Inorg. Chem. **1996,** *35,* 1535−1539 **1535**

Coordinatively and Electronically Unsaturated Tungsten(0) Carbonyl Complexes Stabilized by π-Donating Amido Ligands

Donald J. Darensbourg,* Kevin K. Klausmeyer, and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received August 2, 1995⊗

Novel, coordinatively and electronically unsaturated tungsten tricarbonyl dianions of 2-aminophenol and 1,2-diaminobenzene have been synthesized from the reaction of photogenerated $W(CO)_5THF$ and $[Et_4N][OC_6H_4NH_2]$ with subsequent deprotonation by $[Et_4N][OH]$ accompanied by facile CO dissociation, and the reaction of $W(CO)_5THF$ and 2 equiv of $[Et_4N][NHC_6H_4NH_2]$, respectively. These air-sensitive derivatives have been fully characterized both in solution (ν(CO) and ^{13}C NMR) and in the solid-state (X-ray crystallography). These metal dianions which have formally 16e$^-$ configurations are stabilized by π-donation from the amido groups of the chelating ligands, as evident from short W−N bond distances. Both solution (ν(CO) and ^{13}C NMR) and solid-state (W−N vs W−O bond distances) data on these derivatives indicate the amido ligand to be a better π-donor than the oxo ligand. Complex **2** crystallized in the monoclinic space group $P2_1/n$ with $a = 14.499(5)$ Å, $b = 14.708(5)$ Å, $c = 15.137(4)$ Å, $\beta = 114.13(2)°$, $V = 2946(2)$ Å^3, and $d_{calc} = 1.433$ g/cm^3, for $Z = 4$. Complex **3** crystallized in the triclinic space group $P\bar{1}$ with $a = 11.479(6)$ Å, $b = 11.786(8)$ Å, $c = 13.148(7)$ Å, $\alpha = 102.41(5)°$, $\beta = 91.27(4)°$, $\gamma = 99.96(5)°$, $V = 1708(2)$ Å^3, and $d_{calc} = 1.444$ g/cm^3, for $Z = 2$.

Introduction

Recently we proposed that interactions of bases or appropriate solvents with the amine protons in glycinate tungsten carbonyl complexes are responsible for the enhanced CO lability noted in these anions (eq 1).[1] That is, base-assisted deprotonation of

$$W(CO)_4(O_2CCH_2NHR)^- + {}^{13}CO \rightleftharpoons W({}^{13}CO)_4(O_2CCH_2NHR)^- + {}^{12}CO \quad (1)$$

$$R = H, Me$$

the amine ligand concomitantly affords an amide intermediate which upon CO dissociation is stabilized by π-donation from the amido group to the metal center. This resembles the well-documented conjugate base mechanism for ligand substitution in metal amine complexes.[2−8] As anticipated, on the basis of this mechanistic interpretation of the CO ligand lability, the *N*,*N*-dimethylglycinate derivative did not exhibit similar CO lability.

In order to further investigate this phenomenon, we have begun to examine the CO-substitutional processes associated with tungsten carbonyls which contain deprotonated amine functionalities. Because of the successful synthesis and characterization of group 6 metal carbonyl catecholates[9,10] and benzene-1,2-dithiolates[11,12] we chose to focus initially on the ligands 2-aminophenol and 1,2-diaminobenzene. Both of these ligands when deprotonated at the amine group have been shown to stabilize metal centers, generally low-valent late transition metals or high-valent early transition metals.[13,14] The complex $Mo(PPh_3)_2(CO)_2(NHC_6H_4NH)$, which has molybdenum in a +2 oxidation state, is coordinatively saturated but electronically "formally" unsaturated.[15] This electronic unsaturation can be satisfied by π-donation from the amido ligands.

Herein, we wish to communicate our results on the synthesis and characterization of tungsten carbonyl complexes derived from the dianions of 2-aminophenol and 1,2-diaminobenzene.

