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Reactions of molybdenum and tungsten alkyl and aryl complexes that contain a triamidoamine ligand with carbon monoxide

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Abstract

$[N_3N_F]W(Ph)$ and $[N_3N_F]W(3,5\text{-}Me_2C_6H_3)$ ($[N_3N_F]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) react with one equivalent of CO to yield the η^2 acyl complexes, $[N_3N_F]W(COPh)$ (**1a**), and $[N_3N_F]W(CO\text{-}3,5\text{-}Me_2C_6H_3)$ (**1b**), while $[N_3N]MoMe$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) reacts with CO to give what is believed to be a simple CO adduct, $[N_3N]Mo(CO)Me$, and then with additional CO, a species that has been identified as the dicarbonyl complex, $[N(CH_2CH_2NSiMe_3)_2CH_2CH_2N{=}C(Me)(OSiMe_3)]MO(CO)_2$, in which three equivalents of CO have been incorporated. © 2001 Elsevier Science B.V. All rights reserved.

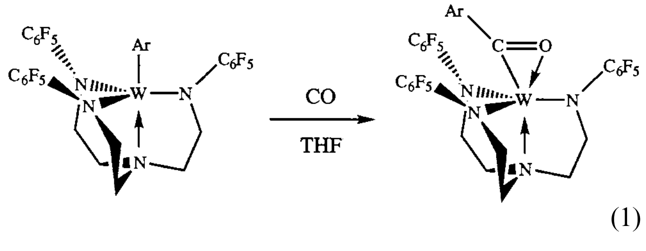
Keywords: Molybdenum; Tungsten alkyl complexes; Tungsten Aryl complexes; Carbon monoxide

1. Introduction

Triamidoamine ligands, $[(RNCH_2CH_2)_3N]^{3-}$, can bind to a variety of transition metals, especially in oxidation states +3 or higher [1,2]. The best known versions currently are those where $R = SiMe_3$ ($[N_3N]^{3-}$) or $R{=}C_6F_5$ ($[N_3N_F]^{3-}$). Such ligands usually bind to a metal in a tetradentate manner, thereby creating a sterically protected, threefold symmetric 'pocket' in which only three orbitals are available to bond to additional ligands in that pocket, two degenerate π orbitals (approximately d_{xz} and d_{yz}) and a σ orbital (approximately d_{z^2}). Recently several papers have appeared that explore the organometallic chemistry of tungsten and molybdenum complexes that contain $[N_3N]^{3-}$ or $[N_3N_F]^{3-}$ ligands [3–5],as well as papers that explore the activation and reduction of dinitrogen [6–8]. In this paper we report some reactions of Mo and W alkyl and aryl complexes that contain $[N_3N]^{3-}$ or $[N_3N_F]^{3-}$ ligands with carbon monoxide. We found reactions that we expected, i.e. acyl formation, but one that was unexpected, one in which a TMS group in a $[N_3N]^{3-}$ ligand became intimately involved in the chemistry.

2. Results

Both $[N_3N_F]W(Ph)^5$ and $[N_3N_F]W(3,5\text{-}Me_2C_6H_3)^5$ react with one equivalent of CO to yield the acyl complexes, $[N_3N_F]W(COPh)$ (**1a**) and $[N_3N_F]W(CO\text{-}3,5\text{-}Me_2C_6H_3)$ (**1b**), as diamagnetic black microcrystalline solids (Eq. (1)). Only one equivalent of carbon monoxide must be employed during the synthesis, since both **1a** and **1b** react further upon exposure to additional CO; the products of reactions involving excess CO could not be identified. IR spectra of **1a** and **1b** display no obvious ν_{CO} absorption that can be assigned to an η^1 acyl ligand, although it could be located



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coincidentally under the strong C_6F_5 absorption at ~ 1510 cm^{-1}. However, the diamagnetism of **1a** and **1b** would appear to rule out the presence of an η^1-acyl ligand and consequently two unpaired electrons in the d_{xz} and d_{yz} orbitals. NMR spectra (^1H, ^{19}F, ^{13}C) show that **1a** and **1b** are C_{3v}-symmetric on the NMR time scale at 22°C and have low-field ^{13}C resonances (256.9 ppm in **1a** and 252.3 ppm in **1b**) consistent with formation of an η^2-acyl ligand. The C_{3v}-symmetry suggests that the η^2-acyl ligand must be able to rotate about the pseudo threefold axis ($W–N_{ax}$) rapidly on the NMR time scale. This type of fluxional process is not uncommon for triamidoamine complexes that have C_s-symmetry in the solid state [1], e.g. $[N_3N]W(H)(CO)$ [9]. One could invoke formation of a η^1 acyl complex as an intermediate in a fluxional process, although that is not necessary.

An X-ray study of **1b** confirmed that the acyl is bound to the metal in an η^2 manner. Table 1 contains the crystallographic data and Table 2 contains selected bond lengths and angles. A drawing of the structure can be found in Fig. 1. The W–O, W–C(40), and C(40)–O distances of 2.177(4), 1.931(7), and 1.296(8) Å, respectively, are more consistent with an alkylidene or oxytungstacyclopropene resonance form, in which the tungsten formally has been oxidized to W(VI), viz.

