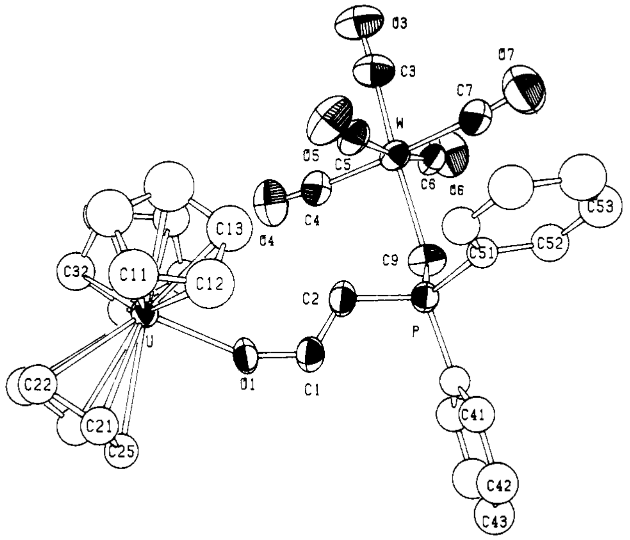
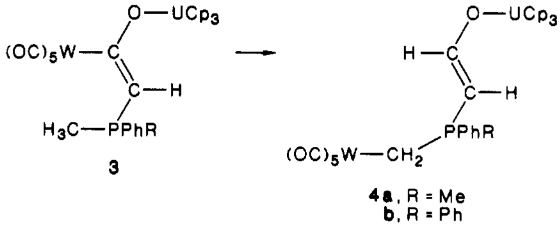


Figure 2. An ORTEP drawing of Cp$_3$UOCH=CHPPh$_2$CH$_2$W(CO)$_5$ (**4b**). Some important bond distances (Å) and angles (deg): U–O1, 2.207 (9); O1–C1, 1.31 (1); C1–C2, 1.37 (2); P–C2, 1.76 (1); P–C9, 1.79 (1); W–C9, 2.36 (1); U–O1–C1, 156.1 (8); O1–C1–C2, 123 (1); P–C2–C1, 124 (1); C2–P–C9, 110.1 (6); W–C9–P, 116.8 (7).

display different chemistries. When **2** is heated to 80 °C, the elements of Cp$_3$UOH are eliminated and Cp(OC)$_2$MnC≡CP(Ph)(R)(Me) is formed in nearly quantitative yield.[4] While NMR peaks consistant with a WC≡CPMePhR moiety[4,5,12] appeared when THF solutions of **3** were heated to 90 °C for 48 h, another compound, **4**,[13] was also produced. NMR and IR spectra of **4** indicate W(CO)$_5$, CpU, PPh, and HCP units.[13] However, **4** could not be unambiguously identified from these data so an X-ray crystal structure of **4b** was determined[7] using crystals (space group $P2_1/c$, unit-cell parameters a = 17.176 (4) Å, b = 11.804 (2) Å, c = 17.588 (2) Å, β = 114.49 (1)°, and V = 3245 (1) Å^3) precipitated from a THF solution onto which a 1:20 toluene–pentane mixture had been layered. An ORTEP of molecule **4b** is shown in Figure 2; a summary of the crystal, data collection, and refinement appears in Table I, a complete listing of bond distances and angles in Tables V, the positional and thermal parameters in Table VI, and the observed and calculated structure factors in Table VII (supplementary material).

The W–C(9) bond distance of 2.36 (1) Å indicates a single bond,[8] and the 1.37 (2) Å C(1)–C(2) separation is typical for a double bond. Other metrical parameters are normal for the resonance form drawn below for **4**. In both **3b** and **4b** the metrical parameters within the enolate portion of the ligands are indistiguishable from those in Cp$_2$Ti(OCH=CH$_2$)$_2$.[14]

Reaction 3 involves the interchange of hydrogen and (OC)$_5$W moieties. While the mechanism of this reaction



(3)

has not been determined, NMR peaks of **3** disappear within 24 h at 90 °C leaving broad resonances which undergo complex changes, finally sharpening to the characteristic peaks of **4** after about 48 h. When solutions of **3** are heated in the presence of PPh$_3$, the rate of reaction is not markedly influenced and the final product is a phosphine complex which also can be obtained by heating solutions of **4** with PPh$_3$. These observations imply that the conversion occurs through several intermediates and probably does not involve (OC)$_5$W dissociation. The mechanism of the reaction is still under study.

