The crystal structures do confirm the previous suggestion[7] that the tendency of the C_5Me_4Et complex to undergo carbonyl substitution at a faster rate than the C_5H_5 complex arises from a stabilization of the transition state rather than from a ground-state effect; i.e., there is no evidence from the crystal structures that the carbonyl ligands in $Ru(C_5Me_4Et)(CO)_2Br$ are bonded any less strongly than in $Ru(C_5H_5)(CO)_2Br$. It is intriguing to speculate that the observed difference in reactivity results from the differences in the two structures. For instance, one could argue that in the case of the C_5Me_4Et complex, where there is evidence of a diene structure, dissociation of a carbonyl ligand is favored since this would reduce the steric constraints in the complex and so allow the C_5Me_4Et ligand to adopt a preferred η^5 coordination. The validity of such an argument must await further kinetic and structural studies on related compounds.

Acknowledgment. We thank the SERC for funds to purchase the diffractometer and Johnson Matthey for the generous loan of ruthenium trichloride.

Registry No. Ia, 32613-75-5; Ib, 72339-70-9.

Supplementary Material Available: Listings of hydrogen atom positional parameters, anisotropic thermal parameters, and observed structure amplitudes and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Binuclear Cationic Complexes of Rhodium. 8. Crystal and Molecular Structure of the Dimetalated-Olefin Isocyanide Complex $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2{\cdot}2(CH_3)_2CO$

JOEL T. MAGUE

Received July 17, 1982

The complex $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2{\cdot}2(CH_3)_2CO$ crystallizes in the space group $C2/c$ with $a = 27.575$ (7) Å, $b = 11.432$ (5) Å, $c = 27.027$ (7) Å, $\beta = 103.07$ (2)°, $V = 8299$ (5) Å^3, and $Z = 4$. Diffraction data ($2\theta \leq 50.7$, Mo Kα) were collected on a Nicolet four-circle autodiffractometer, and the structure was solved by conventional methods. Discrepancy indices are $R_F = 0.045$ and $R_{wF} = 0.066$ for 6228 reflections with $I > 3\sigma(I)$. The dimeric dication has crystallographically imposed C_2 symmetry. The two rhodium atoms are bridged by two bis(diphenylphosphino)methane ligands and the fluorocarbon moiety, which is bound as a cis-dimetalated olefin. Neglecting the position of the second metal atom, the coordination about each metal approximates a square pyramid with one end of each phosphine ligand occupying trans basal sites. The other two basal sites are occupied by one end of the fluorocarbon moiety and one *tert*-butyl isocyanide ligand. The second isocyanide ligand occupies the apical site. The rhodium–rhodium distance of 2.9653 (6) Å is consistent with the presence of a single, albeit weak, metal–metal bond.

Introduction

Recently it was reported that electronegatively substituted acetylenes react with $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$ (DPM = bis(diphenylphosphino)methane) to form adducts having the composition $[Rh_2(CNC(CH_3)_3)_4(\text{acetylene})(DPM)_2](B(C_6H_5)_4)_2$.[1] From their ^{31}P NMR spectra it was evident that the acetylene had become bound in a symmetrical fashion and although the spectral parameters suggested binding as a cis-dimetalated olefin, the data were also consistent with its being bound with the central carbon–carbon axis perpendicular to the metal–metal vector. Also unexplained was the observation that although brownish orange solutions of the acetylene adduct became yellow on exposure to carbon monoxide, no evidence for coordinated carbon monoxide was found in the yellow product. The present study was undertaken to confirm the proposed mode of binding of the acetylene and to ascertain the course of the reaction with carbon monoxide. Since suitable crystals of the tetraphenylborate salts could not be obtained, we chose to study the hexafluorophosphate analogues. No difference in behavior between the two sets of salts was noted.

Experimental Section

Synthesis of $[Rh_2(CNC(CH_3)_3)_4(C_4F_6)(DPM)_2](PF_6)_2$. A solution of 0.40 g of $[Rh(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$[2] in 25 mL of dichloromethane was stirred under an atmosphere of hexafluorobut-2-yne in a septum-capped flask for 18 h, by which time the original purple color had changed to orange. The product was precipitated by addition of diethyl ether and recrystallized from dichloromethane/diethyl ether to give brownish microcrystals. Crystals of the acetone solvate suitable for the X-ray diffraction study were grown by the slow diffusion of diethyl ether into an acetone solution of the complex under nitrogen and obtained as dark orange-brown prisms (hereafter referred to as the brown crystals).

Reactions with Carbon Monoxide. A sample of the original recrystallized material prepared as described above was dissolved in acetone and the solution flushed with carbon monoxide whereupon it became bright yellow. Slow diffusion of diethyl ether into this solution under a carbon monoxide atmosphere yielded large yellow prisms (hereafter referred to as the yellow crystals).

