is the total peak count in t_p sec, and B_1 and B_2 are the individual background counts in $(t_b/2)$ sec; $\sigma(I)$ (reflection significance) = $[CT + (t_p/t_b)^2(B_1 + B_2)]^{1/2}$; $\sigma(F_o)$ (the reflection esd) = $\{[\sigma(I)/Lp]^2 + (\rho|F_o|^2)^2\}^{1/2}/2|F_o|$; $\sigma_s(F_o)$ (the reflection esd from counting statistics alone) = $[\sigma(I)/2(Lp)(|F_o|)]$; R_s (the statistical R factor) = $\sum\sigma_s(F_o)/\sum|F_o|$; background rejection ratio = $[|B_1 - B_2|/(B_1 + B_2)^{1/2}]$.
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Preparation and Fluxional Behavior of New Rhodiacyclopentadiene Complexes Containing Trifluorophosphine

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Dimethyl acetylenedicarboxylate, $CH_3O_2CC_2CO_2CH_3$, and methyl propiolate, $HC_2CO_2CH_3$ (ac), react with dirhodium octakis(trifluorophosphine), $Rh_2(PF_3)_8$, below room temperature to give red complexes of empirical formula $Rh_2(PF_3)_5(ac)_2$ (**1**, ac = $CH_3O_2CC_2CO_2CH_3$; **2**, ac = $HC_2CO_2CH_3$). Above room temperature explosive polymerization of the acetylenes ensues. The complexes are assigned a metallocyclopentadiene structure $(F_3P)_3Rh(\mu\text{-}C_4X_2Y_2)Rh(PF_3)_2$ (X = Y = CO_2CH_3; X = CO_2CH_3, Y = H) on the basis of ^1H and ^{19}F NMR spectra and a preliminary single-crystal X-ray study of the bis(triphenylphosphine) complex of **2**, the acetylene units in **2** being arranged in a "head-to-tail" manner. The $Rh(PF_3)_3$ unit in **1** and **2** shows fluxional behavior in the ^{19}F NMR spectra while the $Rh(PF_3)_2$ unit remains essentially unchanged, and an intramolecular tritopal rearrangement is suggested. Line shape analysis gives the free energy of activation ($\Delta G^\ddagger$) of the process in **1** and **2** as ca. 10.5 kcal/mol.

Introduction

In previous papers[1-3] we showed that a wide range of acetylenes (ac) react with dirhodium octakis(trifluorophosphine), $Rh_2(PF_3)_8$, to give binuclear complexes $Rh_2(PF_3)_6(ac)$. Single-crystal X-ray analysis of the bis(triphenylphosphine) derivative $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$[1,3] showed that the complexes are structurally analogous to the well-known cobalt carbonyl complexes, $Co_2(CO)_6(ac)$, obtained from $Co_2(CO)_8$ and acetylenes. The $Co_2(CO)_6(ac)$ complexes can react with an excess of acetylene to give complexes of empirical formula $Co_2(CO)_6(ac)_4$ or $Co_2(CO)_4(ac)_3$ in addition to cyclopentadienones, aromatic trimers, and polymers,[4] whereas, with only a few exceptions, the $Rh_2(PF_3)_6(ac)$ complexes are the only organometallic products which can be isolated from the reaction of $Rh_2(PF_3)_8$ with acetylenes. Two of these exceptions are dimethyl acetylenedicarboxylate, $CH_3O_2CC_2CO_2CH_3$, and methyl propiolate, $HC_2CO_2CH_3$, which form the subject of this paper.

Experimental Section

Experimental and spectroscopic procedures are as previously described.[2,3]

Preparations. *Warning*! The following reactions become violently explosive if carried out at or above room temperature. It is important to keep to the specified temperatures.

