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PERSPECTIVE

"Rollover" cyclometalation – early history, recent developments, mechanistic insights and application aspects

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"Rollover" cyclometalation constitutes a special case among the well-known class of cyclometalation reactions. An overview is given that covers the very first description of this reaction type, as well as recent developments. In addition, not only condensed-phase experiments are reviewed, but also investigations based on mass spectrometric techniques, together with "in silico" studies using DFT-based calculations are considered. While the latter two methods allow for a detailed analysis of the intrinsic factors that affect the reaction mechanisms, consideration of all three regimes permits to develop a coherent mechanistic picture and to address the often noted gap between condensed- and gas-phase studies. Moreover, the quite unexpected reactivity of "rollover" cyclometalated complexes in gas-phase experiments, as well as potential applications, *e.g.* in synthetic procedures, are discussed in some detail.

1. Introduction

The transformation of non-activated hydrocarbons into value-added products constitutes a long-standing goal for chemists[1–3] and regioselective activation of inert C–H bonds is regarded as one of the key steps for introducing a functional group into a particular position of a substrate. Common to the otherwise different approaches, such as directed *ortho*-metalation,[4] remote functionalization,[5–14] or cyclometalation,[15–30] is the precoordination of the substrate to a metal center, followed by the activation of geometrically accessible C–H bonds, which can be adjacent or remote, to generate a template for further functionalization. In particular, cyclometalation has attracted much attention and, not surprisingly, formed the subject of several review articles.[15–30] The popularity of this reaction type and, in

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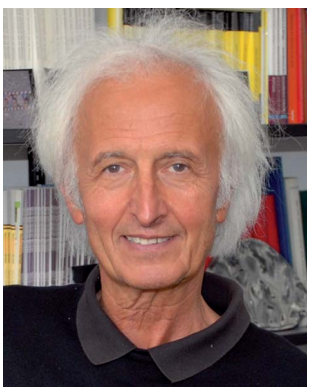


Helmut Schwarz

Helmut Schwarz read chemistry at the Technische Universität Berlin (TUB) from 1966–1971. After having completed his Ph. D. in 1972 under the supervision of Ferdinand Bohlmann and his habilitation in 1974 (both at TUB), he spent some time abroad (ETH Zürich, Cambridge University and MIT Cambridge) before he returned in 1978 to his alma mater *to join the Institute of Chemistry. Dr Schwarz has occupied visiting positions at 14 academic institutions worldwide, has published close to 950 peer-reviewed articles and has delivered more than 900 invited or name lectures. As of January 2008, he serves as President of the Alexander von Humboldt-Stiftung.*

particular, of cyclopalladation,[24,28,31] is due to the facts that i) the outcome of the reaction is highly predictable because predominantly five-membered rings are formed in a strictly intramolecular process, and ii) the resulting compounds are versatile intermediates for further transformations, *e.g.* carbonylations, alkenylations, alkynylations, acylations, isocyanations, or halogenations. If the substrate exhibits more than one coordination site, a special variant of the classical course may become accessible, which is "rollover" cyclometalation. A comparison of both reaction types is depicted in Fig. 1 for a 6-phenyl-2,2′-bipyridine metal complex **1**. While in the classical process the C–H bond of the adjacent phenyl ring is activated concomitant with the loss of HX (**1** → **2**), for the "rollover" cyclometalation, **1** → **3**, partial decomplexation and rotation of a heteroaryl ring constitute prerequisites for the metal-mediated activation of the unactivated, remote C–H bond at C(3).

Depending on the nature of the components M, X and the bidentate ligand in complexes like **1**, rotation around the C(2)–C(2′) bond can be quite demanding energetically; moreover, the choice of the reaction conditions has proved crucial. As a consequence, "rollover" cyclometalation reactions are still quite rare, although the first example was already described in 1977, but not initially correctly recognized.[32] "Rollover" cyclometalation is historically connected with the enormously popular 2,2′-bipyridine (bipy) ligand that was described by Blau already in 1888[33,34] and which, over the ensuing decades, has attracted growing interest.[35–42] Actually, a review article was even entitled "*Bipyridine: The Most Widely Used Ligand*"[36] and also chiral derivatives of 2,2′-bipyridine were developed.[43,44] The attractiveness of this ligand is certainly a consequence of i) its rich and intriguing coordination chemistry, ii) the easiness of functionalization of the pyridine rings and iii) the high stability of many of its transition-metal complexes against moisture and oxygen.

In the first sections of this article, a brief historical overview concerning the discovery of "rollover" cyclometalation is given, followed by more recent studies on the generation of "rollover" cyclometalated complexes in the condensed phase, as well as in gas-phase experiments. Then, detailed mechanistic aspects of the "rollover" cyclometalation process are discussed from different viewpoints, including fundamental, as well as more practical aspects. Although "rollover" cyclometalated complexes are nowadays easily prepared, in-depth reactivity studies have been scarce. However, this situation has changed in recent years, and quite a few condensed phase as well as mass spectrometry-based experiments (ion/molecule reactions) have been conducted in several laboratories. The insight derived from these studies may guide synthetic applications.

While classical cyclometalated complexes have also attracted much attention, *e.g.* in the field of supramolecular chemistry,[45–52] or as chemosensors,[53–59] switches,[60–62] metallomesogens[63–68] and also due to their photoluminescent and electronic properties,[69–83] no attempts will be made to include these aspects, even when related to "rollover" cyclometalated complexes, because the "rollover" cyclometalated ligands in these systems mostly act as mere spectators. In this review, the focus will be rather on the "rollover" process itself. Similarly, although the M–C bond in "rollover" cyclometalated complexes can be regarded as covalent, during the last few years a debate arose as to whether such compounds should not be better classified as abnormal remote-carbene complexes.[84] While of some interest, this aspect will also not be addressed because we prefer to emphasize the structural and mechanistic aspects of the "rollover" cyclometalation process itself rather than elaborating details concerning the precise bonding situation in the cyclometalated products.

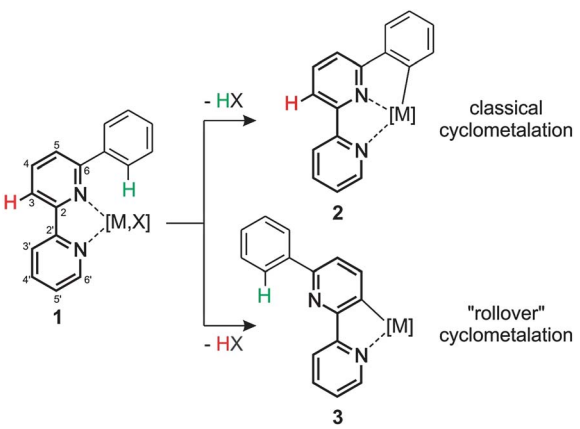


Fig. 1 Classical cyclometalation (**1** → **2**) *versus* "rollover" cyclometalation (**1** → **3**) for a metal complex containing 6-phenyl-2,2′-bipyridine as a ligand.

2. The early history

In 1974, Flynn and Demas reported the isolation of the first tris-2,2′-bipyridyl complexes of iridium, *i.e.* $[Ir(bipy)_3](NO_3)_3$ and $[Ir(bipy)_3](ClO_4)_3$.[85,86] In both complexes, all bipy ligands coordinate in a bidentate fashion, *i.e. via* both nitrogen atoms, to the Ir(III) center.[87] Shortly afterwards, Watts *et al.* described the unprecedented generation of "*A Stable Monodentate 2,2′-Bipyridine Complex of Iridium(III)*" the structure of which was assigned to $[Ir(bipy)_2(H_2O)(bipy)]Cl_3 \cdot 3H_2O$ ("Watts complex").[32] While in this complex two bipyridine ligands were suggested to act as classical bidentate nitrogen donors, the coordination mode of the third heterocyclic ligand remained ambiguous. Several structures were proposed and two were judged to be in agreement with the experimental data (Fig. 2a): i) complex **4**, in which water is directly bound to the iridium center, while one bipy ligand coordinates in a monodentate fashion and ii) structure **5** in which one bipy ligand is "covalently hydrated", thus also acting as a monodentate ligand.[32,88] Despite the controversies about the structural assignment of the third bipy ligand in the "Watts complex",[89–93] the correct structure remained shrouded in mystery

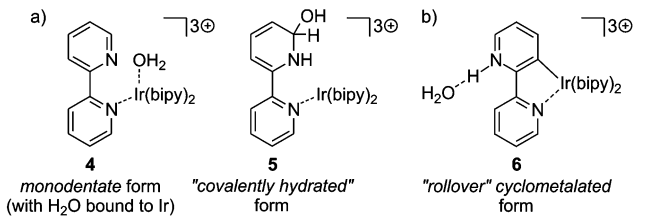


Fig. 2 a) Initially proposed structural representations of the monodentate (**4**) and the "covalently hydrated" form (**5**) of "Watts complex", as suggested in ref. 32 together with b) the actual "rollover" cyclometalated structure **6**.

and the puzzle it caused was even denoted "A Jekyll and Hyde Story".[94] This unsatisfying situation was, however, a consequence of the fact that only those structures were considered that had already been suggested in ref. 32 and alternatives had not been taken into account.

However, a breakthrough occurred in 1981 when Wickramasinghe, Bird and Serpone reported the crystal structure of the perchlorate salt of $[Ir(bipy)_2(H_2O)(bipy)]^{3+}$.[95] One bipy ligand was suggested to be rotated around the central bond and bound in a bidentate fashion to the iridium center *via* one nitrogen and one carbon atom (Fig. 2b). Although there was no clear-cut crystallographic evidence for this particular, novel structural motif, a hydrogen bonded water molecule in the crystal structure gave an idea as to the position of the uncoordinated nitrogen atom. Moreover, both the monodentate coordination mode (**4**) as well as the "covalently hydrated" form (**5**) could be unequivocally excluded based on the X-ray crystallographic data. Following this study, Spellane, Watts and Curtis provided ^{1}H- and ^{13}C-NMR-based support for a covalent Ir–C bond and confirmed the structural suggestion $[Ir(bipy)_2(bipy - H)]^{3+}$ for this complex also in solution (note that the notation (bipy – H) stands for (bipy-C^3,N') and that, throughout this article, (L – H) denotes "rollover" cyclometalated ligands L).[96] Later, a combined crystallographic, NMR and IR study by Nord *et al.* revisited the results obtained so far,[97] and electrochemical, as well as NMR studies conducted by Heath, Peacock and co-workers,[98] as well as a crystallographic study by Hazell and Hazell on both $[Ir(bipy)_3](ClO_4)_3 \cdot 2^1/_3\ H_2O$ and $[Ir(bipy)_2(bipy - H)](ClO_4) \cdot H_2O$[87] further confirmed the presence of a C^3,N'-coordinated 2,2′-bipyridine ligand in "Watts complex". In 1985, Skapski, Sutcliffe and Young investigated the thermal rearrangement of $[Pt(bipy)(Ar)_2]$ (**7**; Ar = C_6H_5, *p*-^{t}Bu-C_6H_4, *p*-CF_3-C_6H_4) that gave rise to the elimination of ArH concomitant with the presumed formation of [Pt(bipy – H)(Ar)] (**8a/8b**) *via* rotation of one pyridyl ring followed by C(3)–H bond activation at the metal center (Fig. 3); in this context, the term "rollover" 3-metalation was coined.[99] The intermediates **8a/8b** were proposed to undergo further ArH loss to produce **9**. However, monomeric species were not isolated. Instead, the polymeric products **10a–c** were suggested to be formed, presumably *via* intermolecular association processes involving complexes **8a/8b** and **9** as intermediates. In contrast, in the presence of a large excess of pyridines, dinuclear complexes, such as **11**, were isolated and characterized *via* X-ray crystallography (Fig. 4).[99]

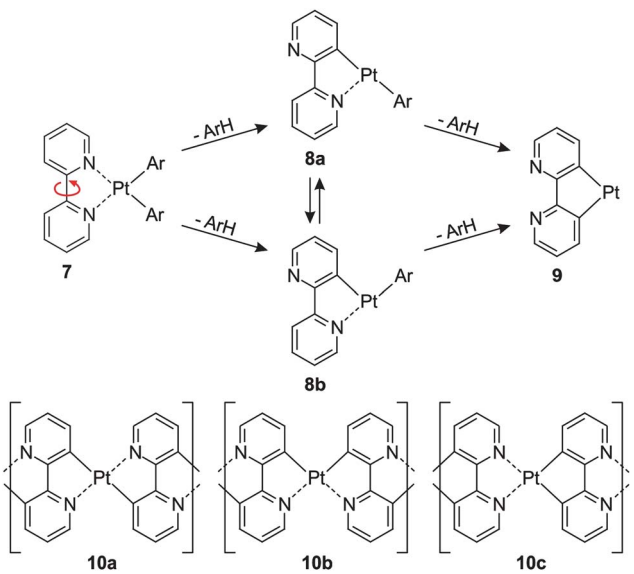


Fig. 3 Processes suggested to occur in the thermal rearrangement of [Pt(bipy)$(Ar)_2$] (**7**) to eventually produce polymeric species **10a–c**, as proposed in ref. 99.

