Synthesis and Crystal and Molecular Structure of Bis(trimethylsilylmethylidyne)tetrakis(trimethylsilylmethyl)dirhenium (*Re–Re*)[†]

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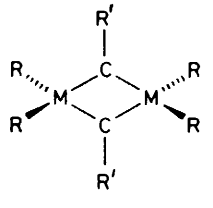
The complex $Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ has been isolated as green crystals in small yield from the reaction of $ReCl_4(thf)_2$ (thf = tetrahydrofuran) with Me_3SiCH_2MgCl and characterised by *X*-ray diffraction analysis. Crystals are triclinic, space group $P\bar{1}$, with a = 10.312(2), b = 10.703(6), c = 11.625(5) Å, α = 117.04(4), β = 64.71(3), and γ = 115.89(3)°. The structure was determined using observed data and refined to an R of 0.0376. The molecule has $\bar{1}$ (C_i) symmetry with a planar, central Re_2C_2 ring. The carbyne ligands bridge symmetrically with the Re–C multiple bond component delocalised. The Re–Re distance of 2.557 Å is rather long, but is still considered compatible with a metal–metal double bond.

During further studies on the dinitrogen complex[1] $[Re(CH_2SiMe_3)_4]_2N_2$, obtained from the interaction of $ReCl_4(thf)_2$ (thf = tetrahydrofuran) and Me_3SiCH_2MgCl under nitrogen, we obtained, in addition to the red-purple major product, a small amount of a highly petroleum-soluble and air-sensitive, green crystalline solid. The compound was chloride-free, and the i.r. spectrum showed bands characteristic of trimethylsilylmethyl ligands (1 246s, 943m, 906m, 830vs, 740m, 680m, 618w, 510w, and 458w cm^{-1}). Unfortunately, the amount of pure material obtained was insufficient for n.m.r. investigations and it was therefore identified by an *X*-ray diffraction study. This revealed that the compound belongs to the class of complexes with bridging alkylidyne groups of type (1), first characterised for niobium and tantalum.[2,3]

Similar compounds are now known for tungsten[4-6] and titanium.[7] The molecular structure of the complex is shown in the Figure; important bond lengths and angles are given in Table 1.

The central Re_2C_2 ring is planar by virtue of the $\bar{1}$ (C_i) molecular symmetry. The bridging Re–C bonds in this ring [1.926(6) and 1.932(6) Å] are shorter than the terminal Re–C bonds [2.059(8) and 2.092(8) Å] and approximately equal. These features are consistent with a model in which the π-bonding component in the Re–C bridge system is delocalised. The distribution of angles in the Re_2C_2 ring, with Re–C–Re = 83.0(3)° and C–Re–C = 97.0(4)°, strongly supports the existence of a Re–Re bonding interaction. Since the compound is formally a derivative of Re^V, we have two electrons available on each metal and therefore expect a Re–Re double bond. The assignment of metal–metal bond orders on the basis of bond length is open to question, as has been discussed elsewhere,[8,9] so the Re–Re distance here, which is a little long compared with values in other systems to which a bond order of two has been assigned, *e.g.*, $[Re_3Cl_{12}]^{3-}$ (2.48 Å)[10] and $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ (2.386 Å),[11] might still be considered compatible with the proposed bond order. Thus we may reasonably describe the electronic structure by the form (2) and so the compound constitutes the third link in the related series of compounds $M_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ with, formally at least, the same double, six-electron bridge system $[M\{\cdots C(R)\cdots\}_2M]$ and then M–M bond orders of zero (the niobium compound),[2] one (the tungsten compound),[6] and two (the rhenium compound).


(1)

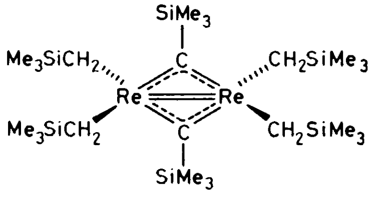

(2)

Table 1

Selected interatomic distances and interbond angles

(*a*) Bond lengths (Å)

Re–Re	2.557(1)	C(1)–Si(1)	1.852(7)
Re–C(1)	1.932(6)	C(2)–Si(2)	1.876(9)
Re–C(1)	1.926(6)	C(3)–Si(3)	1.869(8)
Re–C(2)	2.092(8)		
Re–C(3)	2.059(8)		

(*b*) Bond angles (°)

Re–C(1)–Re′	83.0(3)	C(1)′–Re–C(2)	108.8(4)
C(1)–Re–C(2)	109.0(4)	C(1)′–Re–C(3)	111.0(3)
C(1)–Re–C(3)	114.6(3)	Re–C(1)–Si(1)	136.5(4)
C(2)–Re–C(3)	114.8(4)	Re–C(2)–Si(2)	118.9(5)
C(1)′–Re–C(1)	97.0(4)	Re–C(3)–Si(3)	129.6(5)

* The primed atom is related to the unprimed one by the centre of symmetry at 0,0,0.

