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Low-Temperature Neutron Diffraction Study of $[ReH_5(PPh^iPr_2)_2(SiHPh_2)_2]$ and Low-Temperature X-ray Diffraction Study of $[ReH_5(PCyp_3)_2(SiH_2Ph)_2]$

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Abstract

Crystals of bis[diisopropyl(phenyl)phosphine]bis(diphenylsilyl)pentahydridorhenium $[ReH_5(PPh^iPr_2)_2(SiHPh_2)_2]$ (I) grow as transparent prisms from *n*-hexane in the space group $P\bar{1}$. $M_r = 946.38$, $a = 11.879\,(1)$, $b = 16.754\,(1)$, $c = 12.637\,(1)$ Å, $\alpha = 96.824\,(3)$, $\beta = 116.169\,(3)$, $\gamma = 87.313\,(4)^\circ$, $U = 2238.8\,(6)$ Å^3 (15 K), $Z = 2$, $D_x = 1.41$ g cm^{-3} (293 K), $\lambda = 1.3168$ Å (thermal neutrons; Ge monochromator), $\mu = 2.74$ cm^{-1}, $F(000) = 208 \times 10^{13}$ cm, $R = 0.072$ (3160 reflections used). Crystals of pentahydridobis(phenylsilyl)bis(tricyclopentylphosphine)rhenium $[ReH_5(PCyp_3)_2(SiH_2Ph)_2]$ (II) grow from *n*-hexane as transparent prisms in the space group $P2_12_12_1$. $M_r = 882.38$, $a = 12.448\,(2)$, $b = 17.579\,(4)$, $c = 19.433\,(4)$ Å, $U = 4252\,(3)$ Å^3 (200 K), $Z = 4$, $D_x = 1.36$ g cm^{-3} (293 K), $\lambda = 0.71073$ Å (X-rays: Mo $K\alpha$; graphite monochromator), $\mu = 30.2$ cm^{-1}, $F(000) = 1832.0$, $R = 0.041$ (6014 reflections used). For (I), the Re—P bond lengths and P—Re—P bond angle are 2.444 (8), 2.444 (7) Å and 141.2 (3)°, and the Re—Si bond lengths and Si—Re—Si bond angle are 2.500 (8), 2.510 (9) Å and 117.9 (3)°. For (II), the corresponding lengths and angles are 2.439 (1), 2.444 (1) Å, 139.5 (1)° and 2.501 (2), 2.490 (2) Å, 97.9 (1)°. The closest intramolecular contact between hydride ligands in (I) is 2.002 (29) Å, and that between a hydride ligand and a silicon atom is 2.048 (13) Å.

Introduction

In recent years, a great deal of work has been devoted to investigating the possibility that some transition-metal polyhydride complexes may be 'non-classical', *i.e.* that they may contain molecular hydrogen ligands (Desrosiers, Cai, Lin, Richards & Halpern, 1991, and references therein). Much of this effort has involved spectroscopic techniques, but reliable information usually requires the study of isotopomeric series of several related complexes. Accurate information on the positions of metal-bound hydride positions in single complexes of this type has been obtained from single-crystal diffraction studies (Teller & Bau, 1981; Hlatky & Crabtree, 1985); often using neutrons (for example Brammer, Howard, Johnson, Koetzle, Spencer & Stringer, 1991, and references 7 to 11 therein), but in some cases from X-ray diffraction (for example Luo, Baudry, Boydell, Charpin, Nierlich, Ephritikhine & Crabtree, 1990; Hazel, Howard & Spencer, 1984).

With one exception (Brammer, Howard, Johnson, Koetzle, Spencer & Stringer, 1991), no crystallographic study of a transition-metal polyhydride complex, in which the hydride ligands were located, has shown a structure in which two hydride ligands are less than about 1.6 Å apart. We have been investigating the possibility that, in high-coordination-

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number complexes with bulky ligands, the coordination of the metal might be reduced so as to lower the steric interactions. Thermal reactions of the $[ReH_7(PR_3)_2]$ complexes, in which H_2 dissociates from the molecule, and the resulting transient species reacts with an appropriate substrate, are well established (Zeiher, DeWit & Caulton, 1984). We have found (Dix & Spencer, 1988) that under appropriate conditions, such reactions with silanes (Luo, Baudry, Boydell, Charpin, Neirlich, Ephritikhine & Crabtree, 1990) continue a stage further, forming novel complexes of the type $[ReH_5(PR_3)_2(SiR_3)_2]$.

Experimental

$[ReH_7(PPh^iPr_2)_2]$ and $[ReH_7(PCyp_3)_2]$ were prepared by reaction of the corresponding $[ReOCl_3(PR_3)_2]$ compounds with $LiAlH_4$ in tetrahydrofuran, according to the general method of Chatt & Coffey (1969).

Synthesis of (I): $[ReH_7(PPh^iPr_2)_2]$ (150 mg, 0.158 mmol) and SiH_2Ph_2 (1.0 ml, 5.4 mmol) were sealed in a flask with 6 ml dry *n*-hexane, under dry nitrogen gas. The vessel was held at 328 K for 17 h, then allowed to cool to room temperature. Crystals suitable for the neutron study were deposited directly from the reaction mixture on leaving the unopened reaction vessel to stand for two days. Further material was obtained by concentration of the supernatant. Analysis (%), measured (calculated): C 60.98 (60.92), H 6.92 (7.07).

Synthesis of (II): $[ReH_7(PCyp_3)_2]$ (1 020 mg, 1.523 mmol) and SiH_3Ph (1.0 ml, 8.1 mmol) were sealed in a flask with 22 ml dry *n*-hexane, under dry nitrogen gas. The vessel was held at 339 K for a total of 38 h. Twice during this period, the reaction was allowed to return to room temperature, and the reaction mixture was freeze-thaw degassed to remove H_2. At the end of the reaction, the mixture was allowed to cool slowly to room temperature. Crystals suitable for the X-ray study were deposited directly from the reaction mixture, with further material being obtained by concentration of the supernatant. Analysis (%), measured (calculated): C 56.97 (57.17), H 8.60 (8.34).

