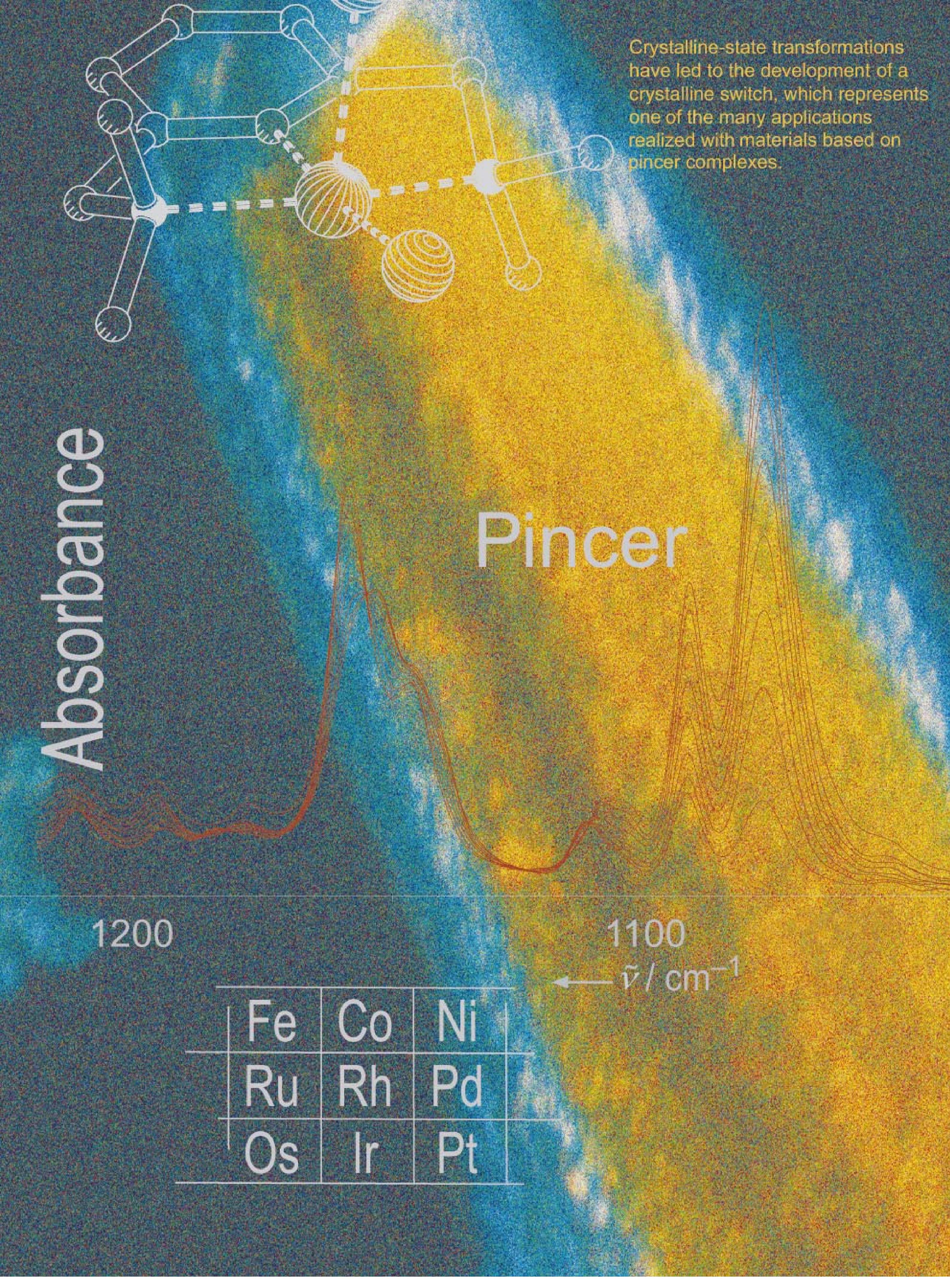

Crystalline-state transformations have led to the development of a crystalline switch, which represents one of the many applications realized with materials based on pincer complexes.

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

Platinum Group Organometallics Based on “Pincer” Complexes: Sensors, Switches, and Catalysts[**]

Martin Albrecht and Gerard van Koten[*]

Since the first reports in the late 1970s on transition metal complexes containing pincer-type ligands—named after the particular coordination mode of these ligands—these systems have attracted increasing interest owing to the unusual properties of the metal centers imparted by the pincer ligand. Typically, such a ligand comprises an anionic aryl ring which is *ortho*,*ortho*-disubstituted with heteroatom substituents, for example, CH_2NR_2, CH_2PR_2 or CH_2SR, which generally coordinate to the metal center, and therefore support the M−C σ bond. This commonly results in a terdentate and meridional coordination mode consisting of two metallacycles which share the M−C bond. Detailed studies of the formation and the properties of a large variety of pincers containing platinum group metal complexes have provided direct access to both a fundamental understanding of a variety of reactions in organometallic chemistry and to a range of new applications of these complexes. The discovery of alkane dehydrogenation catalysts, the mechanistic elucidation of fundamental transformations (for example, C−C bond activation), the construction of the first metallodendrimers for sustainable homogeneous catalysis, and the engineering of crystalline switches for materials processing represent only a few of the many highlights which have emanated from these numerous investigations. This review discusses the synthetic methodologies that are currently available for the preparation of platinum group metal complexes containing pincer ligands and especially emphasizes different applications that have been realized in materials science such as the development and engineering of sensors, switches, and catalysts.

Keywords: catalysis · cyclometalation · materials science · pincer ligands · platinum group metals

1. Introduction

The control of the properties of metal centers by a well-defined ligand system is an ultimate goal of inorganic and organometallic chemistry. Chelation, that is, the binding of a ligand to a metal through two or more bonds, is a versatile method to realize this. In organometallic complexes containing a direct (transition) metal–carbon bond, chelation leads to the formation of metallacycles, which provide additional stabilization of the M−C bond.[1] The first organometallic complexes containing terdentate monoanionic ligands were reported in the late 1970s.[2] These so-called “pincer”[3] ligands have the general formula $[2,6\text{-}(ECH_2)_2C_6H_3]^-$ (ECE) and comprise a potentially *E*,*C*,*E* terdentate coordinating, monoanionic array, where E is a neutral two-electron donor such as $N(R^2)_2$, $P(R^2)_2$ $As(R^2)_2$, OR^2, or SR^2, while C represents the anionic aryl carbon atom of the 2,6-disubstituted phenyl ring (Scheme 1, further examples are shown in Tables 1 and 2).[4] R^1 is a substituent on the aryl ring, most frequently in the 4-position, and is in this review $R^1 = H$, unless otherwise stated.

This review is restricted to an overview of the pincer chemistry of platinum group metals (Ru, Os, Rh, Ir, Pd, Pt), but includes some aspects of the chemistry of nickel complexes as representatives of the first row metals.[5] Metal complexation with pincer ligands usually occurs with formation of two five-membered metallacycles to afford complexes $[MX_n(ECE)L_m]$ (Scheme 1). A few examples are known that contain a two-carbon linkage between the aryl-carbon and the E-donor atoms, which results in the formation of six-membered metallacycles. These systems are included in the discussion where appropriate. A large variety of binding modes has been observed for the complexation of (transition) metals to NCN pincer ligands, ranging from η^1-*C* monodentate to η^3-*N*,*C*,*N* terdentate bonding as shown in Figure 1, together with one of the metals, for which a particular NCN–

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[**] In memory of Prof. Dr. Luigi M. Venanzi and his pioneering work in organometallic chemistry, particularly in PCP pincer chemistry.

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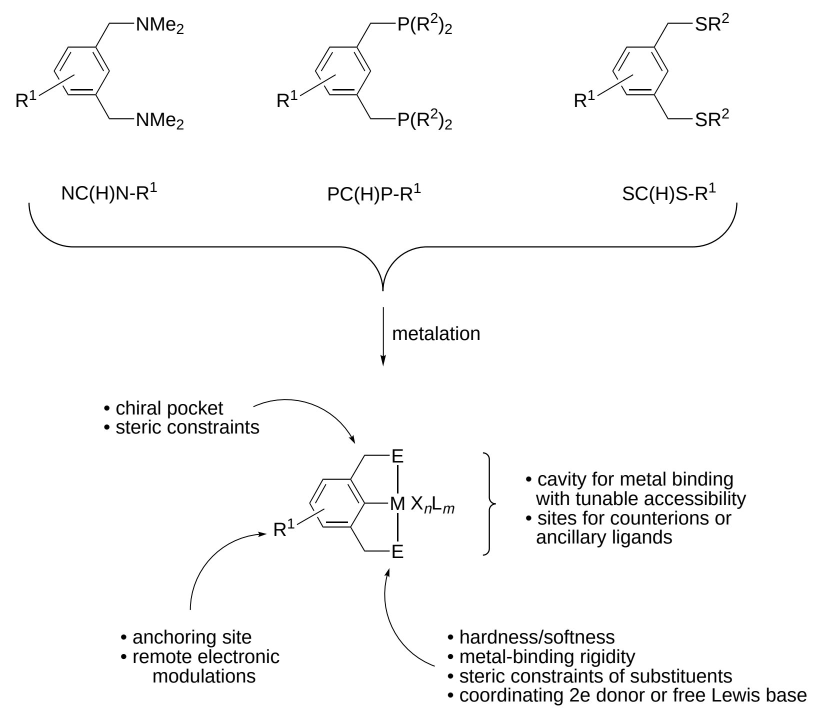


Scheme 1. Potential modification sites in pincer ligands and their effects on the properties of the metal center.

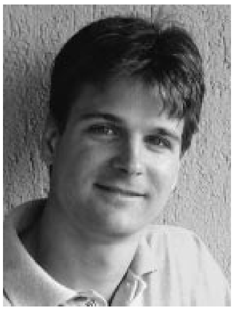
metal binding mode has been found.[6] It seems that this versatility in ECE binding is a unique feature of the NCN system, since until now neither in related PCP nor SCS pincer chemistry has such a diversity been encountered.

By far the most frequently observed is the meridional η^3-*E*,*C*,*E*-coordination mode, in which the ligand bonds to the metal center in a terdentate manner as a six-electron donor with *trans*-positioned neutral donors E. This bonding mode forces the aryl ring of the pincer ligand into a conformation which is approximately coplanar with the coordination plane of d^8 square-planar metal centers (Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}) or with the basal plane of d^6 square-pyramidal metal geometries (Ru^{II}, Rh^{III}, Ir^{III}). Modification of various ligand parameters allows for a refined adjustment of the steric and electronic properties of the complexed metal center without changing its bonding pattern significantly. In such pincer systems, the correlation of modifications in the ligand with the properties of the metal center is exceptionally high (see Scheme 1). These facts have been essential for the realization of most of the concepts and applications described herein.[7] For example, steric influences may be varied by alterating the size of the donor substituents or by introducing functional groups in the benzylic positions. Clearly, some of these modifications will also have electronic consequences. Strong electronic effects are attributed to the type of donor atoms E and the electron-withdrawing or -releasing character of their substituents. Fine-tuning of electronic properties can also be achieved by further substitution of the aromatic ring. Sites which do not exhibit significant or undesirable influences on the metal center may be used for other purposes, for example, for the introduction of molecular recognition sites or for the anchoring of the ECE–metal group to a support (see Sections 3 and 5).

Thus far, the majority of investigations have been carried out with pincer ligands containing nitrogen, phosphorus, or sulfur donor groups (that is, $E = N(R^2)_2$, $P(R^2)_2$, or SR^2.[8] Related OCO-type pincer ligands have not been used as frequently,[9] and no applications have been reported for these complexes thus far.

Gerard van Koten has been Professor of Organic Synthesis at the Debye Institute of the Utrecht University since 1986. He is Scientific Director of the Netherlands Institute for Catalysis Research (NIOK). His research interests comprise the study of fundamental processes in organometallic chemistry, the application of organometallic complexes as homogeneous catalysts (in particular for fine-chemical synthesis), and as materials with special physicochemical properties (molecular wires and switches). The preparation and use of the first examples of homogeneous metallodendrimer catalysts demonstrate his interest in supramolecular systems with (organometallic) catalytically active functionalities.


G. van Koten


M. Albrecht

Martin Albrecht was born in Geneva, Switzerland, in 1971. After obtaining his M.S. in Chemistry from the University of Bern, Switzerland, in 1996, he carried out Ph.D. research under the guidance of Professor G. van Koten. These studies focused on platinum group metals containing pincer ligands and included fundamental aspects of C–H and C–C bond activation as well as the application of organoplatinum complexes as functional devices in materials, which led to new sensors and the first crystalline switches. He was the recepient of the Backer prize for the best Ph.D. thesis in the Netherlands in 2000. Currently, he is a postdoctoral fellow with Professor R. H. Crabtree at Yale University.

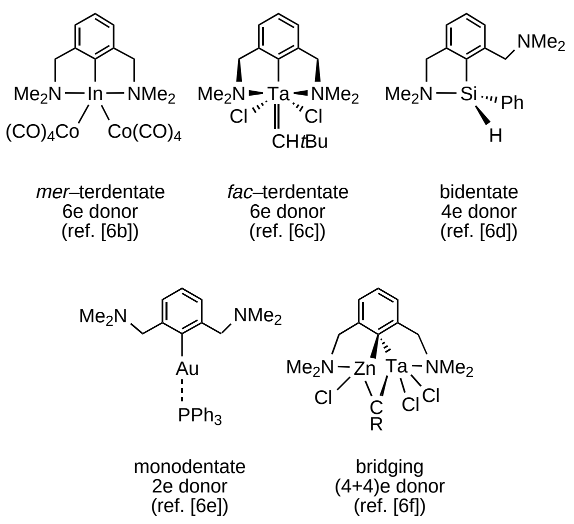


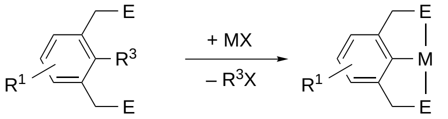
Figure 1. Observed coordination modes for NCN pincer ligands.

2. Strategies for the Metalation of Pincer Ligands

Various methods have been developed for the metalation of pincer ligands and the creation of a new transition metal–carbon σ bond. The applicability of any of these methods is strongly dependent on the transition metal M and the donor sites E of the pincer ligand.

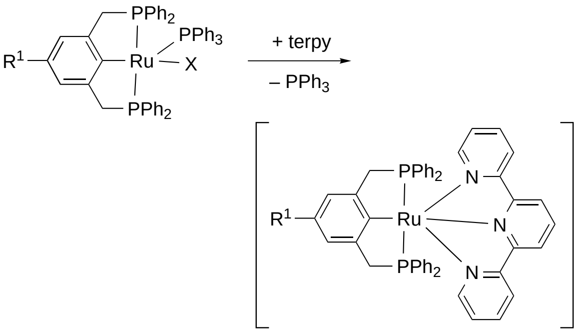
2.1. Direct Cyclometalation by C–R^3 Bond Activation

Direct cyclometalation [Eq. (1), $R^3 = H$, CR_3, SiR_3] is a particularly attractive method for the formation of a new M–C bond, since it does not require prefunctionalization of the pincer ligand in order to achieve regioselective metalation.[7b, 10] C–H bond activation and subsequent biscyclometalation was successfully used as early as 1976 for the complexation of various Group IX (Rh, Ir) and Group X metal centers (Ni, Pd, Pt) with PCP ligands ($E = P(tBu)_2$).[2a] Long reaction times and high temperatures were usually necessary. Milder reaction conditions in terms of reaction time and temperature could be used when the electron-releasing *tert*-butyl substituents on the phosphorus donors were replaced by weakly electron-withdrawing phenyl substituents ($E = PPh_2$).[11] Since then, a wide variety of phosphanes $P(R^2)_2$ ($R^2 = i$Pr, *t*Bu, Ph, Bn, for example) and metal precursors (predominantly Pd and Pt) were successfully used for direct cyclometalation.[12] However, some metal precursors failed to induce C–H bond activation even after prolonged heating, and coordination complexes containing a η^2-*P,P* bidentate coordinating pincer ligand were formed.[13] Such species have been suggested to be intermediates preceding the cyclometalation.



(1)

PCP pincer complexes of ruthenium have only recently been prepared by direct cyclometalation.[12d, 14] The ruthenium complexes [RuX(PCP)L] ($L = PPh_3$, X = Cl, OTf (Tf = trifluoromethanesulfanyl)) are highly oxygen sensitive, but can be significantly stabilized by conversion into the cationic terpyridine (terpy) complex [Ru(PCP)L′](X) (L′ = 2,2′:6′,2″-terpyridine) according to Equation (2). Remarkably, modification of the phosphane donors from PPh_2 to the more bulky $P(tBu)_2$ reduces the oxygen sensitivity of the neutral complexes dramatically. Moreover, this change of phosphane donors allowed for the borohydride-mediated preparation of various hydride complexes [RuH(PCP)L] (L = CO, μ-N_2).[15]

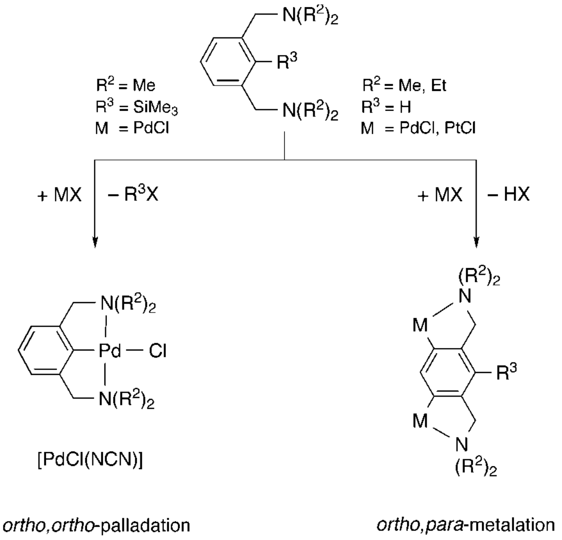


(2)

The corresponding PCP–osmium complexes are very rare, and suitable protocols for the direct metalation of PCP ligands with osmium(II)[16a] and -(IV)[16b] precursors appeared only recently. The lower valent complexes [OsX(PCP)L] have been found to readily react with terminal acetylenes to form vinylidenes and carbynes.

