anisotropic thermal parameters, structure factor amplitudes, and calculated hydrogen atom positions, phenyl carbon positions, etc. are available for both structures in the supplementary material.

Registry No. $CpMo(CO)_2(endo\text{-}\eta^3\text{-}2\text{-}MeC_3H_4)$, 95781-86-5; $CpMo(CO)_2(exo\text{-}\eta^3\text{-}C_6H_9)$, 84117-08-8; $CpMo(CO)_2(exo\text{-}\eta^3\text{-}C_7H_{11})$, 84117-12-4; $(\eta^5\text{-}Cp)W(CO)_2(\eta^3\text{-}Cp)$, 65862-57-9; $InMo(CO)_2(exo\text{-}\eta^3\text{-}1\text{-}MeC_3H_4)$, 95781-87-6; $(In)_2Ti(CH_3)_2$, 49596-02-3; $(In)_2Zr(CH_3)_2$, 49596-04-5; $(In)_2HF(CH_3)_2$, 49596-06-7; $[(1,3\text{-}Me_2In)_2Fe]^+$, 56285-02-0; $(In)Cr(NO)(CO)_2$, 60260-19-7; $(In)Mo(CO)_3I$, 31870-77-6; $(In)_3UCl$, 11082-70-5; $[(In)Mo(CO)PEt_3)(MeC_2Me)]^+$, 78090-93-4; $[(In)Mo(PMe_3)_2(MeC_2Me)]^+$, 78091-05-1; $[(In)Rh\{C_6H_3(CF_3)_4C(CH_2)CH_3\}]$, 63428-47-7; $[(In)_2Rh_2(CO)_2(C_3H_4)]$, 81249-02-7; $[InIr(PPh_3)_2H]BF_4$, 95616-25-4; $\{(C_9H_7)Ir[P(C_6H_5)_3]_2H\}BF_4\cdot CH_2Cl_2$, 95616-26-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, structure factor amplitudes, and calculated hydrogen atom positions, phenyl carbon positions, etc. for both structures (21 pages). Ordering information is given on any current masthead page.

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(40) Crabtree, R. H.; Parnell, C. P. *Organometallics* **1985**, *4*, 519–523.

(41) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.3.1, pp 146–50; (b) Table 2.2B, pp 99–101.

(42) We wish to acknowledge the National Science Foundation for financial support and Johnson Matthey for a loan of iridium. We also wish to thank the National Science Foundation for support of the NSF Northeast Regional NMR Facility.

Communications

Hydrido Heterobimetallic Bis(diphenylphosphino)methane-Bridged Ru–Rh Complexes. Activation of a P–C Bond of Bis(diphenylphosphino)methane To Give a Heterobimetallic Ru–Rh Complex Containing a *trans*-Hydridophenylruthenium Moiety. X-ray Crystal Structure of $RuRhH(C_6H_5)(C_8H_{12})[C_6H_5PCH_2(C_6H_5)_2]\text{-}[(C_6H_5)_2PCH_2P(C_6H_5)_2]\cdot 0.5C_6H_5CH_3$

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Summary: $RuH_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) reacts with $[RhCl(COD)]_2$ (COD = cyclooctadiene) in toluene to give quantitatively $RuRhH_2Cl(COD)(dppm)_2$ (**1**), a heterobimetallic complex shown to contain a single bridging dppm ligand as well as one bridging hydride and one bridging chloride group. The same reaction occurs with $[IrCl(COD)]_2$ but in this case some redistribution to $RuHCl(dppm)_2$ is also observed. **1** does not react with ethylene but decomposes slowly under H_2; it reacts with CO to give the bis dppm-bridged complex $RuRhCl(CO)_3(dppm)_2$ (**4**) and with $P(OMe)_3$ to give $RhH[P(OMe)_3]_4$ and $RuHCl[P(OMe)_3](dppm)_2$ (**5**) which contains a monodentate dppm group. Finally, with CH_3Li a quantitative yield of $RuRhH(C_6H_5)(C_8H_{12})[C_6H_5PCH_2P(C_6H_5)_2][(C_6H_5)_2PCH_2P(C_6H_5)_2]$ (**6**) is obtained. This complex is shown to contain a bridging phosphido group and a *trans*-hydridophenylruthenium moiety.

