Contribution from the W. R. Kenan, Jr. Laboratory, Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514,
and Contribution No. 735 from the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387

Oxotungsten(IV)-Acetylene Complexes: Synthesis via Intermetal Oxygen Atom Transfer and Nuclear Magnetic Resonance Studies

JOSEPH L. TEMPLETON,*[1a] BENNETT C. WARD,[1a] GRACE J.-J. CHEN,[1b] JOHN W. McDONALD,*[1b] and WILLIAM E. NEWTON[1b]

Received October 10, 1980

The first synthesis of oxotungsten(IV)-acetylene complexes, $OW(R^1C\equiv CR^2)(S_2CNR_2)_2$, has been effected by controlled oxidation of $W(CO)(R^1C\equiv CR^2)(S_2CNR_2)_2$ with the dimeric oxygen atom transfer reagent $Mo_2O_3[S_2P(OEt)_2]_4$. These complexes, including the parent C_2H_2 derivative, are stable toward alkyne dissociation (cf. $OMo(HC_2H)(S_2CNR_2)_2$) and have been characterized by elemental analysis, infrared spectroscopy, and variable-temperature nuclear magnetic resonance techniques. Dynamic NMR studies support the premise that a single molecular process is responsible for coalescence of the acetylenic proton signals and the dithiocarbamate alkyl signals. Neither acetylene rotation nor rotation around the C-N bond of the dithiocarbamate ligands is adequate to account for the experimental observations. A rearrangement of the chelating ligands, perhaps via dissociation of the sulfur trans to oxygen to form a fluxional five-coordinate intermediate, is compatible with the data obtained for $OW(C_2H_2)(S_2CNEt_2)_2$, $OW(C_2H_2)(S_2CNMe_2)_2$, and $OW(PhC_2H)(S_2CNMe_2)_2$.

Introduction

The synthesis and characterization of a number of molybdenum(II)[2,3] and tungsten(II)-acetylene[4,5] complexes of the form $M(CO)(R^1C_2R^2)(S_2CNR_2)_2$ have recently been reported, with the structural, NMR spectral, and reactivity data for these species interpreted in terms of the acetylenes acting as formal four-electron donors toward the metals. For molybdenum, a series of compounds $OMo(R^1C_2R^2)(S_2CNR_2)_2$ is also known[6-9] where an oxo group has been substituted for CO and the metal can be considered Mo(IV). The NMR data for the oxo-acetylene species are quite different from those of the carbonyl-acetylene complexes, suggesting that the acetylenes do not behave as four-electron donors to the oxomolybdenum moiety. All of the above types of complexes were made for $R^1C_2R^2 = C_2H_2$, making them particularly interesting species as only a few mononuclear complexes of unsubstituted acetylene are known.[9]

A natural extension of the above chemistry was the synthesis of the oxotungsten(IV)-acetylene species $OW(R^1C_2R^2)(S_2CNR_2)_2$ so that their chemical and spectral properties could be compared with those of the previously reported complexes. Herein, we report the successful use of the unique atom-transfer reagent $Mo_2O_3[S_2P(OEt)_2]_4$ to prepare these new complexes whose NMR spectra have indeed proven useful in understanding the nature of the tungsten-acetylene bonding. In addition, the temperature dependence of these NMR spectra has been studied and indicates that the fluxional behavior of $OW(R^1C_2R^2)(S_2CNR_2)_2$ is due to a quite different intramolecular process from that of $W(CO)(R^1C_2R^2)(S_2CNR_2)_2$.

Experimental Section

Materials and Methods. All reactions were carried out under an inert atmosphere with use of standard techniques. All solvents were dried over molecular sieves and degassed prior to use. The compounds $Mo_2O_3[S_2P(OEt)_2]_4$, $W(CO)(C_2H_2)(S_2CNR_2)_2$ (R = Me, Et), $W(CO)(PhC_2H)(S_2CNMe_2)_2$, and $Mo(CO)(DTA)(S_2CNEt_2)_2$ (DTA = $MeC_6H_4C(O)C\equiv CC(O)C_6H_4Me$) were prepared as previously described.[3-5,10]

Infrared spectra were recorded on a Beckman IR-20A spectrophotometer, and elemental analyses for CHN were determined with a Perkin-Elmer 240 instrument equipped with a Microjector from Control Equipment Corp. ^1H NMR (100 MHz) and ^{13}C NMR (25.2 MHz) spectra were recorded on a Varian XL-100 spectrometer. ^1H chemical shifts are reported relative to internal 1% HMDS, and ^{13}C chemical shifts are relative to internal 1% Me_4Si. NMR sample temperatures were measured with either a low-temperature thermometer located directly in the probe or with a methanol insert by utilizing the known temperature dependence of the methyl and hydroxyl proton chemical shift difference.

Synthesis of Compounds. $OW(C_2H_2)(S_2CNEt_2)_2$ (1). The complexes $Mo_2O_3[S_2P(OEt)_2]_4$ (0.92 g, 0.94 mmol) and $W(CO)(C_2H_2)(S_2CNEt_2)_2$ (0.50 g, 0.94 mmol) were dissolved in CH_2Cl_2 (60 mL), and the solution was stirred at room temperature for 90 min. The reaction mixture was filtered, the filtrate evaporated to dryness, and the residue triturated with diethyl ether (40 mL). The off-white solid product (0.12 g) was isolated by filtration, washed with diethyl ether, and dried in vacuo. Evaporation of the combined filtrate and washes to ~20 mL gave more product (0.16 g) which was filtered off, washed with hexane, and dried in vacuo. The total yield was 0.28 g (57%). Anal. Calcd for $C_{12}H_{22}N_2OS_4W$: C, 27.6; H, 4.21; N, 5.36. Found: C, 27.7; H, 4.39; N, 5.25.