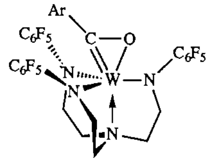


Table 1
Summary of crystal data for **1b** and **3a** [a]

	1b	**3a**
Empirical formula	$C_{34}H_{23}Cl_2F_{15}N_4OW$	$C_{19}H_{42}N_4O_3Si_3Mo$
Formula weight	1043.31	554.78
Temperature (K)	183(2)	188(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	12.32550(10)	18.723(2)
b (Å)	20.6113(5)	9.0802(9)
c (Å)	15.6883(3)	33.390(3)
α (°)	90	90
β (°)	111.4180(10)	93.372(2)
γ (°)	90	90
V (Å^3)	3710.29(12)	5666.8(10)
Z	4	8
ρ_{calc} (mg m^{-3})	1.868	1.301
$F(000)$	2024	2336
Absorption coefficient (mm^{-1})	3.368	0.614
θ range for data collection (°)	1.71–23.26	2.44–20.00
Limiting indices	$-13 \leq h \leq 10$ $-22 \leq k \leq 22$ $-17 \leq l \leq 17$	$-12 \leq h \leq 20$ $-10 \leq k \leq 8$ $-37 \leq l \leq 37$
Reflections collected	14 753	7734
Independent reflections	5314	2606
R_1 (all data) [b]	0.0496	0.0935
wR_2 (all data) [c]	0.0943	0.111
Goodness-of-fit (on F^2)	1.211	1.147

[a] All structures were solved on a Siemens SMART/CCD diffractometer using 0.71069 Å Mo–K_α radiation and ω scans.

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[c] $wR_2 = [(\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, wF_o^2)]^{1/2}$.

Table 2
Selected bond distances (Å) and bond angles (°) in $[N_3N_F]W[C(O)$-3,5-$Me_2C_6H_3]$ (**1b**)

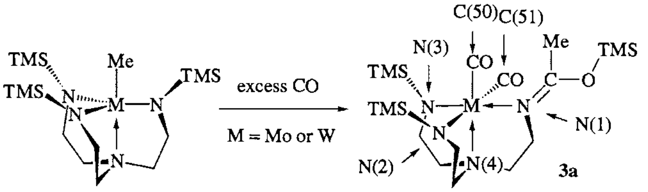
Bond distances			
W–O	2.177(4)	W–C(40)	1.931(7)
W–N(1)	1.988(6)	O–C(40)	1.296(8)
W–N(2)	1.969(6)	C(40)–C(41)	1.464(10)
W–N(3)	1.988(7)	N(1)–C(11)	1.413(9)
W–N(4)	2.227(6)	N(2)–C(21)	1.429(11)
Bond angles			
W–C(40)–O	82.3(4)	N(3)–W–N(1)	117.6(3)
C(40)–W–O	36.2(2)	N(2)–W–N(3)	116.7(3)
C(40)–O–W	61.5(3)	N(2)–W–N(1)	113.1(3)
W–C(40)–C(41)	151.3(5)	N(4)–W–N(3)	79.9(2)
W–N(3)–C(31)	126.6(5)	N(4)–W–N(1)	76.8(2)
W–N(1)–C(11)	125.6(4)	N(3)–W–O	82.0(2)
Dihedral angles [a]			
N(4)–W–N(2)–C(21)	170.5	W–N(1)–C(11)–C(16)	60.0
N(4)–W–N(1)–C(11)	178.0	W–N(2)–C(21)–C(26)	71.4
N(4)–W–N(3)–C(31)	164.0	W–N(3)–C(31)–C(32)	80.0

[a] Obtained from a CHEM 3D drawing.

The xylyl ring lies between two of the three C_6F_5 rings with the shortest distances between carbon atoms in the rings ranging from 3.182 Å (C(42)–C(22)) to 3.497 Å (C(41)–C(11)). There appears to be a stacking interaction between the xylyl ring and the flanking pentafluorophenyl rings, since the N(1)–W–N(2) angle (113.1(3)°) is actually the smallest of the three $N_{eq}–W–N_{eq}$ angles. Attractive interactions between phenyl and perfluorophenyl rings have been shown to lead to π–π distances in the range of 3.4–3.6 Å [10–12]. Large dihedral angles in **1b** ($N(4)–W–N_{eq}–C$ = 178.0, 170.5, and 164.0°) suggest that there is little steric crowding in the trigonal coordination pocket. (A decrease in this dihedral angle, which is equivalent to a 'tipping' of the substituent from vertical, is believed to be the first response to a significant degree of steric crowding in the trigonal pocket in triamidoamine molecules of this general type [1,4].) The $W–N_{eq}$ and W–N(4) distances are also in the range normally observed for triamidoamine complexes.

