Figure 1 compares $D^\circ(M^+-CH_2)$ values to $E_p(sd^{n-1})$ for the first-row transition metals. The slope of the linear regression fit is nearly identical with those previously reported for MH^+ and MCH_3^+.[6] The excellent fit to the data indicates that the promotion energy–bond strength correlation extends to double bonds as well as single bonds of transition metals. The maximum or intrinsic $M^+{=}CH_2$ bond strength is ~101 kcal/mol, such that the intrinsic M^+-C π-bond strength is ~45 kcal/mol. The intrinsic double-bond value corresponds nicely with the lone metal–methylidene bond energy known for a *saturated* metal center, $D^\circ[(CO)_5Mn^+{=}CH_2] = 96 \pm 7$ kcal/mol.[16] Preliminary data indicate that a parallel correlation also holds for M^+-CH triple bonds,[6] with an intrinsic $M^+{\equiv}CH$ BDE of ~130 kcal/mol. It is interesting to note that the ratio of the *intrinsic* M^+-C single-, double-, and triple-bond strengths, 1.0:1.68:2.20, is nearly identical with that for C–C single, double, and triple bonds (as represented by CH_3-CH_3, $CH_2{=}CH_2$, and $CH{\equiv}CH$), 1.0:1.65:2.21.

In their theoretical paper, Carter and Goddard[2] suggest that the M^+-CH_2 BDEs should correspond to the *lower* value of the sd^{n-1} and d^n promotion energies, shown in boldface in Table I. For M = Co and Cr, however, it is clearly the higher $E_p(sd^{n-1})$ value that best matches the periodic trend (Figure 1). In contrast, the $E_p(d^n)$ data point for M = Fe is in better agreement with the best fit than the $E_p(sd^{n-1})$ value, although the latter value is within 2 standard deviations of the line. Overall, this suggests that the bonding character for $M^+{=}CH_2$ bonds involves substantial 4s character. Conversely, the slope of the line in Figure 1 is not unity, which could mean that s–d hybridization may be important in the bonding.

On the basis of the deviation of $D^\circ(FeCH_2^+)$ from the line, a comparison of the bonding in this molecule to neighboring species would be a particularly interesting topic for detailed theoretical characterization. Theoretical studies of $CuCH_2^+$ should also be fruitful since Figure 1 suggests this species could have a covalent M–C double bond, but a comparable bond strength can conceivably arise from a dative interaction where $CH_2(^1A_1)$ donates a pair of electrons into the empty 4s orbital of ground-state $Cu^+(3d^{10})$. Indeed, very recent results of Planelles et al.[17] conclude that the ground state of $CuCH_2^+$ has the latter electronic structure although a $Cu{=}CH_2^+$ species (correlating to excited $Cu^+(^3D,4s^13d^9) + CH_2(^3B_1)$) was not explicitly considered.

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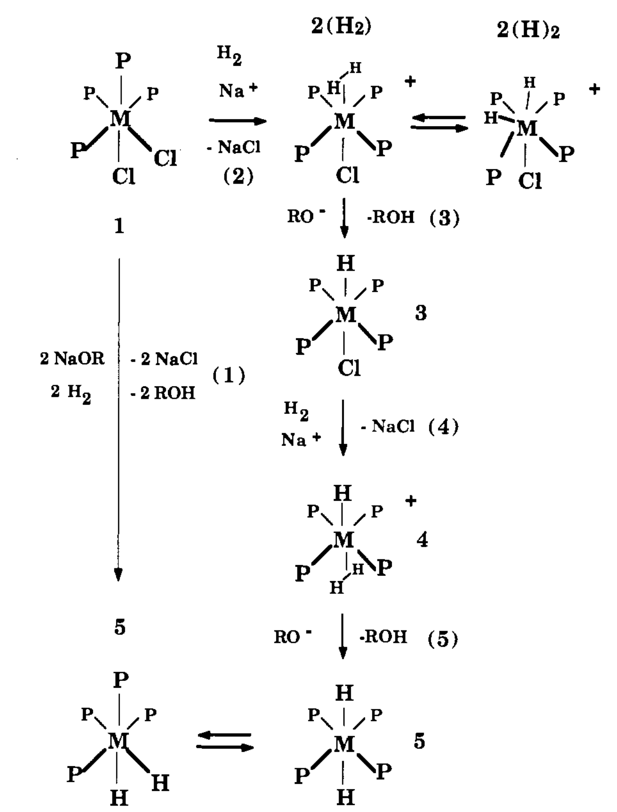
From *cis*-Dichloride Complexes to Dihydride Complexes of the Iron Group Metals via Two Successive η^2-Dihydrogen Intermediates

