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Binuclear methylene- and alkyne-bridged complexes of rhodium not containing accompanying metal–metal bonds

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Abstract

The alkyne-bridged "A-frame" complex, $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (DPM $= Ph_2PCH_2PPh_2$), reacts with diazomethane to give the unusual species, $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (**2**) in which the two DPM ligands, the methylene and the hexafluoro-2-butyne groups bridge the metals with no accompanying Rh–Rh bond. Attempts to produce a methylene-bridged complex from the analogous carbonyl-bridged "A-frame", $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$, were unsuccessful as this species did not react with diazomethane. An X-ray structure determination has been carried out on compound **2**. This complex crystallizes in the tetragonal space group $P4_1$ with a 21.334(3), c 14.574(2) Å, $V = 6633.2$ Å^3 and $Z = 4$. On the basis of 3669 unique observations and 291 parameters varied the structure has converged to $R = 0.034$ and $R_w = 0.039$. The Rh–Rh separation of 3.466(1) Å indicates that there is no Rh–Rh bond and the wide Rh–C–Rh angle at the bridged methylene group (119.5(5)°) is also consistent with the absence of metal–metal bonding. The methylene group in compound **2** is found to be unreactive towards CO, H_2 and protic acids, probably in part because it is protected in the pocket between the two metals, however compound **2** did react with PMe_3 to yield a complex mix of products, from which $[Rh_2Cl(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(PMe_3)_5]$ (**3**) crystallized in low yield. This complex crystallizes with two molar equivalents of CH_2Cl_2 in the monoclinic space group $P2_1/n$ with a 11.519(2), b 14.689(7), c 25.250(5) Å, β 93.00(2)°, V 4266.7 Å^3 and $Z = 4$. Based on 4614 unique observations and 396 parameters varied the structure has converged to $R = 0.063$ and $R_w = 0.095$. Compound **3** is unusual in that it has resulted from the replacement of the two bridging bidentate DPM groups in **2** by five monodentate PMe_3 ligands. Both rhodium atoms have octahedral geometries in which they share a common face, bridged by the methylene, the alkyne and one chloro group. The Rh–Rh separation of 3.1338(7) Å is consistent with the absence of metal–metal bonding, which is substantiated by the relatively large $Rh\text{–}CH_2\text{–}Rh$ angle of 100.1(3)°.

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Introduction

Transition metal complexes containing bridging methylene groups have been widely studied in the past few years [1] owing in a large part to suggestions that such species may be involved in catalytically important processes such as Fischer–Tropsch chemistry [2–6] and olefin metathesis reactions [7]. At the time this work was initiated, a large number of bridging methylene complexes were known, but in all cases these methylene units were accompanied by metal–metal bonds. It was of interest to us to establish whether such complexes without accompanying metal–metal bonds could be prepared, and if so how they differed structurally from their metal–metal bonded counterparts, and whether they would display unusual reactivity. We chose, as a route to these complexes, the insertion of a methylene fragment into a metal–metal single bond in some "A-frame" complexes, since such a strategy had previously proven to be successful in the preparations of the unusual, analogous bridging carbonyl and sulfur dioxide complexes in which there were no metal–metal bonds [8].

An additional aspect of interest in one of these complexes, $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (**1**), was the possibility that methylene insertion into one or more of the Rh–alkyne bonds might occur. Herein we report the results of this study documenting the synthesis and characterization of the methylene-bridged complex $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$, a preliminary report of which has appeared [9]. Attempts to react this methylene-bridged product further are also reported in this paper.

Experimental

All solvents were dried and degassed under an atmosphere of dinitrogen prior to use and all reactions were carried out under Schlenk conditions employing an atmosphere of dinitrogen or the reactant gas. Unless otherwise specified, reactions were carried out at room temperature. Reagent grade chemicals were used as received from Aldrich except for sodium borohydride, which was supplied by BDH Chemicals. Gaseous reactants were supplied by Matheson and were used as received. The compounds $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (**1**) and $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ were prepared according to the published procedures [10,11]. Infrared spectra were obtained by using a Nicolet 7199 Fourier Transform interferometer with samples run as film casts (from CH_2Cl_2) on KBr plates or as KBr disks. The ^1H NMR spectra were obtained using a Bruker WH-400 spectrometer at ambient temperature, unless otherwise noted, and $^{31}P\{^1H\}$ NMR spectra were obtained at 233 K by using Bruker HFX-90 (at 36.4 MHz) and WH-400 (at 162.0 MHz) spectrometers. The chemical shifts were measured relative to tetramethylsilane (^1H) and H_3PO_4 (^{31}P). An internal deuterium lock (CD_2Cl_2) was used for all spectra.

(i) Synthesis of $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ *(2).* To a solution of **1** (262.3 mg, 0.217 mmol) in 90 ml of CH_2Cl_2 at −78°C was added 20 ml of a diethyl ether solution of diazomethane (ca. 4.76 mmol of CH_2N_2 generated by the complete reaction of 1.19 g of Diazald [12*]). The solution was added dropwise over the

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* Reference number with asterisk indicates a note in the list of references.

period of 1 h and resulted in the precipitation of a yellow-brown powder. This mixture was stirred for an additional hour at −78 °C and after warming to room temperature the solvents were evaporated under a stream of N_2, (the desired product decomposed in solution at temperatures greater than ca. 40 °C) leaving a yellow-brown powder which was washed with 5 ml THF and 2 × 5 ml Et_2O. Yield: approx 0.21 g (79%). The $^{31}P\{^1H\}$ NMR spectrum appeared as two major peaks separated by 121.4 Hz and centered at δ 8.1 ppm. Such a spectrum is typical of symmetrical species based on the $Rh_2(DPM)_2$ framework [13]. The ^1H NMR spectrum showed the DPM methylene groups as multiplets at δ 3.15 and 4.02 ppm and the metal-bridged methylene as a quintet at δ 6.07 ppm (^3J(P–H) 10 Hz). Owing to the very limited solubility of the product, satisfactory NMR spectra could be obtained only after a great number of scans (eg. overnight for ^1H). Final characterization of this species was based on an X-ray structure determination. Anal. Found: C, 53.82; H, 3.91; Cl, 5.68. $Rh_2Cl_2P_4F_6C_{55}H_{46}$ calcd.: C, 54.08; H, 3.80; Cl, 5.80%.

(ii) Attempted reaction of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ with diazomethane. This reaction was attempted using the exact conditions listed for the preparation of **2**. No reaction was noted spectroscopically after 4 h at −78 °C nor after allowing the solution to warm to room temperature and to stand for 24 h.

(iii) Attempted reactions of 2 with CO, $HBF_4 \cdot Et_2O$, HCl, and H_2. In each case 50 mg (0.041 mmol) of compound **2** in 7.0 ml CH_2Cl_2 in a 100 ml round-bottom flask was used. With gaseous reactants, the gases were flushed through the solution for 4–5 minutes at a rate of ca. 0.5 ml sec^{-1} then the solution was stored under an atmosphere of the reactant gas for 24 h. In the case of $HBF_4 \cdot Et_2O$, volumes from between 12 to 60 μl (0.083 to 0.417 mmol) were added and left under a dinitrogen atmosphere for 24 h. In each case the ^{31}P NMR spectrum run in the presence of excess reagent (CO, H_2 or acid) indicated that no reaction had taken place.

