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(11) σ(ext), an external estimate of the esd on each bond length, is given by $[\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where N is the number of equivalent bond lengths, d_i is the ith bond length, and $\bar{d}$ is the average bond length. σ(av), the esd of the average bond length, is given by $[\sum(d_i - \bar{d})^2/N(N-1)]^{1/2}$.

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Crystal Structure and Molecular Geometry of $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)$(dmpe), a Mononuclear Tungsten(VI) Complex with Metal–Alkylidyne, Metal–Alkylidene, and Metal–Alkyl Linkages

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[1,2-Bis(dimethylphosphino)ethane](neopentylidyne)(neopentylidene)(neopentyl)tungsten(VI), $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)$(dmpe), previously prepared by Clark and Schrock, has been investigated via a three-dimensional single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 9.784 (3) Å, b = 29.200 (8) Å, c = 9.859 (2) Å, β = 109.54 (2)°, V = 2654 (1) Å^3, mol wt 544.4, Z = 4, and ρ(calcd) = 1.36 g cm^{-3}. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer using Mo Kα radiation and an ω-scan mode of collection. The structure was solved by conventional Patterson, difference Fourier, and full-matrix least-squares refinement techniques, the resulting discrepancy indices being R_F = 3.9% and R_{wF} = 3.1% for all 2475 symmetry-independent reflections with 4.5° < 2θ < 40° (R_F = 3.2% and R_{wF} = 3.1% for those 2199 reflections with $I > 3\sigma(I)$). The tungsten atom is in a distorted square-pyramidal coordination environment, with the neopentylidyne ligand in the apical site and with the neopentylidene and neopentyl ligands in adjacent basal sites. The tungsten–neopentyl bond length is W–C(11) = 2.258 (9) Å (∠W–C(11)–C(12) = 124.5 (7)°), the tungsten–neopentylidene bond length is W–C(6) = 1.942 (9) Å (∠W–C(6)–C(7) = 150.4 (8)°), and the tungsten–neopentylidyne bond length is W–C(1) = 1.785 (8) Å (∠W–C(1)–C(2) = 175.3 (7)°).

Introduction

For the past year or two we have been interested in the bonding of small highly reactive organic fragments to transition metals, and we have reported the results of X-ray diffraction studies on a neopentylidene–tantalum complex $[Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl]$,[1] a benzylidyne–tantalum complex $[Ta(\eta^5\text{-}C_5Me_5)(\equiv CPh)(PMe_3)_2Cl]$,[2] a bis(neopentylidene)–tantalum complex $[Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2]$,[3] and a benzyne–tantalum complex $[Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$.[4]

A number of mixed isoskeletal[5] alkyl–alkylidene complexes have been investigated by others [cf. $Ta(\eta^5\text{-}C_5H_5)_2(=CH_2)(CH_3)$[6] and $Ta(\eta^5\text{-}C_5H_5)_2(=CHC_6H_5)(CH_2C_6H_5)$[7]], as has an isoskeletal alkyl–alkylidyne complex $[Ta(\equiv CCMe_3)(CH_2CMe_3)_3\cdot Li(dmp)]$.[8] However, X-ray and neutron diffraction studies show that transition-metal alkyls, alkylidenes, and alkylidynes have a number of unusual structural characteristics—(i) the M–C(α)–C(β) angles in alkyls are frequently as large as 120–125°; (ii) the M=C(α)—C(β) angles in alkylidenes vary widely (for the *neopentylidene* ligand, these angles are 168.9 (6) and 154.0 (6)° in $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$,[3a] 161.2 (1)° in $[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$,[9] and 150.4 (5)° in $Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl$[1a]); (iii) the M≡C($\alpha$)—C($\beta$) angles in alkylidynes appear to be deformed easily from linearity (an angle of 165 (1)° is found in $Ta(\equiv CCMe_3)(CH_2CMe_3)_3\cdot Li(dmp)$ and an angle of 171.8 (6)° is found in $Ta(\eta^5\text{-}C_5Me_5)(\equiv CPh)(PMe_3)_2Cl$[2]). It is due to these factors, we believe, that several mixed alkyl–alkylidene systems (e.g., $Nb(=CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$)[10] are subject to severe disorder in the solid state.

