(4) R. P. M. Werner and H. E. Podall, *Chem. Ind. (London)*, 144 (1961).
(5) However, ESR and derivatization evidence has been presented for the generation of $(\eta\text{-}C_5H_5)_2Nb$ in solution: D. A. Lemenovski and V. P. Fedin, *J. Organomet. Chem.*, **132**, C11 (1974). The ESR spectrum of this material is reported to be independent of solvent (aromatic or ethereal), a surprising property for a 15-electron, coordinatively unsaturated complex.
(6) (a) B. Sarry and V. Dobrusskin, *J. Organomet. Chem.*, **13**, 1 (1968); (b) B. Sarry and M. Schön, *ibid.*, **13**, 9 (1968). The structures of these compounds are unknown; evidence has been presented that they are M(IV) derivatives containing ortho-disubstituted phenyl groups: (c) B. Sarry and J. Steinke, Abstracts, Fourth International Conference on Organometallic Chemistry, Bristol, 1969, paper C10.
(7) S. Datta and S. S. Wreford, *Inorg. Chem.*, **16**, 1134 (1977).
(8) J. C. Smart and C. J. Curtis, *Inorg. Chem.*, **16**, 1788 (1977).
(9) K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 1118 (1959).
(10) B. M. Foxman, *Inorg. Chem.*, **17**, 1932 (1978).
(11) M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).
(12) (a) "Syntex P2₁ Operations Manual", Syntex Analytical Instruments, Cupertino, Calif., 1973; (b) "Syntex P2₁ FORTRAN Operations Manual", Cupertino, Calif., 1975; (c) "Syntex XTL Operations Manual", 2nd ed, Syntex Analytical Instruments, Cupertino, Calif., 1976.
(13) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99–101; (b) 148–150.
(14) B. M. Foxman, "METHYL, A Program for Calculating Methyl Hydrogen Atom Positions", Brandeis University, 1977.
(15) K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr.* **30**, 2290 (1974), and references therein.
(16) (a) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971); (b) P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, **13**, 1025 (1974); (c) R. A. Forder and K. Prout, *Acta Crystallogr. Sect. B*, **30**, 2778 (1974); (d) F. A. Cotton, D. L. Hunter, and B. A. Frenz, *Inorg. Chim. Acta*, **15**, 155 (1975); (e) M. G. B. Drew and C. J. Rix, *J. Organomet. Chem.*, **102**, 467 (1975); (f) J. O. Albright, L. D. Brown, S. Datta, B. M. Foxman, J. K. Kouba, and S. S. Wreford, *J. Am. Chem. Soc.*, **99**, 5518 (1977); (g) B. M. Foxman, T. J. McNeese, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, in press.
(17) (a) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976); (b) A. J. Schultz, K. L. Stearley, J. M. Williams, R. Mink, and G. D. Stucky, *Inorg. Chem.*, **16**, 3303 (1977).

Contribution from the Department of Chemistry,
University of Southern California,
Los Angeles, California 90007

Crystal Structure of [(Ph₃P)₂N]⁺[HFe₂(CO)₈]⁻

Henry B. Chin and Robert Bau*

As part of our continuing studies on transition-metal hydride complexes[1] and metal carbonyl anions,[2] and as a sequel to our earlier work on the isoelectronic $[Fe_2(CO)_8]^{2-}$ and $[Fe\text{-}Co(CO)_8]^-$ anions,[2c] we wish to report the structure of the $[HFe_2(CO)_8]^-$ anion. This anion was first prepared by Hieber and Brendel in 1957 via the alkaline reduction of $Fe_2(CO)_9$.[3] From the results of Mössbauer and vibrational spectroscopic experiments, Greenwood and co-workers suggested that the structure of $[HFe_2(CO)_8]^-$ is based on that of $Fe_2(CO)_9$, with one of the CO bridges replaced by a bridging hydride.[4] The solution structure of $[HFe_2(CO)_8]^-$ has not been thoroughly investigated until recently, perhaps because of its rapid decomposition in most solvents. It is also probably for this reason (i.e., solution instability) that a definitive single-crystal X-ray study has not been previously reported. In the light of current interest in the chemistry of this anion,[5] it was felt that the solid-state structure of $[HFe_2(CO)_8]^-$ was deserving of a definitive and quantitative X-ray study.