The reaction between $[N_3N]MoMe$ and excess carbon monoxide at 0°C produces a rust-colored product (**2**) in high yield that contains one equivalent of carbon monoxide. NMR spectra reveal that **2** is a diamagnetic C_3-symmetric species (on the NMR time scale). A broad carbonyl carbon resonance is found at 245.7 ppm, while a strong ν_{CO} stretch is found at 1728 cm^{-1}. These data are similar to those found for crystallographically characterized [N_3N]W(H)(CO) (209 ppm, 1760 cm^{-1}) [9] and contrast with those for an η^2-acyl complex analogous to **1a** and **1b**. Therefore it seems most likely that **2** is simply a CO adduct, [N_3N]Mo(Me)(CO) and that migration of the methyl group to the carbonyl is either slow, or readily reversible with the equilibrium lying on the side of [N_3N]Mo(Me)(CO). However, we cannot entirely exclude the possibility that an η^1 acetyl is present in **2**. Reactions between [N_3N]MoMe and one equivalent of CO at 22°C led to mixtures containing [N_3N]MoMe (**2**), and a compound in which three equivalents of CO have been incorporated, **3a** (see below and Eq. (2)). Although further reaction of **2** with CO takes place at room temperature (see below), at 0°C reaction between **2** and more than one CO must be relatively slow.

If three equivalents or more of CO are added to [N_3N]WMe at 0°C, then a compound is obtained in which three equivalents of CO have been incorporated, **3b** (see below). If only one equivalent of CO is added to [N_3N]WMe at 0°C, and the reaction is warmed to room temperature, proton NMR spectra reveal the presence of at least three diamagnetic compounds, one of them being [N_3N]W≡CH formed by α,α-dehydrogenation of [N_3N]WMe ($k \sim 10^{-5}$ s^{-1} at 25°C) [3]. The tendency for [N_3N]WMe to lose dihydrogen to yield [N_3N]W≡CH probably is one of the main reasons why the tungsten analog of **2** cannot be prepared in pure form. Since [N_3N]MoMe is indefinitely stable at room temperature toward α,α-dehydrogenation to give [N_3N]Mo≡CH [4], the reaction between [N_3N]Mo(Me) and CO at 0°C is relatively uncomplicated.



(2)

Addition of excess CO to [N_3N]MMe complexes (M = Mo [4] or W [3]) at 22°C yields purple to blue diamagnetic complexes that have no symmetry. Analytical data suggest that these complexes contain three molecules of carbon monoxide. An X-ray structural study of '[N_3N]MoMe$(CO)_3$' (**3a**; Table 1) revealed that two molecules of carbon monoxide are bound to the metal, while the third has been incorporated to form a trimethylsiloxy-substituted imine (Eq. (2)). A drawing is shown in Fig. 2; selected inter-atomic distances and bond angles are listed in Table 3. The complex has a pseudooctahedral coordination geometry that consists of two equivalents of carbon monoxide and a tren ligand in which an 'acetyl' (C(54), C(53), O(3)) has 'inserted' between the amido nitrogen atom N(1) and Si(1) to give an imine donor. The Mo–N(1) and Mo–N(4) donor bond lengths are virtually identical, as one would expect, since both are two electron donors *trans* to π bonding ligands. The Mo–N(4) distance is typical of complexes that contain the [N_3N]$^{3-}$ ligand [1]. The amido nitrogen (N(2), N(3)) to Mo distances are ~2 Å, which also is charac-

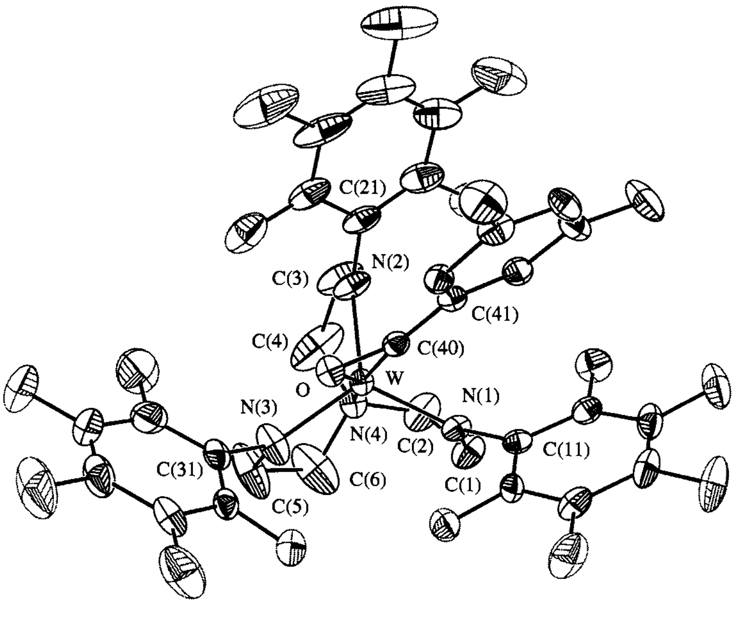


Fig. 1. A view of the structure of [N_3N_F]W[C(O)3,5-$Me_2C_6H_3$] (**1b**) (CH_2Cl_2 removed).

