Synthesis and Crystal Structure of Diphenylcarbene(pentacarbonyl)tungsten(0)

Charles P. Casey,* Terry J. Burkhardt, Charles A. Bunnell, and Joseph C. Calabrese

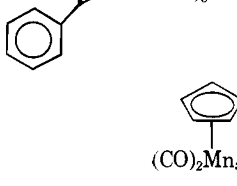
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received June 16, 1976

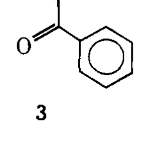
Abstract: Reaction of $(CO)_5WC(OCH_3)C_6H_5$ with phenyllithium at −78 °C followed by treatment with HCl at −78 °C produces a 59% yield of $(CO)_5WC(C_6H_5)_2$, **1**, which was characterized by spectral means and by x-ray crystallography. The carbene carbon–tungsten distance in **1** is 2.15 Å, and the planes of the phenyl rings are twisted ~42° from the plane defined by the carbene carbon atom and the atoms directly bonded to it. **1** reacts with oxidizing agents to give benzophenone, with $CH_2{=}P(C_6H_5)_3$ to give diphenylethylene, and with $P(C_6H_5)_3$ to give $(C_6H_5)_2C{=}P(C_6H_5)_3$. Thermal decomposition of **1** in heptane gives tetraphenylethylene and diphenylmethane.

Stable transition metal-carbene complexes[1] generally have at least one heteroatom (O, N, S) directly bonded to the carbene carbon atom. The heteroatom serves to stabilize the complex by electron donation to the carbene carbon atom. The resulting partial double bond between the heteroatom and the carbene carbon atom is manifested by a shortening of the carbon heteroatom bond[2] and by a substantial rotational barrier about the carbon heteroatom bond.[3] Heteroatom substituted carbene complexes are often thermally stable to over 100 °C[4,5] and have been found to act as cyclopropanating agents only toward α,β-unsaturated esters and vinyl ethers.[6] We began studies of the preparation of a diphenylcarbene complex since we felt that such a complex would be less stable and more reactive in carbene transfer reactions than heteroatom substituted carbene complexes.

Prior to our synthesis of diphenylcarbene(pentacarbonyl)tungsten(0), **1**,[7] the only well-documented reports of carbene complexes not substituted with heteroatoms were (2,3-diphenylcyclopropenylidene)chromium and palladium compounds prepared by Öfele;[8] the high stability of these complexes is undoubtedly related to the aromaticity of the diphenylcyclopropenium cation. Subsequently a number of other stable nonheteroatom stabilized carbene complexes have been prepared. Giering and Sanders prepared the cationic iron-carbene complex, **2**, by hydride abstraction from the corresponding alkyl iron compound;[9] decomposition of **2** via hydride migration to the carbene carbon atom (a normal route for decomposition of metal carbene complexes[4,5]) is unfavorable since a benzocyclobutadiene complex would be produced. Schrock has recently prepared a series of remarkably stable tantalum-carbene complexes including $[(CH_3)_3CCH_2]_3Ta{=}CH[C(CH_3)_3]$ and $(\eta^5\text{-}C_5H_5)_2(CH_3)Ta{=}CH_2$ via α-elimination reactions.[10] Hermann has prepared manganese complexes of α-ketocarbenes such as **3** from the corresponding diazoketone.[11] The synthesis of diphenylcarbene complexes of manganese[12] and of chromium has also been reported.[13]



2

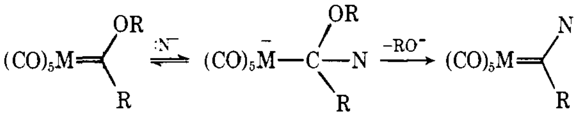


3

Diphenylcarbene(pentacarbonyl)tungsten(0), **1**, has proven to be a valuable compound for model studies of the olefin metathesis reaction.[14,15] Indeed, **1** is a moderately effective catalyst for the metathesis of alkenes[16] and for the ring opening metathetical polymerization of 1-methylcyclobutene.[17] Here we report the full details for the synthesis of $(CO)_5WC(C_6H_5)_2$, **1**, its spectral and chemical characterization, and its single-crystal x-ray structure. The use of **1** as a model compound for the study of the olefin metathesis reaction will be discussed in a subsequent paper.

Results and Discussion

Synthesis of $(CO)_5WC(C_6H_5)_2$. The reaction of phenyllithium with $(CO)_5WC(OCH_3)C_6H_5$, **4**, provided an attractive route to a diphenylcarbene complex in light of the known nucleophilic substitution reactions of metal carbene complexes. For example, alkoxy substituted metal carbene complexes react readily with amines and thiols to produce nitrogen and sulfur substituted carbene complexes.[18] Similarly, $(CO)_5CrC(OCH_3)C_6H_5$ undergoes rapid exchange with CD_3OH in basic solutions.[19] The kinetics of these nucleophilic substitution reactions are consistent with the addition of the nucleophile to the carbene carbon atom followed by elimination of the alkoxy group.[20] Stable addition products have been obtained from the reaction of tertiary amines and phosphines with carbene complexes.[21] Molecular orbital calculations on $(CO)_5CrC(OCH_3)CH_3$ indicate that the lowest unoccupied molecular orbital is highly localized on the carbene carbon atom; the observed attack of nucleophiles on the carbene carbon atom is consistent with frontier orbital control of reactivity.[22]



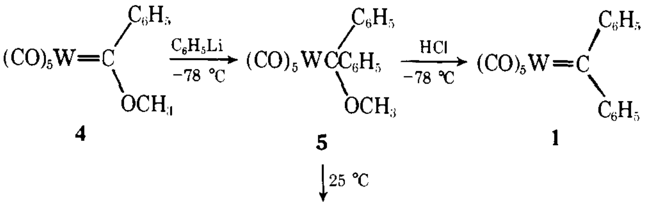
The addition of C_6H_5Li to an orange-red ether solution of $(CO)_5WC(OCH_3)C_6H_5$, **4**, at −78 °C produced a homogeneous red-brown solution. Decomposition to a brown heterogeneous mixture occurred upon warming to room temperature. Benzhydrol methyl ether (20%), 1,2-dimethoxy-1,1,2,2-tetraphenylethane (19%), and hexacarbonyltungsten (37%) were isolated from the reaction mixture. Fischer has reported similar products from the reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with C_6H_5Li at 0 °C.[23] Both of the organic products obtained from the reaction of **4** with C_6H_5Li contained carbons bearing two phenyl groups and a methoxy group. Evidently, methoxide was not spontaneously lost from the presumed intermediate adduct **5**. In view of the reactions of amines and phosphines with carbene complexes to give stable adducts which are resistant to the loss of methoxide, the reluctance of intermediate

Table I. Infrared CO Stretching Frequencies and Force Constants

	A_1^2	B_1	A_1^1	E	k_1	k_2	k_i	Ref
$(CO)_5WC(C_6H_5)_2$[a]	2070 (m)		1971 (s)	1963 (s)	15.87	16.08	0.26	
$(CO)_5WC(OCH_3)C_6H_5$[a]	2070 (m)	1984 (w)	1958 (s)	1945 (s)	15.71	15.90	0.31	
$NEt_4^+(CO)_5WCH_2(C_6H_4)CH_3$-*p*[b]	2034 (m)	1932 (w)	1840 (m)	1889 (s)	15.07	13.83	0.33	27
$(CO)_6W$		(A_{1g} 2121, E_g 2015, T_{1u} 1980)				16.41	0.29	26, 28

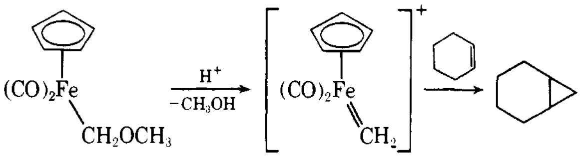
[a] Solution IR spectrum in heptane. [b] Solution IR spectrum in THF.

