Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ni(1)—C(1′)	1·783 (8)	Ni(1)—P(1)	2·215 (2)
Ni(1)—C(1)	2·020 (7)	Ni(1)—P(4)	2·172 (2)
C(1′)—O(1′)	1·114 (10)	P(1)—P(2)	2·228 (3)
P(1)—C(1)	1·785 (6)	P(2)—Cl(2)	2·072 (3)
P(2)—C(20)	1·876 (7)	C(1)—Si(1)	1·888 (8)
C(1)—C(11)	1·511 (10)	Ni(2)—C(2′)	1·744 (10)
Ni(2)—P(2)	2·181 (2)	Ni(2)—P(3)	2·220 (2)
Ni(2)—C(3)	2·017 (7)	C(2)—O(2′)	1·151 (13)
P(3)—P(4)	2·238 (3)	P(3)—C(3)	1·778 (6)
P(4)—Cl(4)	2·063 (3)	P(4)—C(40)	1·885 (7)
C(3)—Si(3)	1·887 (8)		
C(1′)—Ni(1)—P(1)	149·8 (3)	C(1′)—Ni(1)—C(1)	101·3 (3)
P(1)—Ni(1)—C(1)	49·6 (2)	C(1′)—Ni(1)—P(4)	104·7 (3)
P(1)—Ni(1)—P(4)	105·2 (1)	C(1)—Ni(1)—P(4)	153·6 (2)
Ni(1)—C(1′)—O(1′)	177·5 (9)	Ni(1)—P(1)—P(2)	105·0 (1)
Ni(1)—P(1)—C(1)	59·5 (2)	P(2)—P(1)—C(1)	111·3 (3)
P(1)—P(2)—Cl(2)	105·4 (1)	P(1)—P(2)—C(20)	101·2 (3)
Cl(2)—P(2)—C(20)	99·1 (3)	P(1)—P(2)—Ni(2)	117·9 (1)
Cl(2)—P(2)—Ni(2)	114·2 (1)	C(20)—P(2)—Ni(2)	116·5 (3)
Ni(1)—C(1)—P(1)	70·9 (2)	Ni(1)—C(1)—Si(1)	110·2 (3)
P(1)—C(1)—Si(1)	109·2 (3)	Ni(1)—C(1)—C(11)	110·5 (5)
P(1)—C(1)—C(11)	125·4 (5)	Si(1)—C(1)—C(11)	119·5 (5)
P(2)—Ni(2)—C(2′)	103·8 (3)	P(2)—Ni(2)—P(3)	103·6 (1)
C(2)—Ni(2)—P(3)	151·9 (4)	P(2)—Ni(2)—C(3)	152·7 (2)
C(2′)—Ni(2)—C(3)	103·5 (4)	P(3)—Ni(2)—C(3)	49·3 (2)
Ni(2)—C(2′)—O(2′)	176·0 (9)	Ni(2)—P(3)—P(4)	104·1 (1)
Ni(2)—P(3)—C(3)	59·4 (2)	P(4)—P(3)—C(3)	112·2 (2)
Ni(1)—P(4)—P(3)	117·9 (1)	Ni(1)—P(4)—Cl(4)	112·0 (1)
P(3)—P(4)—Cl(4)	107·6 (1)	Ni(1)—P(4)—C(40)	116·1 (2)
P(3)—P(4)—C(40)	101·5 (3)	Cl(4)—P(4)—C(40)	99·9 (2)
Ni(2)—C(3)—P(3)	71·3 (2)	Ni(2)—C(3)—Si(3)	109·2 (3)
P(3)—C(3)—Si(3)	110·5 (3)	Ni(2)—C(3)—C(31)	117·1 (5)
P(3)—C(3)—C(31)	125·4 (5)	Si(3)—C(3)—C(31)	115·2 (5)

Related literature. For complexes on 1,2-diphosphapropene see Appel, Casser & Knoch (1985), Casser (1985), and Dunker (1986). For η^2-coordinated phosphoralkene see Cowley, Jones, Stewart & Stuart (1983), and van der Knapp, Jenneskens, Meeuwissen & Bickelhaupt (1983).