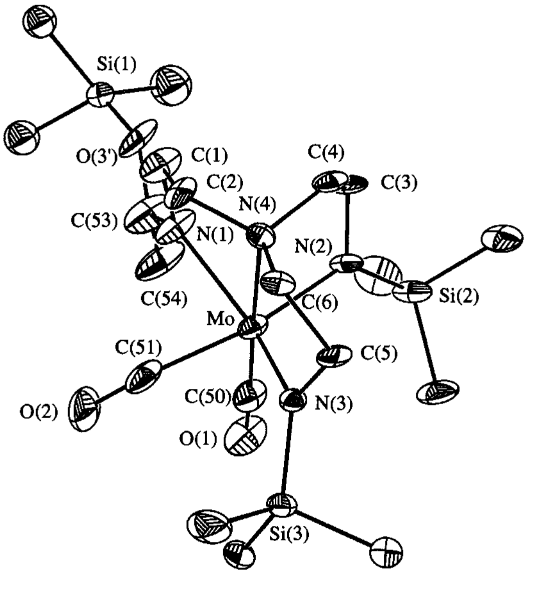


Fig. 2. A view of the structure of [N(CH$_2$CH$_2$)NSiMe$_3$)$_2$-CH$_2$CH$_2$N=C(Me)(OSiMe$_3$)]Mo(CO)$_2$.

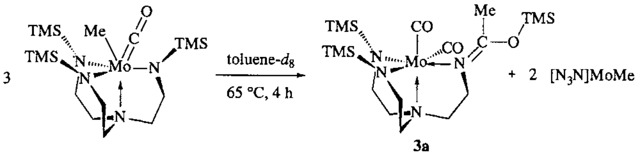
Table 3
Selected distances (Å) and bond angles (°) in [N(CH$_2$CH$_2$NSiMe$_3$)$_2$-CH$_2$CH$_2$N=C(OSiMe$_3$)(Me)]MO(CO)$_2$ (**3a**)

Bond distances			
Mo–N(1)	2.290(7)	Mo–C(51)	2.03(1)
Mo–N(2)	2.060(6)	C(53)–N(1)	1.25(1)
Mo–N(3)	1.987(6)	C(53)–O(3)	1.35(2)
Mo–N(4)	2.289(6)	C(53)–C(54)	1.49(1)
Mo–C(50)	1.90(1)		
Bond angles			
C(50)–Mo–N(1)	106.3(3)	Mo–C(50)–O(1)	177.6(8)
C(50)–Mo–N(3)	99.0(3)	Mo–C(51)–O(2)	172.9(10)
C(50)–Mo–N(2)	99.6(4)	C(51)–Mo–N(4)	106.3(3)
C(50)–Mo–C(51)	75.4(4)	C(51)–Mo–N(2)	164.6(4)
C(50)–Mo–N(4)	178.2(3)	N(1)–C(53)–C(54)	125.2(11)
N(1)–Mo–N(2)	87.7(3)	O(3)–C(53)–N(1)	120.3(12)
N(1)–Mo–N(3)	148.8(3)	C(54)–C(53)–O(3)	112.3(12)
N(1)–Mo–N(4)	74.7(3)	C(53)–O(3)–Si(1)	137.3(13)
N(2)–Mo–N(3)	105.9(3)	Mo–N(2)–Si(2)	126.5(4)
N(2)–Mo–N(4)	78.8(3)	Mo–N(3)–Si(3)	133.9(4)
N(3)–Mo–N(4)	80.6(2)	Mo–N(1)–C(53)	130.7(7)

teristic of metal–amido distances in [N$_3$N]$^{3-}$ complexes that contain a second or third row metal [1]. The Mo–C(51) distance (2.03(1) Å) is significantly longer than the Mo–C(50) distance (1.90(1) Å), most likely as a consequence of competitive π bonding between Mo and N(2).

IR spectra of **3a** reveal terminal CO stretches at 1927 and 1768 cm^{-1} and a ν_{CN} stretch at 1609 cm^{-1}. In **3a**, prepared from [N$_3$N]MoMe and ^{13}CO, these stretches shift to 1883, 1729, and 1574 cm^{-1}. In the ^{13}C-NMR spectrum of the ^{13}C labeled compound the ^{13}C resonances are found at 266.5, 248.1, and 163.9 ppm. The methyl group carbon in the imine (C(54)) is coupled to C(53) ($^1J_{CC}$ = 58 Hz) and C(50) and C(51) are coupled to one another ($^2J_{CC}$ = 11 Hz), all as expected for the structure found in the solid state. IR and NMR data for **3b** are similar to those for **3a**.

When a toluene-d_8 solution of **2** is heated to 65°C in a sealed tube for 4 h, [N$_3$N]Mo(CH$_3$) and **3a** are formed quantitatively in a 2:1 ratio (Eq. (3)). We propose that CO is lost from **2** at 65°C, and the one equivalent of CO reacts with 1/3 of **2** present to form **3a**. These results suggest that an acyl complex can form from **2** and that in the presence of two equivalents of CO the complex is converted into **3a**. It is possible that formation of the acyl complex is induced by coordination of a second equivalent of CO to the metal.



