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Transition metal methylene complexes

LXVII *. Neutron diffraction study of μ-propylidene(2)-bis[carbonyl(η^5-pentamethylcyclopentadienyl)rhodium-(Rh–Rh)], $[\mu\text{-C(CH}_3)_2][\{\eta^5\text{-C}_5(\text{CH}_3)_5\}\text{Rh(CO)}]_2$, at 20 K

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Abstract

The title compound, **3**, is prepared by reaction of $[(\mu\text{-CO})(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2$, **1**, with $N_2{=}CMe_2$, **2**. A neutron diffraction study of the structure of **3** at 20 K reveals a normal dimeric structure with approximate C_2 molecular symmetry and a Rh–Rh single bond (2.66 Å). The geometry of the bridging propylidene ligand shows no exceptional features that might be connected with the unusual photolysis behavior of **3**, wherein a diamagnetic material with complex ^{1}H- and ^{13}C-NMR spectra is formed. Crystallographic data: a 16.856(3), b 15.978(5), c 18.730(11) Å, β 107.50(2)°, $Z = 8$, space group $P2_1/c$ (No. 14), $R(F^2) = 0.141$ for 8514 neutron data.

Introduction

The chemistry of the so-called dimetallacyclopropanes has been established mainly in the context of the long-known catalytic hydrogenation of carbon monoxide called Fischer–Tropsch synthesis [1,2]. A number of synthetic methods for this prominent class of organometallic compounds are nowadays available, with the

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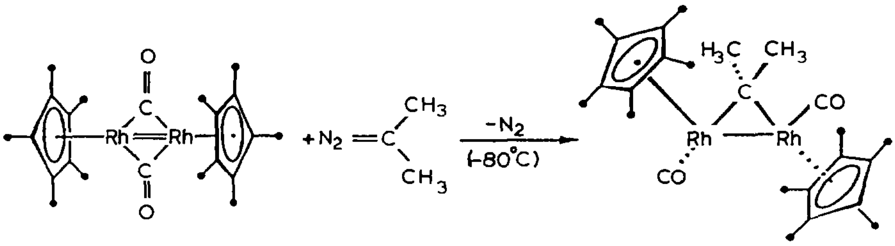
* For Part LXVI see M. Flöel, E. Herdtweck, W. Wagner, J. Kulpe, P. Härter and W.A. Herrmann, *Angew. Chem.*, 99 (1987) 787; *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 787.

most general route being carbene addition to metal–metal double bonds [1,3]. The most extensive series of μ-alkylidene compounds of transition metals is available for rhodium. Due to the work of Herrmann and his group, stable compounds of general composition (μ-CRR')[(η^5-C_5Me_5)Rh(CO)]$_2$ (Me = CH_3) can be synthesized in practically quantitative yields by reacting the corresponding diazoalkane N_2=CRR' with the easily available dinuclear rhodium complex **1** [4–8]. These latter compounds undergo photochemical and thermal decarbonylation to cleanly yield the degradation products of composition (μ-CRR')(μ-CO)[(η^5-C_5Me_5)Rh]$_2$ that once again contain a rhodium-to-rhodium double bond accessible for further carbene addition [9]. In the course of this work, the dimethyl-methylene (2-propylidene) derivative **3** was synthesized according to eq. 1:



(1) (2) (3)

(1)

This particular compound, an air-stable crystalline material, is also photolabile, but the expected decarbonylation product [μ-C(CH_3)$_2$](μ-CO)[(η^5-C_5Me_5)Rh]$_2$ could not be isolated from photolysis experiments. Photolysis of **3** proceeds with elimination of 1 mol of carbon monoxide. However, in contrast to all other alkylidene rhodium complexes of type (μ-CRR')[(η^5-C_5Me_5)Rh(CO)]$_2$, the green product of analytical composition $(C_5Me_5)_2Rh_2(CO)(C_3H_6)$ does not exhibit a simple NMR spectrum but rather a multiline spectrum in the δ 1.6–2.9 ppm range suggesting that the former propylidene ligand is somehow changed in its structure during photolysis. For example, C–H activation and isomerization from $C(CH_3)_2$ to CH_2=$CHCH_3$ is a plausible explanation. It is somewhat puzzling that addition of carbon monoxide to the photolysis product quantitatively converts it back to **3** (color change from dark green to red). In order to see if there is any possible prerequisite in the precursor complex **3** for H ··· Rh interactions, we have carried out a single-crystal neutron diffraction study, the results of which are reported here.

