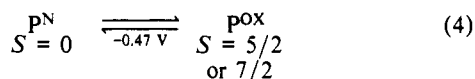


spectral parameters by these ligand sets at a single subsite.

Of all native clusters, the "P-clusters" of nitrogenase are the best candidates for non-cysteinate or otherwise unconventional terminal ligation. Their properties, which are consistent with but do not necessarily prove the Fe_4S_4 cubane-type formulation, are summarized elsewhere.^{12,62} Following the usual practice, we adopt this formulation. Briefly, the clusters exhibit redox couple 4;



$$\delta (\Delta E_Q) = 0.55 (3.03) \text{ mm/s (unique subsite)}$$

$$\delta (\Delta E_Q) = 0.51-0.52 (0.68-1.33) \text{ mm/s (other subsites)}$$

the P^{OX} form is reduced at the indicated potential E_0' .⁶³ The clusters occur as two slightly inequivalent pairs whose P^{N} forms have the Mössbauer parameters⁶⁴ given. Isomer shifts for all subsites are nearly the same, but one subsite is unique because of the large quadrupole splitting, which is closely comparable to that of tetrahedral $\text{Fe}^{\text{II}}\text{S}_4$ units.

Given the diamagnetic ground state of P^{N} , the two possible redox couples are $[\text{Fe}_4\text{S}_4]^{+/0}$ and $[\text{Fe}_4\text{S}_4]^{3+/2+}$ (Figure 10). The redox potential is too low for a normal $3+/2+$ reaction, and much too high for the $+/0$ couple based on analogue data.¹² The first

couple could be displaced to lower values by binding of two negative ligands at one or more subsites as in **10-14**, and isomer shifts could be raised to the observed values by increased coordination numbers at the subsites. With the $+/0$ couple, isomer shifts are entirely consistent with a $[\text{Fe}_4\text{S}_4]^0$ core of a $\text{Fe}_4\text{S}_4(\text{S-Cys})_4$ cluster, as is the observation of a transient $g = 1.94$ -type EPR spectrum corresponding to an unstable $S = 1/2$ $[\text{Fe}_4\text{S}_4]^+$ species produced during oxidation. Unless the redox step is proton-linked (by, e.g., protonation of the all-ferrous core) or is subject to some special protein environmental effect, it is not clear what displaces the potential upward to the observed value. With either couple, it is also difficult to understand how one subsite of the P^{N} form can be differentiated from the other three by a much larger quadrupole splitting. Indeed, we have yet to produce any Fe_4S_4 cluster with a quadrupole splitting as large as 3 mm/s.

In order to accommodate simultaneously the redox potential, ground spin states, and Mössbauer parameters of P-clusters, departure from the ligation mode of a classical $\text{Fe}_4\text{S}_4(\text{S-Cys})_4$ cluster appears to be required. The results presented here provide the first comprehensive study of the effects of non-standard terminal ligation in $[\text{Fe}_4\text{S}_4]^{2+}$ clusters. To provide a more detailed account of these effects, this work is being expanded to oxidized clusters $[\text{Fe}_4\text{S}_4]^{3+}$ whose potential accessibility in the set **10-14** and with other clusters in dichloromethane solution has already been noted.

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Acknowledgment. This research was supported by NIH Grant GM 28856, and by the National Science Foundation at M.I.T. G.C.P. acknowledges support by the Office of Naval Research program on Cluster Science and Dynamics under Contract No. N00014-89-J-1779.

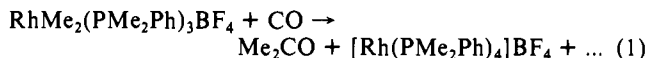
$\eta^3\text{-MeC}(\text{CH}_2\text{PPh}_2)_3/\text{Rhodium}$ Complexes Utilize Phosphine Arm Dissociation Mechanisms at 25 °C

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Abstract: Reaction of $\text{RhMe}_3(\text{triphos})$ ($\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$) with CO generates acetone and $\text{RhMe}(\text{CO})(\text{triphos})$, which reacts with further CO to give $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$. The structure of $\text{RhMe}(\text{CO})(\text{triphos})$ shows one strained P-Rh-P bond angle between equatorial ligands ($90.80 (5)^\circ$) in a trigonal bipyramid, together with intramolecular steric effects that cause a small equatorial CO-Rh-axial(CH_3) C/C angle of $79.09 (25)^\circ$. The acetyl and methyl complexes react with H_2 at 25 °C to produce acetaldehyde and methane, respectively, together with $\text{RhH}(\text{CO})(\text{triphos})$. Reaction of CO with $\text{RhH}_3(\text{triphos})$ is even faster than with $\text{RhMe}_3(\text{triphos})$ to give H_2 and $\text{RhH}(\text{CO})(\text{triphos})$, together with a CO hydrogenation product. These results show that these clean stoichiometric conversions, as well as a variety of isotopic exchange reactions of the Rh(I) and Rh(III) compounds with D_2 and ^{13}CO , occur by preequilibrium dissociation of one arm of the triphos ligand at 25 °C. One such species, $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})_2(\eta^2\text{-triphos})$, is directly detectable and reveals the mechanism of exchange of $\text{Rh}[\text{C}(\text{O})\text{Me}](^{13}\text{CO})(\text{triphos})$ with ^{12}CO . The coordination of CO to $\text{Rh}(\text{H})_3(\eta^2\text{-triphos})$ is proposed to generate a dihydrogen complex, thus accounting for the CO-induced elimination of H_2 . As suggested by these individual reactions, $\text{RhH}(\text{CO})(\text{triphos})$ is a catalyst for olefin hydroformylation. The high n:iso selectivity mimics that of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in the presence of a large amount of added PPh_3 , a beneficial consequence of the chelate effect.

We have been examining the polyhydride and polymethyl chemistry of iridium(III) with monodentate phosphine ligands.¹⁻³ When we attempted to compare these results with the analogous rhodium compounds, the outcome was obscured by phosphine redistribution (eq 1).⁴ We reasoned that this problem might be



avoided if we employed the tridentate phosphine $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$, "triphos". In addition to "tight" binding (i.e., retention) of phosphine due to the chelate effect, the imposed *facial* stereochemistry of this ligand was anticipated to have major influence

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on reaction mechanisms because the quasi-tetrahedral intermediate (triphos)RhX (X = H or Me) would be destabilized; the d^8 electron configuration is more stable when planar. Thus, new reaction products and mechanisms might be expected for tridentate in comparison to monodentate phosphines.

Since our interest was in exploring the comparative reactivity of the two prototypical one-electron ligands hydride and methyl, we selected for study $\text{RhH}_3(\text{triphos})$ and $\text{RhMe}_3(\text{triphos})$. Both are found to react readily (25 °C). Because the commercial application of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ to catalyze olefin hydroformylation shows improved normal/iso ratios for aldehydes in the presence of a large excess of added PPh_3 , we have studied briefly the influence of the chelate effect of triphos on hydroformylation catalysis.

Throughout this paper, we use "triphos" to indicate the ligand coordinated in a η^3 fashion.

Experimental Section

General Procedures. Pentane, tetrahydrofuran, benzene, and toluene were all dried and distilled prior to use from solutions containing sodium/potassium benzophenone ketyl. Methylene chloride was refluxed over P_2O_5 and distilled prior to use. The gases H_2 (Ultra High Purity, Air Products), CO (Ultra High Purity, Air Products), $^2\text{H}_2$ (C.P. Grade, Linde), and ^{13}CO (99% ^{13}C , Monsanto) were used as received. MeLi was purchased from Aldrich. $\text{RhH}_3(\text{triphos})$ was prepared as previously reported.⁵ NMR spectra were recorded on a Bruker AM-500 or a Nicolet NT-360 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer. Gas chromatography was accomplished with a Varian Model 3700 gas chromatograph with a J&W DB-5 (0.25 μM) 30-m fused-silica capillary column. The following abbreviations are used: d (doublet), t (triplet), m (multiplet), FPT (freeze-pump-thaw), wd (full width at half-height).

Synthesis of $\text{RhCl}_3(\text{triphos})$ ($\text{triphos} = \text{CH}_3\text{C}(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_3$). $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.25 g, 4.75 mmol) was added to triphos (3 g, 4.75 mmol) dissolved in THF (75 mL). This mixture was then refluxed for 1 h, after which time the solution was cooled and EtOH (20 mL) was added to raise the reflux temperature and help solubilize the rhodium salt. The reaction mixture was again refluxed with stirring, this time for 7 h (until no dark red crystals of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were noticeable in the bottom of the reaction mixture when it was allowed to stand (~ 1 min) without stirring). The light yellow microcrystalline precipitate was then collected by filtration, washed with EtOH (2×15 mL), and dried in vacuo to yield $\text{RhCl}_3(\text{triphos})$ (2.55 g). The homogeneous yellow filtrate was then stripped in vacuo, and the resulting yellow-green residue was extracted with CH_2Cl_2 (2×20 mL) and filtered through a medium-porosity frit to yield a deep yellow solution, which was then reduced in volume to 5 mL. To this solution was added pentane (40 mL) to precipitate a pale yellow solid and a brown gum. After 7 h of stirring, all that remained was a pale yellow precipitate, which was collected by filtration, washed with pentane (2×15 mL), and dried in vacuo to yield a second batch of $\text{RhCl}_3(\text{triphos})$ (1.33 g). Combined yield 3.86 g (96%). ^1H NMR (360 MHz, CD_2Cl_2 , 22 °C): δ 1.59 (unresolved q, $J_{\text{PH}} = 2$ Hz, CCH_3), 2.6 (d, $J_{\text{PH}} = 1.5$ Hz, PCH_2). ^{31}P NMR (146 MHz, CD_2Cl_2 , 22 °C): δ 9.5 (d, $J_{\text{RHP}} = 104$ Hz).

