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The Monoanionic ECE-Pincer Ligand: A Versatile Privileged Ligand Platform—General Considerations

Gerard van Koten

Abstract During the past 40 years, the monoanionic, tridentate ligand platform that has been named "Pincer" has established itself as a privileged ligand in a variety of research and application areas. Exciting discoveries with NCN and PCP-pincer metal complexes in the late 1970s created a firm basis for the tremendous development of the field. Some of the basic findings are summarized with emphasis on the organometallic aspects of the ECE-pincer metal system.

Keywords Coordination properties · Decomposition pathways · Pincer ligand · Preparation · Reactivity · Stability

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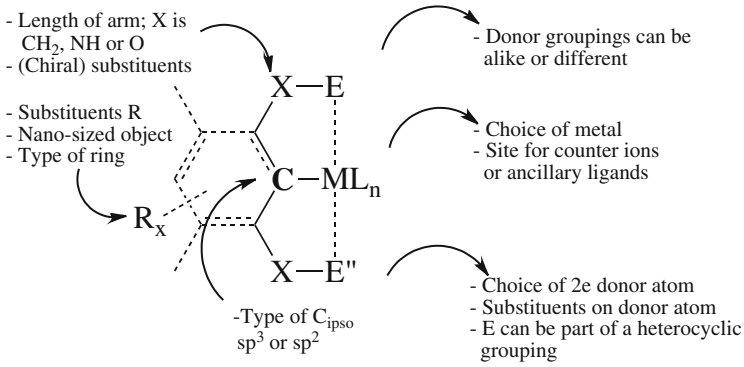

Fig. 1 The pincer-metal platform and the various possibilities to shape and modify it. The ECE-pincer is potentially a six electron donor (similar to the Cp-anion)

1 Introduction

From the beginnings of "Pincer Chemistry" in 1976, the exploration of pincer-metal compounds mainly developed along the lines of the nature of the various donor atoms [1]. Whereas the pincer-transition metal chemistry primarily concentrated on the use of PCP- [2] and SCS-pincer ligands [3] (with the "soft" P- or S-donor sites), it was in the chemistry of copper, lithium, and the group 14 metals that researchers started to apply the NCN-pincer [4, 5] ligand (with the "hard" sp^3 amine donor groupings). During the first 20 years, researchers mainly concentrated on ECE-pincer ligands with a central phenyl (aryl) ring, bonded via its anionic C_{ipso} atom to a ML_n cationic unit and having two similar *ortho*-CH_2E substituents ($E = PR_2$, is PCP; $E = SR$, is SCS; $E = NR_2$, is NCN), coordinating to ML_n via its E-donors, see Fig. 1.

The present situation is an entirely different one; the monoanionic pincer ligand has emerged as a versatile "privileged" ligand platform indeed [1, 6–9]. All pincer-metal complexes have the central connection between the monoanionic site and the ML_n grouping as a common structural feature. The pincer ligands applied nowadays, however, show a striking variation of the nature of the ligand backbone. This includes changes in the formal hybridization of C_{ipso}, (either sp^3 or sp^2), the *ortho*-substituents (including the length and structure of the tether connecting C_{ipso} and the donor atom), the nature of the donor atom sites, as well as the substituents present in the backbone, etc. The available space (i.e., void space) [10] remaining around the metal center after coordination of the ECE′-pincer ligand is determined by both the actual coordination mode of the pincer and the steric requirements of the groupings present as the *ortho*-substituents. A further influence is exerted by the atomic radii of the donor atoms (cf. the atomic radius of N is much smaller than P or S), the form of its formal hybridization, the E–M bond length, and the nature of the X–E connector (e.g., amine or imine, part of a heterocyclic ring, phosphine or phosphite, P = S, etc.). The influence of the nature of the donor atom on the void

space has been studied in some detail for a series of bisamino-pincers [11] and more extensively for the corresponding bisphosphine-pincer ligand [10].

The ECE-pincer can act as a 2e (via C_{ipso}), 4e (via E and C_{ipso}), or as a 6e (via all three sites) donor ligand. A schematic representation of the pincer platform is shown in Fig. 1. A large series of reviews is available describing the various aspects of pincer chemistry from a variety of perspectives (e.g., [1, 6–9, 11–16]).

This chapter serves to illustrate some of the similarities and diversity of the various pincers used in the (now) vast field of pincer-metal chemistry. Various aspects such as the coordination properties, the synthetic routes available, the stability and reactivity properties of pincer-metal compounds in relation to applications as sensors and in catalysis will be touched upon with some illustrative examples. Many of these latter aspects are playing a role in the following chapters of this volume in which the current state of the pincer-metal chemistry in various directions is extensively outlined.

2 Coordination Modes

For square planar ECE-pincer transition metal complexes, a *mer*-E,C,E coordination mode for the terdentate, monoanionic aryl-pincer ligands was anticipated and initially indeed, that is what was also found. Inspection of the Cambridge Crystallographic Data Base [17] reveals about 350 hits for PCP-, 330 for NCN-pincers while SCS- and OCO-pincer metal complexes were represented by about 90 and 50 solid-state structures, respectively. In particular, the fixed, *trans*-orientation of the two phosphorous donor sites in the PCP-pincer metal complexes represented a new structural feature in transition metal chemistry, see Fig. 2. It is noteworthy that a few years after Shaw reported on the well-known *aryl* PCP-pincer metal-d^8 complexes, he followed this up by publishing the synthesis of a series of complementary four- and five-coordinate *alkyl* PCP-pincer (Ir) complexes in which C_{ipso} is a monoanionic C_{sp3}-atom [18]. In five- and in six-coordinate complexes, the acute bonding angles cause a specific binding preference for the pincer. Specifically in five-coordinate complexes in a tbp configuration, an axial-equatorial-axial spanning is observed and for the square planar (sp) structures a binding to three basal sites is noted. In contrast, six-coordinate complexes contain all three binding sites situated in the same plane with the remaining three ligands in a plane perpendicular to it.

