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Organorhodium(I) and -rhodium(III) Complexes Containing the Ligand 1,1,1-Tris((diphenylphosphino)methyl)ethane (triphos)

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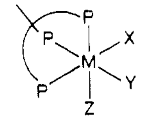
Treatment of the complex $[Rh(CO)_2(triphos)]PF_6$ (triphos = $MeC(CH_2PPh_2)_3$) with the ligands L (L = PMe_3, PMe_2Ph, PEt_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$, *t*-BuNC) resulted in the formation of complexes of the type $[Rh(CO)L(triphos)]PF_6$. The analogous complexes of PPh_3, ethylene, and propylene could not be prepared in this way but were synthesized by displacing molecular hydrogen from the complex $[RhH_2(CO)(triphos)]PF_6$, prepared by the photochemical oxidative addition of H_2 to $[Rh(CO)_2(triphos)]PF_6$. The σ-bonded organorhodium(I) complexes RhR(CO)(triphos) (R = Me, Ph) were prepared by treating RhCl(CO)(triphos) with the appropriate alkyllithium reagent, and these compounds in turn were found to react readily with CO to form the acyl complexes Rh(RCO)(CO)(triphos). Addition of anhydrous HCl to the complex RhCl(CO)(triphos) resulted in the formation of a mixture of $RhHCl_2(CO)(triphos)$ and $RhCl_3(triphos)$, while addition of excess chlorine, bromine, or iodine to $[Rh(CO)_2(triphos)]PF_6$ resulted in the formation of the rhodium(III) complexes $[RhX_2(triphos)]PF_6$ (X = Cl, Br, I). These reacted in turn with methyllithium to form $RhMe_3(triphos)$, and with a variety of neutral ligands L to form the series $[RhX_2L(triphos)]PF_6$.

There have been numerous investigations in recent years into the coordination chemistry of polydentate tertiary phosphines.[1] Of particular interest to ourselves and others has been the tridentate ligand 1,1,1-tris((diphenylphosphino)methyl)ethane, $MeC(CH_2PPh_2)_3$ (henceforth triphos), which forms a wide variety of complexes containing unusual ligands such as P_3, CE_2 (E = S, Se), P_2S_3, etc.[1b,c] Furthermore, as we have earlier noted,[2] octahedral triphos complexes of necessity assume a facial stereochemistry, in contrast to the meridional geometry more commonly assumed by tris-monodentate phosphine complexes. Thus complexes of the type M(triphos)XYZ (XYZ = monodentate ligands) are chiral, i.e.



and we have successfully resolved one example of this type of complex, $[RuMe(CO)(t\text{-}BuNC)(triphos)]^+$.[2b]

In addition, for complexes of the type M(triphos)XYZ, X, Y, and Z are all trans to a phosphorus atom. As phosphorus donors lie high in the trans influence series,[3] we have anticipated that triphos complexes might exhibit chemistry which would differ from that of meridional tris(phosphine) complexes. Consonant with this suggestion, we have found that the complex $[RuH(CO)_2(triphos)]^+$ is surprisingly acidic and that the acetyl complex $[Ru(COMe)(CO)_2(triphos)]^+$ is unstable with respect to elimination of ketene to form the hydride $[RuH(CO)_2(triphos)]^+$.[2b]

In an effort to extend our research in this area, we have carried out an extensive investigation into the chemistry of triphos complexes of rhodium(I) and rhodium(III), the results of which are reported here and in a paper which follows.[4] Relevant to the present investigation, the complexes RhX(CO)(triphos) (X = Cl,[5a,d] Br, I[5d]), $RhCl_3(triphos)$,[5b,d] $RhHCl_2(triphos)$,[5a] $[Rh(CO)_2(triphos)]PF_6$,[5c,d,g] $Rh(CO)(CO_2Me)(triphos)$,[5c] $RhH_3(triphos)$,[5d] RhH(CO)(triphos),[5d] $Rh(CH_2SiMe_3)(CO)(triphos)$,[5e] and $RhX(C_2H_4)(triphos)$ (X = H, Cl, Et)[5f,h] have been reported elsewhere, either prior to or during our work.

Table I. IR Data[a]

complex	$\nu(CO)$, cm^{-1}	other, cm^{-1}
$[Rh(CO)L(triphos)]PF_6$		
L = CO	2060, 1995	
t-BuNC	1975	$\nu(CN) = 2185$
PMe_3	1927	
PEt_3	1928	
$P(n\text{-}Bu)_3$	1931	
PMe_2Ph	1941	
$PMePh_2$	1944	
PPh_3	1946	
$P(OMe_3)$	1956	
$P(OPh)_3$	1969	
C_2H_4	2042	
CH_2CHCH_3	2045	
$(H)_2$	2073[b]	$\nu(RhH) = 1985$ (br)
RhR(CO)(triphos)		
R = Me	1895	
Ph	1915	
MeCO	1909	$\nu(C{=}O) = 1635$
PhCO	1909	$\nu(C{=}O) = 1650$
H	1909[b]	
Rh(MeCO)(*t*-BuNC)(triphos)	$\nu(CN) = 2115$, $\nu(C{=}O) = 1684$	

[a] CH_2Cl_2 solution. [b] THF solution.

Experimental Section

Unless otherwise noted, all operations were performed under an atmosphere of N_2 at room temperature by using standard vacuum line techniques. All yields are based upon the starting rhodium material, and, if a reaction was performed more than once, the range of observed yields is given.

IR spectra were obtained on a Bruker IFS-85 Fourier transform spectrometer and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra on a Bruker AM-400 spectrometer operating at resonance frequencies

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Table II. ^{1}H NMR Data (in ppm)[a]

complex	triphos resonances CH$_2$[b]	triphos resonances CH$_3$[c]	triphos resonances Ph	other[f]
[Rh(CO)L(triphos)]PF$_6$				
L = CO	2.57	1.78	7.12–7.20	
t-BuNC	2.50	1.72	7.11, 7.28	1.22 (CNCMe)
PMe$_3$	2.70	1.83	7.75–7.96	0.84 d (9.9) (PMe)
PEt$_3$	2.69	1.78	7.16–7.20	1.73, 1.05 (Et)
P(*n*-Bu)$_3$	2.69	1.78	7.13–7.28	0.81,1.12, 1.25 (*n*-Bu)
PMe$_2$Ph	2.70	1.81	7.16	0.90 d (7.2) (PMe) 7.50 (PPh)
PMePh$_2$	2.63	1.68	7.05	0.26 d (10.5) (PMe) 7.35 (PPh)
PPh$_3$	2.73	1.71	6.9–7.11	6.9–7.4 (PPh)
P(OMe)$_3$	2.53	1.71	7.11	3.3 d (12) (POMe)
P(OPh)$_3$	2.56	1.70	7.25, 7.1, 6.8[d]	
C$_2$H$_4$	2.55	1.74	7.2, 7.31	3.38 d (9.4), 2.08 d (9.4) (C$_2$H$_4$)
CH$_2$CHCH$_3$	2.37 2.92	1.62	7.1, 7.3	1.96 d (9) (Me) 2.10, 3.09, 3.17 (CH$_2$CH)
(H)$_2$	2.72, 2.92	1.90	7.6–7.1	–7.29 dd (131, 14.5) (Rh–H)
RhR(CO)(triphos)				
R = Me	2.33	1.57	7.7	–0.16 dq (1.9), 6.8 (Rh–Me)
Ph	2.34	1.50	7.2–6.9	7.5, 6.5, 6.6 (Rh–Ph)
Et	2.34	1.58	7.05, 7.27	1.00, 1.15 (Rh–Et)
MeC(O)	2.28	1.52	7.3–7.1	2.13 d (3) (COMe)
PhCO	2.24	1.9	7.3–7.0	7.5–7.0 (COPh)
H[e]	2.30	1.6	7.6–6.9	–8.13 qd (15, 33) (Rh–H)
Rh(MeCO)(*t*-BuNC)(triphos)	2.37	1.58	7.1–7.2	1.83 (MeCO), 1.34 (*t*-Bu)
RhMe$_3$(triphos)	2.74	1.44	7.1	0.35 (Rh–Me)
RhCl$_3$(triphos)	2.60	1.52	7.1–7.7	
[RhX$_2$(triphos)]PF$_6$				
X = Cl	2.86	2.05	7.2–7.4	
Br	2.87	2.07	7.0–7.5	
I	2.87	2.05	7.2–7.4	
[RhCl$_2$L(triphos)]PF$_6$				
L = *t*-BuNC	2.76	1.7	7.9–7.3	1.40 (CNCMe)
PMe$_3$	2.66, 2.77	1.7	7.9–6.8	0.83 dd (10.8, 3) (PMe)
P(OMe)$_3$	2.65	1.52	7.1–7.7	3.58 d (10.2) (POMe)

[a] CD$_2$Cl$_2$ solutions. [b] CH$_2$ resonances appear as doublets (^2J(P–H) = 7.5–9 Hz) unless otherwise noted. [c] CH$_3$ resonances appear as quartets (^4J(P–H) = 3.5–4 Hz). [d] Not possible to distinguish between the phenyl resonances of triphos and the ligand. [e] Acetone-d_6 solution. [f] Coupling constants in parentheses.

of 400, 100.9, and 162.0 MHz, respectively. Spectroscopic data for all new complexes are presented in Tables I–V, where some comparisons are made with known compounds. GC analyses were performed on a Hewlett-Packard Model 5880A gas chromatograph using a flame ionization detector (FID). Elemental analyses were performed by Canadian Microanalytical Services Ltd; analytical data are presented in Table VI.

