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Structure of a Methyldiazo Complex of Tungsten, $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$, at Low Temperature

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The structure of the methyldiazo complex $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$ has been determined at −140 °C by using X-ray diffraction techniques. The complex, prepared by the action of CH_2N_2 on $(\eta^5\text{-}C_5H_5)W(CO)_3H$, appears to have a normal methyl group attached in a singly bent fashion to the N(2)–N(1)–W linkage with W–N(1) = 1.856 (3) Å, N(1)–N(2) = 1.215 (5) Å, W–N(1)–N(2) = 173.3 (3)° and N(1)–N(2)–C(8) = 116.5 (4)°. The complex is monomeric and has the expected "three-legged" stool geometry about the metal. As compared to the CO groups, the methyldiazo ligand exerts a trans shortening influence on part of the C_5H_5 group, causing a shortening of the W–C(7) bond by about 0.03 Å. The title complex crystallized in space group $P\bar{1}$ with $a = 7.003$ (2) Å, $b = 10.988$ (3) Å, $c = 6.542$ (2) Å, $\alpha = 104.56$ (1)°, $\beta = 107.16$ (1)°, $\gamma = 86.76$ (2)°, and $Z = 2$. On the basis of 2059 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ the structure was refined by using full-matrix, least-squares methods to $R(F) = 0.019$ and $R_w(F) = 0.033$.

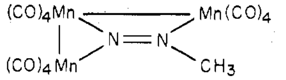
Introduction

There has been considerable interest in organodiazo complexes because they are intermediates in the metal-assisted reduction of dinitrogen to organic amines and because analogous species are postulated intermediates in the synthetic reduction of dinitrogen to ammonia using W(0) and Mo(0) complexes.[1,2] Organodiazo ligands and the nitrosyl ligand are isoelectronic, and the structural properties of aryldiazo complexes seem to parallel those of their nitrosyl analogues although there are some marked differences in the reactions of the coordinated ligands. Because very little structural data were known for alkyldiazo ligands, we undertook the present structural study in order to determine if there are any important differences between aryl- and alkyldiazo ligands in similar coordination environments.

It is noteworthy that there are far fewer aryldiazo complexes than analogous nitrosyl complexes and that there are far fewer yet alkyldiazo complexes. Furthermore, the only known terminal alkyldiazo complexes contain molybdenum or tungsten. Alkylhydrazines are used to produce $Mo(N_2R)(S_2CNEt_2)_3$[3] and $Mo(N_2R)_2(S_2CNEt_2)_2$;[4] alkylation of dinitrogen complexes yields $MoI(N_2R)(diphos)_2$[5] and $WBr(N_2R)(diphos)_2$;[6] the action of diazoalkanes on metal hydride complexes gave the first reported alkyldiazo complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(N_2R)$ and $(\eta^5\text{-}C_5H_5)W(CO_2(N_2R)$.[7,8]

$$(\eta^5\text{-}C_5H_5)WH(CO)_3 + CH_2N_2 \xrightarrow[\text{THF}]{-85\ °\text{C}} (\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3) + CO$$

We now report an improved synthesis for $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$ and its structure using single-crystal X-ray diffraction techniques. Low temperatures were used in order to improve the final structural precision, reduce unwanted thermal motion, and avoid thermal decomposition. The only previously reported structure of a terminal alkyldiazo complex is $MoI(N_2R)(diphos)_2$ where R is cyclohexyl; although the general structural features of the cyclohexyldiazo group were determined, accurate metrical parameters for the diazo ligand could not be obtained.[9] The structure of a three-coordinate, bridging methyldiazo ligand is also known.[10]