A room-temperature X-ray diffraction study of (I) was undertaken, the results of which are not presented here. All atoms other than H atoms were located in this study; during the refinement the organic H atoms were taken to be 'riding' on the attached C atoms. The subsequent neutron study was undertaken on D19 at ILL, Grenoble, at 15 K using a 'Displex' cryorefrigerator (Archer & Lehmann, 1986), and a 64 × 4° position-sensitive detector (Thomas, Stansfield, Berneron, Filhol, Greenwood, Jacobe, Feltin & Mason, 1983). The faces of the crystal were indexed at room temperature, after which the crystal was cooled to 15 K over a period of several hours, the (460) reflection being monitored throughout. $|F^2_{obs}|$ values were calculated by the ILL program *RETREAT* (Wilkinson, Khamis, Stansfield & McIntyre, 1988). During data collection, the intensities of the standard reflections were not observed to vary significantly. The X-ray structure (with C—H distances corrected to 1.08 Å) was used as the starting point for the refinement, during which the remaining H atoms were successfully located. Insufficient data were collected to allow free refinement with a fully anisotropic model, so constraints were placed on the phenyl groups, and only the hydride ligands were assigned anisotropic displacement parameters. Further experimental data are given in Table 1.

Table 1. *Additional crystal and experimental data for* $[ReH_5(PPh^iPr_2)_2(SiHPh_2)_2]$ (I) *and* $[ReH_5(PCyp_3)_2(SiH_2Ph)_2]$ (II)

Complex	$[ReH_5(PPh^iPr_2)_2(SiHPh_2)_2]$	$[ReH_5(PCyp_3)_2(SiH_2Ph)_2]$
Crystal size (mm)	2.50 × 0.82 × 0.16	0.1 × 0.2 × 0.15
Crystal faces	$\bar{2}11$, $0\bar{1}2$, $01\bar{2}$, $\bar{2}0\bar{2}$, $20\bar{2}$, 111, $\bar{1}\bar{1}\bar{1}$	
Diffractometer	D19, ILL, Grenoble	Nicolet *P3m/v*
Scan type	ω	ω:2θ
Data used for determining cell parameters	50 reflections	15 reflections with $30 \leq 2\theta \leq 32°$
Absorption correction	Numerical	Empirical
θ_{max} (°)	50	30
Range of *h,k,l*	±10, ±15, ±12	17, 24, 27
Standard reflections	460, $\bar{4}\bar{6}0$	$2\bar{1}3$, 310, $\bar{3}\bar{1}0$
Data measured	4871	6878
Independent data	3456	6844
Data used	3160	6014*
R_{merge}	0.029	0.020
$I > n\sigma(I)$, *n*	2	4
Structure solution (X-ray)	Heavy-atom methods and electron density difference maps	
Structure refinement	Full-matrix least squares (on $|F^2|$)	
Number of parameters	426	424
R (*R*′)	0.072 (0.076)	0.041 (0.036)
Goodness of fit	3.03	1.00
Weighting scheme $[\sigma^2(F) + g|F^2|]^{-1}$, *g*	0.0002	0.0005
Maximum shift/e.s.d.	0.06	0.16
Maximum and minimum height in Fourier syntheses	$\pm 1.5 \times 10^{-13}$ cm Å^{-3}	±1 e Å^{-3}
Source of atomic scattering factors	Bacon (1975)	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs used	In-house software (ILL) and *SHELXTL-Plus*	*SHELXTL-Plus* (Sheldrick, 1991)

* The (111) reflection exceeded the dead time correction, and was rejected.

The X-ray study of (II) was performed on a Nicolet *P3m/v* four-circle diffractometer at 200 K. The temperature of the crystal was maintained by a dry nitrogen gas flow. During data collection, the intensities of the standard reflections were not observed to vary significantly. After data collection, the crystal was allowed to return to room temperature, and azimuthal (ψ) scans were collected for use in an empirical absorption correction. All non-H atoms were successfully located by heavy-atom methods, and the four silyl H atoms by low sinθ electron density difference maps. During the refinement, the organic H atoms were taken to be 'riding' on the attached C atoms. In the final structure, the H atoms were assigned fixed isotropic displacement parameters, all other atoms being refined with anisotropic displacement parameters. None of the metal-bound hydride ligands were located in this study. Further experimental data are given in Table 1.

Discussion

Figs. 1 and 2 show the molecular structures of (I) and (II), and Fig. 3 shows the core geometry of (I). Atomic coordinates, and important bond lengths and interbond angles, are given in Tables 2 and 3.* The P—Re—P bond angles and Re—P bond lengths of both (I) and (II) are similar to those already observed for [$ReH_7(PR_3)_2$] complexes (Bau, Carroll, Hart, Teller & Koetzle, 1978; Howard, Mead & Spencer, 1983; Howard, 1986; Howard & Johnson, 1988), although the angles are slightly smaller than is typical, and the lengths are slightly greater. As in the monosilyl hexahydride complex [$ReH_6(PPh_3)_2(SiPh_3)$] (Luo, Baudry, Boydell, Charpin, Nierlich, Ephritikhine & Crabtree, 1990), the Re—Si bond lengths are somewhat shorter than the sum of the covalent radii of rhenium and silicon (2.65 Å), and Luo *et al.* suggested that this might be due to a weak interaction between the Si atom and one or more of the hydrides. Unsupported metal–hydrogen–silicon two-electron three-centre bonds typically have a Si···H distance of 1.6 to 1.8 Å (Schubert, Ackerman & Worle, 1986; Schubert, Bahr & Müller, 1987; Schubert, Müller & Alt, 1987). In (I), the closest Si···H distances are 2.048 Å for Si(1)···H(1) and 2.065 Å for Si(2)···H(2), which indicates that any interaction between the Si atoms and these hydrides is weak.

