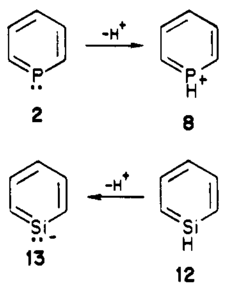
of molecules containing phosphorus-carbon multiple bonds has indicated that acyclic phosphaalkenes have low PA values similar to that of C_5H_5P.[36] These calculations suggest that the low basicity of the heterobenzenes may be due to the particular electronic character of carbon-phosphorus or (C-As) multiple bonds rather than a consequence of geometrical constraints. Since phosphaalkenes are now readily available,[48] an experimental determination of their PA is feasible and should answer this question.

Finally, it is interesting to speculate on the relation of phosphabenzene and its conjugate acid to the isoelectronic silicon compounds. Unlike phosphabenzene, silabenzene 12 is an extremely labile compound.[49,50] The observed low basicity of phosphabenzene suggests that silabenzene may be a strong acid. Perhaps the conjugate base of silabenzene 13 may even possess a kinetic stability that silabenzene does not have.



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Registry No. 2, 289-68-9; 3, 289-31-6.

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Addition of Di-*p*-tolylcarbodiimide to Ditungsten Hexa-*tert*-butoxide. Preparation and Structure of $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$

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Ditungsten hexa-*tert*-butoxide reacts readily with di-*p*-tolylcarbodiimide, $CH_3C_6H_4NCNC_6H_4CH_3$, in toluene at 25 °C to afford in about 80% yield the moderately air-sensitive red-black adduct $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$. This product has been identified and characterized by NMR and X-ray crystallography. The molecule has the carbodiimide group bridging the W-W bond (2.482 (1) Å) and three $OCMe_3$ groups on each W atom, with effective symmetry C_2. The ^{13}C NMR indicates that in solution the molecule is either actually or effectively more symmetrical since the $OCMe_3$ groups form only two sets in 4:2 ratio. The crystalline compound belongs to space group *Pbca* with unit-cell dimensions $a = 18.693$ (4) Å, $b = 17.739$ (7) Å, $c = 26.685$ (8) Å, $V = 8849$ (3) Å^3, and $Z = 8$. The structure was refined to $R = 0.045$ and $R_w = 0.058$. The bonding of the carbodiimide molecule to the W-W unit is discussed, and a simple formulation that leaves a W-W double bond is proposed.

Introduction

We have been pursuing studies on the reactions between compounds containing metal-metal triple bonds (specifically $W_2(OCMe_3)_6$) and heterocumulenes (a-f) and allenes (g) in order to understand how these metallic and non-

$$\underset{a}{O{=}C{=}O} \quad \underset{b}{O{=}C{=}NR} \quad \underset{c}{RN{=}C{=}NR} \quad \underset{d}{S{=}C{=}S}$$

$$\underset{e}{S{=}C{=}O} \quad \underset{f}{S{=}C{=}NR} \quad \underset{g}{R_2C{=}C{=}CR_2}$$

metallic unsaturated compounds interact. Cotton, Chisholm, and co-workers[1] have reported that allenes oxidatively add to $Cp_2M_2(CO)_4$ (M = Mo, W), and they also reported that the order of addition is as follows: $CH_2{=}C{=}CH_2 > MeCH{=}C{=}CH_2 > MeCH{=}C{=}CHMe$, but when $Me_2C{=}C{=}CH_2$ was used, no addition was observed across the M-M triple bond. Cotton, Chisholm, and coworkers also reported that CO_2 could insert into M-OR (M = W, Mo)[2] and $W{-}NR_2$[3] bonds to form either carbonato or carbamato bridging bidentate ligands, respectively. In our most recent work[4] we have reported that organic isocyanates insert into a M-OR (M = W, Mo) bond.

We now report on the reaction of a heterocumulene of type c, *p*-tolylcarbodiimide, with $W_2(OCMe_3)_6$.

Experimental Section

Ditungsten hexa-*tert*-butoxide was prepared[5] by Na/Hg reduction of WCl_4 in THF at -10 °C in the presence of $LiOCMe_3$, followed by recrystallization from hexane at -10 °C. Di-*p*-

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tolylcarbodiimide was purchased from Aldrich Chemical Co. All reactions were done under an argon atmosphere.

