

HETERONUCLEAR (W–Fe) AND HOMONUCLEAR (Fe–Fe) μ -ALKYLIDENE COMPLEXES OF TRANSITION METALS FROM MONONUCLEAR TERMINAL CARBENE COMPLEXES. CRYSTAL STRUCTURES OF $\{WFe[\mu-\eta^1, \eta^3-C(OCH_2CH_3)(CH=CHCH_3)](CO)_8\}$ AND $[Fe_2\{\mu-\eta^2, \eta^3-C[OCH_2CH_3][CH=C(OCH_2CH_3)(CH_3)]\}(CO)_6]$

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Summary

The reactions of mononuclear carbene complexes of W and Fe of the type $CO)_mM=C(OR)(CH_2)_nCH=CR'R''$ ($M = Fe, W$; $m = 4$ and 5 ; $n = 0, 2, 3$; $R', R'' = H, CH_3, OEt$) with $Fe(CO)_5$ have been studied. In all cases the reaction leads to new hetero (W–Fe) or homo (Fe–Fe) μ -alkylidene complexes, the position of the double bond depending strongly on n .

Introduction

In the preceding paper [1], we described the synthesis of homonuclear μ -alkylidene complexes of tungsten. This synthesis was based on the reaction of a tungstabutadiene with coordinatively unsaturated $W(CO)_4$ species, generated in situ. In the present paper we describe the synthesis of the first heteronuclear (W–Fe) μ -alkylidene complexes by the same approach, involving the reaction of conjugated terminal carbene complexes of tungsten with sources of $Fe(CO)_3$ and also by a second route based on the analogy between Fischer-type carbene complexes and esters and on the ability of $Fe(CO)_5$ to bring about isomerization of non-conjugated to conjugated esters.

Results and discussion

Conjugated esters [2] are known to react very readily with $Fe(CO)_5$ to give stable

complexes. We therefore treated conjugated carbene complexes **1** and **3** either photochemically with $\text{Fe}(\text{CO})_5$ or thermally with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$.

Complex **1** ($\text{R} = \text{Me}$) was found to react with $\text{Fe}(\text{CO})_5$ in hexane under UV irradiation to give complex **2** ($\text{R} = \text{Me}$) in 7% yield. Its mass spectrum shows, in addition to the molecular ion (m/z 534), peaks due to the successive loss of 8 CO groups. The ^1H NMR spectrum (Table 1) contains three signals, at 5.02, 1.95 and 1.32 ppm, each due to one proton which clearly show the presence of a coordinated double bond. The ^{13}C NMR spectrum shows, in addition to the signals from the double bond at 60.7 and 43.5 ppm, a characteristic signal at 209.4 ppm due to the bridging carbon atom. Complex **2** ($\text{R} = \text{Et}$) was made analogously from **1** ($\text{R} = \text{Et}$).

The coordination of the two double bonds can also be brought about thermally: thus, complex **3** ($\text{R} = \text{Me}$) reacts with $\text{Fe}_2(\text{CO})_9$ in THF at room temperature to give complex **4** ($\text{R} = \text{Me}$) as black crystals in 15% yield. Signals at 5.14 and 2.20 ppm in the ^1H NMR spectrum again show the presence of a coordinated double bond.

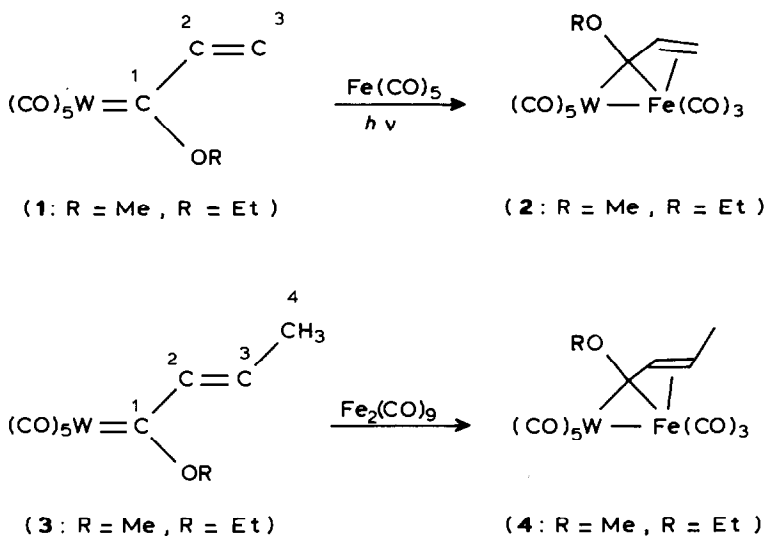


TABLE I
IMPORTANT ^1H NMR DATA (δ , ppm)

	Solvent	C_2H	C_3HR	C_3HR	OCH_2R
1	CDCl_3	7.4	5.72	5.25	4.6
3	C_6D_6	7.3	6.57		4.55
12	CDCl_3	6.95			
2	C_6D_6	5.02	1.95		3.25
4	C_6D_6	5.14	2.20		3.27
6	C_6D_6	5.0	2.0		3.12
13	C_6D_6	4.10			
17	C_6D_6	4.27	2.4		3.27

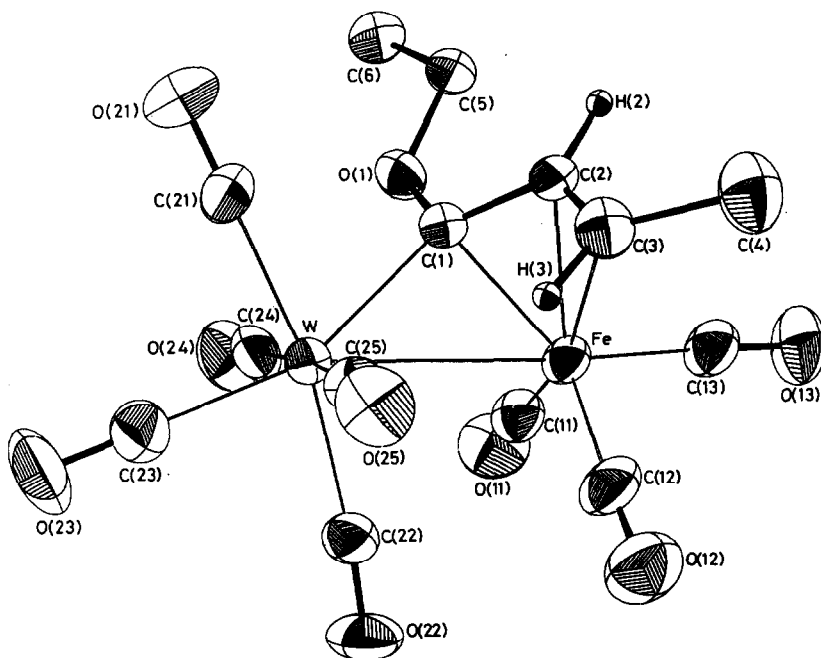
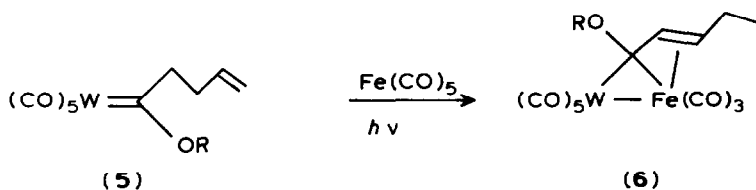