Experimental

The starting compound (**1**) was synthesized by reacting dicarbonyl(η^5-pentamethylcyclopentadienyl)rhodium (2.00 g, 6.8 mmol), (η^5-C_5Me_5)Rh(CO)$_2$ [11], with 700 mg (9.0 mmol) trimethylamine oxide, $(CH_3)_3NO$, in 150 mL of boiling acetone. A yield of 1.65 g (91%) was thus obtained [12]. 2-Diazopropane (**2**) was synthesized according to a literature preparation [13].

1. Preparation of μ-propylidene(2)-bis[carbonyl(η⁵-pentamethylcyclopentadienyl)-rhodium](Rh–Rh) (3)

A solution of 1.33 g (2.5 mmol) **1** in 250 mL of tetrahydrofuran was cooled to −70 °C (acetone/dry ice). At this temperature the violet-colored solution was treated under continued magnetic stirring with a total of 25 mL of a ca. 0.2 molar solution of 2-diazopropane in diethylether. Note that the diazo compound has to be added slowly. Under rapid elimination of nitrogen, the color of the solution changed to red within a few minutes. The solution was then warmed to room temperature. All volatile materials were stripped off in an oil pump vacuum. The brick-red residue thus obtained was purified by crystallization from n-pentane at low temperatures (−35– −78°C). Yield: 1.38 g (91%). The deep-red, air-stable rhomboid crystals melt above 75°C under darkening, with subsequent melting at 162–163°C. The compound is very soluble in all common organic solvents.

Elemental analysis. Found: C, 52.17; H, 6.21; Rh, 35.57. $C_{25}H_{36}O_2Rh_2$ (574.4) Calc.: C, 52.28, H, 6.31, Rh, 35.83%. Molecular weight 574 (electron-impact mass spectrum), 582 (vapor-pressure osmometry). The compound is characterized by the following spectral data: IR (KBr, cm^{-1}): 1937 vs. IR (n-pentane, cm^{-1}): 1948 vs. ^1H NMR (100 MHz, $CDCl_3$, +28°C): $\delta C_5(CH_3)_5$ 1.92 [s, 30 H], $\delta C(CH_3)_2$ 2.11 ppm [s, 6H].

2. *Neutron diffraction study of the μ-propylidene(2) rhodium complex 3*

The data collection crystal had a volume of 7.2 mm^3. Crystal data: $C_{25}H_{36}O_2Rh_2$, M_r 574.4, a 16.856(3), b 15.978(5), c 18.730(11) Å, β 107.50(2)°, V 4811.0(2) $Å^3$ at 20.0(5) K, $Z = 8$, space group $P2_1/c$ (No. 14), D_c 1.59 g cm^{-3}. The sample was mounted on an aluminum pin oriented approximately along the (100) direction, sealed under a helium atmosphere in an aluminum container, and placed in a closed-cycle helium refrigerator [14*] mounted on a four-circle diffractometer [15,16] at the Brookhaven High Flux Beam Reactor. A beryllium (002) single-crystal monochromator was used to select a neutron beam of wavelength 1.05079(3) Å based on KBr ($a_0 = 6.6000$ Å at $T = 298$ K [17]). The temperature of the sample was maintained at 20.0(5) K [18*] during the experiment, and unit cell dimensions were determined by a least-squares fit of the averaged 2θ values of 16 Friedel pairs ($49 < 2\theta < 56°$).

Three-dimensional intensity data were obtained by means of $\theta/2\theta$ step scans over one complete quadrant of reciprocal space with $2\theta \leqslant 80°$ ($\sin\theta/\lambda \leqslant 0.61$ $Å^{-1}$) and sampled out to $2\theta \leqslant 113°$ ($\sin\theta/\lambda \leqslant 0.80$ $Å^{-1}$) by measuring the 456 reflections calculated to be the strongest in this range. The scan range was varied according to $\Delta 2\theta = (1.80 + 1.94 \tan\theta)°$ for the high-angle data ($58 \leqslant 2\theta \leqslant 113°$) and $\Delta 2\theta = 2.8°$ for low-angle data. The step size was adjusted to give between 55 and 80 steps per scan and counts were accumulated for approximately 1.3 s at each step, the exact time interval being determined by monitoring the incident beam intensity. The intensities of three monitor reflections were measured every 200 reflections and showed no significant variation over the course of data collection.

