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TRIARYLSTIBINE COMPLEXES OF RHODIUM(I)

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Summary

The complexes that can be isolated from the reaction of R_3Sb (R = Ph, *o*- or *p*-$CH_3C_6H_4$) with $[RhCl(CO)_2]_2$, $[RhCl(cod)]_2$ and $Rh(acac)(CO)_2$ are $RhClCO(R_3Sb)_n$ ($n = 2$ and/or 3, depending upon solvent and the size of R), $RhCl(cod)(R_3Sb)_2$ and $Rh(acac)CO(R_3Sb)_2$ respectively. Five coordination is favored in the solid state. However, there is considerable dissociation of R_3Sb in solution. $RhClCO(R_3Sb)_n$ ($n = 2$ or 3), $RhCl(cod)(R_3Sb)_2$ and $RhCl(R_3Sb)_3$ react immediately with CO to yield *cis*-$RhCl(CO)_2R_3Sb$.

Introduction

During our investigations of triarylstibine complexes of the platinum metals we have noted confusion concerning the complexes of Rh^I [1]. Reactions of R_3Sb with $[RhCl(CO)_2]_2$ have been reported to give red products formulated at various times as $RhClCO(R_3Sb)_2$ [2], $RhCl(CO)_2(R_3Sb)_3$ [3], $RhClCO(R_3Sb)_3$ [4], $RhClCO(R_3Sb)_4$ [5], and $RhClCO(R_3Sb)_3 \cdot C_6H_6$ [6,7]. Reaction of $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) with R_3Sb has been reported to give no stable product (R = Ph) [8], a stable yellow complex formulated $RhCl(cod)R_3Sb$ (R = Ph, *p*-$CH_3C_6H_4$) [9,10], and an orange complex formulated as $RhCl(cod)(R_3Sb)_2$ described as stable (R = Ph) [11] and unstable (R = Ph or *p*-$CH_3C_6H_4$) [6]. Reaction of $Rh(acac)(CO)_2$ (acac = 2,4-pentanedionato) with Ph_3Sb has been reported to give the 20 electron, six-coordinate Rh^I complex, $Rh(acac)(CO)(Ph_3Sb)_3$ [12].

In view of the above observations, we have reinvestigated these reaction products in order to determine under what conditions triarylstibines favor four, five or six coordination in Rh^I complexes.

Experimental

All reactions were carried out under an atmosphere of argon. Solvents were dried and deaerated prior to use. All compounds were found to be stable to the

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* Contribution no. 2346.

atmosphere except Rh(acac)CO$(R_3Sb)_2$, which was prepared using standard Schlenk-type glassware and stored under argon.

The ligands $(p\text{-}CH_3C_6H_4)_3Sb$ [13], $(o\text{-}CH_3C_6H_4)_3Sb$ [13], and $Ph_2SbCH_2SbPh_2$ [14] and the rhodium complexes $[RhCl(CO)_2]_2$ [15], $[RhCl(cod)]_2$ [16], $Rh(acac)(CO)_2$ [12], and $[RhCl(cyclooctene)_2]_2$ [17] were prepared by literature methods. Ph_3Sb was generously donated by M & T Chemicals, Inc.

Infrared spectra were recorded with a Perkin—Elmer 621 Spectrometer. Proton magnetic resonance spectra were recorded using a Varian HR 220 Spectrometer in $CDCl_3$ unless otherwise noted. Molecular weights were obtained using a Hewlett—Packard 301A vapor pressure osmometer. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee. Analyses, molecular weights measurements and infrared absorptions are presented in Table 1.

Infrared solution studies

The reaction of $[RhCl(CO)_2]_2$ with R_3Sb (R = Ph or $p\text{-}CH_3C_6H_4$) was monitored by IR spectroscopy in the 2100 — 1900 cm^{-1} region during the addition of aliquots of 0.01 mmol of R_3Sb in $CHCl_3$ to a 0.05 mmol solution of the carbonyl dimer in $CHCl_3$. A portion of the solution was withdrawn by syringe one minute after addition of the aliquot and the solution spectrum recorded. The portion was then returned and another aliquot added. At regular intervals, a given portion was set aside for about 5 min and the infrared spectrum examined again. Comparison of the spectra showed that only slight changes had occurred, indicating the reaction was not as time dependent as Poilblanc has observed previously for the analogous triphenylphosphine system [18].

