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Registry No. I, 73440-09-2; II, 73440-08-1; [Ni(1,4-(4-$MeC_6H_4)_2N_4)_2$], 73432-46-9; [Ni(Cp)$_2$], 1271-28-9; 4-$MeC_6H_4N_3$, 2101-86-2.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters (Table IIA), and least-squares planes (Table V) and an ORTEP drawing (Figure 5) (25 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3][CF_3SO_3]$, a Seven-Coordinate Tungsten(II) Complex Produced by Transfer of a PMe_3 Ligand to the $W{=}CH_2$ System

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The title complex, prepared by Schrock and co-workers from the reaction of $[W({=}CH_2)(PMe_3)_4Cl^+][CF_3SO_3^-]$ with CO, crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 9.249$ (2) Å, $b = 11.911$ (3) Å, $c = 13.573$ (3) Å, $\alpha = 81.49$ (2)°, $\beta = 78.63$ (2)°, $\gamma = 84.96$ (2)°, $V = 1447.2$ (6) Å^3, ρ(calcd) = 1.77 g cm^{-3} for $Z = 2$, and mol wt 770.8. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer, and the structure was refined to $R_F = 4.3\%$ and $R_{wF} = 4.8\%$ for all 4048 independent reflections with $3.5° < 2\theta < 46.0°$ (Mo Kα radiation). The coordination environment of the tungsten atom approximates to a monocapped trigonal-prismatic geometry. One triangular face is occupied by atom C(3) of an ordered CO ligand and by atoms P(1) and P(2) of PMe_3 ligands [W–C(3) = 1.957 (8) Å, W–P(1) = 2.548 (2) Å, and W–P(2) = 2.567 (2) Å], while the other triangular face contains P(3) of the third PMe_3 ligand [W–P(3) = 2.495 (2) Å] and disordered CO/Cl ligands, which were successfully resolved [W–C(1) = 1.968 (19) Å, W–Cl(1) = 2.557 (5) Å; W–C(2) = 1.940 (19) Å, W–Cl (2) = 2.527 (5) Å]. The CH_2PMe_3 ligand is linked to tungsten with W–C(4) = 2.305 (7) Å and occupies the capping position on the square face defined by P(1), P(2), C(1)/Cl(1), and C(2)/Cl(2).

Introduction

There are few examples of transition-metal complexes containing terminal methylene ligands, an observation that has, in some cases, been attributed to the high reactivity of the methylene complex under the conditions in which it is formed.[1] The first discovery of such a species, that of $Ta(\eta^5\text{-}C_5H_5)_2({=}CH_2)(CH_3)$ by Schrock and co-workers,[2] has recently been followed by their synthesis of $[W({=}CH_2)(PMe_3)_4Cl^+][CF_3SO_3^-]$, a methylene complex of W(IV).[3] Other examples of methylene ligands exist in tungsten chemistry, although none have been isolated as stable solids. Thus, $[W(\eta^5\text{-}C_5H_5)_2({=}CH_2)(CH_3)^+]$, which is isoelectronic with $Ta(\eta^5\text{-}C_5H_5)_2({=}CH_2)(CH_3)$, was postulated as an intermediate in the formation of $[W(\eta^5\text{-}C_5H_5)_2(C_2H_4)H^+]$ from $[W(\eta^5\text{-}C_5H_5)_2(CH_3)_2^+][PF_6^-]$ upon treatment of the latter with the trityl radical.[4] A similar species, $[W(\eta^5\text{-}C_5H_5)_2({=}CH_2)H^+]$, has also been proposed.[5]