The presence of the two silyl groups does not seem to have a profound effect on the ReP_2 part of the complexes; indeed the P—Re—P bond angle in (I) (141.2°) is the same, within experimental error, as

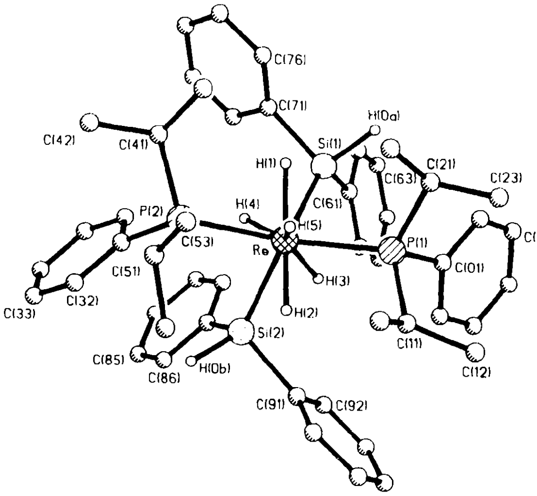

Fig. 1. Molecular geometry of (I), showing atomic numbering scheme. Organic H atoms are omitted for clarity.

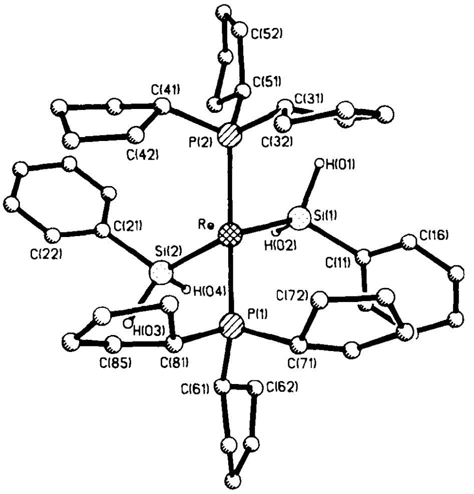

Fig. 2. Molecular geometry of (II), showing atomic numbering scheme. Organic H atoms are omitted for clarity.

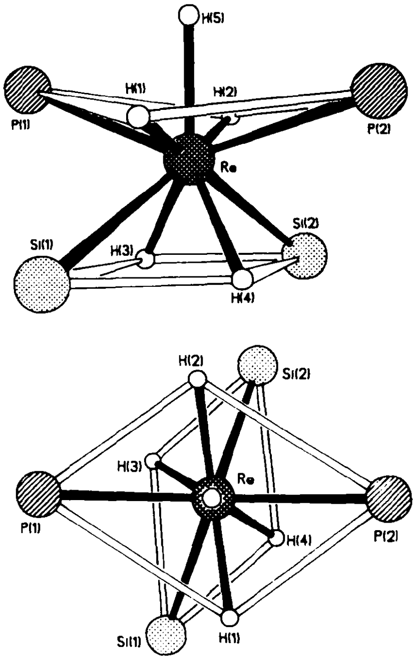

Fig. 3. Coordination sphere of (I), illustrating monocapped twisted rhombic prism geometry.

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* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54825 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0088]

Table 2. *Atomic coordinates* ($\times 10^5$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^4$)

