species with overall trigonal symmetry, having unexceptional, approximately tetrahedral $M^{II}S_4$ chromophores that are magnetically coupled. Determination of the nature and magnitude of the exchange interactions requires extensive measurements over larger temperature intervals than those investigated here.

The complexes $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ show one quasi-reversible oxidation and irreversible reduction (Fe(II)), and a reversible reduction (Co(II)) at a very negative potential (Table IV), properties that tend to restrict further investigations of isolated forms of these complexes to those with the overall 2– oxidation level. In a biological context trinuclear iron–sulfide species are of interest in relation to the cyclic $Fe_3(\mu\text{-}S)_3$ core unit of one Fe–S site in *Azotobacter vinelandii* Fd I.[24a] This unit exists in the $[Fe_3S_3]^{3+,2+}$ oxidation levels,[25] and in the oxidized form the Fe···Fe separations are ~4.1 Å. The complex $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ bears only a distant structural and no electronic relationship to that site (and to subsequently discovered 3-Fe sites in other proteins provided they have the same structure[24b]). Consequently, it should not be described[13] as a model for trinuclear iron–sulfur centers in proteins. However, it and $[Fe_3S_4(SR)_4]^{3-}$ are the only known trinuclear Fe–S–SR species[26] and may serve as precursors to complexes having Fe_3S_3 cores. This possibility is currently under investigation.

Acknowledgment. This research was supported by NIH Grant GM 28856. NMR and X-ray diffraction equipment used in this research were obtained by NSF Grants CHE 80-00670 and CHE 80-08891.

Registry No. $(Et_4N)_2[Co_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$, 83546-51-4; $(Et_4N)_2[Fe_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$, 83546-54-7.

Supplementary Material Available: Crystal structure data for $(Et_4N)_2[M_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$ (M = Fe(II), Co(II)): anisotropic thermal parameters for the anions (Tables S-I, S-II), positional parameters for cations and solvate molecules (Table S-III), anisotropic thermal parameters for cations and solvate molecules (Tables S-IV, S-V), and calculated and observed structure factors (Table S-VI) (51 pages). Ordering information is given on any current masthead page.

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(26) A compound, $Fe_3(\mu\text{-}S)(\mu_3\text{-}S)(S_2C_2(CF_3)_2)_4\cdot{}^1/_2S_8$, has been structurally characterized (Gerst, K.; Nordman, C. E. "Proceedings of the American Crystallographic Association"; American Crystallographic Association: Storrs, CT, 1974; p 225, Abstract E2) but is an unattractive addition to the above compounds because of the presence of dithiolene ligands. This compound may be the same as an incompletely defined material investigated prior to the structural report (Rubinson, K. A.; Palmer, G. *J. Am. Chem. Soc.* **1972**, *94*, 8375).

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405, and the Institut für Chemie, Universität Regensburg, D-8400 Regensburg, West Germany

New Bridging Mode for Organodiazo Ligands. Molecular Structure of $(\eta^5\text{-}C_5H_5)(CO)_2W(N\overline{NCH_3)Cr}(CO)_5$[1]

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The interaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$ with $Cr(CO)_5(THF)$ (THF = tetrahydrofuran) gives a binuclear complex containing a bridging organodiazo ligand. Attachment of the $Cr(CO)_5$ group to the organodiazo ligand causes the W–N(1) distance to decrease (0.03 Å) and the N(1)–N(2) distance to increase (0.03 Å). Structural changes in the carbonyl and cyclopentadienyl ligands attached to tungsten are also observed. The geometry about chromium is typical of $Cr(CO)_5L$, where L is an ordinary sp^2 hybridized σ-donor ligand. This is the first example of an N,N′ bridging organodiazo ligand, and its relationship to isodiazene (hydrazido(2–)) ligands (W–N–NH–R) is discussed. Important structural parameters include W–N(1) = 1.830 (3) Å, N(1)–N(2) = 1.247 (4) Å, Cr–N(2) = 2.106 (3) Å, W–N(1)–N(2) = 174.4 (3)°, N(1)–N(2)–Cr = 122.3 (3)°, N(1)–N(2)–C(8) = 113.8 (3)°, and C(8)–N(2)–Cr = 123.9 (2)°. The X-ray crystal structure of the title complex was determined at –175 °C in space group $P2_1/c$ with $a = 15.257$ (6) Å, $b = 8.874$ (3) Å, $c = 13.279$ (5) Å, $\beta = 111.39$ (1)°, and $Z = 4$. On the basis of 3168 reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by using full-matrix, least-squares methods to $R(F) = 0.021$ and $R_w(F) = 0.029$.

