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Spectroscopic and Calorimetric Titration Studies of the Reactions of Chloro-Bridged Rhodium(I) Dimers with Trimethyl Phosphite

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The reactions of the chloro-bridged rhodium(I) dimers $[Rh(COD)Cl]_2$ (where COD stands for 1,5-cyclooctadiene) and $[Rh(CO)_2Cl]_2$ with trimethyl phosphite in benzene solvent are quantitatively studied by spectroscopic titrations. The spectroscopic titration of these rhodium(I) dimers with trimethyl phosphite is followed via $^{31}P\{^1H\}$ NMR, ^1H NMR, and infrared spectroscopies. Structures of the species in solution are deduced and reaction pathways leading to the products are proposed. A calorimetric study of the titration of $[Rh(COD)Cl]_2$ was also undertaken to determine the thermodynamic data for product formation. The trimethyl phosphite ligand causes simultaneous bridge cleavage and olefin displacement from $[Rh(COD)Cl]_2$ in benzene solvent. The reactions occurring when trimethyl phosphite is added to $[Rh(CO)_2Cl]_2$ in benzene differ in that some of the CO remains bound to rhodium, leading to the formation of $\{Rh(CO)[P(OCH_3)_3]_4\}^+$ in excess trimethyl phosphite.

In the past decade, largely due to the significance in the area of homogeneous catalysis of organometallic systems of group 8 metals having a d^8 configuration, much research has been directed toward elucidating the chemistry of various such complexes. During previous investigations of the Lewis acidities of the chloro-bridged rhodium(I) dimers $[Rh(COD)Cl]_2$[8] (where COD stands for 1,5-cyclooctadiene) and $[Rh(CO)_2Cl]_2$,[9] it was noted that tertiary phosphite ligands behaved in contrast to other monodentate ligands containing either second-row group 5 or group 6 donor atoms. Stoichiometric amounts of the latter ligands cleaved the chloride bridges, but displacement of CO and COD occurred with phosphite. Other workers[10,11] have also reported extensive ligand displacement with phosphite donors, but a thorough solution investigation of the reactions has not yet been undertaken. From the standpoint of both the synthesis of new rhodium(I) and rhodium(III) complexes and establishment of the species and equilibria that may be involved in solution reactions of d^8 systems, the present study was thus undertaken. Clearly, fundamental studies of the species that exist in solution when d^8 complexes are used in homogeneous catalytic reactions are critical to an understanding of the interesting chemistry effected by these materials. This report not only establishes the species that exist in the titration of $[(COD)RhCl]_2$ and $[(CO)_2RhCl]_2$ with $P(OCH_3)_3$ but also provides fingerprint NMR and infrared data for characterization of most of the species formed in these solution reactions.

Experimental Section

Materials. The dimeric complexes $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ were prepared and purified using previously reported procedures.[11-14] Anal. Calcd for $[C_8H_{12}RhCl]_2$: C, 38.97; H, 4.92; Rh, 41.74; Cl, 14.38; mol wt 493. Found: C, 39.09; H, 4.85; Rh, 41.67; Cl, 14.50; mol wt (in benzene) 490. Calcd for $[C_2O_2RhCl]_2$: C, 12.36; Cl, 18.24. Found: C, 12.69; Cl, 18.40. All elemental analyses and molecular weight determinations were preformed by the microanalytical laboratory of the University of Illinois.

Reagent grade benzene was dried over Linde 4-Å molecular sieves for at least 24 h prior to use. Freshly opened ampules of C_6D_6 solvent were used for all NMR studies. C_6H_6 and C_6D_6 were freeze–pump outgassed prior to use. Trimethyl phosphite was fractionally distilled at atmospheric pressure either for immediate use or for subsequent use, in which case it was then stored overnight in a desiccator with calcium sulfate. All NMR samples were prepared in an inert-atmosphere box.

Apparatus and Procedure. $^{31}P\{^1H\}$ NMR Spectra. $^{31}P\{^1H\}$ Fourier transform NMR spectra were recorded on a Varian Associates XL-100 FT spectrometer operating at 40.5 MHz. The spectra were run using an external ^{19}F lock in 12-mm diameter NMR tubes. The ^{31}P NMR chemical shifts were measured relative to an external reference of 85% H_3PO_4.

^1H NMR Spectra. ^1H NMR spectra were recorded using a Varian HR-220 NMR spectrometer equipped with a Nicolet Technology Corp. TT-220 Fourier transform accessory. Precision-grade tubes were used for the 220-MHz spectra whenever possible so as to reduce spinning sidebands. All chemical shifts were measured relative to tetramethylsilane.

IR Spectra. Infrared spectra were recorded in benzene solution using a Beckman IR-12 instrument. The carbonyl stretching region of the infrared spectra was recorded with the scale expanded 10× along the frequency axis. A pair of matched sodium chloride cells of 0.1-mm path length was used. Rough curve resolutions were performed using a Du Pont 310 curve resolver.

Calorimetry. The description of the modified calorimeter and the calorimetric experimental procedure have been previously reported.[16,17]

Titration Experiments. Calorimetric, infrared, and ^1H and $^{31}P\{^1H\}$ NMR titration experiments for the reaction of metal dimer plus freshly distilled trimethyl phosphite in benzene were conducted at ambient temperatures by successively adding increments of the phosphite base to each solution of the metal dimer.

Results and Discussion

Titration of $[Rh(COD)Cl]_2$ with Trimethyl Phosphite. 1. $^{31}P\{^1H\}$ NMR Studies. The results of the $^{31}P\{^1H\}$ NMR titration of a C_6D_6 solution of 0.10 M $[Rh(COD)Cl]_2$ with freshly distilled trimethyl phosphite at 30 °C are summarized in Table I. Figure 1 shows the series of $^{31}P\{^1H\}$ NMR spectra obtained for various ratios of trimethyl phosphite to rhodium in C_6H_6.

The sharp doublets observed for each of the species labeled A, B, and C (refer to Figure 1 and Table I) in the proton-decoupled ^{31}P NMR spectra arise from splitting of sets of equivalent phosphorus nuclei in each compound by rhodium-103 (of 100% natural abundance with a nuclear spin of $^1/_2$). All assignments and values given in Table I are consistent with previous reports[18-21] of ^{31}P NMR chemical shifts and coupling constants for rhodium(I)–phosphine and rhodium(I)–phosphite complexes (see Table II). Systematic trends are evident in the $^{31}P\{^1H\}$ NMR chemical shifts and coupling constants for the various trimethyl phosphite complexes contained in Table II when compared to those for analogous phosphine and phosphite complexes.

