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Intramolecular and Intermolecular Ligand Exchange in Trifluorophosphinerhodium Complexes of Di-*tert*-butylacetylene. Rotation of Trifluorophosphine Groups about a Rhodium–Rhodium Double Bond

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Octakis(trifluorophosphine)dirhodium, $Rh_2(PF_3)_8$, reacts with di-*tert*-butylacetylene, t-Bu_2C_2, to give a yellow, crystalline complex $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$. This is believed to contain a bridging acetylene moiety lying over and perpendicular to $Rh(PF_3)_3$ and $Rh(PF_3)_2$ groups which are joined by a rhodium–rhodium double bond. ^{19}F NMR spectra in the temperature range 24–116° show that the PF_3 groups on each rhodium atom undergo intramolecular exchange with identical activation energies but without exchanging between the rhodium atoms, i.e., the ligands rotate about the metal–metal double bond. The free energy of activation $\Delta G^{\ddagger}$ is estimated from line shape analysis to be 15.1 ± 0.5 kcal/mol, being independent of temperature. The complex $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ reversibly adds PF_3 to give $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ which undergoes both intramolecular and intermolecular exchange of PF_3. The free energy of activation $\Delta G^{\ddagger}$ for the intramolecular process, estimated as 13.3 kcal/mol, is considerably higher than the values found for other $Rh_2(PF_3)_6$(ac) complexes, probably owing to steric hindrance by the bulky *tert*-butyl groups. This feature is probably also responsible for the relative ease of intermolecular PF_3 exchange in $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ and for the stability of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$.

Introduction

A wide variety of acetylenes (ac) react with octakis(trifluorophosphine)dirhodium, $Rh_2(PF_3)_8$, to give bridging acetylene complexes $Rh_2(PF_3)_6$(ac),[1,2] which are structurally analogous to the well-known $Co_2(CO)_6$(ac) complexes obtained from $Co_2(CO)_8$ and acetylenes.[3] Acetylenes which behave exceptionally in their reaction with $Rh_2(PF_3)_8$ are dimethyl acetylenedicarboxylate, $CH_3O_2CC_2CO_2CH_3$, methyl propiolate, $HC_2CO_2CH_3$, and 2,2,5,5-tetramethyl-3-hexyne (di-*tert*-butylacetylene), t-Bu_2C_2.[4] The first two give rhodiacylopentadiene complexes $Rh_2(PF_3)_5(ac)_2$, as already discussed.[5] The reaction of di-*tert*-butylacetylene with $Rh_2(PF_3)_8$ and the inter- and intramolecular exchange behavior of the resulting complexes are discussed in this paper.

Experimental Section

Experimental, spectroscopic, and line-shape fitting procedures are as previously described.[2] ^{19}F NMR data are in Tables I and II.