Introduction

We have maintained a continuing interest in organodiazo complexes because they are intermediates in the metal-assisted, synthetic reduction of dinitrogen to amines,[2] ammonia,[3] and diazenes.[4] The M–N–N linkage in organodiazo complexes has a partially delocalized π-bonding system that is strongly affected by the attached metal and coligands and by the nature of the group attached to the outer nitrogen atom. We undertook the present study to determine the effect on the W–N and N–N distances in $(C_5H_5)W(CO)_2(N_2CH_3)$ (I) when a metal-containing fragment such as $Cr(CO)_5$ was attached to the outer nitrogen atom of the methyldiazo ligand. Accurate structural parameters for the terminal methyldiazo ligand[5] in the parent complex are available for purposes of comparison.

Previous studies have shown that simple protonation (or alkylation) of organodiazo ligands can occur at the inner nitrogen atom, at the outer nitrogen atom, or at both nitrogen atoms. Doubly bent organodiazo ligands always protonate at

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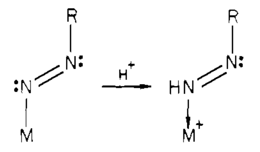
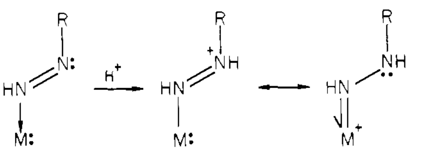
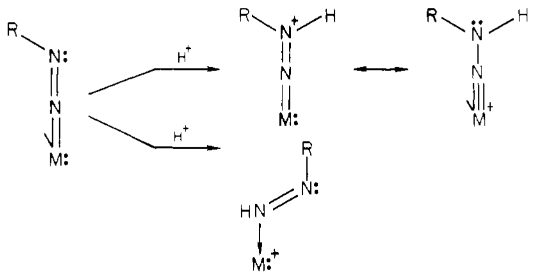
the inner nitrogen atom (eq 1), which seems to be more basic


(1)

than the outer nitrogen atom; $RuCl(CO)_2(N_2Ph)(PPh_3)_2$,[6] $IrCl_2(CO)(N_2Ph)(PPh_3)_2$,[7] $[RhCl(N_2Ph)((Ph_2PCH_2CH_2CH_2)_2PPh)][PF_6]$,[8] and $PtCl(N_2Ph)(PEt_3)_2$[9] are typical examples. Diazene complexes can be further protonated on the outer nitrogen atom (eq 2); $ReCl(CO)_2(NH{=}NPh)(PPh_3)_2$,


(2)

$ReCl_2(NO)(NH{=}NPH)(PPh_3)_2$, and $OsCl_2(CO)(NH{=}NPh)(PPh_3)_2$ are typical examples.[8] A preliminary account indicated that protonation of $W(N_2)_2(PPh_2Me)_4$ with HCl gave $WCl_3(NHNH_2)(PPh_2Me)_2$, but this compound was later reformulated as $WHCl_3(NNH_2)(PPh_2Me)_2$.[10] Contrary to earlier beliefs, the geometry of the organodiazo ligand is not a good indicator of the preferred site of protonation.[11] Singly bent organodiazo ligands can be protonated at either nitrogen atom depending on the nature of the metal and coligands (eq 3). d^4 complexes[15] and low-valent d^6 complexes with linear


(3)

NMR groups protonate at the outer nitrogen atom; $W(N_2Ph)(S_2CNMe_2)_3$,[8] $WBr(N_2CH_3)(diphos)_2$,[12,16] and $ReCl_2(NH_3)(N_2Ph)(PPhMe_2)_2$[13] are typical examples. Similar complexes, $ReCl_2(CO)(N_2Ph)(PPhMe_2)_2$ and $OsCl_3(N_2Ph)(PPh_3)_2$,[14] will *not* protonate. d^8 complexes[15] protonate on the inner nitrogen atom, and protonation is often accompanied by coordination of the couteranion even when weakly coordinating acids like $HClO_4$, HBF_4, or HSO_3CF_3 are used; $Re(CO)_2(N_2Ph)(PPh_3)_2$,[8] $OsH(CO)(N_2Ph)(PPh_3)_2$,[14] and $[Os(CO)_2(N_2Ph)(PPh_3)_2][PF_6]$[14] are typical examples. Protonation of organodiazo ligands is accompanied by geometric changes, and we hoped to see similar changes caused by a metallic class B Lewis acid ($Cr(CO)_5$). We now report the low-temperature crystal structure of $(\eta^5\text{-}C_5H_5)(CO)_2W(NNCH_3)Cr(CO)_5$ (II). This compound represents the first example of an N,N′ *doubly* bridging organodiazo ligand. The structure of a triply bridging methyldiazo ligand in $Mn_3(CO)_{12}(N_2CH_3)$ is known.[17]

