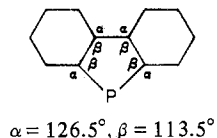


apical in the rectangular pyramid, it was necessary to maintain the biphenylene ring carbon atoms attached to phosphorus coplanar; otherwise the geometry would transform to the trigonal bipyramid with R equatorial. For an energy minimization for I and II in a trigonal-bipyramidal geometry with R axial, coplanarity of the biphenylene group, situated at an axial-equatorial location, and the phosphorus-carbon bond of the attached R group was required to avoid severe distortions from this geometry. The coordinates for the biphenylene ring were representative of those obtained in the X-ray studies; e.g., some angle parameters are shown here.



A strainless bond length of 1.47 Å was assumed for the central C-C bond.

With use of the trigonal bipyramid A as the ground-state structure, reasonable agreement with the X-ray parameters was obtained. Bond angles at phosphorus are compared in Table XII.

For the 8-(CH₃)₂N-1-Np derivative I, the calculated value of the equatorial angle CN1-P-C2' is only 138.3° compared to the X-ray value^{1b} of 151.9°. This results from opening of the angles at CN1, CN9, and CN8 to a greater degree than found experimentally in order to accommodate the presence of the (CH₃)₂N group. If one reduces the equatorial bending force constant at phosphorus, better agreement between observed and calculated exocyclic angles of the α-naphthyl group and that of the equatorial angle at phosphorus is obtained. For both I and II, minimum-energy structures result when the

plane of the naphthyl group is approximately at right angles to the basal plane of B or, in the case of A, when it lies near the equatorial plane, as found in the X-ray analyses.

The calculations show that the rectangular pyramid with R apical (type C) is the most strained and that the strain energy increases progressively, relative to conformation of types A or B, as the size of the R group increases along the series. When viewed relative to the type of structural displacement coordinates found from the X-ray data for I and II as opposed to that for III and IV, the results suggest, in agreement with the conclusion from the X-ray structural studies, that intramolecular ligand exchange through transition states of the type C may become disfavored in preference to pseudorotations proceeding via trigonal bipyramids with R apical (type D). This apparently is the case on going from the 2-isopropylphenyl derivative (VIII) to the 2,4,6-triisopropylphenyl derivative (VII) where ligand exchange was interpreted in terms of a transition state of the type C for VIII and in terms of a transition state or intermediate of the type D for the more sterically hindered phosphorane VII.

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Registry No. III, 3151-21-1; IV, 3572-91-6.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes for III and IV, thermal parameters (Table XIII) and bond angles involving hydrogen atoms (Table XIV) for III, and similar data (Tables XV, XVI) for IV (24 pages). Ordering information is given on any current masthead page.

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Proof of a Linear Fe-N-O Linkage, Perpendicular to the S₄ Plane in Fe(NO)(S₂CN{CH(CH₃)₂})₂. A New (Aerobic) Synthesis of the Complex and Its Crystal Structure

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The title complex [Fe(NO)(i-Prdtc)₂] was prepared by the action of ferric nitrate on Fe(i-Prdtc)₃, and its crystal structure was determined. The meticulously air-free conditions normally used for such syntheses were not required. The crystal structure is by far the most accurate of any "d⁷" M-N-O complex and is the first [Fe(NO)(dtc)₂] complex for which the ligand geometry can be established unambiguously. The controversial Fe-N-O geometry was found to be linear (179°) and perpendicular to the S₄ plane in a rectangular-base pyramid of ligand atoms. The Fe-N and N-O distances are 1.676 (3) and 1.161 (3) Å, respectively. Earlier spectroscopic structural assignments are reevaluated. Crystal data for [Fe(NO)(i-Prdtc)₂]: space group P2₁/n; Z = 4; a = 9.242 (6) Å, b = 16.932 (1) Å, c = 14.223 (4) Å; β = 107.40 (4)°; V = 2124 Å³; R = 4.6% for 2069 reflections.

