Crystal and Molecular Structure of Di-μ-trimethylsilylmethyl-bis[(trimethylphosphine)(trimethylsilylmethyl)chromium(II)] (4 *Cr–Cr*)

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The crystal and molecular structure of the title compound has been determined by direct methods and refined by least squares to *R* 0.029 3 based on 4 345 diffractometer data. Crystals are triclinic with $a = 16.975(7)$, $b = 11.396(6)$, $c = 10.678(6)$ Å, $\alpha = 114.87(7)$, $\beta = 91.75(7)$, $\gamma = 84.98(7)°$, space group $P\bar{1}$, and $Z = 2$. The binuclear molecule possesses an approximate two-fold axis and contains two bridging alkyl groups arranged in a *cis* configuration. One H atom from each bridging CH_2 group makes a close contact (*ca.* 2.25 Å) with one of the metal atoms, introducing a slight asymmetry in the Cr–C bridge bonds. The short Cr–Cr distance [2.1007(5) Å] is consistent with the presence of a quadruple metal–metal bond. However, in order to account for the overall coordination geometry, and in particular the accommodation of the two *cis* electron-deficient bridges, it is suggested that the M$\equiv$M system is bent. A simple description of this in terms of *d*-orbital overlap integrals is presented.

BINUCLEAR transition-metal acetates, $[M_2(O_2CMe)_4]$, and related derivatives are very useful starting materials for the preparation of other binuclear compounds. For example, the acetates $[Mo_2(O_2CMe)_4]$ and $[Re_2Cl(O_2CMe)_4]$ react with methyl-lithium to give the salts $Li_4[M_2Me_8]$ (M = Mo or Re).[1,2] In an attempt to produce neutral alkyl derivatives, Wilkinson and his co-workers[3] have explored the reactions between the binuclear acetates and magnesium dialkyls, MgR_2 (R = Me, CH_2SiMe_3, or CH_2Bu^t). Although the straightforward reaction between the acetates and MgR_2 invariably led to decomposition, in the presence of PMe_3, neutral, crystalline, alkyl derivatives have been obtained which are either monomeric or dimeric. In collaboration with Professor Wilkinson's group, we have been engaged in the structural characterisation of some of these new products, using single-crystal *X*-ray diffraction techniques. The title compound was obtained from the reaction of tetrakis-μ-acetato-dichromium(II) and bis(trimethylsilylmethyl)magnesium in the presence of PMe_3. A preliminary account of this work has appeared;[4] we now report full details of the crystal-structure analysis and the molecular structure thus determined.

EXPERIMENTAL

The compound crystallises as dark red pyrophoric needles, with the needle axis parallel to [100]. Suitable specimens for *X*-ray work were mounted under nitrogen in 0.3-mm Lindemann capillaries.

Crystal Data.—$C_{22}H_{62}Cr_2P_2Si_4$, $M = 605$, Triclinic, $a = 16.975(7)$,† $b = 11.396(6)$, $c = 10.678(6)$ Å, $\alpha = 114.87(7)$, $\beta = 91.75(7)$, $\gamma = 84.98(7)°$, $U = 1\,866.8$ Å^3, D_m not measured, $Z = 2$, $D_c = 1.076$ g cm^{-3}, $F(000) = 656$, space group $P\bar{1}$, $\mu(\text{Mo-}K_\alpha) = 7.5$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

The crystal system and preliminary unit-cell parameters were determined from oscillation and Weissenberg photographs. The accurate cell constants were determined from least-squares refinement of the setting angles of 15 reflections automatically centred on a diffractometer.

Intensity Measurements.—Three-dimensional *X*-ray diffraction data ($1.5 < \theta < 25°$) were collected from a single crystal ($0.52 \times 0.26 \times 0.24$ mm) mounted on a computer-controlled Nonius CAD4 diffractometer using Mo-K_α radiation (graphite monochromator) and an ω—2θ scan technique (scan width = $0.8 + 0.2 \tan\theta$). All the data in one half of the reciprocal space ($\pm h, \pm k, l$) were measured. Two control reflections monitored after every 50 reflections showed a *ca.* 15% decrease in the intensity of the diffracted beam during data collection. All the intensities were corrected for $(Lp)^{-1}$ factors, variable measuring time, and crystal deterioration, but not for absorption or extinction. The total 6 191 data reduced to 5 951 independent intensities (merging $R = 0.014$) of which 4 345 were defined as observed [$I_o > 1.5\sigma(I_o)$] and used in the final refinement.