Experimental Section

The title compound was synthesized in 94% yield by the reaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(NNCH_3)$ with $Cr(CO)_5(THF)$ as described elsewhere.[18] Crystals for the X-ray diffraction study were grown from diethyl ether/methylene chloride (1:10) at −10 °C. Anal. (of crystalline sample from which the crystal for the structural work was selected) Calcd for $C_{13}H_8CrN_2O_7W$: C, 28.91; H, 1.43; Cr, 9.63; N, 5.19; W, 34.04. Found: C, 28.90; H, 1.51; Cr, 9.60; N, 5.17; W, 34.00. The molecular weight is 531 (determined osmometrically in benzene). The infrared and ^1H NMR data agreed with those reported.[18]

Crystallographic Data. The crystals were more air stable than $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$ and could be conveniently handled in air for several hours. In the space of several days' exposure to air, however, the crystals decomposed to an olive green powder. A crystal of the W–Cr complex was mounted on the diffractometer, and monoclinic symmetry was identified after a quick search for intense, low-angle reflections. During data collection, the extinctions $h0l$, l = odd, and $0k0$, k = odd, were observed, which uniquely determined the space group as $P2_1/c\text{-}C_{2h}^5$. X-ray data collection was carried out using a locally constructed diffractometer consisting of a Picker goniostat interfaced to a Texas Instruments T1980B computer and a low-temperature device.[19] On the basis of a least-squares analysis of the angular positions of 12 strong, machine-centered reflections in diverse regions of reciprocal space ($26° > 2\theta > 20°$), accurate unit cell dimensions were determined. See Table I for pertinent crystal information and details of data collection. Background counts were measured at both ends of the scan and both crystal and counter stationary. The intensities of the three standard reflections were measured every 100 reflections and remained constant during the entire data collection. The intensity data were corrected for background effects and for Lorentz polarization effects. An absorption correction was performed by using Gaussian integration.[20] A careful check of F_o and F_c during the least-squares refinements in their later stages showed that a small isotropic extinction correction might be necessary; this correction refined to a value of $9.2\ (6) \times 10^{-7}\ e^{-2}$. Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares calculations. The values of $\sigma(F)$ were estimated by using a value of 0.05 for p.[21] A total of 4174 unique reflections was collected to 55° in 2θ. Owing to an oversight, we collected these diffraction data at −175 °C instead of −140 °C (the temperature at which the structure of $(C_5H_5)W(CO)_2(NNCH_3)$ was determined). We do not believe that this temperature difference significantly changes the ensuing structural comparisons.

Structure Refinement. The structure was readily solved with use of a Patterson synthesis to locate the tungsten atom. Difference Fourier syntheses were used to locate all remaining atoms, including all eight hydrogens. All H atoms were remarkably well-defined in the electron density syntheses, but little was to be gained by their refinement. The eight hydrogen atoms were placed in idealized positions (C–H = 0.95 Å; $B = 1.0 + B$(attached carbon)) and included in the final least-squares calculations;[22] their positional and thermal parameters were

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(6) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369.

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(15) The electronic configurations for the metal are calculated by assuming that the organodiazo ligand is cationic (RN_2^+) when it has a singly bent geometry and acts as a three-electron donor ligand. Although somewhat artifical, this formalism allows one to conventiently classify organodiazo complexes.

(16) Earlier claims that the d^6 complex $WBr(NNH)(diphos)_2$ could be protonated on the inner nitrogen atom have been retracted: Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

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(22) In addition to various local programs for the CDC-6600 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, and the Northwestern full-matrix, least-squares program NUCLS, which, in its nongroup form, closely resembles the Busing and Levy ORFLS program.

