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Contribution from the Research School of Chemistry,
The Australian National University, Canberra, A.C.T. 2600, Australia

Preparation and Fluxional Behavior of μ-Acetylene-hexakis(trifluorophosphine)dirhodium Complexes

M. A. BENNETT,* R. N. JOHNSON, and T. W. TURNEY

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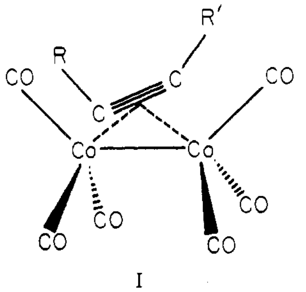
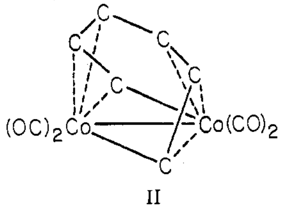
Acetylenes react with octakis(trifluorophosphine)dirhodium, $Rh_2(PF_3)_8$, to give a series of binuclear complexes $Rh_2(PF_3)_6(RC_2R')$ which have been characterized by elemental analysis, ^1H and ^{19}F NMR spectroscopy, and mass spectrometry. Like the well-known $Co_2(CO)_6(RC_2R')$ complexes, the rhodium compounds contain a bridging acetylene ligand lying over and perpendicular to a metal–metal bond. The phenylacetylene derivative ($R = C_6H_5$, $R' = H$) catalyzes the linear polymerization of phenylacetylene, unlike the corresponding cobalt carbonyl complex, which catalyzes cyclotrimerization. Variable-temperature ^{19}F NMR studies show that the PF_3 groups of $Rh_2(PF_3)_6(RC_2R')$ undergo intramolecular exchange leading to NMR equivalence at room temperature. At low temperatures the ^{19}F resonances appear in a 2:1 ratio when $R = R'$ and a 1:1:1 ratio when $R \neq R'$. ^{31}P noise decoupling has been used to simplify the spectra, and the apparatus for removing the large ^{31}P–^{19}F coupling (~1400 Hz) is described. The free energy of activation ($\Delta G^{\ddagger}$) is of the order 6–10 kcal/mol, being higher for electron-withdrawing and for sterically hindered acetylenes. Possible mechanisms for the exchange process are discussed.

Introduction

The reaction of dicobalt octacarbonyl, $Co_2(CO)_8$, with a range of mono- and disubstituted acetylenes (ac) gives two types of complexes of general formulas $Co_2(CO)_6(ac)$ and $Co_2(CO)_4(ac)_3$, the first type being formed at room temperature using stoichiometric quantities of reagents, the second being formed at higher temperatures with excess acetylene.[1-5] Single-crystal X-ray studies of members of the first series, e.g., $Co_2(CO)_6(C_6H_5C_2C_6H_5)$[6] and $Co_2(CO)_6(C_6F_6)$[7] (C_6F_6 = hexafluoro-1,3-cyclohexenyne) and related molecules,[8-11] have shown that the common structural feature is an acetylene moiety bridging two metal atoms and lying above and at right angles to the metal–metal bond axis (I). X-Ray studies of two members of the second series[12,13] have shown that the three acetylene units are joined to form a six-carbon "fly-over" bridge between two dicarbonylcobalt units (II). Thermal decomposition of $Co_2(CO)_4(ac)_3$ gives the 1,2,4-trisubstituted benzene,[2] and complexes of this type may be involved in the cobalt carbonyl catalyzed cyclotrimerization of acetylenes to benzenes.[3,14] Less extensive series of complexes analogous to I are formed by other transition metals, e.g., $Ni_2(C_5H_5)_2(ac)$,[15] $Mo_2(C_5H_5)_2(CO)_2(ac)$,[16] and $Rh_2(C_5H_5)_2(CO)_2(ac)$,[17] but the rhodium analogues of $Co_2(CO)_6(ac)$ are unknown, probably because the precursor, $Rh_2(CO)_8$, is stable only under high pressures of CO.[18] A rhodium(0) complex $Rh_2(CO)_3[P(C_6H_5)_3](C_6H_5C_2C_2H_5)_2$, which has been isolated from the reaction of $Rh_4(CO)_{12}$, diphenylacetylene, and triphenylphosphine, is thought to contain one diphenylacetylene attached to each rhodium atom (III).[19] In view of the well-established similarity of CO and PF_3 as ligands[20,21] and in particular the marked similarities of $Co_2(CO)_8$ and $Rh_2(PF_3)_8$ in their reactions with hydrogen and with group 4 hydrides,[22] it seemed worthwhile to investigate the reactions of $Rh_2(PF_3)_8$ with acetylenes. It was also hoped that ^{19}F NMR studies would reveal intramolecular and intermolecular ligand-exchange processes in the resulting complexes similar to those which have been studied by ^{13}C NMR in analogous carbonyl complexes.[23] Our results, which have appeared in a preliminary report,[24] are described in this series of papers.

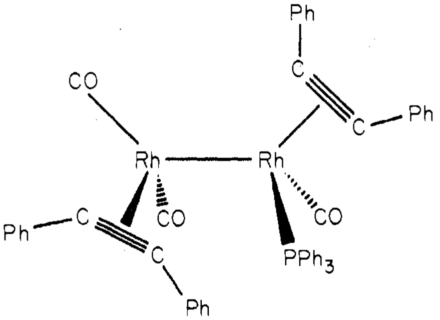


I



II

(substituents on carbon chain omitted for clarity)



III

Experimental Section

Starting Materials. Reactions were carried out either under dry nitrogen or by using standard vacuum-line techniques. Solvents were dried and degassed before use; those which were gaseous at room temperature were condensed into NMR tubes directly from cylinders. The complex $Rh_2(PF_3)_8$ was prepared as described previously[22] but in variable and often poor yields (5–20% based on $[RhCl(PF_3)_2]_2$).

Table I. Preparation, Purification, Analytical Data, and Melting Points of $Rh_2(PF_3)_6(ac)$[a]

Acetylene (ac)	Method of prepn[b]	Color	Mp, °C	Sublimation temp, °C (0.005 mm)	Calcd % C	Calcd % H	Calcd % P	Found % C	Found % H	Found % P	Mol wt[c]
HC_2H	B	Yellow	60–61	RT	3.1	0.3	24.5	3.5	0.5	24.3	759
$C_6H_5C_2H$	B	Dark brown	Oil	80	11.5	0.7	22.2	11.9	0.6	21.9	835
n-$C_4H_9C_2H$	B	Brown	Oil	60					NM[d]		815
t-$C_4H_9C_2H$	B	Orange-brown	18	50	8.8	1.2	22.8	9.3	1.6	22.4	815
$CH_3C_2CH_3$	B	Yellow	118[e]	RT	6.0	0.8	23.6	6.4	0.9	23.4	787
n-$C_3H_7C_2CH_3$	B	Yellow	NM	50					NM[d]		815
$C_6H_5C_2CH_3$	A	Orange	68	f	12.7	1.2	21.9	13.0	1.1	21.8	849
$C_6H_5C_2C_2H_5$	A	Red	Oil	90					NM[d]		863
$C_6H_5C_2C_6H_5$	A	Red	143–145[e]	120	18.4	1.1	20.3	18.2	1.2	20.3	910
$C_6H_5C_2CO_2CH_3$	A	Orange	Oil	d					NM[d]		893
p-$NO_2C_6H_4C_2CO_2C_2H_5$[g]	A	Yellow	58	f	13.9	1.0	19.5	14.5	1.3	19.3	952
$CF_3C_2CF_3$	B	Yellow	159[e]	RT	5.4	0.0	20.2	5.4	<0.4	20.5	895
$CH_3C_2CO_2CH_3$	B	Yellow	NM	RT					NM[d]		831

[a] Abbreviations: NM, not measured; RT, room temperature. [b] A = reaction in refluxing n-hexane; B = reaction in vacuum line (see Experimental Section). [c] By mass spectrometry; values agree with those calculated in all cases. [d] Sample contaminated with free acetylene; identified by presence of parent ion in mass spectrum and by ^1H and ^{19}F NMR. [e] Appreciable sublimation before melting. [f] Purified by recrystallization from isopentane at −78°. [g] Percent N: calcd, 1.5; found, 1.7.