$OW(C_2H_2)(S_2CNMe_2)_2$ (2). The complexes $Mo_2O_3[S_2P(OEt)_2]_4$ (1.16 g, 1.18 mmol) and $W(CO)(C_2H_2)(S_2CNMe_2)_2$ (0.57 g, 1.19 mmol) were dissolved in CH_2Cl_2 (60 mL), and the solution was stirred in vacuo at room temperature for 90 min. The reaction mixture was filtered, the filtrate evaporated to dryness under vacuum, and the residue triturated with diethyl ether (50 mL). The off-white solid product was isolated by filtration, washed with diethyl ether, and dried in vacuo. The yield was 0.44 g (80%). Anal. Calcd for $C_8H_{14}N_2OS_4W$: C, 20.6; H, 3.00; N, 6.01. Found: C, 20.3; H, 3.02; N, 5.63.

$OW(PhC_2H)(S_2CNMe_2)_2$ (3). The complexes $Mo_2O_3[S_2P(OEt)_2]_4$ (0.885 g, 0.90 mmol) and $W(CO)(PhC_2H)(S_2CNMe_2)_2$ (0.50 g, 0.90 mmol) were dissolved in CH_2Cl_2 (50 mL), and the solution was stirred in vacuo at room temperature for 4 h. The reaction mixture was filtered, the filtrate evaporated to dryness under vacuum, and the residue triturated with diethyl ether. The off-white solid product was isolated by filtration, washed with diethyl ether, and dried in vacuo. The yield was 0.43 g (81%). The analytical data indicate that the complex is best formulated as $OW(C_6H_5C_2H)(S_2CNMe_2)_2 \cdot {}^1/_2CH_2Cl_2$. Anal. Calcd for $C_{14.5}H_{19}N_2ClOS_4W$: C, 29.8; H, 3.25; N, 4.79. Found: C, 30.1; H, 3.21; N, 4.97.
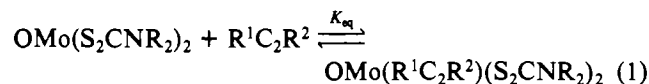
(1) (a) The University of North Carolina. (b) Charles F. Kettering Research Laboratory.
(2) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* **1975**, *97*, 1970.
(3) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25.
(4) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.
(5) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.
(6) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 8640.
(7) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997.
(8) Maatta, E. A.; Wentworth, R. A. D.; Newton, W. E.; McDonald, J. W.; Watt, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 1320.
(9) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 524.
(10) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

OMo(DTA)(S₂CNEt₂)₂ (4). The complexes Mo(CO)-(DTA)(S₂CNEt₂)₂ (0.20 g, 0.293 mmol) and Mo₂O₃[S₂P(OEt)₂]₄ (0.28 g, 0.28 mmol) were dissolved in 30 mL of CH₂Cl₂, and the solution was stirred in vacuo for 1 h. After evaporation of the reaction mixture to dryness under vacuum and trituration of the residue with diethyl ether, the product was obtained as a yellow solid which was isolated by filtration, washed with diethyl ether, and dried in vacuo. The yield was 0.10 g (51%), and the product was identified by comparison of its IR spectrum with that of an authentic sample.[7]

Attempted Preparation of OMo(C₂H₂)(S₂CNEt₂)₂. The solids Mo(CO)(C₂H₂)(S₂CNEt₂)₂ (0.20 g, 0.45 mmol) and Mo₂O₃[S₂P-(OEt)₂]₄ (0.44 g, 0.45 mmol) were dissolved in CH₂Cl₂ (30 mL), and the solution was stirred for 1 h under vacuum. After evaporation of the reaction mixture to dryness and trituration of the residue with diethyl ether, the solid product was isolated by filtration, washed with diethyl ether, and dried in vacuo. The yield was 0.14 g, and the solid was shown by IR spectral comparison to be predominantly OMo-(S₂CNEt₂)₂ contaminated with a small amount of Mo₂O₃(S₂CNEt₂)₄. No evidence for coordinated C₂H₂ was found.

Results and Discussion

Syntheses. The five-coordinate Mo(IV) complexes OMo-(S₂CNR₂)₂ are easily prepared and well characterized for a variety of dialkyldithiocarbamate ligands,[10,11] with a structural study[12] of the complex for R = *n*-Pr showing the species to be square pyramidal in the solid state. In addition to reacting with diazenes,[6] nucleophiles,[13] hydrohalic acids,[14] elemental oxygen[11] and sulfur,[15] and hydrazoic acid,[16] these complexes interact with acetylenes[6–9] (including C₂H₂) according to eq 1. The reaction is an equilibrium with K_{eq} varying over a wide

$$\text{OMo(S}_2\text{CNR}_2)_2 + \text{R}^1\text{C}_2\text{R}^2 \underset{\longleftarrow}{\overset{K_{eq}}{\rightleftharpoons}}$$
$$\text{OMo(R}^1\text{C}_2\text{R}^2)(\text{S}_2\text{CNR}_2)_2 \quad (1)$$

range (from ~20 M⁻¹ for C₂H₂ to ~20 000 M⁻¹ for MeO₂CC≡CCO₂Me) depending on the nature of the substituents R¹ and R². The NMR[7–9] and structural data[7] for these acetylene adducts are consistent with a molybdenum–acetylene bond order of slightly greater than 1.
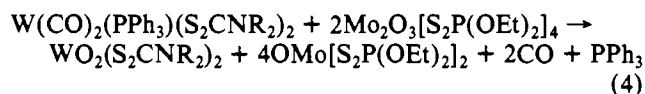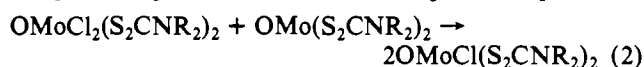
We were interested in preparing the tungsten analogues of these molybdenum–acetylene adducts in order to compare the metal–alkyne bonding in the two systems via NMR spectroscopy studies. Unfortunately, the species OW(S₂CNR₂)₂ are unknown, and all attempts to prepare them in our laboratory have ended in failure. Thus, syntheses of the tungsten–acetylene complexes OW(R¹C₂R²)(S₂CNR₂)₂ via a reaction like that in eq 1 was not possible. Our success utilizing intermetal atom transfer chemistry as a synthetic method[17–19] has, however, led us to an alternative preparative method for these compounds.

