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Structure of the Michael Addition Product of Allylamine and a Vinylidene Phosphine Complex of Tungsten

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Abstract. {*N*-[2,2-Bis(diphenylphosphino)ethyl]allylamine-*P*,*P*}tricarbonyl(triphenylphosphine)tungsten(0) allylamine solvate (1:0·5), $[W(CO)_3(C_{18}H_{15}P)(C_{29}H_{29}NP_2)].\frac{1}{2}C_3H_7N$, $M_r = 1040{\cdot}77$ (includes solvate), triclinic, $P\bar{1}$, $a = 11{\cdot}847\,(1)$, $b = 12{\cdot}335\,(1)$, $c = 17{\cdot}402\,(2)$ Å, $\alpha = 87{\cdot}70\,(1)$, $\beta = 86{\cdot}86\,(1)$, $\gamma = 73{\cdot}28\,(1)^\circ$, $U = 2431{\cdot}0\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}42$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 23{\cdot}87$ cm^{-1}, $F(000) = 1052$, room temperature, $R = 0{\cdot}0322$, 5930 unique reflections with $I > 2{\cdot}0\sigma(I)$. Coordination of the vinylidenebis(diphenylphosphine) (vdpp) ligand to a W atom in the complex *mer*-$[(OC)_3W(vdpp)(PPh_3)]$ activates the C═C bond which readily undergoes Michael addition with allylamine ($C_3H_5NH_2$) to give *mer*-$[(OC)_3W\{(Ph_2P)_2CHCH_2N(H)C_3H_5\}(PPh_3)]$.

Introduction. The C═C double bond of the functionalized diphosphine vdpp is not susceptible to nucleophilic attack by compounds such as amines, hydrazines, carbon nucleophiles, *etc.* (Colquhoun & McFarlane, 1982). However, upon complexation with transition metals such as Cr, W, Mo or Pt the activity of the vinylidene group is increased and it readily undergoes Michael-type additions (Cooper, Hassan, Shaw & Thornton-Pett, 1985). Here we report the structure of the product of the reaction between $[(OC)_3W(vdpp)\ (PPh_3)]$ and allylamine.

Experimental. Crystals of the title compound were obtained directly by dissolving $[(OC)_3W(vdpp)(PPh_3)]$ in allylamine. The crystals were found to be efflorescent and so one of suitable size (*ca* 0·7 × 0·5 × 0·3 mm) was covered in epoxy resin prior to data collection. All measurements were made on a Nicolet *P*3/*F* diffractometer; 25 reflections centred ($35 \leq 2\theta \leq 40{\cdot}0^\circ$), graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scans, ω scan widths $2{\cdot}0^\circ + \alpha$-doublet separation, scan speeds $2{\cdot}0$–$29{\cdot}3^\circ$ min^{-1} subject to a fast pre-scan. Complete data set ($h0\rightarrow13$, $k-14\rightarrow14$, $l-19\rightarrow19$; $4{\cdot}0 \leq 2\theta \leq 45^\circ$) measured over 111 hours with no significant decay of a standard reflection (measured every 50 reflections); 6203 unique data, 5930 with $I > 2{\cdot}0\sigma(I)$ considered observed and used in structure solution and refinement. Structure solution by Patterson synthesis (for W atom) and difference Fourier methods; empirical absorption correction (Walker & Stuart, 1983); full-matrix least-squares refinement on *F* with anisotropic thermal parameters for all non-H atoms with the exception of the terminal —CH_2CHCH_2 group and also a $C_3H_5NH_2$ solvent molecule (which was refined with an occupancy factor of $\frac{1}{2}$) which were refined with isotropic thermal parameters. All H atoms were included in calculated positions and were refined with isotropic temperature factors except for those on the terminal —CH_2CHCH_2 group and the solvent molecule which were not included. Scattering and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Refinement converged to $R = 0{\cdot}0322$, $wR = 0{\cdot}0344$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0002(F_o)^2$, number of parameters = 486;

