(NO) (43% yield) and (η^5-C_5H_5)Cr$(NO)_2(NO_2)$ (35% yield) under identical experimental conditions. It has previously been reported that the carbonyl dimer in benzene reacts with CO (100 atm) to form $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[22] and with phosphines to form unisolable products. Both bimetallic compounds are transformed by ClNO in CH_2Cl_2 to the well-known (η^5-C_5H_5)Cr$(NO)_2$Cl, the sulfur-containing reagent being converted in higher yields (60% vs. 42%).

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Registry No. $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$, 71549-26-3; ($\eta^5$-$C_5H_5$)Cr$(NO)_2$Cl, 12071-51-1; $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$, 54667-87-7; ($\eta^5$-$C_5H_5$)Cr$(CO)_2$(NO), 36312-04-6; ($\eta^5$-$C_5H_5$)Cr$(NO)_2(NO_2)$, 68013-60-5; ClNO, 2696-92-6.

Supplementary Material Available: Table IV, a listing of structure amplitudes (67 pages). Ordering information is given on any current masthead page.

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Organometallic Nitrosyl Chemistry. 10.[1] Synthesis, X-ray Structural Characterization, and Properties of Dicarbonyl(η^5-cyclopentadienyl)(thionitrosyl)chromium

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The novel organometallic thionitrosyl complex (η^5-C_5H_5)Cr$(CO)_2$(NS) can be isolated in 21% yield from the reaction of Na[(η^5-C_5H_5)Cr$(CO)_3$] and $S_3N_3Cl_3$ in tetrahydrofuran at −78 °C. The complex crystallizes in space group $P2_1/m$ of the monoclinic system in a cell of dimensions $a = 6.528$ (1) Å, $b = 9.641$ (1) Å, $c = 7.096$ (1) Å, and $\beta = 99.22$ (1)°. The structure has been refined by full-matrix least-squares methods to values of R and R_w of 0.025 and 0.033, respectively, for 848 observed reflections. Each molecule of the complex has crystallographic m symmetry and is in a "piano stool" configuration with the NS ligand being coordinated essentially linearly to the metal via the nitrogen atom. Important intramolecular dimensions are Cr–N = 1.694 (2) Å, N–S = 1.551 (2) Å, and the angle Cr–N–S = 176.8 (1)°. Several physical and chemical properties of the complex have been determined and have been compared with those displayed by its isostructural nitrosyl analogue, (η^5-C_5H_5)Cr$(CO)_2$(NO). Such a comparison results in a dichotomy concerning the relative electron-accepting and -donating properties of NS and NO ligands.

Introduction

It has been known for many years that nitric oxide can coordinate to transition metals in a wide range of oxidation states to form metal nitrosyls.[2] Analogous thionitrosyl complexes are markedly less abundant, a fact which reflects primarily the present lack of reagents which can be utilized to introduce the thionitrosyl group onto a transition metal. The few thionitrosyl complexes which have been prepared result from the reaction of elemental sulfur, propylene sulfide, or disulfur dichloride with coordinated nitrido ligands in the precursors.[3] We now report that during its reaction with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^-$, trithiazyl trichloride, $S_3N_3Cl_3$, functions as a source of NS to afford the novel organometallic complex (η^5-C_5H_5)Cr$(CO)_2$(NS). We also provide full details of an X-ray investigation of this unique compound and describe some of its characteristic physical and chemical properties. Portions of this work have been communicated previously.[4]

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was confirmed by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use; all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared (IR) spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton and carbon-13 magnetic resonance spectra

Table I. Reactions of $N_3S_3Cl_3$ with Some Transition-Metal Compounds

transition-metal compd (mmol)	Amt of $N_3S_3Cl_3$, mmol	solvent (mL)	Temp, °C	products (yields, %)[b]	isolation and identification
$Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$[5] (5.0)	1.7	THF (150)	−78	$[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (20) $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ (10)	chromatography on Florisil; infrared spectrum[a]
$Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$[5] (6.2)	2.4	THF (120)	−78	$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (25) $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (15)	chromatography on Florisil; infrared spectrum[a]
$Na[Mn(CO)_5]$[7] (5.6)	2.0	THF (100)	20	$Mn_2(CO)_{10}$ (25%)	sublimation at 40 °C (5×10^{-3} mm); infrared spectrum[a]
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[5] (3.0)	1.0	THF (100)	20	$(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ (35)	chromatography on Florisil; infrared spectrum[a]
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$[5] (5.0)	1.6	CH_2Cl_2 (100)	20	$[(\eta^5\text{-}C_5H_5)Mo(NO)Cl]_2$ (<5)	infrared spectrum[a]

[a] By comparison with the infrared spectrum of the authentic compound. [b] Based on metal.

were recorded on Varian Associates T60 and CFT20 spectrometers, respectively, with tetramethylsilane being employed as the standard. Elemental analyses were performed by Mr. P. Borda of this department.

Reaction of $S_3N_3Cl_3$ with $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$. To a stirred tetrahydrofuran (THF) solution (60 mL) containing 2.24 g (10.0 mmol) of $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$[5] cooled to −78 °C was added dropwise a solution of $S_3N_3Cl_3$[6] (0.82 g, 3.35 mmol) in the same solvent. Gas evolution occurred, a precipitate formed, and the reaction mixture developed a red-brown coloration. After the addition of $S_3N_3Cl_3$ was complete (30 min), the mixture was allowed to warm slowly to room temperature over a period of several hours. Removal of the solvent in vacuo produced a green-brown residue. This solid was suspended in toluene (30 mL) and transferred to the top of a 3 × 10 cm Florisil column. Elution of the column with toluene afforded a broad red-green band which was collected and then taken to dryness under reduced pressure. The dried residue was sublimed at 30 °C (5×10^{-3} mm) onto a dry-ice-cooled probe to obtain 0.46 g (2.1 mmol, 21% yield) of red, crystalline $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$.

