(14) R. J. Angelici, S. E. Jacobson, and C. M. Ingemanson, *Inorg. Chem.*, **7**, 2466 (1968).
(15) G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, **2**, 479 (1968).
(16) G. R. Dobson, *Inorg. Chem.*, **8**, 90 (1969).
(17) D. R. Powers, G. C. Faber, and G. R. Dobson, *J. Inorg. Nucl. Chem.*, **31**, 2970 (1969).
(18) M. Dokiya, R. D. Johnson, and F. Basolo, *Inorg. Chem.*, **9**, 996 (1970).
(19) G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **4**, 87 (1970).
(20) G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, **6**, 507 (1972).
(21) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 627 (1974).
(22) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 632 (1974).
(23) B. J. McKerley, G. C. Faber, and G. R. Dobson, *Inorg. Chem.*, **14**, 2275 (1975).
(24) G. R. Dobson, private communication.
(25) R. J. Angelici, *Organomet. Chem. Rev.*, **3**, 173 (1968).
(26) W. Hieber and F. Mühlbauer, *Z. Anorg. Allg. Chem.*, **221**, 337 (1935).
(27) M. H. B. Stiddard, *J. Chem. Soc.*, 4713 (1962).
(28) R. B. King, "Organometallic Synthesis", Academic Press, New York, N.Y., 1965, p 122.
(29) J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organomet. Chem.*, **29**, 105 (1971).
(30) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(31) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, New York, N.Y., 1975.
(32) J. H. Schachtschneider, Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.
(33) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85 (1963).
(34) G. Platbrood and L. Wilputte-Steinert, *J. Organomet. Chem.*, **70** 393 (1974).
(35) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Denenberg, *J. Am. Chem. Soc.*, **93**, 2807 (1971).
(36) A. Berry and T. L. Brown, *Inorg. Chem.*, **11**, 1165 (1972).
(37) J. A. Connor, T. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).
(38) J. A. Connor and G. A. Hudson, *J. Organomet. Chem.*, **73**, 351 (1974).
(39) J. A. Connor and P. E. Riley, *J. Organomet. Chem.*, **94**, 55 (1975).
(40) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).
(41) The calculated spectra are essentially insensitive to an increase in the ratio k_c/k_t beyond about 10. This ratio might in fact be (and indeed we believe it is) much larger than this.
(42) It has recently been reported[43] that *fac*-(glyoxal bis(*tert*-butylimine))tricarbonyl(acetonitrile)chromium loses CH_3CN at 20 °C in the presence of ^{13}CO to yield both cis and trans ^{13}CO labeled (glyoxal bis(*tert*-butylimine))tetracarbonylchromium. This suggests that the bidentate nitrogen ligand in this case is nonstereospecific in directing dissociative CO loss. A more likely explanation is that chelate ring opening occurs.
(43) W. Majunke, D. Leikfritz, T. Mack, and H. Dieck, *Chem. Ber.*, **108**, 3025 (1975).
(44) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

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Mononuclear and Binuclear Carbonyl Complexes of Chromium, Molybdenum, and Tungsten with 2,3-Diazabicyclo[2.2.1]hept-2-ene

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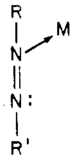
Three series of carbonyl complexes of the group 6B metals with the azo ligand 2,3-diazabicyclo[2.2.1]hept-2-ene, $C_5H_8N_2$ (DBH), have been synthesized. In the compounds *cis*-$(CO)_4M(C_5H_8N_2)_2$ (M = Cr, Mo, W) the azo group is coordinated by only one of the nitrogen lone pairs. Both nitrogen lone pairs are coordinated in the dibridging derivatives $(CO)_4M(C_5H_8N_2)_2M'(CO)_4$ (M, M' = Cr, Mo, W) and in the tribridging $(CO)_3M(C_5H_8N_2)_3M(CO)_3$ (M = Cr, Mo, W). The dibridging compounds include the first examples of mixed-metal azo-bridged complexes. For a given structural type the reactivity is in the order Mo > Cr > W; the stability trend for the three structures is $(CO)_3M(C_5H_8N_2)_3M(CO)_3$ > $(CO)_4M(C_5H_8N_2)_2M(CO)_4$ > *cis*-$(CO)_4M(C_5H_8N_2)_2$. Force constants calculated by the Cotton–Kraihanzel method for *cis*-$(CO)_4M(C_5H_8N_2)_2$ and $(CO)_3M(C_5H_8N_2)_3M(CO)_3$ are interpreted as supporting π-acceptor ability by the azo group in DBH.

Introduction

Organometallic complexes containing a coordinated azo linkage ($-\ddot{N}{=}\ddot{N}-$) have attracted considerable recent attention.[1,2] The two nitrogen lone pairs and the N=N π bond provide for a rich variety of coordination modes for the azo grouping. Four types of complexes have been identified in which the N—N bond remains intact. These involve coordination through one or both nitrogen lone pairs (I, II), coordination through the N=N π bond (III), and coordination through both lone pairs and the π bond simultaneously (IV). Type III coordination, which appears to be the least frequently encountered, is quite sensitive to the nature of the metal center and the identity of other ligands coordinated to it.[1-3] Likewise type IV coordination which retains the N—N σ bond only is limited to systems in which M—M is the $Fe_2(CO)_6$ unit. Coordination types I and II are most widely encountered with examples known for a variety of azo ligands and metal systems. Even diazene, HN=NH, the parent azo compound has been stabilized in type II complexes.[4] Type I and type II complexes may be models for possible metal–diazene intermediates in the biological fixation of nitrogen.[5,6]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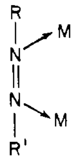
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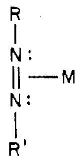
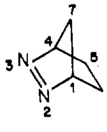

