NMR spectra are referenced to the signals of the deuterated solvent, THF-$d_8$: $^1H$, residual α-H, δ = 3.58 ppm; $^{13}C$, α-C, δ = 67.4 ppm. $^6Li$ spectra are referenced to 1M LiBr in THF/THF-$d_8$. The reference measurements were carried out prior to the sample measurements at the indicated temperatures. The following probe heads were employed: selective 5-mm $^1H$ (Figure 1; 90° pulse width 35 μs, attenuated), dual 5-mm $^{13}C$, $^1H$ (Figure 3; 90° pulse widths 9 μs, $^{13}C$, and 15 μs, $^1H$), and 10-mm multinuclear (Figures 2 and 4; 90° pulse widths 28 μs, $^6Li$, and 28 μs, $^1H$). The States[30] method was employed for quadrature detection in $f_1$ for phase sensitive 2D NMR spectra.

Selected parameters for the individual spectra shown in the figures are as follows:

(a) Figure 1 (phase-sensitive ROESY of **23**): 0.35 M solution in THF-$d_8$, +26 °C, spectral width 2500 Hz ($f_1$ and $f_2$), 512 complex data points in $t_2$, zero filled to 1024 points, 128 $t_1$ increments, zero filled to 256 complex $t_1$ data points, 48 scans per $t_1$ increment, spin lock time 0.6 s (repetitive $[11.7\text{-}\mu s \text{ pulse}, 117\text{-}\mu s \text{ delay}]_{4668}$ sequence), Gaussian window in $t_1$ and $t_2$, interpulse delay 2.0 s.

(b) Figure 2 (phase-sensitive $^6Li$,$^1H$ HOESY of **23**): 0.35 M solution in THF-$d_8$, +26 °C, 5-mm sample tube, spectral widths 400 Hz ($f_2$, $^6Li$) and 2500 Hz ($f_1$, $^1H$), 256 complex data points in $t_2$, 64 increments in $t_1$, zero filled to 256 complex data points, 48 scans per $t_1$ increment, mixing time 2.0 s, Gaussian window in $t_1$ and $t_2$, interpulse delay 2.8 s.

(c) Figure 3 (magnitude mode C,H shift correlation of **23**): 0.35 M solution in THF-$d_8$, −90 °C, spectral widths 14970 Hz ($f_2$, $^{13}C$) and 2500 Hz ($f_1$, $^1H$), 1024 complex data points in $t_2$, zero filled to double size, 128 increments in $t_1$, zero filled to double size, 64 scans per $t_1$ increment, Gaussian window in $t_1$ and $t_2$ interpulse delay 2.2 s.

(d) Figure 4 (phase-sensitive $^6Li$,$^1H$ HOESY of **23**): 0.65 M solution in THF-$d_8$, −110 °C, spectral widths 906 Hz ($f_2$, $^6Li$) and 2500 Hz ($f_1$, $^1H$), 1024 complex data points in $t_2$, zero filled to double size, 128 increments in $t_1$, zero filled to double size, 32 scans per $t_1$ increment, mixing time 2.0 s, Gaussian window in $t_1$ and $t_2$, interpulse delay 3.0 s.

MNDO calculations were carried out on a CONVEX C220 computer by using the VAMP4 (vectorized AMPAC) program. All geometry optimizations involved the keyword EF (Eigenvector following). No symmetry constraints were imposed.

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[30] States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* 1982, *48*, 286.

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# Synthesis of Cyclopentadienyldinitrosyl(trifluoromethyl)chromium(0), $CpCr(NO)_2CF_3$, and Cyclopentadienyldinitrosyl(trifluoromethyl)molybdenum(0), $CpMo(NO)_2CF_3$. Crystal Structure of $CpCr(NO)_2CF_3$

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The new compounds $CpCr(NO)_2CF_3$ (71%) and $CpMo(NO)_2CF_3$ (44%) were prepared from the interactions of $Cd(CF_3)_2$·glyme (glyme = $CH_3OCH_2CH_2OCH_3$) with the chlorides at 65 °C; $CpW(NO)_2CF_3$, however, was not afforded by the analogous reaction with $CpW(NO)_2Cl$. The trifluoromethyl derivatives were characterized by $^{19}F$, $^{13}C$, and $^1H$ NMR, by IR, and by mass spectrometry. X-ray crystallography demonstrated that $CpCr(NO)_2CF_3$ crystallizes in the orthorhombic space group *Pnnm*, with $Z = 4$, $a = 7.770$ (4) Å, $b = 10.200$ (4) Å, and $c = 11.179$ (5) Å. The chromium complex is exceptionally thermally and oxidatively stable, but $CpMo(NO)_2CF_3$ reacts with air immediately upon exposure, and under an inert atmosphere decomposition is evident within 10 h.