(3)

3. Discussion

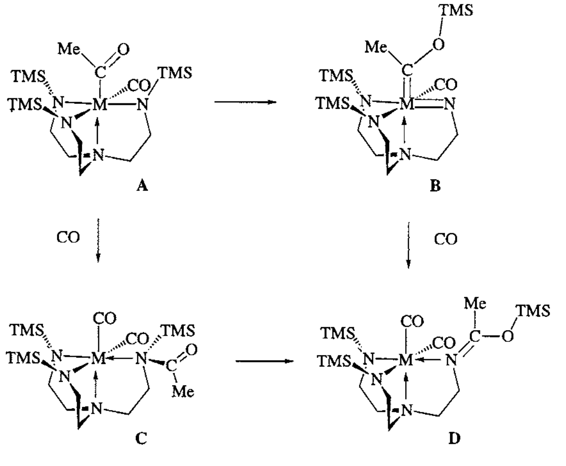
The sequence of reactions that would lead to **3a** and **3b** is clearly complex. At this stage we favor a mechanism in which a second equivalent of CO attacks an acyl complex or causes it to form (**A** in Scheme 1). Strong π bonding between the acyl α carbon atom then leads to silyl migration from N to O to form **B**. One attractive feature of **B** is that imido alkylidene complexes are well-documented for Mo and W, and have been used extensively as olefin metathesis catalysts [13]. However, the manner in which **B** would be converted into **D** is less clear. There is no precedent in the literature that we could find that suggests that alkylidene and imido ligands can be induced to couple in the presence of CO. (Azatantalacyclopropane complexes have been reported in the literature [14], but they are not formed via coupling of carbene and imido fragments.) Coupling of a carbene and an imido ligand is formally a 4-electron reduction of the metal if the carbene is viewed as an alkylidene (a dianion), but only a 2-electron reduction of the metal if the carbene is viewed as a neutral ligand. In contrast there is much precedent for other types of couplings involving two multiply bonded ligands [15,16], some of them induced by coordination of carbon monoxide. Examples are coupling of imido ligands with CO or isonitriles [16–18] coupling of carbyne-like ligands with CO [19–22], or coupling of two carbyne-like ligands [15,23,24]. The coupling observed here is unusual in part because it does *not* involve carbon monoxide, even though CO is present. Coupling of a carbene-like ligand to an imido ligand may also be rare because of the often large substituent on an imido ligand in combination with the presence of a metal–nitrogen triple bond. The 'imido' ligand in **B** not only contains a relatively small substituent, but the imido ligand is held in a 'bent' conformation.

A 'bent' imido ligand that is part of a triamidoamine ligand does have precedent. Decomposition of $[N_3N]W$(cyclopentyl) yields a crystallographically characterized complex (quantitatively) that contains a similar 'bent' ligand, $[(Me_3SiNCH_2CH_2)_2(NCH_2CH_2)$-N]W(1-trimethylsilylcyclopentene) [3]. The latter could be considered a relative of **B**, since an olefin and a carbene ligand bind to a metal in a similar fashion. Although bent imido ligands are somewhat unusual [25,26], they appear to be more common when there is little alternative, i.e. when incorporated into some relatively rigid ligand structure that is sterically protected against bimolecular reactions [3,27,28].

A plausible alternative to the above proposed pathway to obtain **D** is a reductive coupling of an acyl and an amide in the presence of CO to give **C**, which then rearranges to **D** via a 1,3 migration of a TMS group. Coupling of an acyl to an amide is one possible means of forming amides from aryl halides, carbon monoxide, and amines using Group 10 metals as catalysts [29]. The unusual coupling of an alkylidene to an imido ligand thereby could be avoided.

4. Conclusions

We conclude that although many unusual $[N_3N]M$ complexes have been prepared [1], reactions that involve a trimethylsilyl group will continue to lead to complications, even in circumstances that do not involve CO [6]. The C_6F_5 nitrogen substituent may have its own set of problems associated with nucleophilic attack on the C_6F_5 ring, although to our knowledge there are at present no documented cases that illustrate that complication. Therefore we are turning to triamidoamine complexes that contain 'ordinary' aryl groups [30], especially those that are bulky enough to provide a significant degree of steric protection for the 'pocket' in triamidoamine complexes.



Scheme 1.

5. Experimental

5.1. General details

All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox, using standard Schlenk techniques, or on a high vacuum line ($< 10^{-4}$ Torr). Glassware was dried in a 135°C oven overnight. Pentane was washed with HNO_3–H_2SO_4 (5/95 v/v), $NaHCO_3$, H_2O, stored over $CaCl_2$ and then distilled from sodium benzophenone with tetraglyme under nitrogen. Ether and THF were purified by purging with nitrogen and passing through alumina columns [31]. Reagent grade benzene was distilled from sodium benzophenone under nitrogen. Toluene was distilled from molten sodium. Acetonitrile was distilled from P_2O_5. Methylene chloride was distilled from CaH_2. All solvents were stored in the drybox over activated 4 Å molecular sieves. Deuterated solvents were freeze–pump–thaw degassed and vacuum transferred from an appropriate drying agent. $[N_3N]Mo(CH_3)$ [32], $[N_3N]W(CH_3)$ [33], $[N_3N_F]W(Ph)$ [5], and $[N_3N_F]W(3,5\text{-}Me_2C_6H_3)$ [5] were prepared as described in the literature. CO (99.99%) was purchased from Matheson and used directly from the cylinder. ^{13}CO was purchased from Cambridge Isotope Laboratory. ^1H-NMR spectra were recorded at either 250 or 300 MHz at 25°C. ^{13}C- and ^{19}F-NMR spectra were recorded at 75.4 and 282 MHz, respectively. ^1H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced using the solvent peak. ^{19}F-NMR are listed in parts per million downfield of $CFCl_3$ as an external standard. Coupling constants are given in hertz, and routine couplings are not listed. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 2400 CHN analyzer in our own laboratory.