Integrated intensities were obtained with the first and last tenth of each scan taken as background. Lorentz factors and absorption corrections ($\mu = 2.637$ cm^{-1}) calculated by means of numerical integration over a Gaussian grid of points [19] were applied; the absorption correction was checked with reference to azimuthal scan intensity data for reflection $\overline{14}\,\bar{2}\,2$. The data were then averaged over the $2/m$ Laue symmetry to yield squared structure factors, F_o^2, for 8514 unique reflections,

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

Table 1

Summary of crystal data and refinement parameters for $[(\mu\text{-C(CH}_3)_2)][(\eta^5\text{-C}_5\text{(CH}_3)_5)\text{Rh(CO)}]_2$

Neutron data at 20 K	
Cryst. dimensions	3.2×2.2×0.7 mm
Cryst. boundary faces	{011}, (100), $(\bar{1}11)$, $(1\bar{1}\bar{1})$
Range of $e^{-\mu t}$	0.570–0.818
Number of reflections measured	10193 [a]
Number of independent reflections (n)	8514
R_{int}	0.090
Number of variable parameters (m)	1147
Final agreement factors for 4553 reflections with $I > 3\sigma(I)$	
$R(F^2) = \Sigma\left\|F_o^2 - (k^2F_c^2)\right\|/\Sigma\left\|F_o^2\right\|$	0.088
$R_w(F^2) = [\Sigma w(F_o^2 - (k^2F_c^2))^2/\Sigma wF_o^4]^{1/2}$	0.086 [b]
Goodness of fit	1.35
Final agreement factors for all data	
$R(F^2)$	0.141
$R_w(F^2)$	0.110 [b]
Goodness of fit	1.18

[a] A quadrant of data (h, k, $\pm l$) was measured to $\sin\theta/\lambda = 0.61$ Å^{-1} and sampled to $\sin\theta/\lambda = 0.80$ Å^{-1}. [b] Weights chosen as $w = (\sigma^2(F_o^2))^{-1} = (\sigma_{\text{count}}^2(F_o^2) + (0.01\ F_o^2)^2))^{-1}$.

all of which were used in the structure refinement. Further details are given in Table 1.

Initial atomic coordinates were taken from the X-ray results [20]. Least-squares refinements were carried out by a full-matrix procedure [21], minimizing $\Sigma w(F_o^2 - (k^2F_c^2))^2$, with weights taken as $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = \sigma_{\text{count}}^2 + (0.01F_o^2)^2$. While the inclusion of all data in the refinement has resulted in R values that are somewhat higher than normal, due to the fact that almost half of the reflections have intensity less than 3 esd, the results are essentially identical to those from a refinement including only those reflections with $I > 3\sigma(I)$. The refinement including all data is, however, preferred on the basis that the parameter esd's are lower by a factor of ca. 1.3 and the goodness of fit is closer to the ideal value of 1. The final structure model included positional parameters for all 130 atoms, isotropic thermal parameters for Rh1, Rh3, Rh4, C8, and C9 and anisotropic thermal parameters for the remaining 125 atoms, a scale factor k, and a type I isotropic-extinction parameter [22,23] with Lorentzian mosaic for a total of 1147 variable parameters. All correlation factors were less than 0.5, ruling out the possibility of a missed symmetry element relating the two molecules in the asymmetric unit. The most significant extinction correction factor was 1.04 multiplying F_o^2 for reflection 210. When anisotropic thermal parameters were included for Rh1, Rh3, Rh4, C8, and C9, the tensors for these atoms became non-positive definite. Examination of the individual U_{ij} values showed that insignificant small negative off-diagonal terms were responsible; none of these was of magnitude greater than 3 esd.

