Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 35.[1] The Synthesis and Crystal Structures of the Compounds $[N(PPh_3)_2][W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]\cdot0.5\ Et_2O$ and $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$ *

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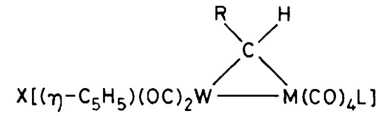
Treatment of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $[N(PPh_3)_2][WH(CO)_5]$ in thf (tetrahydrofuran) affords the salt $[N(PPh_3)_2][W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]$, the structure of which has been established by *X*-ray diffraction. In the anion, the W–W bond [3.111(1) Å] is asymmetrically spanned by the $C(H)C_6H_4Me\text{-}4$ group [μ-C–W 2.127(7) and 2.436(8) Å]. One tungsten atom carries five CO groups at octahedral sites around the metal, while the other tungsten atom is ligated by two CO groups and the cyclopentadienyl ring. The latter and the tolyl group are positioned on opposite sides of the $\mu\text{-}CW_2$ ring. The reaction between $[AsPh_4][WH(CO)_5]$ and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ affords $[AsPh_4][W_2\{C(H)Me\}(CO)_7(\eta\text{-}C_5H_5)]$, and evidence was obtained for the existence in related syntheses of the anions $[MW\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_6(L)(\eta\text{-}C_5H_5)]^-$ [M = Cr, L = CO; M = W, L = $P(OMe)_3$]. Treatment of $[W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]$ with $SnPh_3Cl$ in thf affords the stable alkylidene complex $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$, the structure of which has been established by a single-crystal *X*-ray diffraction study. The W–C and W–Sn separations are 2.032(7) and 2.837(1) Å, respectively, with the $SnPh_3$ and $C(H)C_6H_4Me\text{-}4$ groups in a *transoid* configuration. The molecule is orientated such that the alkylidene hydrogen substituent is adjacent to the cyclopentadienyl ligand. The n.m.r. data for the new compounds are reported and discussed.

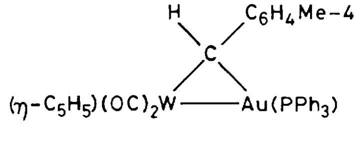
The tungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$ or Me) combine with a variety of metal–ligand fragments isolobal with CH_2 to afford dimetal compounds with bridging alkylidyne ligands.[1,2] The latter are very reactive, and several of the compounds have been protonated at the bridging carbon atoms affording salts in which alkylidene groups bridge the metal–metal bond in the cations.[3,4] In this paper we describe the contrary situation: salts in which alkylidene groups bridge metal–metal bonds in dimetal anions. These species have also been obtained *via* the mononuclear alkylidyne tungsten complexes mentioned above. A preliminary account of this work has been given.[5]

Results and Discussion

Treatment of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $[N(PPh_3)_2][WH(CO)_5]$[6] in tetrahydrofuran (thf) at room temperature affords the dark red crystalline compound (1), characterised by microanalysis and by its spectroscopic properties. The ^1H n.m.r. spectrum showed a resonance at δ 10.15, in the region expected for a μ-C*H*R ligand.[7] Signals for the $C_6H_4Me\text{-}4$ and C_5H_5 groups were also observed (Table 1). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum also provided strong evidence for the presence of a bridging alkylidene group with a resonance for the μ-C nucleus at δ 147.8 p.p.m. with $^{183}W\text{-}^{13}C$ coupling (105 Hz). Four carbonyl signals were also observed (Table 1). On the basis of peak intensities, the resonances at 207.8 and 203.2 p.p.m. are assigned to the axial and radial CO groups of a $W(CO)_5$ fragment.



	X	M	R	L
(1)	$[N(PPh_3)_2]^+$	W	$C_6H_4Me\text{-}4$	CO
(2)	$[AsPh_4]^+$	W	Me	CO
(3)	$[N(PPh_3)_2]^+$	Cr	$C_6H_4Me\text{-}4$	CO
(4)	$[N(PPh_3)_2]^+$	W	$C_6H_4Me\text{-}4$	$P(OMe)_3$



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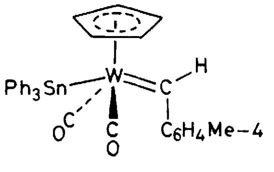

(6)

At the time of synthesis,[5] compound (1) was the first example of a species in which an alkylidene ligand bridged a metal–metal bond in an anion. However, more recently we have reported[8] the salts $[N(PPh_3)_2][ReW\{\mu\text{-}C(H)R\}(CO)_9]$(R = $C_6H_4Me\text{-}4$ or Me), thereby adding to this new class of compound.

An *X*-ray diffraction study was carried out on (1) to establish the structure precisely. The results are summarised in Table 2, and the anion is shown in Figure 1 with the atom numbering scheme. The metal–metal bond is bridged asymmetrically by the $C(H)C_6H_4Me\text{-}4$ group [W(1)–C(1) 2.127(7), W(2)–C(1) 2.436(8) Å]. The relatively short W(1)–C(1) separation is similar to that observed [2.14(2) Å] for the C=W

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* Bis(triphenylphosphine)iminium 1,1,1,1,2,2-heptacarbonyl-2-η-cyclopentadienyl-μ-*p*-tolylmethylene-ditungstate and dicarbonyl(η-cyclopentadienyl)(*p*-tolylmethylene)triphenylstannyltungsten.