5 to produce the diphenylcarbene complex **1** is not surprising. The observed products could arise from homolytic cleavage of the tungsten-carbon bond of adduct **5** to give a $C(OCH_3)(C_6H_5)_2$ radical which either abstracts hydrogen from solvent or dimerizes.



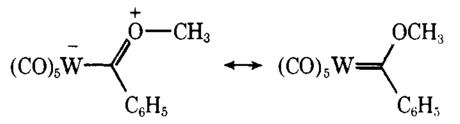
Adduct **5** was treated with acid at low temperature in an effort to protonate it, bring about loss of methanol, and form **1**. The red-brown solution obtained from reaction of **4** with 1.1 equiv of C_6H_5Li at −78 °C was treated with 1.1 equiv of dry HCl in ether at −78 °C to give a dark red solution. Column chromatography of the reaction mixture (silica gel-pentane) at 15 °C gave a rapidly eluted red compound which was recrystallized from pentane at −22 °C to give the desired $(CO)_5WC(C_6H_5)_2$, **1**, in 59% yield as black iridescent crystals. The structure of **1** was assigned on the basis of its spectral properties and chemical reactions and was confirmed by x-ray crystallography.

Presumably, HCl protonates the methoxy group of adduct **4** and brings about the rapid loss of methanol to give **1**. Similarly, the reaction of **4** with $C_6H_5S^-$ yields a stable adduct which is converted to $(CO)_5WC(SC_6H_5)C_6H_5$ only upon treatment with acid.[24] In a related reaction, **6** reacts with HBF_4 in the presence of cyclohexene to give norcarane, presumably via an intermediate cationic carbene complex.[25]



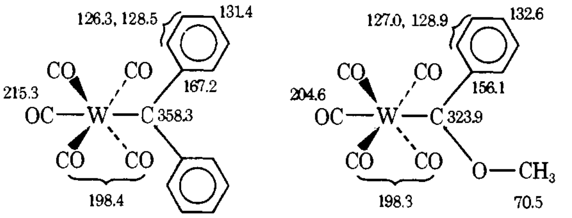
6

Spectral Characterization of $(CO)_5WC(C_6H_5)_2$. The infrared spectrum of **1** (Table I) is consistent with its formulation as a metal pentacarbonyl. The B_1 fundamental vibrational mode, which is not infrared active for rigorous C_{4v} symmetry but gives rise to a weak band in the IR spectrum of **4**, is not seen in the IR spectrum of **1**. The CO stretching frequencies of $(CO)_5WC(C_6H_5)_2$, **1**, appear at higher energy than those of $(CO)_5WC(OCH_3)C_6H_5$, **4**. A Cotton-Kraihanzel force constant analysis[26] of the infrared spectra of **1** and **4** indicates that both the cis and trans carbonyl stretches of **1** are about 0.20 mdyn/Å greater than those of **4**. This indicates that there is less negative charge on the $W(CO)_5$ fragment of **1** than **4**; conversely, there is more positive charge on the $C(OCH_3)C_6H_5$ ligand of **4** than on the $C(C_6H_5)_2$ ligand of **1**. Much of the positive charge in **4** is centered on the oxygen atom of the $C(OCH_3)C_6H_5$ ligand. The difference between cis and trans force constants of **1** is only 0.21 mdyn/Å; this indicates that



while the $C(C_6H_5)_2$ ligand is a good π-acceptor, it is not as good a π-acceptor as CO. If the carbene ligands of **1** and **4** operated only as σ-donors, their infrared spectra would be similar to that of $(CO)_5WCH_2C_6H_4CH_3^-$, which has much lower force constants and a large difference of 1.24 mdyn/Å between its cis and trans force constants.[27] Thus the infrared spectrum of **1** provides strong evidence for extensive back-bonding from tungsten to the $C(C_6H_5)_2$ ligand.

In the ^{13}C NMR spectrum of $(CO)_5WC(C_6H_5)_2$, **1**, the carbene carbon resonance appears at δ 358.3[29] which is 34.4 ppm lower field than $(CO)_5W^{13}C(OCH_3)C_6H_5$. The carbene carbon of metal-carbene complexes appears at characteristically low fields. The factors giving rise to these low field shifts are not well understood.[30] Certainly, the low field shifts cannot be wholly ascribed to the electropositive nature of the carbene carbon atom since the carbonium ion $^{13}C(C_6H_5)_3^+$ appears at δ 211[31] and since $R_3Ta^{13}CH[C(CH_3)_3]$ which has a negatively polarized carbene carbon atom appears at low field also, δ 250.1.[10a] Nevertheless, within limited series of carbene complexes, the ^{13}C chemical shift of the carbene carbon atom decreases with increasing electron donating ability of the substituents attached to the carbene carbon atom.[24,32,33] The 34.4 ppm downfield shift of the carbene carbon atom of **1** relative to **4** can therefore be taken as an indication of greater positive charge on the carbene carbon atom of $(CO)_5WC(C_6H_5)_2$, **1**. Consequently, while the $C(C_6H_5)_2$ ligand of **1** bears less positive charge than the $C(OCH_3)C_6H_5$ ligand of **4**, the carbene carbon atom of **1** is more positive than that of **4**. Evidently the positive charge on the $C(C_6H_5)_2$ ligand is localized on carbon while the positive charge on the $C(OCH_3)C_6H_5$ ligand is largely delocalized onto oxygen.



The ^1H NMR of **1** consists of a broad multiplet at δ 7.4–7.0. These chemical shifts indicate that little positive charge is delocalized into the phenyl rings.

The UV-visible spectrum of **1** in hexane showed bands at 232 (ε 46 500), 285 (sh), and 485 mμ (ε 10 400). The long wavelength band is responsible for the deep red color of **1** in solution.

The mass spectrum of **1** gave a weak parent ion at *m/e* 490 (^{184}W, 1.2%), loss of one, three, four, and five carbon monoxides was observed (for ^{184}W): 462 (8%), 406 (15%), 378 (2%), 350 (15%). This successive loss of CO is typical for group 6 metal-carbene complexes where the base peak usually corresponds to loss of five CO's.[34]

The dipole moment (μ) of **1** was determined in benzene solution at 20.0 °C and found to be 3.48 D. The dipole moment

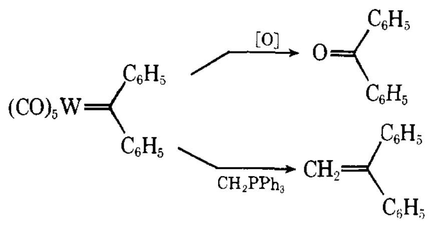
Table II. Bonding Distances (Å) for $(CO)_5WC(C_6H_5)_2$

	Molecule 1	Molecule 2
C(3)-W(1)	2.02 (2)	2.01 (2)
O(4)-C(3)	1.17 (2)	1.15 (2)
C(5)-W(1)	1.98 (2)	1.95 (2)
O(6)-C(5)	1.20 (2)	1.19 (2)
C(7)-W(1)	2.03 (3)	2.06 (2)
O(8)-C(7)	1.13 (3)	1.14 (2)
C(9)-W(1)	2.02 (2)	2.05 (2)
O(10)-C(9)	1.16 (2)	1.16 (2)
C(11)-W(1)	2.06 (2)	2.02 (2)
O(12)-C(11)	1.11 (2)	1.18 (2)
C(13)-W(1)	2.15 (2)	2.13 (2)
C(14)-C(13)	1.45 (2)	1.52 (2)
C(15)-C(14)	1.35 (2)	1.41 (2)
C(16)-C(15)	1.36 (2)	1.42 (3)
C(17)-C(16)	1.37 (2)	1.33 (3)
C(18)-C(17)	1.39 (2)	1.38 (3)
C(19)-C(14)	1.45 (2)	1.39 (2)
C(19)-C(18)	1.39 (2)	1.36 (3)
C(20)-C(13)	1.51 (2)	1.46 (2)
C(21)-C(20)	1.45 (2)	1.42 (2)
C(22)-C(21)	1.41 (2)	1.35 (2)
C(23)-C(22)	1.39 (2)	1.37 (3)
C(24)-C(23)	1.42 (3)	1.40 (3)
C(25)-C(20)	1.33 (2)	1.37 (2)
C(25)-C(24)	1.36 (2)	1.40 (2)

of $(CO)_5WC(OCH_3)C_6H_5$ was found to be 4.39 D, and is in good agreement with 4.08 D (cyclohexane, 20 °C) found for $(CO)_5CrC(OCH_3)C_6H_5$.[35] The smaller dipole moment of $(CO)_5WC(C_6H_5)_2$ compared with $(CO)_5WC(OCH_3)C_6H_5$ is in agreement with the finding from IR spectroscopy that the $C(C_6H_5)_2$ ligand bears less positive charge than the $C(OCH_3)C_6H_5$ ligand.