Experimental Section

Improved Preparation of $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$. The title complex was synthesized by the following improved and scaled-up procedure with the usual Schlenk techniques (N_2 as inert gas; rigorously dried, nitrogen-saturated solvents). A magnetically stirred solution of 10.02 g (30 mmol) of resublimed $(\eta^5\text{-}C_5H_5)WH(CO)_3$[11] in 250 mL of tetrahydrofuran was treated at −85 °C with 70 mmol of diazomethane[12] (0.10 M ethanol-free solution in diethyl ether) by dropwise addition. The slow addition of the diazomethane solution took about 40 min. Under these conditions it was not necessary to precool the diazomethane solution lower than 0 °C. After the addition of diazomethane was complete, the reaction mixture was allowed to slowly warm up to room temperature (ca. 2 h). For completion of the reaction, the mixture was stirred another 2 h at room temperature. After volatile byproducts and the solvents were removed under vacuum, the oily, dark red residue was chromatographed on a silica column ($l = 85$ cm, $\phi = 3$ cm; column temperature ca. +10 °C; silica 60, act. II–III, 70–230 mesh ASTM, Merck 7734) with benzene as eluant. A small amount of $(\eta^5\text{-}C_5H_5)W(CO)_3(CH_3)$ was eluted as a fast-moving yellow band, while the desired product was obtained by eluting the dark red band. The solvent was removed, and the remaining oily residue was crystallized twice from pentane–diethyl ether solutions

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Table I. Summary of Crystallographic Data

compd	W(η^5-C_5H_5)(CO)$_2$(N_2CH_3)	density, g/cm^3	2.482 (calcd)
formula	$C_8H_8N_2O_2W$	temp	−140 (5) °C
fw	348.02	μ	126.372 cm^{-1}
a, Å	7.003 (2)	range of transmission factors	0.627–0.857
b, Å	10.988 (3)	aperature	2.5 mm wide × 3.5 mm high
c, Å	6.542 (2)	takeoff angle	2.0°
α, deg	104.56 (1)	scan speed	3.0°/min
β, deg	107.56 (1)	scan range	1.00° below Kα_1 to 1.20° above Kα_2
γ, deg	86.87 (2)	bkgd counting	10 s
V, Å^3	465.5	2θ limits	4.0–55.0°
Z	2	no. of variables	119
space group	C_i^1-$P\bar{1}$	unique data with $I_o > 3\sigma(I_o)$	2059
cryst size, mm	0.24 × 0.15 × 0.09	error in observn of unit weight	1.21 electrons
cryst vol	3.6 × 10^{-3} mm^3	$R(F)$	0.019
cryst shape	triclinic needle with {100}, {010}, and {0$\bar{1}$1} faces	$R_w(F)$	0.033
radiation	Mo Kα (λ 0.710 69 Å) monochromatized with highly oriented graphite		

(ca. 3:1) at −78 °C, yielding analytically pure dark red crystals of (η^5-C_5H_5)W(CO)$_2$(N_2CH_3), yield 6.89–8.25 g (66–79%, based on (η^5-C_5H_5)W(CO)$_3$H). The yield decreased drastically if the tungsten hydride contained even traces of acetic acid from its preparation; therefore, careful sublimation of this starting material was required. The methyldiazo product is very air sensitive, even in the crystalline state, but it can be stored in a N_2 atmosphere at −35 °C (refrigerator) for months without any decomposition; mp 36–39 °C dec.

Crystal Preparation. Crystals were grown by slow evaporation of a pentane/ether solution. Single crystals could be handled for periods of up to 30 min in the air without visible decomposition. For obtainment of a crystal which was free of significant decomposition and displayed single, acceptably narrow peaks during ω scanning, a long needle was chosen and fractured at one end so that it was about $^1/_4$ mm long. The data crystal was handled briefly (about 10 min) in air and mounted on a glass fiber with silicone grease. The crystal was then immediately placed in a nitrogen cold-stream on the diffractometer. At low temperature under these conditions, the data crystal was quite stable toward decomposition during the entire data collection. Efforts to obtain an experimental density were not entirely successful owing to the high reactivity of the compound, but we obtained a crude experimental density which agreed with the calculated value to within 10%.

X-ray data collection was accomplished by using a locally constructed diffractometer consisting of a Picker goniostat interfaced to a Texas Instruments TI980 computer. The attached low-temperature device has been described.[13]

