

two chlorine atoms of either  $\text{SO}_2\text{Cl}_2$  or  $\text{SOCl}_2$  are then replaced by two deprotonated N atoms of the en complex. For bridging to occur in this manner, the two N atom nucleophiles would be required to occupy a *cis* configuration at some stage during the reaction. The infrared data support these conclusions since S-N stretching frequencies are observed and the  $\text{SO}_2$  stretching frequencies are shifted to much lower values in comparison with those of  $\text{SO}_2\text{Cl}_2$ .

The S-N stretch in  $\{\text{Rh}(\text{en})[(\text{en}-\text{H})_2\text{SO}]\}\text{Cl}_2\text{I}$  occurs at approximately the same frequency as for the sulfonyl chloride reaction product. However  $\nu(\text{SO})$  at  $1265\text{ cm}^{-1}$  is higher than the corresponding vibration for  $\text{SOCl}_2$  indicating an increase in the double-

bond character of the (S=O) group. The influence of resonance hybrid structures responsible for this effect apparently contributes to the instability in air.

The nucleophilic properties of the deprotonated N atoms in  $[\text{Rh}(\text{en}-\text{H})_2\text{en}]\text{I}$  are further demonstrated by its ability to act as a Lewis base toward boron trifluoride. Although Watt and Crum have shown<sup>12</sup> that delocalization does occur to some extent, the deprotonated site must retain a substantial electron density in order for this reaction to proceed.

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## Fluorocarbon Complexes of Rhodium Containing Triphenylstibine and Triphenylarsine

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Tris(triphenylstibine)chlororhodium(I) reacts readily with tetrafluoroethylene to produce the complex  $\text{RhCl}(\text{C}_2\text{F}_4)(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ . With hexafluorobut-2-yne, the complexes  $\text{RhCl}(\text{C}_4\text{F}_6)(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  and  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  are formed. The latter five-coordinate complex contains a rhodiacyclopentadiene ring and being coordinatively unsaturated for rhodium(III) readily forms adducts with donor molecules such as carbon monoxide, phosphorus trifluoride, and pyridine. An analogous rhodiacyclopentadiene derivative is formed from tris(triphenylarsine)chlororhodium(I) and hexafluorobut-2-yne.

### Introduction

The large variety of substitution and oxidative addition reactions undergone by the versatile hydrogenation catalyst tris(triphenylphosphine)chlororhodium(I)<sup>1</sup> suggested that similar results could be obtained with the analogous triphenylarsine and triphenylstibine complexes.<sup>2</sup> In view of the enhanced stability of a number of the derivatives of the complexes  $\text{RhCl}(\text{M}(\text{C}_6\text{H}_5)_3)_3$  (M = As, Sb) over that noted for the analogous triphenylphosphine-containing complexes<sup>2</sup> it was hoped a wider range of derivatives could be prepared from these.

### Experimental Section

Microanalyses were by the Microanalytical Laboratory, Imperial College, London, A. Bernhardt, Mühlheim, Germany, and Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were determined on a Mechrolab osmometer at  $37^\circ$ . Infrared spectra were recorded using Beckman IR-5A and Grubb-Parsons Spectromaster instruments on Nujol mulls unless otherwise stated. All of the compounds reported contain absorptions due to triphenylarsine or -stibine; thus only additional bands are reported. Nmr spectra were taken on a Varian HR-60 spectrometer in chloroform solutions. The  $^{19}\text{F}$  resonances are referred to benzotrifluoride as an internal standard. Melting points were

determined on a conventional hot-stage microscope and are uncorrected. The benzene used was distilled from calcium hydride and stored over sodium. Dichloromethane was distilled from calcium chloride and stored over the same.

**$\text{RhCl}(\text{C}_2\text{F}_4)(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ .**—A dichloromethane solution (5 ml) of  $\text{RhCl}(\text{Sb}(\text{C}_6\text{H}_5)_3)_3$  (0.3 g) was placed in a thick glass tube which was then frozen and evacuated. Tetrafluoroethylene was condensed in and the tube sealed. The tube was shaken for *ca.* 0.5 hr at room temperature, at the end of which time yellow-orange crystals of the *complex* had formed (mp  $154\text{--}156^\circ$ ). These were collected, washed with diethyl ether, and air dried (yield 0.2 g, 85%). Recrystallization was effected from hot 1,1-dichloroethane.