$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_2$

A solution of 300 mg (0.76 mmole) of $(p\text{-}CH_3C_6H_4)_3Sb$ in 10 ml of cyclohexane was added dropwise to a solution of 74 mg (0.19 mmol) of $[RhCl(CO)_2]_2$ in 5 ml of cyclohexane under a gentle flow of argon. Precipitation of an off-yellow solid occurred throughout the addition process. The complex was isolated by filtration, washed with cyclohexane and recrystallized from ether/hexane to yield 65-75% of yellow, crystalline material.

$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_3$

A solution of 250 mg (0.64 mmol) of $(p\text{-}CH_3C_6H_4)_3Sb$ in 10 ml of benzene was added dropwise to 20 mg (0.053 mmol) of $[RhCl(CO)_2]_2$ in 5 ml of benzene. The blood red solution was reduced in volume to ca. 1 ml and pentane was added to induce precipitation. The orange-red precipitate was filtered, washed with cold pentane and dried. The complex could not be recrystallized. This compound can be prepared similarly in $CHCl_3$ in ca. 75% yield.

$RhClCO[(o\text{-}CH_3C_6H_4)_3Sb]_2$

A solution of 160 mg (0.38 mmol) of $(o\text{-}CH_3C_6H_4)_3Sb$ in 20 ml of $CHCl_3$ was added dropwise to 37 mg (0.09 mmol) of $[RhCl(CO)_2]_2$ in 10 ml of $CHCl_3$. The solution turned a golden yellow and a very small amount of black precipitate formed. The solution was reduced in volume to ca. 5 ml and eluted through an acid alumina (grade II) column with diethyl ether. The resulting bright yellow solution was reduced in volume to ca. 10 ml. Hexane was added dropwise to induce precipitation of a yellow crystalline material in 75-85% yield.

[RhClCO(Ph$_2$SbCH$_2$SbPh$_2$)]$_2$

A solution of 110 mg (0.19 mmol) of $Ph_2SbCH_2SbPh_2$ in 10 ml of $CHCl_3$ was added dropwise to 37 mg (0.09 mmol) of $[RhCl(CO)_2]_2$ in 10 ml of $CHCl_3$. The brick red solution was reduced in volume to ca. 2 ml and pentane was added to induce precipitation. The solution was filtered and the compound washed with pentane and vacuum dried, yield ca. 60%.

RhCl(cod)(Ph$_3$Sb)$_2$

$[RhCl(cod)]_2$, 49 mg (0.01 mmol), was added to a refluxing solution of 1.0 g (2.9 mmol) of Ph_3Sb in 10 ml of methanol. Precipitation of the orange crystalline complex was immediate. The complex was filtered, washed with hexane and dried under vacuum, yield ca. 80%.

RhCl(cod)[(p-CH$_3$C$_6$H$_4$)$_3$Sb]$_2$

A solution of 49 mg (0.01 mmol) of $[RhCl(cod)]_2$ and 160 mg (0.04 mmol) of $(p\text{-}CH_3C_6H_4)_3Sb$ in 20 ml of benzene was heated at reflux for 5 h. The resulting amber solution was then reduced in volume to ca. 2 ml and 15 ml of pentane was added. Precipitation was induced by cooling in a dry-ice acetone bath. The orange crystalline material which precipitated was washed with cold pentane and vacuum dried, yield 50-60%.

Rh(acac)CO(Ph$_3$Sb)$_2$

Ph_3Sb, 100 mg (0.035 mmole), in 10 ml of hexane was added dropwise in a Schlenk filtration apparatus to 26 mg (0.01 mmol) of $Rh(acac)(CO)_2$ in 10 ml of hexane. The orange solution was stirred at room temperature for 2 h. The solution then was reduced to ca. 3 ml, inducing precipitation of an orange powder which was filtered, dried and stored under argon, yield ca. 60%.