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Table 1. *Atom coordinates* (× 10^4) *and isotropic and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^4$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{iso}/U_{eq}
W	1242·5 (2)	1247·4 (2)	2070·5 (1)	44 (1)
P(1)	1558 (1)	−772 (1)	1777 (1)	46 (9)
P(2)	2757 (1)	1007 (1)	3085 (1)	50 (1)
P(3)	1467 (1)	3057 (1)	2442 (1)	57 (1)
C(111)	2681 (3)	−1333 (3)	1008 (2)	54 (3)
C(112)	3816 (3)	−1242 (3)	1088 (2)	75 (4)
C(113)	4685 (3)	−1617 (3)	507 (2)	100 (5)
C(114)	4421 (3)	−2083 (3)	−153 (2)	94 (5)
C(115)	3286 (3)	−2174 (3)	−233 (2)	85 (5)
C(116)	2417 (3)	−1799 (3)	348 (2)	64 (3)
C(121)	290 (3)	−1217 (3)	1471 (2)	50 (3)
C(122)	−522 (3)	−493 (3)	994 (2)	64 (3)
C(123)	−1417 (3)	−855 (3)	696 (2)	71 (4)
C(124)	−1502 (3)	−1942 (3)	877 (2)	74 (4)
C(125)	−691 (3)	−2666 (3)	1354 (2)	103 (5)
C(126)	204 (3)	−2304 (3)	1652 (2)	84 (4)
C(131)	2062 (3)	−1816 (3)	2567 (2)	52 (3)
C(132)	1448 (3)	−1597 (3)	3277 (2)	72 (4)
C(133)	1751 (3)	−2374 (3)	3890 (2)	95 (5)
C(134)	2668 (3)	−3370 (3)	3792 (2)	95 (6)
C(135)	3282 (3)	−3588 (3)	3082 (2)	83 (5)
C(136)	2979 (3)	−2812 (3)	2469 (2)	71 (4)
C(211)	2479 (3)	809 (3)	4121 (1)	52 (3)
C(212)	1353 (3)	808 (3)	4401 (1)	69 (4)
C(213)	1120 (3)	718 (3)	5192 (1)	83 (4)
C(214)	2013 (3)	628 (3)	5702 (1)	93 (5)
C(215)	3138 (3)	629 (3)	5422 (1)	93 (5)
C(216)	3372 (3)	719 (3)	4631 (1)	78 (4)
C(221)	4254 (3)	49 (3)	2934 (2)	66 (3)
C(222)	4482 (3)	−1058 (3)	3228 (2)	76 (4)
C(223)	5574 (3)	−1842 (3)	3069 (2)	95 (6)
C(224)	6437 (3)	−1518 (3)	2616 (2)	112 (7)
C(225)	6208 (3)	−411 (3)	2323 (2)	112 (6)
C(226)	5117 (3)	373 (3)	2482 (2)	92 (5)
C(231)	2848 (5)	2496 (5)	2953 (3)	65 (3)
C(232)	3082 (7)	3133 (6)	3646 (4)	87 (4)
N(1)	4335 (6)	2693 (6)	3821 (4)	116 (5)
C(233)*	4422 (13)	3296 (12)	4593 (8)	165 (5)
C(234)*	5591 (16)	2854 (17)	4757 (12)	256 (8)
C(235)*	6529 (20)	2225 (19)	4410 (12)	284 (9)
C(311)	461 (4)	4070 (3)	3090 (2)	67 (4)
C(312)	−216 (4)	3658 (3)	3646 (2)	110 (4)
C(313)	−974 (4)	4398 (3)	4160 (2)	137 (8)
C(314)	−1055 (4)	5550 (3)	4119 (2)	122 (7)
C(315)	−378 (4)	5961 (3)	3563 (2)	120 (7)
C(316)	380 (4)	5221 (3)	3049 (2)	96 (5)
C(321)	1843 (4)	3979 (4)	1676 (2)	73 (4)
C(322)	1100 (4)	4266 (4)	1059 (2)	130 (7)
C(323)	1371 (4)	4911 (4)	438 (2)	175 (10)
C(324)	2386 (4)	5270 (4)	433 (2)	127 (7)
C(325)	3129 (4)	4984 (4)	1050 (2)	132 (7)
C(326)	2857 (4)	4339 (4)	1671 (2)	120 (6)
C(1)	−181 (5)	1167 (5)	2709 (3)	62 (4)
O(1)	−1074 (4)	1138 (5)	3011 (3)	103 (4)
C(2)	78 (5)	1949 (5)	1299 (3)	59 (3)
O(2)	−605 (4)	2431 (4)	862 (3)	83 (3)
C(3)	2494 (5)	1328 (5)	1254 (3)	60 (3)
O(3)	3137 (4)	1405 (5)	755 (3)	96 (3)
N(1S)*	6188 (17)	3041 (16)	2363 (11)	148 (6)
C(1S)*	6890 (26)	3874 (27)	2433 (17)	184 (10)
C(2S)*	7120 (27)	4758 (29)	2060 (18)	184 (11)
C(3S)*	6595 (22)	5569 (22)	1654 (14)	149 (8)