Chemical Characterization of $(CO)_5WC(C_6H_5)_2$, 1. Several reactions of **1** were carried out to aid in its characterization. The oxidizing reagents, cerric ammonium nitrate,[36] dimethyl sulfoxide,[37] and oxygen,[38] are known to convert the carbene ligand into the corresponding carbonyl compounds. Oxidation of **1** to benzophenone was accomplished with ceric ion (58%), dimethyl sulfoxide (88%), and oxygen (41%). Solid samples of **1** can readily be handled in air at room temperature but solutions of **1** decompose slowly in air.

The reactions of oxycarbene complexes with Wittig reagents yield an olefin and $W(CO)_5PR_3$.[39] Similarly, the reaction of **1** with methylenetriphenylphosphorane gave a 49% yield of 1,1-diphenylethylene. These results indicate that the reactions of **1** parallel those of the oxycarbene complexes. Several exceptions, however, were found.



The thermolysis of **1** was found to be qualitatively much faster than any heteroatom carbene complex. At reflux temperature after several hours in heptane no remaining **1** could be detected. In contrast $(CO)_5CrC(OCH_3)C_6H_5$ must be heated to 135 °C for 12 h for complete decomposition.[4] The products from thermolysis of **1** in heptane were $W(CO)_6$, diphenylmethane, and tetraphenylethylene.

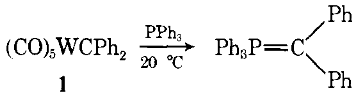
$$(CO)_5WCPh_2 \xrightarrow[\Delta]{\text{heptane}} W(CO)_6 + CH_2Ph_2 + Ph_2C{=}CPh_2$$

Table III. Intramolecular Bond Angles (deg) for $(CO)_5WC(C_6H_5)_2$

	Molecule 1	Molecule 2
C(3)-W(1)-C(5)	178.1 (6)	179.7 (7)
C(3)-W(1)-C(7)	90.2 (7)	88.4 (7)
C(3)-W(1)-C(9)	91.7 (7)	92.0 (8)
C(3)-W(1)-C(11)	87.9 (6)	89.9 (7)
C(3)-W(1)-C(13)	90.4 (6)	90.3 (6)
C(5)-W(1)-C(7)	91.6 (7)	91.6 (8)
C(5)-W(1)-C(9)	86.5 (6)	88.0 (8)
C(5)-W(1)-C(11)	91.5 (7)	89.9 (7)
C(5)-W(1)-C(13)	90.3 (6)	89.9 (6)
C(7)-W(1)-C(9)	177.3 (8)	175.2 (7)
C(7)-W(1)-C(11)	90.8 (8)	87.2 (7)
C(7)-W(1)-C(13)	91.3 (7)	92.5 (7)
C(9)-W(1)-C(11)	87.4 (8)	88.0 (7)
C(9)-W(1)-C(13)	90.6 (7)	92.3 (6)
C(11)-W(1)-C(13)	177.3 (7)	179.6 (7)
W(1)-C(3)-O(4)	173.0 (13)	176.4 (16)
W(1)-C(5)-O(6)	174.1 (13)	174.0 (17)
W(1)-C(7)-O(8)	172.5 (21)	176.9 (17)
W(1)-C(9)-O(10)	174.0 (15)	173.8 (18)
W(1)-C(11)-O(12)	175.1 (20)	177.0 (18)
W(1)-C(13)-C(14)	126.1 (11)	124.4 (11)
W(1)-C(13)-C(20)	120.7 (11)	124.8 (12)
C(14)-C(13)-C(20)	112.3 (13)	110.7 (15)
C(13)-C(14)-C(15)	124.6 (16)	120.5 (17)
C(13)-C(14)-C(19)	117.1 (15)	119.5 (16)
C(15)-C(14)-C(19)	117.9 (15)	120.0 (18)
C(14)-C(15)-C(16)	122.5 (17)	116.2 (20)
C(15)-C(16)-C(17)	121.2 (18)	123.5 (20)
C(16)-C(17)-C(18)	118.4 (16)	118.0 (20)
C(17)-C(18)-C(19)	121.5 (17)	122.6 (20)
C(14)-C(19)-C(18)	118.1 (16)	119.6 (19)
C(13)-C(20)-C(21)	115.1 (14)	120.0 (17)
C(13)-C(20)-C(25)	125.8 (16)	124.4 (17)
C(21)-C(20)-C(25)	118.7 (16)	115.2 (17)
C(20)-C(21)-C(22)	117.8 (15)	122.5 (20)
C(21)-C(22)-C(23)	121.2 (17)	121.2 (21)
C(22)-C(23)-C(24)	119.0 (17)	118.5 (18)
C(23)-C(24)-C(25)	118.3 (16)	118.8 (20)
C(20)-C(25)-C(24)	124.9 (17)	123.5 (20)

The thermolysis of $(CO)_5CrC(OCH_3)C_6H_5$ forms the dimeric products *cis*- and *trans*-α,β-dimethoxystilbene and $Cr(CO)_6$.[4] The thermolysis of $(CO)_5Cr\overline{COCH_2CH_2C}H_2$ proceeds by a bimolecular mechanism not involving a free carbene.[5] Presumably, $(C_6H_5)_2C{=}C(C_6H_5)_2$ arises via a similar pathway.

Another exception was found in the reaction of **1** with triphenylphosphine. To prepare triphenylphosphine substituted oxycarbene complexes, the carbene complex must be heated with triphenylphosphine to 80 °C for 5 h.[40] The reaction of **1** with triphenylphosphine is instantaneous at room temperature, but the phosphine-carbene complex is not formed. Rather,



$$\underset{\mathbf{1}}{(CO)_5WCPh_2} \xrightarrow[20\ ^\circ C]{PPh_3} Ph_3P{=}C(Ph)_2$$

7

attack occurs at the carbene carbon with cleavage of the metal-carbon bond to produce the phosphorane, **7**. In related work, Kreissl and Held have found that PMe_3 reacts with $(CO)_5W{=}C(C_6H_5)_2$ to give an isolable adduct, $(CO)_5WC(C_6H_5)_2PMe_3$.[29]

X-Ray Crystal Structure of $(CO)_5WC(C_6H_5)_2$. The crystal structure of **1** was determined using standard heavy atom techniques and was refined to $R_1 = 0.050$ and $R_2 = 0.055$. The unit cell had $P2_1/c$ symmetry with two similar molecules in the asymmetric unit. The bond distances and angles are shown in Tables II and III. Figure 1 clearly shows that **1** is monomeric

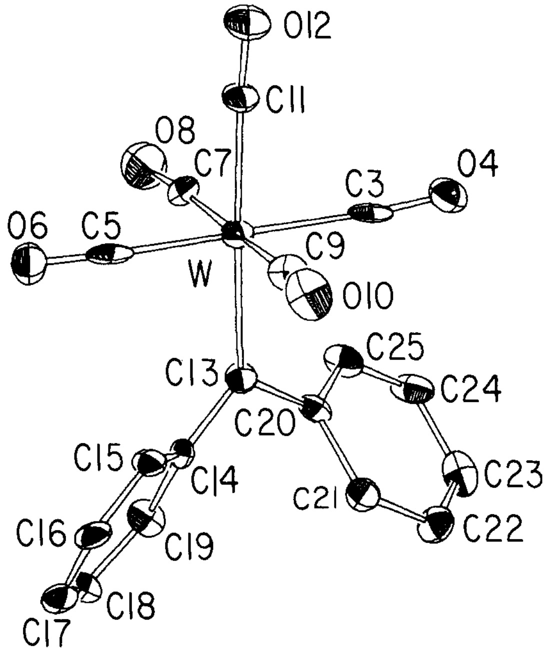


Figure 1. Structure of diphenylcarbenepentacarbonyltungsten(0) with thermal ellipsoids of 30% probability.