III


IV

At the time we began our work no careful investigation of types I and II coordination with any single metal system had been reported, although a brief report of type I benzo[*c*]cinnoline complexes, $LM(CO)_5$ (M = Cr, Mo, W), appeared shortly thereafter.[7] Hence we initiated such a study focusing on group 6B metal carbonyl compounds with the ligand 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) which had previously been demonstrated to coordinate to metal carbonyl systems.[8,9] We now report on a series of group 6B coordination compounds with DBH involving three different modes of types I and II coordination. Included in this set are the first examples of mixed-metal bridging systems. When this work was nearly complete and a preliminary report was already in press,[10] an independent synthesis of the chromium compounds was reported.[11] However, no previous report of the molybdenum,


DBH

tungsten, or mixed-metal systems has appeared.

Experimental Section

Microanalyses were preformed by Atlantic Microlab, Inc., Atlanta, Ga. Molecular weights were determined by Galbraith Laboratories, Inc., Knoxville, Tenn., by vapor pressure osmometry in dichloromethane. Infrared spectra (Table I) of solutions were recorded on a Perkin-Elmer Model 621 spectrometer. Proton NMR spectra were taken on chloroform-*d* solutions and recorded on a Varian A-60 spectrometer. Melting points were taken in open capillaries or on a Kofler hot-stage microscope and are uncorrected.

A nitrogen atmosphere was employed for carrying out all reactions, for filtration and handling of solutions of organometallic compounds, and for filling evacuated flasks. Solvents for carrying out reactions and for recrystallizations were purged with nitrogen before use. Tetrahydrofuran was redistilled under nitrogen from sodium benzophenone ketyl. Alumina (chromatographic grade F-20) and Florisil for chromatography were used as received from Alcoa Chemicals and Fisher Scientific, respectively. Chromatography was performed on a 2 × 25 cm column that was slurry packed using petroleum ether (bp 30–60 °C). All reaction mixtures were stripped to dryness (~20 mm at 25 °C) prior to chromatography and applied to the column using a minimum amount of dichloromethane. Except as otherwise noted recrystallization was accomplished by dissolving the crude material in a minimum amount of dichloromethane followed by addition of petroleum ether to the cloud point. Crystals were obtained by cooling the solution at −20 or −78 °C.

Materials. 2,3-Diazabicyclo[2.2.1]hept-2-ene ($C_5H_8N_2$) was prepared as reported in the literature.[12] The metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) were purchased commercially and sublimed before use. The metal carbonyl derivatives $C_7H_8M(CO)_4$ (C_7H_8 = norbornadiene; M = Cr,[13] Mo,[13] W[14]) and *fac*-$(CH_3CN)_3M(CO)_3$[15] (M = Mo, W) were prepared by published procedures.

Preparation of $M(CO)_4(C_5H_8N_2)_2$. (1) M = Cr. A mixture of 492 mg (1.92 mmol) of $Cr(CO)_4(C_7H_8)$ and 204 mg (2.1 mmol) of $C_5H_8N_2$ in 25 ml of *n*-hexane was stirred at room temperature. An orange-red solid began to precipitate immediately. After 5 h the product was filtered, washed with hexane, and dried. Recrystallization of the crude material yielded 254 mg (0.71 mmol, 68% yield based on $C_5H_8N_2$) of orange-red $Cr(CO)_4(C_5H_8N_2)_2$, mp 96 °C. Anal. Calcd for $Cr(CO)_4(C_5H_8N_2)_2$: C, 47.19; H, 4.53; N, 15.73; mol wt 356. Found: C, 47.29; H, 4.54; N, 15.79; mol wt 316.

(2) M = Mo. A solution of 300 mg (1.0 mmol) of $Mo(CO)_4(C_7H_8)$ in 30 ml of *n*-hexane was cooled to −30 °C after which 192 mg (2.0 mmol) of $C_5H_8N_2$ was added. After 2 h at −30 °C the bright yellow powder was collected by filtration, washed with a generous amount of cold hexane, and dried. A 79% yield (315 mg, 0.79 mmol) of analytically pure $Mo(CO)_4(C_5H_8N_2)_2$ was obtained; mp ~110 °C dec. Anal. Calcd for $Mo(CO)_4(C_5H_8N_2)_2$: C, 42.01; H, 4.02; N, 14.00. Found: C, 42.18; H, 4.11; N, 14.09.

(3) M = W. The reaction was carried out as for the Cr compound with a reaction time of 22 h. A mixture of 198 mg (0.50 mmol) of $W(CO)_4(C_7H_8)$ and 192 mg (2.0 mmol) of $C_5H_8N_2$ gave a recrystallized yield of 75% (184 mg, 0.38 mmol) of orange crystals, mp 148°. Anal. Calcd for $W(CO)_4(C_5H_8N_2)_2$: C, 34.44; H, 3.31; N, 11.48. Found: C, 34.56; H, 3.36; N, 11.54.