Introduction

Preparation and reactivity of heterobimetallic complexes are a largely studied subject, but most of the research has been oriented so far toward CO reduction.[1] Many such species containing dppm as bridging ligand have been prepared recently, mostly by Shaw et al.[2] As part of our interest in hydride complexes as possible precursors for C–H activation reactions,[3] we developed a method for the preparation of ruthenium-containing hydrido bimetallic compounds using the chelated complex $RuH_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane).[4] We have recently shown that this bis dppm-bridged complexes could be obtained from the reaction of $RuH_2(dppm)_2$ or $Ru(COD)(dppm)_2$ (COD = cyclooctadiene) with $[RhCl(CO)_2]_2$.[5] In this paper we describe the reaction of $RuH_2(dppm)_2$ with the analogous carbonyl-free complex $[RhCl(COD)]_2$ and the activation of a P–C bond of dppm to give a bimetallic Ru–Rh complex containing a *trans*-hydridophenylruthenium moiety.

$RuH_2(dppm)_2$ reacted smoothly at room temperature in toluene with $[RhCl(COD)]_2$ to give a quantitative yield of a bright orange compound analyzing for $RuRhH_2Cl(COD)(dppm)_2$ (1).[6] This air-stable complex is very soluble in common organic solvents except alkanes. A terminal hydride on ruthenium as well as a bridging one are observed by ^1H NMR spectroscopy whereas the ^{31}P NMR spectrum shows four different phosphorus atoms, two of which are coupled to rhodium (J_{Rh-P_2} = 130 Hz; J_{Rh-P_3} = 5 Hz). The spectrum is first order and is attributed unambiguously. 1 simply results from the association between $RuH_2(dppm)_2$, after opening of one chelated dppm group, with a "RhCl(COD)" moiety. The presence of one bridging hydride and one bridging chloride is deduced from

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(1) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Permagon Press: Oxford, 1982; Chapter 40.

(2) See for example: Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 1815–1822 and references therein.

(3) (a) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1388–1390. (b) Chaudret, B.; Devillers, J.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1983**, 641–643.

(4) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635–1639.

(5) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Nouv. J. Chim.* **1983**, *7*, 679–681.

(6) Selected spectroscopic data for 1 (all NMR spectra were recorded on a Bruker WH90 or WH250 spectrometer operating in the Fourier transform mode. Chemical shifts are relative to Me_4Si (^1H and ^{13}C NMR) or external H_3PO_4 in D_2O (^{31}P NMR): IR ν(Ru–H) 1990 cm^{-1}; ^1H NMR (in C_6D_6) $\delta(H_1)$ −14.6 (q, J_{P-H} = 21 Hz), $\delta(H_2)$ −15.6 (J_{Rh-H} = 22 Hz), $\delta(CH_2)$ 4.6 (1), 4.1 (2), 2.5 (1); ^{31}P NMR (in C_6D_6/C_7H_8) $\delta(P_1)$ 45.7 (ddd), $\delta(P_2)$ 22.5 (dddd), $\delta(P_3$ 14.1 (ddt), $\delta(P_4)$ 7.1 (ddd), $J_{P_1P_2}$ = 84 H, $J_{P_1P_3}$ = 29.5 Hz, $J_{P_1P_4}$ = 313 Hz, $J_{P_3P_4}$ = 68 Hz, $J_{P_2P_3}$ = 5 Hz, $J_{P_2P_4}$ = 12 Hz, J_{P_2Rh} = 134 Hz, J_{P_3Rh} = 3 Hz; ^{13}C NMR in (C_7D_8) $\delta(CH_2(dppm))$ 30.4, 62.1, $\delta(CH(COD))$ 75.9, $\delta(CH(COD))$ 36.9, 28.5. Anal. Calcd for $RuRhC_{58}ClH_{38}P_4$: C, 62.3; H, 5.29; Cl, 3.2; P, 11.1. Found: C, 62.2; H, 5.2; Cl, 3.0; P, 11.0.