$\text{RhMe}_3(\text{triphos})$. To $\text{RhCl}_3(\text{triphos})$ (0.63 g, 0.76 mmol) in THF (60 mL), with stirring at 0 °C, was added MeLi in Et_2O (1.4 M, 4.2 mL, 5.88 mmol). The reaction mixture was stirred at 0 °C for 3.5 h, during which time the solution changed from orange to a very pale yellow. The reaction mixture was maintained at 0 °C and slowly (dropwise) hydrolyzed with wet THF (until gas evolution ceased), leaving a dark brown solution. The volatiles were then removed in vacuo, and the remaining gray-white solid was extracted with CH_2Cl_2 (70 mL) and filtered to yield a homogeneous yellow-brown solution. This was then reduced in volume (15 mL) until large amounts of a white precipitate ($\text{RhMe}_3(\text{triphos})$) were present. The product was collected by filtration and dried in vacuo. Yield 0.44 g (75%). ^1H NMR (360 MHz, CD_2Cl_2 , 22 °C): δ 0.311 (second-order m, 9 H, RhMe), 1.4 (unresolved q, $J_{\text{PH}} = 7$ Hz, CCH_3),

Table I. Crystallographic Data for $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Rh}(\text{CH}_3)\text{CO}$

chem formula	$\text{C}_{43}\text{H}_{42}\text{OP}_3\text{Rh}$	space group	$P2_1$
a , Å	10.205 (1)	T , °C	-141
b , Å	17.520 (2)	λ , Å	0.71069
c , Å	10.498 (1)	ρ_{calcd} , g cm^{-3}	1.442
β , deg	108.93 (0)	$\mu(\text{Mo K}\alpha)$, cm^{-1}	6.39
V , Å ³	1775.31	R	0.0402
Z	2	R_w	0.0396
formula wt	770.63		

2.35 (d, $J_{\text{PH}} = 4$ Hz, 6 H, CH_2P), 7.6–7.2 (30 H, phenyl H). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, CD_2Cl_2 , 22 °C): δ -2.25 (d, $J_{\text{PRh}} = 75$ Hz).

Reaction of $\text{RhMe}_3(\text{triphos})$ with H_2 . $\text{RhMe}_3(\text{triphos})$ (0.027 g, 0.03 mmol) was placed in C_6D_6 (0.4 mL) and transferred to an NMR tube. The solution was then degassed (FPT, three cycles) and placed under H_2 (1 atm). The tube was then submerged in liquid N_2 to reduce the pressure and the tube was flame sealed. Monitoring this reaction by ^1H NMR showed, after 2 h, significant production of $\text{RhH}_3(\text{triphos})$,⁵ methane (δ 0.149), and a trace amount of ethane (δ 0.791). The ^1H NMR intensities of CH_4 to C_2H_6 integrated 8:1. After 16 h, ^1H NMR revealed a 50:50 mixture of $\text{RhMe}_3(\text{triphos})$ and $\text{RhH}_3(\text{triphos})$.

Reaction of $\text{RhMe}_3(\text{triphos})$ with CO . (a) $\text{RhMe}_3(\text{triphos})$ (0.2 g, 0.26 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed in a high-pressure reaction vessel of local construction. The vessel was then charged with CO (1600 psi), and the reaction mixture was allowed to stir for 24 h. The CO pressure was then released, and the homogeneous yellow solution was transferred to a Schlenk flask. The volatiles were removed in vacuo to yield a pale yellow solid.⁹ Yields are quantitative by ^1H and ^{31}P NMR. ^1H NMR (360 MHz, CD_2Cl_2 , 22 °C) for $\text{Rh}[\text{C}(\text{O})\text{CH}_3](\text{CO})(\text{triphos})$: δ 1.57 (s, 3 H, CCH_3), 2.14 (d, $J_{\text{RH}} = 1.5$ Hz, 3 H, $\text{C}(\text{O})\text{CH}_3$), 2.28 (d, $J_{\text{PH}} = 7.6$ Hz, 6 H, CH_2P), 7.4–7.0 (30 H, phenyl H). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, CD_2Cl_2 , 22 °C): δ 4.9 (br d, $J_{\text{PRh}} = 112$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (-90 °C): 16 (dt, $J_{\text{PRh}} = 72$ Hz, $J_{\text{PP}} = 42$ Hz, 1 P), 0.7 (dd, $J_{\text{PRh}} = 132$ Hz, 2 P). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 22 °C, natural abundance): δ 208 (dq, $J_{\text{RHC}} = 82$ Hz, $J_{\text{PC}} = 15$ Hz, RhCO), 258 (dq, $J_{\text{RHC}} \approx J_{\text{PC}} \approx 24$ Hz, $\text{RhC}(\text{O})\text{CH}_3$). IR (CH_2Cl_2): 1890 and 1600 cm^{-1} .

(b) $\text{RhMe}_3(\text{triphos})$ (0.04 g, 0.05 mmol) was dissolved in a minimum amount of CD_2Cl_2 and placed in an NMR tube. The tube and its contents were then degassed (FPT, three cycles) and placed under CO (1 atm). The solution was then cooled to -196 °C and the tube was flame sealed. Upon thawing of the sample, no visible change was noted. Monitoring the reaction by ^1H NMR showed significant (20%) production of $\text{Rh}[\text{C}(\text{O})\text{CH}_3](\text{CO})(\text{triphos})$ after 24 h. Also present was a sharp singlet at 2.11 ppm (acetone). No signals were present in the region expected for ethane (0.84 ppm in CD_2Cl_2).

$\text{Rh}^{13}\text{C}(\text{O})\text{CH}_3(\text{triphos})$. $\text{RhMe}_3(\text{triphos})$ (0.08 g, 0.1 mmol) was placed in C_6D_6 (1 mL). This solution was then placed in a 50-mL Kontes-valved flask, degassed (FPT, three cycles), and placed under ^{13}CO (99%, ~ 1 atm). After the originally heterogeneous mixture was stirred for 8 days, the solution was completely homogeneous and pale yellow. ^1H NMR (360 MHz, C_6D_6 , 22 °C): δ 1.12 (br s, CCH_3), 1.54 (d, $J_{\text{CH}} = 5.8$ Hz, $\text{C}(\text{O})\text{CH}_3$), 2.12 (d, $J_{\text{PH}} = 7$ Hz, 6 H, CH_2P), 7.7–6.75 ($\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, C_6D_6 , 22 °C): δ 5 (br d, $J_{\text{PRh}} = 110$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, -95 °C): δ 0.36 (ddd, $J_{\text{PRh}} = 130$ Hz, $J_{\text{PP}} \approx J_{\text{PC}} \approx 37$ Hz, 2 P), 16 (br m, 1 P). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was only slightly broadened compared to that of the unlabeled compound, exhibiting no resolvable C/C coupling.

$\text{Rh}(\text{Me})(\text{CO})(\text{triphos})$. $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ (0.2 g, 0.25 mmol) was dissolved in toluene (40 mL), and the solution was heated to 40 °C. N_2 was bubbled through the solution for 1.5 h while the temperature was maintained at 40 °C. After this time, the volatiles were removed in vacuo to yield a pale orange solid. The ^1H and ^{31}P NMR spectra indicated complete conversion to $\text{RhMe}(\text{CO})(\text{triphos})$. ^1H NMR (360 MHz, CD_2Cl_2 , 22 °C): δ -0.12 (qd, $J_{\text{PH}} = 4.83$ Hz, $J_{\text{RH}} = 1.53$ Hz, RhCH_3), 1.59 (unresolved q, $J_{\text{PH}} = 2.3$ Hz, CCH_3), 2.35 (d, $J_{\text{PH}} = 7.25$ Hz, CH_2P), 7.7–6.85 ($\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz,

(8) Degradation of the hydrides and alkyl compounds occurs over time in CH_2Cl_2 . For example, $\text{RhMe}_3(\text{triphos})$ forms $\text{RhClMe}_2(\text{triphos})$ (^1H NMR (CD_2Cl_2): RhMe_2 , δ 0.79, second-order multiplet (br), 2.65–2.5 (CH_2P), 1.5 (CCH_3). ^{31}P NMR (CD_2Cl_2 , 146 MHz): 41.7 (dt, $J_{\text{PRh}} = 147$ Hz, $J_{\text{PP}} = 22$ Hz), -19.3 ppm (dd, $J_{\text{PRh}} = 68.7$ Hz). Many of the five-coordinate carbonyl complexes yielded $[\text{Rh}(\text{CO})_2(\text{triphos})]\text{Cl}$ over time in CH_2Cl_2 . The five-coordinate compounds degrade much more rapidly (2–3 days) than the octahedral six-coordinate species. Tetrahydrofuran is thus a preferred solvent for multiday reactions.

(9) The amount of $\text{RhMe}(\text{CO})(\text{triphos})$ produced through decarbonylation of the acyl product varied with varying lengths of time under vacuum in the solid state. Also, vacuum removal of solvent from $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ always generated small amounts (5% or less) of the methyl carbonyl.

(5) Geerts, R. L.; Huffman, J. C.; Westerberg, D. E.; Folting, K.; Caulton, K. G. *New J. Chem.* **1988**, *12*, 455.

(6) Earlier preparations of $\text{RhCl}_3(\text{triphos})$, performed in EtOH , gave significantly lower yields (60%). It was felt that some of the Rh was lost through decarbonylation of EtOH during reflux. The relatively small amount of EtOH used here increases the solubility of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in comparison to pure THF and avoids decarbonylation of solvent. Large amounts of EtOH should be avoided.

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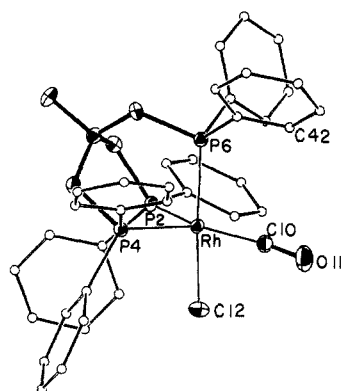


Figure 1. ORTEP drawing of non-hydrogen atoms for RhMe(CO)(triphos), showing selected atom labeling.

