Mechanisms of d^8 Organometallic Reactions Involving Electrophiles and Intramolecular Assistance by Nucleophiles

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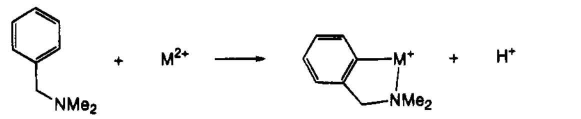
The most attractive and fundamental interaction between metal centers and organic molecules that could lead to new functionalization at carbon is direct activation of the C–H bonds of hydrocarbons,[1] and several significant advances toward realization of this objective using transition metals have been reported.[1c] In particular, transition metal complexes have been used not only in pioneering studies of the synthesis or detection of complexes resulting from C–H activation[1,2] but also in cyclometalation chemistry, exemplified by eq 1, which provided the first examples of C–H activation[3] and which is still providing new insights into mechanisms.[4]



(1)

Scheme 1 illustrates the intermediates and/or products that could be formed in reactions that commence with activation of a C–H bond of CH_4 and C_6H_6 by the metal(II) center of a complex, i.e., reagent pairs **5** and **12**, respectively. Scheme 1 also shows that there is a formal linkage between this reaction chemistry and electrophilic attack by H^+ on a $M–CH_3$ or $M–C_6H_5$ bond (reactions commencing with reagent pairs **1** and **6**, respectively), since both processes may involve related species such as **2–4** and **7–11**. Included in Scheme 1 are reactions such as 1,2-shifts of hydrogen atoms between carbon and metal centers [**7** ⇌ **8**], formation of arenonium species (**7**), and also concepts regarding descriptions of the formal oxidation state for M–H interactions where the hydrogen atom may be regarded as "$H^{(-)}$" or "$H^{(+)}$" (**2** ↔ **3** and **8** ↔ **9**). The hydrogen atom as a ligand is generally classified as a hydrido group, "$H^{(-)}$", but protonation of some metal complexes gives species in which the metal–hydrogen interaction is much weaker and may be regarded as "$M\cdot\cdot H^{(+)}$".

Studies of the interaction of metal centers with X–H bonds where X ≠ C, e.g., N–H in $[NHMe_2R]^+$, which is isoelectronic with the alkane $CHMe_2R$, and of organometallic complexes with electrophiles other than H^+, e.g., Hg^{2+} and Me^+, have also improved our understanding of the mechanisms occurring for the reactions in Scheme 1. In this Account contributions from Tasmania and Utrecht relevant to the reactions in Scheme 1 are discussed for d^8 organometallic complexes, with an emphasis on reactions of M–C σ-bonded species with H^+ (reagent pairs **1** and **6**) and other electrophiles. Research reviewed includes arenonium chemistry,[5] reactions in which the electrophile H^+ as a reagent is modeled by mercury(II),[6] protonation of metal centers assisted by nucleophiles,[7] aspects of organopalladium(IV) chemistry,[8,9] oxidation of M(II) to M(IV) complexes (M = Pd, Pt) by water,[9] and other processes occurring at metal centers that appear to involve intermediates shown in Scheme 1.[10]

Allan Canty is a D.Sc. graduate of Monash University, where he studied as a Ph.D. student with Glen Deacon and Bryan Gatehouse. After a year as an 1851 Overseas Scholar with Jack Lewis in Cambridge (U.K.) he joined the University of Tasmania, where he is now a professor. He has been a Fulbright Senior Scholar at Purdue University, a visiting professor at the Universities of Waterloo and Western Ontario, and a Netherlands Institute for Catalysis Fellow at Utrecht University. His research interests have included ruthenium carbonyl organometallics; the bioinorganic and structural chemistry of mercury; and the coordination and organometallic chemistry of heavy p block and late transition metals, in particular mercury, gold and platinum, and more recently the development of organopalladium(IV) chemistry.

Gerard van Koten obtained his Ph.D. from Utrecht University (Professor G. J. M. van der Kerk) during his stay in the Laboratory for Organic Chemistry (TNO) in Utrecht (1967–1977). After a period in the Inorganic Chemistry Department at the University of Amsterdam, where he was promoted to professor (1984), he went back to Utrecht University (Debye Institute) in 1986 to become professor of organic chemistry. He has been visiting professor in Strasbourg, Heidelberg, and Sassari. Research interests comprise the organometallic chemistry of late (Ni, Pd, Pt, Ru) and early transition metals (Ta, La, Lu) as well as of Cu, Li, and Zn and the development and use of chelating arylamine ("pincer") and aminoarenethiolate bonded organometallic complexes as catalysts for homogeneous catalysis, in particular for fine-chemical synthesis. The preparation and use of the first examples of homogeneous dendrimer catalysts demonstrate his interest in supramolecular systems with (organometallic) catalytically active functionalities.

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Yamamoto, A. *Organotransition Metal Chemistry: Fundamental Concepts and Applications*; John Wiley & Sons: New York, 1986. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (d) Chatt, J.; Davidson, M. *J. Chem. Soc.* **1965**, 843. (e) Halpern, J. *Discuss. Faraday Soc.* **1968**, *47*, 7.

(2) (a) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; *Ibid.* **1983**, *105*, 3929. (c) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (d) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (e) Jones, W. D.; Feher, F. J. *Ibid.* **1982**, *104*, 4240; *Acc. Chem. Res.* **1989**, *22*, 91. (f) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421. (g) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436.

(3) (a) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272. (b) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

(4) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(5) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891.

(6) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.

(7) (a) Wehman-Ooyevaar, I. C, M.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1367. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916. (c) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484. (d) Pregosin, P. S.; Ruegger, H.; Wombacher, F.; van Koten, G.; Grove, D. M.; Wehman-Ooyevaar, I. C. M. *Magn. Reson. Chem.* **1992**, *30*, 548.