*Anal.* Calcd for  $\text{C}_{33}\text{H}_{30}\text{Sb}_2\text{F}_4\text{ClRh}$ : C, 48.3; H, 3.2; mol wt, 945. Found: C, 48.7; H, 3.7; mol wt, 927 ( $\text{CHCl}_3$ ).  $\nu_{\text{max}}$ : 1401 w, 1333 w, 1304 m, 1263 m, 1100 vs, 1020 vs, 855 w, 803 vs, 763 vs  $\text{cm}^{-1}$ .

Reaction of this complex with carbon monoxide produced  $\text{Rh}(\text{CO})\text{Cl}(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ .

*Anal.* Calcd for  $\text{C}_{73}\text{H}_{60}\text{Sb}_2\text{OCIRh}$ : C, 55.53; H, 3.83; Cl, 2.24. Found: C, 55.56; H, 4.21; Cl, 2.89.

**$\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ .**—Hexafluorobut-2-yne was condensed into an evacuated, thick glass tube containing  $\text{RhCl}(\text{Sb}(\text{C}_6\text{H}_5)_3)_3$  (0.3 g) which had been completely dissolved in dry benzene (5 ml). The tube was sealed and held at  $75\text{--}80^\circ$  for 3 hr. The tube was then cooled, left to stand 24 hr, and opened, and the excess fluorocarbon was recovered. The crude crystalline product was filtered off and recrystallized from 1,1-dichloroethane-petroleum ether (bp  $30\text{--}60^\circ$ ) affording yellow-orange crystals, mp  $208\text{--}210^\circ$  dec (0.23 g, 80%).

*Anal.* Calcd for  $\text{C}_{44}\text{H}_{30}\text{Sb}_2\text{F}_{12}\text{ClRh}$ : C, 45.2; H, 2.6; F, 19.5; mol wt, 1170. Found: C, 44.9; H, 2.7; F, 20.4; mol wt,

(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1711 (1966).

(2) J. T. Mague and G. Wilkinson, *ibid.*, 1736 (1966).

1121 (CHCl<sub>3</sub>), 1168 ± 2 (mass spectrometer).  $\nu_{\max}$ : 1538 m, 1365 s, 1333 sh, 1304 w, 1263 sh, 1220 vs, 1202 vs, 1163 sh, 1147 vs, 1121 vs, 913 m, 833 m, 807 m cm<sup>-1</sup>.

**Rh(CO)Cl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>.**—A dichloromethane solution of RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> was treated with carbon monoxide at 25° and 1 atm pressure. The orange-yellow solution rapidly became lemon yellow, and, after petroleum ether (bp 60–80°) had been added, the solution was evaporated in a stream of carbon monoxide to give an essentially quantitative yield of the product as a pale yellow powder. This was recrystallized from 1,1-dichloroethane to give pale yellow needles, mp 189–192° dec.

*Anal.* Calcd for C<sub>40</sub>H<sub>30</sub>Sb<sub>2</sub>OF<sub>12</sub>ClRh: C, 45.16; H, 2.53; Cl, 2.96; F, 19.05; mol wt, 1196. Found: C, 44.68; H, 2.53; Cl, 3.36; F, 19.34; mol wt, 1204 (CHCl<sub>3</sub>).  $\nu_{\max}$ : 2103 sh, 2096 vs ( $\nu_{C=O}$ ), 2101 vs ( $\nu_{C=O}$ , CHCl<sub>3</sub> solution), 1515 w, 1333 s, 1303 w, 1261 w, 1220 vs, 1201 vs, 1162 sh, 1146 vs, 1119 s, 913 w, 805 w cm<sup>-1</sup>.

**RhCl(C<sub>2</sub>F<sub>4</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>.**—When pyridine was added to an orange-yellow solution of RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> in dichloromethane, the color rapidly lightened. The solvent was evaporated under reduced pressure to yield an oil which became solid when washed with petroleum ether (bp 30–60°). The product was recrystallized from dichloromethane–petroleum ether to give lemon yellow needles. Proton nmr measurements confirmed that the ratio of pyridine to triphenylstibine was 2:1.