Introduction

As part of a program on the synthesis, properties, and structure of iron and cobalt dithiocarbamates (dtc),²⁻⁵ we have

been interested in their nitroso derivatives, [M(NO)(dtc)₂], on which there is already a considerable body of literature.⁶⁻¹⁶

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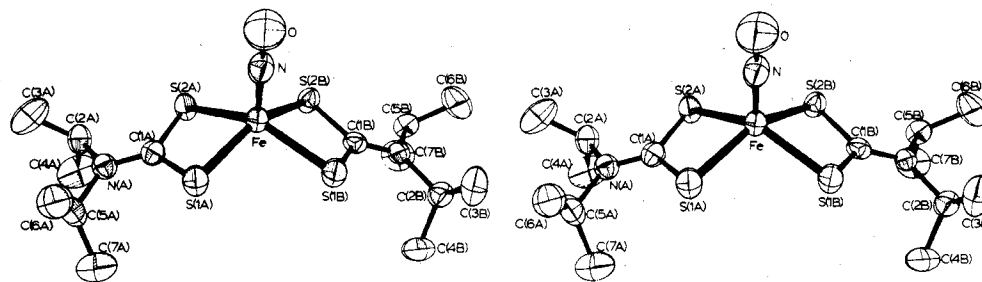


Figure 1. Stereoview of the molecular structure showing nonhydrogen atoms.

The synthesis of the Fe(NO)(dtc)₂ series has required cautious anaerobic processes. We have produced the *N,N'*-diisopropyl derivative, [Fe(NO)(*i*-Prdtc)₂], by a simple reaction analogous to that which produces polynuclear dtc complexes of copper;¹⁷ the tris complex [Fe(*i*-Prdtc)₃] is reacted with ferric nitrate in the open air.

The Fe–N–O angle in the [Fe(NO)(dtc)₂] series and in related compounds has been uncertain and the subject of considerable discussion. In the [Fe(NO)(dtc)₂] crystal structures so far determined, the nitrosyl oxygen has suffered considerable positional disorder.^{7–9} Thus neither linear nor bent Fe–N–O linkages are ruled out in these and related complexes, and the spectral data have been shown to be compatible with either. We report the crystal structure of [Fe(NO)(*i*-Prdtc)₂] in which the nitrosyl oxygen atom has a single and unambiguous position and the Fe–N–O linkage is essentially linear at 179°. This observation permits selection between the various possible molecular orbital models for the system.

Experimental Section

Preparation of the Complex. A total of 10 mmol of Fe(NO₃)₂·9H₂O dissolved in 10 mL of methanol and 10 mL of TEOF was mixed with a solution of 30 mmol of diisopropylamine and 40 mmol of carbon disulfide in 200 mL of methanol and 20 mL of triethoxymethane. A dark green solution resulted. When this was allowed to evaporate to dryness, large well-formed green crystals of two shapes, needles and blocks, resulted, mixed with some red-brown material. The crystals were easily separated from this material by handpicking or by extraction into chloroform. Subsequent X-ray analysis showed that the two crystal types exhibited the same lattice parameters and space group and hence were taken to be the same material. X-ray data collection was carried out on a crystal of the block type. The red-brown material is insoluble in common solvents and was not examined further.

Crystal Data for [Fe(NO)(*i*-Prdtc)₂]: FeS₂ON₃C₁₄H₂₈, mol wt 438.5; space group *P*2₁/*n*; *Z* = 4; *a* = 9.242 (6) Å, *b* = 16.932 (1) Å, *c* = 14.223 (4) Å; β = 107.40 (4)°; *V* = 2124 Å³; ρ_{calcd} = 1.37 g cm⁻³, ρ_{obsd} = 1.39 g cm⁻³; μ(Mo Kα) = 11.1 cm⁻¹; crystal dimensions (distances in mm of faces from centroid) (100) 0.18, (100) 0.18, (010) 0.08, (010) 0.08, (011) 0.08, (011) 0.08, (011) 0.08, (011) 0.08; maximum, minimum transmission coefficients 0.89, 0.86.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used, as previously described,¹⁸ to record the intensities for all nonequivalent reflections for which 1° < 2θ < 46°. Scan widths were calculated as (*A* = *B* tan θ), where *A* is estimated from the mosaicity of the crystal and *B* allows for the increase in width of peak due to Kα₁–Kα₂ splitting. The values of *A* and *B* were 0.6 and 0.35°, respectively.