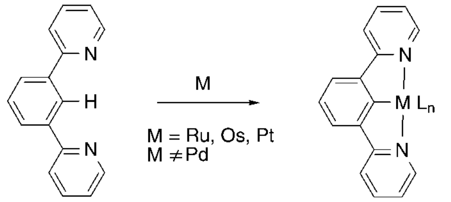
Direct cyclometalation of PCP pincer ligands with rhodium has been extensively studied by Kaska and more recently by Milstein and co-workers, and has resulted in the isolation and characterization of a series of rhodium(I) complexes [Rh(PCP)L] ($L = C_2H_4$, H_2, CO, PPh_3, N_2, carbene, for example).[17] Remarkably, appropriate reaction conditions promoted a direct cyclometalation involving C_{aryl}–C_{alkyl} bond activation [R^3 = Me, Et in Eq. (1); see also Section 4.1], thus providing an elegant access to rhodium(III) complexes of the type [RhX(R^3)(PCP)].[18] Similarly, PCP–iridium complexes can be prepared by direct cyclometalation through C–H or C–C bond activation.[17a, 19]

Direct cyclometalation of NCN pincer ligands is less common, and the topic was reviewed in 1998.[7b] The reduced tendency for cyclometalation with these ligands may be explained by the relatively low bond strength of the M–N bond. Therefore, initial coordination of the NCN pincer ligand to the metal precursor, which is an essential prerequisite for cyclometalation, is less favored than with the corresponding PCP and SCS pincer ligands. Moreover, this situation results in kinetically rather than thermodynamically controlled reaction pathways, and consequently, *ortho,para* doubly metalated products rather than *ortho,ortho*-biscyclometalated species are obtained (Scheme 2).[20, 21] Insertion of a Me_3Si substituent as a directing group on the aromatic system ($R^3 = Me_3Si$) successfully suppresses undesired *ortho*,*para*-metalation.[22]



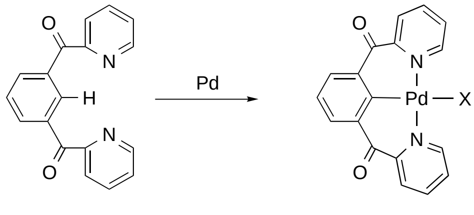
Scheme 2. Site-selective cyclometalation of NCN pincer ligands as a function of the ligand substitution pattern.

In contrast to NCN pincer ligands with amine groups, their pyridine analogues undergo facile cyclometalation with ruthenium, osmium,[23] and platinum[24] precursors to give the corresponding biscyclometalated products [Eq. (3)]. It is noteworthy that the analoguous reaction with palladium precursors did not give *ortho*,*ortho*-biscyclometalation, but resulted in metal insertion into the *ortho*,*para*-positions instead. This reactivity pattern is similar to that observed for NC(H)N ligands with palladium or platinum precursors (Scheme 2). Remarkably, introduction of a C_1 spacer between the central aryl ring and the pyridine unit (either C(=O) or CHMe) facilitated the biscyclopalladation considerably and afforded six-membered metallacycles [Eq. (4)].[25]



(3)

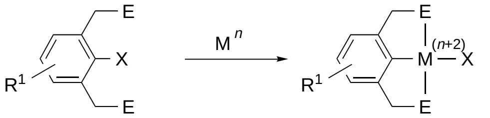
Palladation was reported for sulfur-type SC(H)S pincer ligands as early as 1980.[26] Studies using a variety of SC(H)S arene ligands have revealed that the electronic configuration of the sulfur atom and the cavity size of the SCS unit, imposed by the substituents on the donor atoms, are key factors in the promotion of cyclometalation.[27] Benzyl and aryl substituents on the sulfur donor atoms were found to enhance the rate of cyclometalation, whereas sterically demanding *t*Bu groups required prolonged reaction times to achieve comparable yields. Experiments using SC(H)S pincer ligands containing small alkyl groups (for example, $R^2 = Me$) on the sulfur atom gave the cyclometalated product in low yields only (typically 10%). These results clearly demonstrate the potential of selective and controlled ligand tuning as a means of tailoring the properties of the metal center in such pincer complexes (see Scheme 1). Remarkably, the organometallic chemistry of SCS-type pincer ligands with platinum group metals other than palladium has thus far been virtually unexplored.[28]



(4)

2.2. Oxidative Addition with Low-Valent Metal Precursors

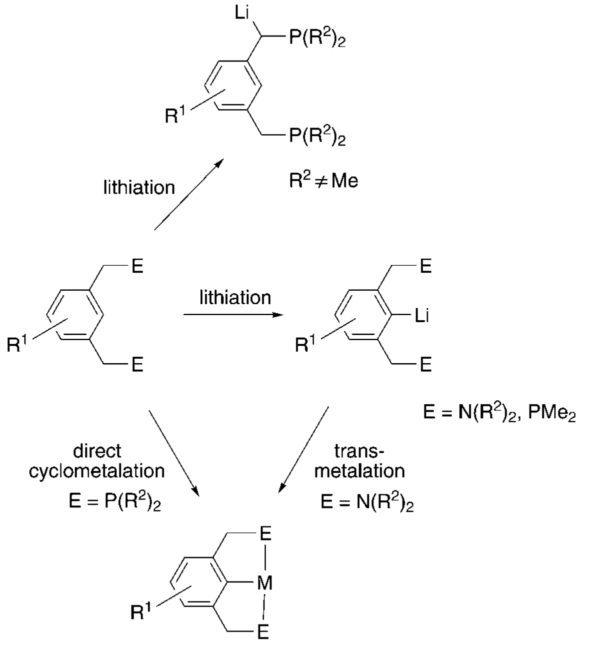
In contrast to direct cyclometalation, oxidative addition to carbon–halogen bonds [Eq. (5)] has hardly been explored in PCP chemistry, presumably because C–H activation has been a successful method for complexation with all platinum group metals. The method might become more important when further functionalization on the pincer ligand is required, for example, with acid-labile or thermally unstable substituents, since direct cyclometalation by C–H bond activation formally releases HX as the by-product [X = Cl, Br, I; see Eq. (1)]. For NC(X)N ligands, which are much more resistant to direct cyclometalation, extensive studies on the oxidative addition of an aryl halide as a means of metalation have been carried out. Synthetic protocols for the preparation of suitable ligand precursors (X = Br, I) have been developed which tolerate a large diversity of functional groups R^1 on the pincer ligand ($R^1 = NR_2$, OR, I, CHO, for example).[29] Successful approaches have included the oxidative addition to nickel (as $[Ni(cod)_2]$ or $[Ni(PPh_3)_4]$),[30] palladium (as $[Pd_2(dba)_3]$), and recently also to platinum (as $[Pt(4\text{-tol})_2(SEt_2)]_2$; dba = dibenzylideneacetone, cod = cycloocta-1,5-diene, 4-tol = 4-methylphenyl).[29c] The reaction with the bis(tolyl)platinum precursor probably involves the formation of a platinum(IV) intermediate, which reductively eliminates 4,4′-bitolyl to give the desired complex [PtX(NCN)].[31]



(5)

2.3. Transmetalation

Lithiation of PC(H)P ligands generally does not occur on the arene, but predominantly yields products arising from lithiation at the benzylic position of the PC(H)P ligand (Scheme 3). The use of an aryl halide precursor improves the



Scheme 3. Reactivity of PC(H)P and NC(H)N pincers towards lithiating agents.

selectivity, since Li/halide exchange is quantitative. However, the aryllithium species is generally not stable and isomerizes to the benzyllithium complex. This migration has been efficiently suppressed only when methyl substituents were used on the phosphorus atom ($E = PMe_2$).[32] In this case, lithiation takes place at the arene and solid-state analyses (X-ray) have shown the presence of a dimeric $[Li_2(PCP)_2]$ species with two Li-C-Li three-center, two-electron (3c-2e) bonds interconnecting the two PCP residues. This structure is closely related to those that have been isolated earlier with NCN pincer ligands (see Figure 2). Transmetalation of the lithium dimer with anhydrous $MgCl_2$ afforded the corresponding magnesium compound $[Mg(PCP)_2]$ as a thermally stable complex, which has been characterized by single-crystal X-ray diffraction studies. Thus far, however, none of these complexes have been used as a precursor for transmetalation reactions.

Lithiation of the NC(X)N ligand precursors has been extensively applied to the preparation of suitable substrates for transmetalation. Early studies showed that the choice of solvent was crucial for the regioselectivity of the reactions.[2c] In hexane, the lithiation (X = H) is an intramolecular, heteroatom-assisted process and favors C–H bond activation in the *ortho*,*ortho*-position. However, in ethereal solvents or using pincer ligands with oxo substituents ($R^1 = OR$), the oxygen-centered lone pairs exert a stronger directional influence than the amine donors and lithiation in the *ortho*,*para*-position is competitive or even dominant.[2c, 33] Selective lithiation of such ligand precursors in the *ortho*,*ortho*-position by Li/halide exchange requires appropriate prefunctionalization of the pincer ligand. Various studies have revealed that the aryllithium species are generally[34] dimers in solution as well as in the solid state (Figure 2).[35] Transmetalation of these aryllithium species is straightforward and has been applied to the synthesis of iridium, nickel,

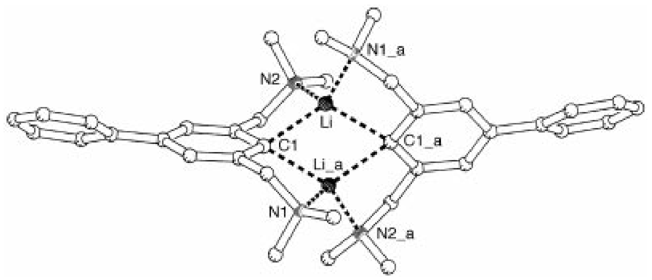
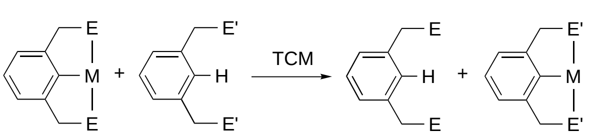


Figure 2. Molecular structure of dimeric $[Li(4\text{-}Ph\text{-}NCN)]_2$ containing a phenyl-substituted NCN pincer ligand as a representative of [Li(NCN)]-type structures.[35a,e]

palladium, platinum, and ruthenium complexes.[36] Significantly, transmetalation is thus far the only available method for the coordination of amine NCN pincer ligands with ruthenium.

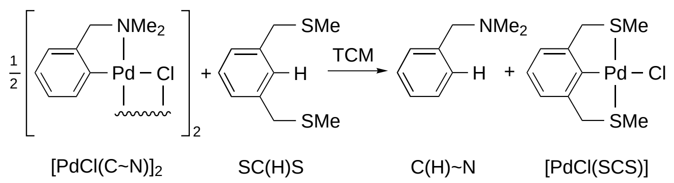
2.4. Transcyclometalation

Recently, transcyclometalation (TCM) has been introduced as a novel method for the preparation of cyclometalated pincer compounds [Eq. (6)].[37] The term is adapted from



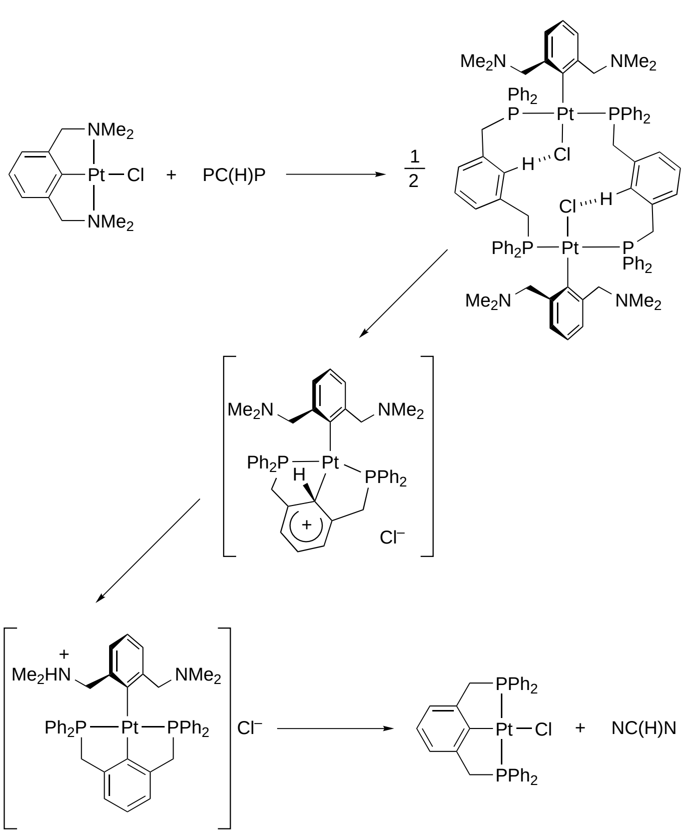
(6)

organic chemistry and is analogous to, for example, the term transesterification.[38] The latter describes the replacement of one ester group by another one without formation of a stable cleavage or addition product (for example, an acid). Accordingly, transcyclometalation describes the substitution of one cyclometalated ligand by another one without the formation of significant and detectable amounts of purely inorganic compounds (dissociated metal salts). TCM reactions were initially investigated with bidentate coordinating ligands,[39] but the concept has subsequently been extended also to terdentate-binding pincer ligands. Preliminary results included the reaction of the pincer ligand precursor SC(H)S with half an equivalent of the biscyclometalated dimer $[PdCl(C\sim N)]_2$ (where $C\sim N$ is the η^2-*C*,*N* bidentate coordinating ligand $[2\text{-}C_6H_4CH_2NMe_2]^-$), which afforded the biscyclometalated palladium complex [PdCl(SCS)] along with two equivalents of the protonated ligand $C(H)\sim N$ [Eq. (7)].[39] The product



(7)

yield was markedly improved when instead of direct cyclometalation conditions ($[Pd(OAc)_2]_3$, <10% yield) the TCM reaction was applied (>90%). Recently, the doubly cyclometalated starting materials [PtCl(NCN)] and [RuCl(NCN)(PPh_3)] have been successfully used as starting materials for the preparation of the corresponding PCP-type complexes by a TCM protocol.[37] The driving force in these reactions is most probably the higher M–E bond strength of $E = PPh_2$ (or SMe) than for $E = NMe_2$.[40] This result shows that complexes containing the NCN pincer ligand are particularly suitable starting materials for TCM reactions. In the case of platinum, this method has been studied in detail and various intermediates have been isolated and characterized.[37b] A mechanism of transcyclometalation has been suggested from these results that involves C–H bond activation through formation of an initial C_{aryl}–H···Cl–Pt hydrogen bonding and formation of a self-assembled dimer (Scheme 4).



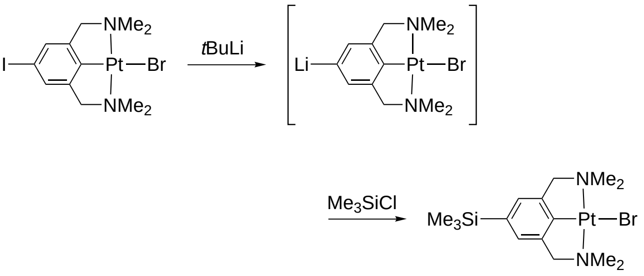
Scheme 4. Proposed reaction trajectory for the formation of a PCP–platinum complex by transcyclometalation.

Subsequent arenium formation and acid-mediated cleavage of the NCN ligand by M–C_{aryl} bond fission finally leads to the formation of [PtCl(PCP)] and NC(H)N. Preliminary investigations in analoguous ruthenium chemistry have indicated a different mechanism, however.[41] It is thus clear that various mechanisms exist for the TCM reaction which are dependent on the ligand array and the metal center. Remarkably, the TCM reaction has enabled the metalation of polyfunctional cartwheel ligands (see Section 5.3), which could not be cyclometalated by any of the three methods described above, which clearly indicates that the TCM reaction presents a different and, in certain cases, superior methodology for metal insertion.[42]

3. New Materials Properties

3.1. Stability—The Key to New Materials

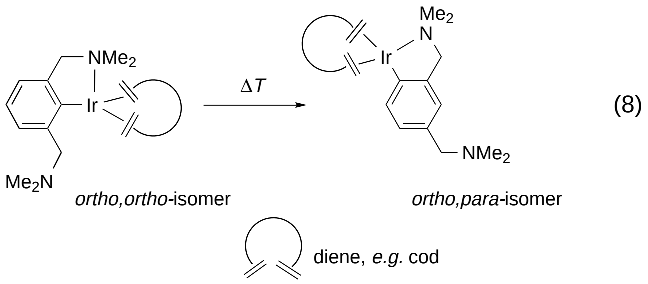
The rigid terdentate binding mode of the pincer ligands provides the metal complexes having a substantially stabilized M–C σ bond. This is best illustrated by the advances achieved in the functionalization of the pincer ligand by aryl substitution ($R^1 \neq H$). The classical protocol uses ligand modification prior to metal insertion.[24] Recent results with NCN complexes have shown that functionalization of the 4-position is possible even on the platinated complex.[43] Related palladium complexes are slightly more sensitive but also tolerate a large variety of functionalizations. For example, esterification and etherification reactions of the hydroxy group ($R^1 = OH$)[44] or amidation of a remote acid functionality (R^1 = linker with a COOH end group)[45] have been shown not to affect the organometallic site of the complex. Most interestingly, the platinum complex [PtBr(I-NCN)] was lithiated selectively at the aryl position without inducing any detectable decomposition, and the heterobimetallic complex was subsequently quenched with Me_3SiCl, which acted as a model substrate for a reactive silyl chloride periphery on carbosilane dendrimers (Scheme 5).[29c]



Scheme 5. Lithiation of NCN–platinum complexes without affecting the organoplatinum site, thus demonstrating the high stability of the Pt–C bond.

The successful performance of these reactions implies there is rigid coordination of the nitrogen atom to the metal center which efficiently protects the M–C σ bond from being cleaved. These $[M(NCN)]^+$ units (M = Pt, Pd) can therefore be envisaged as organometallic synthons for organic synthesis. Notably, strongly nucleophilic bases (for example, NaOMe, *n*BuLi) are not compatible with this synthon, but instead promote M–C bond cleavage and the formation of decomposition products, presumably by hydrogen elimination pathways. These limitations can be avoided, however, by using protecting group strategies, a concept originally developed for organic synthesis. For example, the halide X in [PtX(NCN)] has been quantitatively replaced by an acetylide anion ($X' = C{\equiv}CR$).[46] Removal of the protecting group and formation of the halide complex [PtX(NCN)] again was achieved by the addition of molecular iodine, a CuX_2 salt, or ammonium halides R_4NX (X = Cl, Br, I). These latter results illustrate the high stability of the *trans*-C-M-X arrangement in these complexes, which has also been encountered in other applications (see Sections 3.3 and 4.1). Strong evidence for this remarkable stability came from detailed kinetic investigations on exchange reactions in [PtX(NCN)] complexes and comparison with data obtained from related *cis*-[PtX(CNN)] species (X = halide, solvent molecule; CNN = pincer ligand containing mutually *cis*-coordinating nitrogen donor atoms).[47]

In contrast to the robustness of the palladium and platinum species, the related iridium complexes [Ir(NCN)(diene)] (diene = cod, norbornadiene) are configurationally unstable. A thermal isomerization process has been observed in which the metal migrates from the *ortho*,*ortho*- to the *ortho*,*para*-position of the aryl ring by sequential intramolecular C-H bond-making and -breaking processes [Eq. (8)].[36b] Isotopic labeling revealed that the process is intramolecular and probably not solvent-assisted. A similar rearrangement was observed with analoguous ruthenium complexes [RuX(NCN)(diene)] and [Ru(C_5H_5)(NCN)(PPh_3)].[48] The fluxional behavior of the CH_2NMe_2 donor groups in related rhodium(I) complexes[49] suggested that the coordination of the nitrogen atom in these complexes is much less rigid than in the corresponding platinum and palladium species. Moreover, it also demonstrates that the free CH_2NMe_2 groups represent *ortho* substituents with considerable steric bulk which make the *ortho*,*ortho* to *ortho*,*para* rearrangement an irreversible process in the complexes [Ir(NCN)(diene)] [Eq.(8)].