Preparation of $M_2(CO)_8(C_5H_8N_2)_2$. (1) M = Cr. A mixture of 1.28 g (5.0 mmol) of $Cr(CO)_4(C_7H_8)$ and 192 mg (2.0 mmol) of $C_5H_8N_2$ in 30 ml of *n*-hexane was stirred at room temperature for 10 h. Chromatography on Florisil gave first a yellow band of unreacted $Cr(CO)_4(C_7H_8)$ on elution with petroleum ether. Elution with increasing ratios of dichloromethane–petroleum ether developed three product bands: at a 1:3 ratio a brown band of $Cr_2(CO)_8(C_5H_8N_2)_2$ (158 mg, 30% yield), at a 2:3 ratio an orange-red band of $Cr(CO)_4(C_5H_8N_2)_2$ (62 mg, 36% yield), and with pure dichloromethane a purple band of $Cr_2(CO)_6(C_5H_8N_2)_3$ (54 mg, 14% yield). $Cr_2(CO)_8(C_5H_8N_2)_2$ crystallizes as fine, black, iridescent needles with mp ~120 °C dec. Anal. Calcd for $Cr_2(CO)_8(C_5H_8N_2)_2$: C, 41.54; H, 3.11; N, 10.77. Found: C, 41.36; H, 3.15; N, 10.75.

(2) M = Mo. A mixture of 494 mg (1.79 mmol) of $Mo(CO)_4(C_7H_8)$ and 158 mg (1.79 mmol) of $C_5H_8N_2$ in 30 ml of benzene was stirred at room temperature for 1.5 h to give a dark brown solution. Chromatography on Florisil gave a yellow band (apparently $Mo(CO)_5(C_5H_8N_2)$ from its infrared spectrum but too little to isolate) on elution with 1:9 dichloromethane–petroleum ether, followed by a dark brown band of $Mo_2(CO)_8(C_5H_8N_2)_2$ (352 mg, 70% yield) with a 2:3 solvent ratio. Finally 3:1 dichloromethane–petroleum ether eluted a purple-red band which provided a small amount of $Mo_2(CO)_6(C_5H_8N_2)_3$. Recrystallization gave 240 mg (44% yield) of iridescent, dark red-brown needles of $Mo_2(CO)_8(C_5H_8N_2)_2$, mp ~130 °C dec. Anal. Calcd for $Mo_2(CO)_8(C_5H_8N_2)_2$: C, 35.53; H, 2.63; N, 9.21; mol wt 608. Found: C, 35.52; H, 2.64; N, 9.22; mol wt 615.

(3) M = W. A mixture of 1.60 g (4.1 mmol) of $W(CO)_4(C_7H_8)$ and 192 mg (2.0 mmol) of $C_5H_8N_2$ in 30 ml of benzene was stirred at 45 °C for 24 h. Chromatography on Florisil gave first a yellow band of unreacted $W(CO)_4(C_7H_8)$ on elution with petroleum ether. Elution with increasing ratios of dichloromethane–petroleum ether developed three product bands: at a 1:2 ratio a brown band of $W_2(CO)_8(C_5H_8N_2)_2$ (250 mg, 32% yield), at a 2:3 ratio a red band of $W(CO)_4(C_5H_8N_2)_2$ (50 mg, 11%), and with pure dichloromethane a purple band of $W_2(CO)_6(C_5H_8N_2)_3$ (180 mg, 33% yield). $W_2(CO)_8(C_5H_8N_2)_2$ crystallizes as fine, iridescent, very dark green needles, mp ~130 °C dec. Attempts to run this reaction at a lower temperature gave predominantly $W(CO)_4(C_5H_8N_2)_2$, while at higher temperatures excessive amounts of $W_2(CO)_6(C_5H_8N_2)_3$ were formed. Anal. Calcd for $W_2(CO)_8(C_5H_8N_2)_2$: C, 27.57; H, 2.06; N, 7.15. Found: C, 27.72; H, 1.96; N, 7.16.

Preparation of $M_2(CO)_6(C_5H_8N_2)_3$. (1) M = Cr. A mixture of 147 mg (0.89 mmol) of $Cr(CO)_6$ and 254 mg (2.7 mmol) of $C_5H_8N_2$ was refluxed in 30 ml of *n*-heptane for 22 h. The product was filtered, washed with hexane, and dried to give 115 mg (46% yield) of green $Cr_2(CO)_6(C_5H_8N_2)_3$, mp ~190 °C dec. Anal. Calcd for $Cr_2(CO)_6(C_5H_8N_2)_3$: C, 45.00; H, 4.29; N, 15.00. Found: C, 44.76; H, 4.36; N, 14.79.

(2) M = Mo. A mixture of 210 mg (0.78 mmol) of $Mo(CO)_6$ and 221 mg (2.3 mmol) of $C_5H_8N_2$ in 30 ml of *n*-heptane was refluxed for 22 h. After cooling of the mixture to room temperature, the green product was filtered, washed with hexane, and dried. Recrystallization gave a 58% yield (146 mg) of green $Mo_2(CO)_6(C_5H_8N_2)_3$, mp ~240 °C dec. Anal. Calcd for $Mo_2(CO)_6(C_5H_8N_2)_3$: C, 38.89; H, 3.70; N, 12.96. Found: C, 38.85; H, 3.71; N, 12.89.

In an alternative preparation 221 mg (2.3 mmol) of $C_5H_8N_2$ and 0.78 mmol of freshly prepared $Mo(CO)_3(CH_3CN)_3$ were heated in 25 ml of *n*-heptane at 80 °C for 4 h to give a crude yield of 97% (223 mg, 0.35 mmol) of $Mo_2(CO)_6(C_5H_8N_2)_3$.

