molecular packing can have a substantial effect on the Fe-N-O angle. Further, a comparison of structural parameters with values reported for ν_{N-O} (Table V) show clearly the limited utility of this quantity for structural predictions, as there is no obvious correlation between this latter value and any structural parameter of the FeNO moiety. Thus it is quite clear that only full structure determinations will allow detailed comparisons of electronic properties with M-NO geometries.

Acknowledgment. Support under NSF Grant CHE77-01372 is gratefully acknowledged.

Registry No. Fe(NO)(*i*-Prdtc)$_2$, 72251-12-8; diisopropylamine, 108-18-9; carbon disulfide, 75-15-0; Fe(NO$_3$)$_2$, 14013-86-6.

Supplementary Material Available: A listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Y6

Organometallic Nitrosyl Chemistry. 14.[1] Novel Reactivity of LiEt$_3$BH with [(η^5-C$_5$H$_5$)Cr(NO)$_2$]$_2$: Conversion of a Bridging Nitrosyl Ligand to a Bridging EtNBEt$_2$ Group

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Received May 8, 1980

The reaction between LiEt$_3$BH and [CpCr(NO)$_2$]$_2$ (Cp = η^5-C$_5$H$_5$) produces the following organometallic nitrosyl complexes: CpCr(NO)$_2$Et (5%), Cp$_2$Cr$_2$(NO)$_3$(EtNBEt$_2$) (6%), Cp$_2$Cr$_2$(NO)$_3$(NH$_2$) (15%), Cp$_2$Cr$_2$(NO)$_2$(NH$_2$)$_2$ (5%), and Cp$_2$Cr$_2$(NO)$_2$(NH$_2$)(OH) (2%). The latter three products probably result from the customary reaction mode of Et$_3$BH$^-$ as a hydride source. The formation of the former two products, however, reflects unprecedented modes of reactivity of the hydridoborate. The crystal and molecular structures of the new Cp$_2$Cr$_2$(NO)$_3$(EtNBEt$_2$) complex have been determined by X-ray crystallography. The complex crystallizes in space group $P2_1/n$ of the monoclinic system in a cell of dimensions a = 9.9140 (9) Å, b = 12.8562 (9) Å, c = 15.0903 (13) Å, and β = 94.896 (7)°. The structure has been refined by full-matrix least-squares methods to values of R and R_w of 0.047 and 0.059, respectively, for 2999 observed reflections. The most chemically interesting feature of the molecular structure is the novel EtNBEt$_2$ ligand which is coordinated via N in a symmetrical fashion to the two Cr atoms (mean Cr-N = 2.069 (4) Å). The coordination environment around N is that of a distorted tetrahedron, but the N-B distance of 1.459 (5) Å suggests some degree of multiple bonding between these two atoms. Such an inference is consistent with the stability of the complex and its spectroscopic properties.

Introduction

The reported chemistry of lithium triethylborohydride, LiEt$_3$BH, portrays it exclusively as a very powerful nucleophile which functions as a hydride donor toward organic and organometallic electrophiles. For example, it is an exceptionally clean reagent for the facile reductive dehalogenation of alkyl halides and the regio- and stereospecific reduction of epoxides.[2] It also reacts smoothly with various transition metal carbonyl complexes to form, in the first instance, formyl derivatives in virtually quantitative yields.[3] We now wish to report that, during its reaction with [CpCr(NO)$_2$]$_2$ (Cp = η^5-C$_5$H$_5$), LiEt$_3$BH not only acts as a source of H$^-$ but also displays unprecedented reaction modes.

Experimental Section

The reaction and subsequent manipulations were performed under anaerobic and anhydrous conditions, and all reactants were of reagent grade purity. Melting points were taken in capillaries and are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. ^{1}H and ^{13}C NMR spectra were obtained with the assistance of Dr. S. O. Chan and Mrs. M. M. Tracey on Varian Associates HA-100 or XL-100 and CFT-20 spectrometers, respectively, with reference to the solvent used; but all ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from Me$_4$Si. The ^{11}B magnetic resonance spectrum was recorded on a Bruker WP-80 spectrometer with reference to external BF$_3$·Et$_2$O in CDCl$_3$. Mass spectra were obtained at 70 eV on Atlas CH4B or AEI MS902 spectrometers by using the direct-insertion method with the assistance of Mr. J. W. Nip and Mr. G. Gunn. Elemental analyses were performed by Mr. P. Borda of this department.

Reaction of LiEt$_3$BH with [CpCr(NO)$_2$]$_2$. A stirred tetrahydrofuran solution (30 mL) of [CpCr(NO)$_2$]$_2$[4] (0.90 g, 2.5 mmol) at ambient temperature was treated dropwise with a THF solution of LiEt$_3$BH.[5] A reaction occurred immediately, and the original red-purple solution gradually became dark yellow-brown. IR monitoring of the progress of the reaction indicated that 2 equiv of LiEt$_3$BH was required to consume completely the organometallic reactant. Solvent was removed from the final solution under reduced pressure to obtain a brown residue which was redissolved in a minimum of benzene (~5 mL). For partial separation of the products, the benzene solution was chromatographed on a 3 × 8 cm column of Florisil. A broad orange-brown band was first eluted with benzene, and the remaining products were then eluted with THF.