(8)

One aspect common to all pincer metal complexes is the high electron density on the metal center, which provides the metal with Lewis base properties.[50] The pronounced nucleophilic character is a direct consequence of the monoanionic *E*,*C*,*E* donor motif of the pincer ligand, especially of NCN ligands containing hard electron-donating amine nitrogen atoms that coordinate in a *trans* arrangement. Moreover, the rigid terdentate binding mode forces the anionic aryl ring into an orientation which is almost coplanar with the d^8-metal coordination plane. This is a significantly different situation than the one observed in classical Vaska compounds,[50c] since it enables unusual orbital overlap of the metal-centered (filled) d_{xz} orbital and antibonding π^*-aryl orbitals.[51] Nucleophilic behavior is well-documented (for example, data from UV-photoelectron spectroscopy) for the platinum(II) and palladium(II) species [PtX(NCN)] and [PdX(SCS)], respectively,[52] both of which have a filled d_{z^2} orbital as the HOMO. These Lewis bases are known to coordinate AgX or HgX_2. Confirmation of a direct metal–metal donor bond in the adducts was obtained by X-ray diffraction studies (for a platinum–mercury bond, see Figure 3),[53] and also for platinum···silver interactions by a series of early ^{107}Ag and ^{109}Ag NMR spectroscopic measurements.[54]

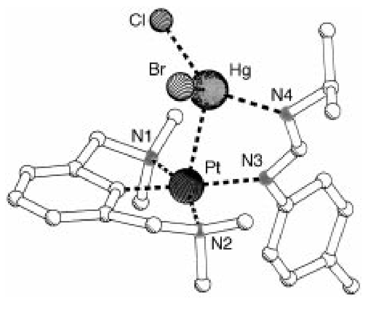
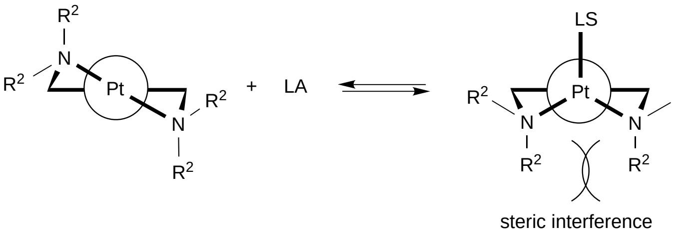


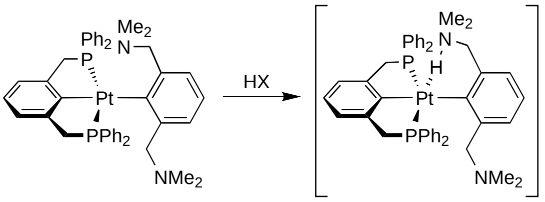
Figure 3. Molecular structure of a heterobimetallic pincer complex containing a direct platinum–mercury bond.[53a]

Another example of Lewis acid–base interaction was found between SO_2 and platinum(II) and nickel(II) (but remarkably not palladium) complexes containing NCN pincer ligands, which resulted in the reversible formation of pentacoordinate adducts.[55] Importantly, the Lewis basic character of NCN pincer complexes is strongly dependent on the functional groups on the donor sites. An increase in the steric bulk from E = NMe_2 to NEt_2 is sufficient to induce an efficient shielding of the metal *z*-axis and therefore prevents the formation of these Lewis acid–base complexes even though NEt_2 is more basic than NMe_2 (Scheme 6).[30b, 56]



Scheme 6. Repulsive interactions of large substituents on the heteroatom would cause steric congestion in Lewis acid/base adducts and therefore prevent the binding of Lewis acids (LA) by the nucleophilic metal center.

Unambiguous evidence for the Lewis basicity of the platinum centers in pincer complexes was deduced from their intriguing ability to bind a proton through a Pt···H^+ interaction.[57] Complexes containing a η^3-*P*,*C*,*P*-coordinating PCP pincer ligand and a η^1-*C*-coordinating NCN pincer ligand created a coordination pocket for reversible bidentate proton fixation through interaction with a lone pair on a noncoordinating nitrogen donor atom and the nucleophilic platinum center [Eq. (9)].[37b] Solid-state and solution measurements on the protonated analogues provided evidence for a η^2-*Pt*,*N*-chelated proton rather than a Pt^{IV}-H hydride species ($\delta_H = 11.8$, $J_{Pt,H}$ not observed, Pt···H 2.82 Å; Figure 4).[37b] Related studies using either PCP- or NCN-ligated platinum complexes containing *N*-acetyl-8-aminoquinoline at the fourth coordination site, that is, a pyridine-type ligand with an amino substituent as a potential proton receptor, confirmed this



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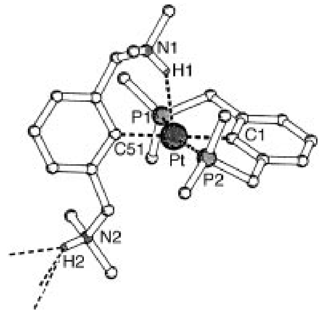
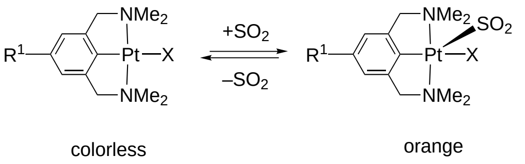


Figure 4. Molecular structure of the protonated form of an organometallic proton sponge comprising a platinum(II) center bound to a η^3-*P,C,P*-coordinating PCP ligand and an η^1-*C*-coordinating NCN ligand. The hydrogen atom is sequestered by *N,Pt* bidentate chelation.[37b]

binding mode. Proton chelation through η^2-*Pt,N* bidentate bonding was identified in the presence of an acid by extensive NMR spectroscopic analyses ($\delta_H = 13.02$, $^1J_{Pt,H} = 55$ Hz for the NCN analogue).[58] These complexes therefore represent a rare type of organometallic proton sponge.[59]

3.2. Gas Sensors

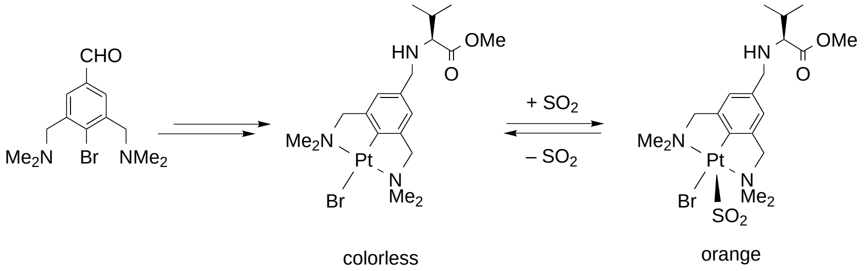
Exposure of square-planar platinum or nickel complexes containing an NCN pincer ligand to an atmosphere of SO_2 results in the instantaneous and reversible formation of the pentacoordinate adduct [MX(NCN)(SO_2)] (Scheme 7).[54, 60] This reaction occurs in the solid state as well as in solution and is fully reversible for the platinum complexes, while the corresponding nickel complexes gradually decompose—probably because of the low stability of the pentacoordinate nickel adduct. Upon binding of SO_2, the organoplatinum material undergoes a reversible color change from colorless to bright orange, which is diagnostic for the presence (or absence) of this gas. This property suggests the use of the Pt(NCN) unit as an active site for the construction of novel sensor materials for the detection of SO_2 gas. Titration measurements have shown that concentrations of SO_2 in the ppm range may be detected qualitatively and quantitatively.[60b] The threshold limit is very sensitive to steric modifications in the pincer ligand. An increase in the bulk on the nitrogen donor substituents from E = NMe_2 to NMeEt significantly lowered the sensor response (see Section 3.1), and a further increase to E = NEt_2 resulted in a complete deactivation of the sensor. On the basis of solid-state (X-ray) and solution (NMR) studies, this behavior was attributed to an efficient shielding of the d_{z^2} orbital of the metal center which is involved in the most relevant interactions with the SO_2 frontier orbitals.[61]



Scheme 7. Reversible binding of SO_2 on NCN–platinum complexes with formation of five-coordinate adducts.

Remarkably, the molecular recognition process between the platinum center and SO_2 is very selective and is not disturbed by the presence of other atmospheric gases (including CO and HCl) or humidity (H_2O). The reversible binding of SO_2 is an extremely fast process at ambient temperature and reaction rates in the order of nanoseconds were established ($k = 2 \times 10^8\,s^{-1}$). [62] Detailed kinetic investigations using low-temperature NMR spectroscopy and ab initio calculations have indicated that SO_2 bonding occurs directly at the metal site and that the metal-bound halide exerts only secondary influences on the reaction.

The high stability of platinum complexes containing the NCN pincer ligand combined with the specific NMR activity of the ^{195}Pt nucleus ($I = 1/2$)[63] suggested the use of these [Pt(NCN)] units for labeling purposes in biochemical and medicinal applications. For example, they are thermally inert in the presence of bases or strong acids (for example, 2 N HCl, 60 °C), conditions which otherwise cause rapid denaturation of proteins. A high stability of the organometallic labeling sequence under physiological conditions is essential for potential biochemical and medical applications, since heavy metal release must be strictly avoided in in vivo applications. For this purpose, the covalent anchoring of organoplatinum sites to the N-terminus of amino acids has been performed (Scheme 8).[64] These organoplatinum-labeled peptide mimics indeed showed a diagnostic NMR signal, whose chemical shift values are strongly dependent on the chemical environment of the biomarker. Hence these biomarkers provide a probe for the localization of the labeled sequence in a complex system. Additionally, they display attractive (bio)sensor properties, since such complexes detect SO_2 reversibly, which is indicated, for example, by a characteristic downfield shift of the ^{195}Pt NMR signal ($\Delta\delta_{Pt} = 1200$, compared to SO_2-free solutions).

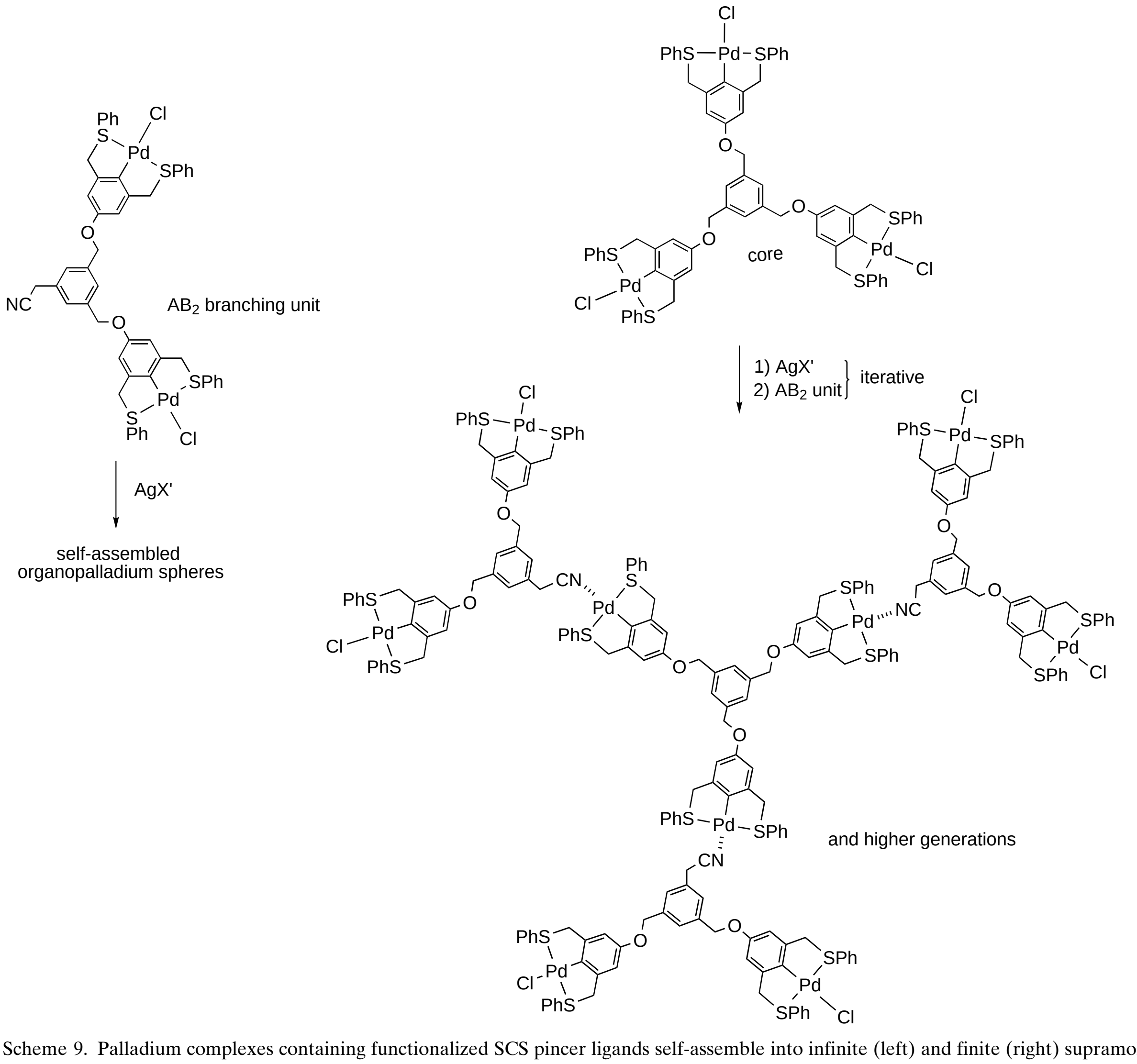


Scheme 8. Biosensors and markers obtained by covalent functionalization of the N-terminus of an α-amino acid with a diagnostic NCN–platinum site.

3.3. Self-Assembled Systems

The excellent stability of the palladium and platinum pincer complexes suggests their potential use as novel building blocks in materials science. In such square-planar d^8 complexes, only one coordination site *trans* to the M–C σ bond is left open, which can be occupied by a variety of neutral or ionic ligands. Interesting possibilities emerge from functionalization of the pincer ligand prior to metalation, for example, by aryl substitution ($R^1 \neq H$). For example, the introduction of coordinating nitrile sites into the aryl system of SCS ligands (R^1 is a linker with a CH_2CN end group) afforded a bifunctional ligand that can bind to a metal center through terdentate ECE coordination and also through weak monodentate nitrile binding. On the basis of these ideas, a bimetallic Pd_2-CN synthon and a trimetallic Pd_3 complex were prepared, which represent an AB_2 building block and a core unit, respectively, for noncovalent metallodendrimer synthesis (Scheme 9).[65] A divergent synthesis (including repetitive halide abstraction in the core molecule and subsequent addition of an AB_2 branching point) provided dendritic structures up to the 5th generation that were fabricated by controlled self-assembly. Substitution of the sulfur donors by phosphanes facilitated the incorporation of different metals and resulted in the construction of homometallic (M = Pd) and heterometallic metallodendrimers (M = Ni, Pd, Pt).[66]

A similar convergent dendrimer synthesis is difficult because of the competitive coordination strength of the focal point of the dendrons and the added branching point. Second generation dendrimers have been prepared convergently, however, by modifying the coordination site from a nitrile to a pyridine-type site.[67] Large self-assembled organopalladium spheres have been generated by halide abstraction and subsequent removal of the coordinating solvent (Scheme 9).[68] Light-scattering techniques and microscopy (TEM, AFM) have revealed self-assembled particles in the submicrometer range (estimated diameter roughly 200 nm). The noncoordinating anions were assumed to play a key role during surface congestion—a process that determines the end-point of the self-assembly and hence the particle size. Moreover, branching of the building blocks seems to be essential for spherical self-assembly. Notably, the noncovalent (that is, coordinating) interactions between the building blocks are formed rever-



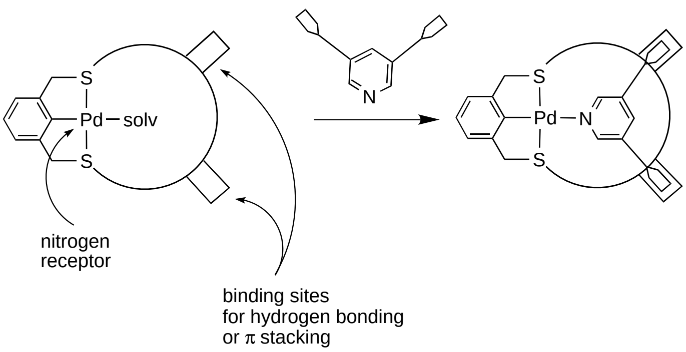
Scheme 9. Palladium complexes containing functionalized SCS pincer ligands self-assemble into infinite (left) and finite (right) supramolecular structures.

sibly and are highly sensitive towards the presence of small coordinating molecules (for example, H_2O, Cl^-), which disrupt the self-assembled structures within a few minutes.

Similar coordination chemistry has been employed for the construction of supramolecular assemblies from bimetallic synthons (Scheme 10).[69] Depending on the pyridine-type ligand occupying the fourth coordination site (pyrazine or 4,4′-bipyridine),[70] either linear polymeric structures or molecular macrocycles can be obtained. The latter result from a [3+3] self-assembly of the bimetallic building block and 4,7-phenanthroline.[71]

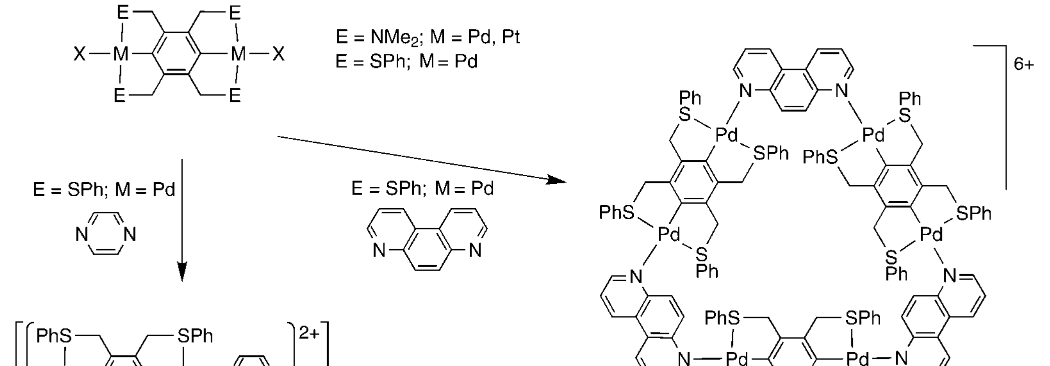
On a supramolecular level, these assemblies correspond to host–guest interactions, where the [Pd(SCS)] moiety serves as a host (receptor) for nitrile and pyridine guests. Loeb and coworkers have refined the host system in order to achieve more-selective binding sites for specific guest molecules.[72] For this purpose, the sulfur donors were functionalized with bridging polyether or calixarene substituents that were to act as receptors for secondary host–guest interactions. As a result, Pd⋯N coordination is assisted by secondary hydrogen bonding of guest protons to crown ether oxygen atoms or π-stacking interactions with calixarenes (Scheme 11). Modification of the ring size and oxygen distribution in the dithiamacrocycle allowed for the optimization of the binding pockets of these metalloreceptors. Various host–guest complexes have been prepared with amines, imines, and water. In most cases, secondary hydrogen-bonding interactions have been established in the solid state. However, competition studies have revealed that selectivity in these reactions is generally low. The most promising results have been obtained for the selective recognition of purine bases. The complexation of cytosine was preferred in these systems, and thymine was efficiently discriminated against, provided that the solvent and macrocyclic ligand system were appropriately chosen.[73] The employment of two sequential extraction steps has also allowed for the differentiation between guanine and adenine, and hence for the specific detection of all DNA nucleobases.