## Introduction

The first trifluoromethyl-containing transition-metal complexes were generated by thermal decarbonylations of $CF_3CO$ ligands, and soon thereafter $CF_3I$ oxidative addition was developed as the second major route to $CF_3$–metal derivatives. While a reasonably large number of compounds have been synthesized by these methods, each has fairly severe limitations and their utility has been largely confined to low-valent, late (electron rich) transition metals.[2]

We have been examining ligand-exchange reactions between $Cd(CF_3)_2$·glyme[3] (glyme = $CH_3OCH_2CH_2OCH_3$) and a number of main-group[4] and transition-metal halides,

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[1] (a) University of Illinois at Chicago. (b) Southern Methodist University.

[2] (a) Morrison, J. A. *Adv. Inorg. Chem. Radiochem.* 1983, *27*, 293. (b) Brothers, P. J., Roper, W. R. *Chem. Rev.* 1988, *88*, 1293. (c) Treichel, P. M.; Stone, F. G. A. *Adv. Organomet. Chem.* 1964, *1*, 143. (d) Morrison, J. A. *Adv. Organomet. Chem.*, submitted for publication.

[3] Krause, L. J.; Morrison, J. A. *J. Am. Chem. Soc.* 1981, *103*, 2995. Ontiveros, C. D.; Morrison, J. A. *Inorg. Synth.* 1986, *24*, 55.

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including the group 11 species $MX(PMe_3)$ (M = Cu, Ag, Au; X = Br, Cl, and OAc)[5] and the group 10 compounds $MX_2(PR_3)_2$ (M = Ni, Pd, Pt; X = Br, I).[6] In both series the stability of the trifluoromethylated products increases from the 3d to the 4d to the 5d transition metal. In addition, the reaction between $CpCo(CO)I_2$ and $Cd(CF_3)_2$·glyme was described; it yielded the previously unknown $CpCo(CO)(CF_3)_2$ (63%) along with $CpCo(CO)I(CF_3)$ (16%). The disubstituted product was also shown to be much more thermally stable than its methylated analog, $CpCo(CO)(CH_3)_2$.[7]

The objective of the present study was to examine the reactions of $Cd(CF_3)_2$·glyme with a series of halides in which the metal atoms had been drawn from an earlier group in the periodic table. For this purpose, the cyclopentadienyl dinitrosyl chlorides of the group 6 elements Cr, Mo, and W were selected, in part because all three homologs are known and in part because it facilitates comparisons between the 18-electron $d^6$ Co(III) complex above and, e.g., an 18-electron $d^6$ Cr(0) species. Other attractive features of this system included the facts that in no case have group 6 complexes that contained both $CF_3$ and NO ligands been described and that while the existence of, e.g., $CpMo(CO)_3CF_3$ and the Cr(III) derivatives $Cr(H_2O)_5(CF_3)^{2+}$,[8] $Cr(CH_3CN)_3Cl_2(CF_3)$,[9] and Cr(py)(Salen)$(CF_3)$[9] has been reported, in no previous case has a $Cr^0$–$CF_3$ or a $Mo^0$–$CF_3$ complex been characterized.

## Experimental Section

All manipulations of air-sensitive materials were carried out in glovebags, gloveboxes, or standard vacuum lines. Mass spectral data at 70 eV were obtained from a Hewlett-Packard 5985A spectrometer. Ambient-temperature $^1H$, $^{13}C$, and $^{19}F$ NMR spectra were obtained with IBM 200-SY or Bruker AM-400 spectrometers from samples that had been dissolved in $CH_2Cl_2$ or $CDCl_3$ and then sealed into 4-mm Pyrex tubing. Positive chemical shifts are deshielded from external $CF_3CO_2H$ or $Si(CH_3)_4$. IR spectra were obtained from an IBM IR-32 FT instrument. Uncorrected melting points are from a Thomas Hoover capillary melting point apparatus.

Cyclopentadiene was prepared from the dimer (Aldrich). Glyme (1,2-dimethoxyethane), THF, and butyl ether were dried with sodium benzophenone ketyl and $CH_2Cl_2$ and $CDCl_3$ over $P_4O_{10}$. Nitrosyl chloride (Matheson) was commercially obtained; nitric oxide was generated from the reaction of $NaNO_2$ with $FeSO_4$ and $H_2SO_4$. Molybdenum hexacarbonyl, $W(CO)_6$, $CrCl_3$, and Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) were all purchased from Aldrich.

Bis(trifluoromethyl)cadmium–glyme was prepared from $Cd(CH_3)_2$ and $Hg(CF_3)_2$ in glyme.[3] Golden yellow $CpCr(NO)_2Cl$[10] ($\nu$(NO) 1815, 1690 $cm^{-1}$), green $CpMo(NO)_2Cl$[11] ($\nu$(NO) 1757, 1649 $cm^{-1}$), and green $CpW(NO)_2Cl$[11] ($\nu$(NO) 1736, 1649 $cm^{-1}$) were synthesized by the literature routes.