Preparation of μ-2,2,5,5-Tetramethyl-3-hexyne-pentakis(trifluorophosphine)dirhodium(0)(*Rh–Rh*), $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$. A mixture of $Rh_2(PF_3)_8$ (0.30 g) and di-*tert*-butylacetylene (0.10 g, excess) in *n*-hexane (20 ml) was heated under reflux in a nitrogen atmosphere for 20 min. The solvent was removed under reduced pressure (100 mm) and the gummy brown residue was allowed to stand in air for several hours to decompose air-sensitive side products. It was then extracted with two 20-ml portions of isopentane, and the combined extracts were filtered. On cooling the filtrate to −78°, orange-yellow crystals slowly formed. These were recrystallized from 5 ml of isopentane and dried in vacuo at 0° for 5 hr to give 0.21 g (82%) of the complex, mp 145–148° (sealed tube under nitrogen; partial sublimation and decomposition). Anal. Calcd for $C_{10}H_{18}F_{15}P_5Rh_2$: C, 15.3; H, 2.3; P, 19.8; mol wt 783. Found: C, 16.0; H, 2.7; P, 20.0; mol wt (by mass spectrometry) 783. ^1H NMR ($CFCl_3$): δ 1.32 (s, CH_3). Mass spectrum (70 eV), *m/e* (relative intensity): 971 impurity (~0.6), 953 impurity (~0.2), $[Rh_2(PF_3)_6(C_{10}H_{18})]^+$ (~0.01), 791 impurity (~0.1), $[Rh_2(PF_3)_5(C_{10}H_{18})]^+$ (41), $[Rh_2(PF_3)_4(C_{10}H_{18})]^+$ (57), $[Rh_2(PF_3)_3(PF_2)(C_{10}H_{18})]^+$ (1), $[Rh_2(PF_3)_3(C_{10}H_{18})]^+$ (95), $[Rh_2(PF_3)_2(PF_2)(C_{10}H_{18})]^+$ (22), $[Rh_2(PF_3)_2(C_{10}H_{18})]^+$ (100), $[Rh_2(PF_3)(PF_2)(C_{10}H_{18})]^+$ (2), $[Rh_2(PF_3)(C_{10}H_{18})]^+$ (71), $[Rh_2(PF_2)(C_{10}H_{18})]^+$ (2), $[Rh_2(C_{10}H_{18})]^+$ (98), $[Rh_2(C_{10}H_{17})]^+$ (D), $[Rh_2(C_9H_{12})]^+$ (D), $[Rh_2(C_8H_9)]^+$ (D), $[Rh_2(C_6H_6)]^+$ (D), $[Rh_2(C_5H_6)]^+$ (D), $[Rh_2(C_4H_6)]^+$ (D), $[Rh_2(C_3H_3)]^+$ (D), $[Rh_2(C_2H_2)]^+$ (D), $[Rh_2C]^+$ (7); metastable ions at 618 for $[Rh_2(PF_3)_5(C_{10}H_{18})]^+ \xrightarrow{*} [Rh_2(PF_3)_4(C_{10}H_{18})]^+$, 531 for $[Rh_2(PF_3)_4(C_{10}H_{18})]^+ \xrightarrow{*} [Rh_2(PF_3)_3(C_{10}H_{18})]^+$, 444 for $[Rh_2(PF_3)_3(C_{10}H_{18})]^+ \xrightarrow{*} [Rh_2(PF_3)_2(C_{10}H_{18})]^+$, 359 for $[Rh_2(PF_3)_2(C_{10}H_{18})]^+ \xrightarrow{*} [Rh_2(PF_3)(C_{10}H_{18})]^+$, 274 for $[Rh_2(PF_3)(C_{10}H_{18})]^+ \xrightarrow{*} [Rh_2(C_{10}H_{18})]^+$. [D indicates ions mixed with dehydrogenation products.]

Table I. ^{19}F NMR Data for $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)^a$

	Chem shift^c (intens)		Coupling constants, Hz	
PF_3 groups^b	ϕ_F(24°)	ϕ_F(116°)	"J_{PF}"(24°)	"J_{PF}"-(116°)
1	−1.52 (2)	+2.34 (3)	1381	1391
2	+12.13 (1)		1353	
3^d	+8.12 (1)	+11.62 (2)	1375	1369
4^d	+14.11 (1)		1324	

^{a} Measured in *n*-octane with $CFCl_3$ as internal reference. ^{b} Numbered as in II. ^{c} Positive to high field of $CFCl_3$. ^{d} These assignments could be reversed.

Table II. ^{19}F NMR Data for $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)^a$

	Chem shift (intens)		Coupling constants, Hz	
PF_3 groups^b	ϕ_F(−40°)	ϕ_F(24°)	"J_{PF}"(−40°)	"J_{PF}"-(24°)
1	+4.93 (2)	+5.34 (3)	1398	1402
2	+3.92 (1)		1327	

^{a} Measured in $CFCl_3$. ^{b} Numbered as in I.