(3) M = W. A mixture of 473 mg (1.21 mmol) of freshly prepared $W(CO)_3(CH_3CN)_3$ and 350 mg (3.65 mmol) of $C_5H_8N_2$ was refluxed in 30 ml of *n*-hexane for 22 h. Chromatography on alumina gave first a yellow band (the amount was too small to isolate) with petroleum ether, followed by the major purple band on elution with 7:3 dichloromethane–petroleum ether. Recrystallization gave 170 mg (0.21 mmol, 34% yield) of green $W_2(CO)_6(C_5H_8N_2)_3$, mp ~250 °C dec. Anal. Calcd for $W_2(CO)_6(C_5H_8N_2)_3$: C, 30.58; H, 2.91; N, 10.20. Found: C, 30.53; H, 2.93; N, 10.16.

Preparation of $MM'(CO)_8(C_5H_8N_2)_2$. (1) M = Mo, M' = Cr. A mixture of 245 mg (0.70 mmol) of $Cr(CO)_4(C_5H_8N_2)_2$ and 470 mg (1.55 mmol) of $Mo(CO)_4(C_7H_8)$ in 30 ml of benzene was stirred at room temperature for 9 h. Chromatography on Florisil gave first a yellow band of unreacted $Mo(CO)_4(C_7H_8)$. A 2:3 dichloromethane–petroleum ether mixture eluted next a dark brown band of $CrMo(CO)_8(C_5H_8N_2)$ followed by a red-brown band of $Cr_2(CO)_6(C_5H_8N_2)_3$ (35 mg, 15% yield). Recrystallization provided 197 mg (0.35 mmol, 50% yield) of fine, iridescent, dark green needles of $CrMo(CO)_8(C_5H_8N_2)_2$, mp ~110 °C dec. Anal. Calcd for $CrMo(CO)_8(C_5H_8N_2)_2$: C, 38.30; H, 2.84; N, 9.93. Found: C, 38.39; H, 2.87; N, 10.03.

(2) M = Mo, M' = W. A mixture of 350 mg (0.72 mmol) of $W(CO)_4(C_5H_8N_2)_2$ and 430 mg (1.44 mmol) of $Mo(CO)_4(C_7H_8)$ in 30 ml of benzene was stirred at 45–50 °C for 21 h. Workup as for the M = Mo, M' = Cr case gave successive bands of yellow $Mo(CO)_4(C_7H_8)$, dark brown $MoW(CO)_8(C_5H_8N_2)_2$ (304 mg, 61% yield), and with pure dichloromethane red-brown $W_2(CO)_6(C_5H_8N_2)_3$ (89 mg, 30% yield). Recrystallization provided 160 mg (32% yield) of fuzzy, very dark green, iridescent crystals of $MoW(CO)_8(C_5H_8N_2)_2$, mp ~120 °C dec. Attempts to run the reaction at a lower temperature to minimize $W_2(CO)_6(C_5H_8N_2)_3$ formation gave lower conversion to the desired product, e.g., 24% crude yield at room temperature. Anal. Calcd for $MoW(CO)_8(C_5H_8N_2)_2$: C, 31.05; H, 2.32; N, 8.05. Found: C, 30.95; H, 2.23; N, 8.00.

(3) M = Cr, M' = W. Method A. A mixture of 273 mg (0.77 mmol) of $Cr(CO)_4(C_5H_8N_2)_2$ and 596 mg (1.54 mmol) of $W(CO)_4(C_7H_8)$ in 30 ml of benzene was stirred at 40 °C for 21 h.

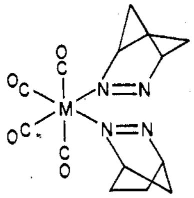
Chromatography on Florisil produced four bands on elution with dichloromethane–petroleum ether in increasing ratios: at a 1:9 ratio yellow $W(CO)_4(C_7H_8)$ (75 mg, 13% recovery), at a 1:3 ratio a brown band of $CrW(CO)_8(C_5H_8N_2)_2$ (259 mg, 52% yield), at a 1:1 ratio a red-brown band of $Cr(CO)_4(C_5H_8N_2)_2$ (32 mg, 12% recovery), and with pure dichloromethane a purple band of $Cr_2(CO)_6(C_5H_8N_2)_3$ (82 mg, 38% yield). Recrystallization gave $CrW(CO)_8(C_5H_8N_2)_2$ as very dark green, iridescent, fine needles, mp ~110 °C dec.

Method B. A mixture of 392 mg (1.54 mmol) of $Cr(CO)_4(C_7H_8)$ and 374 mg (0.77 mmol) of $W(CO)_4(C_5H_8N_2)_2$ in 30 ml of benzene was stirred at 48 °C for 46 h. Chromatography as in method A produced four bands: unreacted yellow $Cr(CO)_4(C_7H_8)$ (78 mg, 20% recovery), a brown band of $CrW(CO)_8(C_5H_8N_2)_2$ (221 mg, 44% yield), a red band of unreacted $W(CO)_4(C_5H_8N_2)_2$ (52 mg, 14% recovery), and a purple band of $W_2(CO)_6(C_5H_8N_2)_3$ (135 mg, 43% yield). Anal. Calcd for $CrW(CO)_8(C_5H_8N_2)_2$: C, 33.15; H, 2.47; N, 8.59. Found: C, 33.40; H, 2.35; N, 8.72.