Whereas the terdentate bonding mode is the dominant one in the complexes with the PCP- and SCS-pincer ligands, in complexes with the NCN-pincer ligand a more diverse variety of binding modes was encountered even in early studies, see Fig. 2 [1, 6, 7]. For example, the monodentate *C*- and bidentate *C, N*-bonding mode was noted in complexes in which the amine ligands could not compete with, or were replaced by, stronger donor ligands. Moreover, when either one or both amine ligands could not bind to the metal, for example due to quaternarization by protonation, the resulting complexes contained a monodentate *C*-bonded NCN-pincer [19].

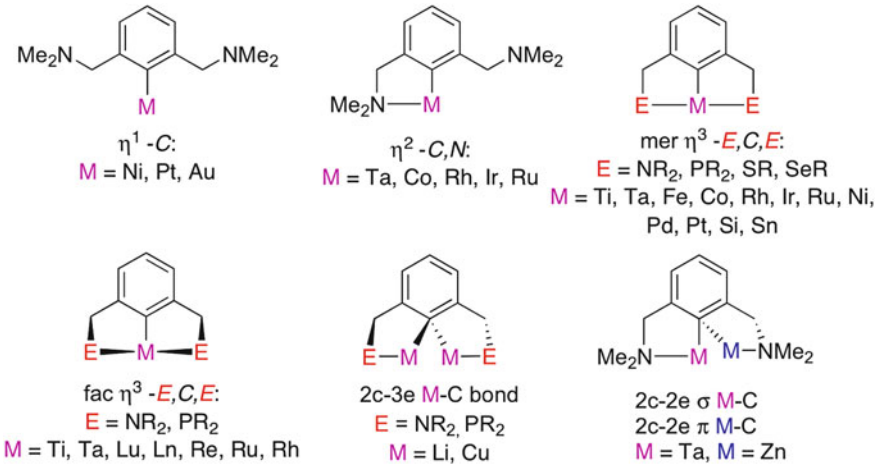

Fig. 2 The coordination modes found for ECE-pincer-metal complexes in the solid state [6]

It is noteworthy that free (noncoordinated) amine substituents can represent a steric constraint at the coordination site *cis* to the C_{ipso}–M bond. This aspect has been observed in NCN-pincer metal-d^8 complexes that contain either a monodentate *C*- or bidentate *C, N*-bonded NCN-ligand. Often this steric interference may cause inter- or intramolecular rearrangements of the pincer-metal motif; a few examples of this are discussed below, cf. Fig. 9.

Many of the differences between the binding observed in the NCN- and OCO-pincers on one hand and the PCP- and SCS-ligands on the other hand are related to the differences in coordination properties of the various donor atoms: the respective N- and O-donor sites are σ-donors while the phosphine donor atoms have both σ-donor and π-accepting properties. Moreover, steric factors also affect the actual binding mode of the pincer ligand. In comparing the NCN- and PCP ligands, it is most likely the difference in atomic radii between N and P that make steric constraints in R_2N- vs. R_2P-groupings dominant, i.e., the M–P bond is longer than the M–N bond while increasing the size of the R groups in the R_2N grouping greatly affects the Lewis basicity of this grouping [11]. The difference in binding properties of the various donor groupings has recently been observed in hybrid ECE′ complexes. For example, in NCP-pincer metal-d^8 complexes the amino-phosphine pincer ligand is *C, P*-chelate bonded through its *ortho*-phosphine substituent whereas the *ortho*-amine substituent remains largely noncoordinating [20, 21].

Initially, the surprising observation was made in the fact that the NCN-pincer ligand can even display a *fac*-terdentate binding mode, see Figs. 2 and 3, a structural feature that on the basis of the presumed rigidity of the central benzene ring was not anticipated [1, 4, 5]. This *fac-NCN*-binding is characterized by a rather acute (amine)N–M–N(amine) bond angle (between 110° and 120°) and in some cases a characteristic bending of the arene C_6-ring [22]. This has been found for, e.g., NCN-pincer Ti [23], Ru [22], and La [24] complexes, see Fig. 3. An early example

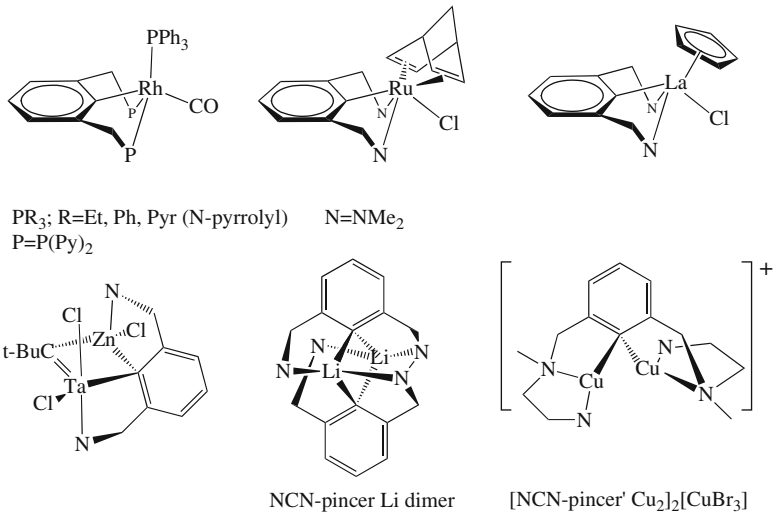

Fig. 3 Some of the bonding modes of the ECE′-pincer ligand

with PCP-pincer ligands is the *fac*-Rh(PCP)(PR_3)(CO) complexes containing (*N*-pyrrolyl)phosphinemethyl *ortho*-substituents as the phosphine donors of the pincer ligand [25]. More recently, several *fac*-PCP-pincer iridium complexes have been prepared and characterized with strongly electron withdrawing phosphine groupings containing organic fragments such as $–CF_3$ [10, 26]. These results indicate that the *fac* binding can be imposed upon the ECE-pincer ligand by selecting the right combination of steric and/or electronic properties (σ-donating or π-accepting or a combination) of the E donor atom groupings. Finally, it appears that this *fac*-binding leads to ECE-pincer metal complexes that have similar structural features to those of the corresponding Cp-metal compounds [6].