5.2. $[N_3N_F]W[C(O)C_6H_5]$ (**1a**)

A 50 ml round bottomed flask was charged with $[N_3N_F]WPh$ (200 mg, 0.222 mmol), 10 ml THF, and a stir bar. It was fitted with a vacuum adapter and attached to a high vacuum line. The solution was degassed by three freeze–pump–thaw cycles and CO (67 mmHg, 0.22 mmol, ca. one equivalent) was introduced. The reaction was sealed and warmed to room temperature (r.t.). Within minutes the reaction had turned black. After 40 min the volatile components were removed in vacuo and the black residue was dissolved in 4 ml of CH_2Cl_2. Pentane (8 ml) was carefully layered on top of the solution and the mixture was chilled to −40°C for 15 h. The black crystalline product was isolated by decanting off the mother liquor; yield, 166 mg in two crops (81%): ^{1}H-NMR (C_6D_6) δ 6.83 (t, 2, H_{ortho}), 6.62 (d, 2, H_{meta}), 6.20 (t, 1, H_{para}), 3.45 (br s, 6, NCH_2N), 2.37 (br s, 6, NCH_2N); ^{19}F-NMR (C_6D_6) δ −150.7 (s, 6, F_o), −163.6 (t, 3, F_p), −164.9 (t, 6, F_m); ^{13}C{^{1}H}-NMR (C_6D_6) δ 256.9, 131.9, 131.6, 125.9, 53.91.

5.3. *$[N_3N_F]W[C(O)\text{-}3,5\text{-}Me_2C_6H_3]$* (**1b**)

A 50 ml round-bottomed flask was charged with $[N_3N_F]W[3,5\text{-}Me_2C_6H_3]$ (200 mg, 0.215 mmol), 10 ml THF, and a stir bar. The flask was fitted with a vacuum adapter and attached to a vacuum manifold. The solution was degassed at −78°C and CO (60 mmHg, ca. one equivalent (headspace volume estimated to be 47 ml)) was introduced and the flask sealed. The reaction was warmed to r.t. with stirring, and after 5 min at r.t. the volatile components were removed in vacuo. The product was recrystallized by layering a concentrated CH_2Cl_2 solution with pentane; yield, 135 mg in two crops (66%): ^{1}H-NMR (C_6D_6) δ 6.31 (s, 2, H_{ortho}), 6.01 (s, 1, H_{para}), 3.49 (t, 6, NCH_2N), 2.42 (t, 6, NCH_2N), 1.76 (s, 6, $3,5\text{-}C_6H_3\mathit{Me}_2$); ^{19}F-NMR ($C_6D_6$) δ −150.9 (s, 6, F_o), −166.4 (t, 3, F_p), −167.1 (s, 6, F_m); ^{13}C-NMR (C_6D_6) δ 252.3, 145.6, 142.3, 139.2, 135.9, 133.6, 132.6, 130.0, 127.3, 58.2, 54.0, 20.7. Anal. Calc. for $C_{33}H_{21}F_{15}N_4OW$: C, 41.36; H, 2.21; N, 5.85. Found: C, 41.09; H, 2.10; N, 5.75%.

5.4. *$[N_3N]Mo(CO)(CH_3)$* (**2**)

Excess CO (105 ml) was added to a solution of $[N_3N]MoCH_3$ (0.16 g, 0.34 mmol) in ether at 0°C and the solution was stirred at 0°C for 3 h. The color changed from deep red to red–brown. The solvent was removed in vacuo and the remaining solid was extracted into pentane. The solution was filtered through a pad of celite and the filtrate was concentrated in vacuo. The solution was cooled overnight at −35°C to yield 135 mg of rust-colored product; yield, 80%: ^{1}H-NMR (C_6D_6) δ 3.35 (t, 6, $NC\mathit{H}_2CH_2N$), 3.19 (s, 3, $C\mathit{H}_3CO$), 2.26 (t, 6, $NCH_2C\mathit{H}_2N$), 0.31 (s, 27, $Si(C\mathit{H}_3)_3$); ^{13}C-NMR (C_6D_6) δ 245.7 (*C*O), 53.3, 56.3 ($N\mathit{C}H_2CH_2N$), 29.2 ($\mathit{C}H_3CO$), 4.1 ($NSi(\mathit{C}H_3)_3$); IR (Nujol) cm^{-1} 1728 (ν_{CO}). Anal. Calc. for $C_{17}H_{42}N_4MoOSi_3$: C, 40.96; H, 8.43; N, 11.24. Found: C, 41.03; H, 8.97; N, 11.10%.

The ^{13}C labeled complex was prepared similarly employing ^{13}CO.