As described below, X-ray diffraction studies on both the brown and yellow crystals showed that the only crystallographically detectable species present in each is $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2](PF_6)_2$. Thus this acetylene adduct appears unaffected by treatment with carbon monoxide. We therefore suspected that the brown crystals contained an impurity which reacted with carbon monoxide to produce the observed color change. Thin-layer chromatography of a sample of the brown crystals showed this to be the case. Elution of samples of the brown and yellow compounds with tetrahydrofuran showed the former to consist of a minor, mobile brownish purple component and major immobile yellow component while the latter consisted only of the yellow, immobile component. The mobile component of the brown compound appeared to move at the same rate as purple $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ under the same conditions, and we tentatively ascribe the brown color of the brown crystals to the presence of a small amount of this complex, which cocrystallizes with the hexafluorobut-2-yne adduct. The color change on reaction of the brown crystals with carbon monoxide can then be attributed to the reaction of this impurity, which we have previously shown to form a yellow carbonyl adduct.[3] The absence

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(1) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.
(2) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049.

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Table I. Summary of Crystal Data and Intensity Collection

compd	$[Rh_2(CNCMe_3)_4(C_4F_6)(DPM)_2](PF_6)_2\cdot 2(CH_3)_2CO$
fw	1875.40
formula	$C_{80}H_{92}P_6F_{18}N_4O_2Rh_2$
cell parameters	
a	27.575 (7) Å
b	11.432 (5) Å
c	27.027 (7) Å
β	103.07 (2)°
V	8299 (5) Å^3
Z	4
density	
obsd	1.54 ± 0.02 g/cm^3
calcd	1.56 g/cm^3
space group	$C2/c$
cryst dimens	0.070 × 0.070 × 0.070 cm
temp	20 ± 1 °C
radiation	Mo Kα (λ = 0.710 73 Å), graphite monochromated
μ	6.33 cm^{-1}
range of transmission factors	0.817-1.000
unique data used	6228
final no. of parameters varied	385
error in observn of unit wt	1.98
R_F	0.045
R_{wF}	0.066

of a carbonyl band in the infrared spectrum of the yellow crystals indicates that the $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}CO)(DPM)_2](PF_6)_2$ impurity thus produced evidently does not cocrystallize with the hexafluorobut-2-yne adduct.

Collection and Processing of X-ray Diffraction Data. Since it was determined that the yellow crystals appeared to be the purer sample of $[Rh_2(CNC(CH_3)_3)_4(C_4F_6)(DPM)_2](PF_6)_2$ and to be of better quality, only the details of the work on this sample will be given. A well-formed yellow parallelepiped approximately 0.70 mm on an edge was sealed in a thin-walled glass capillary and mounted in a random orientation on a computer-controlled four-circle Nicolet autodiffractometer at Crystalytics Co., Lincoln, NE. Final lattice parameters as determined from a least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 15 reflections ($2\theta > 25°$) accurately centered on the diffractometer at 20 ± 1 °C are given in Table I together with other data pertinent to the data collection. From these and the systematic absences observed during the data collection, the space group is either *Cc* (No. 9) or *C*2/*c* (No. 15). The choice of the latter was suggested by the intensity statistics and confirmed by the successful refinement. From the measured density it was then evident that the asymmetric unit consisted of half of the dimer.

Intensity data were collected by the ω-scan technique with use of graphite-monochromated Mo Kα radiation with a takeoff angle of 4° and a normal-focus X-ray tube. For those reflections having $2\theta_{\text{Mo K}\alpha} < 43°$, a scan rate of 6°/min was employed for the scan between ω settings 0.45° above and below the calculated Kα doublet value for each reflection. A scan rate of 4°/min was used for the remaining reflections with $43° < 2\theta < 50.7°$. Each scan was divided into 17 equal time intervals with the 13 contiguous intervals having the highest single accumulated count at their midpont being used to calculate the net intensity. The preliminary survey of the reflections showed them to have a width at half-height of 0.35° in ω. Background counts, each lasting half the total time used for the net scan, were measured at ω settings of 0.90° above and below those calculated for each reflection.