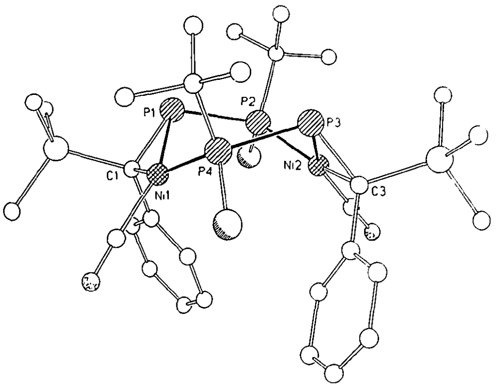

Fig. 2. View on the six-membered NiP ring. The ring adopts a boot conformation (twist conformation of the four P atoms).

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Vaska's Compound[*] – Dichloromethane Solvate (1/2)

BY ALEXANDER J. BLAKE,[†] E. A. V. EBSWORTH,[‡] HENRY M. MURDOCH AND LESLEY J. YELLOWLEES

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

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Abstract. $C_{37}H_{30}ClIrOP_2.2CD_2Cl_2$, $M_r = 954·14$, orthorhombic, *Pcab* (alternative *Pbca*, No. 61), $a = 8·0054\,(21)$, $b = 20·669\,(6)$, $c = 23·170\,(5)$ Å, $V = 3834$ Å^3, $Z = 4$, $D_x = 1·649$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3·94$ mm^{-1}, $F(000) = 1872$, $T = 298$ K, $R = 0·0253$ for 1176 unique observed reflections. Despite disordering of the Cl^- and CO ligands, it was possible to resolve the affected atoms and finally to refine without the need for geometric constraints. The solvate molecules associate with the metal complex *via* O···H and Cl···H contacts of 2·415 (25) and 2·672 (16) Å respectively.

Experimental. Crystals were obtained from a CD_2Cl_2 solution of $IrH(CO)(PPh_3)_3$. Yellow columnar crystal, 0·31 × 0·31 × 0·77 mm, Stoe STADI-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values of 46 reflections measured at $\pm\omega$ ($28 < 2\theta < 30°$). For data collection, ω–2θ scans with ω-scan width (1·65

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[*] *trans*-Carbonylchlorobis(triphenylphosphine)iridium.

[†] Author for correspondence.

[‡] Presently Vice-Chancellor, University of Durham, Old Shire Hall, Durham DH1 3HP, England.

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Table 1. *Atomic coordinates with e.s.d.'s in parentheses*

