dergoes reduction at a higher negative potential than $[(CH_3)_2NH_2]_2MoS_4$ (Table I). A similar trend is observed in the anions under study. The all-sulfur complexes $[M_2S_{11}]^{2-}$ (M = Mo, W) are easily reducible compared to their oxo analogues, $[M_2O_2S_9]^{2-}$ (M = Mo, W). In general, the molybdenum complexes are more easily reducible than their tungsten counterparts. The anodic peak potential is almost nonvariant for all the anions, presumably due to the oxidation of the disulfido group, S_2^{2-}. The reduction step involved in higher negative potentials in the case of $(Ph_4X)_2M_2O_nS_{11-n}$, (X = P or As; M = Mo, W; n = 0, 2) is due to the cation, which has been confirmed by using simple $[Ph_4X]^+$ (X = P or As) salts.

The early work on $[W_2S_{11}H]^-$ [16] and $[W_2S_{11}]^{2-}$ [2] requires some explanation. It is interesting to note that $[W_2S_{11}H]^-$ reacts with elemental sulfur to give $[W_2S_{11}]^{2-}$. Thus acidification of WS_4^{2-} in the presence of elemental sulfur (not filtering out as has been done in the earlier work)[16] produces the desired compound. In all of these acidification reactions, H_2S is one of the byproducts. So, the condensation process in acidic medium in the presence of sulfur may follow the reactions shown in eq 1 and 2. The

$$MS_4^{2-} \xrightarrow{H^+} [M_2S_7]^{2-} + H_2S \tag{1}$$

$$[M_2S_7]^{2-} + S_8 \rightarrow [M_2S_{11}]^{2-} \tag{2}$$

formation of $[Mo_2S_7]^{2-}$ during the acidification of aqueous solutions of MoS_4^{2-} has been proposed previously on the basis of pH and conductometric titrations.[17]

In the present study, it is also of interest to stress that the stoichiometry of the thiometalate and sulfur is not the crucial factor to dictate the course of the reaction. It is the protonated cationic species that drives the reaction resulting in the condensation product (eq 3). The difference in reactivity as described

$$(Et_2NH_2)_2MoS_4 \xrightarrow{S_8} (Et_2NH_2)_2Mo_2S_{11} \tag{3}$$

$$(Et_4N)_2MoS_4 \xrightarrow{S_8} (Et_4N)_2MoS_9{}^{12} \tag{4}$$

in these two equations (eq 3 and 4) may be attributed to an entirely different course of reactions. In the absence of protons, induced electron transfer takes place across the Mo=S bond and the external oxidant S_8 on reduction produces S_4^{2-}, which stabilizes the generated Mo(IV)[12] under ambient conditions. A similar transformation can be brought about in a variety of ways where the oxidation state of the central atom may vary.[18] However for the reaction in the presence of protonated cation or free proton, the condensation reaction with dimerization (eq 1) may be the first stage followed by intramolecular electron transfer between the metal–sulfur bond, which happens in tungsten–sulfur chemistry.[2,5-7,13] In the presence of elemental sulfur the stability of the dimeric condensation product probably is achieved by coordination expansion under ambient conditions as shown in eq 1 and 2.

Acknowledgment. We thank the Department of Science and Technology, Government of India, and The Indian National Science Academy, New Delhi, India, for financial support.

Registry No. $[(C_2H_5)_2NH_2]_2MoS_4$, 59129-76-9; H_2MoO_4, 7782-91-4; H_2S, 7783-06-4; $(AsPh_4)_2Mo_2S_{11}$, 116026-61-0; $(Ph_4As)_2MoS_4$, 14493-05-1; S, 7704-34-9; $(AsPh_4)_2W_2O_2S_9$, 116026-62-1; $[Ph_4As]_2WOS_3$, 116026-66-5; $[(C_2H_5)_2NH_2]_2Mo_2S_{11}$, 116026-64-3; $(NH_4)_2MoS_4$, 15060-55-6; $(AsPh_4)_2Mo_2O_2S_9$, 116026-65-4; $(Ph_4As)_2MoOS_3$, 116026-67-6; $[(CH_3)_2NH_2]_2Mo_2O_2S_9$, 116052-58-5; $(NH_4)_2MoO_2S_2$, 16150-60-0; $(AsPh_4)_2W_2S_{11}$, 116126-35-3; $(AsPh_4)_2WS_4$, 14348-12-0; $(PPh_4)_2Mo_2O_2S_9$, 116026-68-7; $(PPh_4)_2W_2O_2S_9$, 112469-34-8; $(Me_2NH_2)_2MoOS_3$, 116026-69-8; $(Me_2NH_2)_2MoS_4$, 116026-70-1; $Cs_2(MoOS_3)$, 86915-92-6; $Cs_2(MoS_4)$, 15060-35-2; $[(PPh_4)_2W_2S_{11}]$, 106213-35-8; $[(PPh_4)_2Mo_2S_{11}]$, 116026-71-2.