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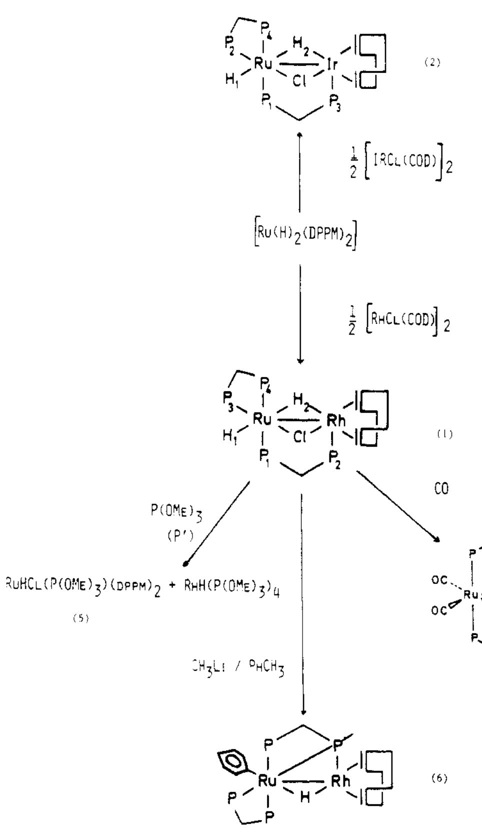
Scheme I. Preparation and Some Reactions of $RuRhH_2Cl(COD)(dppm)_2$ (1)



spectroscopic data. The same reaction using $[IrCl(COD)]_2$ instead of $[RhCl(COD)]_2$ gave $RuIrH_2Cl(COD)(dppm)_2$ (2) whose spectroscopic data[7] are very similar to those of 1. In this case $RuHCl(dppm)_2$[4] (3) and an unidentified iridium hydride also were formed and crystallized out from the reaction mixture prior to 2. This probably indicates that 2 is an intermediate in the redistribution reaction. The same reaction with $PdCl_2(COD)$ affords a quantitative yield of 3.

We attempt some reactions of 1 to test its reactivity and see whether the bimetallic structure is retained during reaction (Scheme I). 1 did not react with ethylene at room temperature, but with H_2 it reacted to give a brown solution from which a very low yield of pink crystals was obtained. This compound contains terminal as well as bridging hydrides as indicated by infrared spectroscopy, but no NMR data were obtained due to extensive decomposition in solution. By reaction of 1 with CO, substitution of COD occurs and the previously characterized complex $RuRhCl(CO)_3(dppm)_2$[5] (4) was obtained. It is noteworthy that this complex adopts a bis dppm-bridged structure which seems thermodynamically more favorable as long as no chelating ligand such as COD prevents its formation. However, with the more basic ligand $P(OMe)_3$ in excess the dinuclear structure was broken and $RhH[P(OMe)_3]_4$ was obtained together with the new complex $RuHCl[P(OMe)_3](dppm)_2$[8] (5) which was shown to contain a monodentate dppm group.

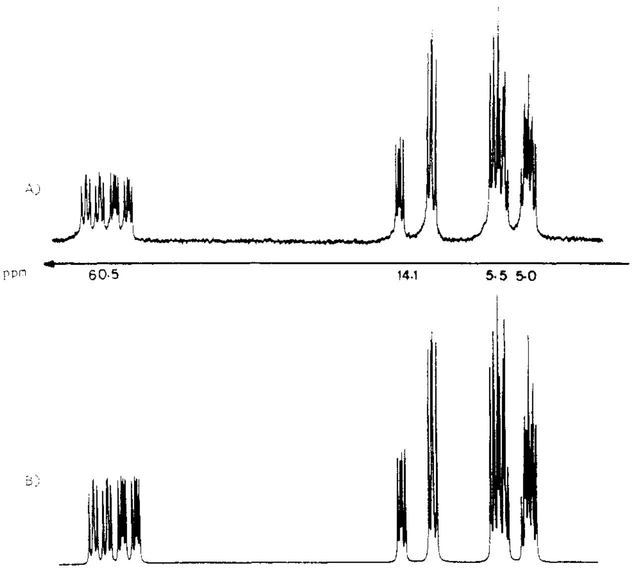


Figure 1. ^{31}P NMR spectrum of $RuRhH(C_6H_5)(C_8H_{12})[C_6H_5PCH_2P(C_6H_5)_2][(C_6H_5)_2PCH_2P(C_6H_5)_2]$ (6): original (A) and simulated (B).