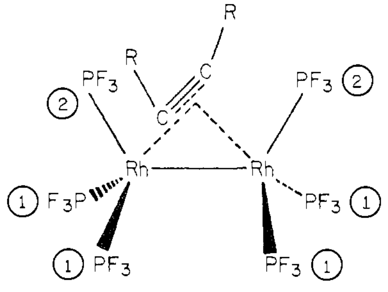
Preparation of μ-2,2,5,5-Tetramethyl-3-hexyne-hexakis(trifluorophosphine)dirhodium(0)(*Rh–Rh*), $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$. When PF_3 was passed into 5 ml of a solution of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ (0.25 g) in *n*-pentane, there was an immediate color change from yellow to red, and on cooling to −78°, a red solid formed. The reaction was reversed by heating the red solid in *n*-hexane, by bubbling nitrogen gas through the solution for 12 hr at room temperature, or by attempted vacuum sublimation. An analytically pure sample of $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ was obtained by passing PF_3 gas over a finely powdered solid sample of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ for 1 hr. Anal. Calcd for $C_{10}H_{18}F_{18}P_6Rh_2$: C, 13.8; H, 2.1; P, 21.3. Found: C, 14.3; H, 2.6; P, 21.1. ^1H NMR ($CFCl_3$, 30° in presence of free PF_3): δ 1.33 (s, CH_3).

A solution of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ in *n*-pentane gave no observable reaction with hydrogen, ethylene, or triphenylphosphine. It readily reacted with carbon monoxide giving first a transient red species which turned yellow on further passage of carbon monoxide. This reaction has not been studied further.

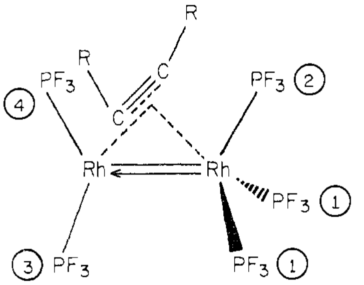
Results and Discussion

The dark brown gum initially formed on reaction of di-*tert*-butylacetylene with $Rh_2(PF_3)_8$ shows a complex spectrum in the δ 0–1.5 region of its ^1H NMR spectrum and an apparently complex ^{19}F NMR spectrum. The only organometallic complex which can be isolated from the gum is a volatile, yellow, crystalline complex $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$, which shows a parent molecular ion in its mass spectrum and fragment ions resulting from the consecutive loss of five PF_3

groups; the appropriate metastable ions are also observed. The fragmentation pattern is typical of transition metal–trifluorophosphine complexes.[6,7] The purified sample shows a singlet ^{1}H NMR resonance due to the methyl protons of the *tert*-butyl groups in equivalent environments, while the room-temperature ^{19}F NMR spectrum, which is identical with that of the crude reaction mixture, consists of four widely spaced doublets ("J_{PF}" ≈ 1400 Hz), the intensity ratios being 2:1:1:1 in order of increasing field strength; for convenience in later discussion, we label these peaks A, B, C, and D. This spectrum supports the stoichiometry given above and shows that, at room temperature, only two of the five PF$_3$ groups are equivalent. The complex reacts reversibly at room temperature with PF$_3$, both in solution and in the solid state, to give a red solid of formula Rh$_2$(PF$_3$)$_6$(*t*-Bu$_2$C$_2$), which shows a singlet methyl resonance in its ^{1}H NMR spectrum and a variable-temperature ^{19}F NMR spectrum (see below) which is similar to those of the known Rh$_2$(PF$_3$)$_6$(ac) complexes.[1,2] Thus the di-*tert*-butylacetylene complex probably has a typical Rh$_2$(PF$_3$)$_6$(ac) structure (I), but its ready loss of PF$_3$ to re-form Rh$_2$(PF$_3$)$_5$(*t*-Bu$_2$C$_2$) is exceptional; the mass spectra of the hexakis and pentakis complexes are identical. The ease with which PF$_3$ is picked up and lost suggests that the two complexes are structurally similar, and we accordingly propose structure II for Rh$_2$(PF$_3$)$_5$(*t*-Bu$_2$C$_2$), in which the acetylene bridges and is bound "sideways-on" to a Rh(PF$_3$)$_3$ and a Rh(PF$_3$)$_2$ unit. Since the PF$_3$ groups of the Rh(PF$_3$)$_2$ moiety are inequivalent, they cannot be coplanar with the acetylene and probably lie in a plane perpendicular to it. In order to account for the diamagnetism of the complex, we must assume that the Rh–Rh single bond is supported by donation of an electron pair from the Rh(PF$_3$)$_3$ group to the Rh(PF$_3$)$_2$ group, thus giving rise to a formal rhodium–rhodium double bond (Rh$\Leftarrow$Rh). A donor–acceptor single bond between two transition metal atoms is believed to be present in the compounds (η-C$_5$H$_5$)$_2$MoH$_2$·M(CO)$_5$ (M = Cr, Mo, or W)[8] and must also be invoked (at least in terms of a simple valence-bond representation) to account for the diamagnetism of ferracyclopentadiene complexes such as (OC)$_3$FeC$_4$H$_4$Fe(CO)$_3$.[9] The formation of complexes containing metal–metal double bonds from metal carbonyl–acetylene reactions is also documented, e.g., Fe$_2$(CO)$_4$(*t*-Bu$_2$C$_2$)$_2$[10] and Nb$_2$(CO)$_2$(η-C$_5$H$_5$)$_2$[(C$_6$H$_5$)$_2$C$_2$],[11] but we know of no previous example of a four-electron metal–metal bond in which three of the electrons are derived from one of the metal atoms. Attempts to obtain crystals of Rh$_2$(PF$_3$)$_5$(*t*-Bu$_2$C$_2$) suitable for X-ray structural analysis have so far been unsuccessful.



