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Synthesis and Crystal Structure of an Iron Nitrosyl Carbonyl Hydride[1]

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Protonation with trifluoroacetic acid of the iron tricarbonyl nitrosyl anion $Fe(CO)_3NO^-Na^+$ in ether in the presence of excess triphenylphosphine yields the iron nitrosyl hydride $FeH(CO)(NO)(P(C_6H_5)_3)_2$ (65–70%) ($\delta_{Fe-H} = -5.0$, $J_{P-H} = 79 \pm 1$ Hz). The structure of this new compound has been determined with X-ray data measured at 115 K. The crystals are orthorhombic, space group $Pbc2_1$, with $a = 13.443$ (1) Å, $b = 23.101$ (2) Å, $c = 20.284$ (4) Å, $V = 6299.1$ (14) Å^3, and $D_{calcd} = 1.35$ g/cm^3 for $Z = 8$ (D_{obsd} at room temperature is 1.32 g/cm^3). Refinement of two independent molecules in the asymmetric unit converged at $R = 0.041$ and $R_w = 0.053$ for the 4464 observed reflections. In both molecules, the five-coordinate 18e Fe(0) complex is a distorted trigonal bipyramid with H, CO, and linear NO in the basal plane and the two P atoms in axial positions but pulled toward the hydride to form a P–Fe–P angle of 140.9 (1)°. The Fe–P lengths of 2.174 (2)–2.188 (2) Å are shorter than in most other similar structures. The Fe–carbonyl and Fe–nitrosyl arrangements are linear with the following mean geometry: Fe–C = 1.753 (8) Å, C–O = 1.140 (3) Å, Fe–C–O = 177.9 (8)°; Fe–N = 1.673 (7) Å, N–O = 1.171 (1) Å, Fe–N–O = 175.1 (8)°. Chemically equivalent valence angles around the Fe atoms are observed with slightly different values, indicating some sensitivity to changes in the packing environment.

Introduction

The fascinating and intriguing chemistry of nitrosyl complexes has attracted considerable attention in recent years.[3] However, although some nitrosyl derivatives have found their application as catalyst precursors in hydrogenation[4,5] or hydroformylation,[6] only a limited number of nitrosyl hydrides have been reported,[5,7] compared to the large number of carbonyl hydrides presently known.[8] This is somewhat surprising in view of the pivotal role of hydrides in several reactions of current interest.[9-11] Following our previous work on the reactivity of the anion $Fe(CO)_3NO^-$,[12] we came to study its protonation reactions in a variety of conditions[13] with the prospect of synthesizing new iron hydrides for future studies of reactions with synthesis gas. In this paper we report the details of the synthesis and crystal structure of the new iron nitrosyl hydride $FeH(NO)(CO)(P(C_6H_5)_3)_2$ at 115 K.

The crystal structures of only two pentacoordinated nitrosyl hydrides $RuH(NO)(P(C_6H_5)_3)_3$[14] and $[IrH(NO)(P(C_6H_5)_3)_3]^+$,[15,16] containing a second- and a third-row element, have been reported. The Ru atom in the first complex has trigonal-bipyramidal coordination with the hydride and a linear NO in axial positions. The second complex occurs in three isomeric forms, two of which have been studied by X-rays. In both forms, the coordination around Ir is distorted trigonal bipyramidal with linear NO. However, in the black form[15] the hydride and NO are axial, while in the brown form[16] two triphenylphosphine groups occupy axial positions. The present study provides the first crystal structure of a pentacoordinated nitrosyl hydride of a first-row transition element.

Experimental Section

Compound Preparation. All operations were done under argon or vacuum. Tetrahydrofuran was refluxed, then distilled from benzophenone/sodium under nitrogen, and used immediately. All the solvents were saturated with argon before use. Anhydrous ether (Mallinkrodt), triphenylphosphine (Aldrich 99%), $Fe(CO)_5$ (Pressure Chemical), $Na^+NO_2^-$ (BDH), and trifluoroacetic acid (MCB or J. T. Baker) were used as received. $Fe(CO)_2(NO)_2$,[17] $Fe(CO)_4(P(C_6H_5)_3)$,[18] and $Fe(CO)_3(P(C_6H_5)_3)_2$[19] were prepared according to published procedures. Thermal decomposition of the cation $[Fe(CO)(NO)(CH_3CN)(P(C_6H_5)_3)_2]^+$[20] in acetonitrile at 50 °C afforded $Fe(NO)_2(P(C_6H_5)_3)_2$,[21] which crystallized. Solutions of $Fe(CO)(NO)_2(P(C_6H_5)_3)$[21] were obtained from the reaction of $Fe(CO)_2(NO)_2$ with triphenylphosphine in hexane or ether at room temperature. SiO_2 plates for analytical chromatography were from Analtech Inc. IR spectra were recorded on a Unicam SP 1100, calibrated with a polystyrene film, or on a Perkin-Elmer 283. ^1H NMR spectra were recorded on a Varian HA 100 with Me_4Si as an internal reference. Elemental analyses were performed by Chemalytics Inc., Tempe, AZ, or MHW Laboratories, Phoenix, AZ.