Structure Solution and Refinement.—The positions of the two Cr, two P, and four Si atoms were obtained from the 'best' *E* map computed with the automatic direct-methods routine in the SHELX program.[5] Two cycles of isotropic least-squares refinement[5] of these atoms was followed by a difference electron-density synthesis which gave the positions of the 22 carbon atoms in the structure. Isotropic and anisotropic refinement of all the non-hydrogen atoms together with an overall scale factor reduced the *R* value to 0.105 and 0.054 respectively (unit weights). The hydrogen atoms were located from a difference map and included in the refinement with isotropic temperature factors. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0002|F_o|^2]$ was applied and gave flat analysis of variance with $\sin\theta$, $(F_o/F_{max.})^{\frac{1}{2}}$, parity groups, and reflection indices. The final values for *R* and *R'* were 0.029 3 and 0.030 1. Atomic scattering factors for neutral Cr, P, Si, and C atoms were taken from ref. 6 and for hydrogen from ref. 7. All the computational work was carried out on the Queen Mary College ICL 1904S and University of London CDC 7600 computers.

RESULTS AND DISCUSSION

The crystal structure (Figure 1) comprises discrete molecules of $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$ held together by

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† Estimated standard deviations are given in parentheses throughout this paper.

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[2] F. A. Cotton, L. D. Gage, K. Mertis, L. W. Shrive, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1976, **98**, 6922.

[3] R. A. Anderson, R. A. Jones, and G. Wilkinson, *J.C.S. Dalton*, 1978, 454.

[4] R. A. Anderson, R. A. Jones, G. Wilkinson, M. B. Hursthouse, and K. M. A. Malik, *J.C.S. Chem. Comm.*, 1977, 283.

[5] SHELX Package of Crystallographic Programs, G. M. Sheldrick, University of Cambridge, 1976.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

van der Waals forces. Figure 2 shows a single molecule and the atom-numbering scheme adopted. Final values of the atomic co-ordinates are listed in Tables 1 and 2 and the derived interatomic distances and angles in Table 3.*

The main features of the molecular structure are the retention of the Cr–Cr multiple bond, the presence of two bridging alkyl groups arranged in a *cis* configuration, and the possession of an approximate two-fold axis passing through the midpoints of the Cr–Cr bond and the line joining the two bridging carbon atoms. The chromium atoms are thus in essentially identical environments, each with bonds to two bridging and one terminal alkyl group and one phosphine, in addition to the metal–metal bond. The Cr–Cr bond [2.1007(5) Å] is in the range found for other binuclear chromium(II) species in which a quadruple bond is assumed, such as $[Cr_2(C_3H_4)_4]$ (1.97),[8] $Li_4[Cr_2Me_8]\cdot 4C_4H_8O$ [1.980(5)],[9] $Li_4[Cr_2(C_4H_8)_2]\cdot 4C_4H_8O$ [1.975(5)],[10] $Mg_2[Cr_2(CO_3)_4(OH_2)_2]\cdot 4H_2O$ (2.22),[11] and $[Cr_2(O_2CMe)_4]\cdot H_2O$ [2.386(1) Å].[12] In the case of the last two structures, however, it has been suggested that the metal–metal bonds are weakened and thus lengthened by the presence of coaxial ligands,[13] or even eliminated by the occupancy of orbitals of an antibonding character.[14]

TABLE 1

Final non-hydrogen atomic fractional co-ordinates (Cr, P, and Si × 10^5; C × 10^4)