A total of 7604 independent reflections was measured with 6 standards being monitored every 300 reflections to check for misalignment and/or crystal deterioration. These showed only a random ±2.0% variation. The intensities were corrected empirically for absorption effects with use of ψ scans on six reflections having $9.83° \leq 2\theta \leq 28.71°$ and were further corrected for Lorentz and polarization effects. By application of the acceptance criterion $I > 3\sigma(I)$, a total of 6228 reflections were considered to be observed. Here, $\sigma(I)$ is the standard deviation in the intensity computed from

$$\sigma^2(I) = C_T + k^2B$$

with C_T the total scan count, B the total background, and k the ratio of scan time to total background time.[4]

Solution and Refinement of the Structure.[5] The structure was refined by a block-diagonal least-squares process. Scattering factors for neutral Rh, P, F, C, N, and O were those tabulated by Cromer and Waber[6] while the values given by Stewart et al.[7] were used for hydrogen. Those for Rh, P, and F included the real and imaginary parts of the correction of the effects of anomalous dispersion. The function minimized was $\sum w\Delta^2$, where $\Delta = K|F_o| - G|F_c|$ (F_o and F_c are respectively the observed and calculated structure factors, and K and G are scale factors ($G = 1.0$)) and $w = 1/\sigma^2(F_o)$. The standard deviation in F_o, $\sigma(F_o)$, was taken as $\sigma(F_o^2)/2F_o$. The conventional and weighted residuals R_F and R_{wF} are defined as $R_F = \sum|\Delta|/\sum F_o$ and $R_{wF} = [\sum w\Delta^2/\sum F_o^2]^{1/2}$.

A three-dimensional, unsharpened Patterson function readily provided coordinates for the unique rhodium atom, and the remainder of the non-hydrogen atoms were rapidly located by the application of least-squares refinement of the positional parameters followed by a difference Fourier synthesis. With all the non-hydrogen atoms included in the calculation, refinement of an overall scale factor and positional and isotropic thermal parameters led to $R_F = 0.086$. Refinement was continued with the introduction of anisotropic thermal parameters of the form $\exp[-B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]$ for all non-hydrogen atoms except the phenyl carbon atoms, resulting in $R_F = 0.065$. A difference Fourier synthesis at this pont revealed reasonable locations for the hydrogen atoms of the DPM ligands, and they were included in fixed positions (C–H = 0.95 Å, B = 1.0 Å^2 greater than that of the attached carbon atom). During the subsequent refinement, these positions were updated every two cycles. Difference Fourier syntheses computed in the idealized planes of the three hydrogen atoms of each methyl group provided reasonable locations for the remaining hydrogen atoms, but as these were rather diffuse (particularly for the solvent molecule), it was decided to place them by using an idealized methyl group geometry with C–H = 0.95 Å, H–C–H = 109.5°, and the plane containing the hydrogen atoms normal to the C–C vector. With use of these constraints, the best rotational orientation of each methyl group was determined from the difference maps just described. The contributions of these atoms, with isotropic thermal parameters 1.2 times greater than those of the attached carbon atoms, were included in subsequent structure factor calculations, but their positions were not refined. Instead they were reset manually by the same procedure used initially to locate them after every two cycles of refinement. The refinement was continued until no parameter changed by more than 10% of its estimated standard deviation. A final difference Fourier synthesis showed no feature greater than ±0.6 e/Å^3. These were primarily in the vicinity of the rhodium atom although some were also indicative of anisotropic thermal motion of some of the phenyl carbon atoms. These were not large enough however to warrant the added time and expense of anisotropic refinement of these atoms. An analysis of the residuals over various ranges of F_o, $(\sin\theta)/\lambda$, and Miller indices showed no unusual trends although there was a tendency for these to be slightly larger for the weakest reflections. The final R factors are given in Table I while Table II (supplementary material) lists the final values of F_o and F_c. The atomic coordinates obtained from the final cycle of least-squares refinement are presented in Table III together with the associated standard deviations as estimated from the inverse

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(3) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743.

(4) Data collection and reduction services were provided by Crystalytics Co., Lincoln, NE. All required calculations were performed on a Data General Eclipse S-200 computer using a local version of the Nicolet (Syntex) E-XTL crystallographic software package.

(5) All computations involved in the solution and refinement of the structure were performed on a Digital Equipment Corp. 2060 computer at the Tulane University Computer Laboratory using the LOKI Crystallographic Computing System by C. J. Fritchie, Jr., B. L. Trus, J. L. Wells, C. A. Langhoff, Jr., M. Guise, W. Lamia, M. Krieger, J. T. Mague, and R. Jacobs. Other programs used were local versions of MGEOM, by J. S. Wood (distance and angle calculations), PACK, by C. J. Fritchie, Jr. (molecular packing), RANGER, by J. A. Ibers (weighting scheme analysis), SFTBL2, by J. T. Mague (preparation of structure factor table for publication), and ORTEP, by C. K. Johnson (graphical illustrations).