Fig. 1. ORTEP view of complex 4 with ellipsoids of 35% probability.

The structures of these complexes were confirmed by an X-ray diffraction study of complex 4 ($R = \text{Et}$), An ORTEP view of which is shown in Fig. 1. The important feature in this structure is the unsymmetrical bonding of the bridging carbon atom to the two metal centers, with $\text{W}-\text{C}(1)$ 2.274(8) Å and $\text{Fe}-\text{C}(1)$ 2.048(8) Å. These values are close to those found in homonuclear μ -alkylidene complexes of W ($\text{W}-\text{C}(1)$ 2.273 Å) and of Fe ($\text{Fe}-\text{C}(1)$ 2.022 Å) [3].

Reaction of complex 5 with $\text{Fe}(\text{CO})_5$: isomerization of the double bond

Complex 5, which can be regarded as a tungstaheptadiene, reacts in an interesting way with $\text{Fe}(\text{CO})_5$ in that its behaviour is like that of a non-conjugated ester; there is isomerization of the double bond to a position in which it is conjugated with the $\text{W}=\text{C}$ double bond, and at the same time coordination of $\text{Fe}(\text{CO})_3$ to the conjugated tungstabutadiene formed. Thus, irradiation of $\text{Fe}(\text{CO})_5$ in hexane in the presence of complex 5 gives a 12% yield of the red complex 6, in which, according to the ^1H

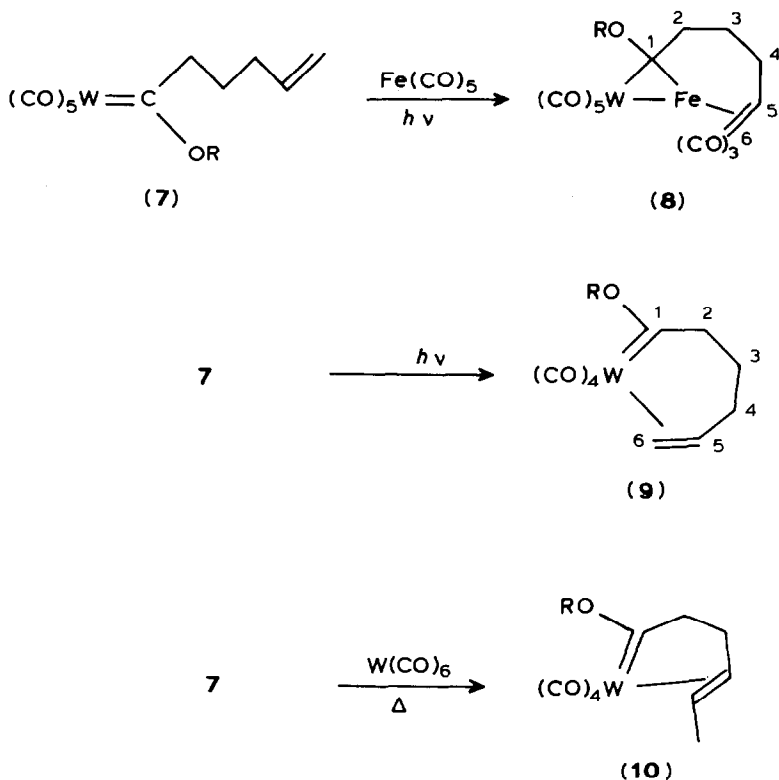


NMR spectrum (Table 1), the double bond is coordinated to the iron: a signal due to one olefinic proton appears at 5.0 ppm as a doublet and the other at 2.0 ppm.

Reaction of complex 7 with $Fe(CO)_5$: formation of a μ -alkylidene complex ($W-Fe$) without isomerization of the double bond

The behaviour of complex 7 towards $Fe(CO)_5$ is unusual. We previously observed that complex 7 reacts with $W(CO)_6$, a carbon-carbon double bond isomerization catalyst, to give, after a shift of the double bond towards an internal position, the new complex 10 [4]. The course of the reaction of 7 with $Fe(CO)_5$, which is also an isomerization catalyst, is quite different: instead of partial or complete isomerization, such as was observed in the case of complex 5, coordination of the two terminal double bonds of the tungstaheptadiene system of 7 to $Fe(CO)_3$ takes place, with formation of a μ -alkylidene complex 8 as a yellow oil. That the double bond is coordinated to one of the metal centres in this case to the iron is shown by the 1H NMR spectra; the signals due to the olefinic protons H(5) appear at 2.93 (3.8 in 9), those from H(6) *cis* at 2.02 (3.21 in 9) and those from H(6) *trans* at 2.29 ppm (3.21 ppm in 9)).