The THF eluate was taken to dryness in vacuo, the resulting residue was dissolved in CH$_2$Cl$_2$ (~5 mL), and the solution was transferred by syringe onto a 1 × 4 cm Florisil column. Elution of the column with CH$_2$Cl$_2$ and removal of the solvent from the eluate under reduced pressure yielded 0.04 g (5% yield) of orange Cp$_2$Cr$_2$(NO)$_2$(NH$_2$)$_2$. Elution with THF afforded 0.02 g (2% yield) of orange-brown Cp$_2$Cr$_2$(NO)$_2$(NH$_2$)(OH) after solvent removal. Both products were readily identifiable by their characteristic IR, ^{1}H NMR, and mass spectra.[1]

The original benzene eluate was also taken to dryness in vacuo, and the residue was extracted with hexanes (4 × 15 mL). The hexane-insoluble matter was dissolved in CH$_2$Cl$_2$, an equal volume

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(1) Part 13: Hames, B. W.; Legzdins, P.; Oxley, J. C. *Inorg. Chem.* **1980**, *19*, 1565-1571.

(2) Brown, H. C.; Krishnamurthy, S. *Aldrichimica Acta* **1979**, *12*, 3-11 and references contained therein.

(3) Gladysz, J. A. *Aldrichimica Acta* **1979**, *12*, 13-17 and references contained therein.

(4) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1979**, *19*, 208-212.

(5) Purchased from the Aldrich Chemical Co. as a 1 M THF solution under the trade name Super-Hydride.

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Table I. Crystal Data and Experimental Conditions for Data Collection

$C_{16}H_{25}BCr_2N_4O_3$	fw 436.207
$a = 9.9140$ (9) Å	space group $P2_1/n$
$b = 12.8562$ (9) Å	$Z = 4$
$c = 15.0903$ (13) Å	$V = 1916.34$ Å^3
$\beta = 94.896$ (7)°	$D_O = 1.482$ (5) g cm^{-3} [a]
$\mu = 94.39$ cm^{-1}	$D_c = 1.512$ g cm^{-3}

radiatn: Cu Kα; graphite monochromator, $\theta = 12.20°$
scan: ω–2θ; range $(0.50 + 0.14 \tan \theta)°$ in ω, extended 25% for backgrounds; speed 0.7–10.1° min^{-1} to give $I/\sigma(I) \geq 20$
aperture: $(3.0 + 0.5 \tan \theta) \times 4$ mm, 173 mm from crystal
stds: reflectns $\bar{1}40$, $0\bar{2}3$, and $\bar{1}61$ monitored every hour of exposure time for intensity fluctns (three reflectns recentered every 100 reflectns for orientation control)
data collected: $h, -k, \pm l$ for $0 < \theta < 70°$
$\sigma(I)$: $\{\text{INT} + 4(\text{BG}) + (0.04I)^2\}^{1/2}$ [b]
boundary planes: 7 faces; $\{001\}$, $\{11\bar{1}\}$, $\{\bar{1}11\}$, $(\bar{1}0\bar{1})$
transmission factors: 0.4805 max and 0.0568 min
cryst size: approximately 0.40 × 0.41 × 0.09 mm

[a] By neutral buoyancy in aqueous $CdSO_4$. [b] INT is the integrated intensity; BG is the sum of the background counts; I is the intensity.

of hexanes was added, and the solution was slowly concentrated under reduced pressure to induce the formation of green crystals (0.13 g, 15% yield) of $Cp_2Cr_2(NO)_3(NH_2)$[6] which were identified by conventional spectroscopic methods.

The dark-red hexane extracts were concentrated in vacuo to ~7 mL and were transferred onto a 1 × 20 cm Florisil column. Elution of the column with hexanes developed a yellow band which afforded ~0.04 g (5% yield) of a yellow oil after complete elution and solvent removal. The oil was identified as $CpCr(NO)_2Et$[7] by its characteristic spectroscopic properties [IR (CH_2Cl_2): ν_{NO} 1770, 1645 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.55 (s, 5 H), 1.4 (m, 5 H)]. A low-resolution mass spectrum of the oil was also identical with that displayed by an authentic sample of $CpCr(NO)_2Et$.

Further elution of the column with benzene (200 mL) afforded a red-brown eluate from which the solvent was removed under reduced pressure. The resulting residue was redissolved in CH_2Cl_2 (5 mL), and hexanes (20 mL) were added. Slow concentration of this solution in vacuo resulted in the crystallization of analytically pure, purple-red $Cp_2Cr_2(NO)_3(EtNBEt_2)$ (0.068 g, 6% yield, mp (in air) 151–153 °C dec).

Anal. Calcd for $C_{16}H_{25}Cr_2N_4O_3B$: C, 44.06; H, 5.78; N, 12.84. Found: C, 44.06; H, 5.95; N, 12.81. IR (CH_2Cl_2): ν_{NO} 1644, 1495 cm^{-1}.

X-ray Diffraction Study of $Cp_2Cr_2(NO)_3(EtNBEt_2)$. Crystals of the title compound suitable for X-ray work were grown by slow evaporation of a CH_2Cl_2–hexanes solution of the complex under a stream of N_2 at ambient temperature. Preliminary photographic examination indicated that the crystals possessed monoclinic symmetry with systematic absences $h + l$ odd for $h0l$ and k odd for $0k0$. This unambiguously determined the space group to be $P2_1/n$ (an alternative setting of $P2_1/c$) with equivalent positions $\pm(x, y, z; 1/2 + x, 1/2 - y, 1/2 + z)$. The crystal chosen for data collection was cut from a larger crystal and was mounted in a nonspecific orientation on an Enraf-Nonius CAD-4 diffractometer. Cell constants and an orientation matrix were determined from a least-squares refinement of the setting angles for 25 reflections with $36° < 2\theta < 98°$. The crystal data and experimental parameters for data collection are given in Table I. The 3830 independent reflections measured were corrected for background Lorentz, polarization, and absorption[8] to give 2999 reflections with $I > 3\sigma(I)$ which were used in the structure solution and refinement.