**Preparation of $CpCr(NO)_2CF_3$ from $CpCr(NO)_2Cl$ and $Cd(CF_3)_2$·glyme.** Freshly sublimed $CpCr(NO)_2Cl$ (0.090 g, 0.42 mmol) and $Cd(CF_3)_2$·glyme (0.432 g, 1.27 mmol) were placed in a 20 × 80 mm cylindrical Pyrex reactor that was then attached to a vacuum line through a 4-mm Teflon valve, cooled to −196 °C, and evacuated. Dry $CH_2Cl_2$ (4 mL) was added, and the vessel was placed in a 65 °C oil bath for 10 h. The reactor contents were transferred to a vacuum sublimator, and the solvent was evaporated. Sublimation at 60 °C yielded $CpCr(NO)_2CF_3$ (0.075 g, 0.30 mmol) in 71% yield.

**Table I. Crystal Data and Structure Refinement Details**

| | |
|---|---|
| compd | $C_6H_5N_2O_2F_3Cr$ |
| fw | 246.1 |
| cryst syst | orthorhombic |
| space group | *Pnnm* |
| *a*, Å | 7.770 (4) |
| *b*, Å | 10.200 (4) |
| *c*, Å | 11.179 (5) |
| *V*, Å$^3$ | 886.0 (8) |
| molecules/unit cell | 4 |
| $\rho$(calcd), g cm$^{-3}$ | 1.84 |
| $\mu$(calcd), cm$^{-1}$ | 12.83 |
| radiation | Mo K$\alpha$ |
| cryst size, mm | 0.20 × 0.10 × 0.30 |
| temp, K | 293 |
| scan type | $\omega$–2$\theta$ |
| scan width, deg | 1.20 plus K$\alpha$ separation |
| 2$\theta$ range, deg | 3.5–42.0 |
| std reflns | 3 measd every 150 reflns |
| decay of stds | none |
| no. of reflns collected | 587 |
| no. of reflns obsd, $I \geq 3.0\sigma(I)$ | 463 |
| no. of params varied | 78 |
| GOF | 2.02 |
| *R* | 0.046 |
| $R_w$ | 0.059 |

Green cyclopentadienyldinitrosyl(trifluoromethyl)chromium(0) melts at 135 °C without decomposition, and no decomposition was observed when $CpCr(NO)_2CF_3$ was heated to 200 °C in an unsealed capillary tube. The $^{19}F$ (70.1 ppm) and the $^1H$ (5.67 ppm) NMR spectra are singlets; the $^{13}C\{^1H\}$ spectrum consists of a singlet at 99.8 ppm ($C_5H_5$) and a quartet at 158.2 ppm ($J_{C-F}$ = 373 Hz ($CF_3$)). The IR spectra contain strong bands at 1817 and 1734 $cm^{-1}$ ($\nu$(NO)), at 1071 and 994 $cm^{-1}$ (C–F stretches), and at 835 $cm^{-1}$. Mass spectrum (*m*/*e*, ion, intensity): 246, $CpCr(NO)_2CF_3$, 3.6%; 227, $CpCr(NO)_2CF_2$, 5.5%; 216, $CpCr(NO)CF_3$, 35.4%; 186, $CpCrCF_3$, 2.1%; 177, $CpCr(NO)_2$, 31.0%; 147, CpCr(NO), 19.1%; 136, CpCrF, 100.0%; 121, $CrCF_3$, 1.8%; 117, CpCr, 18.5%; 90, $CrF_2$, 6.3%; 71, CrF, 39.0%; 69, $CF_3$, 5.4%; 65, Cp, 4.1%; 52, Cr, 26.4%. Anal. (Schwarzkopf, Woodside, NY) calcd (found): C, 29.28 (29.50); H, 2.05 (2.54).

**Stability of $CpCr(NO)_2CF_3$.** When butyl ether (0.25 mL), $C_6H_5CF_3$ (0.1 mg), and $CpCr(NO)_2CF_3$ (2 mg) were all sealed into a 4-mm Pyrex tube and heated to 115 °C, $^{19}F$ NMR integrations indicated that little decomposition occurred during the initial 250 h, that after 400 h ca. half of the $CF_3$ compound had decomposed, and that after 1100 h at 115 °C approximately 2% of the organometallic species remained.

**Crystal Structure.** After recrystallization of $CpCr(NO)_2CF_3$ from $CH_2Cl_2$/hexane, a green crystal was mounted on a Nicolet R3m/V diffractometer. The final unit cell parameters given in Table I were obtained by a least-squares fit of the angles of 24 accurately centered reflections (18° < 2$\theta$ < 25°). The intensity data were collected in the range 3.5° ≤ 2$\theta$ ≤ 42.0° at room temperature using graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation in the $\omega$/2$\theta$ scan mode; 587 reflections were collected, of which 509 were unique. The systematic absences were consistent with the space groups *Pnnm* and *Pnn*2. The structure was solved in the centrosymmetric space group, and the successful refinement confirmed that this was the correct choice. Three standard reflections monitored after every 150 reflections did not show any significant change in intensity during the data collection. The data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied. The minimum and maximum transmission factors were 0.6408 and 1.0000, respectively.