	x	y	z	$U_{\rm eq}$
Compound (I)				
Re	24664 (33)	28557 (21)	23271 (28)	35 (9)
P(1)	23436 (62)	36624 (40)	40167 (56)	75 (16)
P(2)	16395 (60)	27951 (38)	1728 (53)	39 (16)
Si(1)	47807 (75)	30777 (48)	34742 (67)	75 (20)
Si(2)	16485 (76)	14443 (48)	19488 (68)	83 (20)
H(1)	3306 (10)	3584 (7)	2153 (9)	28 (5)
H(2)	1037 (9)	2594 (6)	2200 (9)	22 (5)
H(3)	2936 (11)	2240 (7)	3395 (9)	28 (5)
H(4)	3462 (10)	2275 (7)	1956 (9)	27 (5)
H(5)	1505 (10)	3652 (7)	1857 (10)	26 (5)
C(01)	34063 (26)	33141 (17)	54814 (21)	60 (12)
C(02)	30695	26057	57512	70 (13)
C(03)	38179	23128	68326	86 (13)
C(04)	49030	27283	76443	99 (13)
C(05)	52398	34367	73745	101 (13)
C(06)	44914	37296	62931	75 (13)
C(11)	7647 (46)	35611 (31)	39761 (41)	37 (12)
C(12)	6429 (52)	37591 (33)	51441 (45)	85 (13)
C(13)	2676 (51)	40015 (33)	29927 (45)	90 (13)
C(21)	27651 (50)	47419 (30)	42549 (43)	59 (12)
C(22)	22388 (52)	51739 (33)	31401 (45)	94 (13)
C(23)	24337 (50)	52159 (32)	51989 (44)	66 (13)
C(31)	18088 (26)	17991 (15)	5806 (26)	66 (12)
C(32)	7834	13667	14646	77 (13)
C(33)	9666	6291	−20051	73 (13)
C(34)	21753	3238	−16617	75 (13)
C(35)	32008	7561	7777	63 (12)
C(36)	30175	14937	2372	68 (13)
C(41)	25171 (48)	34120 (30)	−3708 (42)	48 (12)
C(42)	19753 (52)	33306 (33)	−17254 (45)	101 (13)
C(43)	27334 (53)	43205 (32)	1325 (48)	96 (13)
C(51)	459 (47)	30531 (30)	6832 (43)	52 (13)
C(52)	−9396 (51)	25768 (33)	−4101 (46)	87 (13)
C(53)	−2877 (53)	39579 (32)	−4987 (47)	90 (13)
C(61)	58079 (24)	23513 (18)	46137 (26)	90 (13)
C(62)	71037	24367	50532	84 (13)
C(63)	79086	19589	59085	93 (13)
C(64)	74178	13958	63242	101 (13)
C(65)	61220	13104	58847	104 (13)
C(66)	53170	17882	50294	66 (13)
C(71)	56258 (32)	30929 (18)	24720 (27)	92 (13)
C(72)	61028	23864	21259	117 (13)
C(73)	66333	23942	13380	195 (15)
C(74)	66868	31086	8962	230 (15)
C(75)	62098	38151	12423	186 (15)
C(76)	56793	38073	20302	89 (13)
C(81)	27179 (25)	5746 (15)	17973 (28)	70 (13)
C(82)	40248	6185	23248	80 (13)
C(83)	47173	−250	21186	94 (13)
C(84)	41030	7123	13848	88 (13)
C(85)	27962	−7562	8573	93 (13)
C(86)	21036	−1127	10635	74 (13)
C(91)	11504 (28)	11710 (20)	31171 (23)	84 (13)
C(92)	19323	7393	40482	63 (13)
C(93)	15870	6177	49388	96 (13)
C(94)	4598	9278	48983	96 (13)
C(95)	−3221	13595	39672	116 (13)
C(96)	232	14811	30766	72 (13)
Compound (II)				
Re	56452 (1)	51850 (1)	−792 (1)	277 (1)
P(1)	41000 (9)	55772 (8)	6060 (6)	299 (3)
P(2)	61634 (11)	41787 (7)	−8809 (7)	310 (4)
Si(1)	64525 (13)	61366 (9)	−8837 (10)	413 (5)
Si(2)	67976 (14)	54564 (11)	9387 (9)	487 (5)
C(21)	78930 (44)	47556 (40)	11709 (30)	439 (17)
C(12)	56545 (61)	76545 (33)	−8099 (34)	540 (20)
C(13)	50187 (63)	82658 (39)	9965 (43)	641 (26)
C(14)	43352 (75)	82065 (41)	−15560 (40)	662 (26)
C(15)	42815 (74)	75393 (40)	−19203 (36)	634 (24)
C(16)	49173 (57)	69254 (40)	−17192 (34)	531 (21)
C(11)	56073 (53)	69697 (29)	−11673 (27)	414 (15)
C(22)	77420 (56)	42008 (44)	16754 (35)	555 (23)
C(23)	85319 (75)	36739 (52)	18230 (41)	709 (30)
C(24)	94828 (68)	36891 (49)	14933 (42)	680 (28)
C(25)	96766 (59)	42380 (48)	9937 (43)	654 (27)
C(26)	88962 (49)	47630 (44)	8354 (33)	521 (19)
C(42)	53807 (47)	29237 (32)	−500 (35)	502 (18)
C(43)	58889 (86)	25085 (83)	5266 (67)	1394 (64)
C(44)	70294 (71)	24693 (43)	4428 (49)	755 (31)
C(45)	73139 (49)	31255 (34)	−351 (37)	523 (19)
C(41)	63280 (43)	32130 (29)	−4982 (28)	368 (15)

Table 2 (*cont.*)

	x	y	z	$U_{\rm eq}$
C(32)	41251 (51)	36609 (45)	−13924 (36)	566 (23)
C(33)	34532 (77)	37760 (72)	−20186 (49)	918 (42)
C(34)	38891 (66)	44714 (54)	−24012 (42)	765 (30)
C(35)	49768 (63)	46571 (36)	−20618 (34)	573 (23)
C(31)	52268 (50)	39828 (34)	−15878 (29)	410 (16)
C(52)	77702 (61)	36433 (41)	−18554 (42)	617 (25)
C(53)	89739 (63)	37020 (54)	−18913 (43)	694 (29)
C(54)	93030 (60)	44237 (51)	−15409 (45)	750 (29)
C(55)	84096 (48)	45897 (41)	−10121 (35)	525 (21)
C(51)	74088 (44)	43145 (33)	13906 (30)	401 (16)
C(62)	48644 (51)	70904 (34)	9620 (33)	465 (19)
C(63)	46043 (72)	76874 (44)	14906 (45)	758 (31)
C(64)	36868 (59)	74161 (40)	19222 (38)	572 (23)
C(65)	33042 (59)	66792 (41)	15882 (40)	580 (23)
C(61)	42935 (48)	63707 (30)	12189 (25)	368 (14)
C(72)	24515 (53)	52897 (40)	−4002 (36)	553 (21)
C(73)	20086 (141)	57653 (65)	−9656 (69)	1658 (76)
C(74)	22303 (72)	65275 (58)	−8949 (49)	833 (34)
C(75)	30458 (48)	66048 (34)	−3136 (31)	449 (17)
C(71)	28928 (37)	58777 (30)	1142 (29)	367 (14)
C(82)	30533 (61)	41379 (36)	8767 (38)	554 (21)
C(83)	29677 (111)	35947 (56)	14820 (59)	1089 (49)
C(84)	36868 (97)	38554 (53)	20241 (50)	906 (40)
C(85)	42516 (76)	45907 (48)	17813 (37)	773 (30)
C(81)	34961 (46)	48708 (38)	11994 (27)	416 (16)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

that in one of the two crystal forms of its parent heptahydride, $[\mathrm{ReH_7(PPh^iPr_2)_2}]$ (Howard, Mead & Spencer, 1983). (In the other crystal form, the bond angle is 147.0°, the difference of 6.0° presumably arising from crystal packing forces). In the case of (II), the P—Re—P bond angle is 7.2° smaller than that of its parent heptahydride (Howard, 1986). This is in marked contrast to $[\mathrm{ReH_6(PPh_3)_2(SiPh_3)}]$ (Luo, Baudry, Boydell, Charpin, Nierlich, Ephritikhine & Crabtree, 1990), where the P—Re—P angle is 29° smaller than that in $[\mathrm{ReH_7(PPh_3)_2}]$ (Howard, Mead & Spencer, 1983).