3. A renaissance

After Skapski's investigation in 1985,[99] not much attention was paid anymore to "rollover" cyclometalation chemistry. It took five years until Garces and Watts reported a new "rollover" cyclometalated dichloro-bridged complex of iridium(III) with 2,2′-bipyridine (bipy), namely $[Ir(bipy)(bipy - H)Cl]_2$, which turned out to be the second example of a genuine "rollover" cyclometalation reaction involving iridium.[100] In 1999, however, Minghetti and co-workers gave new momentum to the chemistry of "rollover" cyclometalation when they published their landmark paper on the generation of C(3)-metalated palladium and platinum complexes of 6-substituted 2,2′-bipyridines, bipy^R.[101] Reactions of *iso*-propyl and *neo*-pentyl substituted bipy^R with $[Pd(CH_3COO)_2]$ in refluxing benzene for 7 h, followed by treatment with LiCl in water/acetone for *ca.* 1 week resulted in the formation of $[Pd(bipy^R - H)(Cl)]_2$ (**12**; R = *iso*-propyl, *neo*-pentyl; Fig. 5). Under these conditions, only quite low yields (25% and 35% for R = *iso*-propyl and *neo*-pentyl, respectively) were achieved and simple 1 : 1 adducts, as well as sp^3-cyclometalated species were formed as by-products.[101] However, when $Na_2[PdCl_4]$ was used as a precursor, 1 : 1 adducts were formed exclusively.[102] Interestingly, when $Na_2[PdCl_4]$ or $K_2[PtCl_4]$ are reacted with 6-*tert*-butyl-2,2′-bipyridine, C(sp^3)–H activation of the *tert*-butyl group occurs and the corresponding *N*,*N*,*C*-cyclometalated complexes are generated, while formation of simple *N*,*N*-bidentate adduct complexes does not take place.[102–104] In contrast, when $[Pt(CH_3)(Cl)((CH_3)_2S)_2]$ is used as a metal precursor, "rollover" cyclometalated [Pt(bipy^{tBu} – H)(Cl)$((CH_3)_2S)$] (**13**, Fig. 5) is exclusively produced, but only in very low yield (10%) and only after a prolonged reaction time (12 days).[101]

From these experiments, it became obvious that subtle changes of the substituents bound to the bipy ligands, as well as of the reaction conditions and the metal precursors used often cause the reactions to proceed in an unpredictable and difficult-to-control way; simple adduct formation, conventional cyclometalation involving the substituent in C(6)-position, as well as "rollover"

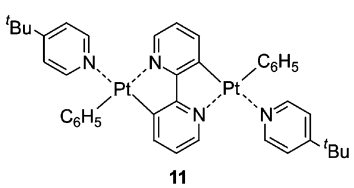


Fig. 4 Dinuclear "rollover" cyclometalated 2,2′-bipyridine complex **11** produced in the thermal rearrangement of $[Pt(bipy)(C_6H_5)_2]$ in the presence of an excess of 4-*tert*-butylpyridine.[99]

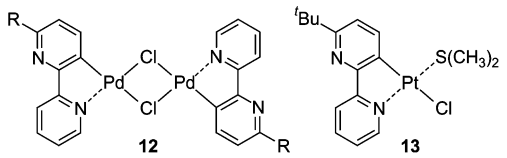


Fig. 5 The first examples of "rollover" cyclometalated complexes containing 6-substituted 2,2′-bipyridines bipy^{R} (R = *iso*-propyl, *neo*-pentyl) as generated and characterized by Minghetti and co-workers.[101]

cyclometalation compete with each other.[102] In fact, it proved difficult to estimate if a $C(CH_3)_2(C_6H_5)$ substituent in the 6-position will undergo $C(sp^2)$–H or $C(sp^3)$–H activation.[102,105] However, the presence of a substituent in the 6-position seems to be crucial to induce "rollover" cyclometalation, and both the bulkiness and the electronic nature of the substituent influence the reaction outcome. For example, Britovsek and co-workers observed a competition between adduct formation and "rollover" cyclometalation when they employed 6-substituted 2,2′-bipyridines bipy^{R} (R = NH_2, $N(CH_3)_2$, CH_3) and [Pt$(CH_3)_2((CH_3)_2S)]_2$ as a metal precursor; for R = NH_2, adduct formation was observed, while "rollover" cyclometalated complexes were produced for R = $N(CH_3)_2$ and CH_3.[106] As already mentioned above, also the choice of the metal precursor affects the reaction outcome quite much,[102,107–109] and C(3)-metalation is achieved for a great variety of 6-substituted 2,2′-bipyridines when electron-rich [Pt$(CH_3)_2(DMSO)_2$] is employed. While this observation suggested the superiority of this particular metal precursor to form "rollover" cyclometalated species,[108] also [Pt$(C_6H_5)_2(DMSO)_2$] is quite versatile.[107] In contrast, the use of [Pt$(Cl)_2(DMSO)_2$] and [Pt$(CH_3)(Cl)(DMSO)_2$] often leads to simple adduct formation,[108] while employment of [Pt$(CH_3)_2(DMSO)_2$] sometimes does not even allow for the isolation of adduct complexes prior to cyclometalation.[110] For example, when 6-phenyl-2,2′-bipyridine is treated with [Pt$(CH_3)_2(DMSO)_2$] in toluene, at 90 °C, "rollover" cyclometalation occurs to produce complex **14** (Fig. 6) in 93% yield after only 2 h;[111] in contrast, when [Pt$(CH_3)(Cl)((CH_3)_2S)_2$] is employed, adduct formation, as well as production of the *N*,*N*,*C*-cyclometalated complex **15** are observed (compare Fig. 1).[111] However, even with [Pt$(CH_3)_2(DMSO)_2$] as a precursor, the presence of a substituent at position C(6) seems to dramatically facilitate metalation at C(3). For example, in the reaction of [Pt$(CH_3)_2(DMSO)_2$] with 5-methyl-2,2′-bipyridine, only adduct formation takes place and for unsubstituted 2,2′-bipyridine, NMR spectrometric evidence points to some minor "rollover" cyclometalated products.[107] Yet, when the reaction conditions were carefully optimized (dry nitrogen, anhydrous toluene as a solvent, 110 °C, 3 h), "rollover" cyclometalation of even unsubstituted 2,2′-bipyridine to produce [Pt(bipy – H)(CH_3)(DMSO)] (**16**; Fig. 6) in almost quantitative yield was achieved.[112] In contrast, with palladium acetate, no evidence for C(3)-metalation of unsubstituted 2,2′-bipyridine was found.[113]

An interesting dinuclear complex **17** (Fig. 7) could be produced after only 3 h, in 97% yield, in the reaction of [Pt$(CH_3)_2(DMSO)_2$] with terpy (terpy = 2,2′:6′,2″-terpyridine) when employed in a 2 : 1 ratio.[114] Interestingly, the same complex is formed when the platinum complex and terpy are used in a 1 : 1 ratio, while the unreacted ligand can be recovered from the reaction mixture; this observation indicates that the central pyridyl ring is activated toward further substitution after the initial Pt–C bond formation.[114] A structural feature that complexes **14** and **16** (Fig. 6) have in common concerns the presence of a non-coordinated nitrogen atom that suggests potential for additional cyclometalation. Indeed, when [Pt$(CH_3)_2(DMSO)_2$] and 2,2′-bipyridine are employed in a 2 : 1 ratio, the dinuclear species **18** (Fig. 7) is formed in an almost quantitative yield after 8 h (reminiscent of the first dinuclear complex **11** reported by Skapski *et al.*,[99] see Fig. 4).[112] When **14** is treated with [Pt$(CH_3)_2(DMSO)_2$] in a 2.5-fold excess, the threefold Pt–C-containing complex **19** is formed in 62% yield; even a complex with four Pt–C bonds, **20**, can be generated by the reaction of 6,6′-diphenyl-2,2′-bipyridine with [Pt$(CH_3)_2(DMSO)_2$] (Fig. 7).[108] Note, however, that the second metalation step in the productions of **18–20** does not correspond to genuine "rollover" cyclometalation; rather, classical cyclometalation takes place, for which the initial "rollover" cyclometalation simply provides a perfect geometrical arrangement.

Minghetti and co-workers have also achieved genuine "rollover" cyclometalation with gold in the oxidation state +III. For example, when 6,6′-dimethoxy-2,2′-bipyridine (bipy^{2OMe}) is treated with [$Au(OAc)_3$] in acetic acid, at 80 °C, "rollover" cyclometalated [Au(bipy^{2OMe} – H)$(OAc)_2$] is formed.[115] Furthermore, it is worth mentioning that Yang and co-workers discovered "rollover" cyclometalation of 2,2′-bipyridine in the presence of Cu^{II} when they tried to synthesize new types of polyoxometalates under hydrothermal conditions, and even

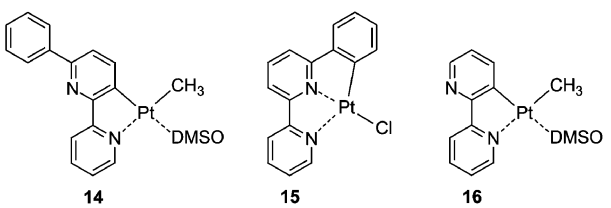


Fig. 6 Examples of mononuclear cyclometalated and "rollover" cyclometalated complexes.

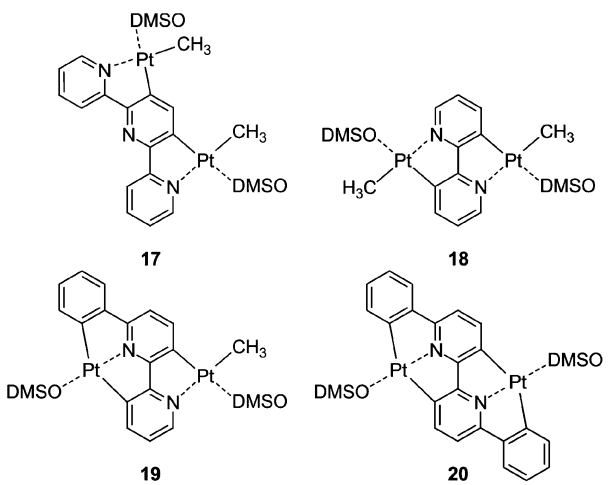


Fig. 7 Examples of dinuclear "rollover" cyclometalated complexes.

double-"rollover" cyclometalated units $[Cu_2(bipy - 2H)]^{2+}$ were formed.[116]

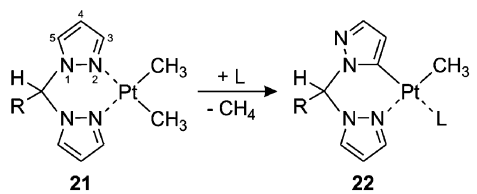
4. "Rollover" cyclometalation without 2,2′-bipyridine ligands

2,2′-Bipyridine is not the only ligand that enables "rollover" cyclometalation; actually, this reaction is, in principle, feasible for all ligands that can adopt an (at least) bidentate coordination mode and that are "flexible" enough to undergo internal rotation ("rollover"). In the following section, examples of "rollover" cyclometalation reactions are given that involve various ligands, among them are polypyrazolylmethanes and 2-(2-thienyl)pyridines. Furthermore, examples are presented that result in structural motifs reminiscent of "rollover" cyclometalated complexes, although a genuine "rollover" cyclometalation did not occur; for these reactions we suggest the term *pseudo*-"rollover" cyclometalation.

