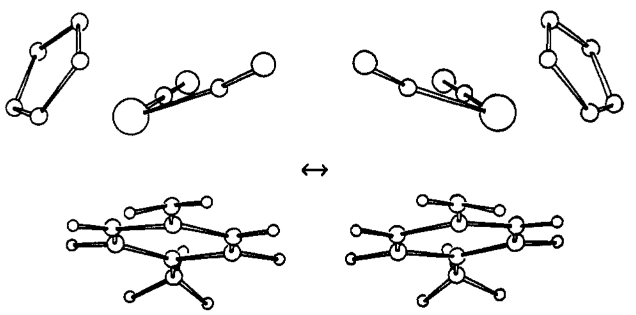

Figure 2. A view of the stylized molecule in its enantiomorphous forms to illustrate the rotation of the $Mo(\pi\text{-}C_5H_5)(CO)_2$ group which must accompany movement of the Mo atom relative to the benzyl moiety as these enantiomorphs are interconverted.

that two isomers which exist in solution in equilibrium most likely differ in a conformational sense, with interconversion of the conformers taking place by internal rotation. The structure we have found for $(CH_3C_6H_4CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$ corresponds to their structure A, which they felt was most likely the predominant one. Of course, the presence of the ring in the π-benzyl molecules creates a very strong steric preference for Davison and Rode's configuration A; the infrared spectrum[8] of $(CH_3C_6H_4CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$ gives no indication of the presence of more than one isomer in hexane solution and we presume that this is the isomer found by us in the crystal.

Finally, it remains to point out the implications of this structure with respect to the fluxional nature of the molecule. Even the simplest and shortest excursion by the metal atom which has the potentiality of producing the observed averaging in the nmr spectrum requires that simultaneously there be a considerable reorientation of the other ligands, $\pi\text{-}C_5H_5$ and the two CO groups. As Figure 2 shows, this set of ligands must rotate by about 150° in order to give a new conformation which is exactly the mirror image of the old one. Thus, at best, the pathway of the rearrangement accounting for the fluxional nature of the molecule will not be simple and, of course, there are more complicated trajectories for the metal atom relative to the benzyl moiety which are not, as yet, ruled out by any experimental data.

Acknowledgments. We are grateful to Mr. Tobin J. Marks for supplying the sample and to him and Dr. M. J. Bennett for stimulating discussions.

The Molecular Configuration of $[H_2NFe(CO)_3]_2$ and Its Identity with the Previously Reported $[HNFe(CO)_3]_2$. The Influence of Bridged Ligands on the Basic Geometry of an Organometallic Complex Containing a Strong Metal–Metal Bond

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Abstract: An X-ray analysis of di-μ-amido-bis(tricarbonyliron), $[H_2NFe(CO)_3]_2$, has been carried out in order to assess the stereochemical consequence of replacement of a second-row nonmetallic bridging atom with a first-row atom in a ligand-bridged binuclear organometallic complex containing a strong metal–metal interaction. This diamagnetic complex, initially formulated and widely accepted as $[HNFe(CO)_3]_2$ with a presumed bridging diimido group, has been conclusively shown from the X-ray work and mass spectrometric analysis to possess a di-μ-amido structure. The two $Fe(CO)_3$ moieties are symmetrically linked to each other by two bridging amido groups and a "bent" iron–iron bond such that the resulting idealized molecular configuration of C_{2v}-2mm symmetry possesses a nonplanar Fe_2N_2 fragment with a sharply acute bridging Fe–N–Fe angle of 74.4° (esd, 0.5°) and Fe–Fe and Fe–N distances of 2.402 (6) and 1.98 (1) Å, respectively. A detailed comparison of its $[NFe(CO)_3]_2$ framework with those of $[C_2H_5SFe(CO)_3]_2$ and other electronically and structurally analogous sulfur-, nitrogen-, and phosphorus-bridged complexes is made. Despite sterically predictable variations in the X–Fe–X angles of the X_2Fe_2 system (X = N, S) in these homologous complexes, there is near-constancy of the Fe–Fe distances and Fe–X–Fe angles for a given X-bridged ligand. The considerably shorter Fe–Fe distances in the nitrogen-bridged dimers (2.37–2.40 Å) compared to the sulfur-bridged dimers (2.51–2.55 Å) are found to be primarily a consequence of the much smaller Fe–X distances (1.94–2.02 *vs.* 2.23–2.27 Å) counterbalanced to some extent by the somewhat larger Fe–X–Fe angles (72–75 *vs.* 67–70°). Crystals of $[H_2NFe(CO)_3]_2$ contain four dimeric molecules in an orthorhombic cell of symmetry $Pna2_1$ and of cell lengths $a = 13.60$ Å, $b = 6.81$ Å, $c = 11.77$ Å. A least-squares refinement of the structure resulted in a final unweighted discrepancy index of $R_1 = 6.5\%$ for the 472 independent nonzero reflections collected photographically.