Crystallographic Data. The crystal of the W complex was mounted on the diffractometer, and no symmetry could be identified. A careful search of all diffraction peaks in the region (4.0° < 2θ < 7.0°) indicated the absence of any symmetry or extinction pattern. A primitive, reduced triclinic unit cell was chosen. The space group was assumed to be centrosymmetric, C_i^1-$P\bar{1}$, and this was verified by successful refinement of the structure and location of all eight hydrogen atoms. 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° < 2θ < 37°), 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 with both the crystal and counter stationary. The intensities of three standard reflections were measured every 100 reflections and remained constant during the data collection. The intensity data were corrected for background effects and for Lorentz–polarization effects. An absorption correction was performed by using Gaussian integration.[14] Owing to the large absorption, a moderately fine grid was chosen in order to improve precision. Some difficulty was encountered in defining the fractured face which was approximately perpendicular to the needle axis. With the aid of 200 redundant reflections and considerable trial-and-error, an acceptable absorption correction was finally accomplished. A careful check of F_o and F_c in the final refined model showed that a small isotropic extinction correction might be necessary; the isotropic extinction correction refined to a value of 3.5 (3) × 10^{-6}. Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares calculations. The values of $\sigma(F_o)$ were estimated by using a value of 0.05 for *p*. A total of 2131 unique reflections were collected out to 55° in 2θ.

Structure Refinement. The structure was easily solved by using a Patterson synthesis to locate the metal atom and difference Fourier syntheses to locate all the remaining lighter atoms including all eight hydrogen atoms. The structure was refined by using full-matrix, least-squares techniques.[15] During the refinements, the quantity minimized was $q = \sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure amplitudes and where the weights, *w*, are taken as $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual sources,[16] and the anomalous dispersion terms for W were included in F_c. All eight hydrogen atoms were clearly located in difference Fourier syntheses. Their positions were idealized, and isotropic thermal parameters were chosen 1.0 Å^2 larger than the isotropic equivalents of the respective carbon atoms to which the H atoms are attached. The C–H distance was chosen to be 0.95 Å. The hydrogen atoms were included in later refinements, and two sets of refinements were carried out. First, the structure was refined until convergence without varying the positional or thermal parameters of hydrogen atoms; $R_w(F)$ was 0.0326. Second, the structure was again refined until convergence, including the refinement of the positional, but not thermal, hydrogen parameters; $R_w(F)$ was 0.0320. Seven of the hydrogen atoms moved very little and refined well; one of the methyl hydrogen atoms tended to oscillate and moved to a chemically unreasonable position 1.5 Å from the methyl carbon atom. The true location of H(2C8) was clear from difference maps, but the presence of a residual of about 0.5 e/Å^3 only 0.6 Å away prevented a satisfactory refinement.

In view of the small improvement in R_w upon refinement of hydrogen atoms, the final and most satisfactory model was that in which the hydrogen atoms were not refined. This model converged with 13 anisotropic nonhydrogen atoms and 8 isotropic unrefined hydrogen atoms to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.0188$ and $R_w(F) = (q/\sum wF_o^2)^{1/2} = 0.0326$. A statistical analysis of the trends of *q* as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed nothing unusual and indicated that the weighting scheme was adequate. A final difference Fourier synthesis showed no significant residual electron density. With the exception of a tungsten residual (1.0 e/Å^3), there were no residuals above 0.5 e/Å^3. Of the reflections with $3\sigma(F_o^2) > F_o^2$, only one had $F_c^2 > 4\sigma(F_o^2)$. A careful examination of F_o and F_c showed that there were four moderately weak reflections which measured about 3 times too large. Omission of these four reflections caused no significant parameter shifts but reduced the discrepancy indices to $R(F) = 0.0186$ and $R_w(F) = 0.0298$. The final refined model included these four reflections.

The final positional and thermal parameters of the refined atoms appear in Table II, and the root-mean-square amplitudes of vibration are given in Table III.[17] Table IV contains the positional and thermal parameters for the unrefined hydrogen atoms.[17] A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[17]

Discussion

The structure of (η^5-C_5H_5)W(CO)$_2$(N_2CH_3) consists of discrete monomeric molecules in the unit cell. There are no significant intra- or intermolecular nonbonded contacts. A perspective view of the complex together with the labeling

Table II. Positional and Thermal Parameters for the Atoms of (Methyldiazo)dicarbonylcyclopentadienyltungsten(0)