The complexes RhCl(CO)(triphos), [Rh(CO)$_2$(triphos)]X (X = Cl, PF$_6$), and RhH(CO)(triphos) were synthesized by literature methods.[5a,c,d]

Preparation of the Complexes [Rh(CO)L(triphos)]PF$_6$. The complexes [Rh(CO)L(triphos)]PF$_6$ (L = PMe$_3$, PMe$_2$Ph, PEt$_3$, P(*n*-Bu)$_3$, P(OMe)$_3$, P(OPh)$_3$, *t*-BuNC) were prepared by addition of ≈1.1 equiv of L to THF solutions of [Rh(CO)$_2$(triphos)]PF$_6$ (no reactions were observed with PPh$_3$, ethylene, or propylene under these conditions). For L = PMe$_2$Ph, P(OPh)$_3$, and P(OMe)$_3$, the complexes precipitated readily from solution. In the other cases, hexane was slowly added to the reaction mixtures until the cloud points were reached. Upon cooling the reaction mixtures in an ice bath, yellow solids precipitated and were filtered, washed with hexane, and dried in vacuo; yields 65–90%.

The relative stabilities of several of the new complexes [Rh(CO)L(triphos)]PF$_6$ with respect to ligand exchange were determined in a series of ^{31}P NMR experiments. In a typical experiment, 50–60 mg of a complex was weighed into an NMR tube and the sample was dissolved in an 80:20 (v/v) mixture of CH$_2$Cl$_2$/CD$_2$Cl$_2$. Between 1 and 2 equiv of a second ligand was added to the NMR tube, and the ^{31}P NMR spectrum was obtained. This procedure was then repeated by adding successively two or three other ligands to the NMR sample.

Preparation of the Complexes RhR(CO)(triphos) (R = Me, Ph, MeCO, PhCO) and Rh(COMe)(*t*-BuNC)(triphos). RhMe(CO)(triphos). A solution of 1.2 g of RhCl(CO)(triphos) in 35 mL of CH$_2$Cl$_2$ was treated with a 5× excess of 1.4 M methyllithium. When the ν(CO) from the starting material (2020, 1940 cm^{-1})[5a,d] had been replaced by the ν(CO) of RhMe(CO)(triphos) (1895 cm^{-1}), 20 mL of ethanol was added to the reaction mixture. Concentrating the solution by removing the solvent under reduced pressure resulted in the precipitation of a yellow solid which was filtered, washed with ethanol, and dried in vacuo. Recrystallization from THF/ethanol gave analytically pure RhMe(CO)(triphos) in 45–75% yield.

RhPh(CO)(triphos). About 1 mL of phenyllithium (1.7 M in cyclohexane/ether) was slowly added to a suspension of 1.3 g of RhCl(CO)(triphos) in 50 mL of THF. After the ν(CO) of the starting material had been replaced by the ν(CO) of RhPh(CO)(triphos) (1915 cm^{-1}), 25 mL of ethanol was added to the reaction mixture. Concentrating the solution by removing the solvent under reduced pressure resulted in the precipitation of a yellow solid which was filtered, washed with ethanol, and dried in vacuo (yield 35–60%).

Rh(MeCO)(CO)(triphos). A solution of 1.5 g of RhMe(CO)(triphos) in 50 mL of THF was saturated with CO for 10–25 min. When the ν(CO) of RhMe(CO)(triphos) had been replaced by a new ν(CO) at 1909 cm^{-1}, attributable to Rh(MeCO)(CO)(triphos), in the IR spectrum, 20 mL of ethanol was added and the solution was concentrated by bubbling CO through the mixture. The yellow product eventually precipitated and was filtered, washed with ethanol, and dried in vacuo (yield 75–85%). It was important that the reaction mixture be concentrated by removing the solvent by bubbling CO through the solution; removing the solvent under reduced pressure or bubbling N$_2$ through the solution resulted in the precipitation of a mixture of Rh(MeCO)(CO)(triphos) and the product of decarbonylation RhMe(CO)(triphos).

Rh(PhCO)(CO)(triphos). The same procedure was used in the preparation of Rh(PhCO)(CO)(triphos), the product being obtained in 75–84% yield.

Table III. ^{31}P NMR Data[a]

complex	triphos δ(P)[b]	triphos ^1J(Rh–P), Hz	other δ(P)[c]	other ^1J(Rh–P), Hz	other ^2J(P–P),[d] Hz
[Rh(CO)L(triphos)]PF_6					
L = CO	9.9	98.9			
t-BuNC	10.3	97.2			
PMe_3	8.5	102.7	−3.30	94.2	61.9
PEt_3	6.8	101	21.5	95.6	58
P(*n*-Bu)$_3$	7.8	100.4	17.5	96.2	58.8
PMe_2Ph	7.1	102	4.6	99	60
$PMePh_2$	6.3	100.4	18.5	103.5	63
PPh_3	3.70	100.7	30.9	105.5	63
P(OMe_3)	7.1	100	128.5	167	114
P(OPh)$_3$	6.2	100	117.4	201	113
C_2H_4	8.1 br	($\nu_{1/2}$ = 300 Hz)			
CH_2CHCH_3	7.0	97			
(H)$_2$	29.1[e]	98.1 (1 P)			35[g]
	9.57[f]	78 (2 P)			
RhR(CO)(triphos)					
R = Me	11.6	113			
Ph	8.10	106.6			
MeCO	5.02	112			
PhCO	3.86	117			
H	18.1[h]	118			
Rh(MeCO)(*t*-BuNC)(triphos)	8.7	117			

	triphos δ(P)	triphos ^1J(Rh–P), Hz	triphos ^2J(P_a–P_b),[i] Hz	other δ(P)	other ^1J(Rh–P), Hz	other ^2J(P–P), Hz
Me_3Rh(triphos)	−2.28	73.6				
$RhCl_3$(triphos)	9.7	103				
[RhX_2(triphos)]PF_6						
X = Cl	39.6	103.7				
Br	37.4	103.2				
I	31.5	103.3				
[$RhCl_2$L(triphos)]PF_6						
L = *t*-BuNC	−9.9 (1 P)[e]	84.5	37			
	16.9 (2 P)[f]	98.8				
PMe_3	−6.5[j] (1 P)[m]	85	38 (16)[j]	−13.5[j]	76	458[k]
	13.5 (2 P)[n]	94				38 (16)[j,l]
P(OMe)	−22 (1 P)[m]	75	35	74.5[e]	140	730[k]
	15 (2 P)[f]	120				≈0[l]

[a] CH_2Cl_2/CD_2Cl_2 (80:20) solutions. [b] Resonances appear as doublets of doublets where L = PR_3 or P(OR)$_3$. [c] Resonances appear as doublets of quartets. [d] Coupling between triphos and ligand. [e] Resonance is doublet × triplet. [f] Resonance is doublet × doublet. [g] Coupling between the two triphos environments. [h] THF/C_6D_6 (80:20 v/v) solution. [i] P_a is the unique triphos phosphorus atom; P_b represents the two equivalent triphos phosphorus atoms. [j] It is not possible to distinguish between P_a and PMe_3. [k] ^2J(P–P_a). [l] ^2J(P–P_b). [m] Resonance is a doublet of doublets of triplets. [n] Resonance is a doublet of doublets of doublets.

Rh(MeCO)(*t*-BuNC)(triphos). A solution of 1.0 g of RhMe(CO)(triphos) in 25 mL of CH_2Cl_2 was treated with a 10-fold excess of *t*-BuNC. After the solution had been stirred for 1–2 h, the ν(CO) of RhMe(CO)(triphos) had been replaced by a ν(CN) at 2115 cm^{-1} attributable to Rh(MeCO)(*t*-BuNC)(triphos). Hexane was added until the cloud point was reached, and the solution was cooled in an ice bath until a yellow solid precipitated. The product was filtered, washed with hexane, and dried in vacuo (yield 35–50%).

In attempts to form other insertion products, 10-fold excesses of PMe_3 and P($OMe)_3$) were added to THF solutions of RhMe(CO)(triphos). In neither case had reaction occurred after a period of 8 h at room temperature or 2 h of refluxing.

Oxidative Addition Reactions of Rhodium(I) Complexes. Acid Halides. One equivalent of CH_3COCl (freshly distilled from *N*,*N*-diethylaniline) was added to a stirred CH_2Cl_2 solution of RhCl(CO)(triphos). Hexane was added to the solution after 1 h, and the resulting yellow precipitate of $RhCl_3$(triphos)[5b,d] was filtered, washed with hexane, and dried in vacuo (yield 50%). A sample suitable for elemental analysis was obtained by recrystallization from THF/ethanol. Reactions of other acid halides RCOCl (R = C_2H_5, $CH_3(CH_2)_5$, C_6H_5) with RhCl(CO)(triphos), carried out as described above, also gave $RhCl_3$(triphos) as the primary product.