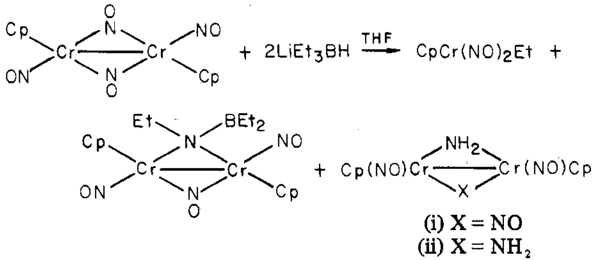
The positional parameters of the two Cr atoms were determined from a three-dimensional Patterson synthesis. Least-squares refinement and a difference Fourier synthesis revelealed the remaining nonhydrogen atoms. Refinement of atomic parameters was carried out by using full-matrix least-squares techniques on F and minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weighting factor, w, is given by $w = 4F_o^2/(\sigma(F_o))^2$. The neutral atom scattering factors were calculated from the analytical expression for the scattering factor curves.[10] The f' and f'' components of anomalous dispersion were those of Cromer and Liberman[11] and were included in the calculations for the Cr atoms. Two cycles of refinement with the nonhydrogen atoms included and assigned anisotropic thermal parameters resulted in agreement factors of $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.071$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|)^{1/2} = 0.101$. A difference Fourier synthesis calculated at this stage revealed the positions of all 25 H atoms, and their positional and isotropic thermal parameters were varied in subsequent refinement cycles. However, H–C(1) and H–C(10) of the cyclopentadienyl rings kept refining to geometrically impossible positions. Hence, it was decided to fix these two H atoms at their calculated positions (assuming a C–H bond length of 0.95 Å and a regular C sp^2 geometry). This model was then refined for two additional cycles, whereupon it converged at residuals of $R = 0.047$ and $R_w = 0.059$.

In the final cycles, 327 variables were refined by using 2999 observations, and no parameter shift exceeded 0.25 times its estimated standard deviation. The error in an observation was 1.73 electrons, and the highest peak in the final difference Fourier map had a density of 0.61 e/Å^3 and was located between the two Cr atoms at fractional coordinates −0.091, 0.271, 0.157. The final atomic positional and thermal parameters are tabulated in Tables II and III. Values of $|F_o|$ vs. $|F_c|$ for the 3830 reflections are given in Table IV.[12]

Results and Discussion

We recently reported[1] that treatment of $[CpCr(NO)_2]_2$ with 2 equiv of $NaAlH_2(OCH_2CH_2OCH_3)_2$ in benzene at room temperature affords, in low yields, a mixture of $Cp_2Cr_2(NO)_3(NH_2)$ (15%), $Cp_2Cr_2(NO)_2(NH_2)_2$ (2%), and $Cp_2Cr_2(NO)_2(NH_2)(OH)$ (3%) as the only isolable nitrosyl-containing complexes. The formation of these amido products can be viewed as arising from the nucleophilic attack of H$^-$ on the nitrogen atoms of the nitrosyl ligands in the organometallic reactant.[1] With the hopes of preparing these product complexes in higher yields and of gaining further insight into the mechanism of reduction of a coordinated NO group, we decided to investigate the reactions of $[CpCr(NO)_2]_2$ with more potent hydride donors. Of particular interest to us were those hydride sources which, unlike $NaAlH_2(OCH_2CH_2OCH_3)_2$, contain only one transferable H$^-$ per mole and should thus provide better defined chemistry.[3] For the reasons cited in the Introduction, our first choice was $LiEt_3BH$.

The reaction of $LiEt_3BH$ with $[CpCr(NO)_2]_2$ at ambient temperature is quite a complex process, i.e., eq 1. Again, 2 equiv of the hydride donor is required to consume completely



(1)

(i) X = NO
(ii) X = NH$_2$
(iii) X = OH

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(6) Flitcroft, N. *J. Organomet. Chem.* **1968**, *15*, 254–256.

(7) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022–1025.

(8) The computer programs used in this and other parts of the analysis include local modifications of the following: ORFLS and ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy for full-matrix least-squares and function and errors, respectively; ORTEP II by C. K. Johnson for crystal structure illustrations; FORDAP by A. Zalkin for Patterson and Fourier syntheses. The absorption correction used the Gaussian integration method based on the Coppens–Leiserowitz–Rabinovich logic.[9]

(9) (a) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–182. (b) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Ibid.* **1965**, *18*, 1035–1038.

(10) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(12) Supplementary material.