Supplementary data available (No. SUP 56214, 14 pp.): complete bond parameters, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Hydrogen-1 and carbon-13 n.m.r. data[a] for the tungsten complexes

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(**1**)	2.18 (s, 3 H, Me-4), 5.30 (s, 5 H, C_5H_5), 6.8—7.0 (m, 4 H, C_6H_4), 7.3—7.8 (m, 30 H, Ph), 10.15 (s, 1 H, μ-CH)	239.4 [CO, *J*(WC) 188], 238.6 [CO, *J*(WC) 173], 207.8 [CO, *J*(WC) 149], 203.2 [4 CO, *J*(WC) 122], 161.0 [C^1 (C_6H_4)], 147.8 [μ-*C*, *J*(WC) 105], 134—126 (Ph and C_6H_4), 93.1 (C_5H_5), 21.0 (Me-4)
(**2a**)[d]	3.27 [d, 3 H, μ-C(H)*Me*, *J*(HH) 7], 5.02 (s, 5 H, C_5H_5), 7.3—7.9 (m, 20 H, Ph), 9.54 [q, 1 H, μ-C(*H*)Me, *J*(HH) 7]	[e]239.1 (CO), 238.7 (CO), 208.4 [CO, *J*(WC) 151], 204.8 [4 CO, *J*(WC) 122], 146.9 (μ-C), 135.1, 133.2, 131.5, 120.4 (Ph), 91.9 (C_5H_5), 44.1 (Me)
(**2b**)[d]	3.11 [d, 3 H, μ-C(H)*Me*, *J*(HH) 8], 5.18 (s, 5 H, C_5H_5), 7.3—7.9 (m, 20 H, Ph), 9.00 [q, 1 H, μ-C(*H*)Me, *J*(HH) 8]	[e]238.7 (CO), 238.4 (CO), 203.7 [CO, *J*(WC) 161], 200.8 [4 CO, *J*(WC) 127], 146.5 (μ-C), 135.1, 133.2, 131.5, 120.4 (Ph), 92.8 (C_5H_5), 42.1 (Me)
(**3**)	2.23 (s, 3 H, Me-4), 5.35 (s, 5 H, C_5H_5), 7.2—8.0 (m, 34 H, Ph and C_6H_4), 10.25 (s, 1 H, μ-CH)	[e]241.7 (WCO), 238.6 (WCO), 219.4 (CrCO), 216.9 (4 CrCO), 159.3 [C^1 (C_6H_4)], 148.5 (μ-C), 134.5—125.6 (Ph and C_6H_4), 93.7 (C_5H_5), 21.2 (Me-4)
(**6**)[f]	2.19 (s, 3 H, Me-4), 5.70 (s, 5 H, C_5H_5), 7.0—7.7 (m, 19 H, Ph and C_6H_4), 14.48 [s, 1 H, C(*H*)C_6H_4Me-4]	282.4 [*C*(H)C_6H_4Me-4, *J*(WC) 92, *J*(SnC) 68], 214.2 [CO, *J*(WC) 156, *J*(SnC) 136], 148.3—127.8 (Ph and C_6H_4), 95.4 (C_5H_5), 22.0 (Me-4)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2 unless otherwise stated. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$; measured in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [d] Isomers of compound (**2**), see text. [e] Spectrum measured at −40 °C. [f] Spectra measured in $CDCl_3$.

Table 2. Selected internuclear distances (Å) and angles (°) with estimated standard deviations in parentheses for the anion $[W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]^-$

W(1)–W(2)	3.111(1)	W(1)–C(14)	1.913(7)	W(2)–C(9)	2.025(8)	W(2)–C(12)	2.040(8)
W(1)–C(1)	2.127(7)	W(1)–C(15)	1.956(7)	W(2)–C(10)	1.975(11)	W(2)–C(13)	2.060(8)
W(2)–C(1)	2.436(8)	W(1)–C(cp)*	2.384(8)	W(2)–C(11)	2.049(7)	C(1)–C(2)	1.475(9)
W(2)–W(1)–C(1)	51.3(2)	W(1)–C(1)–W(2)	85.7(2)	W(1)–W(2)–C(1)	43.0(2)	C(9)–W(2)–C(10)	86.9(4)
C(1)–W(1)–C(14)	84.8(3)	W(1)–C(1)–C(2)	131.3(5)	W(1)–W(2)–C(11)	69.0(2)	C(9)–W(2)–C(12)	88.1(3)
C(1)–W(1)–C(15)	112.1(3)	W(2)–C(1)–C(2)	115.6(5)	C(1)–W(2)–C(9)	75.0(3)	C(11)–W(2)–C(12)	93.0(3)
C(14)–W(1)–C(15)	75.7(3)	C(2)–C(1)–H(1)	115.7(4)	C(9)–W(2)–C(11)	173.1(3)	C(11)–W(2)–C(13)	88.4(3)
W(1)–C(14)–O(14)	176.9(6)	W(1)–C(15)–O(15)	177.7(7)	mean W(2)–C–O	176.8(7)		

* Mean distance to cyclopentadienyl carbons.

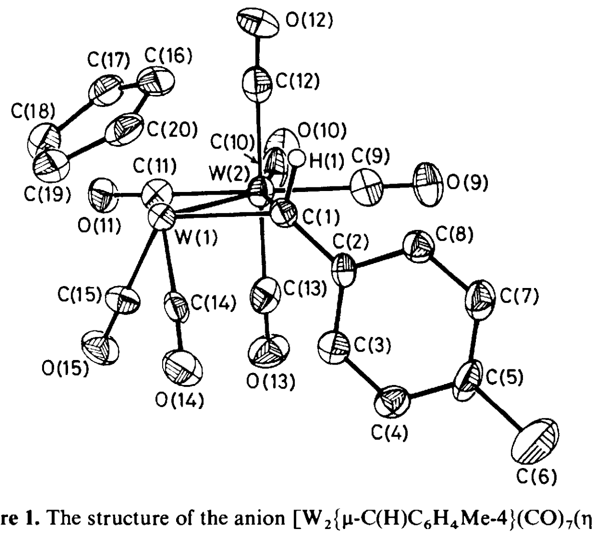


Figure 1. The structure of the anion $[W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]^-$, showing the atom numbering scheme. The atom H(1) is shown at the calculated position (see text)