The existence of the tris(phosphite) monomeric complex $Rh[P(OCH_3)_3]_3Cl$ was established on the basis of the correct relative intensities and the expected chemical shifts of ^{31}P NMR resonances as well as ^1H NMR data (see the next section for a discussion of the ^1H NMR data). A $^{31}P\{^1H\}$ spectrum using a narrow spectral width illustrates a complex second-order splitting pattern, rather than the double triplet and double doublet pattern expected for a simple first-order $^{31}P\{^1H\}$ NMR spectrum of a square-planar $Rh[P(OCH_3)_3]_3Cl$ species (see Figure 2). If rhodium splitting is ignored, the

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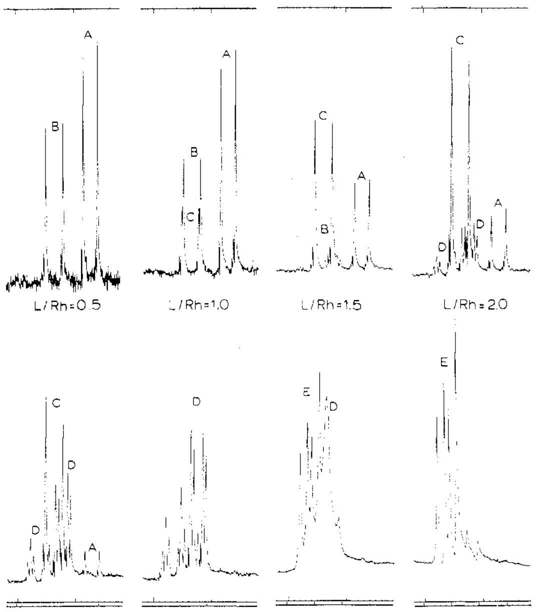
Table I. $^{13}P\{^1H\}$ NMR Data for the Titration of $[Rh(COD)Cl]_2$ + $(CH_3O)_3P$ in C_6D_6 at 28 °C

L/Rh[a]	δ[b]	J_{Rh-P}, Hz	J_{P-P}, Hz	species	symbol[c]
0.5	−122.0 d[d]	249.1		$Rh(COD)[(CH_3O)_3P]Cl$[d]	A
	−137.5 d	298.3		$[(CH_3O)_3P]_2RhCl_2Rh(COD)$	B
1.0–1.5	−122.0 d	249.1		$Rh(COD)[(CH_3O)_3P]Cl$	A
	−137.5 d	298.3		$[(CH_3O)_3P]_2RhCl_2Rh(COD)$	B
	−138.1 d	295.1		$Rh_2Cl_2[(CH_3O)_3P]_4$	C
2.0–2.5	−122.0 d	249.1		$Rh(COD)[(CH_3O)_3P]Cl$	A
	−138.1 d	295.1		$Rh_2Cl_2[(CH_3O)_3P]_4$	C
	−134.2 dd	208.9	52.9	$Rh[(CH_3O)_3P]_3Cl$	D
	−144.9 dt	263.6	52.9		
3.0	−138.1 d	295.1		$Rh_2Cl_2[(CH_3O)_3P]_4$	C
	−134.2 dd	208.9	52.9	$Rh[(CH_3O)_3P]_3Cl$	D
	−144.9 dt	263.6	52.9		
4.0	−137.5 s			$Rh[(CH_3O)_3P]_3Cl$	D
	−148.4 s			Rh cationic species	E
	−145.4 s				
	−143.5 s				
	−140.4 s				
	−87.9 mult				
5.5	−148.5				
	−145.4			Rh cationic species and $(CH_3O)_3P$	E
	−143.5				
	−140.4				
	−87.9 mult				

[a] Ratio of moles of trimethyl phosphite to moles of rhodium. The concentration of $[Rh(COD)Cl]_2$ in C_6D_6 is 0.10 M. [b] Chemical shifts were measured relative to an external sample of 85% H_3PO_4 (contained in a concentric capillary) and are reported in ppm. [c] See Figure 1. [d] Abbreviations: COD, 1,5-cyclooctadiene; d, doublet; dt, double triplet, dd, double doublet; s, singlet; mult, multiplet (see text for further discussion).



L/Rh=0.5 L/Rh=1.0 L/Rh=1.5 L/Rh=2.0

L/Rh=2.5 L/Rh=3.0 L/Rh=4.0 L/Rh=5.5

Figure 1. $^{31}P\{^1H\}$ NMR titration of 0.10 M $[Rh(COD)Cl]_2$ with $(CH_3O)_3P$ in C_6H_6 at 28 °C.

resulting AB_2 system can be described completely[22] by two resonance frequencies ω_A and ω_B and by one coupling constant J_{AB}. The $^{31}P\{^1H\}$ spectrum observed for $Rh[P(OCH_3)_3]_3Cl$ resembles a "pseudo double triplet" and a "pseudo double doublet" further split by second-order splitting.

The coupling constants observed for these rhodium–phosphite complexes are 70–100 Hz larger than values reported previously for similar rhodium–phosphine complexes. Though there has been much controversy[21,23–26] about the interpretation of metal–phosphorus coupling constants, the values suggest stronger rhodium–phosphite bonds than rhodium–phosphine bonds. Such a trend is consistent with the generally accepted belief that phosphites are stronger π acceptors than phosphines.

Factors influencing ^{31}P NMR chemical shifts in similar complexes are no better understood than those affecting coupling constants.[19,20,24,27] From Table II, it is apparent that the chemical shifts for the bis- and tetrakis(phosphite) dimers are similar, the phosphorus nuclei in the latter being only slightly less shielded. In the phosphite dimer, resonances occur ~138 ppm downfield from 85% H_3PO_4. These phosphorus nuclei are substantially less shielded compared with those at −49.5 ppm[19] in the analogous phosphine dimer $[RhCl(P(p\text{-}tol)_3)_2]_2$. The shielding of the phosphorus nucleus (Table II) increases in the order $P(OCH_3)_3 < P(OC_6H_5)_3 < P(C_6H_5)_3 < P(p\text{-}tol)_3$.

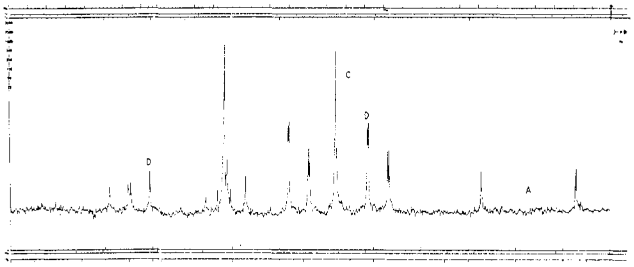


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $[Rh(COD)Cl]_2$ + $(CH_3O)_3P$ in C_6D_6 at ~30 °C for L/Rh = 2.5.

In summary, the $^{31}P\{^1H\}$ NMR data for the titration of $[Rh(COD)Cl]_2$ with stoichiometric amounts of trimethyl phosphite through L/Rh = 3.0 (L/Rh represents the ratio of moles of trimethyl phosphite to moles of rhodium) in benzene indicate bridge cleavage as well as displacement of cyclooctadiene from the dimer. A stepwise dissociation of a bidentate ligand has previously been proposed.[28,29] The formation of the tetrakis(phosphite) dimer at low ligand-to-rhodium ratios could result from two bis(phosphite) dimers which disproportionate to the bis(cyclooctadiene) dimer and the tetrakis(phosphite) dimer. This type of dimer fragment exchange has been observed in the formation of mixed-metal dimers.[30] A monomeric tris(phosphite) species $Rh[P(OCH_3)_3]_3Cl$ is expected in the presence of a L/Rh ratio of greater than 2. The $^{31}P\{^1H\}$ NMR data indicate that for L/Rh = 3.0 the major rhodium–phosphite species present in solution is $Rh[P(OCH_3)_3]_3Cl$. The observations throughout the course of the $^{31}P\{^1H\}$ NMR titration experiment are consistent with the reaction scheme proposed in Figure 3.