Addition Reactions of HCl. About 2 equiv of HCl (generated by the reaction of ethanol with CH_3COCl) was added slowly to a CH_2Cl_2 solution of RhCl(CO)(triphos). As the reaction proceeded, the ν(CO) of the starting material disappeared but no new bands appeared in the region of 2500–1400 cm^{-1}. Following completion of the reaction, hexane was added to precipitate the product. A yellow solid was filtered, washed with hexane, dried in vacuo, and identified as $RhCl_3$(triphos) by its ^{31}P NMR spectrum. If, on the other hand, the reaction was stopped after 1 equiv of HCl had been added, there precipitated a solid which was identified as a mixture of the known[5a] complex $RhHCl_2$(triphos) (85%) and $RhCl_3$(triphos) (15%) (IR and ^{31}P NMR spectroscopy).

In a complementary experiment, gaseous HCl was bubbled through a CH_2Cl_2 solution of [Rh(CO)$_2$(triphos)]PF_6 until the starting material had been consumed. Hexane was added to the solution to precipitate an orange solid, which was filtered, washed with hexane, and dried in vacuo. The solid was subsequently identified as [$RhCl_2$(triphos)]PF_6 by its ^{31}P NMR spectrum (see below) (yield 60%).

Reactions of Cl_2, Br_2, and I_2. Excess halogen was added to CH_2Cl_2 solutions of [Rh(CO)$_2$(triphos)]PF_6 until the colors of the solutions faded from yellow to a reddish color (10–15 min). Hexane was then added until the solutions became cloudy, at which point the solutions were cooled. The resulting solids were filtered, washed with hexane, and recrystallized from THF/ethanol to give the complexes [RhX_2(triphos)]PF_6, incorporating ≈1 mol of THF/rhodium. Drying under vacuum gradually removed the THF from the complexes and produced samples suitable for elemental analyses in 65–75% yields.

Reaction of H_2. A THF solution of [Rh(CO)$_2$(triphos)]PF_6 was placed in a Parr stirring minireactor, and the atmosphere was replaced by an atmosphere of H_2 at a pressure of 50 atm. The temperature was raised to 50 °C (*P* = 68 atm), and the reaction

Table IV. $^{13}C\{^1H\}$ NMR Data (in ppm)[a]

	triphos					
complex	CH_2[b]	CH_3[c]	C	phenyl[d]	CO[e]	other[e]
$[Rh(CO)L(triphos)]PF_6$						
L = CO	33.18	38.3	38.4	132.6, 131.7, 131.1, 129.4	196.3 dq (57.9, 22.4)	
t-BuNC	29.7	34	NA[g]	136.8, 131.8, 129, 128.4	200.8 dq (65.9, 22.1)	184, 58, 30.5 (*t*-BuNC)
PMe_3	35.1	39.4	37.9	135.3, 131.8, 130.3, 129	204.3 ddq (68, 22, 22)	19.3 d (PMe)
PEt_3	36.3	39.2	37.5	135.9, 132.2, 130.3, 128.8	203.8 ddq, (68, 22, 22)	20.2, 9.6 (Et)
$P(n\text{-}Bu)_3$	36.5	39.2	37.5	135.8, 132.2, 130.4, 128.8	203.9 (ddq (68, 23, 23)	13.8, 24.7, 26.6, 36.5 (Bu)
PMe_2Ph	35.7	39.0	37.7	135.3, 132.0, 130.4, 128.9	203.5 ddq (66, 22.4, 22.4)	17.6 d (32) (PMe), 129–131 m (Ph)
$PMePh_2$	35.6	39.2	37.8	135.4, 132, 130.0, 129.2	202.4 ddq (60, 24, 24)	18.4 d (PMe), 129–133 m (Ph)
PPh_3	36.4	38.8	37.2	135.5, 132.0, 130.2, 128.8	201.8 ddq (60, 24, 24)	133.2, 133.9, 130.8, 128.7 (PPh)
$P(OMe)_3$	35.3	38.9	37.8	135.1, 133.2, 130.2, 128.8	201.4 ddq (66, 22, 22)	52.4 (POMe)
$P(OPh)_3$	34.2	37.8	36.5	134.0, 132.2, 130.6, 129.8	199.9 ddq (60, 23, 23)	151.4, 130.2, 124.9, 121.3 (POPh)
C_2H_4	32.5	38.4	37.5	133.1, 131.7, 131.0, 129.3	194 dd (52.5, 33.8)	39.4 br s (C_2H_4)
C_3H_6	32.7	38.4	37.3	133.2, 131.9, 131.6, 131.1, 129.5, 129.3	194.7 dq (54.5, 32.5)	45.0, 59.3, 24.7 (C_3H_6)
$(H)_2$	33.1	38.5	37.8	134.2, 132.1, 131.6, 128.9	NA[g]	
RhR(CO)(triphos)						
R = Me	35.3	39.2	37.8	137.8, 132.5, 128.4, 127.8	212.6 dq (78, 24)	−12.6 dq (15.4, 15.4) (Rh–Me)
Ph	38.3	39.1	38	138.6, 132.9, 128.6, 127.9	209.5 dq (80, 25)	131.6–121 (Rh–Ph)
MeCO	36.7	38.8	37.4	138.9, 132.6, 128.8, 128.1	208.1 dq (83, 15)	251.5 dq (24, 24), 55 m (MeCO)
PhCO	36.9	3994	37.3	138.1, 132.0, 128, 129	207.4 dq (80, 17)	252.7 dq (25, 25), 125–131 (PhCO)
H	35.5	39.5	37.6	137.1, 132.6, 128.7, 128.1	...	
Rh(MeCO)(*t*-BuNC)(triphos)	34.6	38.7	38.0	136.5, 129.6, 128.5	NA[g]	146.6 (*C*NCMe),[f] 30.5 (CN*C*Me), 31.9 (CNC*Me*), 55 *Me*CO
$RhMe_3(triphos)$	35.2	39.2	35.5	138.2, 132.9, 128.6, 128.0		≈10 m (Rh–Me)
$RhCl_3(triphos)$	38.6	37.3	36.4	134.6, 133.7, 131.5, 128.7		
$[RhX_2(triphos)]PF_6$						
X = Cl	40.1	38.9	39.2	128.4, 137.5, 135.5, 128.0		
Br	39.9	38.9	39.1	128.6, 137.9, 135.7, 128.3		
I	39.8	38.6	39.0	128.2, 137.6, 135.9, 128.3		
$[RhCl_2L(triphos)]PF_6$						
L = *t*-BuNC	38.5	37.0	38.4	133.5, 132.6, 131.4, 128.6		34 (CNC*Me*$_3$), 60.2 (CN*C*Me$_3$)
PMe_3	38.7	37.7	39.0	134.1, 132.1, 135–128.6		16.1 d (33.4) (PMe)
$P(OMe)_3$	38.1	37.4	37.2	136.5, 133.2, 129.5, 128.0		55.0 (P(OMe))

[a] CD_2Cl_2 solutions. [b] CH_2 resonances appear as doublets; $^1J(P\text{–}C) = 19\text{–}21$ Hz. [c] CH_3 resonances appear as quartets; $^3J(P\text{–}C) = 10\text{–}12$ Hz. [d] The first resonance given is the ipso C; ^1J(P–ipso C) = 35–40 Hz; the remaining phenyl resonances have the following pattern: doublet ($J(P\text{–}C) = 9\text{–}24$ Hz), singlet, and doublet ($J(P\text{–}C) = 9\text{–}12$ Hz). [e] Coupling constants in parentheses. [f] Resonance is a quartet of doublets; $^1J(Rh\text{–}C) = 25$ Hz, $^2J(P\text{–}C) = 45$ Hz. [g] NA = not available.

was allowed to proceed for 18 h, after which time the H_2 was vented and the contents of the reactor were transferred to a round-bottom flask. The solvent was removed under reduced pressure, and the residual solid was dried in vacuo. The ^{31}P NMR spectrum of the solid (THF/C_6D_6 80:20 v/v) consisted of resonances of the starting material (40%) and of $[RhH_2(CO)(triphos)]PF_6$ (see below) (60%). No reaction occurred at 1 atm of hydrogen.

In alternative procedure, a hydrogen-saturated solution of 1.0 g of $[Rh(CO)_2(triphos)]PF_6$ in 250 mL of THF in a water-cooled quartz reactor was photolyzed with a 200-W Hanovia UV lamp until the starting material had disappeared. The reaction mixture was then canulated into a 500-mL flask, the solvent was removed in vacuo, and the residual solid was recrystallized from THF/hexane to give 75–90% yield of the white product $[RhH_2(CO)(triphos)]PF_6$.