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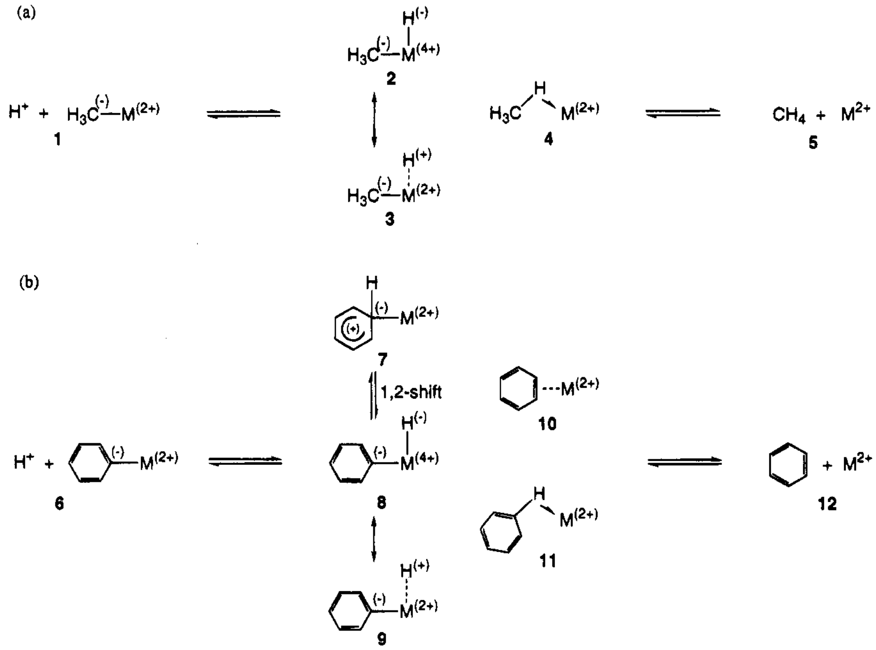
Scheme 1. Species That May Be Formed on Protonation of Organometallic Complexes (Reagent Pairs 1 and 6) and C–H Activation Reactions (Reagent Pairs 5 and 12)[a]



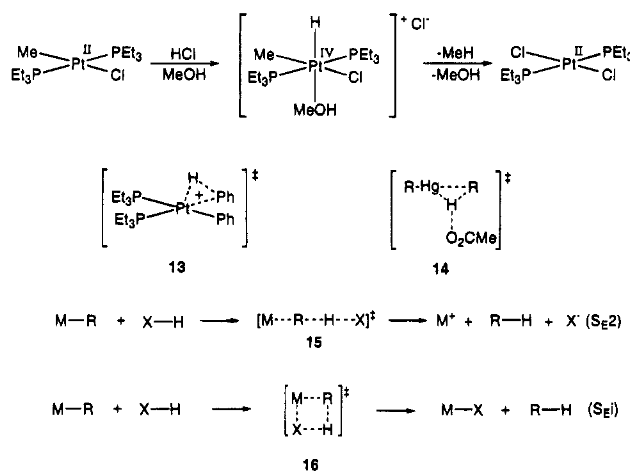
[a] For (a) alkylmetal(II) complexes and alkanes and (b) arylmetal(II) complexes and arenes. Ancillary ligands are omitted, methane and benzene are illustrative as hydrocarbons, and formal charges in organometallic species are shown for metal(II) centers as model reagents. Species containing moieties **2–4** and **7–11** may be intermediates or products of reactions. Relationships between **2** and **3** and **7–9** are emphasized here because of their importance in mechanisms for some reactions described in this Account.

In most of the reactions reviewed here intramolecular assistance by a nucleophile plays a major role in the mechanism and/or in the stabilization of products, and thus they are relevant also to the development of a better understanding of cyclometalation reactions exemplified by eq 1.

Interaction of d^8 M–C Bonds with X–H Bonds Formal Oxidation States (d^6 or d^8) in Key M···H···X Systems

The mechanisms for cleavage of a d^8 M–C σ-bond by a protic reagent HX may be summarized[11] as involving either oxidation/reduction sequences, as proposed for the reaction of HCl with *trans*-[PtClMe(PEt$_3$)$_2$] in methanol (Scheme 2),[11d,12] or three-center transition states,[11c,13] such as **13** proposed for the reaction of *cis*-[PtPh$_2$(PEt$_3$)$_2$] with HCl that affords *cis*-[PtClPh(PEt$_3$)$_2$] and PhH.[13] A three-center intermediate (**14**) similar to that of **13** has also been proposed for the protonolysis of alkylmercury(II) bonds in acetic acid.[14] For alkyl species of p block elements, transition states such as **15** in the S$_E$2 mechanism and **16** in the S$_E$i mechanism have been proposed, whereas for protonation of arylmetal species the proposals include formation of an arenonium intermediate (**7**) followed by reaction with a nucleophile to give the arene and metal–nucleophile complex as products.

Scheme 2



Model complexes for the arenonium intermediate **7** have not been obtained to date, but with Me$^+$ rather than H$^+$ as the electrophile, the (arenonium)platinum(II) cation **18** has been isolated from the reaction of the tetrafluoroborate salt of [Pt{2,6-(NMe$_2$CH$_2$)$_2$C$_6$H$_3$-*N,C,N*}(OH$_2$)]$^+$ (**17**) with methyl iodide (eq 2).[5a] Complex **18** (Figure 1a) and its relatives are the only examples of isolated arenonium complexes, and the

(8) (a) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1722. (b) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83. (c) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (d) Byers, P. K.; Canty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A. *Organometallics* **1992**, *11*, 3085. (e) Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2053. (f) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; Traill, P. R.; White, A. H. *Organometallics* **1995**, *14*, 199. (g) Canty, A. J. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Puddephatt, R. J., Ed.; Pergamon Press: New York, Vol. 9, Chapter 5, in press.

(9) (a) Canty, A. J.; Honeyman, R. T.; Roberts, A. S.; Traill, P. R.; Colton, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *471*, C8. (b) Canty, A. J.; Fritsche, S. D.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *490*, C18. (c) Canty, A. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.*, in press.

(10) (a) Valk, J.-M.; van Belzen, R.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, 2293. (b) Valk, J.-M.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1994**, *483*, 213.

(11) (a) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43. (b) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. (c) Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332. (d) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565.

(12) Belluco, U.; Giustiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494.

(13) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813.

(14) Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5979.