Acetylenes were obtained commercially, except for $RC_2CO_2CH_3$($R = CH_3$ or C_6H_5), which were obtained from the corresponding acids and diazomethane.

Physical Measurements. Microanalyses were carried out by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates). Melting points were measured on a Gallenkamp melting point apparatus on samples in tubes sealed under nitrogen and are uncorrected. Mass spectra were measured at 70 eV on an AEI MS9 instrument using a direct-inlet probe cooled to 0° (Mr. K. W. Goggin). Proton NMR spectra were measured at 100 MHz on Varian HA 100 or Jeol Minimar instruments using TMS as internal reference. Fluorine NMR spectra were measured on a Jeol C60-HL spectrometer at 56.44 MHz in the field sweep mode using a water external NMR lock. Spectra were calibrated by the audio-modulation side-band method using a ^{19}F resonance of the solvent ($CFCl_3$, CF_2Cl_2, or CHF_2Cl). Chemical shifts (ϕ_F) are positive to high field of $CFCl_3$. The relationships $\phi_{CFCl_3} = \phi_{CF_2Cl_2} + 6.6$ and $\phi_{CFCl_3} = \phi_{CHF_2Cl} + 71.7$ were determined by measuring the chemical shift of a few drops of $CFCl_3$ in the appropriate fluorocarbon. Constant low temperatures were achieved in the normal way by controlling the direct boil-off of liquid nitrogen into the vacuum-jacketed probe insert with a thermocouple close to the sample tube (see also comments below). Phosphorus NMR spectra were measured on a modified JEOL C60-HL spectrometer operating at 24.29 MHz; the configuration will be described elsewhere.[25] Spectra were accumulated using a PDP-8S computer and were calibrated by recording the resonance of 85% H_3PO_4 at different frequencies derived from a frequency synthesizer to give a series of peaks across the spectrum. The arrangement for ^{19}F decoupling was similar to that described below for ^{31}P decoupling except that noise modulation could not be used because of the resulting noise modulation of the water external lock frequency (60 MHz).

The "broad-band" heteronuclear decoupling coil supplied with the probe proved unsatisfactory for the difficult ^{31}P decoupling required here and so was modified in the following way. The series-wound 16-turn coil was stripped to give two five-turn coils, one on each of the opposite sides of the probe insert, which were joined in parallel. The coil ends were connected to a suitable radiofrequency connector placed in the top of the probe, and tuning-matching boxes containing two capacitors were fitted between it and a radiofrequency amplifier.[26] Initial tuning matching at the ^{31}P resonance frequency (24.29 MHz) was made with a pickup coil contained in an empty NMR sample tube inserted into the probe and connected to a high-frequency oscilloscope. Final tuning matching was then made with a standing-wave-ratio meter in the line between the power amplifier, JEOL Hetero Spin Decoupler, Model NMM-SD-HC, and the tuning-matching box. The standing wave ratio was always kept ≤1.2.

Noise modulation of the decoupling frequency was achieved by mixing it with the audio output of a General Radio Co. Random-Noise Generator (Model 1381). A Hewlett-Packard mixer (Model 10534A) was used, and the noise bandwidth was determined by a Krohn-Hite filter (Model 3340).

The JEOL thermocouple (copper–constantan) used in conjunction with the temperature controller picked up irradiation from the decoupler which prevented proper temperature control. Another thermocouple was inserted along the inside of the silvered, vacuum-jacketed nitrogen-transfer tube so that the bead remained inside the tube and was shielded from radiofrequency radiation by the silver mirror. In addition a capacitor was connected across the ends of the thermocouple wires. These steps enabled the temperature to be controlled while decoupling at high power levels. The only disadvantage was that temperature equilibration at the sample took a few more minutes than normal because of the greater distance between thermocouple and sample.

Temperatures at which spectra were run were measured directly with a copper–constantan thermocouple inserted into the sample. After equilibration the decoupling field, if any, was momentarily switched off and the emf measured with respect to a second junction kept in an ice–water bath. Temperatures could be measured to better than 0.2°C but are only reported to the nearest 0.5°C.

NMR line shapes were calculated using the program DNMR3[27] modified for use with a CDC-3600 computer and were plotted on a 12-in. Calcomp plotter.

Preparation of Complexes. Method A. A solution of $Rh_2(PF_3)_8$ (0.20 g) in n-hexane (10 ml) was heated under reflux in a nitrogen atmosphere with an equimolar quantity of the acetylene for 15 min. The solvent was evaporated under reduced pressure and the residue was extracted with three 10-ml portions of isopentane. The combined extracts were filtered and cooled to −78° to give crystals of the acetylene complex. Analytically pure samples were obtained by vacuum sublimation at 0.005 mm. Yields were generally 50–70%.

Method B. An excess of the acetylene was condensed onto solid $Rh_2(PF_3)_8$ (0.20 g) in a conventional high-vacuum system. The mixture was heated to between 40 and 90° (depending on the acetylene) until a gas was evolved (PF_3, ir identification) and a dark red or yellow oil was formed. Unreacted acetylene and liberated PF_3 were removed by pumping at room temperature (or below room temperature if the complex was very volatile, as in the case of hexafluoro-2-butyne). The complex was purified by sublimation or distillation at 0.005 mm on to a Dry Ice probe. Terminal acetylenes formed appreciable amounts of involatile polymeric material, and the yields of their complexes were 20–50%, but the complexes of disubstituted acetylenes were isolated almost quantitatively.

Methods of preparation and purification, analytical data, and melting points are in Table I.

Mass Spectra. Representative examples are given as follows; the figures in parentheses represent the intensity relative to that of the most intense ion, which is taken as 100. The designation D indicates that the particular ions are mixed with dehydrogenation products.

$Rh_2(PF_3)_6(C_2H_2)$: $[Rh_2(PF_3)_6(C_2H_2)]^+$ (19), $[Rh_2(PF_3)_5(C_2H_2)]^+$ (21), $[Rh_2(PF_3)_4(PF_2)(C_2H_2)]^+$ (5), $[Rh_2(PF_3)_5]^+$ (0.1),

$[Rh_2(PF_3)_3(PF_2)_2(C_2H_2)]^+$ (0.2), $[Rh_2(PF_3)_4(C_2H_2)]^+$ (12), $[Rh_2(PF_3)_3(PF_2)(C_2H_2)]^+$ (5), $[Rh_2(PF_3)_4]^+$ (0.7), $[Rh_2(PF_3)_2(PF_2)_2]^+$ (0.4), $[Rh_2(PF_3)_3(C_2H_2]^+$ (17), $[Rh_2(PF_3)_3(C_2H)]^+$ (0.5), $[Rh_2(PF_3)_2(PF_2)(C_2H_2)]^+$ (3), $[Rh_2(PF_3)_3]^+$ (4), $[Rh_2(PF_3)(PF_2)_2(C_2H_2)]^+$ (0.4), $[Rh_2(PF_3)_2(C_2H_2)]^+$ (13), $[Rh_2(PF_3)_2(C_2H)]^+$ (2.0), $[Rh_2(PF_3)(PF_2)(C_2H_2)]^+$ (1.1), $[Rh_2(PF_3)_2]^+$ (5), $[Rh_2(PF_3)(C_2H_2)]^+$ (19), $[Rh_2(PF_3)(C_2H)]^+$ (4), $[Rh_2(PF_2)(C_2H_2)]^+$ (12), $[Rh_2(PF_3)]^+$ (3), $[Rh_2(PF)(C_2H_2)]^+$ (3), $[Rh_2(PF_2)]^+$ (1.5), $[Rh_2(PF)]^+$ (0.4), $[Rh_2(C_2H_2)]^+$ (9), $[Rh_2(CH_2)]^+$ (55), Rh_2^+ (100); metastable ions at *m/e* 594 for $[Rh_2(PF_3)_6(C_2H_2)]^+ \xrightarrow{*} [Rh_2(PF_3)_5(C_2H_2)]^+$, 507 for $[Rh_2(PF_3)_5(C_2H_2)]^+ \xrightarrow{*} [Rh_2(PF_3)_4(C_2H_2)]^+$, 489 for $[Rh_2(PF_3)_4(PF_2)(C_2H_2)]^+ \xrightarrow{*} [Rh_2(PF_3)_3(PF_2)(C_2H_2]^+$, 422 for $[Rh_2(PF_3)_4(C_2H_2)]^+ \xrightarrow{*} [Rh_2(PF_3)_3(C_2H_2)]^+$, 336 for $[Rh_2(PF_3)_3(C_2H_2)]^+ \xrightarrow{*} [Rh_2(PF_3)_2(C_2H_2)]^+$, and 193 for $[Rh_2CH_2]^+ \xrightarrow{*} Rh_2^+$.