Table IV. Least-Squares Planes, Displacement (Å), and Selected Angles

		Molecule 1	Molecule 2
1	C3	−0.012	0.040
	C5	−0.012	0.041
	C7	0.012	−0.041
	C9	0.012	−0.041
	W1[a]	−0.022	0.045
2	C3	−0.004	−0.003
	C5	−0.004	−0.003
	C11	0.004	0.003
	C13	0.004	0.003
3	W1	0.005	0.005
	C13	−0.019	−0.018
	C14	0.007	0.006
	C20	0.007	0.007
4	C14	0.027	0.006
	C15	−0.040	−0.001
	C16	0.015	−0.012
	C17	0.021	0.022
	C18	−0.033	−0.018
	C19	0.010	0.004
5	C20	−0.019	−0.002
	C21	0.003	0.015
	C22	0.011	−0.008
	C23	−0.010	−0.010
	C24	−0.006	0.022
	C25	0.021	−0.017
		Dihedral Angles	
Plane 2 and plane 3		17.5°	19.2°
Plane 3 and plane 4		40.3°	41.7°
Plane 3 and plane 5		43.3°	40.7°

[a] Not defined in the plane.

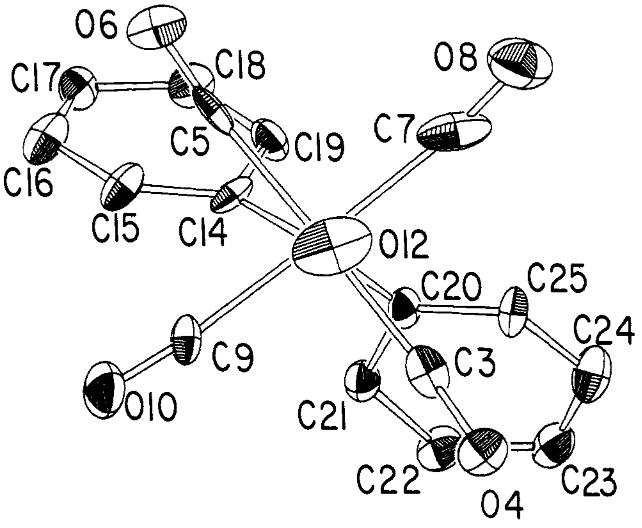


Figure 2. Structure of diphenylcarbene(pentacarbonyl)tungsten(0) viewed down the O(12)-C(11)-W(1)-C(13) bonds.

and contains a diphenylcarbene ligand and five carbon monoxides located pseudooctahedrally about tungsten.

All previous x-ray structures of Group 6 metal-carbene complexes have been determined with chromium as the central metal atom.[41] This precludes any direct comparison of metal-carbon bond lengths with **1**. The length of the tungsten-carbene carbon bond, W-C(13), is 2.15 (2) and 2.13 (2) Å in the two independent molecules. This is substantially shorter than the 2.34 (1) Å C-W single bond in Et_4N^+-$(CO)_5W$-$CH(OCH_3)C_6H_5^-$[42] and substantially longer than the 1.88 Å C-W triple bond in the carbyne complex I-$(CO)_4W{\equiv}CC_6H_5$.[43] Thus the C-W bond of $(CO)_5$-$WC(C_6H_5)_2$ can best be characterized as a carbon-metal double bond. This result confirms the extensive back-bonding from tungsten to carbon in **1** which was deduced from infrared spectroscopy. The average tungsten to CO bond length of 2.02 Å is 0.04 Å shorter in **1** than in $W(CO)_6$,[44,45] indicating that the σ-donor/π-acceptor ratio of the $C(C_6H_5)_2$ ligand is higher than that of CO; this may be due solely to the weaker π-acceptor ability of $C(C_6H_5)_2$. The tungsten to carbene carbon bond is 0.13 Å longer than the tungsten to CO bonds. Since CO has two π^* orbitals available for back-bonding while $C(C_6H_5)_2$ has only a single p orbital available for back-bonding, it is not surprising that there is more back-bonding to CO.

The carbene carbon, C(13), and the atoms bonded to it, W(1), C(14), C(20), are coplanar (Table IV). This plane forms an angle of 17.5° (19.2°, molecule 2) with the plane defined by C(3), C(5), C(11), and C(13), as illustrated in Figure 2. This angle is much smaller than that found in $(CO)_5$-$CrC(OCH_3)C_6H_5$ (45°)[45] or $(CO)_5CrC(SC_6H_5)CH_3$ (36°).[41]

Each phenyl ring is planar and forms angles of 40.3° (41.7°, molecule 2) and 43.3° (40.7°) with the W(1), C(13), C(14), C(20) plane. Electron donation from the phenyl rings to the electron deficient carbon atom is possible in $(CO)_5WC(C_6H_5)_2$ even though the phenyls are twisted ~42° from the p orbital on the carbene carbon atom. The overlap between adjacent p orbitals depends on the cosine of angle between them. For orbitals twisted 42° from planarity, the overlap is reduced to 74% of the maximum overlap. For comparison, the angle of twist in the propeller shaped $(C_6H_5)_3C^+ClO_4^-$ is 32°,[46] indicating ~85% of the maximum stabilization from the phenyl rings. Steric interactions in **1** and $(C_6H_5)_3C^+$ undoubtedly prevent the phenyl rings from being coplanar with the plane defined by the carbene carbon atom and its attached atoms.

In the x-ray structure of $(CO)_5CrC(OCH_3)C_6H_5$, the phenyl ring is twisted 90° from the plane defined by the carbene carbon atom and the atoms directly bonded to it. Because the phenyl ring is orthogonal to the p orbital on the carbene carbon atom there can be no resonance stabilization of the electron deficient carbene carbon by the phenyl group. In $(CO)_5CrC(OCH_3)C_6H_5$, the electronic stabilization originates entirely from oxygen and chromium.

Experimental Section

General. All reactions involving organometallic reagents were carried out under a nitrogen atmosphere. Ether and tetrahydrofuran were distilled from sodium and benzophenone prior to use. Solutions were transferred by syringe or by cannula (hypodermic wire) under positive nitrogen pressure. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian A60A or a Jeolco MH-100 spectrometer. IR spectra were recorded on a Perkin-Elmer 267 spectrometer in the solvent specified and are reported in wavenumbers. Mass spectra were obtained on an AEI-MS-903 mass spectrometer at 70 eV. Analytical vapor phase chromatography was run on a Hewlett Packard 5750 gas chromatograph with flame ionization detector and disk integrator. Preparative vapor phase chromatography was done on a Varian Aerograph 90P instrument.

Reaction of $(CO)_5WC(OCH_3)C_6H_5$, 4, with Phenyllithium. 4 (391.7 mg, 0.885 mmol) was dissolved in 12 mL of ether and cooled to −78 °C. Phenyllithium (0.49 mL, 1.82 M, 0.891 mmol) was added and the reaction mixture was stirred 1 h at −78 °C. The resulting red-brown, homogeneous solution was warmed to room temperature and stirred overnight producing a brown, heterogeneous reaction mixture. The ether was removed under aspirator vacuum, and cold (0 °C) ether was added. Filtration gave white tungsten hexacarbonyl (112.3 mg, 37%): IR ($CHCl_3$) 1970 cm^{-1}. The brown filtrate was evaporated, taken up in a small amount of $CHCl_3$, passed through a short silica gel chromatography column, and purified by preparative TLC (silica gel, two elutions pentane, one elution 10% ether–90% pentane) to give 1,2-dimethoxy-1,1,2,2-tetraphenylethane[23] (19%) and benzhydrol methyl ether (20%).