Considered from the viewpoint of steric properties, the ligands of (I) and (II) fall into two broad groups: one of four (the phosphines and silyls) and one of five (the hydride ligands). It might therefore be expected that the coordination sphere would adopt a structure based on the triangular-faced dodecahedron, with the heavier atoms occupying one of the two types of vertex, four of the hydrides occupying the other type, and the remaining hydride capping a face or bridging an edge. This kind of structure is adopted by $[\mathrm{MoH_4(PMePh_2)_4}]$, for example (Meakin, Guggenberger, Peet, Muetterties & Jesson, 1973). The description of (I) as adopting a monobridged dodecahedral structure would require P(1), P(2), H(3) and H(4) to be coplanar, and also Si(1), Si(2), H(1) and H(2) (Lippard & Russ, 1968, 1972). This, however, is not the case, the mean deviations from the least-squares planes being 0.34 and 0.41 Å respectively. The dihedral angle between these planes is 86.1°, which is intermediate between the values of 90 and 79° required for dodecahedral and square-antiprismatic geometry respectively, and does not conclusively distinguish between the two possibilities.

Table 3. *Principal bond lengths* (Å) *and angles* (°)

Compound (I)

Re—H(1)	1.704 (14)	Re—H(2)	1.707 (13)
Re—H(3)	1.676 (12)	Re—H(4)	1.684 (13)
Re—H(5)	1.698 (11)	Re—P(1)	2.444 (8)
Re—P(2)	2.444 (7)	Re—Si(1)	2.500 (8)
Re—Si(2)	2.510 (9)	H(1)—Si(1)	2.048 (12)
H(2)—Si(2)	2.065 (14)	H(3)—Si(2)	2.146 (12)
P(1)—C(01)	1.868 (6)	P(1)—C(11)	1.869 (10)
P(1)—C(21)	1.853 (8)	P(2)—C(31)	1.868 (7)
P(2)—C(41)	1.879 (10)	P(2)—C(51)	1.867 (8)
Si(1)—H(0*A*)	1.510 (12)	Si(1)—C(61)	1.942 (8)
Si(1)—C(71)	1.935 (11)	Si(2)—H(0*B*)	1.493 (11)
Si(2)—C(81)	1.936 (9)	Si(2)—C(91)	1.923 (11)
C(11)—C(12)	1.542 (9)	C(11)—C(13)	1.543 (7)
C(21)—C(23)	1.539 (9)	C(21)—C(22)	1.524 (8)
C(41)—C(43)	1.565 (7)	C(41)—C(42)	1.531 (7)
C(51)—C(52)	1.533 (9)	C(51)—C(53)	1.539 (7)

H(1)—Re—H(2)	145.4 (6)	H(1)—Re—H(3)	128.5 (5)
H(2)—Re—H(3)	80.8 (6)	H(1)—Re—H(4)	80.4 (6)
H(2)—Re—H(4)	127.8 (6)	H(3)—Re—H(4)	80.7 (6)
H(1)—Re—H(5)	72.1 (6)	H(2)—Re—H(5)	73.3 (6)
H(3)—Re—H(5)	140.2 (7)	H(4)—Re—H(5)	139.2 (7)
H(1)—Re—P(1)	91.9 (5)	H(2)—Re—P(1)	77.1 (4)
H(3)—Re—P(1)	75.1 (5)	H(4)—Re—P(1)	141.6 (4)
H(5)—Re—P(1)	70.1 (4)	H(1)—Re—P(2)	77.1 (4)
H(2)—Re—P(2)	91.0 (4)	H(3)—Re—P(2)	140.0 (4)
H(4)—Re—P(2)	73.8 (4)	H(5)—Re—P(2)	71.1 (4)
P(1)—Re—P(2)	141.2 (3)	H(1)—Re—Si(1)	54.4 (4)
H(2)—Re—Si(1)	152.6 (5)	H(3)—Re—Si(1)	74.6 (5)
H(4)—Re—Si(1)	60.0 (4)	H(5)—Re—Si(1)	119.7 (4)
P(1)—Re—Si(1)	84.9 (3)	P(2)—Re—Si(1)	115.7 (3)
H(1)—Re—Si(2)	152.5 (5)	H(2)—Re—Si(2)	54.7 (4)
H(3)—Re—Si(2)	57.6 (4)	H(4)—Re—Si(2)	74.2 (5)
H(5)—Re—Si(2)	122.4 (4)	P(1)—Re—Si(2)	114.6 (3)
P(2)—Re—Si(2)	85.7 (3)	Si(1)—Re—Si(2)	117.9 (3)
Re—H(1)—Si(1)	83.0 (6)	Re—H(2)—Si(2)	82.9 (6)
Re—H(3)—Si(2)	81.1 (4)	Re—P(1)—C(01)	113.8 (3)
Re—P(1)—C(11)	110.9 (3)	C(01)—P(1)—C(11)	102.1 (4)
Re—P(1)—C(21)	117.2 (4)	C(01)—P(1)—C(21)	102.1 (3)
C(11)—P(1)—C(21)	109.3 (4)	Re—P(2)—C(31)	114.8 (3)
Re—P(2)—C(41)	115.4 (3)	C(31)—P(2)—C(41)	97.4 (4)
Re—P(2)—C(51)	117.6 (4)	C(31)—P(2)—C(51)	104.0 (3)
C(41)—P(2)—C(51)	105.1 (4)	Re—Si(1)—H(1)	42.6 (4)
Re—Si(1)—H(0*A*)	113.0 (5)	H(1)—Si(1)—H(0*A*)	89.5 (6)
Re—Si(1)—C(61)	120.6 (4)	H(1)—Si(1)—C(61)	162.9 (6)
H(0*A*)—Si(1)—C(61)	103.1 (5)	Re—Si(1)—C(71)	113.1 (3)
H(1)—Si(1)—C(71)	85.5 (5)	H(0*A*)—Si(1)—C(71)	102.0 (7)
C(61)—Si(1)—C(71)	102.8 (4)	Re—Si(2)—H(2)	42.4 (4)
Re—Si(2)—H(3)	41.3 (3)	H(2)—Si(2)—H(3)	62.7 (4)
Re—Si(2)—H(0*B*)	115.0 (6)	H(2)—Si(2)—H(0*B*)	91.1 (6)
H(3)—Si(2)—H(0*B*)	153.1 (7)	Re—Si(2)—C(81)	117.9 (4)
H(2)—Si(2)—C(81)	160.4 (6)	H(3)—Si(2)—C(81)	102.8 (5)
H(0*B*)—Si(2)—C(81)	101.0 (6)	Re—Si(2)—C(91)	113.7 (4)
H(2)—Si(2)—C(91)	86.9 (5)	H(3)—Si(2)—C(91)	83.6 (5)
H(0*B*)—Si(2)—C(91)	101.9 (7)	C(81)—Si(2)—C(91)	105.4 (4)
P(1)—C(01)—C(02)	117.0 (2)	P(1)—C(01)—C(06)	123.0 (2)
P(1)—C(11)—H(11*A*)	99.7 (8)	P(1)—C(11)—C(12)	118.2 (4)
P(1)—C(11)—C(13)	112.6 (5)	P(1)—C(21)—H(21*A*)	102.8 (7)
P(1)—C(21)—C(22)	115.3 (4)	P(1)—C(21)—C(23)	112.4 (5)
P(2)—C(31)—C(32)	122.5 (2)	P(2)—C(31)—C(36)	117.5 (2)
P(2)—C(41)—H(41*A*)	99.5 (8)	P(2)—C(41)—C(42)	112.9 (4)
P(2)—C(41)—C(43)	116.7 (5)	P(2)—C(51)—H(51*A*)	104.3 (7)
P(2)—C(51)—C(52)	113.4 (4)	P(2)—C(51)—C(53)	112.1 (4)
Si(1)—C(61)—C(62)	116.4 (3)	Si(1)—C(61)—C(66)	123.6 (3)
Si(2)—C(81)—C(82)	124.0 (2)	Si(2)—C(81)—C(86)	115.9 (2)
Si(2)—C(91)—C(92)	121.8 (2)	Si(2)—C(91)—C(96)	118.0 (3)