Table II. Selected Bond Distances (Å) and Angles (Deg) for MeC(CH₂PPh₂)₃Rh(CH₃)CO

Distances			
Rh(1)–P(2)	2.3683 (12)	Rh(1)–C(10)	1.878 (6)
Rh(1)–P(4)	2.3446 (14)	Rh(1)–C(12)	2.204 (7)
Rh(1)–P(6)	2.3135 (14)	O(11)–C(10)	1.144 (7)
Angles			
P(2)–Rh(1)–P(4)	90.80 (5)	P(4)–Rh(1)–C(12)	94.87 (21)
P(2)–Rh(1)–P(6)	87.14 (5)	P(6)–Rh(1)–C(10)	97.63 (19)
P(2)–Rh(1)–C(10)	138.13 (19)	P(6)–Rh(1)–C(12)	175.78 (21)
P(2)–Rh(1)–C(12)	93.54 (16)	C(10)–Rh(1)–C(12)	79.09 (25)
P(4)–Rh(1)–P(6)	89.28 (5)	Rh(1)–C(10)–O(11)	173.1 (5)
P(4)–Rh(1)–C(10)	130.64 (18)		

CD₂Cl₂, 22 °C): δ 11.5 (br d, $J_{\text{Rhp}} = 106$ Hz). ³¹P{¹H} NMR (THF, –90 °C): δ 7.8 (dd, $J_{\text{PP}} = 40$ Hz, $J_{\text{PRh}} = 123$ Hz, 2 P), 23 (dt, $J_{\text{PRh}} = 85$ Hz, 1 P). IR (CH₂Cl₂) 1900 cm⁻¹. X-ray-quality crystals of the methyl carbonyl were grown by slow evaporation of a C₆D₆ solution of Rh[C(O)Me](CO)(triphos).

Crystallography for Rh(CH₃)(CO)(triphos). A small, almost equidimensional crystal was selected by using inert atmosphere handling techniques. The crystal was transferred to the goniostat, where it was cooled to –141 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of 32 reflections that exhibited monoclinic symmetry (*2/m*). The systematic extinction of *0k0* for *k* = 2*n* + 1 limited the choice of possible space groups to *P2*₁ or *P2*₁/*m*. The choice of the noncentrosymmetric space group *P2*₁ was confirmed by the successful solution and refinement of the structure. Unit cell dimensions were determined by using 76 reflections between 21° and 42° in *2θ*. Data collection¹⁰ was undertaken as detailed in Table I. The upper limit of the data collection range was extended to 60° since the crystal diffracted very well. A plot of the standard reflections showed no systematic trends. No correction for absorption was performed.

The structure was solved by using the usual combination of direct methods and Fourier techniques. The non-hydrogen atoms were readily located and, following initial refinement, almost all of the hydrogen atoms were evident in a difference Fourier map. The full-matrix, least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. Since the space group *P2*₁ is polar, both enantiomorphs were refined and the atomic coordinates reported here are for the preferred absolute configuration. The final difference map was essentially featureless; the largest peak was 0.63 e/Å³. Carbon–hydrogen separations in the phosphine ligand range from 0.64 to 1.07 Å. The results of the structural study are shown in Table II and Figures 1 and 2. Additional information is available as supplementary material.

The Rh[C(O)CH₃](CO)(triphos)/RhMe(CO)(triphos) Equilibrium. A CD₂Cl₂ solution of Rh[C(O)CH₃](CO)(triphos) and RhMe(CO)(triphos) (75:25) sealed in an NMR tube under vacuum was refluxed (40 °C) for 5 h to establish an equilibrium mixture. The ¹H NMR spectrum was then recorded immediately, revealing a 40:60 mixture of the two compounds. The solution was then allowed to stand at room temperature for 3 h, and the ¹H NMR spectrum was again recorded. The initial ratio (75:25) of the two compounds had been reestablished.

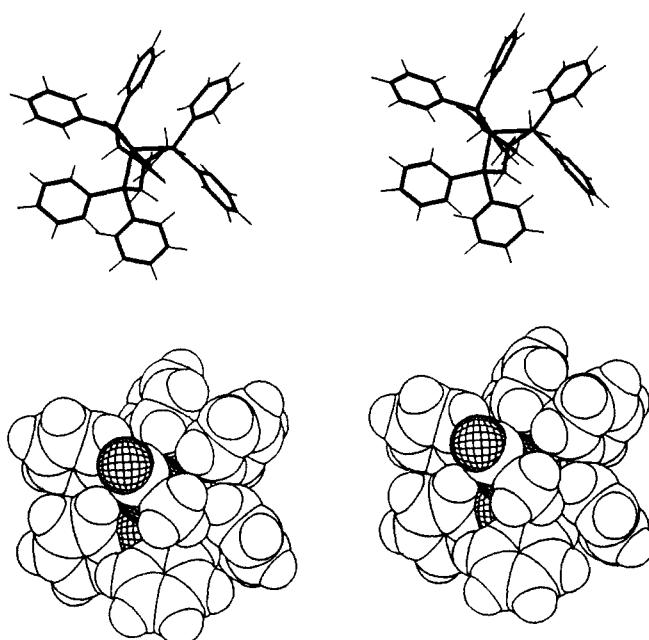


Figure 2. Stereo space-filling and stick figure drawings of RhMe(CO)(triphos), showing contacts between CO and phenyl groups.

Rh(CH₃)(¹³CO)(triphos). This material was prepared in a manner identical with that used for Rh(CH₃)(¹²CO)(triphos), starting from Rh[¹³C(O)CH₃](¹³CO)(triphos). ¹H NMR¹¹ (360 MHz, C₆D₆, 22 °C): δ 0.75 (m, 3 H, RhMe), 1.22 (unresolved q, $J_{\text{PH}} = 2.52$ Hz, CCH₃), 2.21 (d, $J_{\text{PH}} = 6.86$ Hz, 6 H, CH₂P), 7.4–6.7 (P(C₆H₅)₂). ³¹P{¹H} NMR (146 MHz, C₆D₆, 22 °C): δ 11.3 (br dd, $J_{\text{PRh}} = 111$ Hz, $J_{\text{PC}} = 20.1$ Hz). ³¹P{¹H} NMR (CH₂Cl₂, –80 °C): δ 8.3 (dt, $J_{\text{Rhp}} = 120$ Hz, $J_{\text{PC}} \approx J_{\text{PP}} = 42$ Hz, 2 P), 22 (m, 1 P). ¹³C{¹H} NMR (90.8 MHz, C₆D₆, 22 °C): δ 212 (dq, $J_{\text{CRh}} = 77.4$ Hz, $J_{\text{CP}} = 23.8$ Hz).

Reaction of Rh[¹³C(O)Me](¹³CO)(triphos) with ¹²CO. A saturated C₆D₆ solution of Rh[¹³C(O)Me](¹³CO)(triphos) was placed in an NMR tube. The tube was frozen and evacuated, charged with ¹²CO (~1.0 atm), and flame sealed. The solution itself was intentionally not degassed to avoid formation of the decarbonylated species Rh(Me)(¹³CO)(triphos). The tube was then shaken vigorously for 2 min, and the reaction was monitored by ¹³C{¹H} NMR. The terminal ¹³CO was exchanged within 10 min. However, the acyl ¹³CO was exchanged much more slowly, and only after 13 h was a signal not present. ³¹P{¹H} NMR (146 MHz, C₆D₆, 22 °C): showed Rh[C(O)Me](CO)(triphos) (δ 4.8 (br d, dominant resonance)) along with three other broad resonances (δ –28 (br s), 8 (vbr m, 300-Hz wd), 10 (vbr m, ~200-Hz wd)). ³¹P{¹H} NMR (THF, –90 °C): showed Rh[C(O)Me]CO(triphos) and two isomers of Rh[C(O)Me](CO)₂(η²-triphos): δ –29.4 (s), –28 (br s), 7.62 (dd, $J_{\text{PRh}} = 139$ Hz, $J_{\text{PP}} = 55.5$ Hz, 1 P), 9.86 (dd, $J_{\text{PRh}} = 72.5$ Hz, 1 P), 10.8 (d, $J_{\text{PRh}} = 99$ Hz).

Reaction of Rh[C(O)Me](CO)(triphos) with H₂. A saturated CD₂Cl₂ solution of Rh[C(O)Me](CO)(triphos) was placed in an NMR tube. The solution was then degassed (FPT, three cycles), and the tube was charged with H₂ (~1 atm) and flame sealed. The tube was then shaken vigorously for 2 min and allowed to stand for 3.5 h, after which time the ¹H NMR spectrum showed only one metal-containing product, RhH(CO)(triphos). ¹H NMR (360 MHz, CD₂Cl₂, 22 °C): δ –8.2 (qd, $J_{\text{PH}} = 35$ Hz, $J_{\text{RH}} = 13$ Hz, RhH), 1.47 (unresolved q, $J_{\text{PH}} = 2.16$ Hz, CCH₃), 2.18 (d, $J_{\text{PH}} = 7.9$ Hz, CH₂P), 7.5–6.95 (P(C₆H₅)₂). ³¹P{¹H} NMR (146 MHz, CD₂Cl₂, 22 °C): δ 16 (d, $J_{\text{Rhp}} = 116$ Hz). IR (CH₂Cl₂): 1890, 1910 cm⁻¹. Also present in the ¹H NMR spectrum were signals for CH₃C(O)H at δ 9.75 (q, $J_{\text{HH}} = 2.5$ Hz) and 2.16 (d, buried underneath CH₂ protons of the phosphine ligand).

Attempted Reaction of Rh[C(O)Me](CO)(triphos) with RhH(CO)(triphos). Rh[C(O)Me](CO)(triphos) and RhH(CO)(triphos) were both generated separately from equimolar amounts of RhMe₃(triphos) (0.04 g, 0.05 mmol) and RhH₃(triphos) (0.038 g, 0.05 mmol) and carbon monoxide (vide infra). They were then combined by dissolving each in CH₂Cl₂ and placing the resulting solutions in an NMR tube. The solu-

(11) The ¹H NMR chemical shifts for the Rh compounds presented here are extremely solvent dependent. This is especially true for functionalities bound to the Rh atom. For example, the RhMe resonance of RhMe(CO)(triphos) comes at –0.12 ppm in CH₂Cl₂, 0.02 ppm in THF, and 0.75 ppm in C₆D₆.

(10) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

tion was then degassed (FPT, three cycles), and the tube was sealed under vacuum. ^{31}P NMR showed no reaction after 72 h.¹²

Reaction of RhMe(CO)(triphos) with H₂. A saturated C₆D₆ solution of RhMe(CO)(triphos) was placed in an NMR tube. The solution was then degassed (FPT, three cycles) and placed under H₂ (1 atm). The tube was then submerged in a liquid nitrogen bath to reduce the pressure and flame sealed. The solution was warmed to room temperature, shaken vigorously for 5 min, and allowed to stand 4 h, after which time ^1H and ^{31}P NMR showed RhH(CO)(triphos) (70% conversion) and methane (^1H NMR (C₆D₆): δ 0.152).