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Table III. Atomic Coordinates[a]

atom	x	y	z	atom	x	y	z	atom	x	y	z
Rh	479.0 (1)	4250.9 (3)	2883.1 (1)	C_{31}	1359 (2)	8358 (6)	3069 (3)	C_{211}	231 (2)	2578 (4)	3952 (2)
P_1	860.1 (4)	4620 (1)	2217.9 (4)	C_{41}	908 (2)	8539 (5)	3772 (3)	C_{221}	660 (2)	2591 (5)	4335 (2)
P_2	58.3 (4)	3894 (1)	3555.2 (4)	C_{51}	1643 (3)	7214 (7)	3877 (3)	C_{231}	783 (2)	1621 (6)	4653 (2)
P_3	1548.7 (7)	1186 (2)	815.5 (7)	C_{12}	1122 (2)	3631 (4)	3328 (2)	C_{241}	484 (2)	650 (5)	4590 (2)
F_1	1496 (3)	971 (7)	1370 (2)	N_{12}	1491 (2)	3218 (4)	3554 (2)	C_{251}	66 (2)	622 (6)	4207 (2)
F_2	1015 (2)	731 (7)	622 (3)	C_{22}	1952 (2)	2607 (6)	3792 (2)	C_{261}	−66 (2)	1571 (5)	3892 (2)
F_3	1573 (3)	1522 (8)	273 (2)	C_{32}	2335 (3)	3525 (9)	3996 (4)	C_{112}	855 (2)	6124 (4)	1974 (2)
F_4	2077 (2)	1617 (8)	1024 (3)	C_{42}	2112 (3)	1930 (8)	3370 (4)	C_{122}	1231 (2)	6508 (5)	1741 (2)
F_5	1349 (3)	2445 (6)	873 (2)	C_{52}	1845 (3)	1815 (9)	4189 (4)	C_{132}	1227 (2)	7625 (6)	1565 (2)
F_6	1711 (4)	−33 (7)	743 (5)	C_{1S}	1716 (4)	5234 (13)	668 (4)	C_{142}	858 (2)	8398 (6)	1601 (2)
F_7	1022 (1)	1798 (3)	2607 (1)	C_{2S}	1896 (3)	4980 (9)	238 (4)	C_{152}	477 (2)	8039 (6)	1823 (2)
F_8	674 (1)	1119 (3)	3172 (1)	C_{3S}	2294 (3)	4136 (8)	196 (4)	C_{162}	474 (2)	6898 (5)	2007 (2)
F_9	418 (1)	640 (3)	2385 (1)	O_S	1699 (3)	5523 (9)	−140 (4)	C_{212}	119 (2)	5037 (4)	4038 (2)
C_1	237 (2)	2586 (4)	2618 (2)	C_{111}[c]	1529 (2)	4342 (4)	2347 (2)	C_{222}	591 (2)	5475 (5)	4259 (2)
C_2	578 (2)	1544 (4)	2702 (2)	C_{121}	1836 (2)	5051 (5)	2700 (2)	C_{232}	645 (2)	6301 (6)	4645 (2)
C_3	609 (2)	3685 (4)	1678 (2)	C_{131}	2349 (2)	5002 (6)	2781 (2)	C_{242}	239 (2)	6719 (6)	4806 (2)
C_{11}	685 (2)	5895 (4)	3129 (2)	C_{141}	2556 (3)	4233 (6)	2498 (3)	C_{252}	−224 (3)	6293 (7)	4595 (3)
N_{11}	887 (1)	6746 (3)	3285 (1)	C_{151}	2268 (2)	3498 (6)	2158 (2)	C_{262}	−286 (2)	5456 (5)	4215 (2)
C_{21}	1205 (2)	7732 (5)	3506 (2)	C_{161}	1747 (2)	3538 (5)	2018 (2)				

[a] The estimated standard deviation in the least significant digit(s) is given in parentheses. Positional parameters are ×10^4. [b] The atom labeling is that of Figure 1. [c] The labeling scheme C_{ijk} indicates that carbon atom j is part of ring k attached to P_i. Atom C_{i1k} is that attached to phosphorus.

Table VI. Interatomic Distances (Å)[a]

$Rh-P_1$[b]	2.317 (1)	C_2-F_7	1.338 (6)
$Rh-P_2$	2.401 (1)	C_2-F_8	1.328 (6)
$Rh-C_1$	2.089 (4)	C_2-F_9	1.352 (6)
$Rh-C_{11}$	2.031 (4)	$C_{11}-N_{11}$	1.153 (6)
$Rh-C_{12}$	2.031 (4)	$N_{11}-C_{21}$	1.468 (7)
P_1-C_3	1.815 (4)	$C_{21}-C_{31}$	1.521 (8)
P_1-C_{111}	1.826 (5)	$C_{21}-C_{41}$	1.519 (8)
P_1-C_{112}	1.840 (5)	$C_{21}-C_{51}$	1.506 (9)
P_2-C_{211}	1.846 (5)	$C_{12}-N_{12}$	1.162 (6)
P_2-C_{212}	1.828 (5)	$N_{12}-C_{22}$	1.467 (7)
$P_2'-C_3$	1.820 (4)	$C_{22}-C_{32}$	1.502 (11)
C_1-C_1'	1.318 (9)	$C_{22}-C_{42}$	1.523 (11)
C_1-C_2	1.504 (7)	$C_{22}-C_{52}$	1.483 (12)

[a] The estimated standard deviation in the least significant digit(s) is given in parentheses. [b] The atom labeling is that of Figure 1.

least-squares matrix. In a similar fashion the thermal parameters of all atoms refined are presented in Table IV while Table V provides the calculated hydrogen atom positions used (supplementary material).