Experimental Section

$[HFe_2(CO)_8]^-$ was prepared by the method of Hieber[3] and isolated as its bis(triphenylphosphine)iminium salt. All manipulations were carried out in the absence of air and all solvents were deoxygenated prior to use. A 1.4-g sample (25 mmol) of KOH was dissolved in 25 ml of absolute ethanol. Diiron nonacarbonyl ($Fe_2(CO)_9$), 1.8 g (5 mmol), was added to the alcoholic KOH solution and the resultant

mixture was stirred for approximately 15 min to allow all of the iron carbonyl to react. The solution was then cooled to −78 °C by means of a dry ice–acetone bath. Thirty milliliters of a 1 N solution of acetic acid, prepared from glacial acetic acid and absolute ethanol, was cooled to about −50 °C and then added to the stirring iron carbonyl solution. This was followed by the addition of a solution of 1.8 g (3 mmol) of $[(Ph_3P)_2N]^+Cl^-$ [6] in 50 mL of absolute ethanol at −78 °C. The resultant mixture was allowed to warm slowly to room temperature. During the warming period a precipitate of small yellow brown crystals appeared. The mixture was then heated until all of the precipitate just dissolved, and as it cooled again to room temperature, very well formed yellow-brown crystals of $[(Ph_3P)_2N]^+[HFe_2(CO)_8]^-$ were obtained along with small quantities of crystalline $[(Ph_3P)_2N]^+[HFe_3(CO)_{11}]^-$. The crystals were isolated by filtration and washed with water. The compound is remarkably stable in the solid state, showing decomposition only after exposure to air for several days. In solution the compound is unstable, decomposing to $[HFe_3(CO)_{11}]^-$ and other products in several hours.[4b,5b] All attempts to recrystallize the isolated material failed. The yellow-brown crystals were identified as $[(Ph_3P)_2N]^+[HFe_2(CO)_8]^-$ based on the IR spectrum in the carbonyl stretching region (1990 (m), 1920 (s), 1880 (vs), 1790 (m), 1750 (m) cm⁻¹) taken as a fluorocarbon mull. These values are in general agreement with the spectrum obtained by Greenwood et al. for the $[Et_4N]^+$ salt.[4]

Crystallographic Section

X-ray diffraction work was carried out on a specimen of dimensions $0.50 \times 0.27 \times 0.23$ mm, mounted on a glass fiber. Crystals of $[(Ph_3P)_2N]^+[HFe_2(CO)_8]^-$ are monoclinic, space group $P2_1/c$, with $a = 10.687$ (5) Å, $b = 20.470$ (10) Å, $c = 19.421$ (10) Å, $\beta = 107.72$ (3)°, and $V = 4047.0$ Å³; $\rho(\text{obsd}) = 1.422$ g cm⁻³ and $\rho(\text{calcd}) = 1.435$ g cm⁻³ for $Z = 4$. One quadrant of data was collected with Zr-filtered Mo Kα radiation using a θ–2θ scan technique up to a 2θ limit of 44°. The procedure used in data collection is essentially the same as that described in an earlier publication.[2f] A total of 5162 reflections were collected and corrected for Lorentz and polarization effects. Elimination of the weaker data ($I \leq 3\sigma$) and merging of duplicate reflections resulted in 3330 reflections being retained for the subsequent structure analysis. An absorption correction was not carried out, on the basis of the observation that the intensity of an axial reflection (at $\chi = 90°$) showed no significant variation with spindle angle ϕ. The absorption coefficient (μ) is 8.72 cm⁻¹ for Mo Kα X-rays.

The positions of the iron atoms were determined from a Patterson map. A difference Fourier map phased by the iron atoms revealed the positions of the phosphorus atoms. The remaining nonhydrogen atoms were located from successive difference-Fourier maps. This was followed by several cycles of least-squares refinement, in which all the atoms except the carbons of the phenyl rings were assigned anisotropic temperature factors. The R factor at this stage was 0.084.

At this point an attempt was made to locate the bridging hydrogen atom. The coordinates of the phenyl hydrogen atoms were calculated[7] and included in the synthesis of a series of difference-Fourier maps using $((\sin \theta)/\lambda)^2$ limits of 0.278, 0.175, and 0.110 Å⁻², the first value representing all of the data. This technique has been used previously to locate hydrogen atoms in close proximity to metal atoms.[8] In the present case the difference-Fourier maps revealed a single peak in a bridging position between the iron atoms. However, whereas previous examples of the use of this technique allowed one to refine the position of the hydrogen atom using the low-angle data, in the present case the hydrogen atom could be refined only by using the full set of data. The anion, including the hydrogen, was refined by least squares and resulted in a final R factor of 0.081 ($R_w = 0.089$).[9] The positional parameters of the phenyl hydrogens were not refined and their isotropic temperature factors were set arbitrarily to 4.0 Å².