Experimental Section

All manipulations were performed on a double-manifold Schlenk line under an atmosphere of argon or in an argon-filled glovebox (Vacuum Atmospheres) at room temperature unless otherwise noted. THF, diethyl ether, and hexane solvents were dried and deoxygenated by distillation from sodium benzophenone dianion under a nitrogen atmosphere. Acetonitrile was dried over CaH_2 and P_2O_5 and freshly distilled from CaH_2. Photolysis experiments were performed using a mercury arc 450-W UV immersion lamp purchased from Ace Glass Co in a 100 mL water-cooled photochemical reaction vessel obtained from ACE Glass Co. Infrared spectra were recorded on a Mattson 6021 FTIR spectrometer with DTGS and MCT detectors. Solution infrared spectra were collected using a 0.01-mm CaF_2 cell. ^{13}C NMR spectra were collected on a Varian Unity 500 spectrometer. ^{13}CO (99% ^{13}C) was purchased from Cambridge Isotope and used as received. $W(CO)_6$ was purchased from Strem Chemicals Inc. and used without further purification. 2-Aminophenol and 1,2-phenylenediamine were purchased from Aldrich Chemicals and used as received. Et_4NOH, 25% w/w in MeOH, was purchased from Sigma Chemical Co. and stored in the glovebox.

⊗ Abstract published in *Advance ACS Abstracts*, February 15, 1996.

(1) Darensbourg, D. J.; Atnip, E. V.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1994**, *33*, 5230.

(2) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley and Sons: New York, 1967.

(3) Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 1.

(4) Garrick, F. J. *Nature (London)* **1937**, *139*, 507.

(5) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.

(6) Gaudin, M. J.; Clark, C. R.; Buckingham, D. A. *Inorg. Chem.* **1986**, *25*, 2569.

(7) Buckingham, D. A.; Marzilli, P. A.; Sargeson, A. M. *Inorg. Chem.* **1969**, *8*, 1595.

(8) Watson, A. A.; Prinsep, M. R.; House, D. A. *Inorg. Chim. Acta* **1986**, *115*, 95.

(9) Darensbourg, D. J.; Klausmeyer, K. K.; Mueller, B. L.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1503.

(10) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1995**, *34*, 4676.

(11) Sellmann, D.; Ludwig, W.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *294*, 199.

(12) Sellmann, D.; Wilke, M.; Knoch, F. *Inorg. Chem.* **1993**, *32*, 2534.

(13) Kang, H.; Liu, S.; Shaikh, S. N.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 920.

(14) Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1990**, 315.

(15) Anillo, A.; Obeso-Rosete, R.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1993**, *453*, 71.

0020-1669/96/1335-1535$12.00/0

Synthesis of [Et_4N][$OC_6H_4NH_2$]. The synthesis of [Et_4N][$OC_6H_4NH_2$] was accomplished by the reaction of $HOC_6H_4NH_2$ with 1 equiv of Et_4NOH (25% w/w in methanol) in a 100 mL Schlenk flask. The reaction mixture was allowed to stir for 20 min, and the methanol was removed by rotary vacuum; the resulting material was redissolved in methanol and again vacuum-dried. This process was repeated several times, and the reaction mixture was then placed under vacuum overnight, leaving a brown solid product.

Synthesis of [Et_4N][$NHC_6H_4NH_2$]. The synthesis of [Et_4N][$NHC_6H_4NH_2$] was accomplished by the reaction of $NH_2C_6H_4NH_2$ with 1 equiv of Et_4NOH (25% w/w in methanol) in a 100 mL Schlenk flask. The reaction mixture was stirred for 20 min and then was placed under vacuum to remove the solvent. After the solvent was removed, more methanol was added and subsequently removed by rotary vacuum to help remove water, similar to the process used to synthesize [Et_4N][$OC_6H_4NH_2$]. Upon exposure to vacuum overnight, a dark gray solid formed in the flask.

Synthesis of [Et_4N][$W(CO)_4OC_6H_4NH_2$] (1). The synthesis of [Et_4N][$W(CO)_4OC_6H_4NH_2$] was accomplished in yields greater than 90% by the addition of $W(CO)_5THF$ (prepared by photolysis of 0.50 g of $W(CO)_6$ in 60 mL of THF for 35 min) to 1 equiv of solid [Et_4N][$OC_6H_4NH_2$] at ambient temperature. The color of the solution turned from the yellow of $W(CO)_5THF$ to orange for **1**. The reaction mixture was allowed to magnetically stir for 2 h. The THF was removed from the reaction mixture by vacuum, leaving a yellow-brown powder. The powder was washed several times with hexane to remove any $W(CO)_6$ present. A solution of this complex can be exposed to ^{13}CO in order to enrich the sample for NMR data collection.