(iv) Reaction of 2 with $NaBH_4$. Compound **2** (30 mg, 0.025 mmol) and 0.95 mg (0.025 mmol) of $NaBH_4$ were dissolved in a mixture of 5 ml of CH_2Cl_2 and 1.5 ml of MeOH yielding a green-brown solution. A $^{31}P\{^1H\}$ NMR spectrum of this solution showed that the only rhodium- and phosphorus-containing species was the starting material. After an hour a large number of peaks became evident in the baseline of the $^{31}P\{^1H\}$ NMR spectrum corresponding to decomposition products. No attempt was made to identify the many species present. Similar results were obtained for a range in $NaBH_4$: Compound **2** stoichiometries from 1/1 to 10/1 and for the temperature range between ca. −50 +25 °C.

(v) Reaction of 2 with PMe_3. Compound **2** (80 mg, 0.066 mmol) and 8 ml of dry THF were mixed in a 25 ml round-bottom flask resulting in a suspension of the undissolved solid in a yellow solution. The addition of one equivalent of PMe_3 (6.67 μl) in 2 ml of CH_2Cl_2 resulted in no change after 12 h as judged by ^{31}P NMR spectroscopy. A large excess of PMe_3 (0.70 ml, 7.95 mmol) was then added causing a color change to a darker yellow. Upon stirring for 2 h a white precipitate (polymethylene) appeared. The solution was filtered and a $^{31}P\{^1H\}$ NMR spectrum run on the solution showed the presence of many species, most not displaying coupling to Rh. The solvent was removed under a nitrogen stream, the residue extracted with 3 ml acetone and 3 ml hexane was layered on top. Storing the solution overnight in the freezer resulted in the appearance of orange crystals. The solution was decanted and the crystals were washed with 2 ml hexane. Yield: 10 mg.

The $^{31}P\{^1H\}$ NMR spectrum showed 5 resonances (all doublets of multiplets) due to the PMe_3 groups at δ 17.8, 11.2, −18.6, −30.9, and −36.1, in addition to resonances due to small amounts of impurities. The ^1H NMR spectrum showed the methyl resonances at δ 1.05 (d, 9H, J(P–H) 12.3 Hz), 1.10 (d, 9H, J(P–H) 11.8 Hz), 1.28 (s, br, 9H), 1.29 (s, br, 9H), 1.50 (d, 9H, J(P–H) 12.2 Hz). No resonance for the bridging methylene group was obvious. Attempts to obtain this product (**3**) by adding the exact stoichiometry (5 equiv.) to **2** gave no detectable amount (by ^{31}P NMR) of **3**.

(vi) X-ray data collection. Suitable quality, golden-amber prismatic crystals of $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (**2**) were obtained by allowing diethyl ether to slowly diffuse into a saturated CH_2Cl_2 solution of the compound. Orange crystals of **3** (as the methylene chloride disolvate) were obtained from the reaction mixture of **2** and excess PMe_3 as described in the Experimental section. Preliminary film data on **2** showed that the crystal had $4/m$ diffraction symmetry and belonged to the tetragonal system with extinctions $(00l,\ l \neq 4n)$ characteristic of the space groups $P4_1$ and $P4_3$. The space group of **3** was established as $P2_1/n$ by utilizing the automatic peak search, reflection indexing and cell reduction programs of the Nonius CAD4 system, together with the systematic absences of the compound. The non-standard setting was retained because of the convenient β angle. Accurate cell parameters for **2** and **3** were obtained by least-squares analyses of 25 carefully centered reflections chosen from diverse regions of reciprocal space ($9.2° \leqslant 2\theta \leqslant 25.0°$ for **2**; $19.9° \leqslant 2\theta \leqslant 27.4°$ for **3**; Mo-K_α, radiation). See Table 1 for pertinent crystal data and the details of intensity collection.

The intensity data were collected by using $\theta/2\theta$ scans with variable speeds chosen to give $\sigma(I)/I \leqslant 0.03$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1–α_2 wavelength dispersion, and backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. The intensities of three standard reflections were measured every hour of exposure time to assess possible crystal decomposition or movement. No significant variation in these standards was noted for either crystal so no correction was applied to the data. The data were processed in the usual way using a value of 0.04 for p [14]. Absorption corrections for **2** were applied to the data using Gaussian integration [15*], whereas for **3** the method of Walker and Stuart [16] was used.

(vii) Structure solution and refinement. For **2** the structure was originally solved in space group $P4_3$ (instead of $P4_1$), since this was the space group of the precursor $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ [10], using conventional Patterson, Fourier and Full-Matrix Least-Squares techniques. As required in space group $P4_3$, the z-coordinate of one atom (Rh(1)) was fixed. Atomic scattering factors for the atoms [17,18] and anomalous dispersion factors [19] for Rh, Cl, P and F were obtained from the usual sources. For compound **2** the carbon atoms of all phenyl groups were refined as rigid groups having D_{6h} symmetry, C–C distances of 1.392 Å and independent isotropic thermal parameters. All hydrogen atoms of the DPM ligands were located but were included in their idealized positions using a C–H distance of 0.95 Å. These atoms were not refined but were given thermal parameters of 1.0 $Å^2$ greater than the isotropic B (or equivalent B) of their attached carbon atom. The hydrogens of the bridging methylene group were also located but attempts to refine them were not

Table 1

Summary of crystal data and details of intensity collection.

Compound	$[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (**2**)	$[Rh_2Cl(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(PMe_3)_5]\cdot 2CH_2Cl_2$ (**3**)
Formula	$Rh_2Cl_2P_4F_6C_{55}H_{46}$	$Rh_2Cl_6P_5F_6C_{22}H_{51}$
FW	1221.58	1003.04
Cell parameters		
a, Å	21.334(3)	11.519(2)
b, Å	–	14.689(7)
c, Å	14.574(2)	25.250(5)
β, deg	–	93.00(2)
V, Å^3	6633.2	4266.7
d(calc), gcm^{-3}	1.223	1.561
Space Group	$P4_1$, C_4^2 (No. 76)	$P2_1/n$ (non-standard setting of $P2_1/c$ No. 14)
Z	4	4
Temp., °C	22°C	
Radiation	Graphite monochromated Mo-K_α (λ 0.7069 Å)	
Receiving aperture, mm	2.00 × (1.00 tan θ) wide × 4.00 high, 173 from crystal	
Take-off angle, deg	3.10	
Scan speed, deg min^{-1}	variable between 0.65 and 10.06	variable between 1.54 and 6.67
Scan width	0.50 + (0.347 tan θ) in θ	0.70 + (0.347 tan θ) in θ
No. of unique data collected	9129	7768
$2\theta_{max}$, deg	55.0	50.0
No. of unique observations ($F_o^2 \geq 3\sigma(F_o^2)$)	3669	4614
Crystal shape	distorted tetragonal bipyramid with faces of the form {110}, {111}	monoclinic prism with faces of the form {101}, {010}, {001}
Crystal dimensions, mm	0.32 × 0.26 × 0.28	0.32 × 0.52 × 0.19
Absorption coefficient, cm^{-1}	7.103	13.667
Range in transmission factors	0.824–0.845	0.832–1.409
Final no. of parameters varied	291	396
Error in observation of unit weight	0.951	2.947
R [a]	0.034	0.063
R_w [b]	0.039	0.095

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

successful so they also were included as fixed contributions in their idealized positions as above. The final model in space group $P4_3$ converged to $R = 0.040$ and $R_w = 0.048$. Refinement in the enantiomeric space group $P4_1$ converged at $R = 0.034$ and $R_w = 0.039$ suggesting that this is the correct choice so it was adopted and final calculations were carried out with this space group. For **3** the structure was again solved by a combination of Patterson, Fourier and least-squares techniques. All hydrogens of the complex were located but were idealized with an isotropic B of 20% greater than that of the attached carbon atom, and were not refined. Attempts to refine the methylene hydrogens were unsuccessful. Both CH_2Cl_2 molecules of