Table II. Atomic Positional and Thermal Parameters[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	−1862.5 (6)	2607.0 (4)	1979.1 (3)	36.6 (3)	37.6 (3)	35.4 (3)	2.2 (3)	6.1 (2)	0.7 (2)
Cr(2)	459.3 (6)	1854.0 (5)	1473.5 (4)	37.3 (3)	38.3 (3)	37.1 (3)	1.5 (3)	9.5 (2)	2.4 (2)
N(1)	−1427 (3)	1583 (3)	1149 (2)	43 (2)	49 (2)	42 (2)	−2 (2)	4 (1)	−9 (1)
N(2)	−1713 (3)	3673 (3)	1352 (2)	45 (2)	42 (2)	41 (2)	9 (2)	2 (1)	3 (1)
N(3)	687 (3)	633 (3)	1854 (2)	46 (2)	40 (2)	46 (2)	0 (1)	11 (1)	−1 (1)
N(4)	67 (3)	2649 (2)	2616 (2)	41 (2)	30 (1)	36 (1)	−3 (1)	1 (1)	−2 (1)
O(1)	−1985 (3)	881 (3)	749 (2)	59 (2)	77 (2)	88 (2)	−6 (2)	−2 (2)	−44 (2)
O(2)	−1812 (4)	4449 (2)	920 (2)	84 (2)	52 (2)	65 (2)	11 (2)	3 (2)	19 (2)
O(3)	960 (3)	−264 (2)	1992 (2)	76 (2)	33 (1)	82 (2)	6 (2)	13 (2)	2 (1)
B	771 (4)	1863 (3)	3179 (2)	44 (2)	29 (2)	35 (2)	−1 (2)	−1 (2)	−2 (2)
C(1)	−2925 (5)	2218 (5)	3200 (3)	50 (2)	94 (4)	49 (2)	17 (3)	22 (2)	15 (2)
C(2)	−3282 (5)	1478 (4)	2542 (4)	47 (2)	61 (3)	83 (3)	−1 (2)	25 (2)	18 (3)
C(3)	−3940 (4)	1989 (4)	1809 (3)	34 (2)	81 (3)	64 (3)	−8 (2)	5 (2)	−3 (3)
C(4)	−4012 (4)	3049 (4)	2026 (3)	41 (2)	65 (3)	61 (3)	16 (2)	11 (2)	4 (2)
C(5)	−3370 (5)	3183 (5)	2875 (3)	58 (3)	75 (3)	53 (2)	14 (3)	18 (2)	−5 (2)
C(6)	2451 (6)	1874 (5)	941 (4)	52 (3)	91 (5)	88 (4)	15 (3)	32 (3)	32 (4)
C(7)	2161 (6)	2893 (5)	1112 (4)	59 (3)	84 (4)	80 (3)	−19 (3)	26 (3)	15 (3)
C(8)	1016 (5)	3164 (4)	573 (4)	67 (3)	58 (3)	77 (3)	6 (3)	35 (3)	24 (3)
C(9)	604 (6)	2314 (5)	64 (3)	68 (3)	112 (5)	44 (2)	−10 (3)	19 (2)	22 (3)
C(10)	1501 (7)	1494 (4)	293 (4)	111 (5)	63 (3)	78 (3)	3 (3)	66 (4)	−6 (3)
C(11)	−2 (5)	974 (3)	3649 (3)	61 (3)	39 (2)	41 (2)	5 (2)	6 (2)	9 (2)
C(12)	−164 (8)	1290 (6)	4616 (3)	98 (5)	76 (4)	41 (2)	13 (4)	13 (3)	10 (2)
C(13)	2339 (5)	2005 (4)	3507 (3)	53 (3)	50 (3)	62 (3)	1 (2)	−12 (2)	−1 (2)
C(14)	3167 (6)	1011 (5)	3592 (5)	58 (3)	70 (4)	83 (4)	15 (3)	−10 (3)	−12 (3)
C(15)	597 (5)	3730 (3)	2780 (3)	54 (2)	32 (2)	61 (2)	−5 (2)	−8 (2)	0 (2)
C(16)	157 (8)	4170 (5)	3636 (4)	100 (5)	45 (3)	80 (4)	3 (3)	−4 (4)	−21 (3)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional parameters are ×10^4 and the thermal parameters are ×10^3. $U_{ij} = B_{ij}/(2\pi^2 a^*_i a^*_j)$ Å^2. The thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Table III. Positional (×10^3) and Isotropic Thermal (×10^2) Parameters

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
HC(1)	−245	210	377	8	HC(2)	−299 (5)	80 (4)	261 (3)	8 (2)
HC(3)	−421 (5)	177 (4)	126 (3)	6 (1)	HC(4)	−426 (4)	356 (4)	169 (3)	6 (1)
HC(5)	−313 (6)	381 (5)	314 (4)	10 (2)	HC(6)	310 (6)	152 (5)	115 (4)	9 (2)
HC(7)	274 (6)	331 (5)	151 (4)	10 (2)	HC(8)	68 (5)	396 (4)	63 (3)	8 (2)
HC(9)	−20 (8)	225 (5)	−33 (5)	12 (2)	HC(10)	150	87	4	10
H1C(11)	−83 (5)	78 (4)	338 (3)	6 (1)	H2C(11)	50 (4)	31 (3)	366 (3)	5 (1)
H1C(12)	67 (7)	136 (5)	495 (4)	10 (2)	H2C(12)	−40 (5)	207 (4)	468 (3)	7 (1)
H3C(12)	−77 (8)	91 (6)	477 (5)	14 (3)	H1C(13)	279 (5)	243 (3)	310 (3)	6 (1)
H2C(13)	233 (7)	234 (4)	406 (4)	10 (2)	H1C(14)	278 (6)	54 (4)	397 (4)	9 (2)
H2C(14)	326 (6)	72 (4)	308 (4)	9 (2)	H3C(14)	406 (5)	113 (4)	367 (3)	6 (1)
H1C(15)	155 (4)	375 (3)	283 (2)	4 (1)	H2C(15)	26 (4)	412 (3)	233 (2)	3 (1)
H1C(16)	58 (6)	491 (6)	377 (4)	12 (2)	H2C(16)	−76 (7)	418 (5)	368 (5)	11 (3)

the organometallic reactant, and the five nitrosyl-containing products indicated can be isolated in yields ranging from 2–15%.[13] Regrettably, the yields of the last three products (i–iii)[14] are comparable to those obtained when $NaAlH_2(OCH_2CH_2OCH_3)_2$ is employed as the reductant;[1] but their formation in this reaction nevertheless indicates that they probably result from the usual reaction mode of Et_3BH^- as a hydride source. Just as for the transformation involving $NaAlH_2(OCH_2CH_2OCH_3)_2$,[1] it can be demonstrated that $Cp_2Cr_2(NO)_3(NH_2)$ reacts further with $LiEt_3BH$ to yield both $Cp_2Cr_2(NO)_2(NH_2)_2$ and $Cp_2Cr_2(NO)_2(NH_2)(OH)$ and that neither of these latter complexes undergoes further reaction with excess hydride under the conditions of the experiment. Consequently, it seems reasonable to conclude that similar mechanisms for formation of the bimetallic amido compounds are operative in both systems. A plausible mechanism for the conversion of an NO ligand to a coordinated NH_2 group by H^- attack has been previously proposed.[1]

