Table VII. Axial Contacts to Mo and Noncovalent O-O Contacts for $Mo_2(D(-)\text{-man})_4 \cdot 2THF$

atom 1	atom 2	dist, Å	atom 2 coord
Mo(1)	O(18)	2.967 (7)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
	O(22)	2.825 (8)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
Mo(2)	O(24)	2.613 (6)	$-1 + x, y, z$
Mo(3)	O(10)	2.650 (7)	x, y, z
Mo(4)	O(4)	3.010 (6)	$1 - x, -{}^1/_2 + y, {}^1/_2 - z$
	O(12)	2.922 (8)	$1 - x, -{}^1/_2 + y, {}^1/_2 - z$
O(2)	O(22)	2.831 (10)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(4)	O(18)	2.699 (10)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(9)	O(23)	2.867 (14)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(10)	O(27)	2.858[a]	x, y, z
O(12)	O(17)	2.978 (12)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(12)	O(20)	2.906 (10)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(12)	O(25)	2.678[a]	$-{}^1/_2 + x, {}^3/_2 - y, 1 - z$
O(22)	O(28)	2.799[a]	$1 - x, -{}^1/_2 + y, {}^1/_2 - z$
O(24)	O(26)	2.723[a]	$1 + x, y, z$

[a] Since THF molecules were not refined in the last cycle, these esd's are omitted.

at its opposite end: the hydroxyl oxygen O(24) of molecule 2 (at $-1 + x, y, z$) is 2.613 (6) Å from Mo(2) (Mo(1)-Mo(2)-O(24) = 173.1 (2)°); Mo(3) and O(10) are 2.650 (7) Å apart, with the angle Mo(4)-Mo(3)-O(10) equal to 171.6 (2)°.

Table VII is a list of intermolecular contacts. As it shows, the quasi-axial contacts to two of the molybdenum atoms are accompanied by similarly bifurcated interactions centered at the oxygen atoms involved. It can be seen from Figure 2 that the noncovalent contacts form a zigzag pattern beginning with O(12)-O(20) (2.906 (10) Å) and continuing down along the interface of the two molecules, to the short (2.831 (10) Å) contact between coordinated oxygen atom O(2) of molecule 1 and hydroxyl oxygen O(22) of molecule 2.

In accommodation of this array of nonbonded interactions, the mandelate ligands are arranged so that their four alcoholic oxygen atoms are roughly in the coordination plane of one of the molybdenum atoms. The plane of Mo(1) and its respective oxygen atoms (O(1), O(2), O(3), O(4), O(9), O(10), O(11), O(12)) in molecule 1 is nearly parallel to the analogous plane (Mo(4), O(17), O(18), ..., O(24)) of molecule 2. (The dihedral angle is 4.3°.)

Hydrogen bonding allows the identification of the oxygen atom in each of the THF molecules. Although not all of these moieties were refined well, each has a single close contact to one of the mandelate oxygen atoms (Table VII).

Acknowledgment. We are grateful to the Robert A. Welch Foundation and the National Science Foundation for financial support.

Registry No. $Mo_2(D\text{-man})_4 \cdot 2THF$, 83944-23-4.

Supplementary Material Available: Complete tables of bond distances and bond angles, anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Reactions of $Mo_2(O\text{-}i\text{-}Pr)_6$ with *trans*-$WBr(CO)_4(CPh)$ and Pyridine. Structural Characterizations of $WBr(CO)_2(py)_2(CPh)$ and $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$

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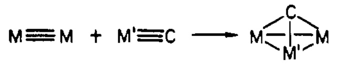
Received June 8, 1982