The structural investigation of $[H_2NFe(CO)_3]_2$ was motivated in large part by the desire to assess the "size effect" of different bridging atoms on the molecular geometry of an organometallic ligand-bridged dimer containing a metal–metal bond.

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Although this compound, prepared by Hieber and Beutner[2] from the reaction of tetracarbonylferrate(−II) anion with either nitrite ion or hydroxylamine, was originally formulated as di-μ-imido-hexacarbonyldiiron from elemental and infrared analyses,[3] it should be noted that these workers specifically stated that this compound possibly contained NH_2– rather than NH– bridging groups. The similarity of both the dipole moment of value 3.28 ± 0.03 D and the carbonyl stretching infrared bands with those in $[SFe(CO)_3]$ and $[SeFe(CO)_3]_2$ led Hieber and Beutner[2] to postulate a molecular model of C_{2v} (or C_s) symmetry involving a nonplanar N_2Fe_2 fragment analogous to that previously suggested by Hieber and Beck[4] for the related sulfur and selenium dimeric complexes of formula $[XFe(CO)_3]_2$ (X = S, Se, SR, SeR). Subsequent X-ray structural work on $[RSFe(CO)_3]_2$ (R = C_2H_5)[5] and $[SFe(CO)_3]_2$[6] not only substantiated the general configuration suggested by Hieber and Beck[4] but also provided detailed molecular parameters compatible with a previously proposal[7] of a "bent" iron–iron bond for each of these complexes. Furthermore, the X-ray characterization of $[SFe(CO)_3]_2$ as a μ-dithio complex with a disulfide group symmetrically linked to the two $Fe(CO)_3$ moieties resulted in the suggestion[6] of a μ-diimido system in the presumed $[HNFe(CO)_3]_2$ in order to make it electronically equivalent as well as stereochemically analogous to the μ-dithio iron complex. Since a rational basis for a distinct iron–iron bond of considerable bond strength in $[RSFe(CO)_3]_2$ and $[SFe(CO)_3]_2$ (in contrast to a superexchange coupling through the bridging ligands) was provided from later structural work[8] on the homologous compounds $[R_2PCoC_5H_5]_2$ and $[R_2PNiC_5H_5]_2$ (R = C_6H_5), an X-ray examination of the nitrogen derivative was especially desirable both to confirm the suggested presence of a HN–NH-bonded bridging system and to ascertain the degree of alteration of the molecular geometry of the X_2Fe_2 fragment due to the replacement of a second-row main-group element with a first-row one as bridging groups. The resulting X-ray investigation together with a mass spectrometric measurement unequivocally showed the actual formula for the nitrogen compound to be $[H_2NFe(CO)_3]_2$.[9–14]

Experimental Section

Single-Crystal X-Ray Data. The compound was prepared by R. B. K. according to the Hieber–Beutner procedure.[2] Reddish-orange crystals were obtained by sublimation under vacuum at 40°. Because of the air sensitivity of the compound, crystals optically selected under an argon atmosphere were wedged in small thin-walled glass capillaries which subsequently were evacuated, filled with argon, and then sealed. After preliminary X-ray examination of several crystals, a needle-like cylindrical crystal of length 0.3 mm and cross section 0.15 mm, with the cylinder axis coincident to the spindle axis, was used in the data collection. For Mo Kα radiation the linear absorption coefficient (μ) of 27.2 cm^{-1} results in a μR_{max} of 0.2. Since the variation of absorption correction factors with θ is negligible for the above μR value,[15] no absorption corrections were applied.