The monomeric product of the reaction, $CpCr(NO)_2Et$, is also well-known, having been synthesized earlier by the action of Et_3Al on $CpCr(NO)_2Cl$.[7] However, its formation during the present conversion is somewhat surprising since the transfer of an ethyl group from boron to chromium is not a common chemical occurrence. In this connection, though, it is of interest to note that treatment of $[CpFe(CO)_2]_2$ (isoelectronic and isostructural with $[CpCr(NO)_2]_2$) with $LiEt_3BH$ in THF–HMPA does not result in formation of any of the corresponding alkyl complex, $CpFe(CO)_2Et$, but rather in quantitative conversion of the carbonyl dimer to the anion $[CpFe(CO)_2]^-$.[15] In contrast, careful IR monitoring of reaction 1 provides no evidence for the formation of anionic nitrosyl products.

The most intriguing product isolated from the final reaction mixture is the novel complex $Cp_2Cr_2(NO)_3(EtNBEt_2)$, a purple-red solid (mp 151 °C dec) which dissolves readily in common organic solvents to yield air-stable, red-brown solutions. Its IR spectrum (in CH_2Cl_2) exhibits strong absorptions at 1644 and 1495 cm^{-1} attributable to terminal and bridging NO ligands, respectively. Its mass spectrum (Table V) confirms its bimetallic nature, and its ambient-temperature ^{1}H and ^{13}C NMR spectra (Table VI) indicate the absence of molecular symmetry and are consistent with the presence of

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(13) The exact nature of the other, nonnitrosyl products formed in this conversion remains to be ascertained.

(14) It has been shown that the physical properties of these compounds are consistent with their possessing the bimetallic structures shown.[1]

(15) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553–558.

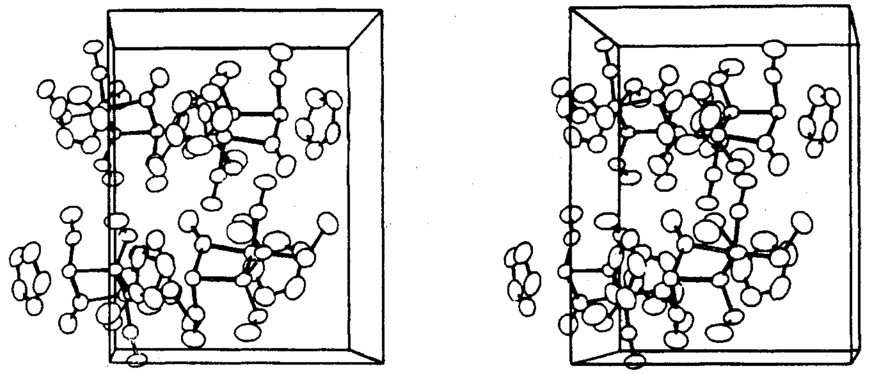


Figure 1. Stereoscopic view of the contents of a unit cell. The view is down *c*, and the hydrogen atoms are omitted for clarity.

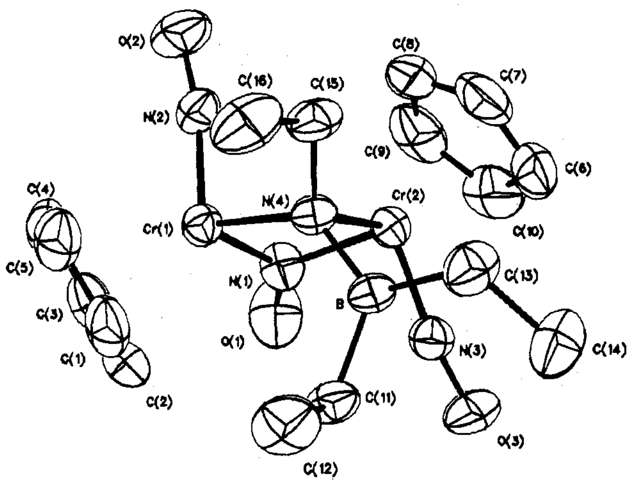


Figure 2. Perspective view of the molecular structure of $Cp_2Cr_2(NO)_3(EtNBEt_2)$ including the atom numbering scheme. Hydrogen atoms are omitted, and thermal ellipsoids are drawn at the 50% probability level.

Table V. High-Resolution Mass Spectral Data for $Cp_2Cr_2(NO)_3(EtNBEt_2)$[a]

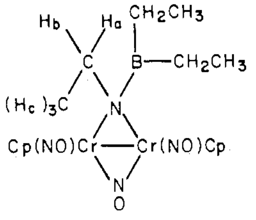
m/z measd[b]	m/z calcd	rel abund	assignt[c]
436.081	436.083	28	$Cp_2Cr_2(NO)_3(EtNBEt_2)^+$
406.087	406.085	5	$Cp_2Cr_2(NO)_2(EtNBEt_2)^+$
376.088	376.087	2	$Cp_2Cr_2(NO)(EtNBEt_2)^+$
351.003	351.001	2	$Cp_2Cr_2(NO)_2(NEt)N^+$
324.964	324.961	15	$Cp_2Cr_2(NO)_3H^+$
320.040	320.044	3	$Cp_2Cr_2(NEt_2)N^+$
319.018	319.017	3	$Cp_2Cr_2(NO)(NBC_2H_6)^+$
294.964	294.963	3	$Cp_2Cr_2(NO)_2H^+$
291.000	291.005	17	$Cp_2Cr_2(NEt)N^+$
264.965	264.965	25	$Cp_2Cr_2(NO)H^+$
258.100	258.100	28	$CpCr(NO)(NBC_6H_{14})^+$
249.973	249.978	23	$Cp_2Cr_2(NH_2)^+$
229.109	229.109	100	$CpCr(EtNBEt_2)^+$
201.078	201.078	75	$CpCr(NBC_4H_{11})^+$
182.019	182.019	60	Cp_2Cr^+
176.975	176.976	1	$CpCr(NO)_2{}^+$
171.031	171.031	18	$CpCr(NBC_2H_5)^+$
116.980	116.980	25	$CpCr^+$

[a] Probe temperature ~150 °C. [b] ±0.001 mass unit. [c] The assignments involve the most abundant naturally occurring isotopes, e.g., ^{52}Cr, in each fragment.

a bridging $EtNBEt_2$ group. To ascertain its molecular structure, we have carried out a single-crystal X-ray structural analysis of the complex.