4.1. Pyrazolylmethanes

Trispyrazolylmethane (pz_3CH; pz = *N*-pyrazolyl) is a potentially tridentate ligand, which, however, mostly coordinates in a bidentate fashion with the third pyrazolyl unit sometimes weakly coordinating to the metal center.[117] Canty, Honeyman, Minchin and co-workers reported the generation of $[Pt(pz_3CH)(CH_3)_2]$ (**21**; R = pz) by treating pz_3CH with $[Pt(COD)(CH_3)_2]$ (or $[Pt(CH_3)_2(SEt_2)]_2$[118]) in refluxing benzene; however, the poor solubility of this compound precluded the determination of the coordination mode of the pz_3CH ligand *via* NMR studies or X-ray crystallography.[119,120] Surprisingly, when recrystallization from boiling pyridine was attempted, crystals of a new compound could be isolated, which was identified as cyclometalated $[Pt(pz_3CH - H)(CH_3)(py)]$ (**22**; R = pz, L = py = pyridine) having been formed *via* loss of methane from **21**.[118–120] Later it was found that this reaction even proceeds at ambient temperature over 5–6 h in pyridine or upon gentle warming in 4-methylpyridine, *N*-methylimidazole, or 3,5-dimethylpyridine, eventually giving rise to the corresponding C(5)-metalated, *i.e.* "rollover" cyclometalated, complexes $[Pt(pz_3CH - H)(CH_3)(L)]$ (**22**; R = pz; L = pyridine, 4-methylpyridine, *N*-methylimidazole or 3,5-dimethylpyridine; Fig. 8).[118,121]

For the analogous $[Pt(pz_2RCH)(CH_3)_2]$ complexes with R = H, C_6H_5 and *N*-methylimidazol-2-yl, the same behavior has been observed.[118] These findings indicate that, at least for R = H and C_6H_5, the mechanism involves a monodentate intermediate in the course of a genuine "rollover" cyclometalation process, rather than an intermediate in which two pyrazolyl groups are coordinated to the platinum center in a bidentate fashion while hydrogen abstraction occurs from the third, weakly coordinating pyrazolyl ring, as suggested in ref. 120. The former scenario is further supported by the fact that the presence of a donor solvent seems necessary for the formation of **22** because all four complexes $[Pt(pz_2RCH)(CH_3)_2]$ (**21**; R = H, C_6H_5, pz, *N*-methylimidazol-2-yl) are unaffected by reflux in toluene or xylene.[118] Donor molecules are presumably required to occupy vacant coordination sites of intermediates and/or the product complexes (for further details, see section 6.2). However, also for this ligand, the choice of an appropriate metal precursor is crucial as, for example, the adduct complex $[Pt(pz_3CH)(C_6H_5)_2]$ dissolves in pyridine without metalation even upon prolonged heating, and NMR experiments in C_5D_5N show that rather $[Pt(py)_2(C_6H_5)_2]$ and the free ligand are produced.[118] Moreover, we would like to mention in passing that "rollover" cyclometalation of bis- and trispyrazolylmethane complexes appear to be the first examples of cyclometalation at a donor ring that is connected to another donor ring *via* a bridging unit, rather than linked directly as in 2,2′-bipyridine; thus, 6-membered rings can also be formed.[118–120,122] Finally, it is worth mentioning that the palladium complex $[Pd(pz_3CH)(CH_3)_2]$, which is analogous to **21**, does not undergo cyclometalation in pyridine; instead, $[Pd(py)_2(CH_3)_2]$ is formed.[122] This observation is in agreement with the lower propensity of palladium(II) toward oxidative addition.[123–125]



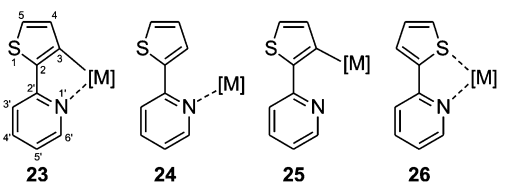
21 **22**

Fig. 8 "Rollover" cyclometalation of platinum(II)–polypyrazolyl complexes $[Pt(pz_2RCH)(CH_3)_2]$ (**21**; R = H, C_6H_5, pz, *N*-methylimidazol-2-yl) in L = pyridine, 4-methylpyridine, 3,5-dimethylpyridine, or *N*-methylimidazole to produce **22**.[118–120]

4.2. 2-(2-Thienyl)pyridines

For metal complexes of 2-(2-thienyl)pyridine (thpy), four structural motifs (Fig. 9) exist, *i.e.* bidentate *N*,*C*(*3*)-coordination (**23**), monodentate *N*-coordination (**24**), monodentate, covalent M–C(3) linkage (**25**) and bidentate *N*,*S*-coordination (**26**). Structure **23** is the most commonly observed,[126–134] and motifs **24**[126,132,135,136] and **25**[130,133] are also often encountered. Most of the complexes contain platinum and palladium as metal centers, but also iridium,[127] rhodium,[128] ruthenium[128,136] and gold[132,136] serve as metal cores. Note that in complexes of type **24** the sulfur atom of the thienyl ring sometimes weakly coordinates to the metal center in an octahedral fashion, as can be nicely observed in the crystal structures of complexes $[Pd(thpy)_2Br_2]$[135] and $[Pt(thpy)(thpy - H)(I)]$;[126] the latter compound is an especially interesting example because it combines both motifs **23** and **24** within one single complex.

Structure **26**, however, while required for the formation of **23** in the course of a "rollover" cyclometalation process, is quite rare;[136] in most cases, **23** is even produced directly and not *via* **26**. Complexes with structure **26** are only known for ruthenium as



23 **24** **25** **26**

Fig. 9 Structural motifs that are encountered for metal complexes of 2-(2-thienyl)pyridine and its derivatives.

a metal center;[136–139,140] surprisingly, the isolation of "rollover" cyclometalated $[Ru(bipy)_2(thpy - H)]^+$ proved impossible,[136] while the analogous cyclometalated 2-phenylpyridine complex $[Ru(bipy)_2(phpy - H)]^+$ is easily produced.[141] Therefore, Constable and his co-workers' observation about the reversible interconversion of $[Ru(terpy)(thpy)]^{2+}$ (**27**) and $[Ru(terpy)(thpy - H)]^+$ (**28**) upon treatment with base (aqueous NaOH) or acid (dilute HCl or AcOH), see Fig. 10, is quite interesting.[139] Furthermore, this example constitutes the first case of a genuine "rollover"/retro-"rollover" cyclometalation process comprising a 2-(2-thienyl)pyridine. Later, Wolf and co-workers came across a similar system where a thiophene ring undergoes reversible and pH-dependent "rollover"/retro-"rollover" cyclometalation (Fig. 11).[142,143]

4.3. Further ligands

Wang and co-workers reported the formation of the supramolecular structure **33** generated upon "rollover" cyclometalation of the platinum–NPA intermediate $[Pt(NPA)(CH_3)_2]$ (**31**) (Fig. 12; NPA = *N*-(2′-pyridyl)-7-azaindole). The latter is accessible by the reaction of $[Pt(CH_3)_2(\mu\text{-}SMe_2)]_2$ and NPA in THF at −10 °C and undergoes spontaneous self-assembly to produce the tetrameric Pt_4 macrocyle **33**.[144] It is assumed that "rollover" cyclometalation is extremely facile for **31** on the ground that NPA is a rather poor *N*,*N*-chelating ligand that strongly tends to dissociate from the metal center.[145] Platinum–diphenyl complexes of substituted NPA^R, *e.g.* **34** (R = $BMes_2$, (*p*-C_6H_4)Si(C_6H_5)$_2$(*p*-$C_6H_4BMes_2$)), also undergo "rollover" cyclometalation upon heating in the presence of donor ligands, such as dimethyl sulfide to produce **35** (Fig. 13);[146] however, aggregation of these complexes does not take place.

Gandelman and co-workers have described "rollover" cyclometalation employing the pincer click ligands **36** (Fig. 14).[147] *N*,*P*-coordinated palladium-chloride complexes **37** are generated *via* reaction of **36** (R = C_6H_5, *o*-$MeOC_6H_4$, *iso*-propyl, cyclohexyl) with an appropriate metal precursor, such as $[PdCl_2(CH_3CN)_2]$, K_2PdCl_4, or $[Pd(tmeda)Cl_2]$ in DMF, at room temperature; for R = C_6H_5 and cyclohexyl, the analogous platinum complexes were also generated using $[Pt(COD)Cl_2]$. When **37** is heated up to 70 °C in the presence of NEt_3, the *P*,*C*,*S*-pincer-type complex **38** is generated smoothly, as described for R = C_6H_5, *o*-$MeOC_6H_4$ (Fig. 14).

When Safari and co-workers treated 2,2′-dimethyl-4,4′-bithiazole (dmbt) with $Tl(NO_3)_3 \cdot 3H_2O$ in methanol, after a few days the formally cyclometalated complex $[Tl(dmbt - H)_2(NO_3)(H_2O)]$ (**39**; L = H_2O; Fig. 15) was formed, which, upon dissolving in dimethylsulfoxide, converts to $[Tl(dmbt - H)_2(NO_3)(dmso)]$ (**39**; L = DMSO) (accompanied by some isomerization).[148] Although, in several instances, 4,4′-bithiazole was shown to act as an *N*,*N*-bidentate ligand,[149–154] it is not possible to unambiguously decide if **39** is the outcome of a genuine "rollover" cyclometalation process because no *N*,*N*-bidentate intermediates were observed. However, when 2,2′-diphenyl-4,4′-bithiazole (dpbt) is treated with $Tl(NO_3)$, the *N*,*N*-bidentate $[Tl(dpbt)(NO_3)_3]$ complex **40** was formed;[155] this observation may thus suggest that genuine "rollover" cyclometalation is also involved in the production of **39**.

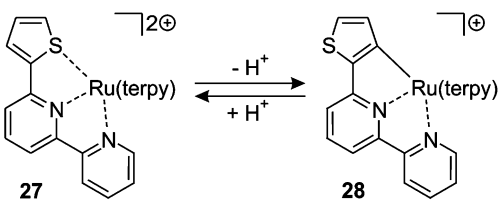


Fig. 10 Reversible "rollover"/retro-"rollover" cyclometalation of a ruthenium(II)-thienylpyridine complex, as studied by Constable and co-workers.[139]

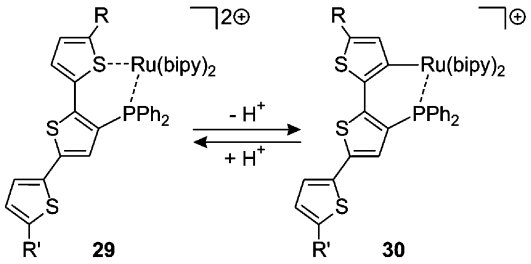


Fig. 11 Reversible "rollover"/retro-"rollover" cyclometalation of ruthenium(II)-thienylpyridine complexes (R, R′ = H, CH_3), as studied by Wolf and co-workers.[142,143]

4.4. *Pseudo*-"rollover" cyclometalation

There exist several reports about cyclometalation reactions that produce "rollover" cyclometalated products and yet their formation proceeds in a mechanistically quite different mode. For instance, *C*,*N*-coordinated 2-(2-thienyl)pyridine complexes **23** are mostly formed directly, rather than from *N*,*S*-bidentate complexes **26**, as described in section 4.2. Another typical example is given in Fig. 16, in which the "rollover" cyclometalation is circumvented *via* direct deprotonation (**41** → **42**);

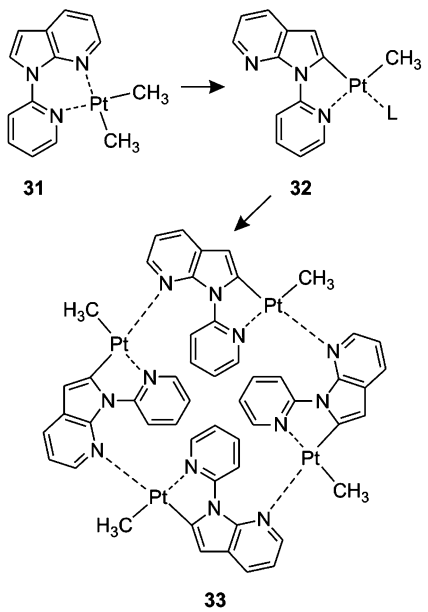


Fig. 12 Spontaneous formation of a tetrameric scaffold (**33**) *via* initial "rollover" cyclometalation of the platinum–NPA complex **31** (NPA = *N*-(2′-pyridyl)-7-azaindole).[144]

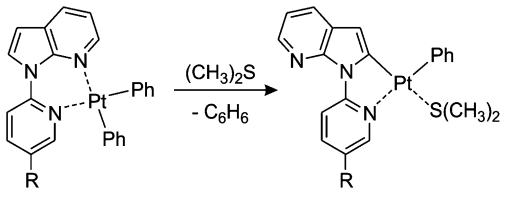


Fig. 13 "Rollover" cyclometalation of substituted NPA^{R} (R = $BMes_2$, $(p\text{-}C_6H_4)Si(C_6H_5)_2(p\text{-}C_6H_4BMes_2)$).[146]

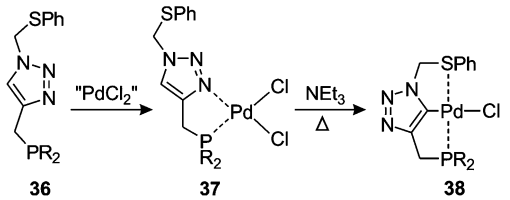


Fig. 14 The generation of the kinetically controlled bidentate palladium–chloride complex **37** (R = C_6H_5, *o*-$MeOC_6H_4$) followed by the formation of the thermodynamically preferred complexes **38** *via* "rollover" cyclometalation in the presence of NEt_3.[147]

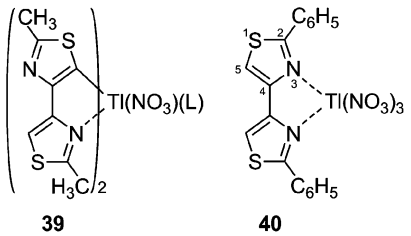


Fig. 15 "Rollover" cyclometalated and *N*,*N*-bidentate thallium(III)-4,4′-bithiazole complexes (L = H_2O, DMSO).