RhCl(CO)$_2$R$_3$Sb, R = Ph, o-CH$_3$C$_6$H$_4$, p-CH$_3$C$_6$H$_4$

When CO is bubbled through a $CHCl_3$ solution of $RhClCO(R_3Sb)_2$ (R = $o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$), $RhCl(cod)(R_3Sb)_2$ (R = Ph, $p\text{-}CH_3C_6H_4$) or $RhCl(Ph_3Sb)_3$ under argon, infrared examination showed the immediate formation of $RhCl(CO)_2R_3Sb$. This species could not be isolated even when solvent was removed by a stream of CO.

Results and discussion

Reactions of [RhCl(CO)$_2$]$_2$

The reaction of R_3Sb with $[RhCl(CO)_2]_2$ was monitored in solution by infrared spectroscopy, during the addition of increasing amounts of R_3Sb, in order to observe and assign structures to the intermediates and isolated products. Fig. 1 shows the results of this study for R = Ph. Only one intermediate was observed having $\nu(CO)$ 2095, 2015 cm^{-1}, and was assigned the structure *cis*-$RhCl(CO)_2Ph_3Sb$ for reasons that will be discussed forthwith. Similar solution studies have been carried out recently using PPh_3 [7,18]. Dinuclear complexes

TABLE 1

ANALYSES, MOLECULAR WEIGHTS AND CO STRETCHING FREQUENCIES

Compound	Color	$\nu(CO)$[a] (cm^{-1})	Analysis found (calcd.) (%)			Mol. wt. found (calcd.)
			C	H	Cl	
$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_2$	Yellow	1955 (1966)	53.67 (53.98)	4.66 (4.43)	3.40 (3.65)	1020[b] (962)
$RhClCO[(o\text{-}CH_3C_6H_4)_3Sb]_2$	Yellow	1952 (1964)	54.48 (53.98)	4.88 (4.43)	3.95 (3.65)	934[c] (962)
$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_3$	Orange-red	1968 (1966)	57.42 (56.93)	5.00 (4.75)		690[b] (1350)
$[RhClCO(Ph_2SbCH_2SbPh_2)]_2$	Red	1960 (1970)	39.61 (39.53)	3.07 (2.97)	4.63 (4.82)	1380[b] (1460)
$RhCl(cod)(Ph_3Sb)_2$	Orange		55.71 (55.82)	4.53 (4.50)	3.52 (3.70)	468[b] (946)
$RhCl(cod)[(p\text{-}CH_3C_6H_4)_3Sb]_2$	Orange					580[b] (1036)
$Rh(acac)CO(Ph_3Sb)_2$	Orange	1962	53.6 (54.2)	4.10 (3.95)		
$RhCl(CO)_2(R_3Sb)$[d]		(2095,2015)				

[a] Nujol ($CHCl_3$). [b] Chloroform. [c] Benzene. [d] R = Ph, $p\text{-}CH_3C_6H_4$.

TABLE 2

PMR SPECTRA OF RHODIUM(I) TRIARYLSTIBINE COMPLEXES

	Chemical shifts (τ)[a]			
	Aryl	CH_3	CH_2	CH
Ph_3Sb	2.65 - 2.80			
$(p\text{-}CH_3C_6H_4)_3Sb$	1.80,2.00[b]	7.68		
$(p\text{-}CH_3C_6H_4)_3Sb$[c]	2.63,3.21[b]	7.98		
$(o\text{-}CH_3C_6H_4)_3Sb$	2.76 - 3.02	7.54		
$[RhCl(cod)]_2$			7.52,8.25	7.59
$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_3$[c]	2.26,3.14[b]	8.02		
$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_2$[c]	2.16,3.10[b]	8.04		
$RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_2$	2.43,2.79[b]	7.66		
$RhClCO[(o\text{-}CH_3C_6H_4)_3Sb]_2$	2.57 - 2.95	7.49		
$[RhClCO(Ph_2CH_2SbPh_2)]_2$	2.46 - 2.72		7.17	
$RhCl(cod)(Ph_3Sb)_2$	2.55 - 2.77		7.59br,8.20br	5.57br
$Rh(acac)CO(Ph_3Sb)_2$[c]	2.50 - 3.02	8.24		4.75

[a] In $CDCl_3$ unless otherwise noted. [b] Doublets. [c] Benzene.