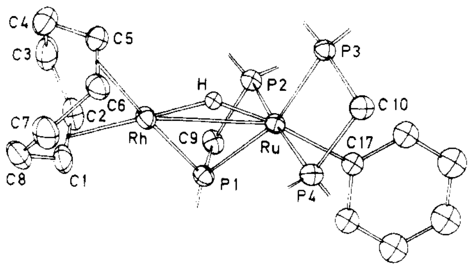


Figure 2. Molecular structure of $RuRhH(C_6H_5)(C_8H_{12})[C_6H_5PCH_2P(C_6H_5)_2][(C_6H_5)_2PCH_2P(C_6H_5)_2]$.

Table I. Selected Bond Distances (Å) and Angles (deg) for $RuRhHPh(COD)(PhPCH_2PPh_2)(Ph_2PCH_2PPh_2)$

Bond Distances

Ru-Ru	2.9413 (8)	Ru-H	1.62 (5)
Rh-H	1.64 (4)	Ru-C(17)	2,191 (5)
Rh-C(1)	2.154 (7)	Ru-P(1)	2,298 (1)
Rh-C(2)	2.138 (6)	Ru-P(2)	2,342 (1)
Rh-C(5)	2.255 (8)	Ru-P(3)	2,320 (1)
Rh-C(6)	2.243 (8)	Ru-P(4)	2,321 (1)
Rh-P(1)	2.260 (2)		

Bond Angles

H-Ru-C(17)	173 (2)	P(1)-Ru-P(4)	112.11 (5)
H-Ru-P(1)	75 (2)	P(1)-Ru-Rh	49.24 (5)
H-Ru-P(2)	92 (1)	P(2)-Ru-P(3)	108.41 (5)
H-Ru-P(3)	87 (2)	P(2)-Ru-P(4)	173.58 (7)
H-Ru-P(4)	94 (1)	P(3)-Ru-P(4)	72.21 (5)
C(17)-Ru-P(1)	100.2 (1)	P(2)-Ru-Rh	80.34 (5)
C(17)-Ru-P(2)	89.9 (1)	P(3)-Ru-Rh	112.28 (5)
C(17)-Ru-P(3)	98.3 (1)	P(4)-Ru-Rh	105.47 (5)
C(17)-Ru-P(4)	83.7 (1)	H-Ru-Rh	25 (2)
P(1)-Ru-P(2)	69.44 (5)	C(17)-Ru-Rh	149.43 (9)
P(1)-Ru-P(3)	161.36 (7)		

In order to eliminate the chloride ligand, 1 was treated with 1 equiv of CH_3Li in toluene, yielding an orange, air-stable (in the solid state) complex of composition $RuRhH(COD)(dppm)_2$[9] (6) in nearly quantitative yield. It

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(7) Selected spectroscopic data for 2: ^1H NMR (in C_6D_6) $\delta(H_1)$ −14.23 (q), $\delta(H_2)$ −15.6; ^{31}P NMR (in C_7H_8/C_7D_8) $\delta(P)_1$ 47.6, $\delta(P_2)$ 17.5, $\delta(P_3)$ 6.6, $\delta(P_4)$ −8.5, $J_{P_1P_2}$ 30.9 Hz, $J_{P_1P_3}$ 78.0 Hz, $J_{P_1P_4}$ 317.6, $J_{P_2P_3}$ 4.4 Hz, $J_{P_2P_4}$ 67.7 Hz, $J_{P_3P_4}$ 10.3 Hz.

(8) Selected spectroscopic data for 5: ^1H NMR (in C_6D_6) δ (hydride) −3.2 (dq, J_{PH}(cis) = 22.5 Hz, J_{PH}(trans) = 162.5 Hz); ^{31}P NMR (in C_6D_6/C_7H_8) $\delta(P(OMe)_3)$ 137.8, $\delta(P_1)$ 39.9, $\delta(P_2)$ 16.7, $\delta(P_3)$ −10.6, $\delta(P_4)$ −26.6. Anal. Calcd for $RuC_{53}ClH_{54}OP_5$: C, 61.7; H, 5.2; Cl, 3.5; P, 15.1. Found: C, 59.7; H, 5.2; Cl, 3.8; P, 14.3.