Synthesis of [Et_4N]$_2$[$W(CO)_3OC_6H_4NH$] (2). The complex [Et_4N]$_2$[$W(CO)_3OC_6H_4NH$] can be prepared in nearly quantitative yields by dissolving all of the powder obtained in the preparation of **1** in 35 mL of THF and 15 mL of acetonitrile; to this solution is added dropwise with vigorous stirring 1 equiv of Et_4NOH (25% w/w in methanol diluted with 5 mL THF). The ratio of THF to acetonitrile is important, for if too much acetonitrile is present, the tricarbonyl is too soluble and it is destroyed by the base. On the other hand, some acetonitrile is necessary in order to dissolve the tetracarbonyl. The yield of product depends greatly on how accurately 1 equiv of base is added. *Note: It is very important that the base be added very slowly; otherwise, additional reactions of base with complex* ***1*** *will occur which destroy the complex.* The reaction mixture is allowed to stir for 2 h, and the solvent is removed by vacuum, leaving an orange oil. The oil is washed several times with THF and then diethyl ether, leaving an orange powder.

Synthesis of [Et_4N]$_2$[$W(CO)_3NHC_6H_4NH$]·[$NH_2C_6H_4NH_2$] (3). The complex [Et_4N]$_2$[$W(CO)_3NHC_6H_4NH$]·[$NH_2C_6H_4NH_2$] was synthesized by the reaction of $W(CO)_5THF$ (produced photochemically; 0.50 g of $W(CO)_6$ in 60 mL of THF) and 2 equiv of [Et_4N][$NHC_6H_4NH_2$]. The reaction mixture was allowed to stir for 3 h, and the product, **3**, precipitated from solution as a bright orange powder. This powder was transferred to a frit *via* cannula to remove the mother liquor. The solid was washed on the frit with three 10 mL aliquots of THF. Isolated yield was 0.85 g or 80.9%.

X-ray Crystallography of 2 and 3. Crystal data and details of data collection are given in Table 1. A dark brown block crystal of **2** and an orange block crystal of **3** were mounted on a glass fiber with epoxy cement at room temperature and cooled to 163 K for **2** and 193 K for **3** in a N_2 cold stream. Preliminary examination and data collection were performed on a Rigaku AFC5 X-ray diffractometer for **2** and a Nicolet R3m/V for **3** (Mo Kα $\lambda = 0.710\,73$ Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 24 reflections. ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \leq 2\theta \leq 50.0°$. Three control reflections collected every 150 reflections for **2** and every 97 for **3** showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were applied to 5407 reflections for **2** and 6103 reflections for **3**. A semiempirical absorption correction was applied. A total of 5192 unique reflections for **2** and 6001 for **3** with $|I| \geq 2.0\sigma I$ were used in further calculations. Both structures were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1988)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.0381$, $R_w(F^2) = 0.0856$, and $S = 1.027$ at convergence for **2** and $R = 0.0387$, $R_w(F^2) = 0.0531$, and $S = 0.895$ for **3**. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

Table 1. Crystallographic Data for **2** and **3**

	2	**3**
formula	$C_{25}H_{45}N_3O_4W$	$C_{31}H_{54}N_6O_3W$
fw	635.49	742.65
space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	14.499(5)	11.479(6)
b, Å	14.708(5)	11.786(8)
c, Å	15.137(4)	13.148(7)
α, deg		102.41(5)
β, deg	114.13(2)	91.27(4)
γ, deg		99.96(5)
V, Å^3	2946(2)	1708(2)
Z	4	2
d_{calc}, g/cm^3	1.433	1.444
abs coeff, mm^{-1}	3.952	3.420
λ, Å	0.710 73	0.710 73
T, K	163	193
transm coeff	0.9999−0.7472	0.999−0.860
R,[a] %	3.81	3.87
R_w,[a] %	8.56	5.31
GOF	1.027	0.895

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. [b] $R_w = \{[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]\}^{1/2}$.