Table I. Summary of Crystallographic Data

compd	$(\eta^5\text{-}C_5H_5)(CO)_2W(N\overline{NCH_3)Cr}(CO)_5$
formula	$C_{13}H_8N_2O_7CrW$
fw	540.06
a, Å	15.257 (6)
b, Å	8.874 (3)
c, Å	13.279 (5)
β, deg	111.39 (1)
V, Å^3	1674
Z	4
space group	$C^5_{2h}\text{-}P2_1/c$
cryst size, mm	0.22 × 0.24 × 0.30
cryst vol, mm^3	1.2×10^{-2}
cryst shape	elongated prism with {001}, {100}, {011}, and $\{11\bar{1}\}$ faces
radiation	Mo Kα (λ = 0.710 69 Å) monochromatized with highly oriented graphite
μ, cm^{-1}	76.73
density, g/cm^3	2.140 (calcd) 2.10 (2) (exptl 21 °C)
temp, °C	−175 (5)
range of transmission factors	0.208-0.296
aperture	2.5 mm wide × 3.5 mm high, 21.5 cm from crystal
takeoff angle, deg	2.0
scan speed, deg/min	3.0
scan range, deg	1.2 below $K\alpha_1$ to 1.3 above $K\alpha_2$
bkgd counting time, s	10
2θ limits, deg	4-55
no. of variables	218
unique data with $F_o^2 > 3\sigma(F_o^2)$	3168
error in observn of unit weight, e	0.94
R(*F*)	0.021
$R_w(F)$	0.029

Table II. Positional Parameters for the Atoms of $(C_5H_5)W(CO)_2(\overline{NNCH_3)Cr}(CO)_5$

atom	x^a	*y*	*z*
W	0.159563 (10)	0.29646 (2)	0.355291 (11)
Cr	0.35490 (4)	0.61732 (7)	0.27017 (5)
N(1)	0.2613 (2)	0.3515 (4)	0.3218 (3)
N(2)	0.3343 (2)	0.3930 (4)	0.3082 (3)
C(8)	0.4052 (3)	0.2705 (5)	0.3243 (4)
C(1)	0.0606 (3)	0.3551 (6)	0.2169 (4)
O(1)	0.0020 (2)	0.3909 (6)	0.1395 (3)
C(2)	0.1447 (3)	0.0977 (6)	0.2815 (4)
O(2)	0.1395 (3)	−0.0172 (4)	0.2404 (3)
C(3)	0.3110 (3)	0.6865 (4)	0.3797 (4)
O(3)	0.2845 (3)	0.7337 (4)	0.4433 (3)
C(4)	0.3744 (3)	0.8126 (4)	0.2382 (3)
O(4)	0.3873 (2)	0.9355 (3)	0.2174 (3)
C(5)	0.3968 (3)	0.5491 (4)	0.1580 (3)
O(5)	0.4212 (2)	0.5147 (4)	0.0905 (2)
C(6)	0.4804 (3)	0.6184 (5)	0.3734 (3)
O(6)	0.5554 (2)	0.6298 (4)	0.4342 (2)
C(7)	0.2295 (3)	0.6359 (5)	0.1668 (3)
O(7)	0.1563 (2)	0.6572 (4)	0.1048 (3)
C(R1)	0.2067 (3)	0.4038 (7)	0.5265 (3)
C(R2)	0.2057 (4)	0.2479 (7)	0.5408 (4)
C(R3)	0.1107 (5)	0.1995 (6)	0.4922 (4)
C(R4)	0.0552 (3)	0.3248 (6)	0.4489 (4)
C(R5)	0.1149 (4)	0.4516 (5)	0.4691 (4)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

not varied. During the refinements, the minimizing function was $Q = \sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes; weights, *w*, were taken as $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual sources,[23] and anomalous dispersion terms for W and Cr were included in F_c. The final structural model converged with 24 anisotropic non-hydrogen atoms to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.021$ and $R_w(F) = (Q/\sum wF_o^2)^{1/2} = 0.029$. A careful statistical analysis of the trends of *Q* as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed expected behavior. The error in an observation of unit weight (0.94 e) was a bit low, but our statistical analyses indicated nothing unusual, and our weighting scheme seemed adequate. A final difference Fourier synthesis showed insignificant residual electron density; the largest peak was a tungsten residual (0.9 e/Å^3) and the remaining residuals were less than 0.6 e/Å^3 in size. Of the weak reflections with $3\sigma(F_o^2) > F_o^2$, only two had $|F_o^2 - F_c^2| > 4\sigma(F_o^2)$.