Overall the reaction of **1** with W(CO)$_6$ represents the conversion of a coordinated carbon monoxide to the enolate of an aldehyde and involves cleavage of the original W–C bond.

Acknowledgment. The support of this work by the National Science Foundation, Grants CHE82-10244 and CHE-8519289 (J.W.G. and R.E.C.) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. **1a**, 77357-85-8; **1b**, 77357-86-9; **3a**, 104807-99-0; **3b**, 104780-30-5; **4a**, 104808-00-6; **4b**, 104780-31-6; W(CO)$_6$, 14040-11-0.

Supplementary Material Available: Table I, crystal, data collection, and reduction parameters for (OC)$_5$WC(OUCp$_3$)CHPPh$_2$Me·$^1/_2$C$_7$H$_8$ and Cp$_3$UOCH=CHPPh$_2$CH$_2$W(CO)$_5$, Table II, bond distances and bond angles for (OC)$_5$WC(OUCp$_3$)CHPPh$_2$Me·$^1/_2$C$_7$H$_8$, Table III, positional and thermal parameters for (OC)$_5$WC(OUCp$_3$)CHPPh$_2$Me·$^1/_2$C$_7$H$_8$, Table V, bond distances and bond angles for Cp$_3$UOCH=CHPPh$_2$CH$_2$W(CO)$_5$, and Table VI, positional and thermal parameters for Cp$_3$UOCH=CHPPh$_2$CH$_2$W(CO)$_5$ (5 pages); Table IV, observed and calculated structure factors for (OC)$_5$WC(OUCp$_3$)CHPPh$_2$Me·$^1/_2$C$_7$H$_8$, and Table VII, observed and calculated structure factors for Cp$_3$UOCH=CHPPh$_2$CH$_2$W(CO)$_5$ (34 pages). Ordering information is given on any current masthead page.

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[12] (a) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F.; Korte, W. D. *J. Am. Chem. Soc.* **1974**, *96*, 2847–2854. (b) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391–402. (c) Blau, H.; Griessman, K.-H.; Malish, W. *J. Organomet. Chem.* **1984**, *263*, C5–C9.

[13] NMR spectra taken on reactions run in THF-d_8 at 90 °C show about equal conversion to the –C≡CPMePhR-containing compound and to **4**. An isolated yield of 32% was obtained after recrystallization of **4b**. ^{1}H NMR (THF-d_8, 300 MHz): **4a**, δ 6.02 (mult, 1 H, Ph), 5.33 (mult, 2 H, Ph), 1.57 (mult, 2 H, Ph) –4.04 (s, 15 H, *Cp*$_3$U), –4.83 (d, 3 H, J_{PCH} = 12.8 Hz, *MeP*), –5.21 (dd, 1H, J_{PCH} = 14 Hz, J_{HCH} = 14 Hz, H$_a$H$_b$CP, H$_a$), –5.91 (dd, 1 H, J_{PCH} = 14 Hz, J_{HCH} = 14 Hz, H$_a$H$_b$CP, H$_b$), –11.51 (dd, 1 H, J_{PCH} = 13.6 Hz, J_{HCCH} = 12.6 Hz, PC*H*=), –26.55 (dd, 1 H, J_{PCCH} = 8.4 Hz, J_{HCCH} = 12.6 Hz, OC*H*=); **4b**, 5.87 (mult, 2 H, Ph), 5.13 (mult, 4 H, Ph), 1.18 (mult, 4 H, Ph) –3.83 (s, 15 H, *Cp*$_3$U), –5.00 (d, 2 H, J_{PCH} = 15.2 Hz, H$_2$C), –11.24 (dd, 1 H, J_{PCH} = 14.8 Hz, J_{HCCH} = 10.6 Hz, PC*H*=), –27.24 (dd, 1 H, J_{PCCH} = 7.7 Hz, J_{HCCH} = 10.6 Hz, OC*H*=). IR (THF solution on NaCl plates, 1800–2100 cm^{-1}): 2051 (m), 1958 (s, sh), 1892 (vs), 1863 cm^{-1} (s). Anal. Calcd: C, 42.10; H, 2.93. Found: C, 42.93; H, 3.61.