As noted earlier, the structure of the brown crystal was also determined and refined to $R_F = 0.052$ with use of 4726 reflections with $I > 3\sigma(I)$. Details of the data collection and refinement closely parallel those described above, and the resulting structure is the same in all respects within experimental error. Attempts were made with difference Fourier syntheses to detect the presence of the presumed $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ impurity, but no definite evidence for it could be found. We therefore conclude that it is not present at a crystallographically significant level.

Results and Discussion

The structures of both the brown and the yellow crystals consist of discrete binuclear cations, $[Rh_2(CNCMe_3)_4(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2]^{2+}$, interspersed with hexafluorophosphate counterions and molecules of solvent acetone. A perspective view of the cation is presented in Figure 1. The contents of the unit cell are shown in Figure 2 (supplementary material). No unusual intermolecular contacts are present. The dimeric cation has crystallographically imposed C_2 symmetry with the symmery axis bisecting the Rh–Rh′ and C_1–C_1' vectors. Pertinent bond distances and interbond angles for the cation are presented in Tables VI and VII, respectively.

The results of the structure determination confirm the conclusions drawn from the spectroscopic data[1] that the hexafluorobut-2-yne molecule has become bound as a dimetalated olefin. The Rh–C_1 distance of 2.089 (4) Å is the same within experimental error as that of 2.053 (12) Å found previously[8] in $[Rh_2(P(OMe)_3)(\mu\text{-}CO)(\mu\text{-}MeO_2CC{=}$

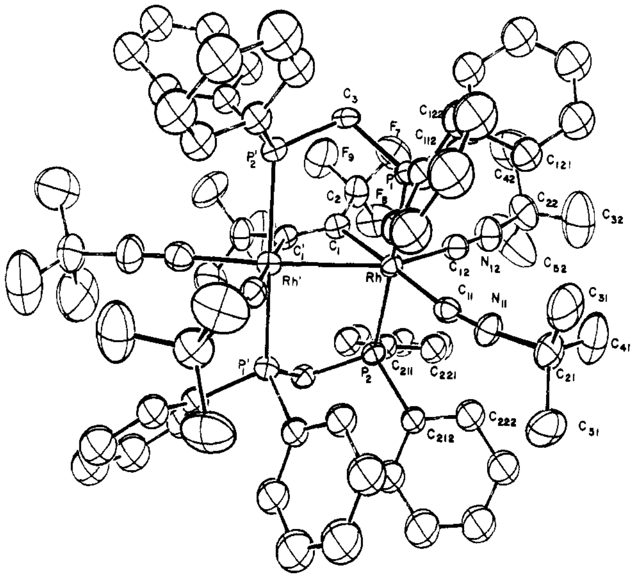

Figure 1. Perspective view of the $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2]^{2+}$ cation with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 50% probability. The numbering of the phenyl carbon atoms continues around the rings as indicated with the second subscript as the running index. Phenyl hydrogen atoms (not shown) are numbered in the same fashion. the atoms P_1', P_2', and C_1' are related to their unprimed counterparts by the C_2 axis. The remaining unlabeled atoms are symmetry related in an analogous fashion.

$CCO_2Me)(O_2CMe)(DPM)_2]^+$ but is significantly longer than those of 1.994 (9) and 1.997 (9) Å found in the closely related neutral complex $[Rh_2(\mu\text{-}CF_3C{=}CCF_3)Cl_2(DPM)_2]$.[9] This lengthening may be ascribed at least in part to a significant trans influence of the *tert*-butyl isocyanide ligand which is situated trans to it. The formulation of the fluorocarbon ligand as a dimetalated olefin is confirmed by the C_1–C_1' distance of 1.318 (9) Å and the angles about C_1 (Table VII). The only one of these deviating markedly from the expected 120° is

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(14) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.