Reaction of $W_2(OCMe_3)_6$ with *p*-Tolylcarbodiimide. A weighed amount of $W_2(OCMe_3)_6$ (160 mg, 0.20 mmol) was dissolved in 20 mL of toluene. A slight excess of the carbodiimide (132 mg, 0.6 mmol) was added to the solution at room temperature. The reaction mixture was stirred at 25 °C for 6 h. Within 1 h after the addition of the $C_7H_7N{=}C{=}NC_7H_7$, the color of the solution changed from red to green-brown. After the solvent was removed under vacuum, the residue was extracted with 10 mL of hexane and the extract concentrated to ca. 3.0 mL. Red-black crystals were deposited overnight at -10 °C. The reaction gives reproducible yields of 75–85% based on tungsten. The same products were obtained when $W_2(OCMe_3)_6$ to carbodiimide ratios of 1:4, 1:2, or 1:1 were used. The 1:3 ratio seems to give the best yields without wasting carbodiimide.

Reaction of $W_2(OCMe_3)_6$ with $C_7H_7NCNC_7H_7$ at 70 °C. The reaction was carried out according to the procedure described above except that the temperature and the reaction time were changed to 70 °C and 3 days, respectively. The product obtained was as above, but the yields were smaller, ca. 45–55%, based on tungsten. Thus, 25 °C seems to be the optimum temperature.

Spectral Measurements. **$^{13}C\{^1H\}$ NMR**: measured on a solution in C_6D_6 at 25 °C using a Varian XL-200 PFT spectrometer. Chemical shifts are specified in parts per million downfield from Me_4Si. Three signals at 30.05, 30.62, and 19.436 ppm with relative intensities very nearly in the ratio 6:3:1 can be assigned to two types of $OCMe_3$ methyl groups and the *p*-tolyl methyl groups, respectively. Two signals at 78.32 and 81.70 ppm in an intensity ratio of 2.03 can be assigned to the central carbon atoms of two types of $OCMe_3$ groups. Signals at 122.92, 128.06, 132.73, and 140.57 ppm with relative intensities of 1.8:2.0:0.72:0.68 may be assigned to the carbon atoms of the $N{-}C_6H_4CH_3$ rings. The spectrum had only a few other very weak peaks and the location of the signal for the carbodiimide central carbon atom is unknown.

IR. The spectrum was recorded on a Perkin-Elmer 783 spectrometer using a hexane solution: 3020 (w), 2950 (vs), 2917 (m), 1708 (s), 1507 (m), 1500 (vs), 1372 (m), 1350 (s), 1337 (m), 1258 (m), 1230 (s), 1172 (vs), 1105 (w), 1021 (w), 998 (m), 975 (m), 960 (s), 925 (s), 899 (w), 870 (w), 810 (s), 790 (w), 770 (m), 580 (m), 558 (w), 482 (w).

X-ray Crystallography. The general procedures used in determining the structure have already been described elsewhere.[6] Single crystals grew as nearly black tablets which appear black-red to purple by transmitted light. A suitable crystal was immersed in epoxy cement inside a Lindemann glass capillary. All geometric and intensity data were taken from the crystal, by a Syntex P$\bar{1}$ automated four-circle diffractometer.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 15 reflections taken from a rotation photograph and located by the diffractometer. Axial photography was used to verify the presence of mirror planes and to verify the unit-cell dimensions. The latter, along with the crystal orientation matrix, was refined by a least-squares fit to 15 accurately located reflections in the range of 15° < 2θ < 30°. The ω–2θ scan technique was used to measure 3840 data in the range of 5° < 2θ < 45°. The scan speed was variable in the range of 2–24°/min. Three standard reflections were remeasured after every 100 data scans and showed no loss in intensity over 71.63 h of X-ray exposure time. The intensity data were corrected for Lorentz and polarization effects before structure factors were derived. An empirical absorption correction was based on azimuthal scans of eight reflections near χ = 90°. Systematically absent data uniquely identified the space group *Pbca*. The positions of the tungsten atoms were obtained by a combination of Patterson and direct methods. The remainder of the structure was located and refined by an alternating sequence of least-squares cycles and difference Fourier maps. The final least-squares cycle included parameters for 49 atoms and did not shift any parameter by more than 0.5 times its estimated standard deviation. The last cycle gave the residuals R = 0.045, R_w = 0.058, and a quality of fit equal to 1.172 for a fit of 417 variables to 3089 observations. Five atoms were refined isotropically because there were residual peaks in the vicinity of the main peaks, suggesting a second rotational conformer. The low residual density (>0.95 e/Å^3) and the nonideal geometry, however, did not warrant refinement of a disorder model. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