$Rh_2(PF_3)_6(CF_3C_2CF_3)$: $[Rh_2(PF_3)_6(C_4F_6)]^+$ (23), $[Rh_2(PF_3)_5(PF_2)(C_4F_6)]^+$ (1), $[Rh_2(PF_3)_5(C_4F_6)]^+$ (29), $[Rh_2(PF_3)_4(PF_2)(C_4F_6)]^+$ (22), $[Rh_2(PF_3)_3(PF_2)(C_4F_6)]^+$ (20), $[Rh_2(PF_3)_3(C_4F_6)]^+$ (33), $[Rh_2(PF_3)_2(PF_2)(C_4F_6)]^+$ (15), $[Rh_2(PF_3)_2(C_4F_6)]^+$ (85), $[Rh_2(PF_3)(PF_2)(C_4F_6)]^+$ (9), $[Rh_2(PF_3)_3]^+$ (7), $[Rh_2(PF_3)(C_4F_6)]^+$ (91), $[Rh_2(PF_2)(C_4F_6)]^+$ (10), $[Rh_2(PF)(C_4F_6)]^+$ (0.5), $[Rh_2(PF_3)_2]^+$ (1), $[Rh_2(C_4F_6)]^+$ (100), $[Rh_2(C_4F_5)]^+$ (15), $[Rh_2(C_4F_4)]^+$ (2), $[Rh_2(C_4F_3)]^+$ (27), $[Rh_2(C_4F)]^+$ (27), $[Rh_2(C_4F)]^+$ (3), $[Rh_2C_2]^+$ (1), $[Rh_2C]^+$ (5), Rh_2^+ (7), Rh^+ (2); metastable ions at *m/e* 728 for $[Rh_2(PF_3)_6(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)_5(C_4F_6)]^+$, 709 for $[Rh_2(PF_3)_5(PF_2)(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)_4(PF_2)(C_4F_6)]^+$, 642 for $[Rh_2(PF_3)_5(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)_4(C_4F_6)]^+$, 623 for $[Rh_2(PF_3)_4(PF_2)(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)_3(PF_2)(C_4F_6)]^+$, 554 for $[Rh_2(PF_3)_4(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)_3(C_4F_6)]^+$, 545 for $[Rh_2(PF_3)_3(PF_2)(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)(PF_2)(C_4F_6)]^+$, 468 for $[Rh_2(PF_3)_3(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)_2(C_4F_6)]^+$, 449 for $[Rh_2(PF_3)_2(PF_2)(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)(PF_2)(C_4F_6)]^+$, 382 for $[Rh_2(PF_3)_2(C_4F_6)]^+ \xrightarrow{*} [Rh_2(PF_3)(C_4F_6)]^+$, 297 for $[Rh_2(PF_3)(C_4F_6)]^+ \xrightarrow{*} [Rh_2(C_4F_6)]^+$.

$Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$: $[Rh_2(PF_3)_6(C_{14}H_{10})]^+$ (2.5), $[Rh_2(PF_3)_5(C_{14}H_{10})]^+$ (12), $[Rh_2(PF_3)_4(C_{14}H_{10})]^+$ (9), $[Rh_2(PF_3)_3(PF_2)(C_{14}H_{10})]^+$ (0.1), $[Rh_2(PF_3)_3(C_{14}H_{10})]^+$ (9), $[Rh_2(PF_3)_2(PF_2)(C_{14}H_{10})]^+$ (4), $[Rh_2(PF_3)_2(C_{14}H_{10})]^+$ (19), $[Rh_2(PF_3)(PF_2)(C_{14}H_{10})]^+$ (0.5), $[Rh_2(PF_3)(C_{14}H_{10})^+$ (15), $[Rh(PF_3)_2(C_{14}H_{10})]^+$ (4), $[Rh_2(PF_2)(C_{14}H_{10})]^+$ (0.9), $[Rh_2(C_{14}H_{10})]^+$ (23), $[Rh_2(PF_3)_2]^+$ (19), $[Rh(PF_3)(C_{14}H_{10})]^+$ (0.5), *m/e* 258? (D), *m/e* 255? (D), *m/e* 230 $[Rh_2C_2]^+$ (0.8), $[Rh_2C]^+$ (3), Rh_2^+ (9), $[Rh(C_7H_5)]^+$ (D), $[C_{14}H_{10}]^+$ (off scale), $[RhC_2]^+$ (45), $[RhC]^+$ (48), Rh^+ (100); metastable ions at *m/e* 744 for $[Rh_2(PF_3)_6(C_{14}H_{10})]^+ \xrightarrow{*} [Rh_2(PF_3)_5(C_{14}H_{10})]^+$, 658 for $[Rh_2(PF_3)_5(C_{14}H_{10})]^+ \xrightarrow{*} [Rh_2(PF_3)_4(C_{14}H_{10})]^+$, 571 for $[Rh_2(PF_3)_4(C_{14}H_{10})]^+ \xrightarrow{*} [Rh_2(PF_3)_3(C_{14}H_{10})]^+$, 485 for $[Rh_2(PF_3)_3(C_{14}H_{10})]^+ \xrightarrow{*} [Rh_2(PF_3)_2(C_{14}H_{10})]^+$, 394 for $[Rh_2(PF_3)_2(C_{14}H_{10})]^+ \xrightarrow{*} [Rh_2(PF_3)(C_{14}H_{10})]^+$, 314 for $[Rh_2(PF_3)(C_{14}H_{10})]^+ \xrightarrow{*} [Rh(C_{14}H_{10})]^+$.

Polymerization of Phenylacetylene. Phenylacetylene (1.0 g) was added to $Rh_2(PF_3)_6(C_6H_5C_2H)$ (0.05 g) in 20 ml of *n*-pentane. The yellow precipitate which formed was separated after 12 hr by centrifugation. After washing with *n*-pentane and drying in vacuo, a yellow-brown powder, mp 216–217°, was obtained. Anal. Calcd for $[C_8H_6]_n$: C, 94.1; H, 5.9. Found: C, 93.3; H, 6.1; mol wt (VPO, C_6H_6, 25°, 43.832 mg/ml) 10531.

Results and Discussion

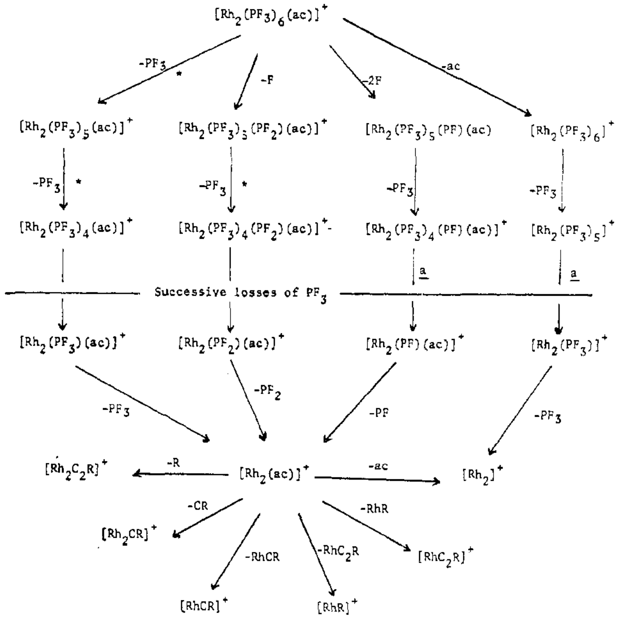


Figure 1. General mass spectral fragmentation pattern of $Rh_2(PF_3)_6(ac)$ complexes (ac = RC_2R) (a: weak or not observed in many spectra).