Reactions of $[RhCl_2(triphos)]PF_6$ with Ligands L. For L = *t*-BuNC, PMe_3, and $P(OMe)_3$, 1.1 equiv of L was added to THF solutions of $[RhCl_2(triphos)]PF_6$, the color of the solutions changing from red/orange to nearly colorless. Ethanol was added to the solutions, which were cooled, and the resulting yellow precipitates were filtered, washed with ethanol, and dried in vacuo.

Table V. Low-Temperature ^{31}P NMR Data[a]

complex	triphos δ(P)	triphos ^1J(Rh–P)[b]	triphos ^2J(P–P)[b]	other δ(P)	other $\nu_{1/2}$[b]
[Rh(CO)L(triphos)]PF_6					
L = CO	10.8	95.6 ($\nu_{1/2}$ = 9 Hz)			
t-BuNC	$\simeq$10 ($\nu_{1/2}$ =230 Hz)				
$P(OMe)_3$	8.1 ($\nu_{1/2}$ = 380 Hz)			131.7 m	
PMe_3	3.3 (2 P)	~99		1.0 m	<30
	21.7 (1 P)	~213			
PPh_3	-3.1 (2 P)	$\nu_{1/2}$ = 1430 Hz		32	390
	8.1 (1 P)	$\nu_{1/2}$ = 780 Hz			
C_2H_4	1.5 dd	108	43.7		
	23.1 dt	87.1	43.7		
RhR(CO)(triphos)					
R = Me	7.7 dd	125	41		
	23.0 dt	84	41		
Ph	2.15 dd	121	39		
	24.9 dt	77.7	39		
H	18.3	$\nu_{1/2}$ = 380 Hz			
MeCO	1.4 dd	132	43		
	15.1 dt	71	43		
PhCO	-0.13 dd	127	43		
	17.2 dt	73	43		

[a] CH_2Cl_2/CD_2Cl_2 solution at -90 °C. [b] In Hz.

Table VI. Elemental Analytical Data

complex	calcd C	calcd H	calcd X	found C	found H	found X
[Rh(CO)L(triphos)]PF_6						
L = *t*-BuNC	57.39	4.92		56.94	4.83	
PMe_3	55.34	4.95		55.08	4.95	
PEt_3	56.60	5.34		56.23	5.31	
P(*n*-Bu)$_3$	58.81	6.03		58.55	5.93	
PMe_2Ph	57.82	4.91		57.92	4.52	
$P(OMe)_3$	52.75	4.72		52.67	5.31	
$P(OPh)_3$	59.52	4.50		59.03	4.96	
$PMePh_2$	60.00	4.76		59.61	4.78	
PPh_3	62.00	4.68		62.90	4.91	
C_2H_4	56.91	4.67		57.29	5.07	
C_3H_6	57.34	4.81		57.26	5.13	
[RhX_2(triphos)]PF_6						
L = Cl	52.20	4.17	7.52	51.81	4.58	7.37
Br	47.70	3.80	15.47	48.01	3.75	15.31
I	43.84	3.50	22.53	43.96	3.30	21.97
[$RhCl_2$L(triphos)]PF_6						
L = *t*-BuNC	53.82	4.71		53.48	4.72	
PMe_3	52.81	5.17		53.37	5.48	
$P(OMe)_3$	49.51	4.53		49.42	5.01	
RhR(CO)(triphos)						
R = Me	67.02	5.49		66.47	5.49	
Ph	69.24	5.33		69.09	5.35	
MeCO	66.17	5.30		66.08	5.41	
PhCO	68.38	5.2		68.19	5.2	
Rh(MeCO)(*t*-BuNC)(triphos)	67.53	6.02		67.71	6.65	
$RhCl_3$(triphos)	59.05	4.71		58.55	4.66	
$RhMe_3$(triphos)	68.40	6.26		67.66	6.29	
RhH_2(CO)(triphos)]PF_6	55.89	4.58		55.53	4.71	

The complexes [$RhCl_2$L(triphos)]PF_6 were obtained in 80–95% yields.

For L = Cl^-, LiCl was added to a THF/ethanol (80:20 v/v) solution of [$RhCl_2$(triphos)]PF_6. The color of the solution became lighter and the ^{31}P NMR spectrum of the solution indicated that the starting material had completely disappeared and that $RhCl_3$(triphos) had formed quantitatively. No reaction occurred with CO (1 atm) or $P(OPh)_3$.

Synthesis of $RhMe_3$(triphos). A solution of 3.5 mL of 1.4 M methyllithium was added to a solution of [$RhCl_2$(triphos)]PF_6 in 50 mL THF, the mixture was stirred for 30 min, and 25 mL of ethanol was added. Concentration of the solution at reduced pressure resulted in the precipitation of a white solid, $RhMe_3$(triphos), which was filtered, washed with ethanol, and dried in vacuo (yield 75%).

Reactions of [RhH_2(CO)(triphos)]PF_6. About 1–2 equiv of L (L = PPh_3, PPh_2Me, LiI) was added to THF solutions of [RhH_2(CO)(triphos)]PF_6. For L = LiI, the IR spectrum of the reaction mixture showed the quantitative conversion of [RhH_2(CO)(triphos)]PF_6 to RhI(CO)(triphos).[5d] For L = PPh_2Me and PPh_3, the yellow products [Rh(CO)($PMePh_2$)(triphos)]PF_6 (yield 75%) and [Rh(CO)(PPh_3)(triphos)]PF_6 (yield 80%) precipitated and were filtered, washed with THF, and dried in vacuo. In an IR experiment, CO was bubbled through a THF solution of [RhH_2(CO)(triphos)]PF_6. After 5 min, the IR spectrum showed the complete displacement of H_2 and conversion of [RhH_2(CO)(triphos)]PF_6 to [Rh$(CO)_2$(triphos)]PF_6.

In a separate series of experiments, ethylene and propylene were bubbled through THF solutions (100 mL) of [RhH_2(CO)(triphos)]PF_6 (1.5 g) for 20–40 min. As the reactions proceeded, the yellow products [Rh(CO)(C_2H_4)(triphos)]PF_6 (yield 85%) and [Rh(CO)(C_3H_6)(triphos)]PF_6 (yield 65%) precipitated and were filtered, washed with THF, and dried in vacuo. The conversion of [RhH_2(CO)(triphos)]PF_6 to [Rh(CO)(C_2H_4)(triphos)]PF_6 is reversible, as treatment of a CH_2Cl_2 solution of the latter with 1 atm of H_2 resulted in the quantitative formation of the former.

The olefin complexes can also be prepared, albeit in an impure state, by the direct reaction of the olefins with [Rh(CO)$_2$(triphos)]PF$_6$ in the presence of Me$_3$NO.

In a series of ^{31}P NMR experiments, ≈1 equiv of lithium diethylamide (LDA), LiOEt, MeLi, NaBH$_4$, or (*i*-Pr)$_2$NH) was added to THF/C$_6$D$_6$ (80:20 v/v) solutions of [RhH$_2$(CO)(triphos)]PF$_6$. For all bases, the ^{31}P NMR spectra of the reaction mixtures exhibited only the resonance of RhH(CO)(triphos). For B = LiOEt, in addition to the resonance of RhH(CO)(triphos), the ^{31}P NMR spectrum indicated that there was still starting material present.

Low-Temperature ^{31}P NMR Spectroscopy. Low-temperature spectra of the complexes [Rh(CO)L(triphos)]PF$_6$ (L = CO, *t*-BuNC, PMe$_3$, P(OMe)$_3$, PPh$_3$, C$_2$H$_4$) and RhR(CO)(triphos) (R = H, Me, MeCO, Ph, PhCO) were obtained utilizing 40–50 mg of the complexes in an 80:20 (v/v) mixture of CH$_2$Cl$_2$/CD$_2$Cl$_2$. Low-temperature ^{31}P NMR spectral data (−90 °C) are given in Table V.

For [Rh(CO)(C$_2$H$_4$)(triphos)]PF$_6$ and the complexes RhR(CO)(triphos) (R = Me, MeCO, Ph, PhCO), additional spectra were obtained at various temperatures between −90 °C and ambient temperature. For Rh(MeCO)(CO)(triphos) and Rh(PhCO)(CO)(triphos), upon completion of the variable-temperature study, the temperature was returned to the initial temperature; in both cases, the initial spectra were regenerated.

Results and Discussion

Complexes of the Type [Rh(CO)L(triphos)]PF$_6$. This class of complexes was prepared in several ways. For L = *t*-BuNC, PMe$_3$, PEt$_3$, P(*n*-Bu)$_3$, PPhMe$_2$, P(OMe)$_3$, and P(OPh)$_3$, the complexes [Rh(CO)L(triphos)]PF$_6$ were prepared by substitution of CO in [Rh(CO)$_2$(triphos)]PF$_6$. For L = C$_2$H$_4$, C$_3$H$_6$, and PPh$_3$, there was no reaction between L and [Rh(CO)$_2$(triphos)]PF$_6$ at room temperature or, for PPh$_3$, in refluxing THF or CH$_2$Cl$_2$ solutions. For L = *t*-BuNC and P(OMe)$_3$, the reactions of L with RhCl(CO)(triphos) gave complexes whose spectral properties were identical with those of [Rh(CO)L(triphos)]$^+$. Metathesis of the counterion resulted in the formation of the complexes [Rh(CO)L(triphos)]PF$_6$.