double bond in $[W(=CPh_2)(CO)_5]$.[9] In contrast, the W(2)–C(1) distance is even longer than the carbon–tungsten σ bond [2.34(1) Å] in the anion $[W\{CH(OMe)Ph\}(CO)_5]^-$, but is comparable with those found for similar linkages in the molecules $[PtW\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$ [2.48(1) Å] and $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ [2.37(1) Å], where the organic groups have also been described as semi-bridging.[10] In the recently reported[11] homonuclear dimetal complex $[W_2\{\mu\text{-}C(H)Ph\}(CO)_{10}]$, however, the alkylidene ligand essentially symmetrically bridges the metal–metal bond [μ-C–W 2.265(8) and 2.290(8) Å]. The metal–metal distances in $[W_2\{\mu\text{-}C(H)Ph\}(CO)_{10}]$ [3.118(1) Å] and in (**1**) [3.111(1) Å] are very similar.

The tungsten atom W(2) is in an essentially octahedral environment defined by the five CO ligands and the midpoint of the W(2)–C(1) vector, the latter lying so that it almost eclipses the radial carbonyl groups C(9)O(9) and C(11)O(11). The angle C(9)–W(2)–C(11) is 173.1(3)°, with the vectors W(2)–C(9) and W(2)–C(11) inclined by only 2 and 3°, respectively, from the plane defined by C(1)W(1)W(2). The terminal carbonyl groups on W(2) are essentially linear [mean W–C–O 176.8(7)°].

The structural data suggest a relationship between the anion of (**1**) and complexes of the type $[W(CO)_4(L)(\text{alkene})]$ [L = CO, PMe_3, or $AsMe_3$].[12] Thus the anion can be viewed as a $W(CO)_5$ complex of the group $(\eta\text{-}C_5H_5)(OC)_2\bar{W}{=}C(H)C_6H_4\text{-}Me\text{-}4$, isolobal with an alkene. This may account for the relatively short W(1)–C(1) distance and the 'eclipsed' structure referred to above. In the complexes $[W(CO)_4(L)(\text{alkene})]$, the preferred structures are those with parallel alignment of the alkene C=C bond and a radial L–W–CO group.[13] A similar structural feature is experimentally observed and theoretically predicted in related chromium– and molybdenum–olefin complexes.[14] The radial CO ligands attached to W(2) give only one signal in the ^{13}C-{^{1}H} n.m.r. spectrum (Table 1), in the temperature range 25 to −40 °C. Presumably this dynamic behaviour is due to a process akin to alkene rotation.[15]

The cyclopentadienyl and tolyl rings are positioned on opposite sides of the plane defined by C(1)W(1)W(2), which makes an angle of 84° with the plane defined by the tolyl ring. The angles about C(1) are not tetrahedral (Table 2) but the W(1)–C(1)–W(2) angle [85.7(2)°] is typical of others found in species with dimetallacyclopropane rings.[10] The two CO groups attached to W(1) are essentially linear [mean W(1)–C–O 177.3(6)°]. The W(1)–C_5H_5 carbon atom distances vary from 2.346(8) Å [W(1)–C(20)] to 2.427(7) Å [W(1)–C(17)], both C(19) and C(20) being significantly closer to W(1) than the other three carbon atoms.

The $[N(PPh_3)_2]^+$ counter ion has a P–N–P angle of 140.1(4)°, a value towards the lower end of the range of these angles (135—180°) found in a variety of salts of this cation.[16] The P–N separations [mean 1.584(6) Å] in (**1**) are typical.[17]

The compound $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ reacts with $[N(PPh_3)_2][WH(CO)_5]$ in a similar manner to its tolylmethylidyne analogue but the resulting complex failed to crystallise from either thf or dichloromethane. These difficulties were circumvented by using the tetraphenylarsonium salt $[AsPh_4][WH(CO)_5]$ and in this manner the salt (**2**) was isolated as red crystals and fully characterised, although it is thermally sensitive, solutions in dichloromethane decomposing at room temperature.

The ^{1}H and $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectra of (**2**) (Table 1) show that two isomeric species (**2a**) and (**2b**) are present in 2:1 ratio. We have previously observed[18] diastereoisomers in related complexes, and these arise from the relative orientations of the substituents on the alkylidene carbon atom with respect to the plane of the dimetallacyclopropane ring and the other ligands present. In (**1**), as mentioned above, the $\eta\text{-}C_5H_5$ and $C_6H_4Me\text{-}4$ groups lie on opposite sides of the $\overline{W(\mu\text{-}C)W}$ ring. In (**2**) the less sterically demanding Me group may allow the existence of an isomer with this substituent on the same side of the ditungstacyclopropane ring as the C_5H_5 ligand. This would be expected to be the minor isomer (**2b**).

Both (**2a**) and (**2b**) show ^{1}H n.m.r. signals characteristic for μ-C(*H*)Me groups at δ 9.54 and 9.00, respectively. Both signals are quartets due to coupling to the methyl group protons, the resonances for which appear as doublets (Table 1). The $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum also shows resonances due to two isomers with peaks at δ 146.9 and 146.5 p.p.m. due to the bridging alkylidene carbon atom.