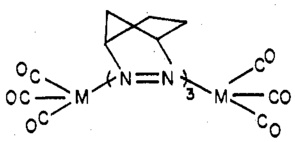
Reaction of $M(CO)_4(C_5H_8N_2)_2$ with $Fe_2(CO)_9$. Equimolar amounts (1–1.5 mmol each) of $Fe_2(CO)_9$ and $M(CO)_4(C_5H_8N_2)_2$ (M = Cr, Mo, or W) in 30 ml benzene were stirred at room temperature until the solid $Fe_2(CO)_9$ had disappeared. Chromatography on Florisil provided an initial band of orange $Fe_2(CO)_6(C_5H_8N_2)$ (~50 mg, identified by its infrared spectrum and melting point[8,9]) followed by the compounds $M_2(CO)_8(C_5H_8N_2)_2$, $M(CO)_4(C_5H_8N_2)_2$, and $M_2(CO)_6(C_5H_8N_2)_3$ in varying amounts. Similar results were obtained with tetrahydrofuran as solvent for M = W run at room temperature and M = Mo run at 0 °C.

Results and Discussion

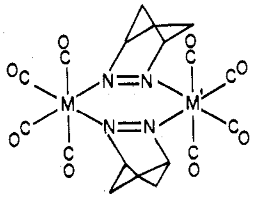
Syntheses and Chemistry. The compounds synthesized in this study are of three types: *cis*-$(CO)_4M(DBH)_2$ (V), $(CO)_3M(DBH)_3M(CO)_3$ (VI), and $(CO)_4M(DBH)_2M'(CO)_4$ (VII) where M, M' = Cr, Mo, W. All are representative of type I or type II coordination in which one or both nitrogen atoms of the DBH azo group serve as two-electron donors.



V



VI



VII

The cis-disubstituted derivatives V (M = Cr, Mo, W) were prepared in high yield from the reaction of excess DBH with the norbornadiene complexes $(C_7H_8)M(CO)_4$ (M = Cr, Mo, W) in *n*-hexane. For M = Cr and W the reactions proceeded satisfactorily at room temperature but with molybdenum the temperature had to be lowered to −25 °C to obtain a pure product. At higher temperatures, even in the presence of excess DBH the type V products are converted to the dibridging complexes VII (M = M') with the relative rates Mo > Cr > W. The chromium and tungsten conversions are slow enough to permit purification by low-temperature recrystallization. Attempts to purify V (M = Mo) were unsatisfactory and invariably resulted in further formation of VII (M = M' = Mo).

The tribridged complexes VI (M = Cr, Mo) were obtained in good yield directly from the metal hexacarbonyls by heating with DBH in *n*-heptane solution. A similar procedure did not work for the tungsten analogue; therefore, it was prepared from the more reactive acetonitrile complex *fac*-$(CH_3CN)_3W(CO)_3$ in refluxing *n*-hexane. This latter method also gave excellent yields of the molybdenum complex.

The dibridged compounds VII (M = M' = Cr, Mo, W) are formed by the reaction of an excess of the norbornadiene complex $(C_7H_8)M(CO)_4$ (M = Cr, Mo, W) with DBH. Since the order of stability appears to be VI > VII > V for the three structural types the temperature was selected to be vigorous enough to cause most of the initially formed V to react further to VII (M = M') without promoting extensive additional conversion to VI. This strategy gives good yields of VII (M = M' = Mo) but only fair yields of the chromium and tungsten analogues. (However, the total yield of V, VI, and VII in any experiment is high.) It seems likely that an even greater excess of $(C_7H_8)M(CO)_4$ will increase the yields of VII (M = M' = Cr, W) but we have not pursued this point.

The ability of the DBH ligand to bridge two equivalent metals as in VI and VII (M = M') suggested that mixed-metal systems might be synthesized starting with V and another reactive metal carbonyl compound. Accordingly the three possible group 6B mixed-metal dibridged compounds VII (M = Cr, M' = Mo, W; M = W, M' = Mo) were obtained from the reaction of V (M = Cr, W) with excess $(C_7H_8)M'(CO)_4$ (M' = Cr, W, Mo; M ≠ M') in benzene at or slightly above room temperature. The compound $(CO)_4Cr(DBH)_2W(CO)_4$ could be prepared conveniently by two routes in equally good yield. However the greater tendency of V (M = Mo) to form only molybdenum-containing bridging species VI and VII (M = M' = Mo) made it less suitable as a precursor. Hence $(CO)_4Cr(DBH)_2Mo(CO)_4$ and $(CO)_4W(DBH)_2Mo(CO)_4$ were synthesized using $(C_7H_8)Mo(CO)_4$ as the source of the $Mo(CO)_4$ moiety.

Spurred by the proposal that diazene may be coordinated simultaneously to both molybdenum and iron during the enzymatic fixation of nitrogen,[5,6] we attempted reactions of V with $Fe_2(CO)_9$ in benzene and tetrahydrofuran at room temperature and below. No evidence for formation of a mixed-metal compound was found. Only the well-known iron complex $Fe_2(CO)_6(DBH)$ and varying amounts of V, VI, and VII (M = M') were obtained. Whether $Fe_2(CO)_6(DBH)$ results from abstraction of coordinated DBH in V by an iron carbonyl species or by reaction of free DBH (formed when V goes to VI and VII) is not known. To date we have not attempted reactions of V with other metal systems. The group 6B compounds VII (M ≠ M') are presently the only known mixed-metal systems bridged by the azo group.