Atom	*x*	*y*	*z*
Cr(1)	78 121(2)	50 895(3)	31 497(3)
Cr(2)	74 562(2)	70 712(3)	42 384(3)
P(1)	79 613(4)	41 200(7)	48 267(7)
P(2)	86 409(4)	82 717(7)	49 765(7)
Si(3)	91 302(5)	30 292(8)	6 541(8)
Si(4)	61 934(5)	91 537(8)	68 330(8)
Si(5)	71 408(5)	75 367(7)	14 175(7)
Si(6)	60 125(4)	42 619(8)	22 209(8)
C(11)	7 132(3)	4 157(5)	5 877(5)
C(12)	8 679(3)	4 874(4)	6 144(4)
C(13)	8 347(3)	2 418(4)	4 136(5)
C(21)	9 376(3)	8 141(7)	3 711(6)
C(22)	9 253(3)	7 818(7)	6 139(8)
C(23)	8 477(3)	16(4)	5 965(6)
C(31)	8 986(2)	4 303(3)	2 418(3)
C(32)	8 808(4)	3 601(6)	−688(4)
C(33)	199(4)	2 411(9)	272(7)
C(34)	8 570(6)	1 590(7)	372(7)
C(41)	7 070(2)	7 960(3)	6 328(3)
C(42)	5 302(2)	8 484(5)	5 813(5)
C(43)	5 924(4)	9 682(7)	8 682(5)
C(44)	6 349(4)	652(5)	6 601(8)
C(51)	7 700(2)	6 414(2)	2 043(2)
C(52)	6 056(3)	7 786(6)	1 795(7)
C(53)	7 561(5)	9 142(5)	2 149(7)
C(54)	7 262(4)	6 859(6)	−503(5)
C(61)	6 546(1)	5 588(2)	3 540(3)
C(62)	6 196(4)	3 997(6)	403(4)
C(63)	6 302(3)	2 674(4)	2 324(6)
C(64)	4 933(2)	4 636(7)	2 573(8)

TABLE 2

Fractional co-ordinates (× 10^4) of the H atoms

Atom	*x*	*y*	*z*
H(11a) *	6 742(19)	3 708(31)	5 333(33)
H(11b)	7 298(22)	3 756(36)	6 468(40)
H(11c)	6 887(25)	5 072(41)	6 318(45)
H(12a)	8 725(17)	4 405(29)	6 670(32)
H(12b)	9 185(18)	4 879(28)	5 711(31)
H(12c)	8 478(18)	5 707(30)	663(31)
H(13a)	8 854(25)	2 257(38)	3 665(42)
H(13b)	7 931(22)	1 941(35)	3 640(37)
H(13c)	8 417(26)	2 163(41)	4 843(45)
H(21a)	9 817(22)	8 615(34)	4 162(35)
H(21b)	9 508(27)	7 260(47)	3 149(51)
H(21c)	9 148(24)	8 613(40)	3 325(44)
H(22a)	9 623(23)	8 443(35)	6 502(38)
H(22b)	8 959(24)	7 897(40)	6 827(40)
H(22c)	9 447(24)	6 979(40)	5 742(44)
H(23a)	8 932(25)	414(40)	6 269(42)
H(23b)	8 255(24)	102(37)	6 738(42)
H(23c)	8 275(34)	330(53)	5 455(61)
H(31a)	9 281(15)	3 949(26)	2 938(27)
H(31b)	9 243(16)	4 984(27)	2 455(28)
H(32a)	8 888(22)	3 034(36)	−1 489(40)
H(32b)	8 222(29)	3 742(47)	−675(48)
H(32c)	9 160(23)	4 349(38)	−473(39)
H(33a)	226(30)	1 846(46)	−468(50)
H(33b)	540(49)	2 961(85)	112(90)
H(33c)	295(41)	1 989(66)	736(65)
H(34a)	9 195(56)	999(87)	540(96)
H(34b)	8 591(32)	1 073(51)	−297(51)
H(34c)	8 093(37)	1 859(63)	473(69)
H(41a)	6 921(14)	7 273(24)	6 513(25)
H(41b)	7 465(16)	8 314(26)	6 978(29)
H(42a)	4 856(22)	9 059(33)	6 227(35)
H(42b)	5 243(24)	7 762(39)	5 919(43)
H(42c)	5 385(23)	8 319(39)	4 856(43)
H(43a)	5 551(21)	293(35)	8 941(37)
H(43b)	6 381(26)	3(41)	9 271(46)
H(43c)	5 810(39)	9 074(57)	8 878(65)
H(44a)	5 888(25)	1 173(40)	6 834(42)
H(44b)	6 547(26)	414(41)	5 690(46)
H(44c)	6 770(32)	1 116(49)	7 158(53)
H(51a)	8 175(13)	6 457(20)	1 827(22)
H(51b)	7 532(13)	5 594(22)	1 366(24)
H(52a)	5 812(26)	8 144(43)	1 267(46)
H(52b)	5 850(32)	6 965(51)	1 221(58)
H(52c)	6 082(50)	8 416(81)	2 647(90)
H(53a)	7 059(19)	9 467(29)	3 129(34)
H(53b)	7 279(27)	9 654(45)	1 829(45)
H(53c)	8 021(42)	9 121(65)	2 166(80)
H(54a)	7 811(40)	6 854(68)	−625(67)
H(54b)	7 134(52)	6 259(75)	−809(83)
H(54c)	7 144(41)	7 666(63)	−728(69)
H(61a)	6 385(14)	5 608(23)	4 332(26)
H(61b)	6 250(15)	6 379(25)	3 480(25)
H(62a)	6 073(28)	4 771(45)	304(46)
H(62b)	5 856(23)	3 406(39)	−222(43)
H(62c)	6 692(35)	3 646(55)	279(60)
H(63a)	6 017(24)	1 926(41)	1 638(44)
H(63b)	6 863(27)	2 369(41)	1 953(46)
H(63c)	6 084(33)	2 850(50)	3 130(56)
H(64a)	4 786(22)	5 481(37)	2 533(39)
H(64b)	4 705(24)	4 106(38)	2 080(41)
H(64c)	4 727(40)	4 580(62)	3 444(62)