$Fe(CO)_3NO^-Na^+$ (1). The published procedure[7j] was followed by reacting $Fe(CO)_5$ with $Na^+NO_2^-$ in absolute methanol in the presence of $CH_3O^-Na^+$. After completion of the reaction, the solvent was removed under reduced pressure and the solid residue dried under vacuum for at least 24 h at room temperature. **1** was extracted with ether and the filtered solution concentrated under vacuum at 0 °C until a few crystals appeared. Further cooling to −10 °C with the addition of hexane and efficient stirring afforded most of the compound in the solid state. The solid was separated from the slightly colored solution, washed with hexane and benzene, and dried under vacuum (3 h). The solid retained approximately 1 mol of methanol/mol of

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(3) (a) Frenz; B. A.; Ibers, J. A. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1973**, *11*, 33. (b) Enemark, J. G.; Feltham, R. S. *Coord. Chem. Rev.* **1974**, *13*, 339. (c) Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26. (d) Caulton, K. G. *Coord. Chem. Rev.* **1974**, *13*, 339. (e) Bottomley, F. *Acc. Chem. Res.* **1975**, *14*, 317. (f) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (g) Hoffmann, R.; Chen, M. M. L.; Thorn, D. L. *Inorg. Chem.* **1977**, *16*, 503.

(4) Giovanitti, B.; Ghedini, M.; Dolcetti, G.; Denti, G. *J. Organomet. Chem.* **1978**, *157*, 457.

(5) Wilson, S. T.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3068.

(6) Sanchez-Delgado, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399.

(7) (a) Hames, B. W.; Legdzins, P.; Oxley, J. C. *Inorg. Chem.* **1980**, *19*, 1565. (b) Legdzins, P.; Martin, D. T. *Ibid.* **1979**, *18*, 1250. (c) Reed, C. A.; Roper, W. R. *J. Chem. Soc. D* **1969**, *155*. (d) Stewart, R. P.; Okamoto, M.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32. (e) Clark, G. R.; Grundy, K. R.; Roper, W. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc. D* **1972**, 119. (f) Lamonica, G.; Freni, M.; Cenini, S. *J. Organomet. Chem.* **1974**, *71*, 57. (g) Giusto, D.; Ciani, G.; Manassero, M. *Ibid.* **1975**, *105*, 91. (h) Kruck, T.; Lang, W. *Chem. Ber.* **1966**, *99*, 3794. (i) Hieber, W.; Tengler, H. *Z. Anorg. Allg. Chem.* **1962**, *318*, 136. (j) Hiebner, W.; Beutner, H. *Ibid.* **1963**, *320*, 91.

(8) (a) McCue, J. P. *Coord. Chem. Rev.* **1973**, *10*, 265. (b) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231. (c) Muetterties, E. L., Ed. "Transition Metal Hydrides"; Marcel Dekker: New York, 1971; Vol. 1.

(9) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319.

(10) Masters, C. A. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(11) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1.

(12) Roustan, J. L. A.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721.

(13) Roustan, J. L. A.; Forgues, A. *J. Organomet. Chem.* **1980**, *184*, C13.

(14) Pierpont, C. G.; Eisenberg, R. *Inorg. Chem.* **1972**, *11*, 1094.

(15) Mingos, D. M. P.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 1479.

(16) Clark, G. R.; Waters, J. M.; Whittle, K. R. *Inorg. Chem.* **1974**, *13*, 1628.

(17) King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1, p 157.

(18) Siegle, O. *J. Organomet. Chem.* **1975**, *92*, 321.

(19) McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 186.

(20) Roustan, J. L. A.; Merour, J. Y.; Forgues, A. *J. Organomet. Chem.* **1980**, *188*, C23.

(21) McBride, D. W.; Stafford, S. L.; Stone, F. G. A. *Inorg. Chem.* **1962**, *1*, 386.

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Table I. Crystal Data

formula	$C_{37}H_{31}NO_2P_2Fe$
formula weight	639.46
space group	$Pbc2_1$ (orthorhombic)^b
equivalent positions	x, y, z
	$-x, -y, {}^1/_2 + z$
	$x, {}^1/_2 - y, {}^1/_2 + z$
	$-x, {}^1/_2 + y, z$
a	13.443 (1) Å
b	23.101 (2) Å
c	20.284 (4) Å
V	6299.1 (14) Å^3
Z	8
calcd density	1.35 g/cm^3
temp	115 K
measd density^a	1.32 g/cm^3
radiation used	Mo Kα (monochromatized)
abs coeff	47.3 cm^{-1}

^{a} By flotation in aqueous KI solution at room temperature.
^{b} $Pbc2_1$ is a nonstandard setting of space group $Pca2_1$ (No. 29).

anion (NMR of a CD_3COCD_3 solution calibrated with a known amount of toluene). The compound was known already to form solvates with dioxane[7j] and acetone.[22] It is sensitive to water (deliquescent), oxygen, and light and was stored under argon at 0 °C. Over several months, the yellow color slightly turned green, presumably reflecting some oxidation (IR: THF—tight ion pairs ν(CO) 1990 s, 1890 s, ν(NO) 1615 s; loose ion pairs ν(CO) 1977 s, 1873 sh, ν(NO) 1648;[23] ether—only tight iron pairs detected[23] ν(CO) 1995 s, 1905 vs, ν(NO) 1585 s cm^{-1}).