Spectroscopic Properties and Structures. The infrared spectra of the complexes in the carbonyl stretching region are summarized in Table I. The pattern for the $(CO)_4M(DBH)_2$ derivatives is typical of other disubstituted metal carbonyl compounds[17] and confirms a cis geometry. The tribridged compounds VI show only two ν(CO) frequencies similar to the pattern of monometallic octahedral tricarbonyl compounds of the type *fac*-$(CO)_3ML_3$.[17] A local C_{3v} symmetry for each metal is therefore indicated in this bridging system. The symmetric dibridged complexes VII (M = M') show five carbonyl stretching bands. This is in excess of the four bands expected if local C_{2v} symmetry prevailed for two independent and identical cis-substituted tetracarbonyl units and suggests significant interaction between them. The spectra of the mixed-metal analogues (VII, M ≠ M') are so similar to those of the non-mixed-metal systems that one cannot confidently distinguish between them on this basis.

The most useful characteristic in the proton NMR spectra of the DBH complexes is the signal(s) associated with the hydrogen atoms at the 1,4 bridgehead positions (Table I). In the bridging derivatives VI and VII (M = M') these 1,4 hydrogens occur as an apparent singlet. This is consistent with their equilvalence when both nitrogen atoms of the azo ligand are coordinated to identical metal atom centers. In the

Table I. Spectroscopic Data

Compd ($L = C_5H_8N_2$)	Infrared, ν_{CO}, cm^{-1} [a]	Ir solvent	^1H NMR, τ [b,c]
cis-$Cr(CO)_4L_2$	2018 m, 1907 vs, 1890 sh, 1848 s	*d*	4.83, 4.95
	2015 m, 1909 vs, 1870 s	*e*	
cis-$Mo(CO)_4L_2$	2023 m, 1911 vs, 1890 sh, 1849 s	*d*	*f*
	2019 m, 1911 vs, 1873 s	*e*	
cis-$W(CO)_4L_2$	2018 m, 1900 vs, 1885 sh, 1845 s	*d*	4.80, 4.95
	2015 m, 1901 vs, 1873 s	*e*	
$Cr_2(CO)_8L_2$	2035 m, 1998 s, 1940 s, 1910 vs, 1872 s	*d*	4.88
	2031 m, 1996 s, 1945 s, 1921 vs, 1884 s	*e*	
$Mo_2(CO)_8L_2$	2043 m, 2010 s, 1948 s, 1920 vs, 1882 s	*d*	4.89
	2033 m, 2004 s, 1950 s, 1927 vs, 1891 s	*e*	
$W_2(CO)_8L_2$	2141 m, 1996 s, 1938 s, 1910 vs, 1874 s	*d*	4.97
$CrMo(CO)_8L_2$	2035 m, 2006 s, 1940 s, 1912 vs, 1872 s	*d*	4.87
	~2035 m, 2001 s, 1948 s, 1923 vs, 1889 s	*e*	
$CrW(CO)_8L_2$	2035 m, 1995 s, 1940 s, 1910 vs, 1873 s	*d*	4.87
$MoW(CO)_8L_2$	2038 m, 2003 s, 1943 s, 1911 vs, 1874 s	*d*	4.89, 4.98
	2027 m, 2000 s, 1949 s, 1921 vs, 1890 s	*e*	
$Cr_2(CO)_6L_3$	1897 s, 1842 m, b	*d*	5.03
$Mo_2(CO)_6L_3$	1905 s, 1842 m, b	*d*	5.11
$W_2(CO)_6L_3$	1897 s, 1840 m, b	*d*	5.25

[a] Abbreviations: v, very; s, strong; m, medium; b, broad; sh, shoulder. [b] Recorded in chloroform-*d* with internal tetramethylsilane as reference. [c] Chemical shift of 1,4 bridgehead protons. All compounds also showed a complex multiplet centered at approximately τ 8.5. [d] Dichloromethane solvent. [e] Cyclohexane solvent. [f] Conversion to $Mo_2(CO)_8(C_5H_8N_2)_2$ occurred too rapidly at the probe temperature to record a satisfactory spectrum.

mixed-metal dibridging complexes VII ($M \neq M'$) the two different metal centers render the 1,4 hydrogens formally inequivalent. Experimentally only the mixed molybdenum–tungsten complex shows two different signals for these protons. In the symmetrically bridged derivatives the chemical shifts were in the order W > Mo > Cr with Mo and Cr having rather similar values. Thus it is not surprising that the chromium–molybdenum compound shows only a single 1,4-hydrogen signal. However, the failure of the chromium–tungsten derivative to show two signals is unexpected. The coordination of only one nitrogen atom in the cis-disubstituted compounds V is supported by the presence of two distinct 1,4-hydrogen peaks.

All of the complexes of types V, VI, and VII are capable of existing in two isomeric forms due to the presence of two different alkyl bridges in the ligand. These isomers are surely noninterconvertible in complexes VI and VII and probably in V as well. However, neither the NMR nor the infrared spectra show any features that may be attributed to the presence of a mixture of isomeric forms. In the case of NMR this may be due to a lack of sufficient sensitivity of the 1,4 hydrogens to their environment since even two of the mixed-metal complexes show only a single resonance for these protons. In the infrared even the sharper spectra taken in cyclohexane show no additional carbonyl peaks. Thus the available evidence does not require more than a single isomeric form, although a mixture of nearly spectroscopically identical isomers which were not separable in our chromatographic procedures cannot be excluded.