Diphenylcarbenepentacarbonyltungsten(0), 1. In a 250-mL flask $(CO)_5WC(OCH_3)C_6H_5$, 4 (1.649 g, 3.72 mmol) was dissolved in 140 mL of ether and cooled to −78 °C. To this orange-red solution phenyllithium (2.3 mL, 1.82 M active base, 4.19 mmol, 1.1 equiv, 2.03 M total base, 4.67 mmol) was added dropwise resulting in a gradual change over 1 h to a red-brown solution. As an ether solution of dry HCl (5.2 mL, 1.01 M, 5.25 mmol, ~10% excess over total base) was slowly added, a dark red color was immediately produced. After 10 min at −78 °C the reaction was warmed to room temperature. During this time the flask was covered with aluminum foil to protect it from light. A small amount (~5 g) of silica gel was added and the ether evaporated. The silica gel with the reaction mixture adsorbed on it was then placed on top of a chromatography column (silica gel, 70 g) with a water-cooled jacket (~15 °C), and eluted with pentane. Isolation of the dark red band and recrystallization from pentane (14 mL) at −22 °C gave dark crystals (1.073 g, 59%) mp 65–66 °C. Anal. Calcd for $C_{18}H_{10}O_5W$: C, 44.11; H, 2.05; W, 37.51. Found: C, 43.94; H, 2.11; W, 37.69. UV-visible (hexane): 232 (46 500), 285 (sh), 485 (10 400). Mass spectrum: 493 (0.4). 492 (1.2), 491 (0.5), 490 (1.8), 489 (0.9), 4.88 (1.2), 465 (1.8), 464 (6.8), 463 (2.1), 462 (8.4), 461 (5.3), 460 (7.4), 409 (3), 408 (12), 407 (3), 406 (15), 405 (9), 404 (12), 381 (1.2), 380 (6), 379 (1.2), 378 (7), 377 (1.4), 376 (2.1), 356 (6), 354 (13), 353 (6), 352 (18), 351 (7), 350 (15), 349 (6), 348 (6), 324 (6), 322 (7), 321 (3), 320 (4), 298 (7), 296 (7), 295 (4), 294 (5), 270 (12), 268 (13), 267 (7), 266 (11), 242 (6), 240 (5), 239 (3), 238 (5), 214 (5), 212 (6), 211 (3), 210 (5), 195 (9), 194 (71), 182 (11), 168 (44), 167 (49), 166 (58), 165 (100), 164 (9), 163 (9), 154 (40), 153 (14), 152 (13), 139 (7), 119 (6), 115 (9), 105 (24), 91 (13), 83 (13), 82.5 (15), 82 (11), 78 (17), 77 (18), 76 (10), 69 (14), 63 (9), 57 (10), 55 (8), 51 (12), 50 (6). The exact mass of the parent ion could not be determined because of its low intensity. However, the exact mass of parent ion minus one CO was determined by high resolution mass spectrometry. Calcd for $C_{17}H_{10}O_4W$, 462.008 84; Found: 462.005 84.

Cerric Ammonium Nitrate Oxidation of 1. A 5-mL portion of a solution prepared from $(NH_4)_2Ce(NO_3)_6$ (0.55 g, 1 mmol) in 7 mL of acetone was added to a dark red solution of **1** (79.1 mg, 0.162 mmol) in 5 mL of ether. The ether solution was quenched with water, washed with saturated sodium chloride, and dried (K_2CO_3). GC analysis (octadecane internal standard) showed a 58% yield of benzophenone.

Oxidation of 1 with Dimethyl Sulfoxide. Dimethyl sulfoxide (0.1 mL, 110 mg, 1.41 mmol) was added to **1** (70.3 mg, 0.144 mmol) and dissolved in 5 mL of ether. The deep red color of **1** faded rapidly (~5 s) to yellow-brown. After 30 min the ether was evaporated. Analysis by GC (octadecane internal standard) showed an 88% yield of benzophenone.

Oxidation of 1 with O_2. **1** (34.7 mg, 0.0708 mmol) was dissolved in 8 mL of ether which was then saturated with oxygen. After stirring for 4 days under an O_2 atomsphere, GC analysis (octadecane internal standard) showed a 41% yield of benzophenone.

Reaction of 1 with Methylenetriphenylphosphorane. A solution of $CH_2P(C_6H_5)_3$ was prepared by adding methyllithium (0.45 mL, 2.0 M, 0.90 mmol) to methyltriphenylphosphonium bromide (324.9 mg, 0.91 mmol) in 15 mL of ether. After stirring 3 h this solution was added to **1** (89.9 mg, 0.202 mmol) in 10 mL of ether. GC analysis (octadecane internal standard) showed a 49% yield of 1,1-diphenylethylene which was isolated by preparative TLC (silica gel, three elutions of pentane, three elutions of 2% ether–98% pentane, two elutions of 5% ether–95% pentane). The IR spectrum was identical with that of an authentic sample.[47]

Thermolysis of 1 in Heptane. **1** (146.1 mg, 0.280 mmol) was dissolved in 10 mL of heptane (dry, distilled) to give a dark red solution. This was protected from light and refluxed for 6 h under a N_2 atmosphere. During the reaction a black precipitate formed. Filtration gave a brown solution which was purified by preparative TLC (silica gel, three elutions of hexane) to give $W(CO)_6$ (18.7 mg, 19%), (mp 148–150 °C, IR ($CHCl_3$) 1980 s), diphenylmethane (4.6 mg, 10%), identified by TLC comparison with an authentic sample, and a third band which was rechromatographed (silica gel preparative TLC, two elutions of 5% ether–95% hexane) to give tetraphenylethylene (16.3 mg, 35%), identified by TLC and IR comparison with an authentic sample.

Reaction of 1 with Triphenylphosphine. **1** (276.7 mg, 0.565 mmol) and triphenylphosphine (628.7 mg, 2.4 mmol) were placed in a flask and 5 mL of ether was added. The carbene complex dissolved to give its characteristic dark red color, but as the triphenylphosphine dissolved the color faded to give after 30 min a red precipitate. The ether was decanted and the solid washed with ether and dryed under vacuum to give diphenylmethylenetriphenylphosphorane as a red-orange solid (195 mg, 81% crude yield, mp 163–170 °C), recrystallization from benzene to give red crystals (112.8 mg, 47%; mp 171.5–173.5 °C, lit.[48] 172–174 °C, mmp with authentic material: 171–174 °C).

Dipole Moment Determinations. The dipole moments for $(CO)_5WC(OCH_3)C_6H_5$ and $(CO)_5WC(C_6H_5)_2$ were determined in benzene on a Wissenschaftlich-Technische Werkstätten Dipolemeter Type DM 01 using a DFL2 measuring cell of approximately 10 mL capacity. Measurements were made on four benzene solutions of either $(CO)_5WC(OCH_3)C_6H_5$ or $(CO)_5WC(C_6H_5)_2$ over a concentration range of 0.2–1.2 weight %.

^{13}C NMR of $(CO)_5WC(OCH_3)C_6H_5$ and $(CO)_5WC(C_6H_5)_2$, 1. The ^{13}C NMR spectra were obtained on a Varian XL-100 spectrometer operating in the Fourier transform mode. All spectra were recorded in chloroform-*d* with tris(acetylacetonato)chromium(III)[49] added (~0.07 M). Spectra were proton noise decoupled. A pulse width of 63 μs (~32 °) was found to maximize the metal carbonyl ^{13}C intensities. A probe temperature of 20.5 °C was used in obtaining spectra of **1**.