Recently, Clark and Schrock[11] reported the synthesis of the species $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2$ and $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)$(dmpe) (dmpe = $Me_2P(CH_2)_2PMe_2$), which are *rigid* on the NMR time scale and thus (hopefully) are likely to be *ordered* in the solid state. These species are unique in possessing metal–alkylidyne, metal–alkylidene and metal–alkyl linkages. Because of this and because of the interest in tungsten–alkylidenes as intermediates in the olefin metathesis reaction,[12] we have undertaken an X-ray diffraction study of $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)$(dmpe); a preliminary report has appeared previously.[13]

Experimental Section

A. Collection and Processing of the X-ray Diffraction Data. Red columnar crystals of $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)$(dmpe) were provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The material decomposes *rapidly* upon exposure to the air, melting and bubbling to form a thick, viscous liquid.

A well-formed crystal of approximate dimensions 0.3 × 0.3 × 0.5 mm was removed from the provided vial in an inert-atmosphere drybox and was carefully wedged into a 0.3-mm diameter thin-walled glass capillary, which was flame-sealed, fixed into an aluminum pin with beeswax, and mounted into an eucentric goniometer. (Preliminary photographs were not taken, since we were concerned about the potential for decomposition of the crystal.) The crystal was centered on our Syntex $P2_1$ automated diffractometer. Determinations of the crystal class, the orientation matrix, and accurate unit cell dimensions were carried out as described previously.[14] Both θ–2θ and ω scans were monitored graphically for selected reflections along (and adjacent to) each of the principal reciprocal axes. As a result of the rather long b axis (ca. 29.2 Å) and concomitantly short spacings of reflections along b^*, we elected to collect data via the "wandering ω-scan" technique,[15] rather than by the customary θ–2θ method. Details of the data collection appear in Table I. A survey of the complete data set revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/n$ is thereby strongly indicated.

All crystallographic computations were carried out on our in-house Syntex XTL system (NOVA 1200 computer; Diablo disk; Versatec printer/plotter), including the XTL interactive program package[16] as modified by our research group at SUNY—Buffalo.

Data were corrected for absorption (μ = 47.3 cm^{-1}) by an empirical method, based upon a set of ψ scans of carefully selected reflections. Each of these reflections was collected at intervals of 10° about its diffraction vector from ψ = 0 to 350°; each was converted to a

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Table I. Experimental Data for the X-ray Diffraction Study of W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)

(A) Crystal Parameters at 26 °C[a]

cryst system: monoclinic	β = 109.544 (19)°
space group: $P2_1/n$	V = 2654.3 (12) Å^3
a = 9.7843 (25) Å	Z = 4
b = 29.2001 (75) Å	mol wt 544.40
c = 9.8586 (21) Å	ρ(calcd) = 1.36 g/cm^3

(B) Measurement of Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite; $2\theta_{mono}$ = 12.2°; equatorial mode
rflcns measd: $\pm h,+k,+l$
scan type: wandering ω scan
2θ range: 4.5–40.0°
scan speed: 1.5°/min
scan width: 1.2° (0.8° offset for bkgd)
bkgd measment: stationary-crystal, stationary-counter at beginning and end of each scan, each for one-fourth of the time taken for the scan
std rflcns: 600; 0,18,0; $\bar{2}06$; these were measured after each 97 rflcns
rflcns collected: 2656 total, yielding 2475 symmetry-independent data
abs coeff: μ = 47.3 cm^{-1}

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections of the forms {145}, {$\bar{6}$23}, {$\bar{4}$,10,3}, {$\bar{4}$55}, {$\bar{1}$,18,1}, and {095} all with 2θ between 20 and 30°.

normalized absorption curve vs. ϕ_c (ϕ, corrected for ω and χ). The reflections used to obtain the normalized absorption curves, their 2θ values, and their maximum:minimum intensity ratios were as follows: $\bar{1}$60 [2θ = 9.47°, (max/min) = 1.239]; $\bar{3}$,10,1 [18.00°, 1.304]; $\bar{4}$,13,1 [24.85°, 1.290]; $\bar{3}$,17,0 [27.42°, 1.234].

Intensity data were corrected for absorption by two-parameter interpolation (in ϕ_c and in 2θ) between the appropriate ψ-scan curves.

Redundant and equivalent data were averaged [$R(I)$ = 1.91%] and were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

B. Solution and Refinement of the Structure. Data were placed on an approximately absolute scale via a Wilson plot, which also provided the average overall thermal parameter ($\bar{B}$ = 3.53 Å^2). The location of the tungsten atom was determined from a three-dimensional (unsharpened) Patterson synthesis. Refinement of the scale factor and positional and isotropic thermal parameters for the tungsten atom led to R_F = 20.9% and R_{wF} = 30.0%. All other nonhydrogen atoms were located (not without considerable difficulty) by a series of difference Fourier syntheses, each being phased by an increasing number of atoms. Refinement of positional parameters for all nonhydrogen atoms, anisotropic thermal parameters for tungsten and isotropic thermal parameters for all other atoms (102 parameters in all), led to R_F = 5.5% and R_{wF} = 5.9%. The introduction of anisotropic thermal parameters for all nonhydrogen atoms (217 parameters) led to convergence with R_F = 4.3%, R_{wF} = 3.8%, and GOF = 2.57.