Reaction of RhMe(CO)(triphos) with ^{13}CO . A saturated C₆D₆ solution of RhMe(CO)(triphos) was placed in an NMR tube and degassed (FPT, three cycles). The tube was then charged with ^{13}CO (~1 atm), flame sealed, and shaken vigorously for 20 min. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C₆D₆, room temperature) showed a broad resonance for dissolved ^{13}CO at 187 ppm and four very broad (>400-Hz wd) resonances between 202 and 191 ppm; also present was a doublet of multiplets at 234 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, C₆D₆, 22 °C): δ 10.9 (dt, $J_{\text{PRh}} = 97$ Hz, $J_{\text{PP}} = 22$ Hz), 7.8 (vbr m, 200-Hz wd), -23.4 (s), -26.8 (s).

Reaction of RhMe(^{13}CO)(triphos) with RhH₃(triphos). RhMe(^{13}CO)(triphos) was prepared as previously stated, starting from RhMe₃(triphos) (0.082 g, 0.106 mmol). ^{31}P showed this material to be mostly RhMe(^{13}CO)(triphos) containing <5% Rh[$^{13}\text{C}(\text{O})\text{Me}$](^{13}CO)(triphos). To this material in C₆D₆ (0.5 mL) was added RhH₃(triphos) (0.077 g, 0.106 mmol). This solution was transferred to an NMR tube and degassed, and the tube was flame sealed. After 2 h at 25 °C, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed resonances for RhH₃(triphos), RhMe(^{13}CO)(triphos), and RhH(^{13}CO)(triphos). The resonance for Rh[$^{13}\text{C}(\text{O})\text{Me}$](^{13}CO)(triphos) was no longer present. The spectrum showed no change after 6 days.¹²

Reaction of RhH₃(triphos) with CO. (a) RhH₃(triphos) (0.04 g, 0.05 mmol) was dissolved in a minimum amount of CD₂Cl₂ and placed in an NMR tube. The solution was degassed (FPT, three cycles) and frozen in a liquid nitrogen bath. The tube was then charged with CO (~1 atm) and flame sealed. Upon thawing of the solution, it immediately turned bright yellow, indicating the formation of RhH(CO)(triphos). The ^1H NMR spectrum (500 MHz, 22 °C) revealed RhH(CO)(triphos) (100%) and also indicated the presence of H₂ (4.6 ppm) and an unidentified resonance at 10.02 ppm.

(b) RhH₃(triphos) was placed in C₆D₆ (0.4 mL), and the solution was transferred to an NMR tube. The solution was then degassed (FPT, three cycles), the tube was charged with CO (~1 atm) and flame sealed, and the solution was shaken vigorously for 15 min. After an additional 20 min, the ^1H NMR spectrum again showed the production of RhH(CO)(triphos) (100%) and the unidentified resonance at 9.68 ppm.

Reaction of RhH₃(triphos) with ^{13}CO . This reaction was performed in a manner identical with that reported above for ^{12}CO . ^1H NMR (500 MHz, CD₂Cl₂, 22 °C) for RhH(^{13}CO)(triphos): δ -8.23 (qdd, $J_{\text{PH}} = 34.4$ Hz, $J_{\text{RH}} = 14$ Hz, $J_{\text{CH}} = 4.4$ Hz, RhH), 1.47 (q, $J_{\text{PH}} = 2.65$ Hz, CCH₃), 2.17 (d, $J_{\text{PH}} = 7.54$ Hz, CH₂P), 7.5-6.95 (m, P(C₆H₅)₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, CD₂Cl₂, 22 °C): δ 17.5 (dd, $J_{\text{RHP}} = 115.7$ Hz, $J_{\text{PC}} = 21.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (90.8 MHz, CD₂Cl₂, 22 °C): δ 210.5 (dq, $J_{\text{RHC}} = 75$ Hz, $J_{\text{PC}} = 21$ Hz). Also present in the ^1H NMR spectrum were signals at δ 10.01 (d, $J_{\text{CH}} = 174.28$ Hz) and 4.6 (H₂). For comparison, *sym*-trioxane in CDCl₃ has a chemical shift of 5.1 ppm.

Reaction of RhD₃(triphos) with CO. A saturated CH₂Cl₂ solution of RhD₃(triphos) was placed in an NMR tube. This solution was degassed (FPT, three cycles) and placed under an atmosphere of CO. The tube was then submerged in a liquid N₂ bath to reduce the pressure and flame sealed. Upon thawing of the solution and shaking the tube, the solution immediately turned bright yellow. ^2H NMR again showed the unidentified resonance at δ 10.04 and $^2\text{H}_2$ (δ 4.65).

Reaction of RhH₃(triphos) with Synthesis Gas. (a) RhH₃(triphos) (0.021 g, 0.029 mmol) was placed in C₆D₆ (0.4 mL). The solution was then transferred to an NMR tube, which was subsequently charged with a CO/H₂ (1 atm, 50:50) mixture. The ^1H NMR spectrum revealed RhH(CO)(triphos) (100%) and no increase in the unidentified resonance at 9.68 ppm.

(b) RhH₃(triphos) (0.026 g, 0.036 mmol) was placed in C₆D₆ (1.5 mL). The solution was then transferred to a high-pressure reaction vessel, which was subsequently charged with a CO/H₂ (50:50, 500 psi) mixture. The vessel was then heated to 75 °C for 4.5 h. No pressure decrease was noted during this period. The pressure was then released, yielding a bright yellow solution. The ^1H NMR spectrum showed RhH(CO)(triphos) (100%) but again no increase in the resonance at 9.68 ppm.

Attempted Reaction of RhH(CO)(triphos) with H₂. RhH₃(triphos) (0.05 g, 0.07 mmol) was dissolved in a minimum amount of C₆H₆ (10

mL) and placed under an atmosphere of CO. The solution immediately turned bright yellow, indicating the formation of RhH(CO)(triphos), and the solution was stirred an additional 10 min to ensure complete conversion. The solution was then transferred to a high-pressure reaction vessel, which was subsequently charged with H₂ (1600 psi). The solution was stirred for 4 h, after which time the H₂ pressure was released. The ^{31}P NMR spectrum showed only resonances for RhH(CO)(triphos).

Exchange of RhH(CO)(triphos) with D₂. RhH(CO)(triphos) was generated in situ from RhH₃(triphos) (0.04 g, 0.055 mmol) and CO in C₆D₆. This solution was then placed in an NMR tube, and the tube was charged with D₂ (~1 atm) and flame sealed. The ^1H NMR spectrum showed only a very weak hydride signal after 45 min. The ^1H NMR signal for the hydride ligand in RhH(CO)(triphos) had completely disappeared after 3 h.

Exchange of RhH₃(triphos) with D₂. A C₆D₆ solution of RhH₃(triphos) (0.04 g) was placed in an NMR tube and degassed. The tube was then charged with ~1 atm of D₂ and flame sealed. After 6 h, ^{31}P NMR showed a broad doublet at δ 25.7, indicating deuterium incorporation. After 18 h, no RhH signal was observable by ^1H NMR, indicating complete production of RhD₃(triphos).

Exchange of RhH(^{13}CO)(triphos) with ^{12}CO . RhH(^{13}CO)(triphos) was synthesized as reported previously and placed in C₆D₆ in an NMR tube. The solution was then degassed and placed under ^{12}CO (~1 atm), and the tube was flame sealed. The tube was then shaken vigorously for 5 min. Only signals for RhH(^{12}CO)(triphos) were observed by ^1H NMR.

Hydroformylation of 1-Hexene with RhH(CO)(triphos). RhH₃(triphos) (0.0195 g, 0.027 mmol) was converted to RhH(CO)(triphos) by placing it in C₆D₆ (1 mL) and stirring under CO for 1 h. The solution of RhH(CO)(triphos) was then transferred to a high-pressure reaction vessel, and 1-hexene (0.45 g, 5.3 mmol) was added. The reaction vessel was then charged with H₂/CO (50:50; 1200 psi), and the reaction was stirred for 18 h. After this time, the pressure was released and the reaction checked by ^1H NMR and gas chromatography. No appreciable reaction was evident. The vessel was then recharged with H₂/CO (50:50; 900 psi) and heated to 67 °C for 1.75 h. The pressure was then released. Gas chromatography indicated the production of *n*-heptanal (0.75 mmol), 2-methylhexanal (0.095 mmol), and 2-hexenes (0.053 mmol). The ^1H NMR spectrum (500 MHz, C₆D₆, 22 °C) showed mostly 1-hexene, but also present were signals for *n*-heptanal (9.31 ppm, t, $J_{\text{HH}} = 1.7$ Hz) and 2-methylhexanal (9.278 ppm, d, $J_{\text{HH}} = 1.8$ Hz).

Reaction of RhH(CO)(triphos) with Ethylene. An NMR tube containing a saturated C₆D₆ solution of RhH(CO)(triphos) was degassed and placed under 1 atm of ethylene. The ethylene was condensed by using liquid nitrogen, and the NMR tube was flame sealed. Within 18 h, the hydride resonance was totally consumed. At 36 h, ^{31}P NMR revealed 98% consumption of RhH(CO)(triphos) and the formation of three major resonances: δ 10.2 (vbr m), 5 (br d, $J_{\text{RHP}} = 109$ Hz), and -1 (vbr m).

Attempted Reaction of RhH(CO)(triphos) with Styrene. RhH₃(triphos) (0.083 g, 0.11 mmol) was placed in C₆D₆ (0.5 mL), degassed, and placed under an atmosphere of CO. The solution was stirred for 45 min to ensure complete conversion to RhH(CO)(triphos). To this solution was added styrene (0.0118 g, 0.11 mmol). After 3 h of stirring at 25 °C, no reaction had occurred (as determined by ^1H NMR). The mixture was then refluxed for 3 h. Again, no reaction was noted.