The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected

from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Of the 2868 independent intensities, there were 2069 with *F*_o² > 3σ(*F*_o²), where σ(*F*_o²) was estimated from counting statistics.¹⁹ These data were used in the final refinement of the structural parameters.

Structure Determination. The position of the iron atom was determined from a three-dimensional Patterson function calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.¹⁸ Anisotropic temperature factors were introduced for nonhydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least-squares refinement and then held fixed.

The model converged with *R* = 4.6% and *R*_w = 5.2%. A final Fourier difference function was featureless. A listing of observed and calculated structure factors is available.²⁰ The principal programs used are as previously described.¹⁸

Results and Discussion

Final positional and thermal parameters for the complex are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 shows a stereoview of the molecule, while Figure 2 shows the molecular packing in the unit cell. The structure consists of well-separated five-coordinated complex molecules, the nearest intermolecular approach being between the nitrosyl oxygen and a ligand carbon of neighboring molecule (O–C(7B) = 3.457 (5) Å). The metal environment is an approximate square pyramid (*vide infra*) which has the four S donor atoms at the base and the nitrosyl oxygen at the apex. There are no features of trigonal-bipyramidal geometry at all. The iron atom is raised 0.65 Å above the base of the pyramid. The SCS ligand planes of the two ligands "A" and "B" make angles of 18.7 and 20.8°, respectively, with the pyramid base and are inclined at 39.5° to each other (Table IV). The iron atom lies approximately in the SCS plane of ligand B but is 0.07 Å above that of ligand A. The structure is unusual among Fe(NO)(dtc)₂-type compounds in having a well-defined nitrosyl group, without positional disorder of the O atom.

The Fe–N–O group is essentially linear (179.0 (3)°). This unambiguous finding is in contrast with previous conclusions about related compounds. The EPR results for [Fe(NO)(S₂CN{C₂H₅})₂] in EPA glass¹³ were interpreted in terms of a single nonlinear FeNO species, on the EPR time scale, or, if the FeNO group were linear, it could be normal to the plane of the four S atoms. In [Fe(NO)(*i*-Prdtc)₂], not only is the FeNO linear, but it is also essentially normal to the S₄ plane. This is indicated by several of the structural details. The four S–Fe–N angles have quite similar values, ranging