The orthorhombic lattice parameters were determined from *h*0*l* and 0*kl* precession photographs which were calibrated by the superposition of a zero-level reciprocal lattice of a NaCl crystal on the same film before development. Multiple-film, equiinclination Weissenberg photographs were obtained with Mo Kα radiation for 13 reciprocal levels (*hk*0 through *hk*12), from which the intensities of 453 independent reflections were measured. Timed-exposure precession photographs of 0*kl*, 1*kl*, *h*0*l*, and *h*1*l* zones, also obtained with Mo Kα radiation, yielded a total of 172 independent reflections of which 19 were experimentally inaccessible by the Weissenberg technique. All intensities were judged visually by comparison with calibrated standard intensity strips made with the same crystal. The Weissenberg and precession intensity data were first corrected for Lorentz-polarization effects and then merged together by least squares[16] to place them on one relative scale.

Unit Cell and Space Group. Crystals of $[H_2NFe(CO)_3]_2$ (mol wt, 311.8) are orthorhombic with lattice parameters $a = 13.60 \pm 0.02$ Å, $b = 6.81 \pm 0.02$ Å, $c = 11.77 \pm 0.02$ Å; volume of the unit cell 1090 Å^3; $\rho_{calcd} = 1.90$ g cm^{-3} for four dimeric molecules per unit cell; total number of electrons in the unit cell, $F(000) = 616$.

The observed systematic absences which are $\{0kl\}$ with $k + = 2n + 1$ and $\{h0l\}$ with $h = 2n + 1$ indicate the probable space groups to be either Pna2$_1$ (C_{2v}^9, no. 33) or Pnam [nonstandard setting of Pnma (D_{2h}^{16}, no. 62)].[17] Our choice of the acentric space group, Pna2$_1$, from the concentration of peaks in the computed Patterson function was later verified by the satisfactory refinement of the determined structure. Since all atoms are in fourfold sets of general positions (*i.e.*, $x, y, z;\ \bar{x}, \bar{y}, {}^1/_2 + z;\ {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z;\ {}^1/_2 + x, {}^1/_2 - y, z$),[17] the structural analysis required the location of two iron, six carbon, six oxygen, two nitrogen, and four hydrogen atoms corresponding to one dimer as the crystallographic asymmetric unit.

Determination of the Structure. A diagnosis of a three-dimensional Patterson function, calculated from the corrected intensities, resulted in two possible self-consistent sets of coordinates for the iron atoms. The ambiguity between these trial sets was resolved by isotropic least-squares refinement with a local version of the Busing–Martin–Levy ORFLS program.[18] After several cycles discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 22.9\%$ and $R_2 = [\Sigma w|| F_o - \| F_o| |^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 30.0\%$ were obtained for one set. The remaining 14 nonhydrogen atoms were

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[2] W. Hieber and H. Beutner, *Z. Naturforsch.*, **15b**, 324 (1960); *Z. Anorg. Allgem. Chem.*, **317**, 63 (1962).

[3] The fact that only two bands are observed in the N–H stretching region was interpreted[2] to favor a complex with two HN– bridging groups, since selection rules for a molecule of C_{2v} symmetry predict four allowed N–H stretching frequencies for two $-NH_2$ groups. In light of the compound's correct formulation (reported here) as a di-μ-amido complex one must rationalize the paucity of resolvable bands as due to accidental degeneracy. *Anal.* Calcd for $[H_2NFe(CO)_3]_2$: Fe, 35.82; N, 8.98; C, 23.11; H, 1.29; CO, 53.90; NH_3, 10.92; mol wt, 311.8. Found:[2] Fe, 36.0; N, 8.97; C, 23.3; H, 0.6; CO, 53.9; NH_3, 10.9; mol wt, 307 (in benzene). Except for the hydrogen analysis the corresponding calculated and experimental values agree well with each other.