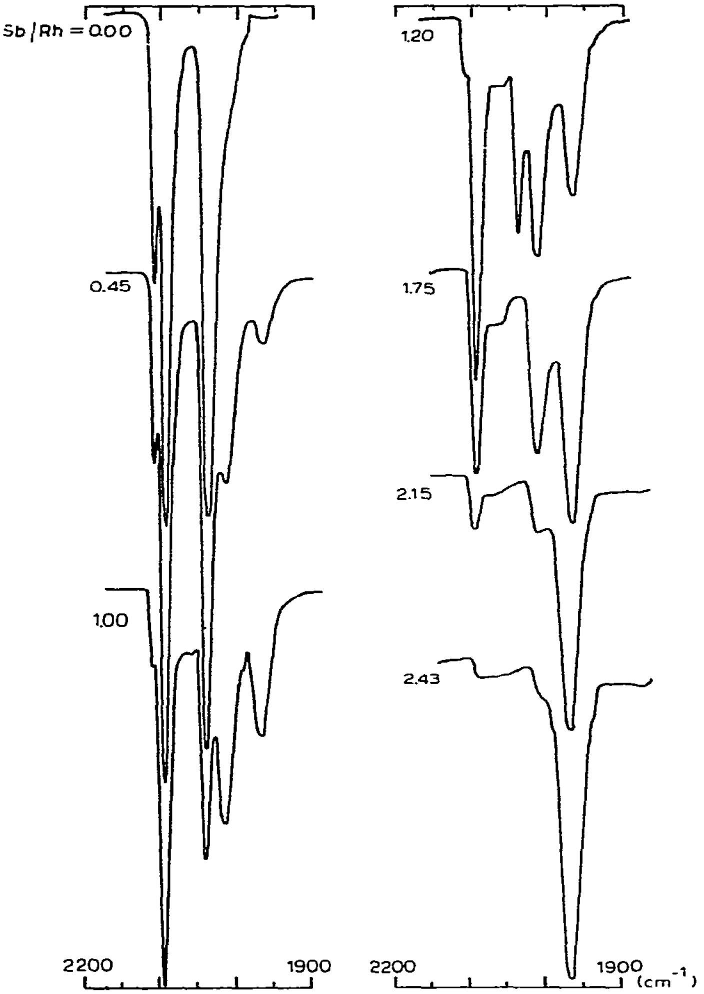


Fig. 1. Infrared spectra in the ν(CO) region of the reaction of Ph_3Sb with $[RhCl(CO)_2]_2$ in $CHCl_3$.

of the type $Rh_2Cl_2(CO)_{4-n}(Ph_3P)_n$ (n = 1,3) and mononuclear $RhCl(CO)_2PPh_3$ were observed [18]. The complex $RhCl(CO)_2PPh_3$, ν(CO) 2095, 2014 cm^{-1} ($CHCl_3$), was assigned a monomeric structure based on IR, gas evolution and molecular weight determinations [19].

Not until an Sb/Rh ratio of 2.43 was reached was there only one ν(CO) stretch, at 1966 cm^{-1} ($CHCl_3$), present, indicating that an Sb/Rh ratio of > 2/1 is necessary to convert all starting and intermediate complexes to the final products. At this ratio the following equilibrium is predominant in solution:

$$RhClCO(R_3Sb)_3 \rightleftharpoons RhClCO(R_3Sb)_2 + R_3Sb \qquad (1)$$

Further addition of R_3Sb caused no further change in the peak at 1966 cm^{-1}.

Attempted isolation of a product at Sb/Rh 2/1 gave a reddish powder having ν(CO) at 1968 and 1955 cm^{-1} (nujol) which contained perceptible amounts of decomposition material.

Reaction at an Sb/Rh ratio of > 10/1 as suggested by Ugo et al. [9] results in a magenta-red powder for R = Ph and an orange-red powder for R = p-CH_3-C_6H_4, both of which analyzed as $RhClCO(R_3Sb)_3$, ν(CO) 1968 (nujol). Although Ugo proposed benzene adducts for both complexes, we have found no evidence for the presence of benzene. It was not detectable in the PMR spectra ($CDCl_3$) of the p-$CH_3C_6H_4$ complex which had been prepared in benzene.