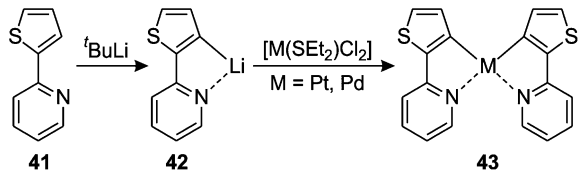


Fig. 16 Transmetalation reaction to generate "rollover" cyclometalated complexes of 2-(2-thienyl)pyridine as an example of a *pseudo*-"rollover" cyclometalation.[129,131]

transmetalation of the lithiated intermediate **42** with a transition metal gives rise to the corresponding cyclometalated compound **43**. While in these processes structures with "rollover" motifs are formed, the reactions should be distinguished from genuine "rollover" processes due to their different mechanisms and we prefer the term *pseudo*-"rollover" cyclometalation.

Another strategy that allows for selective C(3)–H bond activation of 2,2′-bipyridines involves quaternization of one of the nitrogen atoms, for example by monomethylation. Such a procedure was initially developed by Dholakia, Gillard and Wimmer in an attempt to generate "monodentate 2,2′-bipyridine" complexes.[156,157] The reactions of *N*-monomethylated 2,2′-bipyridines [bipyMe]X (X = Cl, Br, I, NO_3, ClO_4) with different metal complexes like Li_2MCl_4 (M = Co, Cu), MX_2 (M = Co, Ni, Cu, Zn, Cd, Hg; X = Cl, Br, I), or K_2MX_4 (M = Pd, Pt; X = Cl, Br) allow for the generations of the corresponding *N*-monodentate [M(bipyMe)X_3] complexes.[156,158,159] When the platinum complexes [Pt(bipyMe)X_3] (X = Cl, Br) are heated up to 90 °C for 12–15 h, together with an equimolar quantity of [bipyMe]NO_3, elimination of HX concomitant with the formations of "rollover" cyclometalated [Pt(bipyMe − H)X_2] (**44**) takes place (Fig. 17).[158] IR spectra exclude the possibility that [Pt(bipy)X_2] was generated due to the loss of MeX. However, although the spectra are in agreement with cyclometalation of [Pt(bipyMe)X_3] at C(3), it could not be rigorously excluded that metalation also occurs at the *N*-methyl group to produce **45** (Fig. 17). Although attempts to afford cyclometalation of the analogous palladium complex [Pd(bipyMe)X_3] (X = Cl, Br) initially failed,[158] heating under reflux in water for 22 h gave rise to the formation of [Pd(bipyMe − H)Cl_2] in 85% yield; the use of water was essential and the conversion did not occur directly but $[Pd(bipyMe)_2Cl_2]^{2+}$ was presumably formed as an intermediate.[160]

5. "Rollover" cyclometalation in the gas-phase

Bursey and co-workers were among the first to explore the capability of fast-atom bombardment (FAB) and field-desorption (FD) mass spectrometry to characterize organometallic compounds.[161,162] In this context, they noted for 2,2′-bipyridine-containing osmium complexes $[Os(bipy)_2(X)(L)]^+$ (L = π-bonding hydrocarbon ligand, CO; X = Cl, HCOO, CF_3COO, $C_6H_5CH_2$, H) a strong signal that corresponds to the combined eliminations of L and HX; this result was interpreted in terms of the formation of a "rollover" cyclometalated [Os(bipy)(bipy − H)]$^+$ fragment ion. The corresponding ruthenium complexes $[Ru(bipy)_2(X)(CO)]^+$ (X = Cl, HCOO, $C_6H_5CH_2$, $(CH_2)_4CH_3$) gave rise to the formations of [Ru(bipy)(bipy − H)]$^+$ and [Ru(bipy − H)]$^+$.[162] Although no attempts were undertaken to verify, *e.g.* by labeling experiments, that hydrogen-atom abstraction indeed involves the 3-position of the bipy ligand, the authors explicitely mentioned the analogy of these gas-phase fragmentation processes to the "rollover" chemistry of such complexes in solution; in fact, for [M(bipy)(bipy − H)]$^+$, a "rollover" cyclometalated structure was suggested based on the X-ray crystallographic study of Wickramasinghe *et al.*[95] A fragmentation scheme was suggested (Fig. 18) that summarizes all of the relevant steps involved in the decomposition of $[M(bipy)_2(X)(L)]^+$ (M = Ru, Os; L = π-bonding hydrocarbon ligands, CO; X = Cl, CF_3COO, H).[162] While this complex can undergo loss of neutral X in the course of a redox-fragmentation process **46** → **47**,[161] elimination of L (**46** → **48**), followed by ejection of HX gives rise

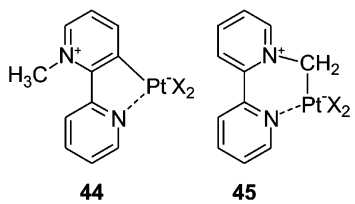


Fig. 17 Conceivable cyclometalation products of *N*-methylated 2,2′-bipyridine.[158]

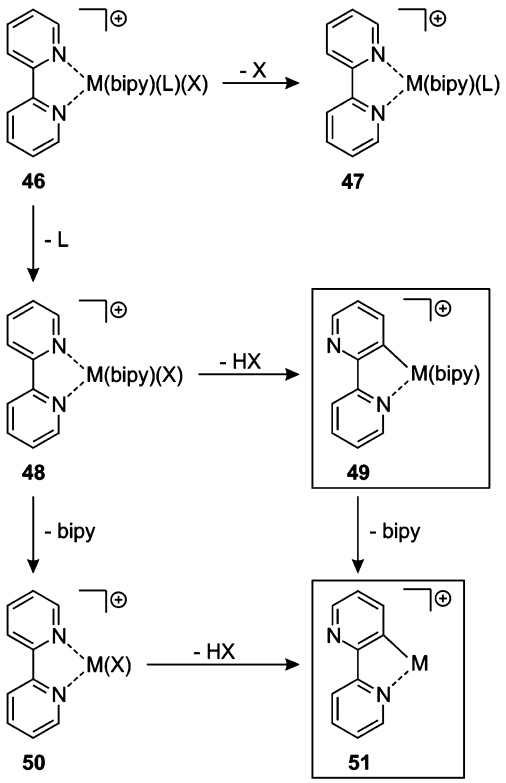


Fig. 18 A fragmentation scheme for the production of $[M(bipy)(bipy - H)]^+$ (**49**) and $[M(bipy - H)]^+$ (**51**) *via* FAB of $[M(bipy)_2(X)(L)]^+$ (M = Ru, Os; L = π-bonding hydrocarbon ligands, CO; X = Cl, CF_3COO, H), as suggested in ref. 162.

to $[M(bipy)(bipy - H)]^+$ (**49**). The cyclometalated complex $[M(bipy - H)]^+$ (**51**) was suggested to be formed by consecutive eliminations of bipy and HX from $[M(bipy)_2(X)]^+$ (**48**) *via* two competing pathways.

Tanaka and Miki interpreted the signals in the secondary-ion mass spectrometry/metastable-ion spectra of $[Ru(bipy)_2(Cl)_2]^+$ in terms of consecutive eliminations of Cl, HCl and bipy; it is quite likely that $[Ru(bipy - H)]^+$ was produced.[163] Further, the authors stated that "*similar ligand-loss processes were observed for* $[Ru(phen)_2(Cl)_2]^+$"; unfortunately, the corresponding data or any other supporting information were not provided. This notion, however, casts some doubt that in the course of HCl loss from $[Ru(bipy)_2(Cl)]^+$, a genuine "rollover" cyclometalation, *i.e.* C(3)-metalation, has taken place because the rigid structure of the phen ligand prevents rotation around the central C–C bond. The same concern applies to the interpretation of the FAB spectra of $[Ru(L)_2(CN)_2]$ (L = bipy, phen), as reported by Bortolini and co-workers.[164] For *both* ligands bipy and phen, formation of the products ions $[Ru(L)(L - H)]^+$ and $[Ru(L - H)]^+$ has been reported, and for L = bipy, their production was interpreted in terms of a genuine "rollover" cyclometalation, although for L = phen this process is not possible on structural grounds.[164–166] Furthermore, Freas and co-workes have reported CID experiments (CID = collision-induced dissociation) employing $[Ru(bipy)_2(terpy)(PF_6)]^+$ as the precursor ion; the loss of neutral PF_5 and of one bipy moiety give rise to the fluoride complex $[Ru(bipy)(terpy)(F)]^+$.[167] CID of the latter species brings about the elimination of HF to produce $[Ru(bipy)(terpy) - H]^+$ and, in addition, the fragment ions $[Ru(terpy - H)]^+$ and $[Ru(L)(F)]^+$ are formed.[167] Analogous processes have also been reported in the studies of $[Ru(bipy)_3(X)_2]$ (X = Cl, PF_6, BF_4, CF_3SO_3, SCN) and $[Os(bipy)_3(X)_2]$ (X = Cl, PF_6).[168,169] It is perhaps interesting to note that "rollover" cyclometalation chemistry in the gas-phase developed nearly independently from the solution-phase studies, and only Bursey and co-workers[162] have mentioned Serpone's crucial X-ray crystallographic study;[95] the subsequent mass spectrometry studies referred exclusively to Bursey's work. Obviously, a mutual perception of the other community's work did not exist for decades. This situation, however, has changed more recently. For example, the gas-phase work conducted in the TU Berlin laboratory of the present authors was initiated by the observation that collision-induced dissociation of cationic $[Pt(bipy)(CH_3)((CH_3)_2S)]^+$ (**52**), generated by electrospray ionization (ESI) of a mixture of bipy with $[Pt(CH_3)_2((CH_3)_2S)]^+$ in methanol, gives rise to "rollover" cyclometalated $[Pt(bipy - H)]^+$ (**55**, Fig. 19).[170] The initial assignment that a genuine "rollover" cyclometalation process is indeed responsible for the formation of **55** was supported by the fact that complexes $[Pt(L - H)]^+$ are produced in the ESI ion source for L = phpy, bipy and pypyrm (Fig. 20), all of which posses a C–H bond in the *ortho*-position relative to the central C–C bond. In contrast, for L = bipyrm and phen only $[Pt(L)]^+$ ions were formed instead.[170] Later, detailed deuterium-labeling studies employing the ligands shown in Fig. 21 reinforced this interpretation because in the CID spectrum of $[Pt([3,3'\text{-}D_2]bipy)(CH_3)]^+$ more than 97% CH_3D are lost concomitant with the formation of $[Pt([3,3'\text{-}D_2]bipy - D)]^+$.[124]

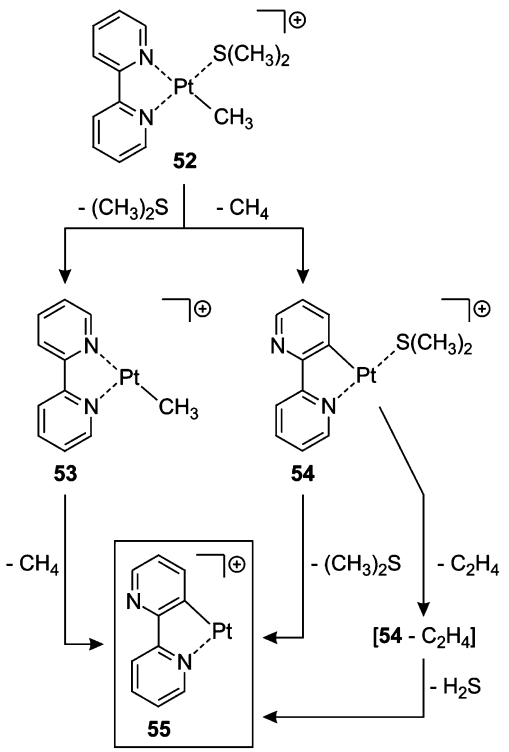


Fig. 19 Gas-phase generation of "rollover" cyclometalated $[Pt(bipy - H)]^+$ (**55**). The pathway **52** → **54** → **55** is lower in energy than the sequence **52** → **53** → **55** and prevails at low collision energies.[170]

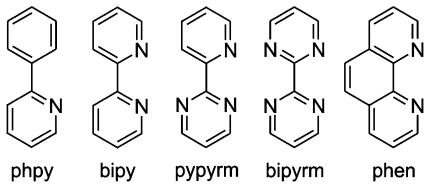


Fig. 20 An overview of the various ligands used for the elucidation of "rollover" cyclometalation processes in mass spectrometric experiments.[170–174]

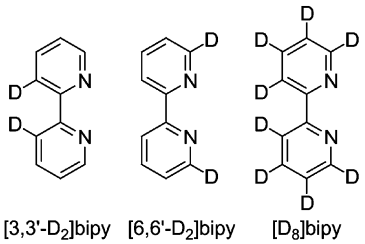


Fig. 21 An overview of deuterated ligands used for the elucidation of "rollover" cyclometalation processes in mass spectrometric experiments.[124]

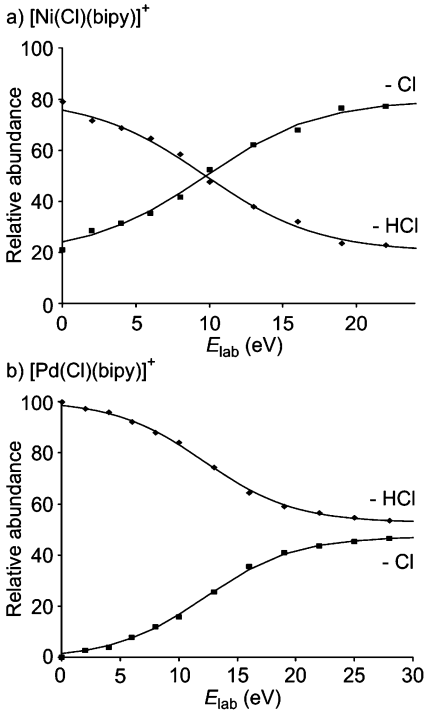


Fig. 22 Relative intensities for the loss of HCl and Cl in the CIDs of mass-selected $[M(bipy)(Cl)]^+$ (M = Ni, Pd).