Results

Synthesis. The reaction of photogenerated $W(CO)_5THF$ with the monodeprotonated 2-aminophenolate anion from [Et_4N][$OC_6H_4NH_2$] carried out at ambient temperature provided in 90% yield the chelated tetracarbonyl derivative [Et_4N][$W(CO)_4OC_6H_4NH_2$] (**1**). Formation of complex **1** was confirmed by infrared spectroscopy, as evidenced by a four-band pattern in the ν(CO) region, which is consistent with approximate C_{2v} symmetry for a *cis*-disubstituted tetracarbonyl derivative.[16] The related coordinatively unsaturated complex [Et_4N]$_2$[$W(CO)_3OC_6H_4NH$] (**2**) was synthesized by the slow addition of 1 equiv of [Et_4N][OH] in methanol to a THF/CH_3CN solution of **1**. This reaction was clean in that no carbonyl-containing species were produced other than the tricarbonyl tungsten dianion.

The diamido coordinatively unsaturated complex, [Et_4N]$_2$[$W(CO)_3NHC_6H_4NH$] (**3**), was prepared by following the procedure previously employed for synthesizing its catecholate analog.[9,17] That is, $W(CO)_5THF$ (produced photochemically in THF) was reacted with 2 equiv of [Et_4N][$NHC_6H_4NH_2$] over a period of 3 h. The long reaction period was required because of the low solubility of [Et_4N][$NHC_6H_4NH_2$] in THF. However, as the reaction mixture was stirred, the amido ligand was slowly drawn into solution as the reaction occurred. This reaction is presumed to occur in a stepwise fashion with the deprotonated amine functionality first displacing the THF from the metal center. This would then be followed by additional loss of CO due to the strong π-donating ability of the amido species. Loss of CO allows the appended NH_2 ligand to bind to the metal center. Once the amine functionality is chelated to the metal, it reacts with the second equivalent of free ligand and is deprotonated, forming the dianionic species (**3**) and re-forming free 1,2-diaminobenzene.

---

(16) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975.

(17) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 1529.

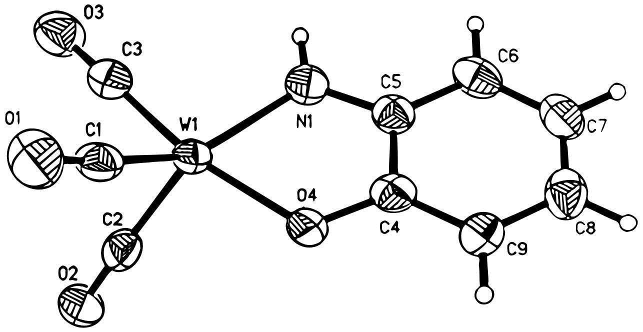

Figure 1. Thermal ellipsoid drawing of the dianion of complex **2** (50% probability) with the atomic numbering scheme.

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for $[Et_4N]_2[W(CO)_3OC_6H_4NH]$, **2**

W(1)−C(1)	1.906(8)	W(1)−C(2)	1.913(7)
W(1)−C(3)	1.937(8)	W(1)−N(1)	2.078(5)
W(1)−O(4)	2.143(5)	O(1)−C(1)	1.179(8)
O(2)−C(2)	1.189(8)	O(3)−C(3)	1.171(9)
O(4)−C(4)	1.333(8)	N(1)−C(5)	1.392(8)
C(1)−W(1)−C(2)	83.3(3)	C(1)−W(1)−C(3)	84.8(3)
C(2)−W(1)−C(3)	87.1(3)	C(1)−W(1)−N(1)	138.6(2)
C(2)−W(1)−N(1)	138.0(3)	(C3)−W(1)−N(1)	96.2(3)
C(1)−W(1)−O(4)	100.5(3)	C(2)−W(1)−O(4)	101.1(2)
C(3)−W(1)−O(4)	170.7(2)	N(1)−W(1)−O(4)	74.7(2)

[a] Estimated standard deviations are given in parentheses.