It was also possible to chemically remove a CO from [Rh(CO)$_2$(triphos)]PF$_6$ by means of Me$_3$NO. Thus the olefin-substituted complexes [Rh(CO)(olefin)(triphos)]PF$_6$ (olefin = C$_2$H$_4$, C$_3$H$_6$) were prepared from [Rh(CO)$_2$(triphos)]PF$_6$ in this way, i.e.

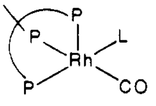
$$[\mathrm{Rh(CO)_2(triphos)}]\mathrm{PF_6} + \text{olefin} + \mathrm{Me_3NO} \rightarrow [\mathrm{Rh(CO)(olefin)(triphos)}]\mathrm{PF_6} + \mathrm{CO_2} + \mathrm{Me_3N} \quad (1)$$

This method did not work for PPh$_3$, and the complex [Rh(CO)(PPh$_3$)(triphos)]PF$_6$ was prepared instead by the reaction of [RhH$_2$(CO)(triphos)]PF$_6$ with PPh$_3$, i.e.

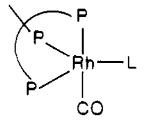
$$[\mathrm{RhH_2(CO)(triphos)}]\mathrm{PF_6} + \mathrm{PPh_3} \rightarrow [\mathrm{Rh(CO)(PPh_3)(triphos)}]\mathrm{PF_6} + \mathrm{H_2} \quad (2)$$

Ethylene, propylene, and PMePh$_2$ were also found to react with [RhH$_2$(CO)(triphos)]PF$_6$ to form the corresponding complexes of the type [Rh(CO)L(triphos)]PF$_6$. In the case of the olefin complexes, this method is preferred over procedures involving substitution of CO on [Rh(CO)$_2$(triphos)]PF$_6$, as the complexes precipitate analytically pure.

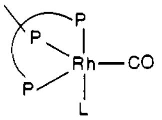
Complexes of the type [Rh(CO)L(triphos)]PF$_6$ may be expected to assume one of two different structure types, square pyramidal (B) or trigonal bipyramidal (C). For the latter, two geometrical isomers are possible, depending on the site of coordination of the CO (C′, C″).



B



C′



C″

An X-ray study of the related complex Ir(CO)Cl(triphos) shows that this compound assumes a structure as in C″ (L = Cl$^-$),[6] and thus a preference for trigonal-bipyramidal structures in the rhodium system seems likely.

The IR spectra of this series of complexes are listed in Table I. In general, ν(CO) varies inversely with the electron-donating ability of L, decreasing in the order CO > olefins > *t*-BuNC > P(OR)$_3$ > PR$_3$. The dihydride [RhH$_2$(CO)(triphos)]PF$_6$, although formally a complex of rhodium(III), is included in the series and, as anticipated, exhibits the highest value of ν(CO).

The ^{1}H NMR spectra of complexes of the type [Rh(CO)L(triphos)]PF$_6$ (Table II) are all similar, the resonances of the triphos ligand being comprised in each case of a multiplet for the phenyl protons, a doublet for the methylene groups, and a quartet for the methyl group. In addition to the triphos resonances, each spectrum exhibits resonances of the ancilliary ligand L, only slightly changed from the chemical shifts of the free ligands on coordination to rhodium. Interestingly, the C$_2$H$_4$ proton spectrum of [Rh(CO)(C$_2$H$_4$)(triphos)]PF$_6$ exhibits two separate resonances, both broad doublets with apparent splittings of ≈9.4 Hz. The implications of this pattern will be discussed below.

The ^{13}C NMR data of complexes of the type [Rh(CO)L(triphos)]PF$_6$ are presented in Table IV. The resonances of the triphos skeletal atoms exhibit similar chemical shifts throughout the series, the methylene resonances being doublets, the methyl resonances quartets, and the quaternary carbon resonances broadened singlets because of couplings to ^{31}P. The resonances of the ancillary ligands are as expected and, as is the case in the ^{1}H NMR spectra, are not normally shifted significantly upon coordination. The olefin carbon resonance of the C$_2$H$_4$ complex is a broadened singlet.

The CO resonances of the complexes [Rh(CO)L(triphos)]PF$_6$ (L = *t*-BuNC, C$_2$H$_4$, C$_3$H$_6$) are split into doublets of quartets, with ^1J(Rh–CO) > ^2J(P–CO). In the complexes where L = phosphorus donors, the CO resonances are further split into complicated patterns which can be described as overlapping doublets of quintets, in which $^2J(\mathrm{OC{-}P_{triphos}}) = {}^2J(\mathrm{OC{-}P_{ligand}})$. The assumption that $^2J(\mathrm{OC{-}P_{triphos}}) = {}^2J(\mathrm{OC{-}P_{ligand}})$ rather than $^2J(\mathrm{OC{-}P_{triphos}}) = {}^1J(\mathrm{OC{-}Rh})$ is based on the observed *J* values from the spectrum of [Rh(CO)$_2$(triphos)]PF$_6$, where $^1J(\mathrm{OC{-}Rh}) > {}^2J(\mathrm{OC{-}P_{triphos}})$.

The ^{31}P NMR spectra (Table III) of the substituted complexes at room temperature are generally similar and show that in all cases the three triphos phosphorus atoms are equivalent on the NMR time scale. For the complexes where L = CO, *t*-BuNC, and C$_3$H$_6$, the phosphorus resonances appeared as simple doublets, while for those containing phosphorus donors, the resonances appeared as doublets of doublets because of spin–spin coupling to the unique P atom. The triphos signals were sharp in all cases except for the complexes of C$_2$H$_4$ and C$_3$H$_6$, for which the triphos resonances were broad.

Consideration of the possible structures B, C′, and C″ suggests that, for the complexes [Rh(CO)L(triphos)]PF$_6$, exchange of the phosphorus atoms must be occurring rapidly on the NMR time scale at room temperature, as has been observed previously for rhodium–triphos and ruthenium–triphos systems.[2b,5g] In no case was nonequivalence of the phosphorus atoms observed, although the broadness of the triphos resonances in the spectrum of the olefin complexes suggests either that the phosphorus

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[6] Janser, P.; Venanzi, L. M.; Bachechi, F. *J. Organomet. Chem.* **1985**, *296*, 229.

atoms of these complexes are exchanging at rates which are slower than for the other substituted complexes or that the chemical shift differences between the various sites of the olefin complexes are larger than for the other complexes. This issue will be considered in greater detail below.

For complexes where L = a phosphorus donor, the ^{31}P NMR spectra of complexes of the type $[Rh(CO)L(triphos)]PF_6$ exhibit additional resonances of the ligand L. These resonances are split into doublets of quartets from coupling to both ^{103}Rh and the three triphos phosphorus atoms (in all cases $^1J(Rh-P_L) > {}^2J(P_{triphos}-P_L)$).

The relative stabilities of complexes of the type $[Rh(CO)L(triphos)]PF_6$ ($L = PR_3$, $P(OR)_3$) with respect to substitution by a different ligand L′ were determined by monitoring the reactions of L′ with $[Rh(CO)L(triphos)]PF_6$ by ^{31}P NMR spectroscopy. On the basis of the ^{31}P NMR spectra of the reaction mixtures, the relative stabilities of the complexes $[Rh(CO)L(triphos)]PF_6$ with respect to ligand substitution were found to follow the order PMe_3 (cone angle[7] 118°) > $P(OMe)_3$ > $P(n\text{-}Bu)_3$ (cone angle 132°) ≈ PMe_2Ph (cone angle 128°) ≈ PEt_3 (cone angle 132°) > $PMePh_2$ (cone angle 138°) > $P(OPh)_3$ > PPh_3 (cone angle 144°). Thus, in general, the smaller the ligand, the more stable is the complex $[Rh(CO)L(triphos)]PF_6$.

Complexes of the Type RhR(CO)(triphos). The reaction of RhCl(CO)(triphos) with methyl- or phenyllithium resulted in the formation of RhR(CO)(triphos) (R = Me, Ph), i.e.

$$RhCl(CO)(triphos) + RLi \rightarrow RhR(CO)(triphos) + LiCl \quad (3)$$

The IR spectrum of RhMe(CO)(triphos) exhibits $\nu(CO)$ at 1895 cm^{-1}, which is in the region expected for a five-coordinate complex of this type. Thus Dahlenburg et al. have prepared the similar complex $Rh(CH_2SiMe_3)(CO)(triphos)$ ($\nu(CO) = 1875$ cm^{-1} (Nujol)).[5e] The $\nu(CO)$ of RhPh(CO)(triphos) occurs at 1915 cm^{-1}, at a somewhat higher frequency relative to RhMe(CO)(triphos).