(11) Jowitt, R. N.; Mitchell, P. C. H. *J. Chem. Soc. A* **1969**, 2632.

(12) Ricard, L.; Estienne, J.; Karagrannidis, P.; Toledano, P.; Mitchell, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277.

(13) Newton, W. E.; McDonald, J. W.; Watt, G. D., "Proceedings of the Climax 3rd International Conference of the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, Mich., 1979; p 259.

(14) Newton, W. E.; Bravard, D. C.; McDonald, J. W. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 553.

(15) McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1980**, *44*, L81.

(16) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1978**, *17*, 922.

(17) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta*, in press.

(18) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1979**, *35*, 93.

(19) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1976**, *19*, L67.

Table I. Infrared Spectral Data for the Complexes OW(R¹C₂R²)(S₂CNR₂)₂[a]

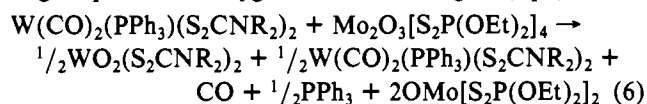| complex	ν		
	W=O	C≡C	C=N
OW(C₂H₂)(S₂CNEt₂)₂ (1)	930 s	1620 m	1500, 1530
OW(C₂H₂)(S₂CNMe₂)₂ (2)	930 s	1615 m	1515, 1550
OW(PhC₂H)(S₂CNMe₂)₂ (3)	930 s	1725 w	1515, 1540

[a] Spectra obtained on KBr pellets; frequencies in cm⁻¹.

Previously, we demonstrated that it was possible to prepare OMoCl(S₂CNR₂)₂,[17] OMoCl(acac)₂,[18] and WO₂(S₂CNR₂)₂[19] utilizing direct atom transfer between two different metal complexes (eq 2–4). The reaction in eq 4 was of particular

$$\text{OMoCl}_2(\text{S}_2\text{CNR}_2)_2 + \text{OMo(S}_2\text{CNR}_2)_2 \rightarrow$$
$$2\text{OMoCl(S}_2\text{CNR}_2)_2 \quad (2)$$

$$\text{MoO}_2(\text{acac})_2 + \text{MoCl}_2(\text{acac})_2 \rightarrow 2\text{OMoCl(acac)}_2 \quad (3)$$

$$\text{W(CO)}_2(\text{PPh}_3)(\text{S}_2\text{CNR}_2)_2 + 2\text{Mo}_2\text{O}_3[\text{S}_2\text{P(OEt)}_2]_4 \rightarrow$$
$$\text{WO}_2(\text{S}_2\text{CNR}_2)_2 + 4\text{OMo[S}_2\text{P(OEt)}_2]_2 + 2\text{CO} + \text{PPh}_3 \quad (4)$$

relevance to the planned synthesis of OW(R¹C₂R²)(S₂CNR₂)₂ because it demonstrated the feasibility of transferring oxygen atoms to W(II) species and suggested that a similar oxidation of the easily prepared, well-characterized complexes[4,5] W-(CO)(R¹C₂R²)(S₂CNR₂)₂ might take place. Indeed, reaction of W(CO)(C₂H₂)(S₂CNMe₂)₂ with 1 equiv of Mo₂O₃[S₂P-(OEt)₂]₄ in CH₂Cl₂ proceeded smoothly to yield the desired species in high yield (eq 5). Preparation of OW-

$$\text{W(CO)(C}_2\text{H}_2)(\text{S}_2\text{CNR}_2)_2 + \text{Mo}_2\text{O}_3[\text{S}_2\text{P(OEt)}_2]_4 \rightarrow$$
$$\text{OW(C}_2\text{H}_2)(\text{S}_2\text{CNR}_2)_2 + 2\text{OMo[S}_2\text{P(OEt)}_2]_2 + \text{CO} \quad (5)$$
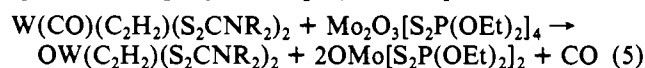
(C₂H₂)(S₂CNEt₂)₂ and OW[PhC₂H)](S₂CNMe₂)₂ was readily accomplished via analogous reactions.

The Mo(V) complex Mo₂O₃[S₂P(OEt)₂]₄ is particularly well suited for its role as an oxygen atom transfer agent since its reduction product OMo[S₂P(OEt)₂]₂ is soluble in diethyl ether, facilitating separation of the metal-containing products. Spectroscopic evidence[20] has indicated that the Mo(V) species dissociates in solution to Mo(IV) and Mo(VI) complexes with the latter postulated to be the actual reactive entity. It should also be noted that oxygen atom transfer from Mo₂O₃[S₂P-(OEt)₂]₄ to the W(CO)(R¹C₂R²)(S₂CNR₂)₂ species is much more rapid than O₂ oxidation as evidenced by the fact that these complexes are relatively air stable, even in solution. The Mo(V) complex can thus be viewed as a source of kinetically activated oxygen atoms with other applications of its reactivity possible in the future.

Infrared spectroscopic data for the three oxotungsten-acetylene complexes are given in Table I. The spectra are characterized by strong bands at 930 cm⁻¹ assigned to the W=O stretch and bands in the 1600–1750-cm⁻¹ region which are due to the C≡C stretch of the coordinated acetylene. The relative positions of these latter bands are consistent with those of the analogous molybdenum species[8,9] in that the C≡C stretching frequency for the phenylacetylene complex is found ~100 cm⁻¹ higher in energy than those for the two acetylene complexes.

The most striking feature of the chemistry of these new complexes is their complete stability toward dissociation of acetylene. This behavior contrasts directly with their molybdenum analogues[7–9] where dissolution of the adducts results in ~50% dissociation into acetylene and OMo(S₂CNR₂)₂ (eq 1). Thus oxidation of Mo(CO)(C₂H₂)(S₂CNR₂)₂ with

(20) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 697.