I (R = *t*-Bu)



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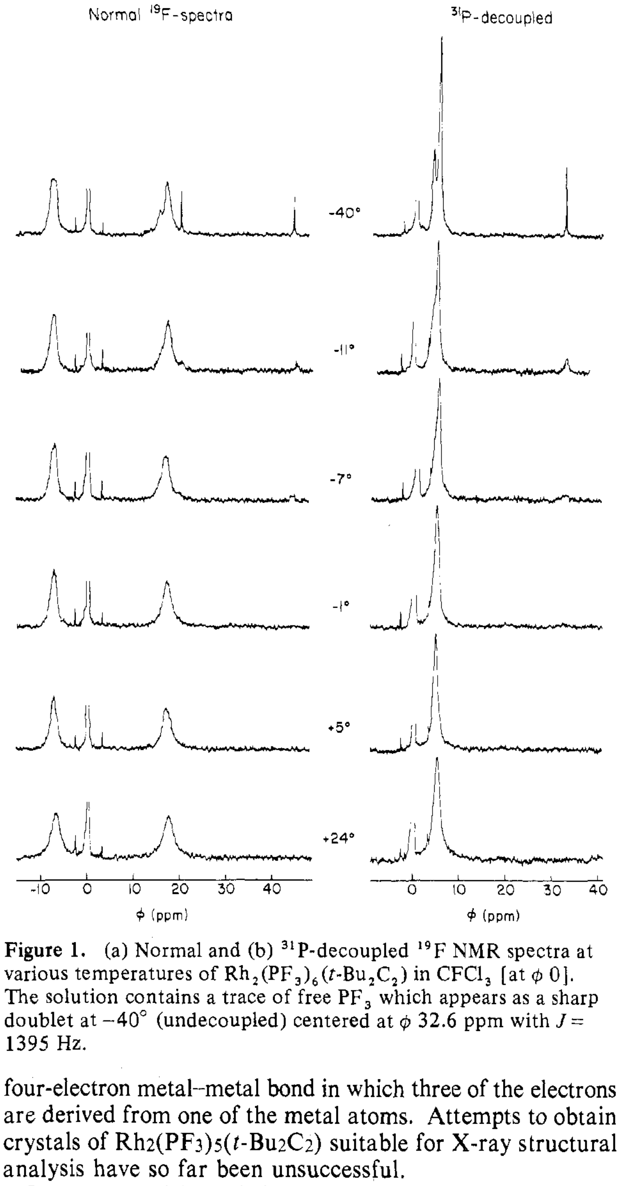