An attempt to form an addition product of $Mo_2(O\text{-}i\text{-}Pr)_6$ with *trans*-$WBr(CO)_4(CPh)$ by reaction in the presence of pyridine led instead to $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ (**1**) and $WBr(CO)_2(py)_2(CPh)$ (**2**); both are new compounds that have been characterized by X-ray crystallography. It has been shown that **1** may be obtained by reaction of $Mo_2(O\text{-}i\text{-}Pr)_6(CO)$ with pyridine alone and **2** by reaction of *trans*-$WBr(CO)_4(CPh)$ with pyridine alone. Compound **1** crystallizes in space group $C2/c$ with four molecules in a cell of the following dimensions: a = 10.674 (10) Å, b = 18.502 (13) Å, c = 18.238 (14) Å, β = 91.50 (7)°; V = 3600 (5) $Å^3$. The structure of **1** was solved and refined, showing that the $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ molecule is simply the bis(pyridine) adduct of the O-*i*-Pr homologue of the previously characterized $Mo_2(O\text{-}t\text{-}Bu)_6(CO)$ molecule. It is a confacial bioctahedron with the two O-*i*-Pr and the CO as bridging groups. The Mo=Mo distance is 2.487 (1) Å. The bridging and terminal Mo-O distances are 2.104 [7] and 1.908 [2] Å. The Mo-C and Mo-N distances are 2.045 (3) and 2.341 (4) Å. Compound **2** crystallizes in space group $P2_1/n$ with Z = 4 and the following unit cell dimensions: a = 10.298 (6) Å, b = 13.372 (5) Å, c = 16.861 (9) Å, β = 98.35 (4)°. The molecular structure is derived from an octahedron with Br and CPh trans and the pairs of CO groups and py groups cis. The metal-ligand distances are as follows: W-CPh, 1.84 (2) Å; W-Br, 2.696 (2) Å; W-CO, 2.00 (2), 2.01 (2) Å; W-N, 2.26 (1), 2.28 (1) Å.

Introduction

trans-Bromo(tetracarbonyl)(phenylcarbyne)tungsten has been found to be a synthon for trinuclear clusters.[1] It is isolobal with alkynes and expected to add across metal-metal multiple bonds analogously, i.e.



The expected products are alkylidyne-capped trinuclear clusters. We have demonstrated earlier that $Cp_2Mo_2(CO)_4$ and *trans*-$WBr(CO)_4(CPh)$ form a benzylidyne capped heteronuclear trimer.[1] Although $Mo_2(O\text{-}i\text{-}Pr)_6$ has been observed to react with *trans*-$WBr(CO)_4(CPh)$, no defined addition

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[1] Cotton, F. A.; Schwotzer, W. *Angew. Chem.* **1982**, *94*, 652; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 629. We have been informed by Prof. F. G. A. Stone that he has used the closely related *trans*-$WBr(CO)_4CC_6H_4CH_3$ carbyne to synthesize trinuclear clusters capped by $CC_6H_4CH_3$.

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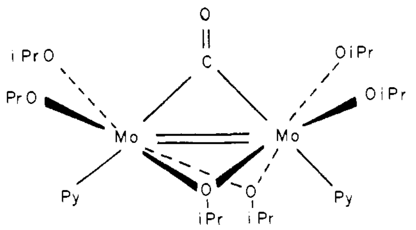

Figure 1. Schematic drawing of the molecule for $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$.

products could be isolated. By following Chisholm's improved procedure[2] for the addition of acetylenes to $Mo_2(O\text{-}i\text{-}Pr)_6$, we were able to isolate two crystalline products in high yields. The orange crystals that formed during the reaction at about −30 °C turned out to be the substitution product (**2**) obtained by replacing two carbonyl groups in *trans*-$WBr(CO)_4(CPh)$ by pyridine molecules.[3] The dark brown material that crystallized within 3 days at −20 °C from the mother liquor was identified as $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ (**1**), with the carbonyl group in a bridging position. Compound **1** is a bis(pyridine) adduct of the O-*i*-Pr homologue of $Mo_2(O\text{-}t\text{-}BuO)_6(CO)$, earlier reported[4] as an intermediate in the conversion of $Mo_2(O\text{-}t\text{-}Bu)_6$ to $Mo(CO)_6$ and $Mo_2(O\text{-}t\text{-}Bu)_8$.

Results and Discussion

Carbonyl-Transfer Reaction. A reasonable way of explaining the formation of products **1** and **2** involves rapid substitution of carbonyl by pyridine on the carbyne compound, *trans*-$WBr(CO)_4(CPh)$, followed by addition of the liberated CO to $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2$, itself formed by rapid addition of pyridine to $Mo_2(O\text{-}i\text{-}Pr)_6$:

$$WBr(CO)_4(CPh) \xrightarrow{py} WBr(CO)_2(py)_2(CPh) + 2CO$$

$$Mo_2(O\text{-}i\text{-}Pr)_6 \xrightarrow{py} Mo_2(O\text{-}i\text{-}Pr)_6(py)_2 \xrightarrow{CO} Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$$