Results

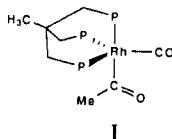
Synthesis and Characterization of RhMe₃(triphos). Under carefully controlled conditions, RhMe₃(triphos) may be obtained in good yield (75%) from the reaction of excess MeLi and RhCl₃(triphos) in tetrahydrofuran. Isolated pure samples of RhMe₃(triphos) are nearly colorless and hydrocarbon solutions (and the solid) are stable under N₂. Proton and ^{31}P NMR patterns and integrations are fully consistent with the formula given, with exclusively a *facial* octahedral structure. The rhodium/phosphorus coupling constant of 75 Hz for RhMe₃(triphos) is significantly reduced in comparison to RhCl₃(triphos) (104 Hz) and RhH₃(triphos) (89 Hz). These spectral data agree with those recently reported for RhMe₃(triphos) from a different synthesis.^{13c}

Reactivity of RhMe₃(triphos). (a) **Toward CO.** RhMe₃(triphos) reacts with CO at 1 atm over the course of days (or in 6 h at 1600 psi CO) to eliminate 1 mol of acetone and produce the acetyl compound Rh[C(O)Me](CO)(triphos). It is important to note that under no condition was the formation of ethane ever observed.

(13) (a) Mercer, W. C.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 1418. (b) Bonnesen, P. V.; You, P. K. L.; Hersch, W. H. *Organometallics* **1987**, *6*, 1587. (c) Johnston, G. G.; Baird, M. C. *Organometallics* **1989**, *8*, 1894.

(12) The reactants began to degrade significantly after this time.

This molecule exhibits one terminal carbonyl and one acetyl infrared stretch. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a doublet of quartets at 208 ppm for the terminal carbonyl and a doublet of quartets at 258 ppm for the acetyl carbonyl, both of which are in the range of chemical shift values reported for such functionalities^{13c} and consistent with the values recently reported for this species.^{13c} As implied by these quartets, the molecule is fluxional (P site exchange): the ^{31}P NMR spectrum is a broad doublet at 22 °C but shows a 2:1 intensity pattern at -90 °C. All these data are consistent with structure I for this molecule.

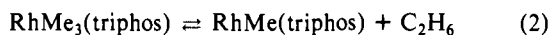


In the absence of CO, $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ is readily decarbonylated, both in the solid state (very slowly) and in solution, to yield $\text{RhMe}(\text{CO})(\text{triphos})$.^{13c} This is undoubtedly an intermediate on the reaction pathway to the acetyl complex since in the presence of stoichiometric amounts of CO in solution, $\text{RhMe}(\text{CO})(\text{triphos})$ rapidly (<3.5 h) reverts back to the Rh-acetyl complex. The Rh-methyl proton resonance of $\text{RhMe}(\text{CO})(\text{triphos})$ displays coupling to both phosphorus and rhodium. The quartet coupling to phosphorus suggests a fluxional molecule (rapid P site exchange). The room temperature ^{31}P NMR shows only a very broad doublet; however, at -90 °C the spectrum shows the pattern of an A_2BX spin system. Since the unique phosphorus atom displays the smaller J_{RhP} value, it was proposed to be situated trans to the methyl group in a trigonal-bipyramidal ground-state structure. To verify this structural assignment, an X-ray structural study was performed.

The molecule is reasonably well described as being trigonal bipyramidal, subject to the geometric constraints of the triphos ligand. The CO ligand is equatorial and the methyl group is axial. In particular, the P-Rh-P angles are all within the typical¹⁴ narrow range 87.14 (5)-90.80 (5)°, and thus the angles in the equatorial plane about Rh are significantly different from 120°: the angles C(O)-Rh-P are 130.64 (18) and 138.13 (19)°. In spite of these distortions, the equatorial plane is rigorously planar; the angles sum to 359.6°. The axial/axial angle P(6)-Rh-C(12) is nearly ideal at 175.78 (4)°. As in $\text{Ir}(\text{CO})\text{Cl}(\text{triphos})$,⁷ the $\text{P}_{\text{axial}}\text{-Rh}$ distance is shorter than the two $\text{P}_{\text{equatorial}}\text{-Rh}$ distances. This clearly shows that $J_{\text{P-Rh}}$ values (larger to the equatorial phosphorus) do not correlate with bond length but rather with orbital hybridization.

The Rh-CO distance (1.878 (6) Å) is much shorter than the Rh-CH₃ distance (2.204 (7) Å). The H₃C-Rh-CO angle, at 79.09 (25)°, is both small and notably smaller than the Cl-Ir-CO angle (86.0 (6)°) in $\text{Ir}(\text{CO})\text{Cl}(\text{triphos})$. In addition, the Rh-C-O angle is noteworthy at 173.1 (5)°. Such bending may be in response to the encroachment on the CO by phenyl ring hydrogens (e.g., C(42)H(37)···C(10) = 2.78 (9) Å and C(42)H(37)···O(11) = 2.86 (8) Å. This is evident in a space-filling model (Figure 2).

(b) **Toward H₂.** The reaction of $\text{RhMe}_3(\text{triphos})$ with CO must involve some preequilibrium creation of a 16-electron complex. Since no ethane is produced in this reaction, we rule out eq 2 as



the operative preequilibrium. We are left to consider the possibility of phosphine arm dissociation (eq 3) and to seek additional support



for its occurrence. Reasoning that an "arm-off" process would cause loss of P-Rh coupling in the $^{31}\text{P}\{^1\text{H}\}$ NMR, we recorded the spectrum of $\text{RhMe}_3(\text{triphos})$ at 60 °C in benzene. A doublet remains at this temperature. This sets an upper limit on the rate

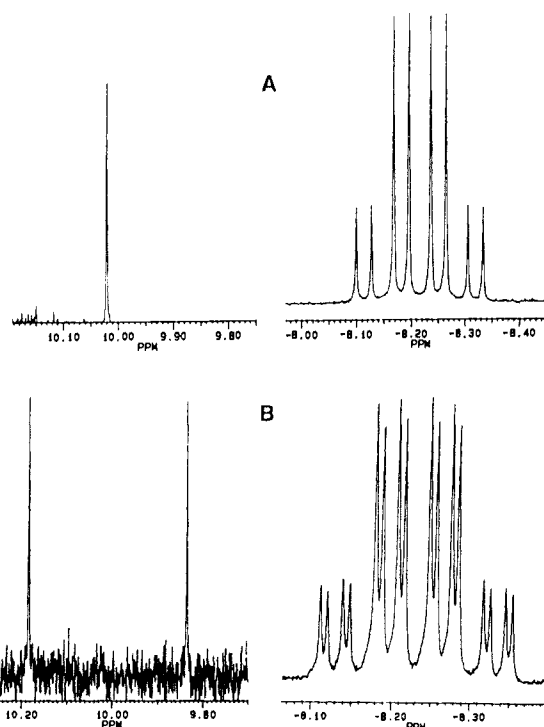


Figure 3. ^1H NMR (CD_2Cl_2) resonances for the CO hydrogenation product and the hydride of $\text{RhH}(\text{CO})(\text{triphos})$ from the reaction of CO and $\text{RhH}_3(\text{triphos})$: (A) from natural-abundance CO; (B) from ^{13}CO .

of any arm-off process as less than $\sim 10^2 \text{ s}^{-1}$.

We next sought to trap the proposed η^2 -triphos transient with H₂. If $\text{RhMe}_3(\text{triphos})$ is placed under 1 atm of H₂, after a very short time (2 h) ^1H NMR reveals significant production of $\text{RhH}_3(\text{triphos})$, methane, and trace amounts of ethane. After 16 h, 50% of the $\text{RhMe}_3(\text{triphos})$ has been converted to $\text{RhH}_3(\text{triphos})$, with no detectable change in the ratio of methane to ethane concentration. This result strongly supports the participation of a $\text{RhMe}_3(\eta^2\text{-triphos})$ intermediate. The production of traces of ethane in this hydrogenolysis reaction is surprising and contrasts to the reaction of CO and $\text{RhMe}_3(\text{triphos})$, which never evolves ethane.

Reactivity of $\text{RhH}_3(\text{triphos})$ with CO. The facile reaction of $\text{RhMe}_3(\text{triphos})$, a d^6 octahedral system anticipated to be kinetically inert, with carbon monoxide to yield only acetone and no ethane prompted a reinvestigation of the reaction between $\text{RhH}_3(\text{triphos})$ and carbon monoxide in CH_2Cl_2 . We confirm the previous⁷ report that this reaction leads exclusively to the formation of $\text{RhH}(\text{CO})(\text{triphos})$, and we have established H₂ as one co-product (eq 4). Since we were interested in possible CO hy-

drogenation in this reaction, it is of interest that a minor (<5%) additional product was also observed as a ^1H NMR singlet at 10.02 ppm. The resonance for this unidentified species is quite weak but is also produced when the reaction is run in C_6D_6 (δ 9.68), indicating it is not a product of reaction with CD_2Cl_2 . The fact that this product is wholly CO derived is verified by employing ^{13}CO in the reaction with $\text{RhH}_3(\text{triphos})$. Figure 3 shows the change in both the unidentified ^1H signal (d, δ 10.02, $J_{\text{CH}} = 174 \text{ Hz}$) and the hydride signal of $\text{RhH}(\text{CO})(\text{triphos})$ when ^{12}CO is replaced by ^{13}CO in eq 4. To ascertain that the resonance at 10.02 ppm originated from the hydride ligands of $\text{RhH}_3(\text{triphos})$, the reaction in eq 4 was performed starting with $\text{RhD}_3(\text{triphos})$. Indeed the resonance was present in the ^2H NMR (CH_2Cl_2 , δ 10.04), together with evolved D₂. Independent experiments show no net reaction of $\text{RhH}(\text{CO})(\text{triphos})$ with H₂ even at 1600 psi. This suggests that the unidentified resonance is not somehow derived from the hydrido carbonyl species and liberated H₂. In an attempt to determine whether or not the material giving rise to the resonances at 10 ppm was volatile, the products from a

(14) (a) Sacconi, L.; Mani, F. In *Transition Met. Chem.* **1982**, *8*, 179. (b) DiVaira, M.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 330.