* Hydrogen atoms are numbered according to the parent carbon atom, distinguished by suffices a, b, or c if more than one is present.

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* Temperature factors and observed and calculated structure factors are deposited in Supplementary Publication No. SUP 22292 (32 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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The Cr–C bond lengths to the terminal alkyl groups are almost equal and average 2.131 Å. In contrast, the bonds to the bridging alkyls are longer and, within each bridge, asymmetric, with average values of 2.181 [Cr(1)–C(61), Cr(2)–C(51)] and 2.266 Å [Cr(1)–C(51), Cr(2)–C(61)]. Similar asymmetric bridges have been found for other alkyls or related species, *e.g.* $[Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4]$ [15] and $[\{Mn(CH_2SiMe_3)_2\}_\infty]$, $[Mn_4(CH_2CMe_3)_8]$, and $[Mn_2(CH_2CMe_2Ph)_4]$,[16] but in the tetrameric copper(I) cluster $[\{Cu(CH_2SiMe_3)\}_4]$ [17] the bridges

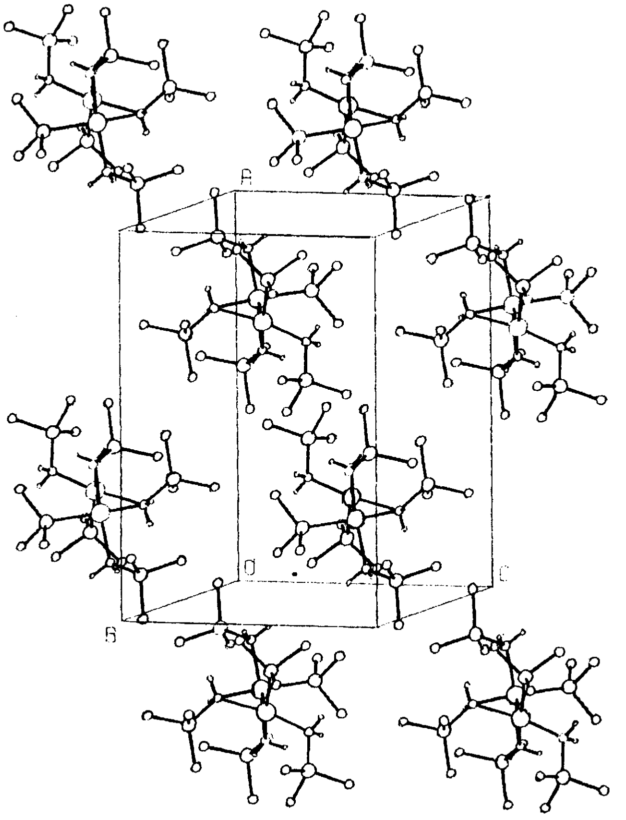

FIGURE 1 The crystal structure of $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$