Table 2

Parameters for the independent non-hydrogen atoms of compound **2**

Atom	x	y	z	B (Å^2) [a]
Rh(1)	−0.01145(4)	0.27756(4)	0.0	2.96
Rh(2)	0.07729(4)	0.39114(4)	−0.10982(8)	3.10
Cl(1)	−0.1109(1)	0.2209(1)	−0.0059(2)	4.47
Cl(2)	0.0739(1)	0.4559(1)	−0.2465(2)	5.00
P(1)	−0.0570(1)	0.3611(1)	0.0792(2)	3.02
P(2)	0.0264(1)	0.4645(1)	−0.0149(2)	3.32
P(3)	0.0454(1)	0.2036(1)	−0.0866(2)	3.21
P(4)	0.1252(1)	0.3089(1)	−0.1873(2)	3.64
F(1)	0.0425(3)	0.2376(3)	0.1685(4)	5.63
F(2)	0.1379(3)	0.2307(3)	0.1208(5)	6.03
F(3)	0.1091(4)	0.3081(3)	0.2038(5)	6.61
F(4)	0.1648(3)	0.4086(3)	0.1152(5)	6.42
F(5)	0.2097(3)	0.3276(3)	0.0604(5)	6.37
F(6)	0.1969(3)	0.4097(3)	−0.0227(5)	5.88
C(1)	−0.0012(6)	0.3372(6)	−0.1029(9)	3.82
C(2)	0.0907(6)	0.2713(6)	0.1346(10)	4.16
C(3)	0.0717(5)	0.3062(5)	0.0475(8)	3.38
C(4)	0.1062(5)	0.3493(5)	0.0077(8)	2.91
C(5)	0.1688(6)	0.3728(6)	0.0399(9)	4.28
C(6)	−0.0066(5)	0.4290(4)	0.0902(7)	3.26
C(7)	0.1224(5)	0.2325(4)	−0.1256(8)	3.35

[a] Equivalent isotropic B for atoms refined anisotropically.

crystallization were found to be disordered such that for each there were three Cl positions of occupancy 2/3. Hydrogen atoms on the solvent molecules were not located so were not included in the model. The final positional and isotropic thermal parameters of the individual non-hydrogen atoms in **2** are given in Table 2 whilst the phenyl group parameters are given in Table 3. For **3** the positional and isotropic thermal parameters are given in Table 4. In Tables 5–8 are given the relevant intramolecular contacts and selected bond angles in compound **2** and selected bond distances and angles in compound **3**. The derived hydrogen parameters, the anisotropic thermal parameters and listings of the observed and calculated structure factor amplitudes used in the refinements are available from M.C. on request.

Results and discussion

(a) Description of structures

(i) $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (2). The unit cell of $[\mathrm{Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2}]$ (**2**) contains four discrete molecules of the complex separated by normal Van der Waals contacts. As suggested by the spectroscopic data (vide infra) and as shown in Fig. 1, compound **2** is a symmetric species in which the two metal centers are held together by the two bridging diphosphines and the bridging methylene and hexafluoro-2-butyne groups. The DPM ligands have a *trans* arrangement normally found in these DPM-bridged binuclear species and the other two bridging groups occupy equatorial positions on opposite faces of the

Table 3

Parameters for the rigid groups of compound **2**

Atom	x	y	z	B (Å^2)
(a) Derived positions and thermal parameters				
C(11)	−0.0767(4)	0.3412(3)	0.1969(4)	3.4(2)
C(12)	−0.1301(3)	0.3050(4)	0.2112(6)	5.3(3)
C(13)	−0.1447(3)	0.2839(3)	0.2991(7)	6.2(3)
C(14)	−0.1058(4)	0.2989(4)	0.3725(5)	8.9(4)
C(15)	−0.0524(4)	0.3350(4)	0.3582(5)	5.6(3)
C(16)	−0.0379(3)	0.3562(3)	0.2704(6)	5.4(3)
C(21)	−0.1305(3)	0.3935(4)	0.0339(6)	3.8(3)
C(22)	−0.1562(4)	0.3718(3)	−0.0479(6)	4.6(3)
C(23)	−0.2093(4)	0.4004(4)	−0.0843(5)	6.8(4)
C(24)	−0.2368(3)	0.4507(4)	−0.0387(7)	8.8(4)
C(25)	−0.2112(4)	0.4724(3)	0.0431(7)	6.7(4)
C(26)	−0.1581(4)	0.4438(4)	0.0795(4)	6.5(3)
C(31)	−0.0389(3)	0.5126(3)	−0.0579(6)	3.3(2)
C(32)	−0.0638(4)	0.5009(3)	−0.1445(5)	4.6(3)
C(33)	−0.1123(4)	0.5379(4)	−0.1781(4)	5.8(3)
C(34)	−0.1361(3)	0.5866(4)	−0.1251(6)	7.6(4)
C(35)	−0.1113(4)	0.5984(3)	−0.0385(6)	5.3(3)
C(36)	−0.0627(4)	0.5614(4)	−0.0049(4)	5.0(3)
C(41)	0.0828(3)	0.5233(3)	0.0301(6)	3.5(2)
C(42)	0.0770(3)	0.5508(4)	0.1163(5)	5.4(3)
C(43)	0.1201(5)	0.5957(4)	0.1448(5)	10.2(5)
C(44)	0.1690(4)	0.6132(3)	0.0870(7)	7.7(4)
C(45)	0.2748(3)	0.5857(4)	0.0008(7)	6.7(3)
C(46)	0.1317(4)	0.5408(4)	−0.0276(4)	4.6(3)
C(51)	0.0085(4)	0.1723(3)	−0.1915(4)	4.0(3)
C(52)	0.0425(3)	0.1300(4)	−0.2446(6)	5.8(3)
C(53)	0.0175(4)	0.1076(3)	−0.3265(6)	6.6(4)
C(54)	−0.0414(4)	0.1275(4)	−0.3554(4)	7.6(4)
C(55)	−0.0753(3)	0.1698(4)	−0.3023(6)	5.4(3)
C(56)	−0.0504(4)	0.1922(3)	−0.2203(5)	4.2(3)
C(61)	0.0676(4)	0.1340(3)	−0.0212(4)	3.0(2)
C(62)	0.0237(2)	0.1121(3)	0.0418(5)	4.8(3)
C(63)	0.0386(3)	0.0623(4)	0.0995(5)	5.5(3)
C(64)	0.0974(4)	0.0343(3)	0.0942(5)	6.8(4)
C(65)	0.1413(3)	0.0561(3)	0.0312(5)	5.0(3)
C(66)	0.1264(3)	0.1060(3)	−0.0265(4)	3.9(3)
C(71)	0.0986(4)	0.2891(4)	−0.3053(5)	3.9(3)
C(72)	0.1357(3)	0.2494(4)	−0.3584(8)	8.5(4)
C(73)	0.1141(5)	0.2286(4)	−0.4432(7)	9.9(5)
C(74)	0.0556(6)	0.2474(4)	−0.4750(5)	11.6(5)
C(75)	0.0185(3)	0.2870(4)	−0.4220(7)	6.9(4)
C(76)	0.0401(4)	0.3079(3)	−0.3371(6)	5.2(3)
C(81)	0.2093(3)	0.3232(5)	−0.1993(7)	4.3(3)
C(82)	0.2266(5)	0.3764(4)	−0.2482(6)	9.7(4)
C(83)	0.2896(6)	0.3925(4)	−0.2561(7)	11.3(5)
C(84)	0.3353(3)	0.3553(5)	−0.2151(8)	10.9(5)
C(85)	0.3179(4)	0.3020(5)	−0.1661(7)	8.3(4)
C(86)	0.2549(5)	0.2860(3)	−0.1582(5)	6.3(3)