Table II. ¹H and ¹³C NMR Data for OW(R¹C≡CR²)(S₂CNR₂)₂ Complexes[a]

complex	NMR	δ(≡C–H)	δ(R of ⁻S₂CNR₂)
OW(HC₂H)(S₂CNEt₂)₂ (1)	¹H[b]	10.69 (s, 1), 10.56 (s, 1)	3.90 (q, 6, J = 7, CH₂), 3.56 (q, 2, J = 7, CH₂), 1.38 (t, 9, J = 7, CH₃), 1.12 (t, 3, J = 7, CH₃)
OW(HC₂H)(S₂CNEt₂)₂ (1)	¹³C[c]	154.1, 146.9	46.38 (CH₂), 46.24 (CH₂), 46.13 (CH₂), 44.85 (CH₂), 12.87 (CH₃), 12.54 (CH₃), 12.28 (CH₃), 11.98 (CH₃)
OW(HC₂H)(S₂CNMe₂)₂ (2)	¹H[d]	10.73 (s, 1), 10.56 (s, 1)	3.41 (s, 3, CH₃), 3.38 (s, 3, CH₃), 3.36 (s, 3, CH₃), 3.06 (s, 3, CH₃)
OW(PhC₂H)(S₂CNMe₂)₂ (3)	¹H[e]	10.91 (s, 2), 10.68 (s, 1)	3.43 (s, 3, CH₃), 3.40 (s, 6, CH₃), 3.36 (s, 6, CH₃), 3.35 (s, 9, CH₃), 3.21 (s, 3, CH₃), 3.10 (s, 6, CH₃), 2.93 (s, 3, CH₃)

[a] Chemical shift values are reported in ppm relative to Me₄Si with multiplicity, relative intensity, coupling constants (in Hz), and assignments listed sequentially in parentheses. [b] Spectrum recorded in acetone-d_6 at 2 °C. [c] Spectrum recorded in CH₂Cl₂–CD₂Cl₂–C₆D₆ (75:5:20) at −25 °C. [d] Spectrum recorded in CDCl₃ solvent at −10 °C. [e] Spectrum recorded in CDCl₃ solvent at −38 °C.

Mo₂O₃[S₂P(OEt)₂]₄ followed by a workup procedure which involved evaporation of the reaction mixture under vacuum (thereby removing free C₂H₂ from the solution) yielded only OMo(S₂CNEt₂)₂. A similar oxygen atom transfer to Mo-(CO)(DTA)(S₂CNEt₂)₂ (DTA = MeC₆H₄C(O)C≡CC-(O)C₆H₄Me) did yield OMo(DTA)(S₂CNEt₂)₂. The ability to isolate the DTA complex was due to both the higher value of K_{eq} in eq 1 for this acetylene and the fact that DTA was not removed on evaporation of the reaction mixture.

The large difference in the stability of the M–R¹C₂R² linkage for the molybdenum and tungsten systems is likely due to a greater π donation from R¹C₂R² to tungsten in the OW-(R¹C₂R²)(S₂CNR₂)₂ complexes. It has been postulated that the degree of π donation from acetylene to metal can be estimated from both ¹H[2–4] and ¹³C[21] NMR spectral measurements. This concept and its application to the OM-(R¹C₂R²)(S₂CNR₂)₂ (M = Mo, W) systems will be discussed in the next section. From chemical studies alone, however, it can be concluded that the OW(S₂CNR₂)₂ moiety is extremely reactive toward π-donor ligands. Thus, it has been shown[19] that reaction of W(CO)₂(PPh₃)(S₂CNR₂)₂ with a single equivalent of oxygen atom transfer agent (eq 6) did not

$$W(CO)_2(PPh_3)(S_2CNR_2)_2 + Mo_2O_3[S_2P(OEt)_2]_4 \rightarrow$$
$$^1/_2WO_2(S_2CNR_2)_2 + ^1/_2W(CO)_2(PPh_3)(S_2CNR_2)_2 +$$
$$CO + ^1/_2PPh_3 + 2OMo[S_2P(OEt)_2]_2 \quad (6)$$

yield OW(S₂CNR₂)₂ as expected but instead produced 0.5 equiv of the dioxotungsten(VI) complex. This result was interpreted as indicating that, once formed, the transient species OW(S₂CNR₂)₂ reacted much more rapidly with the oxygen atom transfer agent than did the W(II) species itself. This result and the high stability of the OW-(R¹C₂R²)(S₂CNR₂)₂ complexes described herein imply that the reactivity of the OW(S₂CNR₂)₂ moiety may well prevent its isolation as a monomeric complex.

**Nuclear Magnetic Resonance Studies.** Chemical shift data for OW(R¹C₂R²)(S₂CNR₂)₂ (for **1**, R = Et and R¹ = R² = H; for **2**, R = Me and R¹ = R² H; for **3**, R = Me, R¹ = H, R² = Ph) are reported in Table II (¹H and ¹³C for **1**, ¹H for **2** and **3**). A tabulation of ¹H δ values for acetylenic protons in over 20 molybdenum– and tungsten–alkyne complexes (Table III) supports the suggested qualitative correlation between the electrophilicity of the metal moiety and the observed ¹H chemical shift value.[2–4] The extreme δ values, which differ from one another by more than 6 ppm, are associated with formal 18-electron complexes of the type (π-C₅H₅)₂Mo(η²-alkyne) at the low end (7–8 ppm) and with formal 16-electron Mo(CO)(η²-alkyne)(S₂CNR₂)₂ compounds at the opposite end of the range (12–14 ppm). The intermediate chemical shift region (8–11 ppm) is composed entirely of metal oxo–alkyne derivatives and bis(alkyne) complexes (where each alkyne ligand can reasonably be considered a three-electron donor[3,21]).