Supplementary Material Available: A table of interplanar (d) spacings of the most prominent peaks (Å) for all four complexes as tetraphenylphosphonium salts (1 page). Ordering information is given on any current masthead page.

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Metathesis-like Reactions between the Carbene Complex $(CO)_5W{=}C(OMe)Ph$ and Organic Nitroso Reagents

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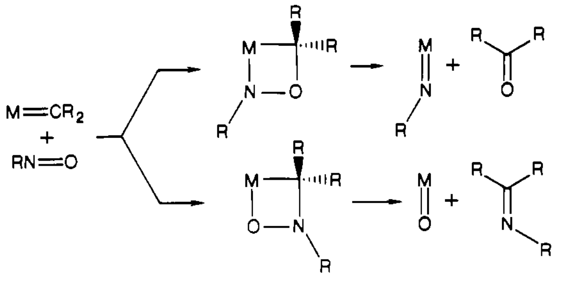
Nitrene (NR, imido) ligands invariably assume bridging positions, typically μ_3, in low-valent, electron-rich metal complexes. Mononuclear nitrene complexes are known only for the more electron-deficient metals.[1] Carbonyl–nitrene complexes such as $(CO)_5Cr{=}NR$ have been invoked as reactive intermediates,[2] but such compounds have never been characterized, apparently because the metal–nitrogen bond is too weak and the nitrogen too poor a π-acceptor to give stability to such species. Nevertheless, if such complexes could be generated as reactive transients, it might prove possible to trap the nitrene ligand with added organic substrates and thereby accomplish useful synthetic chemistry, much like the impressive syntheses that have resulted from the corresponding metal carbene complexes.[3]

We reasoned that a possible route to such $(CO)_xM{=}NR$ species would be through metathesis-like reactions between carbene complexes and nitroso reagents, eq 1a. Metathesis could also proceed in the opposite sense as illustrated in eq 1b to generate an oxo complex and an imine. Herein we present results that indicate that the metathesis-like reaction of eq 1 does occur to generate transient nitrene complexes, although such species have proven too elusive to characterize. However, one such reaction has led to the formation of the first metal complex possessing an azoxy ligand, and this species has been structurally characterized.



(1a)

(1b)

Results and Discussion

The carbene complex $(CO)_5W{=}C(OMe)Ph$ (**1**)[4] was chosen for initial study since it was expected to yield a more stable third-row metal nitrene complex. Complex **1** reacts immediately with PhNO in toluene solution to give the products shown in eq 2, along with organometallic residues containing some $W(CO)_6$. Even at −78 °C the reaction is rapid, and the carbene complex **1** is completely consumed if a slight excess of nitrosobenzene is used. ^1H NMR analysis indicated that all of the carbene ligand was converted into methyl benzoate (**2**) and the imidate **3**, with an approximate 1.75:1 ratio of these products. The high yield

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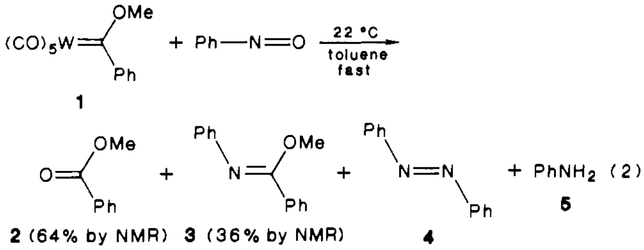
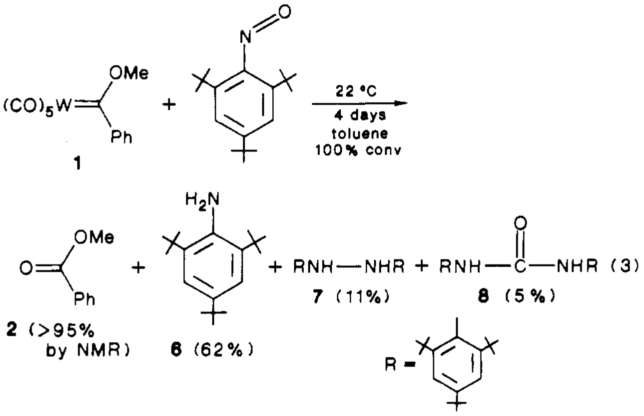