It has been noted earlier that carbon monoxide adds readily to $Mo_2(O\text{-}i\text{-}Pr)_6$ in hydrocarbon solvents,[4] leading in the absence of a coordinating solvent to a molecule with a tetranuclear chain-like structure. This compound is unstable in solution, and complete cleavage of the metal–metal bond is observed. The reaction of CO with the sterically more demanding $Mo_2(O\text{-}t\text{-}Bu)_6$, which leads ultimately to $Mo(CO)_6$ and $Mo(O\text{-}t\text{-}Bu)_4$, can be interrupted at the intermediate stage represented by $Mo_2(O\text{-}t\text{-}Bu)_6(CO)$. Our experimental conditions favor the carbonyl adduct in two ways. First, the pyridine present in solution occupies vacant ligand sites both in $Mo_2(O\text{-}i\text{-}Pr)_6$ and in the product. Second, the supply of CO is limited, thus decreasing the possibility of total cleavage of the metal–metal bond.

Table I. Crystallographic Data Collection Parameters

	$Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$	$WBr(CO)_2(py)_2(CPh)\cdot CH_2Cl_2$
fw	$C_{29}H_{52}N_2O_7Mo_2$, 732.6	$WBrCl_2O_2N_2C_{20}H_{17}$, 652.0
space group	*C*2/*c* (No. 15)	$P2_1/n$
a, Å	10.674 (10)	10.298 (6)
b, Å	18.502 (13)	13.372 (5)
c, Å	18.238 (14)	16.861 (9)
β, deg	91.50 (7)	98.35 (4)
V, Å^3	3600 (5)	2297 (2)
Z	4	4
d_{calcd}, g/cm^3	1.351	1.885
cryst size, mm	0.5 × 0.5 × 0.3	0.4 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	7.183	71.116
data collection instrument	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation	Mo Kα	Mo Kα
scan method	θ/2θ	θ/2θ
data collection range, deg	4–50 (2θ)	4–50 (2θ)
abs corr		semiempirical (ψ-scan)
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	2190	2056
no. of parameters refined	191	226
R^a	0.041	0.053
$R_w{}^b$	0.053	0.077
quality-of-fit indicator^c	1.411	1.907
largest shift/esd, final cycle	0.26	0.86

^{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} The quality of fit is equal to $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)^a$

atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.11212 (5)	0.16474 (3)	0.23314 (3)	2.916 (8)
O(1)	−0.0296 (4)	0.2286 (2)	0.1850 (2)	4.9 (1)
O(2)	0.1631 (4)	0.1264 (2)	0.1414 (2)	3.95 (9)
O(3)	0.000	0.0123 (3)	0.250	4.3 (1)
O(4)	0.2405 (4)	0.1299 (2)	0.2987 (2)	3.99 (9)
N(1)	0.2716 (5)	0.2455 (3)	0.2031 (3)	3.8 (1)
C(1)	0.2609 (7)	0.3178 (3)	0.2075 (4)	4.7 (2)
C(2)	0.3578 (8)	0.3637 (4)	0.1852 (5)	6.4 (2)
C(3)	0.4675 (8)	0.3321 (5)	0.1576 (4)	7.0 (2)
C(4)	0.4779 (7)	0.2573 (5)	0.1547 (4)	6.3 (2)
C(5)	0.3763 (6)	0.2164 (4)	0.1775 (4)	4.9 (2)
C(6)	0.439 (1)	0.2561 (7)	0.6162 (7)	4.6 (3)
C(6A)	0.451 (1)	0.2128 (8)	0.6406 (8)	5.1 (3)
C(7)	−0.1848 (7)	0.2937 (5)	0.1136 (5)	6.3 (2)
C(8)	0.0418 (8)	0.2882 (5)	0.0751 (4)	6.3 (2)
C(9)	0.1249 (7)	0.0678 (4)	0.0949 (4)	4.9 (2)
C(10)	0.2067 (9)	0.0027 (5)	0.1116 (5)	7.5 (2)
C(11)	0.134 (1)	0.0933 (5)	0.0151 (4)	8.1 (3)
C(12)	0.2569 (6)	0.0707 (4)	0.3479 (4)	4.6 (2)
C(13)	0.3593 (8)	0.0229 (5)	0.3191 (6)	8.4 (3)
C(14)	0.290 (1)	0.1002 (5)	0.4247 (5)	8.8 (3)
C(15)	0.000	0.0770 (4)	0.250	3.1 (2)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The easy replacement of one or two carbonyl groups in metallocarbynes has been reported by Fischer et al.[3] The substitution products exhibit increased kinetic and thermodynamic stability. Retrospectively, the relative stability of the parent compound seems surprising as there are only two electrons available for the back-bonding into the four CO's, four electrons being involved in the W≡C and W—Br bonds. The stabilization resulting from replacement of two CO's by two pyridines makes it likely that the substituted carbyne may be a much more convenient and versatile reagent. Experiments are planned to probe the reactivity of the stabilized carbynes with respect to addition to multiple metal–metal bonds.