Anal. Calcd for $C_7H_5CrO_2NS$: C, 38.36; H, 2.30; N, 6.39. Found: C, 38.64; H, 2.20; N, 6.37. IR (hexanes): ν(CO) 2033, 1962 cm^{-1}; ν(NS) 1180 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.08 (s). ^{13}C NMR ($CDCl_3$): δ 239.43 (s, CO), 92.75 (s, C_5H_5). Melting point (under N_2): 68–69 °C.

Reactions of $S_3N_3Cl_3$ with Other Transition-Metal Carbonyl Complexes. Other transition-metal compounds were treated with trithiazyl trichloride in a manner similar to that described above. The experimental procedures are summarized in Table I.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ with Triphenylphosphine. Two different experiments were performed. In the first, solid PPh_3 (0.52 g, 2.0 mmol) was added to a toluene solution (30 mL) of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ (0.22 g, 1.0 mmol), and the mixture was held at reflux for 70 h. At the end of this time, an IR spectrum of the cooled reaction mixture indicated that no reaction had occurred. The toluene was removed in vacuo, and the remaining residue was sublimed onto a dry-ice-cooled probe (30 °C, 5×10^{-3} mm) to recover quantitatively the unaltered organometallic reactant.

The second experiment involved photolysis of a stirred benzene solution (200 mL) containing $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ (0.22 g, 1.0 mmol) and PPh_3 (0.52 g, 2.0 mmol) in a photoreactor using a medium-pressure mercury lamp (Hanovia SOL-100W) housed in a water-cooled Pyrex immersion well. Monitoring by IR spectroscopy indicated that the thionitrosyl complex was completely destroyed after 6 h, during which time a precipitate formed. Solvent was removed from the reaction mixture under reduced pressure, and the resulting residue was extracted with CH_2Cl_2. No new complexes containing either CO or NS ligands could be detected by IR spectroscopy in the concentrated extracts.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ with Nitrosyl Chloride. A stirred solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ (0.88 g, 4.0 mmol) in dichloromethane (60 mL) at room temperature was treated dropwise with a dichloromethane solution of ClNO (containing 2.0 g of ClNO in 30 mL of CH_2Cl_2).[8] Gas evolution occurred and a green-brown solid precipitated. The reaction was monitored by IR spectroscopy, and just enough ClNO was added to react with all the thionitrosyl complex. The final reaction mixture was stirred at ambient temperature for 3 h and then was concentrated in vacuo to ~15 mL in total volume and transferred to the top of a 3 × 8 cm Florisil column. Elution with CH_2Cl_2 produced three components: (1) a rapidly moving yellow-orange band which yielded ~0.05 g of solid when collected and taken to dryness in vacuo (the solid was discarded because its IR spectrum (Nujol mull) did not exhibit any carbonyl or nitrosyl absorptions); (2) a golden-brown band which afforded 0.23 g (27% yield) of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ (identified by its distinctive physical properties[5]) after collection and addition of hexanes; (3) a blue-green band which remained at the top of the column (this band could not be eluted even with highly eluotropic solvents).

Preparation of $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)_2]PF_6$. An orange solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[5] (0.61 g, 3.0 mmol) in CH_2Cl_2 (15 mL) and CH_3CN (5 mL) was cooled to −78 °C. Solid $NOPF_6$ (0.54 g, 3.1 mmol) was added, and the mixture was stirred for 2 h. During this time the solution became green and a similarly colored solid was deposited. The addition of cold $(C_2H_5)_2O$ (25 mL) precipitated more solid which was collected by filtration, washed with $(C_2H_5)_2O$, and dried in vacuo. The product, $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)_2]PF_6$ (0.97 g, 93% yield), was identified by its characteristic physical properties.[9]

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)_2]PF_6$ with KI. To an acetone solution (30 mL) containing 0.35 g (1.0 mmol) of $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)_2]PF_6$ was added 0.20 g (1.2 mmol) of solid KI. The reaction mixture was stirred at room temperature for 2 h during which time it became yellow-brown and a gray precipitate formed. The acetone was removed in vacuo, and the residue was extracted with CH_2Cl_2. The extracts were filtered through a 2 × 3 cm column of Florisil, and the filtrate was taken to dryness under reduced pressure to obtain 0.21 g (77% yield) of $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$ which was identified by its spectral properties.[10]

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ with $NOPF_6$. A stirred CH_2Cl_2–CH_3CN solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ was treated at −78 °C with $NOPF_6$ in a manner identical with that described above for its nitrosyl analogue. However, the isolated blue-green product reacted with solvents in which it was soluble and could not be purified. Consequently, 0.50 g of the solid product was added to a stirred acetone solution (40 mL) containing NaI (0.30 g, 2.0 mmol). The original green solution slowly became green-brown, gas evolution occurred, and a green solid precipitated. The mixture was stirred for 2 h at room temperature, and then the acetone was removed in vacuo. The blue-green residue was extracted with CH_2Cl_2, and the extracts were filtered through a 2 × 3 cm column of Florisil to obtain a golden brown filtrate. The filtrate contained 0.14 g (~25% yield based on NO) of $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$.[10]

Decomposition of $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$. A solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$[11] (0.37 g, 1.0 mmol) in benzene (40 mL) was stirred at room temperature for 20 h during which time a blue-green precipitate formed. The final mixture was filtered through a 2 × 3 cm column of Florisil to obtain a golden filtrate. Solvent was removed from the filtrate in vacuo, and the residue was dried for 1 h at 25 °C (5×10^{-3} mm). The gold-brown solid (0.19 g, 45% yield) was identified spectroscopically as $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.[5]