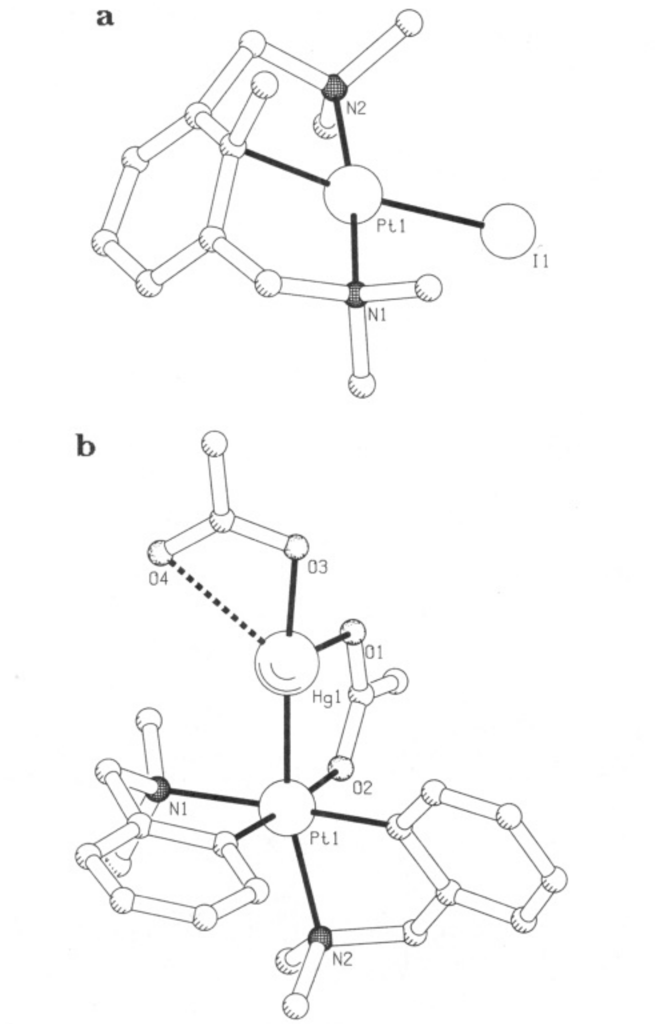
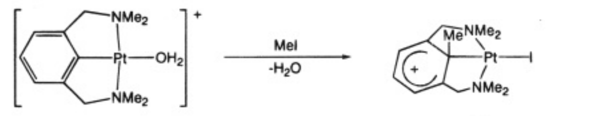


Figure 1. Crystallographic studies of (a) [Pt{2,6-$(NMe_2CH_2)_2$-MeC_6H_3-*N,C,N*}I]$^+$ (**18**)[5a] and (b) [Pt{2-$(NMe_2CH_2)C_6H_4$-*C,N*}$_2$-{Hg(O_2CMe)}(O_2CMe)].[6] The latter complex crystallizes in space group *Pccn* containing equal numbers of enantiomers. Part b shows the enantiomer drawn in ref 6; the other enantiomer is shown as **19** to facilitate comparisons with other diagrams.

two intramolecular (dimethylamino)methyl donor groups are clearly important in stabilizing such species. On the basis of synthetic[5] and theoretical[15] studies it is likely that the reaction of eq 2 models the sequence **6** → **8** → **7** in Scheme 1. In this sequence there is initial oxidative addition of MeI at the Pt(II) center of **17** (cf. **6**) to afford a cationic aryl(methyl)-platinum(IV) species (cf. **8**) that is followed by a 1,2-shift of the methyl group from the Pt(IV) center to the ipso carbon and generation of the Pt(II) arenonium cation **18** (cf. **7**). The reverse process, i.e., C–C bond cleavage in **18** involving a 1,2-shift of the methyl group from C_{ipso} to platinum, occurs in the reaction of **18** with nucleophiles such as halide ions.[5b] In a related 1,2-shift process, reversible hydrogen atom migration between rhodium and pyrrolic nitrogen atoms has been documented for an octaphenylphthalocyaninato complex, i.e., RhH(Ph_8Pc-N_4) ↔ Rh(Ph_8Pc-N_3,*N*H).[16]

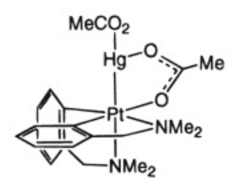
Electrophilic attack by H^+ on d^8 metal–carbon σ-bonded organometallic complexes that contain moieties such as **1** or **6** to give model species containing

(15) Ortiz, J. V.; Havlas, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.
(16) Chen, M. J.; Rathke, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 308.



17 18 (2)

the moieties (**2** ↔ **3**) or (**8** ↔ **9**) also does not appear to have been reported, although polyhapto organometallic[17] and coordination complexes as substrates for H^+ attack have been studied. Systems based on Ir(I)[18] and Pt(II) as representative d^8 metal ions[19] include the reaction of IrBr(cod)$(PMePh_2)_2$ with HPF_6 to form [IrH(Br)(cod)$(PMePh_2)_2$]PF_6[18c] and the reaction of [PtH$(PEt_3)_3$]$^+$ with HCl to form [$PtH_2Cl(PEt_3)_3$]$^+$.[19] However, metal–carbon σ-bonded organometallic complexes react with simple electrophiles other than H^+, and some of these reactions can serve as models for the protonation reaction,[6,20] e.g., the reaction of square-planar *cis*-[Pt{2-$(NMe_2CH_2)C_6H_4$-*C,N*}$_2$] with mercury(II) acetate to give the six-coordinate species **19** (Figure 1b).[6] In this reaction the bridging acetate group may provide intramolecular assistance both for attack by electrophilic mercury(II) and for stabilization of the product. Examples of Me^+ as an electrophile include the reaction of methyl triflate with square-planar $PdMe_2$(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) in acetone-d_6 to form octahedral [$PdMe_3$(tmeda)(acetone-d_6)]$^+$ [8c] and analogous reactions of CD_3I with MMe_2(bpy) (M = Pd,[8d] Pt[21a]) in acetone-d_6 at low temperature to give [$MMe_2(CD_3)$-(bpy)(acetone-d_6)]$^+$ prior to iodide coordination and formation of $MIMe_2(CD_3)$(bpy). These reactions of MMe_2(bpy) are two of the very few examples in which detection of intermediate cations in S_N2 reactions of organohalides with d^8 organometallic substrates has proved possible.[8d,21]