The crystal structure of $Cp_2Cr_2(NO)_3(EtNBEt_2)$ consists of a well-separated array of discrete molecular units, the intermolecular distances corresponding to normal van der Waals contacts. The molecular packing within the crystal is illustrated in Figure 1, and the shortest nonbonded contacts are tabulated in Table VII. Each molecule (Figure 2) adopts a trans configuration of the nitrosyl and cyclopentadienyl ligands with respect to the mean plane of the central, cyclic Cr_2N_2 fragment and has an overall geometry similar to that displayed by *trans*-$[CpCr(NO)(NMe_2)]_2$,[16] *trans*-$[CpCr(NO)_2]_2$,[17] and

Table VI. NMR Data for $Cp_2Cr_2(NO)_3(EtNBEt_2)$ in $CDCl_3$



^1H Data

δ[a]	rel intens	assignt[b]
5.34 (s)	5	Cp
5.27 (s)	5	Cp
4.94 (m, $J_{ab} = 12$ Hz)	1	$N{-}CH_a$
4.62 (m)	1	$N{-}CH_b$
1.51 (t, $J_{ac} = J_{bc} = 7$ Hz)	3	$N{-}CH_2{-}C(H_c)_3$
0.81 (br, m)	8	B-Et, $B{-}CH_2{-}CH_3$
−0.06 (br)	2	$B{-}CH_2$

^{13}C Data

δ[a]	$^1J_{^{13}C-H}$, Hz	assignt[b]
102.53	177	Cp
102.04		Cp
62.86	137	$N{-}CH_2{-}CH_3$
24.33	126	$N{-}CH_2{-}CH_3$
14.0 (br)		$B{-}CH_2{-}CH_3$
9.27	123	$B{-}CH_2{-}CH_3$

[a] The indicated chemical shifts are in ppm downfield from Me_4Si. [b] These assignments have been confirmed by a series of homonuclear and heteronuclear decoupling experiments.

Table VII. Shortest Nonbonded Contacts[a] (Å)

	Intramolecular		
N(1)· · ·C(3)	2.81	N(1)· · ·N(3)	2.58
N(1)· · ·C(9)	2.86	N(1)· · ·N(2)	2.72
O(1)· · ·Cr(2)	2.86	O(1)· · ·C(3)	2.98
O(1)· · ·Cr(1)	2.89	O(1)· · ·C(9)	3.39
	Intermolecular		
$O(2)\cdots C(2)^{i}$	3.49	$O(3)\cdots C(5)^{iv}$	3.27
$O(2)\cdots C(14)^{ii}$	3.56	$O(3)\cdots C(4)^{iv}$	3.34
$C(1)\cdots C(9)^{iii}$	3.33	$C(5)\cdots C(9)^{iii}$	3.59

[a] Symmetry code: (i) $-^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; (ii) $-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$; (iii) $-^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (iv) $-^1/_2 - x, -^1/_2 + y, {}^1/_2 - z$.

Table VIII. Selected Bond Distances (Å) and Bond Angles (Deg) for $Cp_2Cr_2(NO)_3(EtNBEt_2)$

Bond Distances

Cr(1)–Cr(2)	2.6680 (8)	Cr(1)–C(1)	2.255 (4)
Cr(1)–N(1)	1.892 (3)	Cr(1)–C(2)	2.238 (4)
Cr(1)–N(2)	1.679 (3)	Cr(1)–C(3)	2.202 (4)
Cr(1)–N(4)	2.068 (3)	Cr(1)–C(4)	2.212 (4)
Cr(2)–N(1)	1.924 (3)	Cr(1)–C(5)	2.226 (4)
Cr(2)–N(3)	1.680 (3)	Cr(2)–C(6)	2.194 (5)
Cr(2)–N(4)	2.070 (3)	Cr(2)–C(7)	2.256 (5)
N(1)–O(1)	1.196 (4)	Cr(2)–C(8)	2.262 (4)
N(2)–O(2)	1.191 (4)	Cr(2)–C(9)	2.225 (4)
N(3)–O(3)	1.199 (4)	Cr(2)–C(10)	2.183 (4)
N(4)–B	1.459 (5)	C(11)–C(12)	1.536 (6)
N(4)–C(15)	1.498 (5)	C(13)–C(14)	1.519 (7)
B–C(11)	1.578 (5)	C(15)–C(16)	1.508 (7)
B–C(13)	1.601 (6)		

Bond Angles

N(1)–Cr(1)–N(4)	94.1 (1)	Cr(1)–N(1)–Cr(2)	88.7 (1)
N(1)–Cr(2)–N(4)	93.1 (1)	Cr(1)–N(4)–Cr(2)	80.3 (1)
Cr(1)–N(1)–O(1)	137.6 (3)	N(4)–B–C(11)	122.5 (4)
Cr(2)–N(1)–O(1)	131.5 (3)	N(4)–B–C(13)	120.3 (3)
Cr(1)–N(2)–O(2)	170.0 (3)	C(11)–B–C(13)	116.1 (3)
Cr(2)–N(3)–O(3)	168.4 (3)	B–C(11)–C(12)	109.2 (4)
Cr(1)–N(4)–B	129.0 (2)	B–C(13)–C(14)	115.7 (4)
Cr(2)–N(4)–B	91.6 (2)	N(4)–C(15)–C(16)	111.5 (4)
B–N(4)–C(15)	113.8 (3)		

trans-$Cp_2Cr_2(NO)_3(NH_2)$.[18] Selected bond distances and interbond angles are given in Table VIII.