Electron-Impact Experiments. The low-resolution mass spectra of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ and its nitrosyl analogue[5] were measured with the assistance of Mr. J. W. Nip at 70 eV on an Atlas CH4B spectrometer by using the direct-insertion method and an ionization chamber temperature of 70 °C. The ionization potentials of the complexes and the appearance potentials of the fragment ions were determined with the assistance of Dr. G. Eigendorf by the vanishing-current method[12] from ionization efficiency curves obtained at maximum sensitivity on a Kratos/AEI MS902 mass spectrometer equipped with a standard EI source. The compounds were introduced

Table II. Final Positional Fractional Parameters ($\times 10^4$; for Cr and S $\times 10^5$; for H $\times 10^3$) with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z
Cr	44617 (5)	25000 (0)	−14831 (5)
S	73020 (14)	25000 (0)	27083 (10)
N	6003 (3)	2500 (0)	677 (3)
O	6841 (2)	224 (2)	−3084 (2)
C(1)	5945 (3)	1090 (2)	−2513 (3)
C(2)	1655 (16)	2500 (0)	−313 (17)
C(3)	1641 (16)	1296 (13)	−1383 (26)
C(4)	1582 (10)	1780 (8)	−3314 (9)
C(2′)	1815 (23)	2500 (0)	−3903 (23)
C(3′)	1684 (27)	1354 (15)	−2674 (33)
C(4′)	1332 (34)	1796 (24)	−998 (43)
H(2)	161 (9)	250 (0)	111 (10)
H(3)	165 (6)	39 (5)	−88 (6)
H(4)	168 (7)	124 (5)	−434 (6)
H(2′)	240	250 (0)	−520
H(3′)	160	30	−300
H(4′)	150	120	0

[a] Primed atoms designate the $^1/_3$ η^5-C_5H_5 ring.

directly into the source held at 80 °C and 1×10^{-7} mm. Iodomethane (I = 9.55 eV) and argon (I = 15.75 eV) were used as calibrants and were admitted to the sample chamber through a gas-inlet system at a pressure of $\sim 10^{-7}$ mm from a reservoir held at 70 °C.

X-ray Diffraction Study of (η^5-C_5H_5)Cr(CO)$_2$(NS). Crystals of the thionitrosyl complex suitable for X-ray analysis were grown by sublimation at 35 °C under a static vacuum ($\sim 10^{-2}$ mm) onto a water-cooled probe. A well-formed, regularly shaped crystal of approximate dimensions $0.45 \times 0.35 \times 0.15$ mm was mounted in a Lindemann glass capillary under an argon atmosphere. A series of precession photographs provided a preliminary unit cell, the Laue symmetry $2/m$, and the systematic absence $0k0$ for $k \neq 2n$, indicating the space group $P2_1$ or $P2_1/m$. On the basis of possible molecular m symmetry, the latter was chosen and later confirmed by the structure analysis. The crystal was transferred to an Enraf-Nonius CAD4 diffractometer where automatic location and centering of 25 reflections ($20° < 2\theta < 27°$, graphite-monochromated Mo Kα_1 radiation, λ = 0.709 30 Å) provided the unit cell parameters a = 6.528 (1) Å, b = 9.641 (1) Å, c = 7.096 (1) Å, and β = 99.22 (1)°. These dimensions correspond to a unit cell volume of 440.84 Å^3 and a calculated density of 1.65 g cm^{-3} for Z = 2 and a formula weight of 219.2.

Intensities were collected to 2θ = 55° by using the ω–2θ scan method and a scan range determined by $\Delta\omega = (1.1 + 0.35 \tan \theta)°$ with a 25% extension at either end for background determination. These parameters were ascertained from a peak profile analysis. The scan rate was computed from a fast prescan at 6.66° min^{-1} such that a count of $\sim 5 \times 10^3$ was obtained, if possible, in a maximum time of 120 s. An aperture 4 mm high and $(1.5 + 0.5 \tan \theta)$ mm wide was placed 173 mm from the crystal. The intensities of three reflections measured after every 100 reflections showed no systematic variation during the data collection. A total of 1074 independent intensities were measured; Lorentz and polarization corrections were applied; and standard deviations were assigned according to $\sigma^2(I) = S + B + (0.05S)^2$ where S = total scan count and B = the time-averaged background count. Of the 1074 intensities, 849 had $I > 3\sigma(I)$ and were classified as observed. The crystal was found to be bounded by the (100), (010), (001), (011), and (0$\bar{1}$1) faces and their inverses, and measurement of interfacial distances was followed by absorption corrections using BICABS[13] which gave transmission factors for $|F|^2$ ranging between 0.5912 (100) and 0.8089 (020) with μ(Mo Kα) = 14.50 cm^{-1}.

The structure was solved and refined in the following manner. The positions of the chromium and sulfur atoms were determined by a combination of Patterson synthesis and direct methods,[14] both of which indicated the centrosymmetric space group $P2_1/m$ with Cr and S in the mirror plane. Two cycles of anisotropic full-matrix least-squares refinement using unit weights and the data not corrected for absorption gave $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ = 0.32 and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o{}^2|)^{1/2}$ = 0.40 for the observed reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$, and scattering factors were taken from ref 15. The remaining nonhydrogen atoms were located from a difference Fourier synthesis, and isotropic followed by anisotropic least-squares refinement gave R = 0.044 and R_w = 0.070 using weights $1/\sigma^2(F)$. At this stage, a difference Fourier synthesis contained peaks at the expected positions of the η^5-C_5H_5 hydrogen atoms and others which suggested a disorder of this ligand. The hydrogen atoms were included in the model, with scattering factors from ref 16; and two cycles of least-squares refinement, including isotropically refining hydrogens and anomalous dispersion corrections for Cr and S,[17] gave R = 0.040 and R_w = 0.053. The absorption-corrected intensity data were introduced, and further full-matrix least-squares refinement gave R = 0.031 and R_w = 0.047. Evidence for η^5-C_5H_5 disorder was still present in a difference Fourier synthesis. Therefore, the carbon atoms in this ring were refined isotropically, thereby producing a clear indication of the alternative configuration in a subsequent difference Fourier synthesis. A series of refinements, alternating between fixed population parameters and fixed thermal parameters for the disordered η^5-C_5H_5 rings, converged on an occupancy ratio of 2:1 which gave B values between 4.1 and 5.1 Å^2 for the individual carbon atoms. With the population parameters fixed at $^2/_3$ and $^1/_3$, full anisotropic refinement (except for the $^2/_3$ H atoms which were isotropically refined) gave R = 0.026 and R_w = 0.034. The $^1/_3$ hydrogen atoms were included at positions indicated by a difference Fourier synthesis and were fixed in the final cycles of least-squares refinement which gave R = 0.025 and R_w = 0.033 for the 848 observed reflections, with R = 0.036 and R_w = 0.036 for all 1073 reflections. The 20$\bar{1}$ reflection with $|F_o|$ = 8.0 and $|F_c|$ = 2.0 was omitted in these final stages. The error in an observation of unit weight was 0.89, and the average

