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A Study of Substitution Reactions in $Rh_6(CO)_{16}$ Using Simple and Polymer Bound Phosphine Ligands

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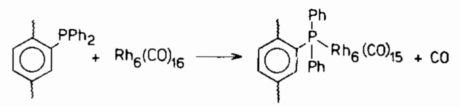
Substitution of phosphines for CO on $Rh_6(CO)_{16}$ has been studied. Controlled addition of triphenylphosphine or of tris-(2-diphenylphosphinoethyl)phosphine to $Rh_6(CO)_{16}$ resulted in displacement of 1–3 carbonyl ligands to form compounds of general formula $Rh_6(CO)_{16-n}L_n$. Increased substitution to $n > 6$ produced unstable materials which were difficult to characterize. These reactions are compared with the reaction of $Rh_6(CO)_{16}$ with phosphine substituted polystyrene to produce polymer bound Rh_6 clusters. Spectroscopic evidence for a very close similarity between the polymer bound rhodium species and the homogeneous phase complexes is presented.

Introduction

Several studies of substitution reactions with polynuclear rhodium carbonyls have been reported. Both $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ appear to undergo substitution of carbonyls by other ligands with retention of the integrity of the metal cluster framework. Substitution by π-acid phosphines and phosphites occurs to produce compounds formulated as $Rh_6(CO)_7L_9$ and $Rh_6(CO)_{10}L_6$ on the hexanuclear cluster,[1,2] while substitutions on the tetranuclear cluster have been reported to yield the complexes $Rh_4(CO)_{10}L_2$, $Rh_4(CO)_9L_3$, and $Rh_4(CO)_8L_4$.[2] Substitution by halides and pseudohalides into $Rh_6(CO)_{16}$ seems to be largely limited to the monosubstituted product $[Rh_6(CO)_{15}X]^-$ and one stable disubstituted product $[Rh_6(CO)_{14}(CN)_2]^{2-}$.[3,4] The limited substitution by halides is attributed to the buildup of electron density on the metal atoms due to the donor properties of the X^- group. Complexes in which an acyl group substitutes for one carbonyl ligand have also been isolated.[5] These are presumably intermediates in hydroformylation reactions catalyzed by the rhodium cluster carbonyls.

We have been interested in catalytic behavior of rhodium cluster compounds as heterogenized catalysts under conditions leading to limited substitution and partial or complete decarbonylation of the cluster carbonyl.[6] Collman and coworkers recently communicated a study of the binding of $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ to phosphine modified polystyrene to give materials which display catalytic activity.[7] The clusters are apparently bound to the polystyrene surface *via* a simple ligand substitution reaction in which phosphines attached to the polymer replace carbonyls of the cluster compound as in reaction 1.



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In order to better understand the reactions of rhodium cluster carbonyls with these and other support materials, we have undertaken a study of limited substitution reactions of phosphine ligands on the hexarhodium cluster compound in solution. Earlier studies of phosphine substitutions on $Rh_6(CO)_{16}$ reported complexes in which a minimum of six phosphine ligands were substituted for CO. We report here the evidence for formation of products of formula $Rh_6(CO)_{16-n}L_n$ where n = 1, 2, or 3; and we compare the properties of these products, formed in solution, with those of Rh_6 clusters bound to modified polystyrene.

Experimental

Preparation of $Rh_6(CO)_{16}$

Rhodium chloride trihydrate was purchased from Englehard Industries and was used to prepare $Rh_2(CO)_4Cl_2$ according to the method of McCleverty and Wilkinson.[8] This dimeric species was purified by recrystallization prior to use in the atmospheric pressure synthesis of $Rh_6(CO)_{16}$ as described by Chini and Martinengo.[9,10]

Phosphine Ligands

All phosphines were purchased from Pressure Chemical Company. They were generally used as received

TABLE I. Reactions of Phosphines with $Rh_6(CO)_{16}$[a].