The ^1H NMR (Table II) and ^{13}C NMR (Table IV) spectra of the two complexes are similar to the spectra of the substituted complexes, $[Rh(CO)L(triphos)]PF_6$, with the triphos resonances exhibiting essentially the same patterns. The rhodium-methyl resonance of RhMe(CO)(triphos) occurs as a quartet of doublets at δ -0.16 in the ^1H NMR spectrum and as a doublet of quartets at δ -12.6 in the ^{13}C NMR spectrum. The resonances of the rhodium-phenyl ligand of RhPh(CO)(triphos) can be distinguished from the phenyl groups of the triphos only in the ^1H NMR spectrum.

The ^{31}P NMR spectra (Table III) of the two complexes each exhibits a doublet, broader ($\nu_{1/2} = 60$ Hz for RhR(CO)(triphos) than are the resonances of the substituted complexes mentioned in the previous section ($\nu_{1/2} < 10$ Hz for $[Rh(CO)L(triphos)]PF_6$) and indicating either that the rate of phosphorus site exchange is slower or that the frequency separation between the two sites is larger in the alkyl/aryl complexes. Variable-temperature ^{31}P NMR experimental results are discussed below.

Both RhMe(CO)(triphos) and RhPh(CO)(triphos) reacted with CO at 1 atm and room temperature to yield the corresponding acyl products Rh(RCO)(CO)(triphos) (R = Me, Ph). The carbonylation reactions were found to be reversible, and applying vacuum to, or purging with N_2, solutions of the acyl complexes gradually but quantitatively regenerated the methyl or phenyl complexes. The IR spectra (Table I) of the acyl complexes exhibit the characteristic acyl $\nu(C{=}O)$ at about 1650 cm^{-1} as well as $\nu(CO)$ at 1909 cm^{-1}. The ^1H NMR data are given in Table II. The triphos resonances exhibit features similar to those exhibited by the other series of substituted and alkyl products discussed above, while the acyl methyl resonance exhibits a downfield chemical shift relative to the methyl resonance in RhMe(CO)(triphos).

The ^{31}P NMR spectra (Table III) of the acyl complexes are characterized by shifts to higher field with respect to the parent alkyl complexes. As with the latter complexes, the triphos signals appear as broad doublets ($\nu_{1/2} = 120$ Hz), indicating again an exchange process involving the phosphorus sites. The ^{13}C NMR spectra (Table IV) of the acyl complexes are also similar to those previously discussed. Although the natural abundance ^{13}C NMR spectra do not show the acyl or carbonyl resonances, bubbling ^{13}CO through a solution of RhR(CO)(triphos) (R = Me, Ph) did allow the observation of both resonances. The CO resonances are split into doublets of quartets with $^1J(Rh-C) > {}^2J(P-C)$. Likewise, the acyl carbon resonances appear as quintets (or overlapping quartets), with $^1J(Rh-C) \approx {}^2J(P-C)$. Interestingly, exposure of the complexes RhR(CO)(triphos) to ^{13}CO results in near equal incorporation of the label into the acyl and terminal CO sites of the acyl products. Since CO "insertion" is generally believed to proceed via alkyl migration,[8] this observation suggests that the incoming CO does not merely induce alkyl migration but that a more random process, possibly involving a fluxional dicarbonyl intermediate, occurs.

In attempts to form complexes of the type Rh(MeCO)L(triphos) ($L \neq CO$), RhMe(CO)(triphos) was reacted with the ligands t-BuNC, PMe_3, and $P(OMe)_3$. For the PMe_3 and $P(OMe)_3$ systems, there were no reactions, while for t-BuNC, a reaction did occur, i.e.

$$RhMe(CO)(triphos) + t\text{-}BuNC \rightarrow Rh(MeCO)(t\text{-}BuNC)(triphos) \quad (4)$$

The IR spectrum of Rh(MeCO)(t-BuNC)(triphos) exhibits a $\nu(CN)$ at 2115 cm^{-1} and a $\nu(C{=}O)$ at 1684 cm^{-1} attributed to the acyl group. The triphos resonances in both the ^1H (Table II) and ^{13}C NMR spectra (Table IV) follow similar patterns to those previously discussed. While the resonance of the acyl CO was not observed in the ^{13}C NMR spectrum, the resonances for the three t-BuNC carbons and the acetyl methyl group were well resolved and in the expected regions. In contrast to complexes of the type Rh(RCO)(CO)(triphos), the ^{31}P NMR spectrum of Rh(MeCO)(t-BuNC)(triphos) exhibits a sharp doublet with $\nu_{1/2} = 10$ Hz, indicating that the phosphorus exchange process is faster in Rh(MeCO)(t-BuNC)(triphos) than in the other acyl complexes.

Oxidative Addition Reactions. The oxidative addition of hydrogen halides, halogens and alkyl halides to square-planar d^8 complexes to produce octahedral d^6 complexes has been extensively studied,[9] but, while several oxidative addition reactions of RhCl(CO)(triphos) were examined by Seigl et al.,[5a] few tractable products could be identified. In contrast, the complex $Ru(CO)_2(triphos)$ was found to react smoothly with several electrophilic reagents to give corresponding ruthenium(II) complexes.[2] Since $[Rh(CO)_2(triphos)]PF_6$ is isoelectronic with $Ru(CO)_2(triphos)$, and as Siegl et al. reported few details of the studies which they carried out, it seemed that a reexamination of the oxidative addition chemistry of RhCl-

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[7] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[8] Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195.

[9] Stille, J. K. in *The Chemistry of Metal-carbon Bonds*; Hartley, F. R., Patai, S. Eds.; Wiley: New York, 1985; Vol. 2.

(CO)(triphos) and [Rh(CO)$_2$(triphos)]PF$_6$ was in order.

It was anticipated that reactions of MeI with RhCl(CO)(triphos) and [Rh(CO)$_2$(triphos)]$^+$ would result in the formation of methyl- or acetylrhodium(III) complexes, as occurs with many analogous systems. However, RhCl(CO)(triphos) did not react with 2 equiv of MeI over a period of 30 min, and while the starting material disappeared when a large excess of MeI was added to a CH$_2$Cl$_2$ solution of RhCl(CO)(triphos), the IR spectrum of the product exhibited no ν(CO) and no resonances in the ^{31}P NMR spectrum could be identified. Similar results were obtained for the complex [Rh(CO)(*t*-BuNC)(triphos)]PF$_6$; refluxing MeI/CH$_2$Cl$_2$ solutions were necessary to force a reaction, but the solid produced by the reaction contained no carbonyl bands in the IR spectrum and could not be identified. In general, reactions of MeI with a variety of rhodium(I)–triphos complexes were found not to proceed under mild conditions, and, under the conditions necessary to force a reaction to occur, the products could not be identified.

The reaction of CH$_3$COCl with RhCl(CO)(triphos) did proceed smoothly but gave RhCl$_3$(triphos)[5b,d] rather than the expected acetyl complex. There was no evidence in the IR spectrum of the reaction mixture that the complex Rh(MeCO)(CO)(triphos) had been formed. The reaction of HCl with RhCl(CO)(triphos) to give RhHCl$_2$ (triphos) was the only oxidative addition reaction reported by Siegl et al.[5a] in which an identifiable product was formed. However, we found that bubbling HCl through a CH$_2$Cl$_2$ solution of RhCl(CO)(triphos) again gave RhCl$_3$(triphos). Only on adding a stoichiometric amount of HCl to a solution of RhCl(CO)(triphos) in CH$_2$Cl$_2$ was RhHCl$_2$(triphos) produced, albeit as a mixture with RhCl$_3$(triphos). [Rh(CO)$_2$(triphos)]PF$_6$ reacts with excess HCl to give [RhCl$_2$(triphos)]PF$_6$, but attempts to observe and/or isolate a hydride intermediate were unsuccessful. The structure and characterization of [RhCl$_2$(triphos)]PF$_6$ will be discussed below.

Although [Rh(CO)$_2$(triphos)]PF$_6$ did not react with H$_2$ at room temperature and 1 atm, placing a THF solution under ≈70 atm of H$_2$ at a temperature of 50 °C did result in slow oxidative addition (60% yield after 18 h), i.e.

$$[\mathrm{Rh(CO)_2(triphos)}]\mathrm{PF_6} + \mathrm{H_2} \rightarrow [\mathrm{RhH_2(CO)(triphos)}]\mathrm{PF_6} + \mathrm{CO} \quad (5)$$

Details concerning a better synthesis and the characterization and chemistry of [RhH$_2$(CO)(triphos)]PF$_6$ will be discussed below.

