trianglar cluster of three osmium atoms with two osmium-osmium bonds, Os(1)-Os(2) = 2.793 (1) Å and Os(1)-Os(3) = 2.873 (1) Å. The nonbonding osmium-osmium distance, Os(2)···Os(3) = 3.492 (1) Å, is bridged by the methoxide ligand. The hydride ligand, located crystallographically, bridges the Os(1)-Os(3) bond, Os(1)-H = 1.8 (1) Å and Os(3)-H = 2.0 (1) Å. The most interesting and unusual feature of this structure is the C,N η^2 triply bridging (dimethylamino)carbene ligand, H(1),C,N,C(2),C(3). The carbon atom symmetrically bridges the Os(1)-Os(3) bond on the side of the cluster opposite that of the bridging hydride ligand, Os(1)-C = 2.11 (2) Å and Os(3)-C = 2.15 (2) Å. The nitrogen atom is coordinated only to the third metal atom, Os(2)-N = 2.15 (1) Å. η^2-Carbene ligands are very unusual but have been observed previously in some mononuclear[21] and dinuclear[22] metal complexes. The compound $Ru_3(CO)_7(dppm)(\mu_3\text{-}CHPPh_2)(\mu_3\text{-}PPh)$ contains a triply bridging $C(H)PPh_2$ ligand which could be viewed as a (diphenylphosphino)carbene ligand.[23] The hydrogen atom H(1) was located crystallographically, but its position was not refined. It exhibits a low-field shift, δ +7.62, but this position is shifted upfield considerably from that of the terminal carbene ligand in **1** and related carbene complexes.[18,19] An interesting structural feature is the unusually long length of the C-N bond, 1.54 (2) Å, which is 0.25 Å longer than the corresponding distance in **1** and even longer than the C-N single bond lengths to the methyl groups, C(2)-N = 1.49 (2) Å and C(3)-N = 1.47 (2) Å in **2**. The bond lengthening effects induced by polynuclear ligand coordination are well-known.[13]

Since compounds **1** and **2** are isomers, attempts were made to interconvert them. When **2** was heated to reflux in heptane under a CO atmosphere for 4 h, **1** was obtained in 60% yield. The pathway for this transformation has not yet been determined but by necessity must involve CO and hydride ligand shifts and a closing of the cluster. Further experiments to elucidate upon this are in progress.

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy. We wish to thank Johnson Matthey Inc. for a loan of osmium tetraoxide. NMR measurements were made on a Brüker AM-300 spectrometer purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters and selected interatomic distances and angles for both structural analyses (14 pages); listings of structure factor amplitudes for both structural analyses (33 pages). Ordering information is given on any current masthead page.

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(19) Crystals of **2** were grown by slow evaporation of hexane solutions at -20 °C. Compound **2** crystallizes in the monoclinic crystal system: space group $P2_1/n$, a = 8.878 (2) Å, b = 26.287 (8) Å, c = 9.243 (2) Å, β = 115.19 (1)°. The structure was solved by direct methods (MULTAN) and was refined (2226 reflections) to the final residuals R = 0.0381 and R_w = 0.0387.

(20) Selected interatomic distances (Å) and angles (deg) for **2** as follows: Os(1)-Os(2) = 2.793 (1), Os(1)-Os(3) = 2.873 (1), Os(2)···Os(3) = 3.492 (1), Os(1)-H = 1.8 (1), Os(3)-H = 2.0 (1), Os(1)-C = 2.011 (2), Os(3)-C = 2.15 (2), Os(2)-N = 2.15 (1), C-N = 1.54 (2); Os(1)-H-Os(3) = 97 (5), Os(1)-C-Os(3) = 85.0 (6), Os(1)-C-N = 110 (1), Os(3)-C-N = 116 (1), Os(2)-N-C = 97.7 (9).

(21) (a) Clark G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1983**, *259*, 215. (b) Kim, H. P.; Sangsoo, K.; Jacobsen, R. A.; Angelici, R. J. *Organometallics* **1986**, *5*, 2481.