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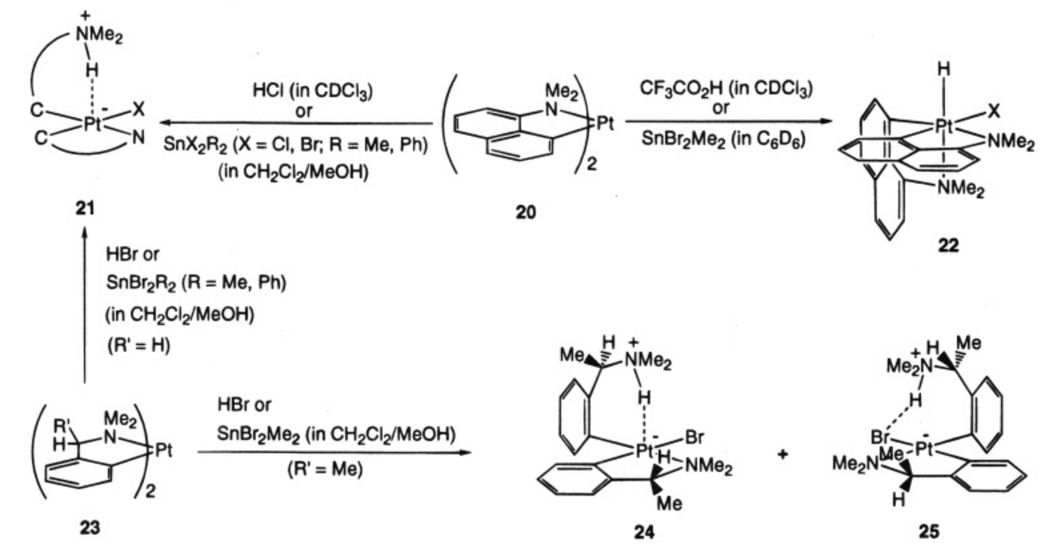
A wide range of M···H–C geometries have been observed for the interaction of metal centers with C–H bonds,[22] and a three-center–two-electron (3c–2e) bonding model for agostic interactions (**4** and **11**) involving

(17) (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. (b) Herrmann, W. A.; Plank, J.; Bauer, Ch.; Ziegler, M. L.; Guggolz, E.; Alt, R. *Z. Anorg. Allg. Chem.* **1982**, *487*, 85. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927. (d) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185. (e) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51.
(18) (a) Blake, D. M.; Kubota, M. *Inorg. Chem.* **1970**, *9*, 989. (b) Ashworth, T. V.; Singleton, J. E.; de Waal, D. J. A.; Louw, W. J.; Singleton, E.; van der Stok, E. *J. Chem. Soc., Dalton Trans.* **1978**, 341. (c) Crabtree, R. H.; Quirk, J. M.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *181*, 203.
(19) Blacklaws, I. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877.
(20) (a) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 1458. (b) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2739. (c) Arsenault, G. J.; Anderson, C. M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 2094. (d) Uson, R.; Fornies, J. *Adv. Organomet. Chem.* **1988**, *28*, 219. (e) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Sutton, D. *Can. J. Chem.* **1989**, *67*, 1832.
(21) (a) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (b) Puddephatt, R. J.; Scott, J. D. *Organometallics* **1985**, *4*, 1221.
(22) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

Scheme 3



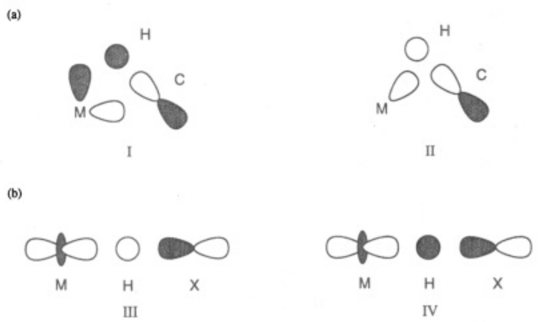


Figure 2. Bonding orbitals for (a) the 3c–2e M··H–C interaction and (b) the 3c–4e M··H–X interaction in d^8 complexes.

$d \rightarrow \sigma_{(CH)}^*$ (I) and $\sigma_{(CH)} \rightarrow d$ (II) in which II is dominant may be applied to these systems (Figure 2a).[1c,23] However, there are several d^6, d^8, and d^{10} complexes[7,24] for which structural or spectroscopic data for M··H–X interactions cannot be readily interpreted in terms of the 3c–2e model, and for some of these complexes a 3c–4e model closely related to hydrogen bonding may be more appropriate. Whereas M··H–X geometries are markedly bent for 3c–2e bonding, in 3c–4e bonding this geometry is close to linear. With linear geometry, as illustrated in Figure 2b, overlap of the d_{z^2} orbital with $\sigma_{(XH)}^*$ (III) and σ_{XH} (IV) occurs to give predominantly electrostatic bonding with minimal interaction of M and H–X orbitals. In contrast to 3c–2e M··H–X interactions, characterized by upfield shifts for the proton resonance, complexes proposed as containing 3c–4e interactions exhibit a downfield shift for this proton compared with free ligand values.

The best explored M··H–N systems containing d^8 metal ions include an organoplatinum(II) complex with an intramolecularly coordinated group Pt··H–N~C which has distances of Pt··H = 2.11(5) Å and N–H = 0.88(5) Å, with a Pt··H–N angle of 168(4)°, as illustrated in **21** (Scheme 3) and Figure 3a.[7] Complexes **21**, which have been shown to possess a zwitterionic Pt^{II-}··H–N^+ unit, may be considered as models for the lower oxidation state species **9** in Scheme 1. Complexes **21** can be formed by reaction of **20** or **23** (R′ = H) with HCl, or with SnX_2R_2 in the presence of methanol which also generates HX as the protic reagent. Under slightly different conditions **20** reacts with the protic reagent CF_3CO_2H to afford the hydridoplatinum(IV) tautomer **22**, which is related to **8**. The assignment of oxidation state and the presence of 3c–4e bonding in complex **21** (X = Br, from **20**) follow directly from structural and spectroscopic data; e.g., δ(H) for Pt··H–N is at +16 ppm with J(H–Pt) 180 Hz compared to −20.35 ppm with 1540 Hz for the Pt(IV) complex **22** (X = Br). Complex **22** appears to be the first isolated organoplatinum(IV) hydride.[7,25] Complexes **23** (R′ = H, Me), similar to **20**, react with HBr (or $SnBr_2R_2$ in the presence of methanol generating HBr) to form either **21** (R′ = H) with a Pt··H–N interaction or, when R′ = Me, the analogous complex **24** together with complex **25** having a N–H interaction with the Pt–Br bond. Complex **25** has H··Br = 2.486(13) Å with the N–H vector pointing between Pt and Br [N–H··Br = 157.4(1.5)°] (Figure 3b).

