final electron density difference synthesis showed no peaks >1 e Å^{-3}. Scattering factors were used and anomalous dispersion corrections were applied to all non-hydrogen atoms.[29] All computations were carried out on an "Eclipse" (Data General) minicomputer with the "SHELXTL" system of programs.[28] Atomic coordinates are given in Table IV.

(b) $PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)\cdot{}^1/_2CH_2Cl_2$. A well-formed red parallelepiped crystal of **7a** was obtained from a CH_2Cl_2–hexane solution. Details are given in Table III, and the solution and refinement of the structure were as described for **5**, but with the cyclopentadienyl and aryl rings treated as rigid groups (C–C(C_5H_5) = 1.420 Å and C–C(C_6H_4) = 1.395 Å). Refinement converged at R = 0.048 (R' = 0.051) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|]^{-1}$. The final electron-density difference synthesis showed no peaks >1.4 e Å^{-3}. Atomic coordinates are listed in Table V.

Acknowledgment. C.S. and M.F.S. are grateful to the Deutscher Akademischer Austauschdienst for support during the period spent at Bristol University. This work was supported in part by the Air Force Office of Scientific Research (Grant No. 82-0070).

Registry No. 2a, 61202-59-3; **2c**, 83114-97-0; **2d**, 83114-98-1; **2e**, 83114-99-2; **3**, 83115-00-8; **4**, 83115-01-9; **5**, 83134-38-7; **6**, 83115-03-1; **7a**, 83115-04-2; **7b**, 83115-05-3; **7c**, 83115-07-5; **9**, 83115-06-4; **10**, 83115-08-6; **11**, 83115-10-0; $Rh(CO)(PMe_3)(\eta^5\text{-}C_9H_7)$, 83114-96-9; $PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{PMe_2(CH_2Ph)\}_2(\eta\text{-}C_5H_5)$, 83115-09-7; $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$, 63428-46-6; $W{\equiv}CC_6H_4Me\text{-}4\text{-}(CO)_2(\eta\text{-}C_5H_5)$, 60260-15-3; $Pt(\eta\text{-}C_8H_{12})_2$, 12130-66-4; $Co_2(CO)_8$, 10210-68-1; Co, 7440-48-4; W, 7440-33-7; Rh, 7440-16-6; Pt, 7440-06-4.

Supplementary Material Available: Observed and calculated structure factor tables for compounds **5** and **7a** as well as tables of anisotropic thermal parameters and a full list of bond lengths (59 pages). Ordering information is given on any current masthead page.

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(Pentamethylcyclopentadienyl)rhodium and -iridium Complexes. 37.[1] Synthesis and X-ray Structure Determination of Bis(μ_3-methylidyne)tris[(η^5-pentamethylcyclopentadienyl)rhodium][†]

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Under appropriate conditions reaction of $[(C_5Me_5Rh)_2Cl_4]$ with Al_2Me_6 gives bis(μ_3-methylidyne)tris[(η^5-pentamethylcyclopentadienyl)rhodium], $[(C_5Me_5Rh)_3(CH)_2]$, 4, in 50% yield rather than *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CH_3)_2]$. The stoichiometry of formation is formally represented by the equation $3[(C_5Me_5Rh)_2Cl_4] + 2Al_2Me_6 = 2[(C_5Me_5Rh)_3(CH)_2] + 2Al_2Cl_6 + 8CH_4$. Complex 4 was characterized spectroscopically and by an X-ray structure determination [rhombohedral, a = 11.918 (7) Å, α = 101.91 (4)°, Z = 2, and space group $R\bar{3}$ (C_{3i}^2, No. 148); 1441 reflections with $I > 3\sigma(I)$; R = 0.027]. This showed an equilateral triangle of rhodiums each η^5 bonded to a C_5Me_5 and capped top and bottom by a μ_3-CH ligand. From its dimensions the Rh_3C_2 skeleton appears to be very tightly bound; this may account for the high thermal stability of 4.