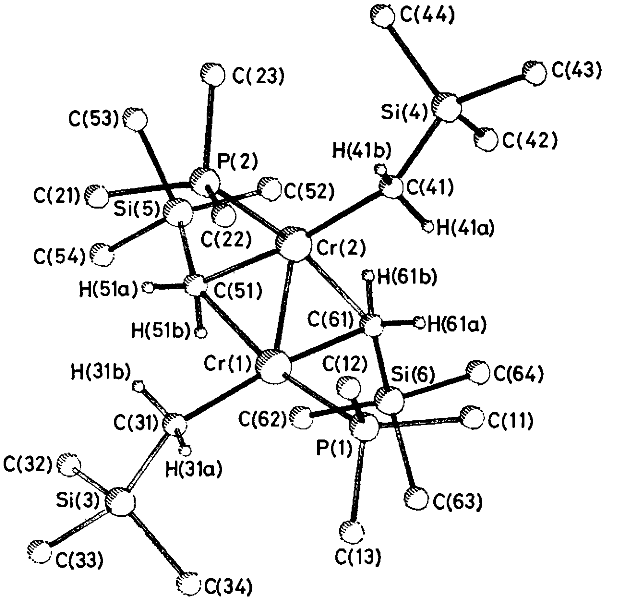

FIGURE 2 A view of the molecule down its approximate two-fold axis. Methyl hydrogen atoms are omitted for clarity

TABLE 3

Intramolecular interatomic distances (Å) and angles (°)

(*a*) Bond distances

Cr(1)–Cr(2)	2.100 7(5)	Si(3)–C(31)	1.839(3)
Cr(1)–P(1)	2.466(1)	Si(3)–C(32)	1.859(6)
Cr(2)–P(2)	2.453(1)	Si(3)–C(33)	1.881(7)
Cr(1)–C(51)	2.269(3)	Si(3)–C(34)	1.878(9)
Cr(1)–C(61)	2.181(2)	Si(4)–C(41)	1.853(3)
Cr(2)–C(51)	2.181(3)	Si(4)–C(42)	1.860(4)
Cr(2)–C(61)	2.263(3)	Si(4)–C(43)	1.864(5)
Cr(1)–C(31)	2.140(3)	Si(4)–C(44)	1.866(7)
Cr(2)–C(41)	2.123(3)	Si(5)–C(51)	1.858(3)
		Si(5)–C(52)	1.869(5)
P(1)–C(11)	1.813(5)	Si(5)–C(53)	1.860(6)
P(1)–C(12)	1.806(4)	Si(5)–C(54)	1.874(5)
P(1)–C(13)	1.827(4)	Si(6)–C(61)	1.860(2)
P(2)–C(21)	1.818(6)	Si(6)–C(62)	1.866(5)
P(2)–C(22)	1.804(8)	Si(6)–C(63)	1.881(5)
P(2)–C(23)	1.816(4)	Si(6)–C(64)	1.858(4)
C(31)–H(31a)	0.926(32)	C(41)–H(41a)	0.940(31)
C(31)–H(31b)	0.910(32)	C(41)–H(41b)	0.936(27)
C(51)–H(51a)	0.856(24)	C(61)–H(61a)	0.888(30)
C(51)–H(51b)	0.971(21)	C(61)–H(61b)	1.018(30)

(*b*) Non-bonding short distances

Cr(1) · · · H(31a)	2.679(26)	Cr(2) · · · H(41a)	2.531(28)
Cr(1) · · · H(31b)	2.540(28)	Cr(2) · · · H(41b)	2.661(27)
Cr(1) · · · H(51a)	2.622(28)	Cr(2) · · · H(61a)	2.604(28)
Cr(1) · · · H(51b)	2.236(29)	Cr(2) · · · H(61b)	2.262(25)
Cr(1) · · · H(61a)	2.669(25)	Cr(2) · · · H(51a)	2.671(23)
Cr(1) · · · H(61b)	2.874(30)	Cr(2) · · · H(51b)	2.811(30)