Table I. Crystallographic Data

formula	$W_2(OCMe_3)_6[C_7H_7NCNC_7H_7]$
fw	1028.69
space group	*Pbca*
systematic absences	$00l$, $l = 2n$; $0k0$, $k = 2n$; $h00$, $h = 2n$ $h0l$, $l = 2n$; $0kl$, $k = 2n$; $hk0$, $h = 2n$
a, Å	18.693 (4)
b, Å	17.739 (7)
c, Å	26.685 (8)
V, Å^3	
Z	
d_{calcd}, g/cm^3	8849 (3)
cryst size, mm	8
μ(Mo Kα), cm^{-1}	1.544
data collection instrument	0.4 × 0.5 × 0.2 53.485
radiatn (monochromated in incident beam)	Syntex P$\bar{1}$
orientation, reflctns, no. range (2θ)	Mo Kα
temp, °C	15, 15 < 2θ < 30°
scan method	
data col range, 2θ, deg	5 ± 1
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	ω-2θ 5-45
no. of parameters refined	3089
trans factors, max. min	
exptl	417
R^a	99.87%, 75.94%
$R_w{}^b$	
quality-of-fit indicator^c	0.045
largest shift/esd, final cycle	0.058 1.172
largest peak, e/Å^3	0.5
	0.95

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Table II lists the positional parameters, and Table III gives important bond distances and angles. Tables of anisotropic thermal parameters, complete bond lengths and angles, and structure factors are available as supplementary material.

Results and Discussion

In undertaking this study, we had in mind the reactions whereby other heterocumulenes, viz., CO_2[2,3] and RNCO,[4] have been inserted into M–OR and M–NR_2 bonds to generate three-atom bridging ligands that span the two metal atoms with retention of the M≡M bond order. The well-established reactions of this type are shown in eq 1–4.

$$Mo_2(OR)_6 + 2CO_2 \rightleftarrows Mo_2(OR)_4(O_2COR)_2 \qquad (1)$$

$$R = Me_3C,\ Me_2CH$$

$$W_2(NMe_2)_6 + 6CO_2 \rightleftarrows W_2(O_2CNMe_2)_6 \qquad (2)$$

$$W_2Me_2(NEt_2)_4 + 4CO_2 \rightleftarrows W_2Me_2(O_2CNEt_2)_4 \qquad (3)$$

$$M_2(OR)_6 + R'NCO \rightarrow M_2(OR)_4[R'NC(OR)O]_2 \qquad (4)$$

$$M = W,\ R = OCMe_3,\ R' = Ph;\ M = Mo,\ R = CHMe_2,\ CH_2CMe_3,\ R' = Me,\ Ph$$

While there is a prompt reaction between $W_2(OCMe_3)_6$ and $CH_3C_6H_4NCNC_6H_4CH_3$, the only product we have

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[6] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

Table II. Positional Parameters and Their Estimated Standard Deviations for $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$[a]