Table III. Final Thermal Parameters and Their Estimated Standard Deviations

(a) Anisotropic Thermal Parameters ($U_{ij} \times 100$ Å^2)[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	3.92 (2)	7.03 (3)	3.76 (2)	0.0 (0)	0.07 (1)	0.0 (0)
S	8.25 (5)	9.48 (6)	4.21 (4)	0.0 (0)	−1.23 (3)	0.0 (0)
N	5.0 (1)	7.1 (1)	4.0 (1)	0.0 (0)	0.2 (1)	0.0 (0)
O	7.0 (1)	9.2 (1)	7.5 (1)	0.9 (1)	1.1 (1)	−1.6 (1)
C(1)	4.7 (1)	7.9 (1)	4.5 (1)	−0.2 (1)	0.0 (1)	−0.4 (1)
C(2)	4.6 (5)	11.2 (10)	6.4 (4)	0.0 (0)	1.6 (4)	0.0 (0)
C(3)	4.8 (4)	9.2 (6)	7.8 (4)	−0.7 (3)	0.3 (3)	1.7 (5)
C(4)	4.4 (2)	10.7 (7)	4.8 (4)	−0.4 (5)	−0.4 (2)	−1.2 (3)
C(2′)	4.7 (6)	12.6 (16)	3.8 (7)	0.0 (0)	−0.4 (4)	0.0 (0)
C(3′)	4.7 (4)	6.1 (6)	12.6 (19)	−1.0 (4)	−1.2 (11)	1.3 (8)
C(4′)	3.5 (5)	13.4 (29)	14.3 (34)	−1.3 (11)	0.2 (9)	7.7 (26)

(b) Isotropic Thermal Parameters ($U \times 100$)

atom	U, Å^2	atom	U, Å^2
H(2)	9.0 (16)	H(2′)	8.9
H(3)	8.3 (12)	H(3′)	8.9
H(4)	9.6 (14)	H(4′)	8.9

[a] The anisotropic thermal parameters employed in the refinement are U_{ij} in the expression $f = f^0 \exp(-2\pi^2\Sigma_{i,j=1}^3 U_{ij}h_ih_ja_i{}^*a_j{}^*)$; for isotropic atoms $f = f^0 \exp(-8\pi^2U(\sin^2\theta)/\lambda^2)$.

shift/error on the last cycle was 0.21. A final difference synthesis showed random fluctuations of up to ±0.25 e/Å^3.

Final positional and thermal parameters are tabulated in Tables II and III. Values of $|F_o|$ vs. $|F_c|$ for the 1073 reflections are given in Table IV.[18]

Results and Discussion

Preparation of (η^5-C_5H_5)Cr(CO)$_2$(NS). The reaction of trithiazyl trichloride, $S_3N_3Cl_3$, with Na[(η^5-C_5H_5)Cr(CO)$_3$] produces (η^5-C_5H_5)Cr(CO)$_2$(NS) (I), the first organometallic thionitrosyl complex, in 21% yield:[19]

$$\mathrm{Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3] + {}^1/_3S_3N_3Cl_3 \xrightarrow[-78\ ^\circ C]{THF} (\eta^5\text{-}C_5H_5)Cr(CO)_2(NS) + CO + NaCl} \quad (1)$$

This reaction resembles a procedure previously used in this laboratory to synthesize various nitrosyl complexes, namely, the treatment of organometallic carbonylates with ClNO.[20] Indeed, we believe that an important feature of our preparation of I is that in THF the trithiazyl trichloride reagent probably exists as a solvated monomer, NSCl(THF)$_x$. This belief is based on the following observations. Yellow $S_3N_3Cl_3$ dissolves in $CHCl_3$ to give yellow-green solutions that exhibit a ν(NS) at 1010 cm^{-1} which is comparable to the 1008-cm^{-1} band observed in an IR spectrum of the solid compound in a Nujol mull. In donor solvents such as CH_3CN and THF, $S_3N_3Cl_3$ dissolves to give mint green solutions. The CH_3CN solution displays a ν(NS) at 1245 cm^{-1}, but a similar band cannot be detected in the IR spectrum of the THF solution because of pronounced solvent absorptions in this frequency range. Pyrolysis of $S_3N_3Cl_3$ at 80 °C is known to result in the formation of monomeric, green NSCl which exhibits a ν(NS) at 1322 cm^{-1} in the gas phase.[21]