A difference Fourier synthesis at this stage *did not* indicate the positions of any hydrogen atoms. These were, nevertheless, included in the model in idealized positions with d(C–H) = 0.95 Å[17] and (where appropriate) with perfectly staggered conformational geometry. Three cycles of full-matrix refinement (with hydrogen atoms not refined but up-dated after each cycle of refinement) led to final convergence with R_F = 3.9%, R_{wF} = 3.1%, and GOF = 2.04 for all 2475 reflections (none rejected). The discrepancy indices are R_F = 3.2% and R_{wF} = 3.1% for those 2199 reflections with $I > 3\sigma(I)$. The data-to-parameter ratio was 11.4:1. The largest peak on a final difference Fourier synthesis was of height 0.5 e Å^{-3} and was close to the position of the tungsten atom. The usual tests of the residual ($\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, (sin θ)/λ, sequence number, and identity or parity of the Miller indices) suggested that the weighting scheme was satisfactory. Final positional and thermal parameters are collected in Tables II and III.

Throughout the analysis the analytical scattering factors[18a] for neutral W, P, C, and H were used; both the real and imaginary components of anomalous dispersion[18b] were applied to all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during

Table II. Positional Parameters, with Esd's, for W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)[a]

atom	x	y	z
W	−0.00050 (3)	0.11456 (1)	0.10206 (3)
P(1)	0.2306 (3)	0.10520 (9)	0.3231 (3)
P(2)	0.1827 (3)	0.16057 (10)	0.0453 (3)
C(1)	−0.0711 (8)	0.1645 (3)	0.1593 (9)
C(2)	−0.1401 (10)	0.2040 (3)	0.2080 (12)
C(3)	−0.2887 (14)	0.1953 (5)	0.1898 (22)
C(4)	−0.1277 (18)	0.2466 (4)	0.1302 (23)
C(5)	−0.0574 (17)	0.2165 (6)	0.3567 (18)
C(6)	−0.1063 (9)	0.1045 (3)	−0.1008 (10)
C(7)	−0.2190 (14)	0.1186 (5)	−0.2376 (12)
C(8)	−0.2978 (22)	0.1588 (7)	−0.2294 (16)
C(9)	−0.166 (3)	0.1250 (12)	−0.3490 (23)
C(10)	−0.332 (3)	0.0841 (7)	−0.287 (3)
C(11)	−0.0527 (10)	0.0529 (3)	0.2139 (11)
C(12)	−0.1999 (11)	0.0321 (3)	0.1783 (11)
C(13)	−0.1901 (16)	−0.0044 (4)	0.2885 (16)
C(14)	−0.2437 (14)	0.0053 (4)	0.0397 (15)
C(15)	−0.3182 (12)	0.0646 (4)	0.1746 (15)
C(21)	0.3247 (11)	0.0507 (3)	0.3577 (11)
C(22)	0.2147 (12)	0.1180 (4)	0.4954 (10)
C(23)	0.3766 (11)	0.1438 (4)	0.3110 (14)
C(24)	0.3238 (12)	0.1808 (4)	0.2077 (15)
C(25)	0.1261 (15)	0.2134 (4)	−0.0534 (16)
C(26)	0.2881 (13)	0.1342 (4)	−0.0548 (14)
H(3A)	−0.3286	0.2210	0.2218
H(3B)	−0.3407	0.1899	0.0908
H(3C)	−0.2954	0.1691	0.2444
H(4A)	−0.1721	0.2712	0.1627
H(4B)	−0.0282	0.2534	0.1484
H(4C)	−0.1747	0.2423	0.0297
H(5A)	−0.1030	0.2415	0.3854
H(5B)	0.0384	0.2248	0.3630
H(5C)	−0.0537	0.1910	0.4180
H(6)	−0.0665	0.0770	−0.1238
H(8A)	−0.3669	0.1651	−0.3213
H(8B)	−0.2327	0.1839	−0.1998
H(8C)	−0.3464	0.1543	−0.1617
H(9A)	−0.2433	0.1339	−0.4328
H(9B)	−0.0942	0.1482	−0.3239
H(9C)	−0.1251	0.0972	−0.3673
H(10A)	−0.4028	0.0940	−0.3744
H(10B)	−0.3774	0.0797	−0.2162
H(10C)	−0.2911	0.0560	−0.3029
H(11A)	−0.0240	0.0608	0.3129
H(11B)	0.0082	0.0290	0.2019
H(13A)	−0.2823	−0.0184	0.2691
H(13B)	−0.1604	0.0089	0.3817
H(13C)	−0.1213	−0.0268	0.2843
H(14A)	−0.3377	−0.0072	0.0216
H(14B)	−0.2445	0.0249	−0.0372
H(14C)	−0.1762	−0.0188	0.0474
H(15A)	−0.4073	0.0485	0.1512
H(15B)	−0.3254	0.0875	0.1039
H(15C)	−0.2971	0.0787	0.2662
H(21A)	0.3396	0.0403	0.2724
H(21B)	0.4157	0.0543	0.4317
H(21C)	0.2681	0.0289	0.3870
H(22A)	0.1659	0.1464	0.4904
H(22B)	0.3086	0.1198	0.5657
H(22C)	0.1609	0.0944	0.5211
H(23A)	0.4238	0.1568	0.4032
H(23B)	0.4447	0.1262	0.2834
H(24A)	0.4022	0.1927	0.1822
H(24B)	0.2853	0.2044	0.2505
H(25A)	0.0689	0.2306	−0.0106
H(25B)	0.2092	0.2306	−0.0508
H(25C)	0.0705	0.2066	−0.1504
H(26A)	0.3246	0.1055	−0.0125
H(26B)	0.3667	0.1536	−0.0522
H(26C)	0.2280	0.1296	−0.1518