*Anal.* Calcd for C<sub>36</sub>H<sub>26</sub>N<sub>2</sub>F<sub>12</sub>SbClRh: C, 44.40; H, 2.58; N, 2.88. Found: C, 44.78; H, 2.70; N, 3.06.  $\nu_{\max}$ : 1602 m, 1516 w, 1445 vs, 1334 s, 1220 vs, 1195 vs, 1162 sh, 1150 vs, 1088 m, 1040 sh, 1033 s, 903 w, 818 s, 805 sh, 760 m cm<sup>-1</sup>.

**Reaction of RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> with PF<sub>3</sub>.**—Treatment of a dichloromethane solution of RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> with PF<sub>3</sub> at 25° and 1 atm pressure caused a change in color from orange-yellow to lemon yellow. Addition of petroleum ether (bp 30–60°) and cooling to –5° caused the slow precipitation of a mixture of orange-yellow and lemon yellow crystals whose infrared spectra showed them to be starting material and a PF<sub>3</sub> adduct, respectively. The adduct is unstable and loses PF<sub>3</sub> too rapidly for precise analytical data to be obtained; however, the best carbon, hydrogen, and fluorine analyses obtained were within 2% of the theoretical values for RhCl(PF<sub>3</sub>)(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>.

*Anal.* Calcd for C<sub>44</sub>H<sub>30</sub>F<sub>15</sub>Sb<sub>2</sub>PClRh: C, 42.01; H, 2.41; F, 22.75. Found: C, 40.82; H, 2.84; F, 20.92. In addition to bands due to the parent complex, this complex exhibits bands at 913 sh, 899 sh, 890 s, 873 vs, 858 m, 844 w cm<sup>-1</sup>.

**Reaction of RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> with CN<sup>-</sup>.**—The general behavior of dichloromethane solutions of RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> when treated with cyanide ion is to produce yellow solutions and intractable whitish solids. No definite compounds could be isolated. However, in the presence of the diphenyldibenzylphosphonium cation, fine yellow crystals can be obtained whose analysis indicates that they should be formulated as [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>P][RhCl(CN)(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>].

*Anal.* Calcd for C<sub>58</sub>H<sub>37</sub>F<sub>12</sub>NPSbClRh: C, 52.65; H, 3.26; N, 1.16. Found: C, 52.61; H, 3.48; N, 1.42.

In addition to bands due to the parent complex and to the phosphonium cation, the compound exhibits a band of medium intensity in the infrared region at 2122 cm<sup>-1</sup> ( $\nu_{C=N}$ ).

**RhCl(C<sub>2</sub>F<sub>6</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>.**—A solution of RhCl(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> (0.3 g) in 5 ml of dry dichloromethane was shaken with excess hexafluorobut-2-yne in an evacuated, sealed tube at room temperature for approximately 0.5 hr. The orange powder which had formed was collected and recrystallized from dichloromethane–diethyl ether to give dark red-orange crystals, mp 173–175° (0.2 g, 80%).

*Anal.* Calcd for C<sub>58</sub>H<sub>46</sub>Sb<sub>3</sub>F<sub>6</sub>ClRh: C, 51.23; H, 3.34; F, 8.36; mol wt, 1360. Found: C, 50.52; H, 3.62; F, 8.56; mol wt, 1136 (CHCl<sub>3</sub>).  $\nu_{\max}$ : 1824 s (C≡C str), 1820 s (C≡C str, CHCl<sub>3</sub> solution), 1770 sh, 1330 w, 1305 w, 1266 w, 1242 vs, 1217 vs, 1130 vs, 1111 vs, 890 w, 848 w, 799 m cm<sup>-1</sup>.

When treated with carbon monoxide, this complex is converted into Rh(CO)Cl(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>4</sub>.

*Anal.* Calcd for C<sub>73</sub>H<sub>60</sub>OCISb<sub>4</sub>Rh: C, 55.53; H, 3.83; Cl, 2.24. Found: C, 55.34; H, 4.12; Cl, 2.68.