Compound (II)

Re—P(1)	2.439 (1)	Re—P(2)	2.444 (1)
Re—Si(1)	2.501 (2)	Re—Si(2)	2.490 (2)
P(1)—C(61)	1.850 (5)	P(1)—C(71)	1.858 (5)
P(1)—C(81)	1.854 (6)	P(2)—C(41)	1.865 (5)
P(2)—C(31)	1.834 (6)	P(2)—C(51)	1.855 (6)
Si(1)—C(11)	1.886 (6)	Si(2)—C(21)	1.892 (6)
C(21)—C(22)	1.396 (10)	C(21)—C(26)	1.409 (8)
C(12)—C(13)	1.383 (10)	C(12)—C(11)	1.391 (8)
C(13)—C(14)	1.384 (12)	C(14)—C(15)	1.372 (10)
C(15)—C(16)	1.394 (10)	C(16)—C(11)	1.376 (9)
C(22)—C(23)	1.381 (12)	C(23)—C(24)	1.346 (12)
C(24)—C(25)	1.390 (12)	C(25)—C(26)	1.375 (10)
C(42)—C(43)	1.479 (15)	C(42)—C(41)	1.552 (8)
C(43)—C(44)	1.431 (14)	C(44)—C(45)	1.523 (11)
C(45)—C(41)	1.529 (8)	C(32)—C(33)	1.490 (12)
C(32)—C(31)	1.531 (9)	C(33)—C(34)	1.530 (15)
C(34)—C(35)	1.541 (11)	C(35)—C(31)	1.533 (9)
C(52)—C(53)	1.503 (11)	C(52)—C(51)	1.553 (10)
C(53)—C(54)	1.497 (13)	C(54)—C(55)	1.542 (10)
C(55)—C(51)	1.526 (8)	C(62)—C(63)	1.504 (10)
C(62)—C(61)	1.535 (8)	C(63)—C(64)	1.495 (11)
C(64)—C(65)	1.425 (10)	C(65)—C(61)	1.525 (9)
C(72)—C(73)	1.487 (15)	C(72)—C(71)	1.539 (9)
C(73)—C(74)	1.375 (16)	C(74)—C(75)	1.525 (11)
C(75)—C(71)	1.537 (8)	C(82)—C(83)	1.519 (13)
C(82)—C(81)	1.535 (9)	C(83)—C(84)	1.456 (16)
C(84)—C(85)	1.545 (13)	C(85)—C(81)	1.551 (10)

Table 3 (*cont.*)