We have recently described the syntheses of the *cis*- and *trans*-dimethylbis(μ-methylene)dirhodium complexes **2a** and **2b** from reaction of $[(C_5Me_5Rh)_2Cl_4]$ (**1**) and Al_2Me_6 (or LiMe) in hydrocarbon solvents.[2,3] Recent studies of the mechanism by which **2** were formed showed that the kinetically controlled product was the cis-isomer **2a** which isomerized, in the presence of a Lewis acid, into the thermodynamically more stable trans-isomer **2b**. The cis-complex **2a** was, in turn, obtained from an intermediate, identified by low-temperature ^{13}C NMR spectroscopy as $C_5Me_5RhMe_2MeAlMe_xCl_{2-x}$, **3**, by careful oxidation or addition of a hydrogen acceptor such as acetone.[3,4] Under different conditions, however, the trinuclear bis(μ_3-methylidyne) complex **4** is formed in this reaction (Scheme I).

Results and Discussion

Structure of 4. Complex **4** crystallized from chloroform in orange needles and was air stable in both solid and solution. It was readily soluble in hydrocarbons, dichloromethane, and ether but less so in acetone or methanol. Elemental analysis and the mass spectrum gave the formula $C_{32}H_{47}Rh_3$ (the molecular ion at m/e 740 was also the parent ion). The ^1H NMR spectrum showed the presence of a singlet at δ 1.88 and a quartet at δ 13.18 (J = 5.5 Hz), with relative intensity ratio close to 45:2. The very low-field chemical shift of the latter resonance suggested the presence of a methylidyne ligand; for example, in $[(CpRh)_3(\mu_3\text{-}CH)(\mu\text{-}CO)_2]BF_4$ the μ_3-CH resonates at δ 16.28,[5] while in $[Co_3(\mu_3\text{-}CH)(CO)_9]$ it is at δ 12.08.[6] The multiplicity of the signal indicated that it was coupled, and

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[†] To Rowland Pettit, a brilliant and dedicated chemist, whom we remember with affection.

[1] Part 36: Moreto, J.; Maruya, K.-I; Bailey, P. B.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1341.

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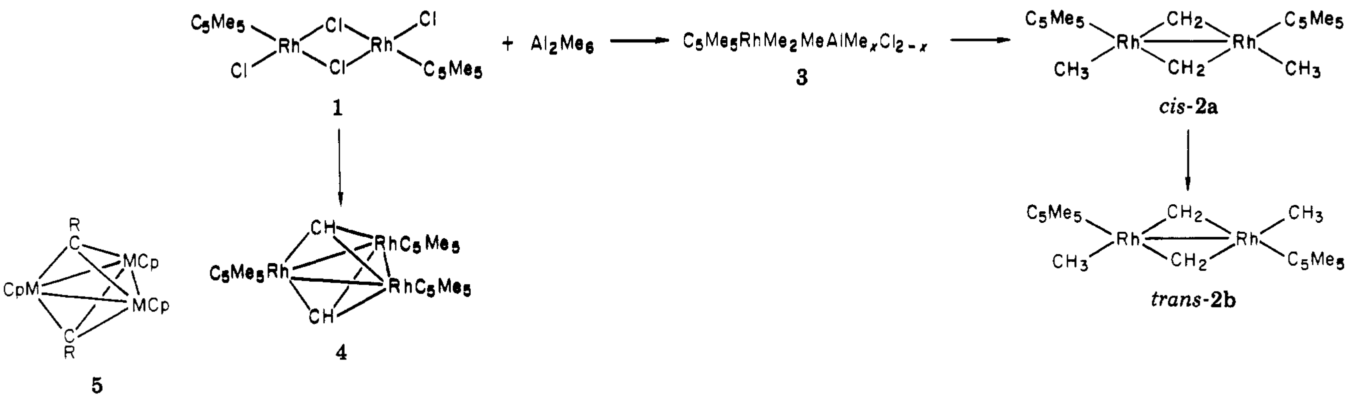
0276-7333/82/2301-1604$01.25/0