(*c*) Bond angles

P(1)–Cr(1)–Cr(2)	107.9(1)	P(2)–Cr(2)–Cr(1)	108.6(1)
C(31)–Cr(1)–Cr(2)	125.3(1)	C(41)–Cr(2)–Cr(1)	124.8(1)
C(31)–Cr(1)–P(1)	89.0(1)	C(41)–Cr(2)–P(2)	88.0(1)
C(51)–Cr(1)–Cr(2)	59.7(1)	C(61)–Cr(2)–Cr(1)	59.8(1)
C(51)–Cr(1)–P(1)	166.8(1)	C(61)–Cr(2)–P(2)	167.3(1)
C(51)–Cr(1)–C(31)	94.9(1)	C(61)–Cr(2)–C(41)	94.9(1)
C(61)–Cr(1)–Cr(2)	63.8(1)	C(51)–Cr(2)–Cr(1)	64.0(1)
C(61)–Cr(1)–P(1)	93.5(1)	C(51)–Cr(2)–P(2)	94.2(1)
C(61)–Cr(1)–C(31)	169.1(1)	C(51)–Cr(2)–C(41)	169.7(1)
C(61)–Cr(1)–C(51)	85.1(1)	C(51)–Cr(2)–C(61)	85.2(1)
C(11)–P(1)–Cr(1)	120.9(2)	C(21)–P(2)–Cr(2)	120.2(2)
C(12)–P(1)–Cr(1)	112.5(2)	C(22)–P(2)–Cr(2)	113.3(2)
C(13)–P(1)–Cr(1)	115.9(2)	C(23)–P(2)–Cr(2)	116.4(2)
C(11)–P(1)–C(12)	100.8(2)	C(21)–P(2)–C(22)	100.5(3)
C(11)–P(1)–C(13)	102.5(3)	C(21)–P(2)–C(23)	102.3(3)
C(12)–P(1)–C(13)	101.4(2)	C(22)–P(2)–C(23)	101.4(3)
C(31)–Si(3)–C(32)	112.8(2)	C(41)–Si(4)–C(42)	112.5(2)
C(31)–Si(3)–C(33)	111.9(2)	C(41)–Si(4)–C(43)	111.4(3)
C(31)–Si(3)–C(34)	111.5(3)	C(41)–Si(4)–C(44)	112.9(2)
C(32)–Si(3)–C(33)	106.1(4)	C(42)–Si(4)–C(43)	106.5(3)
C(32)–Si(3)–C(34)	107.4(3)	C(42)–Si(4)–C(44)	106.3(3)
C(33)–Si(3)–C(34)	106.7(4)	C(43)–Si(4)–C(44)	106.9(3)
C(51)–Si(5)–C(52)	114.7(3)	C(61)–Si(6)–C(62)	114.4(2)
C(51)–Si(5)–C(53)	110.3(3)	C(61)–Si(6)–C(63)	110.7(2)
C(51)–Si(5)–C(54)	108.5(2)	C(61)–Si(6)–C(64)	108.9(2)
C(52)–Si(5)–C(53)	108.9(3)	C(62)–Si(6)–C(63)	106.8(3)
C(52)–Si(5)–C(54)	107.2(3)	C(62)–Si(6)–C(64)	108.3(3)
C(53)–Si(5)–C(54)	106.9(3)	C(63)–Si(6)–C(64)	107.5(3)
Si(3)–C(31)–Cr(1)	119.2(1)	Si(4)–C(41)–Cr(2)	119.7(2)
Si(3)–C(31)–H(31a)	102.4(1.4)	Si(4)–C(41)–H(41a)	104.4(1.4)
Si(3)–C(31)–H(31b)	106.3(1.6)	Si(4)–C(41)–H(41b)	107.3(1.5)
Cr(1)–C(31)–H(31a)	116.1(1.7)	Cr(2)–C(41)–H(41a)	104.7(1.3)
Cr(1)–C(31)–H(31b)	105.6(1.6)	Cr(2)–C(41)–H(41b)	115.2(1.8)
H(31a)–C(31)–H(31b)	106.3(2.6)	H(41a)–C(41)–H(41b)	103.6(2.7)
Cr(2)–C(51)–Cr(1)	56.3(1)	Cr(2)–C(61)–Cr(1)	56.4(1)
Si(5)–C(51)–Cr(1)	153.6(2)	Si(6)–C(61)–Cr(2)	153.9(2)
Si(5)–C(51)–Cr(2)	108.9(1)	Si(6)–C(61)–Cr(1)	108.1(1)
Cr(1)–C(51)–H(51a)	104.8(1.8)	Cr(2)–C(61)–H(61a)	102.5(1.5)
Cr(2)–C(51)–H(51a)	116.1(1.5)	Cr(1)–C(61)–H(61a)	114.1(1.6)
Si(5)–C(51)–H(51a)	101.5(1.8)	Si(6)–C(61)–H(61a)	103.3(1.5)
Cr(1)–C(51)–H(51b)	75.7(1.8)	Cr(2)–C(61)–H(61b)	76.9(1.5)
Cr(2)–C(51)–H(51b)	121.3(1.7)	Cr(1)–C(61)–H(61b)	123.7(1.6)
Si(5)–C(51)–H(51b)	99.5(1.6)	Si(6)–C(61)–H(61b)	100.7(1.3)
H(51a)–C(51)–H(51b)	106.5(1.8)	H(61a)–C(61)–H(61b)	104.4(2.2)

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are symmetrical. In the present compound the asymmetry could be due to the presence of short Cr · · · H contacts [2.24(3) and 2.26(3) Å] to one hydrogen atom of each bridging CH_2 group [H(51b) and H(61b)], these contacts presumably arising from the particular orientation of the bulky CH_2SiMe_3 group adopted.