(22) (a) Huttner, G.; Regler, D. *Chem. Ber.* **1972**, *105*, 2726. (b) Matachek, J. R.; Angelici, R. J.; Schugart, K. A.; Haller, K. J.; Fenske, R. F. *Organometallics* **1984**, *3*, 1038. (c) Davis, J. H., Jr.; Lukehart, C. M.; Sacksteder, L. *Organometallics* **1987**, *6*, 50.

(23) Lavigne, G.; Bonnet, J. J. *Inorg. Chem.* **1981**, *20*, 2713.

New Hydrido-Carbonyl Rhenates by Reduction of $[Re_2(CO)_{10}]$ with Bases. X-ray Crystal Structure of the Anion $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$

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Summary: The reaction of $[Re_2(CO)_{10}]$ with OH^- gives first $[Re_2H(CO)_9]^-$ and then, under more drastic conditions, the novel anion $[Re_2H_2(CO)_8]^{2-}$, which can be reversibly protonated to give $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$, whose structure has been elucidated by a X-ray investigation. Variable-temperature NMR spectra indicate that both the new hydrido carbonylates are fluxional in solution.

The reduction of $[Re_2(CO)_{10}]$ with bases was studied for the first time about 30 years ago,[1] and several compounds have been successively isolated by this route.[2] However, none of the products expected on the basis of the classical mechanism involving CO_2 elimination from an unstable hydroxycarbonyl intermediate was so far obtained. The use of the strong bases NR_4OH (R = Et or Bu) allowed us to fill in this gap and to discover a rapid and high yield route to two novel hydrido-carbonyl rhenates, the anions $[Re_2H_2(CO)_8]^{2-}$ and $[Re_2H_3(CO)_8]^-$, which can play a relevant role in the chemistry of polynuclear hydrido carbonylates of rhenium.

The first stable product expected from this type of reduction is the anion $[Re_2H(CO)_9]^-$ (compound **1**), previously obtained[3] by photochemical decomposition of the formyl $[Re_2(CHO)(CO)_9]^-$. We have now found that on simply refluxing a tetrahydrofuran solution of $[Re_2(CO)_{10}]$ in the presence of a stoichiometric amount of NR_4OH, the anion **1** is rapidly and nearly quantitatively produced.[4]

Further attack of OH^- on **1** is obviously more difficult because of the negative charge. However, using highly concentrated tetraalkylammonium hydroxides, we succeeded in synthesizing, directly from $[Re_2(CO)_{10}]$, the species resulting from this second attack.[5] Depending on

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(1) Hieber, W.; Schuster, L. *Z. Anorg. Allg. Chem.* **1956**, *285*, 205; **1956**, *287*, 214.

(2) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1978**, *152*, 85. Ciani, G.; Sironi, A.; Albano, V. G. *Ibid.* **1977**, *136*, 339.

(3) Casey, C. P.; Neuman, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544.

(4) Typically, a solution of $[Re_2(CO)_{10}]$ (50 mg, 0.077 mmol) in 5 mL of THF was treated under N_2 with aqueous NEt_4OH (1.37 M 0.7 mL, 0.096 mmol) and refluxed for 15 min. The solution was then concentrated under vacuum and *n*-heptane added, causing the precipitation of a cream solid, which was washed with water and dried (47 mg, 0.062 mmol, isolated yield 81%). Elemental and spectroscopic analyses showed it to be pure $[NEt_4][Re_2H(CO)_9]$. The structure of the compound has been also investigated by X-ray analysis, and the results will be published elsewhere.

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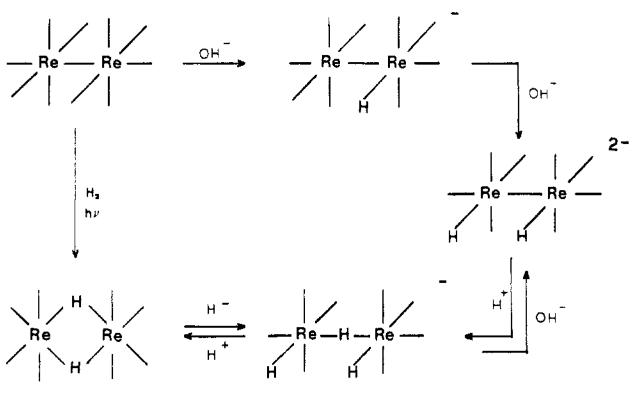
Scheme I. Rhenium Hydrides $[Re_2H_x(CO)_y]^{m-}$ Originated from $[Re_2(CO)_{10}]$