Table 3 (continued)

Ring	x_c [a]	y_c	z_c	φ [b]	θ	ρ
(b) Group parameters						
1	−0.0913(2)	0.3200(2)	0.02847(4)	−1.065(5)	−2.776(6)	1.394(5)
2	−0.1837(2)	0.4221(2)	−0.0024(4)	0.027(9)	−2.262(5)	−2.502(8)
3	−0.0875(2)	0.5496(2)	−0.0915(4)	−0.018(9)	−2.136(5)	−2.426(9)
4	0.1259(2)	0.5683(2)	0.0586(4)	−0.975(5)	2.964(6)	1.981(5)
5	−0.0164(2)	0.1499(2)	−0.2734(4)	0.981(5)	−2.995(5)	−2.092(4)
6	0.0825(2)	0.0841(2)	0.0365(3)	−1.631(5)	2.716(4)	0.725(5)
7	0.0771(3)	0.2682(3)	−0.3902(4)	1.022(5)	−3.013(7)	−2.031(5)
8	0.2723(3)	0.3392(3)	−0.2072(4)	−2.838(9)	−2.566(5)	−3.043(8)

[a] x_c, y_c and z_c are the fractional coordinates of the group centroid. [b] The rigid group angles, φ, θ and ρ (radians), are the angles by which the rigid body is rotated with respect to a set of axes X, Y, and Z. The orgin is the centre of the ring, X is parallel to $a^\star$, Z is parallel to c, and Y is parallel to the line defined by the intersection of the plane containing $a^\star$ and $b^\star$ with the plane containing b and c.

$Rh_2(DPM)_2$ core. In addition, each metal has a terminal chloro ligand completing its coordination sphere. The resulting geometry about each metal is a distorted tetragonal pyramid with the bridging methylene group sharing the apical sites of the two adjoining pyramids. Alternately the coordination about the metals can be considered as distorted octahedra in which one site on each metal (opposite the bridging CH_2 group) is vacant.

The structure of compound **2** is essentially superimposable with that of its carbonyl-bridging analogue, $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(DPM)_2]$ (apart

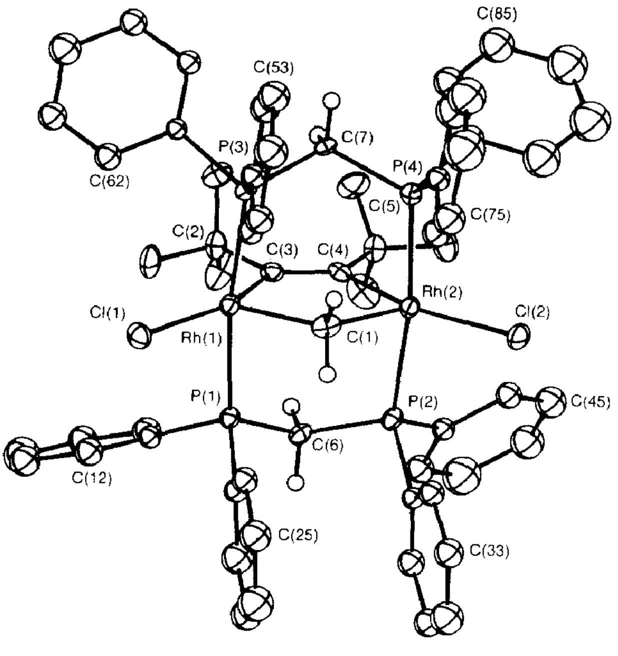

Fig. 1. A perspective view of complex **2** showing the numbering scheme. Numbering of the phenyl carbons starts at the one bound to phosphorus and proceeds sequentially around each ring. Phenyl hydrogens have the same number as their attached carbon atom, but are not shown. 20% thermal ellipsoids are shown, except for methylene hydrogens which are shown arbitrarily small.

Table 4

Parameters for the non-hydrogen atoms of compound 3

Atom	x	y	z	B (Å^2) [a]
Rh(1)	0.09379(7)	0.19723(6)	0.30226(3)	2.66(2)
Rh(2)	−0.02831(7)	0.19434(6)	0.18841(3)	2.81(2)
Cl(1)	0.1000(3)	0.0751(2)	0.2321(1)	3.53(6)
Cl(2)	0.1227(3)	0.2355(3)	0.1240(1)	4.44(7)
Cl(3) [b]	0.4753(5)	0.1568(4)	0.1207(2)	5.4(1)
Cl(4) [b]	0.4260(7)	0.2740(4)	0.0330(2)	7.7(2)
Cl(5) [b]	0.4452(6)	0.1257(6)	0.4843(3)	8.5(2)
Cl(6) [b]	0.6834(8)	0.1025(7)	0.4730(3)	11.5(3)
Cl(7) [b]	0.585(1)	0.2810(5)	0.4652(3)	13.0(3)
Cl(8) [b]	0.3731(6)	0.0832(4)	0.0240(2)	7.1(2)
P(1)	0.1250(3)	0.0671(2)	0.3648(1)	3.74(7)
P(2)	0.0890(3)	0.3200(2)	0.3540(1)	3.77(7)
P(3)	0.2977(3)	0.2152(2)	0.2870(1)	3.30(7)
P(4)	−0.1354(3)	0.3122(2)	0.1591(1)	3.86(7)
P(5)	−0.0833(3)	0.0651(3)	0.1281(2)	4.70(8)
F(1)	−0.2220(6)	0.0902(6)	0.3484(3)	5.9(2)
F(2)	−0.2372(6)	0.2350(6)	0.3499(3)	6.0(2)
F(3)	−0.0968(6)	0.1702(6)	0.3921(3)	5.2(2)
F(4)	−0.3409(6)	0.1819(6)	0.2623(3)	6.4(2)
F(5)	−0.2928(6)	0.1481(6)	0.1847(3)	5.7(2)
F(6)	−0.2734(7)	0.0504(5)	0.2463(4)	6.9(2)
C(1)	0.0447(9)	0.2843(7)	0.2416(4)	2.8(2)
C(2)	−0.162(1)	0.1694(9)	0.3454(6)	4.7(3)
C(3)	−0.0891(9)	0.1789(8)	0.2964(5)	3.7(3)
C(4)	−0.1359(9)	0.1703(7)	0.2483(4)	2.9(2)
C(5)	−0.256(1)	0.140(1)	0.2369(6)	4.8(3)
C(6)	0.257(1)	−0.001(1)	0.3599(6)	5.7(4)
C(7)	0.015(1)	−0.0221(9)	0.3505(7)	6.7(4)
C(8)	0.125(1)	0.074(1)	0.4406(6)	7.1(5)
C(9)	0.142(2)	0.306(1)	0.4239(6)	6.4(4)
C(10)	0.172(1)	0.4176(9)	0.3329(6)	5.4(4)
C(11)	−0.049(1)	0.378(1)	0.3620(7)	6.9(4)
C(12)	0.398(1)	0.238(1)	0.3423(6)	5.8(4)
C(13)	0.338(1)	0.303(1)	0.2405(5)	4.8(3)
C(14)	0.368(1)	0.120(1)	0.2539(5)	4.8(3)
C(15)	−0.243(1)	0.355(1)	0.2024(6)	6.0(4)
C(16)	−0.217(1)	0.299(1)	0.0941(6)	6.7(4)
C(17)	−0.053(1)	0.4155(9)	0.1464(6)	5.7(4)
C(18)	0.043(1)	0.024(1)	0.0933(6)	6.5(4)
C(19)	−0.189(2)	0.068(1)	0.0699(7)	12.9(5)
C(20)	−0.121(2)	−0.041(1)	0.1626(8)	9.1(5)
C(21) [b]	0.377(1)	0.179(1)	0.0676(6)	6.1(4)
C(22) [b]	0.567(2)	0.183(2)	0.4974(6)	9.8(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$. [b] Disordered CH_2Cl_2 of crystallization. See text for explanation.