Evidence supporting the structures of these intermediate methylene complexes was provided by the isolation of stable phosphonium ylide complexes with the formulas $[W(\eta^5\text{-}C_5H_5)_2(CH_2PMe_2Ph)CH_3^+][PF_6^-]$ and $[W(\eta^5\text{-}C_5H_5)_2(CH_2PMe_2Ph)H^+][PF_6^-]$, respectively. Other examples of attack by a tertiary phosphine on an unsaturated carbon producing a phosphoylide are known. Thus the vinyl-bridged cluster $(\mu\text{-}H)Os_3(CO)_{10}(CH{=}CH_2)$ reacts with PMe_2Ph, giving the 1,3-dipolar species $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}C^-\text{-}HCH_2P^+Me_2Ph)$.[6] The bridging formyl ligand in the complex $[Ta(\eta^5\text{-}C_5Me_4Et)_2Cl_2]_2(CHO)(H)$[7] undergoes a reaction with PMe_3, resulting in cleavage of the carbon–oxygen bond and formation of the ylide $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(C^-HP^+Me_3)(O)(H)$.[8] The η^1-alkynyl complex $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C{\equiv}CPh)$ reacts with PPh_3 in the presence of acid to yield $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C(PPh_3)){=}CHPh^+]$.[9]

Table I. Experimental Data for the X-ray Diffraction Study of $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3][CF_3SO_3]$

(A) Crystal Parameters[a] at 23 °C

cryst syst: triclinic	space group: $P\bar{1}$
$a = 9.2494$ (20) Å	$\alpha = 81.487$ (18)°
$b = 11.9113$ (26) Å	$\beta = 78.626$ (18)°
$c = 13.5734$ (32) Å	$\gamma = 84.960$ (18)°
$V = 1447.2$ (6) Å	mol wt 770.8
$Z = 2$	ρ(calcd) = 1.77 g cm^{-3}

(B) Intensity Data

radiation: Mo Kα [$\bar{\lambda} = 0.710\,730$ Å]
monochromator: highly oriented graphite
2θ range: 3.5–46.0°
reflctns measd: $+h, \pm k, \pm l$
scan type: θ(cryst)–2θ(counter)
scan speed: 2.50° min^{-1}
scan range: $[2\theta(K\alpha_1 - 1.0)]\text{–}[2\theta(K\alpha_2 + 1.0)]°$
reflctns collected: 4234 total yielding 4048 independent
abs coeff: 46.5 cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 25 reflections with $2\theta = 25\text{–}31°$.

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Table II. Final Positional Parameters, with Esd's, for $[\mathrm{W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3}][\mathrm{CF_3SO_3}]$

atom	*x*	*y*	*z*	B_{iso}, Å^2
W	0.16861 (3)	0.18681 (2)	0.22177 (2)	
Cl(1)	0.0336 (5)	0.2356 (4)	0.0723 (3)	3.83 (7)
Cl(2)	−0.0428 (5)	0.1674 (4)	0.3715 (4)	3.95 (7)
P(1)	0.2945 (2)	0.1884 (2)	0.3724 (2)	
P(2)	0.3657 (2)	0.2568 (2)	0.0688 (2)	
P(3)	0.0579 (2)	0.0055 (2)	0.2138 (2)	
P(4)	−0.0476 (2)	0.4512 (2)	0.2599 (2)	
O(1)	0.0197 (17)	0.2265 (14)	0.0349 (11)	6.2 (3)
O(2)	−0.0663 (14)	0.1447 (11)	0.4175 (10)	4.8 (2)
O(3)	0.4265 (7)	0.0001 (5)	0.2056 (5)	
C(1)	0.0722 (20)	0.2070 (16)	0.1028 (14)	4.2 (3)
C(2)	0.0211 (21)	0.1552 (16)	0.3439 (14)	4.5 (3)
C(3)	0.3269 (9)	0.0663 (6)	0.2126 (6)	
C(4)	0.1250 (8)	0.3790 (6)	0.2300 (6)	
C(11)	0.4934 (9)	0.2212 (10)	0.3468 (7)	
C(12)	0.2969 (11)	0.0526 (8)	0.4521 (7)	
C(13)	0.2168 (10)	0.2834 (8)	0.4647 (6)	
C(21)	0.3935 (11)	0.1677 (9)	−0.0319 (7)	
C(22)	0.5542 (10)	0.2657 (11)	0.0854 (8)	
C(23)	0.3343 (12)	0.3954 (8)	−0.0007 (7)	
C(31)	0.0724 (10)	−0.1083 (7)	0.3180 (7)	
C(32)	−0.1413 (9)	0.0184 (8)	0.2130 (8)	
C(33)	0.1305 (10)	−0.0665 (8)	0.1031 (7)	
C(41)	−0.1910 (9)	0.3947 (8)	0.2159 (8)	
C(42)	−0.1094 (11)	0.4535 (9)	0.3925 (7)	
C(43)	−0.0383 (11)	0.5965 (7)	0.2051 (8)	
S	−0.3614 (2)	0.3927 (2)	−0.2855 (2)	
F(1)	−0.4002 (9)	0.2369 (7)	−0.3924 (7)	
F(2)	−0.5965 (8)	0.2931 (8)	−0.2956 (7)	
F(3)	−0.5057 (9)	0.3915 (7)	−0.4310 (6)	
O(4)	−0.4547 (9)	0.4864 (7)	−0.2539 (7)	
O(5)	−0.2312 (7)	0.4180 (6)	−0.3589 (5)	
O(6)	−0.3363 (8)	0.3068 (6)	−0.2050 (5)	
C(5)	−0.4685 (11)	0.3258 (8)	−0.3561 (8)	

