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Structure of [$W_2(\mu\text{-}C_2)\{OC(CH_3)_3\}_6$]: a Dimetallabutadiyne

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Abstract. (μ-Dicarbido)-hexa(1,1-dimethylethoxy)-ditungsten, [$W_2(C_2)(C_4H_9O)_6$], $M_r = 830.41$, rhombohedral, $R\bar{3}$, $a = 11.301\ (4)$ Å, $\alpha = 52.93\ (3)$°, $V = 851.40\ (5)$ Å^3, $Z = 1$, $D_x = 1.62$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 71.7$ cm^{-1}, $F(000) = 406$, $T = 223$ K, $R = 0.039$, $wR = 0.055$ for 948 observed [$F_o > 5\sigma(F_o)$] reflections. The structure of the title compound was determined as part of investigations concerning the presence or absence of π conjugation in metal–carbon multiply bonded complexes. The compound undergoes a destructive phase transition at low temperature, but data collected at 223 K were sufficient for refinement. The molecule exhibits a diyne-like structure, with the $W\equiv C$ bond length [1.79 (1) Å] within the range observed for high-oxidation-state alkylidyne complexes. The internal C—C bond is unusually short [1.38 (2) Å] for a single bond, but such shortening has been observed previously in organic diynes. These data are critically compared to those reported for the toluene solvate of the title compound.

Introduction. Molecules and polymers containing conjugated π systems are of current interest in organic chemistry owing to their potential uses in photonics (Prasad & Williams, 1991). A developing facet of this work is the incorporation of transition metals into such molecules, either as pendant groups (Marder, Perry, Tiemann & Schaefer, 1991) or as integral parts of the chain framework (Cayton & Chisholm, 1989; Gilbert & Rogers, 1991). Our interest lies in the latter, and we became interested in those metals for which metal–carbon multiple bonds exist, anticipating that such moieties could be used as templates for conjugated metal–carbon π chains. In an effort to ascertain what types of molecules might

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exhibit unusual electronic structures, we noted that the title complex was described as dark red (Listemann & Schrock, 1985), whereas all alkylidynes previously reported were described as colorless or yellow (Schrock, Clark, Sancho, Wengrovius, Rocklage & Pedersen, 1982). This suggested the possibility that the electron density in this 'dialkylidyne' (also called a μ-dicarbide or a dimetallabutadiyne) is delocalized. To address this question, we determined the molecular structure and report here the results.

Experimental. The material was prepared from $[W_2\{OC(CH_3)_3\}_6]$ and 4,6-decadiyne (Listemann & Schrock, 1985), and crystallized as dark-red cubes by slow cooling of a hot toluene solution under argon. The data crystal measured 0.20 × 0.25 × 0.40 mm and was mounted in a thin-walled glass capillary under argon, whereupon the capillary was flame sealed. The crystal was cooled to 223 K with a cold N_2 stream on an Enraf–Nonius CAD-4 diffractometer. Using graphite-monochromated Mo $K\alpha$ radiation, lattice parameters were obtained from 25 well centered reflections with $\theta > 20°$. 2975 data were collected in the triclinic cell $a = 10.073$ (2), $b = 10.069$ (4), $c = 11.304$ (4) Å, $\alpha = 116.49$ (3), $\beta = 90.01$ (2), $\gamma = 119.97$ (3)° using ω–2θ scans for $2 \leq 2\theta \leq 50°$; h 0 to +11, $k \pm 11$, $l \pm 13$. Intensity standards (700, 060 and 0,0,10) were checked every 3600 s of exposure and showed a maximum deviation of ± 2%. Orientation standards were checked every 500 reflections. The raw data were corrected for Lorentz–polarization effects and were empirically corrected for absorption using ψ-scan data ($\mu = 71.7$ cm^{-1}, range of relative transmission factors 57–100%). The data were then transformed to $R\bar{3}$ (No. 148) and averaged ($R_{\rm int} = 0.098$), providing 977 unique reflections, 948 with $[F_o > 5\sigma(F_o)]$ considered observed. The structure was solved using the *SHELXS*86 (Sheldrick, 1990) direct-methods program, and refined using *SHELX*76 (Sheldrick, 1976), which provided scattering factors and corrections for anomalous dispersion. Non-H atoms were located through difference Fourier techniques and refined anisotropically with full-matrix non-linear least squares; the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma(F_o)^2 + 0.0009(F_o)^2]^{-1}$, varying 52 parameters. Owing to the large thermal parameters exhibited by the methyl C atoms, H atoms were not included in the refinement. An attempt was made to solve the structure in the higher symmetry space group $R\bar{3}m$, but this led to a larger $R_{\rm int}$, larger residuals and required a disordered model. The final residuals were $R = 0.039$, $wR = 0.055$, $S = 2.05$. Δ/σ in the final refinement cycle was less than 0.01, and the largest peak in the final difference Fourier map was 1.0 e Å^{-3} near W.