(9) Selected spectroscopic data for 6: ^1H NMR (in C_7D_8) δ(hydride) −10.95 (J_{Rh-H} = 19.5 Hz, J_{HP_1} = 19.5 Hz, $J_{HP_2} = J_{HP_3} = J_{HP_4}$ = 10 Hz); ^{31}P NMR (in C_7H_8/C_7D_8) $\delta(P_1)$ 60.5, $\delta(P_4)$ 14.1, $\delta(P_2)$ 5.5, $\delta(P_3)$ 5.0, $J_{P_1P_4}$ = 26.9 Hz, $J_{P_1P_2}$ = 31.7 Hz, $J_{P_1P_3}$ = −253.9 Hz, $J_{P_2P_4}$ = −274.7 Hz, $J_{P_3P_4}$ = 42.7 Hz, $J_{P_2P_3}$ = 28.1 Hz, J_{P_1Rh} = 120.85 Hz; ^{13}C NMR (in C_6D_6) δ(CH(COD)) 74.0, 70.1, $\delta(CH_2(COD))$ 30.6, $\delta(CH_2(dppm))$ 52.3, 138.4, δ(CRu) 167.7, δ(CO) 149.3, δ(Cm) 94.2, δ(Cp) 120.05. Anal. Calcd for $RuRhC_{58}H_{57}P_4$: C, 64.4; H, 5.3; P, 11.5; Cl, 0. Found: C, 64.4; H, 5.5; P, 11.3, Cl, <0.1.

was shown to contain a bridging hydride and four different phosphorus atoms. An intriguing feature was the observation by ^{31}P NMR of two trans P–P coupling constants ($J_{P_1P_3}$ = 253.9 Hz, $J_{P_2P_4}$ = 274.7 Hz) whereas only one phosphorus is coupled to rhodium (J_{Rh-P_1} = 120.85 Hz). The spectrum was simulated by using the PANIC program[9] (Figure 1). The only possible structure should contain four phosphorus substituents on ruthenium, one part of a bridging phosphido group. This was confirmed by an X-ray crystal structure determination[10] (Figure 2). Selected bond distances and angles are listed in Table I. The four phosphorus are bonded to ruthenium. P(1) bridges the metal–metal bond together with one hydride. The Ru–Rh distance, 2.9413 (8) Å, is consistent with the presence of a hydrido-bridged metal–metal bond (see 2.933 Å for $Pt_2H(Me)_2(dppm)_2^+$). The most interesting feature is the presence of a phenyl group bonded to ruthenium. This can only arise from the cleavage of a P–C bond mediated by ruthenium. Interestingly, such an intermediate has never been isolated in the decomposition of dppm on clusters.[11] Some products of pyrolysis of clusters in the presence of PPh_3 have been shown to contain coordinated phenyl groups.[12] In our case, the reaction occurs at room temperature and is selective. The same structure remains in solution as confirmed by ^{13}C NMR which shows the phenyl group bonded to ruthenium[13] (C–Ru δ 163.7, C_{ortho} 149.3, C_{meta} 94.2, C_{para} 120.0). The mechanism of formation of this complex probably involves an unstable dihydrido methyl intermediate which after elimination of methane leaves a very reactive 16-electron ruthenium moiety. This is stabilized by insertion into a P–C bond of dppm to achieve an 18-electron configuration. We are presently studying the reactivity of this interesting species.

Registry No. 1, 95531-46-7; 2, 95531-47-8; 3, 34216-12-1; 4, 89613-06-9; 5, 95531-48-9; 6, 95531-49-0; 6·0.5 $C_6H_5CH_3$, 95531-50-3; $RhH[P(OMe)_3]_4$, 59400-49-6; $RuH_2(dppm)_2$, 89613-08-1; $[RhCl(COD)]_2$, 12092-47-6; $[IrCl(COD)]_2$, 12112-67-3; $PdCl_2(COD)$, 12107-56-1.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters, complete bond distances and angles, and structure factors (33 pages). Ordering information is given on any current masthead page.

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(10) Crystal data: $C_{58}H_{57}P_4RhRu\cdot 0.5C_6H_5CH_3$: a = 15.985 (3) Å, b = 18.324 (4) Å, c = 19.496 (4) Å, β = 112.2 (2)°, monoclinic, space group C_{2h}^5—$P2_1/c$, Z = 4. Intensity data were recorded in θ–2θ scan mode on a CAD4 diffractometer using Mo Kα radiation. Full-matrix least-squares refinement with 4751 reflections having $I > 4\sigma(I)$ led to final R = 0.034.