(Tris(trifluorophosphine)rhodia)(1–4-η-2,3,4,5-tetrakis(carboxymethyl)cyclopentadiene)bis(trifluorophosphine)rhodium(*Rh–Rh*), $Rh_2(PF_3)_5(CH_3O_2CC_2CO_2CH_3)_2$, 1. Dimethyl acetylenedicarboxylate (0.6 g, excess) was condensed onto solid $Rh_2(PF_3)_8$ (0.26 g) at liquid nitrogen temperature under a high vacuum. The mixture was allowed to warm to +20°C; gas (PF_3, ir identification) was evolved. The exothermic reaction was kept at or below 20° until no more gas came off. Unreacted acetylene was removed at 20° (0.005 mm) over a 12-hr period to leave a red solid which was extracted with four 5-ml portions of isopentane. The solution was filtered and cooled to −5° to give large red crystals of the complex, mp 162° (0.15 g, 58%).

Anal. Calcd for $C_{12}H_{12}F_{15}O_8P_5Rh_2$: C, 15.5; H, 1.3; P, 16.7; F, 30.6; mol wt 929. Found: C, 15.2; H, 1.4; P, 16.3; F, 29.8; mol wt (by mass spectrometry) 929. ^1H NMR (C_6D_6): δ 3.35 (s, CH_3); cf. $CH_3O_2CC_2CO_2CH_3$ δ 3.80. ^{19}F NMR data are in Table I.

(Tris(trifluorophosphine)rhodia)(1–4-η-2,4-bis(carboxymethyl)cyclopentadiene)bis(trifluorophosphine)rhodium(*Rh–Rh*), $Rh_2(PF_3)_5(HC_2CO_2CH_3)_2$, 2. The reaction was carried out as described above, unreacted acetylene being removed from the complex by trap-to-trap sublimation. The red solid when recrystallized from isopentane at −78° gave a 40% yield of the complex, which was further purified by vacuum sublimation.

Anal. Calcd for $C_8H_8F_{15}O_4P_5Rh_2$: C, 11.8; H, 1.0; P, 19.0; mol wt 813. Found: C, 12.3; H, 1.3; P, 18.7; mol wt (by mass spectrometry) 813. ^1H NMR (C_6D_6): δ 3.31 (s, 3, CH_3), 7.80 (m, 1, =CH), 8.24 (m, 1, =CH); cf. $HC_2CO_2CH_3$ δ 3.41 (s, 3, CH_3), 2.56 (s, 1, ≡CH). ^{19}F NMR data are in Table I.

(Bis(trifluorophosphine)triphenylphosphinerhodia)(1–4-η-2,4-bis(carboxymethyl)cyclopentadiene)(trifluorophosphine)(triphenylphosphine)rhodium(*Rh–Rh*), $Rh_2(PF_3)_3[P(C_6H_5)_3]_2(HC_2CO_2CH_3)_2$, 3. A solution of triphenylphosphine (0.38 g, excess) in *n*-pentane (15 ml) was added to $Rh_2(PF_3)_5(HC_2CO_2CH_3)_2$ (0.23 g) in *n*-pentane in an atmosphere of nitrogen. The mixture rapidly turned red and after 1 day at room temperature had deposited deep red crystals. These were collected by filtration, washed with three 20-ml portions of *n*-pentane, and vacuum dried to give 0.18 g (57%) of the complex, mp 167°.

Anal. Calcd for $C_{44}H_{38}F_9O_4P_5Rh_2$: C, 45.5; H, 3.3; P, 13.3. Found: C, 46.8; H, 4.1; P, 13.4. ^{19}F NMR ($C_6H_5CH_3$, 24°, 90 scans): ϕ (ppm upfield of $CFCl_3$) 13.7 (d, PF_3, "J_{PF}" = 1345 Hz), 14.0 (d, PF_3, "J_{PF}" = 1353 Hz), 17.2 (d, PF_3, "J_{PF}" = 1393 Hz). Note: "J_{PF}" may include a contribution from $^3J_{PF}$ couplings in addition to the main contribution from $^1J_{PF}$.