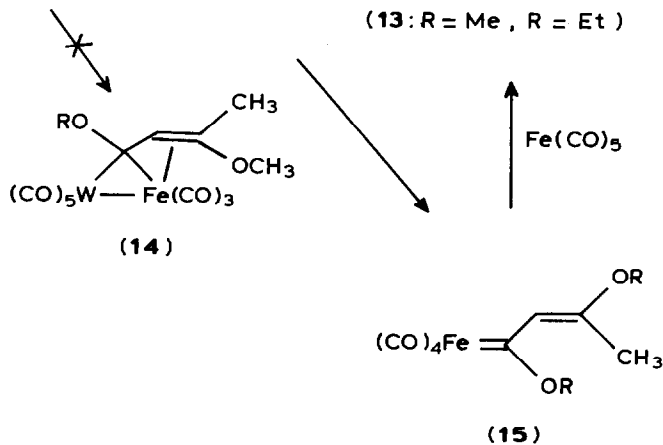
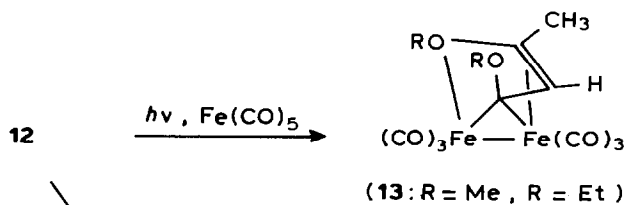
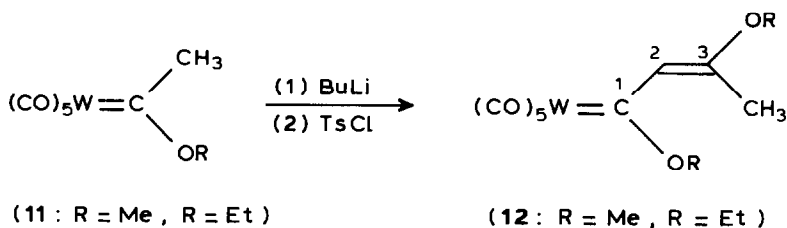
It appears therefore that the photochemical behaviour of 7 is the same in the absence of $Fe(CO)_5$ as in its presence: in both cases, stable cyclic systems are



formed without isomerization of the terminal double bond. We found that complex **8** is not formed by irradiation of complex **9** in the presence of $\text{Fe}(\text{CO})_5$.

Reaction of complex 12 with $\text{Fe}(\text{CO})_5$: formation of a μ -alkylidene complex of iron (Fe-Fe)

Ultraviolet irradiation of $\text{Fe}(\text{CO})_5$ in the presence of complex **12** did not give the expected heteronuclear μ -alkylidene complex **14**, but instead there was an exchange of the metal in complex **12** [5], probably followed by coordination of the tridentate ligand **15** to a second metal center, and complex **13** was formed in 80% yield. The ^1H NMR spectrum of the product contains four signals: there is a one-proton singlet at 4.1 ppm, consistent with a hydrogen on a coordinated double bond, along with three signals, each due to a methyl group, at 3.47, 2.02, and 1.2 ppm. The coordination of the double bond is also confirmed by the ^{13}C NMR spectra, in which the carbons of the double bond are shifted from 166.7 and 123.2 ppm, to 103.7 and 67.1 ppm, respectively, in the new complex. The mass spectrum indicates that there are only six CO groups in the complex, which means that one of the alkoxy groups is also coordinated to one of the metal centers.



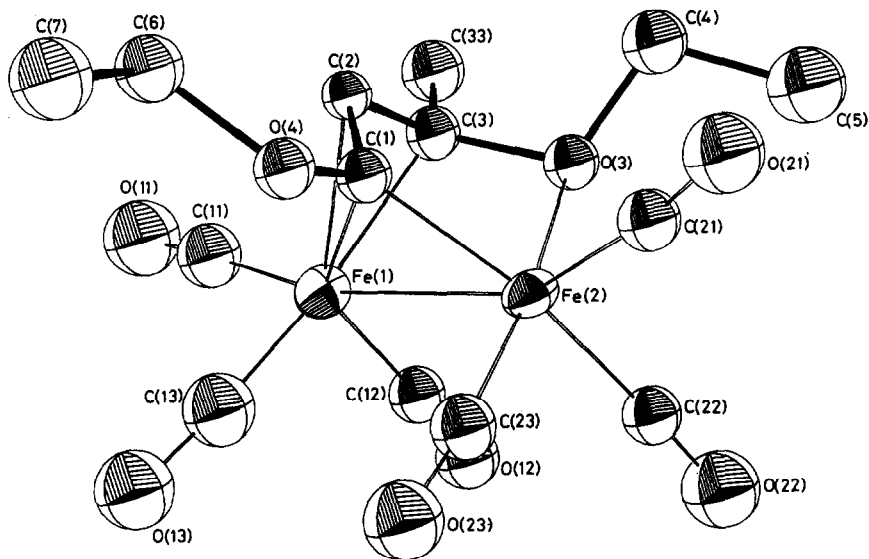
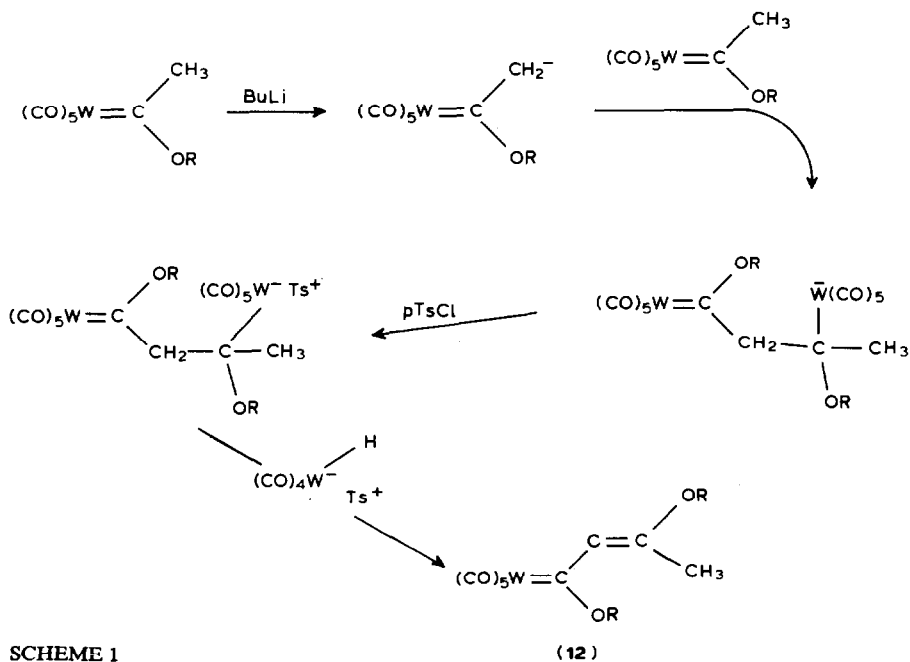


Fig. 2. ORTEP view of complex **13** with ellipsoids of 25% probability.