of methyl benzoate is consistent with the metathesis reaction (1a), and the imidate likely forms via the alternative reaction sequence of eq 1b. Also isolated from reaction 2 were aniline and azobenzene, products expected from generation of transient phenylnitrene,[5] but they do not indicate whether the incipient nitrene was coordinated or free.

A widely used approach to stabilize reactive metal–ligand bonds is to increase the steric crowding. Accordingly, the reaction of **1** with 2,4,6-tri-*tert*-butylnitrosobenzene was examined, but this nitroso reagent gave only a very slow reaction over a 4-day period at 22 °C. No new carbonyl-containing organometallics were produced, but ^{1}H NMR analysis showed the formation of methyl benzoate in >95% yield (eq 3). Also formed were the amine **6**, the hydrazine **7**, and the urea **8**. The latter may have formed via addition of **6** to an isocyanate generated by coupling of carbonyl and nitrene ligands.



Nearly quantitative formation of methyl benzoate also occurred when the carbene complex **1** was allowed to react with Bu^{t}NO (eq 4). The only nitrogen-containing organic product detected was the azoxy compound **9**. This species could form by the addition of the excess Bu^{t}NO to an incipient nitrene. However, Bu^{t}NO exists in CDCl$_3$ solution as a ~1:1.5 monomer/dimer mixture,[6] and oxygen atom transfer *from the dimer* to the carbene complex **1** could directly give the azoxy species **9**. Also formed in modest yield was the nitroso complex **10**, which has been independently prepared by photolysis of (CO)$_5$W(piperidine) in the presence of Bu^{t}NO. Its synthesis and spectroscopic and crystallographic characterization will be separately described.[7]

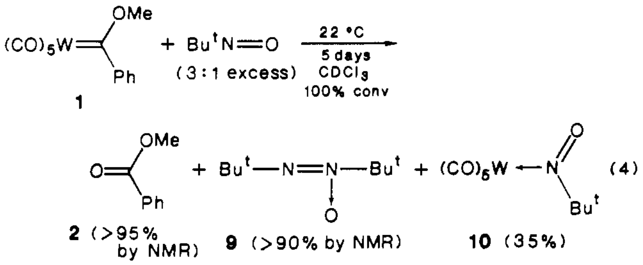


Table I. Crystallographic Parameters for (CO)$_5$W(C$_{12}$H$_9$N{O}C$_{12}$H$_9$) (**14**)

(a) Crystal Parameters			
cryst sysem	triclinic	V, Å^3	2652 (1)
space group	$P\bar{1}$	Z	4
a, Å	12.280 (3)	μ, cm^{-1}	47.1
b, Å	16.013 (4)	ρ, g cm^{-3}	1.689 (calcd)
c, Å	16.439 (4)	size, mm	0.22 × 0.27 × 0.34
α, deg	64.00 (2)	color	red
β, deg	68.06 (2)		
γ, deg	89.15 (2)		
(b) Data Collection			
diffractometer	Nicolet R3m/μ		
radiation	Mo Kα (λ = 0.71073 Å)		
monochromator	graphite		
2θ scan limits, deg	$4 \le 2\theta \le 45$		
scan type	$\theta/2\theta$		
scan spd, deg min^{-1}	4–20		
temp, °C	22		
(c) Data Reduction and Refinement			
no. of rflns collected	7209		
no. of unique rflns	6915		
no. of unique rflns with $F_o \ge 3\sigma(F_o)$	5063		
R(int), %	3.49		
$R(F)$, %[a]	5.16		
$R_w(F)$, % (g = 0.01)[a]	6.06		
GOF	1.231		
highest peak, final diff Fourier, e Å^{-3}	1.07		
Δ/σ	0.032		
N_o/N_v	7.4		

[a] $w^{-1} = \sigma^2(F_o) + g(F_o^2)$; $R(F) = \sum|\Delta|/\sum|F_o|$; $R_w(F) = \sum(|\Delta|w^{1/2})/\sum(|F_o|w^{1/2})$; $\Delta = |F_o| - |F_c|$.