	x	y	z	U_{iso} (Å^2)
Ir	0·0	0·0	0·0	0·03351 (23)
Cl	0·0462 (8)	−0·0941 (4)	−0·0510 (4)	0·083 (3)
C	−0·019 (3)	0·0658 (16)	0·0463 (16)	0·147 (3)
O	−0·0724 (23)	0·1156 (10)	0·0583 (10)	0·102 (3)
P	0·1445 (3)	0·06346 (11)	−0·06535 (10)	0·0337 (11)
C(11)	0·0119 (6)	0·11472 (21)	−0·11029 (19)	0·035 (3)
C(12)	0·0733 (6)	0·14261 (21)	−0·16084 (19)	0·045 (3)
C(13)	−0·0305 (6)	0·18111 (21)	−0·19487 (19)	0·055 (3)
C(14)	−0·1959 (6)	0·19171 (21)	−0·17833 (19)	0·055 (3)
C(15)	−0·2573 (6)	0·16381 (21)	−0·12778 (19)	0·055 (3)
C(16)	−0·1534 (6)	0·12531 (21)	−0·09375 (19)	0·044 (3)
C(21)	0·2741 (6)	0·02265 (21)	−0·11875 (18)	0·037 (3)
C(22)	0·4469 (6)	0·03126 (21)	−0·12055 (18)	0·056 (3)
C(23)	0·5415 (6)	−0·00013 (21)	−0·16266 (18)	0·070 (3)
C(24)	0·4633 (6)	−0·04013 (21)	−0·20294 (18)	0·062 (3)
C(25)	0·2906 (6)	−0·04873 (21)	−0·20114 (18)	0·062 (3)
C(26)	0·1960 (6)	−0·01733 (21)	−0·15904 (18)	0·050 (3)
C(31)	0·2887 (6)	0·11738 (23)	−0·02889 (20)	0·038 (3)
C(32)	0·3045 (6)	0·18290 (23)	−0·04230 (20)	0·046 (3)
C(33)	0·4217 (6)	0·22087 (23)	−0·01335 (20)	0·055 (3)
C(34)	0·5231 (6)	0·19331 (23)	0·02900 (20)	0·062 (3)
C(35)	0·5073 (6)	0·12780 (23)	0·04240 (20)	0·060 (3)
C(36)	0·3901 (6)	0·08984 (23)	0·01345 (20)	0·045 (3)
C(1*S*)	0·1994 (16)	0·1788 (7)	0·1559 (5)	0·119 (3)
Cl(1*S*)	0·1246 (5)	0·13932 (20)	0·21703 (17)	0·1195 (22)
Cl(2*S*)	0·2509 (5)	0·25632 (23)	0·16584 (13)	0·1251 (21)

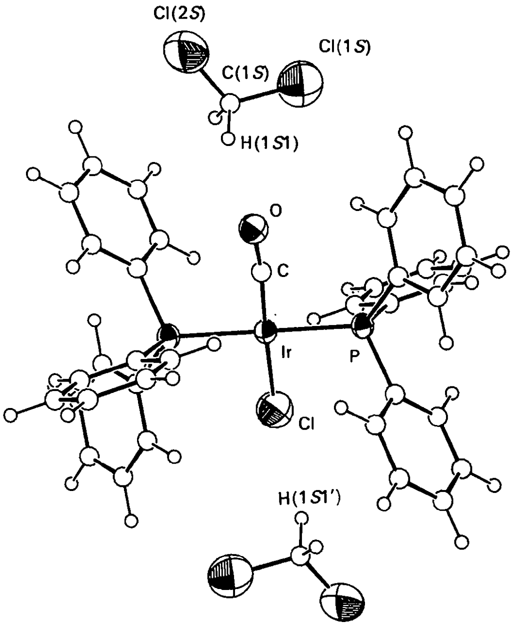

Fig. 1. A general view showing atom-numbering scheme: thermal ellipsoids are drawn at the 30% probability level, excepting those of C and H/D which have artificial radii of 0·15 and 0·10 Å respectively for clarity.

Table 2. *Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.'s in parentheses*