Diphenylacetylene reacts with $Rh_2(PF_3)_8$ in refluxing *n*-hexane to give a dark red solution together with a small amount of insoluble polymeric material. On cooling the solution to −78°, crimson red, platelike crystals of the complex $Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$ separate. Most acetylenes react with $Rh_2(PF_3)_8$ under the same conditions, but the main product is generally polymer, and the organometallic complexes, if formed, are too soluble even in *n*-hexane at −78° to permit isolation. However, if $Rh_2(PF_3)_8$ is heated with an excess of the acetylene in the absence of solvent, the complexes $Rh_2(PF_3)_6(ac)$ (ac = C_2H_2, $C_6H_5C_2H$, *n*-$C_4H_9C_2H$, *t*-$C_4H_9C_2H$, $CH_3C_2CH_3$, *n*-$C_3H_7C_2CH_3$, $CF_3C_2CF_3$, or $CH_3C_2CO_2CH_3$) can be isolated. Yields are almost quantitative using disubstituted acetylenes such as $CH_3C_2CH_3$ and $CF_3C_2CF_3$, but terminal acetylenes such as $C_6H_5C_2H$ and *t*-$C_4H_9C_2H$ give much polymer, and the complexes are formed in poor yield. It proved impossible to separate the complexes formed by *n*-$C_4H_9C_2H$, $C_3H_7C_2CH_3$, and $CH_3C_2CO_2CH_3$ from the excess of acetylene, and in these cases characterization is based only on ^1H and ^{19}F NMR data and on mass spectrometry (see below). The rhodium complexes resemble the well-known complexes $Co_2(CO)_6(ac)$ in being fairly air stable, both in the solid state and in solution. In the absence of free acetylene, they are thermally stable, decomposing only above 200°. Some of the complexes, e.g., $Rh_2(PF_3)_6(CF_3C_2CF_3)$, are appreciably volatile even at room temperature and will evaporate if left in an open vessel for a few days. The complexes catalyze the polymerization of acetylenes, but differ from the analogous $Co_2(CO)_6(ac)$ complexes in that the products appear to be linear polymers rather than cyclic trimers. Thus, polymerization of phenylacetylene in the presence of $Rh_2(PF_3)_6(C_6H_5C_2H)$ gives a yellow-brown, amorphous solid with an average molecular weight of 10000. The degree of polymerization is higher than that of the "polyphenylacetylene" formed from phenylacetylene in refluxing chlorobenzene[28] and is close to that of the product obtained by polymerizing phenylacetylene in the presence of arene–tricarbonyl complexes of the group 6 metals.[29] The acetylene complex $Rh_2(PF_3)_6(C_2H_2)$ catalyzes the formation of a small amount of benzene from acetylene, as shown by proton NMR spectroscopy, but the main product is an insoluble polymer. We have found no evidence for the formation of complexes of the type $Rh_2(PF_3)_4(ac)_3$ in the reaction of acetylenes with $Rh_2(PF_3)_6(ac)$, in contrast with the behavior of the $Co_2(CO)_6(ac)$ complexes. Despite these chemical differences, the overall geometry of the bis(triphenylphosphine) derivative of $Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$[24,30] is very similar to that of a typical $Co_2(CO)_6(ac)$ complex.

The fragmentation patterns in the mass spectra of the $Rh_2(PF_3)_6(ac)$ complexes are outlined in Figure 1. A parent ion is observed in all cases, together with daughter ions arising from the consecutive loss of neutral PF_3 groups and, frequently, fluorine atoms. All complexes show metastable ions for the fragmentation

$$[Rh_2(PF_3)_x(ac)]^+ \xrightarrow{*} [Rh_2(PF_3)_{x-1}(ac)]^+ + PF_3 \quad (x = 1\text{–}6)$$

and they are also frequently observed for the fragmentation

$$[Rh_2(PF_3)_y(PF_2)(ac)]^+ \xrightarrow{*} [Rh_2(PF_3)_{y-1}(PF_2)(ac)]^+ + PF_3 \quad (y = 1\text{–}5)$$

Table II. ^1H NMR Spectra of Acetylenes and Their $Rh_2(PF_3)_6$ Complexes[a]

Acetylene	Proton	Chem shifts (multiplicity), coupling constants in Hz	
		Ligand	Complex
HC_2H	$\equiv CH$	1.80 (s)[b]	4.88 (h), $J_{PH} = 7.3$
$C_6H_5C_2H$	$\equiv CH$	3.15 (s)[c]	5.39 (h), $J_{PH} = 7.2$
$n\text{-}C_4H_9C_2H$	$\equiv CH$	1.99 (m)	5.55 (h), $J_{PH} = 7.5$
	$\equiv CCH_2$	2.21 (m)	2.75 (br m)
	$-CH_2CH_2$	1.50 (m)	1.35 (m)
	$-CH_3$	0.94 (m)	0.83 (m)
$t\text{-}C_4H_9C_2H$	$\equiv CH$	2.04 (s)[c]	5.77 (h), $J_{PH} = 7.2$
	$-CH_3$	1.22 (s)	1.29 (s)
$C_6H_5C_2CH_3$	$\equiv CCH_3$	1.74 (s)	2.75 (h), $J_{PH} = 6.5$
$C_6H_5C_2C_2H_5$	$\equiv CCH_2$	2.15 (q)	3.07 (br m)
	$-CH_3$	1.02 (t), $^3J_{HH} = 7.5$	1.30 (t), $^3J_{HH} = 7.5$
$CH_3C_2CH_3$	$\equiv CCH_3$	1.70 (s)	2.83 (h), $J_{PH} = 6.0$
$n\text{-}C_3H_7C_2CH_3$	$\equiv CCH_3$	1.60 (t), $^5J_{HH} = 2.6$	2.42 (m), $J_{PH} = 6.0$
	$\equiv CCH_2$	2.01 (m)	~2.5 (m)
	$-CH_2-$	1.42 (m)	1.46 (m)
	$-CH_3$	0.91 (t), $^3J_{HH} = 7.0$	0.82 (t)
$CH_3C_2CO_2CH_3$	$\equiv CCH_3$	1.42 (s)	2.73 (h),[d] $J_{PH} = 6.5$
	$-CO_2CH_3$	3.41 (s)	3.72 (s)
$C_6H_5C_2CO_2CH_3$	$-CO_2CH_3$	3.32 (s)	3.20 (s)
$C_6H_5C_2CO_2C_2H_5$	$-CO_2CH_2-$	3.95 (q)	3.95 (q)
	$-CH_3$	0.95 (t), $^3J_{HH} = 7.1$	0.93 (t)
$p\text{-}NO_2C_6H_4C_2CO_2C_2H_5$	$-CO_2CH_2-$	3.94 (q)	3.92 (q)
	$-CH_3$	0.93 (t), $^3J_{HH} = 7.2$	0.88 (t)

[a] Chemical shifts in ppm downfield of internal TMS, measured in C_6D_6 unless stated otherwise. Abbreviations: s, singlet; h, heptet; q, 1:3:3:1 quartet; t, 1:2:1 triplet; br m, broad multiplet. All aromatic signals are in the range δ 6.8–7.7 ppm. [b] Value from E. A. V. Ebsworth and S. G. Frankiss, *J. Chem. Soc.*, 661 (1963); solvent probably cyclohexane. [c] Measured in $CDCl_3$. [d] Measured in $CFCl_3$.