The dependence upon reaction conditions and minor changes in ligand design for the formation of **21**, **22**, **24**, and **25** may be explained in terms of the ease of formation of products under different conditions. For HCl or HBr as reagents in $CDCl_3$, the Pt(II) complexes **21** may be formed directly, most likely via protonation of a dissociated ligand (**26**). Other reaction conditions are assumed to be unable to give **21** directly, and thus the Pt(IV) oxidation product **22** is formed. Thus, for CF_3CO_2H as reagent, reaction of **20** to form **22** may

(23) (a) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(24) (a) Baker, A. W.; Bublitz, D. E. *Spectrochim. Acta*, **1966**, *22*, 1787. (b) Drago, R. S.; Nozari, M. S.; Klinger, R. J.; Chamberlain, C. S. *Inorg. Chem.* **1979**, *18*, 1254. (c) Calderazzo, F.; Fachinetti, G.; Marchetti, F. *J. Chem. Soc., Chem. Commun.* **1981**, 181. (d) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922. (e) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1986**, *5*, 336. (f) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508. (g) Albinati, A.; Anklin, C. G.; Ganazzoli, F.; Ruegg, H.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 503. (h) Yoshida, T.; Tani, K.; Yamagata, T.; Tatsuno, Y.; Saito, T. *J. Chem. Soc., Chem. Commun.* **1990**, 292. (i) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789. (j) Brammer, L.; McCann, M. C.; Bullock, R. M.; McMullan, R. K.; Sherwood, P. *Organometallics* **1992**, *11*, 2339. (k) Shubina, E. S.; Krylov, A. N.; Timofeeva, T. V.; Struchkov, Y. T.; Ginzburg, A. G.; Loim, N. M.; Epstein, L. M. *J. Organomet. Chem.* **1992**, *434*, 329. (l) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069. (m) Brammer, L.; Zhao, D. *Organometallics* **1994**, *13*, 1545. (n) Albinati, A.; Lianza, F.; Pregosin, P. S.; Muller, B. *Inorg. Chem.* **1994**, *33*, 2522.

(25) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13.

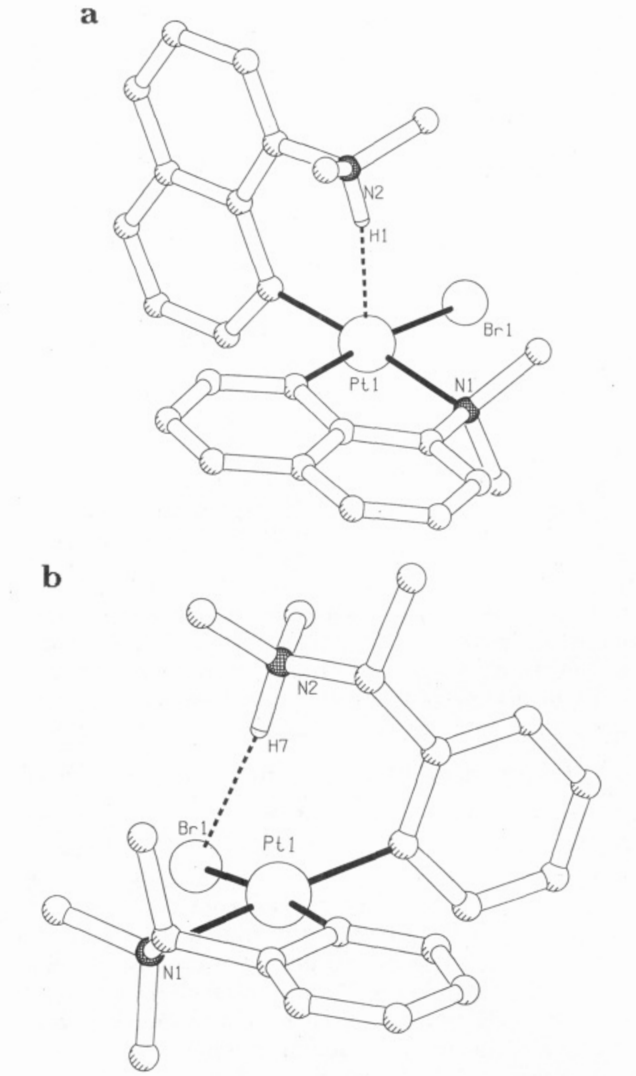
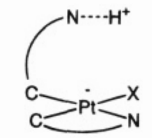


Figure 3. Crystallographic studies of reaction products in Scheme 3: (a) [PtBr{1-(NMe_2)$C_{10}H_6$-*C,N*}{1-($NHMe_2$)$C_{10}H_6$-*C,-H*}] (**21** with X = Br formed from **20**)[7a,b] and (b) [PtBr{(*R*)-2-(NMe_2CHMe)C_6H_4-*C,N*}{(*R*)-2-($NHMe_2CHMe$)C_6H_4-*C*)}] (**25**).[7b]

occur via intermediate **27**, which is modeled by the mercury(II) acetate adduct **19**. For $SnBr_2Me_2$ as a reagent in benzene (**20** → **22**), in which HBr is not formed from $SnBr_2Me_2$, direct oxidative addition to form octahedral $PtBr(C{\sim}N)_2(SnBrMe_2)$ may occur followed by dissociation of bromide, β-elimination from the resulting five-coordinate cation (**28**), and then recoordination of bromide. The homochiral complex **23** (R′ = Me), in which both ligands have the *R* configuration, forms a mixture of diastereoisomers **24** and **25** on reaction with HBr. Steric effects between the methyl-substituted bidentate ligand and the other ligand in **24** and **25** are different, resulting in a preference for the Pt···H−N interaction in **24** and the mainly electrostatic interaction of the N−H moiety with the Pt−Br bond in **25**.