* These atoms are listed with isotropic thermal parameters. All others are listed with equivalent isotropic thermal parameters.

difference synthesis showed max. density of 0·77 e Å^{-3} (min. −0·81 e Å^{-3}); max. $\Delta/\sigma = 0{\cdot}110$ [in U_{iso} of H(325)]. All calculations performed on an Amdahl 5850 computer. Programs used were *SHELX76* (Sheldrick, 1976) and *ORTEPII* (Johnson, 1976).

Discussion. Final fractional coordinates and isotropic and equivalent isotropic thermal parameters are listed in Table 1. A packing diagram looking down the *c* axis, in which the relative positions of the solvent molecules in the unit cell can be seen, is shown in Fig. 1, and its numbering scheme, for clarity, is shown in Fig. 2. Selected bond lengths and angles are given in Table 2.* The W atom is octahedrally coordinated with the three carbonyl groups in a meridional plane and a triphenylphosphine *trans* to

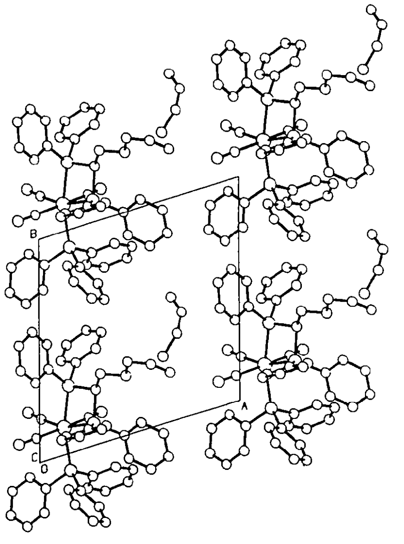

Fig. 1. Packing diagram for the title compound.

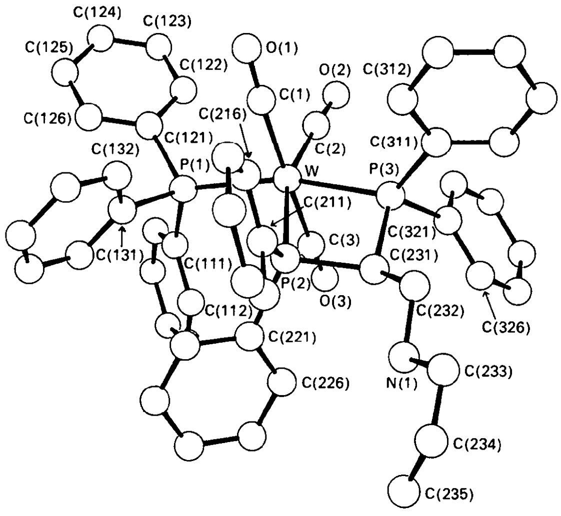

Fig. 2. The molecular structure of the title compound illustrating the atomic numbering scheme.