Ir—Cl	2·306 (8)	P—C(21)	1·822 (5)
Ir—C	1·74 (3)	P—C(31)	1·813 (5)
Ir—P	2·3133 (24)	C(1*S*)—Cl(1*S*)	1·740 (14)
C—O	1·15 (4)	C(1*S*)—Cl(2*S*)	1·671 (14)
P—C(11)	1·826 (5)		
Cl—Ir—C	171·8 (10)	C(21)—P—C(31)	103·80 (24)
Cl—Ir—P	93·58 (21)	P—C(11)—C(12)	120·9 (4)
C—Ir—P	90·2 (10)	P—C(11)—C(16)	119·1 (4)
Ir—C—O	151·8 (27)	P—C(21)—C(22)	121·7 (4)
Ir—P—C(11)	114·30 (18)	P—C(21)—C(26)	118·3 (3)
Ir—P—C(21)	117·83 (18)	P—C(31)—C(32)	123·4 (4)
Ir—P—C(31)	111·21 (18)	P—C(31)—C(36)	116·6 (4)
C(11)—P—C(21)	102·27 (23)	Cl(1*S*)—Cl(1*S*)—Cl(2*S*)	115·0 (8)
C(11)—P—C(31)	106·21 (24)		
Cl—Ir—P—C(11)	106·9 (3)	C(31)—P—C(21)—C(22)	6·4 (5)
Cl—Ir—P—C(21)	−13·2 (3)	C(31)—P—C(21)—C(26)	−172·7 (4)
Cl—Ir—P—C(31)	−132·8 (3)	Ir—P—C(31)—C(32)	−134·2 (4)
C—Ir—P—C(11)	−80·3 (10)	Ir—P—C(31)—C(36)	47·6 (4)
C—Ir—P—C(21)	159·5 (10)	C(11)—P—C(31)—C(32)	−9·2 (5)
C—Ir—P—C(31)	39·9 (10)	C(11)—P—C(31)—C(36)	172·5 (4)
Ir—P—C(11)—C(12)	−163·2 (3)	C(21)—P—C(31)—C(32)	98·2 (4)
Ir—P—C(11)—C(16)	16·1 (4)	C(21)—P—C(31)—C(36)	−80·1 (4)
C(21)—P—C(11)—C(12)	−34·8 (4)	P—C(11)—C(12)—C(13)	179·4 (4)
C(21)—P—C(11)—C(16)	144·6 (4)	P—C(11)—C(16)—C(15)	−179·4 (4)
C(31)—P—C(11)—C(12)	73·8 (4)	P—C(21)—C(22)—C(23)	−179·1 (4)
C(31)—P—C(11)—C(16)	−106·9 (4)	P—C(21)—C(26)—C(25)	179·1 (4)
Ir—P—C(21)—C(22)	−117·1 (4)	P—C(31)—C(32)—C(33)	−178·2 (4)
Ir—P—C(21)—C(26)	63·9 (4)	P—C(31)—C(36)—C(35)	178·3 (4)
C(11)—P—C(21)—C(22)	116·7 (4)		
C(11)—P—C(21)—C(26)	−62·4 (4)		

$+ 0{\cdot}35\tan\theta)^\circ$, $2\theta_{\max} = 45^\circ$, h 0→8, k 0→22, l 0→24, linear isotropic crystal decay (*ca* 6%) corrected for during data processing, initial absorption correction using ψ scans (minimum, maximum transmission factors 0·203, 0·253 respectively), 3844 reflections measured, 1969 unique (R_{int} 0·054), giving 1176 with $F > 6\sigma(F)$ for structure solution [intensity statistics indicated the Ir to lie on an inversion centre and using this information *DIRDIF* (Beurskens, Bosman, Doesbury, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasarathai, 1983) located the remaining non-H atoms] and refinement [using full-matrix least squares on F (Sheldrick, 1976)]. At isotropic convergence, final absorption corrections (minimum 0·915, maximum 1·085) were applied empirically using *DIFABS* (Walker & Stuart, 1983). Anisotropic thermal parameters for Ir, Cl, P and phenyl C, phenyl rings refined as rigid, idealized hexagons, H/D atoms in fixed, calculated positions, no secondary-extinction parameter. In order to resolve the disorder, constraints (Ir—Cl 2·36, Ir—C 2·00, C—O 1·15 Å, ∠Ir—C—O 180°) were initially applied; however, these could be removed in the latter stages of refinement. At final convergence, $R = 0{\cdot}0253$, $wR = 0{\cdot}0305$, $S = 1{\cdot}072$ for 186 parameters, $(\Delta/\sigma)_{\max}$ in final cycle 0·16, maximum and minimum residues in final ΔF synthesis 0·49, $-0{\cdot}32$ e Å^{-3} respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}000237F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976) except for Ir (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while selected bond lengths and angles appear in Table 2.* The atom-numbering scheme is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985).