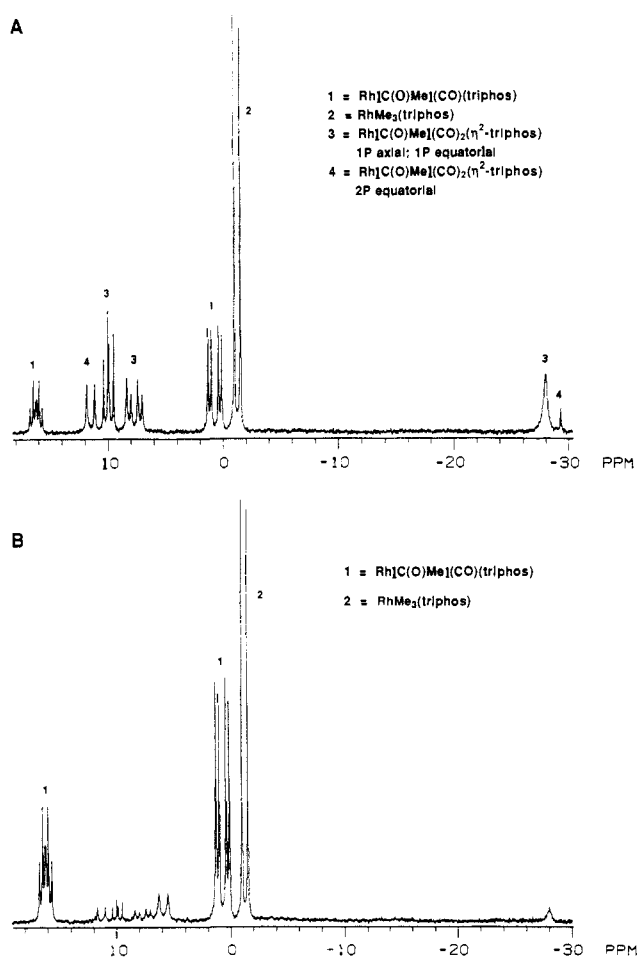
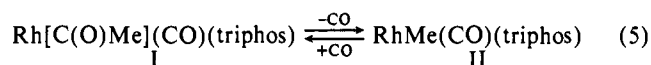


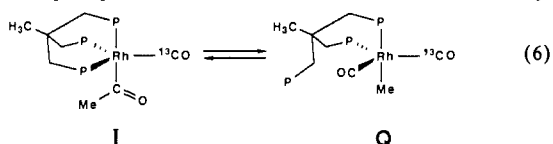
Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, -90°C) spectra: (A) of $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos}) + \text{CO}$; (B) generated by removal of CO atmosphere from NMR tube in spectrum A.

reaction between $\text{RhH}_3(\text{triphos})$ and CO in CD_2Cl_2 were vacuum transferred to an NMR tube. The ^1H NMR spectrum of the resulting solution showed no resonance at 10.02 ppm. This suggests that the unknown compound is coordinated to rhodium. Attempts to produce greater amounts of the unidentified material by reacting $\text{RhH}_3(\text{triphos})$ with CO in the presence of added H_2 or by placing $\text{RhH}(\text{CO})(\text{triphos})$ under 500 psi of an H_2/CO mixture showed no increase in yield.

Reactivity of $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ (I) and $\text{RhMe}(\text{CO})(\text{triphos})$ (II). (a) **With CO.** To gain further mechanistic insight into the lability of the triphos ligands (but now on Rh(I)), several exchange reactions were carried out. As mentioned above, $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ (I) and $\text{RhMe}(\text{CO})(\text{triphos})$ (II) are readily interconverted by the removal or addition of 1 equiv of CO (eq 5). Both I and II also show rapid exchange (i.e., minutes)



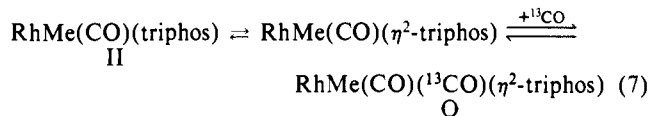
between free CO and the terminal carbonyl ligand; however, I also exchanges CO into the acetyl position at a much slower rate (i.e., hours). Exchange into the acyl position proves that, even under a CO atmosphere, the methyl group of the acyl ligand must migrate to the metal without loss of ^{13}C and thus encounter chemically equivalent (but isotopically distinct) CO ligands (eq 6). Again, a phosphine "arm-off" mechanism is demanded by



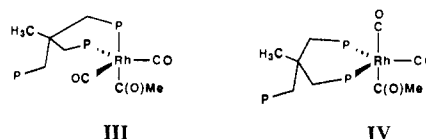
the data. By the principle of microscopic reversibility, we conclude

that executing eq 6 from right to left is the mechanism of carbonylation of $\text{RhMe}(\text{CO})(\text{triphos})$; the mechanism is *not* a preequilibrium formation of $\text{Rh}[\eta^2\text{-C}(\text{O})\text{Me}](\text{triphos})$.

Formation of Q, via eq 7, is also central to accomplishing the fast exchange of ^{13}C with II. Note that this arm-off mechanism seems superior to eq 8 based on independent reasoning: the four-coordinate species $\text{RhMe}(\text{triphos})$, of C_{3v} (T_d derived) symmetry, is a high-energy (possibly paramagnetic) geometry for a d^8 configuration.

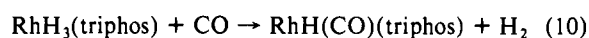
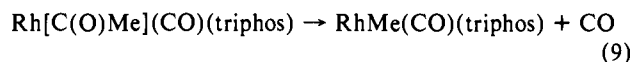


Direct detection of an arm-off species is in fact possible. If I or II (containing ^{12}C) is placed under an atmosphere of ^{13}C , the ^{13}C NMR (22°C , C_6D_6) recorded under CO shows an acetyl resonance, enriched to the same level as the reagent ^{13}C , which is 13 ppm upfield of that of $\text{Rh}[\text{C}(\text{O})\text{Me}]\text{CO}(\text{triphos})$. Also seen are four terminal carbonyl signals (202–191 ppm), each broadened by exchange with dissolved ^{13}C (which itself is broad at 187 ppm). The intensity of the acetyl resonance indicates that all ^{12}C of the reagent $\text{RhMe}(\text{CO})(\text{triphos})$ has been exchanged into the pool of (excess) ^{13}C ; this exchange is therefore faster than the formation of the acetyl group. The $^{31}\text{P}\{^1\text{H}\}$ NMR at 22°C also shows a variety of broad resonances, including one at $\delta -28$ which is in the region of free triphos. The ^{31}P NMR data suggested the possibility of an $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})_2(\eta^2\text{-triphos})$ species that is fluxional at room temperature. Indeed, if I is placed under an atmosphere of ^{12}C in THF and the $^{31}\text{P}\{^1\text{H}\}$ NMR of this solution is recorded at -90°C (Figure 4A) resonances for $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})_2(\eta^2\text{-triphos})$ (III) are observed [$\delta -28$ (dangling P), 7.62 (dd, $J_{\text{PRh}} = 139$ Hz, $J_{\text{PP}} = 55.5$ Hz, 1 P), 9.86 (dd, $J_{\text{PRh}} = 72.5$ Hz, 1 P)]. It also appears that a less stable isomer IV is present ($\delta 10.8$ (d, $J_{\text{PRh}} = 99$ Hz), -29.4 (s)). The other resonances in



this spectrum are due to residual $\text{RhMe}_3(\text{triphos})$ and I as labeled. That the new species are richer in CO than $\text{Rh}[\text{C}(\text{O})\text{Me}]\text{CO}(\text{triphos})$ is established (Figure 4B) by removing the CO atmosphere from the NMR tube sample, which produced the spectrum in Figure 4A. Compound I grows at the expense of both III and IV. It should be mentioned that if II is placed under a ^{12}C atmosphere, the identical spectra are obtained, suggesting that CO migratory insertion occurs in <5 min.

(b) **With H_2 .** Both I and II also react readily (<4 h) with H_2 at atmospheric pressure to yield acetaldehyde and methane, respectively, together with the same metal complex, $\text{RhH}(\text{CO})(\text{triphos})$. While I reacts with $\text{RhH}_3(\text{triphos})$ to generate $\text{RhH}(\text{CO})(\text{triphos})$ by eqs 9 and 10, II shows no reaction with

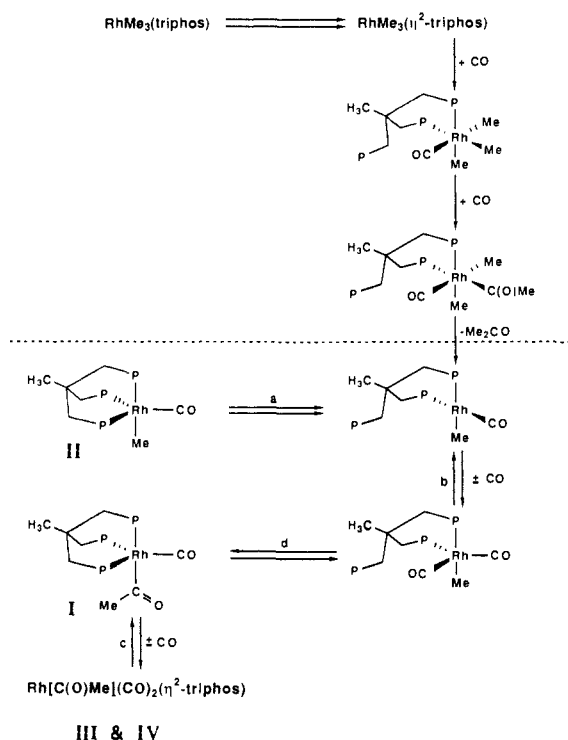


$\text{RhH}_3(\text{triphos})$ even at reaction times >1 week. These results constitute a very sensitive test of the equilibrium shown in eq 11, since any liberated H_2 from such a process would rapidly react with $\text{RhMe}(\text{CO})(\text{triphos})$ (II). The persistence of II proves that $\text{RhH}_3(\text{triphos})$ does *not* participate in the reductive elimination process of eq 11.