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* Full lists of bond lengths and angles, and lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52083 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic bond distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

W—P(1)	2·481 (3)	W—C(1)	1·993 (8)
W—P(2)	2·533 (4)	W—C(2)	1·968 (8)
W—P(3)	2·439 (3)	W—C(3)	2·018 (9)
P(2)—C(231)	1·876 (8)	P(3)—C(231)	1·845 (8)
⟨P—C(phenyl)⟩	1·836 (5)	⟨P(1)—C(phenyl)⟩	1·846 (5)
⟨C—O⟩	1·154 (8)	C(232)—N(1)	1·471 (11)
C(231)—C(232)	1·544 (10)	C(233)—N(1)	1·583 (17)
C(233)—C(234)	1·377 (11)	C(234)—C(235)	1·292 (26)
P(1)—W—P(2)	99·1 (2)		
P(1)—W—P(3)	165·1 (1)	P(2)—W—P(3)	67·9 (2)
P(1)—W—C(2)	99·2 (3)	P(3)—W—C(2)	93·5 (3)
C(1)—W—C(3)	169·2 (2)	P(2)—C(231)—P(3)	96·6 (4)
P(2)—C(231)—C(232)	120·1 (6)	P(3)—C(231)—C(232)	119·7 (6)
W—C(1)—O(1)	172·8 (6)	W—C(3)—O(3)	175·0 (5)
W—C(2)—O(2)	175·4 (5)	C(232)—N(1)—C(233)	103·7 (9)
C(231)—C(232)—N(1)	108·8 (7)		

one P atom of the chelated diphosphine and a carbonyl *trans* to the other. The W—C distances are not significantly different at 1·993 (8), 1·968 (8) and 2·018 (9) Å and are comparable to those in other tungsten(0) carbonyl complexes (Blagg, Hutton, Shaw & Thornton-Pett, 1985); the two W—P(vdpp) distances are significantly different: 2·439 (3) Å (*trans* to P) and 2·533 (4) Å (*trans* to C), and reflect the differing *trans* influence of the phosphine and carbonyl ligands. Because of the bite restriction of the diphosphine chelate the equatorial valence angles at the W atom are not equal, ranging from 67·9 (2) to 99·2 (3)°, although the W atom remains in the plane defined by the three P atoms (sum of angles 359·7°). The C—C bond distance of the diphosphine is 1·544 (10) Å in contrast to the same distance in free vdpp 1·327 (6) Å (Schimdbaur, Herr & Riede, 1985). The angle P(2)—C(231)—P(3) is considerably reduced from 119·0 (3) to 96·6 (4)°; the C atom does not retain its planar sp^2 configuration upon addition since the deviation of this atom from the plane of its attached atoms [P(3), P(2) and C(232)] is 0·486 (6) Å. The angle at C(232) [C(231)—C(232)—N(1)], an initially sp^2 C atom, is now 108·8 (7)°, typical of an sp^3 configuration. Steric effects are apparent for two of the carbonyl groups which are bent slightly away from the diphosphine chelate leading to a C(1)—W—C(3) angle of 169·2 (2)°.

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Structure of [Bis(diphenylphosphino)methane]bis(trifluoroacetato)palladium(II)

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Abstract. $[Pd(C_2F_3O_2)_2(C_{25}H_{22}P_2)]$, M_r = 720·86, monoclinic, $P2_1/n$, a = 10·459 (2), b = 13·592 (2), c = 20·927 (2) Å, β = 90·46 (1)°, V = 2974·8 (7) Å^3, Z = 4, D_x = 1·61 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 7·89 cm^{-1}, F(000) = 1448, T = 296 K, R = 0·069 for 3195 unique data with $I > 3\sigma(I)$. The refinement of the structure was complicated by disorder of one of the trifluoromethyl groups, which was treated by the introduction of two partially occupied rigid rotors. The molecular structure consists of a pseudo-square plane with remarkably short Pd—P bonds [2·219 (3) and 2·233 (3) Å] and a narrow O—Pd—O angle [84·4 (4)°], which are ascribed to the weak *trans* influence of the trifluoroacetate and the strong *trans* influence of the phosphine.

Introduction. We have conducted the synthesis of a simple molecular palladium trifluoroacetate, $[Pd(Ph_2PCH_2PPh_2)(O_2CCF_3)_2]$, which is of interest as a catalyst and cluster precursor, stabilized by the dppm ligand (McAuliffe, 1988; Puddephatt, 1983). This strategy has already been used for the construc-

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