The final positional and thermal parameters of the refined atoms appear in Tables II and S-III, and the root-mean-square amplitudes of vibration are given in Table S-I.[24] Table S-II contains positional and thermal parameters for the unrefined hydrogen atoms.[24] A listing of observed and calculated structure amplitudes for those data used in the refinements is available.[24]

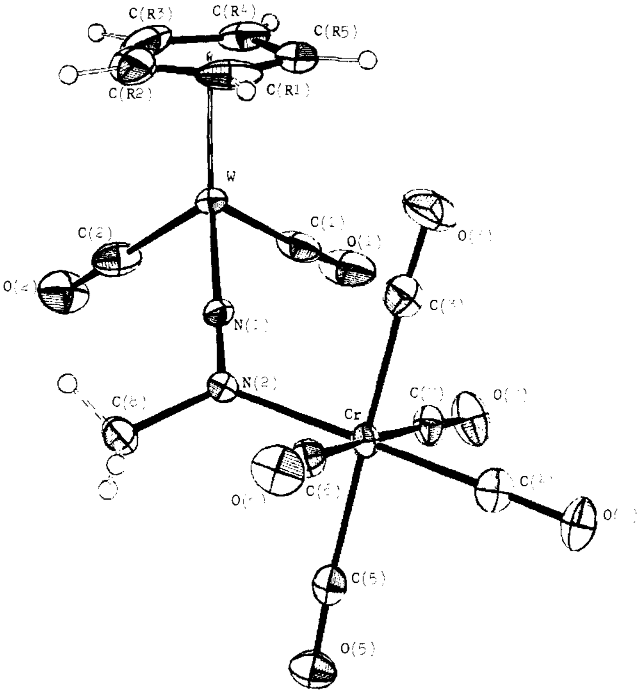

Figure 1. Complete drawing of a molecule of $(C_5H_5)(CO)_2W(N\overline{NCH_3)Cr}(CO)_5$. The vibrational ellipsoids have been drawn at the 50% probability level except for those of the hydrogen atoms, which have been drawn artificially small.

Discussion

The methyldiazo complex $(\eta^5\text{-}C_5H_5)(CO)_2W(NNCH_3)^5$ (I) contains a singly bent CH_3N_2 moiety whose outer nitrogen atom has a geometry suggesting the presence of a stereochemically active lone pair of electrons. Although we were able to demonstrate the susceptibility of this compound to proton attack by strong acids like HBF_4 and CF_3SO_3H, it has not yet been possible to isolate pure, metal-containing products.[25,26] By reacting I with the Lewis acid metal carbonyl fragment $Cr(CO)_5$, we have been able to obtain the heterodinuclear, thermally stable addition product, whose structure shows some interesting differences when compared to that of the tungsten starting material.

The structure of $(\eta^5\text{-}C_5H_5)(CO)_2W(N\overline{NCH_3)Cr}(CO)_5$

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(24) Supplementary material.

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(26) Reaction of $(\eta^5\text{-}C_5H_5)(CO)_2W(NNCH_3)$ with HX (X = Cl, Br) quantitatively gives $(\eta^5\text{-}C_5H_5)(CO)_2WX_3$ as the organometallic product.

Table III. Selected Bond Distances (Å) in $(C_5H_5)W(CO)_2(NNCH_3)Cr(CO)_5$

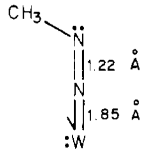
atoms	dist	av	atoms	dist	av
W-N(1)	1.830 (3)		Cr-N(2)	2.106 (3)	
W-C(1)	1.976 (4)	1.983	Cr-C(3)	1.910 (4)	1.912
W-C(2)	1.990 (5)		Cr-C(5)	1.920 (4)	
W-C(R1)	2.323 (4)	2.343	Cr-C(6)	1.906 (4)	
W-C(R2)	2.342 (5)		Cr-C(7)	1.912 (4)	
W-C(R3)	2.365 (4)		Cr-C(4)	1.834 (4)	
W-C(R4)	2.363 (4)		C(3)-O(3)	1.142 (5)	1.137
W-C(R5)	2.323 (4)		C(5)-O(5)	1.130 (5)	
C(1)-O(1)	1.134 (5)	1.140	C(6)-O(6)	1.139 (5)	
C(2)-O(2)	1.145 (6)		C(7)-O(7)	1.136 (5)	
N(1)-N(2)	1.247 (4)		C(4)-O(4)	1.160 (5)	
N(2)-C(8)	1.494 (5)				
C(R1)-C(R2)	1.398 (8)	1.402			
C(R2)-C(R3)	1.420 (8)				
C(R3)-C(R4)	1.388 (8)				
C(R4)-C(R5)	1.410 (7)				
C(R5)-C(R1)	1.395 (7)				