$FeH(NO)(CO)(P(C_6H_5)_3)_2$ (4). CF_3COOH (0.52 mL, 0.8 g, 7 mmol, 1.5 equiv was added dropwise with a syringe to a stirred solution of $Fe(CO)_3NO^-Na^+$ (1.04 g, 4.6 mmol) and $P(C_6H_5)_3$ (7.1 g, 27 mmol, ~6 equiv) in 175 mL of dry diethyl ether, in a three-necked round-bottomed flask surrounded by a water-ice bath. Stirring was maintained until gas evolution was no longer detected (2 h). The solid was filtered, washed with 3 × 10 mL of cold ether, and dried. A small amount of the hydride **4** dissolved in ether, but it was not recovered. Selective extraction of the residue with benzene at room temperature followed by crystallization in benzene/pentane at 10 °C afforded the hydride **4** as a microcrystalline orange powder (2.3 g, 70%). (Anal. Calcd for $C_{37}H_{31}FeNO_2P_2(C_6H_6)$: C, 72.0; H, 5.2; N, 1.9. Found: C, 71.9; H, 5.2; N, 1.6.) Removal of the benzene solvate molecule occurred at room temperature when the solid was kept under the high vacuum of a mass spectrometer. The mass spectra were not very informative. Ionized fragments containing iron could be detected only at temperature above 120 °C when thermal decomposition of **4** was occurring in the solid.

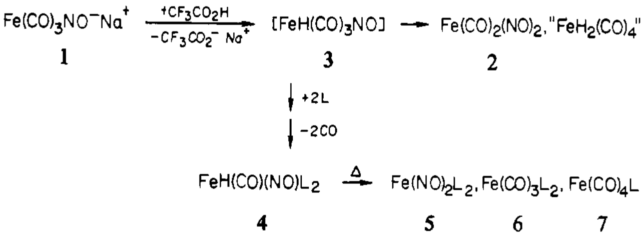
Thermal Decomposition of Hydride 4 in THF. A solution of 0.5 g of **4** in 30 mL of THF was heated at reflux under argon; samples were withdrawn periodically for IR analysis. Thermal degradation was complete after 4 h. The CO- and/or NO-containing products consisted mainly of $Fe(NO)_2(P(C_6H_5)_3)_2$ (**5**), $Fe(CO)_3(P(C_6H_5)_3)_2$ (**6**), and $Fe(CO)_4(P(C_6H_5)_3)$ (**7**). They were identified by their characteristic infrared spectra[19,21] and by their R_f values on analytical thin-layer chromatography (SiO_2, hexane:benzene = 3:1, revelation with iodine vapors). $Fe(CO)(NO)_2(P(C_6H_5)_3)$ was not detected. No separation on a preparative scale was attempted.

Crystallographic Study

Single crystals of **4** were grown by slow evaporation of CS_2/hexane solutions at room temperature. Data for the prismatic crystals formed are presented in Table I. The systematic absences determined from precession photographs were $0kl$ for k odd and $h0l$ for l odd, which are common to space groups $Pbcm$ and $Pbc2_1$. The latter space group was chosen since the $|E|$ statistics were indicative of a noncentrosymmetric space group and the Patterson map had no strong peaks on the 0, 0, W line.

Preliminary X-ray analysis was carried out with room-temperature data, but the final refinement was performed with data measured at 115 K, which comprised a higher ratio of observed reflections (78.2% compared to 57.5%). The low-temperature data, summarized in Table I, were measured on a Picker four-circle diffractometer using monochromatized Mo radiation and a crystal of dimensions 0.33 × 0.43 × 0.46 mm. The cell parameters were derived from the angular settings of 34 reflections with 2θ = 40–47°. Intensities of the hkl quadrant were obtained from θ–2θ scans ($2\theta \leq 50°$) for scan ranges of $\Delta\theta = (0.9 + 0.35 \tan \theta)°$ at a 2θ scan speed of 2°/min and from application of the profile analysis method.[24] Intensities for three standard reflections, which were monitored after every 100 reflections, decreased by 9% during data collection. Of 5721 reflections measured, 4464 were considered observed at the $2\sigma(I)$ level. The net intensities were corrected for crystal decay and the Lorentz and polarization effects but not for absorption.

Scheme I^a



^{a} L = $P(C_6H_5)_3$.

Structure Determination and Refinement. The asymmetric unit cell in this structure contains two independent molecules (86 non-hydrogen atoms). Structure solving was begun by application of the direct method to the 444 reflections with $|E| \geq 1.50$. The E map for the best phase set contained six strong peaks, which were accepted as the Fe and P atoms in the two molecules. The corresponding interatomic vectors were in good agreement with the highest peaks in the Patterson map. The remaining 80 C and N atoms were located in two stages from Fourier maps. The distinction between the C and N atoms of the CO and NO groups was decided by first assuming them to be C atoms and refining their occupancy factors, which shifted to 1.30 and 1.22 for N compared to 1.00 and 1.09 for C. The H atoms, except for the two hydrides, were located later from a difference map but were not refined.