Phosphine	Ligand Quantity (mg)	Product	%C[b]	%H[b]	%P[b]	%Rh[b]	%Cl[b]
$P(C_6H_5)_3$	26.2 (0.1 mmol)	$Rh_6(CO)_{14}[P(C_6H_5)_3]_2$	40.60 (39.1)	2.89 (1.95)	4.38 (4.04)	42.83 (40.3)	–
$P(C_6H_5)_3$	78.6 (0.3 mmol)	$Rh_6(CO)_{13}[P(C_6H_5)_3]_3$	45.82 (45.5)	2.98 (2.54)	4.94 (5.26)	35.08 (34.9)	–
$P(C_6H_5)_3$	157.2 (0.6 mmol)						
$P(C_6H_5)_3$	235.8 (0.9 mmol)	$Rh(CO)[P(C_6H_5)_3]_2Cl$[d]	63.88 (64.2)	4.52 (4.34)	9.21 (8.90)	–	5.92 (5.13)
TP[c]	67.0 (0.1 mmol)	$Rh_6(CO)_{13}(TP)$	40.61 (40.0)	3.36 (2.54)	–	–	–
TP[c]	134.0 (0.2 mmol)	$Rh_6(CO)_{10}(TP)_2$					

[a] All reactions used 106.6 mg (0.1 mmol) of $Rh_6(CO)_{16}$. [b] Analyses by Galbraith Laboratories, Knoxville, Tennessee. Calculated values are in parentheses. [c] TP is tris(2-diphenylphosphinoethyl)phosphine (Tetraphos-II). [d] Product obtained from reaction in chloroform solution is identical to product originally obtained by McCleverty and Wilkinson by an alternative route.[8]

since further purification produced no evidence for increased yield or purity of the reaction products.

Preparation of Modified Polystyrene

The phosphine modified polystyrene was prepared by bromination of the polymer (Biobeads 5x-2, 2% crosslinked) with bromine and ferric bromide followed by treatment with butyl lithium and chlorodiphenyl phosphine according to methods described in the literature to produce phosphine substituted polystyrene.[7, 11]

Reactions of $Rh_6(CO)_{16}$ with Phosphines

Reactions of triphenylphosphine with the rhodium carbonyl to obtain the limited substitution products were achieved by dropwise addition of the indicated quantity (Table I) of the phosphine in 20 ml of benzene to 0.1 mmol of the rhodium carbonyl in 80 ml of benzene at reflux temperature. Addition was carried out over a period of an hour or more under a continuous flow of dry nitrogen. The dark red-black reaction solution was then cooled to room temperature and filtered to remove unreacted $Rh_6(CO)_{16}$. Solvent was removed under vacuum and the remaining solid was washed with Skelly B. The reaction of $Rh_6(CO)_{16}$ with tris(2-diphenylphosphinoethyl)phosphine (tetraphos II) was carried out in a similar manner except that chloroform was used as solvent rather than benzene.

All products were unstable to air and water. It was discovered that long term storage was best attained by placing the product under alkanes (in which the samples are insoluble) and keeping them refrigerated under N_2 in a stoppered bottle. All products decomposed before melting.

Reaction of Modified Polystyrene with $Rh_6(CO)_{16}$

The phosphine modified polystyrene (0.53 g) was treated with $Rh_6(CO)_{16}$ (0.102 g) in 25 ml THF and the mixture was covered in an inert atmosphere and stirred occasionally for three weeks. At the end of this period a grey–black insoluble material was filtered, washed repeatedly, vacuum dried, and stored under dry nitrogen.

Carbonylation of Polymer Supported Cluster

The black powder obtained by addition of $Rh_6(CO)_{16}$ to the modified polymer was treated with CO at pressures from 1–100 atm. After carbonylation the powder was placed in refluxing chloroform for about one hour and filtered. The chloroform filtrate was reduced in volume and an infrared spectrum was taken to look for evidence of dissolved metal carbonyl species.

