Reconsideration of the Crystal Structure Refinement of the Complex $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ †

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An *X*-ray crystal structure determination of $[PPh_4][W(C\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ has been reported recently in this journal. The data have now been re-evaluated and the amended structure is described.

The chemistry of the complexes $[X][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [X = $N(PPh_3)_2$, NEt_4, or PPh_4; R = C_6H_4Me-4, C_6H_4Me-2, or $C_6H_3Me_2$-2,6] has been reported in earlier papers and it has been shown that variation of both the alkylidyne group and the cation leads to different reactivity patterns.[1,2] The crystal structure refinement of the complex $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ was previously[1] carried out in the non-centrosymmetric space group *P*1 (no. 1) where the asymmetric unit required two independent molecules (Figure). This space group assignment was made based almost solely, and erroneously, on the diffraction intensity statistics. At that time the refinement was noted to be poor due to the high correlations produced by refinement of equivalent parameters in the two centrosymmetrically related molecules of the asymmetric unit. However, a redefinition of the unit-cell origin relates these two molecules by a crystallographic inversion centre and re-refinement in space group $P\bar{1}$ (no. 2) ‡ with 4 781 unique data [$F > 6\sigma(F)$] converges at $R(R') = 0.034$ (0.033) with much more satisfactory derived molecular parameters. The fractional atomic co-ordinates are given in Table 1 with selected bond lengths and interbond angles in Table 2.

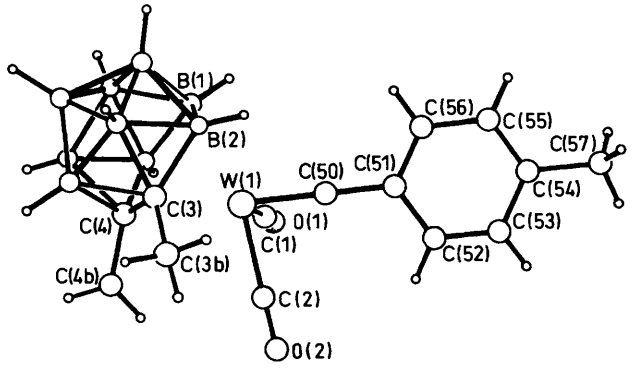

Figure. The molecular structure of the anion of the complex $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ showing the atomic numbering scheme

† Tetraphenylphosphonium dicarbonyl[7—11-η-nonahydro-7,8-dimethyl-7,8-dicarba-*nido*-undecaborato(2−)](*p*-tolylmethylidyne)-tungstate(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ *Crystal data*: $[P(C_6H_5)_4]^+[C_{14}H_{22}B_9O_2W]^-$, M = 842.9, triclinic, a = 12.395(2), b = 13.120(4), c = 12.533(4) Å, α = 101.10(3), β = 82.04(2), γ = 104.48(2)°, U = 1 928(1) Å^3, D_c = 1.46 g cm^{-3}, Z = 2, $F(000)$ = 840, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 31.33 cm^{-1}.

Table 1. Atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
W(1)	7 294(1)	8 527(1)	6 948(1)
C(1)	6 620(6)	7 621(5)	5 682(6)
O(1)	6 199(5)	7 053(4)	4 943(4)
C(2)	8 041(6)	9 583(6)	6 012(5)
O(2)	8 459(5)	10 253(5)	5 499(5)
C(50)	6 169(5)	9 229(4)	7 093(4)
C(51)	5 289(4)	9 784(4)	7 174(4)
C(52)	5 288(5)	10 420(5)	6 417(6)
C(53)	4 415(6)	10 912(6)	6 453(6)
C(54)	3 533(5)	10 803(4)	7 249(5)
C(55)	3 564(5)	10 213(5)	8 030(5)
C(56)	4 424(5)	9 703(5)	7 997(5)
C(57)	2 561(6)	11 291(6)	7 250(6)
B(1)	6 902(6)	7 270(5)	8 207(6)
B(2)	7 431(6)	8 621(5)	8 828(5)
C(3)	8 736(5)	9 009(4)	8 152(5)
C(4)	9 027(5)	8 037(5)	7 221(5)
B(5)	7 955(6)	6 975(5)	7 165(6)
B(6)	7 826(7)	6 520(6)	8 426(7)
B(7)	7 519(7)	7 552(6)	9 457(6)
B(8)	8 645(7)	8 666(6)	9 444(6)
B(9)	9 650(7)	8 302(7)	8 420(7)
B(10)	9 156(7)	6 989(7)	7 786(7)
B(11)	8 890(7)	7 369(7)	9 213(7)
C(3b)	9 358(6)	10 132(5)	8 069(6)
C(4b)	9 856(6)	8 260(7)	6 234(6)
P(1)	12 593(1)	5 577(1)	7 654(1)
C(12)	10 378(3)	4 806(3)	8 451(3)
C(13)	9 373	4 034	8 450
C(14)	9 314	3 036	7 797
C(15)	10 260	2 810	7 144
C(16)	11 265	3 582	7 145
C(11)	11 324	4 580	7 798
C(22)	13 764(3)	4 304(3)	8 240(3)
C(23)	14 673	3 837	8 169
C(24)	15 543	4 014	7 343
C(25)	15 506	4 657	6 589
C(26)	14 598	5 123	6 660
C(21)	13 727	4 947	7 486
C(32)	13 627(3)	6 810(3)	9 463(3)
C(33)	13 778	7 680	10 309
C(34)	13 061	8 376	10 495
C(35)	12 194	8 203	9 834
C(36)	12 043	7 333	8 987
C(31)	12 760	6 636	8 802
C(42)	11 819(3)	5 664(3)	5 703(3)
C(43)	11 777	6 170	4 832
C(44)	12 473	7 174	4 752
C(45)	13 209	7 672	5 543
C(46)	13 251	71 65	6 414
C(41)	12 556	6 162	6 494

Table 2. Selected bond distances (Å) and interbond angles (°) for $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$

W(1)–C(1)	1.942(7)	C(1)–O(1)	1.166(9)
W(1)–C(2)	1.959(7)	C(2)–O(2)	1.16(1)
W(1)–C(50)	1.826(7)	W(1)–cage *	2.42(4)
C(50)–C(51)	1.437(9)	P(1)–C(Ph) *	1.783(8)
W(1)–C(1)–O(1)	177.8(6)	C(1)–W(1)–C(50)	87.3(3)
W(1)–C(2)–O(2)	176.1(6)	C(2)–W(1)–C(50)	82.7(3)
W(1)–C(50)–C(51)	178.4(4)	C(1)–W(1)–C(2)	88.6(3)

* Mean values with estimated standard deviations from the mean.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

The phenyl rings of the cation were constrained to be regular hexagons. The hydrogen atoms of the *p*-tolyl group, the cation, and the methyl groups of the carbaborane cage were placed geometrically and refined by a 'riding' model approximation. All hydrogen atoms were refined with fixed isotropic thermal parameters.

References

1 F.-E. Baumann, J. A. K. Howard, O. Johnson, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2661.
2 F.-E. Baumann, J. A. K. Howard, R. J. Musgrove, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1879 and refs. therein.

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