P(1)—Re—P(2)	139.5 (1)	P(1)—Re—Si(1)	118.0 (1)
P(2)—Re—Si(1)	88.8 (1)	P(1)—Re—Si(2)	88.1 (1)
P(2)—Re—Si(2)	119.6 (1)	Si(1)—Re—Si(2)	97.9 (1)
Re—P(1)—C(61)	117.2 (2)	Re—P(1)—C(71)	115.9 (2)
C(61)—P(1)—C(71)	102.8 (2)	Re—P(1)—C(81)	118.0 (2)
C(61)—P(1)—C(81)	99.1 (3)	C(71)—P(1)—C(81)	100.5 (2)
Re—P(2)—C(41)	115.7 (2)	Re—P(2)—C(31)	116.5 (2)
C(41)—P(2)—C(31)	101.4 (3)	Re—P(2)—C(51)	117.9 (2)
C(41)—P(2)—C(51)	103.8 (3)	C(31)—P(2)—C(51)	98.9 (3)
Re—Si(1)—C(11)	118.6 (2)	Re—Si(2)—C(21)	118.7 (2)
Si(2)—C(21)—C(22)	121.7 (5)	Si(2)—C(21)—C(26)	121.5 (5)
C(22)—C(21)—C(26)	116.8 (6)	C(13)—C(12)—C(11)	121.2 (7)
C(12)—C(13)—C(14)	119.9 (7)	C(13)—C(14)—C(15)	120.0 (7)
C(14)—C(15)—C(16)	119.3 (7)	C(15)—C(16)—C(11)	121.9 (6)
Si(1)—C(11)—C(12)	120.2 (5)	Si(1)—C(11)—C(16)	122.1 (4)
C(12)—C(11)—C(16)	117.7 (6)	C(21)—C(22)—C(23)	121.2 (7)
C(22)—C(23)—C(24)	120.9 (8)	C(23)—C(24)—C(25)	119.9 (8)
C(24)—C(25)—C(26)	120.0 (7)	C(21)—C(26)—C(25)	121.1 (7)
C(43)—C(42)—C(41)	105.2 (6)	C(42)—C(43)—C(44)	111.2 (9)
C(43)—C(44)—C(45)	105.3 (8)	C(44)—C(45)—C(41)	104.4 (5)
P(2)—C(41)—C(42)	116.0 (4)	P(2)—C(41)—C(45)	114.5 (4)
C(42)—C(41)—C(45)	104.3 (5)	C(33)—C(32)—C(31)	104.5 (6)
C(32)—C(33)—C(34)	107.8 (8)	C(33)—C(34)—C(35)	105.8 (7)
C(34)—C(35)—C(31)	105.8 (6)	P(2)—C(31)—C(32)	116.9 (4)
P(2)—C(31)—C(35)	115.7 (4)	C(32)—C(31)—C(35)	104.6 (5)
C(53)—C(52)—C(51)	105.3 (6)	C(52)—C(53)—C(54)	108.1 (7)
C(53)—C(54)—C(55)	105.4 (6)	C(54)—C(55)—C(51)	102.0 (5)
P(2)—C(51)—C(52)	117.1 (4)	P(2)—C(51)—C(55)	117.8 (4)
C(52)—C(51)—C(55)	106.6 (5)	C(63)—C(62)—C(61)	104.7 (5)
C(62)—C(63)—C(64)	109.0 (6)	C(63)—C(64)—C(65)	105.7 (6)
C(64)—C(65)—C(61)	104.5 (6)	P(1)—C(61)—C(62)	118.2 (4)
P(1)—C(61)—C(65)	117.8 (4)	C(62)—C(61)—C(65)	103.5 (5)
C(73)—C(72)—C(71)	103.6 (7)	C(72)—C(73)—C(74)	113.6 (11)
C(73)—C(74)—C(75)	107.1 (9)	C(74)—C(75)—C(71)	104.1 (5)
P(1)—C(71)—C(72)	115.6 (4)	P(1)—C(71)—C(75)	114.5 (4)
C(72)—C(71)—C(75)	104.6 (5)	C(83)—C(82)—C(81)	103.7 (6)
C(82)—C(83)—C(84)	108.6 (9)	C(83)—C(84)—C(85)	108.8 (8)
C(84)—C(85)—C(81)	102.3 (7)	P(1)—C(81)—C(82)	117.0 (4)
P(1)—C(81)—C(85)	114.9 (5)	C(82)—C(81)—C(85)	104.4 (6)

Another possibility for the coordination geometry of (I) is the tricapped trigonal prism. There are two possible descriptions, the first with H(3), H(4) and H(5) in the capping positions, and the second with Si(1), Si(2) and H(5). We consider the first description to be unsatisfactory, since two of the three rectancular faces are not formed by atoms which are coplanar (the deviations from the least-squares planes being 0.28 and 0.26 Å), and the angles between the vectors joining Re and the capping atoms are 141, 139 and 80°. In the second description, these objections are met, but the vectors Re—Si(1) and Re—Si(2) are not normal to the faces which they cap, the angles being 76.4 and 75.8°. In neither description are the triangular faces mutually parallel, making angles of 25.7 and 23.7° respectively.

These considerations lead us to examine (I) in terms of monocapped square-antiprismatic geometry. Although P(1), P(2), H(1) and H(2) are not coplanar, the mean deviation from the least-squares plane (0.15 Å) is considerably less than the deviations from the planes referred to in the previous two paragraphs. Also, Si(1), Si(2), H(3) and H(4) are almost coplanar, the mean deviation being 0.01 Å. The angle between these two planes is 0.7°, and the angle between the first of the two planes and the vector joining Re and H(5) is 89.4°. However, with such a wide disparity between the different types of ligand, the distortion of these 'square' faces is severe. In contrast to $[ReH_7(PMePh_2)_2]$ (Diamond, Howard, Keller, Mason, Spencer & Taylor, 1991), this distortion is not symmetrical: the two angles H(1)—Re—P(1) and H(2)—Re—P(2) are equal within the sum of the errors, as are H(1)—Re—P(2) and H(2)—Re—P(1), but these pairs of angles differ by about 14.4°. The H(3)—H(4)—Si(1)—Si(2) face is similar, with the difference in angles being 15.6°. In view of this, and since the two 'square' faces are parallel and the capping atom is positioned normally above the centre of the capped face, we describe the geometry of (I) as a monocapped twisted rhombic prism.