Table II. Comparison of ^{31}P NMR Data for Rhodium(I)-Phosphine and Rhodium(I)-Phosphite Complexes

	Rh(CO)Cl-(phosphite)$_2$		Rh(COD)Cl-(phosphite)		(phosphite)$_2$-RhCl$_2$Rh(COD)		Rh$_2$Cl$_2$(phosphite)$_4$		Rh(phosphite)$_3$Cl		
phosphite	δ^a	J_{Rh-P}, Hz	δ^a	J_{Rh-P}, Hz	δ^a	J_{Rh-P}, Hz	δ^a	J_{Rh-P}, Hz	δ^a	J_{Rh-P}, Hz	J_{P-P}, Hz
P(OCH$_3$)$_3$	−128.9	195.0^b	−122.0	249.1^b	−137.5	298.3^b	−138.1	295.1^b	−144.9 pdt^g	263.4	52.9^b
	−130.5	195.0^c					−141.7	294.3^c	−135.0 pdd	209	
P(OC$_6$H$_5$)	−115.2	217.4^c			−117.0	311.5^c					
P(C$_6$H$_5$)$_3$	−28.9	129.4^c									
	−29.1	124.0^e	−30.8	152.4^c					−48.9 dt	192	37.5^d
	−29.3	129.0^f							−32.2 dd	146	
									−48.0 dt	189	38^e
									−31.5 dd	142	
P(p-tol)$_3$	−27.3	124.0^d					−49.5	196.0^d	−46.2 dt	189	38^d
									−30.2 dd	143	

[a] All chemical shifts are reported in ppm from 85% H_3PO_4. [b] Taken from this work. Chemical shifts were measured relative to free trimethyl phosphite (contained in a concentric capillary) and then reported relative to 85% H_3PO_4. [c] Taken from ref 18. [d] Taken from ref 19. [e] Taken from ref 20. [f] Taken from ref 21. [g] Abbreviations: d, doublet; dd, double doublet; dt, double triplet; p, pseudo.

Table III. 220-MHz ^1H NMR Data for the Titration of [Rh(COD)Cl]$_2$ + (CH$_3$O)$_3$P in C$_6$D$_6$ at 28 °C

	δ, from Me$_4$Si				
L/Rh^a	olefinic protons of COD	phosphite methyl protons	J_{P-H}, Hz	species	symbol^d
0.5–1.0	4.30			Rh$_2$(COD)$_2$Cl$_2$^{f}	A
	5.83,^{b} 3.86^c	3.62 d^f	11.8	Rh(COD)[(CH$_3$O)$_3$P]Cl	B
	4.36	3.64 t	12.2^e	Rh$_2$(COD)[(CH$_3$O)$_3$P]$_2$Cl$_2$	C
	5.56			COD	D
1.5–2.0	4.30			Rh$_2$(COD)$_2$Cl$_2$	A
	5.83,^{b} 3.86^c	3.62 d	11.8	Rh(COD)[(CH$_3$O)$_3$P]Cl	B
	4.36	3.64 t	12.2^e	Rh$_2$(COD)[(CH$_3$O)$_3$P]$_2$Cl$_2$	C
	5.56			COD	D
		3.67 t	12.2^e	Rh$_2$[(CH$_3$O)$_3$P]$_4$Cl$_2$	E
		3.72 t, 3.53 d	11.0,^{e} 12.6	Rh[(CH$_3$O)$_3$P]$_3$Cl	F
2.5	5.83,^{b} 3.86^c	3.62 d	11.8	Rh(COD)[(CH$_3$O)$_3$P]Cl	B
	4.36	3.64 t	12.2^e	Rh$_2$(COD)[(CH$_3$O)$_3$P]$_2$Cl$_2$	C
	5.56			COD	D
		3.67 t	12.2^e	Rh$_2$[(CH$_3$O)$_3$P]$_4$Cl$_2$	E
		3.72 t, 3.53 d	11.0,^{e} 12.6	Rh[(CH$_3$O)$_3$P]$_3$Cl	F
3.0	5.56			COD	D
		3.67 t	12.2^e	Rh$_2$[(CH$_3$O)$_3$P]$_4$Cl$_2$	E
		3.72 t, 3.53 d	11.0,^{e} 12.1	Rh[(CH$_3$O)$_3$P]$_3$Cl	F
4.0	5.56			COD	D
		3.65 s		Rh[(CH$_3$O)$_3$P]$_3$Cl, [(CH$_3$O)$_3$P], and {Rh[(CH$_3$O)$_3$P]$_4$}$^+$	G

[a] Ratio of moles of trimethyl phosphite to moles of rhodium. The concentration of [Rh(COD)Cl]$_2$ in C$_6$D$_6$ is 0.10 M. [b] Protons trans to (CH$_3$O)$_3$P in (COD)RhPCl. [c] Protons trans to Cl in (COD)RhPCl. [d] See Figure 4. [e] J value is distance between outer peaks. [f] See Table I for abbreviations.

Both the ^1H and $^{31}P\{^1H\}$ NMR data indicate that for L/Rh > 3.0 the resonances for [P(OCH$_3$)$_3$]$_3$RhCl collapse to a singlet, indicating the complex is undergoing phosphite exchange or exists in rapid equilibrium with a new rhodium–phosphite species. Four new resonances are observed in the region near −145 ppm, in addition to a new low-intensity broad multiplet near −88 ppm in the $^{31}P\{^1H\}$ NMR spectrum for L/Rh ≥ 4.0. Cationic rhodium species are probably formed by excess phosphite and are not undergoing fast exchange (see the section on the titration of [(CO)$_2$RhCl]$_2$). The specific identity of the compound or compounds cannot be made because the ^1H NMR spectra at L/Rh > 4.0 remain a broad singlet.

2. ^1H NMR Studies. The 220-MHz ^1H NMR data obtained for an analogous titration of [Rh(COD)Cl]$_2$ with trimethyl phosphite in benzene are shown in Table III and Figure 4. The results obtained are consistent with the reaction scheme offered in the preceding section. The observed chemical shifts are also consistent with previous reports in the literature.[14,31] For the monomeric complex Rh(COD)[P(OCH$_3$)$_3$]Cl, the chemical shifts corresponding to the olefinic protons trans to phosphorus and trans to chlorine of 5.90 and 3.89 ppm, respectively, are similar to those reported for Rh(COD)(PClPh$_2$)Cl at 5.63 and 3.93 ppm[32] downfield from Me$_4$Si. The similar chemical shift observed for the olefinic protons in the dimers (COD)Rh$_2$Cl$_2$[P(OCH$_3$)$_3$]$_2$ and (COD)Rh$_2$Cl$_2$(CO)$_2$[31] support the previous findings from the ^{31}P NMR observations that long-range inductive effects felt across the dimer are small.

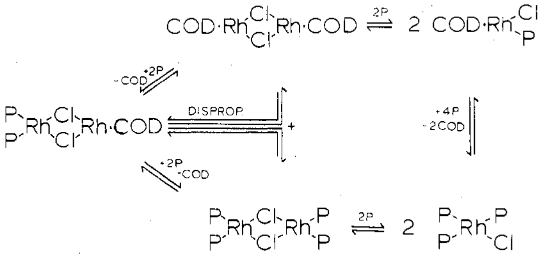


Figure 3. Proposed reaction scheme for [Rh(COD)Cl]$_2$ through the addition of 6 equiv of (CH$_3$O)$_3$P in benzene at room temperature. Abbreviations: "P" = (CH$_3$O)$_3$P, COD = 1,5-cyclooctadiene, disprop = disproportion of 2 equiv of [P(CH$_3$O)$_3$]$_2$Rh$_2$Cl$_2$(COD).