An X-ray structure of the complex **13** (R = Et), an ORTEP view of which is shown in Fig. 2, confirms these conclusions. It can be seen that it is the terminal ethoxy group which is coordinated to the metal center. Complexes **13** belong to a



SCHEME 1

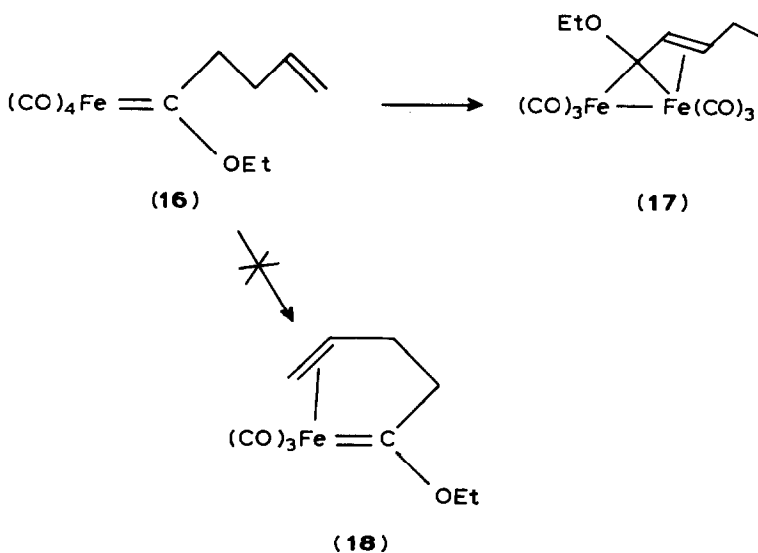
well documented family of dinuclear complexes of iron. The Fe–Fe bond length (2.550 Å) can be compared to that of the corresponding bond in various other dinuclear complexes [7–10].

Comment on the formation of complex 12 from complex 11

Formation of complex **12** was observed during attempts to alkylate complex **11** with alkyl tosylates in the presence of BuLi. We showed that the formation of complex **12** was in fact due to the presence of traces of *p*-toluenesulfonyl chloride in the starting material. A mechanism which could account for this unexpected reaction, and which is closely related to a reaction observed by Casey [6], is shown in Scheme 1.

Thermal and photochemical transformations of terminal iron carbene complexes

During our study aimed at the synthesis of carbene complexes bearing a coordinated carbon–carbon double bond in an alkyl chain, we synthesized complex **16** [11] and tried to coordinate the double bond to the metal center. We found that the expected complex **18** was not formed during the thermal (or photochemical) reaction, but that instead a new homonuclear μ -alkylidene complex **17** was obtained. The same result is observed when the reaction is carried out in the presence of $\text{Fe}(\text{CO})_5$. The ^1H NMR spectrum shows again the presence of a coordinated double bond (Table 1) and the mass spectrum is consistent with the presence of six CO groups. It thus appears, that in the case of carbeneiron(0) complexes the terminal carbene function is unstable with respect to the bridging carbene complexes. Formation of a μ -alkylidene complex of Fe during attempts to prepare a mononuclear complex of this metal, has been observed previously by Huttner [12].



Experimental

Preparation of complex 12 ($R = CH_3$)

A solution of BuLi (2.5 ml, 1.4 *N*) in hexane was added to a solution of pentacarbonyl(methylmethoxycarbene)tungsten(0) (1 g, 2.6 mmol), in THF (30 ml) at -60°C . To the mixture was added a solution of *p*-toluenesulfonyl chloride (0.42 g, 2.6 mmol) in THF (10 ml). After the usual work-up, the residue was taken up in light petroleum and chromatographed on silica gel. Elution with light petroleum first gave the starting material (0.838 g), then complex 12 (0.15 g, 13%) as yellow crystals. M.p. 58°C . IR (CHCl_3): $\nu(\text{CO})$ 2050, 1985, 1935 cm^{-1} . ^1H NMR (CDCl_3): δ 6.95 (1H, s, $\text{CH}=\text{C}$), 4.42 (3H, s, $\text{W}=\text{C}(\text{OCH}_3)$), 3.55 (3H, s, $=\text{C}-\text{OCH}_3$), 2.05 (3H, s, $=\text{C}(\text{CH}_3)$) ppm. ^{13}C NMR (CDCl_3): 298.4 (carbene), 203.6, 198.5, 195.7 (CO), 166.4 (C(3)), 122.5 (C(2)), 69.0 (OCH_3), 56.5 (OCH_3), 23.5 (CH_3) ppm. Mass spectrum: m/z 438 (M^+).

Complex 12 ($R = \text{CH}_2\text{CH}_3$). M.p. 45°C . ^1H NMR (CDCl_3): δ 6.95 (1H, s, $\text{CH}=\text{C}$), 4.90 (2H, q, OCH_2), 4.05 (2H, q, OCH_2), 2.3 (3H, s, CH_3), 1.7 (3H, t, CH_2CH_3), 1.5 (3H, t, CH_2CH_3) ppm. Mass spectrum m/z 466 (M^+).

Preparation of complex 2 ($R = CH_3$)

A solution of complex 1 ($R = \text{CH}_3$) (0.650 g, 1.67 mmol) and $\text{Fe}(\text{CO})_5$ (0.328 g, 3.34 mmol) in hexane (50 ml) was irradiated for 40 h. After evaporation of the solvent, the residue was chromatographed on silica gel to give complex 2 ($R = \text{CH}_3$) (60 mg, 7%) as black crystals. M.p. 96°C . ^1H NMR (60 MHz, C_6D_6): δ 5.02 (1H, dd, J 7.5 and 6.8 Hz, C_2H), 3.25 (3H, s, OCH_3), 1.95 (1H, dd, J 6.8 and 3 Hz, C_3H), 1.32 (1H, dd, J 7.5 and 3 Hz, C_3H) ppm. ^{13}C NMR (90 MHz, C_6D_6): δ 209.5 (C(1)), 196.3 (CO), 73.9 (C(2)), 60.7 (OCH_3), 43.5 (C(3)). Mass spectrum: m/z 534 (M^+).