Numerous phosphoylide adducts of transition-metal compounds, formed by reacting a Wittig-type ylide reagent with a suitable metal complex, have also been reported.[10] For example, the unusual species $\mathrm{Mn(Br)(CO)_4(C{\equiv}CPPh_2)}$ was produced by reacting $\mathrm{Mn(CO)_5Br}$ with $\mathrm{(Ph_3P)_2C}$.[11] Recently lithiated Wittig reagents were used to synthesize phosphoylide complexes of uranium;[12] the ylide group was cited as a stabilizing factor for the actinide–carbon σ bond.

In this paper we report the X-ray structural analysis of the phosphoylide derivative (I) of the W(IV) methylene complex $[\mathrm{W({=}CH_2)(PMe_3)_4Cl^+}][\mathrm{CF_3SO_3^-}]$. This material was produced[13] through a unique reaction involving intramolecular transfer of a trimethylphosphine ligand from tungsten to the methylene carbon, which occurs upon reaction of the methylene complex with CO (eq 1). Note that this "insertion" reaction leads to formal reduction of W(IV) to W(II).

$$[\mathrm{W({=}CH_2)(PMe_3)_4Cl^+}][\mathrm{CF_3SO_3^-}] \xrightarrow{\mathrm{CO}} \underset{\mathrm{I}}{[\mathrm{W(CH_2PMe_3)(PMe_3)_3(CO)_2Cl^+}][\mathrm{CF_3SO_3^-}]} \quad (1)$$

Experimental Section

Data Collection. A bright yellow fragment measuring approximately 0.20 × 0.30 × 0.33 mm, sealed into a glass capillary in an inert-atmosphere (Ar) drybox, was mounted and aligned on a Syntex $P2_1$ diffractometer. Data were collected as described previously[14] (see Table I) and were corrected for absorption and for Lorentz and polarization effects;[15] all subsequent calculations were performed on a CDC Cyber 173 computer with software described earlier.[16]

Table IV. Interatomic Distances (Å), with Esd's, for $[\mathrm{W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3}][\mathrm{CF_3SO_3}]$