The phosphite methyl proton resonances are extensively overlapped for L/Rh < 3.0, even in the 220-MHz ^1H NMR spectra. Probable assignments for the resonances also appear

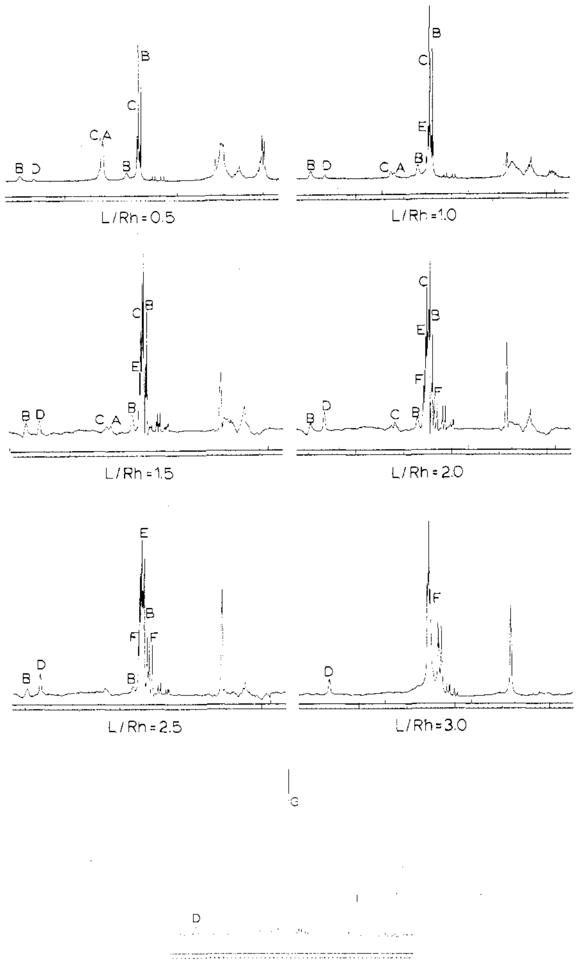


Figure 4. 220-MHz ^1H NMR titration of 0.10 M $[Rh(COD)Cl]_2$ with $(CH_3O)_3P$ in C_6D_6 at 28 °C.

Table IV. Relative Concentrations of Rhodium Species[a] Determined from ^1H and ^{31}P NMR Data from the Titration of $[Rh(COD)Cl]_2$ + $(CH_3O)_3P$ in Benzene at Room Temperature

L/Rh	$[Rh(COD)Cl]_2$	$(COD)RhCl[P(CH_3O)_3]$	$(COD)Rh_2Cl_2[P(CH_3O)_3]_2$	$[P(CH_3O)_3]_2Rh_2Cl_2[P(CH_3O)_3]_2$	$Rh[P(CH_3O)_3]_3Cl$
0.5	54	27	19		
1.0	12	54	27	7	
1.5	2	41	16	38	3
2.0		25	7	50	8
2.5		10	2	38	50
3.0				4	96

[a] Estimate based on integrated areas and intensities from both ^1H and ^{31}P NMR data; accuracy is within ±5%.

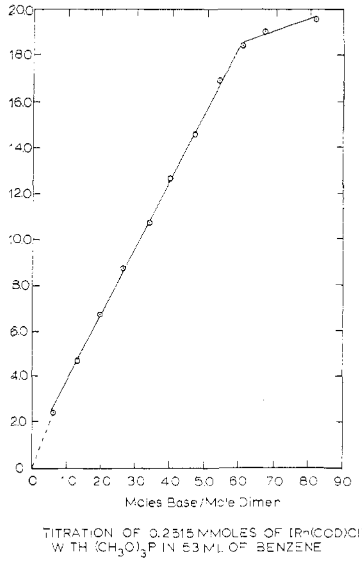
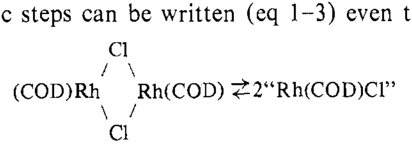


Figure 5. Titration of 0.2515 mmol of $[Rh(COD)Cl]_2$ with $(CH_3O)_3P$ in 53 mL of benzene.

in Table III. As observed in an earlier report, the resonances for the dimers with cis phosphites appear as triplets.[31] When L/Rh = 3.0, however, the phosphite region consists only of a distinct triplet and a doublet of half-intensity at 3.71 and 3.55 ppm, respectively. These features are expected from $[P(OCH_3)_3]_3RhCl$ as a result of the "virtual coupling" of the two trans phosphorus atoms. In the complex, the protons on the phosphites trans to each other are split into a triplet, while the doublet results from the phosphite trans to the chloride. The spectra for L/Rh > 3.0 in the phosphite methyl proton region consist only of a broad singlet. The distinct doublet of free $(CH_3O)_3P$ is not observed even when L/Rh = 5.5. The spectra indicate a system in near fast exchange.

The ^{31}P NMR data enabled us to monitor the various phosphite species formed in solution, while the ^1H NMR data allowed us to follow the various COD species. Thus, the relative concentration of each rhodium species at a given ratio of L/Rh could be estimated using the integrated intensities of both the ^1H NMR and ^{31}P NMR data. (Whenever possible, data from both ^1H and ^{31}P NMR spectra served as mutual checks.) Intensities of ^{31}P NMR resonances are proportional to the number of species in a proton-decoupling experiment only if differences in T_1 and nuclear Overhauser effects are taken into account. A recent study of the $^{31}P\{^1H\}$ nuclear Overhauser effect for several phosphorus compounds shows a 10% enhancement of the signal intensity for trimethyl phosphite.[33] With similar enhancements for the various phosphite complexes under consideration, one can obtain fair estimates of the relative concentrations of the various phosphite species. The estimates for the relative concentrations of rhodium species at each point in the titration of 0.10 M $[Rh(COD)Cl]_2$ with $(CH_3O)_3P$ derived from both the ^{31}P and ^1H NMR data are shown in Table IV. A recent report[19] of $^{31}P\{^1H\}$ NMR data for $Rh_2Cl_2[P(OCH_3)_3]_4$ corresponds closely to the coupling constant and chemical shift obtained in this study (see Table II). The ^{31}P NMR chemical shifts and J_{Rh-P} reported[19] for $[P(OPh)_3]_2Rh_2Cl_2(COD)$ and $Rh(COD)Cl(PPh_3)$ compare favorably with those found in this study for the analogous trimethyl phosphite complexes.

3. Calorimetric Studies. The calorimetric titration curve for $[Rh(COD)Cl]_2$ plus added amounts of $(CH_3O)_3P$ in benzene at room temperature is shown in Figure 5 as a plot of heat evolved vs. moles of base per moles of Rh dimer. The data show that the reaction of $(CH_3O)_3P$ with $[Rh(COD)Cl]_2$ is essentially complete for L/Rh = 3.0, to form $[(CH_3O)_3P]_3RhCl$. The total enthalpy change measured in this reaction is the sum of the enthalpy to cleave the bis(cyclooctadiene) dimer, coordinate a phosphite to the COD monomer, and displace the COD molecule by two phosphites. These thermodynamic steps can be written (eq 1–3) even though the



$$(COD)Rh(\mu\text{-}Cl)_2Rh(COD) \rightleftarrows 2\text{"}Rh(COD)Cl\text{"} \qquad (1)$$

$$\text{"}Rh(COD)Cl\text{"} + (CH_3O)_3P \rightleftarrows Rh(COD)[(CH_3O)_3P]Cl \qquad (2)$$

$$Rh(COD)PCl + 2(CH_3O)_3P \rightleftarrows Rh[(CH_3O)_3P]_3Cl + COD \qquad (3)$$