Solid-State Structure of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ (1). Crystals of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ consist of discrete molecules, shown in Figure 1. Atomic coordinates with equivalent isotropic temperature factors are listed in Table II. Bond angles and distances are listed in Table III. Each molecule possesses a crystallographically imposed twofold axis and has virtual C_{2v} symmetry. The coordination polyhedron of the Mo

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(2) Chisholm, M. H.; Huffman, J. H.; Rothwell, I. P. *J. Am. Chem. Soc.* **1981**, *103*, 4245.

(3) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 805.

(4) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

Table III. Bond Distances (Å) and Angles (deg) for $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$[a]

A. Distances

Mo(1)-Mo(1)′	2.487 (1)	C(1)-C(2)	1.406 (9)
-O(1)	2.094 (4)	C(2)-C(3)	1.413 (11)
-O(1)′	2.114 (4)	C(3)-C(4)	1.391 (11)
-O(2)	1.910 (3)	C(4)-C(5)	1.394 (8)
-O(4)	1.907 (4)	C(6)-C(7)	1.61 (2)
-N(1)	2.341 (4)	C(6)-C(8)	1.576 (15)
-C(15)	2.045 (5)	C(6A)-C(7)	1.52 (2)
O(1)-C(6)	1.323 (14)	-C(8)	1.56 (2)
-C(6A)	1.367 (13)	C(9)-C(10)	1.514 (9)
O(2)-C(9)	1.429 (6)	-C(11)	1.536 (9)
O(3)-C(15)	1.198 (8)	C(12)-C(13)	1.512 (9)
O(4)-C(12)	1.423 (6)	-C(14)	1.537 (9)
N(1)-C(1)	1.345 (6)		
-C(5)	1.336 (7)		

B. Angles

Mo(1)′-Mo(1)-O(1)	54.1 (1)	N(1)-Mo(1)-C(15)	166.9 (2)
-O(1)′	53.4 (1)	C(1)-N(1)-C(5)	119.6 (5)
-O(2)	121.0 (1)	N(1)-C(1)-C(2)	121.3 (7)
-O(4)	121.7 (1)	C(1)-C(2)-C(3)	118.4 (7)
-N(1)	140.2 (1)	C(2)-C(3)-C(4)	119.5 (7)
-C(15)	52.6 (1)	C(3)-C(4)-C(5)	117.8 (7)
O(1)-Mo(1)-O(1)′	70.8 (2)	N(1)-C(5)-C(4)	123.3 (6)
-O(2)	93.5 (2)	O(1)-C(6)-C(7)	110 (1)
-O(4)	162.3 (2)	-C(8)	113 (1)
-N(1)	93.6 (2)	C(7)-C(6)-C(8)	105.7 (9)
-C(15)	95.3 (2)	O(1)-C(6A)-C(7)	113 (1)
O(1)′-Mo(1)-O(2)	163.7 (2)	-C(8)	112 (1)
-O(4)	93.0 (2)	C(7)-C(6A)-C(8)	111 (1)
-N(1)	97.3 (2)	O(2)-C(9)-C(10)	109.3 (5)
-C(15)	94.7 (1)	-C(11)	107.7 (5)
O(2)-Mo(1)-O(4)	101.9 (2)	C(10)-C(9)-C(11)	112.5 (6)
-N(1)	78.8 (2)	O(4)-C(12)-C(13)	108.1 (5)
-C(15)	91.0 (1)	-C(14)	108.9 (5)
O(4)-Mo(1)-N(1)	81.2 (2)	C(13)-C(12)-C(14)	111.8 (6)
-C(15)	92.9 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