Similar macrocyclic NCN ligands without additional recognition sites have been metalated with rhodium, palladium, and platinum.[74] Detailed NMR and X-ray studies revealed a high flexibility of the macrocycle and indicated that the metal coordination site *trans* to the metal–carbon bond is significantly shielded.[74b,c]

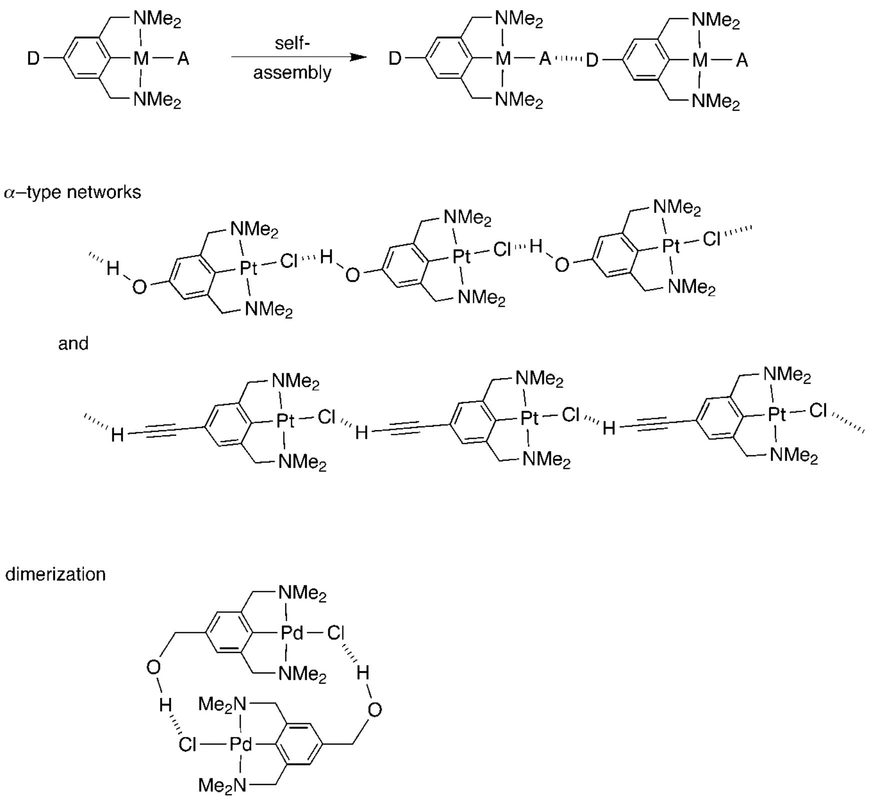


Scheme 11. Schematic representation of palladium complexes containing SCS pincer ligands that are functionalized with secondary recognition sites for substrate discrimination.

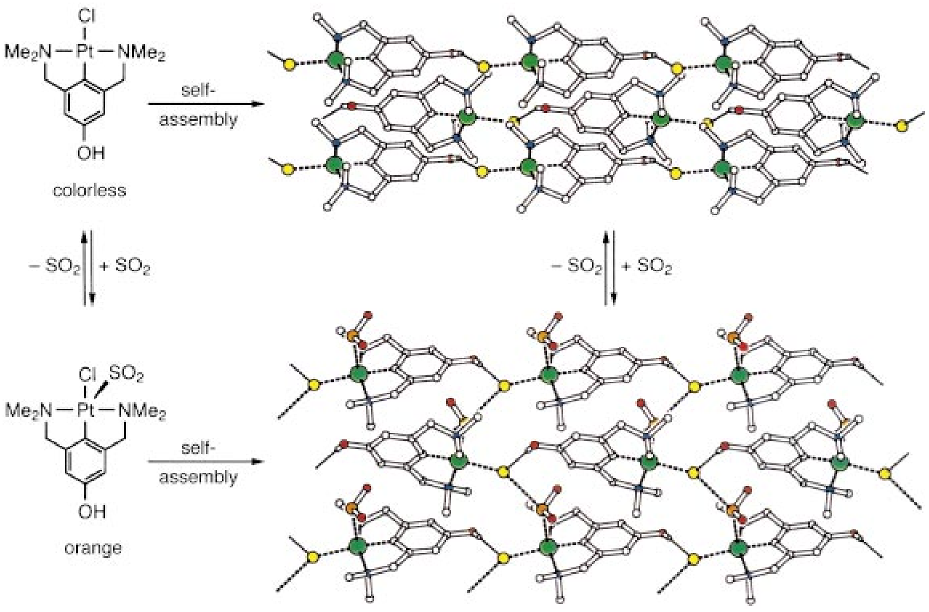
A different supramolecular synthon, which proved to be suitable for crystal engineering, has been prepared by incorporating directional hydrogen bond donor (D) and acceptor (A) sites on the metal–pincer complex. One suitable design has involved the introduction of hydroxyl or acetylene substituents onto the aryl unit of the NCN pincer ligand (D = OH, C≡CH, or CH_2OH, Scheme 12) as hydrogen donor groups and a platinum-bound chloride ion as the hydrogen acceptor.[75] This configuration promoted the hydrogen-bond-mediated self-assembly of these building blocks through O–H⋯Cl–M or C≡C-H⋯Cl–M interactions (M = Pd, Pt). The specific architectures that are formed by this self-assembly are strongly dependent on the flexibility of the hydrogen bond donor and acceptor sites. For example, the CH_2OH donor promoted the formation of discrete dimers, whereas hydroxy or acetylene donors induced the formation of infinite linear, α-type networks. Interestingly, these networks are present in the solid state as well as in solution, as has been demonstrated by IR spectroscopy.[75a] The addition of gaseous SO_2 to the hydroxyl complex resulted in the formation of the corresponding adducts. The O–H⋯Cl–Pt hydrogen-bonding motif is also conserved in the adduct in the solid state. In addition, these chains are superimposed by orthogonal Pt–$S(O)_2$⋯Cl interactions.[60a] Hence, the addition of SO_2 interconnects the self-assembled hydrogen-bond chains and results in the formation of β-type networks (Scheme 13).



Scheme 10. Pyridine derivatives control the self-assembly of bimetallic SCS–palladium building blocks into hexametallic cycles and polymetallic chains.



Scheme 12. Appropriate ligand functionalization with donors (D) or acceptors (A) promotes the self-assembly of palladium and platinum complexes through formation of M–Cl···H hydrogen bonds.

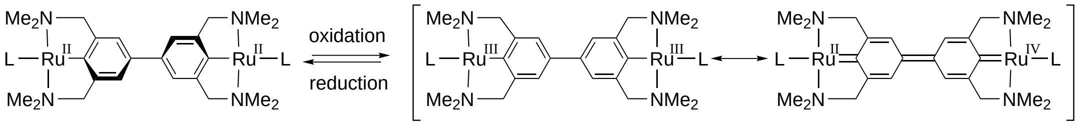


Scheme 13. A SO_2-triggered switch that operates in the crystalline phase.

3.4. Switches

Since the bonding of gaseous SO_2 to the platinum complexes [PtX(R^1-NCN)] occurs both in solution and in the solid state, the gas fixation process was further explored by using crystalline material. Remarkably, exposure of the crystalline material to an atmosphere of SO_2 resulted in adduct formation without destruction of the crystalline organization (R^1 = H, OH).[76] Removal of the SO_2 atmosphere promoted the reverse crystalline transformation and the crystalline starting material was recovered in quantitative yield. Spectroscopic (IR) and X-ray diffraction studies have provided unambiguous evidence that the molecular structure of the crystalline material changes significantly on SO_2 addition. Moreover, gas bonding and release are accompanied by an expansion and shrinkage, respectively, of the unit cell by more than 15 %, without affecting the materials crystallinity. Importantly, the presence of a supramolecular hydrogen-bonding network which is conserved during the crystalline transformations opens interesting applications for crystal engineering, but is not essential for the observed crystalline transformations.[77] The binding and release of SO_2 in the crystalline material of the complexes [PtX(NCN)] (R^1 = H; X = Cl, Br, I) also occurs with full conservation of crystallinity. Hence, these materials represent gas-triggered crystalline switches that are based on the self-assembly of single [PtX(R^1-NCN)] building blocks in the solid state. The color and the characteristic IR absorption bands serve as diagnostic signals to indicate the "on" and "off" positions of the switch. The development of such devices is a unique combination of crystal engineering and sensor properties of the platinum complexes [PtX(R^1-NCN)]. Such switches, which are triggered by environmentally relevant gases, have been suggested as functional devices for (opto-)electronic applications.

A different type of molecular switch is based on the redox activity of ruthenium centers that are complexed to NCN pincer dimers (R^1 = NCN; Scheme 14). Such bimetallic complexes have been prepared successfully through a $CuCl_2$-mediated C_{aryl}–C_{aryl} bond coupling of pincer ruthenium–terpyridine complexes.[78] Remarkably, these bimetallic Ru_2 complexes change their color and molecular conformation in response to the oxidation state of the metal centers (Scheme 14).[78b] For example in a reducing environment, the ruthenium centers are present in the blue Ru^{II}/Ru^{II} oxidation state and the aryl rings of the two pincer ligands are tilted by more than 20°. In the green, oxidized Ru^{III}/Ru^{III} state, however, these aryl rings are virtually coplanar and allow for metal–metal π-electron

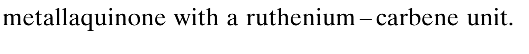


Scheme 14. Redox-active molecular switch that reversibly changes its color and conformation. L = terpy.

conjugation. This latter state is illustrated by a resonance structure comprising a C=C bond between the two aryl rings (emphasizing their coplanarity) and a mixed-valence Ru^{II}/Ru^{IV} species (Scheme 14). Importantly, the slow reduction enabled the characterization of a Ru^{II}/Ru^{III} complex in solution (cyclic voltammetry), which indicated that the oxidation and reduction are stepwise processes and that the ruthenium centers are not independent.

This latter property has been addressed by Sauvage and co-workers.[23, 79] They used homobimetallic ruthenium and osmium complexes containing dimeric NCN ligands with pyridine donors, $[M_2(NCN\text{-}NCN)(terpy)_2]^{n+}$ [see Eq. (3)], in which the two biphenyl-bridged metal centers were able to "communicate" with each other. Huge molecular extinction coefficients resulted from the stabilization of the mixed-valence M^{II}/M^{III} complexes, which points to particularly strong intermetallic interactions. Such bimetallic systems, in which the metal–metal communication may be turned on and off by applying an oxidizing or reducing environment, have a high potential for application in molecular electronics, for example, as redox-sensitive gates in conducting molecular wires.

A solvent-triggered molecular switch based on monometallic PCP–ruthenium complexes has been developed recently.[80] The prefunctionalization of the arene moiety of the PCP ligand with an acidic hydroxy group is essential for the remarkable properties of these complexes. Abstraction of the phenolic proton by an appropriate base afforded a ruthenium(II) complex which displays two limiting resonance structures [Eq. (10)]. Analysis by UV/Vis and multinuclear NMR



(10)

spectroscopy clearly indicated that the prefered resonance form is highly solvent dependent. In polar solvents, such as MeOH and acetone, the complex is yellow, and formulated as a zwitterionic species, whereas in less polar solvents (for example, THF, benzene) it is red, and formulated as a metallaquinone with a ruthenium–carbene unit.

4. Slow and Fast Catalysts

4.1. Trapping of Intermediates

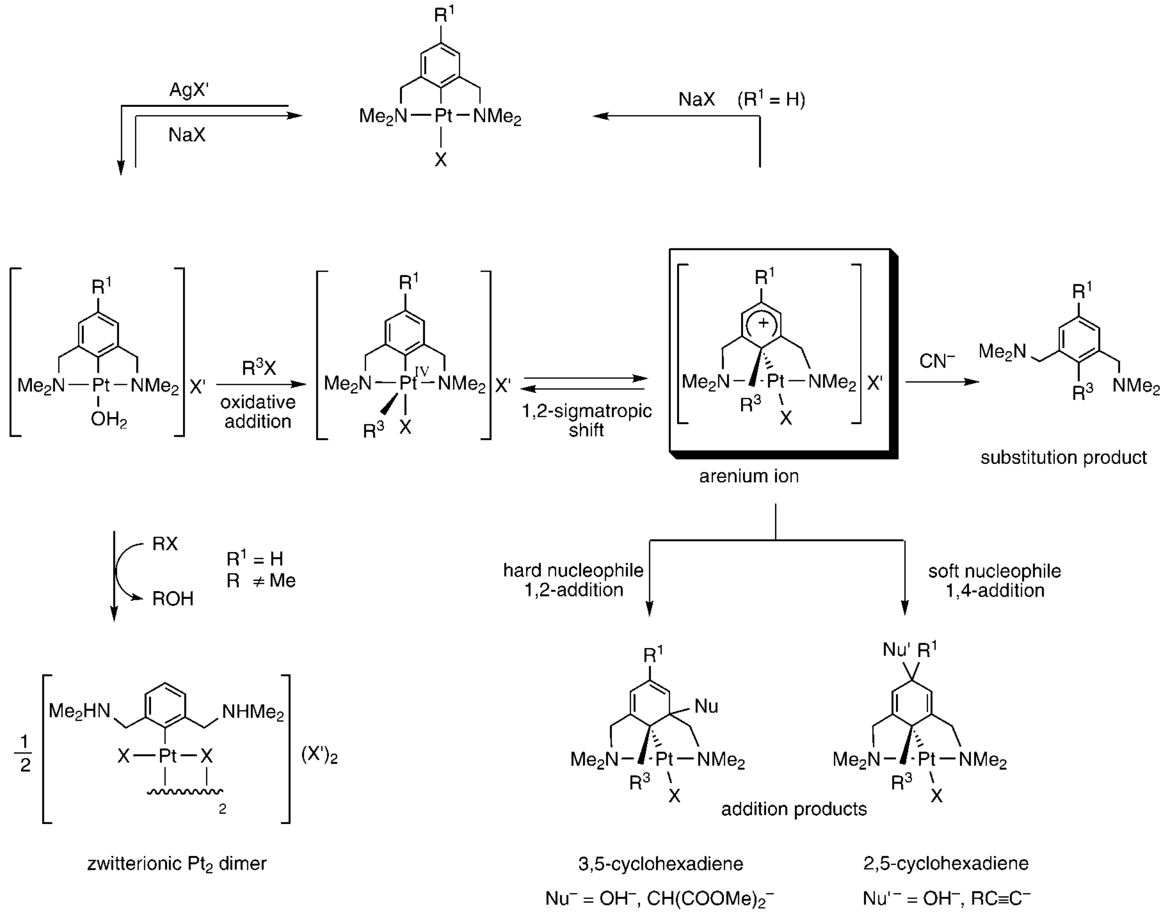
The particular electronic and steric configuration of pincer ligands has been used in several studies to tune the properties of a metal center. A particular consequence emanating from this approach is that complexes with a restricted reactivity have been generated. These complexes have resulted in reactions that were markedly slowed and sometimes even halted at a certain stage, thus providing valuable information about the mechanistic details of the reaction coordinate and about the precise configuration of key intermediates.

4.1.1. C–C Bond Activation

Major efforts have been directed towards the elucidation of the mechanistic aspects of metal-mediated C_{aryl}–C_{alkyl} bond formation and cleavage. Milstein and co-workers have focused predominantly on C–C bond cleavage (by using alkylated $PC(R^3)P$ pincer ligands; R^3 = alkyl), whereas we have concententrated on the reverse process, namely, C–C bond formation with NCN-ligated complexes and alkyl halides. Despite these different approaches, the resultant conclusions are generally congruent and indicate a uniform process that is essentially independent of the metal center and ligand system.

Upon treatment of the aqua complex $[Pt(NCN)(OH_2)](X')$ with methyl iodide (Scheme 15), the platinum-stabilized arenium complex $[Pt(1\text{-}Me\text{-}NCN)](X')$ was isolated and characterized (Figure 5).[2b, 36d, 81] As expected for arenium structures, the *ipso*-carbon atom was considerably rehybridized with sp^3 rather than sp^2 character. Consequently, the platinum coordination plane was significantly tilted with respect to the aryl plane (by more than 80°). This complex was thus proposed as a key intermediate of a C_{aryl}–C_{methyl} bond-forming process, and furthermore represents a frozen Wheland-type intermediate in electrophilic aromatic substitution. Theoretical considerations have suggested that the oxidative addition of MeI to the metal center and formation of an (alkyl)(aryl)platinum complex occurs prior to a 1,2-sigmatropic shift of the alkyl group to form the arenium product (Scheme 15).[51] These arenium compounds are stable towards air and water, as a result of the intramolecular stabilization of the platinum center by nitrogen atoms, and their reactivity could be investigated in full detail.[82] Selective bond cleavage of either the newly formed C_{aryl}–C_{alkyl} bond or the Pt–C_{aryl} bond can be triggered by a careful choice of reagents (Scheme 15). Alternatively, neutral cyclohexadiene derivatives with conserved C_{aryl}–C_{alkyl} and the Pt–C_{aryl} σ bonds can be generated by trapping the arenium intermediate with a nucleophile. The hardness of the nucleophile determines whether 1,2- or 1,4-addition products are obtained, that is, 3,5- or 2,5-cyclohexadiene pincer ligands with an sp^3 hybridized metal-bound carbon.

This reactivity pattern of platinum-stabilized arenium ions shows remarkable analogies to that of Wheland-type intermediates, which suggests there is a similar mechanism for the formation of these species. However, arenium formation was initially restricted to reactions with methyl halides, which



Scheme 15. Intermediates and product variation in platinum-mediated C–C bond-making and -breaking processes.