[14] Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855–1859.

Intra- and Intermolecular Activation of sp^2 C–H Bonds at Rhodium(I) and Iridium(I) Metal Centers. X-ray Structure of the Cis σ-Cyclooctadienyl Hydride [{N(CH$_2$CH$_2$PPh$_2$)$_3$}IrH(σ-C$_8$H$_{11}$)]BPh$_4$·CH$_3$COCH$_3$

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Summary: The metal–ligand fragment [(np$_3$)Ir]$^+$ [np$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$] intermolecularly activates one sp^2 C–H

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bond of 1,5-cyclooctadiene to give the cis σ-cyclooctadienyl hydride $[(np_3)IrH(\sigma\text{-}C_8H_{11})]BPh_4{\cdot}CH_3COCH_3$ (2) whose structure has been established by X-ray methods. The Rh(I) hydride $(np_3)RhH$ undergoes electrophilic attack by $MeSO_3CF_3$ to give CH_4 and the ortho-metalated complex $[(Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4)RhH]SO_3CF_3$ (5) through the intramolecular activation of a phenyl C–H bond.

Most of the metal systems that are capable of cleaving hydrocarbon C–H bonds belong to the d^8 ML_4 category.[1] Within the latter, remarkable efficiency is exhibited by the metal fragments formed by rhodium(I) and iridium(I) with the $[(C_5R_5)L]$ ligand set (R = H, Me; L = CO, PMe_3).

We have now found another donor atom set, namely, that of the tripodal ligand $N(CH_2CH_2PPh_2)_3$, np_3, which forms Rh(I) and Ir(I) fragments capable of activating aromatic and olefinic C–H bonds under very mild conditions.

The plain reaction of np_3 with $[Ir(COD)Cl]_2$ [COD = 1,5-cyclooctadiene] in THF yields red-orange crystals of the trigonal-bipyramidal Ir(I) complex $(np_3)IrCl$[2] (1). On addition of $NaBPh_4$ in acetone to the reaction mixture containing 1 and COD, NaCl immediately precipitates and colorless crystals of the cis σ-cyclooctadienyl hydride $[(np_3)IrH(\sigma\text{-}C_8H_{11})]BPh_4{\cdot}CH_3COCH_3$ (2) are quantitatively obtained on slow evaporation of the solvent (Scheme I). The structure of 2 has been determined by X-ray methods.[4] The structure consists of discrete cations $[(np_3)IrH(\sigma\text{-}C_8H_{11})]^+$, tetraphenylborate anions, and acetone solvent molecules. Figure 1 shows an ORTEP drawing of the complex cation. As expected from the chemical-physical characterization of the complex,[6] the metal has a pseudooctahedral coordination given by all four donor atoms of np_3, a hydride ligand, and a carbon atom from the σ-bonded cyclooctadienyl ligand. The latter group adopts the boat conformation. The Ir–H and Ir–C bond lengths of 1.59 (6) and 2.09 (1) Å, respectively, are consistent with those reported for the cis alkyl hydride $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(Cy)(H)$[1e] [1.55 (6) and 2.125 (4) Å, respectively].