Table II. Calculated Carbonyl Force Constants (mdyn/Å) for *cis*-$M(CO)_4(C_5H_8N_2)_2$ and $M_2(CO)_6(C_5H_8N_2)_3$ [a]

Compd ($L = C_5H_8N_2$)	k_1	k_2	k_i
cis-$Cr(CO)_4L_2$	14.16	15.43	0.37
cis-$Mo(CO)_4L_2$	14.13	15.39	0.32
cis-$W(CO)_4L_2$	14.13	15.36	0.39
$Cr_2(CO)_6L_3$	14.02		0.26
$Mo_2(CO)_6L_3$	14.05		0.30
$W_2(CO)_6L_3$	13.96		0.29

[a] The force constants k_1 refer to carbonyls trans to L; the force constants k_2 refer to carbonyls cis to L; k_i is the CO–CO interaction constant.

Azo Group Bonding. In order to compare the azo system with other nitrogen ligands we have calculated the stretching (k_1 and k_2) and interaction (k_i) force constants for the compounds *cis*-$(CO)_4M(DBH)_2$ (V) using the Cotton–Kraihanzel approximations[18,19] for the carbonyl stretching frequencies recorded in dichloromethane. The four carbonyl frequencies for *cis*-$(CO)_4ML_2$ complexes have been assigned in two different ways. When L is a strong π acceptor, the ν(CO) frequencies decrease in the order $A_1^a > B_1 > A_1^b > B_2$, and when L is a poor π acceptor, $A_1^a > A_1^b > B_1 > B_2$.[16,17] On the basis of the intensity arguments presented by Orgel, we prefer the first assignment with the shoulder near 1890 cm^{-1} attributed to the A_1^b mode. The A_1^a, B_1, and B_2 frequencies were used to calculate the force constants presented in Table II. As required all force constants are positive and $k_2 > k_1$ As a further check on the assignment the frequency of the A_1^b band may be calculated to be at 1878, 1877, and 1876 cm^{-1} for the Cr, Mo, and W compounds, respectively. Given the uncertainty in the frequencies and the approximations in the method,[18] these values are in reasonable agreement with those observed.

In addition to the σ bond formed by nitrogen lone pair donation to the metal, the azo group in DBH may also π bond to the metal through its vacant π^* molecular orbital. Whether such π bonding is significant can be explored by comparing the force constants for the *cis*-$(CO)_4M(DBH)_2$ compounds with structurally similar compounds in which a nitrogen ligand is coordinated that has σ-bonding capability only. Ethylenediamine is such a ligand and the force constants k_1 and k_2 (all in mdyn/Å) for the complexes *cis*-$(CO)_4M(en)$ have been calculated as 13.68 and 15.07 for Cr, 13.76 and 15.25 for Mo, and 13.68 and 15.01 for W.[19] The comparable values for the DBH complexes V are 0.35–0.50 mdyn/Å larger for both k_1 and k_2 and provide evidence for π-acceptor ability for the azo group in DBH. Herberhold et al. have recently arrived at the same conclusion based on a comparison of the carbonyl stretching frequencies for a series of compounds of the type $C_6(CH_3)_6Cr(CO)_2L$ where L represented a wide range of ligands including DBH.[21]

The tribridging complexes $(CO)_3M(DBH)_3M(CO)_3$ (VI) may also be treated by the Cotton–Kraihanzel method assuming that the two observed carbonyl frequencies correspond to the A_1 (higher frequency) and E modes of C_{3v} symmetry.[16-18] In this case σ-bonding-only models are the compounds *fac*-$(CO)_3M(dien)$ (M = Cr, Mo, W; dien = diethylenetriamine). The k_1 values for the dien complexes of 13.1 ± 0.1 mdyn/Å[18] are about 0.9 mdyn/Å smaller than those of the DBH complexes (Table II). Substantial π-bonding ability by the azo group is again indicated.

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Registry No. *cis*-$Cr(CO)_4(C_5H_8N_2)_2$, 54067-83-3; *cis*-$Mo(CO)_4(C_5H_8N_2)_2$, 58641-30-8; *cis*-$W(CO)_4(C_5H_8N_2)_2$, 58641-31-9;

$Cr_2(CO)_8(C_5H_8N_2)_2$, 54067-84-4; $Mo_2(CO)_8(C_5H_8N_2)_2$, 55016-44-9; $W_2(CO)_8(C_5H_8N_2)_2$, 58602-27-0; $CrMo(CO)_8(C_5H_8N_2)_2$, 55016-43-8; $CrW(CO)_8(C_5H_8N_2)_2$, 58602-28-1; $MoW(CO)_8(C_5H_8N_2)_2$, 58602-29-2; $Cr_2(CO)_6(C_5H_8N_2)_3$, 30931-85-2; $Mo_2(CO)_6(C_5H_8N_2)_3$, 58602-30-5; $W_2(CO)_6(C_5H_8N_2)_3$, 58602-31-6; $Cr(CO)_4(C_7H_8)$, 12146-36-0; $Mo(CO)_4(C_7H_8)$, 12146-37-1; $W(CO)_4(C_7H_8)$, 12129-25-8; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_3(CH_3CN)_3$, 16800-47-8; $Fe_2(CO)_9$, 15321-51-4.