Table III. ¹H Chemical Shifts for Acetylenic Protons Bound to Molybdenum and Tungsten

complex	δ(≡C–H)av[a]	ref
(π-C₅H₅)₂Mo(MeC₂H)	7.05	b
(π-C₅H₅)₂Mo(HC₂H)	7.68	c
OMo(S₂CNMe₂)₂(HC₂H)	8.68	9
OMo(S₂CNEt₂)₂(HC₂H)	8.77	8
OMo(S₂CNMe₂)₂(MeO₂CC₂H)	8.78	7
OMo(S₂CNEt₂)₂(PhC₂H)	8.80	9
Mo(S₂CNEt₂)₂(HC₂H)₂	10.15	3
Mo(S₂CNEt₂)₂(PhC₂H)₂	10.45	3
OW(S₂CNEt₂)₂(HC₂H)	10.56	this work
OW(S₂CNMe₂)₂(HC₂H)	10.58	this work
OW(S₂CNMe₂)₂(PhC₂H)	10.77	this work
(η⁵-C₉H₇)W(CO)(Me)(MeC₂H)	11.70	d
(π-C₅H₅)W(CO)(Me)(HC₂H)	12.25	e
(η⁵-C₉H₇)W(CO)(Me)(HC₂H)	12.28	d
Mo(CO)(S₂CNEt₂)₂(HC₂H)	12.30	3
Mo(CO)(S₂P-i-Pr₂)₂(HC₂H)	12.33	2
Mo(CO)(S₂CNEt₂)₂(PhC₂H)	12.6	3
W(CO)(S₂CNEt₂)₂(HC₂H)	13.04	4
W(CO)(S₂CNMe₂)₂(HC₂H)	13.05	5
W(CO)(S₂CNEt₂)₂(PhC₂H)	13.34	5
W(CO)(S₂CNMe₂)₂(PhC₂H)	13.48	5

[a] Relative to Me₄Si at δ 0.00. [b] Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507. [c] Tang Wong, K. L.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694. [d] Alt, H. G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1139. [e] Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349.

The oxygen lone-pair electrons on terminal oxo groups are available for ligand π donation to appropriate metal dπ orbitals. Indeed, the geometry of *cis*-OM(alkyne) moieties determined to date has been adequately rationalized in terms of π donation from both the oxo group and the filled perpendicular π orbital of the alkyne occurring concomitantly with retrodative metal to ligand bonding into the π*-parallel orbital of the coordinated alkyne from the d² metal center.[6–9,22]

d$_{yz}$ (3c–4e)   d$_{xz}$ (2c–2e)

d$_{xy}$ (2c–2e)
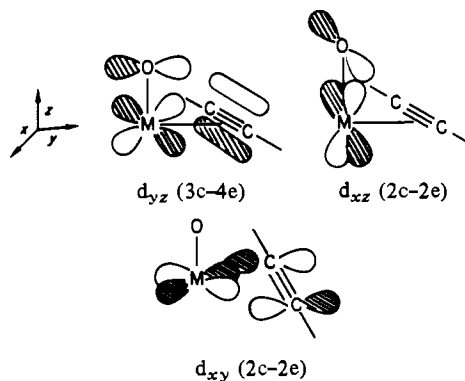
A correlation between ¹³C chemical shifts of alkyne carbons in monomeric molybdenum(II) and tungsten(II) complexes

(21) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(22) (a) Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246. (b) Bokiy, N. G.; Gatilov, Yu. V.; Struchkov, Yu. T.; Ustynyuk, N. A. *J. Organomet. Chem.* **1973**, *54*, 213.

and the extent of electron donation from the alkyne to the metal has been reported.[21] The ^{13}C shifts of 154.1 and 146.9 ppm measured for **1** are indicative of three-electron donation[23] and parallel the proton NMR chemical shift inferences. The data discussed above correlate roughly with a three-electron donor role for the acetylene ligand in **1**. This contrasts with the four-electron donor role of acetylene in the carbonyl complex $W(CO)(HC_2H)(S_2CNR_2)_2$.[4,5,21] Of course both carbon monoxide and atomic oxygen formally provide two electrons to the metal, but only the neutral oxo moiety can furnish additional electron density to the metal by π donation.

The assumption that the Fermi contact term determines the magnitude of $^1J_{CH}$ allows one to estimate the amount of s character in the C–H bond from eq 7.[24] The average value

$$\rho_{C-H} = {}^1J_{^{13}C-H}/500 \text{ Hz} \qquad (7)$$

of 215 Hz observed here for $^1J_{^{13}C-H}$ leads to $\rho = 0.43$ which is consistent with rehybridization of the free acetylene from sp toward sp^2 upon coordination to the metal. This result is similar to that of the $W(CO)(HC_2H)(S_2CNR_2)$ case where a coupling constant of 210 Hz was observed for the bound acetylene. Additional coupling constants of interest include $^2J_{^{183}W-C-H} = 11$ Hz and $^2J_{^{13}C\equiv C-H} = 9.7$ and 12.5 Hz for the low-field and high-field ^{13}C nuclei, respectively.