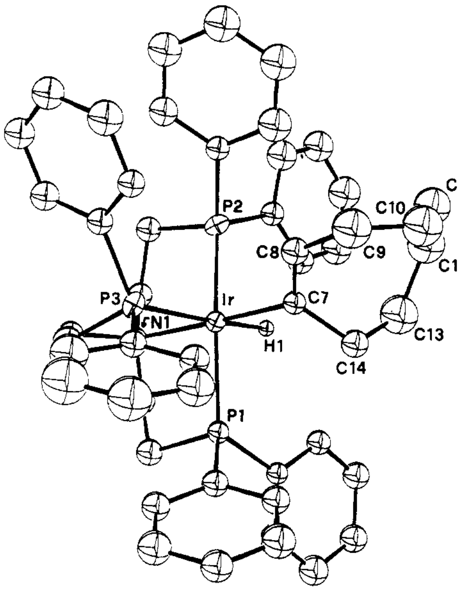
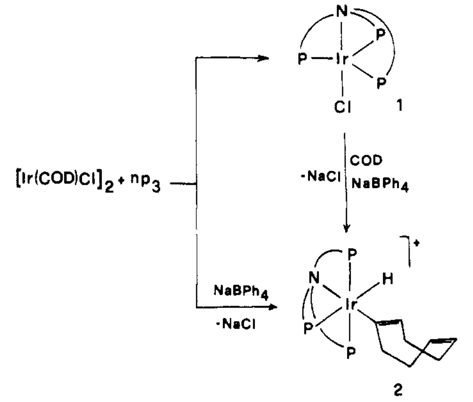


Figure 1. Perspective view of the $[(np_3)IrH(\sigma\text{-}C_8H_{11})]^+$ cation. Important bond distances (Å) are as follows: Ir–P1 = 2.325 (3), Ir–P2 = 2.325 (3), Ir–P3 = 2.374 (3), Ir–N1 = 2.250 (9), Ir–H1 = 1.59 (6), Ir–C7 = 2.09 (1), C7–C8 = 1.33 (2), C11–C12 = 1.23 (3).

Scheme I



Neither X-ray structures of σ-cyclooctadienyl complexes nor metal activation of COD of the present type has been so far reported.

The trigonal-bipyramidal Rh(I) hydride $(np_3)RhH$[3] (3) reacts with HSO_3CF_3 in THF to give the Rh(III) cis dihydride $[(np_3)RhH_2]SO_3CF_3$[7] (4) as colorless crystals. When the electrophilic attack on 3 is carried out with $MeSO_3CF_3$, the reaction yields CH_4 (determined by GC) and colorless crystals of the ortho-metalated complex $[(Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4)RhH]SO_3CF_3$ (5) (Scheme II). The structure of 5 has been unequivocally established by IR and NMR spectroscopy. The appearance of new bands at 2000 and 1560 cm^{-1} provides evidence for the formation of a Rh–H bond and a change in the

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(1) (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723. (c) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1982**, *104*, 352. (d) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *Ibid.* **1983**, *105*, 7190. (e) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *Ibid.* **1986**, *108*, 1537. (f) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562. (g) Perlana, R. A.; Bergman, R. G. *Ibid.* **1984**, *3*, 508. (h) Antberg, M.; Dahlenburg, L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 260.

(2) The solubility of 1 is low so as to preclude any spectroscopic characterization. However, the compound is isomorphous with the trigonal-bipyramidal rhodium derivative $(np_3)RhCl$.[3]

(3) Di Vaira, M.; Peruzzini, M.; Zanobini, F.; Stoppioni, P. *Inorg. Chim. Acta* **1983**, *69*, 37.