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
W	0.15427(2)	0.231044(12)	0.24592(2)	87.8(6)	32.1(2)	100.2(7)	5.6(2)	23.7(4)	12.6(2)
C-1	0.0274(6)	0.1869(4)	0.4482(6)	107.(9)	51.(4)	116.(9)	-11.(4)	19.(7)	11.(5)
O-1	-0.0475(6)	0.1571(4)	0.5661(6)	176.(9)	96.(4)	153.(9)	-15.(5)	68.(7)	37.(5)
C-2	0.1993(6)	0.3929(4)	0.4712(7)	108.(9)	44.(4)	162.(11)	4.(4)	24.(8)	11.(5)
O-2	0.2332(5)	0.4851(3)	0.6043(6)	166.(8)	56.(3)	201.(10)	8.(4)	19.(7)	-10.(4)
C-3	0.4900(6)	0.2226(5)	0.2320(7)	97.(8)	56.(4)	169.(11)	-4.(5)	39.(8)	15.(5)
C-4	0.3647(7)	0.1857(5)	0.0099(7)	155.(10)	67.(4)	136.(11)	0.(5)	72.(9)	14.(5)
C-5	0.2597(7)	0.0727(4)	-0.0139(7)	138.(10)	46.(4)	157.(11)	5.(5)	56.(8)	-13.(5)
C-6	0.3220(7)	0.0410(4)	0.1933(8)	138.(10)	41.(4)	228.(13)	32.(5)	67.(9)	28.(6)
C-7	0.4624(6)	0.1327(5)	0.3440(8)	106.(9)	62.(4)	188.(12)	42.(5)	50.(8)	31.(6)
N-1	-0.0835(5)	0.2742(3)	0.0639(5)	93.(7)	34.(3)	111.(8)	2.(3)	38.(6)	5.(4)
N-2	-0.2386(5)	0.2906(4)	-0.0700(6)	124.(8)	56.(4)	144.(9)	0.(4)	35.(7)	29.(5)
C-8	-0.2500(8)	0.4076(5)	-0.1462(9)	166.(11)	62.(4)	213.(13)	25.(6)	14.(10)	62.(6)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: EXP[-(B11H^2 +B22K^2 +B33L^2 +2B12HK+2B13HL+2B23KL)]. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table V. Selected Bond Distances (Å) in (η^5-C_5H_5)W(CO)$_2$(N_2CH_3)

W-N(1)	1.856 (3)		C(1)-O(1)	1.167 (5)	1.154(av)
W-C(1)	1.960 (4)	1.967(av)	C(2)-O(2)	1.141 (5)	
W-C(2)	1.975 (4)		N(1)-N(2)	1.215 (5)	
W-C(3)	2.376 (4)	2.361(av)	N(2)-C(8)	1.481 (6)	
W-C(4)	2.383 (4)		C(3)-C(4)	1.427 (6)	1.422(av)
W-C(5)	2.361 (4)		C(4)-C(5)	1.429 (7)	
W-C(6)	2.348 (4)		C(5)-C(6)	1.422 (7)	
W-C(7)	2.339 (4)		C(6)-C(7)	1.411 (7)	
			C(7)-C(3)	1.421 (7)	

Table VI. Selected Bond Angles (deg) in (η^5-C_5H_5)W(CO)$_2$(N_2CH_3)

W-C(1)-O(1)	178.1 (4)	C(2)-W-C(5)	151.1 (2)	
W-C(2)-O(2)	177.2 (4)	C(2)-W-C(6)	136.0 (2)	
W-N(1)-N(2)	173.3 (3)	C(2)-W-C(7)	102.3 (2)	
N(1)-N(2)-C(8)	116.5 (4)	C(3)-C(4)-C(5)	107.9 (4)	108.0(av)
C(1)-W-C(2)	81.6 (2)	C(4)-C(5)-C(6)	107.4 (4)	
C(1)-W-N(1)	94.3 (2)	C(5)-C(6)-C(7)	108.7 (4)	
C(2)-W-N(1)	96.2 (2)	C(6)-C(7)-C(3)	108.2 (4)	
N(1)-W-C(3)	133.2 (2)	C(7)-C(3)-C(4)	107.9 (4)	
N(1)-W-C(4)	102.7 (2)	C(3)-W-C(4)	34.9 (2)	35.0(av)
N(1)-W-C(5)	99.8 (2)	C(4)-W-C(5)	35.0 (2)	
N(1)-W-C(6)	127.8 (2)	C(5)-W-C(6)	35.2 (2)	
N(1)-W-C(7)	158.1 (2)	C(6)-W-C(7)	35.0 (2)	
C(1)-W-C(3)	132.5 (2)	C(7)-W-C(3)	35.0 (2)	
C(1)-W-C(4)	152.1 (2)	C(3)-W-C(5)	58.3 (2)	58.3(av)
C(1)-W-C(5)	120.7 (2)	C(3)-W-C(6)	58.2 (2)	
C(1)-W-C(6)	93.9 (2)	C(4)-W-C(6)	58.2 (2)	
C(1)-W-C(7)	99.8 (2)	C(4)-W-C(7)	58.2 (2)	
C(2)-W-C(3)	93.3 (2)	C(5)-W-C(7)	58.5 (2)	
C(2)-W-C(4)	117.7 (2)			