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53494 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Related literature. During the structure determination on unsolvated Vaska's compound, *trans*-$\mathrm{IrCl(CO)(PPh_3)_2}$, Cl/CO disorder was also identified and successfully resolved (Churchill, Fettinger, Buttrey, Barkan & Thompson, 1988). The solvated and unsolvated forms show similar structures for the metal complex.

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The Structure of a Complex Containing a Chelating $\mathrm{S_3^{2-}}$ Ligand: $[\mathrm{(C_5Me_5)_2TiS_3}]$

By Alan Shaver and James M. McCall

Department of Chemistry, McGill University, 801 *Sherbrooke Street West, Montreal, Quebec,*
*Canada H*3*A* 2*K*6

and Peter H. Bird[†] and Upali Siriwardane

Department of Chemistry, Concordia University, 1455 *De Maisonneuve Blvd West, Montreal, Quebec,*
*Canada H*3*G* 1*M*8

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Abstract. Bis(η^5-pentamethylcyclopentadienyl)(trisulfido)titanium(IV), $[\mathrm{Ti(C_{10}H_{15})_2(S_3)}]$, M_r = 414·3, monoclinic, $P2_1/c$, a = 8·770 (8), b = 13·885 (6), c = 17·20 (1) Å, β = 103·75 (6)°, V = 2034·4 Å^3, Z = 4, D_x = 1·353 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 7·11 cm^{-1}, $F(000)$ = 879·9, T = 293 K, R = 0·057 for 1829 reflections with $I > 3\sigma(I)$. The structure is a typical 'slipped sandwich' type with two η^5-$\mathrm{C_5Me_5}$ rings and a novel chelating $\mathrm{S_3^{2-}}$ ligand which results in a non-planar $\mathrm{TiS_3}$ ring with a dihedral angle of 49° between the plane formed by the Ti atom and the two bonded S atoms and that formed by the three S atoms [Ti—S av. 2·413 (4) Å, S—S av. 2·041 (5) Å, $\mathrm{C_5Me_5TiC_5Me_5}$ 136·85 (3)°, STiS 84·44 (9)°, TiSS av. 76·34 (1)°, SSS 105·3 (1)°]. The Ti—S(2) distance is 2·77 Å; it would lengthen to about 3·0 Å if the $\mathrm{TiS_3}$ ring were planar.

Experimental. The complex was prepared by treating $\mathrm{Cp_2^*TiCl_2}$, where Cp* = $\mathrm{C_5Me_5}$, with $\mathrm{Li_2S_5}$ in THF (Bird, McCall, Shaver & Siriwardane, 1982; Shaver & McCall, 1984) and recrystallized from $\mathrm{CH_2Cl_2}$/pentane to give large red-black crystals. Data were collected using a crystal 0·40 × 0·20 × 0·50 mm; Picker FACS-1 diffractometer; monochromated Mo $K\alpha$ radiation; θ–2θ scan mode; cell parameters from 40 reflections with $14 \le 2\theta \le 40°$. The maximum value of $(\sin\theta)/\lambda$ reached in intensity measurements was 0·54 Å^{-1} ($3{\cdot}5 \le 2\theta \le 45{\cdot}0°$); the ranges of h, k and l were $-8 \le h \le 9$, $0 \le k \le 14$ and $0 \le l \le 18$; the standard reflections were 500, 080 and 010 and their intensity variation was 3·5%; number of reflections measured = number of unique reflections = 2678, number of unobserved reflections = 849 ($I < 3\sigma I$). The structure was solved using *MULTAN*; F magnitudes were used in least-squares refinement, with 218 parameters refined; R = 0·057, wR = 0·100, $w = 1/\sigma^2F$, S = 0·999, using counting statistics. $(\Delta/\sigma)_{\max}$ = 0·1, $(\Delta\rho)_{\max}$ = 0·3, $(\Delta\rho)_{\min}$ = −0·18 e Å^{-3}. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV); all programs used for the data collection,

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[†] To whom correspondence should be addressed.

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