[4] W. Hieber and W. Beck, *Z. Anorg. Allgem. Chem.*, **304**, 274 (1960).

[5] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

[6] C. H. Wei and L. F. Dahl, *ibid.*, **4**, 1 (1965).

[7] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

[8] J. M. Coleman and L. F. Dahl, *ibid.*, **89**, 542 (1967).

[9] Since completion of our X-ray work, we have learned that Hieber, Mills, and Frey[10] have also unambiguously established this compound as $[H_2NFe(CO)_3]_2$ from mass spectrometric studies.

[10] W. Hieber, O. S. Mills, and V. Frey, private communication to L. F. Dahl, Sept 1967. Since submission of this manuscript, this work has been published: V. Frey, W. Hieber, and O. S. Mills, *Z. Naturforsch.*, **23b**, 105 (1968).

[11] These studies also suggest that the corresponding nitrogen–iron nitrosyl dimer[2] formulated analogously from infrared and elemental analyses as $[HNFe(NO)_2]_2$ instead is $[H_2NFe(NO)_2]_2$. Its over-all molecular configuration no doubt is similar to that found from X-ray work for the electronically equivalent $[RSFe(NO)_2]_2$[12] and $[IFe(NO)_2]_2$.[13] Further indirect support for a di-μ-amido iron nitrosyl complex is that Hayter and Williams[14] have shown the congener elements phosphorus and arsenic to form only R_2E-bridged dimers $[R_2EFe(NO)_2]_2$ (E = P, R = CH_3, C_6H_5; E = As, R = CH_3).

[12] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, **11**, 599 (1958).

[13] E. Rudulfo de Gil, L. F. Dahl, and R. D. Feltham, to be submitted for publication.

[14] R. G. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 717 (1964).

[15] "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

[16] P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604 Computer," University of Wisconsin, 1964.

[17] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 119.

[18] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS. A Fortran Crystallographic Least-Squares Program," ORN-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1963.

Table I. Final Atomic Parameters and Standard Deviations

	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
Fe(1)	0.1285 (3)	0.2929 (5)	0.1796 (4)	*a*
Fe(2)	0.1529 (2)	0.4769 (5)	0.0084 [b]	*a*
O(1)	0.2912 (16)	0.0146 (30)	0.1643 (19)	8.0 (5)
O(2)	0.1010 (14)	0.3049 (28)	0.4248 (20)	7.3 (5)
O(3)	−0.0220 (16)	0.0004 (33)	−0.1202 (19)	8.6 (5)
O(4)	0.0375 (14)	0.2675 (30)	−0.1599 (16)	6.5 (4)
O(5)	0.1482 (14)	0.8653 (31)	−0.1008 (19)	7.6 (5)
O(6)	0.3258 (17)	0.3134 (29)	−0.0953 (19)	8.0 (6)
C(1)	0.2261 (21)	0.1149 (41)	0.1792 (28)	6.9 (6)
C(2)	0.1128 (19)	0.3061 (42)	0.3201 (25)	6.0 (6)
C(3)	0.0403 (25)	0.1100 (50)	0.1494 (27)	8.5 (9)
C(4)	0.0834 (19)	0.3555 (34)	−0.0943 (21)	4.4 (5)
C(5)	0.1572 (18)	0.7098 (44)	−0.0560 (24)	5.2 (6)
C(6)	0.2599 (21)	0.3864 (39)	−0.0571 (22)	5.5 (6)
N(1)	0.0406 (11)	0.4963 (26)	0.1148 (15)	4.5 (4)
N(2)	0.2201 (15)	0.5194 (31)	0.1534 (18)	5.7 (5)

[a] Anisotropic temperature factors of the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were utilized for the iron atoms; the resulting thermal coefficients ($\times 10^4$) with esd of the last significant figure given in parentheses are

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	62 (2)	253 (9)	56 (2)	21 (5)	−1 (2)	5 (5)
Fe(2)	59 (2)	224 (9)	56 (2)	19 (4)	7 (2)	12 (5)

[b] Since this space group $Pna2_1$ does not specify the unit-cell origin in the c lattice-vector direction, the z coordinate of Fe(2) arbitrarily was fixed.