Attempts to prepare other organometallic thionitrosyl complexes by reactions analogous to eq 1 have not succeeded as yet because $S_3N_3Cl_3$ appears to be a stronger oxidizing agent than ClNO. Thus, treatment of the more nucleophilic anions[22] [(η^5-C_5H_5)M(CO)$_3$]$^-$ (M = Mo or W) with $S_3N_3Cl_3$ in THF at −78 °C results in the formation of [(η^5-C_5H_5)M(CO)$_3$]$_2$ and (η^5-C_5H_5)M(CO)$_3$Cl as the only isolable organometallic products in yields of ~25 and ~15% (based on M), respectively. The former product is probably formed by the oxidation of the anionic reactant, and the latter product could result from the reaction of the dimer with NSCl(THF)$_x$ in a manner similar to that reported for ClNO.[11] Consistent with this interpretation is the fact that [Mn(CO)$_5$]$^-$ is simply oxidized to $Mn_2(CO)_{10}$ by trithiazyl trichloride in THF. However, the reactions of $S_3N_3Cl_3$ with the neutral complexes (η^5-C_5H_5)M(CO)$_2$(NO) (M = Cr or Mo) in THF or CH_2Cl_2 to produce (η^5-C_5H_5)Cr(NO)$_2$Cl and [(η^5-C_5H_5)Mo(NO)Cl]$_2$ are inexplicable in terms of the presently available information on the reactivities of the sulfur reagent.

Physical Properties of (η^5-C_5H_5)Cr(CO)$_2$(NS). A comparison of the physical properties of the new thionitrosyl complex (I) with those exhibited by its nitrosyl analogue (II) permits a direct contrast of the bonding properties of the NS and NO ligands in similar environments. Dicarbonyl(η^5-cyclopentadienyl)(thionitrosyl)chromium is a dark red-brown, diamagnetic solid which is freely soluble in common organic solvents to give blood-red solutions that eventually deposit some decomposed matter when exposed to air for several hours. The pure solid is reasonably stable in air but is best stored in an inert atmosphere. It is quite thermally stable, melting reversibly at 68–69 °C; and it is quite volatile, subliming readily onto a dry-ice-cooled probe at ambient temperature (5 × 10^{-3} mm) without attendant decomposition.

The IR spectrum of I in hexanes displays the expected three strong bands attributable to terminal CO and NS groups. The ν(NS) band at 1180 cm^{-1} occurs in the frequency range (i.e., 1120–1280 cm^{-1}) observed for other thionitrosyl complexes.[3] The ν(CO) bands of I at 2033 and 1962 cm^{-1} occur at slightly higher frequencies than those of II (2028, 1955 cm^{-1}), thereby suggesting that the NS ligand is more effective in removing electron density from the metal center than is the NO ligand. This conclusion is supported by the results of an electron-impact study carried out on both I and II.

Table V. Relative Abundances and Appearance Potentials (AP) of the Major Metal-Containing Ions in the Mass Spectra of (η^5-C_5H_5)Cr(CO)$_2$(NX) (X = S or O)

I, X = S			II, X = O	
rel abund	AP, eV[a]	ion	AP, eV[a]	rel abund
36	7.8_3	$C_5H_5Cr(CO)_2(NX)^+$	8.5_1	26
8	8.1_5	$C_5H_5Cr(CO)(NX)^+$	9.3_7	21
74	9.0_7	$C_5H_5Cr(NX)^+$	10.5_3	13
100	13.4_5	$C_5H_5Cr^+$	12.7_9	100
63		Cr^+		37

[a] The given values are an average of ten indenpendent measurements and have a precision of ±0.1 eV.

Low-resolution mass spectral data for both complexes are displayed in Table V. The two compounds were found to be sufficiently thermally stable to conclude that the observed fragmentation patterns result from electron bombardment and not from thermal decomposition. The major fragmentation pattern for both complexes involves two consecutive unimolecular carbonyl dissociation steps followed by loss of the NX (X = S or O) group to produce the $C_5H_5Cr^+$ ion. This ion fragments further by losing a neutral C_5H_5 group to give the Cr^+ ion. Consistent with this pattern are the observation of appropriate metastable ions for the nitrosyl complex and the absence of the ions $C_5H_5Cr(CO)_2^+$ and $C_5H_5Cr(CO)^+$ from the mass spectra of both the nitrosyl and thionitrosyl compounds.

Since both complexes I and II exhibit similar stabilities in the mass spectrometer and undergo parallel fragmentation processes, the appearance potentials of some of the fragment ions may be used to obtain a relative estimate of the Cr^+–CO and Cr^+–NX (X = S or O) ionic bond dissociation energies. These can be calculated from the difference between the appearance potential of the product ion and that of the reactant ion for a particular dissociation reaction. When such calculations are performed, two important results emerge, namely: (1) the average ionic bond dissociation energies, $\bar{D}$(Cr^+–CO), for the processes

$$\mathrm{C_5H_5Cr(CO)_2(NX)^+ \rightarrow C_5H_5Cr(CO)(NX)^+ + CO}$$

$$\mathrm{C_5H_5Cr(CO)(NX)^+ \rightarrow C_5H_5Cr(NX)^+ + CO}$$

are 1.0 and 0.6 eV for X = O and X = S, respectively, and (2) the ionic bond dissociation energies, D(Cr^+–NX), for the processes

$$\mathrm{C_5H_5Cr(NX)^+ \rightarrow C_5H_5Cr^+ + NX}$$

are 2.2 and 4.4 eV for X = O and X = S, respectively. In terms of the relative bonding properties of the NO and NS ligands, these results indicate two features. First, the Cr–N bond in the thionitrosyl complex appears to be stronger than the Cr–N bond in the nitrosyl complex. In accord with the existence of a stronger Cr–NS linkage is the fact that the $C_5H_5Cr(NS)^+$ ion is markedly more abundant in the mass spectrum of I than is the $C_5H_5Cr(NO)^+$ ion in the spectrum of II (Table V). The second inference that can be drawn from these results is that the NS ligand is a better π acceptor than the NO ligand. Consistent with this view is the observation that the Cr–CO bonds are apparently weaker in the thionitrosyl complex, reflecting poorer π back-donation from the