Scheme I



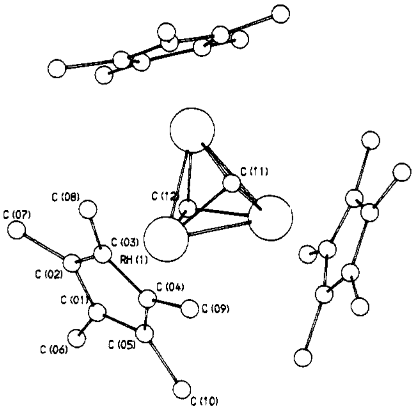


Figure 1. View of the structure of [(C$_5$Me$_5$Rh)$_3$(CH)$_2$] (hydrogens omitted for clarity).

hence bonded to, three rhodiums. This conclusion was supported by the ^{13}C{^{1}H} spectrum which showed an unresolved multiplet (probably a quartet) at δ 291.5. The ^{103}Rh{^{1}H} NMR showed a singlet at δ −990.9 ppm [with respect to frequency of $\Xi(^{103}\text{Rh})$ of 3.16 MHz].

Final proof for the structure of complex 4 came from the X-ray structure determination (Figure 1). This showed the three rhodiums to be at the apices of an equilateral triangle [∠RhRhRh = 60°; Rh–Rh = 2.6363 (5) Å] which is capped top and bottom by a μ_3-methylidyne (CH). The methylidyne carbons lie on the crystallographic three fold axis. Each rhodium is η^5 bonded to a C$_5$Me$_5$ ligand (mean Rh–C = 2.227 Å).

The Rh$_3$C$_2$ core of the molecule is compressed to an unanticipated degree. This can be seen in the unexpectedly short Rh–Rh interactions as well as in the short Rh–C(methylidyne) bonds [1.970 (19) Å].[7] For comparison the Rh–Rh distances in the μ_3-oxy-capped trinuclear trihydride [(C$_5$Me$_5$Rh)$_3$(μ-H)$_3$(μ_3-O)]PF$_6$·H$_2$O average 2.7584 (10) Å.[5] In fact the Rh···Rh distance of 2.6363 Å is very similar to the Rh–Rh bond lengths in the molecules [(C$_5$Me$_5$Rh)$_2$(μ-H)$_2$(μ-OAc)]PF$_6$,[8] 2.680 (1) Å, *cis*-[(C$_5$Me$_5$Rh)$_2$(μ-CH$_2$)$_2$(CH$_3$)$_2$],[4] 2.620 (1) Å, *trans*-[(C$_5$Me$_5$Rh)$_2${μ-C(CO$_2$Me)$_2$}(CO)$_2$],[9] 2.663 (1) Å, [(C$_5$Me$_5$Rh)$_2$(μ-CO)$_2$(μ-$\overline{\text{CCBr:CBrCBr:C}}$Br)],[9] 2.612 Å, and [(C$_5$Me$_5$Rh)$_2$(CO)$_2$(μ-CH$_2$)],[9] 2.672 Å, where the diamagnetism and electron bookkeeping requirements indicate the existence of Rh–Rh bonds. This is not formally required in complex 4 where each Rh would appear to be in the (+III) oxidation state (d^6, low spin) and therefore not to need any metal–metal bonding.

The Rh–C(methylidyne) bond is very short when compared to a normal Rh–C (sp^3, terminal) bond, 2.12 Å as in *cis*-[(C$_5$Me$_5$Rh)$_2$(μ-CH$_2$)$_2$(CH$_3$)$_2$],[4] or to a Rh–C (sp^3, bridging) bond of 2.03 Å in the same molecule or 2.08 Å in [(C$_5$Me$_5$Rh)$_2$(CO)$_2${μ-C(CO$_2$Me)$_2$}].[9]

If the skeletal Rh–C bonds were any longer, then the angles at the methylidyne carbon would be even less than the 84° found. This will be strongly disfavored for what is formally at least a tetrahedrally hybridized carbon, and this may explain the short Rh–C bonds found. Since an increase in the Rh–Rh distances would widen the angle at carbon and could also lead to an increase in the Rh–C bond lengths we must presume that this does not happen for electronic reasons. This in turn implies that there is substantial metal–metal bonding and, probably, that the best description of the oxidation state of the rhodiums is *not* +III. Some support for this is also provided by the metal ring distances in 4, 1.872 Å, which are rather longer than expected for Rh(III) (1.75–1.79 Å) but are reasonably consistent with values for Rh(I) complexes (1.85–1.91 Å).[10]

In the skeleton of the monocapped μ_3-methylidyne complex [(CpRh)$_3$(μ_3-CH)(μ-CO)$_2$]$^+$ the Rh–CH distances (mean 1.962 Å) and the Rh–Rh distances (mean 2.691 Å)[5] are very similar to those in 4 while the angles Rh–C–Rh^1 (average 86.6°) have opened out a little more than in 4.