Table VII. Interbond Angles (deg)[a]

P_1-Rh-P_2[b]	178.06 (6)	F_7-C_2-F_9	103.1 (4)
P_1-Rh-C_1	93.8 (1)	F_8-C_2-F_9	107.0 (4)
P_1-Rh-C_{11}	86.8 (1)	F_7-C_2-C_1	111.6 (4)
P_1-Rh-C_{12}	92.0 (1)	F_8-C_2-C_1	114.6 (4)
P_2-Rh-C_1	86.1 (1)	F_9-C_2-C_1	113.9 (4)
P_2-Rh-C_{11}	93.2 (1)	Rh-C_{11}-N_{11}	167.6 (4)
P_2-Rh-C_{12}	90.0 (1)	C_{11}-N_{11}-C_{21}	172.3 (4)
C_1-Rh-C_{11}	177.6 (2)	N_{11}-C_{21}-C_{31}	106.9 (4)
C_1-Rh-C_{12}	93.1 (2)	N_{11}-C_{21}-C_{41}	108.9 (4)
C_1-Rh-Rh′	66.1 (2)	N_{11}-C_{21}-C_{51}	106.5 (5)
C_{11}-Rh-C_{12}	89.3 (2)	C_{31}-C_{21}-C_{41}	110.9 (5)
C_{11}-Rh-Rh′	111.6 (2)	C_{31}-C_{21}-C_{51}	112.3 (5)
C_{12}-Rh-Rh′	159.0 (2)	C_{41}-C_{21}-C_{51}	111.1 (5)
P_1-Rh-Rh′	86.96 (4)	Rh-C_{12}-N_{12}	175.0 (4)
P_2-Rh-Rh′	91.24 (4)	C_{12}-N_{12}-C_{22}	173.6 (5)
C_3-P_1-C_{111}	103.7 (2)	N_{12}-C_{22}-C_{32}	107.2 (6)
C_3-P_1-C_{112}	106.9 (2)	N_{12}-C_{22}-C_{42}	106.4 (5)
C_3-P_1-Rh	111.1 (2)	N_{12}-C_{22}-C_{52}	108.3 (5)
C_{111}-P_1-C_{112}	99.0 (2)	C_{32}-C_{22}-C_{42}	109.3 (6)
C_{111}-P_1-Rh	115.9 (2)	C_{32}-C_{22}-C_{52}	113.6 (6)
C_{112}-P_1-Rh	118.7 (2)	C_{42}-C_{22}-C_{52}	111.7 (6)
C_{211}-P_2-C_{212}	101.4 (2)	C_{121}-C_{111}-P_1	117.6 (4)
C_{211}-P_2-Rh	118.2 (1)	C_{161}-C_{111}-P_1	123.7 (4)
C_{212}-P_2-Rh	115.9 (2)	C_{122}-C_{112}-P_1	120.5 (4)
C_3-P_2'-Rh′	112.6 (1)	C_{162}-C_{112}-P_1	121.1 (4)
P_1-C_3-P_2'	111.9 (2)	C_{221}-C_{211}-P_2	119.4 (3)
C_2-C_1-Rh	122.0 (3)	C_{261}-C_{211}-P_2	122.4 (4)
C_1'-C_1-C_2	126.2 (5)	C_{222}-C_{212}-P_2	119.2 (4)
C_1'-C_1-Rh	111.8 (3)	C_{262}-C_{212}-P_2	122.6 (4)
F_7-C_2-F_8	105.7 (4)		

[a] The estimated standard deviation in the least significant digit(s) is given in parentheses. [b] The atom labeling is that of Figure 1.

C_1'–C_1–Rh, and this deviation can be attributed to compression due to the close approach of the rhodium atoms. The fact that the angle C_2–C_1–C_1' is larger than C_2–C_1–Rh can be ascribed to the relatively close contact of 2.52 Å between F_9 and F_9', which forces the two trifluoromethyl groups apart.

As is evident from Figure 1, the rhodium atom has slightly distorted square-pyramidal coordination with C_{12} at the apex. If the second metal is included, the coordination can be described as distorted octahedral with the major distortion being an inclination of this last atom by 21° from the Rh–C_{12} vector. This distortion is presumably due in part to the constraints imposed by the binding of the fluorocarbon moiety, but intramolecular contacts of 2.41 Å between H_{152} and H_{413}' and of 2.56 Å between C_{11} and H_{162}' (primed atoms refer to those related by the C_2 axis) probably also serve to prevent the isocyanide ligands based on C_{11} and C_{11}' from closing up on the front face of the molecule.