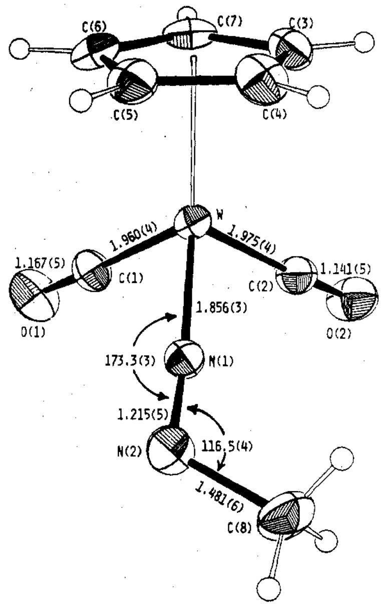


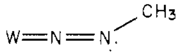
Figure 1. Complete drawing of a molecule of (η^5-C_5H_5)W(CO)$_2$(N_2CH_3). The vibrational ellipsoids have been drawn at the 50% probability level except for the hydrogen atoms which have been drawn artificially small.

scheme is shown in Figure 1. The complex adopts the usual "three-legged" stool geometry with the two carbonyls and the methyldiazo group at the base. The two carbonyl ligands are linear with averaged parameters of W–C = 1.967 Å, C–O = 1.154 Å, and W–C–O = 177.7° (see Tables V and VI).

The cyclopentadienyl ligand is attached through all five carbon atoms to the central tungsten atom. The C_5 unit is absolutely planar; no atom deviates more than 0.002 (4) Å from the least-squares plane through all five carbon atoms. The C–C distances in the C_5 ring vary from 1.411 (7) to 1.429 (7) Å (average 1.422 Å) in an irregular fashion around the ring; in [(η^5-C_5H_5)W(CO)$_3$]$_2$ the average C–C distance is 1.41 Å. The well-behaved C_5H_5 group combined with the reduced thermal motion at −140 °C causes the apparent C–C distances to be slightly longer than in most η^5-C_5H_5 complexes whose structures were determined at room temperature.

The W–C distances to the cyclopentadienyl group show a small but distinct variation around the ring. The shortest distance is W–C(7) at 2.339 (4) Å and the longest are W–C(3) at 2.376 (4) Å and W–C(4) at 2.383 (4) Å. This variation is quite regular around the C_5 ring and seems to be caused by the presence of methyldiazo ligand which is approximately trans to C(7). This apparent trans shortening influence of the CH_3N_2 ligand amounts to about 0.02–0.04 Å and is consistent with CH_3N_2 being a better π acceptor than CO. Similar variations can be found in [(η^5-C_5H_5)W(CO)$_3$]$_2$[18] which has W–C distances ranging from 2.32 (C trans to W) to 2.38 Å (C trans to CO). Other cyclopentadienyltungsten complexes also show a range of W–C distances, but mediocre precision prevents any reliable conclusion: e.g., $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_5H_5)$, 2.31–2.47 Å;[19] $(\eta^5\text{-}C_5H_5)W(CO)_2(C_{15}H_{15})$, 2.23–2.44 Å;[20] $(\eta^5\text{-}C_5H_5)W(CO)_3(AuPPh_3)$, 2.32–2.39 Å.[21]