The individual molecular dimensions of $Cp_2Cr_2(NO)_3(EtNBEt_2)$ are also comparable to those found in the other cyclopentadienylchromium nitrosyl complexes mentioned above. Specifically, the bond lengths and angles within each molecule are consistent with the views that (a) the Cp rings function as formal five-electron donors to the metal centers [The rings have normal geometries,[19] being essentially planar with mean C–C distances of 1.39 (1) Å and internal angles of 108 (1)°; and the mean Cr–C distance is 2.22 (4) Å.], (b) both the terminal and bridging nitrosyl groups are normal three-electron donor ligands in their respective bonding environments [The two terminal NO groups are of the linear type,[20] having Cr–N–O angles of approximately 170°, a mean Cr–N distance of 1.680 (4) Å, and a mean N–O distance of 1.195 (6) Å. A slight asymmetry in the bonding of the bridging NO ligand is indicated by the difference in the Cr–N(1) bond lengths of 0.032 Å (or 8σ) whereas no other chemically equivalent bonds differ by more than 3σ.], and (c) a Cr–Cr single bond exists in the molecule [The existence of this linkage is indicated not only by the Cr–Cr separation of 2.6680 (8) Å but also by the dihedral angle of 167.3° between the N(1)–Cr–N(4) planes and the acute Cr–N–Cr angles of 88.7 (1) and 80.3 (1)°.].[21,22] Consequently, in order that each chromium atom in the complex may attain the favored 18-electron configuration, the bridging $EtNBEt_2$ group (like the bridging NO, NH_2, and NMe_2 groups in the related complexes) apparently functions as a formal three-electron donor.

The most chemically interesting feature of the structure is the novel $EtNBEt_2$ ligand. It is coordinated via N in a symmetrical fashion to the two Cr atoms, the mean Cr–N bond distance being 2.069 (4) Å. This distance is similar to the Cr–N(sp^3) bond lengths of 1.99 (2)–2.04 (2) Å in $[CpCr(NO)(NMe_2)]_2$.[16] The coordination environment around the N atom is distorted from an ideal tetrahedral geometry in a manner which can be viewed as arising from a rotation of the C(15)–N(4)–B plane away from being perpendicular to the Cr(1)–N(4)–Cr(2) plane. Such a distortion is consistent with minimizing the nonbonded repulsions between the cyclopentadienyl rings and the methylene hydrogens of the $EtNBEt_2$ ligand. Within the group itself, the C–C, N–C, and B–C bond lengths are those expected for normal single bonds. For instance, the B–C distances of 1.578 (5) and 1.601 (6) Å are within the range of values, 1.577 (5)–1.619 (3) Å,[23] commonly observed for single B–C bonds. However, the N(4)–B distance of 1.459 (5) Å is intermediate between the values of 1.44 and 1.57 Å for B–N double[24] and single bonds,[25] respectively, and suggests some degree of multiple bonding between the B and N atoms. Consistent with this view are the observed planar (sp^2) geometry around the boron atom and the air stability of the compound (rationalizable in terms of $N \rightarrow Bp\pi$ interaction). Hence, within this bimetallic complex, there appears to be a competition between the two Cr atoms and the B atom for the "lone pair" of electrons on N. However, the resulting feature of a four-coordinate nitrogen atom engaging in concomitant multiple bonding cannot be rationalized in terms of localized, two-center bonds.

The spectroscopic properties of $Cp_2Cr_2(NO)_3(EtNBEt_2)$ can be more fully understood in terms of its molecular structure. Its mass spectra contain peaks assignable to the parent ion and ions resulting from the sequential loss of ligands from both the parent and monometallic species arising from cleavage of the parent; high-resolution data are presented in Table V. Similar fragmentation patterns have been reported for related molecules.[26] Hence, ions resulting from losses of NO, C_2H_4 (from either N–Et or B–Et), NBC_6H_{14}, and $EtNBEt_2$ are observable; and the occurrence of peaks due to metastable ions in the low-resolution mass spectrum of the complex provides direct evidence for several of these fragmentation modes. Thus, peaks at m/z 242, 215, 176, and 153 correspond to the respective fragmentations eq 2–5. Indeed, the whole series of

$$Cp_2Cr_2(NO)_3(EtNBEt_2)^+ \rightarrow Cp_2Cr_2(NO)_3H^+ + NBC_6H_{14} \quad (2)$$

$$CpCr(EtNBEt_2)^+ \rightarrow CpCr(NBC_4H_{11})^+ + C_2H_4 \quad (3)$$

$$Cp_2Cr_2(NO)_2H^+ \rightarrow CpCr^+ + CpCr(NO)_2H \quad (4)$$

$$CpCr(EtNBEt_2)^+ \rightarrow CpCr^+ + EtNBEt_2 \quad (5)$$

ions $Cp_2Cr_2(NO)_xH^+$ (x = 1–3) is observable. Of particular interest is the occurrence of the nitride-containing ions $Cp_2Cr_2(NO)_2(NEt)N^+$, $Cp_2Cr_2(NEt_2)N^+$, and $Cp_2Cr_2(NEt)N^+$. In each of these ions NEt or NEt_2 groups remain, thereby suggesting that the N atom has resulted from fragmentation of a nitrosyl ligand. The elimination of electron-

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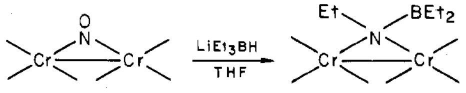
deficient BEt or BEt_2 fragments from the various precursor ions may assist this unusual fragmentation process. In general, oxo ions are more abundant than nitride ions in the mass spectra of chromium nitrosyls.[27] Finally, it can be noted that migration of the cyclopentadienyl group between metal atoms occurs more readily for $Cp_2Cr_2(NO)_3(EtNBEt_2)$ than for $Cp_2Cr_2(NO)_4$[28] (cf. the relative abundances of the Cp_2Cr^+ ion); and ions containing two Cr atoms are less abundant in the mass spectra of the former compound.