Two significant features of the molecule are the twist of the two halves of the dimer about the Rh–Rh′ axis, resulting in a torsional angle between the P_1–P_2 and P_1'–P_2' vectors of 20.3°, and the 0.08-Å difference in length between the two independent Rh–P distances. In the majority of the A-frame type complexes of rhodium and their derivatives containing bridging DPM ligands, the two P–Rh–P units are nearly eclipsed with the torsional angles between them being in the range 1–8°. A virtually identical twist of 20.2° has been found however in $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$[15] while in $[Pd_2Br_2(DPM)_2]$ the twist is 39°.[16] That the whole coordination sphere of the rhodium atom is rotated about the metal–metal axis relative to the other side of the dimer can be seen from the fact that the C_1–C_1' vector is inclined from the Rh–Rh′ vector by 14.7° (see Figure 1) and that the intrabasal angles about rhodium are close to 90°. As no short intermolecular contacts occur, the observed twist must either be an inherent feature of the molecule or be the result of attempts to minimize intramolecular contacts. However, with the data available it is not possible to make a clear choice between these alternative explanations. If the twist were an inherent feature, then the ^{31}P NMR spectrum ought to reflect a chemical shift difference between the two pairs of phosphorus atoms (P_1, P_1' and P_2, P_2') although we have no data to suggest how large this might be expected to be. The observed $^{31}P\{^1H\}$ NMR spectrum is quite similar to the symmetrical pattern observed by us for $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$, where the twist is very small. Unfortunately the substantial overlap of all of the weak lines made a full analysis impossible and this together with the rather poor quality of the spectrum made it difficult to determine if the pattern is in fact completely summetrical. Thus although the NMR spectrum suggests that the twist is not retained in solution, it does not provide convincing evidence that this is the case.

From an inspection of models, an untwisted conformation appears to generate closer contacts between the phenyl rings and the methyl groups of the isocyanide ligands than does the observed twisted conformation. Thus as can be seen from Figure 1 (and also Figure 2, supplementary material) the phenyl rings attached to P_1 are staggered with respect to the equatorial ligands. This conformation does however result in relatively close contacts of 2.41 Å between H_{152} and H_{413}' and between H_{162} and H_{162}'. If steric factors are in fact important in determining the observed conformation, then these close contacts generated by the twist must be less important than those that would be present in the untwisted conformation, but as mentioned earlier, the argument for steric factors determining the conformation is not strong.

In the DPM-bridged dirhodium complexes studied to date, the Rh–P distances are generally in the rather narrow range 2.30–2.35 Å[9-15,17] although in $[Rh_2(P(OMe)_3)(\mu\text{-}CO)(\mu\text{-}MeO_2CC{=}CCO_2Me)(O_2CMe)(DPM)_2]PF_6$ one Rh–P distance was found to be 2.379 (4) Å.[8] This was attributed to intramolecular steric interactions. A similar argument may be made for the fact that the Rh–P_2 distance is significantly longer than the Rh–P_1 distance. The observed conformation of the molecule causes the phenyl rings on P_2 to eclipse the equatorial ligands while those on P_1 are staggered with respect to these ligands. Thus a lengthening of Rh–P_2 distance to minimize their contacts with the phenyl rings could be expected.

The Rh–C_{11} and Rh–C_{12} distances are equal and slightly longer than the range 1.860 (10)–1.991 (3) Å observed previously in rhodium isocyanide complexes.[18-21] The lengthening of the former can be attributed to a significant trans influence of the σ-bonded carbon trans to it. The length of the other is not so easily explained, but if as suggested above the coordination about rhodium can be considered as basically square pyramidal, C_{12} occupies the apical site and hence would be expected to be somewhat lengthened.

The Rh–Rh separation of 2.9653 (6) Å is considerably longer than that found in related A-frame derivatives considered to contain a Rh–Rh single bond, viz., 2.7447 (9) Å in $[Rh_2Cl_2(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2]$,[9] 2.7838 (8) Å in $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$,[10] 2.7566 (9) Å in $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$,[12] 2.8415 (7) Å in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]BPh_4$,[13] and 2.731 (2) Å in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}H)(DPM)_2]((p\text{-}tolyl)SO_3)$,[17] but significantly shorter than in

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those where no explicit metal–metal bonding is thought to occur, viz., 3.2386 (5) Å in $[Rh_2(CO)_2Cl_2(DPM)_2]$,[11] 3.1520 (8) Å in $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$,[22] and 3.154 (2) Å in $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$.[15] The observed diamagnetism of the complex indicates that at the very least there must be a spin-pairing interaction between the formally 17-electron metal atoms, and the fact that the metal–metal distance is significantly shorter ($\Delta/\sigma = 7.2$) than the P_1–P_2' separation within the DPM ligand (3.012 (6) Å) suggests that a metal–metal bond exists. This compression along the metal–metal axis is not the result of constraints of the fluorocarbon bridge since in $[Rh_2(P(OMe)_3)(\mu\text{-}CO)(\mu\text{-}MeO_2CC{=}CCO_2Me)(O_2CMe)(DPM)_2]PF_6$, which contains basically the same bridging ligand and no Rh–Rh bond, the metal–metal distance is 3.386 (1) Å.[8] Also, it should be noted that in $[Rh_2(CNPh)_8]^{2+}$, where a metal–metal bond is required, the metal atoms are separated by 3.193 Å.[18]