IR Spectra

All solution spectra were obtained using a Beckman IR-9 spectrophotometer with resolution and accuracy of about 1 cm^{-1}. The spectrometer was calibrated periodically in the $\nu(CO)$ region using deuterium chloride vapor frequencies. Solid spectra of nujol mull or KBr disc samples generally were taken using the same spectrometer settings as for solutions. Some carbonylation studies of the polymer supported rhodium cluster compound were conducted using jointed ir gas cells in which a pellet of the polymer material was suspended inside the cell. In other cases the polymer material was simply deposited on the inside of the gas cell window by evaporation of solvent from a slurry of polymer in the appropriate solvent. For these gas cell samples it was usually necessary to increase the spectrometer slit width to obtain sufficient signal level. Resolution in these cases is 3–5 cm^{-1}.

Results

Solution Substitution Reactions

The dropwise addition of solutions of tertiary phosphine ligands to a benzene slurry of $Rh_6(CO)_{16}$ in 1 : 1 and 3 : 1 molar ratios of ligand to rhodium carbonyl produced products of limited substitution which could then be separated from the parent carbonyl. More rapid addition of the ligand appeared to lead to products of greater substitution which were unstable and rapidly broke down to give impure materials. The products of the slow addition of ligand in 1 : 1 and 3 : 1 molar ratios were dark red–black in color and displayed sufficient solubility in benzene to allow separation from insoluble $Rh_6(CO)_{16}$ but solubilities in both benzene and chloroform were too limited for accurate molecular weight determinations. Attempts were made to determine molecular weight in highly polar solvents such as DMF where the products appear to be more soluble. However, these solvents apparently dissolve the products only as dissociated ionic species.

The reproducibility of the synthesis, the identity of the ir spectrum from one preparation to the next, and the analytical results all indicate the formation of a pure product of formula $Rh_6(CO)_{13}[P(C_6H_5)_3]_3$ from the 3 : 1 reaction of $P(C_6H_5)_3$ with $Rh_6(CO)_{16}$. Similarly, the reaction of tris(2-diphenylphosphinoethyl)phosphine (TP) with the rhodium carbonyl in 1 : 1 ratio gave a product of formula $Rh_6(CO)_{13}$ TP in which the TP is acting as a tridentate ligand.[12] Results were not as reproducible when the triphenylphosphine to rhodium carbonyl ratio was 1 : 1. However, the high rhodium content and the analyses for other elements all indicate retention of the Rh_6 cluster in a product of limited substitution. It is quite likely that a mixture of $Rh_6(CO)_{16-n}[P(C_6H_5)_3]_n$ products with n = 1–3 is being formed in this case. A considerable quantity of unreacted $Rh_6(CO)_{16}$ always remains after workup of the 1 : 1 reaction.

The color and physical properties of the substitution products change systematically as the extent of substitution increases. Products of 1 : 1 and 3 : 1 reactions were dark red–black in color with limited solubility. These products could be kept under an inert atmosphere for extended periods of time. The higher substitution products are lighter in color and exhibit very limited stability, even under nitrogen, when in solution.

Addition of phosphine to rhodium carbonyl in a 6 : 1 ratio yielded a red product of insufficient purity to give good analytical data. The instability of these products is consistent with previous results.[2] Addition of triphenylphosphine to rhodium carbonyl in mole ratios of 9 : 1 produced materials which could not be characterized if the reaction was carried out in benzene. These are probably unstable mono- or dinuclear products. Reaction or workup in chloroform of the 9 : 1 ratio reaction yielded the yellow mononuclear product $Rh[P(C_6H_5)_3]_2(CO)Cl$. Because of this tendency toward chlorine substitution, benzene was chosen as the reaction solvent and chloroform was avoided in workup of the products for all limited substitution reactions. The only exposure to chloroform occurred when it was used as the solvent for recording ir solution spectra of freshly prepared samples. The absence of any reaction of the metal carbonyl with chloroform while recording ir spectra was established by comparison of the solution spectra with nujol mull spectra of samples not exposed to chloroform. The ir frequencies in the ν(CO) region for the products isolated and studied are listed in Table II.