(A) Distances from the Tungsten Atom			
W–P(1)	2.548 (2)	W···O(2)	3.091 (13)
W–P(2)	2.567 (2)	W···O(3)	3.114 (6)
W–P(3)	2.495 (2)	W–C(1)	1.968 (19)
W–Cl(1)	2.557 (5)	W–C(2)	1.940 (19)
W–Cl(2)	2.527 (5)	W–C(3)	1.957 (8)
W···O(1)	3.076 (15)	W–C(4)	2.305 (7)
(B) Phosphorus–Carbon Distances			
P(1)–C(11)	1.868 (8)	P(3)–C(32)	1.838 (8)
P(1)–C(12)	1.809 (9)	P(3)–C(33)	1.824 (8)
P(1)–C(13)	1.814 (8)	P(4)–C(4)	1.748 (7)
P(2)–C(21)	1.819 (9)	P(4)–C(41)	1.776 (9)
P(2)–C(22)	1.815 (10)	P(4)–C(42)	1.782 (9)
P(2)–C(23)	1.806 (10)	P(4)–C(43)	1.782 (9)
P(3)–C(31)	1.826 (9)		
(C) Carbon–Oxygen Distances			
C(1)–O(1)	1.110 (21)	C(3)–O(3)	1.158 (9)
C(2)–O(2)	1.153 (21)		
(D) Distances within the Triflate Ligand			
S–O(4)	1.414 (7)	C(5)–F(1)	1.295 (11)
S–O(5)	1.427 (6)	C(5)–F(2)	1.353 (13)
S–O(6)	1.422 (7)	C(5)–F(3)	1.273 (12)
S–C(5)	1.810 (10)		

Table V. Interatomic Angles (Deg), with Esd's, for $[\mathrm{W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3}][\mathrm{CF_3SO_3}]$

(A) Interligand Angles about Tungsten			
P(1)–W–P(2)	103.35 (7)	P(1)–W–Cl(1)	166.49 (11)
P(1)–W–C(3)	73.6 (2)	P(1)–W–C(1)	172.6 (6)
P(2)–W–C(3)	73.9 (2)	P(1)–W–Cl(2)	76.88 (11)
P(3)–W–Cl(1)	76.37 (12)	P(1)–W–C(2)	72.7 (6)
P(3)–W–C(1)	71.3 (6)	P(1)–W–P(3)	115.82 (7)
P(3)–W–Cl(2)	74.75 (12)	P(2)–W–Cl(1)	74.33 (12)
P(3)–W–C(2)	72.0 (6)	P(2)–W–C(1)	73.8 (5)
Cl(1)–W–Cl(2)	102.20 (15)	P(2)–W–Cl(2)	166.4 (11)
Cl(1)–W–C(2)	107.8 (6)	P(2)–W–C(2)	171.6 (6)
C(1)–W–C(2)	109.2 (8)	P(2)–W–P(3)	116.3 (7)
C(1)–W–Cl(2)	104.2 (5)	C(4)–W–Cl(1)	82.3 (2)
C(3)–W–Cl(1)	117.6 (3)	C(4)–W–C(1)	88.6 (6)
C(3)–W–C(1)	111.5 (6)	C(4)–W–Cl(2)	84.3 (2)
C(3)–W–Cl(2)	118.5 (3)	C(4)–W–C(2)	89.9 (6)
C(3)–W–C(2)	111.2 (6)	C(4)–W–P(3)	145.8 (2)
C(3)–W–P(3)	71.9 (2)	C(4)–W–P(1)	84.2 (2)
		C(4)–W–P(2)	84.3 (2)
		C(4)–W–C(3)	142.3 (3)
(B) Angles within the Phosphine Ligands			
W–P(1)–C(11)	118.4 (3)	W–P(3)–C(32)	114.9 (3)
W–P(1)–C(12)	113.2 (3)	W–P(3)–C(33)	116.9 (3)
W–P(1)–C(13)	118.5 (3)	W–C(4)–P(4)	126.4 (4)
W–P(2)–C(21)	113.1 (3)	C(4)–P(4)–C(41)	113.9 (4)
W–P(2)–C(22)	119.7 (3)	C(4)–P(4)–C(42)	113.4 (5)
W–P(2)–C(23)	118.4 (3)	C(4)–P(4)–C(43)	109.9 (4)
W–P(3)–C(31)	116.2 (3)		
(C) Angles within the Carbonyl Ligands			
W–C(1)–O(1)	174.9 (22)	W–C(3)–O(3)	176.0 (8)
W–C(2)–O(2)	175.0 (20)		