Several workers have noted that acetylenes can be cleaved to give trinuclear bis(μ_3-methylidyne) complexes 5 (M = Co or Rh)[11–13] under appropriate conditions and the structures of two such complexes (5, M = Co, R^1 = Me, R^2 = CO$_2$Me, and M = Co, R^1 = SiMe$_3$, R^2 = Me$_3$SiC≡C) have been determined.[12,13] In both cases the geometries found were very similar to those for 4 and in particular the methylidyne–methylidyne separations (RC···CR), 2.546 (9) and 2.544 (14) Å, respectively, were very close to that observed for 4, 2.502 (25) Å. These values clearly show that there can be little direct C–C bonding in any of these complexes since even a C sp^3–C sp^3 bond is only 1.54 Å long. The structural evidence therefore points, certainly in the rhodium complex 4 and probably in general for the

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(7) Owing to the fact that C(11) and C(12) sit on the threefold axis of the molecule their esd's are unrealistically large, by a factor of ca. 3. This is then reflected in unreasonably high esd's for bond lengths and angles involving C(11) or C(12).

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other complexes, to an unexpected stabilisation of the M_3C_2 48-electron cluster.

Although the molecule 4 appears chemically quite reactive, thermally it is very stable. For example, under pyrolysis conditions (375 °C) where the cis and trans complexes **2a** or **2b** rapidly broke down (>90% decomposition) and gases (methane, propylene, ethylene, and ethane) were obtained,[2] the decomposition of 4 was less than 1% and only a trace of methane could be detected.

Mode of Formation of 4. The first indicator to the route whereby complex 4 was formed was the observation that gas (found to be methane) was evolved more copiously from experiments that gave a higher yield of 4 and less from those in which 4 was a byproduct and the chief product was the trans complex **2b**.[14] This was later put on a more quantitative basis (see Experimental Section) which showed that the amount of methane given off during the addition of Al_2Me_6 to complex 1 was very close to that implied by eq 1. That is, 4 mol of methane are produced

$$\underset{1}{3[(C_5Me_5Rh)_2Cl_4]} + 2Al_2Me_6 \rightarrow \underset{4}{2[(C_5Me_5Rh)_3(CH)_2]} + 2Al_2Cl_6 + 8CH_4$$

per mole of complex 4. Furthermore, separate experiments have shown no methane to be produced during the formation of the intermediate 3 from 1 and Al_2Me_6.

The precise differences in the conditions needed to form 4 on the one hand and 3, and thence 2, on the other, are subtle, and for this reason an optimum preparation of 4 is described rather carefully. It appears that formation of 4 is favored by low amounts of solvent, i.e., high concentrations of 1, as might be anticipated. We find addition of a 10% solution of Al_2Me_6 in benzene to solid 1 gives best yields. The formation of the black and green oils seems to be critical but because of their extreme sensitivity (even to hydrocarbon solvents) it was not possible to obtain useful spectroscopic measurements on them.

Although the reaction of preformed intermediate 3 with excess of 1 did give rise to some trinuclear complex 4, the yields (ca. 15–20%) were lower than those by the method indicated.[15] This may be due to the need to use more solvent in the preparation of 3 than to make 4. Thus we cannot say for certain whether 3 is involved directly.