The structure was solved by direct methods with the SHELXTL-Plus package.[12a] Scattering factors with anomalous dispersion corrections for Cr were taken from ref 12b. Full-matrix

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(4) Morrison, J. A. Paper presented at the 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 1992.

(5) Nair, H. K.; Morrison, J. A. *J. Organomet. Chem.* **1989**, *376*, 149.

(6) Krause, L. J.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* 1981, 1292.

(7) Ontiveros, C. D.; Morrison, J. A. *Organometallics* **1986**, *5*, 1446.

(8) Malik, S. K.; Schmidt, W.; Spreer, L. O. *Inorg. Chem.* **1974**, *13*, 2986.

(9) Van Den Bergen, A. M.; Murray, K. S.; Sheahan, R. M.; West, B. O. *J. Organomet. Chem.* **1975**, *90*, 299.

(10) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(11) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

(12) (a) Sheldrick, G. M. Siemens Analytical Software Package, Siemens Corp., Madison, WI, 1990. (b) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K.; 1974; Vol. IV.

**Table II. Atomic Coordinates ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^4$)**

| | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cr | 30 328 (9) | −31 831 (13) | 50 000 | 331 (6) |
| N | 40 508 (34) | −29 873 (48) | 37 768 (40) | 495 (15) |
| O | 47 610 (39) | −29 684 (59) | 29 198 (43) | 844 (18) |
| C(1) | 15 415 (43) | −43 229 (64) | 38 873 (56) | 493 (17) |
| F(1) | 19 748 (28) | 481 (47) | 60 476 (30) | 736 (14) |
| F(2) | 35 843 (44) | 4 410 (52) | 50 000 | 911 (21) |
| C(4) | 26 128 (67) | −6 054 (82) | 50 000 | 474 (22) |
| C(2) | 10 852 (67) | −35 728 (125) | 50 000 | 528 (30) |
| C(3) | 22 977 (48) | −56 538 (61) | 43 161 (48) | 485 (14) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III. Bond Lengths and Bond Angles for $CpCr(NO)_2CF_3$**

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Cr–N | 1.696 (4) | Cr–C(1) | 2.203 (5) |
| N–O | 1.181 (6) | Cr–C(2) | 2.198 (8) |
| Cr–C(4) | 2.057 (7) | Cr–C(3) | 2.202 (5) |
| F(1)–C(4) | 1.356 (5) | C(1)–C(2) | 1.374 (7) |
| F(2)–C(4) | 1.357 (9) | C(1)–C(3) | 1.405 (7) |
| | | C(3)–C(3A) | 1.395 (10) |
| | Bond Angles (deg) | | |
| N–Cr–C(1) | 99.5 (2) | N–Cr–C(4) | 93.8 (2) |
| C(1)–Cr–C(4) | 102.6 (2) | N–Cr–C(2) | 132.6 (1) |
| C(1)–Cr–C(2) | 36.4 (2) | C(4)–Cr–C(2) | 84.7 (3) |
| N–Cr–C(3) | 95.5 (2) | C(1)–Cr–C(3) | 37.2 (2) |
| C(4)–Cr–C(3) | 139.8 (2) | C(2)–Cr–C(3) | 60.7 (3) |
| N–Cr–N(0A) | 94.8 (3) | N–Cr–C(1A) | 157.4 (2) |
| C(1)–Cr–C(1A) | 62.0 (3) | N–Cr–C(3A) | 124.2 (2) |
| C(1)–Cr–C(3A) | 62.0 (2) | C(3)–Cr–C(3A) | 36.9 (3) |
| Cr–N–O | 175.6 (4) | Cr–C(1)–C(2) | 71.6 (4) |
| Cr–C(1)–C(3) | 71.4 (3) | C(2)–C(1)–C(3) | 106.2 (5) |
| Cr–C(4)–F(1) | 115.5 (3) | Cr–C(4)–F(2) | 113.6 (5) |
| F(1)–C(4)–F(2) | 103.3 (4) | Cr–C(2)–C(1) | 72.0 (4) |
| F(1)–C(4)–F(1A) | 104.0 (6) | Cr–C(3)–C(1) | 71.4 (3) |
| C(1)–C(2)–C(1A) | 111.4 (7) | C(1)–C(3)–C(3A) | 108.1 (3) |
| Cr–C(3)–C(3A) | 71.5 | | |