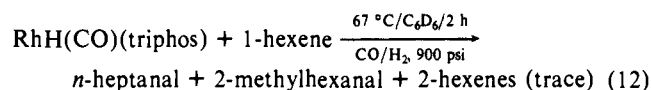


Hydroformylation of 1-Hexene. Because of the ease with which $\text{Rh}[\text{C}(\text{O})\text{CH}_3](\text{CO})(\text{triphos})$ undergoes hydrogenation (H_2 , 1 atm,

Scheme I



3 h) to produce $\text{RhH}(\text{CO})(\text{triphos})$ and acetaldehyde, and the fact that $\text{RhH}(\text{CO})(\text{triphos})$ reacts with excess ethylene (vide infra), $\text{RhH}(\text{CO})(\text{triphos})$ was tested as a hydroformylation catalyst. Using 1-hexene for ease of handling and comparison to industrial processes, we effected hydroformylation under mild conditions (eq 12). Only trace amounts of 2-hexenes (and no



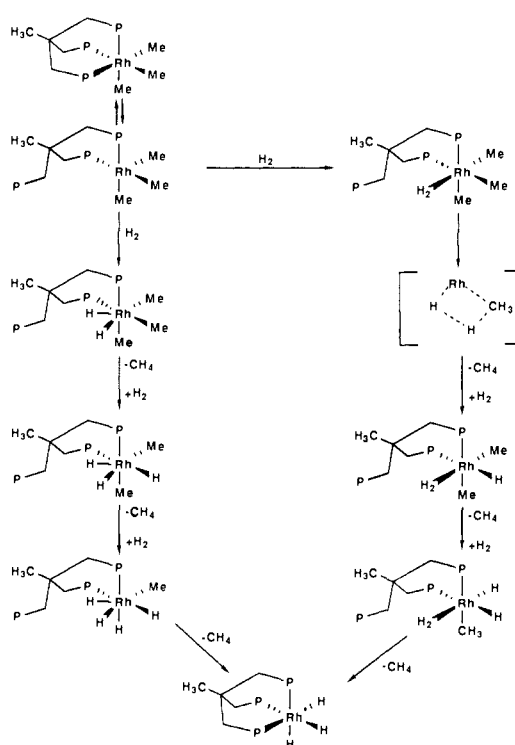
hexane) were produced. The normal/iso ratio for the aldehyde products was 8:1. After the hydroformylation reaction was stopped (heat removed and CO/H_2 pressure released), the solution was still bright yellow and homogeneous, but the ^1H NMR spectrum did not show any RhH resonance. This probably results from the large excess of 1-hexene present, leaving an acyl or alkyl complex as the dominant species. Attempts to model this insertion process for $\text{RhH}(\text{CO})(\text{triphos})$ using styrene (refluxing in C_6D_6) led to no reaction. However, when ethylene was employed, three major (new) broad resonances were observed in the ^{31}P NMR. Two of these resonances (10.2 and 5 ppm) are very close to the ^{31}P (22 $^\circ\text{C}$) resonances reported for $\text{RhMe}(\text{CO})(\text{triphos})$ (11.5 ppm, br d, in CH_2Cl_2) and $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ (5 ppm, br d, in C_6D_6). These results suggest the products of the ethylene reaction to be $\text{RhEt}(\text{CO})(\text{triphos})$ and $\text{Rh}[\text{C}(\text{O})\text{Et}](\text{C}_2\text{H}_4)(\text{triphos})$.

Discussion

Synthesis of $\text{RhMe}_3(\text{triphos})$. While compounds of formula IrP_3Me_3 have been known for over 30 years, an early attempted synthesis of the rhodium analogue met with failure.¹⁵ Only recently have such rhodium compounds been made for $\text{P} = \text{PMe}_3$ ¹⁶ and PMe_2Ph .¹⁷ While this report was being prepared, $\text{RhMe}_3[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]$ was prepared from $[\text{RhCl}_2(\text{triphos})]\text{BF}_4$ and MeLi .^{13c}

Reactivity of $\text{RhMe}_3(\text{triphos})$. (a) **Toward CO.** This 18-electron complex displays reactivity under very mild conditions. The experimental results reported here imply the existence of the network of reactions shown in Scheme I. Above the dotted line

Scheme II



are Rh(III) compounds; below are Rh(I) compounds. The Rh(III) arm-off mechanism is justified by the absence of ethane as a source of a 16-electron intermediate. Equilibria a and b together accomplish the rapid exchange of free and coordinated CO in $\text{RhMe}(\text{CO})(\text{triphos})$. Equilibrium c accomplishes the same for the acetyl carbonyl complex. All require an arm-off process. Equilibrium d exchanges coordinated carbonyl and acetyl carbons in $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$.¹⁸ While this work was being prepared for publication, Johnston and Baird reported¹⁹ the detection of $\text{RhMe}(\text{CO})(\text{PMe}_3)(\eta^2\text{-triphos})$ by attack of PMe_3 on II, showing the generality of the kinetic importance of arm-off processes with $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$.

(b) **Toward H_2 .** Additional evidence in support of a preequilibrium arm-off behavior by $\text{RhMe}_3(\text{triphos})$ comes from its facile hydrogenation, to generate $\text{RhH}_3(\text{triphos})$, methane, and traces of ethane. For such "hydrogenolysis" to occur in nonpolar solvents, the generation of a vacant coordination site is necessary. We exclude accomplishing this by reductive elimination of ethane since it would generate an intermediate ($\text{RhMe}(\text{triphos})$) with approximately tetrahedral symmetry, clearly unfavorable for Rh^{I} . In addition, the mole ratio of ethane to methane produced in this reaction is 0.08 but should be 1.0 if reductive elimination occurred from $\text{RhMe}_3(\text{triphos})$. Scheme II, predicated on the arm-off preequilibrium already supported by Schemes I, outlines two possible mechanisms for hydrogenolysis of $\text{RhMe}_3(\text{triphos})$.

The mechanism on the right side of Scheme II involves the trapping of an η^2 -triphos intermediate by H_2 to form a dihydrogen complex; in this way, $\text{Rh}(\text{V})$ is avoided. This is consistent with the many octahedral d^6 complexes of dihydrogen²⁰ and the propensity for such species to avoid the higher oxidation state in a dihydride structure. The second step of this mechanism could then proceed by a metathesis mechanism similar to that proposed

(18) Although the interconversion of $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ and $\text{Rh}[\text{C}(\text{O})\text{Me}](^{13}\text{CO})(\text{triphos})$ is observed (under 1 atm of CO) to be slow (13 h) compared to the rate of carbonylation of $\text{RhMe}(\text{CO})(\text{triphos})$ to $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$, this is because of the low concentration of I under CO. The equilibrium constant for the arm-off process of I to make $\text{RhMe}(\text{CO})_2(\eta^2\text{-triphos})$ is certainly small (based on spectra of I), and thus $k_d \gg k_{-d}$.

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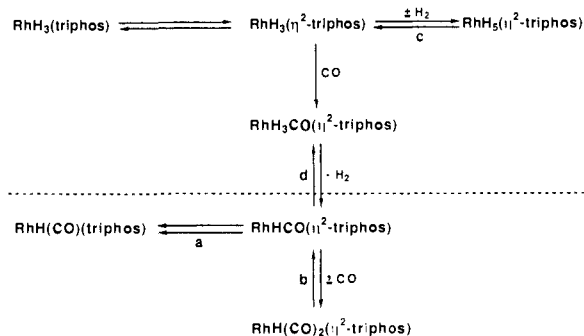
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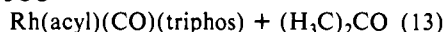
Scheme III



for the hydrogenation of d^0 early transition metal alkyls such as Cp_2ZrMe_2 .²¹ Alternatively, it could be considered as intramolecular proton (H^+) transfer, since the H_2 ligand has been shown²² to exhibit Brønsted acid character. The low-yield path to ethane is not explicitly indicated in Scheme II but could arise from reductive elimination from any intermediate with at least two bound methyl groups.

Since Maitlis has recently shown the existence of a variety of Rh^{IV} and Rh^{V} organometallic species,²³ including the rhodium dihydride $\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)_2$,^{23b} the left-hand side of Scheme II considers oxidative addition of H_2 to generate a variety of Rh^{V} intermediates. It is attractive to hypothesize that the generation of ethane in this reaction, and not in the reaction with CO, is a result of high oxidation state (Rh^{V}) intermediates (generated from H_2 oxidative addition) which promote reductive elimination of ethane.

Reactivity of $\text{RhH}_3(\text{triphos})$. (a) **Toward CO.** The production of ketone in eq 13 prompted us to reexamine the carbonylation of $\text{RhH}_3(\text{triphos})$ for possible hydrogenation of CO. We confirm $\text{RhMe}_3(\text{triphos}) + 3\text{CO} \rightarrow$



(eq 4) the production of $\text{RhH}(\text{CO})(\text{triphos})$ and established the liberation of H_2 . However, this reaction consistently produces an additional material in very low yield (<2%) which has a ^1H NMR singlet (CD_2Cl_2) of 10.02 ppm. Repeating this reaction (eq 4) with ^{13}CO split the resonance at 10.02 ppm into a doublet (Figure 3B) with a C/H coupling constant of 174 Hz. This J value is very close to that of acetaldehyde (173 Hz) and that reported by Wayland²⁴ for free formaldehyde (176 Hz). If eq 4 is carried out in C_6D_6 , this resonance occurs at 9.68 ppm, whereas formaldehyde in C_6D_6 has a chemical shift of 8.68 ppm;²⁴ we have verified this value independently by generating gaseous CH_2O from paraformaldehyde and bubbling it through a C_6D_6 solution (8.67 ppm). Since the species producing this resonance does not vacuum transfer with solvent, we conclude that it is bound to rhodium. We feel that this resonance is not a metal-bound formyl for several reasons. One reason is that the resonance at 10.02 ppm is very sharp and shows no signs of unresolved coupling to either Rh or the three phosphorus nuclei (the RhCH_3 resonance for $\text{RhMe}(\text{CO})(\text{triphos})$ is a quartet of doublets showing coupling to both Rh and P). Moreover, it is reported that $\text{Rh}(\text{CHO})(\text{CO})(\text{triphos})$ ²⁵ is unstable above -60°C and gives rise to a formyl resonance at 12 ppm in THF. Unfortunately, the material causing the resonance at 10.02 ppm is produced in such low yields (even under H_2/CO mixtures) that attempts at further characterization

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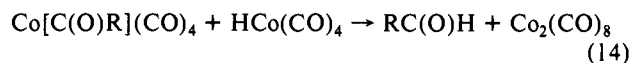
have been unsuccessful. We are currently exploring the possibility that the species is coordinated formaldehyde or formate.

We feel that eq 4 proceeds by an arm-off mechanism (Scheme III). Support for the arm-off preequilibrium comes from the fact that the proposed $\text{RhH}_3(\eta^2\text{-triphos})$ can be trapped with D_2 : $\text{RhH}_3(\text{triphos})$ exchanges with D_2 . This must proceed via $\text{RhH}_3\text{D}_2(\eta^2\text{-triphos})$ as in eq c of Scheme III.