The spectroscopic evidence lends further support for the isolation of rhodium cluster products of limited substitution. Middle and low frequency infrared data were also obtained for the products of 1 : 1 and 3 : 1 reactions of triphenylphosphine with $Rh_6(CO)_{16}$. Bands in the 400–1200 cm^{-1} region are listed for $Rh_6(CO)_{13}[P(C_6H_5)_3]_3$ in Table III along with frequencies for $Rh_6(CO)_{16}$ and $P(C_6H_5)_3$. The product isolated from the 1 : 1 reaction gave a very similar spectrum throughout this region with reduced intensity for bands associated with phosphine ligands as expected. Assignments in the 400–1200 cm^{-1} region are based upon previous studies of phosphines and phosphine complexes.[13–20] The behavior of the X-sensitive bands at 490–520 and 1065–1100 cm^{-1} is especially indicative of the formation of metal phosphine complexes.

TABLE II. CO Stretching Frequencies.

Compound	ν(CO) Frequencies	
	Terminal CO	Bridge CO
$Rh_6(CO)_{13}[P(C_6H_5)_3]_3$[a]	2095w[d], 2079s, 2066s, 2030sh, 2025sh, 2005s	1850s, 1820sh, 1780m
$Rh_6(CO)_{13}TP$[b]	2055s, 2020w, 1985s	1835w, 1785s
$Rh_6(CO)_n$ · polystyrene[c]	2080s, 2000s	1855s

[a] Spectrum in $CHCl_3$ solution. [b] Spectrum of nujol mull sample. [c] Spectrum of solid sample plated on inside of gas cell window. [d] s = strong, m = medium, w = weak, sh = shoulder.

TABLE III. Low Frequency IR Bands.[a]

$Rh_6(CO)_{16}$[b]	$P(C_6H_5)_3$[b]	$Rh_6(CO)_{13}[P(C_6H_5)_3]_3$[b]	Assignment
407 w[c]			Rh–C str
430 m			Rh–C str
	430 w		P–Φ str
	490 m	500 m, sh	X-sensitive P–C bands
	512 m	525 s	
512 s			Rh–C–O bend
	590 w		Φ ring bend
	690 s	670 w	
	740 s	690 s	Φ ring bend
	745 sh	745 s	C–H wag
	751 m	762 w	
	990 w		ring breathing
	1020 w		C–H wag
	1065 w	1075 w, sh	C–H wag
	1085 w	1095 m	X-sensitive P–C band

[a] Frequencies in cm^{-1}. [b] Spectra recorded as nujol mulls. [c] w = weak, m = medium, s = strong, sh = shoulder.

These bands involve motion of the phosphorus–phenyl bond and usually show more influence of complex formation by triphenylphosphine than do other phosphine ligand bands. The shifts in frequency and intensity which we observe parallel those quoted for metal complexes of several metal phosphines.[13]

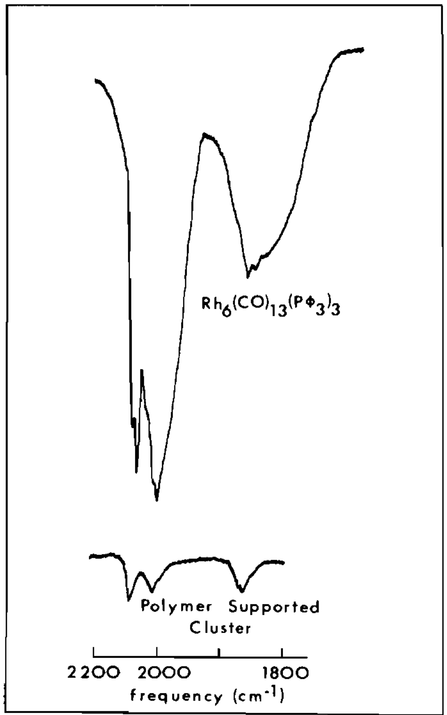


Figure 1. Ir spectrum in the ν(CO) region. Spectrum of $Rh_6(CO)_{13}(P\Phi_3)_3$ was recorded as a chloroform solution. Spectrum of the polymer supported cluster was obtained by pressing a KBr pellet of the polymer material and exposing this sample to one atm CO, followed by evacuation.