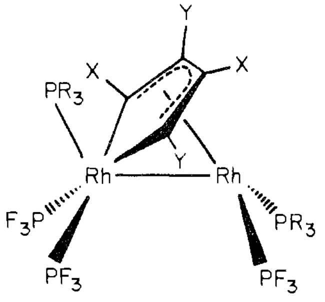
Mass Spectra. The 70-eV mass spectrum of $Rh_2(PF_3)_5(CH_3O_2CC_2CO_2CH_3)_2$ is listed as an example (the symbol D indicates that the ion is mixed with dehydrogenation products): $Rh_2(PF_3)_5(C_{12}H_{12}O_8)^+$ (32), $Rh_2(PF_3)_4(PF_2)(C_{12}H_{12}O_8)^+$ (0.1), $Rh_2(PF_3)_5(C_{11}H_9O_7)^+$ (9), $Rh_2(PF_3)_5(C_{10}H_{10}O_6)^+$ (3), $Rh_2(PF_3)_4(C_{12}H_{12}O_8)^+$ (31), $Rh_2(PF_3)_3(PF_2)(C_{12}H_{12}O_8)^+$ (11), $Rh_2(PF_3)_4(C_{11}H_9O_7)^+$ (3), $Rh_2(PF_3)_4(C_{10}H_{10}O_6)^+$ (2), $Rh_2(PF_3)_3(C_{12}H_{12}O_8)^+$ (61), $Rh_2(PF_3)_2(PF_2)(C_{12}H_{12}O_8)^+$ (3), $Rh_2(PF_3)_3(C_{11}H_9O_7)^+$ (6), $Rh_2(PF_3)_3(C_{10}H_{10}O_6)^+$ (6), $Rh_2(PF_3)_2(C_{12}H_{12}O_8)^+$ (100), $Rh_2(PF_3)(PF_2)(C_{12}H_{12}O_8)^+$ (5), $Rh_2(PF_3)_2(C_{11}H_9O_7)^+$ (1), $Rh_2(PF_3)_2(C_{10}H_{10}O_6)^+$ (11), $Rh_2(PF_3)(C_{12}H_{12}O_8)^+$ (49), $Rh_2(PF_2)(C_{12}H_{12}O_8)^+$ (3), $Rh_2(PF_3)(C_{11}H_9O_7)^+$ (D), $Rh_2(PF_3)(C_{10}H_{10}O_6)^+$ (D), $Rh_2(C_{12}H_{12}O_8)^+$ (52), $Rh_2(C_{11}H_9O_7)^+$ (D), $Rh_2(C_{10}H_{10}O_6)^+$ (38), $Rh_2(C_9H_7O_5)^+$ (D), $Rh_2(C_8H_8O_4)^+$ (D), $Rh_2(C_7H_5)_3^+$ (D), $Rh_2(C_6H_6O_2)^+$ (D), $Rh_2(C_5H_3O)^+$ (D), $Rh_2(C_4H_4)^+$ (D), *m/e* 191 (?), $Rh(C_4H_4)^+$ (16).

Results and Discussion

If an excess of either dimethyl acetylenedicarboxylate, $CH_3O_2CC_2CO_2CH_3$, or methyl propiolate, $HC_2CO_2CH_3$, is condensed onto solid $Rh_2(PF_3)_8$ and the mixture is warmed to about +40°, a violent explosion nearly always occurs. The reaction can be controlled at or below 20°, and red crystalline solids of empirical formula $Rh_2(PF_3)_5(ac)_2$ (ac = $CH_3O_2CC_2CO_2CH_3$, **1**, or $HC_2CO_2CH_3$, **2**,) can be isolated. Under similar conditions, most other acetylenes (ac), including $C_6H_5C_2CO_2CH_3$ and $CH_3C_2CO_2CH_3$, react with $Rh_2(PF_3)_8$ to give $Rh_2(PF_3)_6(ac)$.[1,2] Complexes of this type may be intermediate in the formation of $Rh_2(PF_3)_5(ac)_2$, but they could not be detected. In the absence of the acetylenes, the $Rh_2(PF_3)_5(ac)_2$ complexes are stable; they decompose only above 200° and can be sublimed in vacuo. However, they catalyze the polymerization of the acetylenes just above room temperature in an unpredictably violent manner.