from the different alkyne substituents); even the orientations of the phenyl groups are similar in the two species [20]. In both complexes the methylene groups of the DPM ligands are folded towards the bridging alkyne groups in order to allow the

Table 5

Relevant intramolecular contacts (Å) in compound **2**

Bonded contacts			
Rh(1)–Cl(1)	2.442(3)	C(5)–F(4)	1.34(1)
Rh(2)–Cl(2)	2.425(3)	C(5)–F(5)	1.34(1)
Rh(1)–P(1)	2.335(3)	C(5)–F(6)	1.35(1)
Rh(1)–P(3)	2.356(3)	P(1)–C(6)	1.811(10)
Rh(2)–P(2)	2.355(3)	P(1)–C(11)	1.817(7)
Rh(2)–P(4)	2.324(3)	P(1)–C(21)	1.837(7)
Rh(1)–C(1)	1.980(13)	P(2)–C(6)	1.847(10)
Rh(2)–C(1)	2.033(11)	P(2)–C(31)	1.840(7)
Rh(1)–C(3)	1.999(11)	P(2)–C(41)	1.859(8)
Rh(2)–C(4)	2.027(11)	P(3)–C(7)	1.845(10)
C(2)–F(1)	1.35(1)	P(3)–C(51)	1.844(7)
C(2)–F(2)	1.34(1)	P(3)–C(61)	1.829(7)
C(2)–F(3)	1.34(1)	P(4)–C(7)	1.863(10)
C(2)–C(3)	1.53(1)	P(4)–C(71)	1.860(8)
C(3)–C(4)	1.31(1)	P(4)–C(81)	1.828(7)
C(4)–C(5)	1.50(1)		
Non-bonded contacts			
Rh(1)–Rh(2)	3.466(1)	Rh(1)–F(1)	2.843(6)
P(1)–P(2)	3.147(4)	Rh(2)–F(6)	2.878(6)
P(3)–P(4)	3.177(4)	Rh(2)–H(42)	2.85

phenyl groups to avoid unfavourable contacts with the alkyne substituents. As a result, four phenyl groups are aimed into the space between the bridging methylene group and the terminal chloro ligands, resulting in one rather short contact (2.85 Å) between an *ortho*-hydrogen atom and Rh(2). Other parameters within the DPM groups are as expected.

The alkyne ligand in **2** bridges the metals in the more common geometry for these DPM-bridged species [21], being parallel to the metal–metal axis instead of perpendicular to it. In this geometry the alkyne moiety is better viewed as a *cis*-dimetallated olefin, and certainly its metrical parameters are totally consistent with such an interpretation. The C(3)–C(4) distance (1.31(1) Å) is close to that of an olefinic double bond and the angles about C(3) and C(4) suggest sp^2 hybridization of these atoms. Crystallographically the CF_3 groups are well behaved. However, one fluorine atom on each CF_3 moiety comes into rather close contact with the adjacent Rh atom (2.843(6) and 2.878(6) Å) (shown clearly in Fig. 2). By comparison, the closest Rh–F contact in the precursor is greater than 3.1Å [10], and in the sterically more congested species $[Rh_2Cl(CNMe)_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]^+$ the closest such contact is 3.033(5) Å [8]. It is possible that in the present compound the formally rhodium(III) metal centers (considering the bridging methylene and alkyne groups as dianionic) form a weak interaction with the fluorine lone pairs by utilizing the vacant sixth coordination site opposite the bridging CH_2 group on each metal. Such a proposal is consistent with the more favorable ligand field stabilization energy for octahedral vs. either trigonal bipyramidal or square pyramidal coordination for a d^6 system [22] and with the known preference of rhodium(III) compounds to be octahedral [23]. Calculations by Hoffman and Hoffmann [24] on a similar species suggest that the LUMO, which might give the metals Lewis acid properties, would be located in this position *trans* to the CH_2 group.

Table 6

Selected angles in compound **2**

P(1)–Rh(1)–P(3)	171.8(1)	Rh(2)–P(2)–C(6)	113.0(3)
P(1)–Rh(1)–Cl(1)	91.9(1)	Rh(2)–P(2)–C(31)	121.3(3)
P(1)–Rh(1)–C(1)	86.0(4)	Rh(2)–P(2)–C(41)	110.9(2)
P(1)–Rh(1)–C(3)	88.0(3)	Rh(2)–P(4)–C(7)	114.3(3)
P(3)–Rh(1)–Cl(1)	95.6(1)	Rh(2)–P(4)–C(71)	119.2(3)
P(3)–Rh(1)–C(1)	88.1(4)	Rh(2)–P(4)–C(81)	110.6(3)
P(3)–Rh(1)–C(3)	86.2(3)	C(6)–P(1)–C(11)	104.0(4)
Cl(1)–Rh(1)–C(1)	112.8(3)	C(6)–P(1)–C(21)	103.8(4)
Cl(1)–Rh(1)–C(3)	159.0(3)	C(11)–P(1)–C(21)	103.3(4)
C(1)–Rh(1)–C(3)	88.2(5)	C(6)–P(2)–C(31)	102.9(4)
P(2)–Rh(2)–P(4)	172.1(1)	C(6)–P(2)–C(41)	103.4(4)
P(2)–Rh(2)–Cl(2)	95.2(1)	C(31)–P(2)–C(41)	103.5(3)
P(2)–Rh(2)–C(1)	88.1(4)	C(7)–P(3)–C(51)	104.2(4)
P(2)–Rh(2)–C(4)	86.4(3)	C(7)–P(3)–C(61)	101.6(4)
P(4)–Rh(2)–Cl(2)	92.5(1)	C(51)–P(3)–C(61)	104.3(3)
P(4)–Rh(2)–C(1)	87.7(4)	C(7)–P(4)–C(71)	103.8(4)
P(4)–Rh(2)–C(4)	86.8(3)	C(7)–P(4)–C(81)	102.9(4)
Cl(2)–Rh(2)–C(1)	109.7(4)	C(71)–P(4)–C(81)	104.4(4)
Cl(2)–Rh(2)–C(4)	162.5(3)	P(1)–C(6)–P(2)	118.7(5)
C(1)–Rh(2)–C(4)	87.7(4)	P(3)–C(7)–P(4)	117.9(5)
Rh(1)–C(1)–Rh(2)	119.5(5)	F(1)–C(2)–C(3)	111(1)
Rh(1)–C(3)–C(2)	112.0(8)	F(1)–C(2)–F(2)	106(1)
Rh(1)–C(3)–C(4)	124.0(9)	F(1)–C(2)–F(3)	105(1)
C(2)–C(3)–C(4)	124 (1)	F(2)–C(2)–C(3)	113(1)
Rh(2)–C(4)–C(3)	120.7(8)	F(2)–C(2)–F(3)	106(1)
Rh(2)–C(4)–C(5)	112.9(8)	F(3)–C(2)–C(3)	115(1)
C(3)–C(4)–C(5)	126 (1)	F(4)–C(5)–C(4)	113(1)
Rh(1)–P(1)–C(6)	114.0(3)	F(4)–C(5)–F(5)	106(1)
Rh(1)–P(1)–C(11)	112.6(2)	F(4)–C(5)–F(6)	105(1)
Rh(1)–P(1)–C(21)	113.6(3)	F(5)–C(5)–C(4)	114(1)
Rh(1)–P(3)–C(7)	113.6(3)	F(5)–C(5)–F(6)	106(1)
Rh(1)–P(3)–C(51)	117.9(2)	F(6)–C(5)–C(4)	112(1)
Rh(1)–P(3)–C(61)	113.4(2)		