Unequivocable evidence for the formation of a transient nitrene comes from the reaction of *o*-nitrosobiphenyl with complex **1**. *o*-Biphenylylnitrene is well established to undergo insertion of the reactive nitrogen atom into a C–H bond on the adjacent phenyl group to form carbazole (**11**),[5] and this product was formed in 52% yield from the combination of *o*-nitrosobiphenyl with **1**. Other products include **12**, **13**, and the novel organometallic azoxy complex **14** (eq 5). Complex **14** was spectroscopically and

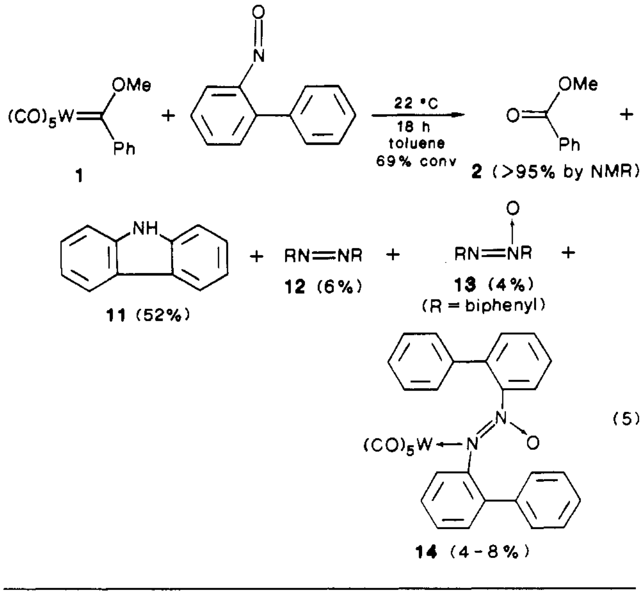


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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U^a		x	y	z	U^a
W(1)	938 (1)	10211 (1)	1410 (1)	56 (1)	C(21)	738 (11)	6268 (11)	5921 (9)	63 (8)
W(2)	7147 (1)	5412 (1)	992 (1)	50 (1)	C(22)	752 (11)	6157 (10)	5141 (10)	68 (8)
O(1)	−336 (10)	11141 (7)	2800 (7)	99 (6)	C(23)	728 (10)	6886 (8)	4286 (8)	46 (6)
O(2)	365 (11)	11899 (8)	−186 (7)	112 (7)	C(24)	781 (11)	6751 (8)	3435 (9)	52 (7)
O(3)	2212 (12)	9567 (9)	−228 (8)	122 (9)	C(25)	1557 (12)	6240 (9)	3119 (10)	62 (8)
O(4)	−1587 (11)	9076 (10)	2011 (9)	117 (9)	C(26)	1616 (14)	6084 (10)	2329 (11)	83 (10)
O(5)	3413 (9)	11531 (8)	526 (8)	107 (7)	C(27)	876 (15)	6469 (11)	1861 (11)	89 (11)
O(6)	−514 (7)	8779 (6)	3703 (6)	64 (5)	C(28)	64 (14)	6976 (10)	2186 (11)	76 (9)
O(30)	4953 (9)	6276 (7)	577 (8)	98 (7)	C(29)	16 (10)	7116 (8)	2981 (8)	55 (7)
O(31)	8847 (10)	7093 (7)	−1027 (7)	100 (6)	C(30)	5729 (11)	5952 (10)	750 (9)	69 (8)
O(32)	7403 (10)	4463 (7)	−394 (7)	101 (7)	C(31)	8246 (11)	6489 (10)	−285 (9)	66 (8)
O(33)	9467 (9)	4687 (8)	1286 (8)	111 (8)	C(32)	7259 (11)	4755 (10)	150 (9)	66 (8)
O(34)	7265 (10)	6639 (8)	2058 (8)	111 (8)	C(33)	8618 (13)	4920 (11)	1201 (11)	85 (10)
O(35)	6985 (7)	4062 (6)	3197 (6)	59 (5)	C(34)	7222 (12	6180 (11)	1699 (11)	76 (9)
N(1)	1341 (8)	9038 (6)	2605 (7)	48 (5)	C(35)	4692 (10)	3868 (8)	2468 (8)	43 (6)
N(2)	513 (8)	8586 (7)	3496 (7)	52 (5)	C(36)	4688 (11)	3444 (8)	1886 (8)	48 (7)
N(3)	5847 (7)	4208 (6)	2379 (6)	40 (5)	C(37)	3597 (12)	3156 (9)	1917 (9)	63 (8)
N(4)	6074 (8)	3757 (7)	3158 (7)	48 (5)	C(38)	2565 (12)	3281 (9)	2500 (9)	62 (8)
C(1)	120 (13)	10771 (9)	2331 (9)	75 (8)	C(39)	2565 (11)	3711 (9)	3059 (9)	57 (7)
C(2)	552 (13)	11248 (11)	400 (10)	82 (9)	C(40)	3625 (9)	4004 (8)	3080 (8)	40 (6)
C(3)	1740 (14)	9764 (10)	398 (10)	80 (9)	C(41)	3548 (11)	4456 (9)	3723 (9)	53 (7)
C(4)	−668 (15)	9445 (12)	1825 (11)	83 (10)	C(42)	2725 (10)	4071 (9)	4676 (8)	53 (7)
C(5)	2515 (13)	11046 (12)	868 (11)	86 (10)	C(43)	2669 (11)	4459 (10)	5270 (9)	60 (8)
C(6)	2522 (10)	8806 (8)	2444 (9)	50 (7)	C(44)	3435 (12)	5259 (11)	4935 (10)	69 (9)