[a] All hydrogen atoms were assigned isotropic thermal parameters of 10.0 Å^2.

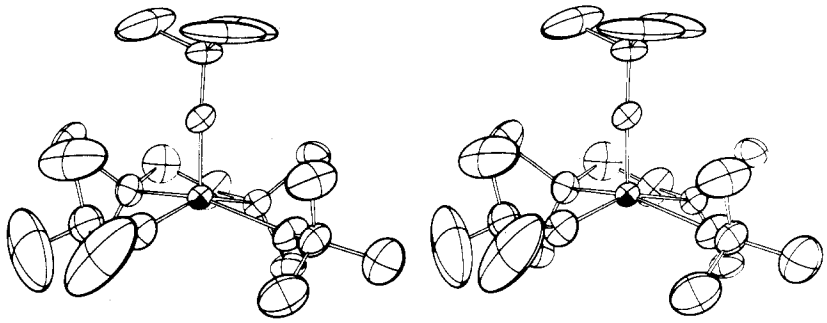

Figure 1. Stereoscopic view of the $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$ molecule, with hydrogen atoms omitted for clarity. The neopentylidyne ligand occupies the axial site, the neopentylidene ligand occupies the left front basal site, and the neopentyl ligand occupies the right front basal site (ORTEP-II diagram; 30% probability ellipsoids).

Table III. Anisotropic Thermal Parameters[a] (with Esd's) for $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	2.866 (16)	3.633 (17)	4.178 (18)	−0.048 (16)	0.945 (12)	0.211 (17)
P(1)	4.85 (12)	5.57 (15)	5.42 (13)	−0.08 (11)	0.42 (10)	−0.01 (11)
P(2)	6.19 (15)	6.57 (15)	7.66 (17)	−1.52 (13)	3.31 (13)	0.89 (13)
C(1)	3.4 (4)	3.9 (4)	6.1 (5)	−0.6 (3)	0.7 (4)	0.3 (4)
C(2)	5.5 (5)	4.2 (5)	8.2 (7)	0.2 (4)	2.4 (5)	−1.7 (5)
C(3)	7.7 (8)	11.6 (10)	39.9 (24)	−2.4 (7)	12.2 (12)	−15.3 (13)
C(4)	17.2 (14)	5.3 (7)	32.1 (23)	2.2 (8)	13.3 (15)	0.1 (11)
C(5)	13.5 (11)	22.2 (17)	15.1 (12)	11.6 (11)	−1.9 (10)	−11.1 (13)
C(6)	4.6 (5)	7.3 (6)	6.3 (6)	−0.3 (4)	−0.9 (4)	0.1 (5)
C(7)	9.4 (8)	7.9 (7)	4.8 (6)	0.9 (7)	−0.4 (6)	−0.0 (6)
C(8)	26.0 (20)	18.9 (15)	10.8 (11)	15.3 (16)	−9.5 (12)	−4.4 (11)
C(9)	22.6 (23)	51.0 (48)	10.7 (13)	15.3 (28)	4.3 (15)	11.0 (21)
C(10)	24.2 (22)	14.8 (15)	23.2 (22)	−2.9 (15)	−15.7 (19)	5.8 (14)
C(11)	5.1 (5)	4.8 (5)	11.1 (7)	−2.8 (4)	3.1 (5)	0.1 (5)
C(12)	6.9 (6)	4.5 (5)	7.6 (6)	−1.0 (5)	2.6 (5)	0.5 (5)
C(13)	14.4 (12)	9.5 (9)	14.2 (11)	−1.6 (8)	6.1 (9)	1.3 (8)
C(14)	9.3 (8)	7.9 (8)	14.2 (11)	−1.8 (6)	2.5 (8)	−1.1 (7)
C(15)	6.6 (7)	8.1 (7)	20.0 (13)	−0.7 (6)	7.9 (8)	−0.2 (8)
C(21)	8.1 (6)	6.6 (6)	7.4 (6)	2.4 (5)	−0.0 (5)	−0.5 (5)
C(22)	10.0 (7)	8.3 (7)	5.6 (6)	1.7 (6)	0.8 (5)	−1.2 (5)
C(23)	5.2 (6)	8.4 (8)	12.0 (9)	−2.7 (5)	−1.8 (6)	0.7 (7)
C(24)	6.8 (7)	10.4 (9)	13.6 (11)	−4.0 (7)	4.0 (7)	−0.8 (8)
C(25)	12.6 (10)	9.4 (8)	18.8 (13)	−0.7 (7)	8.2 (10)	6.4 (8)
C(26)	9.2 (7)	11.2 (9)	12.4 (9)	−2.1 (6)	7.1 (7)	−0.4 (7)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Table IV. Intramolecular Distances (Å) with Esd's for $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$