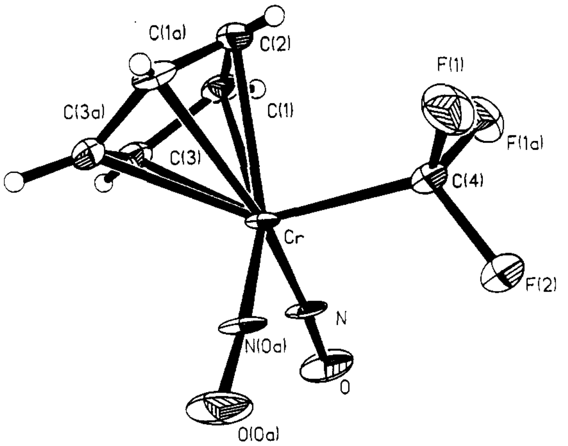

**Figure 1.** Perspective view of $CpCr(NO)_2CF_3$ including the atom-numbering scheme. The thermal ellipsoids of the heavier atoms are drawn at the 40% probability level, but the radii of the hydrogen atoms are arbitrary. The molecular point group is $C_s$ with the mirror plane containing the C(2), Cr, C(4), and F(2) atoms.

**Table IV. Representative Nitrosyl Stretching Frequencies for Cyclopentadienyldinitrosylchromium and -molybdenum Derivatives[a]**

| | $\nu$(NO), cm$^{-1}$ | |
|---|---|---|
| Chromium Complexes | | |
| $CpCr(NO)_2CF_3$ | 1817 | 1734 |
| $CpCr(NO)_2Cl$ | 1815 | 1690 |
| $CpCr(NO)_2CH_2Cl$[19] | 1792 | 1690 |
| $CpCr(NO)_2CH_2OCH_3$[19] | 1775 | 1674 |
| $CpCr(NO)_2CH_3$[15] | 1780 | 1675 |
| $CpCr(NO)_2CH_2PPh_3^+$[19] | 1781 | 1652 |
| Molybdenum Complexes | | |
| $CpMo(NO)_2CF_3$ | 1763 | 1655 |
| $CpMo(NO)_2Cl$ | 1757 | 1649 |
| $CpMo(NO)_2CH_3$[15] | 1728 | 1640 |

[a] Abbreviation: Cp = $\eta^5$-$C_5H_5$.

least-squares refinement was performed. All non-H atoms were refined anisotropically. The H atoms were located from difference Fourier maps, and their positions were refined with fixed isotropic temperature factors ($U = 0.08$ Å$^2$). The weight had the form $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$, where $g = 0.0008$. The final cycles of refinement converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.046$, $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2} = 0.059$, and GOF = 2.02 for 463 observed reflections ($I > 3.0\sigma(I)$). The maximum and minimum residual electron densities shown on the final difference Fourier maps were +0.45 and −0.50 e/Å$^3$, respectively. The final atomic coordinates and the equivalent isotropic thermal parameters are contained in Table II. Bond lengths and angles are contained in Table III. A perspective view of the molecular structure is presented in Figure 1.

**Preparation of $CpMo(NO)_2CF_3$ from $CpMo(NO)_2Cl$ and $Cd(CF)_3$·glyme.** Under an inert atmosphere $CpMo(NO)_2Cl$ (0.064 g, 0.25 mmol) and $Cd(CF_3)_2$·glyme (0.254 g, 0.75 mmol) were placed into the reactor, and $CH_2Cl_2$ (4 mL) was added. The reactor was sealed, and the contents were heated to 65 °C. After 7 h, the reaction was terminated and the vessel contents transferred to a vacuum sublimator. After removal of the material that was volatile under vacuum at −5 °C, sublimation at ambient temperature yielded $CpMo(NO)_2CF_3$ (0.031 g, 0.11 mmol, 44%).

Green cyclopentadienyldinitrosyl(trifluoromethyl)molybdenum(0) decomposes at 70 °C without melting. The $^{19}F$ and $^1H$ NMR chemical shifts are 68.8 (s) and 5.8 (s) ppm, respectively. The $^{13}C\{^1H\}$ spectrum consists of two resonances, a singlet at 102 ppm and a quartet at 152.5 ppm ($^1J_{C-F}$ = 364 Hz). Strong IR absorptions (KBr) are found at 1763 and 1655 cm$^{-1}$ ($\nu$(NO)), at 1094 and 1007 cm$^{-1}$ ($\nu$(CF)), and at 822 cm$^{-1}$. The mass spectrum of the compound was obtained only after it had been briefly exposed to the atmosphere (see below; $m/e$, ion, ion intensity): 292 $CpMo(NO)_2CF_3$, 6.5%; 273, $CpMo(NO)_2CF_2$, 3.8%; 262, $CpMo(NO)CF_3$, 33.1%; 232, $CpMoCF_3$, 28.2%; 223, $CpMo(NO)_2$, 12.5%; 212, CpMoF(NO), 95.8% 182, CpMoF, 94.7%; 167, $MoCF_3$, 16.6%; 163, CpMo, 25.3%; 117, MoF, 9.3%; 98, Mo, 10.8%; 69, $CF_3$, 56.9%; 65, Cp, 93.7%. These ions, however, were accompanied by ions at $m/e$ 77 (100.0%) and at $m/e$ 91 (48.4%). Exact mass determination: calcd for $Cp^{98}Mo(NO)CF_3$ 261.93773, measd 261.93773, $\Delta m/m$ 0.0 ppm.