The other features of the structure appear normal. Thus the carbon–carbon distances in the phenyl rings range from 1.360 (10) (C_{141}–C_{151}) to 1.404 (9) Å (C_{151}–C_{161}) and average 1.382 (8) Å. Also the C–C–C angles average 120.0 (5)° and range from 118.2 (4) (C_{221}–C_{211}–C_{261}) to 121.9 (5)° (C_{131}–C_{121}–C_{111}). The P–F distances in the hexafluorophosphate ion range from 1.490 (7) (P_3–F_6) to 1.560 (7) Å (P_3–F_5) and average 1.532 (7) Å. The cis F–P–F angles range from 86.4 (4) to 93.4 (6)° while the trans F–P–F angles are 173.9 (4), 178.1 (4), and 176.8 (4)°. In all respects, therefore, this ion has a normal geometry. The only unusual aspect of the solvent acetone molecule is a rather short C_{1S}–C_{2S} distance of 1.40 (1) Å, but this is probably the result of the large thermal motion since no evidence could be found to suggest any positional disorder in any portion of the solvent molecule.

In contrast to the case for $[Rh_2Cl_2(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2]$[9] insertion of carbon monoxide into the metal–metal bond of $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2](PF_6)_2$ does not occur even when it is heated at 60 °C under 2 atm of carbon monoxide for 3 h. This lack of reactivity is probably due in large part to this site being blocked by the isocyanide ligands built on C_{11} and C_{11}' and the phenyl groups built on C_{112} and C_{112}'.

Conclusions

Hexafluorobut-2-yne has been shown to bind to $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ as a cis-dimetalated olefin. The adduct thus formed contains a metal–metal bond that is weaker than that found in related complexes but because of steric constraints does not react with carbon monoxide. The color change from brownish orange to yellow, which is observed when even recrystallized samples of the adduct are treated with carbon monoxide, has been traced to the presence of $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ as an impurity that adds carbon monoxide to yield yellow $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}CO)(DPM)_2](PF_6)_2$.

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Registry No. $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2\cdot 2(CH_3)_2CO$, 84848-17-9; Rh, 7440-16-6.

Supplementary Material Available: Listings of observed and calculated structure factors (Table II), thermal parameters (Table IV), and idealized hydrogen atom positions (Table V) and a stereoview of the contents of the unit cell (Figure 2) (25 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of $Os_3(CO)_{12}(SiCl_3)_2$, a Compound with a Linear $SiOs_3Si$ Backbone. Structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$

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The compounds $Os_3(CO)_{12}(SiXCl_2)_2$ (X = Me, Cl) have been isolated from the reaction of $Os_3(CO)_{12}$ with the appropriate silane, Cl_2XSiH, at 140 °C under carbon monoxide pressure (80 atm). The crystal structure of $Os_3(CO)_{12}(SiCl_3)_2$ has been determined by X-ray methods. The space group is $P\bar{1}$ with cell dimensions a = 11.416 (3) Å, b = 9.172 (4) Å, c = 8.443 (4) Å, α = 123.93 (3)°, β = 99.87 (3)°, γ = 98.60 (3)°, V = 689.4 Å^3, and Z = 1. The structure was solved and refined by block-diagonal least-squares methods for 1989 observed reflections to $R = 0.032$ and $R_w = 0.041$. The molecule has a crystallographic center of symmetry with a linear $SiOs_3Si$ chain (Os–Os = 2.912 (1) Å; Os–Si = 2.377 (3) Å); the carbonyl groups on the terminal Os atoms are staggered with respect to those on the central Os. The spectroscopic properties of $Os_3(CO)_{12}(SiXCl_2)_2$ indicate the linear chain is maintained in solution. The crystal structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$ has also been determined: space group *Pnam*, a = 17.312 (2) Å, b = 17.899 (3) Å, c = 9.427 (2) Å, V = 2921.1 Å^3, Z = 4. The structure was refined to $R = 0.054$ and $R_w = 0.061$ for 923 observed reflections. The molecule has a triangular arrangement of osmium atoms in which each Os–Os bond is presumed bridged by a hydrogen atom (Os–Os = 3.132 (3), 3.133 (3), 3.123 (3) Å). The three Os atoms lie on a crystallographic mirror plane, with the Si atoms also lying in the plane (Os–Si = 2.39 (1), 2.39 (1), 2.37 (1) Å).

Introduction

A number of osmium carbonyl derivatives have the formulation $Os_3(CO)_{12}X_2$, e.g., with X = H,[1] CH_3,[2] and halogen.[3] The most probable structures for an $Os_3(CO)_{12}X_2$ compound are shown in **1**–**4**.[4] Spectroscopic evidence suggests that structure **3** is the one commonly adopted. Although structure **4** was thought to pertain to the halogen complexes, subsequent

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[4] The carbonyl groups are omitted and the structures drawn in an eclipsed conformation, for clarity. All crystallographic studies on these compounds have shown that a staggered arrangement is adopted in the solid state.

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