(A) Distances from the Tungsten Atom			
W–C(1)	1.785 (8)	W–P(1)	2.577 (3)
W–C(6)	1.942 (9)	W–P(2)	2.450 (3)
W–C(11)	2.258 (8)		
(B) Distances within the Neopentylidyne Ligand			
C(1)–C(2)	1.492 (13)	C(2)–C(4)	1.488 (19)
C(2)–C(3)	1.426 (19)	C(2)–C(5)	1.464 (20)
(C) Distances within the Neopentylidene Ligand			
C(6)–C(7)	1.487 (15)	C(7)–C(9)	1.373 (27)
C(7)–C(8)	1.422 (25)	C(7)–C(10)	1.457 (28)
(D) Distances within the Neopentyl Ligand			
C(11)–C(12)	1.492 (15)	C(12)–C(14)	1.508 (17)
C(12)–C(13)	1.503 (17)	C(12)–C(15)	1.488 (16)
(E) Distances within the dmpe Ligand			
P(1)–C(21)	1.811 (10)	P(2)–C(24)	1.827 (14)
P(1)–C(22)	1.797 (10)	P(2)–C(25)	1.809 (14)
P(1)–C(23)	1.855 (12)	P(2)–C(26)	1.820 (13)
C(23)–C(24)	1.455 (18)		

least-squares refinement; here $w = [\{\sigma(F_o)\}^2 + \{pF_o\}^2]^{-1}$ and the ignorance factor (p) was 0.01.

Results and Discussion

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table IV; interatomic angles, with esd's, are given in Table V; least-squares planes (and deviations of atoms therefrom) are collected in Table VI. A stereoscopic view of the molecule appears as Figure 1; the labeling of atoms in the core of the molecule is shown in Figure 2.

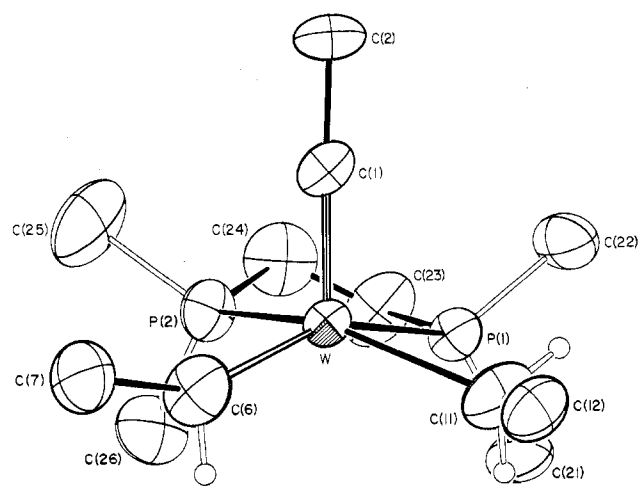

Figure 2. Labeling of atom in the $W(\equiv CC)(=CHC)(CH_2C)(C_2PCCPC_2)$ core of the $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmp)$ molecule. Hydrogen atoms are in estimated positions.