Table IV. Selected Bond Angles (deg) in $(C_5H_5)W(CO)_2(NNCH_3)Cr(CO)_5$

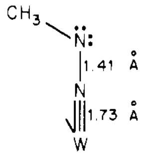
atoms	angle	av
W-C(1)-O(1)	177.5 (4)	177.6
W-C(2)-O(2)	177.7 (4)	
W-N(1)-N(2)	174.4 (3)	
N(1)-N(2)-C(8)	113.8 (3)	
Cr-N(2)-N(1)	122.3 (3)	
Cr-N(2)-C(8)	123.9 (2)	
C(1)-W-C(2)	82.2 (2)	
C(1)-W-N(1)	97.5 (2)	
C(2)-W-N(1)	94.0 (2)	
N(1)-W-C(R1)	98.1 (2)	
N(1)-W-C(R2)	110.5 (2)	
N(1)-W-C(R3)	144.8 (2)	
N(1)-W-C(R4)	153.3 (2)	
N(1)-W-C(R5)	118.5 (2)	
C(1)-W-C(R1)	131.4 (2)	
C(1)-W-C(R2)	149.5 (2)	
C(1)-W-C(R3)	117.6 (2)	
C(1)-W-C(R4)	91.7 (2)	
C(1)-W-C(R5)	98.3 (2)	
C(2)-W-C(R1)	141.6 (2)	
C(2)-W-C(R2)	107.0 (2)	
C(2)-W-C(R3)	92.6 (2)	
C(2)-W-C(R4)	112.1 (2)	
C(2)-W-C(R5)	146.9 (2)	
C(R1)-W-C(R2)	34.8 (2)	34.8
C(R2)-W-C(R3)	35.1 (2)	
C(R3)-W-C(R4)	34.1 (2)	
C(R4)-W-C(R5)	35.0 (2)	
C(R5)-W-C(R1)	34.9 (2)	
C(R1)-W-C(R3)	57.9 (2)	57.9
C(R1)-W-C(R4)	57.9 (2)	
C(R2)-W-C(R4)	57.8 (2)	
C(R2)-W-C(R5)	58.1 (2)	
C(R3)-W-C(R5)	57.7 (2)	
C(R1)-C(R2)-C(R3)	107.3 (4)	108.0
C(R2)-C(R3)-C(R4)	108.2 (4)	
C(R3)-C(R4)-C(R5)	107.9 (4)	
C(R4)-C(R5)-C(R1)	108.1 (4)	
C(R5)-C(R1)-C(R2)	108.4 (4)	
N(2)-Cr-C(3)	89.8 (1)	
N(2)-Cr-C(5)	90.6 (1)	
N(2)-Cr-C(6)	91.8 (2)	
N(2)-Cr-C(7)	93.2 (2)	
C(3)-Cr-C(4)	90.2 (2)	
C(3)-Cr-C(6)	89.4 (2)	
C(3)-Cr-C(7)	89.0 (2)	
C(4)-Cr-C(5)	89.4 (2)	
C(4)-Cr-C(6)	87.5 (2)	
C(4)-Cr-C(7)	87.5 (2)	
C(5)-Cr-C(6)	91.6 (2)	
C(5)-Cr-C(7)	89.9 (2)	
N(2)-Cr-C(4)	179.3 (2)	
C(3)-Cr-C(5)	178.9 (2)	
C(6)-Cr-C(7)	174.8 (2)	
Cr-C(3)-O(3)	177.2 (4)	176.8
Cr-C(4)-O(4)	179.2 (4)	
Cr-C(5)-O(5)	177.3 (4)	
Cr-C(6)-O(6)	175.2 (4)	
Cr-C(7)-O(7)	175.2 (4)	

(II) consists of discrete monomeric molecules in the unit cell. There are no significant intramolecular or intermolecular nonbonded contacts. A perspective view of the complex together with the labeling scheme is shown in Figure 1. The geometry around tungsten is the usual "three-legged" stool geometry with two carbonyl ligands and the methyldiazo group at the base. The geometry at Cr is pseudooctahedral, typical of $Cr(CO)_5L$ complexes. All seven carbonyl ligands are linear with averaged parameters W–C = 1.983 Å, Cr–C = 1.912 Å (CO trans to CO), C–O = 1.14 Å, and M–C–O = 177° (see Tables III and IV for exact values). The gross structural details of the complex will not be discussed further because they are similar to the known structures of I and $Cr(CO)_5L$.