**Stability of $CpMo(NO)_2CF_3$.** When $CpMo(NO)_2CF_3$ is stored at ambient temperature under an inert atmosphere, discoloration is evident within 10 h and the sample completely decomposes to a yellow material after 48 h. Upon exposure to air, the evolution of a brown gas is immediately apparent.

**Spectroscopic Study of the Reaction of $CpW(NO)_2Cl$ with $Cd(CF_3)_2$·glyme.** Methylene chloride (0.2 mL), $Cd(CF_3)_2$·glyme (0.030 g, 0.09 mmol), and $CpW(NO)_2Cl$ (0.010 g, 0.03 mmol) were sealed into a 4-mm Pyrex vessel that was then placed into a 65 °C oil bath, and the reaction was periodically monitored by $^{19}F$ NMR spectroscopy. After 18 h, however, $Cd(CF_3)_2$·glyme remained in solution and no evidence for the formation of $CpW(NO)_2CF_3$ was observed. Similarly, mass spectra obtained from the less volatile material recovered from the reaction contained no ions characteristic of $CpW(NO)_2CF_3$.

## Results and Discussion

**Synthesis of $CpCr(NO)_2CF_3$ and $CpMo(NO)_2CF_3$.** During a series of preliminary experiments, the interactions of $Cd(CF_3)_2$·glyme with $CpCr(NO)_2Cl$, $CpMo(NO)_2Cl$, and $CpW(NO)_2Cl$ at ambient temperature were followed by $^{19}F$ NMR for periods that ranged from 18 to 30 h. Although small amounts (1–10%) of $CpCr(NO)_2CF_3$ and $CpMo(NO)_2CF_3$ were generated, clearly the trifluoromethylations were very slow, and elevated temperatures (65 °C) were

**Table V. Comparisons of Average Bond Lengths (Å) and Bond Angles (deg) for Cyclopentadienyldinitrosylchromium Compounds[a]**

| compd | $\bar{r}$(Cr–N) | $\bar{r}$(N–O) | $r$(Cr–C$_{sp^3}$) | $\bar{r}$(Cr–C$_{ring}$) | ∠Cr–N–O | ∠N–Cr–N | ∠N–Cr–X | X |
|---|---|---|---|---|---|---|---|---|
| (Cp)Cr(NO)$_2$CF$_3$ | 1.696 | 1.181 | 2.057 | 2.20 | 175.6 | 94.8 | 93.8 | C$_{sp^3}$ |
| (Cp)Cr(NO)$_2$Cl[20] | 1.711 | 1.140 | | 2.20 | 168.6 | 94.3 | 99.1 | Cl |
| (Cp$^1$)Cr(NO)$_2$Cl[13] | 1.709 | 1.162 | | 2.22 | 171.7 | 93.5 | 99.2 | Cl |
| (Cp$^1$)Cr(NO)$_2$I[13] | 1.712 | 1.166 | | 2.21 | 175.2 | 96.2 | 95.0 | I |
| (Cp*)Cr(NO)$_2$CH$_2$I[19] | 1.696 | 1.178 | 2.093 | 2.21 | 172.3 | 98.6 | 96.6 | C$_{sp^3}$ |
| (Cp*)Cr(NO)$_2$CH$_2$PPh$_3^+$BPh$_4^-$[19] | 1.699 | 1.173 | 2.115 | 2.21 | 171.2 | 94.4 | 100.5 | C$_{sp^3}$ |
| (Cp)Cr(NO)$_2$NCO[22] | 1.716 | 1.157 | | 2.19 | 171.0 | 94.9 | 99.7 | N |
| (Cp$^2$)Cr(NO)$_2$Cl[23] | 1.716 | 1.151 | | 2.22 | 169.5 | 95.0 | 98.5 | Cl |

[a] Abbreviations: Cp = $\eta^5$-C$_5$H$_5$; Cp$^1$ = $\eta^5$-C$_5$H$_4$CO$_2$CH$_3$; Cp* = $\eta^5$-C$_5$(CH$_3$)$_5$; Cp$^2$ = $\eta^5$-CpFe($\eta^5$-C$_5$H$_4$)C(O)C$_5$H$_4$.

employed thereafter. After 7–10 h of reaction at 65 °C, the new compounds CpCr(NO)$_2$CF$_3$ and CpMo(NO)$_2$CF$_3$, the first group 6 transition-metal complexes containing both CF$_3$ and NO ligands and the first Cr(0) and Mo(0) trifluoromethyl derivatives, were smoothly generated and then isolated in 71 and 44% yields, respectively.