Table V. Interatomic Angles (deg) for $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$

(A) Angles around the Tungsten Atom			
C(1)-W-C(6)	108.68 (38)	P(1)-W-C(6)	150.36 (28)
C(1)-W-C(11)	108.85 (36)	P(1)-W-C(11)	77.31 (25)
C(6)-W-C(11)	104.60 (37)	P(2)-W-C(1)	90.80 (27)
P(1)-W-P(2)	75.47 (9)	P(2)-W-C(6)	91.53 (28)
P(1)-W-C(1)	98.19 (26)	P(2)-W-C(11)	148.36 (26)
(B) Angles within the Neopentylidyne Ligand			
W-C(1)-C(2)	175.34 (69)	C(3)-C(2)-C(4)	109.8 (12)
C(1)-C(2)-C(3)	112.0 (10)	C(3)-C(2)-C(5)	111.7 (12)
C(1)-C(2)-C(4)	110.9 (10)	C(4)-C(2)-C(5)	101.2 (12)
C(1)-C(2)-C(5)	110.9 (10)		
(C) Angles within the Neopentylidene Ligand			
W-C(6)-C(7)	150.44 (79)	C(8)-C(7)-C(9)	106.8 (17)
C(6)-C(7)-C(8)	115.5 (12)	C(8)-C(7)-C(10)	102.9 (15)
C(6)-C(7)-C(9)	113.6 (15)	C(9)-C(7)-C(10)	105.9 (17)
C(6)-C(7)-C(10)	111.3 (13)		
(D) Angles within the Neopentyl Ligand			
W-C(11)-C(12)	124.53 (69)	C(13)-C(12)-C(14)	102.5 (10)
C(11)-C(12)-C(13)	107.2 (9)	C(13)-C(12)-C(15)	109.4 (10)
C(11)-C(12)-C(14)	112.5 (9)	C(14)-C(12)-C(15)	109.1 (10)
C(11)-C(12)-C(15)	115.4 (9)		
(E) Angles within the dmpe Ligand			
W-P(1)-C(21)	120.0 (4)	W-P(2)-C(24)	111.9 (4)
W-P(1)-C(22)	116.6 (4)	W-P(2)-C(25)	118.4 (5)
W-P(1)-C(23)	111.0 (4)	W-P(2)-C(26)	118.8 (4)
C(21)-P(1)-C(22)	101.8 (5)	C(24)-P(2)-C(25)	101.6 (6)
C(21)-P(1)-C(23)	101.1 (5)	C(24)-P(2)-C(26)	102.3 (6)
C(22)-P(1)-C(23)	104.3 (5)	C(25)-P(2)-C(26)	101.3 (6)
P(1)-C(23)-C(24)	113.3 (9)	P(2)-C(24)-C(23)	111.2 (9)

The molecule consists of a pentacoordinate tungsten(VI) atom surrounded by a bidentate 1,2-bis(dimethylphosphino)ethane ligand, a neopentylidyne ligand, a neopentylidene ligand, and a neopentyl ligand. The coordination geometry about the tungsten atom is distorted but is slightly closer to square-pyramidal than to the postulated[11] trigonal-bipyramidal geometry. Within this context, the neopentylidyne ligand occupies the apical site, the apical–basal angles being C(1)–W–C(6) = 108.68 (38)°, C(1)–W–C(11) = 108.85 (36)°, C(1)–W–P(1) = 98.19 (26)°, and C(1)–W–P(2) = 90.80 (27)°. The cis-dibasal angles are P(1)–W–P(2) = 75.47 (9)°, P(2)–W–C(6) = 91.53 (28)°, C(6)–W–C(11) = 104.60 (37)°, and C(11)–W–P(1) = 77.31 (25)°; the trans-dibasal angles are P(1)–W–C(6) = 150.36 (28)° and P(2)–W–C(11) = 148.36 (26)°. The tungsten atom and C(1) (the α carbon of the neopentylidyne ligand) lie −0.4878 (3) and −2.244 (8) Å, respectively, from the least-squares plane through the basally coordinated atoms (P(1), P(2), C(6), C(11): see plane (A), Table VI). The apical group (as defined by W–C(1)–C(2)) makes an angle of 88.92° with the basal plane.

The principal feature of interest in the current structure is the comparison of the geometry of isoskeletal[5] alkyl, alkylidene, and alkylidyne ligands present at a common metal center. The W–C(α) distances for the neopentyl, neopentylidene, and neopentylidyne ligands are, respectively, W–C(11) = 2.258 (9) Å, W–C(6) = 1.942 (9) Å, and W–C(1) = 1.785 (8) Å; the successive decrements are 0.316 [13][19] and 0.157 [12] Å for increases of one unit in bond order.