Solution and Refinement. A Patterson map and several difference-Fourier calculations were used to solve the structure. Full-matrix least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ with $w = [[\sigma(|F_o|)]^2 + (0.02|F_o|^2)]^{-1}$. Neutral-atom analytical scattering

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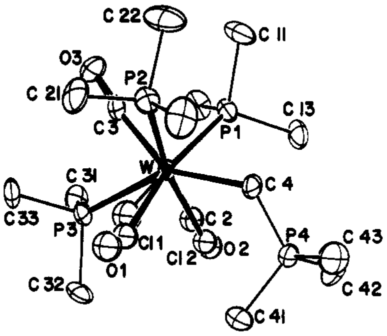

Figure 3. Labeling of atoms in the (disordered) $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3^+]$ cation. Atom C(4) occupies the capping position for capped trigonal-prismatic coordination about W; the capped face is defined by P(1), P(2), C(1)/Cl(1), and C(2)/Cl(2); the 1:4:2 coordination geometry is completed by P(3) and C(3) (ORTEP-II diagram).

factors with corrections for anomalous dispersion were used.[17]

The chloride and one carbonyl ligand are disordered about a noncrystallographic local mirror plane containing atoms P(3), W, C(3)–O(3), C(4), and C(32) (see Figure 1[28]). Both the half-chloride and half-carbonyl were located on both sides of the molecule. The coordinates of each were refined independently along with their isotropic thermal parameters, while their occupancy factors were fixed at $^1/_2$.

All hydrogen atoms were included in calculated positions [d(C–H) = 0.95 Å].[18] Refinement led smoothly to convergence with[19] R_F = 4.3%, R_{wF} = 4.8%, and GOF = 1.82 for 277 parameters refined against all 4048 reflections, with none rejected. Final positional parameters are collected in Table II. Anisotropic thermal parameters are given in Table III (supplementary material).

Description of the Structure

Intramolecular bond distances and angles are presented in Tables IV and V, respectively. The crystal consists of discrete $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3^+]$ cations and $[CF_3SO_3^-]$ anions, well separated by normal van der Waals distances. A projection of the unit cell packing in the a–c plane is shown in Figure 2.[28] The labeling of atoms in the cation is shown in Figure 3.

The tungsten atom is seven-coordinate. Although it is well-known that there are small potential energy differences among the three most common seven-coordinate geometries (defined by the 1:5:1 D_{5h} pentagonal bipyramid, the 1:4:2 C_{2v} capped trigonal prism (CTP), the 1:3:3 C_{3v} capped octahedron),[20] the present structure is considered in the context of a CTP, due to its structural similarity to $[Mo(CNR)_7^{2+}]$,[21] which is an archetypal CTP species. One triangular face is composed of two phosphine ligands (P(1) and P(2)) and an ordered carbonyl ligand (C(3)–O(3)), while the other triangular face is formed by a third phosphine ligand (P(3)) and two sites that are each occupied by disordered carbonyl/chloride ligands (C(1)–O(1)/Cl(1) and C(2)–O(2)/Cl(2)). The CH_2PMe_3 ligand occupies the capping position on the square face defined by P(1), P(2), Cl(1)/CO(1), and Cl(2)/CO(2).

It should be noted that the chloride/carbonyl disorder, which scrambles ligands CO(1)–Cl(1) and CO(2)–Cl(2) across a noncrystallographic mirror plane of symmetry, has little effect on the overall structural results. Interestingly, Figure 1[28] shows that the "half-chlorine atoms" refined to positions not collinear with their respective "half-carbonyl" groups, viz., ∠W-C(1)-O(1) = 175 (2)°, ∠C(1)···Cl(1)···O(1) = 132 (3)° and ∠W-C(2)-O(2) = 175 (2)°, ∠C(2)···Cl(2)···O(2) = 125 (2)°.