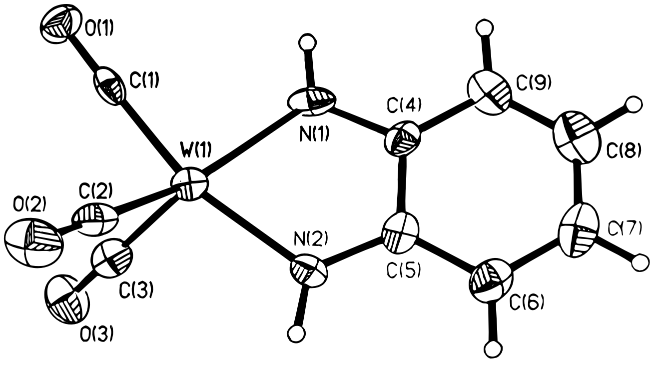

Figure 2. Thermal ellipsoid drawing of the dianion of complex **3** (50% probability) with the atomic numbering scheme.

Table 3. Bond Lengths (Å)[a] and Angles (deg)[a] for $[Et_4N]_2[W((CO)_3HNC_6H_4NH]\ [H_2NC_6H_4NH_2]$, **3**

W(1)−C(2)	1.912(7)	W(1)−C(1)	1.923(6)
W(1)−C(3)	1.942(6)	W(1)−N(1)	2.125(5)
W(1)−N(2)	2.156(5)	O(1)−C(1)	1.222(6)
O(2)−C(2)	1.206(6)	O(3)−C(3)	1.198(6)
N(1)−C(4)	1.418(6)	N(2)−C(5)	1.372(6)
N(3)−C(10)	1.417(6)	N(4)−C(11)	1.418(7)
C(2)−W(1)−C(1)	88.0(2)	C(2)−W(1)−C(3)	82.2(2)
C(1)−W(1)−C(3)	86.5(2)	C(2)−W(1)−N(1)	138.7(2)
C(1)−W(1)−N(1)	93.0(2)	C(3)−W(1)−N(1)	139.0(2)
C(2)−W(1)−N(2)	101.9(2)	C(1)−W(1)−N(2)	166.4(2)
C(3)−W(1)−N(2)	104.0(2)	N(1)−W(1)−N(N2)	73.3(2)
C(4)−N(1)−W(1)	119.2(4)	C(5)−N(2)−W(1)	119.4(4)
O(1)−C(1)−W(1)	178.5(5)	O(2)−C(2)−W(1)	175.8(5)
O(3)−C(3)−W(1)	177.0(5)		

[a] Estimated standard deviations are given in parentheses.

Structures. Crystals of complex **2** were grown from a concentrated acetonitrile solution by slow diffusion of diethyl ether over a period of 2 weeks. Figure 1 shows a drawing of the dianion, and selected bond lengths and angles and are listed in Table 2. The structure of **2** consists of a $W(CO)_3$ fragment chelated by a doubly deprotonated 2-aminophenol ligand. The geometry about the metal center is intermediate between square pyramidal and trigonal bipyramidal, with the most obtuse angle (O4−W1−C3) being 170.7°. The bite angle of the chelating 2-oxidophenylamido is 74.7°, very similar to that noted in the catechol complexes of tungsten we have previously reported.[9,17] The five-membered chelate ring $[WNOC_2]$ is almost planar, with a deviation from planarity of 0.0058 Å. The W−C bond lengths are also similar to those of the catecholate complexes with the average distance being 1.919 Å, the longest of these being the one most *trans* to the oxygen (O4). The C−O bond length of the 2-oxidophenylamido ligand is 1.333 Å, well within that expected for a C−O single bond, and the N−C bond length is 1.392 Å, appropriate for a single bond. Most important for this complex are the W−O and W−N bond lengths. In this complex the W−O distance is 2.143 Å, which is close to that noted for what can be considered a single W−O bond.[9,17,18] The W−N bond length, on the other hand, is much shorter at 2.078 Å, implying that there are additional π-donating interactions of the nitrogen with the tungsten metal center. It is these interactions which are believed to stabilize the unsaturated metal center.