Refinement of the parameters was by block-diagonal least-squares calculations on $\sum w(F_o - F_c)^2$, where $w = [1 + ((|F_o| - 20)/35)^2]^{-1}$ in the final cycles; the constants were chosen to make $\langle w(\Delta F)^2 \rangle$ independent of $|F_o|$. Only the observed reflections were included in the least-squares summations and the R index. The z parameter of Fe in molecule II was kept fixed throughout the refinement. Near the end of the refinement, the two possible absolute configurations were examined by using the anomalous dispersion components of the Fe and P atoms; the one producing the lower R index (0.0416 compared to 0.0432) was refined further until the average and maximum parameter shifts were reduced to 0.1 and 0.6 of their estimated standard deviations. The final difference maps showed peaks of height 0.7 e Å^{-3} near Fe, 0.5 e Å^{-3} near P, and ≤0.3 e Å^{-3} elsewhere. Refined coordinates for the non-hydrogen atoms are listed in Table II. The observed and calculated structure amplitudes, parameters for the H atoms, and U_{ij}'s for the non-hydrogen atoms have been deposited (supplementary material). Calculations were performed with the aid of MULTAN, the NRC program system, and ORTEP.[25] The scattering factor curves were taken from ref 26.

Results and Discussion

Synthesis of the Iron Nitrosyl Hydride $FeH(CO)(NO)(P(C_6H_5)_3)_2$ (4). Protonation of the anion **1** in ether at 5 °C (water-ice bath) (Scheme I) with a limited amount of trifluoroacetic acid (1.5 equiv) led in a few seconds to the volatile

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(22) Chaudhari, F. M.; Knox, G. R.; Pauson, P. L. *J. Chem. Soc. C* **1967**, 2255.
(23) Pannell, K. H.; Sen Chen Yu; Belknap, K. L. *J. Chem. Soc., Chem. Commun.* **1977**, 362.
(24) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.
(25) (a) Main, P.; Woolfson, M. M.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P. "MULTAN 78—A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York and Louvain, 1978. (b) NRC Crystallographic Programs for the IBM/360 System: Ahmed, F. R.; Hall, S. R.; Pippy, M. E.; Huber, C. P. *J. Appl. Crystallogr.* **1973**, *6*, 309 (Accession Nos. 133–147). (c) Johnson, C. K. "ORTEP II", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.
(26) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Fractional Coordinates (×10^5 for Fe, P; ×10^4 for C, N, O) and Equivalent Isotropic Thermal Parameters (Å^2)[a]