The point symmetry of the ML_7 core in the $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3]$ cation closely approaches $C_s(m)$; indeed, the only disruption from this symmetry in the entire cation occurs in the ylide fragment, resulting from freedom of rotation about the W–CH_2 and CH_2–P bonds.

The CTP coordination geometry is characterized by close-to-equivalent L_c–W–L_{qf} angles [L_c = the "capping" ligand, i.e., C(4); L_{qf} = atom defining the quadrilateral face of the trigonal prism capped by C(4)]: C(4)–W–P(1), 84.2 (2)°; C(4)–W–P(2), 84.3 (2)°; C(4)–W–C(1), 88.6 (6)°; C(4)–W–Cl(1), 82.3 (2)°; C(4)–W–C(2), 89.9 (6)°; C(4)–W–Cl(2), 84.3 (2)°. These values compare favorably with the average L_c–M–L_{qf} angle of 82.0° observed in $[Mo(CNR)_7^{2+}]$.[21b] Angles subtended from the C(4)–W vector to the remaining vertices of the trigonal prism [defined as L_c–M–L_e by using the nomenclature of ref 21b; L_c–M–L_e = 144.2 in $[Mo(CNR)_7^{2+}]$] are also nearly equivalent, with C(4)–W–P(3) = 145.8 (2)° and C(4)–W–C(3) = 142.3 (3)°.

Angles involving the central W(II) atom and atoms defining the three quadrilateral faces fall into two distinct sets, with those involving the capped face being substantially larger than the others. Thus, P(1)–W–P(2) = 103.35 (7)° whereas P(1)–W–C(3) = 73.6 (2)° and P(2)–W–C(3) = 73.9 (2)°, and Cl(1)–W–C(2) = 107.8 (6)° [Cl(2)–W–C(1) = 104.2 (5)°] whereas P(3)–W–C(1) = 76.4 (1)° and P(3)–W–Cl(2) = 74.8 (1)°.

The three metal–phosphine bond lengths in the $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3^+]$ cation display some interesting variations. The W–P distances for the pair of PMe_3 ligands trans to the disordered CO/Cl sites are W–P(1) = 2.548 (2) and W–P(2) = 2.567 (2) Å (average 2.558 [13] Å), while the W–P distance trans to the $CH_2P^+Me_3$ ligand is considerably shorter, with W–P(3) = 2.495 (2) Å. While it is important to note that each of the W–P distances trans to the disordered sites is somewhat artificial, and represents the *average* W–P distance for P–W–CO and P–W–Cl systems, it is expected that the trans effect of the carbonyl group would dominate that of the chloride and result in a net bond-lengthening effect on the trans phosphine ligands. We note for comparison that W–PMe_3 distances for the pair of mutually trans phosphine ligands in the $W(\equiv CH\cdot AlMe_{2-x}Cl_{1+x})Cl(PMe_3)_3$ molecule[22] are 2.496 (2) and 2.497 (2) Å. The W–P(3) distance in the present structure is equivalent to these in spite of the trans relationship of P(3) to the $CH_2P^+Me_3$ ligand. σ-Bonded alkyl ligands generally display a trans-lengthening effect,[23] but this must be diminished in the present molecule as a result of the formal positive center of charge on P(4) adjacent to C(4). Further evidence for inductive charge removal within the phosphonium alkyl ligand is presented below.

The W–CH_2P bond length of 2.305 (7) Å is indicative of a tungsten–carbon single bond. The associated W–C–P angle of 126.4 (4)° is similar to the large M–C–C angles (120–130°) found in metal alkyl complexes.[23b] In the $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$ molecule[24,25] the W^{VI}–CH_2CMe_3 bond length is 2.258 (8) Å and the associated W–C–C angle is 124.5 (7)°.