A detailed structural comparison of $(C_5H_5)W(CO)_2(N_2CH_3)$ with and without $Cr(CO)_5$ attached to the outer nitrogen of the methyldiazo ligand shows that the Cr atom is effective at removing electron density from the tungsten atom through the organodiazo linkage. In II, the W–C(cyclopentadienyl) distances became shorter (2.343 vs. 2.361 Å), the W–C(carbonyl) distances became longer (1.983 vs. 1.967 Å), and the C–O distances became shorter (1.140 vs. 1.154 Å). These small structural changes are all consistent with a partial rehybridization as shown by III and IV and indicate that the tungsten atom is more electropositive and less able to engage in W→CO π back-bonding.[31]



III



IV

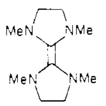
The planar C_5 ring in the title complex is rotated approximately 31° about the W–Cx vector (Cx = center of C_5 ring) in relation to $(C_5H_5)W(CO)_2(N_2CH_3)$; the angle between the N(1)–W–Cx and W–Cx–C(R1) planes is 9.6°. Thus, N(1) is trans to C(7) in I but it is "trans" to the midpoint of the C(R3)–C(R4) bond in the $Cr(CO)_5$ adduct. The C–C distances in the C_5 ring vary from 1.388 (8) to 1.420 (8) Å with an average of 1.402 Å, which is shorter than the 1.422-Å average in I. In both structures, the shortest C–C ring distance(s) occurs between the carbon atoms that are trans or pseudotrans to the methyldiazo group. However, considering the magnitudes of the standard deviations (0.007–0.008 Å) and the effects of libration, we cannot attach extraordinary significance to the variation of C–C distances. The W–C distances in the cyclopentadienyl group show a distinct variation around the ring. The longest distances are W–C(R3) at 2.365 (4) Å and W–C(R4) at 2.363 (4) Å, which are pseudotrans to the methyldiazo group; thus, the C_5 ring is tilted about 0.04 Å *away* from the methyldiazo ligand in $(C_5H_5)W(CO)_2(N_2CH_3)$, but the ring is tilted *toward* the methyldiazo ligand by the same amount in the $Cr(CO)_5$ adduct. These structural effects seem to be caused by the methyldiazo ligand because there are no intra- or intermolecular nonbonded interactions that could explain these observations.

Although the structural features at W are sensitive to the presence of Cr on the methyldiazo ligand, the reverse is *not* true. Table V shows that the $Cr(CO)_5$ moiety has structural parameters quite similar to comparable complexes that contain ordinary σ-donor nitrogen ligands. The Cr–C distances (trans

Table V. Structural Data for Some Chromium Carbonyl Compounds

compd[a]	hybridizn at N	Cr–N, Å	Cr–C, Å N trans to C	Cr–C, Å C trans to C	C–O, Å N trans to C	C–O, Å C trans to C
$Cr(CO)_5(N{\equiv}CSMe)$[b]	sp	2.604 (3)	1.831 (4)	1.905 (5)	1.152 (5)	1.138 (5)
$Cr(CO)_5(N{\equiv}CNEt_2)$[c]	sp	2.603 (3)	1.829 (4)	1.893 (4)	1.164 (5)	1.140 (5)
$(CO)_5CrNH{=}NHCr(CO)_5$[d]	sp^2	2.08 (1)	1.86 (2)	1.91 (2)	1.14 (2)	1.15 (2)
$(C_5H_5)(CO)_2W(NNMe)Cr(CO)_5$[e]	sp^2	2.106 (3)	1.834 (4)	1.913 (4)	1.160 (5)	1.137 (5)
fac-$Cr(CO)_3((NH_2CH_2CH_2)_2NH)$[f]	sp^3	2.185 (7)	1.816 (8)		1.17 (1)	
cis-$Cr(CO)_4(LL)$[g]	sp^3	2.199 (4)	1.820 (6)	1.897 (8)	1.154 (7)	1.140 (10)

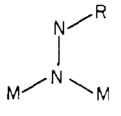
LL =



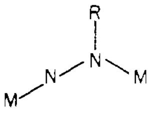
[a] Averaged values are given when appropriate. Abbreviations: Me = CH_3, Et = C_2H_5. [b] Helland, B. J.; Quick, M. H.; Jacobson, R. A.; Angelici, R. J. *J. Organomet. Chem.* **1977,** *132,* 95. [c] Schubert, U.; Neugebauer, D.; Friedrich, P. *Acta Crystallogr., Sect. B* **1978,** *B34,* 2293. [d] Huttner, G.; Gartzke, W.; Allinger, K. *J. Organomet. Chem.* **1975,** *91,* 47. [e] This work. [f] Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1966,** *5,* 1851. [g] Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977,** 2160.

to CO) at 1.91 Å are 0.08 Å longer than Cr–C distances (trans to N) at 1.83 Å because CO has the stronger trans influence; the C–O distances are typical, and as expected, the CO ligands with shorter Cr–C bonds have longer (~0.02 Å) C–O bond lengths. Table V also shows that $Cr{\leftarrow}N(sp^3)$ distances are about 2.19 Å and that $Cr{\leftarrow}N(sp)$ distances are about 2.06 Å. We would estimate a $Cr{\leftarrow}N(sp^2)$ distance to be 2.10–2.12 Å, and we observe a value in the title complex of 2.106 (3) Å; a $Cr{\leftarrow}N(sp^2)$ distance of 2.08 (1.3) Å was observed in $(CO)_5CrNH{=}NHCr(CO)_5$.