C(7)	2975 (11)	8423 (9)	1817 (8)	57 (7)	C(45)	4239 (12)	5699 (10)	3948 (11)	71 (9)
C(8)	4101 (12)	8233 (10)	1581 (10)	65 (8)	C(46)	4313 (11)	5299 (8)	3356 (9)	53 (7)
C(9)	4812 (12)	8471 (10)	1924 (10)	73 (9)	C(47)	5333 (10)	2876 (8)	4028 (8)	45 (6)
C(10)	4419 (12)	8891 (10)	2545 (11)	77 (9)	C(48)	4749 (11)	2933 (9)	4897 (8)	55 (7)
C(11)	3234 (11)	9061 (8)	2826 (8)	56 (7)	C(49)	4039 (12)	2132 (11)	5733 (10)	70 (8)
C(12)	2808 (11)	9488 (8)	3519 (9)	49 (7)	C(50)	3902 (12)	1294 (11)	5704 (10)	71 (9)
C(13)	3002 (11)	9107 (9)	4387 (10)	59 (8)	C(51)	4547 (12)	1237 (9)	4844 (10)	66 (8)
C(14)	2612 (12)	9459 (10)	5058 (11)	72 (8)	C(52)	5275 (11)	2047 (9)	3963 (9)	56 (7)
C(15)	2014 (12)	10220 (10)	4871 (10)	70 (9)	C(53)	5993 (12)	1959 (9)	3062 (11)	60 (8)
C(16)	1859 (12)	10608 (9)	3995 (10)	71 (8)	C(54)	7175 (12)	2379 (10)	2483 (11)	72 (9)
C(17)	2259 (11)	10256 (8)	3319 (9)	59 (7)	C(55)	7821 (16)	2300 (12)	1656 (12)	91 (11)
C(18)	657 (10)	7734 (8)	4307 (8)	47 (6)	C(56)	7283 (19)	1809 (13)	1353 (15)	108 (14)
C(19)	567 (10)	7872 (9)	5101 (8)	57 (7)	C(57)	6100 (19)	1313 (11)	1948 (14)	102 (13)
C(20)	649 (11)	7138 (10)	5901 (9)	63 (8)	C(58)	5474 (15)	1418 (10)	2773 (11)	82 (9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

crystallographically characterized. The yields in eq 5 are given on the basis of the amount of **1** consumed (69%).

To our knowledge, **14** is the first metal complex to be prepared with an azoxy ligand, and thus it was crystallographically characterized.[8] Two independent but structurally similar complexes are present in the asymmetric unit, and an ORTEP drawing of molecule A is shown in Figure 1. Important crystallographic parameters are given in Tables I–III. Tungsten has the usual octahedral geometry with the azoxy ligand bound via a dative interaction through the nitrogen lone pair. Overall, the structural parameters indicate that little change occurs in the azoxy ligand upon metal coordination. The N(1)–N(2) distances of 1.297 (11) and 1.300 (15) Å are slightly longer than typical N–N distances in uncoordinated azoxy molecules (*p*-azoxyanisole, 1.218 (4) Å;[10a] ethyl *p*-azoxybenzoate, 1.155 (6) Å[10b]) whereas the N(2)–O(6) distances of 1.251 (13) and 1.262 (16) Å are typical azoxy values (*p*-azoxyanisole, 1.279 (4) Å;[10a] ethyl *p*-azoxybenzoate, 1.291 (6) Å[10b]). The W(1)–N(1) distances of 2.258 (10) and 2.232 (6) Å for the two independent molecules are similar to the W–N distances found in $WBr(\eta^3\text{-}C_3H_5)(CO)_2(CyNCH{=}CHNCy)$ (2.219 (10) Å)[9a] and $W(CO)_4(N_4P_4(NMe_2)_8)$ (2.33 (2), 2.37 (1) Å).[9b]