Table II. Intramolecular Distances and Standard Deviations (Å)

Fe(1)–Fe(2)	2.402 (6)	C(1)–O(1)	1.13 (3)
		C(2)–O(2)	1.24 (3)
		C(3)–O(3)	1.18 (3)
Fe(1)–N(1)	1.98 (2)	C(4)–O(4)	1.16 (3)
Fe(1)–N(2)	2.01 (2)	C(5)–O(5)	1.19 (3)
Fe(2)–N(1)	1.98 (2)	C(6)–O(6)	1.12 (3)
Fe(2)–N(2)	1.96 (2)		
			1.17 (1) (av)
	1.98 (1) (av)		
		N···N (2)	2.50 (3)
Fe(1)–C(1)	1.80 (3)		
Fe(1)–C(2)	1.67 (3)		
Fe(1)–C(3)	1.76 (4)		
Fe(2)–C(4)	1.74 (3)		
Fe(2)–C(5)	1.77 (3)		
Fe(2)–C(6)	1.76 (3)		
	1.75 (1) (av)		

Table III. Bond Angles and Standard Deviations (Degrees)

N(2)–Fe(1)–N(1)	77.1 (8)	C(1)–Fe(1)–C(3)	91 (1)
N(2)–Fe(2)–N(1)	78.4 (8)	C(4)–Fe(2)–C(6)	89 (1)
	77.8 (6) (av)		90 (1) (av)
		Fe(1)–C(1)–O(1)	170 (3)
Fe(1)–N(2)–Fe(2)	74.4 (7)	Fe(2)–C(2)–O(2)	177 (3)
Fe(1)–N(1)–Fe(2)	74.4 (6)	Fe(1)–C(3)–O(3)	173 (3)
	74.4 (5) (av)	Fe(2)–C(4)–O(4)	177 (2)
		Fe(2)–C(5)–O(5)	172 (2)
N(1)–Fe(1)–C(1)	156 (1)	Fe(2)–C(6)–O(6)	174 (3)
N(2)–Fe(1)–C(3)	159 (1)		174 (1) (av)
N(1)–Fe(2)–C(6)	160 (1)		
N(2)–Fe(2)–C(4)	157 (1)	Fe(2)–Fe(1)–C(1)	104 (1)
	158 (1) (av)	Fe(2)–Fe(1)–C(3)	107 (1)
		Fe(1)–Fe(2)–C(4)	105 (1)
		Fe(1)–Fe(2)–C(6)	107 (1)
N(1)–Fe(1)–C(2)	105 (1)		
N(2)–Fe(1)–C(2)	101 (1)		106 (1) (av)
N(1)–Fe(2)–C(5)	104 (1)		
N(2)–Fe(2)–C(5)	104 (1)	Fe(2)–Fe(1)–C(2)	145 (1)
	104 (1) (av)	Fe(1)–Fe(2)–C(5)	147 (1)
			146 (1) (av
N(1)–Fe(1)–C(3)	90 (1)		
N(2)–Fe(1)–C(1)	93 (1)	N(1)–N(2)–Fe(2)	51.2 (6)
N(1)–Fe(2)–C(4)	93 (1)	N(2)–N(1)–Fe(1)	51.9 (7)
N(2)–Fe(2)–C(6)	93 (1)	N(1)–N(2)–Fe(1)	51.0 (6)
		N(2)–N(1)–Fe(2)	50.4 (7)
	92 (1) (av)		
			51.1 (3) (av)
C(1)–Fe(1)–C(2)	98 (1)		
C(2)–Fe(1)–C(3)	99 (1)	Fe(1)–Fe(2)–N(1)	52.9 (5)
C(4)–Fe(2)–C(5)	98 (1)	Fe(1)–Fe(2)–N(2)	53.7 (7)
C(5)–Fe(2)–C(6)	96 (1)	Fe(2)–Fe(1)–N(1)	52.7 (5)
		Fe(2)–Fe(1)–N(2)	51.9 (6)
	98 (1) (av)		
			52.8 (3) (av)