atom	x	y	z	B, Å^2
W(1)	0.44145 (4)	0.27007 (4)	0.15094 (3)	2.92 (1)
W(2)	0.46430 (3)	0.17338 (4)	0.08564 (3)	2.74 (1)
O(1)	0.3426 (6)	0.2679 (6)	0.1590 (4)	3.2 (2)
O(2)	0.4539 (6)	0.2289 (7)	0.2163 (4)	3.9 (3)
O(3)	0.4333 (6)	0.3569 (6)	0.1065 (4)	3.4 (3)
O(4)	0.4892 (6)	0.2178 (7)	0.0224 (4)	3.8 (3)
O(5)	0.4637 (6)	0.0868 (7)	0.1300 (4)	4.0 (3)
O(6)	0.3745 (6)	0.1498 (6)	0.0613 (5)	4.1 (3)
N(1)	0.5527 (7)	0.2930 (8)	0.1545 (5)	3.3 (3)
N(2)	0.5769 (7)	0.1799 (8)	0.0997)5)	2.9 (3)
C(1)	0.5491 (8)	0.235 (1)	0.1257 (7)	3.6 (4)
C(11)	0.2811 (9)	0.242 (1)	0.1883 (8)	4.7 (5)
C(12)	0.215 (1)	0.276 (1)	0.1590 (9)	6.7 (6)
C(13)	0.288 (1)	0.265 (1)	0.2414 (7)	6.1 (6)
C(14)	0.280 (1)	0.153 (1)	0.1804 (8)	5.8 (6)
C(21)	0.489 (1)	0.186 (1)	0.2531 (7)	4.2 (4)
C(22)	0.566 (1)	0.161 (1)	0.2353 (8)	5.9 (6)
C(23)	0.441 (1)	0.112 (1)	0.2612 (9)	6.9 (6)
C(24)	0.493 (1)	0.231 (2)	0.3005 (7)	7.7 (7)
C(31)	0.410 (1)	0.432 (1)	0.1197 (9)	6.0 (5)
C(32)	0.409 (1)	0.444 (2)	0.178 (1)	7.9 (7)*
C(33)	0.335 (1)	0.440 (1)	0.098 (1)	10.3 (8)
C(34)	0.462 (2)	0.483 (2)	0.093 (1)	9.8 (8)*
C(41)	0.522 (1)	0.274 (1)	−0.0072 (8)	5.0 (5)
C(42)	0.577 (1)	0.322 (1)	0.0247 (8)	6.8 (6)
C(43)	0.465 (1)	0.324 (1)	−0.0283 (9)	7.3 (6)
C(44)	0.560 (1)	0.230 (2)	−0.0508 (9)	9.2 (8)
C(51)	0.466 (1)	0.007 (1)	0.1177 (8)	4.4 (4)
C(52)	0.481 (1)	−0.005 (1)	0.0617 (8)	5.6 (5)
C(53)	0.525 (1)	−0.025 (1)	0.148 (1)	7.1 (6)*
C(54)	0.392 (1)	−0.024 (1)	0.130 (1)	7.7 (6)
C(61)	0.319 (1)	0.159 (1)	0.0243 (7)	4.6 (5)
C(62)	0.256 (1)	0.110 (1)	0.0376 (8)	5.8 (6)
C(63)	0.352 (1)	0.135 (1)	−0.0278 (7)	6.2 (6)
C(64)	0.298 (1)	0.245 (1)	0.0235 (8)	5.1 (5)
C(71)	0.6450 (8)	0.1532 (8)	0.0945 (5)	2.5 (4)
C(72)	0.658 (1)	0.109 (1)	0.0520 (8)	5.1 (5)
C(73)	0.727 (1)	0.073 (1)	0.0472 (9)	5.7 (5)
C(74)	0.777 (1)	0.083 (1)	0.0854 (9)	6.9 (6)*
C(75)	0.767 (1)	0.127 (1)	0.1258 (8)	5.9 (5)
C(76)	0.6982 (9)	0.165 (1)	0.1305 (7)	4.7 (5)
C(77)	0.852 (1)	0.040 (1)	0.080 (1)	7.6 (6)*
C(81)	0.6099 (8)	0.3397 (9)	0.1697 (6)	3.0 (4)
C(82)	0.674 (1)	0.343 (1)	0.1396 (7)	4.7 (5)
C(83)	0.730 (1)	0.394 (1)	0.1577 (9)	6.2 (6)
C(84)	0.721 (1)	0.437 (1)	0.2000 (7)	4.5 (5)
C(85)	0.658 (1)	0.433 (1)	0.2276 (8)	5.0 (5)
C(86)	0.605 (1)	0.386 (1)	0.2127 (7)	4.7 (5)
C(87)	0.784 (1)	0.489 (1)	0.2146 (9)	6.3 (6)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

found, regardless of the mole ratio of reactants employed or the temperature, is an adduct, formed according to eq 5, in which no insertion into W–O bonds has occurred.