The three center-two electron bridge-bonding (via C_{ipso}) to two metals is another bonding mode that was established early on in both NCN-pincer lithium [27, 28] and copper [29] chemistries. In these complexes, C_{ipso} binds to two metal centers while the *ortho*-amine substituents are each coordinated to one of the bridged metal centers, see Figs. 2 and 3. For the corresponding PCP pincer lithium complex, selective bis *ortho*-lithiation of the corresponding (pincer)arene ligand could only be achieved for the ligand in which P represents the (dimethylphosphino)methyl group [30]. Apparently, this grouping has just the appropriate combination of "hard" σ-donating character and steric size to stabilize the final PCPLi compound and prevent alternate deprotonation reactions of, e.g., benzylic protons. Another type of bridge bonding is observed in $TaCl_2$(μ-C*t*Bu)(NCN)(ZnCl) in which C_{ipso} is σ-bonded to the Ta(V) center and π-bonded to Zn, see Fig. 3 [31].

A special structural feature of the pincer platform is the fact that the aryl ring of the *mer*-bonded ECE-pincer ligand (in metal-d^8 complexes) is nearly co-planar with the principal coordination plane of the bonded metal. This can allow for electronic communication between the metal and the aryl σ- and π-systems

[32, 33]. This type of interaction is clearly observable in the trend of the catalytic activity of $NiX(C_6H_2(CH_2NMe_2)_2$-2,6-R-4) catalysts observed in Kharasch reactions (i.e., the addition of halocarbons to alkenes) when the *para*-substituent R in the aryl group is varied from electron donating (−OMe) to electron withdrawing ($-NO_2$) [32, 34]. However, in a similar series of *para*-substituted (PCP)Ir(CO) derivatives ($P{=}CH_2P(t\text{-}Bu)_2$) only a small range of CO IR stretching frequencies is observed for a similar series of R groups [35].

In a number of studies, the *para*-R substituent can be used to bind ECE-pincer metal complex to either insoluble supports or to soluble, supramolecular systems. For example, this technique has been used to make nano-sized homogeneous (dendritic) catalysts [9, 36, 37], or to use the ECE-pincer metal units themselves as building blocks for the construction of supramolecular arrays [9, 38, 39].

3 Preparation of Pincer-Metal Complexes

The actual route for the synthesis of the various types of ECE′-pincer metal compounds depends largely on the nature of the E and E′ donor atoms. In general, when at least one of the donor sites is a soft donor atom, direct and regioselective biscyclometallation (route a, Z = H or Br and M = d^8-metal) of the corresponding arene ligand is observed. In particular, when E=E′ = $-PR_2$ or –SR and M = d^8-metal, the corresponding *mer*-ECE-pincer metal compound can be obtained in high yields. Also in the case of X–E being C=N (e.g., imine [40], oxazoline [41]) regioselective biscyclometallation can be achieved (via C–H bond activation), but in a number of cases the oxidative addition route using C–Br bond cleavage is required or leads to superior product yields. For most of the NCN-diamino pincer ligands, the synthesis of the corresponding pincer metal complex requires a two-step process involving the prior, often in situ, synthesis of the corresponding pincer lithium reagent followed by transmetallation (route a, b in Fig. 4) [6, 42]. In order to avoid separation problems, the bis-*ortho*-lithiation must be quantitative. This can be achieved by the use of an *apolar* solvent and avoiding the presence of any polar or coordinating reagent/solvent(s) in the reaction mixture, cf. the solvent dependence of the yields of the two regioisomers in Fig. 4. As an alternative direct route, lithiation of a bromide-pincer can be used, again followed by transmetallation. For NCN-pincer complexes, $C–SiMe_3$ bond cleavage has likewise been employed for the regioselective introduction of various metal groupings to the NCN-ligand platform [43].

Synthesis of PCP-pincer metal-d^8 complexes by C–Z bond activation (e.g., Z = OR, $OSiR_3$, or CR_3) has been demonstrated and its mechanistic details have been studied in detail ([8], Chapter 5 in [9]).

An alternate route for pincer compounds, that are not easily accessible by other routes, involves a transcyclometallation reaction which also affords for the selective interchange of a C_{ipso}–H for a C_{ipso}–M between *two different* ECE-pincer platforms, see Fig. 5 [44]. This transcyclometallation protocol proved its usefulness

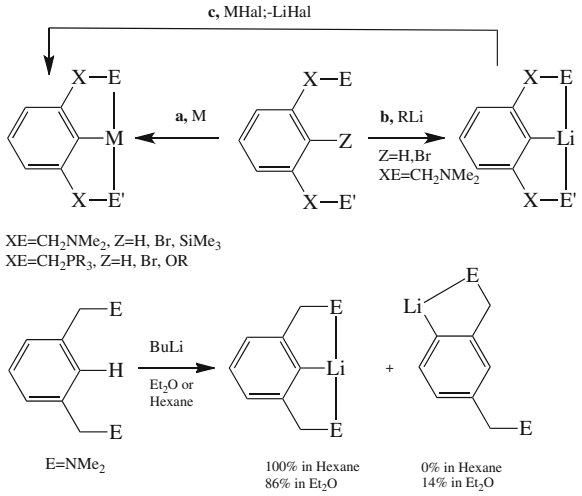

Fig. 4 Summary of some of the (cyclo)metallation routes and starting materials for the various types of ECE-pincer ligands (*top*). Example of the solvent dependence of the regioselective lithiation of NCN-pincers (*below*)

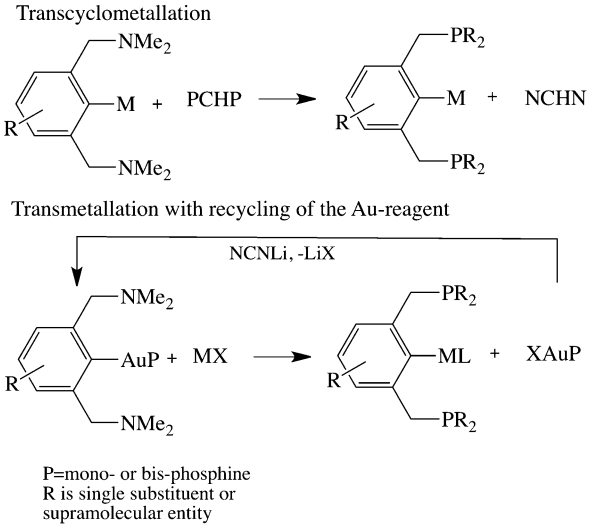

Fig. 5 Two alternate routes for the selective synthesis of pincer metal salts in which the difference in coordination strength of the various donor atoms is the driving force for reaction

in the clean synthesis of, for example, dendritic structures with multiple PCP-pincer ruthenium units [45].