Four distinct ^1H methyl signals are observed for **2** at low temperature in accord with the anticipated ground-state structure (see A and B).[6-9,22] Three of the resonances are
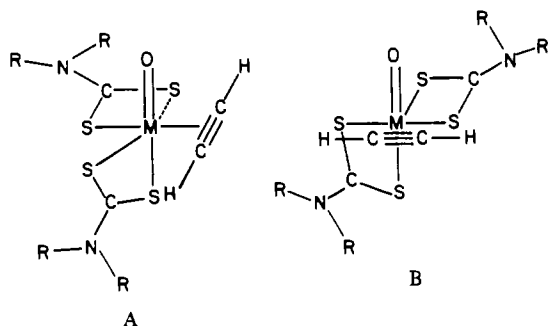
tightly clustered between 3.41 and 3.36 ppm with the remaining resonance at 3.06 ppm.[25] Seven of the eight potential methyl signals expected for the two orientations of $PhC\equiv CH$ in **3** are resolved, and the 2:1 intensity ratio evident for the two isomeric acetylenic protons allows four methyl signals to be assigned to each of the two isomers present on the basis of relative intensities. Both isomers of **3** exhibit three low-field methyl resonances within 0.2 ppm of one another and a remote methyl signal 0.25 ppm or more upfield from the others. Complex **1** exhibits two methylene quartets with a 3:1 intensity ratio and two methyl triplets, also in a 3:1 ratio.[26] Four distinct methylene carbon environments are reflected in the ^{13}C spectrum of **1** with three signals closely packed within a 0.4 ppm range while the fourth is more than 1 ppm further upfield. Likewise, four independent carbon signals are evident for the methyl carbons of the ethyl groups albeit the total spread in chemical shifts is less than 1 ppm.
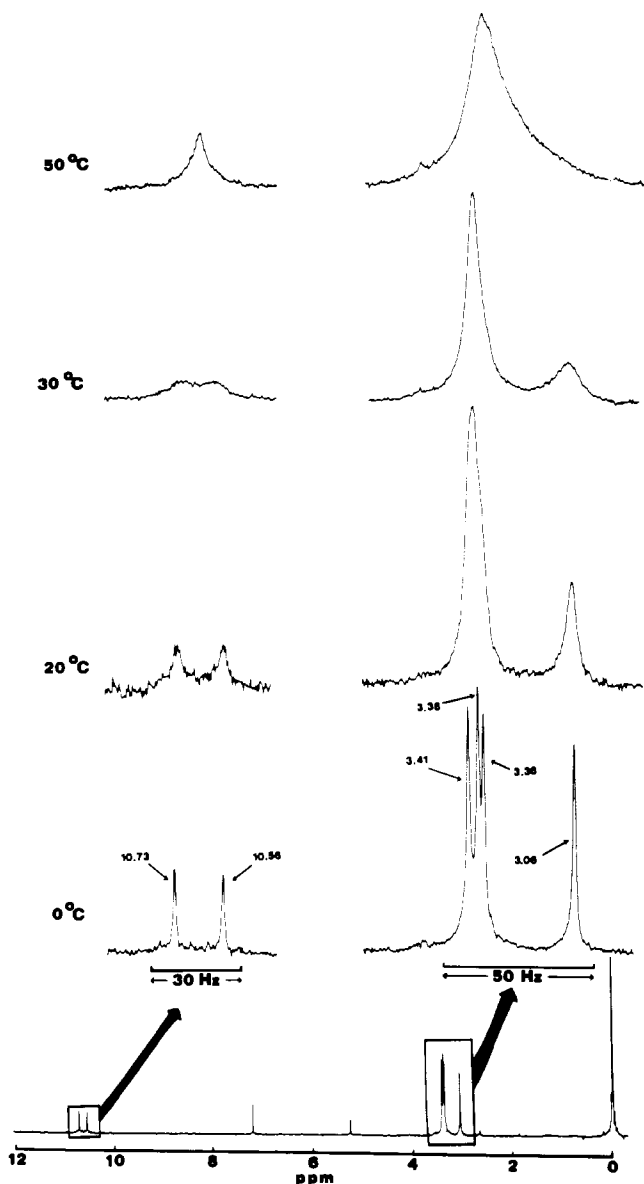

Figure 1. Representative variable-temperature ^1H NMR spectra of **2** over the range 273–323 K which illustrate averaging of the two acetylenic proton signals and the four dithiocarbamate methyl signals, respectively.

All three $OW(R^1C_2R^2)(S_2CNR_2)_2$ complexes which were studied display stereochemical nonrigidity on the NMR time scale. For each compound, two unique acetylenic proton environments are observed at low temperatures prior to the onset of fluxional behavior as the sample is heated. Of equal importance in describing a molecular process responsible for the observed dynamic behavior is the coalescence of the four alkyl resonances which accompanies averaging of the acetylenic protons in each instance (see Figure 1).

Since the alkyl chemical shifts of the dithiocarbamate ligands are independent of any acetylene rotation process, the ^1H NMR data provided two alternative working hypotheses: (i) acetylene rotation and an independent molecular rearrangement of the bidentate ligands occur with very similar activation energies or (ii) a single dynamic process averages the four alkyl groups and both ends of the alkyne ligand simultaneously. Note the contrasting behavior of $W(CO)(HC_2H)(S_2CNR_2)_2$ where the four alkyl signals remain distinct in the high-temperature limit even though acetylene rotation is rapid on the NMR time scale.[5] The unsymmetrical phenylacetylene derivative **3** was selected for study since only one isomer was detected for the analogous carbonyl complex,

(23) Cf. δ_{av} (^{13}C) = 152.0 for $[(\pi\text{-}C_5H_5)W(CO)(RC_2R)_2]^+$ reported by: Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.

(24) Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 218–220.

(25) The unique low-field signal would logically seem to be associated with the methyl group most nearly trans to the oxo ligand while the three proximate methyl signals are tentatively assigned to the methyls lying nearest the pseudo S_3C_2 plane.

(26) The 3:1 ethyl distribution pattern is the same as that observed by Maatta and Wentworth for $OMo(RC_2R)(S_2CNEt_2)_2$ with R = H, Ph, and CH_3CO_2[9] and Newton et al.[7] for a number of complexes of this type.

Table IV. Activation Barriers Calculated for
$OW(S_2CNR_2)_2(R^1C\equiv CR^2)$ Complexes

complex	site probed	T, K	k_{ex},^{a} s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}
$OW(S_2CNEt_2)_2$-	HC≡CH	275	5.2	15.1
(HC_2H) (1)		286	10.8	15.4
		296	31	15.3
		305	34	15.7
		315	50	16.1
		325	142	15.9
				av 15.6 ± 0.5^b
	$S_2CN(CH_2CH_3)_2$	275	2.4	15.6
		286	3.9	16.1
		296	5.7	15.9
				av 15.9 ± 0.3
$OW(S_2CNMe_2)_2$-	HC≡CH	273	0.9	16.0
(HC_2H) (2)		283	3.8	15.8
		293	10.7	15.8
		303	28	15.8
		305	36	15.7
		313	41	16.1
		323	86	16.1
				av 15.9 ± 0.2
	$S_2CN(CH_3)_2$	273	1.6	15.7
		283	4.4	15.7
		293	11.0	15.8
		303	25	15.8
		305	28	15.9
		313	71	15.7
				av 15.8 ± 0.1
$OW(S_2CNMe_2)_2$-	PhC≡CH	278	4.7, 6.6	15.4, 15.2
(PhC_2H) (3)		288	20, 25	15.2, 15.0
		299	29, 38	15.5, 15.4
		309	48	15.8
				av 15.5 ± 0.3, 15.2 ± 0.2
	$S_2CN(CH_3)_2$	278	8.5	15.1
		288	25	15.0
		299	28	15.5
				av 15.2 ± 0.3

^{a} First-order rate constants were calculated as indicated in the text. ^{b} The ± values following $\Delta G^{\ddagger}$ serve only to indicate the range of agreement for determinations at different temperatures and do not represent error limits.