Crystallographic and X-Ray Data. Dark, flat needles of $(CO)_5WC(C_6H_5)_2$, **1**, suitable for the crystal study were obtained by recrystallization from pentane at −22 °C. The crystal chosen had a nearly trapezoidal cross-section and measured 0.09 × 0.20 × 0.45 mm. The crystal faces were defined by ±[100, 010, 001], $\bar{1}10$, and $\bar{1}\bar{1}0$ with the needle direction corresponding to the *b* axis. The sample was mounted on a glass fiber with Elmers Glue, sealed under Ar atmosphere, and placed on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite monochromated Mo Kα source. After careful optical and x-ray tube alignment accurate angle settings were determined for 15 diffraction maxima. From these the Syntex routines indicated the material possessed monoclinic symmetry with cell parameters and their estimated precisions: a = 16.723 (3), b = 14.818 (6), c = 14.246 (8) Å; β = 103.60(3)°; volume = 3431 Å^3.

The C_{2h}-$2/m$ symmetry and associated lattice lengths were verified by partial rotation photographs along each of the three reciprocal axes. The observed density of 1.87 g/cm^3 is in agreement with the calculated 1.90 g/cm^3 for eight molecules per cell.

Intensity data were collected in the usual θ–2θ scan mode with the takeoff angle of the tube set to 4°. Variable scan rates were allowed from 2 to 24 deg/min with total background count time set to 0.6 times the scan time. A total of 4168 reflections in the two unique reciprocal octants (positive l) were measured in the range 2° < 2θ < 45°. During

Table V. Atom Coordinates for $(CO)_5WC(C_6H_5)_2$[a]

	Molecule 1			Molecule 2		
Atom	X[b]	Y	Z	X	Y	Z
W(1)	3839.9 (5)	1710.6 (5)	366.5 (6)	9445.6 (5)	3904.4 (5)	2859.5 (5)
C(3)	4114 (9)	382 (13)	510 (11)	8808 (13)	2782 (13)	2988 (12)
O(4)	4225 (8)	−395 (9)	496 (9)	8428 (11)	2163 (1)	3098 (11)
C(5)	3573 (10)	3013 (13)	180 (11)	10069 (13)	4997 (13)	2741 (12)
O(6)	3381 (8)	3794 (9)	137 (10)	10509 (10)	5623 (10)	2721 (11)
C(7)	3392 (12)	1667 (14)	1576 (20)	10349 (12)	3099 (13)	2542 (13)
O(8)	3102 (11)	1729 (11)	2214 (14)	10824 (8)	2639 (10)	2330 (11)
C(9)	4237 (11)	1787 (11)	−865 (12)	8600 (11)	4706 (14)	3294 (13)
O(10)	4437 (10)	1906 (9)	−1578 (10)	8127 (8)	5105 (10)	3609 (11)
C(11)	2705 (11)	1350 (12)	−478 (15)	10049 (13)	3799 (13)	4264 (15)
O(12)	2102 (9)	1100 (11)	−898 (13)	10368 (9)	3748 (10)	5095 (10)
C(13)	5051 (10)	2046 (11)	1206 (12)	8817 (10)	4016 (11)	1378 (13)
C(14)	5472 (10)	2907 (10)	1224 (13)	8781 (10)	4870 (11)	781 (13)
C(15)	5392 (10)	3464 (10)	459 (13)	8652 (14)	5712 (13)	1174 (16)
C(16)	5794 (10)	4271 (12)	514 (15)	8648 (15)	6475 (13)	566 (17)
C(17)	6246 (11)	4594 (12)	1376 (15)	8734 (14)	6416 (16)	−338 (17)
C(18)	6286 (11)	4082 (11)	2201 (14)	8886 (15)	5583 (16)	−677 (14)
C(19)	5933 (12)	3228 (12)	2155 (12)	8894 (12)	4817 (13)	−154 (14)
C(20)	5582 (10)	1342 (10)	1826 (12)	8400 (11)	3278 (13)	786 (12)
C(21)	6423 (11)	1301 (11)	1731 (13)	7627 (12)	3422 (12)	137 (14)
C(22)	6932 (11)	619 (12)	2239 (14)	7171 (12)	2741 (16)	−351 (14)
C(23)	6639 (13)	8 (12)	2816 (12)	7448 (15)	1866 (16)	−262 (14)
C(24)	5802 (12)	65 (12)	2872 (14)	8222 (15)	1688 (13)	344 (15)
C(25)	5321 (11)	719 (11)	2352 (12)	8661 (13)	2397 (13)	871 (13)
H(15)	5028	3282	−237	1500	764	3143
H(16)	5765	4680	−89	1408	2102	4159
H(17)	6563	5186	1425	1216	1986	5747
H(18)	6597	4323	2860	1068	541	6414
H(19)	6004	2833	2742	977	−790	5440
H(21)	6632	1763	1354	2574	−927	4976
H(22)	7532	604	2188	3426	−2156	5843
H(23)	7034	−488	3190	2873	−3663	5575
H(24)	5619	−391	3273	1541	−3966	4635
H(25)	4692	726	2398	791	−2764	3621

[a] The numbers in parentheses are estimated standard deviations in the last significant digit in this and all other tables. [b] X, Y, Z, are fractional coordinates $\times 10^4$.

Table VI. Anisotropic Temperature Factors for Non-Hydrogen Atoms ($\times 10^4$)[a]

	Molecule 1						Molecule 2					
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	30	48	56	−2	2	−1	35	51	47	−6	1	−6
C(3)	22	84	39	−23	−10	−7	73	69	29	−9	2	−15
O(4)	53	60	78	−10	3	−11	125	72	110	−41	60	−24
C(5)	23	105	34	−29	19	−17	72	68	31	−19	−24	−4
O(6)	62	66	105	12	1	−20	95	87	102	−40	35	−20
C(7)	26	75	176	6	5	−55	54	76	39	−19	9	14
O(8)	88	110	164	−12	62	−33	53	103	111	19	27	11
C(9)	47	57	47	0	4	25	31	92	55	−18	−2	−3
O(10)	105	79	67	1	18	20	46	105	119	7	18	−23
C(11)	34	59	101	−1	−24	−16	56	62	87	2	5	−5
O(12)	50	105	170	−7	−32	−50	82	135	42	−7	5	9
C(13)	33	49	58	7	−19	−12	28	47	71	2	4	−4
C(14)	29	23	83	8	0	4	31	57	57	−9	−3	−9
C(15)	28	37	89	−1	−10	13	78	61	90	−1	−1	−11
C(16)	21	54	110	6	−4	24	98	54	80	4	−8	−8
C(17)	34	57	93	−5	31	10	71	96	78	3	−13	12
C(18)	44	51	75	−13	5	−12	95	106	56	3	44	20
C(19)	59	62	41	−10	23	−8	50	66	71	1	11	−2
C(20)	40	37	52	−15	14	0	44	67	43	−8	0	−2
C(21)	43	46	63	−2	17	8	48	63	75	−14	12	−24
C(22)	44	63	68	13	−2	8	43	110	77	−24	19	−43
C(23)	81	50	42	9	−5	2	87	104	51	−52	36	−39
C(24)	42	61	82	−17	−2	20	99	59	65	−13	28	−23
C(25)	49	47	56	−12	8	20	67	61	63	−15	−7	1

[a] Anisotropic temperature factors are of the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$.

Table VII. Intermolecular Distances (Å) for $(CO)_5WC(C_6H_5)_2$[a]

		Sym[b]	
O(8)	O(10)	5	3.20 (2)
O(10)′	O(8)	1	3.20 (2)
O(12)′	O(10)′	8	3.23 (2)
O(4)	C(9)	2	3.24 (2)
O(4)′	O(6)′	7	3.27 (2)
O(4)	O(10)	2	3.28 (2)
O(6)	C(16)′	3	3.33 (3)
O(6)	C(17)	3	3.37 (2)
C(21)	O(4)	2	3.38 (2)
O(8)′	C(16)′	7	3.39 (3)
O(4)′	C(22)′	5	3.39 (2)
O(8)′	C(17)′	6	3.40 (3)
C(22)	O(4)′	4	3.40 (2)
C(25)′	O(6)′	7	3.40 (2)

[a] Prime indicates atom is located in molecule 2. [b] Symmetry operations: 1, $1 - X$, $\frac{1}{2} + Y$, $\frac{1}{2} - Z$; 2, $1 - X$, $-Y$, $-Z$; 3, $1 - X$, $1 - Y$, $-Z$; 4, $X = Y, Z$; 5, X, $\frac{1}{2} - Y$, $\frac{1}{2} + Z$; 6, $2 - X$, $1 - Y$, $-Z$; 7, $2 - X$, $-\frac{1}{2} + Y$, $\frac{1}{2} - Z$; 8, $2 - X$, $1 - Y$, $1 - Z$.

the collection of the data the two standard peaks monitored every 50 reflections indicated a 13% overall drop in intensity. Examination of the crystal after completion of data collection showed tiny, clear crystals (presumably $W(CO)_6$) on the surface of the needle.