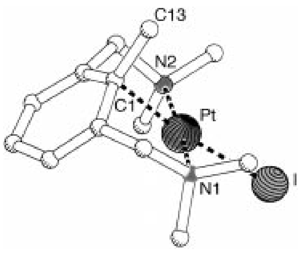
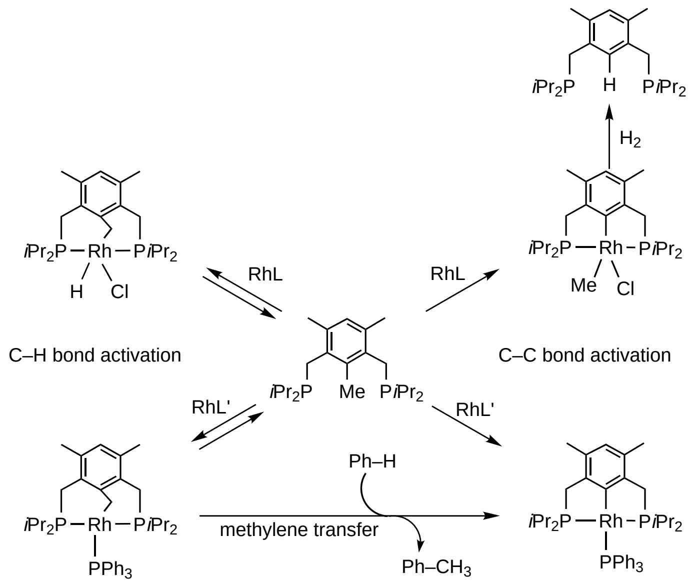


Figure 5. Molecular structure of the cationic methyl arenium complex [PtI(1-Me-NCN)]$^+$ with a newly formed C1–C13 bond as a key intermediate in platinum-mediated C_{aryl}–C_{alkyl} bond formation (the anion X′ = BF_4 is omitted for clarity).[2b, 36]

precluded extensive analyses that would allow a generalization of this reaction.[83] These reactivity limitations have only recently been successfully overcome by the introduction of electron-releasing groups on the aryl ring of the pincer ligand, a concept which is deduced from electrophilic aromatic substitution theory.[84] Arenium formation took place with various alkyl halides when platinum complexes containing oxo-functionalized pincer ligands were used [Pt(R^1-NCN)(OH$_2$)]$^+$ (R^1 = OH, OMe). Moreover, the kinetic and thermodynamic effects of these aromatic substituents, namely, activation of the aromatic ring and stabilization of positive charges, has also allowed for the spectroscopic detection and characterization of the proposed (alkyl)(aryl)-platinum(IV) intermediates, which indeed preceed arenium formation. Direct evidence has been provided for a reversible 1,2-sigmatropic alkyl shift along the Pt–C_{aryl} bond for the final transformation to the arenium species.

Activation of unstrained C_{aryl}–C_{alkyl} bonds, the microscopic reverse process of the reaction sequence described above, has been induced in the presence of a rhodium(I) precursor on an alkyl-functionalized PC(R^3)P pincer ligand (R^3 = Me, Et; Scheme 16).[7a, 18] Surprisingly, the reaction with [RhCl(coe)$_2$]$_2$ (coe = cyclooctene) and under mild H_2 pressure has been performed catalytically. A respectable 106 turnovers were obtained within 72 h when the methyl-functionalized PCP pincer ligand precursor was used.[85] A series of mechanistic investigations[17c, 19, 86] and a theoretical study[87] revealed that C_{alkyl}–H bond activation and formation of a benzylic Rh–C bond may be a competitive reaction, but not an intermediate of the C_{aryl}–C_{alkyl} bond-activation process (Scheme 16). The kinetic preference for one of the two products is strongly dependent on the reaction conditions and can be altered by an appropriate choice of, for example, phosphane substituents, rhodium precursor, solvent, or reaction temperature. In all cases, the thermodynamic product was found to be the five-membered metallacycle resulting from C–C bond cleavage, which, in contrast to C–H bond activation, is irreversible. Hence, the benzylic rhodium complexes obtained from C–H bond activation were transformed to the arylrhodium com-

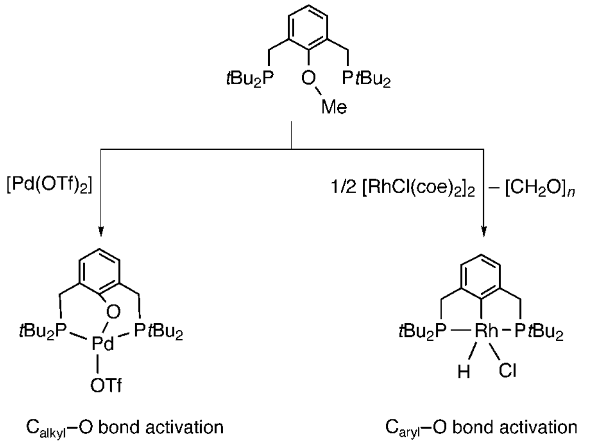


Scheme 16. Selective C–H or C–C bond activation in PC(Me)P ligands as a function of the applied reaction conditions. RhL = $[RhCl(coe)_2]_2$, RhL′ = $[RhH(PPh_3)_4]$.

plexes, a process which can be induced either thermally or by the addition of H_2. This process is presumed to reverse the C–H bond activation and results in the formal release of a CH_2 fragment (for R^3 = Me).[88] Remarkably, this CH_2 group can be selectively delivered to an organic substrate under certain reaction conditions, thus giving, for example, toluene from benzene (Scheme 16).[89] This is an interesting application of a reaction system in which the thermodynamic and kinetic preferences of product formation diverge.

Similar reaction patterns were observed upon changing the active metal center to ruthenium or platinum.[12d] In the latter system, the activation barrier for C–C bond activation is apparently too high and the benzylic complex resulting from C–H bond activation is the exclusive product. The addition of HCl induces the formation of the Pt–C_{aryl} bond, which corresponds to the net transfer of a CH_2 group of the PC(Me)P ligand to HCl. Similar product discrimination was obtained in the reaction of the methoxy-functionalized pincer ligand PC(OMe)P with different metal precursors. Palladation results in the selective formation of six-membered metallacycles by the activation of the O–CH_3 bond, whereas rhodium(I) insertion occurred exclusively into the O–C_{aryl} bond (Scheme 17).[17b, 90]

Detailed analysis of the C–C bond-activation process revealed that the reaction already occurs at low temperature (−40 °C).[91] Coordination of the phosphane donors to the rhodium ion has been established as the first reaction sequence, which results in the formation of a monomeric, or alternatively a dimeric,[13, 37b] coordination compound. No further intermediates have been observed at low temperatures, which clearly shows that the rate-determining step is the activation of this coordination compound, and that subsequent intermediates, if present, would be only weakly stabilized. A cyclopropane-type metallacycle seems to be the most probable transition state on the reaction coordinate of C–C bond activation (Figure 6a). Various structures that could mimic such a transition state have been prepared by independent routes and include rhodium-stabilized quinone methides, xylylenes, and methylene arenium complexes (Figure 6b). In all of these complexes the rhodium center is π bonded to one exocyclic double bond of the arene moiety of the PCP pincer ligand.[92]



Scheme 17. Metal-triggered preferences in C–O bond activation in PC(OMe)P pincer ligands.

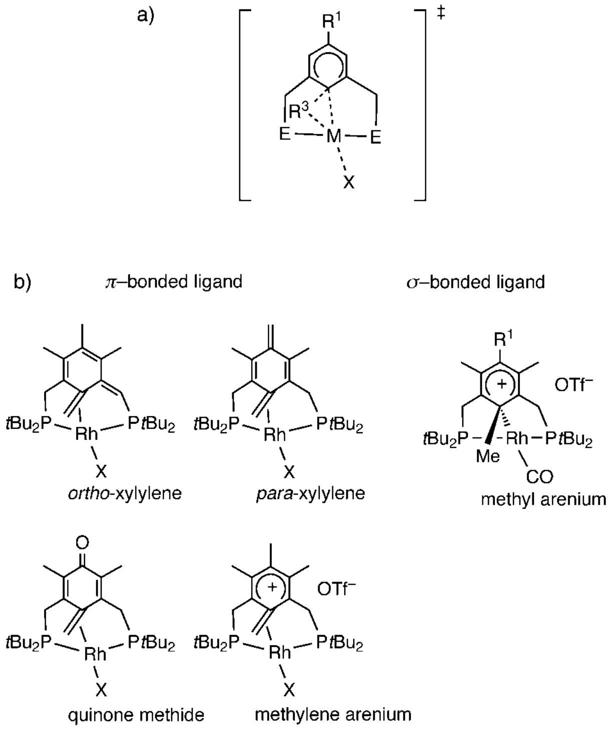
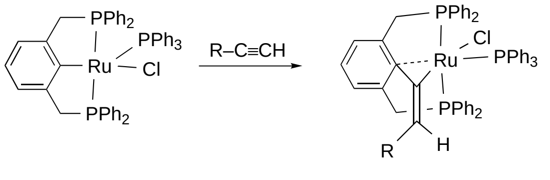


Figure 6. a) Proposed transition state in metal-mediated C–C bond activation. Depending on the substitution pattern on the pincer ligand (E, R^1) and the metal center, one or more of the weak interactions (indicated by dashed lines) is more pronounced, thus giving agostic, methyl, or methylene arenium species with more or less localized π electrons. b) Potential mimics of the proposed transition state: isolated and characterized structures containing a π- or σ-bonded PCP ligand.[92]

Another potential class of intermediates comprises alkyl arenium structures containing a Rh–C σ bond. Such intermediates have been thoroughly analyzed in related platinum chemistry directed towards the mechanism of C–C bond-forming reactions, but they are apparently less stabilized by rhodium. The addition of CO is essential to promote the formation of rhodium–arenium σ complexes from the corresponding π-coordinated methylene arenium complexes.[92c,d] Presumably, the high affinity of the rhodium(I) ion to coordinate to a π acceptor prevents a spontaneous (π → σ) rearrangement in the absence of a CO ligand. Notably, the rhodium-stabilized alkyl arenium complexes do not exhibit the typical reactivity patterns of arenium species, as established, for example, for the platinum analogues. This different behavior has been explained by a relatively strong tendency of the arene to aromatize when coordinated to a rhodium center.

Although the approaches chosen to detail the metal-mediated C_{aryl}–C_{alkyl} bond-making and -breaking process diverge considerably, for example, with respect to the metal center (Rh/Pt), the ligand array (PCP/NCN), and the overall process (C–C bond activation/formation), the results obtained display significant qualitative overlap. In both systems arenium complexes (alkyl)(aryl)metal species have been characterized, the latter only spectroscopically in NCN–platinum complexes. Moreover, the equilibrium established in the platinum-mediated process directly relates these two species to each other and corresponds to the microscopic C–C bond-making and -breaking sequence. These results suggest that C–C bond formation and cleavage have a common reaction coordinate, clearly with opposite directionality, and, depending on the metal used to mediate the reaction, have different preferences for stabilizing certain intermediates along this reaction coordinate.[84b] Therefore, the combination of the recent achievements provides a considerably refined version of a previously suggested mechanism for metal-mediated C_{aryl}–C_{alkyl} bond formation and cleavage (Scheme 15 and Figure 6).[93] Most importantly, coordination of the free ligand to the metal precursor by M–E bond formation is essential for initiating C–C bond activation. Formation of such products has been accomplished with PCP pincer ligands ($E = PR_2$), but it has not been possible so far with nitrogen donors, because of the lower bond strength of the $M–NMe_2$ bond.

A related C–C bond-forming reaction has been observed when PCP–ruthenium complexes were treated with terminal acetylenes.[94] Unusual addition products containing a bridging carbene ligand were obtained instead of vinylidene compounds [Eq. (11)]. Remarkably, these products seem strongly related to the proposed intermediate in rhodium-mediated C–C bond activation (see Figure 6a), and may result from an incomplete insertion of the vinylidene unit into the Ru–C bond. Clearly, the orbital situation at the intermediate carbene stabilizes the bridging conformation and, assisted by the chelating phosphane donors, prevents dissociation of the ruthenium atom.



(11)

4.1.2. C–H and C–Si Bond Activation

Studies directed towards mechanistic elucidation of the C–H bond activation process by using pincer ligands have resulted in the isolation of various intermediates. A compound containing an activated C–H bond was isolated as an intermediate in the transcyclometalation reaction of [PtCl(NCN)] with PC(H)P ligand precursors. The first stable intermediate in this reaction comprised a dimeric structure with two bridging η^2:μ^2-*P,P* bidentate coordinating PC(H)P ligands (see Scheme 4).[37b] Solid-state and solution studies have indicated that the PC*H*P proton was activated by C_{aryl}–H⋯Cl–Pt hydrogen bonding. Moreover, the Pt⋯*ipso*-C distance was shown to be relatively short, which suggested an aromatic substitution of the activated proton by the platinum metal center as a consequent reaction step. Indeed, cyclometalation was observed upon heating this complex and the mechanism is likely to include intermediates with agostic metal⋯ligand interactions.[95] The cationic ruthenium(II) complex [Ru(PCP)(PCHP)](OTf) comprising two PCP ligands represents a potential model of such an intermediate (Figure 7).[41] This complex was characterized by X-ray analysis and extensively by NMR spectroscopy; the latter thus provided additional information about its nature in solution. Deuterium labeling of the PCP ligands has enabled the cyclometalated PCP ligand to be differentiated from the *P,P* bidentate coordinating ligand. Interestingly, these studies pointed to a flexible coordination mode of the ligands, and evidence was obtained for a fluxional behavior of the agostic C_{aryl}–H proton which resulted from a reversible migration from the coordinated PCP ligand to the cyclometalated one.

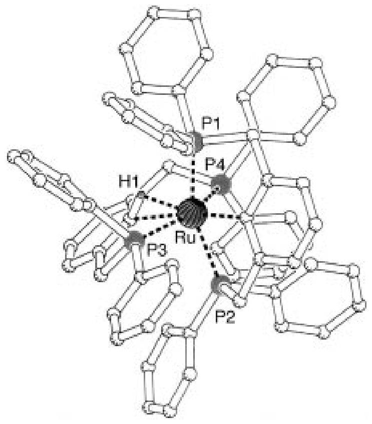
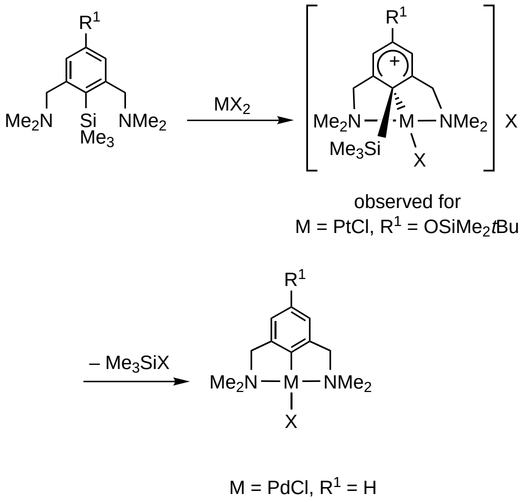


Figure 7. Agostic C–H1⋯Ru interactions in the cation [Ru(PCP){PC(H)P}] (the anion and phosphor-bound phenyl groups are omitted for clarity).[41a]

These observations for C_{aryl}–H bond activation are in good agreement with the mechanistic features established for C_{aryl}–C_{alkyl} bond activation, which suggests that the two processes are mechanistically closely related. The similarities were further underlined by the identification of hydrogen–arenium structures, which were obtained as the products after treatment of the activated platinum aqua complex $[Pt(RO\text{-}NCN)(OH_2)]^+$ with anhydrous HCl.[84b]

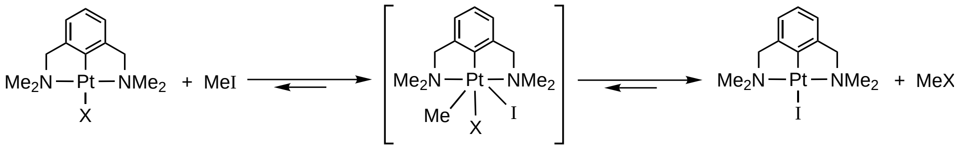
Similar results were obtained when the alkyl group was replaced by a silyl substituent ($R = SiMe_3$). Cyclometalation with a palladium(II) precursor involved selective C–Si bond activation and formation of the complex [PdCl(NCN)] (Scheme 18). This reaction was also proposed to proceed through an arenium intermediate. The kinetic reactivity of the palladium center meant that such structures could not, however, be isolated.[22] In contrast, treatment of the platinum complex [PtI(tBuMe$_2$SiO-NCN)], containing a silyl-protected oxo-group as an activator, with Me_3SiOTf resulted in the formation of highly air- and moisture-sensitive silyl arenium species.[84b] This result shows that the silyl arenium ions are reasonably stable and that such species may also represent key intermediates in silyl-directed cyclopalladation.



Scheme 18. Metal-mediated C_{aryl}–Si bond activation involving an arenium ion as a key intermediate.

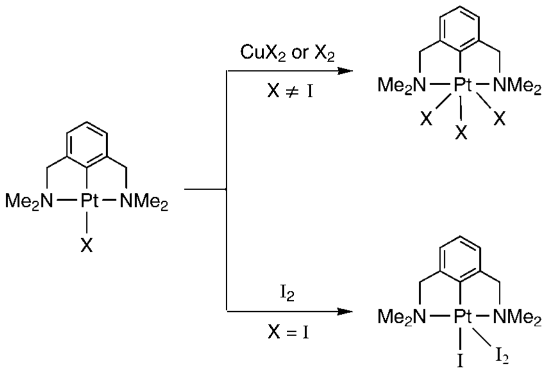
4.1.3. Oxidative Addition

As pointed out in the previous section, the addition of MeX to platinum(II) complexes containing the NCN pincer ligand does not lead to oxidative addition products that can be isolated. However, the fact that neutral platinum complexes [PtX(NCN)] (X = Cl, Br, I) react with MeI to give the complex [PtI(NCN)] along with MeX suggests the transient formation of a platinum(IV) species (Scheme 19).[81] Apparently, the subsequent reductive elimination process is faster than the corresponding oxidative addition, and hence the proposed platinum(IV) intermediate has not been observed thus far for these reactions. This situation contrasts with the reactivity of related platinum(II) complexes containing a *C,N,N,X* ligand array, since those complexes readily form stable oxidative addition products in the presence of RX.[96]



Scheme 19. Halide exchange on NCN–platinum complexes through oxidative addition of an alkyl halide.

Platinum(IV) complexes containing the NCN pincer ligand were only accessible when stronger oxidizing agents such as CuX_2 or X_2 were used.[97] The latter method is restricted to platinum(II) complexes [PtX(NCN)] that are treated with molecular chlorine or bromine. Surprisingly, the addition of iodine afforded a pentacoordinate platinum(II) adduct [PtI(NCN)(I_2)] which contains the iodine molecule bound in an η^1 (end-on) fashion to the metal center (Scheme 20).[98] An X-ray structure analysis on this adduct revealed a considerably stretched I–I bond length in the neutral I_2 ligand compared to that in free I_2 (Figure 8a).



Scheme 20. Reactivity of NCN–platinum complexes towards different oxidizing agents: oxidative addition versus adduct formation.