$W(CO)(PhC_2H)(S_2CNR_2)_2$, and no indication of alkyne rotation was observed at temperatures up to 100 °C.[5]

Data obtained from variable-temperature NMR studies of **1**–**3** are compiled in Table IV where $\Delta G^{\ddagger}$ for the acetylenic protons and $\Delta G^{\ddagger}$ as independently determined from the dithiocarbamate alkyl resonances are listed for each complex. A coalescence temperature near 300 K is exhibited by the acetylenic proton-exchange process for both C_2H_2 complexes *and* for the PhC_2H derivative **3**. The free energy of activation was calculated from the Eyring equation after variable-temperature spectra were analyzed as described previously.[27] The complexity of the alkyl region of the spectra where the exchange process involves four sites for **1** and **2** and eight sites for the unsymmetrical alkyne complex **3** prescribed monitoring of the unique methyl or methylene resonance below T_c to determine accurate $\Delta G^{\ddagger}$ values for the alkyl site exchange at as many temperatures as possible. The Gutowsky–Holm approximation remains valid for coalescence of the alkyl signals based on the magnitude of the chemical shift difference between the unique position and the three similar sites.[28] The temperature range over which useful kinetic data could be obtained was not deemed adequate to attempt extraction of accurate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.[29]

A dissociative process involving reversible loss of the alkyne ligand is incompatible with the observed retention of coupling between the metal and the acetylene proton in the fast-exchange limit ($^2J_{^{183}W-C-H}$ = 11 Hz). Neither alkyne rotation relative to the metal nor rotation around the dithiocarbamate C–N bond axis is a sufficient dynamic process to account for the experimental data since a single alkyl resonance would not result in the fast-exchange limit for these processes whether by themselves or in concert with one another. Note that C–N bond rotation in related dithiocarbamate complexes typically exhibits activation energies near 20 kcal mol^{-1}.[30] The two independent determinations of $\Delta G^{\ddagger}$ for the acetylenic protons and methyl signals, respectively, for **2** are within experimental error of one another. This result lends strong support to the premise that the stereochemical nonrigidity of these oxo complexes has its origin in the chelating ligands rather than in the metal–alkyne linkage.

The most definitive experimental evidence in support of the singular role of a dithiocarbamate rearrangement in equilibrating the two ends of the bound alkyne was supplied by **3**. The $\Delta G^{\ddagger}$ value of 15.6 kcal mol^{-1} calculated for averaging the two unsymmetrical alkyne proton signals not only is within experimental error of $\Delta G^{\ddagger}$ for the alkyl groups of **3** but also is nearly the same as the free energies of activation determined for fluxionality of **1** and **2**. We propose that a rearrangement of the chelate ligands occurs which is independent of the metal–alkyne moiety. Since none of the NMR data provides information about acetylene rotation once the two ends of the alkyne have been equilibrated by this extraneous process, only a lower limit for the activation energy of acetylene rotation in **1**–**3** can be deduced from this work.

The primary conclusion of this analysis is that acetylene rotation in $OW(R^1C\equiv CR^2)(S_2CNR_2)_2$ is not implied by our dynamic NMR studies even though coalescence of the two distinct acetylenic proton signals takes place.[31] Given this result, it is then tempting to speculate on what might loosely be termed secondary conclusions by postulating a plausible mechanism for exchange of the alkyl sites. It is important to realize that the data do not establish any irrefutable guidelines in this respect,[32] but the high trans influence of terminal oxo ligands[33] makes a dissociative mechanism involving dechelation of the unique sulfur trans to oxygen to form a fluxional five-coordinate intermediate an attractive possibility. The ground-state trans influence of oxo and related ligands in group 6 dithiocarbamate complexes has been well documented.[34] Distances of 2.4–2.5 Å are typical of M–S bonds cis to oxygen

(27) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211.
(28) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc. Chem. Commun.* **1971**, 656.
(29) Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760.
(30) (a) Davis, R.; Hill, M. N. S.; Holloway, C. E.; Johnson, B. F. G.; Al-Obaidi, K. H. *J. Chem. Soc. A* **1971**, 994. (b) Johnson, B. F. G.; Al-Obaidi, K. H.; McCleverty, J. A. *J. Chem. Soc. A* **1969**, 1668. (c) Dean, W. K. *J. Organomet. Chem.* **1977**, *135*, 195. (d) Hunt, M. M.; Kita, W. G.; Mann, B. E.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1978**, 467. (e) Edgar, B. L.; Duffy, D. J.; Palazzotto, M. C.; Pignolet, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 1125. (f) Duffy, D. J.; Pignolet, L. H. *Inorg. Chem.* **1974**, *13*, 2045. (g) Pignolet, L. H. *Top. Curr. Chem.* **1975**, *56*, 91. (h) Fackler, J. P., Jr.; Lin, I. J. B.; Andrews, J. *Inorg. Chem.* **1977**, *16*, 450. (i) Bhat, A. N.; Fay, R. C.; Lewis, D. F.; Lindmark, A. F.; Strauss, S. H. *Inorg. Chem.* **1974**, *13*, 886. (j) Bruder, A. H.; Fay, R. C.; Lewis, D. F.; Sayler, A. J. *Am. Chem. Soc.* **1976**, *98*, 6932. (k) Bishop, E. O.; Butler, G.; Chatt, J.; Dilworth, J. R., Leigh, G. J.; Orchard, D.; Bishop, M. W. *J. Chem. Soc., Dalton Trans.* **1978**, 1654.
(31) The coalescence of the acetylenic proton signals in the analogous oxo-molybdenum–acetylene complexes has been interpreted in terms of acetylene rotation.[8] However, $\Delta G^{\ddagger}$ measurements were not carried out on these systems, and it would seem possible that a dissociative mechanism, like that postulated herein for the oxotungsten–acetylene complexes, is operative in the molybdenum species as well.
(32) An attempt to unravel the permutational details of the alkyl exchange process with spin-saturation transfer measurements was unsuccessful due to the proximity of the four methyl signals of **2** to one another.
(33) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience Publishers: New York, 1972.
(34) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, 301 and references therein.