**RhCl(C<sub>2</sub>F<sub>4</sub>)(As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>.**—This complex was prepared from RhCl(As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> in the same manner as the triphenylstibine analog. It was obtained as bright yellow crystals upon recrystallization from hot 1,1-dichloroethane, mp 195–197°.

*Anal.* Calcd for C<sub>44</sub>H<sub>30</sub>As<sub>2</sub>F<sub>12</sub>ClRh: C, 49.1; H, 2.8; F, 21.2; mol wt, 1075. Found: C, 49.5; H, 3.2; F, 20.4; mol wt, 1046 (CHCl<sub>3</sub>).  $\nu_{\max}$ : 1538 m, 1354 s, 1333 sh, 1305 w, 1263 sh, 1220 vs, 1204 sh, 1145 vs, 1121 vs, 915 m, 833 w, 804 m cm<sup>-1</sup>.

## Results and Discussion

**Interaction with Tetrafluoroethylene.**—Tetrafluoroethylene reacts readily at room temperature with dichloromethane solutions of tris(triphenylstibine)chlororhodium(I) to yield orange-yellow crystals of stoichiometry RhCl(C<sub>2</sub>F<sub>4</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>. Molecular weight measurements indicate that the complex is monomeric and undissociated in chloroform solution. The infrared spectrum is essentially identical with the spectra reported previously for the complexes RhCl(C<sub>2</sub>F<sub>4</sub>)(M(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> (M = As<sup>2</sup> and P<sup>3</sup>). The <sup>19</sup>F nmr spectrum of the complex shows a doublet ( $J_{Rh-F} = 9$  cps) centered at +34.5 ppm. This corresponds well to the results found previously for the triphenylphosphine<sup>3</sup> and -arsine<sup>2</sup> analogs. As in these cases, no band was observed in the infrared spectrum in the 1500–2000-cm<sup>-1</sup> region which could be attributed to a coordinated carbon–carbon double bond. All of the evidence is in accord with a square-planar Rh(I) structure analogous to the triphenylphosphine and -arsine complexes reported previously.<sup>2,3</sup>

The complex reacts readily with carbon monoxide (25°, 1 atm) in benzene to yield the known complex Rh(CO)Cl(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>4</sub><sup>4</sup> which was identified by its infrared spectrum and elemental analysis.

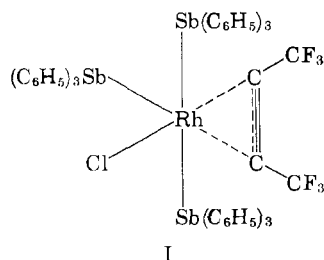
**Interaction with hexafluorobut-2-yne.**—When tris(triphenylstibine)chlororhodium(I) is treated with excess hexafluorobut-2-yne in dichloromethane or benzene solution at room temperature, a red-orange product results which analyzes as RhCl(C<sub>2</sub>F<sub>6</sub>)(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>. When recrystallized from dichloromethane, the complex apparently retains a small amount of solvent as evidenced by consistently high values found for chlorine. This solvent is not readily removed, and its presence has been demonstrated by nmr. The complex shows a tendency to dissociate in solution, as shown by the low value for the molecular weight. The fact that losses on recrystallization can be reduced if performed in the presence of excess triphenylstibine indicates that the dissociation probably involves loss of triphenylstibine.

The infrared spectrum of the complex exhibits a strong band at 1824 cm<sup>-1</sup> which can most reasonably be assigned to the carbon–carbon stretching mode of coordinated hexafluorobut-2-yne. This value does not correspond to those previously reported as characteristic of “ $\pi$ -bonded” (ca. 1920 cm<sup>-1</sup>) or of “doubly  $\sigma$ -

(3) M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 6629 (1965).

(4) R. Ugo, F. Bonati, and S. Cenini, *Rend. Ist. Lombardo Sci. Lettere*, A, **98**, 627 (1964).

bonded" hexafluorobut-2-yne (*ca.* 1775  $\text{cm}^{-1}$ ).<sup>5</sup> However, Collman has recently pointed out<sup>6</sup> that the modes of bonding of acetylenes to metals should not be so rigorously divided into these two extreme types. Thus, it is concluded that there should exist a gradual progression in the strength of the interaction of which the above examples happen to be two extremes. On this basis, then, we conclude that in our case, the hexafluorobut-2-yne moiety is bound to the rhodium in a manner intermediate to those which occur in the two examples cited above. It is probable that since the carbon-carbon stretching frequency here lies toward the low end of the range, the hexafluorobut-2-yne tends to occupy two coordination positions about the rhodium, yielding an effectively six-coordinated complex (I).