$$W_2(OCMe_3)_6 + RNCNR \rightarrow W_2(OCMe_3)_6(RNCNR) \quad (5)$$

$$R = p\text{-}CH_3C_6H_4$$

Failure to observe an insertion reaction was surprising considering the formal similarity of an RNCNR compound to OCO and RNCO. It is also surprising since di-*p*-tolylcarbodiimide has been found to react with $Ti(O\text{-}i\text{-}Pr)_4$, over a range of mole ratios (1:1 to 1:4, of alkoxide to carbodiimide) to give the two-step reaction shown in eq 6.[7]

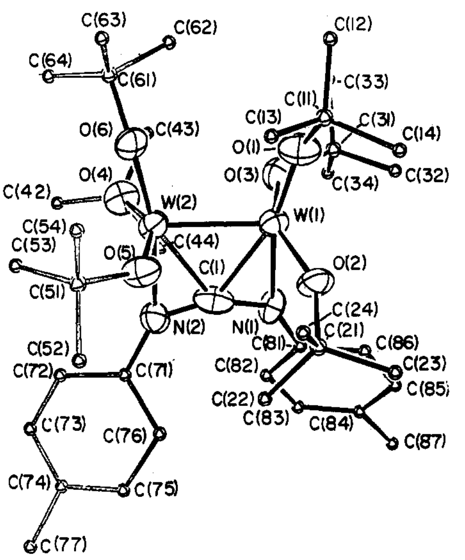


Figure 1. An ORTEP drawing of the entire molecule, giving the atomic labeling scheme. All carbon atoms are represented by arbitrarily tiny spheres to avoid covering up other atoms. All other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

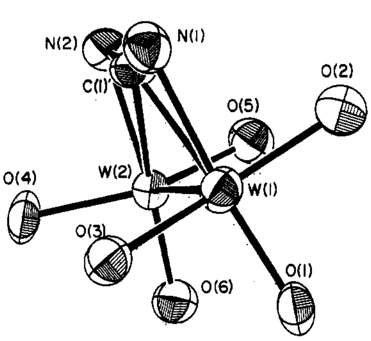
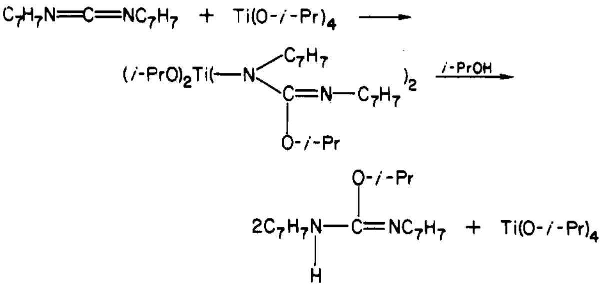


Figure 2. An ORTEP drawing of only the tungsten atoms and those ligand atoms bonded to them.

It is possible that the diimide, in contrast to PhNCO, is just too bulky to allow an insertion reaction to occur.



$$C_7H_7N{=}C{=}NC_7H_7 + Ti(O\text{-}i\text{-}Pr)_4 \longrightarrow (i\text{-}PrO)_2Ti\Big(\!-\!N\begin{matrix}C_7H_7\\ C(O\text{-}i\text{-}Pr){=}N{-}C_7H_7\end{matrix}\Big)_2 \xrightarrow{i\text{-}PrOH} 2C_7H_7N(H){-}C(O\text{-}i\text{-}Pr){=}NC_7H_7 + Ti(O\text{-}i\text{-}Pr)_4 \quad (6)$$

Characterization of $W_2(OCMe_3)_6(CH_3C_6H_4NCNC_6H_4CH_3)$. Infrared and $^{13}C\{^1H\}$ NMR spectral data show that the crystallographic characterization is generally valid for the sample at large and for solutions as well as the solid phase. With regard to the NMR there is one small difference to be discussed later. The entire molecular unit, as seen in the crystal, is shown in Figure 1, where all carbon atoms have been drawn as arbitrarily small spheres to minimize their tendency to obscure other parts of the structure. The more important bond lengths and angles are listed in Table III. Figure 2 shows just the two tungsten atoms and the light atoms that are directly bonded to them. The molecule as a whole is the crystallographic asymmetric unit and thus has no required crystallographic symmetry.

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(7) Cohn, M. O.; Thormpe, D.; Twitchett, H. J. *J. Chem. Soc.* **1970**, 132.