Preparation of complexes 4 ($R = \text{CH}_3$) and 4 ($R = \text{Et}$)

A solution of complex 3 ($R = \text{CH}_3$) (0.74 g, 1.8 mmol) in THF (50 ml) was stirred under N_2 in the presence of $\text{Fe}_2(\text{CO})_9$ (1.092 g, 3 mmol) at room temperature, for 24 h. After evaporation of the solvent, the residue was taken up in light petroleum and chromatographed at -10°C on silica gel to give complex 4 (0.15 g, 15% yield) as black crystals, which were recrystallized from hexane. M.p. 75°C . ^1H NMR (60 MHz, C_6D_6): δ 5.14 (1H, d, J 7 Hz, $-\text{CH}=\text{C}$), 3.27 (3H, s, OCH_3), 2.20 (1H, m, CHCH_3), 1.25 (1H, d, J 6 Hz, CHCH_3) ppm. Mass spectrum: m/z 548 (M^+).

Complex 4 ($R = \text{Et}$) was obtained according to the same procedure, from complex 3 ($R = \text{Et}$) in 11% yield. M.p. 34°C . IR (CHCl_3): $\nu(\text{CO})$ 2280, 2260 cm^{-1} . RMN ^1H (60 MHz, C_6D_6): δ 5.10 (1H, d, J 8 Hz, $\text{CH}=\text{C}$), 3.42 (2H, q, J 6.8 Hz, OCH_2), 2.15 (1H, m, CHCH_3), 1.25 (3H, d, J 6.1 Hz, CHCH_3), 1.08 (3H, t, J 6.8 Hz, OCH_2CH_3) ppm.

Preparation of complex 6

A solution of $\text{Fe}(\text{CO})_5$ (1.486 g, 7.6 mmol) in hexane (30 ml) was irradiated in the presence of complex 5 ($R = \text{CH}_3$) (1.6 g, 3.8 mmol) at room temperature for 12 h. The solution was then filtered through Celite and then evaporated and the residue taken up in light petroleum and chromatographed on silica gel to give complex 6

(R = Me) (0.26 g, 12% yield) as a brown oil. IR (CHCl₃): $\nu(\text{CO})$ 2080, 2060, 2020, 2000, 1945 cm⁻¹. ¹H NMR (60 MHz, C₆D₆): δ 5.0 (1H, d, *J* 12 Hz, C₂H), 3.12 (3H, s, OCH₃), 2.0 (1H, m, C₃H), 1.5 (2H, m, CH₂CH₃), 0.73 (3H, t, *J* 8 Hz, CH₂CH₃) ppm. Mass spectrum *m/z* 562 (*M*⁺).

Preparation of complex 8

A solution of Fe(CO)₅ (1.96 g, 10 mmol) in hexane (40 ml) was irradiated at room temperature in the presence of complex 7 (R = Et) (2.25 g, 5 mmol) for 12 h. After the usual work up, culminating in silica gel chromatography, complex 8 (R = Et) was obtained as a yellow oil (0.510 g, 18%). IR (CHCl₃): $\nu(\text{CO})$ 2085, 2070, 2005, 1980, 1938 cm⁻¹. ¹H NMR (250 MHz, C₆D₆): 4.46 (2H, q, *J* 8 Hz, OCH₂), 2.93 (3H, m, C₅H and C₂H), 2.29 (1H, d, *J* 5.6 Hz, C₆H), 2.02 (1H, d, *J* 11.2 Hz, C₆H), 1.60 (2H, m, C₄H₂), 1.45 (2H, m, C₃H₂), 1.05 (3H, t, *J* 8 Hz, CH₂CH₃) ppm. Irradiation at 2.93 ppm transforms the two doublets at 2.29 and 2.02 ppm into two singlets. ¹³C NMR (90 MHz, C₆D₆): δ 212 (C(1)), 197.7 (CO), 80.9 (OCH₂), 64.4 (C(5)), 61.8 (C(6)), 39.4 (C(2)), 38.5 (C(4)), 29.7 (C(3)), 14.3 (OCH₂CH₃) ppm. Mass spectrum *m/z* 562 (*M*⁺).

Preparation of complex 13

A solution of Fe(CO)₆ (2.5 ml, 15 mmol) in hexane (40 ml), was irradiated at room temperature in the presence of complex 12 (0.648 g, 1.4 mmol) for 2 days. After filtration of the solution through Celite and evaporation of the solvent, the residue was taken up in light petroleum and chromatographed on silica gel. Elution with light petroleum first gave traces of starting material, then complex 13 (R = CH₃) (0.47 g, 80% yield) as orange crystals. M.p. 61° C. ¹H NMR (60 MHz, C₆D₆): δ 4.10 (1H, s, C₂H), 3.47 (3H, s, OCH₃), 2.02 (3H, s, OCH₃), 1.20 (3H, s, CH₃) ppm. Mass spectrum *m/z* 394 (*M*⁺). Complex 13 (R = Et) was prepared by the same procedure (34% yield). M.p. 37° C. Mass spectrum *m/z* 422 (*M*⁺).

Preparation of complexes 16

A solution of butenylmagnesium bromide (16.6 ml, 20 mmol) in THF was added at -78° C to a solution of Fe(CO)₅ (3.92 g, 20 mmol) in THF (100 ml). The temperature of the mixture was raised to 0° C and HMPA (26 ml) was added, and the temperature was then lowered to -78° C. Ethylfluorosulfonate (9.6 ml, 10 mmol) was then added and the mixture was stirred for 3 h at -78° C then allowed to warm to room temperature. The solvent was evaporated, and the residue extracted with light petroleum. Silica gel chromatography gave complex 14 (1.76 g, 30% yield). ¹H NMR (60 MHz, C₆D₆): δ 5.97–5.12 (1H, m, C₄H), 4.97 (2H, m, C₃H₂), 4.8 (2H, q, *J* 8 Hz, OCH₂), 3.2 (2H, m, C₂H₂), 2.2 (2H, m, C₃H₂), 1.1 (3H, t, *J* 8 Hz) ppm. ¹³C NMR (90 MHz, C₆D₆): δ 334.7 (C(1)), 214.2 (CO), 136.1 (C(4)), 115.9 (C(5)), 78.2 (OCH₂), 61.7 (C(2)), 29.2 (C(3)), 14.1 (CH₃) ppm. Mass spectrum *m/z*: 264 (*M*⁺).