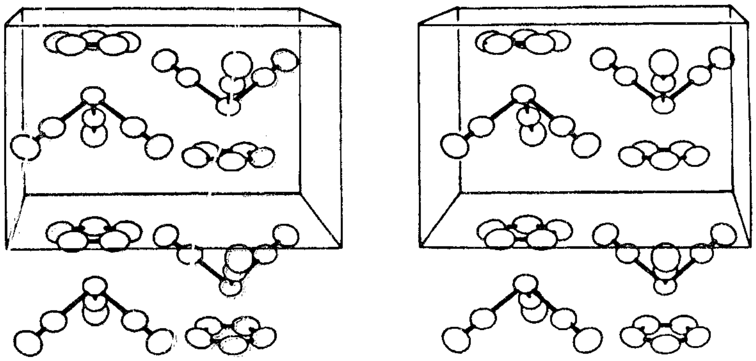

Figure 1. Stereoscopic view of the crystal packing. The cell origin is at the lower right, back corner with *a* running vertically from bottom to top, *b* from right to left, and *c* toward the viewer. Thermal ellipsoids are drawn at the 50% probability level.

metal to the CO ligands. The weaker Cr–CO linkages could also arise because of diminished σ donation by the NS group. However, this would result in relatively weaker Cr–NS than Cr–NO bonding in I and II, a feature which is contradictory to the first inference above. The greater π-accepting ability of the NS ligand is also reflected in the higher ν(CO) values observed in the IR spectrum of the thionitrosyl complex (vide supra).

NMR data for $CDCl_3$ solutions of the $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NX)$ complexes are as follows. For I (X = S): ^1H δ 5.08 (s); ^{13}C δ 92.75 (C_5H_5), 239.43 (CO). For II (X = O): ^1H δ 5.03 (s); ^{13}C δ 90.18 (C_5H_5), 237.05 (CO). Surprisingly, we observe a downfield shift in the carbonyl ^{13}C resonances in going from II to I. The replacement of a ligand in a carbonyl complex by a better π-accepting group generally results in an upfield shift of these resonances.[23] Hence, the observation of more deshielded carbonyl resonances in the spectrum of I seems to imply increased Cr→CO π back-donation resulting from greater electron density on the metal. The lower ionization potential measured for I (Table V) supports such a view of its electron distribution but contrasts directly with the ν(CO) data discussed previously.

The observed physical properties of I and II thus present an interesting dichotomy concerning the ligating properties of NS and NO. On the one hand, IR and electron-impact data suggest that NS is a better remover of electron density from the chromium atom than is NO. On the other hand, NMR and ionization potential measurements imply that it is a better provider of electrons to the metal center. A similar apparent contradiction in experimental observations has been reported for the related complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ (isoelectronic with I) and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (isoelectronic with II). For these compounds, IR spectral data indicate that the presence of the CS group decreases the Mn–CO bond strength (i.e., increases the carbonyl-stretching force constant),[24] and yet the thiocarbonyl complex has a lower first ionization potential.[25,26] It has been suggested[26] that the occurrence of π donation by the CS ligand may account for the observed anomaly. However, such an explanation cannot be invoked for the NS ligand in I since currently accepted bonding formulations require an increase in electron density at the metal center (whether by σ or π donation from the ligands) to be manifested in increased M→CO π back-donation. The assessment of the relative π-acceptor to σ-donor ratios of NS and NO ligands must thus await a detailed theoretical analysis.

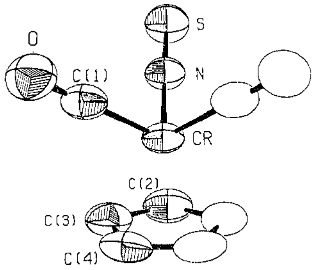

Figure 2. Molecular structure of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ as viewed down the crystallographic mirror plane. Only the $^2/_3$ cyclopentadienyl ring is shown, and hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 50% probability level.

Table VI. Bond Distances (Å) and Bond Angles (deg) for $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$

	Bond Distances		
Cr–N	1.694 (2)	N–S	1.551 (2)
Cr–C(1)	1.883 (2)	C(1)–O	1.131 (2)
Cr–C(2)	2.13 (1)	Cr–C(2′)	2.23 (2)
Cr–C(3)	2.19 (1)	Cr–C(3′)	2.18 (2)
Cr–C(4)	2.22 (1)	Cr–C(4′)	2.23 (2)
Cr–CP[a]	1.85	C(2′)–C(3′)	1.42 (2)
C(2)–C(3)	1.39 (2)	C(3′)–C(4′)	1.32 (3)
C(3)–C(4)	1.44 (2)	C(4′)–C(4′)[b]	1.36 (5)
C(4)–C(4)[b]	1.39 (1)	C(2′)–H(2′)	1.05
C(2)–H(2)	1.02 (7)	C(3′)–H(3′)	1.04
C(3)–H(3)	0.95 (5)	C(4′)–H(4′)	0.90
C(4)–H(4)	0.91 (5)		
	Bond Angles		
N–Cr–C(1)	94.78 (7)	C(2)–C(3)–C(4)	104 (1)
C(1)–Cr–C(1)[b]	92.4 (1)	C(3)–C(2)–C(3)[b]	114 (2)
N–Cr–CP[a]	130.1	C(3)–C(4)–C(4)[b]	109 (1)
C(1)–Cr–CP[a]	118.2	C(2′)–C(3′)–C(4′)	110 (2)
Cr–N–S	176.8 (1)	C(3′)–C(2′)–C(3′)[b]	102 (2)
Cr–C(1)–O	178.1 (2)	C(3′)–C(4′)–C(4′)[b]	109 (1)

[a] CP represents the unweighted centroid of the disordered η^5-C_5H_5 ring. [b] Symmetry-related atom at x, $^1/_2 - y$, z.