Figure 1. (a) Normal and (b) ^{31}P-decoupled ^{19}F NMR spectra at various temperatures of Rh$_2$(PF$_3$)$_6$(*t*-Bu$_2$C$_2$) in CFCl$_3$ [at ϕ 0]. The solution contains a trace of free PF$_3$ which appears as a sharp doublet at −40° (undecoupled) centered at ϕ 32.6 ppm with J = 1395 Hz.

In contrast with the behavior of Rh$_2$(PF$_3$)$_6$(*t*-Bu$_2$C$_2$), the analogous complex Co$_2$(CO)$_6$(*t*-Bu$_2$C$_2$) can be sublimed unchanged at 103° (1.5 mm) and is stable up to 220° in a sealed tube[12] (other authors[13] reported a decomposition temperature of 115–120° under unspecified conditions). Probably steric interaction between the *tert*-butyl substituents and the PF$_3$ groups, which are bulkier than CO groups, provides the driving force for the loss of one PF$_3$ ligand. It is worth noting for comparison that Co$_2$(CO)$_5$(ac) has been postulated as an intermediate in the reactions of the Co$_2$(CO)$_6$(ac) complexes with ^{14}CO and with triphenylphosphine.[14]

Fluxional Behavior. At −40°C the ^{19}F NMR spectrum of Rh$_2$(PF$_3$)$_6$(*tert*-Bu$_2$C$_2$) consists of a doublet due to P–F coupling, each component of which is broad and has shoulders suggestive of several overlapping signals (Figure 1a). The ^{31}P-decoupled spectrum shows two resolved peaks with an intensity ratio of 1:2, the weaker signal being at lower field (Figure 1b). This type of limiting spectrum is similar to those observed for Rh$_2$(PF$_3$)$_6$(RC$_2$R) complexes (R = alkyl or aryl group),[1,2] except that the latter have the weaker signal to higher field. Addition of excess PF$_3$ at −40° gives rise to the characteristic sharp doublet for that molecule at higher field, showing that intermolecular exchange is very slow. The excess of PF$_3$ can be removed by bubbling nitrogen through the

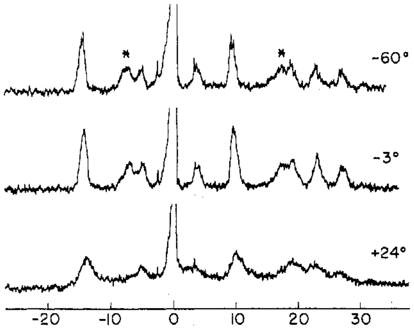

Figure 2. ^{19}F NMR spectra of a 5:1 mixture of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ and $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ in $CFCl_3$ at different temperatures showing intermolecular exchange between them. One peak of the first compound is obscured by the $CFCl_3$ resonance at ϕ 0 and the doublet of the hexakis complex at −60° is starred.