The mass spectra of **1** and **2** show parent molecular ions, $[Rh_2(PF_3)_5(ac)_2]^+$, which fragment primarily by losing consecutively five PF_3 groups; i.e., ions of the type $[Rh_2(PF_3)_x(ac)_2]^+$ (x = 0–5) are most intense in the spectra. A series of less intense fragments $[Rh_2(PF_3)_y(PF_2)(ac)_2]^+$ (y = 0–4) resulting from loss of fluorine atoms is also present; this type of fragmentation also occurs in the $Rh_2(PF_3)_6(ac)$ complexes.[2] In addition the spectrum of **1** shows two minor fragmentation pathways involving the loss of OCH_3 and CO_2CH_2, respectively, from $[Rh_2(PF_3)_x(C_{12}H_{12}O_8)]^+$ (x = 0–5). The ion $[RhC_{12}H_{12}O_8]^+$ progressively loses OCH_3 or CO_2CH_2 until $[Rh_2C_4H_4]^+$ is obtained, which fragments further to give $[RhC_4H_4]^+$, which is presumably the rhodiacyclopentadiene ion.

In the ^1H NMR spectra of **1** and **2**, the carboxymethyl protons appear as a singlet slightly upfield of the values for the free acetylenes. The "acetylenic" protons of **2** consist of two groups of multiplets, which are shifted well downfield of the value for the free ligand, suggesting that the protons are inequivalent and are attached to sp^2-hybridized carbon atoms. The spectrum sharpens somewhat on heteronuclear noise decoupling of ^{103}Rh, showing that coupling to this nucleus is weak, and the upfield proton now appears as a more clearly resolved doublet (J = 3.5 Hz) owing to coupling with the other proton. ^{31}P noise decoupling results in two broad, poorly resolved doublets; the broadness may be due to incomplete decoupling or, more likely, to coupling with ^{103}Rh and ^{19}F. The ^{19}F NMR spectra of **1** and **2** are similar (Table I) and consist at room temperature of two pairs of doublets with fine structure, the ratio being 2:3. The chemical shifts and the large splitting (~1350 Hz), mainly due to $^1J_{PF}$, are characteristic of coordinated PF_3.[5] There thus appear to be only two different chemical environments for the five PF_3 groups at room temperature, and we assume that three of them are attached to one rhodium atom and the other two are bound to the other rhodium atom.



1: R = F, X = Y = CO_2CH_3
2: R = F, X = H, Y = CO_2CH_3
3: R = C_6H_5, X = H, Y = CO_2CH_3

Figure 1. Rhodiacyclopentadiene structure.

The structure most consistent with the available evidence consists of a rhodiacyclopentadiene unit to which the second rhodium atom is attached via a metal–metal bond and two metal–olefin μ bonds (Figure 1). The inert-gas rule is obeyed if we put three PF_3 ligands on the rhodium atom in the metallocyclopentadiene ring and two on the other rhodium atom; the reverse assignment would lead to a deficiency of electrons on the rhodium atom in the ring and an excess on the other. The "head-to-tail" arrangement of acetylene units in **2** is suggested by the observed inequivalence of the ring protons. Since the PF_3 groups in the $Rh(PF_3)_2$ unit of both **1** and **2** are equivalent even at low temperature, they are probably disposed symmetrically with respect to the ring; i.e., there is a mirror plane bisecting the ring and the two pairs of PF_3 groups and containing the unique PF_3 group. This can only be strictly true for **1**, in which all of the substituents on the rhodiacyclopentadiene ring are identical, but the asymmetry introduced by the different ring substituents in **2** is evidently not sufficient to affect the shieldings of the PF_3 nuclei. The ^{19}F NMR spectra of the $Rh(PF_3)_2$ groups in **1** and **2** can be analyzed on the basis of an $AA'MX_3X'_3$ spin system (Table I), but the spectrum of the $Rh(PF_3)_3$ unit was not well enough resolved to permit detailed analysis. The expected inequivalence of the PF_3 groups in the $Rh(PF_3)_3$ unit is observed only at low temperature (see below).