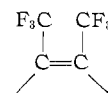


The acetylene is readily replaced by carbon monoxide (1 atm) in benzene solution at room temperature to yield the known complex,  $\text{RhCl}(\text{CO})(\text{Sb}(\text{C}_6\text{H}_5)_3)_4$ ,<sup>4</sup> which was identified by its elemental analysis and infrared spectrum. As would be expected, not all of the rhodium initially present could be recovered in the form of the carbonyl complex.

The  $^{19}\text{F}$  nmr spectrum consists of two rather broad complex signals centered at  $-9.8$  and  $-12.7$  ppm whose areas are in the ratio 1:1, indicating that the two trifluoromethyl groups are not equivalent. This supports the formulation of the complex as isomer I rather than that in which the chlorine is *trans* to a triphenylstibine. Both the nmr and infrared data are in contrast to those found for the complex  $\text{RhCl}(\text{C}_4\text{F}_6)(\text{P}(\text{C}_6\text{H}_5)_3)_2$  which results from the analogous reaction of hexafluorobut-2-yne with tris(triphenylphosphine)chlororhodium(I).<sup>3</sup> In this latter case, only a single resonance is observed and the carbon-carbon stretching frequency occurs at  $1917$   $\text{cm}^{-1}$ . It was concluded that there the hexafluorobut-2-yne occupies only one coordination position.

If the reaction of tris(triphenylstibine)chlororhodium(I) with excess hexafluorobut-2-yne is carried out in benzene at *ca.*  $80^\circ$ , the  $\text{RhCl}(\text{C}_4\text{F}_6)(\text{Sb}(\text{C}_6\text{H}_5)_3)_3$  initially formed reacts further to form an air-stable, yellow-orange compound of empirical formula  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ . This complex is monomeric in chloroform and benzene solutions and appears to be thermally stable up to its melting point. The molecular weight has been further confirmed by mass spectrometry, but as no recognizable fragmentation pattern could be discerned, no further structural information could be derived from this experiment. It is signifi-

cant, however, that no fragment corresponding to  $\text{C}_4\text{F}_6^+$  or  $\text{C}_8\text{F}_{12}^+$  could be detected, indicating that the compound probably does not contain either coordinated hexafluorobut-2-yne or tetrakis(trifluoromethyl)cyclobutadiene. Furthermore, the infrared spectrum of the complex exhibits no bands in the  $1600$ – $2000$ - $\text{cm}^{-1}$  region which could be attributed to a coordinated acetylene moiety (*vide supra*). There is, however, a sharp band of medium intensity at  $1538$   $\text{cm}^{-1}$  which we consider to be the double-bond stretching frequency of a



group adjacent to the rhodium. Similar systems have exhibited bands at  $1535$   $\text{cm}^{-1}$  ( $(\text{CH}_3)_3\text{SnC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Fe}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2$ )<sup>7</sup> and  $1603$   $\text{cm}^{-1}$  ( $\text{PtCl}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H})$ )<sup>8</sup> which have been assigned to  $\text{C}=\text{C}$  stretching frequencies.

The  $^{19}\text{F}$  nmr spectrum of the compound consists of two complex multiplets centered at  $-5.1$  and  $-10.9$  ppm and of relative area 1:1. This is consistent with the presence of two nonequivalent pairs of trifluoromethyl groups.

