Organometallics **1989**, *8*, 2073–2074

lone pair with a half-filled d orbital on chromium.

The free phosphine moiety made **2** susceptible to electrophilic attack. Reaction with $Me_3O^+BF_4^-$, for example, yielded the phosphonium salt **3**.[16] As expected, ^1H NMR resonances for only one isomer of **3** were observed. This compound may also be viewed as an ylide complex[17] and is closely related to Werner's structurally characterized $Cp(I)\overline{RhCH_2P(CH_3)_2CH_2CH_2P}(CH_3)_2$,[18] which was shown to adopt a chair configuration very similar to that of **2**. In addition several chromium compounds reported by Weber et al. serve as precedent for this unusual six-membered heterocycle.[19] Protonation of **2** did not regenerate **1** but rather yielded a mixture of compounds (ca. 2:1 ratio) to which we tentatively assign the structures **4a,b** (Scheme I).[20]

We conclude that the C–H bonds of ligands in cationic chromium(III) complexes are strongly activated with respect to deprotonation. Judicious choice of deprotonation resistant supporting ligands should ultimately lead to proton abstraction from alkyl ligands, thus generating chromium(III) alkylidenes. Efforts to isolate and characterize such compounds are currently underway in our laboratory.

Acknowledgment. This research was supported by the National Science Foundation (CHE-8512710).

Supplementary Material Available: Tables of crystal data and summary of data collection and refinement, fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for **2** (8 pages). Ordering information is given on any current masthead page.

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(16) **3**: ^1H NMR (CD_2Cl_2) 43.9 (1 or 2 H), 22.5 (1 or 2 H), 10.7 (3 H), 8.0 (15 H), −4.7 (3 H), −14.3 (3 H), −34.5 ppm (3 H); IR (KBr) 2960 (m), 2914 (s), 2894 (m), 1424 (m), 1379 (m), 1298 (m), 1057 (vs), 960 (s), 892 (m), 818 (w), 730 (w), 520 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{36}BCrF_4P_2$: C, 47.70; H, 8.01. Found: C, 47.67; H, 8.20.

(17) For a review of ylide complexes see: Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980.

(18) (a) Werner, H.; Hofmann, L.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C65. (b) Werner, H.; Hofmann, L.; Paul, W.; Schubert, U. *Organometallics* **1988**, *7*, 1106.

(19) Weber, L., Wewers, D. *Organometallics* **1985**, *4*, 841.

(20) **4**: ^1H NMR (CD_2Cl_2) **4a**, 8.6 (15 H), 0.1 (3 H), −15.7 (3 H), −30.3 ppm (3 H); **4b**, 6.7 (15 H), −6.2 (3 H), −25.8 (3 H), −37.3 (3 H). IR (KBr): 2922 (m), 2914 (m), 1486 (w), 1420 (s), 1410 (m), 1300 (m), 1058 (vs), 952 (s), 894 (s), 842 (w), 740 (w), 520 (m), 427 (w) cm^{-1}. FAB-MS: *m/e* 352. Several attempts to obtain an elemental analysis of **4** gave erratic results. Deprotonation of **4** with $LiN(SiMe_3)_2$ regenerated **2**.

Facile Olefin Hydrogenation with an Osmium Dihydrogen Complex

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Summary: The cation $OsH_5P_3^+$ (P = PMe_2Ph) is shown to contain and reversibly dissociate H_2 and to hydrogenate ethylene and 1,5-cyclooctadiene with production of $OsH(C_2H_4)_2P_3^+$ and $OsH(COD)P_3^+$. The structure of the ethylene complex is analyzed by extended Hückel methods. $OsH_5P_3^+$ catalytically hydrogenates cyclohexene.

We have shown,[1] before the demonstration that H_2 can exist intact as a ligand,[2] that the tetrahydride[3] OsH_4P_3 (P = PMe_2Ph) can be protonated to $OsH_5P_3^+$. Success in working with this cation is critically dependent on employing a "noncoordinating" solvent (e.g., CH_2Cl_2) and a "nonnucleophilic" partner for the acid (e.g., $HBF_4 \cdot OEt_2$). We now report new observations concerning this polyhydride cation.