Routes that make use of transmetallation via either tin or mercury intermediates are less advantageous for environmental reasons. However, the reaction of the

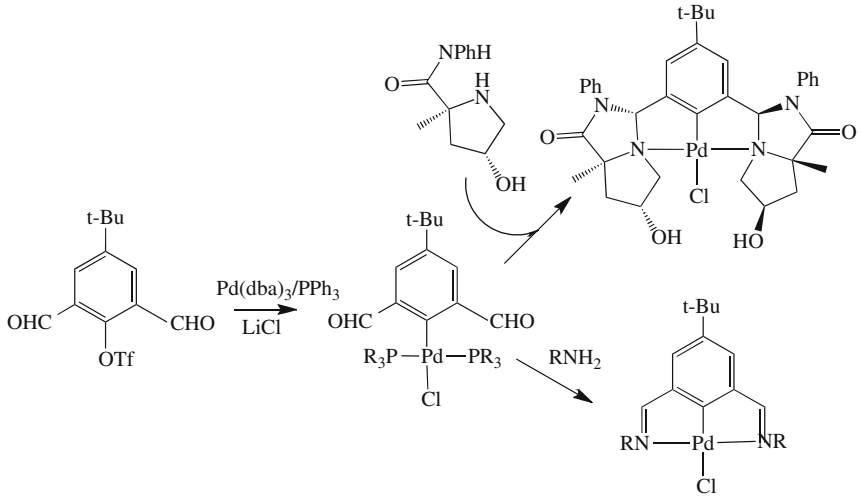

Fig. 6 Synthesis of a chiral NCN-pincer palladium complex by postderivatization

corresponding pincer gold(I) derivative with even highly electrophilic metal salts leads to the direct synthesis of the corresponding pincer metal derivative. It has been demonstrated that the gold(I) phosphine salt that is quantitatively formed can be recovered and recycled, see Fig. 5 [41, 46].

When more elaborate pincer metal platforms are needed, a choice can be made between either a route in which the organic pincer ligand is synthesized first which is then followed by the regioselective introduction of the metal grouping or an alternate protocol involving prior introduction of the metal center followed by functionalization of the resulting organometallic ECE-pincer metal compound. For example, the chiral pincer palladium compound shown in Fig. 6 has been synthesized by making first the bis-*ortho*-hydrocarbonylpincer palladium compound (which in itself is an interesting case with monodentate-*C*-coordination of the OCO-pincer ligand) followed by a condensation reaction that creates the final ligand framework [47].

In the next step, the aldehyde groupings have been selectively converted into the chiral *ortho*-scaffolds. The resulting enantiopure compound was one of the first chiral pincer-metal complexes to be successfully used in enantioselective catalysis [41, 47].

Further examples of postderivatization of pincer metal compounds are shown in Fig. 7 [48]. Starting from the iodo–bromo pincer compound, a chemoselective biscycloplatination has been carried out followed by a selective lithiation through a lithium–iodide exchange reaction (with *t*-BuLi) at low temperature. Subsequently, the lithium–platinum pincer intermediate is quenched in situ with an appropriate electrophile. This is the preferred route for the synthesis of materials carrying a large number of pincer metal entities, e.g., in the case of the synthesis of metallodendrimers for which purification procedures are cumbersome or

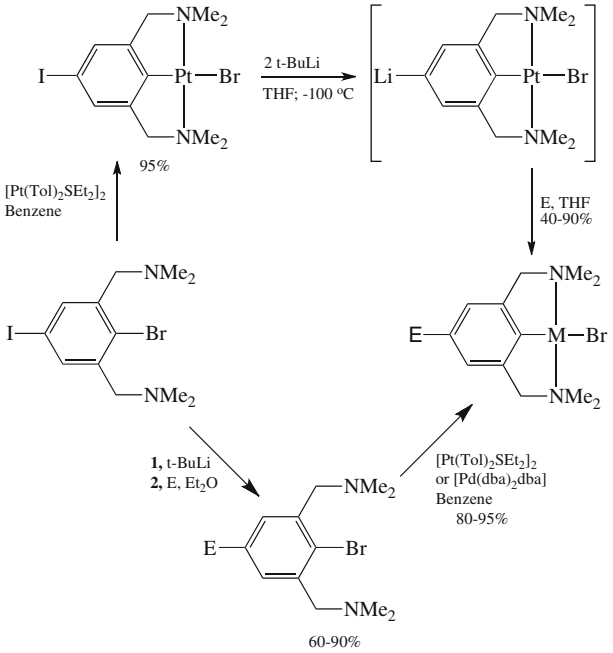

Fig. 7 Electrophile E is, e.g., CO_2, MeSSMe, $ClP(OEt)_2$, $ClSiMe_3$, M = Pd or Pt. Comparison of the synthesis of *para*-E-NCN-pincer palladium and platinum complexes by either prior metal introduction and then functionalization or synthesis of the complete pincer ligand and then metal introduction (postderivatization)

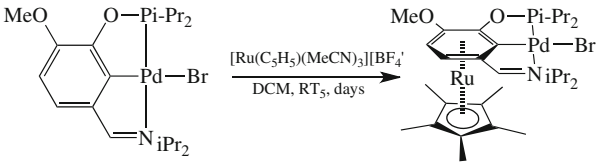

Fig. 8 Example of postderivatization resulting in the direct synthesis of a chiral η^5-Cp*-η^6-(PCN-pincer Pd bromide)Ru complex

impossible. Moreover, starting from the in situ prepared lithium–platinum pincer intermediate (see Fig. 7), N-, O-, and α-C-pincer metal substituted α-aminoacids are accessible as well as polypeptides having distinctly positioned pincer metal moieties [48].

Another example of postderivatization, i.e., the direct synthesis of a chiral ruthenium–palladium–pincer derivative, as exemplified in Fig. 8, has recently been reported. Its synthesis involves an electrophilic attack of the arenophile $[Cp^*RuL_3]^{3+}$ on the arene ring of a planar chiral imine-phosphite pincer palladium bromide compound [49].