Table V. Infrared Data for the Titration of $[Rh(CO)_2Cl]_2$ + $(CH_3O)_3P$ in C_6H_6 at Room Temperature (See Figure 6)

L/Rh[a]	obsd ν(CO), cm^{-1}	lit. ν(CO), cm^{-1} [g]	possible species
0 (–)	2108 s,[h] 2092 vs, 2035 vs, 2002 w	2106 s, 2090 vs, 2034 vs, 2002 w[b]	$Rh_2Cl_2(CO)_4$
		2103 s, 2088 vs, 2032 vs, 2002 w[c]	
0.5 (· ·—· ·)	2107 vw(other bands masked)	2106, 2090, 2034[b]	trace of $Rh_2Cl_2(CO)_4$
	2094 vs, 2025 vs, 2000 m	2089 s, 2022 s, 2000 s[d]	$Rh_2Cl_2(CO)_3[P(CH_3O)_3]$
		2089 vs, 2028 vs, 2021 s[e]	
	2094 vs, 2000 m	2094 vs, 2003 vs[d]	*cis*-$RhCl(CO)_2[P(CH_3O)_3]$
		2092 s, 2003 s[c]	
	2025 vs, 2011 vs	2020 sh, 2012 vs[e]	$Rh_2Cl_2(CO)_2[P(CH_3O)_3]_2$
	2011 vs		*trans*-$RhCl(CO)[P(CH_3O)_3]_2$
	1966 w		^{13}C isomers
1.5 (· · ·)	2010 vs		$Rh(CO)[P(CH_3O)_3]_2Cl$
	1968 w		$RhCl(CO)[P(CH_3O)_3]_2$
			^{13}C isomers
2.0 (- - -)	2010 s	2014[e]	$Rh(CO)[P(CH_3O)_3]_2Cl$
	1980 br	1975[f]	$\{Rh(CO)[P(CH_3O)_3]_4\}^+Cl^-$
3.0 (·–·)	2010 m		$Rh(CO)[P(CH_3O)_3]_2Cl$
	1980 br	1975[f]	$\{Rh(CO)[P(CH_3O)_3]_4\}^+Cl^-$
3.5 (·—·)	2010 w		$Rh(CO)[P(CH_3O)_3]_2Cl$
	1980 br	1975[f]	$\{Rh(CO)[P(CH_3O)_3]_4\}^+Cl^-$
4.0 (—·—)	1980 br	1975[f]	$\{Rh(CO)[P(CH_3O)_3]_4\}^+Cl^-$

[a] Ratio of moles of trimethyl phosphite to moles of rhodium. The concentration of $[Rh(CO)_2Cl]_2$ in C_6H_6 is 0.042 M. [b] Reference 38. [c] Reference 39. [d] Reference 40. [e] Reference 41. [f] Reference 42. [g] Literature references include both phosphine and phosphite species and should be used as a rough guide. [h] Abbreviations: vs, very strong; m, medium; w, weak; br, broad; sh, sharp.

actual reaction mechanisms are more involved. The dimer cleavage enthalpy (eq 1), which includes differences in benzene solvation energy, has previously been determined to be 12.6 kcal/mol of dimer.[34] The complexity of the reactions of the dimer does not allow a value for the reaction in eq 2 to be derived from the data. However, the enthalpy of this step can be estimated using the E and C equation:

$$-\Delta H = E_A E_B + C_A C_B$$

The values for the acid "Rh(COD)Cl" ($E_A = 4.9$, $C_A = 1.25$)[34] and the values for the base $(CH_3O)_3P$ ($E_B = 1.03$, $C_B = 5.99$)[35] yield an enthalpy of –12.5 kcal/mol of monomer. This calculated value does not include the effects of π back-bonding (including a synergistic enhancement of σ bonding), which should result in an additional enthalpic contribution of –5 to –8 kcal/mol of monomer as observed for similar systems.[34,36,37] If an intermediate value of –6.5 ± 1.5 kcal/mol of monomer is assumed, the total enthalpy for eq 2 is –38.0 ± 3.0 kcal. The calorimetric data show a total exothermic heat of –73.3 kcal/mol of $[Rh(COD)Cl]_2$ at L/Rh = 3.0 to form $Rh[(CH_3O)_3P]_3Cl$. The resulting enthalpy for the displacement of COD by two phosphites from $Rh(COD)[(CH_3O)_3P]Cl$ (eq 3) is –24.0 ± 1.0 kcal/mol of monomer. If this value is not much different than the enthalpy to displace COD from the dimer $[Rh(COD)Cl]_2$, then the enthalpies to form either $Rh(COD)[(CH_3O)_3P]Cl$ or $Rh_2(COD)[(CH_3O)_3P]_2Cl_2$ from $[Rh(COD)Cl]_2$ are similar (sum of eq 1 and 2, –25.4 ± 1.0 kcal/mol vs. –24.0 ± 1.0 kcal/mol). This observation provides an enthalpic explanation for the multiple reaction pathways observed for this system.

Titration of $[Rh(CO)_2Cl]_2$ with Trimethyl Phosphite. 1. Infrared Studies. The titration of 0.042 M solutions of $[Rh(CO)_2Cl]_2$ in benzene with incremental 1-mol equiv additions of freshly distilled trimethyl phosphite was followed via infrared spectroscopy. The infrared spectra of all solutions were run within 2–3 min of mixing. The infrared absorptions in the region 1950–2200 cm^{-1} are shown in Figure 6. Tentative assignments of the observed carbonyl stretches to various species in solution are shown in Table V.

A previous report of the X-ray crystal structure of $Rh_2(CO)_4Cl_2$[41] has established the C_{2v} symmetry of this molecule. If we assume this structure in solution, group theory predicts three infrared-active carbonyl stretching vibrations (a_1, b_1, b_2).[43] Three strong bands are observed at 2108, 2092, and 2035 cm^{-1}, respectively, in benzene solution (see Table V). The weak band at 2002 cm^{-1} has been assigned to a naturally occurring ^{13}CO species.[38] Thus, the spectra are consistent with C_{2v} symmetry. The Cotton–Kraihanzel parameters previously calculated[38] for this molecule have been used to estimate the splittings expected for various isomers of $[RhCl(CO)L]_2$ complexes.[31]

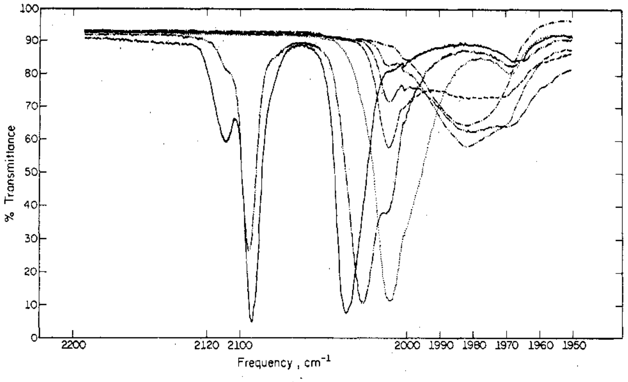


Figure 6. Infrared behavior of $CO_4Rh_2Cl_2$ + $(CH_3O)_3P$ in C_6H_6 (see Table V for symbols and L/Rh ratios).