Discussion

The final atomic parameters of $[(Ph_3P)_2N]^+[HFe_2(CO)_8]^-$ are given in Table I and the interatomic distances and angles for the anion and cation are given in Tables II and III, respectively. An ORTEP plot of the anion is presented in Figure 1. A listing of the observed and calculated structure factors is available as supplementary material.

As predicted from the spectroscopic studies,[4] the carbonyl hydride anion has a structure very similar to $Fe_2(CO)_9$. The anion consists of two approximately octahedrally coordinated

Table I. Final Atomic Parameters for [(Ph$_3$P)$_2$N]$^+$[HFe$_2$(CO)$_8$]$^-$ (Standard Deviations in Parentheses)

(a) Atomic Positions (in Fractional Coordinates)

atom	x	y	z	atom	x	y	z
Fe(1)	−0.2228 (1)	0.1670 (1)	0.0561 (1)	C(22)	0.1283 (11)	0.3657 (6)	0.2804 (6)
Fe(2)	−0.0479 (1)	0.1551 (1)	0.1757 (1)	C(23)	0.0284 (12)	0.3671 (6)	0.3153 (6)
C(1)	−0.1903 (10)	0.1974 (5)	−0.0247 (6)	C(24)	0.0607 (12)	0.3907 (6)	0.3850 (7)
C(2)	−0.3181 (11)	0.0976 (5)	0.0262 (6)	C(25)	0.1800 (12)	0.4126 (6)	0.4225 (7)
C(3)	−0.3613 (10)	0.2182 (5)	0.0566 (5)	C(26)	0.2810 (11)	0.4104 (6)	0.3874 (6)
C(4)	−0.0775 (10)	0.1947 (4)	0.2529 (6)	C(31)	0.4929 (10)	0.4464 (5)	0.3128 (5)
C(5)	−0.0469 (9)	0.0740 (5)	0.2083 (5)	C(32)	0.6273 (11)	0.4325 (6)	0.3343 (6)
C(6)	0.1210 (10)	0.1734 (5)	0.1950 (5)	C(33)	0.7185 (12)	0.4855 (7)	0.3616 (7)
C(7)	−0.1012 (9)	0.2347 (5)	0.1175 (5)	C(34)	0.6756 (13)	0.5463 (7)	0.3678 (7)
C(8)	−0.0591 (11)	0.1187 (5)	0.0805 (6)	C(35)	0.5416 (13)	0.5601 (7)	0.3469 (7)
O(1)	−0.1674 (8)	0.2125 (5)	−0.0746 (5)	C(36)	0.4491 (11)	0.5096 (6)	0.3186 (6)
O(2)	−0.3797 (8)	0.0512 (4)	0.0086 (4)	C(41)	0.2821 (9)	0.3641 (5)	0.0500 (5)
O(3)	−0.4532 (8)	0.2477 (4)	0.0550 (5)	C(42)	0.2974 (11)	0.3792 (6)	−0.0177 (6)
O(4)	−0.0929 (9)	0.2178 (5)	0.3016 (5)	C(43)	0.2556 (11)	0.3299 (6)	−0.0731 (6)
O(5)	−0.0504 (9)	0.0216 (4)	0.2282 (4)	C(44)	0.2026 (12)	0.2717 (6)	−0.0576 (7)
O(6)	0.2300 (8)	0.1868 (5)	0.2086 (5)	C(45)	0.1895 (11)	0.2584 (6)	0.0074 (7)
O(7)	−0.0765 (8)	0.2904 (4)	0.1184 (4)	C(46)	0.2301 (10)	0.3059 (6)	0.0642 (6)
O(8)	−0.0005 (8)	0.0839 (4)	0.0526 (4)	C(51)	0.2302 (10)	0.4951 (5)	0.0916 (5)
H	−0.198 (7)	0.144 (4)	0.140 (4)	C(52)	0.1301 (11)	0.5055 (6)	0.1214 (6)
P(1)	0.3758 (2)	0.3850 (1)	0.2731 (1)	C(53)	0.0484 (13)	0.5636 (7)	0.0997 (7)
P(2)	0.3302 (2)	0.4246 (1)	0.1204 (1)	C(54)	0.0742 (13)	0.6067 (7)	0.0510 (7)
N	0.3060 (7)	0.3941 (4)	0.1902 (4)	C(55)	0.1721 (13)	0.5964 (6)	0.0216 (7)
C(11)	0.4566 (9)	0.3076 (5)	0.2916 (5)	C(56)	0.2549 (12)	0.5398 (6)	0.0412 (7)
C(12)	0.5103 (11)	0.2818 (6)	0.2407 (6)	C(61)	0.4975 (9)	0.4483 (5)	0.1313 (5)
C(13)	0.5783 (11)	0.2201 (6)	0.2543 (7)	C(62)	0.5421 (11)	0.5094 (6)	0.1604 (6)
C(14)	0.5936 (12)	0.1898 (6)	0.3198 (7)	C(63)	0.6797 (13)	0.5218 (7)	0.1783 (7)
C(15)	0.5383 (12)	0.2138 (6)	0.3670 (7)	C(64)	0.7601 (13)	0.4761 (7)	0.1650 (7)
C(16)	0.4690 (11)	0.2746 (6)	0.3552 (6)	C(65)	0.7197 (13)	0.4163 (7)	0.1347 (7)
C(21)	0.2526 (9)	0.3877 (5)	0.3176 (5)	C(66)	0.5815 (11)	0.4015 (5)	0.1182 (6)