The large value of $R_{\rm int}$ compared to the final agreement factors R and wR prompted a review of the original data. Splitting the data into unaveraged reciprocal-space octants and comparing ΔF values revealed only a random distribution of e.s.d.'s. We thus cannot fully explain the large difference between $R_{\rm int}$ and R/wR. The crystal quality, mosaic spread, extinction and incomplete modeling of absorption utilizing ψ scans may all contribute to the problem. It is equally impossible to ascertain if the determined structure is an averaged one.

Discussion. Fractional coordinates and anisotropic thermal parameters are given in Table 1, bond distances and angles in Table 2, and an *ORTEP*II (Johnson, 1976) illustration of the molecule is presented in Fig. 1.*

The title complex crystallizes in the rhombohedral space group $R\bar{3}$ with molecules in special positions having $\bar{3}$ point symmetry. Atoms W and C1 lie on the crystallographic threefold axis; as a result, the dimetallabutadiyne moiety W≡C1—C1≡W within the molecule is strictly linear. The molecules almost exhibit the additional mirror planes expected for the symmetry $\bar{3}m$; however, the torsion angle W—O1—C2—C3, which is rigorously 180° for $\bar{3}m$ symmetry, is actually 167.7° in the crystal structure. The molecular pseudo-mirror planes do not coincide with the true mirror planes which would be introduced if the crystals had the higher symmetry space group $R\bar{3}m$.

The W≡C1 triple-bond length of 1.79 (1) Å is consistent with those observed previously in 'W^{VI},d^0' alkylidynes such as $[C_6H_5C{\equiv}W\{OC(CH_3)_3\}_3]$ (Cotton, Schwotzer & Shamshoum, 1984) and $[(CH_3)_3CC{\equiv}W\{OC(CH_3)_3\}_3]$ (Gilbert & Hopkins, 1992), suggesting that no loss of metal–carbon bond order occurs upon bonding to an identical group. The W—O bond length is typical as well (Cotton *et al.*, 1984; Gilbert & Hopkins, 1992) and suggestive of π-type interaction between these atoms (Chisholm, Cotton, Murillo & Reichert, 1977). The W—O and W≡C bond lengths and the O—W≡C and O—W—O angles are sufficiently similar that the coordination geometry around W is nearly tetrahedral. The considerable steric interaction between the three *tert*-butoxide ligands results in a large W—O—C2 angle [142.7 (4)°], and in the 'bending-in' of these ligands; the *tert*-butyl group lies *over* the W≡C1—C1≡W fragment rather than being tipped away from it.

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* A list of structure factors and an *ORTEP*II side view of the title compound have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55731 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0421]

Table 1. *Fractional coordinates and anisotropic thermal parameters* (Å^2) *for the title compound*