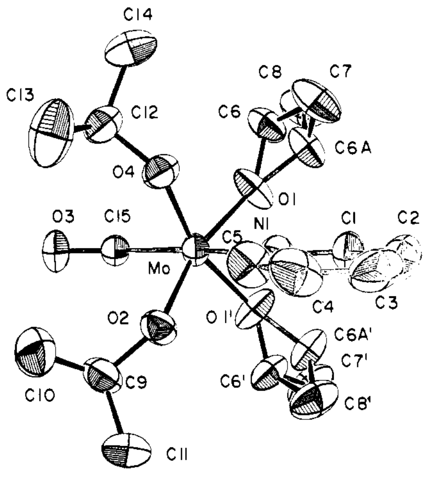


Figure 2. ORTEP view of the molecule along the Mo═Mo bond for $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$.

atoms is a distorted octahedron, and the entire molecule is composed of two such octahedra sharing a face. Figure 2 is a projection along the Mo–Mo bond. We note that the bridging isopropoxide group appears as an approximately 50:50 superposition of two conformers, the disorder manifesting itself only in C(6), which was refined in positions C(6) and C(6A) with occupancies 0.5. The intermetallic distance of 2.487 (1) Å is closely similar to the one encountered in $Mo_2(O\text{-}t\text{-}Bu)_6(CO)$ (2.498 (1) Å), as are comparable metal–oxygen and metal–carbon distances. The order of the metal–metal bond is considered to be 2 for the reasons stated in the $Mo_2(O\text{-}t\text{-}Bu)_6(CO)$ case.[4]

Table IV. Positional Parameters and Their Estimated Standard Deviations for $WBr(CO)_2(py)_2(CPh)$[a]

atom	x	y	z	B_{eqv}, Å^2
W(1)	0.17270 (8)	0.91841 (7)	0.34347 (5)	4.75 (2)
Br(1)	0.3218 (2)	0.7635 (2)	0.4053 (1)	6.26 (6)
O(1)	0.234 (2)	1.028 (1)	0.5100 (8)	8.5 (5)
O(2)	−0.069 (2)	0.812 (1)	0.4017 (10)	9.0 (5)
N(1)	0.352 (2)	0.985 (1)	0.3005 (9)	4.8 (4)
N(2)	0.151 (2)	0.834 (1)	0.2246 (8)	4.5 (4)
C(1)	0.340 (2)	1.045 (2)	0.234 (1)	5.9 (5)
C(2)	0.441 (2)	1.100 (2)	0.205 (1)	8.1 (7)
C(3)	0.564 (2)	1.082 (2)	0.245 (1)	7.1 (6)
C(4)	0.579 (2)	1.025 (2)	0.320 (2)	8.6 (8)
C(5)	0.477 (2)	0.975 (2)	0.343 (1)	6.7 (6)
C(6)	0.253 (2)	0.787 (1)	0.197 (1)	5.0 (5)
C(7)	0.238 (2)	0.743 (1)	0.123 (1)	5.7 (5)
C(8)	0.113 (2)	0.741 (2)	0.078 (1)	6.6 (6)
C(9)	0.009 (2)	0.788 (2)	0.107 (1)	7.9 (7)
C(10)	0.028 (2)	0.832 (2)	0.181 (1)	5.9 (6)
C(11)	0.061 (2)	1.025 (2)	0.320 (1)	6.3 (5)
C(12)	−0.027 (2)	1.114 (1)	0.310 (1)	5.9 (6)
C(13)	−0.057 (2)	1.163 (2)	0.234 (1)	6.7 (6)
C(14)	−0.134 (2)	1.242 (2)	0.224 (2)	9.5 (9)
C(15)	−0.180 (3)	1.282 (2)	0.290 (2)	11 (1)
C(16)	−0.152 (3)	1.248 (2)	0.359 (2)	11.4 (9)
C(17)	−0.080 (2)	1.152 (2)	0.379 (1)	7.5 (6)
C(18)	0.213 (2)	0.985 (2)	0.450 (1)	5.8 (6)
C(19)	0.521 (2)	0.652 (2)	0.882 (1)	6.0 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table V. Bond Distances (Å) and Angles (deg) for $WBr(CO)_2(py)_2(CPh)$[a]