(b) Anisotropic Temperature Factors[a]

atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe(1)	70 (2)	21 (1)	20 (1)	13 (1)	10 (1)	3 (1)
Fe(2)	73 (2)	18 (1)	21 (1)	6 (1)	6 (1)	3 (1)
C(1)	99 (13)	29 (3)	31 (4)	16 (10)	23 (12)	18 (6)
C(2)	114 (14)	29 (3)	28 (4)	1 (11)	35 (12)	2 (6)
C(3)	98 (12)	29 (4)	35 (4)	22 (10)	14 (11)	−15 (6)
C(4)	137 (13)	16 (3)	33 (4)	4 (9)	27 (12)	−8 (5)
C(5)	108 (12)	20 (3)	26 (4)	−3 (10)	28 (11)	1 (5)
C(6)	106 (12)	23 (3)	31 (4)	1 (10)	−3 (10)	2 (5)
C(7)	94 (13)	29 (4)	30 (4)	6 (11)	30 (11)	3 (6)
C(8)	128 (13)	30 (3)	26 (4)	−5 (11)	13 (11)	6 (6)
O(1)	190 (12)	54 (4)	40 (3)	43 (10)	82 (11)	41 (6)
O(2)	181 (12)	34 (3)	44 (4)	−50 (10)	24 (10)	−4 (5)
O(3)	132 (10)	47 (3)	65 (4)	73 (10)	35 (10)	−18 (6)
O(4)	230 (14)	47 (3)	48 (4)	−15 (11)	109 (12)	−40 (6)
O(5)	240 (14)	27 (3)	48 (4)	−28 (10)	23 (10)	17 (5)
O(6)	99 (10)	54 (4)	74 (5)	−44 (10)	10 (10)	−7 (6)
O(7)	94 (13)	29 (4)	30 (4)	6 (11)	30 (11)	3 (6)
O(8)	143 (10)	55 (3)	34 (3)	77 (10)	25 (9)	−20 (5)
P(1)	67 (3)	17 (1)	20 (1)	3 (2)	15 (2)	4 (1)
P(2)	77 (3)	16 (1)	18 (1)	8 (2)	19 (2)	2 (1)
N	75 (8)	21 (2)	23 (2)	6 (7)	22 (7)	13 (4)

(c) Isotropic Temperature Factors

atom	B, Å^2	atom	B, Å^2	atom	B, Å^2	atom	B, Å^2
C(11)	2.9 (2)	C(25)	5.1 (3)	C(41)	3.2 (2)	C(54)	5.8 (3)
C(12)	4.5 (3)	C(26)	4.4 (3)	C(42)	4.6 (3)	C(55)	5.8 (3)
C(13)	4.7 (3)	C(31)	3.1 (2)	C(43)	4.8 (2)	C(56)	5.3 (3)
C(14)	4.7 (3)	C(32)	4.1 (2)	C(44)	5.2 (3)	C(61)	3.3 (2)
C(15)	5.0 (3)	C(33)	5.3 (3)	C(45)	5.1 (3)	C(62)	4.7 (2)
C(16)	4.1 (2)	C(34)	5.4 (3)	C(46)	4.2 (2)	C(63)	6.2 (3)
C(21)	2.6 (2)	C(35)	5.6 (3)	C(51)	3.4 (2)	C(64)	6.4 (3)
C(22)	4.3 (2)	C(36)	4.6 (3)	C(52)	5.0 (3)	C(65)	6.2 (3)
C(23)	4.6 (3)	H	3.3 (18)	C(53)	6.1 (3)	C(66)	4.3 (2)
C(24)	5.1 (3)						