4 Stability and Decomposition Pathways of Pincer-Metal Complexes

Many of the ECE-pincer metal compounds have a surprising thermal stability (decomposition on heating far above 100 °C) in comparison to similar compounds having the same set of E- and C-bonded groupings that are not, however, connected to one another as is the case in the ECE-pincer platform. Moreover, this stability is often accompanied with unmatched chemical stability of the central σ–M–C and the tridentate pincer motif, i.e., the pincer metal interaction is retained in reactions of pincer metal complexes with materials such as water, weak acids; small molecules such as CO, SO_2, isocyanides, dihydrogen, dihalides; oxidizing agents such as dioxygen, iodosobenzene, peroxides; and reducing agents such as organolithiums or even Na metal. However, these reagents can facilitate changes in the formal oxidation state of the metal or may lead to a modification of the pincer arene moiety, cf. Figs. 7 and 8. An interesting example is the reaction of PdCl (i–Pr–PCP) with Na in THF that leads to collapse of the mononuclear complex to an unprecedented bispincer bispalladium complex containing one nonplanar diamagnetic Pd(II) center P,C-bonded to two PCP ligands whereas the second palladium center is a 14e Pd(0) center that binds the remaining P ligands of each of the two PCP ligands (for an X-ray, see Fig. 7 in [21]). Regeneration into the original PdCl (i–Pr–PCP) complex occurs on oxidation of the $(PCP)_2Pd(II)Pd(0)$ complex with either a silver salt or electrophile such as benzyl chloride [50].

A seminal discovery was the extremely high catalytic activity (5×10^5 t) of PCP-pincer palladium complexes such as 2,6-bis[(diiso-propylphosphino)methyl] phenylpalladium TFA in Heck coupling reactions (e.g., the reaction of iodobenzene with methyl acrylate in NMP) at temperatures around 140 °C during extended reaction times (>300 h) [51]. Extensive research followed this observation and clarified both the mechanistic aspects of this and led to the study of related C–C coupling reactions (e.g., Heck, Suzuki–Miyaura reactions, etc.). Hence, the search for the optimum structure reactivity relationship of the pincer palladium precursor in this catalysis area was undertaken. At first, a Pd(II)/Pd(IV) cycle, with retention of the pincer palladium platform, was proposed as a likely mechanism. However, consensus seems to have revised these hypotheses on consideration that the pincer metal compound acts simply as a precatalyst. The pincer-metal species decompose gradually thereby producing palladium nanoparticles (NPs) upon which the actual conversion of reagents to products occurs on the NP surface [52–54]. This view is supported by experiments with supported pincer–palladium catalysts, through experiments with poisoning reagents (e.g., Hg), the results of kinetic and spectroscopic studies as well as from the application of computational techniques. Ample evidence is now available that pincer palladium complexes function as sacrificial species that gradually produce Pd NPs. The rate at which this decomposition occurs is important for the size and constitution of the resulting Pd NPs. If the decomposition of the pincer palladium precursor is too fast, catalytically inactive Pd black is formed. Finally, it cannot be excluded that the pincer–arene species formed (next to

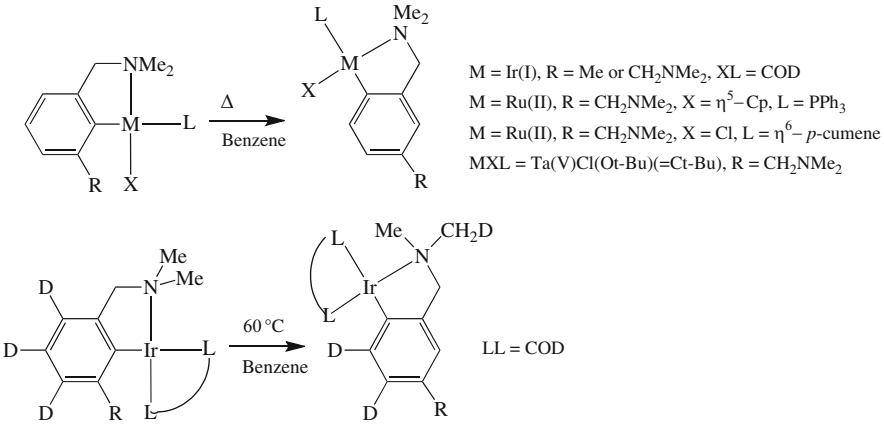

Fig. 9 Documented rearrangements of the NCN-pincer metal platform in NCN-pincer Ir(I), Ru (II), Ta(V) compounds

the Pd NPs) will ultimately also affect the size and constitution of the NPs by absorbing onto their surfaces. Consequently, this interaction can be expected to affect the aggregation rate of these particles as well as the activity of the Pd(0) species at the surface in subsequent catalytic cycles.

In the above-mentioned reactions, it is the cleavage of the M–C_{ipso} bond that is the cause for the (controlled) decomposition of the ECE-pincer metal compound at higher temperatures. This (homolytic) bond cleavage leads to destruction of the pincer metal platform. However, loss of the unique stability and reactivity properties of the ECE-pincer metal motif can also occur as a result of selective rearrangement of the bis-*ortho*-E, C, E arrangement to an *ortho*-E, *para*-E, C one.

In addition to the decomposition by homolytic C–M bond cleavage, occurrence of this selective rearrangement is of particular importance when ECE-pincer metal compounds are used as catalysts or, for example, in sensor devices. So far, these rearrangements have been observed for NCN-diamino pincers if the metal is Ir(I) [55], Ru(II) [56], or Ta(V) [57], again emphasizing the importance of the nature of the donor atoms E. In Fig. 9 a number of the observed rearrangements are summarized. The observed rearrangement of the pincer anion from the bis-*ortho*-N, C_{ipso}, N arrangement to an *ortho*-N, *para*-N, C_{ipso} could be extensively documented by model experiments and selective deuterium-labeling protocols. With all three metals, this rearrangement was kinetically driven by the fact that in the final *ortho*-N, *para*-N-isomer, the other *ortho*-position next to the C_{ipso}-metal bond is occupied by a C–H functionality rather than a free, sterically demanding CH_2NMe_2-grouping, as would be the case in the bis-*ortho* chelated-isomer. This makes the C–H activation and subsequent oxidative addition processes irreversibly running towards the formation of a thermodynamically most stable isomer. It must be noted that these processes occur intramolecularly and provide almost quantitative yield of the rearranged product. For the NCN-pincer Ir COD compound, the result

of ^{2}H-labeling is shown. The process of apparent 1, 3-Ir migration involves four separate C–H bond activations in concert, see [55] for details of this rearrangement mechanism.