References and Notes

(1) A. J. Carty, *Organomet. Chem. Rev. A*, **7**, 191 (1972).
(2) M. Kilner, *Adv. Organomet. Chem.*, **10**, 115 (1972).
(3) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **57**, 389 (1973).
(4) D. Sellmann, *Angew. Chem. Int. Ed. Engl.*, **13**, 639 (1974), and references therein.
(5) R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Adv. Chem. Ser.*, **No. 100**, 219 (1971).
(6) G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **8**, 650 (1969).
(7) M. Kooti and J. F. Nixon, *J. Organomet. Chem.*, **76**, C29 (1974).
(8) R. J. Bennett, *Inorg. Chem.*, **9**, 2184 (1970).
(9) M. Herberhold and W. Golla, *J. Organomet. Chem.*, **26**, C27 (1971).
(10) M. Ackermann and L.-J. Kou, *J. Organomet. Chem.*, **86**, C7 (1975).
(11) M. Herberhold, W. Golla, and K. Leonhard, *Chem. Ber.*, **107**, 3209 (1974).
(12) P. G. Gassman and K. T. Mansfield, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., p 96.
(13) R. B. King, "Organometallic Syntheses", Vol. I, Academic Press, New York, N.Y., 1965.
(14) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).
(15) D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, **1**, 433 (1962).
(16) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4422 (1974).
(17) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
(18) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(19) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).
(20) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).
(21) M. Herberhold, K. Leonhard, and C. G. Kreiter, *Chem. Ber.*, **107**, 3222 (1974).

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Vanadium(IV) Gluconate Complexes

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The complexes formed by oxovanadium(IV) with gluconate have been studied by spectrophotometry, circular dichroism, and polarography between pH 5 and pH 14. The stoichiometry of the complexes varies from a vanadium-to-gluconate ratio of 1:1 at pH 6.0 to 1:2 above pH 12. Both species give well-defined polarographic oxidation waves. The apparent formation constant, K_1', of the 1:1 complex at pH 6.0 is $2.2 \times 10^3\ M^{-1}$; K_2' for the 1:2 complex in 0.5 M NaOH is $1.8 \times 10^5\ M^{-2}$. The apparent equilibrium constant between the 1:1 and 1:2 complexes is $6.7 \times 10^3\ M^{-2}$. Polarographic data indicate that oxovanadium(V) forms a transient complex with gluconate at pH 6 but is not complexed at pH 14.

There is increasing evidence that vanadium has a significant biological role, although it has been established as an essential element for only a few organisms.[1] Vanadium ions also can be substituted for the metals of metalloenzymes without loss in enzymatic activity and thereby provide an ESR probe.[2] Recently, the complexes of oxovanadium(IV) and vanadium(V) with uridine have been proposed as transition state analogues for ribonuclease.[3] The successful coupling of ATP hydrolysis with the ($VO_2^+ + H_2O_2$) redox system[4] provides support for the proposition that electron-transfer reactions occur simultaneously with the ATP–ADP reaction and for the conclusion that vanadium chemistry has substantial relevance to biology.

Gluconic acid (the carboxylic acid derivative of D-glucose) retains the polyhydroxy character of saccharides but is stable to oxidation. Most multicharged metal ions form stable complexes with gluconate ion, especially in alkaline media. A number of these have been studied in terms of electrochemistry, solution equilibria, and reaction stoichiometries.[5] Use of proton NMR has provided insight to the most likely ligand coordination sites.[6] For lead(II) and bismuth(III) the carboxylate oxygen and the α-, β-, and γ-hydroxy oxygens of gluconate are bonded to the metal under basic conditions.

Although several ligands that contain one hydroxyl group and a carboxylate group form complexes with oxovanadium(IV),[7] data for alkaline conditions are limited. Because the formation of stable complexes by saccharides with oxovanadium(IV) in basic media has been known for a long time, similar behavior is to be expected of gluconate ion.

The present study has been undertaken to characterize the electrochemistry and solution equilibria of the complexes of oxovanadium(IV) and oxovanadium(V) with gluconate ion over a wide range of pH values. It results from a continuing interest in model complexes that mimic the chemistry of biological transition metals that are involved in oxidation–reduction reactions.

Experimental Section

Equipment. Spectrophotometric data were obtained with a Cary Model 14 recording spectrophotometer. The circular dichroism measurements were made with a Jasco Model ORD/CD/UV-5 optical rotatory dispersion spectrometer. Polarographic data were recorded with a Sargent Model XV recording polarograph at 25 ± 0.1 °C. The diffusion currents were determined for maximum current (envelope of the tops of the oscillations) and were corrected for residual current. Potentials were measured and reported vs. the saturated calomel electrode (SCE). For the dropping-mercury electrode, the rate of flow of mercury was 2.32 mg/s and the drop time was 3.50 s (without an applied potential). pH measurements were made either with a Corning Model 12 pH meter or a Leeds and Northrup pH meter; the meters were standardized with NBS buffers. Magnetic susceptibility determinations were made by NMR[9] with diamagnetic corrections through use of Pascal's constants.[10] NMR spectra were recorded on a Varian A-60D spectrometer.

Reagents. The vanadium(IV) solutions were prepared from vanadyl sulfate, $VOSO_4 \cdot 1.5H_2O$ (Fisher Scientific Co.) which was found to be 99.4% pure on the basis of permanganate titrations. Vanadium(V) solutions were made from purified NH_4VO_3 (Fisher Scientific Co.); $NaVO_3 \cdot nH_2O$ also was used for some qualitative experiments. Sodium gluconate solutions were prepared determinately from D-glucono-δ-lactone (Matheson Coleman and Bell). The purity of the lactone was determined by back-titrating with standard acid a solution to which excess standard base had been added. The lactone was found to be 99.7% pure and to have a melting point of 152–153 °C.

Above pH 4, solutions that contain oxovanadium(IV) are highly sensitive to air oxidation. To prevent this, the reagent solutions were degassed with and protected by an argon atmosphere. During the preparation of a solution to be examined, argon was bubbled through the initial and resulting solutions. Uv cells were stoppered tightly