For convenience of comparison, we present the relevant data for the three compounds in Table 2. Apart from the variations in metal–metal distances, the most significant differences between the three compounds are the geometries of the bridges.

Whilst it might be argued that in terms of the bond lengths the fairly large differences in the niobium and tungsten compounds are on the borderline of significance, the M–C–Si angles in all three compounds are definitely not equal and in the case of the niobium compound[2] the bridge carbons are not planar. Cotton and co-

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[†] No reprints available.

workers[6] have suggested that the distortion is most likely due to steric factors and have also drawn attention to the fact that the crystal and molecular conformations of the niobium and tungsten compounds are different. Surprisingly, the conformation and crystal structure of the rhenium analogue are different again and we must assume that not only is the intramolecular packing of the alkyl ligands very finely balanced but also that the positioning of the carbon atoms in the bridge may be susceptible to change. Analysis of intramolecular interactions in our compound shows no unusually close contacts and so we presume that the symmetrical bridging found is however the electronically preferred structure.

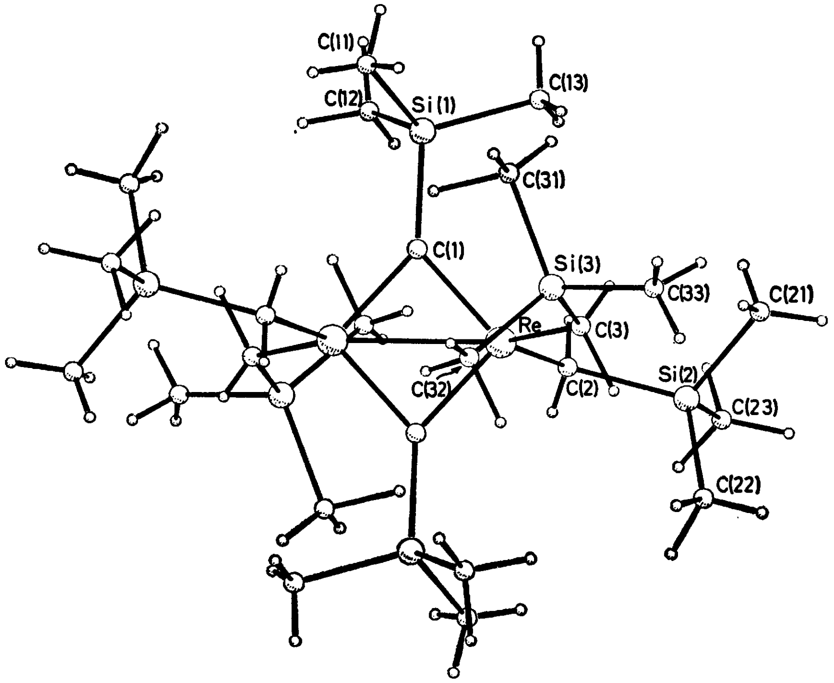

FIGURE Molecular structure of the complex $Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$

TABLE 2

Structural characteristics of complexes $M_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ [a]

	Nb	W	Re
(*a*) Bond lengths (Å)			
[M(1)–M(1)′]	2.897	2.535	2.557(1)
[M(1)–C(1)]	1.995	1.85(3)	1.932(6)
[M(1)–C(1)′]	1.954	1.97	1.92(6)
[M(1)–C(term.)] [b]	2.16	2.1	2.076(8)
(*b*) Angles (°)			
M(1)–C(1)–M(1)′	94.4(4)	84(1)	83.0(3)
C(1)–M(1)–C(1)′	85.6(4)	96(1)	97.0(4)
M(1)–C(1)–Si(1)	142.4	146(2)	136.5(4)
M(1)′–C(1)–Si(1)	119.8	130(2)	

[a] Atomic numbering as in the Figure. [b] Average metal–terminal carbon distance.