Crystals of complex **3** suitable for an X-ray crystallographic study were grown from a concentrated acetonitrile solution by slow diffusion of diethyl ether. Figure 2 depicts an ORTEP representation of the dianion of **3**, and selected bond lengths and angles are listed in Table 3. The structure of **3** consists of a $W(CO)_3$ fragment chelated by the doubly deprotonated $[NHC_6H_4NH]^{2-}$ ligand. Two tetraethylammonium cations are present to balance the charge on the complex. The geometry about the metal center is between square pyramidal and trigonal bipyramidal, very similar to that noted for complex **2**. The W−N bond lengths are 2.125 and 2.156 Å, somewhat longer than the W−N distance found in **2** but still shorter than that found in neutral amine complexes. For example, the W−N bond distance in $W(CO)_4(O_2CCH_2NH_2)^-$ was determined to be 2.33 Å.[1] The average W−C bond length is 1.93 Å. The bite angle of the chelating ligand is 73.3°, slightly smaller than that observed in the 2-oxidophenylamido and catecholate complexes. The $[WN_2C_2]$ chelate ring is nearly planar, deviating from planarity by only 0.0106 Å.

An additional feature contained within the structural data for complex **3** is the presence in the crystal lattice of 1,2-diaminobenzene. It is notable that when the analogous catecholate complexes are crystallized in the presence of free catechol, the catechol is strongly hydrogen-bonded through the oxygen atoms of the bound catecholate ligand.[9,10] However, in this instance the free 1,2-diaminobenzene is *not* hydrogen-bonded to the diamido ligand, being at least 5 Å from the closest atom associated with the metal dianion complex (see ball-and-stick drawing in the Supporting Information). Important information may be gleaned from a comparison between intraligand bond distances in the bound phenylenediamido ligand and free diaminobenzene (Figure 3). In the free diaminobenzene moiety the N−C bond distances are 1.417(6) and 1.418(7) Å. On the other hand, the chelated phenylenediamido ligand in **3** has N−C bond lengths of 1.418(6) and 1.372(6) Å; i.e., one of the bonds has shortened slightly. Parenthetically it should be noted that the crystal structure of 1,2-diaminobenzene has previously been determined, and the N−C bond lengths were found to be 1.406(2) and 1.408(2) Å, very close to those reported herein.[18] In the coordinatively saturated chelated complex $Mo(NHC_6H_4NH)(PPh_3)_2(CO)_2$, the N−C bond lengths were found to be 1.36(3) and 1.39(3) Å and were suggested to have partial N−C double-bond character.[15] The results presented here for complex **3** are also indicative of double-bond character in

---

(18) Stahandske, C. *Cryst. Struct. Commun.* **1981**, *10*, 1081.