the workup conditions, the dihydridic dianion $[Re_2H_2(CO)_8]^{2-}$ (**2**) or its conjugated acid $[Re_2H_3(CO)_8]^-$ (**3**) was obtained. The intermediacy of compound **1** in the synthesis of **2** was confirmed by preparing **2** starting from **1**, by the same method.

While a full characterization of compound **3** was possible (elemental analysis, IR and NMR spectroscopy,[5] and a single-crystal X-ray investigation[6]), compound **2** was characterized only spectroscopically (IR and ^1H and ^{13}C NMR):[5] the compound is quite sensitive to oxygen and to moisture and any attempt to isolate it as a pure solid (removing all NR_4OH) failed. Its formulation, however, is well-supported by the reactivity: treatment of **2** with water or methanol, readily generates quantitatively compound **3**, while reaction of **3** with a stoichiometric amount of NR_4OH, in anhydrous THF, restores compound **2**.

Further protonation of **3** (with stoichiometric CF_3SO_3H) caused hydrogen evolution, affording quantitatively the already known[7] unsaturated neutral species $[Re_2(\mu\text{-}H)_2(CO)_8]$ (compound **4**), identified spectroscopically (IR and ^1H NMR), which was previously synthesized[7b] by photochemical hydrogenation of $[Re_2(CO)_{10}]$. The new method parallels that recently discovered[8] for the transformation of $[Re_4H_6(CO)_{12}]^{2-}$ into the unsaturated $[Re_4H_5(CO)_{12}]^-$. As in that case, the process can be reversed and treatment of the unsaturated species **4** with a slight excess of $NaBH_4$ readily restored the saturated anion **3**.

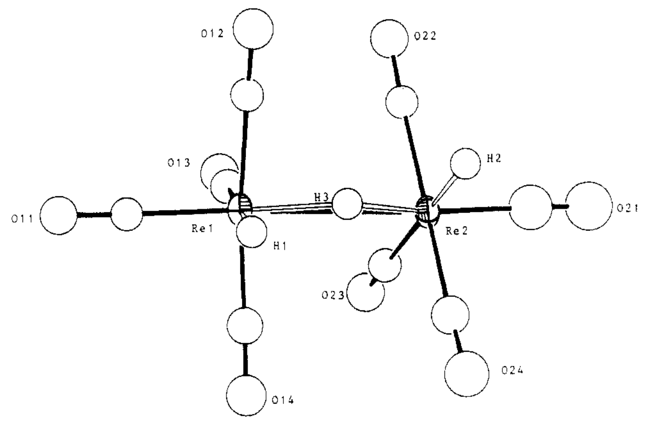


Figure 1. A view of the $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ anion, with the calculated hydrogen atoms positions. The carbonyl groups are indicated by the number of their oxygen atoms.

The series of reactions shown in Scheme I were then proven. In this way, all the known dinuclear hydridocarbonyl complexes of rhenium[9] are chemically related.

The structure of the $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ anion is shown in Figure 1. It possesses an idealized C_2 symmetry and a staggered (torsion angle C13–Re1–Re2–C23 = 39.8°) conformation of the two $Re(CO)_4H$ square-pyramidal units (with the H atom in equatorial position) that are held together by a Re–H–Re linkage (Re–Re bond distance of 3.272 (1) Å). The two terminally bonded H atoms lie trans to two (C13 and C23) syn carbonyl ligands, while the third H atom has been postulated to be transoid to the two axial carbonyl groups in a bent, off-axis position (C11–Re1–Re2 = 173.3°, C21–Re2–Re1 = 174.2°), which is consistent with the presence of a closed 3-center–2-electron bond. The resulting stereochemistry has the three hydrogen atoms on the same side of the molecule.