Formation of complex 17 from complex 16

A solution of complex 16 (1.76 g, 6 mmol) in hexane was irradiated for 6 h at room temperature. The usual work-up and silica gel chromatography of the residue gave complex 16 as a red oil (0.2 g, 8.5% yield). RMN ¹H (C₆D₆): δ 4.27 (1H, d, *J* 12 Hz, C₂H), 3.27 (2H, q, *J* 8 Hz, OCH₂), 2.4 (1H, m, C₃H), 1.67 (2H, q, *J* 8 Hz,

C_4H_2), 1.07 (6H, d.t, J 8 Hz, C_5H_3 and OCH_2CH_3). Mass spectrum m/z 392 (M^+).

X-ray studies

For each compound preliminary unit cell dimensions and symmetry information were derived from precession photographs. Compound **13** was set up on a laboratory-made, automatic three circle diffractometer; cell dimensions and orientation matrix were obtained by least-squares analysis from the setting angles of 6 reflections. A Philips PW 1100 diffractometer was used for compound **4**; accurate cell dimensions were derived from a least-squares refinement of 22 reflections.

Crystal data and data collection parameters are listed in Table 2. For compound **4**, intensities of three standard reflections were monitored every 2 h whereas in **13**, two standards were measured every 100 reflections; these showed no appreciable change during the data collections. Data were processed using a locally written program. No absorption corrections were applied.

Computations were performed by using the SHELX 76 system [13] adapted on an IRIS 80. Atomic scattering factors for neutral Fe, W, O and C were taken from international Tables for Crystallography [14], those for H were taken from Stewart et al. [15], and anomalous dispersion terms for Fe and W were included.

(Continued on p. 384)

TABLE 2
CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR COMPLEX **4** AND **13**

	4	13
Formula	$C_{14}H_{10}O_9FeW$	$C_{14}H_{14}O_8Fe_2$
Mol. wt.	561.9	422
Space group	$P2_1/n$	$Pna2_1$
a (Å)	8.945(2)	17.006(7)
b (Å)	17.028(4)	7.626(7)
c (Å)	12.027(3)	14.06(3)
β (°)	99.36	
V (Å ³)	1808	1823
Z	4	4
Cryst. size (mm)	$0.3 \times 0.2 \times 0.36$	$0.23 \times 0.24 \times 0.4$
μ (Mo- K_α) (cm ⁻¹)	75.1	15.5
ρ_{calcd} (g/cm ³)	2.06	1.54
Temperature (°C)	20	20
Diffractometer	Philips PW 1100	three circle
Radiation	Mo- K_α	Mo- K_α
Scan width	$1.0 + 0.345 \text{tg } \theta$	$1.2 + 0.345 \text{tg } \theta$
2θ range (°)	4–50	3–40
Scan type	$\theta - 2\theta$	$\theta - 2\theta$
Reflections collected	3483	1527
Reflections merged	3039	1527
Reflections observed	2496	1246
Criteria	$F \geq 6\sigma(F)$	$F \geq 6\sigma(F)$
$R = \sum F_o - F_c / \sum F_o $	0.0456	0.103
$R_w = \{ \sum w(F_o - F_c)^2 / \sum w F_o^2 \}^{1/2}$	0.0617	0.122
Weighting scheme	$1.22 / (\sigma^2[F_o] + 0.004 F_o^2)$	$1.0 / (\sigma^2[F_o] + 0.005 F_o^2)$
Shift e.s.d.	0.6	0.1

TABLE 3

FINAL POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS OF COMPLEX 4 (C₁₄H₁₀O₉FeW) AND COMPLEX 13 (C₁₄H₁₃O₈Fe₂)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
<i>Complex 4</i>			
W	0.12970(4)	0.43569(2)	0.24100(3)
Fe	0.4007(1)	0.34966(8)	0.3415(1)
C(11)	0.341(1)	0.3654(6)	0.4751(9)
O(11)	0.305(1)	0.3731(6)	0.5597(7)
C(12)	0.529(1)	0.4264(7)	0.317(1)
O(12)	0.612(1)	0.4732(6)	0.2982(9)
C(13)	0.551(1)	0.2895(7)	0.4091(9)
O(13)	0.6439(9)	0.2529(6)	0.4583(7)
C(21)	-0.022(1)	0.3758(7)	0.125(1)
O(21)	-0.106(1)	0.3431(6)	0.0592(8)
C(22)	0.252(1)	0.5142(6)	0.3490(9)
O(22)	0.312(1)	0.5626(4)	0.4052(7)
C(23)	-0.001(1)	0.5292(8)	0.193(1)
O(23)	-0.078(1)	0.5826(6)	0.164(1)
C(24)	0.002(1)	0.4133(6)	0.367(1)
O(24)	-0.065(1)	0.4067(6)	0.4359(8)
C(25)	0.249(1)	0.4676(6)	0.1201(8)
O(25)	0.309(1)	0.4915(5)	0.0508(7)
O(1)	0.0877(7)	0.2677(4)	0.3148(6)
C(1)	0.193(1)	0.3071(5)	0.2693(7)
C(2)	0.311(1)	0.2641(6)	0.2276(8)
C(3)	0.414(1)	0.3032(6)	0.1775(8)
C(4)	0.561(1)	0.2613(8)	0.150(1)
C(5)	0.082(1)	0.1832(5)	0.3093(9)
C(6)	-0.062(1)	0.1584(7)	0.352(1)
<i>Complex 13</i>			
Fe(1)	0.0387(2)	0.2004(4)	0
Fe(2)	0.0379(2)	0.1518(3)	0.1796(3)
C(11)	0.053(2)	0.274(4)	-0.115(2)
O(11)	0.064(2)	0.314(4)	-0.193(2)
C(12)	0.096(1)	0.007(3)	-0.004(2)
O(12)	0.133(1)	-0.117(3)	-0.014(2)
C(13)	-0.054(2)	0.116(5)	-0.024(2)
O(13)	-0.118(1)	0.068(3)	-0.046(2)
C(21)	0.025(1)	0.221(3)	0.298(2)
O(21)	0.012(1)	0.286(3)	0.373(2)
C(22)	0.086(1)	-0.055(3)	0.204(2)
O(22)	0.118(2)	-0.185(3)	0.215(2)
C(23)	-0.055(1)	0.055(3)	0.184(2)
O(23)	-0.118(1)	-0.004(2)	0.179(2)
C(1)	-0.005(1)	0.355(3)	0.116(1)
C(2)	0.053(1)	0.443(2)	0.063(1)
C(3)	0.123(1)	0.349(3)	0.059(2)
C(4)	0.181(2)	0.383(4)	0.217(2)
C(5)	0.220(2)	0.272(5)	0.296(3)
C(6)	-0.107(1)	0.565(3)	0.080(2)
C(7)	-0.194(2)	0.593(4)	0.104(3)
O(3)	0.1425(8)	0.264(2)	0.152(1)
O(4)	-0.0784(8)	0.407(2)	0.131(1)
C(33)	0.197(2)	0.415(4)	0.006(3)