The data were corrected[50] for Lorentz-polarization effects as previously described[51] and treated for intensity decay by linear interpolation. Later the data were also corrected for crystal absorption effects since with $\mu = 71.6\ \text{cm}^{-1}$, the transmission factors varied from 0.28 to 0.54. Finally, the data were merged to yield 4048 reflections of which 2707 had $I > 2\sigma(I)$.

Inspection of the data revealed systematic absences $h0l$, l odd, and $0k0$, k odd, characteristic of the space group $P2_1/c$.[52] Since $Z = 8$ as determined from the density, this required the location of two molecules of the compound per independent unit.

Solution and Refinement. The structure was solved by the heavy atom method. A Fourier map phased on one tungsten obtained from a Patterson map revealed the coordinates for the second tungsten atom ($R_1 = 22.2$). Repeated Fourier calculation revealed the entire structure. Isotropic full-matrix refinement[53] converged at $R_1 = 0.085$ and $R_2 = 0.091$.[54] At this stage a difference map revealed only 4 of the 20 hydrogen atoms. Hence ideal coordinates for the hydrogens were calculated at 1.0 Å distances ($B = 7.0$ Å^2) from their respective carbons and refinement was continued block diagonally with six blocks of eight atoms per block. The refinement allowed anisotropic thermal motion for all non-hydrogen atoms and included terms $f' = -1.0$ and $f'' = 8.0$ for the anomalous dispersion of tungsten.[55] No correction for extinction was made. After convergence of the block-diagonal refinement, one last full-matrix least-squares cycle varying all non-hydrogen atom coordinates only was run to check the block-diagonal convergence and to allow calculation of errors from full variance-covariance matrix. This cycle indicated no shift greater than 0.6σ and gave $R_1 = 0.050$ and $R_2 = 0.055$. The final standard deviation of an observation of unit weight was 1.23. The ratio of data to the total number of parameters varied for the anisotropic refinement was 6.3:1.

The final atomic coordinates and thermal parameters are given in Tables V and VI. Nonbonding distances are shown in Table VII. The observed and calculated structure factor amplitudes are given in Table VIII (supplementary material).

Acknowledgment. Support by the National Science Foundation through Grants GP-32160 and GP-41259X and a departmental instrument grant, which allowed the purchase of the automated diffractometer, is gratefully acknowledged. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is also gratefully acknowledged.

Supplementary Material Available: Table VIII, structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For recent reviews of transition metal–carbene complexes see D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 575 (1972); F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 243 (1972).

(2) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 642 (1968); J. A. Connor and O. S. Mills, *ibid.*, 334 (1969).

(3) E. O. Fischer and E. Moser, *J. Organomet. Chem.*, **13**, 387 (1968); E. O. Fischer and C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, **8**, 761 (1969).

(4) E. O. Fischer, B. Heckl, K. H. Dötz, H. Müller, and H. Werner, *J. Organomet. Chem.*, **16**, P29 (1969); E. O. Fischer and D. Plabst, *Chem. Ber.*, **107**, 3326 (1974).

(5) C. P. Casey and R. L. Anderson, *J. Chem. Soc., Chem. Commun.*, 895 (1975).

(6) K. H. Dötz and E. O. Fischer, *Chem. Ber.*, **105**, 1356, 3966 (1972).

(7) A preliminary communication has appeared. C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).

(8) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, **7**, 950 (1968); *J. Organomet. Chem.*, **22**, C9 (1970).

(9) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973).

(10) (a) R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796 (1974); (b) *ibid.*, **97**, 6577 (1975); (c) R. R. Schrock and L. J. Guggenberger, *J. Am. Chem. soc.*, **97**, 6578 (1975).

(11) W. A. Hermann, *Angew. Chem., Int. Ed. Engl.*, **13**, 599 (1974).

(12) W. A. Hermann, *Chem. Ber.*, **108**, 486 (1975).

(13) E. O. Fischer, W. Held, S. Riedmüller, and F. Köhler, unpublished results, referred to by E. O. Fischer, *Angew. Chem.*, **86**, 651 (1974).

(14) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

(15) C. P. Casey, H. E. Tuinstra, and M. C. Saeman, *J. Am. Chem. Soc.*, **98**, 608 (1976).

(16) J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Am. Chem. Soc.*, **98**, 605 (1976).

(17) T. J. Katz, J. McGinnis, and C. Altus, *J. Am. Chem. Soc.*, **98**, 606 (1976).

(18) U. Klabunde and E. O. Fischer, *J. Am. Chem. Soc.*, **89**, 7141 (1967); J. A. Connor and E. O. Fischer, *Chem. Commun.*, 1024 (1967); E. O. Fischer, M. Leupold, C. G. Kreiter, and J. Müller, *Chem. Ber.*, **105**, 150 (1972).

(19) U. Schubert and E. O. Fischer, *Justus Liebigs Ann. Chem.*, 393 (1975).

(20) H. Werner, E. O. Fischer, B. Heckl, and C. G. Kreiter, *J. Organomet. Chem.*, **28**, 367 (1971).

(21) F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and K. Weiss, *Angew. Chem., Int. Ed. Engl.*, **12**, 563 (1973); F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fischer, *Chem. Ber.*, **106**, 1262 (1973).

(22) T. F. Block, R. F. Fenske, and C. P. Casey, *J. Am. Chem. Soc.*, **98**, 441 (1976).

(23) E. O. Fischer and S. Riedmüller, unpublished results referred to by E. O. Fischer, *Pure Appl. Chem.*, **30**, 353 (1972).

(24) C. T. Lam, C. V. Senoff, and J. E. H. Ward, *J. Organomet. Chem.*, **70**, 273 (1974).

(25) P. W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, **88**, 5044 (1966).

(26) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(27) C. P. Casey, S. W. Polichnowski, and R. L. Anderson, *J. Am. Chem. Soc.*, **97**, 7375 (1975).

(28) A. Danti, F. A. Cotton, *J. Chem. Phys.*, **28**, 736 (1958).

(29) The ^{13}C spectrum of **1** has been reported. F. R. Kreissl and W. Held, *J. Organomet. Chem.*, **86**, C10 (1975).

(30) J. Evans and J. R. Norton, *Inorg. Chem.*, **13**, 3042 (1974).

(31) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).

(32) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973).

(33) C. G. Kreiter and V. Formacek, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972).

(34) J. Müller and J. A. Connor, *Chem. Ber.*, **102**, 1148 (1969).

(35) E. O. Fischer and A. Massböl, *Chem. Ber.*, **100**, 2445 (1967).

(36) C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Am. Chem. Soc.*, **94**, 8947 (1972).

(37) C. P. Casey, R. A. Boggs, W. R. Brunsvold, unpublished results.

(38) E. O. Fischer and S. Reidmüller, *Chem. Ber.*, **107**, 915 (1974).

(39) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **94**, 6543 (1972).

(40) E. O. Fischer and H. Fischer, *Chem. Ber.*, **107**, 657 (1974).

(41) R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 653 (1972), and references therein.

(42) C. P. Casey, S. W. Polichnowski, L. D. Albin, and J. C. Calabrese, unpublished results.

(43) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973).

(44) S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, **20**, 2711 (1966), and references therein.