5 Reactions with Electrophiles

Organometallic complexes often undergo M–C bond cleavage in the presence of acids. In contrast to this common observation, a great variety of ECE-pincer metal complexes are stable in acidic media. However, in the case of NCN-pincers the *ortho*-amine substituent can become quaternarized (with retention of the M–C_{ipso} bond), see Fig. 10. As it is exclusively the free amine donor that undergoes quaternarization, this observation indicates that the M–N bond undergoes regular dissociation–association [19].

Reactions with electrophiles (e.g., H_2, X_2, alkyl halides) can lead to oxidative addition at the metal center of a pincer-metal complex with concomitant change of its formal oxidation state. Subsequent reductive elimination either involves the ancillary ligands or C_{ipso} of the pincer itself. Exchange of the ancillary halide ligands, as shown in Fig. 10, is observed in the reaction of Me–I with the neutral NCN-platinum halides [58]. However, the reaction of the cationic NCN-pincer platinum water complex with Me–I [58, 59] (and, e.g., benzyl iodide) [60, 61] takes an entirely different course (Fig. 10). This reaction results in quantitative formation of the arenium species via a 1, 2-shift of the methyl group along the Pt–C_{ipso} bond thus *making* a new C–C bond. In this process the formal Pt(II) oxidation state remains unchanged. During the entire process the *N, C, N*-terdentate bonding mode is retained. This is even the case when, in a subsequent reaction, the arenium cation is reacted with, for example, a strong but sterically large nucleophile. As shown in Fig. 10, the regioselective attack of the nucleophile at the 4-position converts the arenium ring into a 2, 5-cyclohexadien-1-yl. Smaller nucleophiles attack at the kinetically more favorable 2-position (not shown in the figure). These processes, including the C–C bond *cleavage*, are reversible [62]. However, once the C_{aryl}–C_{methyl} product has dissociated from the Pt center, the reaction becomes irreversible. That is, the free 1-Me-2,6-$(Me_2NCH_2)_2C_6H_3$ cannot recoordinate to a suitable Pt salt in the proper coordination geometry to effect cleavage of the C_{aryl}–C_{methyl} bond and hence re-enter in the reaction scheme shown in Fig. 10. This observation underscores the great importance on activation processes that are governed by the coordination power of the *ortho*-donor atoms in pincer-metal complexes and pincer-type starting materials. This is nicely demonstrated in reactions of 1-alkyl-2, 6-$(R_2PCH_2)_2$benzene compounds with $PtCl_2COD$ as studied extensively by Milstein et al., see Fig. 11 [21].

This reaction occurs via prior P, P-bidentate chelate bonding of the arene pincer and then proceeds to initiate alkyl-C bond cleavage which produces the corresponding PCP-pincer Pt(II)Cl compound [63]. This reaction is only one of the many examples documented in which cleavage of the C_{aryl}–C_{methyl} bond in

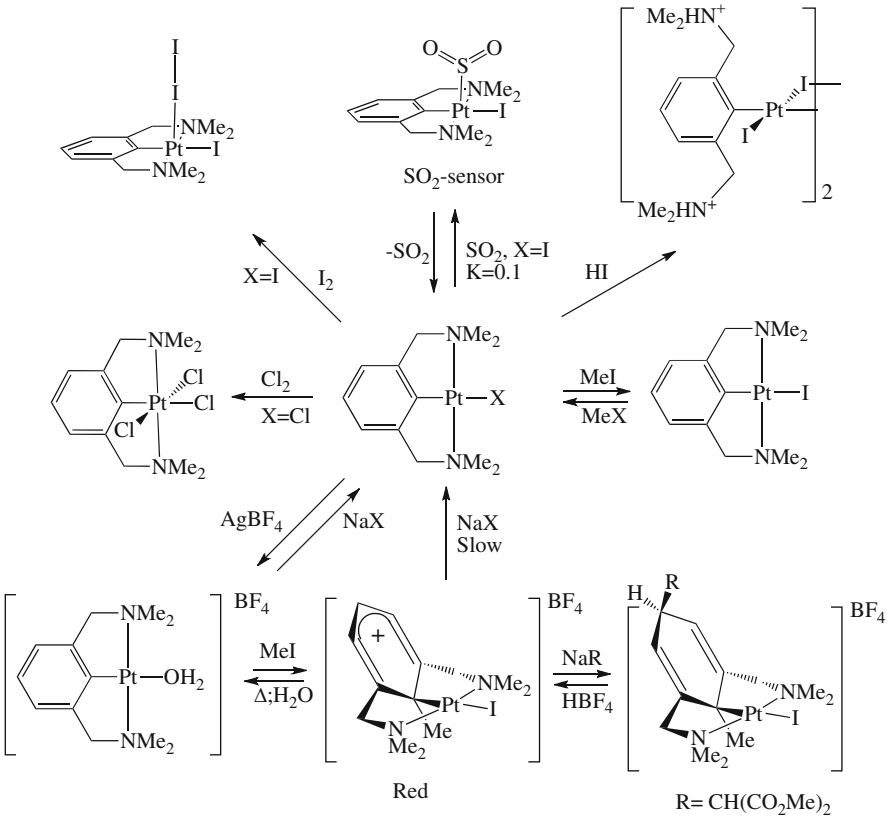

Fig. 10 Some reactions of NCN-pincer Pt(II) halide with electrophiles

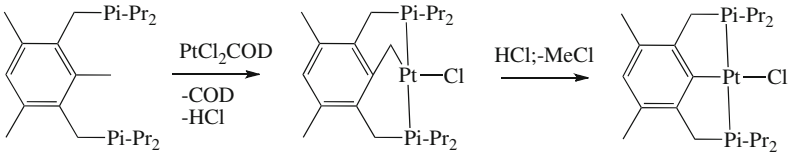

Fig. 11 C_{aryl}–C_{methyl} bond cleavage with a platinum salt

1-alkyl-2, 6–$(R_2PCH_2)_2$benzene compounds is demonstrated for a range of different metal salts (i.e., Ni, Rh, Ir, Ru, and Os). More importantly, detailed thermodynamic, kinetic, and computational studies of these processes led to vital mechanistic insights into the conditions facilitating such C–C bond cleavage processes [16]. Emerging from these studies are catalytic C–C bond activation chemistry of relevance to a number of areas of organic synthesis (see Fig. 12) [64].