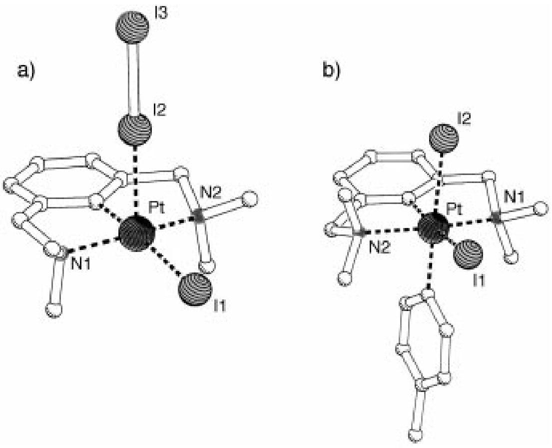
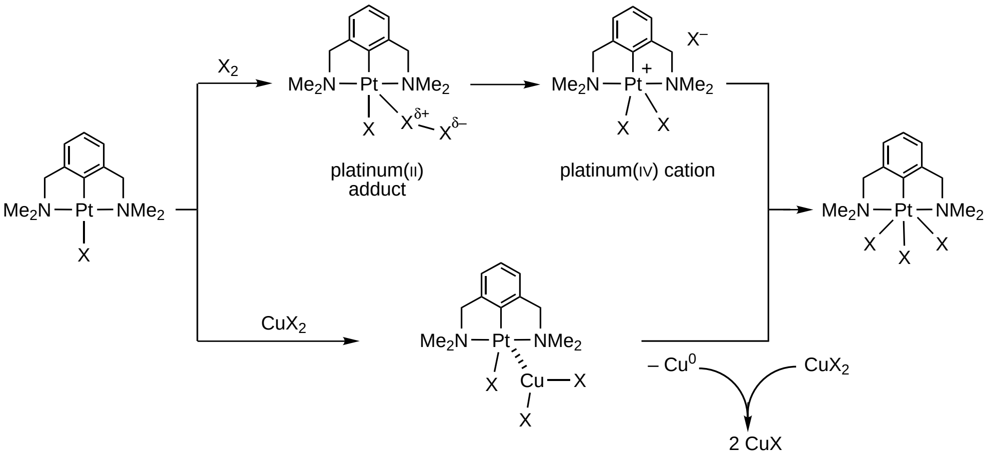


Figure 8. a) End-on (η^1) bound I_2 in the pincer platinum complex [PtI(NCN)(I_2)] as a model species for the initial stage of oxidative addition of dihalogen molecules to a square-planar d^8 metal center.[98] b) The platinum(IV) complex [Pt(I)$_2$(NCN)(4-tolyl)] obtained from oxidative addition of I_2 to [Pt(NCN)(4-tolyl)].[97]

Similar adduct formation with I_2 occurs with platinum complexes containing modified nitrogen substituents on the pincer ligand (for example, E = NMetBu).[99] Two iodine molecules bind to the platinum complex on exposure to I_2: one through η^1 coordination to the platinum center as described above and a second to the platinum-bound iodide ion to form an I_3^- ion. The presence of an iodide ligand in the starting material [PtX(NCN)] (X = I) is important for adduct formation. In the case of the corresponding chloride and bromide complexes or if ICl or IBr is used as the oxidizing agent, halide scrambling takes place to give the oxidative addition product [PtX_3(NCN)] along with the platinum(II) adduct [PtI(NCN)(I_2)].[98] The relevance of the metal-bound iodide is further underlined by the results from the reaction of the halide-free platinum(II) complex [Pt(NCN)(4-tol)] with I_2, which afforded the oxidative addition product [Pt(I)$_2$(NCN)(4-tol)] exclusively (Figure 8b).[97]

Complexes containing end-on-bound iodine have therefore been suggested as representatives of the initial stage of dihalogen oxidative addition to a (late) transition metal center.[100] Subsequent two-electron oxidation of the metal and concomitant heterolytic cleavage of the I–I bond is anticipated to lead to the platinum(IV) intermediate [PtI_2(NCN)]$^+$ and I^- (Scheme 21). A rapid trapping of the released iodide ion finally results in the neutral oxidative addition product. In the case of I_2, this process is probably halted at the first stage because of the soft character of I_2 as an oxidizing agent (relative to other dihalogen reagents), paired with the special electronic configuration of the platinum(II) center imposed by the NCN pincer ligand (the aryl plane of the pincer ligand coincides with the platinum coordination plane, thus allowing unusual overlap between the aryl π^* orbitals and the metal d_{xz} orbitals, see Section 3.1).



Scheme 21. Distinct reaction pathways for the oxidative addition of dihalogen and CuX_2 to NCN–platinum complexes.

Metal oxidation by means of CuX_2 (Scheme 21) is supposed to follow a different reaction pathway, which probably involves Pt–Cu interactions.[100] The dimetallic Pt–Hg structure shown in Figure 3 may be considered as a model intermediate in such a process. Subsequent transfer of two halide ions from copper to platinum (either stepwise or concerted) would then result in the formal oxidative addition ($Pt^{II} \rightarrow Pt^{IV}$) and reductive elimination ($Cu^{II} \rightarrow Cu^0$; Scheme 21). A fast comproportionation reaction between the formed Cu^0 species and residual CuX_2 salts is assumed to occur as the last step of this platinum oxidation process.

4.2. Catalytic Applications

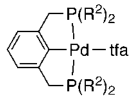
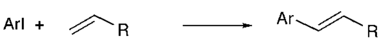
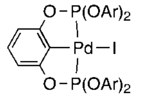
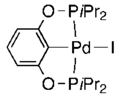
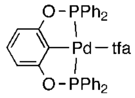
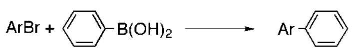
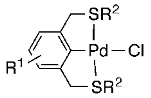
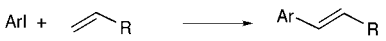
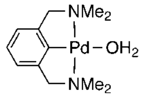
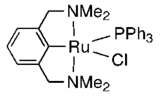
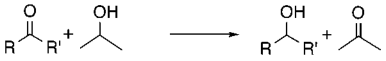
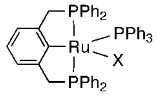
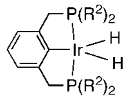
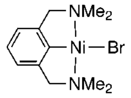
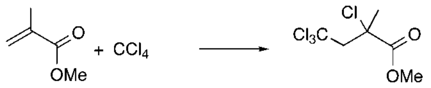
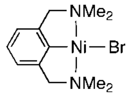
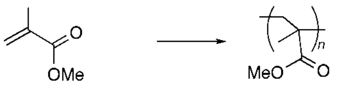
Complexes containing biscyclometalated pincer ligands offer particularly attractive possibilities for catalytic applications, since the tailoring of catalytic properties is readily achieved (see also Scheme 1): First, the terdentate binding mode and the covalent M–C σ bond stabilize the catalytically active (metal) site. This stabilization is assumed to efficiently prevent metal leaching, and hence circumvents a problem common to most catalysts containing exclusively heteroatom-coordinated metals. Second, the electronic properties of the metal center are highly sensitive towards modifications in the donor array (substitution patterns and hybridization of the donor atom E, element alteration). Electronic fine-tuning through variation of the aromatic substituent R^1 represents an additional option in some cases. Third, the steric requirements around the catalytic site may be modified to discriminate against some substrates or to create a chiral pocket for asymmetric catalysis.

When these aspects are taken into account, the availability of a broad range of powerful catalysts containing pincer ligands is no surprise. Table 1 summarizes the reactions promoted by these catalysts.

4.2.1. C–C Bond-Forming Reactions

In line with recent trends in catalysis research, the activity of various palladacycles was explored extensively and successfully.[101] Particularly impressive conversions were obtained with PCP–palladium catalysts in the arylation of alkenes, which is commonly referred to as the Heck reaction.[102] The complex [PdCl(PCP)] with $R^2 = i$Pr has a remarkable effectiveness, with turnover numbers (TON) exceeding 5×10^5 (Table 1, entry 1).[103] However, 1,4-dienes were observed to poison the catalytic activity of these PCP–palladium complexes, thus limiting their application for intramolecular Heck coupling in complex systems.[104] The use of phosphite rather than phosphane donors, that is, replacement of the methylene spacer between the aryl ring and the phosphorus donor by oxygen, and introduction of aryloxy substituents on phosphorus, E = P(OAr)$_2$, had a dramatic effect on catalyst performance (Table 1, entry 2).[105] A minimal catalyst loading (0.1 ppm) resulted in unprecedentedly high rates being obtained for the Heck reaction (TON 8.9×10^6, TOF 4×10^5), that is, more than 100 coupling reactions per second.[105a] A PCP–palladium complex with $R^2 = i$Pr provided one of the most active catalysts known so far for the olefination of aryl chlorides (entry 3).[105b] In addition, similar phosphinite catalysts proved highly efficient in the Suzuki coupling of aryl boronic acids with aryl

Table 1. Catalytic activity of pincer complexes.[a]

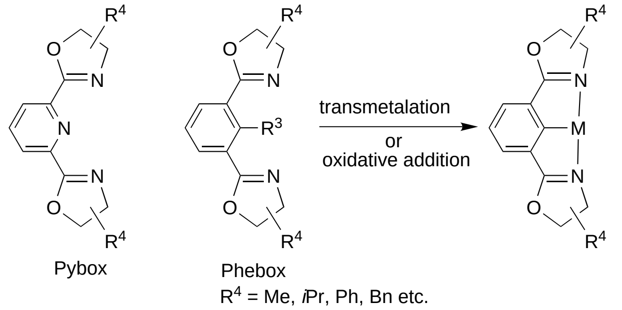
Entry	Catalyst	Catalyzed reaction	TON	Ref.	
1			520000	[103a]	$R^2 = i\mathrm{Pr}$
2			8900000	[105a]	$\mathrm{Ar} = 4\text{-}\mathrm{MeOC_6H_4}$
3			150	[105b]	
4			190000	[105d]	
5a 5b			48500 1000	[108] [45]	$R^2 = t\mathrm{Bu}$ $R^2 = \mathrm{Ph}$
6			100	[109]	
7			1000	[115]	
8			10000	[115]	X = Cl, OTf
9			400	[117]	$R^2 = t\mathrm{Bu}, i\mathrm{Pr}$
10			310	[120]	
11			–	[123]	

[a] tfa = CF_3COO^-; OTf = $CF_3SO_3^-$.

bromides, and—to a lesser extent—also with activated aryl chlorides (entry 4).[105d]

No colloidal palladium was observed and the catalyst precursor was recovered, irrespective of whether phosphane or phosphinite donors were used. Therefore, it indicated that the Pd–C bond was conserved throughout the reaction and a catalytic cycle involving palladium(0) intermediates was discarded, since metal reduction was supposed to induce Pd–C bond fission. The absence of any evidence for Pd–C bond cleavage and concomitant Pd^0 formation is a strong indication, but clearly does not yet prove, the formation of a Pd^{II}-Pd^{IV}-Pd^{II} cycle, since other intermediate structures (for example, molecular ensembles with cluster-type configurations, or palladates such as [Pd(PCP)]$^-$ that may or may not have one phosphane donor dissociated[106]) must also be considered as potential, highly reactive palladium(0) sources.[106, 107] Catalytic activity in the Heck reaction has also been observed with palladium(II) catalysts containing SCS pincer ligands (Table 1, entry 5).[45, 108] In these cases, catalyst performance is considerably lower than with PCP ligands. Comparative studies further demonstrated that the terdentate ligands were inferior to the corresponding *S,C* bidentate coordinating analogues. Palladium complexes of the NCN pincer ligand were used for the aldol condensation (entry 6).[109]

As a consequence of the excellent catalytic performance of related complexes containing *N,N,N* terdentate coordinating Pybox ligands,[110] their organometallic (Phebox) counterparts were explored in detail for catalytic applications (Scheme 22). The introduction of a covalent M–C σ bond was anticipated to suppress metal leaching, which is an issue in the corresponding Pybox complexes because of the coordinative and more labile M–N bonds. However, the steric modifications were only marginal and, therefore, a similar catalytic activity was



Scheme 22. Metalation of Phebox ligands by transmetalation ($R^3 = Li$) or oxidative addition ($R^3 = Br$).

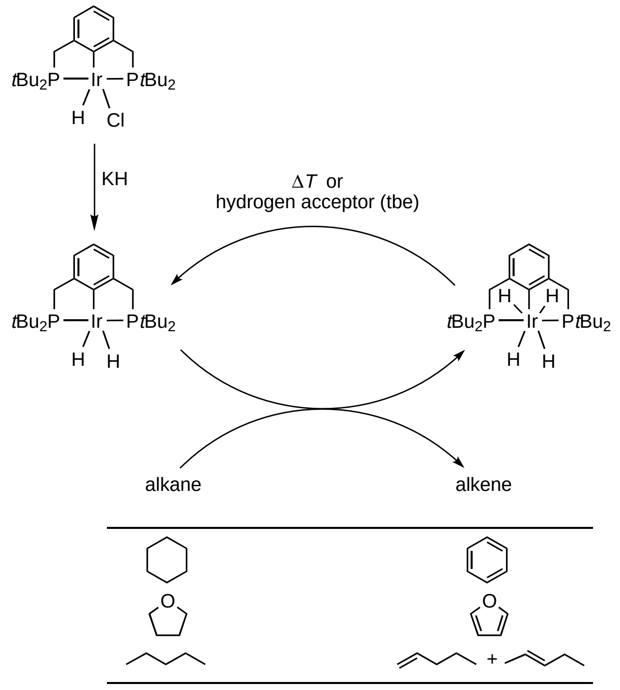
expected. Metalation of Phebox ligands was achieved by lithiation of the ligand precursor with LDA followed by transmetalation with a suitable rhodium(I),[111] palladium(II),[112] or platinum(II)[113] salt. The palladium complex with M = PdBr, $R^4 = Bn$, *t*Bu (Scheme 22) was also obtained by oxidative addition of the Phebox ligand with $R^3 = Br$ to $[Pd(dba)_2]$.[114] These complexes have been successfully used as catalysts for various C–C bond-forming reactions (see Table 2). Direct cyclometalation of Phebox ligands by C–H bond activation has been reported for rhodium(III) precursors.[111]

4.2.2. Transfer Hydrogenation

Ruthenium(II) complexes containing either NCN or PCP pincer ligands are effective catalysts in the transfer hydrogenation reaction of ketones (Table 1, entries 7 and 8).[115] The complex [RuCl(PCP)(OTf)], which contains a weakly bound triflate ligand, has been shown to be the most active catalyst system. Both aryl and alkyl ketones have been transformed into the corresponding alcohols.

4.2.3. Alkane Dehydrogenation

Iridium complexes of the type [IrCl(H)(PCP)] have been identified as precursors for efficient dehydrogenation catalysts (Table 1, entry 9). The corresponding rhodium complexes are thermally less stable and displayed low activity as dehydrogenation catalysts (TON for the formation of cyclooctene from cyclooctane was 0.8). The formal abstraction of HCl (mediated by $NaN(SiMe_3)_2$ or KH, for example) in the presence of a hydrogen atmosphere provides the dihydride complex $[Ir(H)_2(PCP)]$ as the active catalyst.[17a] A similar reactivity pattern towards molecular hydrogen has also been observed with [Ir(NCN)(cod)] at low temperatures, and afforded the thermally unstable complex $[Ir(H)_2(NCN)(cod)]$.[116] These iridium pincer complexes thus represent novel organometallic devices for reversible H_2 storage. More remarkably, catalytic C–H bond activation of alkanes has been accomplished with the complex $[Ir(H)_2(PCP)]$. A variety of unstrained substrates can be dehydrogenated using this catalyst in the presence of a sacrifizing alkene, for example, cycloalkanes to cycloalkenes, cyclohexanes to arenes, THF to furan, and alkanes to α-alkenes, which slowly isomerize to internal alkenes (Scheme 23).[117]



Scheme 23. Catalytic functionalization of nonactivated alkanes by metal-mediated dehydrogenation using PCP–iridium catalysts.

A hydrogen acceptor substrate (*tert*-butylethene, tbe) was initially used to reduce the intermediate $[Ir(H)_4(PCP)]$, but good performances have also been achieved without a hydrogen acceptor; a reflux temperature promotes the loss of H_2 from solution, thus regenerating the catalytically active iridium complex.[118] Remarkably, an "inert" nitrogen atmosphere was shown to inhibit the reaction, and catalysis must be performed under argon. Investigations in the presence of an N_2 atmosphere have revealed the formation of $[Ir(PCP)]_2(\mu\text{-}N_2)$, an Ir(PCP) dimer containing N_2 as a bridging ligand.[119] Deuterium labeling experiments further indicated that the bulky alkyl groups of the phosphane substituents assist in the catalytic cycle, particularly by promoting the dissociation of the converted hydrogen acceptor (namely, *tert*-butylethane formed from tbe).

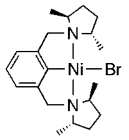
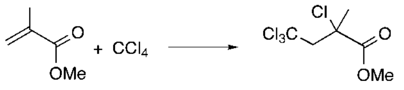
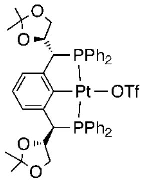
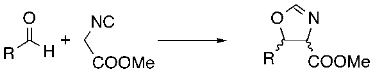
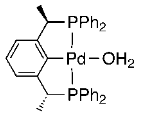
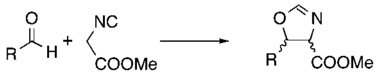
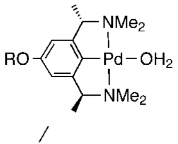
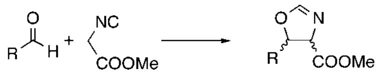
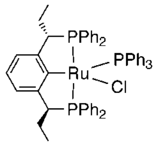
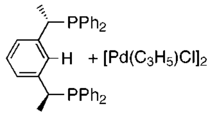
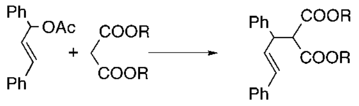
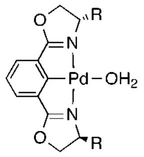
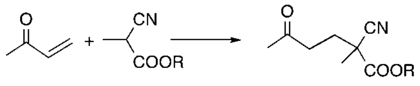
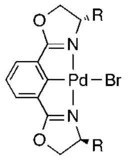
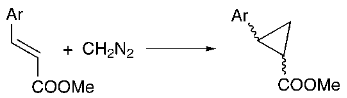
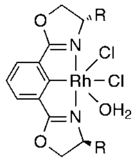
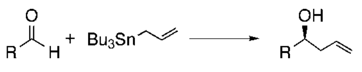
4.2.4. Divalent Catalysts for C–C Bond Formation and Polymerization

Another intriguing system is the nickel(II) complex [NiX(NCN)], since two different reactions are catalyzed by the same complex (Table 1, entries 10 and 11). The reactivity can be regulated by the ratio of the substrate concentrations. These species were initially reported to be catalysts for the Kharasch atom-transfer radical-addition (ATRA) reaction of a polyhalogenated alkane (for example, CCl_4) to a terminal olefin (entry 10).[120] Detailed investigations have revealed that the mechanism follows a radical pathway and includes the formation of the nickel(III) complex $[NiX_2(NCN)]$ as a persistent radical,[121] and $^{\bullet}CCl_3$ as the reactive species for the addition to the olefin to form products containing a novel $C–CCl_3$ bond.[122] However, the prerequisite for the reaction is that both substrates (CCl_4 and olefin) are available in approximately equal ratios. In the presence of a large excess of alkene (for example, methyl methacrylate) and only catalytic amounts of CCl_4, atom-transfer radical polymerization (ATRP) is induced and poly(methyl methacrylate) is formed (entry 11).[123] CCl_4 is essential for the generation of the persistent Ni^{III} and CCl_3 radicals which initiate the polymerization. An intrinsic property of ATRP catalyst systems is that the radicals are slowly but irreversibly consumed (predominantly by polymer-chain recombination), which results in the gradual deactivation of the catalyst. In this case this is identified by isolation of the catalytically inactive nickel(III) complex $[NiX_2(NCN)]$ at the end of the reaction.[124]

4.2.5. *Catalysts Containing Chiral Pincer Ligands*

Chiral analogues of some of the above-mentioned catalysts were also prepared from C_2-symmetric pincer ligands for asymmetric catalysis (Table 2). The earliest achievements in this area were the syntheses of nickel complexes with NCN ligands containing substituents derived from chiral pyrrolidine derivatives on the amine nitrogen atom (entry 1).[125] The absence of any significant asymmetric induction in the Kharasch addition provided the most substantial motivation at that time for postulating a radical mechanism.