This confirms that the loss of PF_3 is at least in part successive, as has generally been found in the mass spectra of other PF_3 complexes.[21,31] Successive losses of CO are commonly observed in the mass spectra of metal carbonyl complexes.[32] Minor pathways involving the loss of acetylene or of more than one fluorine atom occur in a few cases, e.g., $Rh_2(PF_3)_6(C_2H_2)$. Very few mononuclear PF_3-containing ions are observed in the mass spectra of any of the complexes. This fact, taken with the high intensity often observed for the ion $[Rh_2(ac)]^+$, suggests that the $[Rh_2(ac)]$ moiety is very stable. It can fragment in various ways depending on the acetylene, but in the case of $[Rh_2C_2R_2]^+$, ions of the types $[Rh_2C_2R]^+$, $[Rh_2CR_2]^+$, $[Rh_2R]^+$, $[Rh_2]^+$, $[RhC_2R]^+$, and $[RhR]^+$ are common.

As shown in Table II, acetylene coordination causes deshielding of $C{\equiv}C{-}H$ and $C{\equiv}C{-}C{-}H$ protons, the resonances being split into symmetrical septets by coupling with six apparently equivalent phosphorus atoms [$J(P, {\equiv}CH) \approx 7.3$ Hz, $J(P, {\equiv}C{-}CH) \approx 6.5$ Hz)]; this was verified by ^{31}P heteronuclear decoupling. The constancy of these values over the range of complexes studied suggests that there are no marked structural changes as the acetylene is varied. At room temperature the ^{19}F NMR spectra of all the complexes consist of a widely spaced doublet arising from coupling with the ^{31}P nuclei ($|^1J_{PF} + 2(^3J_{PF})| \approx 1400$ Hz, Table III). Each half of the doublet is quite broad (as much as 80 Hz at half peak height), probably owing to the complexity of the spin system. The chemical shift of PF_3 in all of the acetylene complexes is to low field of that of free trifluorophosphine, as is generally observed for transition metal complexes of this ligand.[21] It is clear from the asymmetric line shape of the doublets at room temperature that many lines of the spectrum fall outside the main doublet ($^1J_{PF} + 2(^3J_{PF})$), so that $^1J_{PF}$ and $^3J_{PF}$ are opposite in sign;[33] this is also the case for complexes containing the $Rh(PF_3)_2$ group.[22]

Table III. ^{19}F NMR Spectra of $Rh_2(PF_3)_6(ac)$ Complexes Undergoing Fast Intramolecular Exchange[a]

Acetylene	ϕ_F	"J_{PF}"	Solvent, temp
HC_2H	5.2	1385	CHF_2Cl, −65°
	7.1	1400	$CFCl_3$
$C_6H_5C_2H$	6.1	1385	CHF_2Cl, −145°
$n\text{-}C_4H_9C_2H$	6.5	1400	$CFCl_3$
$t\text{-}C_4H_9C_2H$	6.1	1400	CF_2Cl_2, −40°
$C_6H_5C_2CH_3$	8.6	1405	$CFCl_3$
$C_6H_5C_2C_2H_5$	7.3	1385	CHF_2Cl, −55°
$C_6H_5C_2C_6H_5$	8.4	1415	$(C_2H_5)_2O{-}C_6F_5Br{-}CFCl_3$ (3:3:1), −9°
$CH_3C_2CH_3$	7.5	1380	CHF_2Cl, −70°
$n\text{-}C_3H_7C_2CH_3$	8.9	1405	$CFCl_3$
	7.6	1405	CF_2Cl_2, −68°
$CH_3C_2CO_2CH_3$	8.6	1400	$CFCl_3$
$C_6H_5C_2CO_2C_2H_5$	9.0	1400	$CFCl_3$
$p\text{-}NO_2C_6H_4C_2CO_2C_2H_5$	8.7	1405	$CFCl_3$
$CF_3C_2CF_3$[b]	7.0	1400	CF_2Cl_2, −40°

[a] Chemical shifts (ϕ_F) in ppm upfield of internal $CFCl_3$ measured at 24° unless indicated otherwise. "J_{PF}" = $|^1J_{PF} + 2(^3J_{PF})|$ in Hz although the transitions having this separation were not properly resolved: E. G. Finer and R. K. Harris, *J. Chem. Soc. A*, 1972 (1969). [b] CF_3 resonance was a broad singlet at ϕ 52.9 ppm.

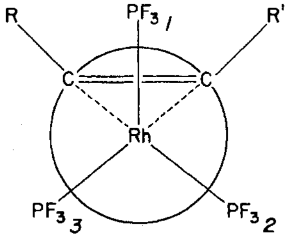


Figure 2. Newman projection of $Rh_2(PF_3)_6(RC_2R')$ along the Rh–Rh bond axis. The second $Rh(PF_3)_3$ moiety is behind and eclipses the one shown.

We assume that the complexes resemble their $Co_2(CO)_6(ac)$ counterparts in adopting an eclipsed conformation and represent them in the form of a Newman projection along the Rh–Rh bond axis (Figure 2). It may be noted that the PF_3 groups in $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$[24,30] are almost eclipsed, though the triphenylphosphine groups depart considerably from this idealized conformation. It is evident from Figure 2 that, for a complex containing an unsymmetrical acetylene RC_2R' ($R \neq R'$), there should be three inequivalent PF_3 groups; for a complex containing a symmetrical acetylene ($R = R'$), two of the PF_3 groups become equivalent. Since the room-temperature ^1H and ^{19}F NMR spectra indicate

Table IV. ^{19}F NMR Spectra of $Rh_2(PF_3)_6$(ac) Complexes Undergoing Slow Intramolecular Exchange[a]

	ϕ_F			"J_{PF}"			
Acetylene	A	B	C	A	B	C	Solvent, temp
HC_2H		5.4			1385		CHF_2Cl, −150°
$C_6H_5C_2H$		6.1			1385		CHF_2Cl, −145°
n-$C_4H_9C_2H$	4.4	6.6	7.0	1390	1405	(1370)	$CFCl_3$-CF_2Cl_2 (1:1), −147°
t-$C_4H_9C_2H$	3.4	4.9	6.4	1380	1340	1395	CF_2Cl_2, −128°
$C_6H_5C_2CH_3$	5.4	7.7	11.2	1390	1405	1360	$CFCl_3$, −129°
$C_6H_5C_2C_2H_5$	4.4	6.4	10.8	1375	1370	1335	CHF_2Cl, −128°
$C_6H_5C_2C_6H_5$	6.5		10.9	1405		1350	$(C_2H_5)_2O$-C_6F_5Br-$CFCl_3$ (3:3:4), −104°
$CH_3C_2CH_3$	6.4		9.7	1355		1335	CHF_2Cl, −146°
n-$C_3H_7C_2CH_3$	4.1	7.8	9.8	1360	1380	1335	CHF_2Cl, −142°
	4.3	8.0	10.4	1365	1380	1340	CF_2Cl_2, −145°
$CH_3C_2CO_2CH_3$	7.1	7.3	11.2	1410	1385	1360	$CFCl_3$, −122°
$C_6H_5C_2CO_2C_2H_5$	6.6	8.0	12.0	1360	1390	1335	$CFCl_3$, −115°
p-$NO_2C_6H_4C_2CO_2C_2H_5$	6.0	7.1	10.9	1360	1385	1340	CHF_2Cl, −103°
$CF_3C_2CF_3$[b]	6.3		7.7	1395		1355	CF_2Cl_2, −104°

[a] See footnote *a*, Table III. For the symmetrical acetylenes the A and B doublets were identical. Numbers in parentheses were estimated when parameter could not be obtained accurately due to overlap. [b] CF_3 resonance was a broad triplet (J = 18 Hz) at ϕ 51.7 ppm.