When a dichloromethane solution of the complex is treated with carbon monoxide at  $25^\circ$  and 1 atm pressure, it does not lose fluorocarbon, in contrast to I, but instead *adds* one molecule of CO, to give  $\text{RhCl}(\text{CO})(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ . The infrared spectrum of this carbonyl adduct is essentially the same as that of the parent complex with two exceptions. There is a strong, sharp band at  $2096$   $\text{cm}^{-1}$  which can be assigned to a terminal carbonyl stretching frequency. The position of this band is in the range usually associated with Rh(III) carbonyls.<sup>9a</sup> (The behavior of  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  here greatly resembles that of the vinyl complex  $\text{RhCl}_2(\text{C}_2\text{H}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_2$  which gives a Rh(III) carbonyl adduct under similar conditions ( $\nu_{\text{C}=\text{O}} = 2082$   $\text{cm}^{-1}$ ).<sup>9b</sup>) In addition, the band at  $1538$   $\text{cm}^{-1}$  now appears at  $1515$   $\text{cm}^{-1}$  and has become broader. The  $^{19}\text{F}$  nmr spectrum of the adduct consists of three complex multiplets which are centered at  $-7.0$ ,  $-13.5$ , and  $-14.6$  ppm and have areas in the ratio 2:1:1, respectively. At first sight this appears to indicate that the two trifluoromethyl groups in one of the pairs have become nonequivalent.

Dichloromethane solutions of the complex  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  also react with pyridine, tri-fluorophosphine, and (in the presence of a large cation) cyanide ion, to give analogous adducts. In each case, a change from orange to lemon yellow accompanied the reaction and the infrared spectra of the products showed, in addition to bands due to the parent complex, bands characteristic of the particular coordinated

(7) R. J. E. Bichler, M. R. Booth, and H. C. Clark, *Inorg. Nucl. Chem. Letters*, **3**, 71 (1967).

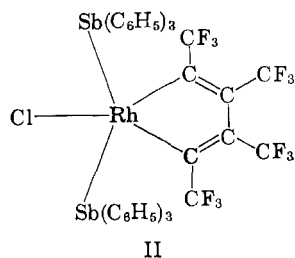
(8) H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, **89**, 533 (1967).

(9) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc., Sect. A*, 1437 (1966); (b) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *ibid.*, 1347 (1967).

(5) J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 3468 (1963).  
 (6) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

group. In particular, the adduct with diphenyldibenzylphosphonium cyanide showed a band at  $2122\text{ cm}^{-1}$  which can be assigned to the  $\text{C}\equiv\text{N}$  stretching frequency. This value is  $18\text{ cm}^{-1}$  lower than that observed for diphenyldibenzylphosphonium cyanide itself, indicating that the cyanide is coordinated to the rhodium and that this is not simply a mixture of the two compounds. The infrared spectrum of the product resulting from reaction with trifluorophosphine showed two strong bands at  $890$  and  $873\text{ cm}^{-1}$  and, in addition, several other bands of medium intensity in the  $920\text{--}840\text{-cm}^{-1}$  region. Free  $\text{PF}_3$  exhibits two strong bands at  $892$  and  $848\text{ cm}^{-1}$  and upon coordination either one or both is generally observed to shift to higher energies.<sup>10</sup> Furthermore, in complexes of low symmetry, other bands of medium intensity are observed in this region. The data thus strongly support the presence of coordinated trifluorophosphine in this complex. In all cases, the  $1538\text{-cm}^{-1}$  band was observed to shift to lower energies paralleling the behavior noted for the carbonyl adduct.

All of the evidence is best consistent with structure II which contains a tetrakis(trifluoromethyl)-



rhodiacyclopentadiene ring with the metal formally  $\text{Rh(III)}$ . The coordination about the rhodium is most probably in the form of a slightly distorted trigonal bipyramid. Further support for this geometry comes from the preliminary results of an X-ray crystallographic structure determination now being undertaken on  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$ ,<sup>11</sup> which indicate that the  $\text{RhSb}_2$  portion of the molecule is nearly linear. Other examples of variously substituted metallocyclopentadiene systems have been reported by Hübel,<sup>12</sup> but this appears to be the first instance of this type of complex containing (a) a heavy transition metal and (b) no carbonyl groups. A perfluoroferracyclopentene ring has been recently reported<sup>13</sup> and an intermediate of this nature has been proposed in the cyclotrimerization of various acetylenic esters by  $\text{RhCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ .<sup>6</sup> A similar rhodium complex,  $\text{RhCl}(\text{C}_4\text{F}_4)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ , which evidently merely has F in place of  $\text{CF}_3$  groups, has also been prepared.<sup>14</sup>