The physical and spectroscopic properties of the two new compounds are as expected in light of their formulation. For example, the mass spectrum of each contains M, M – F, M – NO, and M – 2NO ions and the $^{19}$F, $^{13}$C, and $^1$H chemical shifts, as well as the $^1J_{C-F}$ coupling constants, are entirely appropriate for trifluoromethyl transition-metal species.[2,7]

The yield of the related d$^6$ Co(III) complex CpCo(CO)(CF$_3$)$_2$ (73%) from CpCo(CO)I$_2$ and Cd(CF$_3$)$_2$·glyme was similar to that of the chromium derivative (71%), but the second trifluoromethylation of CpCo(CO)I$_2$ required only 12 h at ambient temperature,[7] a clear indication that the Co(III) substrate is more reactive than the d$^6$ Cr(0) reagent examined here.

The initial methylations of the CpCr(NO)$_2$ halides with Grignard reagents were carried out by Piper and Wilkinson, who also reported that the CpMo(NO)$_2$ halides could not be alkylated by Grignard reagents.[10] Later studies have confirmed these findings,[13–15] and Legzdins has shown that the milder aluminum alkyl reagents do alkylate both CpMo(NO)$_2$Cl and CpW(NO)$_2$Cl in 30–50% yield.[15] These data indicate that, at least toward the CpM(NO)$_2$Cl system (M = Cr, Mo), Cd(CF$_3$)$_2$·glyme is a milder, less disruptive reagent than CH$_3$MgX.

**Stability of CpCr(NO)$_2$CF$_3$ and CpMo(NO)$_2$CF$_3$.** Fluorine-19 NMR data indicate that, when it is exposed to air, CpCr(NO)$_2$CF$_3$ in CH$_2$Cl$_2$ solution is unaffected for ca. 15 days and that in crystalline form no decomposition is observed for 6 months. When it is stored at ambient temperature in a sealed container, no change is evident for at least 15 months. Although the analogous CpCr(NO)$_2$CH$_3$ is reasonably inert, it is more reactive toward air since decomposition is evident after 2–3 days.[10]

The exceptional thermal stability of CpCr(NO)$_2$CF$_3$ is well illustrated by the observations that no decomposition was evident after 250 h at 115 °C and that, even after 1100 h at 115 °C, a small amount (ca. 2%) of the substrate remained. These results demonstrate that the d$^6$ trifluoromethyl complex examined here is even more thermally stable than the d$^6$ Co(III) species CpCo(CO)(CF$_3$)$_2$, since only about 50% of the latter survived 261 h of similar treatment. In both cases the limited data available argue that the decompositions are not first-order.

In that decomposition is evident within 10 h, CpMo(NO)$_2$CF$_3$ is much less thermally stable than the Cr complex, but this may well be the result of the decreased stability of the M–NO linkage rather than the metal–carbon bond. King,[14] among others, has discussed the relative instability of CpMo(NO)$_2$Cl in comparison to CpCr(NO)$_2$Cl and observed that the molybdenum compound slowly evolves NO at room temperature. Similarly, the relative air stability of the methylated complexes CpM(NO)$_2$CH$_3$ has been reported to diminish in the order Cr > Mo > W.[15]

**Nitrosyl Stretching Frequencies.** Like CO stretching frequencies, the differences in $\nu$(NO) for related complexes are commonly interpreted in terms of the electronic $\sigma$-donating and/or $\pi$-withdrawing effects of the ancillary ligands. Although a back-bonding role for the CF$_3$ group in transition-metal complexes has been advocated by some,[16] others have argued that the only significant electronic contributions of trifluoromethyl groups occur through the $\sigma$ manifold.[17] The NO stretching frequencies of CpCr(NO)$_2$CF$_3$ and CpMo(NO)$_2$CF$_3$ are presented in Table IV along with the frequencies of a number of related complexes. The NO frequencies of the (trifluoromethyl)chromium complex are the highest reported for a CpCr(NO)$_2$X species, and they are consistent with a lesser electron-donating ability for the CF$_3$ group than for the Cl ligand. The nitrosyl stretching frequencies of CpMo(NO)$_2$CF$_3$ are also higher than those of CpMo(NO)$_2$Cl (see Table IV). These findings are in accord with a CF$_3$ group electronegativity higher than that of Cl, as has been suggested by Huheey,[18] among others.

**Structure of CpCr(NO)$_2$CF$_3$.** For comparative purposes, some of the more important average bond lengths and angles and, for the alkyl derivatives, the Cr–C$_{sp^3}$ bond lengths from related cyclopentadienyldinitrosylchromium derivatives have been collected in Table V along with the corresponding data from CpCr(NO)$_2$CF$_3$ itself. In CpCr(NO)$_2$CF$_3$ (Table III) the variation of the Cr–C$_{ring}$ distances is less than 0.3%, the variation of the C–C distances within the Cp ring is small (ca. 2%), and the average value (1.39 Å) is near the 1.41 Å found in CpCr(NO)$_2$Cl.[20] The Cr–N and the N–O bond lengths of CpCr(NO)$_2$CF$_3$ appear to be somewhat shorter and longer, respectively, than average, but each is within the expected range; neither is significantly different from the corresponding bond lengths found for Cp*Cr(NO)$_2$CH$_2$I, for example.