With the conclusion that CO reacts with $\text{RhH}_3(\text{triphos})$ via CO attack on an arm-off transient (eq 11 has been excluded by our observations), the question arises as to why $\text{Rh}(\text{CO})\text{H}_3(\eta^2\text{-triphos})$ proceeds further by H_2 loss while the corresponding $\text{Rh}(\text{CO})\text{Me}_3(\eta^2\text{-triphos})$ does not eliminate ethane. While the latter may be due to thermodynamic factors, we suggest that the strong π acidity of CO makes $\text{Rh}(\text{CO})\text{H}_3(\eta^2\text{-triphos})$ a good candidate to be a dihydrogen complex because of the inability of hydrogen to maintain the $\text{Rh}(\text{CO})(\text{P})_2$ fragment as Rh^{III} . The species $\text{Rh}(\text{CO})\text{H}(\text{H}_2)(\eta^2\text{-triphos})$ would then show behavior common to dihydrogen complexes: H_2 loss. Loss of H_2 (eq d, Scheme III) is a reversible reaction, since we detect the (unfavorable) reverse reaction via isotopic exchange of D_2 with $\text{RhH}(\text{CO})(\text{triphos})$ via eqs a and d. It is thus the kinetic mobility of hydride and the availability of an intermediate (coordinated H_2) that create a reaction channel unavailable to $\text{Rh}(\text{CO})\text{Me}_3(\eta^2\text{-triphos})$.

Reactivity of $\text{RhH}(\text{CO})(\text{triphos})$. We sought to promote CO hydrogenation with $\text{RhH}(\text{CO})(\text{triphos})$ by reaction with H_2 but find no detectable reaction. To test whether this failure originates in the absence of an arm-off process in $\text{RhH}(\text{CO})(\text{triphos})$, we treated it with D_2 . Exchange with the metal-bound hydrogen is facile,²⁶ which permits addition of a reversible reaction arrow at d in Scheme III and the conclusion that the lack of CO hydrogenation originates in thermodynamic, not kinetic, limitations of $\text{RhH}(\text{CO})(\text{triphos})$. Exchange of ^{13}CO with $\text{RhH}(\text{CO})(\text{triphos})$ occurs by reactions a and b. However, under 1 atm of CO, ^1H and ^{31}P NMR spectra show no $\text{RhH}(\text{CO})_2(\eta^2\text{-triphos})$. Thus, the acetyl ligand stabilizes this $\text{RhX}(\text{CO})_2(\eta^2\text{-triphos})$ type in a way that hydride does not. We also sought direct observation of the consequences of phosphine arm dissociation via loss of P/Rh spin coupling. However, at $+60^\circ\text{C}$ in C_6D_6 , $\text{RhH}(\text{CO})(\text{triphos})$ showed only slight broadening of the components of its 117-Hz doublet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The rate of eq a at 60°C is therefore $<10^2\text{ s}^{-1}$.

Reactivity of $\text{RhMe}(\text{CO})(\text{triphos})$ and $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$. The intermediates in Scheme I suffice to explain the rapid exchange of these $\text{Rh}(\text{I})$ species with ^{13}CO . Since each of these is in equilibrium with a 16-electron arm-off transient, reaction with H_2 to liberate aldehyde and alkane follows naturally from the species available in Scheme I. The production of acetaldehyde, not methane, from $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ indicates that $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\eta^2\text{-triphos})$ is formed and trapped faster by hydrogenation than I disappears by reaction d of Scheme I. Since a central question in olefin hydroformylation chemistry is whether aldehyde forms by reaction of H_2 with an acyl complex or by a reaction between two metal complexes (e.g., eq 14), we

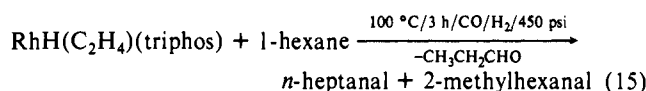


were pleased to have one pathway (the former) clearly established in the Rh/triphos system. We did test the reaction of $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$ with $\text{RhH}(\text{CO})(\text{triphos})$, and find no reaction.

Against this background, we proceeded to test $\text{RhH}(\text{CO})(\text{triphos})$ as a possible olefin hydroformylation catalyst. Indeed, this is successful. $\text{RhH}(\text{CO})(\text{triphos})$ in the presence of CO and H_2 (50:50) effectively converts 1-hexene to *n*-heptanal and 2-methylhexanal in an 8:1 ratio under relatively mild conditions (67°C , 900 psi). Isomerization to 2-hexene occurs to only a small extent. The results reported here are similar to those reported by Bianchini et al. for the hydroformylation of 1-hexene as outlined

(26) Exchange, which is complete within 3 h, is faster than it is for $\text{RhH}_3(\text{triphos})$.

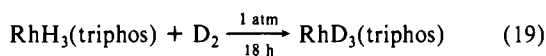
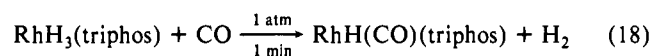
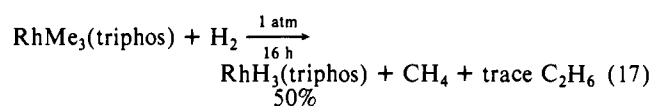
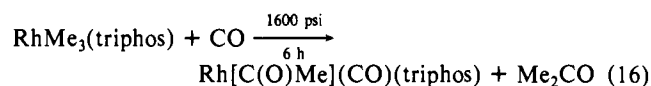
in eq 15.²⁷ Their system produces a linear:branched aldehyde



ratio of 4. The fact that propionaldehyde is liberated to this reaction suggests that both systems involve the same catalytic species. The high selectivity for the linear aldehyde reported here using $\text{RhH}(\text{CO})(\text{triphos})$ as the catalyst is most likely a result of the lower temperature employed here (65 °C) as compared to 100 °C with $\text{RhH}(\text{C}_2\text{H}_4)(\text{triphos})$. The high selectivity for linear aldehyde in the hydroformylation of 1-hexene with $\text{RhH}(\text{CO})(\text{triphos})$ mimics that for $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in the presence of a large excess of PPh_3 . This suggests that triphos fairly effectively mimics the excess PPh_3 and is undoubtedly a direct result of the chelating ability of triphos and its steric bulk (i.e., compare the structure of $\text{RhMe}(\text{CO})(\text{triphos})$).

Conclusions

The reactivity of $\text{RhH}_3(\text{triphos})$ toward either H_2 or CO is significantly higher than that of $\text{RhMe}_3(\text{triphos})$ (eq 16–19). This



is probably a result of several factors. The ligand with the higher trans-effect ability, H^- , should more readily generate the $16e^-$ η^2 -triphos species necessary for nucleophilic attack. Secondly, the approach of an incoming ligand in these reactions will be sensitive to the diminished steric demands of the three hydride ligands, as compared to the three methyl ligands; the rate of trapping of the arm-off transient $\text{RhX}_3(\eta^2\text{-triphos})$ is thus influenced by X. We have already seen that steric crowding exists in $\text{RhMe}(\text{CO})(\text{triphos})$, and that in $\text{RhMe}_3(\text{triphos})$ is undoubtedly greater. Also clearly assisting the reactions of $\text{RhH}_3(\text{triphos})$ is the facile reductive elimination of H_2 subsequent to nucleophilic attack; ethane reductive elimination is only observed to a small extent in the reaction between H_2 and the trimethyl complex.

Phosphine arm dissociation has been proposed previously for reactions of triphos metal complexes,^{7,28} but direct evidence was

lacking. While we initiated these studies with the (now verified) expectation that triphos would eliminate phosphine redistribution reactions (eq 1), we underestimated the *mechanistic* importance of transients where one phosphine arm dissociates. The question thus arises as to why one Rh–P bond is so labile. We feel that a partial answer is contained in the structural parameters of $\text{RhMe}(\text{CO})(\text{triphos})$. Triphos is not well suited to the trigonal-bipyramidal geometry of Rh(I). This is evident in the “pinched” (90.8°) angle between the equatorial phosphines. In becoming η^2 , the tridentate phosphine can open up to an acceptable six-membered ring²⁹ on planar Rh(I). Since rhodium–phosphorus bond cleavage on Rh(III) cannot be due to angle strain in an octahedron, the reason there probably lies more in the unattractive tetrahedral geometry in the alternative reductive elimination product (η^3 -triphos)RhX as well as the trans effect of the hydride and methyl ligands. We have reported an example of dissociation of phosphine from $\text{RhClMe}_2(\text{PMePh}_2)_3$. It may be that diminished back-bonding to phosphine–Rh(III) contributes also.

The generality of arm-off processes appears to extend even to $\text{P}(\text{C}_2\text{H}_4\text{PPh}_2)_3$, where $\text{RhCH}_3(\text{tetraphos})$ has been shown³⁰ to form $\text{RhCH}_3(\text{CO})(\eta^3\text{-tetraphos})$ at –60 °C.

This work provides the opportunity to compare semiquantitatively the barrier to stereochemical nonrigidity of four related five-coordinate complexes.³¹ While $\text{RhMe}(\text{CO})(\text{triphos})$, $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})(\text{triphos})$, and the isomeric $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})_2(\eta^2\text{-triphos})$ species can all be frozen out by ³¹P NMR at –90 °C, $\text{RhH}(\text{CO})(\text{triphos})$ cannot. This higher mobility of hydride than alkyl and acetyl ligands is a poorly understood but general phenomenon worthy of theoretical investigation. The fact that any of these triphos complexes could be frozen out is surprising, since Dahlenburg has shown³² that, among tridentate phosphine ligands attached to Rh(I), $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ gives a uniquely *low* barrier to pseudorotation.

Acknowledgment. This work was supported by the National Science Foundation and Johnson Matthey. We thank M. Baird for a useful discussion and S. Horn for skilled technical assistance.

Supplementary Material Available: Tables giving full crystallographic details, anisotropic thermal parameters, and atomic positional parameters for $\text{RhMe}(\text{CO})(\text{triphos})$ (5 pages); listing of observed and calculated structure factors for $\text{RhMe}(\text{CO})(\text{triphos})$ (13 pages). Ordering information is given on any current masthead page.

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