The properties of the iron group hydride complexes of the type $[M(H_2)(H)L_2]^+$ (M = Fe, Ru, Os; L = di(tertiary phosphine)[1]) are being studied to understand the bonding and reactivity of the unusual η^2-dihydrogen ligand.[2] There is also interest in the use of the neutral complexes $MXHL_2$ (X = H,[3] alkyl[4]) for the activation of C–H bonds. We describe here how the heterolytic cleavage of dihydrogen provides a convenient route to the complexes of $MH_2(PR_2CH_2CH_2PR_2)_2$ (R = Et, M = Fe, Os; R = Ph, M = Ru, Os) as well as MH_2(*rac*-tetraphos-1) (M = Ru, Os), some of which are quite difficult to prepare by using standard hydride reagents, $LiAlH_4$ or $NaBH_4$. The conditions for the reactions are surprisingly mild (1 atm, 20 °C), especially for the d^6 Os complexes. The preparative methods developed from the following observations: (a) *cis*-β-$OsCl_2$(*meso*-tetraphos-1) is converted directly to $[Os(H_2)(H)($*meso*-tetraphos-1$)]BPh_4$ when it is treated with $NaBPh_4$ in THF under 1 atm H_2;[1d] (b) $[Fe(H_2)(H)L_2]^+$ complexes can be deprotonated to give dihydrides (eq 5, Scheme I);[1a,5] (c) coordinated H_2 is generally considered to be more acidic than a hydride ligand in the same molecule.[2a,b] This is the first example of two successive heterolytic cleavages

Scheme I[a]



[a] The substituents on the phosphine ligands have been left out for clarity. The stereochemistries of 2 are tentative.

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of dihydrogen where the dihydrogen intermediates have been identified. One of the intermediates represents a new series of dihydrogen complexes $[MCl(H_2)(PR_2CH_2CH_2PR_2)_2]^+$ which must be as acidic as HCl.

The known complexes $MH_2(depe)_2$[6] (M = Fe, Ru, Os; depe = $PEt_2CH_2CH_2PEt_2$ (**5a–c**)) and $MH_2(dppe)_2$[9] (M = Ru, Os (new complex); dppe = $PPh_2CH_2CH_2PPh_2$ (**5d,e**)) are prepared in good yield from the dichlorides *cis*-MCl_2L_2 (**1a–e**)[11] according to eq 1 in Scheme I. Here solutions of **1** in EtOH or THF/^{t}BuOH (80/20 v/v) react with 2 equiv of base (NaOEt or NaO^tBu) under H_2 (1 atm) at 20 °C. The reactions of **1c** and **1e** also require the addition of $NaBPh_4$ (1 equiv) to ensure the complete removal of chloride from complexes **3c** and **3e**. The dihydrides are separated from the sodium salts by extraction into benzene and filtration through Celite. The use of the base NaO^tBu demonstrates that the hydrides come from H_2 gas and not from the alcohol (since β-elimination is not possible). The use of an Ar atmosphere does not give the products except for the case when **1d** is reacted with NaOEt; here **5d** is obtained in excellent yield. The complexes MH_2(*rac*-tetraphos-1) (M = Ru,[12] Os[1d,13]) have also been prepared by this method.