As to the actual mechanism for the fragmentation of $[Pt(bipy)(CH_3)((CH_3)_2S)]^+$ (**52**) to produce $[Pt(bipy - H)]^+$ (**55**), two scenarios are conceivable (Fig. 19): i) initial loss of $(CH_3)_2S$ to give rise to $[Pt(bipy)(CH_3)]^+$ (**53**), from which the liberation of CH_4 *via* "rollover" cyclometalation produces **55**, or ii) $[Pt(bipy - H)((CH_3)_2S)]^+$ (**54**) is generated first, followed by the elimination of $(CH_3)_2S$;[175] experimentally, both intermediates **53** and **54** are detected.[170] According to DFT calculations, the sequence **52** → **53** → **55** is more than 149 kJ mol^{-1} more demanding than the alternative route and thus not relevant at low collision energies.[170] Note, that the sequences **52** → **53** → **55** and **52** → **54** → **55** resemble the decomposition scheme depicted in Fig. 18, *i.e.* paths **48** → **50** → **51** and **48** → **49** → **51**, respectively. In addition, in a more systematic investigation, we have later focused on selectively probing the steps **46** → **47** and **50** → **51** by generating complexes of the type $[M(bipy)(X)]^+$ (M = Ni, Pd, Pt; X = CH_3, F, Cl, Br, I, OAc) *via* electrospray ionization and subjecting them to CID experiments.[124] Only the platinum complexes, *i.e.* $[Pt(bipy)(CH_3)]^+$ and $[Pt(bipy)(Cl)]^+$, undergo genuine "rollover" cyclometalation, *i.e.* CH_4 and HCl are lost, respectively, with the hydrogen atom originating from the C(3)-position of the bipy ligand; redox-type elimination of neutral X does not occur.[124] In contrast, $[Ni(bipy)(CH_3)]^+$ and $[Pd(bipy)(CH_3)]^+$ exclusively undergo cleavage of the M–CH_3 bond (compare path **46** → **47** in Fig. 18), thus producing the metal(I) complexes $[Ni(bipy)]^+$ and $[Pd(bipy)]^+$, respectively. However, the analogous chloro complexes $[Ni(bipy)(Cl)]^+$ and $[Pd(bipy)(Cl)]^+$ are prone to competitive eliminations of HCl and Cl, and HCl loss decreases in importance upon increasing the collision energy E_{lab}, as illustrated in Fig. 22. While, at $E_{lab} = 0$, CID of $[Ni(bipy)(Cl)]^+$ results in less than 80% HCl elimination, for $[Pd(bipy)(Cl)]^+$ exclusively HCl is lost. At high collision energies (E_{lab} > 25 eV), the ratio for HCl and Cl ejection changes to 20 : 80 and 55 : 45 for $[Ni(bipy)(Cl)]^+$ and $[Pd(bipy)(Cl)]^+$, respectively. These observations indicate that C–H bond activation is significantly more efficient for M = Pd than for M = Ni. Interestingly, HCl loss for these two complexes is not strictly due to "rollover" cyclometalation, as revealed by experiments employing [3,3′-D_2]bipy and [6,6′-D_2]bipy (Fig. 21). For example, at a collision energy of E_{lab} = 10 eV, hydrogen atom abstraction occurs from the 3-, 4/5- and 6-position(s) with 67, 18 and 15% for $[Ni(bipy)(Cl)]^+$ and with 79, 15 and 6% for $[Pd(bipy)(Cl)]^+$, while > 98% C(3)-metalation was observed for $[Pt(bipy)(Cl)]^+$.

The acetate complexes of nickel and palladium, *i.e.* $[Ni(bipy)(OAc)]^+$ and $[Pd(bipy)(OAc)]^+$, do not undergo any cyclometalation; rather, OAc is lost as a neutral fragment, while at moderate collision energies, the formation of CO_2 gives rise to the production of the corresponding methyl complexes $[M(bipy)(CH_3)]^+$ (M = Ni, Pd).[176] Also, for the nickel precursors $[Ni(bipy)(Br)]^+$ and $[Ni(bipy)(I)]^+$, cyclometalation does not occur; rather, redox eliminations of Br and I, respectively, take place. In contrast, when $[Ni(bipy)(F)]^+$ is subjected to CID, rather than neutral F, only HF is eliminated. Interestingly, in the decomposition of this complex the hydrogen atom is preferentially abstracted (92%) from the C(6)-position. This observation was completely unexpected, and a satisfying explanation for this high selectivity is still missing, mostly due to the lack of structural information about the product species. The occurrence of a radical pathway, rather than metal-mediated C–H bond activation, cannot be excluded, and further investigations are indicated for a definitive explanation.

It is tempting to use these gas-phase experiments as a guide to speculate about the solution-phase behavior of related complexes; in particular, the trend observed for the chloro complexes $[M(bipy)(Cl)]^+$ (M = Ni, Pd, Pt) suggests that platinum is superior for "rollover" metalation compared to the

other two metals. This claim is born out by the fact that, for example, $[Pt(pz_3CH)(CH_3)_2]$ undergoes "rollover" cyclometalation,[118–120] while under the same conditions $[Pd(pz_3CH)(CH_3)_2]$ is inert (see section 4.1).[122] Finally, we would like to mention two further examples of "rollover" cyclometalation in gas-phase experiments. The first one deals with the fragmentation of the dinuclear gold-μ-oxo-bis-2,2′-bipyridine complex **56** that has been suggested to undergo a twofold "rollover" 3-metalation **56** → **57** concomitant with the liberation of H_2O (Fig. 23).[177] The second example concerns a rare case in which it is not a heterocyclic ligand, but rather a diimin ligand that is involved in a "rollover" cyclometalation (**58** → **59**, Fig. 24).[178]

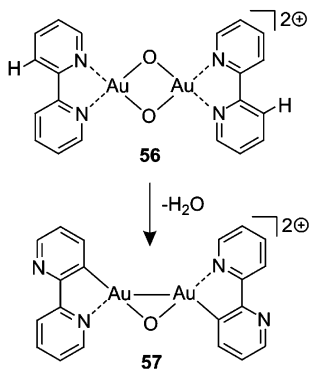


Fig. 23 "Rollover" cyclometalation involving a dinuclear gold-μ-oxo-bis-2,2′-bipyridine complex.[177]

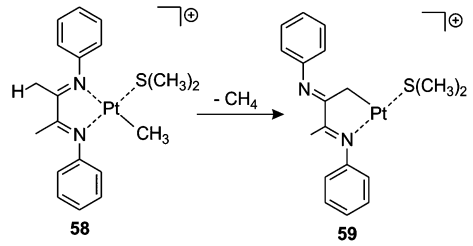


Fig. 24 "Rollover" cyclometalation involving the backbone of a diimin ligand.[178]

6. Mechanistic considerations

6.1. Intrinsic aspects

The crucial mechanistic difference between classical *versus* "rollover" cyclometalation results from the internal ligand rotation that has to take place prior to C–H bond activation. Thus, "rollover" cyclometalation must, by definition, commence with a complex in which the ligand coordinates in an (at least) bidentate fashion (compare section 4.4). This reasoning is in agreement with the studies of Minghetti and co-workers, who have investigated the reactions of $[Pt(CH_3)_2(DMSO)_2]$ with 6-R-2,2′-bipyridines (R = CH_3 and $CH_2C(CH_3)_3$), as well as a chiral pinene-derived 2,2′-bipyridine using NMR spectrometry.[107,110] These studies unequivocally reveal the existence of a two-step scenario that commences with initial *N*,*N*-coordination to produce $[Pt(L)(CH_3)_2]$, followed by rapid methane loss. Isolation of adduct complexes, however, was not possible when $[Pt(CH_3)_2(DMSO)_2]$ was employed, but could be achieved with $[Pt(C_6H_5)_2(DMSO)_2]$.[107] For the elimination of methane, a mechanism was proposed that involves the rotation of a pyridyl ring followed by an oxidative-addition/reductive-elimination sequence to eventually liberate methane.[107] Ring rotation is suggested to be induced by the destabilization of the adduct complex as a consequence of the steric hindrance caused by the 6-substituent in the bipy ligand; moreover, ring rotation is supposed to be facilitated by the operation of a *trans*-effect of the methyl group that weakens the opposing Pt–N interaction.[110] However, for the oxidative-addition/reductive-elimination scenario, experimental evidence, as provided by the detection of hydride intermediates, is lacking.[107] In contrast, Zuber and Pruchnik reported the NMR-based detection of hydride intermediates when they treated $[Rh(bipy)_2Cl]$ with CD_3ONa/CD_3OD. The hydrogen atoms in the 3,3′-positions of the bipy ligand were selectively exchanged for deuterium, and the process was interpreted in terms of a reversible "rollover"/retro-"rollover" cyclometalation process (for further details, see section 6.3).[179] In order to gain a deeper insight into the actual mechanism of C–H bond activation in the sequence $[M(bipy)(X)]^+ \rightarrow [M(bipy - H)]^+ + HX$ (M = Ni, Pd, Pt; X = CH_3, Cl), we have conducted rather extensive DFT calculations.[124] The potential-energy surfaces show a clear preference for an oxidative-addition/reductive-elimination scenario for M = Pt, while σ-bond metathesis is favored for M = Ni; also, for $[Pd(bipy)(CH_3)]^+$ the latter scenario prevails, while for $[Pd(bipy)(Cl)]^+$ both mechanisms compete. These results are in line with the fact that palladium(IV)-hydride complexes were found to be much less stable than the analogous platinum complexes.[109] In Fig. 25, the key steps of the "rollover" cyclometalation mechanism are schematically summarized. Only the intrinsic features of the reaction are displayed; the possible role of solvent effects, substituents on the heterocyclic ligand, or the influence of M and X, as well as the actual mechanism for C–H activation (oxidative addition/reductive elimination *versus* σ-bond metathesis) are ignored.[180] 2,2′-Bipyridine was chosen as a representative ligand just because of its prototypical role in "rollover" cyclometalation. We assume that the basic mechanistic and energetic implications are the same for any comparable ligands. After the formation of the bidentate adduct complex **60**, ring rotation can produce two different kinds of monodentate intermediates, *i.e.* ***cis*-61** and ***trans*-61**, in which the ligand X is in a *cis*- or *trans*-position, respectively, relative to the rotated ring. The transition state ***trans*-TS(60/61)** is lower in energy than ***cis*-TS(60/61)** because of the operation of a *trans*-effect of the ligand X that weakens the Pt–N interaction in **60** for the ring that is in *trans*-position to X. In **61**, due to the proximity of the C(3)–H bond and the metal center, perhaps as a consequence of an agostic interaction, the arrangement is ideal for subsequent C–H bond activation to produce the "rollover" cyclometalated complex **62**. Without any specification of the actual mechanism of C–H bond activation during the transformation **61** → **62**, coordination of the C(3)–H bond in ***trans*-61** is, due to the *trans*-effect of X, weaker and therefore the C–H bond is less pre-activated (elongated) compared with ***cis*-61**. Thus, in the formation of **62**, a cross-over of the two pathways occurs, *i.e.* ***trans*-TS(61/62)** > ***cis*-TS(61/62)**. However, if the monodentate intermediates ***cis*-61** and ***trans*-61** can be interconverted *via* a transition state that is

located below ***cis*-TS(60/61)**, the sequence **60** → ***trans*-61** → ***cis*-61** → **62** can compete with **60** → ***cis*-61** → **62**. Such a situation is encountered in the processes $[M(bipy)(Cl)]^+ \rightarrow [M(bipy - H)]^+ + HCl$ (M = Pd, Pt), but not for the analogous CH_3 complexes.[181] In the very last step, **62** → **63** + HX, at least in gas-phase experiments, simple elimination of HX gives rise to **63**, while in solution-phase experiments the vacant coordination site at the metal core will be occupied by the solvent.