Oxidation of d^8 Organometal Species by Water

The oxidation of complexes by water is assumed to involve either protonation of the metal center or oxidative addition to form two additional metal−ligand bonds. The protonation and oxidative addition reactions have been reported for a small number of d^8 coordination complexes,[26] in particular the reaction



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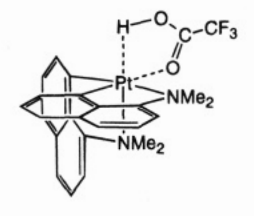

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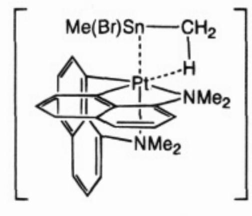

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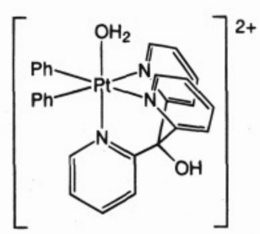
of $RhH(PEt_3)_3$ to form $[RhH_2(PEt_3)_3]^+$ [26b] and of $[Ir(PMe_3)_4]^+$ to form *cis*-$[IrH(OH)(PMe_3)_4]^+$.[26c,d] The only reported oxidation reactions of d^8 M−C σ-bonded complexes by water to give well characterized products appear to be for Pt(II)[9ab;27] and more recently for Pd(II).[9a,b] For example, the reaction of water with the tris(pyridin-2-yl)methanol complex $PtPh_2\{(py)_3COH\text{-}N,N'\}$, which has one uncoordinated pyridine group, leads to $[Pt(OH)Ph_2\{(py)_3COH\text{-}N,N',N''\}][OH]{\cdot}H_2O$; this complex is readily protonated in dilute nitric acid to form $[PtPh_2\{(py)_3COH\text{-}N,N',N''\}(OH_2)]^{2+}$ (**29**),[9a] which has been characterized by X-ray crystallography.[28] The formation of hydroxometal(IV) complexes in oxidations by water is assumed to occur via formation of hydridometal(IV) intermediates which are rapidly hydrolyzed with the release of hydrogen.[9a,b,27a] A neutral hydroxoplatinum(IV) complex $Pt(OH)Me_2\{(pz)_3BH\}$ (**30**), also characterized by X-ray diffraction, has been obtained recently on addition of the anionic tris(pyrazol-1-yl)borate ligand to $[PtMe_2(SEt_2)]_2$ in acetone followed by reaction with water.[9b] Structures **29** and **30** represent the first crystallographic studies of M−C σ-bonded organometallics that have been formed using water as an oxidant.



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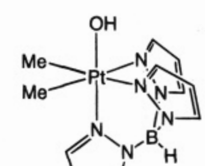

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The tris(pyrazol-1-yl)borate ligand is now known to form some of the most stable palladium(IV) complexes, and several have been studied by X-ray crystallography.[8f] For example, $PdMe_2Et\{(pz)_3BH\}$ formed on oxidative addition of EtI to $[PdMe_2\{(pz)_3BH\}]^-$ has a stability similar to that of the most stable ethylpalladium(II) complexes, and the pallada(II)cyclopentane species $[\overline{Pd(CH_2CH_2CH_2C}H_2)\{(pz)_3BH\}]^-$ reacts with the electrophiles chlorine, bromine, and iodine to provide the first reported stable diorganopalladium(IV) complexes $\overline{Pd(CH_2CH_2CH_2C}H_2)(X)\{(pz)_3BH\}$ (X = Cl, Br, I).[9b] The anion $[\overline{Pd(CH_2CH_2CH_2C}H_2)\{(pz)_3BH\}]^-$

(26) (a) Gillard, R, D.; Heaton, B. T.; Vaughan, D. *J. Chem. Soc. A* **1970**, 3126. (b) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411. (c) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (d) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.

(27) (a) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444. (b) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1990**, *406*, 261. (c) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Williams, M. A. *J. Organomet. Chem.* **1984**, *276*, C73.

(28) Canty, A. J.; Fritsche, S.; Honeyman, R. T.; Jin, H.; Roberts, A. S.; Skelton, B. W.; White, A. H. Unpublished results.

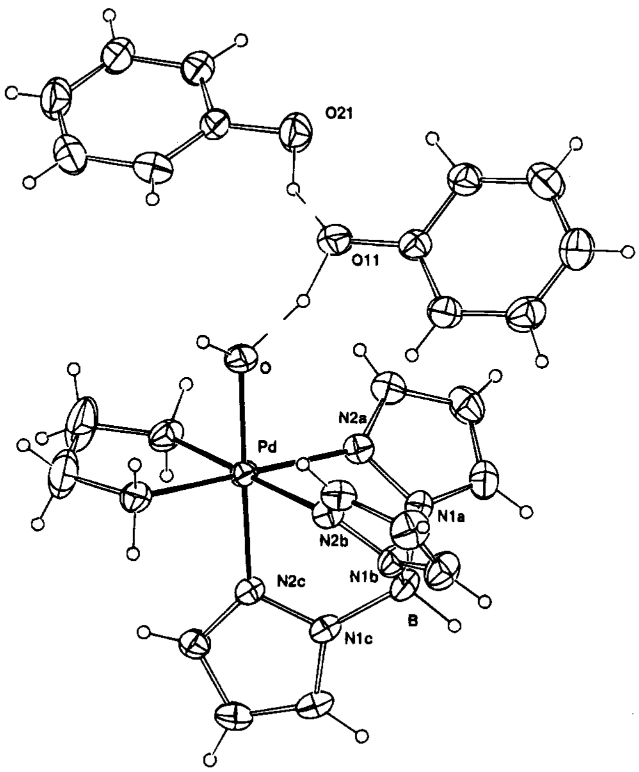


Figure 4. Crystallographic study of the pallada(IV)cyclopentane complex $\overline{Pd(CH_2CH_2CH_2CH_2)}(OH)\{(pz)_3BH\}\cdot 2(PhOH)$ illustrating the hydrogen-bonding to phenol groups where O···O11 and O11···O21 distances are 2.471(5) and 2.648(5) Å, respectively.[28]

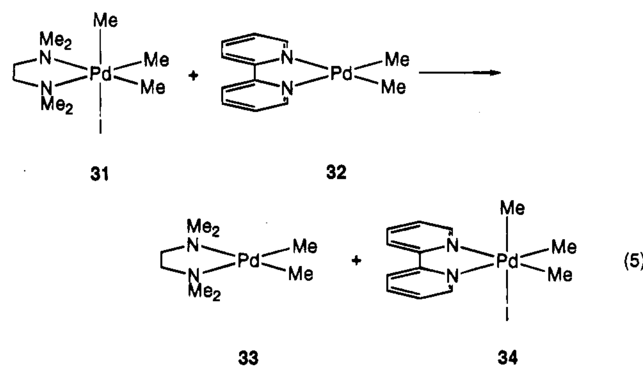
also reacts with water to form the hydroxo complex $\overline{Pd(CH_2CH_2CH_2CH_2)}(OH)\{(pz)_3BH\}$, presumably via an intermediate hydridopalladium(IV) species which is hydrolyzed by water to give the product complex and hydrogen (eq 3). This reaction and others below appear to be the first reports of oxidation of any Pd(II) species by water.[9a,b] This hydroxopalladium(IV) complex forms hydrogen-bonded adducts with phenols,[9c] as illustrated in Figure 4.

