Paramagnetic 1,3-Dimetallacyclobutadienes of Tungsten(VI): 2,4-Bis(trimethylsilyl)-1,3-dihalogeno-1,1,3,3-tetrakis(trimethylsilylmethyl)-1,3-ditungstacyclobutadienes

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Addition of halogens, X_2, to hydrocarbon solutions of $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$ leads to the novel paramagnetic W^{VI} containing compounds $[X(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$, where X = Cl, Br, and I, which contain tungsten atoms in a pseudo trigonal bipyramidal environment (X axial) joined along a common axial–equatorial edge by the μ-$CSiMe_3$ ligands (W–W 2.75 Å).

The d^1–d^1 dimer $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$, (**1**), has been known for several years.[1,2] Recently we have found that alkynes,[3,4] allenes,[5] and diazoalkanes[6] add to (**1**) to give compounds of type (**2**), wherein the electron pair of the W–W bond is used in back bonding to the π-acceptor ligand, un. It was of interest to attempt an oxidative-addition of an X_2 substrate across the W–W centre since d^0–d^0 1,3-ditungstacyclobutadienes are possible intermediates in the interconversion of ditungstatetrahedrane and tungsten alkylidyne containing compounds.[7,8]

The addition of 1 equiv. of the halogens, X_2, to (**1**) in hexane solutions at −40 °C yields the new class of d^0–d^0 1,3-ditungstacyclobutadienes, (**3**), according to equation (1). The compounds (**3**) can be crystallized from hexanes as dark brown air-sensitive solids in *ca.* 40% yield. They are extremely air-sensitive in solution.† A related reaction involving (**1**) and $Pr^iO_2Pr^i$ yielded a non-crystalline product which like the halogeno compounds (**3**), described below, appeared paramagnetic.

$$[(Me_2SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2 + X_2 \rightarrow [X(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2 \quad (1)$$

(**3**)

a; X = Cl
b; X = Br
c; X = I

The molecular structure of the chloro and bromo compounds, (**3a**) and (**3b**), respectively, were determined by single crystal *X*-ray crystallography.‡ The molecular structure of (**3a**) and (**3b**) is depicted in Figure 1. It seems likely that the iodo compound (**3c**) is similarly related. Pertinent structural data are summarized in Table 1. Each tungsten atom is in a distorted trigonal bipyramidal environment. The halogeno atoms and the Me_3SiCH_2 ligands occupy terminal axial and equatorial sites, respectively. The two halves of the centrosymmetric molecules are joined by the μ-$CSiMe_3$ ligands which occupy common axial–equatorial edges. The W–W

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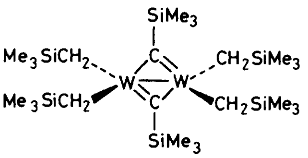
† Dry and oxygen-free atmospheres (N_2) and solvents were used throughout. Satisfactory elemental analyses were obtained.

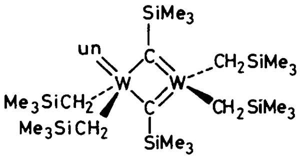
‡ *Crystal data:* (**3a**) at −160 °C: space group $P2_1/n$, $a = 9.960(4)$, $b = 18.438(9)$, $c = 11.743(4)$ Å, $\beta = 114.84(2)°$, $Z = 4$, $D_c = 3.251$ g cm^{-3}. Of 3449 unique intensities, 2985 having $F > 3.00\sigma(F)$ were used to solve the structure by Patterson and Fourier techniques. Excessive thermal motion was evident in the Me_3Si groups even at −160 °C. As hydrogen atoms were not found in the difference Fourier, they were included in the final refinement as fixed atom contributors. Final residuals were $R(F) = 0.044$ and $R_w(F) = 0.049$. (**3b**) at −157 °C: space group $P2_1/a$, $a = 11.807(3)$, $b = 18.321(5)$, $c = 10.072(2)$ Å, $\beta = 115.18(1)°$, $Z = 2$, $D_c = 1.763$ g cm^{-3}. Of 2580 unique intensities, 2030 having $F > 3.00\sigma(F)$ were used to solve the structure by Patterson and Fourier techniques. Significant thermal motion was evident even at −157 °C and hydrogen atoms were included as fixed atom contributors in the final cycles of the least squares refinement. The final residuals were $R(F) = 0.066$ and $R_w(F) = 0.075$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Pertinent bond distances and angles for the centrosymmetric $W_2X_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ molecules [X = Cl and Br: (**3a**) and (**3b**), respectively].