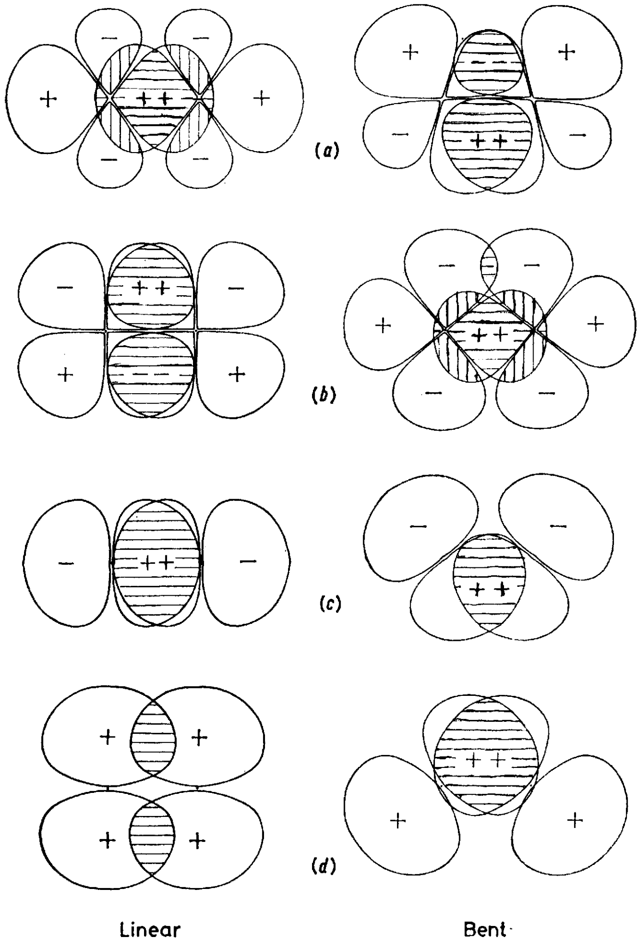
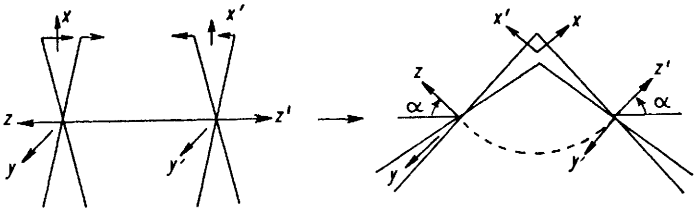


FIGURE 3 Wave function overlaps of *d* orbitals considered to be involved in quadruple bonding for the linear and bent Cr≣Cr systems: (*a*) d_{z^2}–σ; (*b*) d_{xz}–π; (*c*) d_{yz}–π; and (*d*) $d_{x^2-y^2}$–δ bonding. The boundaries shown are all for $|\psi| = 0.015$; positive and negative overlaps are shown by horizontal and vertical hatching respectively. The *x*, *y*, and *z* axes and tilt angle α are defined on the diagram in the text. For (*a*), (*b*), and (*d*) the plots are for sections through the *xz* plane ($y = 0$) and for (*c*) the plots are for a section parallel to *xz* but at $y = 2$ Bohrs (Bohr ≈ 5.29×10^{-11} m). In (*d*) the overlap between the lobes of the orbitals along the *y* axes, which does not vary much with α, is not shown

The *cis* arrangement of the two bridging alkyl groups appears to be rather unusual, compared with other systems containing double bridges (*e.g.* the compounds of Nb and Mn mentioned above and the well known and polymeric or dimeric alkyls of Be and Al). Such a comparison, however, is not strictly valid as these other compounds are MCMC heterocycles with no direct metal–metal bond. In fact the main point of interest is not so much the *cis* arrangement but the actual occurrence of electron-deficient alkyl bridges in association with the multiple M–M bond, and as far as we can ascertain this is the first such example. However, it is interesting to compare the structure of our molecule with the tetra-allyldichromium structure.[8] In this two of the allyl groups are bridging and two are terminal, and here also the two bridging ligands adopt an essentially *cis* configuration.