Anisotropic thermal parameters are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.08553 (1)	0.08553 (1)	0.08553 (1)	0.0457 (3)	0.0457 (3)	0.0457 (3)	−0.0200 (1)	−0.0200 (1)	−0.0200 (1)
O(1)	0.2862 (6)	0.0958 (6)	−0.0650 (6)	0.050 (3)	0.064 (3)	0.062 (3)	−0.025 (2)	−0.020 (2)	−0.030 (3)
C(1)	0.0238 (4)	0.0238 (4)	0.0238 (4)	0.037 (3)	0.037 (3)	0.037 (3)	−0.014 (2)	−0.014 (2)	−0.014 (2)
C(2)	0.4089 (9)	0.075 (1)	−0.2157 (9)	0.043 (4)	0.066 (5)	0.056 (4)	−0.023 (4)	−0.010 (3)	−0.032 (4)
C(3)	0.551 (2)	0.078 (3)	−0.238 (2)	0.100 (9)	0.33 (3)	0.13 (1)	−0.14 (1)	0.031 (8)	−0.14 (1)
C(4)	0.432 (2)	−0.079 (2)	−0.204 (2)	0.10 (1)	0.13 (1)	0.20 (2)	−0.051 (9)	0.007 (9)	−0.13 (1)
C(5)	0.331 (3)	0.221 (2)	−0.339 (2)	0.18 (2)	0.15 (2)	0.086 (9)	−0.02 (1)	−0.07 (1)	−0.03 (1)

Table 2. *Bond distances* (Å) *and angles* (°)

W—O(1)	1.865 (5)	C(2)—C(3)	1.49 (1)
W—C(1)	1.79 (1)	C(2)—C(4)	1.53 (1)
O(1)—C(2)	1.457 (9)	C(2)—C(5)	1.55 (2)
C(1)—C(1^{i})	1.38 (2)		

O(1)—W—C(1)	108.3 (1)	O(1)—C(2)—C(4)	107.5 (8)
O(1)—W—O(1^{ii})	110.6 (1)	O(1)—C(2)—C(5)	103.0 (9)
W—O(1)—C(2)	142.7 (4)	C(3)—C(2)—C(4)	116 (1)
W—C(1)—C(1^{i})	180.0	C(3)—C(2)—C(5)	113 (1)
O(1)—C(2)—C(3)	105.8 (7)	C(4)—C(2)—C(5)	110 (1)

Symmetry code: (i) $-x, -y, -z$; (ii) z, x, y.

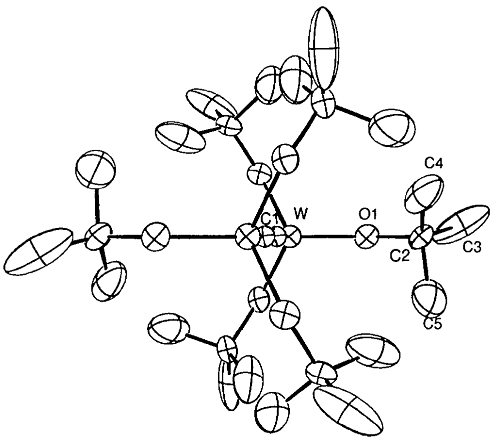

Fig. 1. *ORTEP*II (Johnson, 1976) illustration of the title compound with 30% probability ellipsoids for thermal motion.

As this work was in progress, we learned that other workers had determined the structure of the title complex at 102 K as a toluene solvate $[\mathrm{C{\equiv}W\{OC(CH_3)_3\}_3}]_2\cdot2\mathrm{C_6H_5CH_3}$ (Caulton, Cayton, Chisholm, Huffman, Lobkovsky & Xue, 1992), which crystallized in the low-symmetry space group $P\bar{1}$. Comparison of these distance and angle data with ours allows a more complete evaluation of the experimental errors present in the structure determinations and of possible structure–property relationships.

In the solvated molecule, the W≡C triple-bond distance was found to be 1.819 (16) Å, and was therefore felt to be slightly longer than expected. Our finding a shorter length (though equivalent within 3σ) for the same bond in the same molecule suggests that this interpretation is incorrect, and that the previous value is typical within the bounds of experimental error.

The C1—C1 bond length of 1.34 (3) Å in the solvated molecule appeared short for a C—C single bond, even one between two *sp*-hybridized C atoms. This led Caulton *et al.* to suggest that this, along with theoretical studies and NMR spectroscopic data, represented evidence of delocalization of electron density along the dimetallabutadiyne chain. We are skeptical of this, since our data give a value of 1.38 (2) Å for this bond, again within experimental error of the previous value, but more in line with distances determined for C—C 'single' bonds in organic polyynes (Dale, 1969). It is not entirely clear whether these short bond distances reflect delocalization or simply the considerable *s*-orbital character in the bond. We are attempting to prepare longer chain molecules to address this issue.