Structure of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. The crystal structure of the complex consists of a well-separated array of discrete molecular units, the intermolecular distances corresponding to normal van der Waals contacts. The crystal packing is illustrated in Figure 1. Each molecule has crystallographic *m* symmetry and is in a "piano stool" configuration. The molecular structure as viewed down the mirror plane is presented in Figure 2 with only the $^2/_3$ η^5-C_5H_5 ring, described by C(2), C(3), and C(4), being shown. Bond distances and interbond angles are given in Table VI with primed atoms designating the $^1/_3$ η^5-C_5H_5 ring.

The disordered cyclopentadienyl ring seems reasonably represented as found. It has a mean C–C distance of 1.39 Å and a mean C–C–C angle of 108.0°; none of the individual values differ significantly from these averges. The mean C–H distance is 0.97 Å and average H–C–C angles are 126° for the $^2/_3$ η^5-C_5H_5 ring and 125° for the $^1/_3$ ring. The average Cr–C(cp) distance is 2.20 Å. The Cr–C–O linkages are inherently linear, and the Cr–C(O) and C–O bond lengths are comparable to those found in other cyclopentadienylchromium carbonyls.[27]

The most chemically interesting feature of the structure is the fact that the thionitrosyl ligand coordinates essentially linearly to the metal via the nitrogen atom. The Cr–N bond length of 1.694 (2) Å falls in the range of values (i.e., 1.630–1.717 Å)[27] reported for Cr–N bonds formed by linear, terminal nitrosyl ligands. Hence, in a formal sense, the thionitrosyl group (an overall three-electron donor in this bonding configuration) can be considered to be bonded as NS^+, a mode of coordination that is directly analogous to metal–thiocarbonyl bonding and involves synergistic coupling of σ- and π-bonding components.[28] Consistent with the occurrence of back-donation from Cr π orbitals to NS π^* orbitals is the fact that the N–S distance of 1.551 (2) Å in the complex is longer than the NS^+ equilibrium bond length of 1.440 ± 0.005 Å determined spectroscopically in the vapor state.[29] In view of the conflicting evidence concerning the relative bonding properties of NS and NO ligands provided by a comparison of the physical properties of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ and its nitrosyl analogue (vide supra), it would be of interest to contrast the Cr–NX (X = S or O) bond lengths in the two molecules. Regrettably, an effective comparison of these distances is precluded by crystallographic disorder among the CO and NO groups in the solid-state structure of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$.[30]

Chemical Properties of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. Since the infrared absorptions due to the carbonyl ligands in the thionitrosyl complex (I) are of only slightly higher energy than those exhibited by its nitrosyl analogue (II), it can be reasonably expected that the CO groups in I will not be significantly more labile. Indeed, this is found to be true as I does not react with PPh_3 even in refluxing toluene; after several days, the unaltered organometallic reactant can be recovered quantitatively from the reaction mixture. This is comparable to the reactivity of II which requires 160 °C and neat PPh_3 to be converted to $(\eta^5\text{-}C_5H_5)Cr(CO)(PPh_3)(NO)$.[31] This phosphine complex can also be prepared from II photochemically, but photolysis of I in the presence of PPh_3 results in the complete removal of the CO and NS ligands from the starting material. Furthermore, solutions of I and II do not react with nitric oxide at room temperature.

Nitrosyl chloride is known to displace the carbonyl ligands from II, i.e.[5]

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + ClNO \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)Cr(NO)_2Cl + 2CO \tag{2}$$

Interestingly, the analogous reaction with I does not produce the still unknown $(\eta^5\text{-}C_5H_5)Cr(NO)(NS)Cl$ but rather affords the ubiquitous $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ in 27% yield. Infrared monitoring of the latter reaction indicates that it probably proceeds via $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ (ν(NO) 1680 cm^{-1}). In an independent experiment, we have verified that this dimeric complex does indeed slowly disproportionate to the observed product.

Treatment of II with $NOPF_6$ results in the production of green $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)_2]PF_6$ in 93% yield. This reaction parallels exactly those reported[32] for $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ [M = Mo or W] with the same nitrosonium salt. The product of reaction 3 is a water-sensitive, green-black solid

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS) + NOPF_6 \xrightarrow[-78\ °C]{CH_2Cl_2/CH_3CN} [(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6 + CO \tag{3}$$

which is insoluble in all but those solvents with which it reacts. It can be formulated as $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6$ on the basis of its IR spectrum (Nujol mull) which exhibits a ν(CO) at 2122 cm^{-1}, a ν(NO) at 1790 cm^{-1}, and a ν(NS) at 1243 cm^{-1}. In accord with this formulation, the carbonyl- and nitrosyl-stretching frequencies are in the range previously observed for carbonylnitrosyl cations,[32] and the thionitrosyl-stretching frequency occurs at higher energy than that displayed by the neutral $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. This latter feature is consistent with a decrease in electron density at the metal center which manifests itself in less back-donation from the metal to the NS π^* orbitals. Like the dinitrosyl cation, the nitrosyl(thionitrosyl) cation undergoes nucleophilic attack by I^-, finally producing $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$ in ~25% yield. However, in contrast to the dinitrosyl cation, this conversion involves the initial formation of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$[33] which then slowly disproportionates to the isolated complex.

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Registry No. $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$, 66539-91-1; $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$, 12203-12-2; $S_3N_3Cl_3$, 5964-00-1; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)_2]PF_6$, 69439-82-3; $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$, 53504-57-7; $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$, 64024-33-5; $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$, 12107-36-7; $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$, 12107-35-6; $Na[Mn(CO)_5]$, 13859-41-1; $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, 36312-04-6; $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$, 12128-13-1; $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, 12566-66-4; $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, 12128-24-4; $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, 12091-64-4; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, 12128-23-3; $Mn_2(CO)_{10}$, 10170-69-1; $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl]_2$, 71685-63-7.