Neutron scattering lengths ($\times 10^{-12}$ cm) were taken to be $b_{\text{Rh}} = 0.5930$, $b_{\text{O}} = 0.5805$, $b_{\text{C}} = 0.6648$, and $b_{\text{H}} = -0.3741$ [24]. The refinement was terminated when the maximum shift/esd for positional and thermal parameters was less than 0.03. A difference synthesis computed at this stage was essentially featureless with the highest positive residual peak approximately 0.04 times the height of a carbon peak and the highest negative residual peak approximately 0.1 times the height of a

Table 2

Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters [a,b] with estimated standard deviations at 20 K

Atom	*x*	*y*	*z*	B_{iso} (Å^2)
Rh1	1830(2)	1499(2)	2286(2)	0.27(0.05) [c]
Rh2	1001(2)	2052(2)	927(2)	0.43(0.09)
C1	853(2)	2346(2)	1954(2)	0.46(0.08)
C2	1003(2)	3259(2)	2180(2)	0.75(0.09)
C3	61(2)	2067(3)	2123(2)	0.76(0.09)
C4	2613(2)	2310(2)	2349(2)	0.63(0.08)
O4	3172(3)	2746(3)	2454(2)	1.21(0.11)
C5	238(2)	1206(2)	771(2)	0.54(0.08)
O5	−275(3)	703(3)	574(2)	0.82(0.10)
H2A	1566(5)	3538(5)	2087(5)	2.03(0.22)
H2B	1061(7)	3339(6)	2779(5)	2.70(0.26)
H2C	476(5)	3645(5)	1879(5)	2.24(0.22)
H3A	−92(5)	1410(5)	1995(5)	2.03(0.23)
H3B	−468(5)	2451(6)	1805(5)	2.21(0.22)
H3C	130(5)	2175(6)	2720(4)	2.31(0.24)
C11	1353(2)	172(2)	2420(2)	0.41(0.08)
C13	1542(2)	599(2)	3129(2)	0.44(0.08)
C15	2403(2)	816(2)	3347(2)	0.55(0.08)
C17	2757(2)	487(2)	2788(2)	0.43(0.08)
C19	2113(2)	94(2)	2218(2)	0.46(0.08)
C12	567(2)	−296(2)	2059(2)	0.83(0.10)
C14	958(2)	712(2)	3584(2)	0.70(0.09)
C16	2868(2)	1243(2)	4064(2)	0.70(0.09)
C18	3659(2)	526(3)	2822(2)	0.90(0.09)
C20	2192(2)	−363(2)	1542(2)	0.70(0.09)
C21	2016(2)	2353(2)	339(2)	0.49(0.08)
C23	1320(2)	1956(2)	−171(2)	0.29(0.08)
C25	596(2)	2476(2)	−252(2)	0.49(0.08)
C27	856(2)	3204(2)	200(2)	0.68(0.09)
C29	1725(2)	3122(2)	578(2)	0.77(0.09)
C22	2895(2)	2045(3)	552(2)	0.98(0.10)
C24	1329(2)	1143(2)	−570(2)	0.75(0.09)
C26	−255(2)	2335(3)	−788(2)	1.10(0.10)
C28	323(3)	3952(3)	233(2)	1.31(0.11)
C30	2270(3)	3824(3)	981(2)	1.17(0.10)
H12A	500(6)	−431(6)	1471(5)	2.44(0.24)
H12B	584(6)	−904(6)	2334(5)	2.68(0.26)
H12C	29(5)	35(6)	2090(5)	2.58(0.25)
H14A	1108(6)	1278(6)	3925(5)	2.69(0.26)
H14B	1008(7)	178(6)	3968(6)	3.11(0.29)
H14C	307(5)	759(7)	3238(5)	2.44(0.23)
H16A	3389(6)	1593(7)	4009(5)	3.02(0.28)
H16B	3121(6)	784(6)	4513(5)	2.82(0.25)
H16C	2454(6)	1660(7)	4250(5)	2.71(0.25)
H18A	3746(6)	597(7)	2265(5)	2.84(0.26)
H18B	3982(5)	−60(6)	3075(5)	2.63(0.24)
H18C	3983(6)	1029(7)	3176(6)	3.22(0.28)
H20A	2752(6)	−163(6)	1399(5)	2.99(0.28)
H20B	1657(6)	−251(7)	1056(5)	2.90(0.26)
H20C	2252(7)	−1040(5)	1638(5)	2.63(0.28)
H22A	3260(6)	2276(9)	1084(5)	3.86(0.31)
H22B	3201(6)	2229(7)	146(5)	3.14(0.28)