Attempts to prove the presence of the rhodiacyclopentadiene ring by chemical degradation (e.g., halogenation) have been unsuccessful. However, a single-crystal X-ray study[6] of the bis(triphenylphosphine) complex **3** obtained from **2** and triphenylphosphine at room temperature has established the structure shown in Figure 1. Because of small crystal size, it has not yet been possible to extract accurate molecular parameters, but the basic arrangement is beyond doubt. The ^{19}F NMR spectrum of **3** shows the presence of three nonequivalent PF_3 groups, of which two have very similar chemical shifts, in agreement with the structure shown.

The rhodium complexes are structurally similar to a variety of metallocyclopentadiene complexes isolated from the reaction of metal carbonyls with acetylenes (ac), of which the $Fe_2(CO)_6(ac)_2$ types are probably the most numerous.[7,8] Although a number of mononuclear rhodiacyclopentadiene complexes are known,[9,10] the only binuclear complexes of this type previously described are $[Rh_2Cl_2(CO)(C_2H_5C_2C_2$-

Table I. NMR Parameters Obtained from ^{19}F Spectra of **1** and **2**[a]

		1	2
$Rh(PF_3)_2$ at +24° or −90°	ϕ	13.0	10.0[b]
	$^1J_{PF}$	−1337	−1337
	$^3J_{PF}$	+14	+13
	$^2J_{PP}$	107	109
	$^2J_{RhF}$	24	25
	$^4J_{PF}$[c]	8	10
$Rh(PF_3)_3$ at +24° (time-averaged)	ϕ	15.6	13.9
	$^1J_{PF} + 2(^3J_{PF})$	1378	1369
	$^2J_{RhF}$	11	12
$Rh(PF_3)_3$ at −90° ("frozen")[d]	ϕ (major peak)	16.2	15.5
	"J_{PF}"[e]	1372	1381
	Splitting[f]	24	20
	ϕ (minor peak)	12.9	12.2
	"J_{PF}"[e]	1461	1468

[a] Measured in $CFCl_3$; ϕ in ppm upfield from $CFCl_3$, ±0.1 ppm; $^1J_{PF}$ and $^3J_{PF}$ ±5 Hz, other couplings ±2 Hz. [b] Equivalence of PF_3 groups fortuitous (see text). [c] Splitting observed only at −90° and could be due to J_{RhF} or J_{HF}, though assignment given is considered most likely. [d] Two PF_3 groups equivalent (major peak) and one unique (minor peak). [e] "J_{PF}" includes a contribution from $^3J_{PF}$ couplings in addition to the main contribution from $^1J_{PF}$. [f] Probably due to $^2J_{RhF}$. Note that $^2J_{RhF}$ to the unique PF_3 group is not resolved, thus accounting for the smaller averaged $^2J_{RhF}$ observed at +24°.

$H_5)_2]_2$,[11] obtained from $[RhCl(CO)_2]_2$ and 3-hexyne, and $Rh_2(\eta\text{-}C_5H_5)_2(CF_3C_2CF_3)_2$, **4**,[12] isolated from the reaction of $Rh(\eta\text{-}C_5H_5)(CO)_2$ with hexafluorobut-2-yne. The complex $Rh_2(CO)_3[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)_2$,[13] formed from the reaction of $Rh_4(CO)_{12}$, diphenylacetylene, and triphenylphosphine, may be similar to our PF_3 complexes, though the authors preferred a formulation involving two coordinated diphenylacetylene molecules on the basis of infrared evidence. Metallocyclopentadiene complexes are almost certainly intermediates in metal-catalyzed cyclotrimerizations of acetylenes;[9] the cobalt carbonyl catalyzed reactions are believed to proceed successively via the acetylene complex $Co_2(CO)_6(ac)$ and the bis(allyl) "fly-over" complex $Co_2(CO)_4(ac)_3$, and thermal degradation of the latter gives the 1,2,4-trisubstituted benzene.[4,8] Although it has not been isolated, a cobaltacyclopentadiene complex $Co_2(CO)_5(ac)_2$, analogous to $Rh_2(PF_3)_5(ac)_2$, seems a likely precursor to the "fly-over" complex. We do not know why dimethyl acetylenedicarboxylate and methyl propiolate are the only acetylenes of those studied to give rhodiacyclopentadiene complexes on reaction with $Rh_2(PF_3)_8$.