Another aspect that deserves a brief mention concerns the origin of the driving force for "rollover" cyclometalation. The processes $[M(bipy)(CH_3)]^+ \rightarrow [M(bipy - H)]^+ + CH_4$ for M = Ni, Pd and Pt, for example, are calculated to be endothermic by 174, 95 and 108 kJ mol^{-1}, respectively.[124] However, coordination with a donor L as, for example, a solvent molecule, may turn the reactions exothermic. Moreover, when CH_4 is liberated, in the gas-phase experiments the process becomes irreversible; if HCl is the leaving species, in solution a base might "trap" the acid. Furthermore, metalloaromaticity has been suggested to stabilize the resulting metallacycle.[78]

6.2. Influence of the solvent

The seemingly simple ring-rotation step, **60** → **61**, which is crucial for any "rollover" cyclometalation to occur, is only trivial from a gas-phase chemist's viewpoint; indeed, this step is associated with a variety of subtleties when solvent effects come into play. In the course of this transformation, an *n*-dentate ligand ($n > 1$) is converted to interact with the metal center in an $(n - 1)$-dentate fashion. Therefore, some flexibility within the ligand is essential for this process and it was shown by Griffiths and Young that bipy and bipyrm possess a significantly higher conformational flexibility than phen,[182] thus facilitating monodentate binding modes of the intermediates. Furthermore, Bortolini and co-workers have shown in gas-phase experiments that cationic ruthenium complexes containing bipy and phen preferentially lose bipy.[164,165] Schröder and co-workers have made similar observations in CID studies involving mono- and dicationic, manganese containing, mixed bipy/phen complexes and, according to their complementing DFT calculations, bipy loss from $[Mn(bipy)(phen)]^{2+}$ is 43 kJ mol^{-1} easier than ejection of phen.[183] Moreover, several experimental results suggest that "rollover" cyclometalation is eased by the use of donor solvents or the presence of donors in the reaction mixture. For example, the polypyrazolylmethane complexes $[Pt(pz_2RCH)(CH_3)_2]$ (**21**; R = H, C_6H_5, pz, *N*-methylimidazol-2-yl, Fig. 8) undergo "rollover" cyclometalation only in solvents like pyridine, 4-methylpyridine, 3,5-dimethylpyridine, or *N*-methylimidazole, but are unaffected, even under reflux, when toluene or xylene are employed as solvents as described in section 4.1. This observation was interpreted as support for a mechanism that involves

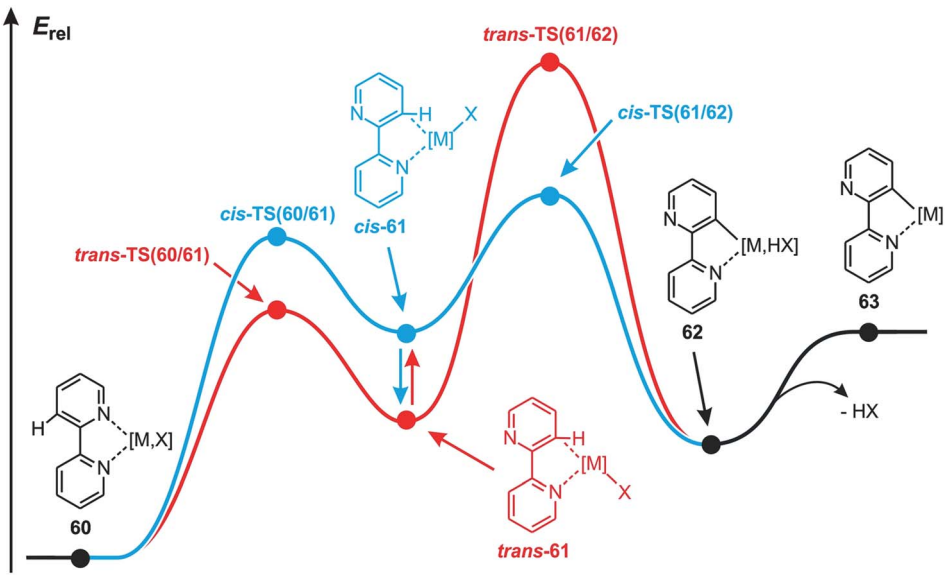


Fig. 25 A schematic potential-energy surface for the "rollover" cyclometalation process $[M(bipy)(X)] \rightarrow [M(bipy - H)] + HX$. Note that the relative energies depend on the nature of M, X and the heterocyclic ligand (here bipy).

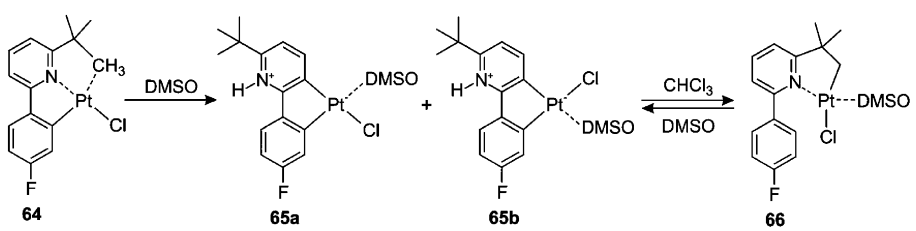


Fig. 26 Solvent-switchable "rollover" cyclometalation, as described by Rourke and co-workers.[184]

stabilization of the monodentate intermediates in the course of the "rollover" step **60** → **61**.[118] Also, Gandelman and co-workers demonstrated that "rollover" cyclometalation of the pincer-click ligand **36** (Fig. 14, section 4.3) requires the addition of NEt_3.[147] However, it is not clear if, in these cases, NEt_3 acts as a base or if the amine actively takes part in the "rollover" process, *e.g.* to occupy empty coordination sites at the metal center. Furthermore, Rourke and co-workers reported the solvent-switchable formation of the exotic "rollover" complexes **65** (Fig. 26) that do not contain a metal–heteroatom interaction.[184] Dissolving **64** in the polar solvent DMSO produces **65**, which, in the less polar solvent $CHCl_3$, is transformed into the classically cyclometalated complex **66**. Complex **65** can be reversibly regenerated by treatment of **66** with DMSO. These observations have been explained in terms of a delicate balance (induced by the bulkiness of the *tert*-butyl group) that can be controlled by solvent polarity. Based on calculations, **65a** and **65b** are favored over **66** in polar DMSO by 6 and 12 kJ mol^{-1}, respectively, while they are disfavored by 11 and 4 kJ mol^{-1} in chloroform.

Surprisingly, in several instances, quite weakly polar solvents, like benzene, toluene, or dichloromethane, have been used for the generation of "rollover" cyclometalated bipy complexes.[101,107,108,110–114,185] Nevertheless, at least traces of a stabilizing agent seem to be mandatory for the reactions to proceed. Although [Pt(bipy − H)(CH_3)(DMSO)] (**16**) is formed in the reaction of [Pt$(DMSO)_2(CH_3)_2$] with 2,2′-bipyridine in anhydrous toluene, heating of the adduct complex [Pt(bipy)$(CH_3)_2$] in toluene, in the complete absence of DMSO, results in partial decomposition, and a mixture of unidentified products is produced; however, when a small amount of DMSO is added to the reaction mixture, the "rollover" species **16** is formed.[112] This result points to the role of [Pt(bipy)$(CH_3)_2$] as an intermediate, but the detailed interplay of DMSO is not yet obvious, *i.e.* does DMSO stabilize the product complex or is the formation of the monodentate intermediate aided by coordination of DMSO? As described in section 4.3, [Pt$(NPA^R)(C_6H_5)_2$] (**34**) undergoes "rollover" cyclometalation upon heating in the presence of donor ligands such as dimethyl sulfide (see Fig. 13).[146] Furthermore, "rollover" cyclometalation is facile for [Pt(NPA)$(CH_3)_2$] (**31**; Fig. 12) and the solvent has been suggested to actively participate in the mechanism.[144] A possible sequence of events is given in Fig. 27.[144] Although ring rotation is facilitated for NPA due to its poor *N*,*N*-chelating performance,[145] coordination of the solvent L to the metal center is supposed to facilitate the dissociation of one nitrogen atom from the platinum center even more, and in the next step, **67** → **68**, L is replaced by an agostic interaction with the rotated ligand. Afterwards, oxidative addition followed by reductive elimination is suggested to take place to eventually form the "rollover" cyclometalated methane complex **70**, from which liberation of methane is facilitated by exchange with another solvent molecule to produce **32**. Deuterium-labeling experiments using 2-D-NPA (deuteration in the 2-position of the azaindole moiety) revealed a primary kinetic isotope effect (KIE) of 2.8 at 24 °C; this result suggests that oxidative addition, **68** → **69**, rather than ring rotation, corresponds to the rate-determining step. Moreover, CH_3D is eliminated exclusively, thus indicating that no H/D exchange either of the CH_3 groups or with deuterated solvents (CD_2Cl_2, C_6D_6, CD_3CN, CD_3OD, or D_2O) occurs. Consequently, the formation of methane from **69** is irreversible and much faster than H/D exchange.[144]

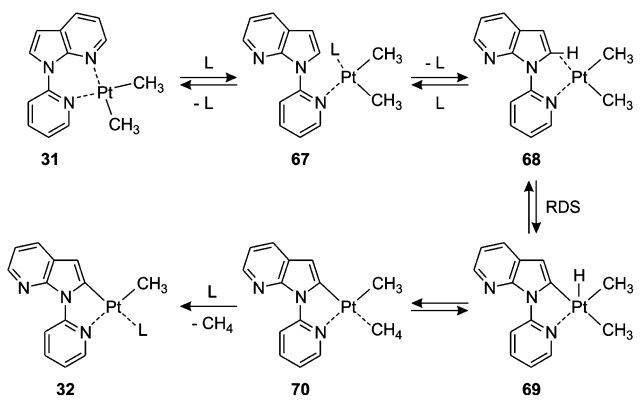


Fig. 27 The suggested mechanism for "rollover" cyclometalation of [Pt$(NPA)(CH_3)_2$] (**31**) taking an active participation of the solvent L into account.[144]

A computational study on the fragmentation of cationic [Pt$(bipy)(CH_3)((CH_3)_2S)]^+$ (**52**) to produce "rollover" cyclometalated $[Pt(bipy - H)]^+$ (**55**) *via* sequential ejection of methane and dimethyl sulfide suggests that methane loss followed by the evaporation of $(CH_3)_2S$ is energetically favored over the reverse sequence by at least 149 kJ mol^{-1} (compare section 5, Fig. 19).[170] Another viewpoint on the energetic effects of dimethyl-sulfide coordination to the metal center during "rollover" cyclometalation is provided by a comparison of the processes **52** → **54** + CH_4 and **53** → **55** + CH_4. In Fig. 28, the lowest-energy pathways for both processes (based on the data in ref. 170) are given. The weak *trans*-influence of the dimethyl-sulfide ligand in **52** results in a slightly more favorable (24 kJ mol^{-1}) "rollover" barrier compared to that for **53**. However, for the very same reason, the oxidative-addition step for **71** is disfavored by 36 kJ mol^{-1}, while its influence on reductive elimination is negligible. The energy gain for the transformation **73** → **54** + CH_4 results from a switch of the $(CH_3)_2S$ ligand from the position *trans* to the platinum-bound carbon atom to the *cis*-position after methane is liberated; this reorientation is a consequence of the *trans*-effect exhibited by the carbon atom of the cyclometalated pyridyl ring.[110] Thus, coordination of $(CH_3)_2S$ to the platinum center in **52** makes "rollover" cyclometalation kinetically slightly easier. However, the quite high "rollover" barriers of more than 150 kJ mol^{-1} that have to be overcome (starting from both **52** and **53**) prior to C–H bond activation suggest that a donor solvent might not only stabilize the product complex, but rather actively supports the "rollover" step in solution-phase experiments, as depicted in Fig. 27. Consequently, while "rollover" cyclometalation, in principle, works without the participation of additional donors, as clearly demonstrated in gas-phase experiments,[124,170] solvent effects have to be carefully considered in solution as they may affect both the barrier of ring rotation, as well as the stability of the resulting intermediates and product species. While in gas-phase experiments, ring rotation is a strictly unimolecular, single-step process, in solution, due to the interplay with solvent molecules, "rollover" becomes much more complex and might well involve several elementary steps; consequently, such a multi-step scenario could result in barriers