Supplementary Material Available: Table IV, a listing of structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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The Tungsten–Tungsten Triple Bond. 9.[1] Bis(1,3-diphenyltriazenido)tetrakis(dimethylamido)ditungsten

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$W_2(NMe_2)_6$ reacts in hydrocarbon solvents with 1,3-diphenyltriazine, PhNNNHPh, to give the title compound $W_2(NMe_2)_4(PhN_3Ph)_2$ as a brick red, crystalline solid. An X-ray study shows that in the solid state each tungsten atom is coordinated to four nitrogen atoms which lie in a plane; there is an unbridged tungsten-to-tungsten triple bond with a W–W distance of 2.314 (1) Å. The two $W(NMe_2)_2(PhN_3Ph)$ units are joined together so that the molecule has C_2 symmetry. The molecule may be viewed as one of the class of *gauche*-$M_2X_2(NMe_2)_4$ compounds ($M\equiv M$). The low-temperature limiting ^1H NMR spectrum at 220 MHz is attained at −40 °C and is consistent with the structure found in the solid state: apparently the rotamers (the two enantiomers) with C_2 symmetry are favored relative to other isomeric forms of the molecule. On increase of temperature, rotations about the W–N bonds interconvert proximal and distal methyl groups of the two types of NMe_2 ligands at different rates. However, these processes do not cause enantiomerization (gauche to gauche isomerization) on the NMR time scale. These observations are compared with earlier findings in dimolybdenum and ditungsten chemistry.

Introduction

Early transition metal dimethylamides exhibit high reactivity toward substrates with active (protic) hydrogen atoms.[2] The general equation for this type of reaction may be represented by eq 1.

$$M(NMe_2)_x + yLH \rightarrow M(NMe_2)_{x-y}(L)_y + yHNMe_2 \qquad (1)$$

Ligand substitution reactions of this type have been extended to dinuclear dimethylamides in our laboratory and have proved important in the synthesis of dinuclear metal alkoxides $M_2(OR)_6$ ($M\equiv M$, M = Mo,[3] W[1]). The insertion of CO_2 into the $M–NMe_2$ bond in the formation of the dinuclear *N,N*-dimethylcarbamato compounds, e.g.,[4] $W_2Me_2(O_2CNMe_2)_4$ and $W_2(O_2CNMe_2)_6$, has been found[5] to proceed by an amine-catalyzed mechanism shown in eq 2. This is also a form of reaction 1.

$$HNMe_2 + CO_2 \rightleftharpoons Me_2NCOOH$$
$$MNMe_2 + Me_2NCOOH \rightarrow M(O_2CNMe_2) + HNMe_2 \qquad (2)$$

The insertion of carbon dioxide into M–OR bonds in reaction 3 has been shown[6] to proceed by both direct and catalyzed mechanisms.

$$Mo_2(OR)_6 + CO_2 \rightleftharpoons Mo_2(OR)_4(O_2COR)_2 \qquad (3)$$

In this paper we report the preparation and characterization of a triazenidoditungsten compound, formed according to reaction 4. This, to our knowledge, is the first preparation

$$M_2(NMe_2)_6 + 2PhNNNHPh \rightarrow M_2(NMe_2)_4(PhN_3Ph)_2 + 2HNMe_2 \qquad (4)$$

of a triazenido compound from a triazene and a transition metal dimethylamide. The structural aspects of this work are compared with those reported for alkylcarbonato and dimethylcarbamato complexes of dimolybdenum and ditungsten ($M\equiv M$).

Results and Discussion

Synthesis. In hydrocarbon solvents, $W_2(NMe_2)_6$ and 1,3-diphenyltriazene, PhNNNHPh, react upon mixing at room temperature. This rapid reaction is accompanied by color changes of the solutions from pale yellow, $W_2(NMe_2)_6$, and pale orange, PhNNNHPh, to deep red, $W_2(NMe_2)_4(PhN_3Ph)_2$. The triazenidoditungsten compound was obtained as deep red crystals by crystallization from toluene–hexane solvent mixtures.

Crystals of $W_2(NMe_2)_4(PhN_3Ph)_2$ are stable in the atmosphere for several hours. We attribute this unusual insensitivity toward hydrolysis to (i) steric congestion in the molecule and (ii) the hydrophobic nature of the *N*-phenyl and *N*-methyl groups.

In the mass spectrometer the compound shows a molecular ion $Mo_2(NMe_2)_4(PhN_3Ph)_2^+$ followed by loss of one and two NMe_2 groups, $[M - 44]^+$ and $[M - 88]^+$. In addition there is an intense mononuclear ion $W(NMe_2)_2(NPh)_2^+$ which is possibly formed by a process in which molecular nitrogen is eliminated: $W_2(NMe_2)_4(PhN_3Ph)_2 \rightarrow 2W(NMe_2)_2(NPh)_2 + N_2$. This reaction has not been realized on the bench top, however.

Analytical data, infrared data, and other spectroscopic data are recorded in the Experimental Section.

Solid-State Structure. In the crystalline state the compound is composed of discrete molecules of $W_2(NMe_2)_4(PhN_3Ph)_2$. ORTEP views indicating the coordination geometry and the atom numbering scheme are shown in Figures 1 and 2. Final atomic coordinates and thermal parameters are given in Table I. Complete listings of bond distances and angles are given in Tables II and III, respectively. A table listing a number of least-squares planes calculated for this molecule and the deviations of atoms from these planes is available as supplementary material.

From the view of the molecule shown in Figure 1, it can be seen that the molecule consists of two $W(NMe_2)_2(PhN_3Ph)$ units fused together by an unbridged tungsten–tungsten bond. Furthermore, it is seen that the molecule has C_2 symmetry and

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