5.5. *$[N(CH_2CH_2NSiMe_3)_2CH_2CH_2N{=}C(CH_3)(OSiMe_3)]Mo(CO)_2$* (**3a**)

Carbon monoxide (105 ml, 180 Torr) was added to a solution of $[N_3N]MoCH_3$ (0.19, 0.21 mmol) in ether at 25°C. The color changed from deep red to red–brown, and then to blue. After 1 day the solvent was removed from the mixture in vacuo and the blue solid was dissolved in a minimum of ether. The ether solution was cooled to −35°C to yield 70 mg of blue crystals; yield, 60%: ^{1}H-NMR (C_6D_6) δ 3.92 (td, 2, $NC\mathit{H}_2CH_2N$), 3.37 (td, 1, $NC\mathit{H}_2CH_2N$), 3.2 (m, 1, $NC\mathit{H}_2CH_2N$), 3.05 (m, 1, $NC\mathit{H}_2CH_2N$), 2.89 (td, 1, $NC\mathit{H}_2CH_2N$), 2.56 (td, 1, $NC\mathit{H}_2CH_2N$), 2.4 (m, 3, $NC\mathit{H}_2CH_2N$), 2.20 (s, 3, CH_3), 2.05 (m, 1, $NC\mathit{H}_2CH_2N$), 1.64 (td, 1, $NC\mathit{H}_2CH_2N$), 0.55 (s, 9, $NSi(C\mathit{H}_3)_3$), 0.40 (s, 9, $NSi(C\mathit{H}_3)_3$), −0.12 (s, 9, $OSi(C\mathit{H}_3)_3$); ^{13}C-NMR (C_6D_6) δ 266.5 (CO), 248.1 (CO), 163.9 ($CH_3\mathit{C}O$), 65.2, 63.1, 58.7, 58.1, 57.0, and 50.6 ($N\mathit{C}H_2CH_2N$), 25.9 ($\mathit{C}H_3CO$), 3.9, 2.8 ($NSi(CH_3)_3$) and 0.6 ($OSi(CH_3)_3$); IR (Nujol) cm^{-1} 1927 (ν_{CO}), 1769 (ν_{CO}), 1609 (ν_{CN}). Anal. Calc. for $C_{19}H_{42}N_4MoO_3Si_3$: C, 41.15; H, 7.58; N, 10.11. Found: C, 41.27; H, 7.84; N, 10.08%.

The same procedure was used to prepare the ^{13}CO-labeled complex; yield 60%: ^{1}H-NMR (C_6D_6) 2.20 (d, 1, $^2J_{H^{13}C} = 6.8$, CH_3); ^{13}C-NMR (C_6D_6) δ 266.4 and 248.1 (d, $^2J_{^{13}C^{13}C} = 11$, ^{13}CO), 163.9 (CH_3, ^{13}CO), 25.9 (d, $^1J_{C^{13}C} = 58$, $\mathit{C}H_3$, ^{13}CO); IR (Nujol) cm^{-1} 1883 ($\nu_{^{13}CO}$), 1845 ($\nu_{^{13}C^{18}O}$), 1729 ($\nu_{^{13}CO}$), 1696 ($\nu_{^{13}C^{18}O}$), 1574 ($\nu_{^{13}CN}$).

5.6. *$[N(CH_2CH_2NSiMe_3)_2CH_2CH_2N{=}C(CH_3)(OSiMe_3)]W(CO)_2$* (**3b**)

Carbon monoxide (105 ml, 220 Torr) was added to a solution of $[N_3N]WCH_3$ (0.135 g, 0.24 mmol) in ether. The color changed from red to purple. After 1 day the solvent was removed in vacuo and the purple solid was dissolved in a minimum of ether. The solution was cooled to −35°C to yield 70 mg of purple crystals; yield, 50%: ^{1}H-NMR (C_6D_6) δ 4.03 (m, 2, $NC\mathit{H}_2CH_2N$), 3.07 (m, 3, $NC\mathit{H}_2CH_2N$), 2.2–2.61 (m, 6, $NC\mathit{H}_2CH_2N$), 2.30 (s, 3, $C\mathit{H}_3$) 1.75 (td, 1, $NC\mathit{H}_2CH_2N$), 0.54 (s, 9, $NSi(C\mathit{H}_3)_3$), 0.41 (s, 9, $NSi(C\mathit{H}_3)_3$), −0.15 (s, 9, $OSi(C\mathit{H}_3)_3$); ^{13}C-NMR (C_6D_6) δ 273.3, 248.6 (CO), 165.3 (CN), 66.1, 64.7, 59.7, 59.0, 57.7, and 52.3 ($N\mathit{C}H_2CH_2N$), 27.5 ($\mathit{C}H_3CO$), 4.1, 3.2 ($NSi(\mathit{C}H_3)_3$), 0.6 ($OSi(CH_3)_3$); IR (Nujol) cm^{-1} 1907 (ν_{CO}), 1752 (ν_{CO}), 1600 (ν_{CN}). Anal. Calc. for $C_{19}H_{42}N_4O_3Si_3W$: C, 35.51; H, 6.54; N, 8.72. Found: C, 35.37; H, 6.63; N, 8.45%.