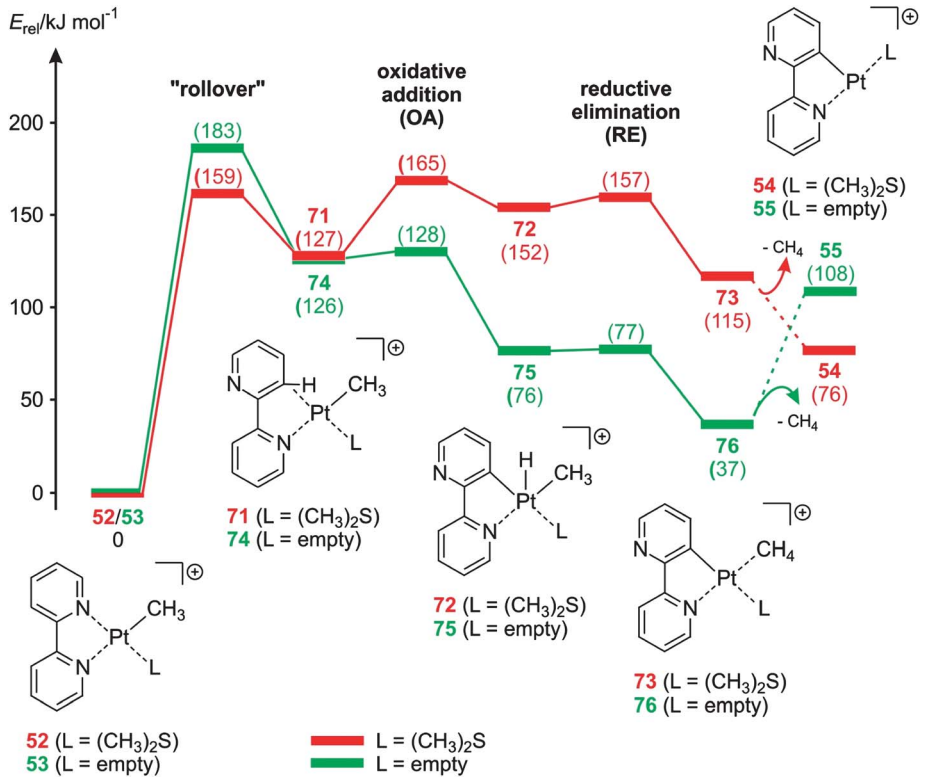


Fig. 28 A schematic potential-energy surface for the reactions $[Pt(bipy)(CH_3)(L)]^+ \rightarrow [Pt(bipy - H)(L)]^+ + CH_4$ (L = $(CH_3)_2S$, empty) based on the data given in ref. 170.

that are easier to overcome than those involved in gas-phase experiments.

6.3. Mechanistic riddles – H/D exchange in 2,2′-bipyridine complexes

When Constable and Seddon treated a solution of $[Ru(bipy)_3]^{2+}$ in $(CD_3)_2SO$ with CD_3ONa/CD_3OD they observed the selective and reversible exchange of the hydrogen atoms at the 3,3′-positions of the bipy ligands.[186] The authors interpreted these results as "*Evidence for the Acidity of the 3,3′-Protons*" within the complex, and the high steric strain exerted on the C(3,3′)–H bonds was suggested to be responsible for this process; the exchange was explained in terms of a conventional acid–base reaction rather than a reversible "rollover" cyclometalation process.[186] Although it was stated that "*once exchange at the 3,3′-positions is complete, no further exchange at any other position is observed*",[186] later, more detailed studies revealed that 95% of the 3,3′-positions are exchanged after 24 h without any other positions being involved, while 70% H/D exchange at the 5,5′-positions was observed after one week.[187,188] Similar observations were made by Wernberg for the analogous osmium complex, $[Os(bipy)_3]^{2+}$, with the order of reactivity being 3,3′ ≫ 5,5′ > 6,6′ > 4,4′.[189] Wernberg also interpreted the H/D exchange in terms of

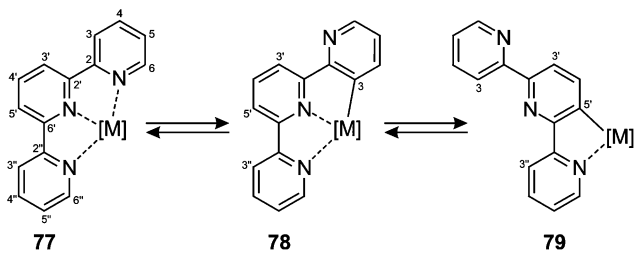


Fig. 29 The suggested stepwise mechanism to explain the preferential exchange of hydrogen atoms in positions 3, 3′, 5′, and 3″. The observation, however, that the 3′- and 5′-positions are exchanged more rapidly than the 3- and 3″-sites rather discounts such a "rollover" cyclometalation mechanism as the major pathway for H/D exchange.[190]

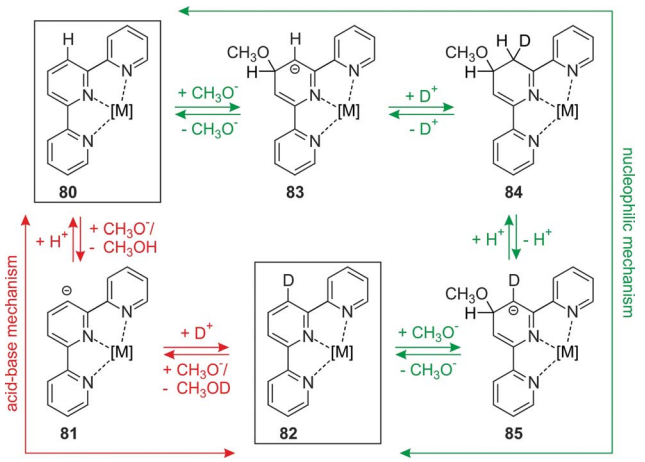


Fig. 30 Suggested mechanisms for H/D exchange at the 3′-position of terpy, **80** → **82** with CH_3O^- acting i) as a base (red arrows) or ii) as a nucleophile (green pathway).[190]

a classical acid–base mechanism. Both studies did not consider the possibility of "rollover"/retro-"rollover" processes as a mechanistic alternative to account for the H/D exchange, at least for the 3,3′-positions, even though Wernberg cited ref. 95–98 that are so central for the discovery of "rollover" cyclometalation. In fact, based on similar studies dealing with H/D-exchange in $[Ru(terpy)_2]^{2+}$, it may indeed seem justified to discount a "rollover" cyclometalation pathway, although the hydrogen atoms in the 3-, 3′-, 5′- and 3″-positions are preferentially exchanged (Fig. 29). A mechanism that accounts for this particular situation is shown in Fig. 29,[190] but the observation that exchange is easier at the central pyridyl unit than at the terminal rings is in disagreement with this mechanism because **79** should be energetically less favorable than **78** and, therefore, a "rollover" cyclometalation pathway was excluded as the dominant pathway.[190] Nevertheless, based on the experimental results, it was stated that no distinction between the two remaining mechanistic alternatives was possible, i.e. i) an acid–base mechanism that involves deprotonation by methoxide followed by reprotonation (red arrows in Fig. 30) or ii) nucleophilic attack of methoxide at a pyridyl ring to produce, for example, a 3′,4′-dihydropyridyl anion as an intermediate, followed by H/D exchange and rearomatization (green arrows in Fig. 30). On the other hand, the two latter mechanisms do not explain the preferential exchange of the 3,3″-positions compared with the 5,5″-positions.

Nevertheless, the conclusion that in H/D-exchange reactions "rollover"/retro-"rollover" cyclometalation mechanisms should be excluded as dominant pathways was reinforced by the fact that for a $[Rh(bipy)_3]^{3+}$ complex (under otherwise identical conditions) hydrogen exchange in the 6,6′-positions precedes the exchange of the hydrogen atoms in the 3,3′-positions, while those in the 5,5′-positions are exchanged only after prolonged reaction times; an acid–base mechanism was suggested in which methoxide acts as a base rather than as a nucleophile.[191] In contrast, when $[Rh(bipy)_2Cl]$ is treated with CD_3ONa/CD_3OD, H/D exchange of the hydrogen atoms in the 3,3′-positions of the bipy ligands takes place, and this observation has been interpreted in terms of a "rollover" cyclometalation process based on NMR studies; in the latter, hydride intermediates were identified.[179] However, after prolonged reaction times, H/D exchange also occurs at the other positions, and the exchange rate decreases in the order 3,3′ ≫ 4,4′ > 6,6′ ≈ 5,5′; this observation suggests that different mechanisms are operative. Interestingly, when 4,4′-dimethyl-2,2′-bipyridine was used as a ligand, no H/D exchange occurs at the rings but at the methyl groups this takes place; in this case, hydride intermediates were not formed, and the exchange mechanism should therefore be different to that proposed for the exchange of the 3,3′-positions in unsubstituted bipy.[179] Hence, a consistent interpretation of the reported H/D-exchange experiments does not seem possible for the time being.

7. Reactions of "rollover" cyclometalated complexes

7.1. Modifications of "rollover" cyclometalated complexes

Based on the "rollover" cyclometalated structural motifs given in Figs 5–7, several new complexes can be produced by ligand exchange reactions; the dimer **12**, for example, can be converted into [Pd(bipy − H)(Cl)(PPh_3)] by treatment with PPh_3 and the DMSO ligands in **14** and **16–20** are easily exchanged for various ligands, *e.g.* PPh_3, PCy_3, CO, 3,5-dimethylpyridine, quinoline, or CH_3CN.[101,107,108,110,112,114,185,192,193] Platinum(II)-hydride complexes can be generated *via* treatment of the corresponding chlorides with $NaBH_4$,[109,185,193] while the chloride analogues are generated either directly by using an appropriate chloride containing precursor,[101,109] *via* ligand exchange with LiCl,[101,102] or by treatment of the methyl complexes with hydrochloric acid (accompanied by some coordinative rearrangements).[107,110,112,185,192,193] However, reaction with HCl can also cause decyclometalation,[109,192] and in some cases, even new types of "rollover" cyclometalated complexes are accessible by this method:[109] for example, **86** and HCl give rise to **87** (Fig. 31), which bears an "unrotated" 6-substituted pyridyl ring; complex **88** is suggested to be the product of a retro-"rollover" cyclometalation process. "Rollover" cyclometalated complexes, like **87**, that contain "unrotated" 6-substituted pyridyl rings are normally not accessible by "rollover" cyclometalation because, in general, C(3)-metalation occurs at the 6-substituted ring, most probably due to steric reasons. A similar structural motif can, in principle, also be achieved by double-"rollover" cyclometalation of 6-substituted 2,2′-bipyridines, as demonstrated for the pinene-derived bipy complex **89** (Fig. 32).[110] This example, however, constitutes the very first case where second metalation is observed in the presence of aliphatic substituents at the C(6)-position.[107]

7.2. "Rollover" cyclometalated ligands as spectators in bond-activation reactions

Periana and co-workers have investigated the reactions of the "rollover" cyclometalated complexes [Ir($bipy^{Ph}$ − H)($bipy^{2tBu}$)(CH_3)(OTf)] ($bipy^{Ph}$ = 6-phenyl-2,2′-bipyridine, $bipy^{2tBu}$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) with hydrocarbons RH (benzene, toluene, mesitylene); C–H bond activation gives rise to

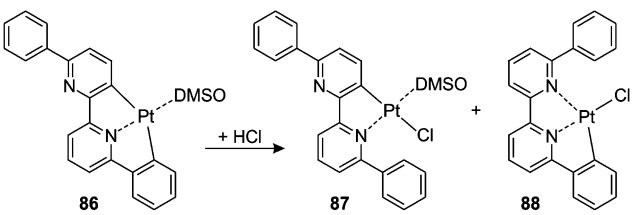


Fig. 31 Decyclometalation of **86** to produce the unusual "rollover" cyclometalated complex **87** that contains an "unrotated" 6-substituted pyridyl ring; **88** is formed *via* retro-"rollover" cyclometalation.[109]

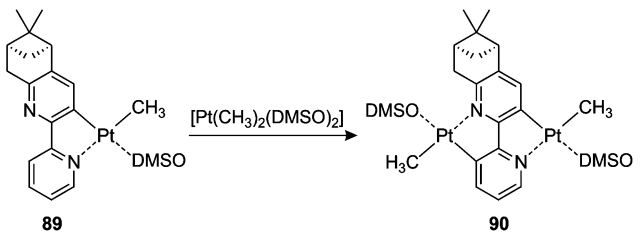


Fig. 32 Double-"rollover" cyclometalation of a pinene-derived 2,2′-bipyridine ligand.[110]

complexes [Ir(bipy^{Ph} – H)(bipy^{2tBu})(R)(OTf)] concomitant with the release of methane.[194,195] Furthermore, Minghetti and co-workers have reported the reactions of "rollover" cyclometalated [Au(bipy^{2OMe} – H)(OAc)(X)] (X = OAc, Cl; bipy^{2OMe} = 6,6′-dimethoxy-2,2′-bipyridine) with acetone to produce the σ-acetonyl complexes [Au(bipy^{2OMe} – H)(CH_3COCH_2)(X)] *via* C–H bond activation.[115] In both cases, however, the "rollover" cyclometalated ligands serve as mere spectators that do not actively participate in the reaction mechanism; the only effect of the C(3)-metalated ligand concerns the strength of the Pt–OTf bond and the Pt–OAc interactions due to the operation of a *trans*-effect by C(3).