The cation $OsH_5P_3^+$ is a fluxional species that shows (360-MHz ^1H or 146-MHz ^{31}P NMR) a single $H_5(Os)$ and a single phosphorus resonance down to −85 °C. The T_1 values of OsH_4P_3 and $OsH_5P_3^+$ are 270 and 68 ms, respectively, at 360 MHz and −70 °C in toluene-d_8 and CD_2Cl_2, consistent with[4] the presence of one (or more) H_2 ligands in the cation. If this H_2 ligand is reversibly dissociated (eq 1),[5,6] this serves as a mechanism for the rapid

$$OsH_5P_3^+ \rightleftarrows H_2 + OsH_3P_3^+ \qquad (1)$$

deuteration of the hydride ligands observed when $OsH_5P_3^+$ is treated with D_2 at 25 °C. More important, eq 1 furnishes a *rare*[7,8] example of a 16-valence electron polyhydride complex. The observation that $OsD_5P_3^+$,[9] in CH_2Cl_2 solution over 10 h, shows deuteration of the ortho phenyl sites, is an indication of the high reactivity (i.e., ortho metalation) of $OsD_3P_3^+$.[10]

Ethylene (1 atm) reacts at 25 °C with $OsH_5P_3^+$ to give ethane and *cis,mer*-$OsH(C_2H_4)_2P_3^+$.[11] No H_2 is observed (^1H NMR). Both olefins rotate rapidly at 25 °C in this stereochemically rigid octahedron, but the olefins show no mutual site exchange on the NMR time scale. Olefin rotation is slowed by −40 °C, but the number (four) of ethylene proton resonances fails to uniquely establish the ground-state orientation of the ethylene C=C vectors. The crystal structure[12] (Figure 1) shows that the C=C vectors (1) eclipse the Os–ligand directions, (2) are mutually orthogonal, and (3) leave the Os—H and one C=C bond coplanar (i.e., in a geometry suited to β-hydrogen migration). In spite of this third point, the long (2.26 (7) Å) H1–C3 distance excludes an agostic ethyl ground-state geometry.

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(1) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(2) Kubas, G. J.; Ryan, R. R.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(3) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

(4) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(5) This preequilibrium was also established by a kinetic study[1] of the conversion of $OsH_5P_3^+$ + MeCN → $OsH_3(MeCN)P_3^+$ + H_2.

(6) D_2 shows no exchange with the "classical" hydride ligands in OsH_4P_3.

(7) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165.

(8) Marinelli, G.; Rachidi, El-I.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346.

(9) D_4OsP_3, from $LiAlD_4$, shows no deuterium scrambling to ortho phenyl positions. This compound was then treated with $DBF_4 \cdot OMe_2$.

(10) Ortho metalation of PMe_2Ph is rare and is a much more stringent test of reactivity than ortho metalation of PPh_3. See: Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39.

(11) Spectral data for $OsH(C_2H_4)_2P_3^+$: ^1H NMR (360 MHz, 24 °C, CD_2Cl_2): δ −6.77 (dt, *J*(PH) = 30, 21 Hz, 1 H), 1.32 (d, *J*(PMe) = 8 Hz, 6 H), 1.40 (br s, C_2H_4 cis to H, 4 H), 1.47 (vt, 3 Hz, 6 H), 1.61 (vt, 3 Hz, 6 H), 2.94 (dt, C_2H_4 trans to H, $J(C_2H_4\text{–}P) = J(C_2H_4\text{–}H)$ = 3 Hz, 4 H), 7.30 (m, PPh). $^{13}C\{^1H\}$ NMR of the ethylene carbons: δ 40.28 (d, *J*(C–P) = 11 Hz), 40.83 (s). $^{31}P\{^1H\}$ (146 MHz, 24 °C, CD_2Cl_2): δ = −41.5 (t, *J*(P–P) = 14 Hz, 1 P), −36.5 (d, *J*(P–P) = 14 Hz, 2 P).