	x	y	z	B_{eq}		x	y	z	B_{eq}
		Molecule I					Molecule II		
Fe	93234 (6)	62483 (3)	61966 (5)	2.5 (1)	Fe	55120 (6)	78596 (3)	88480	2.4 (1)
P(1)	99643 (10)	71185 (5)	61683 (8)	2.1 (1)	P(1)	47256 (9)	86816 (5)	88778 (7)	1.9 (1)
P(2)	95575 (10)	53794 (6)	57966 (7)	2.1 (1)	P(2)	54014 (10)	69757 (6)	92155 (7)	2.1 (1)
C(1)	9818 (5)	6092 (2)	6980 (3)	2.9 (1)	C(1)	5137 (4)	7661 (3)	8056 (3)	2.5 (1)
O(1)	10104 (4)	6000 (2)	7501 (2)	4.4 (1)	O(1)	4905 (4)	7522 (3)	7541 (2)	4.3 (1)
N(2)	8110 (4)	6370 (2)	6102 (3)	3.3 (1)	N(2)	6647 (4)	8100 (2)	9060 (3)	2.7 (1)
O(2)	7257 (3)	6474 (2)	6090 (4)	5.7 (2)	O(2)	7417 (3)	8301 (2)	9201 (3)	3.7 (1)
C(11)	11327 (4)	7143 (2)	6273 (3)	2.3 (1)	C(11)	3372 (4)	8640 (2)	8871 (3)	2.4 (1)
C(12)	11944 (4)	7176 (3)	5740 (3)	3.4 (2)	C(12)	2784 (5)	8928 (3)	9326 (3)	3.5 (2)
C(13)	12970 (5)	7162 (4)	5818 (4)	4.3 (2)	C(13)	1761 (5)	8862 (4)	9317 (4)	4.6 (2)
C(14)	13368 (4)	7097 (3)	6446 (4)	3.8 (2)	C(14)	1308 (4)	8520 (4)	8847 (4)	4.3 (2)
C(15)	12749 (5)	7055 (3)	6980 (3)	3.4 (2)	C(15)	1876 (5)	8243 (4)	8396 (4)	4.5 (2)
C(16)	11724 (5)	7076 (3)	6894 (3)	2.9 (2)	C(16)	2910 (5)	8309 (3)	8402 (4)	3.9 (2)
C(21)	9515 (4)	7608 (2)	6816 (3)	2.3 (1)	C(21)	5051 (4)	9115 (3)	9601 (3)	2.3 (1)
C(22)	8644 (4)	7472 (3)	7152 (3)	2.7 (1)	C(22)	5403 (7)	9674 (3)	9543 (4)	4.8 (2)
C(23)	8249 (5)	7847 (3)	7623 (4)	3.6 (2)	C(23)	5727 (9)	9975 (4)	10094 (5)	6.5 (3)
C(24)	8714 (5)	8367 (3)	7748 (3)	3.3 (2)	C(24)	5697 (6)	9734 (3)	10693 (4)	4.2 (2)
C(25)	9584 (5)	8495 (3)	7431 (4)	3.3 (2)	C(25)	5358 (5)	9183 (3)	10768 (3)	3.3 (2)
C(26)	9991 (5)	8127 (3)	6972 (3)	3.0 (1)	C(26)	5063 (4)	8871 (3)	10216 (3)	2.8 (1)
C(31)	9748 (4)	7538 (3)	5416 (3)	2.4 (1)	C(31)	5020 (4)	9175 (2)	8196 (3)	2.3 (1)
C(32)	10185 (6)	8088 (3)	5331 (4)	4.0 (2)	C(32)	4356 (5)	9603 (3)	7995 (3)	3.0 (2)
C(33)	10009 (6)	8407 (3)	4762 (4)	3.8 (2)	C(33)	4664 (5)	10011 (3)	7530 (3)	3.5 (2)
C(34)	9405 (6)	8176 (4)	4277 (4)	4.7 (2)	C(34)	5578 (5)	9989 (3)	7268 (3)	3.2 (2)
C(35)	9036 (9)	7655 (5)	4342 (5)	8.2 (4)	C(35)	6249 (5)	9558 (3)	7461 (3)	2.7 (1)
C(36)	9183 (7)	7333 (4)	4918 (4)	6.0 (3)	C(36)	5947 (4)	9158 (3)	7924 (3)	2.4 (1)
C(41)	9330 (4)	5296 (2)	4913 (3)	2.3 (1)	C(41)	4190 (4)	6644 (2)	9033 (3)	2.3 (1)
C(42)	9965 (5)	5004 (3)	4486 (3)	3.0 (1)	C(42)	3331 (5)	6954 (3)	9182 (4)	4.2 (2)
C(43)	9731 (5)	4940 (3)	3833 (3)	3.3 (2)	C(43)	2399 (5)	6735 (3)	9020 (5)	4.8 (2)
C(44)	8866 (5)	5158 (3)	3579 (3)	3.1 (2)	C(44)	2320 (5)	6212 (3)	8715 (4)	3.8 (2)
C(45)	8224 (5)	5448 (3)	3996 (3)	3.4 (2)	C(45)	3164 (6)	5915 (3)	8550 (4)	4.0 (2)
C(46)	8443 (5)	5525 (2)	4657 (3)	2.9 (2)	C(46)	4108 (4)	6123 (2)	8700 (3)	2.9 (2)
C(51)	8758 (4)	4804 (2)	6141 (3)	2.5 (1)	C(51)	6310 (4)	6450 (2)	8890 (3)	2.5 (1)
C(52)	8262 (5)	4399 (3)	5750 (4)	3.2 (2)	C(52)	6647 (5)	5999 (3)	9267 (3)	3.4 (2)
C(53)	7682 (5)	3974 (3)	6036 (4)	3.7 (2)	C(53)	7309 (5)	5588 (3)	9011 (4)	3.8 (2)
C(54)	7568 (5)	3946 (3)	6706 (4)	3.9 (2)	C(54)	7658 (5)	5656 (3)	8381 (4)	3.6 (2)
C(55)	8060 (6)	4348 (3)	7096 (4)	4.3 (2)	C(55)	7324 (5)	6109 (3)	7991 (4)	3.8 (2)
C(56)	8638 (5)	4774 (3)	6809 (4)	3.6 (2)	C(56)	6656 (5)	6511 (3)	8245 (3)	3.4 (2)
C(61)	10809 (4)	5076 (3)	5893 (3)	2.4 (1)	C(61)	5564 (5)	6898 (2)	10106 (3)	2.7 (1)
C(62)	11613 (4)	5451 (3)	5906 (3)	3.0 (2)	C(62)	4991 (5)	6539 (3)	10495 (3)	3.7 (2)
C(63)	12571 (5)	5228 (3)	5909 (3)	3.7 (2)	C(63)	5172 (6)	6469 (4)	11150 (4)	4.8 (2)
C(64)	12728 (5)	4640 (4)	5911 (3)	3.8 (2)	C(64)	5944 (7)	6765 (3)	11436 (4)	5.0 (2)
C(65)	11941 (5)	4270 (3)	5922 (4)	4.3 (2)	C(65)	6519 (9)	7124 (3)	11068 (4)	6.2 (3)
C(66)	10985 (5)	4488 (3)	5926 (3)	3.3 (2)	C(66)	6329 (8)	7200 (3)	10407 (4)	5.0 (2)

[a] $B_{eq} = {}^8/_3\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

iron dinitrosyl complex **2** (ν(CO) 2090 s, 2040 s; ν(NO) 1810 s, 1770 vs cm^{-1}),[21] one of the decomposition products of the very unstable hydride FeH(CO)$_3$NO (**3**) (reported[7j] to decompose around −45 °C, sometimes explosively; the other decomposition product FeH$_2$(CO)$_4$ was not detected in our reaction conditions). This qualitative observation was taken as good evidence for the efficient generation of the hydride **3**. Conducting the same protonation in the presence of 5–6 equiv of triphenylphosphine dramatically altered the course of the reaction. The new iron nitrosyl hydride **4** precipitated from the solution over a period of 2 h together with most of the sodium trifluoroacetate. Selective extraction with benzene followed by crystallization in benzene/pentane afforded the compound as a dark orange solid in 65–70% yield. In the solid state, the compound was routinely stored under argon at room temperature, although no degradation was noticeable upon exposing the solid to air for several weeks. It dissolved in a number of solvents such as benzene, tetrahydrofuran, acetone, CH$_2$Cl$_2$, CHCl$_3$, or CS$_2$ but was sparingly soluble in acetonitrile.