A possible reason why compound (**2**) is thermally less stable than compound (**1**) is that the methyl substituent gives rise to decomposition pathways involving beta elimination. Such a pathway has been suggested to explain the thermal decomposition of $[Fe_2\{\mu\text{-}C(H)Me\}(CO)_8]$ to $[Fe_3(CO)_{12}]$ and ethylene.[19]

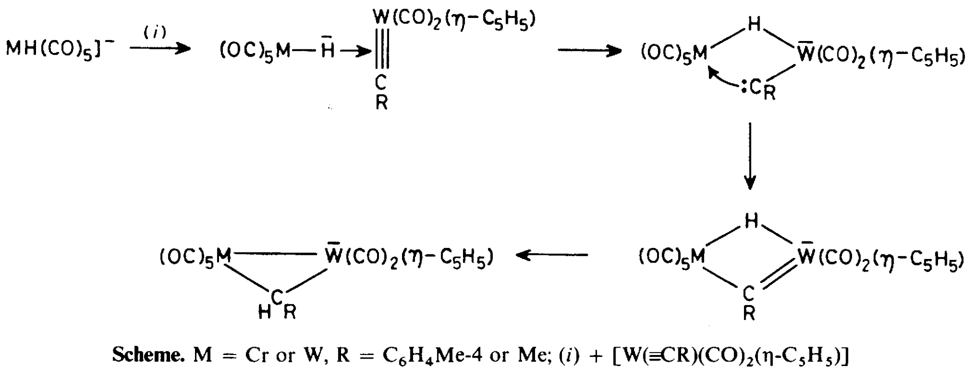
The reaction of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $[N(PPh_3)_2][CrH(CO)_5]$ in thf or dichloromethane initially produces dark red solutions. The i.r. spectrum of the reaction mixture suggests the presence of the salt (**3**). However, attempts to isolate this compound even at low temperatures afforded the salt $[N(PPh_3)_2][W(CO)_3(\eta\text{-}C_5H_5)]$,[20] possibly formed by CO and alkylidene group transfer across the Cr–W bond accompanied by fission of the latter. A similar decomposition pathway has been observed in solution for the complex $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$.[21]

The $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum of (**3**) (Table 1), with the characteristic signal for the μ-*C* nucleus at 148.5 p.p.m., was obtained by mixing the reagents in CH_2Cl_2–CD_2Cl_2 and measuring the spectrum at −40 °C. The spectrum also contained signals due to the species $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, $[N(PPh_3)_2][CrH(CO)_5]$, and $[N(PPh_3)_2][Cr_2(\mu\text{-}H)(CO)_{10}]$, the latter an impurity in the synthesis of the hydridomonochromium complex.

Treatment of $[N(PPh_3)_2][WH(CO)_4\{P(OMe)_3\}]$[22] with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in thf affords a red solution of (**4**). The latter, with i.r. bands in the CO region at 2 039w, 1 913s, 1 874vs, 1 833m, and 1 778w cm^{-1}, is thermally unstable in the solid state, and difficult to purify. However, ^{1}H and $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectra could be obtained before decomposition became too extensive. The $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectrum showed four signals of roughly equal intensity at δ 155.7, 151.8, 151.3, and 130.8 p.p.m., indicative of isomers. Since the anion $[WH(CO)_4\{P(OMe)_3\}]^-$ has the phosphite and hydrido-ligands *cis* to each other,[22] the existence of four isomers of (**4**) could be explained by the $P(OMe)_3$ ligand occupying any one of the four radial sites. In the ^{1}H n.m.r. spectrum there were four resonances {δ 10.13 (s), 9.50 [d, *J*(PH) 9], 9.10 [d, *J*(PH) 2], and 8.17 [d, *J*(PH) 1 Hz]} assignable to a μ-C(*H*)C_6H_4Me-4 proton, as well as signals due to C_5H_5 groups (δ 5.24, 5.27, and 5.31). Broad and unresolved peaks due to Me-4 (δ 2.8—3.2) and C_6H_4 (δ 6.5—7.2) protons were also observed.

The chemistry of the anions $[M(H)(CO)_5]^-$ is dominated by their acting as hydride donors.[23] It seems likely, therefore, that the species (**1**)—(**4**) result from nucleophilic attack of the hydrido-ligand of the anions on the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me). Various pathways are possible depending on whether the initial step is charge controlled or frontier-orbital controlled.[24] A possible route to the alkylidene-bridged dimetal species is shown in the Scheme.

Some reactions of (**1**) have been studied. Treatment with $[CPh_3][BF_4]$ affords the unstable complex $[W_2(\equiv CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)]$,[25] a reaction which can be reversed with $K[BH(CHMeEt)_3]$. Protonation of (**1**) with $HBF_4\cdot Et_2O$ at −78 °C does not afford an isolable neutral ditungsten complex; decomposition to $[W(CO)_6]$ and unidentified products being observed. However, as reported previously,[26] (**1**) reacts with $[AuCl(PPh_3)]$ to afford the gold–tungsten complex (**5**). This prompted a study of a related reaction between (**1**) and $SnPh_3Cl$ in thf, in the presence of $Tl[PF_6]$ to remove chloride ion. Chromatography of the reaction mixture on alumina gave a yellow crystalline compound (**6**). The i.r. spectrum showed two