The reactions of Cl$_2$ with RhCl(CO)(triphos) or [Rh(CO)$_2$(triphos)]Cl gives a solid which is reported to be a polymer of [Rh(triphos)Cl$_3$] units.[5a,b] In contrast, we found that reactions of X$_2$ (X = Cl, Br, I) with [Rh(CO)$_2$(triphos)]PF$_6$ resulted in the formation of the complexes [RhX$_2$(triphos)]PF$_6$ (X = Cl, Br, I), i.e.

$$[\mathrm{Rh(CO)_2(triphos)}]\mathrm{PF_6} + \mathrm{X_2} \rightarrow [\mathrm{RhX_2(triphos)}]\mathrm{PF_6} + 2\mathrm{CO} \quad (6)$$

The ^{1}H NMR (Table II) and ^{13}C NMR (Table IV) spectra of the complexes [RhCl$_2$(triphos)]PF$_6$ exhibit triphos resonances which are very similar to those previously discussed for complexes of the types [Rh(CO)L(triphos)]PF$_6$ and RhR(CO)(triphos). The ^{31}P NMR spectra (Table III) of the complexes [RhX$_2$(triphos)]PF$_6$ exhibit doublet resonances, but at chemical shifts significantly downfield relative to the ^{31}P resonances of the other triphos–rhodium(III) complexes discussed here. Thus the average values of the triphos ^{31}P resonances of RhCl$_3$(triphos) and [RhCl$_2$L(triphos)]PF$_6$ are ≈20–25 ppm to higher field of the resonance of the parent complex [RhCl$_2$(triphos)]PF$_6$, suggesting that the complexes [RhX$_2$(triphos)]PF$_6$ have structures markedly different than the six-coordinate complexes. The downfield shifts may in fact suggest that the 16-electron complexes are five-coordinated, and we note that the five-coordinated, monomeric 16-electron complexes [Rh(X$_2$C=O)(triphos)]$^+$ (X = S, Se)[10a,b] and [Rh$_2$(μ-C$_2$X$_4$)(triphos)$_2$]$^{2+}$ (X = S, Se)[10c,d] exhibit similar low-field phosphorus chemical shifts.

Evidence that the complexes [RhX$_2$(triphos)]PF$_6$ may be coordinatively unsaturated arises from the finding that there may be a marked degree of solvent interaction. Recrystallization from a mixture of THF/ethanol yielded the THF adducts [RhX$_2$(triphos)]PF$_6$·THF, from which the THF of solvation could be removed by drying the complexes in vacuo for several days. The possibility that the complexes are halogen-bridged dimers seems to be reduced by the observation that the far-IR spectrum of [RhCl$_2$(triphos)]PF$_6$ exhibits terminal ν(Rh–Cl) at 260 and 255 cm^{-1} but no apparent bridging ν(Rh–Cl) down to 200 cm^{-1}.[11]

Reactions of [RhCl$_2$(triphos)]PF$_6$ with Nucleophiles. [RhCl$_2$(triphos)]PF$_6$ reacted with nucleophiles, L (L = *t*-BuNC, P(OMe)$_3$, PMe$_3$), to form six-coordinate complexes of the type [RhCl$_2$L(triphos)]PF$_6$, i.e.

$$[\mathrm{RhCl_2(triphos)}]\mathrm{PF_6} + \mathrm{L} \rightarrow [\mathrm{RhCl_2L(triphos)}]\mathrm{PF_6} \quad (7)$$

The ^{1}H (Table II) and ^{13}C (Table IV) NMR spectra of the complexes [RhCl$_2$L(triphos)]PF$_6$ are as expected, with the typical resonances for the triphos ligand and additional resonances from the ligahd L. The only anomaly is the existence of two multiplets for the methylene resonances of the triphos ligand when L = PMe$_3$, resulting from the nonequivalent nature of the triphos phosphorus atoms. In fact it is curious that this nonequivalence is not observed when L = P(OMe)$_3$ and *t*-BuNC. The resonance for the terminal carbon of the ligand *t*-BuNC was not observed in the ^{13}C NMR; either the multiplicity of the signal (expected ddt) or coupling to the quadrupolar ^{14}N nucleus could have prevented its observation.

The ^{31}P NMR spectra of complexes of the type [RhCl$_2$L(triphos)]PF$_6$ (Table III) show that these complexes are stereochemically rigid on the NMR time scale. The triphos phosphorus atoms exist in two different environments, with the resonance of the unique phosphorus atom being to higher field. This is probably due to the larger trans influences of the ligands L vs the chloride ligands.[3] For L = PMe$_3$, it is not possible to distinguish between the resonances of this ligand and of the unique triphos phosphorus atom, as both couple equally strongly to the other triphos phosphorus atoms. For L = P(OMe)$_3$, it is reasonable to assume that the resonance at δ 74.5 is that of P(OMe)$_3$. The P–P coupling constants follow the expected pattern, with trans ^2J(P–P) ≫ cis ^2J(P–P).[12]

In an attempt to prepare a rhodium(III) alkyl complex, [RhCl$_2$(triphos)]PF$_6$ was reacted with 3 equiv of MeLi; the complex RhMe$_3$(triphos) was formed in good yield. The ^{1}H NMR spectrum of RhMe$_3$(triphos) exhibits typical

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[10] (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* 1985, 1024. (b) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Am. Chem. Soc.* 1985, *107*, 5317. (c) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* 1984, *23*, 4125. (d) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* 1984, 1647.

[11] An anonomous reviewer claims that these complexes are dimeric, although no evidence is given. It is not true, as the reviewer claims, that low-temperature ^{31}P NMR spectroscopy would settle the matter, as both dimeric and five-coordinated fluxional species would give single ^{31}P resonances.

[12] Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, NMR Basic Principles and Progress*; Springer-Verlag: New York, 1979; Vol. 16.

triphos resonances and a resonance from the methyl groups. The latter is a broad multiplet, as it is the AA′A″ portion of an $A_3A'_3A''_3KXX'X''$ spin system. A similar complex, *fac*-$RhMe_3(PMe_3)_3$, has been prepared and exhibits a similar ^1H NMR resonance for the rhodium–methyl groups.[13]

The ^{31}P NMR spectrum of $RhMe_3$(triphos) shows the expected equivalence of the triphos environments and the ^{31}P chemical shift of the triphos ligand is the largest average upfield chemical shift observed for the rhodium(III) complexes. The ^{13}C NMR spectrum (Table IV) of $RhMe_3$(triphos) also exhibits resonances typical of the triphos ligands. The rhodium–methyl resonance is a multiplet which is not sufficiently resolved to allow extraction of coupling constants.

Preparation and Reactions of [RhH_2(CO)(triphos)]PF_6. The complex [RhH_2(CO)(triphos)]PF_6, which was prepared by the reaction of [$Rh(CO)_2$(triphos)]PF_6 with H_2 at high pressure, is better prepared by the photolysis of [$Rh(CO)_2$(triphos)]PF_6 in the presence of H_2, i.e.

$$[Rh(CO)_2(triphos)]PF_6 + H_2 \xrightarrow{h\nu} [RhH_2(CO)(triphos)]PF_6 + CO \quad (8)$$

The IR spectrum of [RhH_2(CO)(triphos)]PF_6 exhibits ν(CO) at 2073 cm^{-1} and ν(Rh–H) at 1985 cm^{-1}. The latter assignment compares well with the value of ν(Rh–H) found for the complex RhH_3(triphos) (1965 cm^{-1}).[5d] The triphos resonances in the ^1H and ^{13}C NMR spectra exhibit the typical patterns discussed previously, but the CO resonance was not observed in the ^{13}C NMR spectrum. The hydride resonance in the ^1H NMR spectrum consists of an apparent doublet of doublets, with separations of 131 and 14.5 Hz. The hydride resonance is the AA′ portion of an AA′KPP′X system, where K = ^{103}Rh and P = ^{31}P atoms trans to the hydride ligands, and X = ^{31}P trans to the CO. A similar pattern was observed for RhH_3(triphos), where the hydride resonance was also an apparent doublet of doublets (separations of 130 and 20 Hz).[5d]

During the investigation of [RhH_2(CO)(triphos)]PF_6, it was found that the H_2 is readily displaced from this complex by other ligands. Thus treatment of [RhH_2(CO)(triphos)]PF_6 with PPh_3, $PMePh_2$, CO, C_2H_4, and C_3H_6 resulted in facile formation of the substituted complexes [Rh(CO)L(triphos)]PF_6, i.e.

$$[RhH_2(CO)(triphos)]PF_6 + L \rightarrow [Rh(CO)L(triphos)]PF_6 + H_2 \quad (9)$$

With I^-, Rh(CO)I(triphos) is formed. Since complexes of the type [Rh(CO)L(triphos)]PF_6 could not be prepared directly by treating [$Rh(CO)_2$(triphos)]PF_6 with PPh_3, C_2H_4, or C_3H_6, this reaction provides a convenient route for their syntheses.

The high frequency of the ν(CO) of [RhH_2(CO)(triphos)]PF_6 suggests that the carbonyl ligand should be susceptible to nucleophilic attack.[14] However, upon reaction with either $NaBH_4$ or MeLi, the isolated product was RhH(CO)(triphos), i.e.

$$[RhH_2(CO)(triphos)]PF_6 \xrightarrow[-PF_6^-]{+Me^- \text{ or } +BH_4^-} RhH(CO)(triphos) \quad (10)$$

The acidic nature of [RhH_2(CO)(triphos)]PF_6 was confirmed by its reaction with several different bases, LDA, $(i\text{-}Pr)_2NH$, and LiOEt, which reacted to form RhH(CO)(triphos). Thus the products of the reactions of various nucleophiles with [RhH_2(CO)(triphos)]PF_6 are dependent upon the basicity of the nucleophiles; the more basic nucleophiles deprotonate [RhH_2(CO)(triphos)]PF_6 to form RhH(CO)(triphos), while less basic nucleophiles coordinate and induce elimination of H_2.