solution at −78° without any change in the spectrum of the complex, but experimentally a small amount was usually left in solution as a monitor for intermolecular exchange. Between −50 and −30° there was no change in the relative chemical shifts of the PF_3 groups. At higher temperatures (−17 to 0°) the two peaks of the complex broaden and coalesce to a single broad signal. The process responsible for this change must be *intra*molecular since the resonance due to free PF_3 is still detectable, but the latter shows broadening owing to the onset of *inter*molecular exchange. The concentration of free PF_3 relative to that of the complex is so low, however, that intermolecular exchange would have very little effect on the spectrum of the complex in this particular temperature range. Approximate line-shape analysis of the ^{19}F NMR spectrum[2] gives a free energy of activation $\Delta G^{\ddagger}$ of 13.3 ± 0.2 kcal/mol, this being independent of temperature within experimental error over the temperature range studied (−17 to 0°). As the temperature is raised from 0 to ~15°, the spectrum continues to sharpen (Figures 1), but now the doublet due to free PF_3 cannot be seen owing to the increased rate of intermolecular exchange. Between 15 and 30° the spectrum begins to broaden again, because of intermolecular exchange of PF_3 between the hexakis complex and traces of the pentakis complex formed by loss of PF_3. The rate of this process cannot be estimated because the relative amounts of PF_3 present in the complexes and present as free ligand are not known. If some of the PF_3 is removed by bubbling nitrogen through the solution for 5–10 min, an extremely broad spectrum is obtained at 24° but on cooling to −40° a spectrum attributable to a mixture of the hexakis and pentakis complexes, with no free PF_3, is obtained (Figure 2). The rapid intermolecular exchange processes observed with $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ are not observed with other acetylene complexes of this series[2] and are probably due to the steric bulk of the *tert*-butyl groups. The same factor is probably responsible for the higher $\Delta G^{\ddagger}$ observed for intramolecular exchange of PF_3 groups in the same complex.

The signals in the ^{19}F NMR spectrum of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ at 24° (see above) are quite broad, but at −60° in $CFCl_3$ considerable fine structure is evident; analysis of this complex spectrum was not attempted. Clearly, even at 24°, the pentakis complex undergoes some PF_3 exchange. At higher temperatures in *n*-octane the spectrum continues to broaden until signals A and C on the one hand, and B and D on the other, coalesce. These two signals continue to sharpen as the temperature is increased, and at +116°C two clearly resolved resonances (doublets due to P–F coupling) in the ratio 3:2 are obtained (Figure 3). The process is completely reversible, the original spectrum being regained on cooling to room temperature. There is no sign of coalescence between the two resonances at the upper limit, so that, as in the $Rh_2(PF_3)_6(ac)$ complexes[2] and in the rhodiacyclopentadiene complexes,[5] both intermolecular exchange of PF_3 and exchange of PF_3 between the metal atoms must be ruled out. Likewise the carbonyl ligands in the complex $Fe_2(CO)_5$(acenaphthylene) do not exchange between the metal atoms, though the $Fe(CO)_3$ group of this molecule shows fluxional behavior.[15] In our compounds, the process must involve the permutation of PF_3 sites on the $Rh(PF_3)_3$ *and* $Rh(PF_3)_2$ moieties without exchange between them. Line shape analysis based on the same assumptions as previously discussed[2] gives the same free energy of activation for the intramolecular process in each fragment of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$, viz., $\Delta G^{\ddagger}$ = 15.1 ± 0.5 kcal/mol, measured at ten different temperatures between 38 and 100°C. This strongly suggests that the same mechanism is responsible for both processes, and the simplest proposal is internal rotation about the Rh═Rh double bond, i.e., rotation of the $Rh(PF_3)_2$ unit by 180° and rotation of the $Rh(PF_3)_3$ unit by 120°.

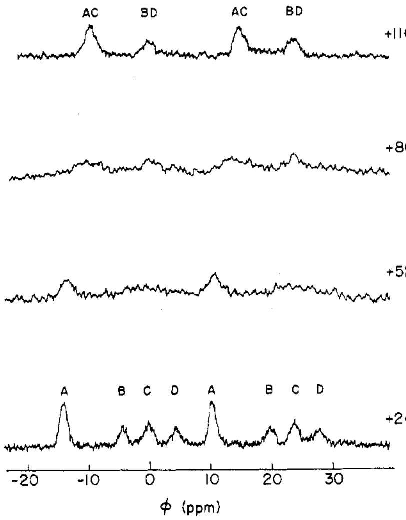

Figure 3. Variable-temperature ^{19}F spectra of $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ in *n*-octane. The labels A, B, C, and D are used to show the collapse of signals at high temperature.