TABLE 4
 INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR COMPLEX 4

W-Fe	2.920(1)	C(11)-O(11)	1.12(1)
W-C(21)	2.05(1)	C(12)-O(12)	1.14(1)
W-C(22)	2.05(1)	C(13)-O(13)	1.13(1)
W-C(23)	2.01(1)	C(21)-O(21)	1.14(1)
W-C(24)	2.08(1)	C(22)-O(22)	1.14(1)
W-C(25)	2.01(1)	C(23)-O(23)	1.16(1)
W-C(1)	2.274(8)	C(24)-O(24)	1.10(1)
		C(25)-O(25)	1.14(1)
Fe-C(11)	1.80(1)		
Fe-C(12)	1.79(1)	C(5)-C(6)	1.53(1)
Fe-C(13)	1.78(1)	C(5)-O(1)	1.44(1)
Fe-C(1)	2.048(8)	O(1)-C(1)	1.34(1)
Fe-C(2)	2.067(9)	C(1)-C(2)	1.44(1)
Fe-C(3)	2.147(9)	C(2)-C(3)	1.35(1)
		C(3)-C(4)	1.57(1)
Fe-W-C(21)	116.4(3)	W-Fe-C(11)	86.9(3)
Fe-W-C(22)	75.2(3)	W-Fe-C(12)	94.3(3)
Fe-W-C(23)	157.5(3)	W-Fe-C(13)	173.2(3)
Fe-W-C(24)	97.1(3)	W-Fe-C(1)	50.8(2)
Fe-W-C(25)	86.2(3)	W-Fe-C(2)	82.7(2)
Fe-W-C(1)	44.3(2)	W-Fe-C(3)	88.4(2)
C(21)-W-C(22)	168.3(4)	C(11)-Fe-C(12)	109.4(5)
C(21)-W-C(23)	84.7(4)	C(11)-Fe-C(13)	89.4(4)
C(21)-W-C(24)	91.3(4)	C(11)-Fe-C(1)	92.8(4)
C(21)-W-C(25)	90.7(4)	C(11)-Fe-C(2)	123.9(4)
C(21)-W-C(1)	75.3(4)	C(11)-Fe-C(3)	161.3(4)
C(22)-W-C(23)	83.7(4)	C(12)-Fe-C(13)	92.3(5)
C(22)-W-C(24)	87.5(4)	C(12)-Fe-C(1)	138.3(4)
C(22)-W-C(25)	89.5(4)	C(12)-Fe-C(2)	126.2(5)
C(22)-W-C(1)	116.0(3)	C(12)-Fe-C(3)	89.0(5)
C(23)-W-C(24)	89.6(5)	C(13)-Fe-C(1)	123.7(4)
C(23)-W-C(25)	85.9(4)	C(13)-Fe-C(2)	94.5(4)
C(23)-W-C(1)	158.1(4)	C(13)-Fe-C(3)	93.2(4)
C(24)-W-C(25)	174.9(4)	C(1)-Fe-C(2)	41.0(3)
C(24)-W-C(1)	82.3(3)	C(1)-Fe-C(3)	70.4(3)
C(25)-W-C(1)	102.8(4)	C(2)-Fe-C(3)	37.4(4)
Fe-C(11)-O(11)	178(1)	Fe-C(1)-W	84.9(3)
Fe-C(12)-O(12)	177(1)	Fe-C(1)-O(1)	130.8(6)
Fe-C(13)-O(13)	176(1)	Fe-C(1)-C(2)	70.2(5)
		W-C(1)-O(1)	111.5(5)
W-C(21)-O(21)	179(1)	W-C(1)-C(2)	127.9(6)
W-C(22)-O(22)	174.5(9)	Fe-C(2)-C(1)	68.8(5)
W-C(23)-O(23)	179(1)	Fe-C(2)-C(3)	74.5(6)
W-C(24)-O(24)	175(1)	Fe-C(3)-C(2)	68.1(5)
W-C(25)-O(25)	174.2(9)	Fe-C(3)-C(4)	122.1(7)
C(6)-C(5)-O(1)	106.7(8)	C(1)-C(2)-C(3)	119.9(9)
C(5)-O-C(1)	120.0(7)	C(2)-C(3)-C(4)	121(1)
O-C(1)-C(2)	119.5(8)		