(11) Lavigne, G.; Lugan, N.; Bonnet, J. J. *Organometallics* **1982**, *1*, 1040–1050.

(12) See for example: Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87–89.

(13) These values are similar to that found for mononuclear phenylruthenium complexes: see, for example: Saunders, D. R.; Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1473–1477.

Steric Effects in Carbon Monoxide Insertion into Manganese–Carbon Bonds

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Summary: The reactivity of the manganese–benzyl complexes $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ toward carbon monoxide insertion induced by tertiary phosphines in polar solvents has been studied. The steric influences of the alkyl group, solvent, and the phosphine are discussed.

Earlier we have drawn attention to steric effects in the tertiary phosphine induced insertion of carbon monoxide into transition metal to carbon bonds for series of alkyl complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$[1,2] and $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$.[3] We have noted a rate enhancement with increase in the size of the alkyl group, R, in the k_1 step of the reaction schematically represented as eq 1, where L

$$[(CO)MR] \xrightleftharpoons[k_{-1},\,-S]{k_1,\,S} [SM(COR)] \xrightleftharpoons[k_{-2},\,-L]{k_2,\,L} [LM(COR)] + S \qquad (1)$$

= tertiary phosphine and S = solvent. This step, on strong kinetic and stereochemical grounds,[2-6] is believed to involve a solvent-induced migration of the alkyl group to a carbonyl carbon atom. Interestingly a substantial diminution in k_1 has also been observed for the reaction of diphenylmethylphosphine with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$ as the effective size of the solvent in a series of α-substituted tetrahydrofurans increases, which is thought to reflect increasing steric hindrance to the coordination of the tetrahydrofuran to molybdenum.[6] We have also detected[2] a large decrease in the rate constant k_2 for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$ systems when the cone angle of the tertiary phosphine,[7] which replaces the solvent molecule in the intermediate acyl in this stage of the reaction, exceeds a critical value. This effect is enhanced in the corresponding (pentamethylcyclopentadienyl)molybdenum benzyl complex and only relatively small ligands, such as dimethylphenylphosphine, react. In the belief that the substantial steric effects may largely be reflecting the influence of the large, nonlabile cyclopentadienyl group, we extended our work to a metal alkyl system which contains only CO ligands and which should be less restricted sterically at the metal center. Specifically, carbon monoxide insertion has been followed, in acetonitrile, tetrahydrofuran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran at 30 °C, for a series of manganese–benzyl complexes, $[(CO)_5Mn(CH_2C_6H_{5-n}X_n)]$, strategically substituted in the aromatic ring, using tertiary phosphines of different cone angles.[10]

The effect of the size of the alkyl group was examined by comparing the effect on k_1 of substitution of an alkyl group, for which electronic effects are small,[1,11] in the ortho

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(6) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(7) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(8) Cotton, J. D.; Kimlin, H. A., unpublished data.

(9) Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.

(10) In a typical experiment, a solution of 0.023 g (0.08 mmol) of $[(CO)_5MnCH_2Ph]$ and 0.20 g (0.76 mmol) of triphenylphosphine in 10 ml of acetonitrile was degassed in a Schlenk tube in a constant temperature bath (30.0 ± 0.1 °C). Periodically, a sample was withdrawn, by syringe, through a serum cap and reaction followed by monitoring the disappearance of the highest energy CO stretching vibration (2111 cm^{-1}) of the starting material. Reaction was followed for around 3 half-lives and, at this high relative concentration of tertiary phosphine, was effectively first order in $[(CO)_5MnCH_2Ph]$. The reaction was repeated for different phosphine concentrations which tyically ranged from 0.025 to 0.2 M. A plot of the reciprocal of the observed first-order rate constant, i.e., $1/k_{obsd}$ vs. $1/[L]$, where L = tertiary phosphine, was linear and enabled the calculation of k_1 and k_{-1}/k_2, based on the overall rate expression,[4] $k_{obsd} = k_1k_2[L]/(k_{-1} + k_{-2}[L])$, appropriate for polar solvents. Uncertainty parameters vary with the system, but a general guide is ±5% for k_1 and ±10% for the ratio k_{-1}/k_2. In this concentration range, the direct reaction (k_3 path) of tertiary phosphine with $[(CO)_5MnR]$ was insignificant.

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