The bond between the Cr and the trifluoromethyl carbon (Cr–C$_{sp^3}$) is short, some 0.04 Å less than the analogous bond in the iodomethyl complex and 0.06 Å less than that

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(13) Wang, Y.; Yang, Y.; Wang, S; Liao, F. *J. Organomet. Chem.* **1991**, *419*, 325.

(14) King, R. B. *Inorg. Chem.* **1968**, *7*, 90.

(15) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.

(16) Clark, H. C.; Tsai, J. H. *J. Organomet. Chem.* **1967**, *7*, 515. Cotton, F. A.; Wing, R. M. *J. Organomet. Chem.* **1967**, *9*, 511. See also: Chen, H. W.; Jolly, W. L.; Xiang, S. F.; Legzdins, P. *Inorg. Chem.* **1981**, *20*, 1779.

(17) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315.

(18) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983, p 144ff.

(19) Hubbard, J. L.; McVicar, W. K. *Organometallics* **1990**, *9*, 2683.

(20) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1966**, 1095.

Table VI. Comparisons of Bond Lengths (Å) and Angles (deg) for Trifluoromethyl Transition-Metal Derivatives[a]

| compd | r(M–C) | r(C–F) | ∠F–C–F | ∠M–C–F |
|---|---|---|---|---|
| $CpCr(NO)_2CF_3$ | 1.696 | 1.356 | 103.5 | 114.7 |
| $CpNi(PPh_3)CF_3$[24] | 1.948 | 1.35 | 104.7 | 113.7 |
| $Pt(SP)(CF_3)_2$[21] | 2.057 | 1.343 | 104.1 | 114.4 |
| $Cp^*Mo(CO)_3CF_3$[25] | 2.248 | 1.363 | 103.0 | 115.3 |
| $Cp(Cp^3)Mo\{CNC(CH_3)_3\}CF_3$[26] | 2.236 | 1.36 | | |
| $Ru(CO)_2(PPh_3)(HgCF_3)CF_3$[27] | | | | |
| M = Ru | 2.084 | 1.38 | | |
| M = Hg | | 1.29 | | |

[a] Abbreviations: Cp = $\eta^5$-$C_5H_5$; $Cp^3$ = $\eta^5$-$C_5(CF_3)_4\{CNC(CH_3)_3\}$; Cp* = $\eta^5$-$C_5(CH_3)_5$; SP = $\eta^3$-(2-vinylphenyl)diphenylphosphine.

in the $CH_3PPh_3^+$ derivative. Short M–C bonds in trifluoromethyl transition-metal species are common,[2] and the differences in the M–C bond lengths for the chromium alkyl complexes are comparable to the 0.05-Å difference between the average Pt–C bond lengths found for analogous dimethyl- and bis(trifluoromethyl)platinum(II) compounds.[21]

As shown in Table VI, the average C–F bond lengths (1.356 Å), F–C–F bond angles (103.5°), and Cr–C–F bond angles (114.7°) all fall within the ranges previously established by other trifluoromethyl transition-metal compounds; no significant distortion of the $CF_3$ group in $CpCr(NO)_2CF_3$ is evident. The relatively small F–C–F bond angles are consistent with a hybridization at the $CF_3$ carbon in which the p character of the bonds directed toward fluorine is greater than 75% while the bond directed toward the metal contains more than 25% s character, as anticipated from Bent's rule. The expected results of the variation of the hybridization at carbon include a $Cr–C_{sp^3}$ bond somewhat shorter than that found in hydrocarbyls and, ultimately, a $\nu$(NO) value that is larger than that of the hydrocarbon derivatives (see Table IV).

Collectively, all of the chemical, physical, and structural properties of $CpCr(NO)_2CF_3$ examined here appear to be representative of those found in very thermally stable trifluoromethyl derivatives of low-valent transition metals.

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**Supplementary Material Available:** Anisotropic displacement coefficients (Table S-1) and H atom coordinates and isotropic displacement coefficients (Table S-2) (1 page). Ordering information is given on any current masthead page.

OM9202682

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(21) Bennett, M. A.; Chee, H.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1071.

(22) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1970**, 605.

(23) Wang, Y.; Hwu, J.; Wang, S. *Acta Crystallogr.* **1990**, *C46*, 2305.

(24) Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1970**, 161.

(25) Koola, J. D.; Roddick, D. M. *Organometallics* **1991**, *10*, 591.

(26) Davidson, J. L.; Green, M.; Nyathi, J. Z.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans* **1977**, 2246.

(27) Clark, G. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9.