In summary, under some conditions C_5Me_5Rh methyls each possess two sufficiently acidic hydrogens to react with Al methyls giving methane and, eventually bis(μ_3-methyne) complex 4.[16] This represents a useful alternative route to μ_3-methyne complexes. Further extensions of this work and an investigation of the chemistry of 4 are under study. This is likely to be rich since, although it is thermally very stable, it seems quite reactive. For example, it reacts readily with acid to give methane, essentially quantitatively, according to eq 2.

$$[(C_5Me_5Rh)_3(CH)_2] + 6CF_3CO_2H \rightarrow 2CH_4 + 3C_5Me_5Rh(O_2CCF_3)_2$$

Experimental Section

Microanalyses were determined by the University of Sheffield Microanalytical Service; NMR spectra were measured on a Perkin-Elmer R-12B (60 MHz, ^1H), Bruker WH-400 (400 MHz ^1H and ^{103}Rh courtesy of the SERC National Service), and JEOL PFT-100 (^{13}C) spectrometers. Solvents were rigorously dried, distilled and stored under argon.

Table I. Atomic Coordinates ($\times10^7$)[a]

atom	*x*	*y*	*z*
Rm	20886 (3)	18108 (3)	33533 (3)
C(01)	1047 (5)	199 (5)	3717 (5)
C(02)	707 (5)	1206 (5)	4243 (5)
C(03)	1715 (5)	2035 (5)	5118 (5)
C(04)	2684 (5)	1511 (5)	5145 (5)
C(05)	2270 (5)	399 (5)	4287 (5)
C(06)	253 (8)	−889 (6)	2847 (6)
C(07)	−547 (6)	1328 (7)	3990 (7)
C(08)	1737 (8)	3181 (6)	5917 (6)
C(09)	3919 (7)	2025 (9)	5960 (7)
C(10)	2994 (8)	−505 (7)	4081 (7)
C(11)	3209 (14)	3209 (14)	3209 (14)
C(12)	1627 (16)	1627 (16)	1627 (16)

[a] Those marked with an asterisk are $\times10^5$.

Bis(μ-methylidyne)tris[(pentamethylcyclopentadienyl)-rhodium] (4). A number of different methods gave 4; this one gave a high yield and worked consistently well. A sample of $[(C_5Me_5Rh)_2Cl_4]$ (0.30 g, 0.49 mmol) in a dry Schlenk tube (35 mL) containing a magnetic stirrer was heated in vacuo (60–80 °C (0.05 mm pressure)) for a few minutes; dry argon was then admitted. This procedure was repeated 10–12 times over the course of 1 h and until the complex $[(C_5Me_5Rh)_2Cl_4]$ had a powdery orange appearance; the tube was cooled to 20 °C. A 10% solution of Al_2Me_6 in benzene (1.2 cm^3, 0.6 mmol. *CAUTION*! Great care needs to be used in making up and handling these solutions, and the reactions should only be attempted by experienced workers) was then injected dropwise over 15 min at 20 °C with stirring. Reaction occurred to give a black oily solid, and methane was evolved. Stirring was continued for a further 2 h, and then another 1.2 cm^3 of the above solution of Al_2Me_6 in benzene was added over 15–20 min at 20 °C. This gave a green oil and a further, but much smaller, quantity of methane was given off. The green oil was stirred (3 h) and then cooled to 0 °C; tetrahydrofuran (2 cm^3) was added with vigorous stirring to yield a dark brown-orange solution. This solution was then evaporated to dryness and extracted with pentane (2 × 35 cm^3), hot benzene (2 × 35 cm^3), and dichloromethane (35 cm^3). Reextraction with pentane of the residues remaining when these solutions were evaporated to dryness gave essentially pure complex 4 (0.125 g, 0.17 mmol, 51% yield).

A further experiment was carried out to monitor the amounts of methane given off at various stages of the reaction. In this case 0.49 mmol of $[(C_5Me_5Rh)_2Cl_4]$ was reacted initially with 0.4 mmol of Al_2Me_6 in benzene as described above. GC analysis (Poropak Q) showed the presence of methane and integration against a standard sample showed that 0.63 mmol of methane had been formed. A further 0.14 mmol of methane was given off during the addition of the second aliquot of Al_2Me_6. In this experiment acetone (1.5 cm^3) was then added to quench the reaction releasing a further 0.65 mmol of methane, followed by water (0.2 cm^3) which gave a further 1.4 mmol of CH_4. Upon workup, this reaction yielded 50% of complex 4 and 15% of complex **2b**.