The ease of addition of small donor molecules further supports the formulation  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  as a five-coordinate complex of  $\text{Rh(III)}$ . The great majority of complexes of  $\text{Rh(III)}$  are six-coordinate

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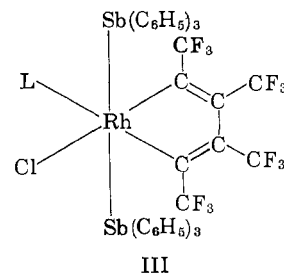
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and the ready addition of another group suggests that the rhodium is initially coordinatively unsaturated. This addition of an extra group, L, would most likely give species such as III since attack adjacent to the



chlorine would involve the least amount of rearrangement of the other groups present.

A comparison of the nmr spectra of  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  and its carbonyl adduct shows that, besides the splitting of the low-field band, the centers of both resonances have shifted downfield. This is as expected since the introduction of a carbonyl group would tend to drain some electron density out of the fluorocarbon  $\pi$  system. At first sight, one would expect that the introduction of a sixth group into the coordination sphere of the metal would result in nonequivalence within both sets of trifluoromethyl groups. However, this effect could be expected to be much less for the pair which is further from the metal. In support of this, one notes that the line of intensity 2 has become somewhat broader in the carbonyl adduct, suggesting an overlapping of peaks and a slight nonequivalence of the two trifluoromethyl groups furthest from the metal as well. A similar phenomenon has been noted for the complex  $\text{RhCl}(\text{C}_4\text{F}_4)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ .<sup>14</sup>

The downward shift in the position of the  $1538\text{-cm}^{-1}$  band on forming the carbonyl adduct is also in accord with a decrease in the ring  $\pi$ -electron density resulting from the  $\pi$ -bonding requirements of the added carbonyl group.

The analogous triphenylarsine complex,  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{As}(\text{C}_6\text{H}_5)_3)_2$ , has been prepared and exhibits an infrared spectrum identical with that of II. Its  $^{19}\text{F}$  nmr spectrum is also virtually the same, showing complex multiplets of equal intensity at  $-12.2$  and  $-5.2$  ppm. In contrast to the triphenylstibine analog, this complex does not form stable adducts with  $\text{CO}$ ,  $\text{PF}_3$ , etc.

It is significant to note that whereas in the reaction of hexafluorobut-2-yne with tris(triphenylphosphine)chlororhodium(I) at room temperature the excess fluorocarbon is polymerized to a high polymer,<sup>8</sup> no appreciable polymerization of this nature occurs in the cases reported here. In the reactions involving  $\text{RhCl}(\text{Sb}(\text{C}_6\text{H}_5)_3)_3$ , one obtains an initial adduct of one molecule of fluoroacetylene per rhodium. Under more strenuous conditions, a maximum of two molecules of the fluoroacetylene can be made to couple but no significant amount of further coupling is observed, the developing polymer apparently being intercepted and stabilized as a complex at any early stage. Occasionally a small amount of hexakis(trifluoromethyl)benzene

was found in the reaction mixture, but it is quite possible that this was a result of the known tendency of hexafluorobut-2-yne to trimerize at elevated temperatures under autogenous pressure and not from the reaction of  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{Sb}(\text{C}_6\text{H}_5)_3)_2$  with a third molecule of the acetylene.<sup>15</sup> The reaction involving  $\text{RhCl}(\text{As}(\text{C}_6\text{H}_5)_3)_3$  represents an intermediate case in which the primary product, even at room temperature, is  $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{As}(\text{C}_6\text{H}_5)_3)_2$  with no complex corresponding to I being found. It thus appears that the tendency

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of  $\text{RhCl}(\text{As}(\text{C}_6\text{H}_5)_3)_3$  and  $\text{RhCl}(\text{Sb}(\text{C}_6\text{H}_5)_3)_3$  to form more stable derivatives than  $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ <sup>2</sup> is once more illustrated with this isolation of a probable intermediate in the polymerization of hexafluorobut-2-yne by rhodium complexes.