The W–C(α)–C(β) angles for the neopentyl, neopentylidene, and neopentylidyne ligands are, respectively, W–C(11)–C(12) = 124.53 (69)°, W–C(6)–C(7) = 150.44 (7)°, and W–C(1)–C(2) = 175.34 (69)°—all in accordance with previous information on primary alkyls, alkylidenes, and alkylidynes of tantalum (vide supra).

Previously determined tungsten–alkylidyne (carbyne) bond distances include W–C(α) = 1.90 Å in *trans*-$W(\equiv CC_6H_5)(CO)_4I$[20] and W—C(α) = 1.82 Å in $W(\equiv CC_6H_4Me)(\eta^5\text{-}C_5H_5)(CO)_2$.[21] The W–C($\alpha$)–C($\beta$) angles in these species are 162 (4) and 177 (2)°, respectively. The only previously determined tungsten–"alkylidene" distances are those of W–C(α) = 2.13 (2) and 2.15 (2) Å (two independent molecules) determined for the *secondary* "alkylidene" derivative $W(=CPh_2)(CO)_5$.[22] The W–C(α)–C(β) angles here are, as expected, normal for an sp^2-hybridized carbon atom (120.7 (11)–126.1 (11)°).

It should be noted that the terminal methyl groups of the neopentylidyne (i.e., atoms C(3), C(4), C(5)), neopentylidene (i.e., C(8), C(9), C(10)), and, to a lesser extent, neopentyl (i.e., C(13), C(14), C(15)) ligands are subject to substantial libration motions about the appropriate C(α)–C(β) axis. This is clearly seen in Figure 1; numerical data are available from Table IV. Thus, while the C(α)–C(β) distances are reasonable [C(1)–C(2) = 1.492 (13) Å, C(6)–C(7) = 1.487 (15) Å, C(11)–C(12) = 1.492 (15) Å], the calculated C(β)–Me distances are shortened artificially due to librational motion.

The dmpe ligand is linked to tungsten via the bonds W–P(1) = 2.577 (3) Å and W–P(2) = 2.450 (3) Å. The longer of these is for the phosphorus atom that is trans to C(6) of the alkylidene ligand; the shorter is that for the phosphorus atom trans to C(11) of the alkyl ligand.

All other distances and angles in the complex are normal.

Table VI. Least-Squares Planes[a] and Atomic Deviations Therefrom and Dihedral Angles for $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$

Planes and Deviations (Å)			
(A) Square Pyramidal Base: $0.6325X - 0.7035Y - 0.3242Z + 2.3888 = 0$[b]			
P(1)*	0.008 (3)	C(2)	−3.728 (10)
P(2)*	−0.010 (3)	C(7)	−0.192 (14)
C(6)*	0.099 (9)	C(12)	−0.418 (11)
C(11)*	−0.114 (9)	C(23)	0.179 (12)
W	−0.4878 (3)	C(24)	−0.380 (13)
C(1)	−2.244 (8)		
(B) $-0.2191X + 0.2148Y - 0.9518Z + 0.1091 = 0$[b]			
W*	0.000	C(2)*	0.000
C(1)*	0.000		
(C) $0.8094X + 0.5356Y - 0.2410Z - 1.2867 = 0$			
W*	0.000	C(7)*	0.000
C(6)*	0.000		
(D) $0.4412X - 0.6003Y - 0.6671X + 2.7912 = 0$			
W*	0.000	C(12)*	0.000
C(11)*	0.000		
(E) $0.4279X - 0.7973Y - 0.4256Y + 3.2170 = 0$			
W*	0.000	C(23)	−0.224 (12)
P(1)*	0.000	C(24)	−0.751 (13)
P(2)*	0.000	C(25)	−0.937 (14)
C(21)	1.476 (10)	C(26)	1.593 (12)
C(22)	−1.289 (11)		
Dihedral Angles (deg)			
A/B = 88.92	B/C = 80.38	C/D = 78.67	
A/C = 77.69	B/D = 65.84	C/E = 88.75	
A/D = 23.42	B/E = 81.95	D/E = 17.95	
A/E = 14.18			

[a] Atoms used in calculating the plane are marked with an asterisk. [b] Cartesian (orthonormalized, Å) coordinates.

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Registry No. $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$, 70878-65-8.

Supplementary Material Available: A table of data-processing formulas and a listing of observed and calculated structure factor amplituded (13 pages). Ordering information is given on any current masthead page.