Fluxional Behavior. The room-temperature ^{19}F NMR spectrum of **2** (Figure 2) shows that the PF_3 groups on each rhodium atom are apparently equivalent, although the postulated metallocyclopentadiene structure implies that two of the PF_3 groups of the $Rh(PF_3)_3$ unit, which are related by the mirror plane, are in a different environment from the third (we again neglect asymmetry introduced by the different ring substituents of **2**). At lower temperatures (Figure 2) the ^{19}F resonance of the $Rh(PF_3)_3$ unit broadens and below −55° begins to separate into two peaks which sharpen on further cooling. The low-temperature limiting spectrum is reached at about −80° and consists essentially of two doublets in a ratio of 2:1 as expected. The $Rh(PF_3)_2$ resonance remains essentially unchanged over the same temperature range except for the resolution of one further coupling, possibly due to the ^{31}P nucleus of the unique PF_3 group of the $Rh(PF_3)_3$ unit. Similar behavior is also observed in the variable-temperature ^{19}F NMR spectrum of **1**, and in both cases the changes are reversible. The room-temperature spectra are unaffected by the presence of free PF_3 and are doubled by coupling with ^{103}Rh, showing that the exchange process is intramolecular, not intermolecular. The separate resonances for the $Rh(PF_3)_2$ and $Rh(PF_3)_3$ moieties do not coalesce above room temperature so that PF_3 groups are not transferred between the rhodium atoms. Although a full density matrix line shape analysis is not possible owing to the complexity of the spin system in **1** and **2**, we have carried out an approximate line shape analysis using previously described assumptions.[2] Values of $\Delta G^{\ddagger}$ for **1** and **2** were calculated over a range of temperatures from the Eyring equation

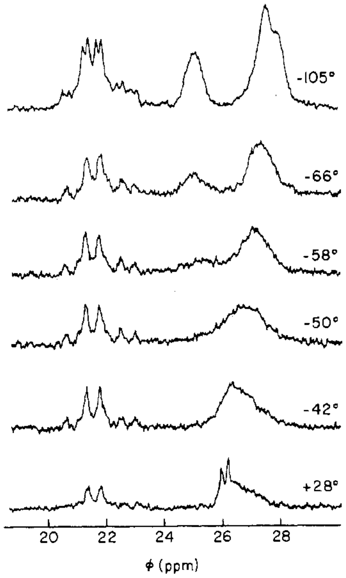


Figure 2. High-field half of the ^{19}F NMR spectrum of $Rh_2(PF_3)_5(HC_2CO_2CH_3)_2$ in $CFCl_3$ at various temperatures. At 28° the low-field halves of the $(PF_3)_2$ and $(PF_3)_3$ spectra are mirror images of the respective high-field halves shown here.

Table II. Intramolecular Exchange Parameters for **1** and **2**

Complex	Temp range, °C	Rates, sec^{-1}	$\Delta G^{\ddagger}$, kcal/mol
1	−78 to −32	20–400	10.5 ± 0.5
2	−76 to −50	20–300	10.3 ± 0.2

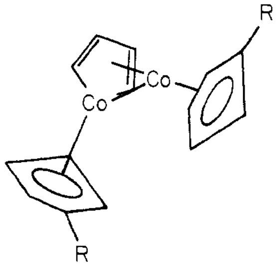
$$\text{rate } (k) = \kappa\left(\frac{kT}{h}\right)\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

the transmission coefficient being taken as unity. The values are independent of temperature within experimental error and about 3 kcal/mol higher than those calculated for the intramolecular exchange in $Rh_2(PF_3)_6(ac)$ complexes.[2]