A. Distances

W(1)-Br(1)	2.696 (2)	C(3)-C(4)	1.47 (3)
-N(1)	2.263 (12)	C(4)-C(5)	1.35 (3)
-N(2)	2.283 (12)	C(6)-C(7)	1.37 (2)
-C(11)	1.84 (2)	C(7)-C(8)	1.40 (2)
-C(18)	2.00 (2)	C(8)-C(9)	1.39 (3)
-C(19)	2.01 (2)	C(9)-C(10)	1.37 (2)
O(1)-C(18)	1.15 (2)	C(11)-C(12)	1.50 (2)
O(2)-C(19)	1.14 (2)	C(12)-C(13)	1.43 (2)
N(1)-C(1)	1.37 (2)	C(12)-C(17)	1.45 (2)
N(1)-C(5)	1.38 (2)	C(13)-C(14)	1.32 (3)
N(2)-C(6)	1.36 (2)	C(14)-C(15)	1.38 (4)
N(2)-C(10)	1.37 (2)	C(15)-C(16)	1.24 (4)
C(1)-C(2)	1.42 (2)	C(16)-C(17)	1.51 (3)
C(2)-C(3)	1.36 (3)		

B. Angles

Br(1)-W(1)-N(1)	88.9 (3)	C(1)-C(2)-C(3)	115 (2)
-N(2)	86.4 (3)	C(2)-C(3)-C(4)	119 (2)
-C(11)	169.4 (5)	C(3)-C(4)-C(5)	121 (2)
-C(18)	87.9 (5)	N(1)-C(6)-C(4)	121 (2)
-C(19)	86.7 (5)	N(2)-C(6)-C(7)	122 (1)
N(1)-W(1)-N(2)	83.9 (4)	C(6)-C(7)-C(8)	118 (2)
-C(11)	97.9 (6)	C(7)-C(8)-C(9)	120 (2)
-C(18)	92.3 (6)	C(8)-C(9)-C(10)	120 (2)
-C(19)	175.3 (6)	N(2)-C(10)-C(9)	119 (2)
N(2)-W(1)-C(11)	102.4 (5)	C(11)-C(12)-C(13)	120 (2)
-C(18)	173.2 (6)	-C(17)	118 (2)
-C(19)	94.3 (6)	C(13)-C(12)-C(17)	121 (2)
C(11)-W(1)-C(18)	83.7 (7)	C(12)-C(13)-C(14)	121 (2)
-C(19)	86.7 (8)	C(13)-C(14)-C(15)	119 (3)
C(18)-W(1)-C(19)	89.0 (7)	C(14)-C(15)-C(16)	124 (3)
C(1)-N(1)-C(5)	117 (2)	C(15)-C(16)-C(17)	125 (3)
C(6)-N(2)-C(10)	120 (1)	C(12)-C(17)-C(16)	110 (2)
N(1)-C(1)-C(2)	127 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Solid-State Structure of $WBr(CO)_2(py)_2(CPh)$ (2). Crystals of this compound consist of discrete molecules, shown in Figure 3. Atomic coordinates with equivalent temperature factors are listed in Table IV and bond lengths and angles in Table

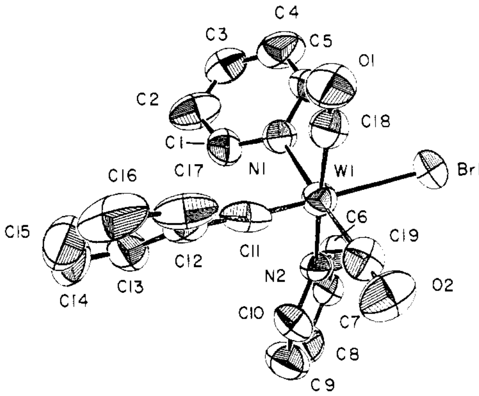
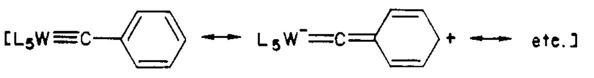


Figure 3. ORTEP view of the molecule for $WBr(CO)_2(py)_2(CPh)$.