If we adopt the standard description[18] of the quadruple metal–metal bond, with the bond defining the *z* axis and comprising one σ (using d_{z^2}), two π (using d_{xz} and d_{yz}), and one δ (using $d_{x^2-y^2}$) bonds, the bonds to the ligands are then formed using essentially *s*, p_x, p_y, and d_{xy} orbitals, with the ligands thus lying mainly in the *xy* plane. Clearly, the formation of effective electron-deficient bridges, as in our compound, can be accounted for by assuming that the metal-orbital hybridisation scheme must be modified in some way, so that the metal orbitals used in bonding to the ligands now have some component in the *z* direction. A simple way of representing this situation is to consider the idea of a bending of the M≣M system similar to the model used to describe single M · · · M interactions in such molecules as $[Co(CO)_8]$. In our compound we imagine the *xy* planes at each metal to be tilted in such a way that two *cis* ligand sites on each coincide.



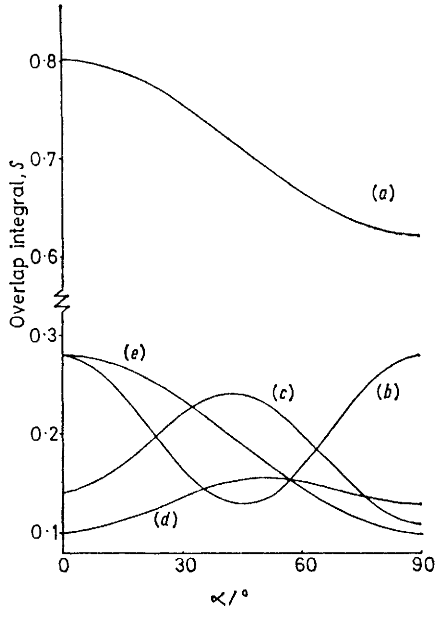


FIGURE 4 Plots of individual and total overlap integrals as a function of the *xy*-tilt angle α: (*a*) $z^2 + xz + yz + (x^2 - y^2)$; (*b*) xz; (*c*) z^2; (*d*) $x^2 - y^2$; and (*e*) yz

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[18] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334.

In order to examine the effect of this bending on the quadruple bond we have calculated overlap integrals using Slater orbitals for each chromium(II) atom, with a screening constant of 4.95. Figure 3 represents the overlap between each of the *d* orbitals considered to be involved in the M≣M bonding for both the ' linear ' and ' bent ' configurations. A more precise idea is obtained from Figure 4 where we plot the overlap integrals for each of the bonds, and the total overlap, as a function of the tilt angle α. These integrals were calculated using the appropriate internuclear distance (2.101 Å) from formulae derived from ref. 19, and the values obtained check with those given in ref. 20. It is interesting to note that in our compound (α 51°) the σ and δ overlaps are almost at their maximum, whereas the two π overlaps are decreased. The total integral has decreased slightly, from 0.80 to 0.71. We would therefore not expect the net bonding to be much reduced and, indeed, part of any loss might be balanced against the probable reduction of interligand steric repulsions in going from the eclipsed L_4M-ML_4 system to our bent $L_2ML_2ML_2$ configurations. Although this model is very simple, neglecting as it does any involvement in the M–M bonding of the p_z orbital, the geometry of the molecule, in which the CrC_3P systems are fairly planar, does seem to agree with it.

Bond lengths and angles within the ligands are normal. In all cases the CH–Si–Me angles are >109° (mean 111.7°) with Me–Si–Me angles averaging 107.1°, and the Si–C distances range from 1.839(3) to 1.881(7) Å with an average of 1.864 Å.

In the phosphine ligands the P–C bond lengths range from 1.804(8) to 1.827(4) Å, with a mean of 1.814 Å, and the C–P–C angles range from 100.5(3) to 102.5(3)° with a mean of 101.5°. On the other hand the Cr–P–C angles show a wide variation, from 112.5(2) to 120(2)°, and probably are affected by intramolecular steric factors.

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