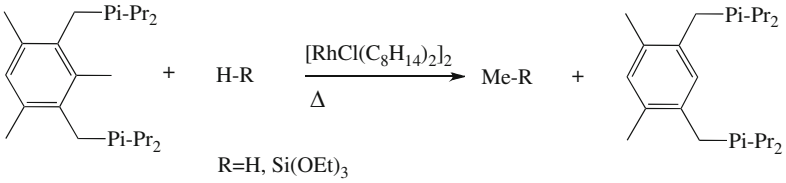

Fig. 12 Example of catalytic methyl transfer using C_{aryl}–C_{methyl} bond activation

6 Reactions with Small Molecules

During the past two decades, the pincer metal platform is increasingly used as a homogeneous (pre-)catalyst in organic synthesis and as a building block in supramolecular chemistry. This successful use of the pincer motif as a privileged ligand derives from the fact that the M–C_{ipso} bond of many ECE-pincer metal compounds appears to be relatively unreactive. In addition, because of its compact size and flexible and versatile bonding properties, the pincer ligand leaves a number of well-defined coordination sites and space available for other reactivity. Small molecules that are commonly used in homogeneous catalysis coordinate and react at the metal site of the pincer metal platform without interfering with the M–C_{ipso} bond. For example, reactions with CO yield CO complexes, whereas complexes with a similar binding set of monodentate ligands would readily undergo insertion chemistry to yield the corresponding acyl complexes. Similarly NCN-pincer platinum compounds bind *reversibly* SO_2 (in solution [65] and in the solid-state [66]) yielding the corresponding η^1-SO_2 coordination complexes (see Fig. 11) rather than yielding the otherwise expected SO_2-insertion products. Most interestingly, σ-coordination of CH_4 to the Rh center of PNP pincer Rh complexes has been recently documented [67].

Reactions with molecular hydrogen yield initially the H_2-coordination complexes and subsequently hydride derivatives. In many cases, the pincer-metal platform shows surprising stability toward reductive elimination of the hydride with C_{ipso} that would otherwise lead to formation of the arene pincer, i.e., would lead to destruction of the catalyst [cf. 21, 55]. An interesting example is the reaction of PCP-(e.g., bis-phosphine [68] and bis-phosphinite [69]) pincer Ir complexes with alkanes that yield alkenes via dehydrogenation (cf. the σ-coordination of CH_4 mentioned earlier). Crucial in these reactions is the stability of the incipient ECE-pincer Ir manifold in the Ir-hydride intermediates towards decomposition (via C_{ipso}–H bond formation). An PCP-pincer Ir catalyst with considerable stability is shown in Fig. 13 that also visualizes the application of immobilization of homogeneous pincer catalysts on solid supports [70].

These heterogenized pincer catalysts combine the advantage of homogeneous (high reactivity and selectivity) catalysis with those of their immobilized analogues (easy separation of the catalyst from products) as was first demonstrated for dendritic NCN-pincer Ni catalysts [36].

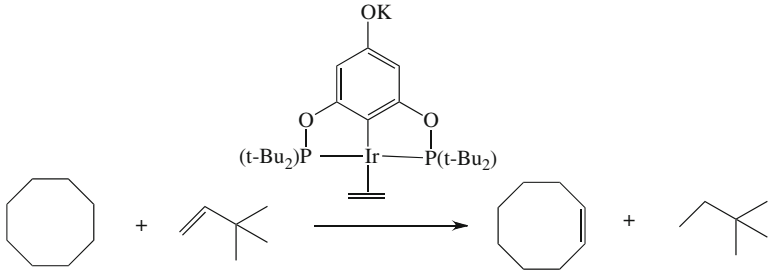

Fig. 13 Example of a highly active and recyclable (immobilized on γ-alumina) PCP-Ir catalyst for transfer dehydrogenation of alkanes

7 Pincer Complexes with Unusual Formal Oxidation States

The actual composition of the pincer platform affects both the reactivity and the thermodynamic stability of the pincer metal manifold particularly with respect to the formal oxidation state of the metal. An early observation represents the isolation of stable, paramagnetic NCN-pincer Ni(III)Br_2, see Fig. 14, from the reaction of NCN-Ni(II)X with X_2.

The facile and selective oxidation of the NCN Ni(II) to the corresponding Ni(III) complex pointed to the effect that the strong σ-donating NMe_2 groupings have on the NCN d^8-metal manifold in facilitating oxidation of the metal and hence stabilization of the resulting higher oxidation state. NCN-Ni(III)X_2 is both water and air-stable whereas related NCN-Ni(II)X oxidizes readily under these conditions to the Ni(III) species [34, 36, 37, 71]. Likewise, the presence of stabilizing *ortho*-phosphine ligands allows for the synthesis of thermally stable low valent platinum species Na[PCP-Pt(0)] [21, 72]. Relatively rare NCN-pincer Rh(II) species (NCN is "benbox") were isolated from the reaction of $RhCl_3(H_2O)_3$ with the corresponding benbox arene precursor via C–H bond activation. The complex is a paramagnetic species with a $S = 1/2$ ground state. These Rh(II) species are thermally unstable and disproportionate via a complex reaction scheme [73]. Following the early synthesis of NCN-pincerSn(II)R (R=Cl, *p*-tolyl) compounds [74], a whole series of pincer compounds were isolated and characterized having a variety of ECE′-pincer ligands [75]. Interestingly, reduction of the Sn(II) compounds with K[$HBEt_3$] afforded, instead of the desired NCNSn(II) hydride, the unusual distannyne NCNSn(I)Sn(I)NCN [76].