$$[\overline{Pd^{II}(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^- + 2H_2O \rightarrow \overline{Pd^{IV}(CH_2CH_2CH_2CH_2)}(OH)\{(pz)_3BH\} + OH^- + H_2 \quad (3)$$

In contrast to dimethylplatinum(II) and pallada(II)cyclopentane complexes of tris(pyrazol-1-yl)borate, the analogous complex ions $[PdMeR\{(pz)_3BH\}]^-$ (R = Me, Ph) undergo remarkable reactions with water involving both oxidation of Pd(II) and methyl group transfer between palladium centers.[9a] The reactions proceed in high yield (100% for R = Me), and the Pd(II) products have been characterized as PPh_3 complexes $PdR\{(pz)_3BH\}(PPh_3)$ (eq 4);[9a] the complex with R = Ph has been the subject of an X-ray crystallographic study.[29]

$$2[Pd^{II}MeR\{(pz)_3BH\}]^- + 2H_2O + PPh_3 \rightarrow Pd^{IV}Me_2R\{(pz)_3BH\} + Pd^{II}R\{(pz)_3BH\}(PPh_3)\ (R = Me, Ph) + 2OH^- + H_2 \quad (4)$$

Methyl group transfer from Pd(IV) to Pd(II) centers was first observed in our laboratories, with eq 5 illustrating a typical reaction in which the Pd(IV) bpy product (**34**) is more stable than the Pd(IV) tmeda reactant (**31**).[8e] The reactions are retarded by additional halide ion, and this evidence, together with kinetic studies of related reactions,[30] indicates that transfer of Me^+ occurs via interaction of nucleophilic $PdMe_2(bpy)$ (**32**) with an electrophilic methylpalladium(IV) group of a new species which has been formed by iodide dissociation from $PdIMe_3(tmeda)$ (**31**), $[\{(tmeda)Me_2Pd\cdots Me\cdots PdMe_2(bpy)\}^+]^{\ddagger}$.

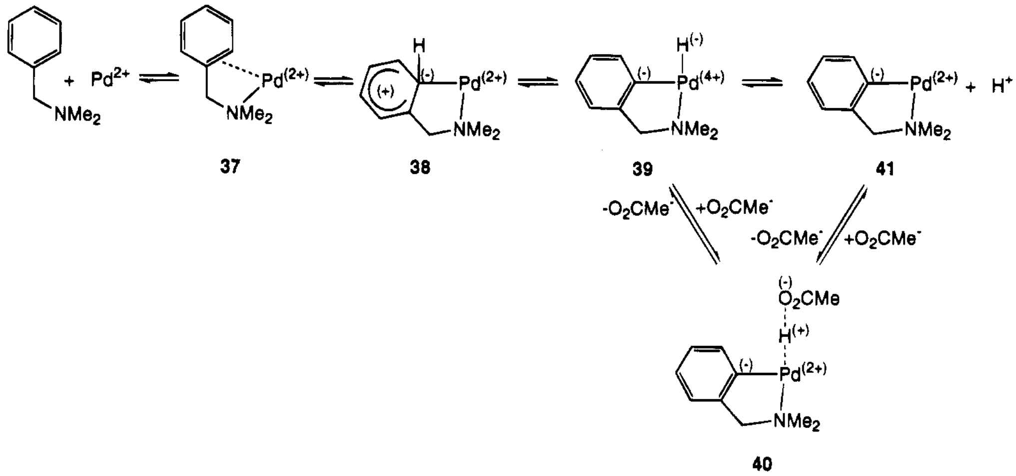


Thus, in the overall reaction described by eq 4, oxidation by water forms a $Pd^{IV}(OH)MeR$ intermediate closely related to stable $\overline{Pd(CH_2CH_2CH_2CH_2)}(OH)\{(pz)_3BH\}$, and this is followed by fast methyl group transfer from the Pd(IV) species to the Pd(II) reagent $[PdMeR\{(pz)_3BH\}]^-$ to form more stable $PdMe_2R\{(pz)_3BH\}$.

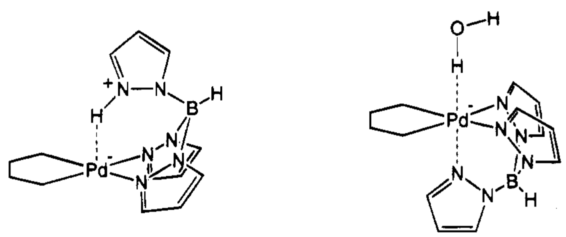
The uncoordinated pyridine group in $PtPh_2\{(py)_3COH\text{-}N,N'\}$ or the pyrazole group in the other square-planar metal(II) substrates, e.g., $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\text{-}N,N'\}]^-$, may provide intramolecular assistance in reactions with water either by delivering a proton to the metal center (**35**) or by increasing the nucleophilic character of the metal(II) center on coordination (**36**). The possible intermediate **35** is closely related to **21**, which has Pt···N 2.982(4) Å, and a similar Pd···N geometry is feasible for **35** since the isoelectronic complex $[AuMe_2\{(pz)_3CH\text{-}N,N'\}]^+$ with an electrophilic Au(III) center and a ligand skeleton closely related to $[(pz)_3BH]^-$ has a weak axial Au···N interaction of 3.139(7) Å.[31] The uncoordinated pyrazole group in complexes of $[(pz)_3BH]^-$ and in closely related ligands is known to be easily protonated;[32] e.g., $[AuMe_2\{(pz)_2(pzH)BH\}]^+$ has a pK_a of 3.69.[32a] For the potential intermediate **36** a water molecule is shown hydrogen-bonded to the metal center, with Pd···H–O similar to Pt···H–N in **21**. For this intermediate the axial Pd···pz interaction is expected to ease the transition to an octahedral product, and this intermediate is consistent with observations of rate enhancement for oxidative addition of MeI to square-

(29) Canty, A. J.; Jin, H.; Roberts, A. S.; Traill, P. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *489*, 153.
(30) Aye, K.-T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518.
(31) Canty, A. J.; Minchin, N. J.; Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1795.
(32) (a) Byers, P. K.; Canty, A. J.; Minchin, N. J.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1183. (b) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 423. (c) Rheingold, A. L.; Haggerty, B. S.; Trofimenko, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1983.