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[\text{Fe}(\text{NO})(i\text{-Prdte})_2]^{1a}$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.15087 (7)	-0.12522 (4)	0.29064 (4)	2.82 (2)	2.48 (2)	3.39 (2)	0.06 (2)	0.94 (2)	0.10 (2)
S(1A)	0.2922 (1)	-0.02865 (7)	0.38968 (9)	2.54 (5)	3.13 (5)	4.86 (6)	0.04 (4)	0.45 (4)	-0.14 (5)
S(2A)	-0.0165 (1)	-0.02481 (7)	0.28478 (9)	2.69 (5)	2.89 (5)	4.77 (6)	0.04 (4)	0.60 (4)	-0.42 (5)
S(1B)	0.2816 (1)	-0.22930 (7)	0.37833 (9)	2.69 (5)	2.79 (5)	4.42 (5)	-0.08 (4)	0.36 (4)	0.13 (5)
S(2B)	-0.0274 (1)	-0.22243 (7)	0.27296 (9)	2.79 (5)	2.89 (5)	4.17 (5)	-0.02 (4)	0.09 (4)	0.44 (4)
O	0.2282 (5)	-0.1230 (3)	0.1121 (3)	12.7 (2)	7.8 (3)	6.8 (2)	0.9 (3)	6.5 (1)	0.8 (2)
N	0.1963 (4)	-0.1232 (2)	0.1851 (3)	4.6 (2)	3.1 (2)	4.5 (2)	0.3 (2)	2.0 (1)	0.5 (2)
N(A)	0.1191 (4)	0.1020 (2)	0.3905 (3)	3.4 (2)	3.2 (2)	3.4 (2)	-0.1 (1)	1.2 (1)	-0.1 (1)
N(B)	0.0957 (4)	-0.3558 (2)	0.3703 (3)	2.9 (1)	2.4 (2)	2.7 (1)	-0.3 (1)	0.5 (1)	0.1 (1)
C(1A)	0.1315 (5)	0.0288 (3)	0.3606 (3)	3.0 (2)	3.0 (2)	3.2 (2)	0.0 (2)	1.2 (1)	0.3 (2)
C(2A)	-0.0314 (6)	0.1430 (3)	0.3561 (4)	4.3 (2)	3.3 (2)	5.2 (2)	0.6 (2)	2.0 (2)	-0.3 (2)
C(3A)	-0.0236 (6)	0.2193 (4)	0.3042 (4)	4.5 (2)	7.6 (4)	7.8 (3)	2.2 (2)	2.5 (2)	3.4 (3)
C(4A)	-0.0988 (6)	0.1501 (4)	0.4408 (4)	5.2 (2)	10.4 (5)	6.4 (3)	2.2 (3)	3.6 (2)	0.9 (3)
C(5A)	0.2478 (6)	0.1463 (3)	0.4578 (4)	5.9 (3)	3.7 (2)	4.3 (2)	-1.3 (2)	1.4 (2)	-1.2 (2)
C(6A)	0.3709 (6)	0.1652 (3)	0.4118 (4)	4.8 (2)	5.7 (3)	5.3 (3)	-1.9 (2)	0.9 (2)	0.7 (2)
C(7A)	0.3022 (7)	0.1113 (4)	0.5615 (4)	5.8 (3)	8.0 (4)	4.0 (2)	0.1 (3)	0.6 (2)	0.6 (3)
C(1B)	0.1143 (5)	-0.2826 (3)	0.3451 (3)	2.3 (2)	3.2 (2)	2.5 (2)	0.1 (2)	0.4 (1)	-0.4 (2)
C(2B)	0.2187 (5)	-0.4034 (3)	0.4375 (3)	4.1 (2)	2.8 (2)	3.6 (2)	0.0 (2)	0.3 (2)	0.5 (2)
C(3B)	0.3475 (6)	-0.4221 (3)	0.3946 (4)	4.5 (2)	3.4 (2)	7.6 (3)	1.0 (2)	1.7 (2)	0.7 (2)
C(4B)	0.2693 (7)	-0.3690 (3)	0.5423 (4)	6.1 (3)	5.0 (3)	3.3 (2)	-0.2 (3)	-0.8 (2)	0.3 (2)
C(5B)	-0.0580 (5)	-0.3927 (3)	0.3335 (3)	2.9 (2)	3.5 (2)	3.8 (2)	-0.4 (2)	0.7 (2)	0.5 (2)
C(6B)	-0.0531 (6)	-0.4714 (3)	0.2822 (4)	5.1 (3)	4.7 (3)	6.9 (3)	-1.3 (2)	1.9 (2)	-1.8 (2)
C(7B)	-0.1306 (6)	-0.3977 (4)	0.4142 (4)	5.0 (2)	6.9 (3)	6.3 (3)	-0.9 (3)	2.3 (2)	0.4 (3)