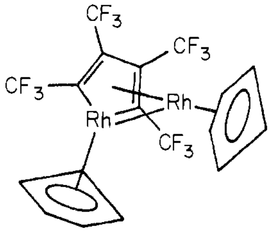
As previously discussed, there are two distinct permutational possibilities, viz, a pairwise exchange of PF_3 groups or simultaneous permutation of all three PF_3 groups (tritopal exchange). The fact that at room temperature two distinct ^{19}F signals are observed corresponding to the PF_3 groups of the $Rh(PF_3)_2[P(C_6H_5)_3]$ moiety in **3** suggests that the first alternative is unlikely for **1** and **2**, though it cannot be completely excluded. In principle the two processes should give rise to different line shapes unless the rate constants for the three pairwise exchanges happen to be equal, but the complexity of the spin system and the relatively poor resolution of the spectra do not justify an attempt to distinguish between the mechanisms by this means.

The PF_3 scrambling in **1** and **2** is probably similar to the ligand scrambling observed in olefiniron tetracarbonyls, in dieneiron tricarbonyls, and in PF_3 derivatives of the latter (see discussion in ref 2), to account for which a process of concerted ligand rotation about a general axis, coupled with some bending, has been suggested.[14-16] We offer the same explanation and note that bending or distortion of the effectively tridentate (metallocyclopentadiene)$Rh(PF_3)_2$ group cannot make a significant contribution to the stereochemical nonrigidity. Most of the reported examples of intramolecular ligand scrambling refer to formally five-coordinate complexes. It is therefore surprising at first sight that **1** and **2** show fluxional behavior of this type, for if we count the two σ-bonded carbon atoms and the other rhodium atom as occupying three coordination sites, the rhodium atom carrying the three PF_3 groups is six-coordinate. The CO groups in the six-coordinate complexes $M(CO)_3(C_7H_8)$ (M = Cr or Mo; C_7H_8 = cycloheptatriene) do show fluxional behavior[17] though the suggested possibility of rotation of the organic ligand relative to the CO groups cannot apply in our compounds.

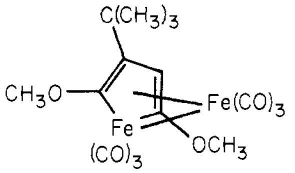
A mechanism involving the "flipping" of the organic moiety from one metal atom to the other, or ring tautomerism, has been postulated to occur in a number of metallocyclopentadiene complexes, e.g., complexes **4**–**6**,[18–20] in which each metal atom has the same number of CO or C_5H_5 ligands. If such a mechanism were operative in complexes **1** and **2**, each rhodium atom would lose its rare gas configuration, unless the process were accompanied by transfer of one PF_3 group, which we have shown does not take place. Moreover, the activation energies for ring flipping appear to be ca. 10 kcal/mol higher than those we observe. Thus the simplest explanation for the stereochemical nonrigidity of complexes **1** and **2** is a tritopal rearrangement of the PF_3 groups of the $Rh(PF_3)_3$ moiety without severe distortion of the rest of the molecule, a possibility which was also considered for the $Rh_2(PF_3)_6(ac)$ complexes.[2] A more complicated mechanism involving the rotation of a rigid $Rh_2(PF_3)_5$ moiety about the Rh–Rh bond axis is also possible. This would interchange the two PF_3 groups of the $Rh(PF_3)_2$ unit, but as these are in any case equivalent, they provide no mechanistic information. The fluxional behavior of the $Rh_2(PF_3)_5(ac)_2$ complexes is very similar to that recently reported[21] for the complex $Fe_2(CO)_5$(acenaphthylene), in which the CO groups of the $Fe(CO)_3$ unit permute among themselves without transferring to the other iron atom.



5, R = H or CO_2CH_3



4



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Registry No. **1**, 56783-52-9; **2**, 56783-53-0; **3**, 56783-54-1; $Rh_2(PF_3)_8$, 14876-96-1; $CH_3O_2CC_2CO_2CH_3$, 762-42-5; $HC_2CO_2CH_3$, 922-67-8; $P(C_6H_5)_3$, 603-35-0.

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