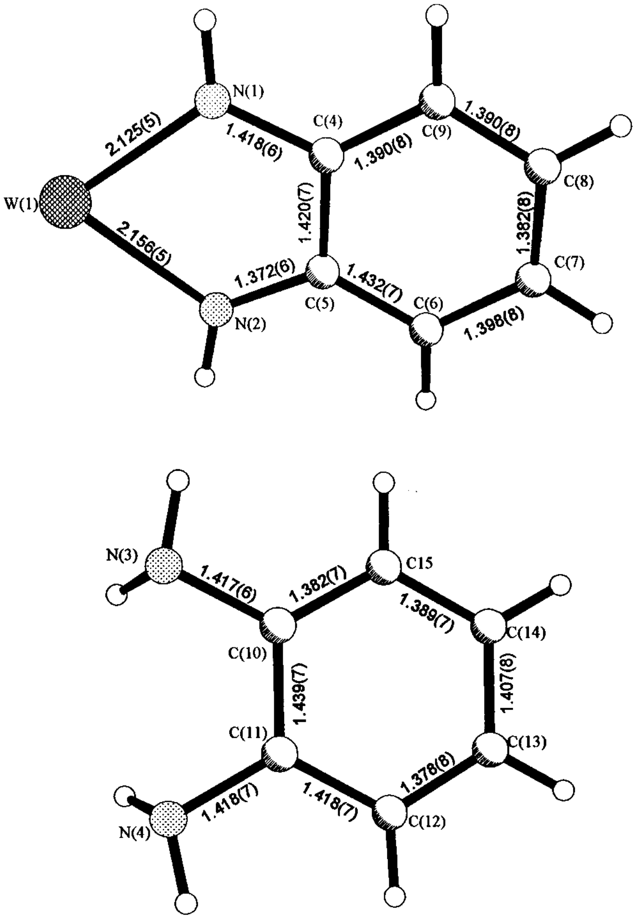

Figure 3. Intraligand bond distances in the bound phenylenediamido ligand and in free diaminobenzene.

the N(2)−C(5) bond (1.372(6) Å) but none in the N(1)−C(4) bond (1.418(6) Å). The nature of the N−W interaction can aid in explaining the asymmetry in the N−C bonds. That is, the W−N(1) bond length of 2.125(5) Å is shorter than the W−N(2) bond length of 2.156(5) Å, suggestive of additional π-donating interactions of N(1) with the metal center.

Spectral Properties. As indicated earlier, complex **1** exhibits a four-band pattern in the carbonyl region of the infrared of the appropriate intensity pattern consistent with a *cis*-disubstituted metal center with ν(CO) bands at 1985 (w), 1848 (s), 1827 (sh), and 1794 (m) cm^{-1}. The ^{13}C NMR spectrum of **1** displays three signals for the carbonyl carbons in an approximate 2:1:1 intensity ratio. An intense resonance for the two carbonyl ligands *cis* to both the nitrogen and the oxygen atoms of the aminophenolate ligand is observed at 206 ppm with satellites due to coupling with the ^{185}W nucleus (J_{C-W} = 132 Hz). The two smaller signals of approximately equal intensity are present at 216 and 217 ppm and are assigned to the carbonyl ligands *trans* to the nitrogen and oxygen donors. The tungsten satellites are weak and overlapping, making accurate determinations of J_{C-W} difficult.

Deprotonation of the amine functionality in complex **1** to afford the coordinatively and electronically deficient complex **2** results in the anticipated change in the ν(CO) infrared spectrum. A two-band pattern of the appropriate intensity ratio consistent with a tricarbonyl complex of *approximately* C_{3v} local symmetry was observed with bands at 1851 (s) and 1714 (vs) cm^{-1}. The ^{13}C NMR spectrum of **2** at ambient temperature exhibits a broad resonance due to quadrupolar coupling to nitrogen centered at 239 ppm. Upon lowering of the temperature to −35 °C, this signal sharpens due to temperature decoupling of the nitrogen quadrupole, and satellites due to coupling with the ^{185}W nucleus (J_{C-W} = 176 Hz) are observed. Hence, the three carbonyl ligands are fluxional at −35 °C in **2**, as has been observed for the catecholate analogs.[9,10,17] This is indicative of a low-energy barrier for intramolecular CO exchange, as is generally noted in five-coordinate metal carbonyl derivatives. In proceeding from **2** (the oxidophenylamido complex) to **3** (the diamido complex), the two ν(CO) vibrational modes decrease in frequency by an average of 10 cm^{-1} to 1839 and 1707 cm^{-1}. Similarly, the broad signal observed in the ^{13}C NMR spectrum for the CO ligands of complex **3** appears downfield from **2** at 241 ppm.[19] A summary of the ν(CO) infrared and ^{13}C carbonyl NMR data in acetonitrile for complexes **1**−**3** is provided in Table 4.

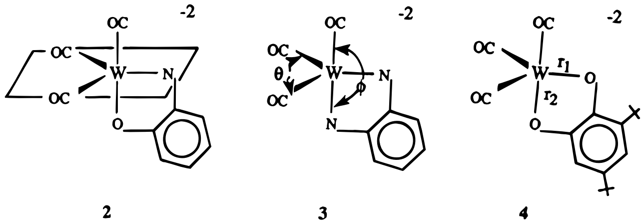

Figure 4. Schematic drawings of complexes **2**−**4** where the dianions are represented ideally as having trigonal bipyramidal geometry.