Scheme 4



planar Rh(I) and Ir(I) complexes in the presence of coordinating nucleophiles,[33] including *N*-methylimidazole.[33b]



Concluding Remarks

This Account summarizes recent research that implicates the occurrence of electrophilic attack at the metal center in reactions leading to metal−electrophile bonding, i.e., the sequence **1** → (**2** ↔ **3**) and **6** → (**8** ↔ **9**) → **7** in Scheme 1, and in some reactions subsequent transfer of the electrophile to organic groups. In several of these reactions delivery of the electrophile to the metal center is mediated by a nucleophile (X) which may be part of an intramolecularly bonded coordination system, and 3c−4e M··H−X interactions play a role in some cases. When the electrophile is H^+ and is delivered to an aryl group via bonding to the metal center, a hydrocarbon may be released from an arenonium species (**7**) and thus the overall reaction (reagent pair **6** forming **12** in Scheme 1) involves some steps that are the reverse of C−H activation of arenes. Conversely, for arenes interacting with d^8 centers (reagent pair **12** in Scheme 1) evidence for preliminary η^2-coordination (**10**) is well documented,[2ad,34] and therefore, η^2-bonded species may be assumed to occur as intermediates in the loss of arene from species such as **7**.

As is always the case for reaction mechanisms modeled by isolated species, the structures of the model complexes may not reflect the geometries of intermediates, but when their chemistry is closely related to reactions of mechanistic interest they are expected to represent geometries that are close to those for the true intermediates.

Application of the above principles to C−H activation assisted by intramolecular coordination, i.e., the classical cyclometalation system exemplified by eq 1, is shown in Scheme 4 using *N,N'*-dimethylbenzylamine as a representative substrate. Several complexes that model the η^2-interaction in **37** have been reported,[35] and additional possible intermediates include species with agostic (**11** in Scheme 1) and η^1-*ipso*-carbon interactions, where the latter is exemplified by $Pd(C_6F_5)_2(PhCH_2NMe_2\text{-}C,N)$.[36] An electrophilic process is generally considered to give,[4] perhaps via η^1- and η^2-interactions (**37**), an arenonium species (**38**) followed by loss of H^+ to afford **41**. Loss of H^+ from **38** may be assisted by a nucleophile,[4] e.g., the ubiquitous acetate ion commonly present in cyclopalladation chemistry. However, a 1,2-shift process to form **39** with a higher oxidation state for palladium may also be accessible, in particular in view of the recent synthesis of arylpalladium(IV) complexes that are stable up to 60 °C in solution,[8f] the expected intermediacy of hydridopalladium(IV) species in the oxidation of organopalladium(II) complexes by water,[9a,b] and spectroscopic evidence for the formation of hydrido(alkyl)palladium(IV) species on the reaction of $PdBr_2(PPh_3)_2$ with cyclohexane.[37] Alternatively, or in addition, the presence of a nucleophile such as the acetate ion may allow the formulation of intermediate **39** as a Pd(II) species **40**, in which a Pd··H··O_2CMe interaction closely related to the Pt··H−N interaction in **21** could lead to facile loss of H^+ from palladium to form **41**.

Other situations in which intermediates in Scheme 1 may occur include (a) cyclopalladation to cleave C−Si bonds,[10,38] which is favored over C−H attack in trimethylsilyl-substituted arenes;[10b] (b) zeolite catalysis where Pd or Pt atoms interact with protons (M··H−

(33) (a) de Waal, D. J. A.; Gerber, T. I. A.; Louw, W. J. *Inorg. Chem.* **1982**, *21*, 1259. (b) Hickey, C. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1609. (c) Murphy, M. A.; Smith, B. L.; Torrence, G. P.; Aguilo, A. *Inorg. Chim. Acta* **1985**, *101*, L47. (d) Basson, S. S.; Leipoldt, J. G.; Purcell, W.; Schoeman, J. *Inorg. Chim. Acta* **1990**, *173*, 155. (e) Haynes, A.; Mann, B. E.; Gulliver, D. J.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 8567.
(34) (a) Klabunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 9081. (b) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429.
(35) (a) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169. (b) Li, C.-S.; Cheng, C.-H.; Liao, F.-L.; Wang, S. L. *J. Chem. Soc., Chem. Commun.* **1991**, 710.
(36) Falvello, L. R.; Fornies, J.; Navarro, R.; Sicilia, V.; Tomas, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3143.
(37) Vedernikov, A. N.; Kuramshin, A. I.; Solomonov, B. N. *J. Chem. Soc., Chem. Commun.* **1994**, 121.
(38) (a) Nishiyama, H.; Matsumoto, M.; Matsukura, T.; Miura, R.; Itoh, K. *Organometallics* **1985**, *4*, 1911. (b) Pereira, M. T.; Pfeffer, M.; Rotteveel, M. A. *J. Organomet. Chem.* **1989**, *375*, 139.

O),[39] and (c) C−C coupling reactions occurring at metal centers. Thus, for the latter reactions concerted reductive elimination of aryl and alkyl groups may proceed via 1,2-shifts, with an alkyl group in place of H for **8** → **7** → **10** → **12**. A specific example is provided by the selective reductive elimination of toluene from the first reported Pd(IV) complexes containing three different organic groups, i.e., $PdXMePh(CH_2Ph)(bpy)$ (X = Br, I).[8e]

In addition to further elucidation of mechanistic details of the chemistry described here, challenges arising from this research in d^8 organometallic chemistry include the development of arenonium chemistry for palladium(II), observation of 1,2-shifts for systems where both the reactant and product are isolable, the synthesis of complexes containing stable 3c−4e M···H−X interactions for X ≠ N, the isolation of d^6 (hydrido)-organometal complexes from reactions in which water is an oxidizing agent, and the exploration of the differences between systems in which nucleophilic assistance for electrophilic attack is provided by an intramolecular or external nucleophile.

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(39) (a) Xu, L.; Zhang, Z.; Sachtler, W. M. H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2291. (b) Zholobenko, V. L.; Lei, G.-D.; Carvill, B. T.; Lerner, B. A.; Sachtler, W. M. H. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 233.