Table 2 (continued)

Atom	x	y	z	B_{iso} (Å^2)
H22C	2937(6)	1373(7)	595(7)	3.76(0.33)
H24A	1812(6)	731(6)	−242(5)	2.62(0.24)
H24B	1443(7)	1243(6)	−1105(5)	2.92(0.28)
H24C	737(6)	804(6)	−693(5)	2.87(0.26)
H26A	−417(6)	1662(6)	−824(6)	2.91(0.27)
H26B	−291(6)	2565(9)	−1339(5)	3.61(0.30)
H26C	−729(6)	2643(6)	−612(5)	2.63(0.24)
H28A	563(7)	4289(6)	756(5)	3.39(0.30)
H28B	−320(7)	3765(7)	182(6)	3.78(0.33)
H28C	280(9)	4394(6)	−234(6)	4.21(0.37)
H30A	2895(7)	3601(7)	1325(6)	3.72(0.29)
H30B	2017(8)	4175(7)	1357(6)	4.00(0.36)
H30C	2367(7)	4262(7)	578(5)	3.28(0.29)
Rh3	3289(2)	7428(2)	3790(2)	0.31(0.05) [c]
Rh4	3724(2)	6100(2)	3144(2)	0.24(0.05) [c]
C6	4023(2)	7351(2)	3071(2)	0.43(0.08)
C7	3716(2)	7720(2)	2285(2)	0.57(0.09)
C8	4916(2)	7645(2)	3423(2)	0.56(0.05) [c]
C9	4675(2)	5942(2)	3928(2)	0.52(0.05) [c]
O9	5271(2)	5756(2)	4386(2)	0.89(0.10)
C10	2366(2)	7615(2)	2988(2)	0.42(0.08)
O10	1759(2)	7790(3)	2531(2)	0.71(0.10)
H7A	3081(5)	7547(6)	1968(4)	1.96(0.21)
H7B	4113(5)	7512(6)	1946(4)	2.11(0.22)
H7C	3753(6)	8415(5)	2315(5)	2.60(0.26)
H8A	5213(4)	7429(6)	3996(4)	1.76(0.19)
H8B	4937(5)	8329(5)	3430(5)	2.12(0.22)
H8C	5304(5)	7440(6)	3072(4)	1.97(0.21)
C31	2759(2)	7393(2)	4785(2)	0.46(0.08)
C33	2901(2)	8242(2)	4574(2)	0.49(0.08)
C35	3776(2)	8356(2)	4726(2)	0.52(0.08)
C37	4173(2)	7576(2)	4993(2)	0.45(0.08)
C39	3537(2)	6981(2)	5030(2)	0.45(0.08)
C32	1945(2)	7025(3)	4785(2)	0.74(0.09)
C34	2244(2)	8911(2)	4341(2)	0.82(0.09)
C36	4217(2)	9159(2)	4666(2)	0.73(0.09)
C38	5087(2)	7466(2)	5351(2)	0.72(0.09)
C40	3683(2)	6116(2)	5344(2)	0.60(0.09)
C41	2706(2)	5738(2)	2055(2)	0.48(0.08)
C43	3481(2)	5399(2)	2045(2)	0.46(0.08)
C45	3751(2)	4838(2)	2670(2)	0.37(0.08)
C47	3120(2)	4807(2)	3052(2)	0.45(0.08)
C49	2477(2)	5368(2)	2675(2)	0.44(0.08)
C42	2127(2)	6246(2)	1439(2)	0.69(0.09)
C44	3896(2)	5530(2)	1449(2)	0.68(0.09)
C46	5419(2)	4294(2)	2846(2)	0.67(0.09)
C48	3135(2)	4278(2)	3710(2)	0.72(0.09)
C50	1669(2)	5501(3)	2838(2)	0.82(0.10)
H32A	1401(5)	7359(7)	4430(5)	2.90(0.25)
H32B	1874(6)	7013(7)	5356(5)	2.77(0.26)
H32C	1871(6)	6380(6)	4590(6)	3.11(0.30)
H34A	2395(6)	9357(6)	3955(5)	2.53(0.25)