(12) Crystallographic data for $[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4 \cdot CH_2Cl_2$ at −155 °C: a = 13.134 (7) Å, b = 13.300 (8) Å, c = 11.011 (7) Å, α = 111.25 (2)°, β = 113.15 (3)°, γ = 89.26 (3), Z = 2 in $P\bar{1}$. $R(F)$ = 0.0280 for 4050 reflections with $F > 2.33\sigma$ refining all atoms including hydrogens.

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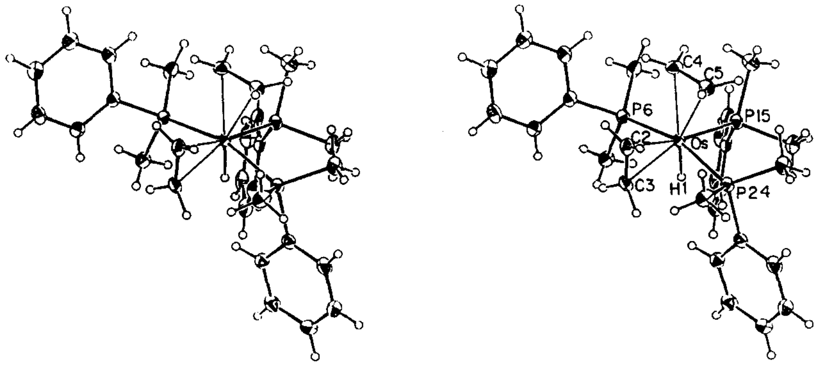
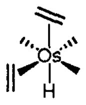


Figure 1. Stereo ORTEP drawing of $OsH(C_2H_4)_2(PMe_2Ph)_3^+$. Unlabeled ellipses are carbon; open circles are hydrogen. Selected distances (Å) and angles (deg): Os–C2 = 2.207 (6), Os–C3 = 2.220 (6), Os–C4 = 2.235 (6), Os–C5 = 2.247 (6), C2–C3 = 1.390 (9), C4–C5 = 1.401 (9), Os–H1 = 1.36 (6), Os–P = 2.374 (2)–2.400 (2); P6–Os–P24 = 162.09 (5).

However, a weak H1–C3 interaction is not wholly excluded, as shown by extended Hückel calculations performed on the four conformations shown below. The



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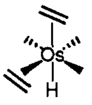

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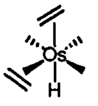

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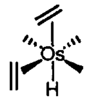
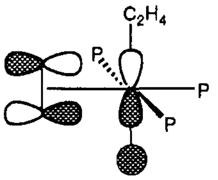


4

observed structure (1) is found to be more stable than 2 or 3 by 2 kcal/mol, with 4 over 20 kcal/mol less stable than the ground state. This preference originates in the back-bonding from the pseudo t_{2g} d orbitals to the olefin π^* orbitals. In 1, 2, and 3, two d orbitals are stabilized in this way, while in 4, only one has the proper symmetry to overlap with the two π^* orbitals (i.e., two olefins compete for back bonding from a single d orbital). Olefin/olefin steric repulsion is also worst in 4. The preference for 1 over 2 and 3 is due to a stabilizing cis interaction (5) between the high-lying occupied σ(Os–H) orbital and π^* of the cis olefin;[13] this is absent by symmetry in both 2 and 3. Since the observed rapid rotation at 25 °C cannot involve surmounting a 20 kcal/mol barrier, it follows that rotation of the olefin trans to hydride can only occur in concert with simultaneous rotation of the second olefin; such correlated rotation also diminishes steric repulsion between the rotating olefins.