It has been shown[16,17] that the binuclear cyclopentadienyl group 6 metal carbonyls $[M(\eta\text{-}C_5H_5)(CO)_3]_2$ (M = Cr or Mo) exist as mixtures of gauche and trans isomers, probably as a result of steric repulsions between the ligands across the metal–metal single bond. The barriers to interconversion are 13.7 and 15.3 kcal/mol, respectively, for the chromium and molybdenum compounds, the higher barrier corresponding to the shorter metal–metal bond, as expected. It seems reasonable to guess that the Rh–Rh bond length in $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ will be about 2.4 Å, i.e., about 0.3 Å shorter than the Rh–Rh distance in $Rh_2(PF_3)_4[P(C_6H_5)_3]_2[(C_6H_5)_2C_2]$,[1] since Fe—Fe distances are usually about 2.5 Å, and the Fe═Fe distance in $Fe_2(CO)_4(t\text{-}Bu_2C_2)_2$ is 2.215 Å.[10] Thus, if we assume that the PF_3 permutation observed in $Rh_2(PF_3)_6$(ac) complexes can be described as an internal rotation about the metal–metal bond, then the higher barrier to rotation in $Rh_2(PF_3)_5\text{-}t\text{-}Bu_2C_2)$ relative to that in $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ can be ascribed to an electronic effect, viz., the necessity to break a d_π–d_π bond, and to the increased steric interaction of the bulky *tert*-butyl groups and the PF_3 groups caused by the shorter Rh–Rh bond. The latter effect is presumably sufficient to offset the expected increase in steric interaction in $Rh_2(PF_3)_6(t\text{-}Bu_2C_2)$ owing to the extra PF_3 group. The behavior in our complexes is analogous to the well-known fact in organic chemistry that barriers to rotation are lower for single bonds, as in ethane (C—C) or methylamine (C—N), than for bonds with multiple character, as in olefins (C═C) or amides (C$\overset{\cdots}{—}$N).

A further point of similarity with cyclopentadienylmetal carbonyls is worth noting. The stabilization of the coordinately unsaturated species $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ containing a metal–metal double bond as a consequence of steric interactions between the *t*-butyl and the PF_3 groups is paralleled by the stabilization of *di*carbonyl complexes $[M[\eta\text{-}C_5(CH_3)_5](CO)_2]_2$ (M = Cr or Mo) containing metal–metal triple bonds when cyclopentadienyl is replaced by pentamethylcyclopentadienyl.[18–20]

Registry No. $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$, 56783-55-2; $Rh_2(PF_3)_6\text{-}t\text{-}Bu_2C_2)$, 56783-56-3; $Rh_2(PF_3)_8$, 14876-96-1.

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Group 5 Boranes. II. Phosphaundecaboranes and Their η-Cyclopentadienylcobalt(III) Complexes[1,2]

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In the presence of excess sodium hydride, decaborane reacts with $RPCl_2$ (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, C_6H_5) to give $7\text{-}B_{10}H_{11}PR^-$, which on protonation gives $7\text{-}B_{10}H_{12}PR$. Pure $(CH_3)_4N^+$ salts of $7\text{-}B_{10}H_{11}PR^-$ are prepared by dissolving $7\text{-}B_{10}H_{12}PR$ in aqueous dilute ammonia solution and precipitating with $(CH_3)_4NCl$ solution. Reacting $7\text{-}B_{10}H_{12}PR$, $CoCl_2$, C_5H_6, and excess KOH in anhydrous ethanol produces the complexes $(\eta\text{-}C_5H_5)Co(\eta\text{-}7\text{-}B_{10}H_{10}PR)$ and the unsubstituted complex $(\eta\text{-}C_5H_5)Co(\eta\text{-}7\text{-}B_{10}H_{10}P)^-$. The P-methyl, -ethyl, and -propyl complexes are obtained in high yield by alkylation of $(\eta\text{-}C_5H_5)Co(\eta\text{-}7\text{-}B_{10}H_{10}P)^-$ in THF.