The mechanism proposed in Scheme I is based on the reactions of the dichlorides with 1 equiv of $NaBPh_4$ and H_2 (1 atm) in ethanol or THF in the absence of added base. Here mixtures of the hydrides *trans*-$MHClL_2$[7,8] (**3**) and the dihydrogen complexes $[M(Cl)(\eta^2\text{-}H_2)L_2]^+$[14,15] (**2**) and *trans*-$[M(H)(\eta^2\text{-}H_2)L_2]BPh_4$ (**4**)[1] form in amounts that vary depending on the starting complex **1** (eq 6; see also the supplementary material). For the reaction of

$$cis\text{-}MCl_2L_2 + NaBPh_4 + H_2 \rightarrow \mathbf{2} + \mathbf{3} + \mathbf{4} + NaCl + HCl \tag{6}$$

cis-$RuCl_2(depe)_2$ (**1b**) with $NaBPh_4$, the first product observed by ^{31}P NMR is **2b** as expected from Scheme I. The chloride must be labilized by the trans phosphorus; *trans*-**1b** does not react. If 1 equiv of base (NaOEt or NEt_3) is added to the mixture from reaction 6, then the dihydrogen complexes **4a** and **4c** become the major products for the Fe and Os complexes with R = Et as expected from eq 3 and 4. Hydrogen uptake of 1.7 mol/mol of Fe occurs in less than 5 min when **1a** is reacted with $NaBPh_4$ and NaOEt in EtOH at 13 °C to give pure **4a**[1b] as a white precipitate. The reverse of eq 3, the protonation of **3** with $HBF_4{\cdot}Et_2O$, yields BF_4^- salts of the stable dihydrogen complex **2c**[14a] and the unstable complexes **2b**[15a] and **2a**.[16] The reaction of **3a–c** with H_2 and $NaBPh_4$ to give **4** (eq 4) has already been reported.[1b] This reaction also explains the formation of **4a** by reaction of **3a** with traces of H_2 and lithium salts as observed by Baker and Field.[17] The deprotonation step 5 has been demonstrated with the bases HOEt for **4a**,[5] BuLi for **4b**,[12] and NaO^tBu for **4c**.[13] Five-coordinate complexes $[MClL_2]^+$[18] from eq 2 and $[MHL_2]^+$[1a,19] from eq 4 are likely responsible for hydrogen uptake. Equation 6 implies that the dihydrogen complexes **2** are very acidic since HCl is produced in the reaction.

The new complexes $[MClH_2L_2]^+$ (**2**) are thermally stable for M = Os[14] but decompose slowly in solution when M = Ru[15] and rapidly when M = Fe,[16] even under H_2. These complexes give quintets in the high-field region of the ^1H NMR spectra that broaden as the solution is cooled to 200 K. The short minimum T_1 values for these resonances for **2b**[15] and **2c**[14] are indicative of H–H bonding in the complex.[1e,2b] H–H distances of 0.95 and 1.06 Å are calculated from the T_1(min) values of **2b**[15a] and **2c**,[14a] respectively, assuming rapid spinning of the H_2 ligand.[1e] However these are long enough to suspect that the dihydrogen complex, **2**(H_2), may be in rapid equilibrium with a significant amount of a dihydride isomer, **2**$(H)_2$ (Scheme I). The observed couplings $^2J(H,P)$ would be averaged by such an equilibrium. This would explain why they are smaller (7.2 Hz for **2b**, 11.8 Hz for **2c**) than expected for hydride–^{31}P couplings (~20 Hz), but they are larger than usual dihydrogen–^{31}P couplings $^2J(H_2,P) < 6$ Hz. If $^2J(H_2,P) = 0$ Hz for **2b**(H_2), and $^2J(H,P) = 20$ Hz for **2b**$(H)_2$, then the fraction of **2b**(H_2) is 0.7 and a more reasonable H–H distance of 0.86 Å[1e] is calculated from $T_1(H_2, \text{min}) = 20$ ms (T_1(H of **2b**$(H)_2$) ~ 280 ms). The ratio **2c**(H_2)/**2c**$(H)_2$ is likely to be less than 1.0, but more work is needed. Judging from their larger $^2J(H,P)$ couplings, **2d** and **2e** are predominately in the dihydride form. Attempts to observed $^1J(H,D)$ couplings for complexes **2**(HD) at low temperatures are in progress.

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Supplementary Material Available: A table of yields from reaction 6 (1 page). Ordering information is given on any current masthead page.