The best single diagnosis of the presence of a hydride ligand is a characteristic high-field resonance in ^{1}H NMR.[8] In C$_6$D$_6$ at 37 °C, for example, the resonance of the hydride ligand of **4** appears as a 1:2:1 binomial triplet ($|J_{P-H}|$ = 79 ± 1 Hz) centered at δ −5.0. No significant changes in the δ and J values resulted from a change of solvent (CDCl$_3$, CDCl$_3$/CS$_2$ mixture, CH$_2$Cl$_2$) or from lowering the temperature. When the solution was cooled to −50 °C, only a slight broadening of the signals was observed, most likely due to viscosity effects. This behavior is consistent with the presence in solution of a major isomer with two magnetically equivalent phosphorus atoms and contrasts with that of other pentacoordinated hydrides such as IrH(CO)$_2$(P(C$_6$H$_5$)$_3$)$_2$.[27] In those cases, equilibration

Table III. Selected ν(CO) and ν(NO) Frequencies (cm^{-1}) of Some Iron Carbonyl Complexes Containing the Metallic Fragment Fe(CO)(NO)L$_2$ (L = P(C$_6$H$_5$)$_3$)

compd	ν(CO)	ν(NO)	solvent	ref
FeH(CO)(NO)L$_2$	1915	1690	THF	this work
	1910	1680	CHCl$_3$, CH$_2$Cl$_2$	this work
	1910	1690	KBr	this work
Fe(CF$_3$CO)(CO)(NO)L$_2$	1931	1710	KBr	28
Fe(Cl)(CO)(NO)L$_2$	1922	1690	CH$_2$Cl$_2$	29
Fe(CN)(CO)(NO)L$_2$	1930	1700	Nujol	30

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(27) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5272.

(28) Hieber, W.; Klingshirn, W.; Beck, W. *Chem. Ber.* **1965**, *98*, 307.

(29) Carroll, W. E.; Deeney, F. A.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1430.

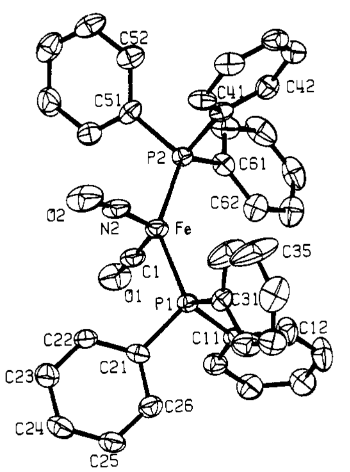

Figure 1. Perspective view of molecule I showing the molecular conformation and atom numbering.

in solution into several isomeric species was inferred from the dependence of their ^{1}H NMR spectra upon a change of solvent and/or temperature.[27] In the IR spectra (Table III), the $\nu(CO)$ and $\nu(NO)$ values of hydride **4** in solution and in KBr (made up from crushed single crystals) are quite similar, suggesting alike structures in solution and in solid state. The IR data are also comparable to those of other derivatives containing the same metallic fragment, suggesting a similar mode of bonding of the NO. Because no crystal structure was available for any of these compounds, an X-ray single-crystal analysis of the hydride was undertaken to establish unambiguously the nature of the NO linkage and the overall stereochemistry.

Description of the Structure. Each pair of crystallographically independent molecules is approximately related by one of four pseudo centers of symmetry located near (0,0,0; $^{1}/_{2}$, $^{1}/_{2}$, $^{1}/_{2}$) + (0.25, 0.175, 0.5; 0.25, 0.325, 0.5), but there is no unique center that relates the eight molecules of the unit cell. This fact and the success of refinement in $Pbc2_1$ eliminate the possibility of the space group being *Pbcm*.

The general structural features are consistent in the two independent molecules, and a perspective view of molecule I is presented in Figure 1. A summary of the bond lengths and valence angles for both molecules is given in Table IV; the full list has been deposited (supplementary material). The differences among equivalent bond lengths are not significant except for Fe–P, which has mean values 2.188 (2) and 2.177 (2) Å in molecules I and II, respectively. However, some significant differences observed in the P–Fe–N and C–Fe–N angles may indicate some sensitivity of these coordination angles to the packing environment.

Although the hydride atoms have not been located, the geometry of the others indicates that the coordination around each iron atom is a distorted trigonal bipyramid with the triphenylphosphine groups in apical positions while the H, CO, and NO form the basal plane. The NO ligands are linear, therefore being formally NO^+, and the complex is an overall five-coordinate 18e Fe(0) complex. The axial ligands bend toward the hydride, forming a P–Fe–P angle of 140.9 (1)° in both molecules. The other angles around the Fe atoms have values P–Fe–C = 92.8 (2)–96.6 (2)°, P–Fe–N = 98.4 (2)–106.5 (2)°, and C–Fe–N = 120.6 (3)° in molecule I and 125.8 (3)° in II.