Table 7

Bond distances [a] (Å) in compound **3**

Rh(1)–Cl(1)	2.525(2)	Cl(5)–C(22) [b]	1.65(1)	P(4)–C(16)	1.860(8)
Rh(1)–P(1)	2.493(2)	Cl(6)–C(22) [b]	1.91(1)	P(4)–C(17)	1.826(8)
Rh(1)–P(2)	2.230(2)	Cl(7)–C(22) [b]	1.67(1)	P(5)–C(18)	1.84(1)
Rh(1)–P(3)	2.415(2)	Cl(8)–C(21) [b]	1.78(1)	P(5)–C(19)	1.861(9)
Rh(1)–C(1)	2.052(6)	P(1)–C(6)	1.831(8)	P(5)–C(20)	1.85(1)
Rh(1)–C(3)	2.122(7)	P(1)–C(7)	1.844(9)	F(1)–C(2)	1.356(8)
Rh(2)–Cl(1)	2.510(2)	P(1)–C(8)	1.917(9)	F(2)–C(2)	1.302(9)
Rh(2)–Cl(2)	2.517(2)	P(2)–C(9)	1.848(9)	F(3)–C(2)	1.366(9)
Rh(2)–P(4)	2.230(2)	P(2)–C(10)	1.819(9)	F(4)–C(5)	1.348(9)
Rh(2)–P(5)	2.495(2)	P(2)–C(11)	1.83(1)	F(5)–C(5)	1.371(9)
Rh(2)–C(1)	2.036(6)	P(3)–C(12)	1.795(8)	F(6)–C(5)	1.360(9)
Rh(2)–C(4)	2.036(7)	P(3)–C(13)	1.816(8)	C(2)–C(3)	1.54(1)
Cl(3)–C(21) [b]	1.738(9)	P(3)–C(14)	1.836(8)	C(3)–C(4)	1.309(9)
Cl(4)–C(21) [b]	1.76(1)	P(4)–C(15)	1.806(9)	C(4)–C(5)	1.47(1)

[a] The non-bonded contact between Rh(1) and Rh(2) is 3.1338(7) Å. [b] Atoms Cl(3), Cl(4), Cl(5), Cl(6), Cl(7), Cl(8), C(21), and C(22) are from the two disordered CH_2Cl_2 molecules. See text for explanation.

Table 8

Selected angles (deg.) in compound **3**

Cl(1)–Rh(1)–P(1)	83.77(6)	C(1)–Rh(2)–C(4)	82.5(3)	C(18)–P(5)–C(19)	97.8(5)
Cl(1)–Rh(1)–P(2)	171.27(7)	Rh(1)–Cl(1)–Rh(2)	76.99(5)	C(18)–P(5)–C(20)	98.9(5)
Cl(1)–Rh(1)–P(3)	84.38(6)	Rh(1)–P(1)–C(6)	117.9(3)	C(19)–P(5)–C(20)	103.6(6)
Cl(1)–Rh(1)–C(1)	86.4(2)	Rh(1)–P(1)–C(7)	110.2(3)	Rh(1)–C(1)–Rh(2)	100.1(3)
Cl(1)–Rh(1)–C(3)	85.7(2)	Rh(1)–P(1)–C(8)	125.5(3)	F(1)–C(2)–F(3)	106.8(6)
P(1)–Rh(1)–P(2)	104.86(7)	C(6)–P(1)–C(7)	99.4(4)	F(1)–C(2)–F(3)	102.6(7)
P(1)–Rh(1)–P(3)	94.35(7)	C(6)–P(1)–C(8)	98.3(4)	F(1)–C(2)–C(3)	115.0(7)
P(1)–Rh(1)–C(1)	167.3(2)	C(7)–P(1)–C(8)	101.5(5)	F(2)–C(2)–F(3)	104.9(7)
P(1)–Rh(1)–C(3)	93.2(2)	Rh(1)–P(2)–C(9)	116.9(3)	F(2)–C(2)–C(3)	113.4(7)
P(2)–Rh(1)–P(3)	93.40(7)	Rh(1)–P(2)–C(10)	115.9(3)	F(3)–C(2)–C(3)	113.1(6)
P(2)–Rh(1)–C(1)	85.4(2)	Rh(1)–P(2)–C(11)	119.6(3)	Rh(1)–C(3)–C(2)	122.6(5)
P(2)–Rh(1)–C(3)	95.1(2)	C(9)–P(2)–C(10)	102.3(4)	Rh(1)–C(3)–C(4)	115.9(5)
P(3)–Rh(1)–C(1)	92.6(2)	C(9)–P(2)–C(11)	101.1(5)	C(2)–C(3)–C(4)	121.4(6)
P(3)–Rh(1)–C(3)	166.8(2)	C(10)–P(2)–C(11)	97.8(4)	Rh(2)–C(4)–C(3)	115.9(5)
C(1)–Rh(1)–C(3)	78.1(3)	Rh(1)–P(3)–C(12)	119.1(3)	Rh(2)–C(4)–C(5)	120.7(6)
Cl(1)–Rh(2)–Cl(2)	92.34(7)	Rh(1)–P(3)–C(13)	117.7(3)	C(3)–C(4)–C(5)	123.4(7)
Cl(1)–Rh(2)–P(4)	172.20(7)	Rh(1)–P(3)–C(14)	116.4(3)	F(4)–C(5)–F(5)	102.8(6)
Cl(1)–Rh(2)–P(5)	82.08(7)	C(12)–P(3)–C(13)	101.3(4)	F(4)–C(5)–F(6)	103.6(7)
Cl(1)–Rh(2)–C(1)	87.1(2)	C(12)–P(3)–C(14)	102.4(4)	F(4)–C(5)–C(4)	118.3(7)
Cl(1)–Rh(2)–C(4)	85.5(2)	C(13)–P(3)–C(14)	96.4(4)	F(5)–C(5)–C(6)	101.8(7)
Cl(2)–Rh(2)–P(4)	89.31(8)	Rh(2)–P(4)–C(15)	117.0(3)	F(5)–C(5)–C(4)	114.3(7)
Cl(2)–Rh(2)–P(5)	87.13(8)	Rh(2)–P(4)–C(16)	117.2(3)	F(6)–C(5)–C(4)	114.0(7)
Cl(2)–Rh(2)–C(1)	89.7(2)	Rh(2)–P(4)–C(17)	114.8(3)	Cl(3)–C(21)–Cl(4) [a]	108.6(5)
Cl(2)–Rh(2)–C(4)	171.9(2)	C(15)–P(4)–C(16)	103.9(5)	Cl(3)–C(21)–Cl(8) [a]	109.1(5)
P(4)–Rh(2)–P(5)	105.64(8)	C(15)–P(4)–C(17)	101.2(4)	Cl(4)–C(21)–Cl(8) [a]	108.5(5)
P(4)–Rh(2)–C(1)	85.3(2)	C(16)–P(4)–C(17)	100.3(4)	Cl(5)–C(22)–Cl(6) [a]	103.1(8)
P(4)–Rh(2)–C(4)	91.9(2)	Rh(2)–P(5)–C(18)	111.2(3)	Cl(5)–C(22)–Cl(7) [a]	117.8(8)
P(5)–Rh(2)–C(1)	168.7(2)	Rh(2)–P(5)–C(19)	126.6(4)	Cl(6)–C(22)–Cl(7) [a]	105.5(6)
P(5)–Rh(2)–C(4)	100.2(2)	Rh(2)–P(5)–C(20)	114.4(4)		

[a] Atoms Cl(3), Cl(4), Cl(5), Cl(6), Cl(7), Cl(8), C(21), and C(22) are from the disordered CH_2Cl_2 molecules.