Table III. Some Bond Distances (Å) and Angles (deg) in $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$

Bond Distances, Å			
W(1)-W(2)	2.482 (1)	W(2)-O(6)	1.848 (11)
-O(1)	1.860 (10)	-C(1)	2.20 (2)
-O(2)	1.905 (11)	-N(2)	2.141 (12)
-O(3)	1.950 (10)	N(1)-C(1)	1.29 (2)
-C(1)	2.21 (2)	N(2)-C(1)	1.30 (2)
-N(1)	2.121 (13)	N(2)-C(71)	1.37 (2)
W(2)-O(4)	1.919 (10)	N(1)-C(81)	1.41 (2)
-O(5)	1.938 (11)	N(1)-N(2)	2.52 (2)
Bond Angles, deg			
W(2)-W(1)-O(1)	103.7 (3)	O(3)-W(1)-N(1)	87.3 (5)
-O(2)	110.9 (4)	-C(1)	96.2 (5)
-O(3)	97.6 (3)	N(1)-W(1)-C(1)	34.5 (6)
-N(1)	89.8 (4)	O(6)-W(2)-O(5)	91.7 (5)
-C(1)	55.6 (5)	-O(4)	90.2 (5)
W(1)-W(2)-O(4)	112.0 (4)	-N(2)	165.2 (5)
-O(5)	96.8 (3)	-C(1)	159.5 (6)
-O(6)	104.3 (4)	O(5)-W(2)-O(4)	149.6 (5)
-N(2)	90.5 (4)	-N(2)	86.6 (5)
-C(1)	56.0 (5)	-C(1)	95.8 (5)
W(1)-O(1)-C(11)	148.0 (1)	O(4)-W(2)-N(2)	83.9 (5)
-O(2)-C(21)	155.0 (1)	-C(1)	92.7 (5)
-O(3)-C(31)	127.0 (1)	W(1)-C(1)-W(2)	68.4 (4)
W(2)-O(4)-C(41)	152.0 (1)	-N(1)-C(1)	76.6 (9)
-O(5)-C(51)	129.0 (1)	-C(1)-N(1)	69.0 (1)
-O(6)-C(61)	150.0 (1)	-C(1)-N(2)	137.0 (1)
O(1)-W(1)-O(2)	90.5 (4)	W(1)-N(1)-C(81)	150.0 (1)
-O(3)	90.5 (4)	C(1)-N(1)-C(81)	133.0 (2)
-N(1)	166.5 (5)	W(2)-N(2)-C(71)	152.0 (1)
-C(1)	158.9 (6)	-C(1)	75.9 (1)
O(2)-W(1)-O(3)	150.4 (5)	-C(1)-N(1)	136.0 (1)
-N(1)	85.0 (5)	N(1)-C(1)-N(2)	154.0 (2)
-C(1)	93.4 (5)	C(1)-N(2)-C(71)	133.0 (1)

In fact, the molecule in the crystal has essentially C_2 symmetry, with the twofold rotation axis passing through the central carbon atom of the carbodiimide group and the midpoint of the W–W bond. With C_2 symmetry rigorously in force the $OCMe_3$ ligands would be of three types, each consisting of one pair, which we may identify by using the numbers assigned to their oxygen atoms: (1,6), (2,4), and (3,5). The fact that the last four, i.e., 2, 3, 4, and 5, are not all equivalent is clearly seen in Figure 2 to be due to the slight twist about the W–W axis. As a result of this twist, 2 and 3 differ in the sense that 2 can be projected onto the other end of the molecule so as to lie between an O and an N atom, O(5) and N(2), whereas 3 projects so as to lie between two oxygen atoms, O(4) and O(6).

The $^{13}C\{^1H\}$ NMR spectrum shows that in solution the six $OCMe_3$ groups form only two distinguishable groups, whose populations are in the ratio of 2:1. A reasonable explanation for this is that the barrier for a rotation about the W–W axis sufficient to exchange the environments of the (2,4) and (3,5) pairs of $OCMe_3$ ligands is low enough (<12 kcal/mol) that this interchange proceeds rapidly on the NMR time scale at room temperature. NMR measurements at lower temperatures might supply direct proof of this, but it is not at present feasible for us to pursue further this point, which does not seem to be one that is in any great doubt.