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[19] Definitions: $R_F = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$ (%); $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%); GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

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Phosphorus–carbon linkages within three PMe_3 ligands are normal, ranging from 1.806 (10) to 1.868 (8) Å and averaging 1.824 [19] Å. Contrasting significantly with this are the phosphorus–carbon distances within the phosphonium ylide moiety, ranging from 1.748 (7) to 1.782 (9) Å and averaging 1.772 [16] Å. Furthermore, the P(4)–C(4) linkage is the shortest of these, accounting for the diminished inductive trans effect of the alkyl ligand. The decrease in phosphorus–carbon bond lengths within a phosphoylide has been observed previously.[26]

Other geometrical features within the molecule are normal. Structural parameters for the ordered CO ligand are W–C(3) = 1.957 (8) Å, C(3)–O(3) = 1.158 (9) Å, and W–C(3)–O(3) = 176.0 (8)°; bond lengths for the disordered carbonyls are similar, with W–C(1) = 1.968 (19) Å, C(1)–O(1) = 1.110 (21) Å, W–C(2) = 1.940 (19) Å, and C(2)–O(2) = 1.153 (21) Å. These values are entirely consistent with previously obtained results[27] on seven-coordinate tungsten carbonyl complexes. The tungsten–chlorine distances are also normal, with W–Cl(1) = 2.557 (5) Å and W–Cl(2) = 2.527 (5) Å.

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Registry No. $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3][CF_3SO_3]$, 82880-78-2.

Supplementary Material Available: Tables of calculated hydrogen atom positions (Table II-S), anisotropic thermal parameters (Table III), and observed and calculated structure factor amplitudes and Figures 1 and 2 (28 pages). Ordering information is given on any current masthead page.

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Bridgehead Phosphorane Structure of a Chlorodiazadiphosphetidine with Fused Five-Membered Rings[1]

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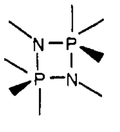
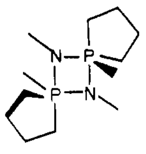
Single-crystal X-ray analysis of 10-chloro-9,10-dihydro-1,2′,9-trimethyl-3,5′,7-triphenylspiro[1*H*-[1,3,2λ^5,4λ^5]diazadiphospheto[2,1-*c*:2,3-*c*′]bis[1,2,4,3λ^5]triazaphosphole-5,3′-[2*H*][1,2,4,3λ^5]triazaphosphole], $(PhCN_3Me)_3P_2Cl$ (IX), containing both a pentacoordinate and tetracoordinate phosphorus center incorporated in the phosphetidine ring with attached 1,2,4,3-triazaphosphole rings, reveals a partial meridonal, partial cis-facial ring arrangement around the five-coodinated phosphorus atom. The compound crystallizes in the monoclinic crystal system, space group *C*2/*c*, with $Z = 8$, $a = 33.229$ (4) Å, $b = 9.685$ (2) Å, $c = 17.677$ (3) Å, and $\beta = 111.96$ (1)°. Refinement including all hydrogen atoms gave $R = 0.035$, $R_w = 0.045$ for the 2881 reflections having $I \geq 2\sigma_I$. The geometry around the pentacoordinate phosphorus atom is about 40% along the coordinate from an idealized trigonal bipyramid with the chlorine atom situated equatorially toward a square pyramid with the chlorine atom in the apical position. The tendency of tricoordinated nitrogen atoms to reach planarity in the partially unsaturated rings is cited as the principal influence leading to the observed structure. NMR data indicate the structure is retained in solution.

Introduction

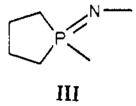
Diazadi-λ^5-phosphetidines I are stabilized relative to a monomeric formulation if substituents of sufficient electronegativity are attached[2,3] to phosphorus. The addition of cyclic substituents, as in II, contributes to the stabilization of the diazadiphosphetidine, presumably due to ring strain reduction relative to the monomeric form III.[4,5]



I

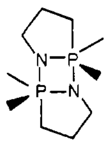


II

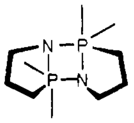


III

Recent work with fused-ring systems revealed two variations of the dimeric form, a meridonal conformer[6,7] IV and a facial-cis placement of the fused rings V.[3] The use of acyclic



IV



V

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[‡] Universität München.

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