5.7. X-ray study of **3a**

A crystal was mounted in oil and placed in a cold stream of nitrogen attached to a Siemens SMART/CCD diffractometer. Unit cell dimensions were obtained from more than 25 reflections that were harvested from three sets of 5° frames scanned about omega. Integration of greater than one-half hemisphere of data using the SAINT program revealed monoclinic Laue symmetry and a C-centered lattice consistent with the unit cell dimensions. Systematic absences indicated $C2/c$ as the space group. Solution (Patterson) and refinement of the structure was performed with SHELXTL set of programs. Crystallographic details are provided in Table 1 and selected interatomic distances and angles in Table 3.

The X-ray study of **1b** was carried out in an analogous manner. One molecule of CH_2Cl_2 was found in the unit cell. It is not shown in Fig. 1.

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References

[1] R.R. Schrock, Acc. Chem. Res. 30 (1997) 9.

[2] J.G. Verkade, Acc. Chem. Res. 26 (1993) 483.

[3] R.R. Schrock, S.W. Seidel, N.C. Mösch-Zanetti, D.A. Dobbs, K.-Y. Shih, W.M. Davis, Organometallics 16 (1997) 5195.

[4] R.R. Schrock, S.W. Seidel, N.C. Mösch-Zanetti, K.-Y. Shih, M.B. O'Donoghue, W.M. Davis, W.M. Reiff, J. Am. Chem. Soc. 119 (1997) 11876.

[5] S.W. Seidel, R.R. Schrock, W.M. Davis, Organometallics 17 (1998) 1058.

[6] M.B. O'Donoghue, W.M. Davis, R.R. Schrock, Inorg. Chem. 37 (1998) 5149.

[7] M.B. O'Donoghue, W.M. Davis, R.R. Schrock, W.M. Reiff, Inorg. Chem. 38 (1999) 243.

[8] M. Kol, R.R. Schrock, R. Kempe, J. Am. Chem. Soc. 116 (1994) 4382.

[9] D.A. Dobbs, R.R. Schrock, W.M. Davis, Inorg. Chim. Acta 263 (1997) 171.

[10] G.W. Coates, A.R. Dunn, L.M. Henling, D.A. Dougherty, R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 36 (1997) 248.

[11] T. Dahl, Acta Chem. Scand. 48 (1994) 95.

[12] J.H. Williams, Acc. Chem. Res. 26 (1993) 593.

[13] J. Feldman, R.R. Schrock, Prog. Inorg. Chem. 39 (1991) 1.

[14] M.V. Galakhov, M. Gómez, G. Jiménez, P. Royo, M.A. Pellinghelli, A. Tiripicchio, Organometallics 14 (1995) 1901.

[15] A. Mayr, C.M. Bastos, Prog. Inorg. Chem. 40 (1992) 1.

[16] S.H. Han, J.S. Song, P.D. Macklin, S.T. Nguyen, G.L. Geoffroy, Organometallics 8 (1989) 2127.

[17] D.S. Glueck, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 111 (1989) 2719.

[18] Y.W. Ge, P.R. Sharp, Inorg. Chem. 31 (1992) 379.

[19] J.D. Protasiewicz, A. Masschlelein, S.J. Lippard, J. Am. Chem. Soc. 115 (1993) 808.

[20] J.D. Protasiewicz, B.S. Bronk, A. Masschelein, S.J. Lippard, Organometallics 13 (1994) 1300.

[21] G.L. Geoffroy, S.L. Bassner, Adv. Organomet. Chem. 28 (1988) 1.

[22] M.R. Churchill, H.J. Wasserman, S.J. Holmes, R.R. Schrock, Organometallics 1 (1982) 766.

[23] Y. Wang, J. Dasilva, A.J.L. Pombeiro, M.A. Pellinghelli, A. Tiripicchio, R.A. Henderson, R.L. Richards, J. Chem. Soc. Dalton Trans. (1995) 1183.

[24] A. Mayr, C.M. Bastos, N. Daubenspeck, G.A. McDermott, Chem. Ber. 125 (1992) 1583.

[25] D.E. Wigley, Prog. Inorg. Chem. 42 (1994) 2239.

[26] B.L. Haymore, E.A. Maatta, R.A.D. Wentworth, J. Am. Chem. Soc. 101 (1979) 2063.

[27] W.A. Herrmann, D.W. Marz, E. Herdtweck, Zeits. Naturforsch. B 46 (1991) 747.

[28] T.I. Gountchev, T.D. Tilley, J. Am. Chem. Soc. 119 (1997) 12831.

[29] Y.-S. Lin, A. Yamamoto, Organometallics 17 (1998) 3466.

[30] G.E. Greco, A.I. Popa, R.R. Schrock, Organometallics 17 (1998) 5591.

[31] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518.

[32] K.-Y. Shih, R.R. Schrock, R. Kempe, J. Am. Chem. Soc. 116 (1994) 8804.

[33] K.-Y. Shih, K. Totland, S.W. Seidel, R.R. Schrock, J. Am. Chem. Soc. 116 (1994) 12103.