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Effects of Crystal Packing on the Coordination Geometry of Eight-Coordinate Metal Chelates. Crystal and Molecular Structure of Tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV)

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The crystal and molecular structure of tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV), $Zr(bzbz)_4$, has been determined by single-crystal X-ray diffraction and has been refined anisotropically by least-squares techniques to $R_1 = 0.080$ and $R_2 = 0.072$ by using 5168 independent diffractometer-recorded reflections having $2\theta(\text{Cu K}\bar{\alpha}) \leq 110.03°$ and $|F_o| > 2\sigma(|F_o|)$. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 25.241$ (5), $b = 10.324$ (1), and $c = 19.395$ (4) Å; $\beta = 101.72$ (1)° ($\rho_{obsd} = 1.31$, $\rho_{calcd} = 1.321$ g cm^{-3}). The crystal contains discrete eight-coordinate molecules in which the bidentate dibenzoylmethanate ligands span the *s* edges of a slightly distorted D_{4d}-$\bar{8}2m$ square antiprism to give the *ssss*-D_2 stereoisomer. Distortions are in the direction of the bicapped trigonal-prismatic $h_1h_1p_2p_2$-C_2 stereoisomer. The distortions, presumably due to the effects of crystal packing, are compared with the somewhat different distortions in the analogous $Zr(acac)_4$ complex. The Zr–O bonds in $Zr(bzbz)_4$ fall into two symmetry-inequivalent sets: Zr–O(outer) = 2.153 Å and Zr–O(inner) = 2.192 Å. The C_3O_2 portions of the chelate rings are planar, but the rings are folded (by 21.7 ± 2.2°) about the edges (O···O) of the square antiprism; all four rings are bent away from the quasi-$\bar{8}$ axis of the antiprism. The phenyl groups are twisted out of the C_3O_2 planes by angles that vary from 17.3 to 41.9°.

Introduction

Because the more common eight-coordination polyhedra are of comparable energy,[1-7] the choice of coordination polyhedron and ligand wrapping pattern in eight-coordinate tetrakis(bidentate) chelates is usually determined by secondary factors such as the matching of ligand bite with polyhedral edge lengths.[1,4] Crystal packing considerations may also influence the coordination geometry,[1] but the effects of crystal packing have not yet been well documented.

In the case of tetrakis(dithiocarbamate) complexes, the dodecahedral *mmmm*-D_{2d} stereoisomer is found in a variety of crystalline environments. Thus the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation exists as the *mmmm* stereoisomer in $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$ and $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$, and the dimensions of the dodecahedral coordination polyhedra in the two salts are closely similar.[8] The same can be said for the $[Mo(S_2CN(C_2H_5)_2)_4]^+$ cation in $[Mo(S_2CN(C_2H_5)_2)_4]Cl$ and $[Mo(S_2CN(C_2H_5)_2)_4]_2[Mo_6O_{19}]$.[9] Evidently the small normalized bite of the dithiocarbamate ligand (S···S/M–S = 1.11) favors the dodecahedral *mmmm* stereoisomer so strongly that the effects of crystal packing are unimportant.

On the other hand, crystal packing does influence coordination geometry in tetrakis(acetylacetonate) complexes, $M(acac)_4$. Two crystalline forms are known, an α form for M = Ce, Th, and U and a β form for M = Zr, Hf, Ce, Th, U, and Np.[10] The β form contains the well-established square-antiprismatic *ssss*-D_2 stereoisomer, but the α form contains the bicapped trigonal-prismatic $h_1h_1p_2p_2$-C_2 stereoisomer.[11-13] The latter isomer is related to the former by folding about the diagonal of one of the square faces of the antiprism.

The present work is prompted by an early report of still another stereoisomer in the tetrakis(β-diketonate) series. On the basis of an analysis of the badly overlapped (001) and (100) electron density projections of tetrakis(dibenzoylmethanato)cerium(IV), $Ce(bzbz)_4$, Wolf and Barnighausen[14] proposed that the isomorphous tetrakis(dibenzoylmethanates) of Ce, Th, and U have a dodecahedral *mmmm* structure. The structure of the analogous $Zr(bzbz)_4$ is unknown, but our studies of mixed-ligand complexes of the type $Zr(acac)_2(NO_3)_2$[15] and $Zr(acac)_3(NO_3)$[16] suggested that the dodecahedral *mmmm* stereoisomer is unlikely for Zr(β-diketonate)$_4$ complexes because the relatively large bite of β-diketonate ligands does not permit two such ligands to be located on the same trapezoid of a ZrO_8 dodecahedron. Brief conflicting reports that propose a square-antiprismatic structure for

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