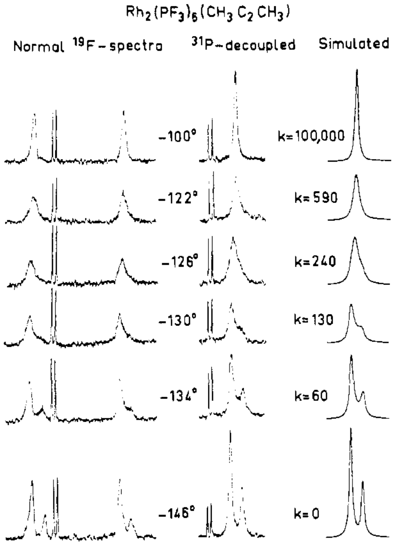


Figure 3. Normal and ^{31}P-noise-decoupled ^{19}F NMR spectra at 56.44 MHz of $Rh_2(PF_3)_6(CH_3C_2CH_3)$ at various temperatures with calculated NMR line shapes at rates (k) shown. The small sharp doublet at ϕ 0.8 in the experimental spectra is the second low-field 4-kHz modulation side band of the solvent CHF_2Cl.

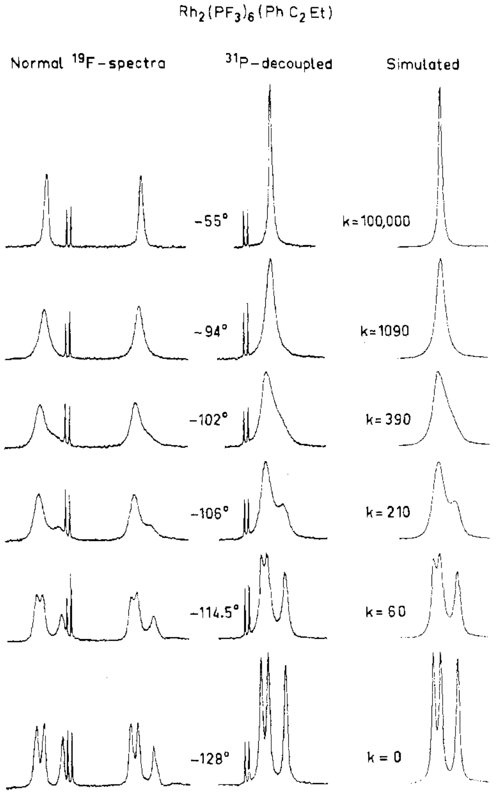


Figure 4. Normal and ^{31}P-noise-decoupled ^{19}F NMR spectra at 56.44 MHz of $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$ at various temperatures with calculated NMR line shapes at rates (k) indicated. The small sharp doublet in the experimental spectra is a second modulation side band of solvent CHF_2Cl.

equivalence for all of the PF_3 groups, some form of chemical exchange must be taking place. At low temperatures the expected nonequivalence of the PF_3 groups is observed in the ^{19}F NMR spectra (Table IV). Thus, on cooling a solution of any of the complexes, each half of the doublet begins to broaden and eventually splits into two (R = R') or three (R ≠ R') resonances. Figures 3 and 4 show the variable-temperature ^{19}F NMR spectra of $Rh_2(PF_3)_6(CH_3C_2CH_3)$ and $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$, respectively, which are representative of the two types. The phenomenon is reversible and the coalescence temperature is very dependent on the nature of the acetylene. As shown in Figures 3 and 4, the signal to highest field in each half of the spectrum is somewhat less intense than expected; i.e. the observed ratio is about 2.8:1 instead of 2:1 for the complex of a symmetrical acetylene and about 1.4:1.4:1 instead of 1:1:1 for the complex of an asymmetrical acetylene. These nonintegral ratios could be due either to the presence of isomers in unequal amounts or, alternatively, to the fact that the spectrum arises from such a complex spin system. ^{31}P-Decoupling experiments (see below) show that the second explanation is correct.

The following observations establish that the process which averages the PF_3 groups must be intramolecular, not intermolecular. At room temperature the doublet in the ^{19}F NMR spectrum of each complex is broad, indicating the presence of many small couplings; these would be expected to disappear if rapid intermolecular exchange were occurring. Addition of PF_3 gives rise to a separate sharp doublet resonance characteristic of that species, showing that there is no exchange between free and coordinated PF_3; in this respect, the $Rh_2(PF_3)_6$(ac) complexes resemble their $Co_2(CO)_6$(ac) analogs, which exchange very slowly with carbon monoxide.[34] Finally, the observation of well-resolved ^{31}P coupling to the C≡C—*H* and C≡C—C—*H* protons rules out intermolecular exchange of either PF_3 or the acetylene ligand. The possibility of rapid intramolecular exchange of PF_3 groups between the two rhodium atoms is excluded on the basis of the room-temperature ^{31}P NMR spectrum of $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$

in fluorobenzene, which consists of a quartet of doublets arising from coupling to three ^{19}F nuclei and to *one* ^{103}Rh nucleus (δ 125.0 ppm downfield from external 85% H_3PO_4, J_{RhP} = 235 ± 10 Hz). If PF_3 scrambled between two rhodium atoms, we would expect to observe a quartet of *triplets* arising from equal coupling with *two* ^{103}Rh nuclei, and the fact that only one ^{31}P resonance is observed at room temperature provides further evidence that rapid exchange of PF_3 groups is occurring. The observed doublet also indicates that $^1J_{RhRh} << {}^1J_{RhP}$ (if $^1J_{RhRh} >> {}^1J_{RhP}$ one would again have expected a quartet of triplets). Trifluorophosphine thus appears to differ from carbon monoxide[35,36] and isocyanides[37] in its inability to pass from one metal atom to another via a bridging intermediate, and it is therefore not surprising that no complexes containing bridging PF_3 groups have so far been isolated.

Even if we neglect the spin-active nuclei of the acetylene, there are 26 spin-active nuclei (2 Rh, 6 P, and 18 F, all 100% abundance, $I = {}^1/_2$) in the complexes, and for such a complex spin system a complete density-matrix line-shape analysis is not possible. We have however obtained approximate rates for site exchange by treating the line-shape effects separately in each half of the P–F doublet with the exchange process involving the cyclic permutation of the three PF_3 sites. Our assumption is probably justified; since $^1J_{PF} >> {}^3J_{PF}$ and $^2J_{PP}$, there will be little mixing of states differing in their phosphorus m_I components. To this approximation the halves of the spectrum can be regarded as independent. As noted briefly above, the broad envelopes observed for the separate halves of each ^{19}F resonance are due to coupling with ^{103}Rh, ^{31}P, ^{19}F, and ^{1}H nuclei and have approximately the same widths at half peak height in both low- and high-temperature spectra; these widths are generally much smaller than the chemical shift differences between the different environments. We therefore treat the halves of the ^{19}F NMR spectrum as being represented by three-spin systems with zero coupling, each having an appropriately constant broad line width in the absence of exchange [related to the transverse relaxation time by the equation $T_2 = [\pi(\Delta_{1/2})]^{-1}$]. Because of the difficulty in predicting the errors inherent in our assumptions and also as a check on the nonintegral ratios observed, we have tried to obtain ^{31}P-decoupled ^{19}F NMR spectra. The difficulty involved in removing such large couplings (a $^1J_{PF}$ of ~1400 Hz will spread the ^{31}P resonance over 4 kHz) is evident from the fact that the technique has so rarely been used. Even with 20-W power (noise decoupling, bandwidth ±2 kHz), complete decoupling was not achieved, but the line shapes were reasonable and the lines were sharper than in the undecoupled spectra. (Complete ^{31}P decoupling would still leave coupling of ^{19}F to ^{103}Rh and ^{1}H nuclei.) This suggests that the exchange between the spin states is fast enough to allow the remaining extra width to be included in a suitable choice of T_2.[38] The decoupled spectra gave excellent integral ratios for the different resonances (1:1:1 for unsymmetrical acetylenes, 2:1 for symmetrical acetylenes), showing that the anomalous integrals observed in the undecoupled spectra are a consequence of the complex spin system and not of the presence of isomers. We have neglected any effects due to temperature dependence of chemical shifts in the line-shape analysis since we found that there was no change in the chemical shifts at temperatures up to 30° below those of the low-temperature limiting spectra. Excellent agreement between calculated and ^{31}P-decoupled spectra was obtained and our assumptions with regard to the undecoupled spectra are also seen to be justified (Figure 3 and 4). The rate data derived in each case for $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$ are plotted in Figure 5 according to the Arrhenius equation: rate $(k) = Ae^{-E_a/RT}$. The parameters $A = 9 \times 10^{12}$ and E_a = 8.1 kcal/mol were derived from the more accurate data from the ^{31}P-decoupled spectra.