[a] The form of the anisotropic thermal ellipsoid is exp$[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

iron atoms joined through a common triangular face of the octahedra by two bridging carbonyl ligands and a bridging hydrogen atom. The six remaining carbonyl groups complete the octahedral coordination about the iron atoms. The [(Ph$_3$P)$_2$N]$^+$ cation is in the usual bent configuration, with P–N–P = 140.9 (5)° and P–N = 1.566 (7) and 1.583 (7) Å.
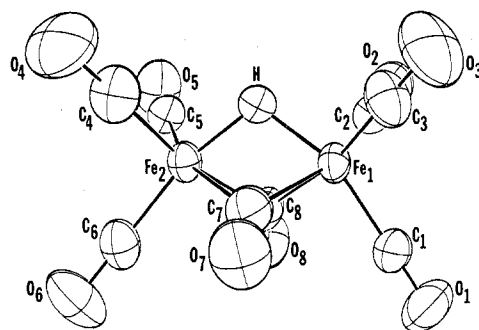
The hydrogen atom as located from the X-ray data is essentially bridging the metal atoms symmetrically. There is little reason to believe the hydrogen bridge to be asymmetric, and the large standard deviations in the individual metal–

Table II. Interatomic Distances and Angles for the
$[HFe_2(CO)_8]^-$ Anion (Standard Deviations in Parentheses)

(a) Interatomic Distances, Å

Fe(1)-Fe(2)	2.521 (1)		
Fe(1)-C(1)	1.798 (11)	Fe(2)-C(4)	1.820 (11)
Fe(1)-C(2)	1.791 (11)	Fe(2)-C(5)	1.777 (10)
Fe(1)-C(3)	1.782 (11)	Fe(2)-C(6)	1.759 (11)
Fe(1)-C(7)	1.981 (11)	Fe(2)-C(7)	1.966 (12)
Fe(1)-C(8)	1.971 (12)	Fe(2)-C(8)	1.961 (10)
Fe(1)-H	1.65 (7)	Fe(2)-H	1.57 (8)
C(1)-O(1)	1.114 (14)	C(4)-O(4)	1.114 (15)
C(2)-O(2)	1.147 (14)	C(5)-O(5)	1.146 (13)
C(3)-O(3)	1.145 (14)	C(6)-O(6)	1.146 (15)
C(7)-O(7)	1.169 (15)	C(8)-O(8)	1.182 (14)

(b) Interatomic Angles, Deg

Fe(1)-H-Fe(2)	103 (4)		
Fe(1)-C(7)-Fe(2)	79.4 (5)	Fe(1)-C(8)-Fe(2)	79.7 (4)
C(1)-Fe(1)-C(2)	102.5 (5)	C(4)-Fe(2)-C(5)	95.8 (4)
C(1)-Fe(1)-C(3)	102.3 (5)	C(4)-Fe(2)-C(6)	99.1 (5)
C(2)-Fe(1)-C(3)	93.9 (5)	C(5)-Fe(2)-C(6)	103.5 (5)
C(7)-Fe(1)-C(8)	80.8 (5)	C(7)-Fe(2)-C(8)	81.4 (4)
C(1)-Fe(1)-C(7)	92.9 (5)	C(4)-Fe(2)-C(7)	90.5 (4)
C(1)-Fe(1)-C(8)	89.0 (5)	C(4)-Fe(2)-C(8)	165.8 (5)
C(2)-Fe(1)-C(7)	162.3 (5)	C(5)-Fe(2)-C(7)	161.2 (5)
C(2)-Fe(1)-C(8)	90.8 (5)	C(5)-Fe(2)-C(8)	88.5 (4)
C(3)-Fe(1)-C(7)	91.1 (5)	C(6)-Fe(2)-C(7)	92.9 (4)
C(3)-Fe(1)-C(8)	166.5 (4)	C(6)-Fe(2)-C(8)	93.0 (5)
Fe(2)-Fe(1)-C(1)	123.6 (4)	Fe(1)-Fe(2)-C(4)	115.8 (4)
Fe(2)-Fe(1)-C(2)	113.0 (3)	Fe(1)-Fe(2)-C(5)	111.1 (3)
Fe(2)-Fe(1)-C(3)	116.7 (3)	Fe(1)-Fe(2)-C(6)	126.7 (3)
Fe(1)-C(1)-O(1)	177.5 (10)	Fe(2)-C(4)-O(4)	177.7 (10)
Fe(1)-C(2)-O(2)	178.4 (10)	Fe(2)-C(5)-O(5)	178.2 (10)
Fe(1)-C(3)-O(3)	177.4 (10)	Fe(2)-C(6)-O(6)	178.0 (10)
Fe(1)-C(7)-O(7)	140.0 (9)	Fe(2)-C(7)-O(7)	140.7 (8)
Fe(1)-C(8)-O(8)	140.0 (8)	Fe(2)-C(8)-O(8)	140.2 (9)
C(1)-Fe(1)-H	161 (3)	C(4)-Fe(2)-H	90 (3)
C(2)-Fe(1)-H	88 (3)	C(5)-Fe(2)-H	85 (3)
C(3)-Fe(1)-H	93 (3)	C(6)-Fe(2)-H	167 (3)
C(7)-Fe(1)-H	75 (3)	C(7)-Fe(2)-H	77 (3)
C(8)-Fe(1)-H	75 (3)	C(8)-Fe(2)-H	77 (3)