Table 2 (continued)

Atom	x	y	z	B_{iso} (Å^2)
H34B	2190(6)	9264(6)	4822(5)	2.84(0.26)
H34C	1649(6)	8646(6)	4051(5)	2.52(0.24)
H36A	3800(6)	9592(6)	4283(6)	2.91(0.27)
H36B	4734(6)	9074(5)	4459(5)	2.39(0.24)
H36C	4466(7)	9459(6)	5210(5)	3.18(0.29)
H38A	5288(5)	6826(6)	5272(5)	2.55(0.25)
H38B	5251(5)	7577(7)	5955(4)	2.42(0.23)
H38C	5453(5)	7904(6)	5132(5)	2.51(0.24)
H40A	4259(6)	5843(6)	5287(5)	2.73(0.26)
H40B	3158(6)	5696(6)	5066(5)	2.79(0.25)
H40C	3739(7)	6118(6)	5932(5)	2.94(0.27)
H42A	2461(5)	6580(6)	1109(4)	2.14(0.22)
H42B	1769(6)	6695(6)	1641(5)	2.67(0.24)
H42C	1687(6)	5822(6)	1045(5)	2.72(0.24)
H44A	4567(5)	5440(7)	1674(5)	2.62(0.24)
H44B	3799(7)	6165(6)	1219(5)	2.78(0.27)
H44C	3660(7)	5092(7)	981(5)	3.09(0.28)
H46A	5043(5)	4605(6)	2732(5)	2.35(0.24)
H46B	4392(6)	3719(6)	2529(5)	2.79(0.25)
H46C	4722(6)	4109(6)	3426(4)	2.49(0.24)
H48A	3765(6)	4138(7)	4057(5)	2.80(0.25)
H48B	2830(7)	3671(6)	3528(5)	2.97(0.27)
H48C	2827(6)	4576(6)	4066(5)	2.65(0.25)
H50A	1722(6)	5428(7)	3421(5)	2.97(0.27)
H50B	1217(6)	5054(6)	2541(6)	2.81(0.26)
H50C	1423(6)	6128(6)	2675(6)	2.77(0.27)

[a] $B_{iso} = (8/3)\pi^2(U_{22} + (U_{11} + U_{33} + 2U_{13}\cos\beta)/\sin^2\beta)$ for atoms refined anisotropically. [b] Tables of anisotropic thermal parameters (Table 4) and structure factors (Table 5) have been deposited with NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017, USA. [c] Refined isotropically.

Table 3

Selected interatomic distances (Å) [a,b] and bond angles (deg) in $[\mu\text{-C(CH}_3)_2][\{\eta^5\text{-C}_5(\text{CH}_3)_5\}\text{Rh(CO)}]_2$

	Molecule 1	Molecule 2
Rh–Rh	2.660(5)	2.652(5)
Rh–C(propylidene)$_{av}$	2.072(5)	2.082(5)
Rh ··· C(ring center)$_{av}$	1.918(4)	1.926(4)
Rh ··· Me(ring center)$_{av}$	2.044(4)	2.070(4)
Rh–CO$_{av}$	1.828(5)	1.834(5)
C–C(propylidene)$_{av}$	1.524(5)	1.525(5)
C–H(propylidene)$_{av}$	1.099(9)	1.100(10)
C–H(ring)$_{av}$	1.091(13)	1.089(11)
Shortest Rh ··· propylidene H	3.122(9)	3.149(8)
Rh–C–Rh	79.9(2)	79.1(2)
C–C–C(ring)$_{av}$	108.0(3)	108.0(3)
C–C–C(propylidene)	107.8(3)	107.6(3)
Rh–C–O$_{av}$	170.9(4)	172.6(4)

[a] Standard deviations of mean values are given as the larger of the individual esd's or $\sigma(\chi_{av}) = [\Sigma_{i=1}^{n}(\chi_i - \chi_{av})^2/(n(n-1))]^{1/2}$ where χ_{av} is the mean value and χ_i are the individual values. [b] A more extensive table of interatomic distances (Table 6) has been deposited.

hydrogen peak. Final indices of fit are included in Table 1, while positional and equivalent isotropic thermal parameters for all atoms are given in Table 2. Selected interatomic distances and bond angles are given in Table 3.