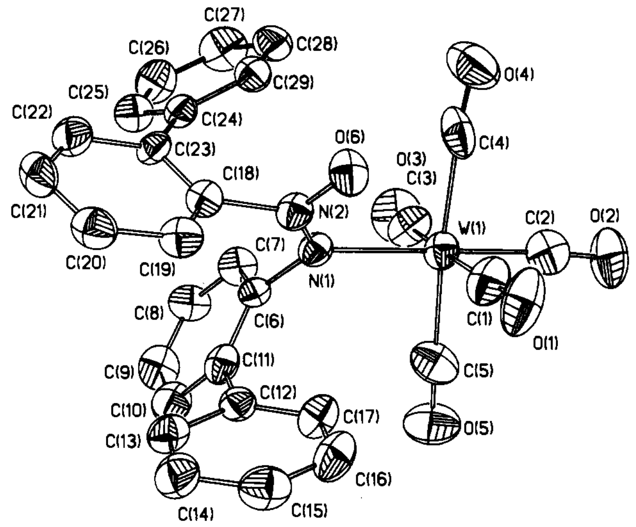

Figure 1. ORTEP drawing of $(CO)_5W(C_{12}H_9N_2\{O\}C_{12}H_9)$ (**14**).

We suggest that azoxy complex **14** forms via the addition of nitrosobiphenyl to a coordinated biphenylylnitrene ligand generated by the metathesis reaction of eq 1a. Alternatively, the azoxy molecule could form by combination of free biphenylylnitrene with nitrosobiphenyl followed by coordination to a $W(CO)_x$ fragment released during the carbene–nitroso reaction. To test this hypothesis, commercially available *p*-azoxyanisole was allowed to react with $(CO)_5W(NH_3)$ and $(CO)_5W(THF)$ under both thermal and photochemical conditions, but in no case was evidence obtained

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(8) All specimens of **14** diffracted very weakly; data were collected to the limits of availability (2θ = 45°). Of 6915 independent data collected (Nicolet R3m/μ, 23 °C, $R(\text{int}) = 3.5\%$) and corrected for absorption (empirical, transmission range 0.266–0.186), 5063 with $F_o \geq 3\sigma(F_o)$ were used for solution (heavy atom) and refinement. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were placed in idealized locations. All computations used the SHELXTL (5.1) program library (Nicolet Corp., Madison, WI).

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Table III. Important Bond Lengths and Angles for the Two Independent Molecules of $(CO)_5W(C_{12}H_9N_2\{O\}C_{12}H_9)$

molecule A		molecule B	
	Bond Distances (Å)		
W(1)–N(1)	2.258 (10)	W(2)–N(3)	2.32 (6)
N(1)–N(2)	1.297 (11)	N(3)–N(4)	1.300 (15)
N(1)–C(6)	1.448 (16)	N(3)–C(35)	1.459 (17)
N(2)–O(6)	1.251 (13)	N(4)–O(35)	1.262 (16)
N(2)–C(18)	1.498 (14)	N(4)–C(47)	1.469 (11)
W(1)–C(1)	2.033 (16)	W(2)–C(30)	2.027 (15)
W(1)–C(2)	1.971 (15)	W(2)–C(31)	1.995 (10)
W(1)–C(3)	2.011 (17)	W(2)–C(32)	2.042 (18)
W(1)–C(4)	2.047 (19)	W(2)–C(33)	2.046 (17)
W(1)–C(5)	2.019 (16)	W(2)–C(34)	2.042 (21)
	Bond Angles (deg)		
C(2)–W(1)–N(1)	178.0 (6)	C(31)–W(2)–N(3)	176.7 (6)
W(1)–N(1)–C(6)	122.7 (6)	W(2)–N(3)–C(35)	122.3 (7)
W(1)–N(1)–N(2)	119.7 (8)	W(2)–N(3)–N(4)	122.2 (7)
Nn2)–N1)–C(6)	117.4 (9)	N(4)–N(3)–C(35)	115.5 (7)
N(1)–N(2)–O(6)	121.1 (9)	N(3)–N(4)–O(35)	120.3 (8)
C(18)–N(2)–O(6)	115.1 (7)	C(47)–N(4)–O(35)	115.7 (10)
N(1)–N(2)–C(18)	123.4 (9)	N(3)–N(4)–C(47)	124.0 (11)