Scheme. M = Cr or W, R = C_6H_4Me-4 or Me; (*i*) + $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$

bands at 1 948 and 1 886 cm^{-1} in the carbonyl stretching region. In the ^{1}H n.m.r. spectrum a resonance at δ 14.48 suggested the presence of a proton attached to a terminally bound alkylidene group. Signals were also observed for C_5H_5, Ph, and C_6H_4Me-4 groups. The ^{13}C-{^{1}H} n.m.r. spectrum was also informative. A resonance at δ 282.4 p.p.m. with two sets of satellite peaks was in the region for a terminally bound carbon of an alkylidene group. The satellites were ascribed to ^{183}W–^{13}C (92 Hz) and $^{117/119}Sn$–^{13}C (68 Hz) couplings. There was one signal (214.2 p.p.m.) in the region for CO ligands, and again ^{183}W–^{13}C (156 Hz) and $^{117/119}Sn$–^{13}C (136 Hz) couplings were observed. Generally ^{117}Sn and ^{119}Sn two-bond couplings are not resolved.[27,28]

The analytical and spectroscopic data for (**6**) suggested that it had the formulation shown. The species (**1**), (**5**), and (**6**) are then mapped by the isolobal relationship shown below. The

$$W(CO)_5 \longleftrightarrow Au(PPh_3)^+ \longleftrightarrow SnPh_3^+$$

trans arrangement of the alkylidene and triphenyltin ligands in (**6**) is suggested by the spectroscopic data with only one CO resonance in the ^{13}C-{^{1}H} n.m.r. spectrum and with a pattern in the CO stretching region of the i.r. with the higher frequency symmetric absorption being less intense than the lower energy asymmetric stretch.[29] However, in order to establish firmly the structure of (**6**) an *X*-ray diffraction study was carried out.

The results are summarised in Table 3 and the molecular structure is shown in Figure 2 with the atom numbering scheme. As suggested by the spectroscopic data, the $C(H)C_6H_4Me$-4 and $SnPh_3$ ligands adopt a *transoid* configuration. Moreover, the alkylidene ligand is orientated such that the bulky C_6H_4Me-4 group is away from the C_5H_5 ring. The W–C(01) separation [2.032(7) Å] is significantly shorter than that found [2.14(2) Å] for the tungsten–carbon bonding of the alkylidene group in $[W(=CPh_2)(CO)_5]$,[9] probably due to the higher formal oxidation state of the tungsten in (**6**). The Sn–W bond [2.837(1) Å] may be compared with that (2.81 Å) found in the complex $[Sn\{W(CO)_3(\eta\text{-}C_5H_5)\}_2Ph_2]$.[30]

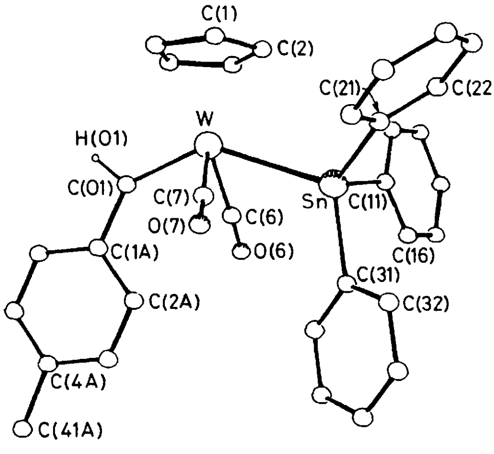


Figure 2. The molecular structure of $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$ (**6**), showing the atom numbering scheme

Some complexes related to (**6**) have been reported.[31] These are the molybdenum and tungsten compounds $[M\{=C(OR')R\}(M'Ph_3)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W, M′ = Ge or Sn, R = Me or Ph, R′ = Me or Et). An *X*-ray crystallographic study on $[Mo\{=C(OEt)Ph\}(GePh_3)(CO)_2(\eta\text{-}C_5H_5)]$ showed that in the crystal the $GePh_3$ and C(OEt)Ph ligands are *transoid*, and in the latter the ethoxy group is adjacent to the cyclopentadienyl ring. However, i.r. studies in heptane solution revealed four bands in the CO stretching region, indicating the existence of two conformers under these conditions. These species rapidly interconvert on the n.m.r. time-scale.

Compound (**6**) is relatively insoluble in hydrocarbon solvents, but a weak i.r. spectrum was measured in methylcyclohexane. Four CO stretching bands were observed at 1 958, 1 937, 1 896, and 1 866 cm^{-1}, suggesting the presence of two conformers, arising through rotation of the $C(H)C_6H_4Me$-4 group about the carbon–tungsten bond. The behaviour of (**6**) and the molybdenum species, mentioned above, contrasts with the properties of the salt $[W\{=C(H)Ph\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)][AsF_6]$ which exists as one conformer in which it is assumed that the Ph substituent lies away from the C_5H_5 ring.[32]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experimental techniques and instrumentation used were as described in the preceding paper.[1] Salts of the anions $[MH(CO)_5]^-$ (M = Cr or W) were prepared as reported elsewhere.[6]

Synthesis of $[N(PPh_3)_2][W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]$ (**1**).—A mixture of $[N(PPh_3)_2][WH(CO)_5]$ (0.44 g, 0.52 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.21 g, 0.52 mmol) in thf (10 cm^3) was stirred for 1 h, after which time the solution had turned dark red. The solution was filtered through a Celite pad (*ca.* 1.5 × 3 cm), and then the solvent was removed *in vacuo*. The residue was washed with light petroleum (2 × 20 cm^3) and crystallised from thf–diethyl ether (1:5) to afford dark red *crystals* of (**1**) (0.53 g, 80%) (Found: C, 53.1; H, 3.5; N, 0.9. $C_{56}H_{43}NO_7P_2W_2 \cdot 0.5C_4H_{10}O$ requires C, 53.2; H, 3.7; N, 1.1%); $\nu_{max.}$(CO) at 2 039m, 1 955w, 1 913s, 1 875m, and 1 789w cm^{-1} (thf).