(45) The chromium to CO bond distance in $(CO)_5CrC(OCH_3)C_6H_5$ is 0.04 Å shorter than in $Cr(CO)_6$.[44] O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 642 (1968).

(46) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Crystallogr.*, **18**, 437 (1965).

(47) F. H. Allen and S. Converse, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 226.

(48) L. Horner and E. Lingnau, *Justus Liebigs Ann. Chem.*, **591**, 135 (1955).

(49) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).

(50) Programs used in the structure solution were written by J. C. Calabrese. In addition DEAR, the J. F. Blount absorption correction program; ORFLS and ORFEE, the Busing, Martin, Levy least-squares and error analysis program; ORTEP, the Johnson thermal ellipsoid plotting program were used.

(51) T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, **13**, 1895 (1974).

(52) "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, The Kynoch Press, Birmingham, England, 1965, p 99.

(53) All least-squares refinement were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors used for all non-hydrogen atoms are from H. P. Hanson, F. Herman,

J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); those for the hydrogen atoms are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(54) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}$.

(55) Reference 52, Vol. III, 1962, p 215.

Reactions of Two-Coordinate Phosphine Platinum(0) and Palladium(0) Compounds. Ligand Exchange and Reactivities toward Small Molecules

T. Yoshida and Sei Otsuka*

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560. *Received August 13, 1976*

Abstract: Reactions of two-coordinate complexes PdL_2 (**1**, L = $P(t\text{-Bu})_3$; **2**, L = $PPh(t\text{-Bu})_2$; **3**, L = $P(c\text{-}C_6H_{11})_3$) and PtL_2 (**4**, L = $P(t\text{-Bu})_3$; **5**, L = $PPh(t\text{-Bu})_2$; **6**, L = $P(c\text{-}C_6H_{11})_3$; **7**, L = $P(i\text{-Pr})_3$) were studied. The thermal reaction of **2** and **5** gives no evidence for ortho C metalation. Ligand exchange of **2** and **5** with $PPh(t\text{-Bu})_2$ takes place through an associative mechanism at high temperature with activation energies of 7.8 and 12.1 kcal mol^{-1}, respectively. These complexes, except **1** and **4**, are sensitive to dioxygen and react even in the solid state to produce MO_2L_2. Dioxygen coordination in $PdO_2[PPh(t\text{-Bu})_2]_2$ is reversible, while that in the corresponding Pt complex is irreversible. **1** reacts very slowly with dioxygen to give a red polynuclear oxygen-containing compound of formula $[PdOP(t\text{-Bu})_3]_n$. The reaction of **1**, **2**, and **5** with CO gives $M_3(CO)_3L_3$ (M = Pd, L = $P(t\text{-Bu})_3$, $PPh(t\text{-Bu})_2$; M = Pt, L = $PPh(t\text{-Bu})_2$). Dimethyl fumarate (DF) with **2** or **5** gives $M(DF)_2PPh(t\text{-Bu})_2$ (M = Pd, Pt), while maleic anhydride (MA) affords $M(MA)[PPh(t\text{-Bu})_2]_2$. Oxidative addition of HX (X = Cl, $OCOCF_3$) to **1**, **2**, and **5** produces *trans*-$MH(X)L_2$ (M = Pd, L = $P(t\text{-Bu})_3$, $PPh(t\text{-Bu})_2$; M = Pt, L = $PPh(t\text{-Bu})_2$). MeOH reacts with PtL_2 to give stable dihydride complexes *trans*-PtH_2L_2 (L = $PPh(t\text{-Bu})_2$, $P(c\text{-}C_6H_{11})_3$, $P(i\text{-Pr})_3$), which can be obtained also by molecular hydrogen addition to the appropriate PtL_2 at room temperature under normal pressure. **4** and **5** do not add H_2. All the PdL_2 complexes are inert toward MeOH and H_2. Factors determining the observed reactivities of these ML_2 complexes are discussed in terms of steric and electronic effects.

In previous papers[1,2] we reported syntheses of two-coordinate complexes ML_2 (Table I) and the molecular structures of **2** and **5**. The successful isolation is possible because of the stability of these complexes in solution. The x-ray analysis of $PPh(t\text{-Bu})_2$ complexes **2** and **5** revealed nonbonding contacts (2.7 ~ 2.8 Å) of ligand hydrogen atoms to the metals, which apparently prevent approach of solvent molecules.[2] The extent of kinetic stabilization in this series depends critically upon the ligand bulk. For example, complexes of exceedingly bulky $P(t\text{-Bu})_3$ (cone angle[3] 182°), **1** and **4**, are fairly air stable in the solid state, while all the other ML_2 compounds are readily dioxygenated. The two-coordinate complexes of moderately bulky phosphines (cone angle <170°) exhibit high reactivity toward small molecules such as H_2, CO, HX (X = halogen, RCO_2, RO), olefins, etc. Even when the cone angle of phosphines in ML_2 exceeds 170°, four-coordinate complexes $MH(X)L_2$ are formed, suggesting considerable ligand compressibility.[2] Enhanced reactivity can thus be expected for most of the ML_2 complexes. The electronic properties of both the ligand and the metal also influence the reactivity. With strongly electron-donating phosphines it is possible to prepare ML_2 capable of absorbing a hydrogen molecule under normal pressure, a phenomenon unusual for Pd(0) or Pt(0) compounds.[4] In this paper the reactivity of ML_2 species toward a wide range of compounds will be described and discussed in terms of steric and electronic factors.

It has been recognized that the reactivity, particularly substitution, of coordinatively saturated complexes ML_4 is governed by the propensity for dissociation to form ML_3 and ML_2 species.[4-7] Tolman[8] has stressed the importance of the 16- and 18-electron rule and argued against dissociation of NiL_3. It is then of interest to examine mechanisms of ligand exchange reactions in the present ML_2 system.

Results and Discussion

Innate Reactivity and Ligand Exchange. The short nonbonded contacts (2.83 Å)[1,2] between the metal and two hydrogen atoms of the phenyl groups in the solid and solution state (at low temperature) prompted us to examine if the thermal reaction of **2** and **5** leads to the aromatic substitution.[9,10] Prolonged heating of **2** and **5** in xylene under gentle reflux results in the decomposition of **2** or the complete recovery of **5** and no evidence for ortho C metalation is obtained. This contrasts to a facile metalation of the corresponding divalent complex $PtCl_2[PPh(t\text{-Bu})_2]_2$[11] and suggests that the facile intramolecular aromatic substitution occurs through a mechanism involving electrophilic substitution by metal[9,10,12] rather than an electrophilic, oxidative addition of the C–H to metal.[9,10,13] In support of this view, facile ortho C metalation of azobenzene occurs upon complexation with divalent nickel triad metal, e.g., $Ni(\eta^5\text{-}C_5H_5)_2$[14] and $PdCl_2$,[12] whereas the zerovalent complexes, $Ni(t\text{-BuNC})_2$[15] and $Ni(PPh_3)_4$[16] give side-on coordination $Ni(\eta^2\text{-PhN{=}NPh})L_2$ (L = *t*-BuNC, PPh_3).

In view of the compressibility of these tertiary phosphine ligands, we were initially interested in the maximum or minimum coordination number that can be seen in isolable species. With $P(i\text{-Pr})_3$ (cone angle, 160 ± 10°[3]) both PtL_2 (**7**) and PtL_3 (**8**) complexes could be obtained, but not the PtL_4.[2] With $PPh(t\text{-Bu})_2$ (cone angle, 170 ± 2°[2]) only ML_2 (**2**, M = Pd; **5**, M = Pt) was isolated, but not ML_3. Their absence was confirmed by ^1H NMR of a mixture of free $PPh(t\text{-Bu})_2$ and **2** or **5** recorded as low as −80 °C.[2,17] Interestingly, however, slow ligand exchange was observed in benzene or anisole at high temperature. A 1:3 mixture of **2** and $PPh(t\text{-Bu})_2$ shows the *tert*-butyl proton signals of **2** as a sharp triplet (δ 1.45) and