	Distance/Å			Angle/°	
Atoms	(**3a**)	(**3b**)	Atoms	(**3a**)	(**3b**)
W(1)–W(1′)	2.760(1)	2.757(1)	X–W(1)–C(13)	172.6(3)	176.5(3)
W(1)–X	2.481(5)	2.650(5)	X–W(1)–C(3)	78.5(6)	72.9(14)
W(1)–C(3)	2.07(1)	2.07(3)	X–W(1)–C(8)	73.0(7)	77.4(12)
W(1)–C(8)	2.05(1)	2.04(3)	C(3)–W(1)–C(8)	122.7(6)	122.2(13)
W(1)–C(13)(ax.)	1.970(9)	2.01(2)	C(3)–W(1)–C(13′)	111.1(5)	100.3(15)
W(1)–C(13′)(eq.)	1.967(10)	1.92(2)	C(8)–W(1)–C(13′)	119.7(5)	106.8(14)
			C(13)–W(1)–C(13′)	91.0(4)	90.9(9)
			W(1)–C(13)–W(1′)	89.0(4)	89.1(9)



(**1**)



(**2**)

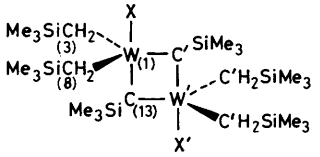


Figure 1. A schematic representation of the molecular structure of (**3a**) and (**3b**) as determined by single crystal *X*-ray crystallography (see Table 1).

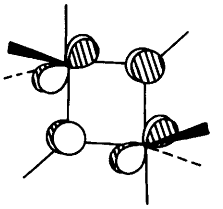


Figure 2. A schematic representation of the HOMO for (**3a—c**).

distances in (**3a**) and (**3b**), 2.76 Å, are intermediate between the distances seen previously for d^1–d^1 and d^0–d^0 1,3-dimetallacyclobutadienes of tungsten, which are typically *ca.* 2.54 and 2.90 Å, respectively.[1,2,4,6]

The compounds (**3a—c**) show similar ^1H n.m.r. spectra in [$^2H_8$]toluene solutions. At 22 °C there are pairs of broad resonances centred at δ *ca.* 3 and 13 downfield from Me_4Si. Upon lowering the temperature these resonances undergo further broadening and shift downfield, suggestive of paramagnetic behaviour. Measurements of solution magnetic susceptibilities by the Evan's method[9] gave $\mu_{eff.} = 1.6 \pm 0.1$ μ_B for (**3a**) and (**3b**) at 22 °C, *i.e.* nearly one unpaired electron per dinuclear unit. The $\mu_{eff.}$ value of the iodide, (**3c**), was slightly lower, *ca.* 1.2 ± 0.1 μ_B.

A cryoscopic molecular weight determination of (**3b**) in benzene indicated the dinuclear species is retained in solution and electrochemical studies in CH_2Cl_2 and tetrahydrofuran showed only a broad irreversible reduction wave suggesting that the formation of radical cation–radical anion pairs of the type ($3^{\cdot +}$)–($3^{\cdot -}$) in solution is unlikely. Compound (**3b**) displays a broad e.s.r. signal in toluene centred at *g* 2.03 having a half-width of *ca.* 680 Hz.

Crystalline samples of (**3a**) and (**3b**) exhibit a broad featureless e.s.r. signal at ambient temperatures, *g ca.* 2.0. Magnetic susceptibility measurements on solid samples of (**3b**) employing the Faraday balance method show a steady decrease in the magnitude of $\mu_{eff.}$ from 1.48 μ_B at 301 K to 0.63 μ_B at 91 K. Considering the temperature dependence of $\mu_{eff.}$ and the non-integral electron count necessary to generate the observed $\mu_{eff.}$ values, the paramagnetism of compounds (**3**) most probably arises from an equilibrium between a singlet ground state and a thermally accessible triplet excited state. In a formal sense compounds (**3**) contain W^{VI}, if the ligands are assigned charge −1 for X and CH_2SiMe_3 and −3 for $CSiMe_3$. The paramagnetism would, therefore, appear to be associated with the planar M_2C_2 ring, an inorganic analogue of cyclobutadiene except in that the degeneracy of the e orbitals is removed. An extended Hückel calculation using weighted H_{ij} values[10] and previously published tungsten parameters[11] indicates that the HOMO in compounds (**3a**) and (**3b**) is an orbital of b_u symmetry having a M–M δ–δ type interaction with contributions from carbon p orbitals; see Figure 2. At a distance of 2.75 Å, overlap of δ type orbitals will be very small and the resultant spin-equilibrium could, therefore, parallel the classic example seen for the copper acetate dimer.[12]

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