7.3. Gas-phase reactions

Nord and co-workers claimed: "*It seems to us that the [Watts] complex is best considered as the end product of a reaction series in which the kinetically unexplored and mechanistically interesting step is the proton loss from the C3 of an* N,N′*-coordinated bipyridine*".[97] However, "rollover" cyclometalated ligands can also actively take part in reactions and such processes may involve the transfer of hydrogen atoms or of other functional groups to the metal-bound carbon atom. Further, these steps might then be followed by processes such as retro-"rollover" cyclometalation or bond activation involving the transferred group. Thus, products may become accessible that are otherwise difficult to make. During our investigations of the gas-phase fragmentation of [Pt(bipy)(CH_3)((CH_3)$_2$S)]$^+$ (**52**), we realized that, upon CID of the "rollover" cyclometalated intermediate [Pt(bipy – H)((CH_3)$_2$S)]$^+$ (**54**), elimination of C_2H_4 occurs, as already indicated in Fig. 19.[178] Indeed, attempts to react "rollover" cyclometalated [Pt(bipy – H)]$^+$ (**55**) in an ion/molecule reaction directly with (CH_3)$_2$S gave rise to the spectrum given in Fig. 33.[171,178]

Obviously, the main reaction channel corresponds to the liberation of neutral C_2H_4 from the adduct complex [Pt(bipy – H)((CH_3)$_2$S)]$^+$ in an oxidative C–C bond coupling process concomitant with the formation of [Pt(bipy)(SH)]$^+$, as supported by quantum chemical calculations and detailed labeling experiments.[170,173] For higher alkyl sulfides, however, C–C bond coupling seems to be restricted to methyl sulfides (*e.g.* propene loss occurs in the reaction of **55** with ethyl methyl sulfide),[171] because higher sulfides R_2S (R = ethyl, *iso*-propyl, *tert*-butyl)

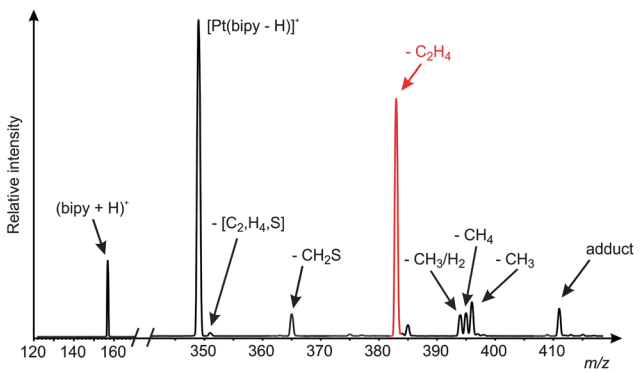


Fig. 33 Thermal ion/molecule reactions of mass-selected [Pt(bipy – H)]$^+$ (**55**) with (CH_3)$_2$S.

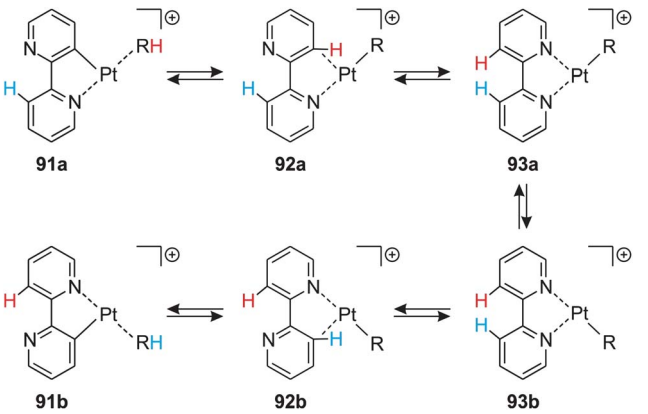


Fig. 34 A mechanistic scheme to explain the reversible hydrogen exchange between the (bipy – H) ligand in [Pt(bipy – H)]$^+$ and a substrate RH, *e.g.* in the reaction of [Pt(bipy – H)]$^+$ (**55**) with (CH_3)$_2$S.[170]

preferentially undergo consecutive losses of two alkene units (ethene, propene, isobutene).[171] An interesting feature of these reactions concerns the occurrence of a reversible "rollover"/retro-"rollover" process prior to product formation that becomes obvious, for example, in the reaction of **55** with (CD_3)$_2$S: losses of both C_2D_4 and C_2HD_3 are observed in a ratio of *ca.* 1.3 : 1; eliminations of $C_2H_nD_{4-n}$ (*n* = 2, 3, 4) are not detected. However, when [Pt(pypyrm – H)]$^+$ (see Fig. 20) is employed, only C_2D_4 is eliminated. A reasonable mechanism for the specific H/D exchange is given in Fig. 34: initial hydrogen transfer from RH, *e.g.* dimethyl sulfide, produces a monodentate bipy ligand (**92a**) that undergoes a retro-"rollover" process **92a** → **93a** to be followed by "rollover" of the adjacent ring to eventually transfer the C(3′)-bound hydrogen atom back to R. The main reaction, *i.e.* formation of C_2H_4, occurs at the bipy complex [Pt(bipy)(C_2H_5S)]$^+$ and all relevant steps exclusively take place at the Pt(C_2H_5S) unit while the bipy ligand acts as a mere spectator.[170,173] It is important to note that the intermediate [Pt(bipy)(C_2H_5S)]$^+$ is located *ca.* 300 kJ mol^{-1} below the separated reactants [Pt(bipy – H)]$^+$ and (CH_3)$_2$S; this is a result of recovering the bidentate coordination mode. Thus, it is the retro-"rollover" process that,

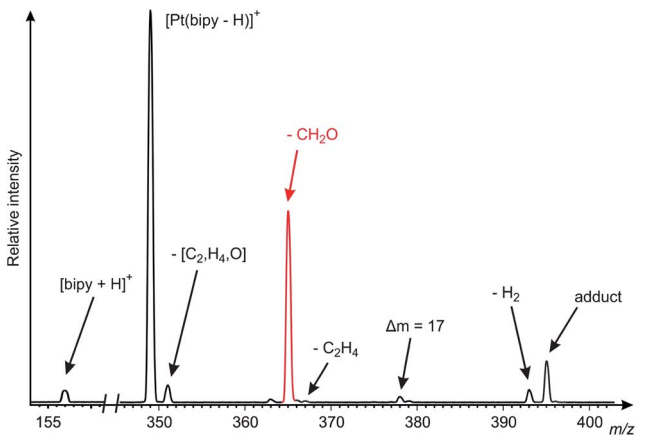


Fig. 35 Ion/molecule reactions of mass-selected [Pt(bipy – H)]$^+$ (**55**) with (CH_3)$_2$O.

due to the associated re-complexation, provides enough energy to drive the reaction to completeness. In contrast, when [Pt(phpy − H)]$^+$ is reacted with $(CH_3)_2S$, elimination of C_2H_4 does not take place because, due to the absence of a re-complexation step, there is not enough energy available.[171]

In the reaction of $(CH_3)_2O$ with [Pt(bipy − H)]$^+$ (Fig. 35), ethene is not generated. Instead, CH_2O loss constitutes the main reaction channel producing cationic [Pt(bipy)(CH_3)]$^+$.[173] The different behavior of $(CH_3)_2O$ in comparison with $(CH_3)_2S$ can be explained in terms of DFT-derived potential-energy surfaces for the reactions of both substrates, as described in detail in ref. 173. In brief, the weaker interaction of platinum with oxygen in comparison with sulfur and the higher thermochemical stability of CH_2O as compared with CH_2S constitute the origin of this distinct behavior. In contrast to the reactions of **55** with thioethers and dimethyl ether, the reactions with higher ethers, as well as with ethanol are much richer and diverse in terms of the products formed.[172]

Furthermore, we have also investigated the reactions of chloromethanes $CH_{4-n}Cl_n$ (n = 1 − 4) with [Pt(bipy − H)]$^+$.[174] HCl loss is observed for CH_3Cl, for CH_2Cl_2 eliminations of one or two HCl moieties, as well as of $PtCl_2$ occur, and for $CHCl_3$, additionally, formation of $CHCl_2^{0/+}$ takes place. In the reaction of **55** with CCl_4, the losses of $PtCl_2$, as well as neutral and cationic $CCl_3^{0/+}$ compete. For all reactions, mechanisms were suggested that mainly start with the insertion of the platinum center into the C–Cl bond of the substrate followed, in most cases, by transfer of the $CH_{3-n}Cl_n$ (n = 0–3) moiety to the platinum-bound carbon atom.

7.4. Synthetic applications

Cyclometalated compounds have attracted much attention as synthetic intermediates due to their rather high reactivity and especially due to the fact that functional groups can be introduced in a highly regioselective fashion *via* attacking the M–C bond;[16,17,24,27–29] cyclopalladated compounds have proven especially useful in synthetic applications. For example, carbonylation followed by appropriate workup gives rise to substituted alkyl esters or carboxylic acids. Alkenylations generate intermediates that can be used for the formation of heterocyclic compounds *via* cyclization reactions. Alkynylations can directly produce new heterocycles. Insertions of acyl halides into the M–C bond give rise to acyl compounds, while reactions with isocyanates, followed by appropriate workup allow for the synthesis of amines and ketones. Halogenation reactions occur regioselectively in the *ortho*-position. However, although such procedures are quite common for classically cyclometalated compounds, to the best of our knowledge, Minghetti and co-workers were the first and, so far, the only researchers to make use of "rollover" cyclometalated complexes for this particular purpose. They have reported carbonylation of "rollover" cyclometalated palladium complexes of 6-substituted 2,2′-bipyridines bipy^R (Fig. 36; R = methyl, ethyl, *iso*-propyl, *neo*-pentyl).[113] Under quite harsh conditions, *i.e.* 40 bar CO pressure and 60 °C in ethanol, the palladium complex **12** is transformed into the ethyl ester **94** or the corresponding acid **95** after basic workup. This procedure is interesting as 3,6′-disubstituted 2,2′-bipyridines are produced, which are difficult to synthesize otherwise. Moreover, nicotinic-acid derivatives, such as **95**, are of biological and pharmaceutical interest.[110]

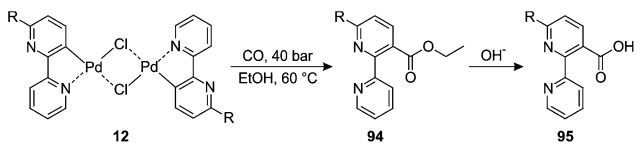


Fig. 36 The procedure for the synthesis of alkyl esters **94** and acids **95** *via* carbonylation of "rollover" cyclometalated palladium–bipy^R complexes **12** (R = methyl, ethyl, *iso*-propyl, *neo*-pentyl).[113]

Another feature of "rollover" cyclometalated complexes that deserves a mention concerns the uncoordinated heteroatom, which offers the possibility for additional coordination, protonation, or other kinds of functionalization reactions. Interestingly, protonation of that site is not achieved when HCl is used, but with HBF_4·18-crown-6 selective protonation of the uncoordinated nitrogen atom occurs; the proton can be reversibly removed upon treatment with Na_2CO_3.[110,112] The properties of the resulting ligand, which can be regarded as a tautomer of 2,2′-bipyridine, are a matter of debate; it can be described as a zwitter-ionic ligand but also classification in terms of an (abnormal) carbene has been suggested.[84,110] Moreover, nitrogen ligands that contain N–H bonds were reported to respond to pH variations and other changes in the solution environment, so that it is conceivable to tune the properties of the transition metal center. "*Ligands with multiple personalities*"[196] have attracted some interest during the last years and such species exhibit perspectives for C–H bond activation reactions[197] or for the design of molecular devices.[198] Also, "rollover" cyclometalation was shown to be reversible,[139,142,143,184] thus offering in principle the possibility to design catalytic cycles that are based on "rollover"/retro-"rollover" processes, employing, for example, the (bipy − H) ligand to serve as a hydrogen atom reservoir.

8. Conclusions

"Rollover" cyclometalation is no longer an exotic phenomenon of metal complexes that contain 2,2′-bipyridine and related ligands as, for example, polypyrazolylmethane- or 2-(2-thienyl) pyridine-based ligands. However, structural motifs that are reminiscent of genuine "rollover" cyclometalated complexes can also be the product of *pseudo*-"rollover" processes, as described in section 4.4. Donor solvents or the presence of donors in the reaction mixture are crucial for efficient "rollover" cyclometalation to occur in solution, presumably due to stabilization of intermediates and product complexes by occupation of vacant coordination sites. In mass spectrometric studies, the reactions of mass-selected "rollover" cyclometalated complexes, especially of [Pt(bipy − H)]$^+$, with several substrates have opened up prospects for studies in solution-phase experiments that may lead to the development of new synthetic methods. Although quite promising, functionalization reactions employing "rollover" cyclometalated complexes, *e.g.* carbonylations, alkenylations, alkynylations, acylations, isocyanations, or halogenations, are currently unexplored and deserve further investigation.

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