**Figure 1.** The molecular structure of the $[HFe_2(CO)_8]^-$ anion.

known that M–H distances determined from X-ray data are about 0.1 Å shorter than their actual values because of the perturbing influence of the electron density of the M–H σ bond.[1]

The metal–metal distance in the carbonyl hydride anion, 2.521 (1) Å, is in very good agreement with the metal–metal distances found in the carbonyl-bridged compounds $Fe_2(CO)_9$ [M–M = 2.523 (1) Å][10] and $Co_2(CO)_8$ [M–M = 2.524 (2) Å][11] and is significantly shorter than that in the nonbridged $[Fe_2(CO)_8]^{2-}$ anion [M–M = 2.787 (2) Å].[2c] The agreement in the iron–iron distances between $[HFe_2(CO)_8]^-$ and $Fe_2(CO)_9$ parallels that observed in the distances between bridged iron atoms in $[HFe_3(CO)_{11}]^-$ [2.577 (3) Å][12a] and $Fe_3(CO)_{12}$ [2.560 (6) Å].[12b]

Another interesting feature common to bridging carbonyl structures and also seen in this structure is the acute M–C-(bridge)–M angle. In $[HFe_2(CO)_8]^-$ the average Fe–C–Fe angle is 79.6 (5)°. The corresponding angle in $Fe_2(CO)_9$ is 77.6 (1)°.[10] In contrast, the angles at the carbon atom in organic carbonyl compounds are typically between 120 and 124°. It has been pointed out by Braterman,[13] and reemphasized by Cotton,[10] that these structural effects indicate a fundamental difference between organic and inorganic carbonyl groups and that the M–C(O)–M bridging system behaves in many respects as though it were a three-center bond (I). As mentioned in the previous paragraph, the replacement of a bridging CO group by H⁻ leaves the M–M distance virtually unchanged, whereas the replacement of Cl⁻ by H⁻

hydrogen distances prohibit one from assigning much credence to the observed differences in iron–hydrogen distances between the two metal atoms. The average Fe–H distance [1.61 (7) Å] is probably a little lower than its true value. It is well-

Table III. Interatomic Distances (Å) and Angles (deg) for the $[(Ph_3P)_2N]^+$ Cation (Standard Deviations in Parentheses)

N-P(1)	1.566 (7)	N-P(2)	1.583 (7)
P(1)-N-P(2)	140.9 (5)		
P(1)-C(11)	1.788 (10)	P(2)-C(41)	1.801 (10)
P(1)-C(21)	1.781 (10)	P(2)-C(51)	1.779 (10)
P(1)-C(31)	1.776 (11)	P(2)-C(61)	1.802 (11)

	phenyl(1) C(11)-C(16)	phenyl(2) C(21)-C(26)	phenyl(3) C(31)-C(36)	phenyl(4) C(41)-C(46)	phenyl(5) C(51)-C(56)	phenyl(6) C(61)-C(66)
1-2	1.39 (2)	1.38 (2)	1.40 (2)	1.41 (2)	1.38 (2)	1.40 (2)
2-3	1.44 (2)	1.38 (2)	1.45 (2)	1.44 (2)	1.46 (2)	1.43 (2)
3-4	1.38 (2)	1.43 (2)	1.35 (2)	1.39 (2)	1.38 (2)	1.35 (2)
4-5	1.33 (2)	1.38 (2)	1.39 (2)	1.34 (2)	1.35 (2)	1.37 (2)
5-6	1.43 (2)	1.34 (2)	1.42 (2)	1.44 (2)	1.44 (2)	1.45 (2)
6-1	1.38 (2)	1.44 (2)	1.39 (2)	1.38 (2)	1.42 (2)	1.39 (2)
a	120.3 (10)	120.9 (10)	120.4 (10)	123.0 (10)	121.3 (10)	122.2 (10)
b	119.8 (10)	119.1 (10)	118.3 (11)	116.5 (10)	118.6 (11)	117.2 (11)
c	118.3 (11)	118.2 (11)	121.1 (12)	119.4 (11)	119.4 (12)	120.0 (12)
d	121.2 (12)	124.3 (13)	120.7 (13)	123.1 (12)	122.1 (13)	124.6 (14)
e	122.0 (11)	117.3 (11)	119.8 (12)	119.5 (11)	120.5 (12)	116.7 (12)
f	118.2 (10)	120.2 (11)	119.7 (11)	118.6 (10)	118.2 (11)	119.3 (10)
g	118.2 (8)	118.2 (8)	120.7 (8)	118.1 (8)	117.5 (8)	119.5 (8)