When fractional recrystallization of the mixture obtained at Sb/Rh 2/1, (R = p-$CH_3C_6H_4$), was attempted from cyclohexane it was found that $RhClCO(R_3Sb)_3$ was soluble, leaving behind a yellow complex (ca. 10—15%) ν(CO) (nujol) 1955 cm^{-1} which analyzed as $RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_2$. We therefore examined the reaction of $[RhCl(CO)_2]_2$ and R_3Sb in cyclohexane. When R = p-$CH_3C_6H_4$, $RhClCO(R_3Sb)_2$ was obtained as a result of its immediate precipitation upon formation. When R = Ph, however, the solubilities are such that a mixture of four- and five-coordinate complexes was again obtained. All attempts, including column chromatography, to separate $RhClCO(R_3Sb)_3$ from $RhClCO(R_3Sb)_2$ when R = Ph failed. We feel that this difficulty in separation has been the problem encountered by others in the past. A small amount of reddish $RhClCO(R_3Sb)_3$ masks the yellow color of the four-coordinate complex.

Isolation of an appreciable amount of $RhClCO(R_3Sb)_3$ from an Sb/Rh reaction ratio of 2/1 indicates the five-coordinate complex is favored in the solid state and the four-coordinate complex can only be obtained under special circumstances (i.e., insolubility in cyclohexane for R = p-$CH_3C_6H_4$).

Reaction with $(o\text{-}CH_3C_6H_4)_3Sb$ was attempted in the belief that the steric influence of the o-$CH_3C_6H_4$ group would favor four-coordination. With Sb/Rh ≥ 2/1, yellow $RhClCO[(o\text{-}CH_3C_6H_4)_3Sb]_2$ was obtained in good yield, indicating that the tendency towards five-coordination can be overcome with sufficiently bulky ligands.

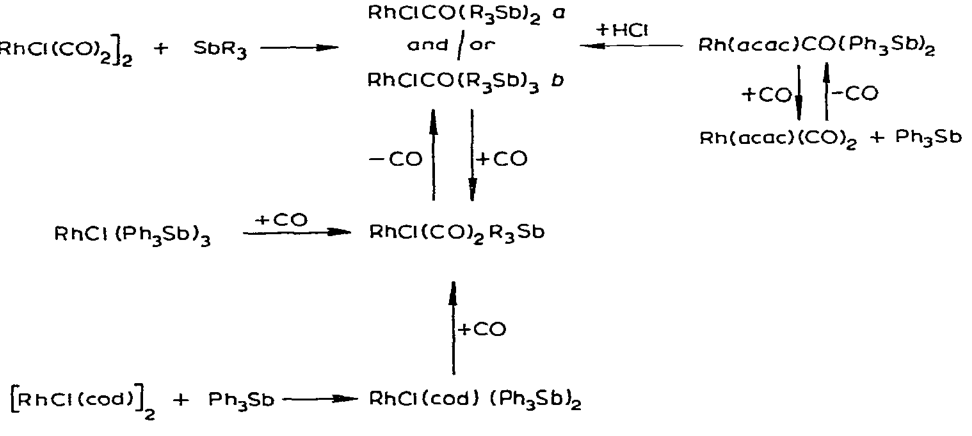
Molecular weight measurements indicate that the yellow four-coordinate complexes are indeed monomeric and undissociated in solution. The five-coordinate complex, $RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_3$, however, is nearly completely dissociated in benzene, to the four-coordinate complex, as observed previously [6]. This is consistent with the observation that the yellow four-coordinate and reddish five-coordinate complexes give the same ν(CO) in solution where they undoubtedly are present as the same solvated, four-coordinate species.

Reaction of $RhCl(CO)(PPh_3)_2$ with CO was found to proceed only slowly at 60° (no reaction at room temperature) to form a mixture of complexes including $RhCl(CO)_2PPh_3$ and $[RhClCOPPh_3]_2$ [18]. Reaction of $RhClCO(R_3Sb)_x$ (R = Ph, p-$CH_3C_6H_4$ for $x = 3$; R = o- or p-$CH_3C_6H_4$ for $x = 2$] with CO at room temperature resulted in the immediate formation of cis-$RhCl(CO)_2R_3Sb$, as identified by solution IR spectroscopy. This CO can be removed from the complex in solution by either applying a vacuum or passing nitrogen gas through it. The mild conditions necessary for this transformation become significant in light of the recent report that cis-$RhCl(CO)_2PPh_3$ is a very active hydroformylation catalyst [20]. We have examined the carbonylation of $RhClCO(Ph_3As)_2$ and found that it too is reversible at room temperature and one atmosphere, giving cis-$RhCl(CO)_2Ph_3As$ with ν(CO) ($CHCl_3$) 2095 and 2017 cm^{-1}.