while M–S bonds trans to oxo ligands generally fall in the range of 2.6–2.7 Å.[35] Furthermore, the isolation of stable five-coordinate oxomolybdenum(IV)–dithiocarbamate complexes, $OMo(S_2CNR_2)_2$,[10,11] provides literature precedent for the putative $OW(S_2CNR_2)(R^1C_2R^2)(SC(=S)NR_2)$ intermediate. Following formation of the intermediate, the ensuing ligand rearrangement could take place along one of several plausible pathways, the only requirement being that all four alkyl groups on the two bidentate ligands must eventually exchange with one another. The general reticence of octahedral metal complexes to isomerize without bond cleavage,[36] the high trans influence of the oxo ligand, the stability of

five-coordinate group 6 oxo species, and the propensity of five-coordinate complexes to undergo facile intramolecular rearrangements[37] merge to offer a plausible molecular explanation for the dynamic behavior of these complexes in solution.

(35) (a) Ricard, L.; Estienne, J.; Karagiannidis, P.; Toledano, P.; Fischer, J.; Mitschler, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277. (b) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalle, M. *J. Less-Common Met.* **1977**, *54*, 487. (c) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.
(36) (a) Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097. (b) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.
(37) (a) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. (b) Muetterties, E. L. *Acc. Chem. Res.* **1970**, *3*, 266.

Contribution from Naval Biosciences Laboratory, University of California, Berkeley, Oakland, California 94625, the Department of Chemistry, Radford Univeristy, Radford, Virginia 24142, and the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Characterization and Electrochemistry of Manganese(III) Complexes Containing Pentadentate Ligands

W. M. COLEMAN, R. K. BOGGESS, J. W. HUGHES, and L. T. TAYLOR*

Manganese(III) complexes incorporating linear potentially pentadentate Schiff base ligands have been prepared from their manganese(II) precursors. Magnetic susceptibility, visible spectra, and conductivity measurements suggest the manganese(III) ion is in a pseudooctahedral environment. The reduction potentials of the Mn(III)/Mn(II) couple as measured by cyclic voltammetry show a dependence upon the donor atom set as well as an aromatic ring substituent effect. The electrochemistry of complexes containing potential hexadentate ligands is also discussed. Several complexes wherein one of the ligand donor groups may be dangling exhibit a unique ligand oxidative wave.

Introduction

In the last few years, we have been concerned with the reaction of small molecules such as O_2 and NO with manganese complexes which may mimic certain biological processes. One of the most widely studied group of compounds in this regard is the Mn(II) and Mn(III) complexes of Schiff base ligands derived from a substituted salicylaldehyde (ZSAL) and dipropyltriamine (DPT). Differences in chemical reactivity of the Mn(II) compounds toward O_2 have been observed and attributed in part to the Z component on the SAL ring.[1] If Z is an electron-withdrawing group, oxygenation is relatively slow and stops at an O_2:Mn ratio of 0.5. If Z is an electron-donating group, continued oxidation of the complex (presumably the ligand itself) occurs. Reaction of Mn(II) with NO results in a reduction to Mn(I).[2] the resulting reversible NO adducts were found to be most stable with electron-withdrawing substituents on the SAL portion of the Ligand.

Electronic effects no doubt account in part for these reactivity patterns. Manganese(III) complexes of SALDPT and its derivatives have been studied[3] via electrochemical techniques, and it was observed that the Mn(III)/Mn(II) reduction is clearly related to the Z component on the SAL portion of the ligand. Electron-withdrawing groups make the Mn-

(III)/Mn(II) reduction easier while the electron-donating groups make it more difficult. We have now expanded our electrochemical studies to other systems and report some of these results herein.

The pentadentate ligand modifications include the number of carbon atoms in the amine portion of the ligand and substituents on the salicylaldehyde ring (structure I). We have also studied the electrochemistry of four similar complexes previously reported[4] which contain potential hexadentate ligands (structure II).

Experimental Section

Materials. Salicylaldehyde (SAL) was obtained from Fisher Scientific Co. 5-Nitrosalicylaldehyde and 3-nitrosalicylaldehyde were obtained from Eastman Chemical Co. Bis(3-aminopropyl) ether (DAPE) was prepared by a catalytic hydrogenation similar to that reported previously.[5] *N*-(2-Aminoethyl)-1,3-propanediamine (EPT) and *N*-(3-aminopropyl)-1,4-butanediamine were obtained from Aldrich Chemical Co. All other chemicals and solvents were reagent grade or equivalent.

Synthesis of the Complexes. The following is a general method for the preparation of all of the complexes cited here. To a 30-mL

(1) W. M. Coleman and L. T. Taylor, *Inorg. Chem.* **16**, 1114 (1977).
(2) W. M. Coleman and L. T. Taylor, *J. Am. Chem. Soc.*, **100**, 1705 (1978).
(3) W. M. Coleman, R. R. Goehring, L. T. Taylor, J. G. Mason, and R. K. Boggess, *J. Am. Chem. Soc.*, **101**, 2311 (1979).
(4) W. M. Coleman and L. T. Taylor, *J. Inorg. Nucl. Chem.*, **42**, 683 (1980).
(5) M. Israel, J. S. Rosenfield, and E. J. Modest, *J. Med. Chem.*, **7**, 710 (1964).

*To whom correspondence should be addressed at Virginia Polytechnic Institute and State University, Blacksburg, VA.