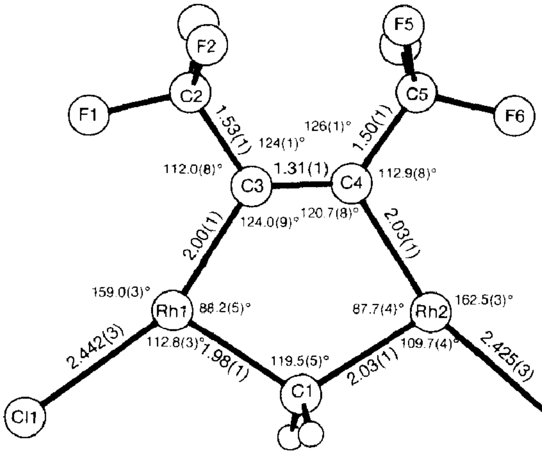

Fig. 2. A representation of the plane approximately perpendicular to the Rh–P vectors, showing some relevant parameters.

The structural determination of compound **2** clearly establishes that insertion of the methylene unit of diazomethane into the Rh–Rh bond of the precursor, $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$, has occurred, and the resulting Rh–Rh separation (3.466(1) Å) is much too long to correspond to any metal–metal bonding. Normal Rh–Rh single bonds in similar compounds occur at ca. 2.7 Å [8,10,25,26]. This Rh–Rh separation is longer than the intraligand P–P separation (av. 3.162(4) Å) showing that there is little or no mutual attraction of the metals as is clearly shown in Fig. 1. As a consequence of the large Rh–Rh separation, the Rh(1)–C(1)–Rh(2) angle at the bridging methylene group (119.5(5)°) is much larger than observed in metal–metal bonded analogues where comparable angles between 76 and 81° seem typical [1]. Although, at the time this work was undertaken, there were no known examples of methylene units bridging metals which were not bonded to each other, several such examples [27–34] have since appeared. As expected, this latter class of methylene-bridged complexes is distinguished from the metal–metal bonded analogues by significantly greater angles at the methylene group (93.4 to 123°). Although, like the present species, most of the bridging methylene groups are supported either by accompanying metal–metal bonds or other bridging groups, there is one exceptional case, $[(CpRu(CO)_2)]_2(\mu\text{-}CH_2)$, in which there are no additional supporting bonds or groups [32]. In this case the Ru–C–Ru angle (123°) is even larger than observed in our complex and the Ru–Ru separation (ca. 3.8 Å) is extremely long. The large angle at the methylene group in our complex is much larger than the angles observed (94(1), 103.4(7)°) in two closely related DPM-bridged Pt_2 complexes [31] so it may be that the bridging dimetallated olefin group in our species forces the metals apart compared to the Pt_2 species. It also appears that the Rh–Rh separation in **2** is large owing to movement apart of the metals in order to optimize interactions with the fluorine atoms close to the vacant sites, and based on a comparison of this structure with that of **3** (vide infra) we feel that this may be the dominant effect. The $Rh\text{–}CH_2$ distances are rather similar to the Rh–C distances involving the dimetallated olefin moiety and are comparable to those reported in other Rh-methylene complexes [1].

(ii) $[Rh_2Cl(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(PMe_3)_5]$ *(3).* This complex crystallizes with two molecules of methylene chloride in the asymmetric unit. Although both solvent molecules are disordered, as described earlier, their geometries are normal once the disorder is taken into account. There are no unusual non-bonded contacts between solvent and complex molecules. The complex (shown in Fig. 3) can be described as two octahedrally coordinated Rh centers which are sharing a face, bridged by the chloro, methylene and hexafluorobutyne ligands. Viewing the bridging methylene and alkyne groups as dianionic, the metals are in a +3 oxidation state. Distortions from octahedral geometry are relatively minor and appear to result from a combination of constraints due to the bridging groups and differences in bulk of the different ligands. In particular, the three phosphines on Rh(1) are bent away from each other resulting in P–Rh(1)–P angles of greater than 90°.

Replacing the bridging DPM groups in **2** by a bridging chloro ligand in **3** has resulted in a compression of the Rh–Rh distance to 3.1338(7) Å, which although much shorter than in **2** is still outside the normal range for Rh–Rh bonding (compare for example the Rh–Rh single bond of 2.7447(9) Å in compound **1** [10]). This compression has resulted in a more acute angle at the bridging methylene

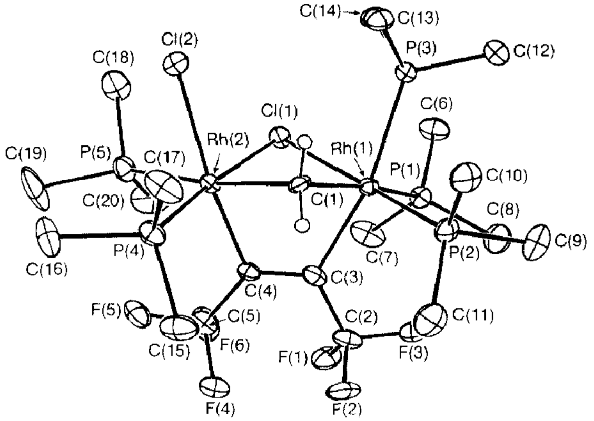

Fig. 3. A perspective view of compound **3** showing the numbering scheme. Methyl hydrogens are omitted. Thermal ellipsoids are shown at the 20% level except for those of the methylene hydrogens, which are drawn artifically small.

group (100.1(3)°) and also more acute angles at the alkyne (115.9(5)°). Although it is tempting to attribute the compression of the Rh–Rh distance as due to the presence of the additional bridging group (Cl(1)) in **3** (ignoring the rather flexible DPM groups), this does not appear to be the case. The Rh(1)–Cl(1)–Rh(2) angle of 76.99(5)° is not particularly abnormal and is in fact more acute than typically observed (ca. 80–95°) in cases in which Cl bridges two metals which are not bonded to each other [35–39], suggesting that it is not responsible for drawing the metals together. More likely it is the bridging methylene group which causes the compression, with the Rh(1)–C(1)–Rh(2) angle in **3** being normal while that in **2** is abnormally large. The unusually large methylene angle in **2** is probably due to movement apart of the metals which are attempting to maximize overlap with the fluorine atoms of the hexafluorobutyne group (vide supra).

Bond distances within the alkyne moiety agree rather well with those in **2**, again suggesting the dimetallated olefin formulation. The Rh–alkyne distances (2.122(7), 2.036(7) Å) differ appreciably, with the larger one (Rh(1)–C(3)) being *trans* to a phosphine group while the other is opposite Cl(2). This probably reflects the higher *trans* influence of PMe_3 compared to Cl. Consistent with this proposal the shorter Rh–alkyne distance in **3** corresponds closely to both such distances in **2** in which the *trans* ligands are both Cl. Both Rh–CH_2 distances (2.036(6), 2.052(6) Å) in **3** compare well with those in **2**. The Rh–Cl distances (2.510(2), 2.525(2) Å) involving the bridging ligand are longer than normally observed (2.30–2.45 Å [35–39]) in such compounds, possibly reflecting the *trans* influence of the PMe_3 groups in the present example. In addition the terminal Rh(2)–Cl(2) distance is also long for such a bond and no doubt reflects the high *trans* influence of the metallated olefin moiety. This bond is even longer than those in **2**, which are also opposite the hexafluorobutyne group.