The bridging methyldiazo ligand has the familiar singly bent geometry and acts as a three-electron donor to W and two-electron donor toward Cr. This is the first time that this mode of bridging (VI) has been observed. A different mode of



V



VI

bridging (V) has been observed three times before.[27,28] The $Cr(CO)_5$ unit may be regarded as a Lewis acid, and its attachment at the outer nitrogen atom in I is analogous to the protonation or alkylation of similar alkyldiazo complexes that contain tungsten or molybdenum. Consistent with our earlier discussion, we find that attaching $Cr(CO)_5$ to the methyldiazo ligand in $(C_5H_5)W(CO)_2(NNCH_3)$ causes a lengthening of the N–N distance (1.247 (4) vs. 1.215 (5) Å) and a shortening of the W–N distance (1.830 (3) vs. 1.856 (3) Å). Similarly, proton (H^+) of MoI(NN-*n*-octyl)(diphos)$_2$[29] causes the N–N distances to increase from 1.18 to 1.26 Å and the Mo–N distance to decrease from 1.84 to 1.80 Å; ethylation ($C_2H_5^+$) of $Mo(NPh)(S_2CNR_2)_3$[30] causes the N–N distance to increase from 1.23 to 1.37 Å and the Mo–N distance to decrease from 1.78 to 1.72 Å. The nature of the Lewis acid that attacks the organodiazo ligand and the ancillary ligands on the metal both determine the extent to which formal structures like $M{=}N{=}NHR$ are stabilized with respect to those like $M{\equiv}N{-}NHR$. In the case where the Lewis acid is $C_2H_5^+$ and the ancillary ligands are dithiocarbamate groups, the largest changes in geometry are observed. Using similar compounds to estimate expected bond distances[31] for formalisms III and IV (see drawings), we see that the bond distances in $(C_5H_5)W(CO)_2(NNCH_3)$ closely approximate those expected for III while those in $(C_5H_5)(CO)_2W(\overline{NNCH_3)Cr}(CO)_5$ represent about an 80:20 mixture of III and IV. Thus, the N_2CH_3 ligand in the title complex retains most of its "diazo" character. The geometry at N(2) is strictly planar. The N(2)–C(8) distance lengthened slightly (1.494 (5) vs. 1.481 (6) Å) and the N(1)–N(2)–C(8) angle decreased (113.8 (3) vs. 116.5 (4)°). These changes are small and not unexpected in view of the increased coordination number from 2 to 3 at N(2).

The changes in the C–O and N–N stretching frequencies in the infrared spectra when $Cr(CO)_5$ is attached to the methyldiazo ligand are in harmony with the changes in the structural data. The carbonyl bands (at W) increased in energy from 1905 and 1981 to 1915 and 1996 cm^{-1}, indicating less $W{\rightarrow}CO$ π back-donation. The $\nu(NN)$ band decreased from 1627 to 1552 cm^{-1}, indicating a weakening of the N–N bond. In isodiazene (hydrazido(2–)) complexes, $\nu(NN)$ is usually not seen or unambiguously identified probably because the band has dropped well below 1500 cm^{-1}.

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Supplementary Material Available: Listings of the observed and calculated structure factor amplitudes, rms amplitudes of vibration, structural parameters for H atoms, and thermal parameters for the refined atoms (18 pages). Ordering information is given on any current masthead page.

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(31) The N–N single-bond distance in NH_2NH_2 is 1.45 Å,[32a] but it is shortened by 0.04 Å when the nitrogen atoms (sp^2) are engaged in π bonding in azines[32b] ($RCH{=}N{-}N{=}CHR$; R = Ph, N–N = 1.41 Å). This shortening is well documented for C–C single bonds. Diazines have an $-N{=}N-$ double-bond distance of 1.23 Å,[32c] and there should be some shortening (~0.01 Å) in singly bent RN_2 complexes for the same reason noted above. Knowing that Mo and W have nearly identical bonding radii, we can estimate $W{\equiv}N-$ at 1.73 Å[32d] and $W{=}N{<}$ at 1.85 Å.

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