Results and discussion

The molecular structure of one of the two independent molecules of $[\mu\text{-}C(CH_3)_2][\{\eta^5\text{-}C_5(CH_3)_5\}Rh(CO)]_2$, **3**, and its numbering scheme are illustrated in Fig. 1. The agreement between the X-ray [20] and neutron results is generally good; the neutron results, which are of higher precision, are used exclusively in the discussion below.

The C1, C2, C3 and Rh1, Rh2, C1 planes are nearly perpendicular, as expected, with a torsion angle of 86.0(2)° (the corresponding angle in molecule 2 is 84.9(2)°). There is an approximate local twofold axis relating the halves of the dimer, passing through the methylene carbon and bisecting the Rh–Rh bond. The C_5Me_5 rings are regular pentagons within experimental error and are η^5 bonded to the metals.

The two independent molecules have essentially the same geometry, with Rh–Rh distances of 2.660(5) and 2.652(5) Å; application of the 18-electron rule predicts a formal Rh–Rh bond order of one. The carbonyl groups are normal with Rh–C–O angles near 180°. The geometry about the bridging propylidene ligand reveals no exceptionally short Rh ··· H–C contacts involving the methyl groups, the shortest (Rh1 ··· H3A) being 3.122(9) Å. There is in fact no obvious structural feature which might be connected with the unusual photolysis behavior of **3**. The Rh–C–Rh

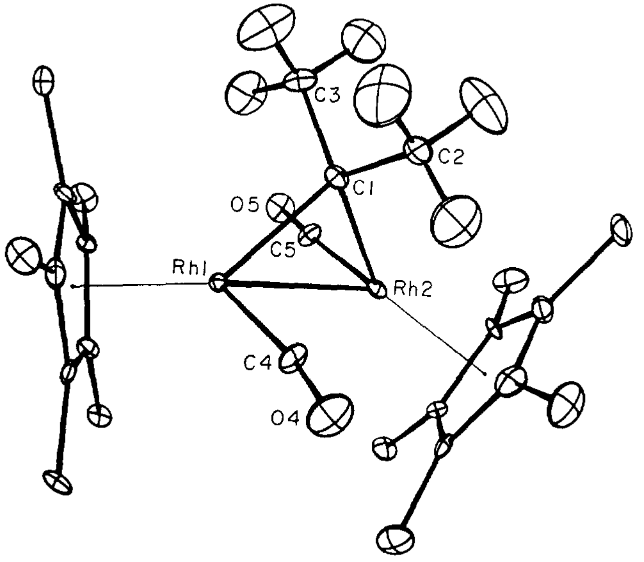

Fig. 1. A view [27] of molecule 1, showing the atom numbering scheme, with atoms drawn to enclose 67% probability. Methyl hydrogens on the Cp rings have been omitted for clarity. Figure 2 giving an analogous view of molecule 2, for which the atom numbering scheme is Rh3, Rh4; C6, C7, C8 (propylidene); C9, O9, C10, O10 (carbonyls), has been deposited. The conformation of molecule 2 is very similar to that observed for molecule 1. The principal difference is a 25° rotation of the C_5Me_5 ring bonded to Rh_3 relative to the orientation of the ring bonded to Rh_1.

angles of 79.9(2) and 79.1(2) fall in the range (75–87°) observed for a series of μ methylene complexes while the CH_3–C–CH_3 angles of 107.8(3) and 107.6(3)° are (perhaps surprisingly) less than the 110.4(1)° for H–C–H in the methylene analog [25].

It may be noteworthy that the C_5Me_5 ring is not especially tightly bound; the distance from rhodium to the C_5 ring plane averages 1.922(4) Å and is substantially longer than for the majority of C_5Me_5–Rh complexes (mean 1.856 Å) [26].

There are no unusually short intermolecular contacts; the shortest is 2.27(1) Å between methyl hydrogens on two of the C_5Me_5 rings. The shortest intramolecular contact is 2.03(1) Å between a propylidene methyl hydrogen and a C_5Me_5 ring methyl hydrogen.

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