Synthesis of $[AsPh_4][W_2\{\mu\text{-}C(H)Me\}(CO)_7(\eta\text{-}C_5H_5)]$ (**2**).—Freshly prepared $[AsPh_4][WH(CO)_5]$ (0.92 g, 1.30 mmol) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.43 g, 1.30 mmol) were stirred in thf (10 cm^3) for 45 min. The solution was concentrated *in vacuo*

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$ (**6**)

W–Sn	2.837(1)	W–C(01)	2.032(7)	C(01)–C(1A)	1.462(9)	Sn–C(11)	2.187(4)
W–C(6)	1.988(6)	C(6)–O(6)	1.158(7)	C(01)–H(01)	1.08(8)	Sn–C(21)	2.177(5)
W–C(7)	1.991(7)	C(7)–O(7)	1.143(8)	W–C(cp)*	2.371(5)	Sn–C(31)	2.185(4)
Sn–W–C(01)	137.8(2)	C(01)–W–C(6)	80.5(3)	W–Sn–C(11)	112.2(1)	W–C(01)–C(1A)	137.7(5)
Sn–W–C(6)	71.3(2)	C(01)–W–C(7)	80.8(3)	W–Sn–C(21)	110.0(1)	W–C(01)–H(01)	115(5)
Sn–W–C(7)	72.7(2)	C(6)–W–C(7)	97.4(2)	W–Sn–C(31)	114.8(1)	C(1A)–C(01)–H(01)	107(5)
W–C(6)–O(6)	174.7(6)	W–C(7)–O(7)	177.1(7)				

* Mean distance to cyclopentadienyl carbons.

Table 4. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.388 53(3)	0.111 68(2)	0.202 61(2)	C(25)	0.434 8(9)	0.537 9(7)	0.110 6(5)
W(2)	0.605 62(3)	0.181 81(2)	0.132 26(2)	C(26)	0.351 8(8)	0.563 6(6)	0.157 8(4)
C(1)	0.478 4(8)	0.250 0(5)	0.221 2(4)	C(27)	0.329 9(7)	0.758 8(6)	0.332 2(4)
C(2)	0 555 4(7)	0.304 3(5)	0.287 6(4)	C(28)	0.375 2(8)	0.708 3(6)	0.392 0(4)
C(3)	0.640 1(8)	0.261 7(6)	0.342 6(4)	C(29)	0.451 2(9)	0.755 0(7)	0.454 3(5)
C(4)	0.708 5(8)	0.316 1(6)	0.405 2(4)	C(30)	0.484 8(10)	0.850 3(7)	0.458 3(5)
C(5)	0.696 3(9)	0.418 1(6)	0.415 9(5)	C(31)	0.443 0(10)	0.899 8(7)	0.399 0(5)
C(6)	0.772 7(12)	0.478 3(9)	0.481 4(6)	C(32)	0.363 1(9)	0.855 5(6)	0.336 1(5)
C(7)	0.610 5(9)	0.462 8(6)	0.361 2(5)	C(33)	0.107 3(7)	0.775 5(5)	0.207 1(4)
C(8)	0.543 0(8)	0.407 6(6)	0.299 0(4)	C(34)	0.084 7(8)	0.779 9(6)	0.132 2(5)
C(9)	0.663 4(8)	0.321 6(6)	0.160 2(5)	C(35)	−0.025 5(9)	0.833 0(6)	0.098 5(5)
O(9)	0.699 3(6)	0.401 7(4)	0.175 1(4)	C(36)	−0.113 0(9)	0.877 4(7)	0.139 7(6)
C(10)	0.721 8(10)	0.170 9(7)	0.062 1(5)	C(37)	−0.091 5(9)	0.873 1(6)	0.212 0(6)
O(10)	0.788 9(8)	0.164 7(6)	0.019 3(5)	C(38)	0.020 0(8)	0.822 9(6)	0.247 5(5)
C(11)	0.564 4(8)	0.038 3(6)	0.096 7(5)	C(39)	0.087 9(8)	0.438 9(6)	0.311 3(4)
O(11)	0.550 8(6)	−0.042 7(4)	0.072 0(3)	C(40)	−0.009 7(8)	0.387 2(6)	0.328 4(5)
C(12)	0.453 3(10)	0.230 0(6)	0.057 0(5)	C(41)	0.026 7(9)	0.304 2(6)	0.363 9(5)
O(12)	0.368 6(7)	0.260 3(5)	0.015 2(4)	C(42)	0.160 9(9)	0.276 4(6)	0.382 3(5)
C(13)	0.755 9(9)	0.136 7(6)	0.212 3(5)	C(43)	0.256 6(9)	0.327 9(6)	0.365 3(5)
O(13)	0.843 0(7)	0.112 7(5)	0.255 3(4)	C(44)	0.221 5(8)	0.409 0(6)	0.330 7(4)
C(14)	0.410 9(8)	0.124 8(5)	0.305 4(4)	C(45)	−0.067 5(7)	0.620 1(6)	0.309 1(4)
O(14)	0.422 9(6)	0.128 4(4)	0.368 5(3)	C(46)	−0.202 9(8)	0.628 3(6)	0.280 7(5)
C(15)	0.516 2(8)	0.007 8(6)	0.232 6(4)	C(47)	−0.279 2(10)	0.639 4(7)	0.319 7(6)
O(15)	0.590 8(6)	−0.054 2(4)	0.252 6(4)	C(48)	−0.223 8(11)	0.745 3(7)	0.383 5(6)
C(16)	0.199 8(8)	0.173 1(6)	0.121 8(5)	C(49)	−0.090 8(10)	0.736 2(7)	0.412 4(6)
C(17)	0.242 0(8)	0.086 9(6)	0.083 9(5)	C(50)	−0.011 1(9)	0.672 6(7)	0.375 8(5)
C(18)	0.229 4(9)	0.006 9(7)	0.121 9(5)	C(51)	−0.033 3(7)	0.504 9(5)	0.172 3(4)
C(19)	0.177 2(8)	0.043 5(6)	0.181 8(5)	C(52)	−0.102 8(8)	0.570 4(6)	0.127 1(5)
C(20)	0.159 8(8)	0.147 5(6)	0.183 7(5)	C(53)	−0.150 2(8)	0.540 7(7)	0.054 7(5)
P(1)	0.234 3(2)	0.693 30(13)	0.250 17(10)	C(54)	−0.127 8(9)	0.446 6(7)	0.025 6(5)
P(2)	0.046 3(2)	0.545 10(13)	0.264 81(10)	C(55)	−0.059 1(9)	0.381 8(7)	0.069 3(5)
N	0.181 8(6)	0.598 1(5)	0.270 9(4)	C(56)	−0.011 7(8)	0.410 6(6)	0.142 9(5)
C(21)	0.346 1(7)	0.659 9(6)	0.188 8(4)	O	−0.000 00	−0.000 00	0.500 00
C(22)	0.421 2(9)	0.729 3(7)	0.171 4(5)	C(57)	0.206(3)	−0.038(2)	0.556 7(11)
C(23)	0.504 2(9)	0.701 8(8)	0.122 8(5)	C(58)	−0.068(4)	0.020(3)	0.441(2)
C(24)	0.510 0(9)	0.607 9(8)	0.093 4(5)	C(59)	0.133(4)	−0.021(3)	0.493(2)