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## The Preparation and Nuclear Magnetic Resonance Spectra of Hydridophosphine Complexes of Ruthenium and Rhodium

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The preparations of the complexes  $\text{H}_2\text{Ru}((\text{C}_6\text{H}_5)_2\text{PCH}_3)_4$ ,  $\text{H}_2\text{Ru}(\text{CO})((\text{C}_6\text{H}_5)_2\text{PCH}_3)_3$ ,  $\text{HRh}((\text{C}_6\text{H}_5)_3\text{P})_4$ ,  $\text{HRh}((\text{C}_6\text{H}_5)_3\text{P})_3$ ,  $\text{HRh}((\text{C}_6\text{H}_5)_2\text{PCH}_3)_4$ ,  $((\text{C}_6\text{H}_5)_2\text{PCH}_3)_3\text{RhCl}$ , and  $((\text{C}_6\text{H}_5)_2\text{PCH}_3)_2(\text{CO})\text{RhCl}$  are described. The nmr spectra of these complexes are discussed with regard to possible structures. The results confirm a rapid ligand exchange in these types of compounds.

### Introduction

Hydrido complexes of the transition metals have been extensively investigated during the past decade.<sup>2</sup> Recently there has been considerable interest in the hydrido and chloro complexes of ruthenium and rhodium from the standpoint of their significance in homogeneous catalytic reactions.<sup>3-5</sup> It has been shown that compounds with a ruthenium or rhodium metal-to-hydrogen bond are the active intermediates in the homogeneous hydrogenation of olefins. There is relatively little information in the literature concerning low-valent ruthenium and rhodium hydrides, and still less is known about the stereochemistry of these types of complexes.

Molecular stereochemistries of transition metal hydrides have in many cases been deduced from nmr measurements.<sup>6,7</sup> From the P-H nuclear spin-spin coupling constants derived from the fine structure of the hydride resonance it is often possible to draw some

firm conclusions about the geometrical arrangement of the phosphine ligands.

In the present paper we wish to report the synthesis and nmr studies of some novel hydrido and chloro complexes of ruthenium and rhodium, with special emphasis on structural elucidation.

### Experimental Section

The nmr spectra were determined on a field-frequency stabilized Varian HR 100 using hexamethyldisiloxane as an internal reference (unless otherwise stated). The infrared spectra were determined *via* potassium bromide films. All preparations were carried out under an argon atmosphere.

**Preparation of Compounds. *cis*-Dihydridotetrakis(diphenylmethylphosphine)ruthenium(II).**—A mixture consisting of 2.5 g of  $[(\text{C}_6\text{H}_5)_2\text{PCH}_3]_4\text{Ru}_2\text{Cl}_3\text{Cl}$ ,<sup>8</sup> 2.5 ml of diphenylmethylphosphine, 25 ml of benzene, 25 ml of ethanol, and 10 ml of anhydrous hydrazine was pressured with 600 psig of hydrogen and warmed at 80° for 30 min. Upon cooling, the white separated solid was filtered and recrystallized from ethanol (2 g, 83% yield). *Anal.* Calcd for  $((\text{C}_6\text{H}_5)_2\text{PCH}_3)_4\text{RuH}_2$ : C, 69.1; H, 6.0; Ru, 11.2. Found: C, 68.8; H, 6.1; Ru, 11.0; mp 188–190°;  $\gamma(\text{Ru-H})$  1940, 1885  $\text{cm}^{-1}$ .

***cis*-Dideuteriotetrakis(diphenylmethylphosphine)ruthenium(II).**—A benzene solution containing 1 g of  $\text{H}_2\text{Ru}((\text{C}_6\text{H}_5)_2\text{PCH}_3)_4$  and a trace of hexene-1 was treated at 120° with 200 psig of deuterium for 3 hr. Upon cooling, a white solid separated which was subsequently filtered (0.6 g, 60% yield);  $\gamma(\text{Ru-D})$  1390, 1355  $\text{cm}^{-1}$ .

***cis*-Dihydridocarbonyltris(diphenylmethylphosphine)ruthenium(II).**—A benzene solution containing 0.5 g of  $\text{H}_2\text{Ru}((\text{C}_6\text{H}_5)_2\text{P}$

(1) To whom inquiries should be addressed.

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