On the basis of an analysis of the infrared spectral evidence shown in Table V, it is obvious that with the addition of 1 mol of $(CH_3O)_3P$ to $[Rh(CO)_2Cl]_2$ in benzene at room temperature, more than just simple substitution of a carbonyl ligand by phosphite occurs in solution. In fact, the data obtained lends support to some observations on reactions of dimethylphenylphosphine with $[Rh(CO)_2Cl]_2$ reported[40] while this work was being completed. It is suggested that the following reactions may be occurring in solution, thus giving rise to all the species observed at L/Rh = 0.5 (shown in Table V):

$$RhCl_2(CO)_4 \xrightleftharpoons{+P(CH_3O)_3,\ -CO} Rh_2Cl_2(CO)_3[P(CH_3O)_3] \xrightleftharpoons{+P(CH_3O)_3,\ -CO} Rh_2Cl_2(CO)_2[P(CH_3O)_3]_2 \xrightleftharpoons{+2P(CH_3O)_3} 2RhCl(CO)[P(CH_3O)_3]_2 \quad (4)$$

$$Rh_2Cl_2(CO)_4 \xrightleftharpoons{+2P(CH_3O)_3} 2RhCl(CO)_2[P(CH_3O)_3] \xrightleftharpoons{+2P(CH_3O)_3,\ -2CO} 2RhCl(CO)[P(CH_3O)_3]_2 \quad (5)$$

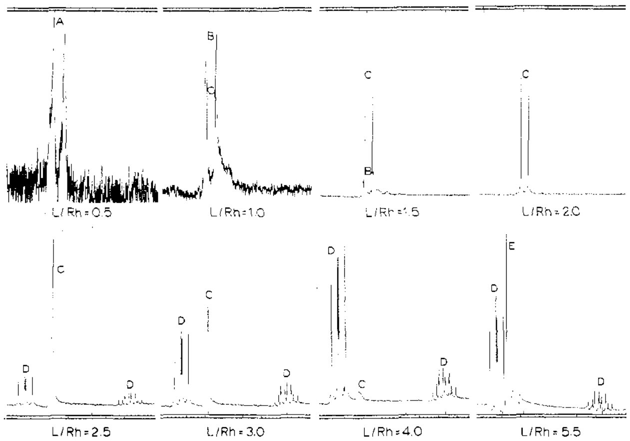


Figure 7. $^{31}P\{^1H\}$ NMR titration of 0.10 M $[Rh(CO)_2Cl]_2$ with $(CH_3O)_3P$ in C_6H_6 at 28 °C.

Since the bands for some of these complexes may overlap, it is difficult to distinguish from the present data which complexes exist in solution. One can offer tentative conclusions at best at low phosphite-to-rhodium ratios. Nevertheless, the existence of complexes analogous to those proposed in eq 4 and 5 has been documented in the literature.[39,40,44]

During the early stages of the titration with trimethyl phosphite, there is evidence for the existence in solution of both the mono- and bis(phosphite) dimers as well as some monomeric complexes. When L/Rh = 1.5, the infrared spectrum shows one major carbonyl absorption (the weak absorption at 1968 cm^{-1} can be attributed to the ^{13}CO isomer). In accordance with eq 4 and 5, this absorption can be assigned to *trans*-$Rh(CO)[P(OCH_3)_3]_2Cl$. The π-acceptor nature of the phosphite ligands in the complex decreases the π donation to the cis carbonyl by the rhodium, leading to a higher frequency infrared absorption than in the analogous phosphine complexes.[39,45]

With increasing concentration of added phosphine, one witnesses a decrease in intensity of the strong band attributed to *trans*-$Rh(CO)[P(OCH_3)_3]_2Cl$. A broad absorption at ~1980 cm^{-1} becomes the dominant feature in the carbonyl region for L/Rh $\geq$ 3.0. The species attributed to this absorption was determined to be $\{Rh[P(OCH_3)_3]_4(CO)\}^+$ from evidence in the $^{31}P\{^1H\}$ NMR titration experiment. A report[42] of the infrared absorption for a mull of solid $\{Rh[P(OCH_3)_3]_4(CO)\}[B(C_6H_5)_4]$ supports this assignment.

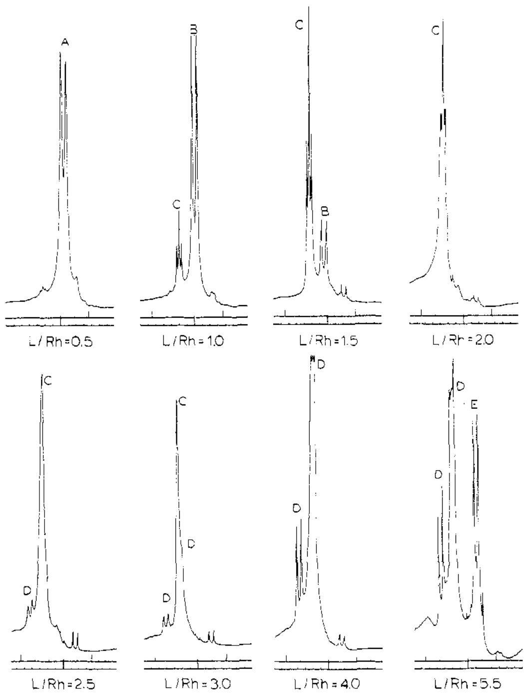


Figure 8. 220-MHz ^1H NMR titration of $[Rh(CO)_2Cl]_2$ with $(CH_3O)_3P$ in C_6D_6 at 28 °C.

2. $^{31}P\{^1H\}$ and ^1H NMR Studies. Results obtained from $^{31}P\{^1H\}$ NMR data confirmed the complexity of the $[Rh(CO)_2Cl]_2$ and trimethyl phosphite system. The $^{31}P\{^1H\}$ and 220-MHz ^1H NMR spectra obtained for the titration of 0.10 M $[Rh(CO)_2Cl]_2$ in benzene with freshly distilled $(CH_3O)_3P$ are shown in Figures 7 and 8, respectively, and are summarized in Table VI. The discernible doublet in the broad absorptions for L/Rh = 0.5 in the $^{31}P\{^1H\}$ NMR spectrum is assignable to $Rh_2(CO)_3[(CH_3O)_3P]Cl_2$ due to its large and distinct J_{Rh-P} = 277.9 Hz. The sharp doublet in the ^1H NMR spectrum is also attributed to the mono(phosphite) dimer. From the magnitudes of J_{Rh-P} = 195 Hz and J_{Rh-P} = 272 Hz shown in the $^{31}P\{^1H\}$ spectrum for L/Rh = 1.0, the two doublets observed in Figure 7 have been assigned to monomeric and dimeric species, respectively. The sharp doublet agrees well with the previous report[19] of J_{Rh-p} = 195.0 Hz for $RhCl(CO)[P(OCH_3)_3]_2$. A comparison of the observed coupling constants and ^{31}P NMR chemical shifts with those obtained for analogous compounds reported in the literature is summarized in Table II. The ^1H NMR spectrum at L/Rh = 1.0 shows a triplet at 3.52 ppm which can be assigned to *trans*-$Rh(CO)[P(OCH_3)_3]_2Cl$. The broad doublet in the $^{31}P\{^1H\}$ NMR spectrum (labeled B in Figure 7) and the doublet in the ^1H NMR spectrum can be assigned to a mixture of *cis*- and predominantly *trans*-$Rh_2(CO)_2[P(OCH_3)_3]_2Cl_2$. At L/Rh = 2.0, the dominant species in solution is *trans*-$Rh(CO)[P(OCH_3)_3]_2Cl$, as indicated by both $^{31}P\{^1H\}$ and ^1H NMR spectra. When L/Rh = 2.5, the *trans*-$Rh(CO)[P(OCH_3)_3]_2Cl$ resonances have collapsed to broad singlets in both spectra. New resonances are also observed at this concentration which become the dominant spectral features at L/Rh = 4.0. However, no resonances attributable to free $(CH_3O)_3P$ are observed. The $^{31}P\{^1H\}$ NMR spectrum of the new species has a doublet of doublets at low field (−146.5 ppm) with an integrated intensity of 3 and a complicated multiplet of 12 peaks at high field (−81.0 ppm) with an integrated intensity of 1. The combined $^{31}P\{^1H\}$ NMR and IR data suggested the presence of $\{Rh(CO)[P(OCH_3)_3]_4\}^+$ in solution. In analogy to the structure proposed[46] for the similar cation $\{Rh(CO)[As(CH_3)_2C_6H_5]_4\}^+$, a trigonal bipyramid with axial CO is proposed for $\{Rh(CO)[P(OCH_3)_3]_4\}^+$. Since the $^{31}P\{^1H\}$ NMR spectrum is second order in nature, "first-order" chemical shifts and coupling constants taken from the observed spectrum at L/Rh = 4.0 were used, assuming an AB_3X pattern, to compute a theoretical spectrum.[47] The theoretical spectrum fit the observed spectrum extremely well in both peak positions and intensities. An iterative calculation, using the restrictions of an AB_3X pattern, was performed to obtain a set of chemical shifts and coupling constants from the experimental peaks (values appear in parentheses in Table VI).