to *ca.* 5 cm^3, and diethyl ether (10 cm^3) added. The solution was then filtered through a Celite pad (*ca.* 1.5 × 3 cm) and solvent removed *in vacuo.* The residue was washed with light petroleum (2 × 20 cm^3) and crystallised from thf–diethyl ether (1:5) to afford red *microcrystals* of (**2**) (0.82 g, 61%) (Found: C, 43.6; H, 2.8. $C_{38}H_{29}AsO_7W_2$ requires C, 43.9; H, 2.8%); $\nu_{max.}$(CO) at 2 037m, 1 947w, 1 909s, 1 885m, 1 868m, and 1 784w cm^{-1} (thf).

Reaction of $[N(PPh_3)_2][CrH(CO)_5]$ *with* $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.—Although attempts to isolate $[N(PPh_3)_2][CrW\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]$ (**3**) afforded $[N(PPh_3)_2][W(CO)_3(\eta\text{-}C_5H_5)]$, the chromium–tungsten species could be observed by i.r. and n.m.r. spectroscopy in solutions formed by mixing equimolar amounts of $[N(PPh_3)_2][CrH(CO)_5]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$; $\nu_{max.}$(CO) at 2 023m, 1 945w, 1 912s, 1 897s, 1 879s, and 1 792w cm^{-1} (thf).

Reaction of $[N(PPh_3)_2][WH(CO)_4\{P(OMe)_3\}]$ *with* $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.—Treatment of $[N(PPh_3)_2][WH(CO)_4\{P(OMe)_3\}]$ with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in a similar manner to the synthesis of (**1**) affords the unstable red compound $[N(PPh_3)_2][W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_6\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**4**); available spectroscopic data are given in the Results and Discussion section.

Synthesis of $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$. (**6**).—A mixture of compound (**1**) (0.76 g, 0.60 mmol), $SnPh_3Cl$ (0.65 g, 1.68 mmol), and $Tl[PF_6]$ (0.70 g, 2.01 mmol) in thf (10 cm^3) was stirred for 16 h, after which time the solution had turned yellow and i.r. analysis showed an absence of (**1**). The reaction mixture was then filtered through an alumina pad (*ca.* 1.5 × 3 cm) and the solvent removed *in vacuo.* The product was purified by chromatography on alumina (1.5 × 20 cm column), eluting with a light petroleum–CH_2Cl_2 mixture (4:1). The desired product was eluted as a yellow band, removal of the solvent *in vacuo* affording yellow *microcrystals* of (**6**) (0.21 g, 45%) (Found: C, 52.2; H, 3.5. $C_{33}H_{28}O_2SnW$ requires C, 52.2; H, 3.7%); $\nu_{max.}$(CO) at 1 948m and 1 886s cm^{-1} (thf).

Crystal Structure Determinations.—(*a*) $[N(PPh_3)_2][W_2\{\mu\text{-}C(H)C_6H_4Me\text{-}4\}(CO)_7(\eta\text{-}C_5H_5)]$ (**1**). Crystals of (**1**) grow as red prisms from thf–diethyl ether. Diffracted intensities were recorded at 200 K from a crystal of dimensions *ca.* 0.15 × 0.15 × 0.40 mm (faces ⟨0 1 0⟩, ⟨0 0 1⟩, and ⟨1 0 $\bar{1}$⟩). Of the total of 8 374 independent reflections ($2.9 \leqslant 2\theta \leqslant 55°$, θ–2θ scans), measured on a Nicolet *P*3*m* four-circle diffractometer, 6 361 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and final refinement of the structure. Lorentz, polarisation, and *X*-ray absorption (analytical) corrections were applied.

Crystal data for (**1**). $C_{56}H_{43}NO_7P_2W_2 \cdot 0.5C_4H_{10}O$, M = 1 308, triclinic, a = 10.326(3), b = 13.856(4), c = 19.114(4) Å, α = 97.62(2), β = 102.72(2), γ = 86.98(2)°, U = 2 643(2) Å^3, D_m (flotation) = 1.68 g cm^{-3}, Z = 2, D_c = 1.70 g cm^{-3}, $F(000)$ = 1 282, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 45.6 cm^{-1}.