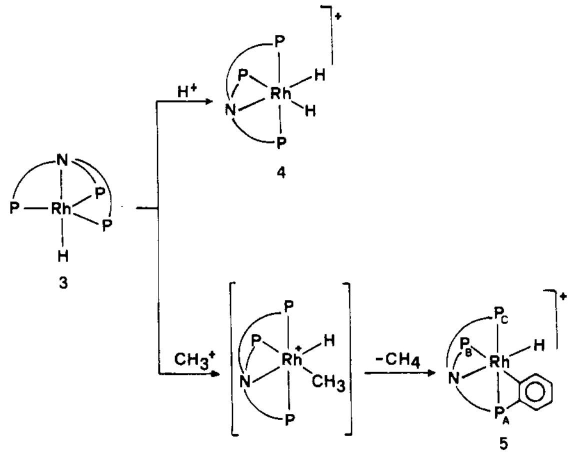
(4) Crystallographic data for 2: monoclinic, $a = 34.542$ (9) Å, $b = 12.824$ (3) Å, $c = 30.183$ (9) Å, $\beta = 91.34$ (2)°, space group $C2/c$, $Z = 8$, $\rho_{calcd} = 1.32$ g cm^{-3}, $\mu(Mo\ K\alpha) = 0.71069$ cm^{-1}. Intensity data were collected by standard methods at this institute. During data collection three reflections were periodically monitored. No crystal decay was observed. The structure was solved by Patterson and Fourier techniques using the SHELX76 program package.[5] Refinement converged at $R = 0.063$ and $R_W = 0.075$ for 4494 absorption corrected reflections with $I > 3\sigma(I)$ measured on a Philips PW 1100 diffractometer with Mo Kα radiation ($2.5 < \theta < 20°$). Final number of variables was 248. The hydrogen atoms except for H1 were inserted in the calculated positions and not refined. The phenyl rings were treated as rigid groups of D_{6h} symmetry. A peak which may be attributed to the hydride ligand appears in the final ΔF maps at a distance of ca. 1.60 Å from the metal. After several trials, we have deviced a reasonable strategy for refining the hydrogen ligand. The Ir–H distance is constrained to vary within the limits 1.55–1.65 Å. A refined value of 0.02 $Å^2$ for the temperature factor U of the hydrogen atom accounts for the reliability of the hydrogen ligand refinement.

(5) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determinations, University of Cambridge, Cambridge, England 1976.

(6) $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 293 K): AB_2 pattern, doublet at 6.59 ppm ($J(P_A\text{–}P_B) = 12$ Hz), triplet at 7.35 ppm, np_3 ligand. ^1H NMR (CD_3COCD_3, 293 K): doublet of triplets at −10.64 ppm ($J(H\text{–}P_{trans}) = 130$ Hz, $J(H\text{–}P_{cis}) = 18$ Hz), Ir–H. IR (Nujol mulls): 2160 cm^{-1} (ν(Ir–H)), 1600, 1570 cm^{-1} (ν(C=C)).

(7) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 223 K): AB_2X pattern, doublet of doublets at 47.97 ppm ($J(P_B\text{–}P_A) = 21$ Hz, $J(P_B\text{–}Rh) = 113$ Hz), doublet of triplets at 37.13 ppm ($J(P_A\text{–}Rh) = 99$ Hz), np_3 ligand. ^1H NMR (TDF, 293 K): multiplet at −14.60 ppm (1 H), doublet of multiplets at −9.0 ppm ($J(H\text{–}P_{trans}) = 100$ Hz) (1 H), N–Rh–H and P–Rh–H, respectively. IR (Nujol mulls): 2000 cm^{-1} (ν(Rh–H)).

Scheme II



substitution pattern of one of the phenyl groups of the ligand,[8] respectively. The ^1H NMR spectrum (TDF, 293 K) of **5** exhibits an unresolved multiplet at −11.5 ppm in the hydride region. The absence of J(H–P) values >20 Hz indicates that the hydride ligand lies trans to the nitrogen atom of np$_3$. Finally, the $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 293 K) consists of a typical ABCX pattern as expected for the obvious nonequivalence of the three phosphorus atoms of np$_3$. The ^{31}P NMR assignments[9] are as follows (see Scheme II): $\delta(P_A)$ 25.70 ($J(P_A{-}P_B)$ = 22.6 Hz, $J(P_A{-}P_C)$ = 436.1 Hz, $J(P_A{-}Rh)$ = 104.3 Hz), $\delta(P_B)$ 12.95 ($J(P_B{-}P_C)$ = 13.2 Hz, $J(P_B{-}Rh)$ = 80.9 Hz), $\delta(P_C)$ −34.08 ($J(P_C{-}Rh)$ = 74.8 Hz).

On the basis of the experimental evidence summarized in Scheme II, the complex $[(np_3)RhH(Me)]^+$ is the most likely product of the straightforward methylation of **3**. Evidently, under the conditions employed, such a cis methyl hydride is not stable and reductively eliminates CH_4 to give the 16-electron cis-unsaturated fragment $[(np_3)Rh]^+$. Finally, the latter species intramolecularly activates a phenyl C–H bond of the ligand to give **5**. Interestingly, the ortho-metalated derivative is obtained also when the reaction of **3** with $MeSO_3CF_3$ is carried out in the presence of COD.