The bending of the two P–Fe bonds toward the hydride has been observed in the brown form of $[IrH(NO)(PPh_3)_3]^+$ (P–Ir–P = 141.6 (2)°),[16] $RuHCl(PPh_3)_3$ (P–Ru–P = 153.1 (2)°),[31] $RhHCl(PPh_3)_2{\cdot}xSiCl_3$ (P–Rh–P = 161.7 (1)°),[32] and

Table IV. Selected Bond Lengths (Å) and Valence Angles (deg)[a]

	molecule I	molecule II	mean values
Fe-P(1)	2.188 (2)	2.174 (2)	2.182 (7)
Fe-P(2)	2.188 (2)	2.179 (2)	
Fe-C(1)	1.760 (6)	1.745 (6)	1.753 (11)
Fe-N(2)	1.666 (5)	1.680 (6)	1.673 (10)
C(1)-O(1)	1.144 (7)	1.136 (8)	1.140 (6)
N(2)-O(2)	1.172 (7)	1.170 (7)	1.171 (1)
P(1)-C(11)	1.845 (6)	1.822 (6)	1.835 (8)
P(1)-C(21)	1.836 (6)	1.829 (7)	
P(1)-C(31)	1.831 (7)	1.835 (6)	
P(2)-C(41)	1.828 (6)	1.837 (6)	
P(2)-C(51)	1.847 (5)	1.845 (5)	
P(2)-C(61)	1.833 (6)	1.828 (6)	
⟨C-C⟩	1.380 (18)	1.378 (16)	
⟨C-H⟩	0.98 (8)	0.95 (11)	
P(1)-Fe-P(2)	140.9 (1)	140.9 (1)	140.9 (1)
P(1)-Fe-C(1)	93.6 (2)	96.6 (2)	94.6 (17)
P(2)-Fe-C(1)	95.3 (2)	92.8 (2)	
P(1)-Fe-N(2)	103.2 (2)	98.4 (2)	103.2 (35)
P(2)-Fe-N(2)	104.6 (2)	106.5 (2)	
C(1)-Fe-N(2)	120.6 (3)	125.8 (3)	123.2 (37)
Fe-C(1)-O(1)	177.1 (5)	178.6 (6)	177.9 (11)
Fe-N(2)-O(2)	174.2 (5)	175.9 (5)	175.1 (12)
Fe-P(1)-C(11)	114.6 (2)	116.1 (2)	115.1 (14)
Fe-P(1)-C(21)	114.7 (2)	112.6 (2)	
Fe-P(1)-C(31)	116.5 (2)	114.6 (2)	
Fe-P(2)-C(41)	115.9 (2)	112.5 (2)	
Fe-P(2)-C(51)	115.9 (2)	116.7 (2)	
Fe-P(2)-C(61)	116.3 (2)	115.0 (2)	
⟨C-P-C⟩	102.7 (7)	103.9 (15)	
⟨P-C-C⟩	120.8 (21)	120.7 (18)	
⟨C-C-C⟩	120.0 (11)	120.0 (11)	

[a] The estimated standard deviations are from the least-squares refinement, except for the quoted mean values calculated from the spreads in the individual measurements

$OsH(CO)(N_2Ph)(PPh_3)_2{\cdot}CH_2Cl_2$ (P–Os–P = 164.4 (1)°).[33] In the latter three molecules, the hydride is located in or near the basal plane.

Distortion toward a tetrahedral coordination also is common in six-coordinated dihydride complexes. The P–M–P angle, which is formed between ligands that are axial to the plane containing the two H atoms and the metal atom M, is observed in the range 151.4 (2)° in $[IrH_2(CO)(PPh_3)_3]^+$[34] to 116.4 (2)° in $RuH_2(PPh_3)_4$.[35] The latter value is very close to P–M–P angles in four-coordinated complexes, e.g. 111.9 (1)° in $Fe(NO)_2(PPh_3)_2$[36] and 103.5 (1)° in $Os(NO)_2(PPh_3)_2{\cdot}{}^{1}/_{2}C_6H_6$.[37]

Despite the broad range of P–M–P angles mentioned above, those observed in five- [$[IrH(NO)(PPh_3)_3]^+$,[16] $FeH(NO)(CO)(PPh_3)_2$ present structure] and six-coordinated ($ReH_2(NO)(PPh_3)_3$)[38] nitrosyl hydrides fall in a narrow range of 140.5 (2)–143.4 (3)°. In the Ir and Re complexes, the bending of the P–M–P ligands toward the compact hydride[5] was attributed to steric interaction with a bulky PPh_3 group in the basal plane. However, in the present Fe complex there is no such bulky group in the basal plane, yet the P–M–P angle is just about the same as in the other two complexes.

Another distortion is observed in the orientation of the P–Fe–P plane relative to the ligands forming the basal plane, as shown by the angles in Table IV and the projections in Figure 2. Thus, the mean P–Fe–C angle (94.6°) is 8.6° smaller than the mean P–Fe–N angle (103.2°), and the P–

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(30) Dolcetti, G.; Busetto, L.; Palazzi, A. *Inorg. Chem.* **1974**, *13*, 222.

(31) Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* **1968**, 1230.

(32) Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 440.

(33) Cowie, M.; Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2617.

(34) Bird, P.; Harrod, J. F.; Than, K. A. *J. Am. Chem. Soc.* **1974**, *96*, 1222.

(35) Immirzi, A.; Lucherini, A. *Cryst. Struct. Commun.* **1972**, *1*, 317.

(36) Albano, V. G.; Aranco, A.; Bellon, P. L.; Ciani, G.; Manassero, M. *J. Organomet. Chem.* **1974**, *67*, 413.

(37) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2610, Table V.

(38) Ciani, G.; Giusto, D.; Manassero, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1943.