Table 2. Asymmetric catalysis using enantiopure pincer complexes as catalysts.

Entry	Catalyst	Catalyzed reaction	*ee* [%]	Ref.
1			17	[125]
2			65	[126]
3			77	[127]
4			<10	[33]
5			14	[33]
6			79	[128]
7			34	[112]
8			<2	[114]
9			80	[129]

At the same time, Venanzi and co-workers reported chiral PCP ligands which were functionalized on the benzylic positions with acetals that were generated by enantioselective Sharpless epoxidations. The corresponding platinum complexes were probed as catalysts for the asymmetric aldol condensation of methyl isocyanoacetate and aldehydes and produced substituted oxazolines with up to 65% *ee* (entry 2).[126] Recently, related C_2-symmetric ligands containing alkyl groups on the benzylic positions of PCP ligands were prepared by enantioselective reduction of the ketone precursors and subsequent nucleophilic substitution of the resulting hydroxy groups by phosphanes.[127] The catalytic activity and enantioselectivity of the corresponding palladium(II) complexes in the aldol condensation (entry 3) were slightly higher than the data obtained by Venanzi and co-workers with a platinum(II) catalyst precursor.[126] Remarkably, catalysis with palladium complexes containing the corresponding C_2-symmetric NCN ligands resulted in a marked drop of asymmetric induction and the product distribution was nearly racemic (*ee* < 10%, entry 4).[33] Clearly, methyl groups on the benzylic positions of either PCP or NCN pincer ligands do not induce sufficiently pronounced chiral pockets for distinct substrate recognition by the metal center. However, studies on the influence of methyl and ethyl substituents on these ligands demonstrated a strong influence of this functionalization on the accessibility of the *ipso*-carbon atom, and hence provided a methodology for adjusting the metal-binding cavity (see Scheme 1).[33] These conclusions were independently confirmed by the results from experiments using ruthenium complexes containing a similarly alkylated C_2-symmetric PCP ligand as catalysts for the asymmetric transfer hydrogenation reaction (entry 5).[33, 37a] The activities and rates (TON, TOF) of the chiral catalysts were identical to those observed with the achiral complex, and the enantioselectivity was low (14% *ee*).

Better asymmetric induction was observed by using palladium complexes of the same ligand as catalysts for allylic alkylation (entry 6).[128] Products were obtained in up to 79% *ee* depending on the reaction conditions. It should be noted, however, that in these experiments the catalyst is not a well-defined species since it has been prepared in situ by mixing the ligand and the metal salt. Consequently, the catalytically active species may consist of coordination compounds in which the ligand actually behaves as a chiral diphosphane rather than a *P,C,P* terdentate-bonding pincer ligand.

A different synthetic strategy for the formation of chiral pincer ligands has used α-amino acids as a chiral pool. The corresponding β-amino alcohols were suitable building blocks for the synthesis of C_2-symmetric Phebox ligands. Complexation to palladium has been reported to provide catalysts for the asymmetric Michael addition and for the synthesis of chiral cyclopropanes. Whereas the former reaction proceeded with some enantioselectivity (up to 34% *ee*; entry 7),[112] the latter produced only racemic product mixtures, regardless of ligand modifications, reaction conditions, and additives used (entry 8).[114]

The corresponding rhodium(III) complexes have recently been used in the asymmetric allylation of aldehydes (maximum 80% *ee*).[129] Stoichiometric amounts of the cationic platinum complex $[Pt(Phebox)(OH_2)]^+$ have also been described as efficient chiral auxilaries in the asymmetric alkylation of aldimines.[113]

5. Recycling of Functional Pincer–Metal Units by Immobilization

5.1. Identification of Suitable Anchoring Points

One of the most challenging issues of catalysis represents the successful combination of the advantages of homogenous (selectivity, rate control) and heterogeneous catalysis (product/catalyst separation, recycling). Straightforward methods for convenient and quick catalyst recovery and recycling of (precious) metal systems are highly desirable, both from an environmental and from an economic point of view, in processes involving toxic and/or expensive catalysts. A few different approaches have been pursued during the last few years to achieve this combination of beneficial aspects of homogeneous and heterogeneous catalyst systems. Common to most of these attempts is that they aim to immobilize the homogeneous catalyst through a covalent linker to a soluble or heterogeneous support without influencing its homogeneous mode of action.[130]

Suitable linker positions on the reactive pincer metal complexes ideally exert no influence on the desired application. They are readily identified as such while optimizing the properties of the metal center by ligand tuning. In many cases it has been shown that functionalization of a selected *para* substituent of the aryl unit of these pincer ligands ($R^1 = OCR_3$, $OSiR_3$, NCOR) had only marginal direct influence on the electronic configuration of the metal center and on the stability of the M–C bond.[60, 84] Consequently, this position has predominantly been used as the anchoring point for the introduction of suitable linkers.

5.2. Heterogeneous and Polymeric Supports

Gold surfaces have been suggested as heterogeneous supports because of their strong interaction with thiols, thioethers, and other sulfur-containing organic molecules. For these purposes, SCS pincer ligands were functionalized with a thioether tail and, after cyclopalladation, were self-assembled on gold to provide organometallic monolayers.[131] These surface-confined organopalladium units have been used as new cores for the construction of self-assembled metallodendrimers. A strict control of the degree of functionalization and hence the number of immobilized units could be achieved by monitoring the adsorption by atomic force microscopy.

Carbon nanotubes are increasingly attractive supports for catalysts and other functional molecules. Selective monoaddition of NCN pincer ligands to fullerene C_{60} (as a representative model for carbon nanotubes in many respects) and subsequent metalation by nickel or palladium provided catalysts containing a backbone with a particular electronic configuration (Figure 9).[132] These fullerene-containing cata-

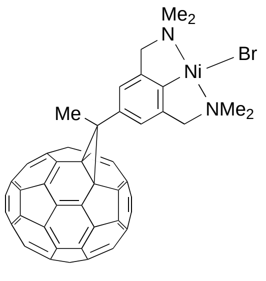


Figure 9. The [NiBr(NCN)] catalyst immobilized on fullerene as a model for functionalized carbon nanotubes.[132]

lysts are easily traced by spectroscopic techniques as a consequence of their strong color.

Silica represents an alternative, cheap, and ubiquitous support. Direct immobilization of the pincer ligand on commercially available silica has been achieved with urea-type linkers containing protected silanol end groups.[133] The grafting of these substituted pincer ligands on silica colloids occurs by covalent Si-O-Si bond formation (Figure 10, left). A model system, which allowed a more detailed investigation of the influence of this specific support on the catalyst, was provided by soluble siloxane polymers, on which pincer ligands were attached by using an amide linker (Figure 10, right).[134] Nickel insertion was achieved by oxidative addition to give homogeneous, polymer-supported catalysts. The performance of this immobilized system compared well with the monomeric material, and retrieval of the catalyst (in its irreversibly deactivated Ni^{III} form) was conveniently achieved by precipitation and filtration.

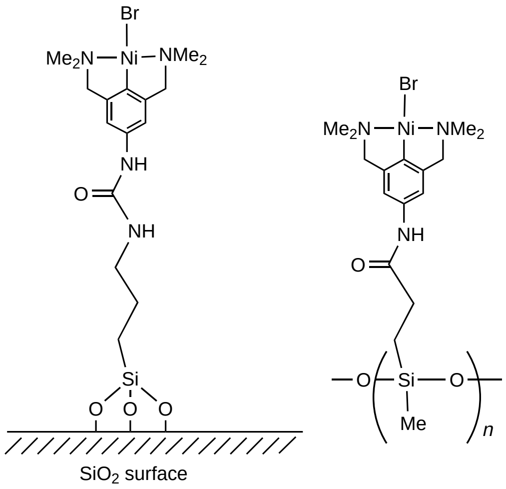


Figure 10. Catalytically active [NiBr(NCN)] sites confined on different silica supports.[133, 134]

In a similar approach, a soluble ethylene glycol polymer containing hydroxide side-chain functionalities was used for the attachement of SCS pincer ligands.[45] Subsequent palladation resulted in the formation of multisite catalysts for the Heck reaction, which were successfully recycled by precipitation/filtration procedures. Repetitive catalytic cycles did not show any loss of activity, which is in accordance with a rigid immobilization of the palladium center which prevents catalyst leaching and metal dissociation. An elegant improvement of this procedure, which avoids the precipitation of the polymeric catalyst but guarantees its recovery, has recently been presented by performing the catalyzed reaction under thermomorphic conditions.[135] A careful choice of solvents (for example, dimethylacetamide and heptane) provides a mixture that is homogeneous at the elevated temperatures required for catalysis, but biphasic at room temperature. This difference allows the facile separation of the organic products (soluble in heptane) from the polymeric catalyst, which remains in the dimethylacetamide phase (Figure 11).

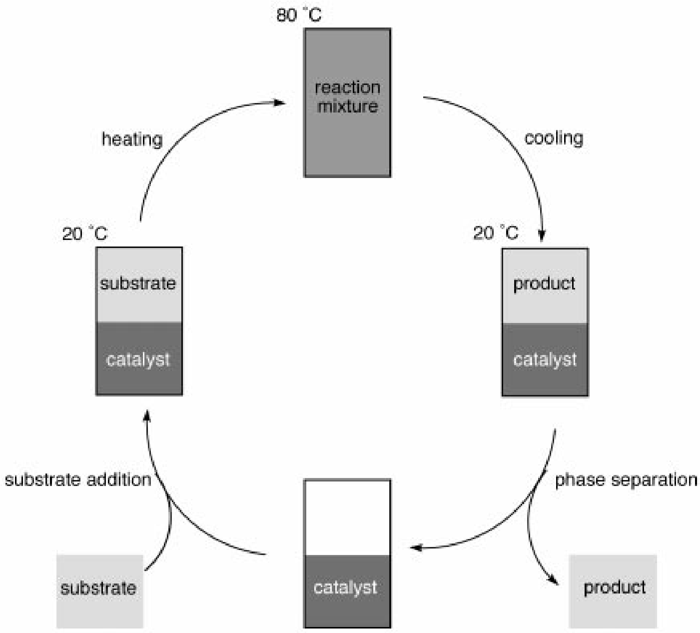
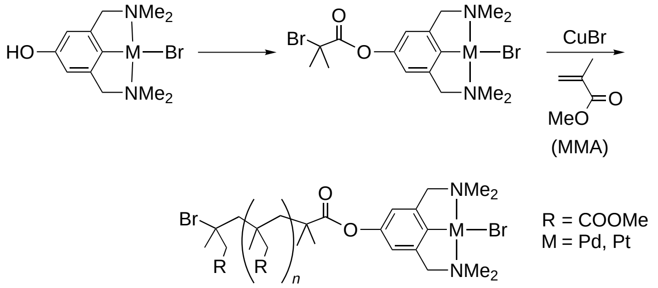


Figure 11. Heck catalysis mediated by a SCS–palladium complex under thermomorphic conditions:[135] At room temperature (left), the polymer-supported catalyst dissolves in dimethylacetamide, whereas the substrates (for example, ArI and methyl methacrylate) are soluble in heptane. At elevated temperatures (top), the system becomes homogeneous, which allows for homogeneous catalysis. Upon cooling, the biphasic system is regenerated (right) and the products are easily separated from the catalyst by phase separation (bottom). The addition of a fresh substrate-containing solution allows for repetitive use of the catalyst.

A valuable synthetic modification of this immobilization approach on polymers was demonstrated by using *metalated* pincer systems as monomer substrates for polymerization. This method eliminates difficulties associated with metal insertion in the polymer-supported pincer sites—insertion may be incomplete or may be accompanied by the formation of undesirable side products (for example, from interactions of the metal center with the polymer support). Clearly, for this latter method there must be no dissociation of the metal–ligand bond (C or N) during the polymerization. The strong M–N and M–C bonds in platinum and palladium complexes containing the NCN pincer ligand have thus far been shown to fulfill these requirements. Functionalization of the aromatic *para* position of these complexes [MBr(4-R^1-NCN)] (M = Pd, Pt) with an initiator group ($R^1 = OC(O)CMe_2Br$) and subsequent ATRP in the presence of methyl methacrylate gave end-group functionalized poly(methyl methacrylate) containing functional end groups (Scheme 24) for either repetitive catalytic applications (M = Pd) or for reversible gas detection (M = Pt).[43] The diagnostic color of the platinum complex in the presence of SO_2 displays a novel probe for the fast assessment of the average molecular weight M_w of the polymer produced.



Scheme 24. Transition metal labeled poly(methyl methacrylate) polymers obtained from radical polymerization with an initiator containing a NCN–metal functionality.

Improved separation methods by filtration techniques are expected for polymers that have a spherical rather than a linear shape. Such a polymer constitution has been achieved by the polymerization of branching monomers to give so-called hyperbranched polymers.[136] For steric reasons, not all the polymeric chains propagate in every possible direction, thus leaving unreacted functional groups at the periphery and in the inner sphere of the hyperbranched polymer. These groups have been employed for the attachment of NCN pincer ligands through a direct C_{aryl}–Si bond (R^1 = hyperbranched carbosilane polymer).[109] Interestingly, low molecular weight fractions can be conveniently separated by dialysis experiments; this caused a significant narrowing of the polydispersity of the material. Lithiation and subsequent transpalladation afforded polymetalated spheres containing active catalysts for the aldol condensation (Figure 12). Preliminary catalytic runs revealed the immobilized catalyst had only a slightly lower activity compared to that of a mononuclear model species. The reduced performance was attributed to steric constraints imposed by the hyperbranched support, which is likely to shield some palladium centers and thus prevent substrate binding to these sites. Alternatively, the microenvironment of some catalytic sites may be defined entirely by the polymeric support and not by the solvent. This leads to locally modified solubility effects, which may influence the reactivity and product selectivity of these metal centers.

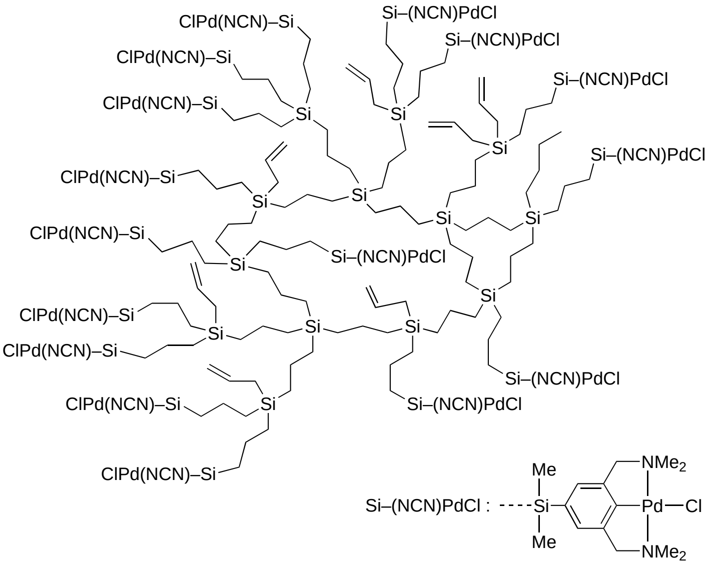


Figure 12. Hyperbranched polymer containing catalytically active pincer palladium sites at the periphery. Note that some of the metal centers are encapsuled and have therefore a different environment from those at peripheral sites.[109]

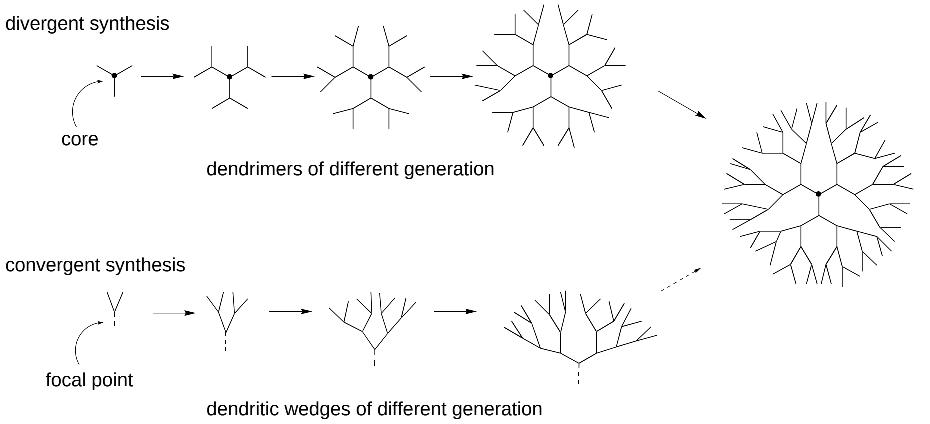
5.3. Homogeneous Dendritic Supports

Improvement of such undesired effects can be achieved when dendrimers are used as macromolecular supports.[137] These treelike macromolecules are prepared by a regular and stepwise growth using repetitive synthesis sequences. Consequently, they are characterized by a well-defined connectivity pattern and a precise number of functional sites, which are located at the periphery and/or in the core. A consequence of this highly regular architecture is that the polydispersity of dendrimers ideally equals 1.[138] Variations in the generation number and/or interconnection of dendrimers or dendritic wedges are appropriate methodologies to tailor the size of these materials. This has been illustrated by the engineering of such macromolecules into nanometer-sized spheres and cylinders.[139] It was therefore assumed that nanofiltration techniques would provide a facile methodology for the separation of these nanodimensional structures from reaction solutions, and that these properties would hence enable the use of heterogeneous separation techniques for homogeneously operating catalysts.[140]

Two principally different concepts are available for the preparation of periphery-functionalized organometallic dendrimers (Scheme 25):[141]

1. A divergent synthetic approach consisting of repeated functionalization of a dendrimer core with branching units,[137a] subsequent anchoring of the pincer ligand precursor at the periphery, and finally metal insertion.
2. A convergent synthesis[137c] starting with the functionalized (and metalated) pincer ligands as zero-generation dendritic wedges and branching units, which are repetitively attached at the focal site of the dendrons. The synthesis is then completed by the coupling of the dendrons to a core unit.