Notes

I   II

III   IV
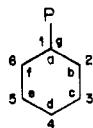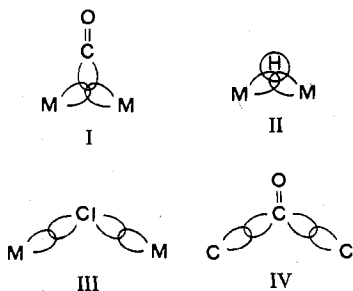
does cause large differences in the M–M distance.[14-16] This fact underscores the similarities between the three-center bonding patterns of the M–C(O)–M and M–H–M[17] linkages (I and II), as opposed to the M–X–M bridging halide system, which represents a system with two localized σ bonds (III). The fluxionality of the M–C(O)–M[18] and M–H–M[19] systems, in contrast to the relative rigidity of the M–X–M and organic carbonyl (IV) systems, is also consistent with this idea.

Finally, we note that the coordination about Fe is not strictly octahedral. In [HFe$_2$(CO)$_8$]$^-$ the terminal carbonyl groups are not collinear with the bridging atoms, as evidenced by the C(t)–Fe–C(b) and C(t)–Fe–H angles of 164 (1) and 164 (3)°, respectively. The bridging CO and H groups are situated closer to the Fe–Fe bond than they would be if the above angles were 180°. This, again, is consistent with the general pattern of ligands found in Fe$_2$(CO)$_9$ [C(t)–Fe–C(b) = 172.1 (1)°].[10]

While Co$_2$(CO)$_8$ is known to exist in solution in both the carbonyl-bridged and nonbridged forms,[20] there is no evidence that either [FeCo(CO)$_8$]$^-$[21,2c] or [HFe$_2$(CO)$_8$]$^-$ exists in a similar equilibrium. The Nujol mull spectrum of [(Ph$_3$P)$_2$N]$^+$[HFe$_2$(CO)$_8$]$^-$ [1990 (m), 1920 (s), 1880 (vs), 1790 (m), 1750 (m), cm^{-1}] somewhat resembles the compound's THF solution spectrum[5b] [1987 (s), 1940 (s), 1880 (s), 1802 (s), 1770 (m) cm^{-1}]: the peaks of the solid-state spectrum are shifted to higher energies by varying amounts (between 0 and 20 cm^{-1}) in solution. Collman and co-workers have further shown that the Li$^+$ and Na$^+$ salts of [HFe$_2$(CO)$_8$]$^-$ in THF solution contain an additional band (1680 cm^{-1} for the Li$^+$ salt and 1730 cm^{-1} for the Na$^+$ salt) that can be attributed to ion-pairing effects. At any rate, all spectra clearly show the presence of bridging carbonyls, and, thus, it is likely that the structure described in this paper persists in solution.

Registry No. [(Ph$_3$P)$_2$N]$^+$[HFe$_2$(CO)$_8$]$^-$, 66016-59-9.