for a complex with an azoxy ligand. Azoxy molecules are apparently not sufficiently strong ligands to compete for a coordination site. Thus, it is likely that the azoxy ligand in **14** is formed within the coordination sphere by addition of nitrosobiphenyl to a coordinated biphenylylnitrene ligand.

We have shown in this work that organic nitroso reagents rapidly react with $(CO)_5W{=}C(OMe)Ph$ and probably with other Fischer-type carbene complexes as well, and the reaction products are consistent with the metathesis reaction (1a). However, it is clear that nitrene complexes of the type $(CO)_5W{=}NR$ are too unstable to be characterized. Binuclear nitrene complexes should be considerably more stable, and experiments are in progress to prepare such species.

Experimental Section

The complex $(CO)_5W{=}C(OMe)(Ph)$[4] and *o*-nitrosobiphenyl[11] were prepared by the literature procedure. PhNO, $2,4,6\text{-}(Bu^t)_3C_6H_2NO$, $[Bu^tNO]_2$, and *p*-azoxyanisole were purchased from Aldrich Chemical Co. and used as received. All manipulations were performed in standard Schlenk glassware under prepurified N_2 or in a nitrogen-filled drybox with the use of predried solvents. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reaction of 1 with Nitrosobenzene. A 0.5-mL C_6D_6 solution of **1** (0.050 g, 0.11 mmol) was added to a 0.5-mL C_6D_6 solution of PhNO (0.024 g, 0.22 mmol). This gave an immediate darkening of the initial red color, and ^1H NMR analysis showed that the δ 4.08 methoxy resonance of **1** had been completely replaced by the characteristic resonances of methyl benzoate (δ 3.50) and the imidate **3** (δ 3.79). TLC chromatography (SiO_2) also showed the formation of aniline, azobenzene and methyl benzoate, which were identified by their characteristic mass and IR spectra.

Reaction of 1 with $2,4,6\text{-}(Bu^t)_3C_6H_2NO$. This reaction was conducted exactly as described above by using $2,4,6\text{-}(Bu^t)_3C_6H_2NO$ (0.060 g, 0.22 mmol). NMR monitoring showed complete reaction over a period of 4 days. Chromatography of the reaction mixture on a SiO_2 TLC plate with 2:1 hexane/CH_2Cl_2 as eluent gave **6** (18.4 mg, 62%), **7** (6.5 mg, 11%), and **8** (3.4 mg, 5%) which were identified by their characteristic IR, ^1H NMR, and mass spectra. The methyl benzoate product was quantified by NMR integration and was observed by TLC chromatography, but no attempt was made to isolate this volatile liquid in pure form.

6. ^1H NMR ($CDCl_3$): δ 1.24 (s, 9 H), 1.43 (s, 18 H), 2.85 (broad s, 2 H), 7.17 (s, 2 H). IR (KBr): ν_{N-H} = 3516 (m), 3445 (m); ν_{C-H} = 2957 (s), 2803 (s); other bands at 1618 (m), 1510 (m), 1433 (s), 1238 (s) cm^{-1}. *m/z* 261 (M^+), 246 ($M^+ - NH_2$).

7. ^1H NMR ($CDCl_3$): δ 1.32 (s, 36 H), 1.39 (s, 18 H), 3.35 (s, 2 H), 7.22 (s, 2 H), 7.36 (s, 2 H). IR (KBr): ν_{N-H} = 3450 (m); ν_{C-H} = 2960 (s), 2750 (s); other bands at 1510 (m), 1430 (m), 1235 (m) cm^{-1}. *m/z* 520 (M^+), 492, 462, 446.