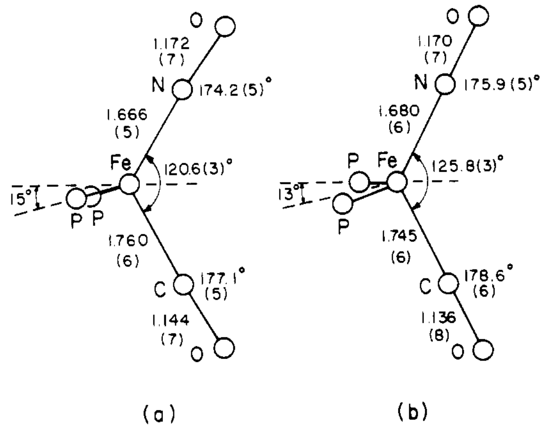

Figure 2. Inner coordination shown in projection along the normals to the C–Fe–N planes for (a) molecule I and (b) molecule II. The quoted bond lengths are in angstroms, and the angles, in degrees.

Fe–P plane is tipped toward the CO group by ~15° in molecule I and by ~13° in molecule II. In the closely related $Ir(CO)(NO)(PPh_3)_2$ complex[39] a similar distortion was observed, with the P–Ir–P plane tipped by 15° toward CO. Such a distortion was rationalized on the basis of nonbonded repulsion between ligands, by assuming that the nonbonded radius of the ligand atom increases as its electron density decreases due to back-donation from the central atom.[37–40] The greater accepting ability of NO^+ over CO makes the former group display a larger nonbonded radius.

In molecules I and II, the Fe, NO, and CO atoms are less than 0.033 (5) Å from the mean basal plane that they form. This plane makes a dihedral angle of 89.4° in molecule I and 86.6° in molecule II with the corresponding P–Fe–P plane.

The geometries of the $Fe{-}C{\equiv}O$ and $Fe{-}N{\equiv}O$ ligands in molecules I and II are well within the range of reported values,[41,37] except for the $Fe{-}N{\equiv}O$ angles of 174.2 (5) and 175.9 (5)°, which are just outside the range 176.9 (7)–178.2 (7)° for other linear nitrosyl ligands.

The Fe–P bond lengths (2.174 (2)–2.188 (2) Å) are among the shortest on record for iron complexes containing a triphenylphosphine and compare to those found in $Fe(C_5H_5)(CO)(COC_6H_5)P(C_6H_5)_3$ (2.17 (1) Å)[42] and in $Fe(C_5H_5)(CO)(CH_2O\text{-menthyl})P(C_6H_5)_3$ (2.181 (2) Å).[43] They are significantly shorter than in the phenyl diazenide cation $[Fe(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2]^+$ (2.261 (2), 2.266 (2) Å),[44] the closest structurally related compound that could be found for comparison. Similar contractions of M–P bond lengths below the average values also have been observed in other penta-[33] and tetracoordinated[45] hydrides containing two triphenylphosphines in an approximate trans relationship.

A final comment concerning the magnitude of the $|J_{P-H}|$ coupling constants is appropriate. The $|J_{P-H}|$ values fall in the ranges 5–30 (P and H cis) and 60–180 Hz (P and H trans) in many octahedral and square-planar complexes of the second- or third-row metals.[8,47] The same rule holds in some bipyramidal complexes. $OsH(CO)(N_2C_6H_5)(P(C_6H_5)_3)_2$ has two mutually cis P and H atoms[33] and a $|J_{P-H}|$ of 21 Hz[33,47] close to the value of 25 Hz found in $OsH(CO)(NO)(P(C_6H_5)_3)_2$.[7e] Similarly, in one of the isomers of $IrH(CO)_2(P(C_6H_5)_3)_2$,[27] one P was assigned cis to H ($J_{P-H} = \pm 24$ Hz) and the other one trans ($J_{P-H} = \pm 94$ Hz). The iron nitrosyl hydride with a large value of $|J_{P-H}|$ (79 ± 1 Hz) and a cis disposition of the H and P atoms provides an example of the breakdown of this stereochemical rule in five-coordination.

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Supplementary Material Available: Listings of observed and calculated structure amplitudes, H coordinates, anisotropic thermal parameters for the non-hydrogen atoms, C–C bond lengths, and P–C–C and C–C–C angles (30 pages). Ordering information is given on any current masthead page.

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(39) Pratt Brock, C.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 2812.

(40) Albano, V. G.; Bellon, P. L.; Ciani, G. *J. Organomet. Chem.* **1972**, *38*, 155.

(41) Reisner, G. M.; Bernal, I.; Brunner, H.; Muschiol, M. *Inorg. Chem.* **1978**, *17*, 783, Table IX.

(42) Semion, V. A.; Struchkov, Yu. T. *J. Struct. Chem.* (*Engl. Transl.*) **1969**, *10*, 80.

(43) Chou, C. K.; Miles. D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271.

(44) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 1369, Table VI.

(45) (a) Del Pra, A.; Forsellini, E.; Bombieri, G.; Michelin, R. A.; Ros, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1862. (b) Immirzi, A.; Bombieri, G.; Toniolo, L. *J. Organomet. Chem.* **1976**, *118*, 355.

(46) Breakdown of the stereochemical rules in octahedral complexes have been observed with "octahedral" cis dihydride complexes of iron: Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 75.

(47) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2784.