Table 4. Infrared[a] and 13CO NMR[b] Data for **1**−**3**

complex	ν(CO), cm^{-1}	δ(^{13}CO), ppm
1	1985 (w), 1848 (s), 1827 (m), 1794 (m)	206, 216, 217
2	1851 (s), 1714 (vs)	239
3	1839 (s), 1707 (vs)	241

[a] Spectra determined in CH_3CN. [b] Spectra determined in CD_3CN.

Table 5. Comparative Structural Parameters for Five-Coordinate Tungsten Tricarbonyl Dianions

complex	r_1, Å	r_2, Å	θ, deg	ϕ, deg	dev from planarity, Å
2	2.078(5)	2.143(5)	83.3(3)	170.7(2)	0.005
3	2.125(5)	2.156(5)	82.2(2)	166.4(2)	0.003
4[a]	2.059(6)	2.154(6)	85.6(6)	166.7(3)	0.026

[a] Taken from refs 9 and 17.

Discussion

The schematic drawings of the three closely related tungsten tricarbonyl dianions, which are coordinatively and electronically unsaturated, are provided in Figure 4, where their geometries are represented simplistically as trigonal bipyramidal. The structural parameters, which are defined in Figure 4 and summarized in Table 5, indicate the significant distortions from ideal TBP geometry observed. The π-donor ligand in the trigonal plane, which contains as well the metal center and two carbonyl ligands, has the shorter metal−ligand distances of the two chelating linkages. That is, $r_1 < r_2$ in each instance with Δr = 0.065 Å for **2**, 0.031 Å for **3**, and 0.095 Å for **4** (the $W(CO)_3DTBCat^{2-}$ anion). Furthermore, it is apparent from these data and structural data elsewhere[10−12] that when the chelating ligand is symmetric, i.e., an unsubstituted catecholate, benzene-1,2-dithiolate, or 1,2-benzenediamidate, Δr is small, indicative of a more equal sharing of π-donation by the coordinating groups of the chelated ligand. Nevertheless, in all instances thus far structurally investigated, when there is a

---

(19) Because of the instability of complex **3** in the presence of a CO atmosphere, it was not possible to enrich this complex with ^{13}CO by a simple ligand exchange process. Hence, we do not have quality ^{13}C NMR data for this particular derivative.

difference in the π-donor properties of the coordinating groups of the chelated ligand, the ligand in the equatorial site is the better π-donor.

Consistent with the expectation that the amido group is a better π-donor than the phenolate group, $W(CO)_3(NHC_6H_4NH)^{2-}$ is stable relative to its tetracarbonyl analog whereas $W(CO)_3(O_2C_6H_4)^{2-}$ is not. It is only when the catecholate possesses electron-releasing substituents that the tricarbonyl derivative/carbon monoxide system is thermodynamically more stable than the tetracarbonyl species. In addition, upon proceeding from **4** to **2** to **3**, the ν(CO) frequencies decrease systematically, and concomitantly the ^{13}C resonances for the CO ligands shift downfield. These spectral data are in accordance with an increase in electron density at the CO ligand as one proceeds from complex **4** to **2** to **3**.

Preliminary observations involving the reactions of these rather novel oxidophenylamido and diamido derivatives with carbon dioxide indicate that insertion occurs initially at the amido group. Moreover, on the basis of ^{13}C NMR measurements, several species are afforded during the CO_2 insertion process.[20] Work is underway to unravel the details of these carbon dioxide activation processes.

Acknowledgment. Financial support of this research by the National Science Foundation (Grant CHE91-19737) is greatly appreciated.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic thermal parameters, and complete bond lengths and angles for complexes **2** and **3**, a ball-and-stick drawing of complex **3** indicating, in addition to the dianion, the two Et_4N^+ ions and the free diaminobenzene, and an ORTEP drawing with the atomic numbering scheme for the 1,2-diaminobenzene molecule which cocrystallized with complex **3** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

IC950985Z

---

(20) For a definitive mechanistic study of the CO_2 insertion reaction involving metal−amido complexes, see: Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499.