The NMR spectra[5] of **3** at 173 K are in accord with the C_2 symmetry observed in solid and with the presence of two terminal and one bridging hydrides. The ^{13}C resonance of double intensity is attributable to the CO mutually trans on each Re atom. At higher temperatures, the signals of the hydrides and those of the CO trans to them coalesce (at 223 and 185 K, respectively, indicating a fluxional process interchanging terminal and bridging hydrides ($\Delta G^\ddagger$ = 9.52 and 10.00 kcal/mol at 185 and 225 K, respectively).[10] The rotation, in turn, of each $ReH_2(CO)_4$ fragment around the axis of the two mutually *trans*

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(5) In a typical preparation, 500 mg (0.766 mmol) of $[Re_2(CO)_{10}]$ was dissolved in 5 mL of methanol, containing NEt_4OH (1.5 M, 7.5 mmol), by stirring in an oil bath at 70 °C. A high vacuum was then applied to the heated solution for about 1 min, leaving a pale brown oil. Treatment with an excess of water afforded a cream solid (480 mg, 0.658 mmol, yield of 86%) characterized as $[NEt_4][Re_2H_3(CO)_8]$. Anal. Calcd for $C_{16}H_{23}NO_8Re_2$: C, 26.32; H, 3.15; N, 1.92. Found: C, 26.85; H, 3.28; N, 1.85. Crystals suitable for X-ray analysis were obtained from THF/*n*-heptane at −20 °C. Spectroscopic data for the anion: IR (THF) ν (CO) 2080 vw, 2054 mw, 1973 vs, 1953 sh, 1916 ms cm^{-1}; ^1H NMR (THF-d_8) δ −9.45 (room temperature), δ −6.2 (2), −14.8 (1) (173 K); ^{13}C NMR (THF-d_8) δ 193.0 (1), 192.2 (1) (room temperature), δ 193 (2), 192.4 (1), 192.0 (1) (173 K). When the above reaction was repeated, but the oil was treated with a 1 M aqueous solution of NEt_4OH (instead of with water, to avoid the protonation), $[NEt_4]_2[Re_2H_2(CO)_8]$ was precipitated, contaminated by some NEt_4OH. In both cases, the use of NBu_4OH gave similar results. Spectroscopic data for the anion 2 (only NBu_4^+ salt has a good solubility in THF): IR (THF) ν(CO) 2010 vw, 1990 mw, 1945 s, 1910 vs, 1865 sh, 1825 ms cm^{-1}; ^1H NMR (THF-d_8) δ −8.45; ^{13}C NMR (THF-d_8) δ 209 (room temperature), δ 212.7 (2), 206.5 (1), 203.8 (1) (203 K).

(6) Crystal data: $C_{16}H_{23}NO_8Re_2$, M_r 729.8, triclinic; a = 8.552 (2) Å, b = 11.249 (2) Å, c = 18.911 (3) Å, α = 102.44 (2)°, β = 94.61 (2)°, γ = 104.41 (2)°; U = 2105.7 Å^3; D_{calcd} = 2.134 g cm^{-3} for Z = 3; $F(000)$ = 1828; space group $P\bar{1}$ [No. 2]; λ (Mo K_α) = 0.71073 Å; μ(Mo $K\alpha$) = 108.33 cm^{-1}. Intensities data were measured on a CAD4 Enraf-Nonius diffractometer, by the ω-scan method, within the limits $3 < \theta < 25°$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, on the basis of 3193, absorption-corrected (ψ-scan), independent, significant $[I > 3\sigma(I)]$ data. The asymmetric unit consists of one $[Re_2H_3(CO)_8]^-$ anion and one $[NEt_4]^+$ cation, in general positions, plus one half anion and one half cation disordered about two centers of symmetry (*c* and *d* in Wyckoff notation, respectively). The disorder of the anion lying about the center of symmetry arises from the staggering of the equatorial ligands on the two metal atoms. Attempts to refine an ordered model in the noncentric space group failed to give meaningful results. The three hydridic hydrogens were indirectly located on the basis of stereochemical considerations (for the ordered anion). Approximate hydrogen coordinates were determined by the Orpen program (Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509) but not refined. The current values of R and R_w are 0.043 and 0.050, respectively.