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
H(2A)	-0.098 (5)	0.108 (3)	0.317 (3)	5.1 (12)	H(7A2)	0.224 (5)	0.088 (3)	0.583 (3)	4.4 (11)
H(5A)	0.210 (6)	0.189 (3)	0.468 (4)	7.6 (16)	H(7A3)	0.353 (5)	0.084 (3)	0.563 (3)	5.6 (12)
H(2B)	0.171 (5)	-0.449 (3)	0.445 (3)	3.5 (10)	H(3B1)	0.385 (4)	-0.380 (2)	0.388 (3)	3.1 (9)
H(5B)	-0.117 (5)	-0.358 (2)	0.287 (3)	3.1 (10)	H(3B2)	0.317 (6)	-0.455 (4)	0.333 (4)	8.4 (17)
H(3A1)	-0.112 (4)	0.237 (2)	0.279 (3)	3.2 (10)	H(3B3)	0.414 (7)	-0.461 (4)	0.440 (4)	9.1 (19)
H(3A2)	0.022 (7)	0.214 (4)	0.262 (4)	8.6 (17)	H(4B1)	0.339 (5)	-0.412 (3)	0.582 (3)	4.6 (11)
H(3A3)	0.034 (7)	0.256 (4)	0.363 (4)	8.6 (18)	H(4B2)	0.307 (5)	-0.327 (3)	0.542 (3)	4.3 (11)
H(4A1)	-0.200 (6)	0.172 (3)	0.422 (4)	6.7 (15)	H(4B3)	0.191 (5)	-0.357 (3)	0.570 (3)	5.0 (12)
H(4A2)	-0.028 (7)	0.189 (4)	0.485 (4)	8.6 (17)	H(6B1)	-0.010 (7)	-0.515 (4)	0.320 (4)	8.2 (17)
H(4A3)	-0.114 (7)	0.098 (4)	0.465 (4)	8.1 (18)	H(6B2)	-0.010 (7)	-0.474 (4)	0.239 (4)	8.2 (17)
H(6A1)	0.330 (5)	0.194 (3)	0.361 (3)	6.3 (14)	H(6B3)	-0.172 (7)	-0.485 (4)	0.252 (4)	8.9 (18)
H(6A2)	0.417 (7)	0.116 (3)	0.391 (5)	9.2 (18)	H(7B1)	-0.226 (5)	-0.415 (3)	0.393 (3)	4.7 (11)
H(6A3)	0.446 (7)	0.203 (4)	0.453 (4)	9.0 (18)	H(7B2)	-0.085 (5)	-0.431 (3)	0.461 (3)	4.6 (11)
H(7A1)	0.354 (5)	0.157 (3)	0.603 (3)	4.3 (11)	H(7B3)	-0.128 (7)	-0.346 (4)	0.439 (5)	9.5 (20)

^a The form of the anisotropic thermal parameter is: $\exp[-(B_{11}a^*ahh + B_{22}b^*bkk + B_{33}c^*cII)/4 + (B_{12}a^*b*hh + B_{13}a^*c*hl + B_{23}b^*c*kl)/2]$.

Table II. Bond Distances and Selected Intramolecular and Closest Intermolecular Contacts (Å)

Fe-S(1A)	2.294 (1)	C(2B)-C(3B)	1.525 (5)
Fe-S(2A)	2.283 (1)	C(2B)-C(4B)	1.537 (5)
Fe-S(1B)	2.285 (1)	C(5B)-C(6B)	1.526 (5)
Fe-S(2B)	2.289 (1)	C(5B)-C(7B)	1.494 (5)
Fe-N	1.676 (3)	C-H	0.92
S(1A)-C(1A)	1.719 (3)	S(2B)-C(4B)	3.606 (3) ^a
S(2A)-C(1A)	1.725 (3)	N-C(3B)	3.573 (5) ^b
S(1B)-C(1B)	1.729 (3)	O-C(3B)	3.468 (5) ^b
S(2B)-C(1B)	1.732 (3)	O-C(7B)	3.457 (5) ^c
N-O	1.161 (3)	S(1A)-S(2A)	2.797 (3) ^d
N(A)-C(1A)	1.327 (4)	S(1B)-S(2B)	2.803 (3) ^d
N(A)-C(2A)	1.499 (4)	S(1A)-S(1B)	3.401 (4) ^d
N(A)-C(5A)	1.487 (4)	S(2A)-S(2B)	3.350 (4) ^d
N(B)-C(1B)	1.317 (4)	S(1A)-S(2B)	4.395 (5) ^d
N(B)-C(2B)	1.485 (4)	S(2A)-S(1B)	4.377 (5) ^d
N(B)-C(5B)	1.496 (4)	S(1A)-N	3.205 (4) ^d
C(2A)-C(3A)	1.501 (5)	S(2A)-N	3.213 (4) ^d
C(2A)-C(4A)	1.517 (5)	S(1B)-N	3.179 (4) ^d
C(5A)-C(6A)	1.506 (5)	S(2B)-N	3.195 (4) ^d
C(5A)-C(7A)	1.529 (5)		

^a $x^{-1/2}, -y^{-1/2}, z^{-1/2}$. ^b $1/2 - x, 1/2 + y, 1/2 - z$. ^c $x + 1/2, -y - 1/2, z - 1/2$. ^d x, y, z .