TABLE 5
 INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR COMPLEX 13

Fe(1)–Fe(2)	2.550(4)	C(2)–C(3)	1.39(3)
Fe(1)–C(1)	2.15(2)	C(3)–O(3)	1.50(3)
Fe(1)–C(2)	2.06(2)	C(3)–Me(3)	1.54(4)
Fe(1)–C(3)	2.01(2)	C(4)–C(5)	1.55(4)
Fe(1)–C(11)	1.73(3)	C(4)–O(3)	1.45(3)
Fe(1)–C(12)	1.77(2)	C(6)–C(7)	1.52(4)
Fe(1)–C(13)	1.74(4)	C(6)–O(4)	1.49(4)
Fe(2)–C(1)	1.93(2)	C(11)–O(11)	1.16(4)
Fe(2)–O(3)	2.01(1)	C(12)–O(12)	1.15(3)
Fe(2)–C(21)	1.76(2)	C(13)–O(13)	1.18(4)
Fe(2)–C(22)	1.81(2)	C(21)–O(21)	1.18(3)
Fe(2)–C(23)	1.74(2)	C(22)–O(22)	1.14(3)
		C(23)–O(23)	1.16(2)
C(1)–C(2)	1.41(3)	Fe(1)...O(3)	2.81
C(1)–O(4)	1.32(2)	Fe(1)...O(4)	3.14
		Fe(2)...O(4)	2.86
Fe(2)–Fe(1)–C(1)	47.6(5)	Fe(1)–C(1)–Fe(2)	77.2(7)
Fe(2)–Fe(1)–C(2)	73.0(5)	Fe(1)–C(1)–C(2)	67(1)
Fe(2)–Fe(1)–C(3)	71.4(6)	Fe(1)–C(1)–O(4)	128(1)
Fe(2)–Fe(1)–C(11)	167(1)	Fe(2)–C(1)–C(2)	111(1)
Fe(2)–Fe(1)–C(12)	85(1)	Fe(2)–C(1)–O(4)	122(1)
Fe(2)–Fe(1)–C(13)	98(1)	C(2)–C(1)–O(4)	127(2)
C(1)–Fe(1)–C(2)	39.1(7)		
C(1)–Fe(1)–C(3)	68.0(8)	Fe(1)–C(2)–C(1)	74(1)
C(1)–Fe(1)–C(11)	126(1)	Fe(1)–C(2)–C(3)	68(1)
C(1)–Fe(1)–C(12)	132(1)	C(1)–C(2)–C(3)	112(2)
C(1)–Fe(1)–C(13)	92(1)		
C(2)–Fe(1)–C(3)	39.9(8)	Fe(1)–C(3)–C(2)	72(1)
C(2)–Fe(1)–C(11)	95(1)	Fe(1)–C(3)–O(3)	106(1)
C(2)–Fe(1)–C(12)	134(1)	Fe(1)–C(3)–Me(3)	125(2)
C(2)–Fe(1)–C(13)	121(1)	C(2)–C(3)–O(3)	112(2)
C(3)–Fe(1)–C(11)	96(1)	C(2)–C(3)–Me(3)	124(2)
C(3)–Fe(1)–C(12)	95(1)	O(3)–C(3)–Me(3)	112(2)
C(3)–Fe(1)–C(13)	160(1)		
C(11)–Fe(1)–C(12)	99(1)	O(3)–C(4)–C(5)	108(2)
C(11)–Fe(1)–C(13)	94(2)	O(4)–C(6)–C(7)	109(2)
C(12)–Fe(1)–C(13)	101(1)		
Fe(2)–O(3)–C(3)	99(1)		
Fe(1)–Fe(2)–C(1)	55.2(6)	Fe(2)–O(3)–C(4)	123(2)
Fe(1)–Fe(2)–O(3)	75.1(4)	C(3)–O(3)–C(4)	112(2)
Fe(1)–Fe(2)–C(21)	153.1(7)		
Fe(1)–Fe(2)–C(22)	108.3(7)	C(1)–O(4)–C(6)	118(2)
Fe(1)–Fe(2)–C(23)	95.6(9)		
C(1)–Fe(2)–O(3)	84.5(7)	Fe(1)–C(11)–O(11)	176(3)
C(1)–Fe(2)–C(21)	98.4(9)	Fe(1)–C(12)–O(12)	175(3)
C(1)–Fe(2)–C(22)	163.5(9)	Fe(1)–C(13)–O(13)	174(3)
C(1)–Fe(2)–C(23)	91(1)		
O(3)–Fe(2)–C(21)	99.4(8)	Fe(2)–C(21)–O(21)	172(2)
O(3)–Fe(2)–C(22)	90.4(9)	Fe(2)–C(22)–O(22)	177(2)
O(3)–Fe(2)–C(23)	171(1)	Fe(2)–C(23)–O(23)	175(3)
C(21)–Fe(2)–C(22)	98(1)		
C(21)–Fe(2)–C(23)	89(1)		
C(22)–Fe(2)–C(23)	92(1)		

The positions of tungsten and iron atoms were determined from Patterson maps. All other non-hydrogen atoms were located on subsequent electron density and difference electron density maps. In compound **13**, owing to a very poor set of data, only iron atoms were refined anisotropically, and only hydrogen atoms of CH₂ groups were included in calculated positions, C–H 1.0 Å. Although most hydrogen atoms for compound **4** were located on difference Fourier map, during subsequent refinements their positions were constrained at C–H 1.0 Å and those of methyl and CH₂ were constrained to maintain approximate tetrahedral symmetry about carbon. The criteria for a satisfactory completed analysis were the ratio of the parameter shifts to standard deviations, and no significant features in final difference maps.

Final positional parameters and their standard deviations, obtained from the last cycle of least-squares refinement, are presented in Table 3. Thermal parameters for non-hydrogen atoms, and final values of observed and calculated structure factors are available. Interatomic distances and angles are presented in Tables 4 and 5.

References

- 1 A. Parlier, F. Rose-Munch, M. Rudler, H. Rudler and J.C. Daran, *J. Organomet. Chem.*, 323 (1987) 353.
- 2 R. Damico, *J. Org. Chem.*, 33 (1968) 1550.
- 3 B.B. Meyer, P.E. Riley and R.E. Davis, *Inorg. Chem.*, 20 (1981) 3029.
- 4 C. Alvarez-Toledano, H. Rudler, J.C. Daran and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, (1984) 574.
- 5 K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert and K. Weiss, in *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983, p. 36.
- 6 C.P. Casey, C.D. Albin and T.J. Burkhardt, *J. Am. Chem. Soc.*, 93 (1977) 2533.
- 7 T.A. Mitsudo, H. Watanabe, K. Watanabe and Y. Watanabe, *Organometallics*, 1 (1982) 612.
- 8 R. Aumann, H. Wörmann and C. Krüger, *Angew. Chem. Int. Ed. Engl.*, 15 (1976) 609.
- 9 R. Aumann, H. Averbek and C. Krüger, *Chem. Ber.*, 108 (1975) 3342.
- 10 J.A.D. Jeffreys, C.M. Willis, I.C. Robertson, G. Ferguson and J.C. Sime, *J. Chem. Soc. Dalton*, (1973) 749.
- 11 M.F. Semmelhack and R. Tamura, *J. Am. Chem. Soc.*, 105 (1983) 4099.
- 12 G. Huttner and D. Regler, *Chem. Ber.*, 105 (1972) 2726.
- 13 G.M. Sheldrick, *System of Crystallographic Computer Program*, University of Cambridge, 1976.
- 14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, Vol. 4, 1974.
- 15 R.F. Stewart, *J. Chem. Phys.*, 42 (1965) 3175.