Interestingly, the Si—Re—Si angles in both (I) and (II) are significantly smaller than the P—Re—P angles, in spite of the Re—Si and Re—P bond lengths differing only slightly, and the covalent radii of P and Si being similar (1.10 and 1.17 Å respectively). The P—Re—P bond angle, being similar to those found in the $[ReH_7(PR_3)_2]$ complexes, may be determined by the steric influence of the capping hydride ligand H(5), or by electronic factors which favour the molecular geometry adopted by complexes (I) and (II). In either case, the steric influence of the silyl groups would not be able to close this angle significantly. The Si—Re—Si angle, on the other hand, is likely to be determined by a balance of the steric interactions between the two silyl groups, and the interactions between the silyl groups and the phosphines. The relative orientation of the 'square' faces deviates considerably from the ideal square antiprism; the two planes Re, P(1), P(2) and Re, Si(1), S(2) have a dihedral angle of 71.7° in (I) and 68.7° in (II) (the ideal antiprismatic value is, of course, 45°). This indicates a degree of repulsion between the phosphine ligands and the silyl groups. {In $[ReH_7(PMePh_2)_2]$, the uncapped square face, which is made up of four hydride ligands, is orientated at close to 45° relative to the capped face (Diamond, Howard, Keller, Mason, Spencer & Taylor, 1991).} On the other hand, the Si—Re—Si angle in (II) is 20.0° smaller than that in (I), which is presumably due to a smaller steric interaction between two SiH_2Ph groups than between two $SiHPh_2$ groups.

Concluding remarks

In the accurate structure of (I) presented here, there is no clear evidence of any reduction in coordination number, in spite of the crowding around the metal atom. $[ReH_7\{P(p\text{-tolyl})_3\}_2]$ (Brammer, Howard, Johnson, Koetzle, Spencer & Stringer, 1991) is the only polyhydride complex currently known for which a structural characterization clearly shows an unusually close contact between hydride ligands, or between one hydride and one other ligand. In this case, steric factors are clearly not responsible. The results presented here provide further evidence of the generally strong electronic factors which favour 'classical' polyhydride complexes.

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Structural Studies of Oxygen-Bridged Iron Compounds

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Abstract

Compound (I): *cis*-dichloro[μ-[bis[μ-[[2,6-diacetylpyridine dioximato](2−)-*O*:*O*′]]dihydroxodiphenyldiborato](3−)]-μ-methoxydiiron, [$Fe_2(C_{30}H_{29}B_2N_6O_6)Cl_2(CH_3O)$], M_r = 804.9, monoclinic, Cc, a = 21.228 (6), b = 8.020 (2), c = 20.865 (5) Å, β = 105.2 (1)°, V = 3428 (2) Å^3, Z = 4, D_x = 1.56 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 10.6 cm^{-1}, $F(000)$ = 1648, T = 275 K, R = 0.055 for 3018 unique reflections. Compound (I) contains a pseudo-twofold axis relating the two pyridine dioxime groups bound to the Fe atoms. In addition, two O atoms from the phenylborate moieties bridge the iron atoms, as does a methoxide. The two Cl atoms are bound to the seven coordinate metals axial to the methoxide. Compound (II): *cis*-dichloro[μ-[bis[μ-[[2,6-diacetylpyridine dioximato](2−)-*O*:*O*′]]dihydroxodiphenyldiborato](3−)]-μ-hydroxodiiron, [$Fe_2(C_{30}H_{29}B_2N_6O_6)Cl_2(OH)$].$H_2O$.$2C_2H_3N$, M_r = 891.0, monoclinic, $P2_1/n$, a = 11.860 (2), b = 20.911 (5), c = 16.175 (3) Å, β = 92.88 (1)°, V = 4006 (3) Å^3, Z = 4, D_x = 1.48 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 9.1 cm^{-1}, $F(000)$ = 1832, T = 275 K, R = 0.051 for 7034 unique reflections. Compound (II) contains a hydroxide group replacing the methoxide in compound (I). The crystals also contain two acetonitriles of solvation. The bond lengths in the complex and the hydrogen-bonding pattern in the crystals are consistent with one of the bridging borate O atoms being protonated. Compound (III): μ-chloro-*cis*-dichloro[μ-[bis[μ-[[2,6-diacetylpyridine dioximato](2−)-*O*:*O*′]]dihydroxodiphenyldiborato](3−)]-diiron, [$Fe_2(C_{30}H_{29}B_2N_6O_6)Cl_3$].$2C_4H_8O$, M_r = 953.5, triclinic, $P\bar{1}$, a = 10.535 (13), b = 13.908 (22), c = 15.175 (21) Å, α = 91.67 (12), β = 106.45 (11), γ = 94.53 (12)°, V = 2123 (7) Å^3, Z = 2, D_x = 1.49 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 9.3 cm^{-1}, $F(000)$ = 984, T = 275 K, R = 0.077 for 5536 unique reflections. Compound (III) contains a bridging chloride in place of the bridging methoxide found in compound (I). There are also two tetrahydrofuran molecules in the asymmetric unit of crystals of compound (III).

Introduction

In exploring the chemistry of binuclear iron complexes, some related to metalloproteins such as hemerythrin and ribonucleotide reductase, we have synthesized several members of a new class of compounds containing two seven-coordinate Fe atoms bridged by two O atoms and another ligand (CH_3O^-, OH^-, Cl^-). We report here the crystal structures of three of these compounds.

Experimental

Crystals of compound (I) were obtained from a self-assembly reaction involving phenylboric acid, sodium methoxide, 2,6-diacetylpyridine dioxime and ferric chloride hydrate, all in methanol solution. Compound (II) was generated by dissolving compound (I) in pyridine, drying the solution and recrystallizing the material from water/acetonitrile solutions. Evaporation of the red–brown filtrate obtained from a mixture of phenylboric acid, 2,6-diacetylpyridine dioxime, ferric chloride and sodium hydroxide in water yielded a solid which was extracted with chloroform. Crystals from the chloro-

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