The ^1H NMR spectrum at L/Rh = 4.0 contains a doublet at 3.73 ppm which is one-third the intensity of an overlapping multiplet at 3.57 ppm. These resonances are assigned to the axial and equatorial phosphite methyl protons, respectively.

At L/Rh = 5.5, the resonance for free trimethyl phosphite is observed in both the $^{31}P\{^1H\}$ and ^1H NMR spectra. The observation of a nonfluxional, nonexchanging rhodium phosphite carbonyl cation on the NMR time scale is surprising. This phenomenon could be a result of tight ion pairing to the chloride in the benzene solvent. The ^1H NMR spectrum of $\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$ at 38 °C in $CDCl_3$ was found to be a broad singlet at 3.56 ppm,[42] indicating a fluxional or exchanging cation. If the temperature difference is not the major cause of this difference in observed proton resonances,

Table VI. $^{31}P\{^1H\}$ and ^1H (220-MHz) NMR Data for the Titration of $[Rh(CO)_2Cl]_2$ + $(CH_3O)_3P$ in C_6D_6 at 28 °C

L/Rh[a]	$\delta(^{31}P\{^1H\})$	J_{Rh-P}, Hz	J_{P-P}, Hz	$\delta(^1H)$	J_{P-H}, Hz	species	symbol[b]
0.5	−126.7 br, d[e]	277.9		3.33 d	12.5	$Rh_2(CO)_6[P(CH_3O)_3]Cl_2$	A
1.0–1.5	−128.9 br, d	272.2		3.38 d	12.6	$Rh_2(CO)_2[P(CH_3O)_3]_2Cl_2$	B
	−129.0 sh, d	195.0		3.52 t	6.1	$Rh(CO)[P(CH_3O)_3]_2Cl$	C
2.0	−128.9 d	198.0		3.58 t	5.8	$Rh(CO)[P(CH_3O)_3]_2Cl$	C
2.5	−129.5 br, s			3.60 s		$Rh(CO)[P(CH_3O)_3]_2Cl$[c]	C
	−146.5 dd	188.0	161.0			eq, $\{Rh(CO)[P(OCH_3)_3]\}^+$	D
	−81.1 m	105.0	162.2	3.74 d	11.2	ax	C
3.0	−129.9 br, s					$Rh(CO)[P(CH_3O)_3]_2Cl$[c]	
	−146.6 dd	188.6	161.4	3.60 s		eq, $\{Rh(CO)[P(OCH_3)_3]_4\}^+$	D
	−80.9 m	105.0	162.2	2.74 d	11.2	ax	C
4.0	~−134.0 br, s					$Rh(CO)[P(CH_3O)_3]_2Cl$[c]	
	−146.5 (−146.5) dd[d]	188.0 (188.6)	161.0 (161.7)	3.58 m	~4.7	eq, $\{Rh(CO)[P(OCH_3)_3]_4\}^+$	D
	−81.0 (−81.2) m	105.0 (104.5)	162.2 (161.7)	3.73 d	11.2	ax	
5.5	−146.2 dd	189.7	164.1	3.58 m	~5.1	eq, $\{Rh(CO)[P(OCH_3)_3]_4\}^+$	D
	−81.4 m	105.5	163.7	3.72 d	11.1	ax	
	−140.2 s			3.31 d	10.3	$(CH_3O)_3P$	E

[a] Ratio of moles of trimethyl phosphite to moles of rhodium. The concentration of $[Rh(CO)_2Cl]_2$ in C_6D_6 is 0.10 M. [b] See Figures 7 and 8. [c] Average resonance for exchanging species. [d] Values in parentheses are obtained from LAOCN3 iteration steps.[47] The root-mean-square error between the values calculated and observed is 2.2 Hz. [e] Abbreviations: sh, sharp; d, doublet; s, singlet; m, multiplet, br, broad.

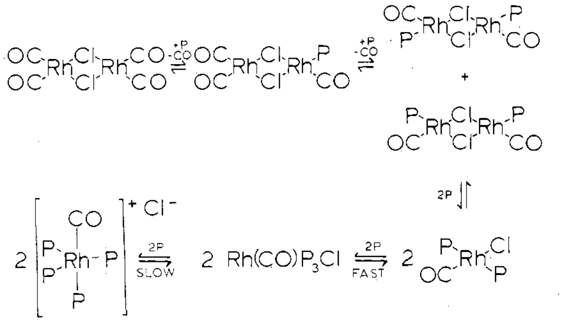


Figure 9. Proposed reaction scheme of $[Rh(CO)_2Cl]_2$ with $(CH_3O)_3P$ in benzene at room temperature. "P" represents $(CH_3O)_3P$.

then the presence of the polar solvent and the large anion aids the fluxional or exchange process in this latter case.

The overall agreement of the infrared and NMR data supports the reaction scheme in Figure 9. The collapse of the resonances for *trans*-$Rh(CO)[P(OCH_3)_3]Cl$ and the distinct resonances of $\{Rh(CO)[P(OCH_3)_3]_4\}^+$ at L/Rh > 2.0 indicate a possible rapid preequilibrium to form a tris(phosphite)rhodium carbonyl. The equilibrium would cause an averaging of the resonances of the Rh species and $(CH_3O)_3P$. The step to form $\{Rh(CO)[P(OMe)]_4\}^+$, however, is most likely a kinetically slow equilibrium on the NMR time scale, leading to the observed distinct resonances.