Supplementary Material Available: A listing of the observed and calculated structure factors for [(Ph$_3$P)$_2$N]$^+$[HFe(CO)$_8$]$^-$ (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle, *Acc. Chem. Res.*, in press.
(2) (a) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973); (b) R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *ibid.*, **96**, 988 (1974); (c) H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *ibid.*, **96**, 5285 (1974); (d) R. D. Wilson and R. Bau, *ibid.*, **96**, 7601 (1974); (e) R. D. Wilson, S. A. Graham, and R. Bau, *J. Organomet. Chem.*, **91**, C49 (1975); (f) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976); (g) R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin, and R. Bau, *ibid.*, **99**, 1104 (1977).
(3) W. Hieber and G. Brendel, *Z. Anorg. Allg. Chem.*, **289**, 324 (1957).
(4) (a) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *Chem. Commun.*, 593 (1968); (b) *J. Chem. Soc. A*, 2339 (1969).
(5) (a) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 4685 (1976); (b) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *ibid.*, **100**, 1119 (1978).
(6) J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, **15**, 84 (1974).
(7) The positions of the phenyl hydrogen atoms were calculated by assuming an idealized sp^2 hybridization of the carbon atoms and a C–H bond distance of 1.1 Å.
(8) (a) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973); (b) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(9) (a) $R = \sum|F_o - |F_c||/\sum F_o$; $R_w = \{\sum w|F_o - |F_c||^2/\sum wF_o^2\}^{1/2}$. (b) The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh and co-workers at the California Institute of Technology.
(10) F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 800 (1974).
(11) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).
(12) (a) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965); (b) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 1351 (1969).
(13) P. S. Braterman, *Struct. Bonding (Berlin)*, **10**, 57 (1972).
(14) One can, for example, make the following sets of comparisons: Mo–Mo = 2.665 Å in [Cl$_3$Mo(μ-Cl)$_3$MoCl$_3$]$^{3-}$ and 2.380 Å in [Cl$_3$Mo(μ-Cl)$_2$(μ-H)MoCl$_3$]$^{3-}$; Mo–Mo = 2.816 Å in [Br$_3$Mo(μ-Br)$_3$MoBr$_3$]$^{3-}$ and 2.439 Å in [Br$_3$Mo(μ-Br)$_2$(μ-H)MoBr$_3$]$^{3-}$;[15] Rh–Rh = 3.719 Å in [(C$_5$Me$_5$)RhCl]$_2$(μ-Cl)$_2$ and 2.906 Å in [(C$_5$Me$_5$)RhCl]$_2$(μ-H)(μ-Cl);[16] Ir–Ir = 3.769 Å in [(C$_5$Me$_5$)IrCl]$_2$(μ-Cl)$_2$ and 2.903 Å in [(C$_5$Me$_5$)IrCl]$_2$(μ-H)(μ-Cl).[16]
(15) F. A. Cotton and B. J. Kalbacher, *Inorg. Chem.*, **15**, 522 (1976).
(16) M. R. Churchill and S. A. Julis, *Inorg. Chem.*, **16**, 1488 (1977).
(17) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. A. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974).
(18) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *Inorg. Chem.*, **14**, 511 (1975), and references therein.
(19) R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 3872 (1977).
(20) (a) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); (b) G. Bor, *ibid.*, **19**, 2065 (1963).
(21) J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968).

Structure of Tris(bis(trimethylsilyl)amido)neodymium(III), Nd[N(Si(CH$_3$)$_3$)$_2$]$_3$[1]

Richard A. Andersen,* David H. Templeton,* and Allan Zalkin*

Neodymium tris(bis(trimethylsilyl)amide) is the only known monomeric, three-coordinate derivative of this lanthanide element.[2] The structures of the europium(III)[3] and ytterbium(III)[4] derivatives have been examined by X-ray crystallographic techniques and they, along with the scandium(III) analogue,[3] have been shown to have MN$_3$ skeletons which are not planar. In contrast all other crystallographically known tris(silylamides) of the type M[N(SiMe$_3$)$_2$]$_3$ are planar.[4] We describe the crystal structure of Nd[N(SiMe$_3$)$_2$]$_3$ and show that it is also nonplanar.

Experimental Section

The Nd[N(SiMe$_3$)$_2$]$_3$ was prepared as previously described,[2] mp 157–161 °C (lit.[2] 161–164 °C). The crystal used in the X-ray analysis was taken from a batch crystallized from pentane (0 °C).

Magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating sample magnetometer employing a homogeneous magnetic field produced by a Varian Associates 12-in. electromagnet capable of a maximum field strength of 12.5 kG. The magnetometer was calibrated with HgCo(CNS)$_4$.[5] A variable-temperature liquid-helium system produced sample temperatures in the range 4–100 K. The temperature was measured with a calibrated GaAs diode.

A hexagonal needle-shaped crystal, 0.09 mm across and 0.3 mm long, was sealed inside a quartz capillary in an argon-filled drybox. It was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube (λ(Kα_1) 0.7093 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.16 and 0.21° for $h00$ and $00l$ type reflections, respectively. The space group was identified as $P\bar{3}1c$. The setting angles of 12 manually centered reflections (19 < 2θ < 25°) were used to determine by least-squares the cell parameters a = 16.476 (13) Å, c = 8.485 (7) Å, and V = 1995 Å^3. For Z = 2 and a molecular