from 105.8 (1) to 107.5 (1)°. The two apical planes made up of a diagonal of the pyramid base and the N atom are essentially perpendicular to the base (88.9°, 89.6°). The two apical planes are inclined at 79.3° to each other rather than 90° because the pyramid base closely approximates a rectangle, rather than a square (long sides 4.395 (5), 4.377 (5)

Table III. Bond Angles (Deg)

S(1A)-Fe-S(2A)	75.3 (1)	C(2B)-N(B)-C(5B)	117.6 (2)
S(1A)-Fe-S(1B)	95.9 (1)	S(1A)-C(1A)-S(2A)	108.6 (2)
S(1A)-Fe-S(2B)	147.0 (1)	S(1A)-C(1A)-N(A)	127.1 (2)
S(1A)-Fe-N	106.6 (1)	S(2A)-C(1A)-N(A)	124.3 (2)
S(2A)-Fe-S(1B)	146.7 (1)	N(A)-C(2A)-C(3A)	112.5 (3)
S(2A)-Fe-S(2B)	94.2 (1)	N(A)-C(2A)-C(4A)	109.8 (3)
S(2A)-Fe-N	107.5 (1)	C(3A)-C(2A)-C(4A)	114.5 (3)
S(1B)-Fe-S(2B)	75.6 (1)	N(A)-C(5A)-C(6A)	113.1 (3)
S(1B)-Fe-N	105.8 (1)	N(A)-C(5A)-C(7A)	113.2 (3)
S(2B)-Fe-N	106.3 (1)	C(6A)-C(5A)-C(7A)	115.4 (3)
Fe-S(1A)-C(1A)	87.9 (1)	S(1B)-C(1B)-S(2B)	108.2 (2)
Fe-S(2A)-C(1A)	88.1 (1)	S(1B)-C(1B)-N(B)	126.6 (2)
Fe-S(1B)-C(1B)	88.2 (1)	S(2B)-C(1B)-N(B)	125.3 (2)
Fe-S(2B)-C(1B)	88.0 (1)	N(B)-C(2B)-C(3B)	113.2 (3)
Fe-N-O	179.0 (3)	N(B)-C(2B)-C(4B)	111.8 (3)
C(1A)-N(A)-C(2A)	119.3 (3)	C(3B)-C(2B)-C(4B)	114.8 (3)
C(1A)-N(A)-C(5A)	123.2 (3)	N(B)-C(5B)-C(6B)	111.7 (3)
C(2A)-N(A)-C(5A)	117.5 (3)	N(B)-C(5B)-C(7B)	110.7 (3)
C(1B)-N(B)-C(2B)	123.4 (2)	C(6B)-C(5B)-C(7B)	113.7 (3)
C(1B)-N(B)-C(5B)	119.0 (2)		

Å; short sides 3.401 (4), 3.350 (4) Å).

A detailed comparison between the structural parameters reported for this complex and those reported previously for other $\{\text{Fe}-\text{NO}\}^7$ five-coordinate crystal structures^{7-9,21-28} shows

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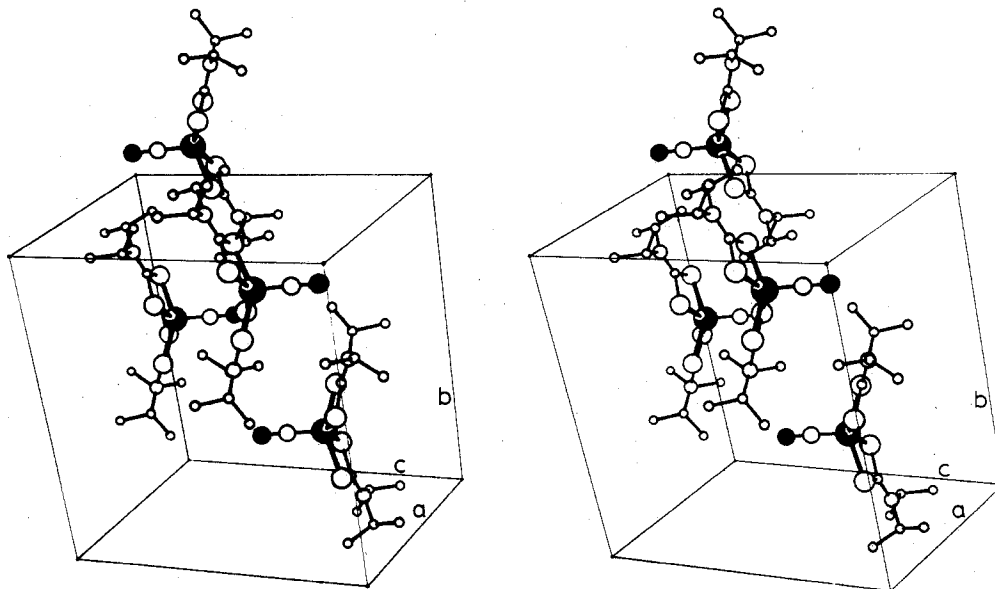