The geometries of the PMe_3 ligands are normal, although they can be grouped into two classes according to their Rh–P distances. Those (P(2) and P(4)) opposite the bridging chloro ligand, of low *trans* influence, have short Rh–P distances (2.230(2) Å), whereas those (P(1), P(3), P(5)) which are opposite the metallated olefin linkage or the methylene group have rather long Rh–P bonds (2.493(2), 2.415(2), 2.495(2) Å). From these latter distances it also appears, at least in this complex, that the bridging CH_2 group has a higher *trans* influence than the metallated olefin, since the Rh–P bonds opposite C(1) are the largest.

(b) Discussion of chemistry

The spectroscopic and X-ray characterization of $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$ (**2**) unambiguously establishes that the only observed Rh(DPM)-containing product in the reaction of **1** with diazomethane has resulted from the insertion of one methylene group into the Rh–Rh bond. The $^{31}P\{^1H\}$ NMR spectrum of compound **2** is characteristic of a symmetrical dirhodium species bridged by two mutually *trans* DPM groups [13]. This is confirmed by the ^1H NMR spectrum which shows the DPM methylene groups as AB quartets with superimposed coupling to the four chemically equivalent phosphorus nuclei, and the metal-bridging methylene group as a quintet (^3J(P–H) 10 Hz). Although these NMR results are straight forward, we were surprised at the ^1H chemical shift of the $Rh_2(\mu\text{-}CH_2)$ group. When methylene groups bridge a metal–metal bond, a wide range of ^1H chemical shifts between δ 5.45 and 10.29 ppm has been reported [1]. However, when there is no accompanying metal–metal bond ^1H chemical shifts at higher field (δ 1.34 to 2.71 ppm), in the region expected for organic methylene groups, seem typical [27–34]. For example, in $[Pt_2(CH_3)(CH_2PPh_3)(\mu\text{-}CH_2)(DPM)_2]^+$ the ^1H chemical shifts of the methylene groups, which bridge one Pt and the PPh_3 group (δ 1.77 ppm) and the two Pt atoms (δ 1.50 ppm), are comparable [31] and in the normal methylene region. In compound **2** the Rh_2CH_2 protons appear at low field in the range previously observed for metal–metal bonded species. Clearly the ^1H chemical shifts of these bridging methylene groups are highly dependent on their chemical environment, and care will have to be taken when using these values to interpret whether or not there is a metal-metal bond.

Further reaction of **2** with additional diazomethane molecules does not seem to occur. We had considered the possibility that the incorporation of more than one CH_2 group and insertion of one or more of these into metal–ligand bonds might occur, but such is not observed. In contrast to this, Puddephatt and coworkers had demonstrated [31] that incorporation of up to three methylene groups into a somewhat analogous diplatinum species could occur, to give CH_2 insertion into the Pt–Pt bond, a Pt–H bond and a Pt–P bond. Similarly it had been demonstrated [40] that two CH_2 fragments could be incorporated into $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ to give a species in which one methylene group bridged the metals and the other linked the alkyne and one metal. Examples of methylene insertion into M–Cl bonds have also been documented [41,42]. In $[Pt_2H(PPh_3)(DPM)_2]^+$, it had been shown that CH_2 insertion occurred first into the Pt–Pt bond, with insertions into the metal–ligand bonds occurring subsequently [31]. In our system, only a single diazomethane group reacts, and results in insertion into the Rh–Rh bond. It seems that insertion into the metal–metal bond is the most favored pathway. Subsequent reaction with CH_2N_2 apparently does not occur, even in the presence of the vast excesses of the molecule. Suprisingly we found that diazomethane did not react with the closely related species $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ over a range of temperatures from −50 to +22°C. Although this carbonyl-bridged species is rather analogous to the alkyne-bridged complex **1**, differences in their reactivity patterns associated with their Rh–Rh bonds, have previously been noted, and have been attributed to the different bridging groups (CO and $CF_3C_2CF_3$) [8].

Although we succeeded in preparing a species in which the bridging methylene group was not accompanied by metal–metal bonding, we are unable to correlate this unusual geometry with any reactivity trends, since this bridging methylene group appears to be rather inert. One major reason for this is probably its inaccessible site in the molecule, where it is shielded from other potential reactants by the chloro groups as well as by the phenyl groups of the DPM ligands. Most notably, the vacant coordination sites on the metals are opposite the bridging CH_2 group. Compound **2** did not react with H_2 at 1 atm. This may not be surprising since the rhodium(III) centers should be relatively unreactive towards oxidative addition. Even if oxidation addition of H_2 had occurred, it is unlikely that production of methane would have been observed, since the methylene and hydride groups would be on opposite faces of the complex. Similarly, attempts to protonate **2** in attempts to yield a methyl-containing species, as was observed for $[CpRh(CO)]_2(\mu\text{-}CH_2)$ [43], met with failure. Again, this is not surprising since not only are the vacant coordination sites remote from the methylene unit, but there does not appear to be any basic site in the molecule; the vacant coordination sites on the metals are themselves apparently acidic [24]. Compound **2** also did not react with CO, and again the low basicity of the metals may be responsible.

Attempts to replace the terminal chloro groups by the more interesting hydrido ligands, by reacting **2** with $NaBH_4$, in hopes of effecting CH_2 insertion to give a methyl complex also failed. The large number of products in the reaction, most of which were shown, by the lack of Rh coupling in the ^{31}P NMR spectra, to be Rh-free species, discouraged us from pursuing this chemistry further.

Consistent with the notion that the vacant coordination sites in **2** are acidic, compound **2** did react with the rather basic PMe_3 ligand, albeit to produce a large number of decomposition products, as witnessed by the polymethylene produced and the large number of phosphine species observed which did not display coupling to Rh. One interesting product (**3**) which was isolated and characterized has resulted from the replacement of the two bridging DPM ligands by monodentate PMe_3 groups. This is the only example, of which we are aware, in which substitution of the DPM groups, on an "A-frame" species, by monodentate ligands has yielded a product which remains binuclear. Apparently the methylene and alkyne bridging groups are sufficiently strongly bound to maintain the binuclear integrity of the complex. It is not surprising that **2** should be reactive towards Lewis bases since, as noted, the 5-coordinate rhodium(III) species should be unfavorable compared to a 6-coordinate product, and the proposed weak interactions involving the fluorines of the hexafluorobutyne group would not be expected to compete effectively with a stronger base such as PMe_3. However, we were surprised that the simple PMe_3 adduct of **2** was not observed since such a species was obtained as the only product in the reaction of PMe_3 with a somewhat analogous diiridium, carbonyl species $[Ir_2Cl_2(CO)(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(DPM)_2]$ [44].

Unfortunately, we have not yet succeeded in devising a rational synthesis of **3** so its reactivity, particularly of the bridging methylene and alkyne moieties, has not yet been investigated.

In conclusion, we have succeeded in synthesizing two of the few known complexes containing a bridging methylene unit and no accompanying metal–metal bond. The first compound is prepared in a rational manner by the direct insertion of a diazomethane-derived CH_2 group into a Rh–Rh single bond. This unusual product $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$, although containing vacant coordination sites adjacent to the bridging alkyne group and opposite the bridging methylene moiety, does not react further with diazomethane. Similarly, the molecule is found to be unreactive to CO, H_2 and to protic acids. This compound was found to be reactive to PMe_3, yielding, among other products, the second methylene-bridged species, $[Rh_2Cl(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}CF_3C_2CF_3)(PMe_3)_5]$ by replacement of the two DPM ligands by five PMe_3 groups.

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