The divergent strategy is the method of choice for the preparation of polyfunctionalized dendrimers containing active (metal) centers which are highly sensitive (for example, towards air or water). Probably the most significant drawback of this method is that the number of reactive (peripheral) sites increases with every repetitive step, and therefore the difficulties in quantitative transformation of the end groups also increases. Consequently, metal insertion by periphery functionalization of higher generation dendrimers is often incomplete and tedious. These difficulties are effectively circumvented by a convergent strategy, where the number of reactive centers is constant in each growing step (independent of the generation number). A high stability of the metal site towards the reaction conditions of the dendrimer synthesis is essential, particularly for the preparation of periphery-functionalized metallodendrimers, since these groups have to be inert to the conditions used for the coupling of the wedges to branching points and to the core.



Scheme 25. Schematic representation of divergent and convergent routes for dendrimer synthesis.

Initial efforts were directed toward divergent metallodendrimer synthesis using relatively inert carbosilane dendrimers. Covalent attachment of the pincer ligand to the dendritic silyl end groups was achieved either directly or using a carbamate linker.[36c, 142] Catalytically active nickel centers were inserted by oxidative addition or a lithiation/transmetalation protocol to afford a model catalyst system (Figure 13) for the ATRA reaction. Nanosize architectures with a diameter of 2–3 nm were fabricated by careful choice of the generation number and the type of branching points on the carbosilane dendritic support employed. Up to 36 nickel centers can be incorporated into the largest of these structures. Complete functionalization of the periphery is difficult to achieve and an average loading of approximately 80% was determined by analytical methods (elemental analysis, integration of NMR signals). Incomplete metalation of the dendritic surface with nickel was rationalized to be a consequence of a subquantitative transmetalation sequence paired with partial decomposition of the highly sensitive polylithiated precursor (for example, by hydrolysis). Nevertheless, the dendrimer-immobilized species were useful catalysts. More importantly, these confined catalysts were efficiently separated from product solutions at the end of the reaction by using nanofiltration membranes. The suitability of this technique was strongly dependent upon the molecular dimension of the dendrimers, which is a direct consequence of the dendrimer generation and of the spacers used to interconnect the branching points (see Scheme 25). Importantly, an increase in the dendrimer generation was paralleled by a drop in catalytic activity, and dendritic catalysts containing 36 nickel centers were deactivated after only one hour and 10% conversion.[143] This dendritic effect may be understood by considering the reduced intramolecular Ni···Ni distance in these macromolecules which favors, in a kinetic sense, the interaction of the activated substrates (for example, $^{\bullet}CCl_3$ radicals in the Kharasch addition reaction) with each other. This interaction promotes the pre-assembly of $^{\bullet}CCl_3$ radicals on the dendritic surface for the formation of, for example, C_2Cl_6 (Scheme 26). This recombination process is competitive with the reaction of the radical with methyl methacrylate, and also lowers the radical concentration, thus preventing the essentially important reduction of the persistent nickel(III) radical to the catalytically active nickel(II) species. This interrupts the catalytic cycle and ultimately leads to a complete deactivation of the catalyst, a feature which is stimulated by surface congestion.

Undesired metal–metal interactions can be avoided by using shape-persistent core units, which force the pincer metal

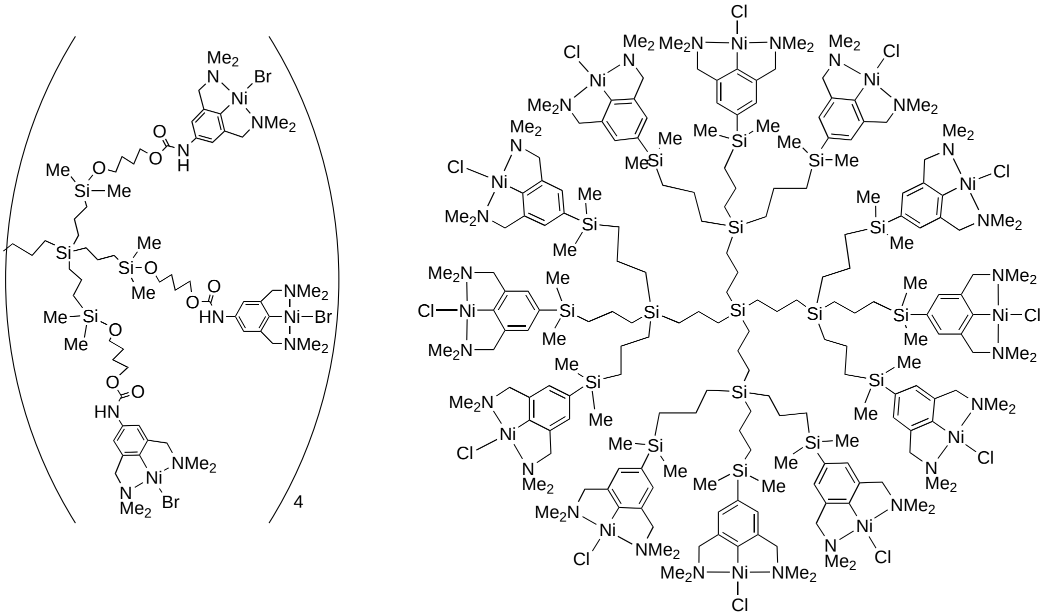
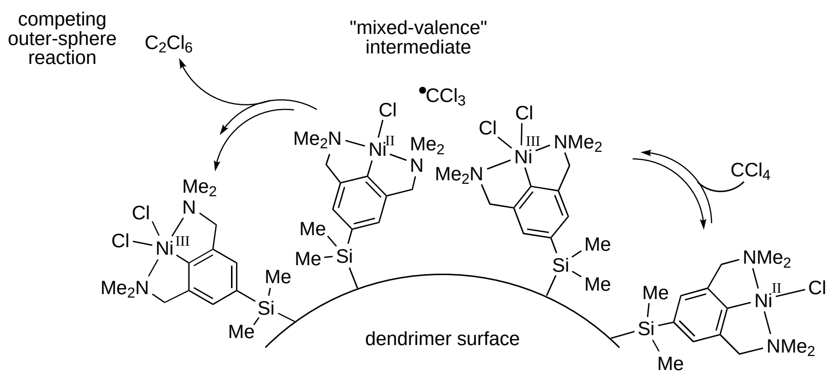


Figure 13. The immobilization of nickel catalysts at the periphery of carbosilane dendrimers affords soluble macromolecular catalysts which operate homogeneously and which can be recovered by nanofiltration techniques.[36c, 142]

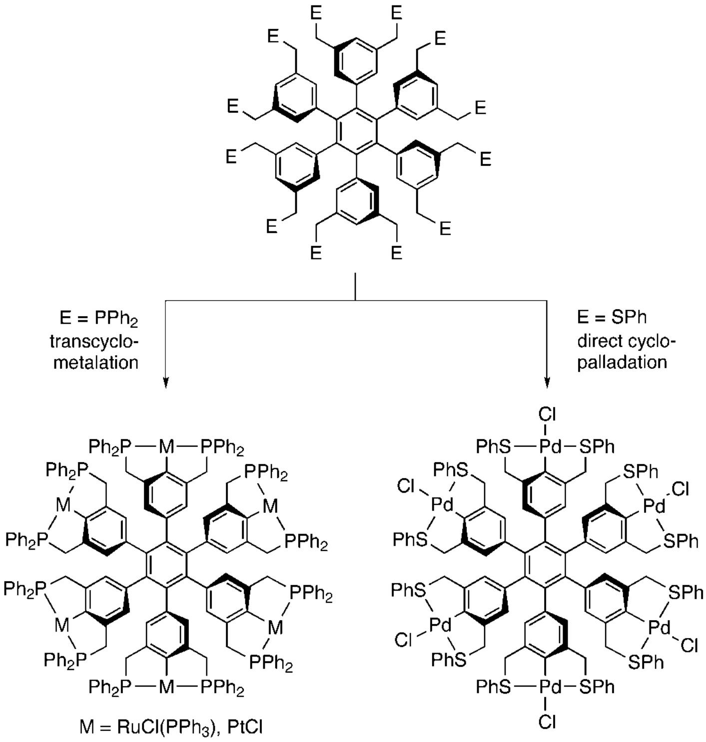


Scheme 26. Deactivation pathways in the nickel-catalyzed Kharasch addition reaction that occur provided that the catalytically active sites are in close proximity, such as at the periphery of high-generation dendrimers.

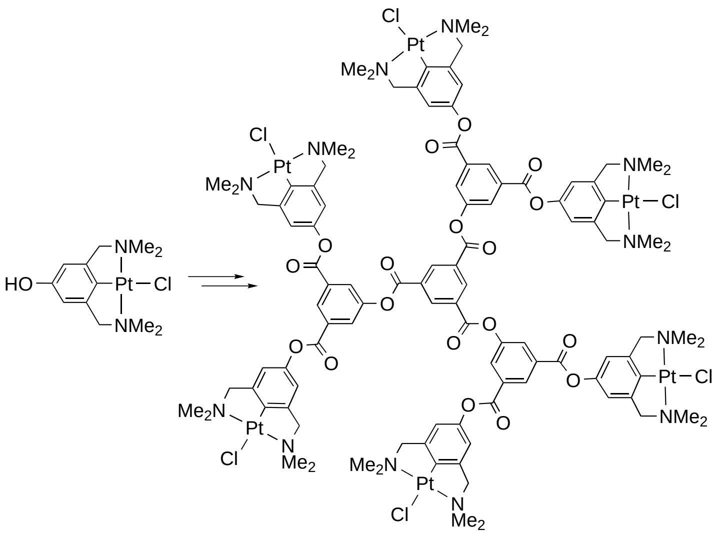
unit into a specific relative orientation. Another advantage of such cores is that metallodendrimers of considerable size are already available at a low generation number. This reduces the laborious multistep preparation of higher generation dendrimers to a few repetitive sequences without losing the required retention properties for nanofiltration membrane applications. Following these lines, a "cartwheel"-like molecule was constructed containing six pincer ligands each connected by a C_{aryl}–C_{aryl} bond to a central benzene core.[144] A synthetic protocol was chosen which allowed the introduction of a variety of donor groups E into the ligand framework.

Complete metalation of all six pincer sites with platinum or ruthenium centers (for E = PPh_2) was only successful by transcyclometalation reactions[37] of the corresponding monomeric [M(NCN)]-type precursor (Scheme 27). Direct cyclometalation or transmetalation procedures failed to give the hexametalated product, probably because of the high local phosphane concentration at the dendritic periphery. By way of contrast, direct palladation was observed for the sulfur analogue (E = SPh, Scheme 27). A single-crystal structure determination of the hexapalladated complex revealed a diameter of 2.1 nm and a torsion angle of approximately 22° between the pincer aryl rings and the core benzene ring, which resulted in a cartwheel-type structure. Modification of the dendritic dimension was demonstrated by the introduction of rigid acetylene spacers, which did not affect the macromolecular shape-persistence.[145] Thus far, however, the low solubility of these hexametallic systems have hampered their application as homogeneous catalysts considerably.

A well-defined connectivity pattern and a strict control of the metal loading is essential for homogeneous sensor applications, since quantitative detection of a substrate requires sensor devices with a precise number of recognition sites.[146] Such materials are available for the reversible detection of SO_2 gas[60] through the selective grafting of dendrimers with sensor-active organoplatinum units, for example, by immobilizing platinum complexes [PtX(HO-NCN)] containing a phenolic functionality onto these macromolecules. The excellent stability properties of this organometallic synthon meant that a fully convergent synthetic strategy could be applied: first the pincer ligand was platinated and then subsequently deprotected/esterified, either to branching points or to a core (Scheme 28). This sequence afforded polymetallic aryl ester dendrimers containing fully functionalized end groups.[44, 60a] All the peripheral arylplatinum sites in these metallodendrimers were shown to be independent sensor sites, which is in accordance



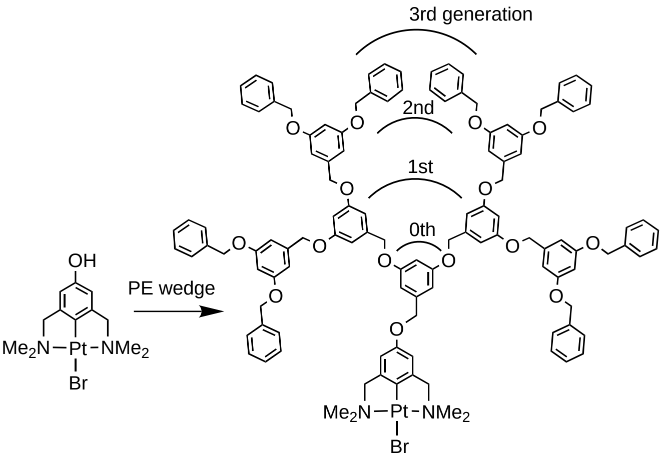
Scheme 27. Different routes for the preparation of hexametalated cartwheel-type macromolecules.



Scheme 28. Convergent synthesis of periphery-functionalized platinum dendrimers starting from robust platinated building blocks.

with a conformationally rigid skeleton of the aryl ester dendrimer and negligible intermetallic interactions. The very low solubility of these macromolecular sensors in common organic solvents is a serious disadvantage for homogeneous applications and parallels the solubility properties of other periphery-functionalized metallodendrimers (for example, "cartwheel"-type structures).[144]

Particular physical properties (surface behavior, size, solubility) of metallodendrimers can be engineered by using core-functionalized dendritic wedges. In such macromolecules, these properties are generally defined by the peripheral constitution and are therefore virtually isolated from the chemical activity since the functional site (sensor, catalyst) is located at the focal point.[147] These unique characteristics allow for the independent tailoring of the physical and chemical properties. This concept was exploited by the core-functionalization of Fréchet-type dendritic wedges with a pincer metal site (Scheme 29).[148] These metallodendritic wedges displayed markedly improved solubility properties relative to the corresponding periphery-functionalized metallodendrimers and were, therefore, appropriate for homogeneous applications in membrane reactors. This scenario was realized by first assessing the permeability of a given membrane by monitoring the diffusion of platinum complexes functionalized with dendritic wedges of different generations through it. These materials are orange colored in the presence of excess SO_2, which facilitates their detection. The retention properties of the dendrimers correlated with their size and molecular weight and allowed for the identification of dendritic wedges that are appropriate for nanofiltration techniques. Substitution of the platinum center at the core by nickel provided dendritic catalysts with defined retention properties. When a solution of metallodendrimers of suitable size is loaded in a membrane-covered vial, a compartmentalized catalyst system is obtained which operates fully homogeneously and which is separated from the product solution simply by removing the vial (Figure 14). Such catalyst compartmentalization was shown to provide a suitable approach for the development of multiple-use catalysts which are conveniently recovered, regenerated, and stored. These applications do not require dendritic supports of exceedingly high generation.



Scheme 29. Core-functionalized metallodenrimers, whose size and retention properties in nanofiltration membranes can be tailored by modification of the generation of the dendritic wedge. PE = polyether.

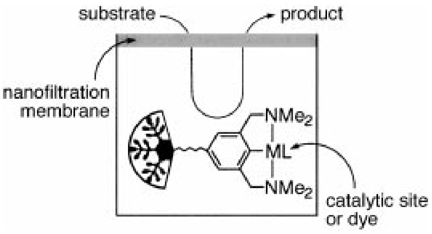


Figure 14. Application of metallodendritic materials that are compartmentalized in a membrane-covered vial, for example, as nanosized dyes or as multiple-use catalysts working at ambient pressure.[148]

6. Perspectives

Early studies directed toward the synthesis of chiral triorganotin halides with a stable configuration led us to use the concept of intramolecular stabilization. The NCN pincer was used for the first time in an attempt to make water-soluble triorganotin compounds.[2b,c] The observed rigid *N,C,N* terdentate coordination mode in this complex suggested that this presumed property (see, however, the different bonding modes in Figure 1) could be exploited to control oxidative addition/reductive elimination cycles in transition metal chemistry and homogeneous catalysis. The first experiments concentrated on the oxidative addition of platinum–pincer complexes [PtX(NCN)], which for X = OTf led to the discovery of the novel arenium–platinum compound (see Figure 5). This was the start of the research described in this review.

After 20 years, many experiments, and surprising results, we may conclude that the transition metal chemistry with pincer ligands has addressed various interesting aspects:

1. Comparative studies of the organometallic chemistry of complexes containing a single $M-C_{aryl}$ bond and some additional ligands versus complexes containing a $M-C_{aryl}$ σ bond which is supported intramolecularly by two neutral ligands.
2. New types and mechanistic details of metal-mediated reactions such as rearrangements of $M-C_{aryl}$ units, C–C bond couplings and selective cleavage, the reactivity of arenium ions, and the stabilization of various proposed intermediates, for example, in oxidative addition.
3. Unprecedented organometallic properties imparted by the presence of well-defined pincer–metal units were used to explore new ideas for the immobilization of homogeneous catalysts, labeling of dendrimers and hyperbranched polymers, the reverse binding of H_2 (H_2 storage), and the sensing of small molecules such as SO_2.
4. New catalytic behaviors, for example, for NCN–nickel complexes acting as redox catalysts which are in many respects superior to alternative systems for similar reactions.

Finally, it should be noted that the concepts described in this review do not apply only for platinum group metals but have also found successful application in the chemistry of early transition metals,[149] lanthanides,[150] and main group metals.[151]

The development and optimization of functional materials, certainly a key challenge in modern chemistry, requires well-defined and tunable systems, namely, functional units that can be specifically tailored on a chemical level. Metal complexes containing the pincer ligand were shown to be outstanding candidates for these purposes. Future research has to concentrate ever increasingly on the incorporation of these functional materials (for example, catalysts, light-harvesting antennas, or sensors) into macroscopic devices for routine applications. Clearly, this requires strong interdisciplinary cooperations with various fields such as physics, biology, engineering, or medicine. A particular issue consists of the appropriate translation of customer needs (that is, physical properties) into (supra)molecular modifications of promising materials. A balanced combination of profound chemical understanding and of serendipity will remain essential to achieve this ambitious aim.

7. Addendum

The continuous interest in pincer chemistry with platinum group metals is manifested by a number of noteworthy articles which have appeared since the submission of this manuscript. Contributions to this research area include the synthesis of new pincer-containing PCP—osmium[152] and NCN—rhodium(II) complexes (Section 2).[153] The diverse coordination chemistry of (immobilized) SCS–palladium units has been used for the construction of self-assembled supramolecular structures (Section 3.3).[154] The mechanism of $C_{aryl}-C_{alkyl}$ bond activation with PCN–rhodium complexes has recently been studied theoretically (Section 4.1).[155] Moreover, pincer-type palladium complexes have been disclosed as novel catalysts for C–C bond-forming reactions (Section 4.2).[156, 157] Finally, chiral Phebox–rhodium(III) species functioned as active catalyst precursors for the asymmetric hetero-Diels–Alder reaction of Danishefsky's dienes and glyoxylates.[158]

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