The methyldiazo ligand has a singly bent geometry and acts as a 3-electron donor to the metal resulting in an 18-electron configuration about the metal similar to the nitrosyl analogue $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$. The location of all three hydrogen atoms in stereochemically reasonable positions on the CH_3 group unequivocally demonstrates that a hydrogen transfer to the methyl carbon atom took place during the preparation. The methyl group on N(2) is not oriented toward the W atom nor away from it, but rather somewhere in between so that the angle between the Cx–W–N(2) and W–N(2)–C(8) planes is 90.2° (Cx is center of C_5 ring). The respective W–N(1) and N(1)–N(2) distances are 1.856 (3) and 1.215 (5) Å, implying multiple bonding between W and N(1) and between N(1) and N(2). This N–N distance is nearly equal to the same distance at 1.224 (11) Å in $Mn_3(CO)_{12}(NNCH_3)$.[10] Indeed, both bonds in the tungsten complex closely approximate bond orders of 2 (I). The W–N(1)–N(2) angle is very nearly linear at 173.3 (3)°, and the N(1)–N(2)–C(8) angle is bent at 116.5 (4)°. These bond distances and angles suggest sp hybridization at N(1) and sp^2 hybridization at N(2). Although the N(1)–N(2)–C(8) angle is somewhat less than 120°, the metrical parameters as a whole are much closer to those expected for I than for II. The N(2)–C(8) distance of 1.481 (6) Å is the expected length of a C–N single bond. By way of comparison, recent structural results show that a hybrid of formalisms I and II best describes the phenyldiazo ligand in $Mo(N_2C_6H_5)(S_2CNMe_2)_3$ and that another formalism



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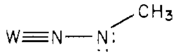
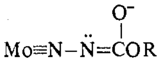


II



$$Mo{\equiv}N{-}\ddot{N}{=}\overset{\overset{\large O^-}{|}}{C}OR$$

is important in $Mo(N_2CO_2Et)(S_2CNMe_2)_3$.[25]

Of special interest to us is the comparison of this methyldiazo ligand with a phenyldiazo ligand in a similar environment. Although the structure of $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2C_6H_5)$[22] has not been determined, the structure of a related complex, $(HBPz_3)Mo(CO)_2(N_2C_6H_5)$ (Pz = $C_3N_2H_3$), is known.[23] In this Mo complex, Mo–N is 1.825 (4) Å and N–N is 1.211 (6) Å. Although a detailed comparison is not warranted owing to the change in metal and ligands, several general observations can be made. Both $N_2C_6H_5$ and N_2CH_3 adopt the same singly bent geometry. The N–N distances in both ligands are identical, but the metal–nitrogen distance is 0.031 (5) Å longer in the $W\text{–}N_2CH_3$ complex. This is an important increase because tungsten is the *same* size as molybdenum or at the most 0.005 Å larger.[18] Although other factors may contribute to this difference, an important one is the reduced π-back-bonding ability of N_2CH_3 as compared to $N_2C_6H_5$. This interpretation is consistent with the trends of ν(CO) in the series of compounds $(C_5H_5)W(CO)_2(N{=}X)$ (X = NCH_3, NC_2H_5, NC_3H_7, NC_6H_5, O).[8] When X = NCH_3, the values of ν(CO) are 1981 and 1905 cm^{-1}, but when X = NC_6H_5, the values increase to 1995 and 1910 cm^{-1}, indicating increased π back-bonding to the carbonyl ligands and decreased back-bonding to the methyldiazo ligand. Thus, replacing the nitrosyl ligand (X = O) by a phenyldiazo ligand (X = NC_6H_5) causes a 20-cm^{-1} drop in the average value of ν(CO); replacing the phenyldiazo ligand by a methyldiazo ligand (X = NCH_3) causes an additional 10-cm^{-1} reduction in ν(CO). The values of ν(NN) seem to follow the expected reverse trend; when X = NCH_3, the value of ν(NN) is 1627 cm^{-1}, and when X = NC_6H_5, the value is 1613 cm^{-1}. Caution must, however, be exercised in using measured values of ν(NN) because vibrational coupling between the N–N stretching vibration and aromatic modes of the C_6H_5 group (and perhaps the CH_3 group) can occur and has been observed in similar complexes.[24]

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Registry No. $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$, 54774-63-9; $(\eta^5\text{-}C_5H_5)WH(CO)_3$, 12128-26-6.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes and Tables III and IV showing root-mean-square amplitudes of vibration and positions and thermal parameters for H atoms (21 pages). Ordering information is given on any current masthead page.

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