When two moles of $Ph_2SbCH_2SbPh_2$ were treated with one mole of $[RhCl(CO)_2]_2$, a deep red powder was obtained which analysed as $[RhClCO(Ph_2SbCH_2SbPh)_2]_2$, ν(CO) 1960 cm^{-1} (nujol). Molecular weight measurements indicated that the complex is dimeric and undissociated in chloroform. We propose that it is a ligand-bridged dimer, analogous to the complexes prepared by Mague [21] with similar P and As containing ligands. $[RhClCO(Ph_2SbCH_2SbPh_2)]_2$ in $CHCl_3$ does not react rapidly with carbon monoxide at atmospheric pressure. After extended periods (ca. 4 h), broad CO peaks due to coordinated CO were observed in the 2060—1960 cm^{-1} region. Attempts to isolate products from these solutions were not successful. Reaction with CO has not been carried out with the P and As analogs [22].

Reactions are summarized in Scheme 1.

SCHEME 1



^{a} R = Ph, p-$CH_3C_6H_4$, o-$CH_3C_6H_4$, ^{b} R = Ph, p-$CH_3C_6H_4$.

Reactions of $[RhCl(cod)]_2$

Cattalini et al. [9] have reported the preparation of $RhCl(cod)R_3Sb$ (R = p-$CH_3C_6H_4$) by the reaction of $[RhCl(cod)]_2$ and R_3Sb at room temperature in CH_2Cl_2, whereas Wilkinson et al. [8] have noted that the Ph_3Sb derivative is not stable enough to be isolated. We have been unable to reproduce either of these results, finding instead that the treatment of $[RhCl(cod)]_2$ with R_3Sb results only in the isolation of starting materials. After prolonged contact at room temperature, the starting materials were isolated, along with $RhCl(cod)(R_3Sb)_2$. We also attempted the replacement of p-$CH_3C_6H_4NH_2$ from $RhCl(cod)(p$-$CH_3C_6H_4NH_2)$ by an equimolar amount of R_3Sb and obtained only $RhCl(cod)(R_3Sb)_2$ and $RhCl(cod)(p$-$CH_3C_6H_4NH_2)$ in a 1/1 ratio. The best preparation for $RhCl(cod)(Ph_3Sb)_2$ is by the addition of $[RhCl(cod)]_2$ to a refluxing solution of excess Ph_3Sb in methanol. Precipitation of the orange crystalline product is immediate. The more soluble $(p$-$CH_3C_6H_4)_3Sb$ complex is best prepared in refluxing benzene. Molecular weight measurements indicate the equilibrium (2) exists far to the right in chloroform.

$$\mathrm{RhCl(cod)(R_3Sb)_2} \rightleftarrows \mathrm{RhCl(cod)(R_3Sb) + R_3Sb} \quad (2)$$

This formulation, a five-coordinate complex with two stibines per rhodium, agrees with the formulation of Takesada et al. [11].

The interaction between the bulky $(o\text{-}CH_3C_6H_4)_3Sb$ and $RhCl(cod)_2$ was investigated in an attempt to synthesize a four-coordinate derivative; but even after extended reflux, there was no reaction.

Reactions of the complexes $RhCl(cod)(R_3Sb)_2$ (R = Ph, $p\text{-}CH_3C_6H_4$) with carbon monoxide resulted in the replacement of the 1,5-cyclooctadiene by CO to give $RhCl(CO)_2R_3Sb$, as identified by solution IR spectroscopy. Only small amounts of $RhClCO(R_3Sb)_2$ along with decomposition materials could be isolated from these solutions.

220 MHz PMR spectra of $RhCl(cod)(Ph_3Sb)_2$ were obtained at +15° and —50°. At +15° two broad peaks were observed for the CH_2 protons and one broad peak for the olefinic protons. This is to be expected, since exchange is occurring in solution (eqn. 2). At —50°, still only one peak was observed for the olefinic protons indicating that the intermolecular exchange has not been stopped. Vrieze et al. [10] have studied the reaction of $RhCl(cod)Ph_3As$ and Ph_3As in 1/1 molar ratio and have found that exchange can be stopped at —65°.