At variance with the $[(np_3)Rh]^+$ fragment, the isoelectronic species $[(np_3)Ir]^+$ prefers to oxidatively add one sp^2 C–H bond of COD through an intermolecular process rather than to intramolecularly activate a phenyl C–H bond of the np$_3$ ligand. Such a metal dependence on C–H activation when all the other conditions are even is not unusual and may depend on steric,[1h] thermodynamic, and kinetic factors.[1e,10]

Registry No. **1**, 104910-88-5; **2**, 104910-94-3; **2**·CH_3COCH_3, 104910-95-4; **3**, 85233-91-6; **4**, 104910-90-9; **5**, 104910-92-1; np$_3$, 15114-55-3; $[Ir(COD)Cl]_2$, 12112-67-3; COD, 111-78-4.

Supplementary Material Available: Listings of final atomic parameters and bond lengths and angles (6 pages); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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[8] Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432.

[9] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

[10] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

Carbonylation of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$

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Summary: The reaction of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$ (**1**) with CO at atmospheric pressure or 40 psi in THF, hexane, or acetone yields *endo*-$(\eta^5\text{-}C_6H(CH_3)_6)Mn(CO)_3$ (*endo*-**2**). This unusual result has been confirmed by determination of the molecular structure of *endo*-**2** by X-ray crystallography. Reaction of **1**, deuteriated at Mn–H, gives *endo*-**2** deuteriated in the exo position in acetone solution, but no deuterium tracing is found for the reaction in THF solution.

Although numerous unsuccessful attempts to insert carbon monoxide into metal–hydrogen bonds have been reported, there are two reports of metal formyls prepared from carbon monoxide and the corresponding metal hydride.[1,2] Evidence for an intermediate formyl complex, formed in a similar manner, by a metal hydride has been reported.[3] The carbonylation study reported here was undertaken to determine if $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$ (1)[4] would form a stable metal formyl or proceed to product formation through a metal formyl intermediate.

The reaction of $P(C_6H_5)_3$ with $(\eta^6\text{-}C_6H_6)Mn(CO)_2CH_3$ leads to migration of methyl from manganese to arene giving the endo-methylated η^5-cyclohexadienyl product.[5] In this reaction the acyl $(\eta^6\text{-}C_6H_6)Mn(CO)(P(C_6H_5)_3,(C(O)CH_3)$ has been identified as an equilibrium participant.[6] This observation suggests that carbonylation of 1 might lead to the formation of a metal formyl which could be involved as an equilibrium participant or intermediate in the formation of *exo*-$(\eta^5\text{-}C_6H(CH_3)_6)Mn(CO)_3$ (*exo*-2). Conversely the formation of a metal formyl would not be expected to play a role in any intramolecular mechanism which would lead to the formation of *endo*-2.

The carbonylation experiments were performed at 25 °C by using dilute rigorously deoxygenated solutions of 1 (10–20 mM) in THF, acetone, or hexane. Carbon monoxide was either bubbled through the solution at atmospheric pressure, or the glass reaction vessel was pressurized to 40 psi. The progress of the reaction was followed by recording the IR spectra of samples removed from the reaction mixture. An induction period in excess of 1 h was always observed during which the concentration of 1 decreased slightly, but no *endo*-2 was formed. The length of the induction period was observed to decrease with

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[1] (OEP)Rh(CHO) is formed from CO and (OEP)RhH. (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. (b) Wayland, B. B.; Woods, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 302.

[2] $(C_5Me_5)ThH(OR)$ adddds CO to form the η^2-formyl derivative. Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

[3] $(\eta\text{-}C_5H_5)Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2](CHO)$ is formed as an intermediate by hydride migration to CO. Davies, S. G.; Simpson, S. J. *J. Organomet. Chem.* **1982**, *240*, C48.

[4] (a) Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445. (b) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; LaBrush, D. M.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 883.

[5] Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *12*, 1730.

[6] Brookhart, M., private communication.

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