By comparison, an experiment under conditions more appropriate for formation of **2b**, in which $[(C_5Me_5Rh)_2Cl_4]$ (0.49 mmol) in benzene (5 cm^3) was reacted with 1.2 mmol of Al_2Me_6 in benzene solution, gave 0.26 mmol of methane. After addition of acetone (1.16 mmol of CH_4) and water (0.71 mmol of CH_4), this yielded 62% of **2b** and 20% (0.07 mmol) of 4. A blank experiment in which a benzene solution of 1.2 mmol of Al_2Me_6 was added to benzene (5 cm^3) in a carefully dried Schlenk tube released 0.03 mmol of methane.

These three experiments indicate that approximately 4 mol of methane per mol of 4 are produced during the addition of Al_2Me_6 to 1:

Anal. Calcd for $C_{32}H_{47}Rh_3$: C, 51.9; H, 6.4; mol wt, 740. Found: C, 51.7; H, 6.5; mol wt (mass spectrometric) *m*/*e* 740 (100%). ^1H NMR ($CDCl_3$) δ 1.63 (s, 45 H, C_5Me_5), 13.18 [q, 2 H, *J*(Rh–H) = 5.5 Hz]; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 11.3 (s, C_5Me_5), 95.5 (s, C_5Me_5), 291.5 (m, CH); $^{103}Rh\{^1H\}$ NMR δ −990.9 (with respect to frequency of $\Xi(^{103}Rh)$ of 3.16 MHz).

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[14] In some cases mixtures of **2a** and **2b** are obtained because the isomerization of **2a** to **2b** is incomplete; neither **2a** nor **2b** gives 4 with Al_2Me_6.

[15] Addition of sodium or magnesium to the reaction of 3 and 1 in toluene raised the yield of 4 to 30–35%. Other variations such as changes in temperature and in quenching solvent did not improve the reaction.

[16] This reaction is probably then rather similar to the reaction $Cp_2TiMe_2 + Al_2Me_6 \rightarrow Cp_2TiCH_2AlMe_2 + CH_4$: Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

Table II. Bond Lengths (Å) and Angles (Deg) in $[(C_5Me_5Rh)_3(CH)_2]$ (4)

Bond Lengths	
Rh(A)–Rh(B) = Rh(B)–Rh(C) etc.	2.6363 (5) Å
Rh(A)–C(1)	2.254 (6)
Rh(A)–C(2)	2.214 (6)
Rh(A)–C(3)	2.212 (6)
Rh(A)–C(4)	2.233 (6)
Rh(A)–C(5)	2.223 (6)
mean Rh–C(C_5Me_5)	2.227
Rh(A)–c.g. (C_5Me_5)	1.872
Rh(A)–C(11)	1.971 (17)
Rh(A)–C(12)	1.970 (19)
C(11)· · ·C(12)	2.502 (25)
Bond Angles	
Rh(A)–C(11)–Rh(B)	84.0 (8)
C(11)–Rh(A)–C(12)	78.8 (7)
Rh(A)–Rh(B)–Rh(C)	60.0 (4)

X-ray Crystal Structure Determination. Crystal data: $C_{32}H_{47}Rh_3$; $M = 740.44$, rhombohedral, $a = 11.918$ (7) Å, $\alpha = 101.91$ (4)°, $U = 1586$ Å^3, $Z = 2$, $D_{calcd} = 1.55$ g cm^{-3}, $F(000) = 748$, space group $R\bar{3}$ (C^2_{3i}, No. 148) (from systematic absences); Mo Kα radiation (graphite monochromator), $\lambda = 0.71069$ Å, μ(Mo Kα) = 15.36 cm^{-1}.

Single-crystal X-ray data in the range $3.5 < 2\theta < 50°$ were collected on a Nicolet Instruments Syntex R3 four-circle diffractometer in the omega scan mode. A total of 1441 reflections with intensity $I > 3\sigma(I)$ and background difference of $\Delta < 4\sigma(B)$ were corrected for Lorentz and polarization but not for absorption or extinction. The structure was solved by Patterson and Fourier methods; block-diagonal-matrix least-squares refinement has reduced R to 0.027 at which stage all the thermal parameters of the non-hydrogen atoms are anisotropic, and those of the hydrogen atoms have fixed isotropic values.