Reaction of Rh(acac)(CO)$_2$

Reinvestigation of the reaction between $Rh(acac)(CO)_2$ and Ph_3Sb has resulted in the isolation of the water-sensitive, five-coordinate complex, $Rh(acac)CO(Ph_3Sb)_2$. The complex is also reactive towards chlorinated solvents. When eluted from an acid alumina column by CH_2Cl_2, $RhClCO(Ph_3Sb)_2$ was obtained and characterized by the ν(CO) of its IR spectrum and by the absence of acac protons in its PMR spectrum in benzene. Reaction with $(o\text{-}CH_3C_6H_4)_3Sb$ in an attempt to obtain the four-coordinate $Rh(acac)CO(R_3Sb)$, analogous to the Ph_3P and Ph_3As systems [12], failed.

Reaction of $Rh(acac)CO(Ph_3Sb)_2$ with CO in benzene resulted in the formation of $Rh(acac)(CO)_2$ and Ph_3Sb. Treatment with HCl cleaved the acac ligand to give monomeric $RhCl(CO)(Ph_3Sb)_2$, as identified by solution and solid state IR spectroscopy. The analogous Ph_3P and Ph_3As complexes yielded the dimers, $[RhCl(CO)L]_2$ [23].

Reaction of [Rh(cyclooctene)$_2$Cl]$_2$

Mague et al. [24] treated $[RhCl(C_2H_4)_2]_2$ with an excess of Ph_3Sb in refluxing methanol to obtain $RhCl(Ph_3Sb)_3$, the stibine analog of Wilkinson's compound. We have reinvestigated this reaction using $[RhCl(cyclooctene)_2]_2$ and have found that an Sb/Rh ratio of 3/1 produces a brown amorphous powder, analyses of which are variable. Only with an Sb/Rh ratio of > 10/1 is the deep purple compound, presumably $RhCl(Ph_3Sb)_3$, formed. Attempted recrystallization of the purple complex resulted in the isolation of a brown, amorphous material, indicating that an excess of Ph_3Sb is necessary to achieve isolation of the complex from solution.

Reaction of $RhCl(Ph_3Sb)_3$ with carbon monoxide resulted in the formation of *cis*-$RhCl(CO)_2Ph_3Sb$ in solution and in the isolation of a mixture of $RhCl(CO)(Ph_3Sb)_3$ and $RhCl(CO)(Ph_3Sb)_2$ in the solid state (characterized by solution and solid state IR spectroscopy). Reaction of $RhCl(C_2F_4)(Ph_3Sb)_2$ with CO has been reported to give $RhCl(CO)(Ph_3Sb)_4$ [25]. In light of our current observations, we feel that this "compound" most assuredly also is a mixture of $RhClCO(Ph_3Sb)_3$ and $RhClCO(Ph_3Sb)_2$.

Conclusions

It seems evident that triarylstibine complexes of Rh^I prefer to be five-coordinate in the solid state but that they exist in solution as an equilibrium mixture of the yellow four-coordinate and reddish five-coordinate species. In the reaction of $[RhCl(CO)_2]_2$ with triarylstibines we have been able to isolate both four- and five-coordinate species by utilizing the insolubility of $RhClCO[(p\text{-}CH_3C_6H_4)_3Sb]_2$ in cyclohexane or the steric restrictions imposed by $(o\text{-}CH_3C_6H_4)_3Sb$. The reaction of $[RhCl(cod)]_2$ or $Rh(acac)(CO)_2$ with triarylstibines resulted in the isolation of five-coordinate complexes. In no case is there evidence for the existence in the solid state of any four- or six-coordinate complexes.

No dinuclear complexes were observed in the reaction of R_3Sb with $[RhCl(CO)_2]_2$; monomeric *cis*-$RhCl(CO)_2R_3Sb$ was the only intermediate observed. This species can also be prepared by the reaction of $RhClCO(R_3Sb)_2$, $RhClCO(R_3Sb)_3$, $RhCl(R_3Sb)_3$ or $RhCl(cod)(R_3Sb)_2$ with carbon monoxide at room temperature.

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