In view of the complex chemistry found for $[Rh(COD)Cl]_2$ reacting with trimethyl phosphite in benzene, calorimetric investigation of the equally complex $[Rh(CO)_2Cl]_2$ system was not undertaken. This latter system is expected to be further complicated by variation in the partial pressure of CO over the solvent.[40]

Conclusions

From the results of this study, the reaction of $[Rh(COD)Cl]_2$ at room temperature with $P(OCH_3)_3$ in C_6H_6 differs from that observed previously for reaction with $P(OC_6H_5)_3$ in CH_2Cl_2[11] and roughly parallels in part that recently reported for $[Rh(COD)Cl]_2$ plus $PCl_x(C_6H_5)_{3-x}$ for $x = 0$–3 in $CHCl_3$.[32] Apparently, then, the trimethyl phosphite ligand possesses the necessary combination of steric and electronic properties to cause simultaneous bridge cleavage and olefin displacement in $[Rh(COD)Cl]_2$ in benzene as shown in Figure 3.

In reactions with $[Rh(CO)_2Cl]_2$, trimethyl phosphite will preferentially displace one carbon monoxide at each rhodium atom and then proceed to cleave the dimer. Further addition of base will cause the displacement of chloride rather than CO from *trans*-$Rh(CO)[P(OCH_3)_3]_2Cl$. It is interesting that no similar phosphite species are formed in the $[Rh(CO)_2Cl]_2$ and $[Rh(COD)Cl]_2$ reaction systems. It would be of interest to further investigate what delicate balance of steric, electronic, and environmental factors determines whether substitution to give dimers or bridge cleavage to give monomers is dominant. Such competitive reactions have recently been reported for $[Rh(CO)_2Cl]_2$ reacting with dimethylphenylphosphine[40] and for $[Rh(C_8H_{14})_2Cl]_2$ reacting with tertiary phosphines.[48]

It should be noted that if the titrations are done in the presence of air (O_2), extensive oxidation of $(CH_3O)_3P$ to $(CH_3O)_3PO$ occurs and very different and complex NMR spectra result.

Futher investigation of the properties of the cationic species formed in the presence of excess phosphite in both these systems, as well as their reaction chemistry, would also be of interest.

Acknowledgment. The authors acknowledge the generous support of this research by the National Science Foundation, a NDEA graduate fellowship to M.L.W., and a University of Illinois fellowship to M.J.D.

Registry No. $[Rh(COD)Cl]_2$, 12092-47-6; $[Rh(CO)_2Cl]_2$, 14523-22-9; $(CH_3O)_3P$, 756-79-6; $Rh(CO)Cl[P(OCH_3)_3]_2$, 32628-33-4; $Rh(COD)Cl[P(OCH_3)_3]$, 66712-35-4; $[P(OCH_3)_3]_2RhCl_2Rh(COD)$, 66712-20-7; $Rh_2Cl_2[P(OCH_3)_3]_4$, 49634-27-7; $Rh[P(OCH_3)_3]_3Cl$, 55000-87-8; $Rh_2(CO)_3[P(OCH_3)_3]Cl_2$, 49634-35-7; $Rh_2(CO)_2[P(OCH_3)_3]_2Cl_2$, 41612-78-6; $\{Rh(CO)[P(OCH_3)_3]_4\}^+Cl^-$, 68832-76-8.

Supplementary Material Available: Data for the calorimetric titration (1 page). Ordering information is given on any current masthead page.

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The Interaction of Hexaphenylcarbodiphosphorane with the Trimethylplatinum(IV) Cation

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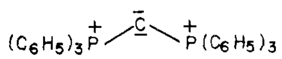
Treatment of $Me_3Pt^+X^-$ ($X^- = PF_6^-$, $OSO_2CF_3^-$, or I^-) with $Ph_3P{=}C{=}PPh_3$, a bis(ylide), gives $[HC(PPh_3)_2]X$, an ortho-metalated ylide–platinum(II) species, and methane. ^{13}C- and ^2H-labeling studies show that methane is formed by the combination of platinum methyl groups and ortho aromatic ylide hydrogen atoms. Methyl group transfer to an aromatic ring of an ylide ligand is also observed. This reaction is an example of ortho metalation in a high-valent transition-metal complex, which continues until all the platinum methyl groups are eliminated.

Introduction

There is considerable physical and chemical interest in bis(phosphoranylidene)methane molecules, such as **1** and **2**,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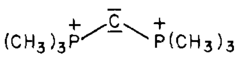
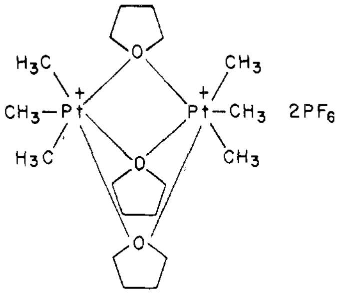

2

with low coordination numbers about the central carbon atom.[2,3] These double ylides have given new insights to the phosphorus–carbon bond with their unusual bent structures.[4] Besides having two different types of molecules in the unit cell with PCP valence angles of 143.8 and 130.1°, **1** shows the phenomenon of triboluminescence (i.e., pressure-induced emission of light from crystals[5]). Chemical reactions of **1** and **2** show a variety of complex ligand species[2] and reactions with organometallic compounds.[6,7] This paper describes yet another facet of **1** in its interaction with the trimethylplatinum cation.

Results

Although bis(triphenylphosphoranylidene)methane (or hexaphenylcarbodiphosphorane), $C(PPh_3)_2$, does interact directly with trimethyliodoplatinum(IV) tetramer, $[(CH_3)_3PtI]_4$, the reaction is sluggish and incomplete. Consequently, the iodoplatinum complex is first metathesized by treatment with silver hexafluorophosphate, $AgPF_6$, or silver trifluoromethanesulfonate, $AgOSO_2CF_3$ (AgOTf), in tetrahydrofuran (THF). This makes the platinum atom more accessible and allows ready substitution of the noncoordinating PF_6^- or weakly coordinating OTf^- anions.

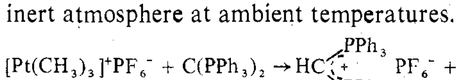
Colorless trimethylplatinum hexafluorophosphate coordinates 1.5 THF molecules per trimethylplatinum unit as evidenced by ^1H NMR integration and thus may possibly exist as a dicationic dimer, **3**, to achieve the characteristic Pt(IV) hexacoordination.[8] The white trifluoromethanesulfonate (triflate) complex, however, does not coordinate solvent and thus probably exists as a tetramer, $[(CH_3)_3PtOTf]_4$, with μ_3-bridging OSO_2CF_3 groups similar to $[(CH_3)_3PtClO_4]_4$.[9]



3

The trimethylplatinum moiety remains intact after metathesis under the conditions employed in this work since the solvated PF_6^- complex is readily converted to $\{(CH_3)_3[(CH_3)_3P]_3Pt\}PF_6$[10] in high yield by addition of trimethylphosphine. The triflate complex is similarly converted to trimethyltris(pyridine)platinum(IV) triflate, $[(CH_3)_3(py)_3Pt]OTf$, by the dissolution of $[(CH_3)_3PtOTf]_4$ in pyridine.[11]

Trimethylplatinum(IV) and Hexaphenylcarbodiphosphorane. Colorless solutions of solvated $[(CH_3)_3Pt]^+PF_6^-$ in THF are treated with 1, 2, 3, or 4 equiv of $C(PPh_3)_2$ in THF under an inert atmosphere at ambient temperatures. As shown in eq 1,



$$[Pt(CH_3)_3]^+PF_6^- + C(PPh_3)_2 \rightarrow HC\overset{+}{\genfrac{}{}{0pt}{}{\nearrow PPh_3}{\searrow PPh_3}}\ PF_6^- + \text{red solution} + CH_4 \qquad (1)$$

the products of the reaction are methane, $[HC(PPh_3)_2]PF_6$,

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