Figure 2. Stereoview of the unit cell contents.

Table IV

		Coefficients of Least-Squares Planes for $AX + BY + CZ = D$					
plane	atoms	A	B	C	D	dist of atoms from plane, Å	
I	S(1A), S(2A), S(1B), S(2B)	0.511	0.032	-0.859	-4.029	S(1A), S(2A), S(1B), S(2B) all 0.0, Fe 0.65, N 2.33, O 3.49	
II	S(1A), S(2A), C(A)	0.484	0.352	-0.802	-3.902	S(1A), S(2A), C(A) all 0.0, Fe 0.07, N(A) -0.01	
III	S(1B), S(2B), C(B)	0.472	-0.324	-0.820	-2.486	S(1B), S(2B), C(B) all 0.0, Fe 0.01, N(A) -0.01	
IV	S(1A), S(2B), N	-0.643	0.665	-0.380	-3.002	S(1A), S(2B), N all 0.00, Fe -0.008, O -0.01	
V	S(2A), S(1B), N	-0.667	-0.611	-0.437	-0.484	S(2A), S(1B), N all 0.00, Fe -0.011, O 0.02	

Interplanar Angles: I-II, 18.7°; I-III, 20.8°; II-III, 39.5°; I-IV, 88.9°; I-V, 89.6°; IV-V, 79.3°

Table V. Comparison of Isoelectronic Pentacoordinate Iron Nitrosyl Complexes

compd ^a	$\nu_{\text{N-O}}$, cm ⁻¹	ordered/ disordered nitrosyl	geometry	Fe-N, Å	N-O, Å	Fe-N-O, deg	ref
Fe(TPP)(NO)	1700	d	SBP, apical NO	1.717 (7)	1.122 (12)	149.2 (6)	21
Fe(N ₂ S ₂)(NO)	1650	o	SBP, apical NO	1.693 (5)	1.170 (6)	155.2 (5)	22
			SBP, apical NO	1.702 (5)	1.130 (6)	158.4 (5)	22
Fe(Me ₂ dtc) ₂ (NO)	1690	d	SBP, apical NO	1.705 (16)	1.016 (19)	173.3 (15)	8, 9
Fe(Me ₂ dtc) ₂ (NO) ^a	1690	o	SBP, apical NO	1.720 (5)	1.102 (7)	170.4 (6)	9
[Fe(S ₂ C ₂ (CN) ₂)(NO)] ²⁻	1645	d	SBP, apical NO	1.56 (2)	1.06 (4)	165 (2)	23, 24
Fe(Et ₂ dtc) ₂ (NO)	1673	d	SBP, apical NO	1.69 (4)	1.16 (5)	174 (4)	7
[Fe(das) ₂ (NO)] ²⁻	1760	o	SBP, apical NO	1.655 (18)	1.141 (27)	172.8 (17)	25
[Fe(CN) ₄ (NO)] ²⁻	1755	o	SBP, apical NO	1.565 ^b	1.161 ^b	177.1 ^b	26
[Fe(TMC)(NO)] ²⁻ c	1840	o	int, ^d apical NO	1.737 (6)	1.137 (6)	177.5 (5)	27
Fe(salen)(NO) ^c	1710	d	SBP, apical NO	1.783 (16)	1.11 (4), 1.09 (2)	144 (5), 150 (4)	28
Fe(salen)(NO) ^{c,e}	1630	d	SBP, apical NO	1.80 (15), 1.81 (11)	1.15 ^f	132 (5), 122 (7)	28
Fe(<i>i</i> -Pr ₂ dtc) ₂ (NO)	1695	o	SBP, apical NO	1.676 (3)	1.161 (3)	179.0 (3)	this work

^a Data collected at -80 °C. ^b No esd's reported; $R_f = 10.2\%$. ^c $S = 3/2 \rightleftharpoons S = 1/2$ temperature-dependent spin equilibrium reported.