The overall geometry of the molecule is shown in Figure 1; atomic coordinates are in Table I and distance and angle values in Table II.

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Registry No. 2b, 80446-42-0; 4, 83350-11-2; $(C_5Me_5Rh)_2Cl_4$, 83377-35-9; Al_2Me_6, 15632-54-9.

Supplementary Material Available: Tables of isotropic and anisotropic thermal parameters, hydrogen atom coordinates, and structure factors (39 pages). Ordering information is given on any current masthead page.

A Heterobinuclear Bridging Methylene Complex: Structures at −110 °C of Two Crystal Forms of (μ-Methylene)(μ-carbonyl)[(cyclopentadienylcarbonyliron)tetracarbonylmanganese], (μ-CH_2)(μ-CO)[Cp(CO)FeMn$(CO)_4$][†]

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The novel heterobinuclear bridging methylene complex (μ-CH_2)(μ-CO)[Cp(CO)FeMn$(CO)_4$] (1) crystallizes in two forms: form A (from pentane), monoclinic, $P2_1/m$ (No. 11), $a = 8.282$ (1) Å, $b = 10.002$ (2) Å, $c = 8.504$ (1) Å, $\beta = 115.70°$ at −110 °C, $Z = 2$; form B (from thermal gradient vacuum sublimation), monoclinic, Cc (No. 9), $a = 15.402$ (2) Å, b = 6.1731 (7) Å, $c = 14.104$ (2) Å, $\beta = 107.36°$ at −110 °C, $Z = 4$. Single-crystal diffraction data (−110 °C) were used to determine and refine (by full-matrix least-squares methods) the crystal structures of both forms: form A, $R_1 = 0.036$, $R_2 = 0.037$ for 1251 reflections with $I/\sigma_I > 2.0$; form B, $R_1 = 0.038$, $R_2 = 0.041$ for 1774 reflections with $I/\sigma_I > 2.0$. Both forms contain disordered molecules with each bridging site occupied (exactly in form A and nearly in form B) by half of μ-CH_2 and half of μ-CO. Principal structural features of the molecule are (1) an unusually short Fe–C(μ) bond (average 1.921 Å), (2) the shortest Fe–Mn bond (average 2.615 Å) yet seen in an organometallic complex, (3) an unusually long Mn–C(μ) bond (average 2.087 Å), (4) an unsymmetrical bridge with Fe-X uncharacteristically shorter than Mn-X, and (5) Mn–CO(terminal) bond lengths which are significantly shorter when trans to μ-CH_2/CO than when trans to CO(terminal). These structural features are related to the strong π-acceptor nature of μ-CH_2 and μ-CO and to the presence on Fe and absence on Mn of the electron-releasing Cp group.

Introduction

Compounds containing unsubstituted (CH_2) or substituted (CHR, CR_2, or CRR′) methylene groups spanning two bonded transition-metal atoms have been the subject of many studies, involving synthesis, reactivity, spectroscopy, and theory, complemented by structural studies of a wide variety of these complexes.[2] Many of the bridging methylene complexes which have been structurally characterized have been substituted with either heteroatoms or aromatic rings (analogous to the mononuclear Fischer carbene complexes); several structures have been deter-

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[†] Dedicated to the memory of Rolly Pettit—mentor, colleague, friend.

(1) Robert A. Welch Foundation Undergraduate Scholar, 1979–1981.

(2) Some reviews and leading references: (a) Herrmann, W. A. "The Methylene Bridge", to appear in "Advances in Organometallic Chemistry". (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. (c) Calderon, N.; Orstead, E. A.; Judy, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 401–409. (d) Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 4128–4139. (e) Creswick, M.; Bernal, I.; Reiter, B.; Herrmann, W. A. *Inorg. Chem.* **1982**, *21*, 645–652. (f) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918. (g) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Ibid.* **1982**, *1*, 1350–1360. (h) Kao, S. C.; Thiel, C. H.; Pettit, R. *Organometallics*, submitted for publication.

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