The asymmetric molecular structure observed for $Cp_2Cr_2(NO)_3(EtNBEt_2)$ in the solid state apparently presists in solution, as evidenced by its ^1H and ^{13}C NMR spectra (Table VI). Hence, in its ambient-temperature ^1H NMR spectrum, the inequivalence of the cyclopentadienyl rings and the diastereotopic nature of the α-H atoms in the N–Et moiety are clearly evident. Also, the ethyl groups attached to the boron atom are seen to be inequivalent, their assignments given in Table VI being based principally on the integration of the spectrum. Similar features are displayed by the ^{13}C NMR spectrum of the complex. However, the methylene carbons of the ethyl groups bonded to boron give rise to a broad ^{13}C signal centered at δ 14.0 presumably due to couplings with the ^{11}B ($I = {}^3/_2$) and ^{10}B ($I = 3$) nuclei which are incompletely relaxed by the quadrupole mechanism.[29] The methyl carbons give rise to only one peak, probably due to coincidental overlap.

The chemical shifts of the different resonances also provide information about the environments of the various nuclei in the novel $EtNBEt_2$ ligand. That the asymmetric nitrogen atom carries at least a partial positive charge is indicated by the downfield position of the resonances due to the protons α to N (i.e., δ 4.62, 4.94). These signals occur at slightly lower fields than the corresponding resonances displayed by typical tetraalkylammonium compounds (δ 3.3–4.8 vs. δ 3.0–3.7 for tertiary amines).[30] The $^{13}C\{^1H\}$ NMR spectrum reinforces this impression, the signal due to the α-carbon nucleus being at δ 62.86 vs. $\delta \sim 52$ for Et_4NX compounds and $\delta \sim 48$ for Et_3N.[30] In addition, the existence of some N–B multiple bonding is suggested by the ^{11}B NMR spectrum of $Cp_2Cr_2(NO)_3(EtNBEt_2)$ in $CDCl_3$ which consists of a single, broad resonance centered at −46.9 ppm from external $BF_3 \cdot OEt_2$ (peak width at half-height = 17.6 ppm). This chemical shift falls in the range (i.e., δ −41.8 to −48.7) previously reported for a series of $R_2N \overset{...}{=} BR'_2$ compounds.[31] It is thus not surpising that the complex as a whole appears to be stereochemically rigid in solution at ambient temperature. Indeed, its ^1H NMR spectrum in toluene-d_8 at 90 °C still displays the principal spectral features listed in Table VI. At this temperature, however, the originally broad peak due to the $B-CH_2$ protons appears as a quartet, thereby confirming its assignment. Admittedly, the ^1H NMR data do not rule out rapid rotation of the Et_2B group about the B–N(4) bond because of the diastereotopic nature of its methylene protons, but in view of the other evidence for some N–B multiple bonding (vide supra), we consider this possibility to be less likely. Interestingly, NMR is more sensitive than IR to the molecular asymmetry as evidenced by the fact that only one terminal NO stretch is observed for the complex whereas two such stretches are expected to be IR active.

The net transformation effected by $LiEt_3BH$ during the formation of this product is thus



namely, the conversion of a bridging nitrosyl ligand to a bridging $EtNBEt_2$ group. The mechanism of this remarkable reaction remains unknown, but we have verified independently that the $EtNBEt_2$-containing product is not obtained from the further reaction of $LiEt_3BH$ with any of the bimetallic amido complexes isolated from the original reaction mixture (vide supra). It may, however, result from the attack of BEt_3 (the byproduct formed when Et_3BH^- functions as a hydride source) on the original organometallic reactant, $[CpCr(NO)_2]_2$. Thus, treatment of the nitrosyl dimer with an equimolar amount of BEt_3 in THF–hexanes at room temperature does afford $Cp_2Cr_2(NO)_3(EtNBEt_2)$ in 4% yield, but the principal isolable product is $CpCr(NO)_2Et$ (20% yield). In any event, the reaction of $LiEt_3BH$ with $[CpCr(NO)_2]_2$ is certainly more complex than with analogous carbonyl compounds, the latter simply being cleaved to anions with the accompanying formation of the volatile byproducts H_2 and BEt_3.[3] The fact that the corresponding nitrosyl anion, $[CpCr(NO)_2]^-$, is not isolable from the present reaction probably reflects upon its inherent instability, it being as yet unknown.[28]

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Registry No. $Cp_2Cr_2(NO)_3(EtNBEt_2)$, 74987-46-5; $[CpCr(NO)_2]_2$, 36607-01-9; $LiEt_3BH$, 22560-16-3; $Cp_2Cr_2(NO)_2(NH_2)_2$, 57673-35-5; $Cp_2Cr_2(NO)_2(NH_2)(OH)$, 73199-21-0; $Cp_2Cr_2(NO)_3(NH_2)$, 39722-97-9; $CpCr(NO)_2Et$, 57034-50-1.

Supplementary Material Available: Table IV, a listing of structure amplitudes (34 pages). Ordering information is given on any current masthead page.

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