Methods for the high-yield preparation of icosahedral η-cyclopentadienylcobalt(III) carborane complexes containing one[3] or two[4] carbons have recently appeared. The two-carbon complexes are very useful reagents for the preparation of lower closo complexes,[5] bimetallo[6] complexes, and nido complexes.[7]

We now report the synthesis of 7-phosphaundecaboranes and their η-cyclopentadienylcobalt(III) complexes. A preliminary report has appeared on the 7-phosphaundecaboranes.[8]

Results and Discussion

Decaborane in diethyl ether in the presence of 4 equiv of sodium hydride reacts with alkyl- or arylphosphorus dichlorides to produce 15–35% yields of the *nido*-phosphaundecaboranes $7\text{-}B_{10}H_{11}PR^-$ (eq 1). The cage numbering system is illustrated in Figure 1. These compounds may also be produced, although in lower yield, using triethylamine as base and THF as solvent (eq 2). Precipitation with aqueous tetramethylammonium chloride solution gives the impure salts $(CH_3)_4N(7\text{-}B_{10}H_{11}PR)$. The impure salts are protonated by dissolving them in acetonitrile and adding concentrated HCl. The protonated form, $7\text{-}B_{10}H_{12}PR$ (R = CH_3 (I), C_2H_5 (II), $n\text{-}C_3H_7$ (III), C_6H_5 (IV)) is extracted from this two-layer system with many portions of 75% hexane–25% ether. The solvent is removed in vacuo, the residue sublimed, and the sublimate crystallized from hexane–ether. Low-resolution mass spectra of crystallized I–IV show cutoffs at *m/e* 168, 182, 196, and 230, corresponding to the parent ions $^{11}B_{10}{}^{1}H_{15}{}^{12}C^{31}P^+$, $^{11}B_{10}{}^{1}H_{17}{}^{12}C_2{}^{31}P^+$, $^{11}B_{10}{}^{1}H_{19}{}^{12}C_3{}^{31}P^+$, and $^{11}B_{10}{}^{1}H_{17}{}^{12}C_6{}^{31}P^+$, respectively.

$$B_{10}H_{14} + RPCl_2 \xrightarrow[(C_2H_5)_2O]{\text{xs NaH}} \xrightarrow{H_2O} NaB_{10}H_{11}PR^- \qquad (1)$$

$$B_{10}H_{14} + RPCl_2 + 3(C_2H_5)_3N \xrightarrow{\text{THF}} 2(C_2H_5)_3NH^+Cl^- + (C_2H_5)_3NHB_{10}H_{11}PR \qquad (2)$$

Boron (^{11}B) NMR spectra (Table I) of I, II, III, and IV are generally in a 1:2:2:2:1:2 pattern, indicative of C_s cage symmetry. I and II show a 1:2:2:2:3 pattern of doublets, but the doublet of area 3 is unsymmetrical, and thus consists of a doublet of area 1 and a doublet of area 2 which are not quite degenerate. Boron NMR spectra of the analogous $7\text{-}B_{10}H_{12}AsR$[2] (R = CH_3, C_6H_5) show the same pattern of doublets, but a slight downfield shift of the resonances for $7\text{-}B_{10}H_{12}AsR$ compared to $7\text{-}B_{10}H_{12}PR$ is observed.

Proton NMR spectra of I, II, and III (Table II) are readily interpreted in terms of a phosphorus alkyl group. I shows a doublet (J_{PCH} = 11 Hz) at τ 7.92, which compares very well with the results for the known compounds[9] $7,8\text{-}B_9H_{10}CHPCH_3$ and $7,9\text{-}B_9H_{10}CHPCH_3$. In the case of II the resonance at lowest field corresponding to the methylene group is a pentet of relative intensity 1:4:6:4:1. Thus $J_{CH} = J_{PCH}$ = 8 Hz, where J_{CH} is the splitting from the methyl protons. The complexity of the spin system in IV has not allowed separation of the multiplet centered at τ 2.2 in the proton NMR spectrum.

Unlike $7\text{-}B_{10}H_{12}AsCH_3$,[2] I is not demethylated by Na in liquid NH_3. The starting material is recovered as a large