V. As in the parent compound, the tungsten atom is octahedrally coordinated with the bromine atom trans to the carbyne ligand. The pyridine ligands are in a cis configuration, thus optimizing the metal–CO back-bonding. The stabilizing effect of σ-donor substitution in metallocarbynes has been discussed by Fischer et al.[5] on the basis of an extended series of structures. We find that our results fit generally into their pattern. The W–CO bond lengths, 2.00 (2) Å, are shorter than those in $WI(CO)_4(CPh)$, 2.07 (2) Å, which we have to use for comparison since data for $WBr(CO)_4(CPh)$ itself are not available. We furthermore find a lengthening of C(11)–C(12) (1.50 (2) and 1.40 (2) Å) as well as a shortening of the W≡C bond (1.84 (2) and 1.90 (2) Å). These changes can be understood in terms of the following resonance formulation, with structure Ia gaining weight within the overall resonance hybrid:



Ia Ib

The angle W–C(11)–C(12) is 173.8 (6)°. It is interesting that while Huttner, Frank, and Fischer[5] had previously stressed an insensitivity of the M≡C bond lengths to changes in the remainder of the coordination sphere, we find here an indication of a change, although the esd's are such that this is not a clean-cut result, viz., 0.06 (3) Å.

Experimental Section

General procedures, including the preparation of $WBr(CO)_4(CPh)$[3] and $Mo_2(O\text{-}i\text{-}Pr)_6$[6] have been reported.

Reaction of $WBr(CO)_4(CPh)$ with $Mo_2(O\text{-}i\text{-}Pr)_6$. Weighed amounts of the carbyne (360 mg) and of $Mo_2(O\text{-}i\text{-}Pr)_6$ (220 mg) were placed in a Schlenk flask and immersed in liquid nitrogen. A mixture of 20 mL of hexane and 0.4 mL of pyridine was slowly added. The flask was transferred to an acetone/dry ice bath and allowed to warm slowly. Formation of an orange crystalline material was observed at a bath temperature of −30 °C. The solution was stirred at room temperature for 15 min and then placed in a cold room at −20 °C overnight. The orange crystals were collected by filtration (yield 90%) and recrystallized from CH_2Cl_2/hexane. The volume of the mother liquor was reduced to half, and the solution was set back into the freezer. Dark brown rhombic tablets, some of them several millimeters long, grew within 3 days (yield 50%).

X-ray Crystallography.[7] **$Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$.** A rhombic tablet of approximate dimensions 0.5 × 0.5 × 0.3 mm was wedged into a glass capillary, which was afterwards sealed at both ends. Cell dimensions were determined from 15 centered reflections with $2\theta \geq 25°$. Parameters pertaining to data collection and refinement are given in Table I. The space group $C2/c$ was consistent with the systematic absences (as was Cc) and confirmed by successful refinement. We note that intensity statistics (NZTEST) suggested an acentric distribution. The structure was solved by heavy-atom techniques and refined by a combination of least-squares and Fourier techniques. No difficulties other than the disordered atom C(6) were encountered, and no residual peak in the final difference Fourier map was larger than 0.76 e $Å^{-3}$.

$WBr(CO)_2(py)_2(CPh)$. A prismatic orange crystal was embedded in epoxy resin in a thin-walled glass capillary. Unit cell dimensions were determined from 15 centered reflections with $2\theta \geq 23°$. The space group $P2_1/n$ was unambiguously determined by the systematic absences. Experimental data are in Table I. The structure was solved by conventional Patterson procedures and refined by combined least-squares and Fourier techniques. After refinement of the tungsten-containing molecule several peaks with intensities up to 1.5 e $Å^{-3}$, which were unconnected to the molecule and were without any chemically feasible connectivity, were left in the difference Fourier map. A 90-MHz ^1H NMR spectrum suggested that these peaks originate from disordered CH_2Cl_2 molecules, but no structurally sensible model could be devised and these peaks were therefore excluded from the refinement. The ^1H NMR data were as follows, where we give in each case the chemical shift in ppm downfield from Me_4Si followed by the type of multiplet, the relative intensity, and the assignment: 9.07, d × t, 1.92, H(C1); 7.71, t × t, 1.0, H(C3); 7.25, t + s, 4.15, H(C2) and C_6H_5; 5.20 s, 0.22, CH_2Cl_2. The CH_2Cl_2 content is nonstoichiometric because the crystals were dried in vacuo.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Registry No. **1**, 83437-00-7; **2**, 83746-84-3; $WBr(CO)_4(CPh)$, 50726-27-7; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; Mo, 7439-98-7.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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(5) Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1976**, *15*, 133.

(6) Chisholm, M. H.; Folting, H.; Huffman, J. C.; Kirkpatrick, C. C.; Raterman, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305.

(7) The Enraf-Nonius Structure Determination Package was used for all crystallographic calculations, which were done on a PDP 11/60 at B. A. Frenz and Associates, Inc., College Station, TX.