The two tungsten atoms were located from a Patterson syn-

Table 5. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.465 52(1)	0.149 73(3)	0.420 48(1)	C(12)	0.436 8(2)	0.255 8(6)	0.286 78(13)
Sn	0.438 63(2)	−0.020 80(5)	0.348 73(1)	C(13)	0.407 8(2)	0.350 5(6)	0.255 62(13)
C(1)	0.588 1(3)	0.176 3(6)	0.420 6(2)	C(14)	0.341 1(2)	0.318 4(6)	0.236 56(13)
C(2)	0.556 1(3)	0.243 1(6)	0.384 7(2)	C(15)	0.303 2(2)	0.191 6(6)	0.248 66(13)
C(3)	0.516 4(3)	0.374 7(6)	0.394 2(2)	C(16)	0.332 2(2)	0.096 9(6)	0.279 82(13)
C(4)	0.523 8(3)	0.389 2(6)	0.436 1(2)	C(11)	0.399 0(2)	0.129 0(6)	0.298 88(13)
C(5)	0.568 1(3)	0.266 6(6)	0.452 4(2)	C(22)	0.560 4(3)	−0.116 2(6)	0.300 39(12)
C(01)	0.422 5(4)	0.173 9(8)	0.471 7(2)	C(23)	0.620 8(3)	−0.195 2(6)	0.292 81(12)
C(1A)	0.362 1(4)	0.113 2(8)	0.489 1(2)	C(24)	0.654 0(3)	−0.298 2(6)	0.320 90(12)
C(2A)	0.315 8(4)	0.000 1(8)	0.470 5(2)	C(25)	0.626 8(3)	−0.322 0(6)	0.356 56(12)
C(3A)	0.257 8(4)	−0.047 0(8)	0.487 7(2)	C(26)	0.566 5(3)	−0.243 0(6)	0.364 14(12)
C(4A)	0.241 6(3)	0.016 0(8)	0.523 0(2)	C(21)	0.533 3(3)	−0.140 1(6)	0.336 06(12)
C(5A)	0.287 7(4)	0.128 2(8)	0.542 1(2)	C(32)	0.372 8(2)	−0.252 7(5)	0.335 24(14)
C(6A)	0.346 1(4)	0.175 6(8)	0.525 0(2)	C(33)	0.322 8(2)	−0.471 5(5)	0.335 75(14)
C(41A)	0.176 9(4)	−0.035 8(9)	0.540 6(3)	C(34)	0.259 3(2)	−0.439 7(5)	0.349 92(14)
C(6)	0.366 0(4)	0.181 7(8)	0.398 5(2)	C(35)	0.245 8(2)	−0.290 0(5)	0.363 57(14)
O(6)	0.308 1(2)	0.210 3(6)	0.387 54(14)	C(36)	0.292 9(2)	−0.172 1(5)	0.363 05(14)
C(7)	0.458 0(3)	−0.074 4(8)	0.434 6(2)	C(31)	0.359 4(2)	−0.203 9(5)	0.348 89(14)
O(7)	0.454 9(3)	−0.203 1(6)	0.444 38(14)				

thesis, and the remaining non-hydrogen atoms from successive electron-density difference syntheses. Blocked-cascade least-squares refinement was performed, with anisotropic thermal parameters for all non-hydrogen atoms except the carbon atoms of the disordered diethyl ether solvent. Hydrogen atoms were incorporated at calculated 'riding' positions with a fixed isotropic thermal parameter 1.2 times $U_{\text{equiv.}}$ of the carbon atom to which they are attached. Individual weights were apportioned according to the scheme $w = [\sigma^2(F) + 0.000\,4|F_o|^2]^{-1}$, and refinement converged at *R* 0.034 (*R′* 0.041). A final electron-density difference synthesis showed no peaks >1.31 or <0.49 e Å^{-3} and these were located close to the tungsten atoms. Atomic scattering factors, with corrections for anomalous dispersion, were taken from ref. 33, and all computations were carried out within the laboratory on an Eclipse (Data General) S230 computer with the 'SHELXTL' system of programs.[34] Atomic co-ordinates for (**1**) are given in Table 4.

(*b*) $[\mathrm{W\{{=}C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)}]$ (**6**). Crystals of (**6**) grow as rectangular prisms from dichloromethane–light petroleum. Diffracted intensities were measured at 210 K from a crystal of dimensions *ca.* 0.10 × 0.35 × 0.45 mm. Of the total of 4 391 independent reflections ($3 \leqslant 2\theta \leqslant 50°$, ω-scans) measured on a Nicolet *P*3*m* four-circle diffractometer, 3 787 satisfied the criterion $I \geqslant 1\sigma(I)$. Lorentz, polarisation, and *X*-ray absorption (empirical, μR = 1.0) corrections were applied.

Crystal data for (**6**). $\mathrm{C_{33}H_{28}O_2SnW}$, *M* = 759, monoclinic, *a* = 19.258(8), *b* = 8.537(2), *c* = 34.06(2) Å, β = 97.05(4)°, *U* = 5 557(4) Å^3, *Z* = 8, D_c = 1.78 g cm^{-3}, *F*(000) = 2 920, space group *C*2/*c* (no. 15), μ(Mo-K_α) = 51.6 cm^{-1}.

The solution and refinement were carried out as for (**1**).[34] The hydrogen atom H(01) was located from an electron-density difference map and refined satisfactorily, while all other hydrogen atoms were incorporated at calculated positions. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\,3|F_o|^2]^{-1}$ gave a reasonable analysis with convergence at *R* 0.037 (*R′* 0.037). Atomic co-ordinates for (**6**) are given in Table 5.

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