(7) (a) Bennet, M. J.; Graham, W. A. G.; Hoyano, J. H.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232. (b) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3260.

(8) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H. *J. Chem. Soc., Chem. Commun.* **1987**, 486.

(9) We think that the species formulated as $[Re_2(\mu\text{-}H)_3(CO)_6]^-$ (Ginsberg, A. P.; Hawkes, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 5930) was indeed the dianion $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$, subsequently characterized (Kaesz, H. D.; Fontal, B.; Bau, R.; Kirtley, S. W.; Churchill, M. R. *J. Am. Chem. Soc.* **1969**, *91*, 1021) and showing identical spectroscopic data. In particular, it would be very surprising the coincidence of the chemical shifts of the hydridic resonances for Re(μ-H)Re and Re(μ-H)$_3$Re systems.

(10) The rate constant for unequally populated sites, at 225 K, was calculated according to the method reported in: Sandstrom, J. *Dynamic NMR Spectroscopy*, Academic: New York, 1982.

carbonyls, leading to the change of the shared hydrogen, could account for this.

As to the stereochemistry of **2**, the δ value of the hydridic resonance, typical of the $Re(\mu\text{-}H)_2Re$ systems, could suggest a bridging location for the H ligands. However, the intensity ratio (2:1:1) of the carbonyl signals, in the low-temperature ^{13}C NMR spectrum, clearly indicates that the hydrogen atoms are terminally bound. At higher temperatures, a dynamic behavior that equilibrates all CO ligands is observed, in contrast to **3**.

The different coordination mode of the H ligands in the two related species **2** and **4** (bridging in the unsaturated neutral **4** and terminal in the saturated anion **2**) is noteworthy. Although it is not unusual in organometallic chemistry to observe relevant stereochemical changes on varying the number of electrons, we think that in the present case this finding confirms that the $M(\mu\text{-}H)_2M$ system is intrinsically two electrons short.

Finally, we remark on the "amphoteric" behavior of compound **3**, whose H ligands (see Scheme I) can be supplied by both H^+ and H^- and can be abstracted by both OH^- and H^+.[11]

Registry No. 1 $[NEt_4]$, 66745-33-3; 1 $[NBu_4]$, 87207-10-1; 2 $[NEt_4]_2$, 107890-40-4; 2 $[NBu_4]_2$, 107982-42-3; 3 $[NEt_4]$, 107890-38-0; 3 $[NBu_4]$, 107982-41-2; 4, 38887-05-7; $Re_2(CO)_{10}$, 14285-68-8; NEt_4OH, 77-98-5; NBu_4OH, 2052-49-5.

Supplementary Material Available: Tables of positional parameters, general temperature factor expressions, bond distances, and bond angles (5 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(11) A similar behavior was observed in $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$: Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666.

Synthesis and Reactivity of $(\eta^5\text{-}C_5H_7)Fe(PMe_3)_3{}^+O_3SCF_3{}^-$. C–C Bond Formation via Nucleophilic Addition to C2 of an η^5-Pentadienyl Ligand[1]

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Received February 23, 1987

Summary: The electron-rich cationic complex $(\eta^5\text{-}C_5H_7)Fe(PMe_3)_3{}^+O_3SCF_3{}^-$ (**1**) has been synthesized via the reaction of $(\eta^3\text{-}C_5H_7)_2Fe(PMe_3)_2$ with $HPMe_3{}^+O_3SCF_3{}^-$. Treatment of **1** with 2,4-dimethylpentadienide ($C_7H_{11}{}^-$) leads to nucleophilic attack at C2 of the η^5-pentadienyl ligand, producing the 1,3,4,5-η-pentenediyl–iron complex $[Fe\text{-}CH_2\text{-}C(H)(C_7H_{11})\text{-}(\eta\text{-}CH\cdots CH\cdots CH_2)](PMe_3)_3$ (**2**), which has been structurally characterized. The attacking nucleophile 2,4-dimethylpentadienide bonds through its central carbon atom to the pentenediyl ligand.