Attempts have been made to isolate the compound in substantial yields by varying the reaction conditions, but without success. No detectable quantities were produced from $ReCl_5$ and $LiCH_2SiMe_3$ in petroleum, from $ReCl(thf)_2$ and an excess of $Mg(CH_2SiMe_3)_2$ in diethyl ether, from $ReCl_4(thf)_2$ and Me_3SiCH_2MgCl in thf, or by thermolysis of $Re_2(CH_2SiMe_3)_8N_2$ in benzene or thf.

EXPERIMENTAL

Synthesis.—The reaction was carried out as before[1] under nitrogen. To a stirred suspension of 1.94 g (4.11 mmol) $ReCl_4(thf)_2$ in a mixture of diethyl ether (20 cm^3) and thf (10 cm^3) was added Me_3SiCH_2MgCl (20.4 mmol) in diethyl ether drop-wise at −70 °C. Stirring was continued for 0.5 h at low temperature, then for 2 h at 0 °C, and the solution allowed to warm slowly to ambient temperature. The red-purple reaction mixture was filtered, the filtrate taken to dryness, and the purple oily residue extracted with petroleum (3 × 10 cm^3), filtered, and cooled to −30 °C. After separation from some oily precipitate the petrol fraction was concentrated to *ca.* 3 cm^3, diethyl ether (5 cm^3) added, and the solution left to crystallise slowly at −30 °C. In addition to crystalline $Re_2(CH_2SiMe_3)_8N_2$, a few green rhombic crystals of $Re_2(CSiMe_3)_2(CH_2SiMe_3)_4$ were obtained and picked out manually; m.p. 145 °C (decomp.).

Crystallography.—Several well formed crystals obtained as described above were sealed under nitrogen in Lindemann capillaries. Preliminary cell data were obtained photographically and accurate parameters from least-squares refinement of setting angles of 25 reflections with $16 < \theta < 18°$ automatically centred on a Nonius CAD4 diffractometer.

Crystal data. $C_{24}H_{62}Re_2Si_6$, $M = 891.67$, Triclinic, $a = 10.312(2)$, $b = 10.703(6)$, $c = 11.625(5)$ Å, $\alpha = 117.04(4)$, $\beta = 64.71(3)$, $\gamma = 115.89(3)°$, $U = 985.3$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 1.50$ g cm^{-3}, $F(000) = 440$, $\mu(\text{Mo-}K_\alpha) = 63.8$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\ 69$ Å.

The intensities of 3 075 unique reflections were recorded on the diffractometer using Mo-K_α radiation and an ω—2θ scan in a manner described in detail elsewhere.[11] The structure was solved by standard heavy-atom methods and refined by full-matrix least squares. The data were corrected for Lorentz and polarisation factors and for absorption and it has proved possible to locate and refine all hydrogen atoms with individual isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically. For the 2 770 data considered observed [$I > 1.5\sigma(I)$], the final R values, $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.037\,6$ and $R' = (\Sigma\omega|F_o - F_c|/\Sigma\omega|F_o|) = 0.035\,5$ with the weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.000\,5|F_o|^2]$, gave flat agreement analyses.

TABLE 3

Fractional co-ordinates (Re × 10^5, others × 10^4) of the non-hydrogen atoms for $Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$

Re	13 290(3)	2 074(3)	−8 089(2)
Si(1)	1 414(3)	588(3)	2 327(2)
Si(2)	4 316(3)	2 570(2)	−2 347(2)
Si(3)	1 760(3)	−3 368(2)	−2 296(2)
C(1)	588(8)	240(7)	1 035(6)
C(2)	2 622(12)	2 335(9)	−867(10)
C(3)	2 340(10)	1 403(9)	−2 167(9)
C(11)	636(18)	−1 019(15)	2 918(14)
C(12)	1 010(22)	2 203(16)	3 782(13)
C(13)	3 484(14)	1 019(19)	1 595(17)
C(21)	5 817(17)	1 949(21)	−2 489(28)
C(22)	3 810(18)	1 570(15)	−3 964(11)
C(23)	5 112(14)	4 593(11)	−2 075(13)
C(31)	1 743(20)	−3 438(16)	−718(12)
C(32)	−100(15)	−4 412(15)	−2 595(18)
C(33)	3 158(17)	−4 238(14)	−3 741(13)

Programs, computers, and scattering-factor data sources used in this work are those described in ref. 11. The final co-ordinates of the non-hydrogen atoms are given in Table 3. Thermal parameters, atomic co-ordinates and isotropic parameters for hydrogen atoms, lists of observed and calculated structure factors, and bond lengths and angles not given in Table 1 have been deposited as Supplementary Publication No. SUP 22803 (16 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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