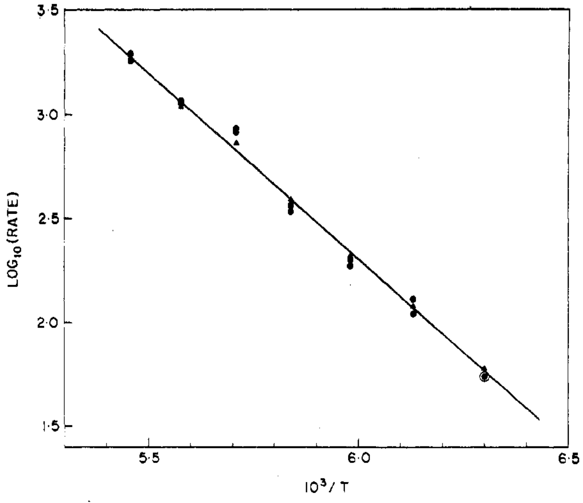


Figure 5. Arrhenius plot for rate data of $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$ obtained from variable-temperature ^{19}F NMR spectra (56.44 MHz): ●, from undecoupled spectra; ▲, from ^{31}P-decoupled spectra.

Table V. Free Energies of Activation for Intramolecular Exchange of Trifluorophosphine Ligands in $Rh_2(PF_3)_6$(ac) Complexes[a]

Acetylene	Temp range, °C	Range of rates, sec^{-1}	$\Delta G^\ddagger$,[b] kcal/mol
HC_2H	Single doublet to −150°		?
$C_6H_5C_2H$	Single doublet to −145°		?
n-$C_4H_9C_2H$	−144 to −125	40–900	6.4
t-$C_4H_9C_2H$	−120 to −101	13–280	8.0
$C_6H_5C_2CH_3$	−122 to −101	85–1100	7.4
$C_6H_5C_2C_2H_5$	−114.5 to −90	55–1950	7.8
$C_6H_5C_2C_6H_5$	−96 to −72	40–700	9.0
$CH_3C_2CH_3$	−138 to −122	20–620	6.8
n-$C_3H_7C_2CH_3$	−132 to −95	40–3600	7.1
$CH_3C_2CO_2CH_3$	−115 to −90	40–2000	7.9
$C_6H_5C_2CO_2C_2H_5$	−101 to −60	40–3500	8.9
p-$NO_2C_6H_4C_2CO_2C_2H_5$	−90 to −52	40–4000	9.2
$CF_3C_2CF_3$	−64 to −48	45–600	10.4

[a] The range of rates given was determined by comparison of experimentally determined spectra with calculated line shapes over the temperature range shown. [b] $\Delta G^\ddagger$ was calculated from the Eyring equation at each temperature and was found to be effectively constant. The largest range of $\Delta G^\ddagger$ values for any of these compounds was only 0.38 kcal/mol. The error in $\Delta G^\ddagger$ at any temperature is estimated to be ±0.15 kcal/mol. The values given here represent the mean of values in the middle of the ranges.

The rates of exchange derived from line-shape analysis can be converted into free energies of activation (Table V) by means of the Eyring equation

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

wherein the symbols have their usual meanings and the transmission coefficient, κ, is assumed to be 1. The agreement between the activation energies derived from undecoupled and decoupled spectra is excellent in all cases, as is shown by the Arrhenius plot in Figure 5, which lends support to the validity of the assumptions made in the approximate line-shape analysis. The values of $\Delta G^\ddagger$ vary very little with temperature; for example, the spectra of $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$ were fitted over the range −90 to −114.5°C and the values of $\Delta G^\ddagger$ varied from 7.75 to 7.79 kcal/mol for the decoupled spectra and from 7.70 to 7.83 kcal/mol for the undecoupled spectra. The differences are within the errors of the rate estimation.

The magnitude of $\Delta G^\ddagger$[39] depends markedly on the acetylene and can be related to electronic and steric effects of the substituents on the acetylene. *tert*-Butyl causes a much higher barrier to exchange than either hydrogen or methyl. Smaller but still significant increases in $\Delta G^{\ddagger}$ occur when hydrogen is replaced by methyl, but lengthening the alkyl chain has little effect, as is shown by comparison of $\Delta G^{\ddagger}$ for the complexes of $CH_3C_2CH_3$ and CH_3C_2-*n*-C_3H_7. The steric effects can be attributed to an increased interaction between one or more of the PF_3 groups and the acetylenic substituents in the transition state, and presumably in the CH_3C_2-*n*-C_3H_7 and $C_2H_5C_2C_6H_5$ derivatives the *n*-alkyl groups can be oriented so as to minimize this interaction. Comparison of $\Delta G^{\ddagger}$ for the complexes of the pairs $CH_3C_2CH_3$–$CF_3C_2CF_3$ and $C_6H_5C_2CO_2C_2H_5$–*p*-$NO_2C_6H_4C_2CO_2C_2H_5$ shows that the barrier to exchange increases with the electron-withdrawing ability of the acetylene and hence presumably with the strength of the metal–acetylene bond.

At this stage we can only speculate about the physical processes which are responsible for the site exchange. We discount the possibility that the PF_3 groups permute pairwise independently of each other, i.e., (12), (23), and (13) permutations (the sites being numbered as shown in Figure 2) on the basis of a study of the triphenylphosphine-substituted derivative $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2CH_3)$, which is reported in the following paper.[30] There are three other obvious possibilities.

(1) A rotation about the Rh–Rh bond of one rigid $Rh(PF_3)_3$ group with respect to the other is a process which is similar in principle to rotation about the C–C bond axis of ethane or, more pertinently, to rotation about the metal–metal bond in molecules such as $Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4$[35,36] and $M_2(\eta^5\text{-}C_5H_5)_2(CO)_6$[40] (M = Cr or Mo). Although the analogy with the latter complexes is appealing, it must be noted that we have evidence for only one stable rotamer in solution, viz., that in which the PF_3 groups on each rhodium atom occupy an eclipsed configuration, whereas in the binuclear cyclopentadienylmetal carbonyls there is evidence for discrete rotamers in solution.

(2) A tritopal rearrangement of each $Rh(PF_3)_3$ group with respect to the acetylene is a process which is not concerted in the sense that it can take place independently in each half of the dimer. The coordination geometry about each rhodium atom in the $Rh_2(PF_3)_6$(ac) complexes and about the cobalt atom in the $Co_2(CO)_6$(ac) complexes can be regarded as approximately trigonal bipyramidal, with the center of the acetylenic bond and two PF_3 groups in equatorial positions and the remaining PF_3 group and a "bent" metal–metal bond in axial positions. It is well known that the axial and equatorial ligands of trigonal-bipyramidal molecules of the type ML_5 undergo pairwise exchange at a rate which is usually fast on the NMR time scale even at the lowest accessible temperatures, though limiting spectra for the complexes $[M[P(OCH_3)_3]_5]^{n+}$ (*n* = 1, M = Co, Rh, or Ir; *n* = 2, M = Ni, Pd, or Pt) have recently been obtained.[41] The simplest explanation for this fluxional behavior involves a square-pyramidal transition state (the Berry mechanism),[42] though a "turnstile" mechanism has also been advocated.[43] Recently it has been shown[44] that the trigonal-bipyramidal complexes $Fe(CO)_4$(olefin), in which the olefin occupies an equatorial site and lies in the equatorial plane, undergo carbonyl group scrambling, the activation energy for the process being considerably higher than for CO scrambling in $Fe(CO)_5$; it appears that carbonyl equilibration and olefin rotation are intimately related. Complexes such as $Fe(CO)_3$(1,--diene)[45-47] and $Fe(CO)(PF_3)_2$(1,3-diene),[48,49] which can be regarded as having square-pyramidal geometry about the metal atom, show fluxional behavior in their ^{13}CO NMR spectra, and a process of carbonyl (or PF_3) group rotation about a general axis together with some bending has been suggested.[45,46,48] In both the tetracarbonyl and tricarbonyl series, electron-withdrawing groups in the olefinic moiety increase the barrier to the equilibration process, an effect which we also observe in the rhodium–acetylene complexes.