Finally, we note an intriguing difference in physical properties between the title complex and the toluene solvate. As is apparent from the *ORTEP*II drawing and the anisotropic thermal parameters, the *tert*-butoxy methyl groups exhibit significant thermal motion. We were unable to develop a static disorder model for this, and attempted several times to attack the problem by cooling the crystals below 223 K. Unfortunately, all the crystals investigated exhibited a large mosaic spread below this temperature (the spread developing over approximately 2 h at temperatures between 183 and 223 K, and within minutes at 173 K), and eventually could not be properly indexed. This appears to result from an irreversible crystalline phase transition through which crystals of the compound pass as they are cooled. It seems likely that the 'slowing down' of the methyl-group rotation plays a significant role in this transition. It is thus interesting that the toluene solvate is stable to 102 K, and suggests that the interstitial solvent may cause the methyl groups to lock near room temperature.

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Diphenylphosphinoferrocene

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Abstact. (η^5-Cyclopentadienyl)[1-(diphenylphosphino)-η^5-cyclopentadienyl]iron, $[Fe(C_5H_5)(C_{17}H_{14}P)]$, $M_r = 370.21$, triclinic, $P\bar{1}$, $a = 8.344$ (1), $b = 9.387$ (1), $c = 12.527$ (2) Å, $\alpha = 97.27$ (1), $\beta = 101.18$ (1), $\gamma = 110.79$ (1)°, $V = 879.2$ (2) Å^3, $Z = 2$, $D_x = 1.398$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.94$ mm^{-1}, $F(000) = 384$, $T = 298$ K, $R = 0.031$ for 2606 observed reflections. The title compound shows an eclipsed geometry for the ferrocenyl rings, with a rotation of 6.6 (1)° from an exact eclipsed conformation. The cyclopentadienyl rings are essentially parallel, the dihedral angle between them being 1.4°. Both phenyl rings are approximately orthogonal to the cyclopentadienyl rings.

Introduction. As part of our studies on unsymmetric ferrocenyl diphosphines, we have synthesized diphenylphosphinoferrocene and determined its X-ray crystal structure in order to compare it with other ferrocenyl mono- and diphosphines.

Experimental. $(C_5H_5)Fe(C_5H_4PPh_2)$ was obtained by the transmetalation of $(C_5H_4SnBu_3)Fe(C_5H_4PPh_2)$ (Wright, 1990) with 1 equiv. of ^{n}BuLi followed by treatment with water. Crystals suitable for X-ray crystallographic studies were obtained by slow evaporation of a dichloromethane solution at 298 K. A prismatic crystal with dimensions 0.41 × 0.39 × 0.48 mm was used. Cell constants were derived from least-squares refinement of 25 reflections in the range $15 \leq 2\theta \leq 32.62°$. Intensity data were collected at 298 K using the $\theta/2\theta$ scan mode on a Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation, with scan width $(0.60 + 0.35\tan\theta)°$ and scan speed 1–8° min^{-1}. A total of 3315 reflections were measured with $2 \leq 2\theta \leq 50°$ $(-9 \leq h \leq 8,\ 0 \leq k \leq 11,\ -14 \leq l \leq 14)$ which were averaged to 2606 unique reflections with $R_{\rm int} = 0.015$. Three standard reflections ($20\bar{5}$, $10\bar{5}$, $21\bar{4}$) were measured every 7200 s and only small (< 1.5%) random variations were observed. Lorentz and polarization corrections were applied. An empirical absorption correction based on a series of ψ scans was applied to the data: $T_{\rm min} = 0.927$, $T_{\rm max} = 0.999$.

The structure was solved by direct methods and refined by full-matrix least-squares routines, initially with isotropic and finally with anisotropic thermal parameters for non-H atoms. All H atoms were located in a difference Fourier synthesis and fixed in the final cycles of refinement. $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + (0.01|F_o|)^2]$. Final $R = 0.031$, $wR = 0.038$, $R_{\rm all} = 0.039$ and $S = 1.84$ were obtained using 217 variables and 2606 observed reflections $[I_o > 2.5\sigma(I_o)]$. The largest Δ/σ was 0.001;

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