8. ^1H NMR ($CDCl_3$): δ 1.37 (s, 36 H), 1.55 (s, 18 H), 7.22 (s, 2 H), 7.36 (s, 2 H), 8.18 (s, 2 H). IR (KBr): ν_{C-H} = 2965 (s), 2870 (s); ν_{CO} = 1694 (s); other bands at 1609 (m), 1464 (m), 1383 (m), 1366 (m), 1242 (m) cm^{-1}. *m/z* 491 ($M^+{-}Bu^t$), 435 ($M^+{-}2Bu^t$), 410, 308.

Reaction of 1 with Bu^tNO. A 0.5-mL $CDCl_3$ solution of **1** (0.050 g, 0.113 mmol) was added to $[Bu^tNO]_2$ (0.030 g, 0.167 mmol). The solution was filtered into an NMR tube in the drybox, and the reaction was monitored by ^1H NMR spectroscopy over a 5–day period, during which time the methoxy resonance of **1** diminished and was replaced by that of methyl benzoate, the azoxy compound **9** [δ 1.48 (s, 9 H), 1.29 (s, 9 H)],[12] and $(CO)_5W(Bu^tNO)$ (**10**; δ 1.44). The last complex was isolated as a black crystalline solid by −30 °C chromatography on SiO_2 and was spectroscopically and crystallographically characterized.[7]

Reaction of 1 with *o*-Nitrosobiphenyl. This reaction was conducted exactly as described above by using *o*-nitrosobiphenyl (0.040 g, 0.22 mmol) and **1** (0.050 g, 0.11 mmol). NMR monitoring showed that the δ 4.08 methoxy resonance of **1** ceased to decrease in intensity after 18 h (69% conversion). Chromatography of the reaction mixture on a SiO_2 TLC plate eluting with 1:1 hexane/CH_2Cl_2 gave carbazole (**11**; 6.6 mg, 52%), the azo compound **12** (1.7 mg, 6%), the azoxy compound **13** (1.0 mg, 4%), and the azoxy complex **14** (2.2 mg, 4%). The yields given are based on the amount of **1** consumed. The organic products were identified by their characterstic mass, IR, and NMR spectra. The methyl benzoate product was quantified by NMR integration and was observed by TLC chromatography, but no attempt was made to isolate this volatile liquid in pure form.

11. ^1H NMR (acetone-d_6): δ 10.34 (broad s, 1 H), 8.2–7.0 (m). IR (KBr): ν_{N-H} = 3420 (s); ν_{C-H} v 2959 (w), 2926 (w), 2860 (w); other bands at 1450 (m), 1327 (m)8 1290 (m), 1096 (m), 1021 (m) cm^{-1}. *m/z* 167 (M^+), 139, 83.

12. ^1H NMR (acetone-d_6): δ 7.6–6.6 (m). IR (KBr): ν_{C-H} = 2952 (w), 2919 (w), 2840 (w); other bands at 1460 (m), 1426 (m), 1260 (m) cm^{-1}. *m/z* 334 (M^+), 181, 167, 152.

13. ^1H NMR (acetone-d_6): δ 7.6–6.6 (m). IR (KBr): ν_{C-H} = 2952 (w), 2919 (w), 2952 (w); other bands at 1481 (m), 1460 (m), 1426 (m), 1261 (m) cm^{-1}. *m/z* 349 (M^+), 333, 167.

14. Anal. Calcd for **14**$\cdot{}^1/_2$(pentane) (shown by ^1H NMR), $C_{31.5}H_{24}N_2O_6W$: C, 53.33; H, 3.38. Found: C, 53.03; H, 3.79. ^1H NMR (acetone-d_6): δ 8.0–7.0 (m, 16 H), 5.77 (d, 2 H, J_{H-H} = 7.83 Hz), 5.63 (d, 2 H, J_{H-H} = 8.1 Hz). IR (pentane): ν_{CO} = 2068 (w), 1941 (s), 1937 (s), 1923 (m) cm^{-1}. *m/z*(FD) 673 (M^+).

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Supplementary Material Available: For **14**, tables of complete bond lengths and angles, anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H atoms (6 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of H_2 to the A-Frame Complex $[Ir_2(CO)_2(\mu\text{-}S)(Ph_2PCH_2PPh_2)_2]$: A Reinvestigation

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"A-Frame" complexes, such as $[Rh_2(CO)_2(\mu\text{-}S)(DPPM)_2]$,[3] $[Ir_2(CO)_2(\mu\text{-}S)(DPPM)_2]$,[4] $[Rh_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$,[5] and

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