Polymer Substitution Reactions

The reaction of $Rh_6(CO)_{16}$ with the phosphine modified polystyrene yielded a polymeric material containing 5% rhodium but which initially exhibited no ν(CO) spectrum. This is consistent with the observations of Collman, *et al.*[7] High pressure carbonylation of this polymer supported material regenerated $Rh_6(CO)_{16}$ which could be removed into refluxing $CHCl_3$. However, exposure to one atmosphere of CO for several hours gave a material with an ir spectrum strikingly similar to that for the $Rh_6(CO)_{16-n}L_n$ products, as shown in Figure 1.

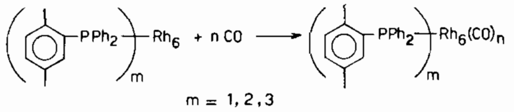
Discussion

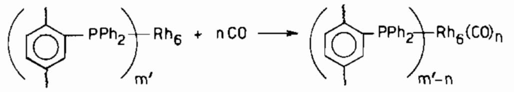
Spectroscopic and analytical data as well as the physical properties of the products all support the conclusion that Rh_6 cluster carbonyls of limited substitution are formed in these reactions. Terminal CO stretching frequencies fall in two regions for all the products: 2060–2100 and 1985–2015 cm^{-1}. Increasing substitution causes a decrease in intensity of bands in the former region relative to the latter as well as small frequency changes within these frequency domains. These results and the usual arguments about the relative π-acidities of phosphine *vs.* CO ligands would suggest that the bands in the 2060–2100 cm^{-1} region are due to vibrations of $Rh(CO)_2$ groups which are largely energy factored from the rest of the CO vibrations in the molecule and that the bands at 1985–2015 are due to energy factored CO vibrations of the $Rh(CO)[P(C_6H_5)_3]$ groups.

Bridging CO frequencies at 1780, 1820, and 1850 cm^{-1} for $Rh_6(CO)_{13}L_3$ are in agreement with the prediction of two or three symmetrically different bridging CO's for a tri-substituted product. The increased frequency of some of these bands relative to bridging bands for $Rh_6(CO)_{16}$ at 1800 cm^{-1} or $Rh_6(CO)_{10}L_6$[2] near 1765 cm^{-1} may indicate that phosphine substitution changes the bridging CO's bonded to a phosphine substituted rhodium from face to edge bridging. Increased substitution by phosphine ligands should then shift these bridging bands back to lower frequencies due to lesser π-acidity of the phosphines as is observed in our studies of impure $Rh_6(CO)_{10}L_6$ species and the studies of Booth, *et al.*[2]

The compounds studied exhibit the expected intensity behavior in the 400–1200 cm^{-1} region; *i.e.,* those bands associated with phosphine vibrations increase in intensity relative to other bands in the spectrum as substitution increases.

This study also supports the earlier conclusion that rhodium cluster species can be bound to a modified polystyrene support with retention of cluster integrity.[7] The very close similarity of the ν(CO) spectrum of $Rh_6(CO)_{16-n}L_n$ species to the spectrum of the polystyrene supported Rh_6 cluster after exposure to 1 atm of CO shows that clusters bound to just a few phosphine side chains must exist under these conditions. It would appear that the polymer bound Rh_6 cluster in the decarbonylated form is either bound to the polymer by just a few phosphine ligands leaving cluster sites available for addition of several moles of CO, or that most of the available complexation sites are occupied by phosphines in the absence of CO but that several of these are easily substituted by CO at pressures of one atm or less:





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