^d Geometry reported to be intermediate between trigonal bipyramidal and square-based pyramid but biased toward the latter. ^e Data

collected at -175 °C. ^f N-O bond distance fixed at 1.15 Å. ^g Abbreviations: SBP = square-based pyramid; TPP = 5,10,15,20-tetraphenyl-

porphinato; N₂S₂ = C₈H₁₆N₂S₂; Me₂dtc = dimethyldithiocarbamate; Et₂dtc = diethyldithiocarbamate; das = *o*-phenylenebis(dimethylarsine);

TMC = tetramethylcyclam (C₁₄H₃₂N₄); salen = *N,N'*-ethylenebis(salicylaldiminato); *i*-Pr₂dtc = diisopropyldithiocarbamate.

quite clearly that this is by far the most accurate determination to date. As such, a detailed analysis of the geometry of this

compound is relevant to the continuing controversy concerning the nature of the {Fe-NO}⁷ group and the FeL₄NO geometry. This is the only iron bis(dithiocarbamate) nitrosyl structure which has been shown to have an ordered nitrosyl group, and from this it seems likely that such groupings in related complexes are linear in at least some cases, though some variety may well exist. In view of the very low bending frequency for the {Fe-NO}⁷ group,²⁹ it seems likely that minor changes in

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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.

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Registry No. Fe(NO)(*i*-Prdtc)₂, 72251-12-8; diisopropylamine, 108-18-9; carbon disulfide, 75-15-0; Fe(NO₃)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.

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Organometallic Nitrosyl Chemistry. 14.¹ Novel Reactivity of LiEt₃BH with [(η^5 -C₅H₅)Cr(NO)₂]₂: Conversion of a Bridging Nitrosyl Ligand to a Bridging EtNBET₂ Group

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The reaction between LiEt₃BH and [CpCr(NO)₂]₂ (Cp = η^5 -C₅H₅) produces the following organometallic nitrosyl complexes: CpCr(NO)₂Et (5%), Cp₂Cr₂(NO)₃(EtNBET₂) (6%), Cp₂Cr₂(NO)₃(NH₂) (15%), Cp₂Cr₂(NO)₂(NH₂)₂ (5%), and Cp₂Cr₂(NO)₂(NH₂)(OH) (2%). The latter three products probably result from the customary reaction mode of Et₃BH⁻ 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 Cp₂Cr₂(NO)₃(EtNBET₂) complex have been determined by X-ray crystallography. The complex crystallizes in space group *P*2₁/*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 EtNBET₂ 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, LiEt₃BH, 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 -C₅H₅), LiEt₃BH 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. ¹H and ¹³C 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 ¹H and ¹³C chemical shifts are reported in ppm downfield from Me₄Si. The ¹¹B magnetic resonance spectrum was recorded on a Bruker WP-80 spectrometer with reference

to external BF₃·Et₂O in CDCl₃. 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 LiEt₃BH with [CpCr(NO)₂]₂. A stirred tetrahydrofuran solution (30 mL) of [CpCr(NO)₂]₂⁴ (0.90 g, 2.5 mmol) at ambient temperature was treated dropwise with a THF solution of LiEt₃BH.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 LiEt₃BH 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 CH₂Cl₂ (~5 mL), and the solution was transferred by syringe onto a 1 × 4 cm Florisil column. Elution of the column with CH₂Cl₂ and removal of the solvent from the eluate under reduced pressure yielded 0.04 g (5% yield) of orange Cp₂Cr₂(NO)₂(NH₂)₂. Elution with THF afforded 0.02 g (2% yield) of orange-brown Cp₂Cr₂(NO)₂(NH₂)(OH) after solvent removal. Both products were readily identifiable by their characteristic IR, ¹H 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 CH₂Cl₂, an equal volume

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