The W–O distances and W–O–C angles each cover a range of values indicative of varying degrees of O to W dative π bonding. The two Me_3CO groups that are trans to the carbodiimide ligand have the shortest W–O bonds, with an average distance of 1.854 [6] Å and rather large W–O–C angles, 149 [1]°. These are presumably the ones with the strongest W–O bonds. The next strongest ones would be those to O(2) and O(4) where the mean distance and angle are 1.912 [7] Å and 153.5 [15]°. The remaining two Me_3CO ligands containing O(3) and O(5) have a mean distance and angle of 1.944 [6] Å and 128 [1]°.

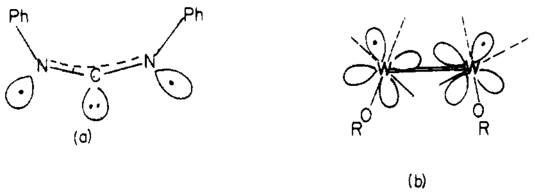

Figure 3. Diagrams of (a) the RNCNR and (b) $W_2(OR)_6$ portions of the molecule in valence states that prepare them for the bonding interaction that occurs in the complete molecule.

Bonding of the Carbodiimide Ligand. The $M_2(OR)_6$ molecules are known to form adducts with neutral donor ligands, L, which have structures of the type $L(RO)_3M{\equiv}M(OR)_3L$. In these molecules the four groups on each metal atom are arranged approximately at the four basal vertices of a square pyramid, with the other metal atom defining the apex. The facts that the carbodiimide could be considered as the source of two linked neutral ligands and the approximately square disposition of four ligands about each metal atom might suggest that the compound reported here could be regarded as a member of this class of adducts, albeit a somewhat unusual example.

However, such a view cannot be sustained when the W–W bond length is taken into consideration. In the case of a simple diadduct, $L(RO)_3M{\equiv}M(OR)_3L$, the $M{\equiv}M$ bond remains essentially a triple bond and its length is only ca. 0.03 Å greater than that in the $M_2(OR)_6$ compounds themselves. For example $Mo_2(OCH_2CMe_3)_6$ has an $Mo{\equiv}Mo$ distance of 2.222 (2) Å[8] while $Mo_2(OCHMe_2)_6py_2$ has an $Mo{\equiv}Mo$ distance of 2.250 (2) Å.[9] It is known that the simple diadduct $W_2(OCHMe_2)_6py_2$ has a $W{\equiv}W$ bond length of 2.334 (1) Å.[10] When we compare these metal–metal bond lengths with the present one, 2.482 (1) Å, it is obvious that the carbodiimide is interacting with the W_2 unit in such a way as to take electrons out of the $W{\equiv}W$ bond and reduce the bond order. A strong interaction between the NCN group and the W_2 unit is also indicated by the short W–N and W–C distances, ca. 2.13 and ca. 2.20 Å, respectively, as well as the marked deviation of the carbodiimide C–N–C–N–C chain from linearity. The N–C–N angle is 154.0 (2)° and the C—N—C angles are 133°.

Bearing in mind the risks attendant upon taking naive pictures of bonding in such complex systems too literally, we nevertheless venture to suggest a simple picture that seems to accommodate the structural facts and orbital symmetry constraints satisfactorily. We can first formulate the carbodiimide ligand as shown in Figure 3a. In addition to the σ bond framework in the plane of the drawing we assume that there is a π system perpendicular to this plane. This π system is formed by pπ orbitals of the two N and the central C atoms, and its bonding and nonbonding orbitals (the latter being localized on the N atoms) are occupied by four electrons. Each nitrogen atom then has an in-plane σ orbital that is singly occupied, and the carbon atom has an in-plane σ orbital that is doubly occupied. This gives a formal charge distribution that is approximately $N(^1/_2+){=}C(1-){=}N(^1/_2+)$.

In Figure 3b is shown the assumed state of the W_2 fragment before interaction with the carbodiimide. We leave intact from the original $W{\equiv}W$ bond the σ bond and one of the π bonds, namely, the one in a plane perpen-

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dicular to that of the drawing. Explicitly represented in Figure 3b are the two d orbitals previously used to form the second π bond, tilted as suggested by the observed geometry of the molecule and with the two electrons uncoupled.