5

Attempts to date to detect the product of a 1:1 reaction between $OsH_5P_3^+$ and substrate have failed to yield $OsH_3P_3(L)^+$. One mole of ethylene gives $OsH(C_2H_4)_2P_3^+$, ethane, and unreacted $OsH_5P_3^+$, while one mole of CO gives *cis,mer*-$OsH(CO)_2P_3^+$.

We have attempted to evaluate the efficiency with which the H_2 evolved in eq 1 is later incorporated into substrate by using 1,5-cyclooctadiene (COD) as a probe. Two equivalents of COD react (eq 2) with $OsH_5P_3^+$ to give exclusively cyclooctane (no monoolefin), together with *fac*-$OsH(COD)P_3^+$[14] and no observable free H_2 in solution.

$$OsH_5P_3 + 2C_8H_{12} \rightarrow OsH(COD)P_3^+ + C_8H_{16} \quad (2)$$

Note that the Os—C and C=C distances in $OsH(C_2H_4)_2P_3^+$ give no evidence of hydride and PMe_2Ph having different trans effects. Consistent with this, facile (1 atm, 25 °C, 5 m) exchange of $^{13}C_2H_4$ is observed with both ethylene ligands. The implied access to an unsaturated species is confirmed since a reactivity cycle can be closed: $OsH(C_2H_4)_2P_3^+$ reacts with 1 atm of H_2 to regenerate $OsH_5P_3^+$ and exclusively ethane; no ethylene is liberated (^1H NMR). Internal monoolefins are also viable substrates for $OsH_5P_3^+$, even in a catalytic mode: under 1000 psi of H_2 at 25 °C, cyclohexene is converted to cyclohexane at a rate (not optimized) of 12.5 turnovers per hour.

In conclusion, the tendency of the H_2 ligand to serve as a good *leaving group* provides ready access of reducible substrates to the coordination sphere. At the same time, the later return of this H_2 to the coordination sphere means that these reducing equivalents are not irretrievably lost. This is a felicitous case of having the best of both worlds and lies at the heart of the appeal of this electrophilic (H^+) activation of transition-metal polyhydrides. In addition, the resulting unsaturated polyhydrides are reactive toward even unactivated olefins.

Acknowledgment. This work was supported by the National Science Foundation, NSF and CNRS under the U.S.–France Cooperative Science Program, and EEC and CNRS for a postdoctoral fellowship (to S.A.J.). We thank Scott Horn for skilled technical assistance and Johnson Matthey for material support.

Supplementary Material Available: A table of positional and thermal parameters for $[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4 \cdot CH_2Cl_2$ (4 pages); a listing of structure factors (11 pages). Ordering information is given on any current masthead page.

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(13) Similar cis interactions have been reported in carbene/olefin complexes (Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1986**, *108*, 2173) as well as in polyhydride complexes.

(14) Spectral data for $OsH(COD)P_3^+$: ^1H NMR (360 MHz, 24 °C, CD_2Cl_2): δ −8.57 (vq, $J PH_{trans}$ = 35 Hz, $J_{PH_{cis}}$ = 28 Hz, 1 H), 1.54 (m, CH_2 4 H), 1.59 (d, J(PMe) = 7.5 Hz, 6 H), 1.87 (d, J(PMe) = 7.5 Hz, 6 H), 2.00 (m, CH_2, 2 H), 2.13 (d, J(PMe) = 7 Hz, 6 H), 2.91 (m, CH, 2 H), 3.86 (br s, CH, 2 H), 7.15–7.50 (m, PPh). $^{13}C\{^1H\}$ NMR of the COD carbons: δ 30.23 (s, CH_2), 33.91 (s, CH_2), 67.73 (dt, CH, $J(CP_{trans})$ = 5 Hz, $J(CP_{cis})$ = 4 Hz), 70.41 (br s, CH). $^{31}P\{^1H\}$ NMR (146 MHz, 24 °C, CD_2Cl_2): δ −46.31 (t, J(P–P) = 28 Hz, 1 P), −40.44 (d, J(P–P) = 28 Hz, 2 P).