Until several years ago, all stable (isolated and characterized) organocopper compounds were copper(I) species [77], whereas organocopper(II) and (III) species were frequently postulated as reaction intermediates and/or transient species. This is also true for the few known pincer copper compounds, e.g., [N′NCNN′Cu(I)$_2$]$_2$[Cu(I)Br_3], see Fig. 3 [29]. This situation changed entirely when researchers started to use macrocyclic pincer type ligand platforms [78–80]. NCNCu(III)X_2 is a representative of new and exciting chemistry that afforded both stable and isolable

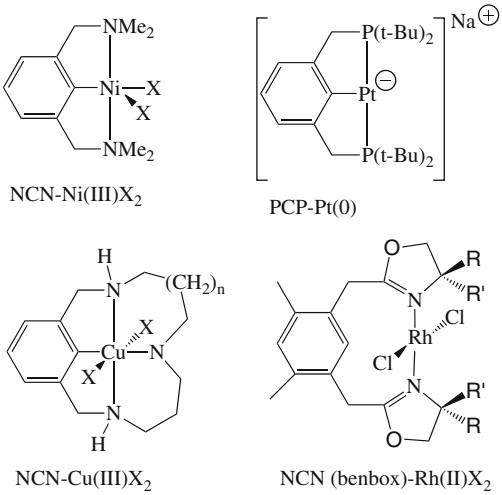

Fig. 14 Four complexes with the metal center in uncommon formal oxidation state

(paramagnetic) organocopper(II) and diamagnetic copper(III) compounds. Synthesis of these materials commonly involves C–H bond activation routes in which the C_{ipso}–Cu bond is directly formed in a reaction of the arene derivative with a Cu(I) or Cu(II) salt. These compounds are frequently used as models in mechanistic studies directed towards the understanding of copper catalyzed C–X bond formation reactions, see for example ref [80].

Unprecedented oxidative coupling process occurred when 4-methylphenolbisphosphine was reacted with $[RhCl(cyclooctene)_2]_2$ (alternately in the presence of an oxidant), see Fig. 15. This reaction afforded the PCP-pincer rhodium chloride complex, resulting from C–O bond cleavage chemistry and a bimetallic stilbenequinone.

This latter complex contains a rare η^2-coordination of the two rhodium centers to the quinonoid C=O double bonds [21, 81]. In the case of NCNRu(II)terpy, oxidative coupling with two equivalents of $Cu(II)Cl_2$ yielded the diruthenium(III) 4, 4′-C–C coupled NCN-pincer compound, and *para*-chloroNCNRu(III)terpy [82]. The detailed mechanism of this reaction has been described. It involves prior one electron oxidation of NCNRu(II)terpy to the corresponding Ru(III) species. In this latter compound, the unpaired electron is partly localized on the *para*-position. In the second step, either dimerization (by oxidative C–C bond formation) or oxidative halogen transfer (from $Cu(II)Cl_2$ with formation of a C–Cl bond at the *para*-position) occurs [83].

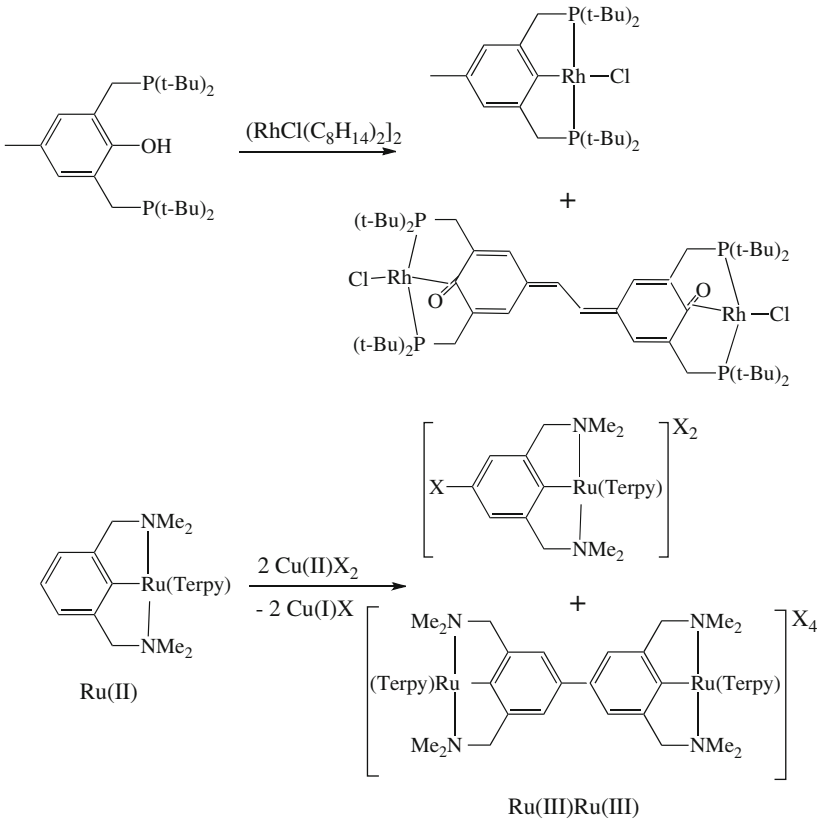

Fig. 15 Two reactions involving oxidative conversion of the pincer metal platform

8 Conclusion

Initially the pincer ligand motif, see Fig. 1, had been considered as a interesting monoanionic, terdentate ligand but with seemingly simple structural features. Since that time however (35 years later), its successful application in organometallic chemistry, materials and catalysis science has led to fascinating and novel chemistry and many unprecedented results. Many of these discoveries are a demonstration of the subtle interplay that occurs in these pincer-metal compounds between the monoanionic pincer ligand and metal center; it has given the pincer ligand motif the status of privileged ligand in organometallic chemistry that it features nowadays. Moreover, in many aspects the properties and structural features of the pincer ligand complement those of the unique cyclopentadienyl anion.

In recent years, novel pincer ligands have been developed, see Fig. 1, different connections X now representing, for example, $(CH_2)_n$ (n is e.g., 1 or 2), NH, or O and in which the anionic ligand site is not C but is a monoanionic N- or P-center

resulting in a central covalent M–N and M–P bond, respectively. Moreover, rather than having similar flanking ligands pincer platforms with two different ligand arms flanking the central covalent bond have been developed, cf. [84]. The understanding of the way these changes of the pincer platform affects both the structural features of the resulting pincer metal complexes and their reactivity is only at its beginning.

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