(3) Rotation of a rigid $Rh_2(PF_3)_6$ moiety with respect to the acetylene (or vice versa) is a process which differs from the preceding two in that the two $Rh(PF_3)_3$ groups retain their eclipsed configuration at all times.

Processes 1 and 2 are based on analogy with the behavior of known compounds, but they represent different descriptions of the same process and are physically indistinguishable. In the di-*tert*-butylacetylene complex $Rh_2(PF_3)_5$(*t*-Bu_2C_2),[50] in which the acetylene is believed to bridge a rhodium–rhodium double bond, the variable-temperature ^{19}F NMR spectrum is most simply explained in terms of an internal rotation of PF_3 groups about the metal–metal bond. The fact that the free energy of activation ($\Delta G^{\ddagger}$) in this case is considerably (~5–8 kcal/mol) higher than that for the $Rh_2(PF_3)_6$(ac) complexes, which contain a metal–metal single bond, suggests that the metal–metal bond plays an important role in the process, and this leads us to choose process 1 or 2 in preference to process 3.

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Registry No. $Rh_2(PF_3)_6(HC_2H)$, 38888-37-8; $Rh_2(PF_3)_6(C_6H_5C_2H)$, 38888-38-9; $Rh_2(PF_3)_6$(*n*-$C_4H_9C_2H$), 38893-61-7; $Rh_2(PF_3)_6$(*t*-$C_4H_9C_2H$), 38893-62-8; $Rh_2(PF_3)_6(CH_3C_2CH_3)$, 38893-59-3; $Rh_2(PF_3)_6$(*n*-$C_3H_7C_2CH_3$), 56792-83-7; $Rh_2(PF_3)_6(C_6H_5C_2CH_3)$, 39015-25-3; $Rh_2(PF_3)_6(C_6H_5C_2C_2H_5)$, 56792-65-5; $Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$, 38893-58-2; $Rh_2(PF_3)_6(C_6H_5C_2CO_2CH_3)$, 56792-66-6; $Rh_2(PF_3)_6$(*p*-$NO_2C_6H_4C_2CO_2C_2H_5$), 56792-67-7; $Rh_2(PF_3)_6(CF_3C_2CF_3)$, 38893-63-9; $Rh_2(PF_3)_6(CH_3C_2CO_2CH_3)$, 38893-60-6; $Rh_2(PF_3)_6(C_6H_5C_2CO_2C_2H_5)$, 56792-68-8; $Rh_2(PF_3)_8$, 14876-96-1; phenylacetylene, 536-74-3; phenylacetylene polymer, 25038-69-1.

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(39) We discuss the barrier to exchange in terms of $\Delta G^{\ddagger}$ rather than the enthalpy of activation, $\Delta H^{\ddagger}$, or the activation energy, E_a, calculated from the Arrhenius equation. Although there is not a strict 1:1 correspondence, any errors should be common to all of the data and it is the *differences* which are significant.
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Contribution from the Research School of Chemistry,
The Australian National University, Canberra, A.C.T. 2600, Australia

Correlated Intermolecular and Intramolecular Ligand Exchange in μ-Acetylene-bis(ligand)tetrakis(trifluorophosphine)dirhodium Complexes and the Crystal and Molecular Structure of the Diphenylacetylene–Triphenylphosphine Derivative $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)\cdot(C_2H_5)_2O$

M. A. BENNETT,* R. N. JOHNSON, G. B. ROBERTSON, T. W. TURNEY, and P. O. WHIMP

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The acetylene complexes $Rh_2(PF_3)_6(ac)$ (ac = $C_6H_5C_2C_6H_5$, $C_6H_5C_2CH_3$, or p-$NO_2C_6H_4C_2CO_2C_2H_5$) react with monodentate tertiary phosphines and arsines (L) to give disubstitution products $Rh_2(PF_3)_4L_2(ac)$ and with o-phenylenebis(dimethylarsine), o-$C_6H_4[As(CH_3)_2]_2$ (diars), to give $Rh_2(PF_3)_2(diars)_2(ac)$ (ac = $C_6H_5C_2C_6H_5$ or $C_6H_5C_2CH_3$). The reaction with monodentate ligands is reversed by the action of PF_3. The crystal and molecular structure of the diphenylacetylene–bis(triphenylphosphine) derivative [L = $P(C_6H_5)_3$; ac = $C_6H_5C_2C_6H_5$] has been determined by three-dimensional X-ray structural analysis using 6834 independent reflections, with $I/\sigma(I) \geq 3.0$, collected by counter methods. The complex crystallizes in the triclinic space group $P\bar{1}$ (C_i^1, No. 2) with a = 21.186 (9) Å, b = 12.994 (5) Å, c = 12.942 (5) Å, α = 114.10 (2)°, β = 64.36 (2)°, γ = 115.33 (2)°, and Z = 2. The structure was solved by conventional heavy-atom methods and was refined by block-diagonal least-squares methods to final weighted and unweighted R factors of 0.046 and 0.042, respectively. The molecule is structurally similar to cobalt–carbonyl–acetylene complexes such as $Co_2(CO)_6(\mu$-$C_6H_5C_2C_6H_5)$ and consists of two $[Rh(PF_3)_2[P(C_6H_5)_3]]$ moieties bridged by diphenylacetylene, the C≡C bond of which is above and approximately normal to the Rh–Rh axis. The triphenylphosphine groups are on the same side of the molecule as the bridging acetylene, and the Rh–Rh distance [2.740 (1) Å] is in the range expected for a rhodium–rhodium single bond. The ^{19}F NMR spectra of the disubstitution products containing unsymmetrical acetylenes, $Rh_2(PF_3)_4L_2(RC_2R')$, show signals due to PF_3 groups in two different environments at or just below room temperature, but on raising the temperature intramolecular PF_3 exchange takes place. This process appears to be initiated by dissociation of the tertiary phosphine or arsine (L). The free energies of activation, $\Delta G^{\ddagger}$, for the intramolecular process have been estimated by approximate line shape analysis of the ^{19}F NMR spectra and are higher for the tertiary phosphine than for the tertiary arsine derivatives. In the one case studied, the electron-withdrawing acetylene ethyl p-nitrophenylpropiolate gives rise to a higher $\Delta G^{\ddagger}$ than either diphenylacetylene or 1-phenylpropyne. Possible mechanisms involving the fluxional behavior of a coordinately unsaturated intermediate are discussed. A 1:1 mixture of $Rh_2(PF_3)_4[As(CH_3)(C_6H_5)_2]_2(C_6H_5C_2CH_3)$ and $Rh_2(PF_3)_6(C_6H_5C_2CH_3)$ undergoes intermolecular PF_3 exchange in the temperature range 50–82°, perhaps via a pentakis intermediate $Rh_2(PF_3)_5[As(CH_3)(C_6H_5)_2](C_6H_5C_2CH_3)$. The diars derivatives $Rh_2(PF_3)_2(diars)_2(ac)$ show temperature-independent ^1H and ^{19}F NMR spectra in the range −90° to room temperature, but their structure could not be determined unambiguously.

Introduction

In the previous paper,[1] we showed that octakis(trifluorophosphine)dirhodium, $Rh_2(PF_3)_8$, reacts with a variety of acetylenes (ac) to give bridging acetylene complexes $Rh_2(PF_3)_6(ac)$, the PF_3 groups of which undergo rapid intramolecular exchange at room temperature. The preparation of tertiary phosphine and arsine substitution products was undertaken in order to obtain crystalline derivatives suitable for X-ray structural analysis. It was also hoped that a study of their variable-temperature ^{19}F NMR spectra would assist in determining the mechanism of intramolecular exchange in the parent compounds. This paper reports the preparation and ligand-exchange behavior of the substitution products, together with a single-crystal X-ray analysis of the diphenylacetyl-