The two fragments shown in parts a and b of Figure 3 can then be combined in an obvious way to result in two W–N single bonds and a three-center two-electron bridge bond extending over the two metal atoms and the carbon atom. Such a bonding picture seems to be consistent with the W–W distance, which is similar to that found in other molecules[11,12] with a σ and π bond as well as bridging ligands between two W^{IV} atoms, and also with the C–N distances, which are in the range of double bonding. The W–C and W–N distances are consistent with the implication from the bonding scheme that bond orders between $^1/_2$ and 1 prevail between these pairs of atoms.

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Registry No. $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$, 94138-23-5; $W2(OCMe_3)_6$, 57125-20-9; $CH_3C_6H_4NCNC_6H_4CH_3$, 1143-91-5.

Supplementary Material Available: A table of observed and calculated structure factors, a table of anisotropic thermal parameters, and complete tables of bond lengths and bond angles (27 pages). Ordering information is given on any current masthead page.

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Preparation, Multinuclear NMR Characterization, and Reactivity of Some *o*-Phenylenebis(dimethylphosphine) Methyl and Acyl Complexes of Iron(II). Steric Effects on Competitive Migratory Carbon Monoxide Insertion and Substitution

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The acyl complex 2 ([Fe(pdmp)$(CO)_2$(C(O)Me)(I)]; pdmp = *o*-phenylenebis(dimethylphosphine)) is prepared by the treatment of [Fe(pdmp)$(CO)_3$] with excess methyl iodide. Acyl 2 decarbonylates on heating in vacuo to give the corresponding neutral methyl complex 5 ([Fe(pdmp)$(CO)_2$(Me)(I)] and affords the CO-extruded cationic alkyl 3 (*fac*-[Fe(pdmp)$(CO)_3$Me]$^+$) in the presence of halide acceptors. Treatment of the alkyl complexes with Lewis bases (L) gives migratory CO insertion in the case of 3 and either migratory CO insertion (L = CO) or sequential substitution (L = P(OMe)$_3$) with final displacement of iodide in the case of 5. Steric factors are suggested to determine the reaction course followed.

Introduction

Cis-bidentate chelation of *o*-phenylene-based ligands of the type *o*-$C_6H_4L_2$ is highly entropically favored, and thus ligands of this class have been extensively used in transition-metal chemistry.[1] Earlier,[2,3] as part of a systematic study of migratory carbon monoxide insertion reactions of octahedral transition-metal complexes which recognizes the ability of arsenical *o*-phenylene bidentates to stabilize a wide range of oxidation states, we reported on the stoichiometric migratory CO insertions of *fac*-[Fe(diars)$(CO)_3$(Me)]$^+$ (diars = *o*-phenylenebis(dimethylarsine)). This paper describes our findings related to the preparation, structural characterization, and reactivity of the new isostructural phosphorus analogue *fac*-[Fe(pdmp)$(CO)_3$(Me)]$^+$ (**3**, pdmp = *o*-phenylenebis(dimethylphosphine)) which extend our earlier stereochemical conclusions[3] and rationalize, on the basis of steric effects, competitive migratory carbonyl insertion and simple substitution previously observed[3–5] for a number of octahedral d^6 complexes.

Results and Discussion

Treatment of [Fe(pdmp)$(CO)_3$], prepared by thermal reaction of iron pentacarbonyl and pdmp[6–8] at 410 K, with an excess of methyl iodide in the dark at 273 K affords[2,9] an isomeric mixture of octahedral neutral acyl–iodo complexes 2 (cf. Scheme I). ^{1}H NMR of the chromatographed product showed three isomeric acyls **2a** (2.51 ppm), **2b** (3.00 ppm), and **2c** (3.13 ppm) in a ratio of 100:18:19, respectively. Two strong ν_{CO} infrared stretches ((CH_2Cl_2) 2006, 1968 cm^{-1}) and a singlet (($CDCl_3$) 53.4 ppm) in the $^{31}P\{^1H\}$ NMR spectrum of samples enriched in the major isomer indicate a *trans*-(acyl, I) geometry for **2a**. Definitive assignments of the remaining isomers could not be made. The reaction presumably proceeds via an initial attack of Fe at carbon to give a six-coordinate cationic methyl complex followed by iodide promoted migratory CO insertion.[2,10,11]

Equilibration of crude samples of 2 in methylene chloride/benzene (ca. 1/1) at 353 K in a sealed tube under CO

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