The reactions of η^5-dienyl ligands with nucleophiles have been extensively investigated during the past decade.[2]

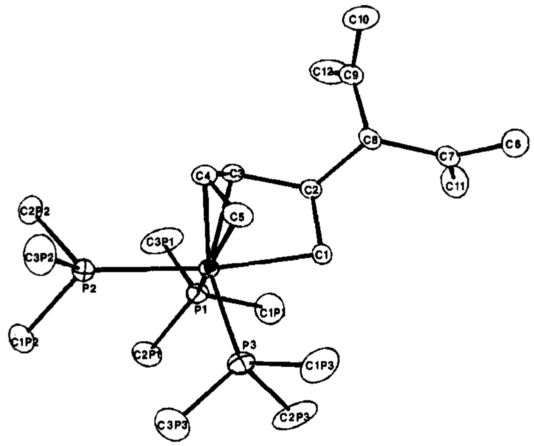
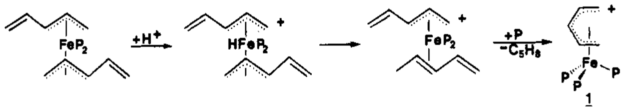
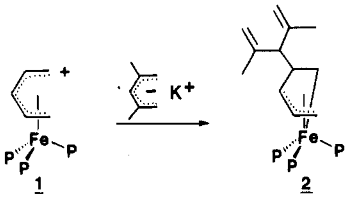


Figure 1. ORTEP drawing of $[Fe\text{-}CH_2\text{-}C(H)(C_7H_{11})\text{-}(\eta\text{-}CH\cdots CH\cdots CH_2)](PMe_3)_3$ (**2**). Thermal ellipsoids are drawn to encompass 15% of the electron density.

Scheme I



Scheme II



However, the vast majority of these studies have involved complexes containing electron-poor $M(CO)_3{}^+$ (M = Fe, Ru) moieties[3] and have resulted primarily in nucleophilic attack at a terminus (C1 or C5) of the η^5-dienyl ligand.[4] We now wish to report that the incorporation of strongly electron-donating PMe_3 ligands into a $(\eta^5\text{-}C_5H_7)FeL_3{}^+$ precursor leads to a clean reversal in the normally observed regiochemistry, i.e., nucleophilic attack at C2 of the dienyl ligand. This result is in accord with the prediction of Davies, Green, and Mingos[5] that nucleophilic attacks on odd open polyenyl ligands in *electron-rich* metal complexes will occur at even-numbered carbon atoms.

The electron-rich η^5-pentadienyl–metal complex $(\eta^5\text{-}C_5H_7)Fe(PMe_3)_3{}^+O_3SCF_3{}^-$ (**1**) is produced in high yield from the reaction of $(\eta^3\text{-}C_5H_7)_2Fe(PMe_3)_2$[6] with

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(1) Pentadienyl–Metal–Phosphine Chemistry. 11. For the previous paper in this series, see: Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.

(2) See, for example: (a) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982; Section 4.1.5. (b) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 4, Chapter 31.3.4. (c) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463.

(3) A variety of synthetic approaches to $(\eta^5\text{-dienyl})M(CO)_3{}^+$ complexes have been developed. See, for example: (a) Fischer, E. O.; Fischer, R. O. *Angew. Chem.* **1960**, *72*, 919. (b) Burton, R.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 594. (c) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 497. (d) Mahler, J. E.; Pettit, R. *Ibid.* **1963**, *85*, 3955. (e) Birch, A. J.; Chamberlain, K. B. *Org. Synth.* **1977**, *57*, 107. (f) Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 2105.

(4) However, attack at C2 or C4 has been observed for several η^5-cycloheptadienyl–metal complexes. See, for example: (a) Edwards, R.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2105. (b) Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *Ibid.* **1975**, 1633. (c) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.

(5) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. (b) This prediction is based on the *charges* of the carbon atoms in the polyenyl ligand.

0276-7333/87/2306-1367$01.50/0