Low-Temperature ^{31}P NMR Studies. Five-coordinate complexes often exhibit stereochemical nonrigidity via a variety of exchange processes.[15] Since most of the ^{31}P NMR spectra of complexes of the types [Rh(CO)L(triphos)]PF_6 and RhR(CO)(triphos) exhibit single resonances (doublets) at room temperature, these complexes clearly undergo exchange processes which are rapid on the NMR time scale and which prevent determination of the ground-state geometries from the room-temperature ^{31}P NMR spectra. If the limiting ^{31}P NMR spectra could be obtained, it should be possible to determine whether the ground state geometries are square-pyramidal (B) or trigonal-bipyramidal (C).

Complexes of the type [Rh(CO)L(triphos)]PF_6 (L = CO, PMe_3, $P(OMe)_3$, PPh_3, *t*-BuNC, C_2H_4) were chosen to examine the effects of changing the size and nature of the substituent. Ott et al. have reported that lowering the temperature had no effect on the ^{31}P NMR spectrum (at 35.6 MHz) of [$Rh(CO)_2$(triphos)]PF_6, as they observed no noticeable line broadening down to a temperature of −90 °C.[5a] We have found that repeating the experiment on a spectrometer with a ^{31}P NMR resonance frequency of 161.9 MHz also had no effect on the line width of the triphos resonance of [$Rh(CO)_2$(triphos)]PF_6 (Table V), indicating either that the exchange process for this complex has a low activation barrier or that the chemical shift difference between the phosphorus sites is small relative to the rate of exchange.[15]

A similar situation exists for the *t*-BuNC and $P(OMe)_3$ derivatives. Although the low-temperature spectra did exhibit significant broadening of the triphos resonances at low temperatures, the spectra still exhibited only one ^{31}P resonance for the triphos ligand. In contrast, the low-temperature ^{31}P NMR spectra of the PMe_3 and PPh_3 derivatives were partially resolved at −90 °C, with the triphos resonances splitting into two broad singlets or doublets of relative intensity 2:1. Although coupling constants could not be accurately discerned from the spectra because of the line widths, the presence of only two resonances suggests that the ground-state geometries are trigonal-bipyramidal.

In the case of the ethylene complex [Rh(CO)(C_2H_4)(triphos)]PF_6, the ^{31}P resonance was already broad at room temperature, suggesting that the limiting spectrum might be easily reached. Indeed, the variable-temperature ^{31}P NMR spectra of [Rh(CO)(C_2H_4)(triphos)]PF_6 exhibited behavior typical of systems undergoing two-site exchange.[15] The doublet at room temperature broadened as the temperature was lowered, finally disappearing into the base line at approximately 0 °C. At approximately −20 °C, two signals (ratio 2:1) separated from the base line and at −60 °C resolved into a double doublet (2 P) and an overlapping double triplet (1 P). As expected, the weighted average of the low-temperature coupling constants is identical with that observed in the high-temperature, fast-exchange spectrum. The difference between the observed fast-exchange chemical shift and that calculated from the low-temperature spectrum can be attributed to slight tem-

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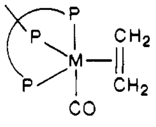
[13] Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

[14] Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691.

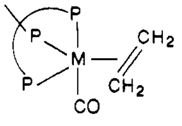
[15] (a) Woods, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227. (b) DoBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076.

perature dependence of the chemical shifts.

Although the ^{31}P NMR spectrum cannot distinguish between trigonal-bipyramidal structures C′ and C″, theoretical calculations suggest that structure C′ would be preferred, with the olefin oriented as in E rather than as in D.[16]

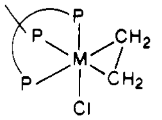


D



E

The related complexes $RhX(C_2H_4)$(triphos) (X = H, Cl) have been reported to exhibit similar ethylene ^1H NMR resonances and, apparently, to have structures essentially as in E.[5f] Compatible with structure E, the room-temperature ^1H NMR spectrum of $[Rh(CO)(C_2H_4)(triphos)]PF_6$ clearly showed that the olefin hydrogen atoms exist in two different environments. The resonances appeared, in fact, to strongly resemble the ethylene resonances of the compound η^5-$C_5H_5Rh(C_2H_4)_2$, for which each pair of cis hydrogen atoms resides in an environment different from the other pair in the same olefin molecule.[17] Also compatible with E, only a single ethylene carbon resonance was observed in the ^{13}C NMR spectrum of $[Rh(CO)(C_2H_4)(triphos)]PF_6$. Thus the coordinated ethylene does not appear to take part in rotation relative to the CO ligand, a conclusion compatible with a suggestion of Bianchini et al.[5f] that the ethylene ligand in $RhCl(C_2H_4)$(triphos) may best considered as a metallocyclopropane fragment, i.e.



The variable-temperature ^{31}P NMR spectra of the complexes RhR(CO)(triphos) (R = Me, Ph, MeCO, PhCO) follow a pattern similar to that exhibited by $[Rh(CO)(C_2H_4)(triphos)]PF_6$, the only differences being the temperature at which the triphos resonances disappeared (≈−50 °C) and the temperature at which the limiting spectra were fully resolved (−90 °C). The limiting spectra of all five complexes are similar to those reported for the complexes MR(CO)(triphos) (M = Ir, R = Me, Ph; M = Rh, R = CH_2SiMe_3), which have been assigned a trigonal-bipyramidal ground state with the CO occupying a position in the equatorial plane.[18] This assignment agrees with the crystal structure and low-temperature ^{31}P NMR spectrum of IrCl(CO)(triphos),[6] which has a trigonal-bipyramidal geometry with an equatorial CO. Although the limiting ^{31}P NMR spectrum of the latter compound was not obtained, the spectrum at −90 °C consisted of two broad resonances in a ratio of 2:1. Thus the observation of two signals in the low-temperature ^{31}P NMR spectrum would seem to be a clear indication that the ground-state geometry is trigonal-bipyramidal.

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Registry No. Me, 2229-07-4; Ph, 2396-01-2; $[Rh(CO)(PMe_3)(triphos)]PF_6$, 121373-92-0; $[Rh(CO)(PMe_2Ph)(triphos)PF_6$, 121374-04-7; $[Rh(CO)(PEt_3)(triphos)]PF_6$, 121374-06-9; $[Rh(CO)(P(n\text{-}Bu_3))(triphos)]PF_6$, 121374-08-1; $[Rh(CO)(P(OMe)_3)(trtphos)]PF_6$, 121373-94-2; $[Rh(CO)(P(oPh)_3)(triphos)]PF_6$, 121374-10-5; $[Rh(CO)(t\text{-}BuNC)(triphos)]PF_6$, 121393-29-1; $[Rh(CO)_2(triphos)PF_6$, 75070-58-5; Rh(Me)(CO)(triphos), 110544-59-7; Rh(Ph)(CO)(triphos), 121373-97-5; Rh(MeCO)(CO)(triphos), 110544-58-6; Rh(PhCO)(CO)(triphos), 121373-95-3; Rh(MeCO)(*t*-BUNC)(triphos), 121393-30-4; RhCl(CO)(triphos), 34440-04-5; CO, 630-08-0; $RhCl_3$(triphos), 62792-06-7; CH_3COCl, 75-36-5; C_2H_5COCl, 79-03-8; $CH_3(CH_2)COCl$, 2528-61-2; PhCOCl, 98-88-4; HCl, 7647-01-0; $RhHCl_2$(triphos), 121374-11-6; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; $[RhCl_2(triphos)]PF_6$, 121374-13-8; $[RhBr_2(triphos)]PF_6$, 121374-15-0; $[RhI_2(triphos)]PF_6$, 121374-17-2; $[RhH_2(CO)(triphos)]PF_6$, 121374-19-4; $[RhCl_2(t\text{-}BUNC)(triphos)]PF_6$, 121374-21-8; $[RhCl_2(PMe_3)(triphos)]PF_6$, 121374-23-0; $[RhCl_2(P(oMe)_3)(triphos)]PF_6$, 121374-25-2; $Rh(Me)_3$(triphos), 121374-26-3; RhI(CO)(triphos), 101075-58-5; $[Rh(CO)(PMe(Ph_2)(triphos)]PF_6$, 121374-28-5; $[Rh(CO)(PPh_3)(triphos)]PF_6$, 121393-32-6; $[Rh(CO)(C_2H_4)(triphos)]PF_6$, 121374-30-9; $[Rh(CO)(C_3H_6)(triphos)]PF_6$, 121374-32-1; RhH(CO)(triphos), 101075-59-6.

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[17] Cramer, R.; Kline, J. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2159.

[18] Dahlenburg, L.; Mirzaei, F.; Yardimcioglu, A. *Z. Naturforsch., B* **1982**, *37B*, 310.