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[6] (a) $FeH_2(depe)_2$:[3a] 50% yield (contaminated with free depe) from **1a**, H_2 and 2 equiv of NaOEt in EtOH, 3 h of stirring. (b) $RuH_2(depe)_2$:[7] 45% (contains a little $RuHCl(depe)_2$) from **1b**, H_2 and 2 equiv of NaOEt in THF/EtOH or 2 equiv of NaO^tBu in THF/^{t}BuOH, 15 h of stirring. (c) $OsH_2(depe)_2$:[8] 67% yield, (cis/trans = 1.8) from **1c**, H_2 and 2 equiv of NaO^tBu and 1 equiv of $NaBPh_4$ in THF/^{t}BuOH, 18 h of stirring. Anal. Calcd for $C_{20}H_{50}OsP_4$: C, 39.73; H, 8.33. Found: C, 39.63; H, 8.02.

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[9] (a) $RuH_2(dppe)_2$:[10] 60% yield (50% overall from $RuCl_3{\cdot}3H_2O$) from **1d**, H_2 and 2 equiv of NaOEt in THF/EtOH, 15 h of stirring. (b) $OsH_2(dppe)_2$: 80% yield (cis/trans = 9) from **1e**, H_2 and 2 equiv of NaO^tBu and 1 equiv of $NaBPh_4$ in THF/^{t}BuOH, 13 h of stirring. Anal. Calcd for $C_{52}H_{50}OsP_4$: C, 63.15; H, 5.09. Found: C, 63.49; H, 5.43. IR (Nujol): 1964 cm^{-1} br, ν(OsH). $^{31}P\{^1H\}$ NMR (162 MHz, THF, vs H_3PO_4): δ 49.6 (*trans*-**5e**, s), 45.7 (P_A or $P_{A'}$ of *cis*-**5e**, t, $J_{AM} = J_{AM'} = J_{A'M} = J_{A'M'} \sim -5$ Hz), 35.9 (P_M or $P_{M'}$ of *cis*-**5e**, t). ^1H NMR (200 Mz, C_6D_6): δ −9.95 (H_X or $H_{X'}$ of *cis*-**5e**, AA′MM′XX′ pattern, $J_{MX} = J_{M'X'} = +54.4$ Hz, $J_{M'X} = J_{MX'} = -14.3$ Hz, $J_{XX'} = -3.5$ Hz, $J_{AX'} = J_{A'X} = -21.8$ Hz, $J_{MM'} = 0$ Hz), −10.85 (*trans*-**5e**, quintet, $J_{PH} = 15.6$ Hz).

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[14] (a) $[OsCl(\eta^2\text{-}H_2)(depe)_2]BF_4$ (**2c**): colorless; prepared also by the reaction of **3c** with $HBF_4{\cdot}Et_2O$ in ether. IR (Nujol): no ν(OsH). ^1H NMR (acetone-d_6, 400 MHz): δ −13.85 (quintet, $J_{PH} = 11.8$ Hz, OsH, T_1(min, 208 K) = 60 ms). ^{31}P NMR (acetone): δ 26.0 (s). Anal. Calcd for $C_{20}H_{50}BClF_4P_4Os$: C, 33.05; H, 6.93. Found: C, 33.39; H, 6.88. (b) **2e** observed in solution. ^1H NMR: δ −16.5 (quintet, $J_{PH} = 16.3$ Hz). $^{31}P\{^1H\}$ NMR (THF): δ 32.8 (s).

[15] (a) **2b** was also generated by reacting **1b** with 1 equiv of $NaBPh_4$ and 1 atm of H_2 in acetone-d_6 for 5 min. ^1H NMR (acetone-d_6, 400 MHz): δ −14.1 (quintet, $J_{PH} = 7.2$ Hz, RuH, T_1(min, 210 K) = 28 ms). $^{31}P\{^1H\}$ NMR (acetone): δ 54.6 (s). (b) **2d** observed in solution. ^1H NMR: δ −15.8 (quintet, $J_{PH} = 18.5$ Hz).

[16] **2a**. ^1H NMR (acetone-d_6): −23.6 (quintet, $J_{PH} = 48$ Hz).

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