determined from successive Fourier syntheses. Seven cycles of isotropic least-squares refinement on all atoms lowered R_1 and R_2 to 7.9 and 9.0%, respectively, with all parameter shifts less than 0.5σ. Since a Fourier difference map indicated some anisotropic electron density around the iron positions, two additional cycles of least-squares refinement were carried out with anisotropic thermal parameters for the two iron atoms and isotropic ones for the other atoms. The discrepancy values were thus reduced to $R_1 = 6.5\%$ and $R_2 = 7.1\%$. During the last cycle no parameter changed by more than 0.2σ. The final positional parameters agreed closely with the ones from the isotropic least-squares refinement; no corresponding coordinates differed by more than 1σ except 6 which differed by $1 - 2\sigma$. The least-squares correlation matrices also showed the positional parameters to be essentially independent of the thermal parameters.

A three-dimensional Fourier difference map based on the anisotropic–isotropic refinement showed no residual density greater than 0.9 e/Å^3 or less than −0.7 e/Å^3. Stereochemical considerations of the probable orientations of the two hydrogen atoms about each nitrogen atom (based on the known directions of the R groups from the bridging atoms in $[C_2H_5SFe(CO)_3]_2$[5] and $[(C_6H_5)_2PCoC_5H_5]_2$[8]) indicated that two distinct positive peaks on this difference map could possibly be interpreted as hydrogen atoms. Nevertheless, since it was felt that the data were not sufficiently reliable to ascertain the hydrogen coordinates, no attempt was made either to confirm the tentative assignments of the two residual peaks or to locate the other two hydrogen atoms by difference maps calculated with the inclusion of unobserved data. Unobserved but experimentally accessible data for which $\sin\theta \leq 0.5$ were generated by the assignment of an intensity equal to the minimum observed intensity for a given reciprocal lattice layer. After Lorentz-polarization and spot-extension corrections, the derived F_o(min) were compared with the corresponding F_c; the fact that no F_c exceeded $1.5F_o$(min) corroborated the over-all correctness of the structure.

In the least-squares refinements the function minimized was $\Sigma w||F_o| - |F_c||^2$ where individual weights were assigned to the observed structure factors according to the function $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o(\text{min})$ and $\sqrt{w} = 1.25I_o^2/F_oI_o^2(\text{min})$ if $I_o < 4I_o(\text{min})$. The scattering factors utilized in this structural analysis were those reported by Hanson, *et al.*[19] No dispersion corrections were made since both the real and imaginary corrections for iron are small (*i.e.*, for Mo Kα radiation $\Delta f' = 0.4$, $\Delta f'' = 1.0$).[20] All Patterson and Fourier summations were computed with the Blount program.[21]

The positional and thermal parameters obtained from the output of the last cycle of the anisotropic–isotropic least-squares refinement are presented in Table I.[22] Intramolecular distances and angles

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(19) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 17, 1040 (1964).

(20) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(21) J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(22) Calculated and observed structure factors for $[H_2NFe(CO)_3]_2$ are deposited as Document No. 10005 with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table IV. Equations of Best Molecular Planes and Distances (Å) of Atoms from These Planes

(a) Plane through N(1), N(2), C(1), and C(3)

$0.163X - 0.127Y - 0.978Z + 1.693 = 0$

N(1)	0.03	C(3)	−0.03	O(3)	0.26
N(2)	−0.03	Fe(1)	−0.34	C(2)	−2.01
C(1)	0.03	O(1)	0.43	O(2)	−3.24

(b) Plane through N(1), N(2), C(4), and C(6)

$-0.006X + 0.935Y - 0.354Z - 2.665 = 0$

N(1)	0.01	C(6)	0.01	O(6)	−0.30
N(2)	0.01	Fe(2)	0.33	C(5)	2.08
C(4)	−0.01	O(4)	−0.30	O(5)	3.25

(c) Plane through Fe(1), Fe(2), and the Midpoint of N(1)–N(2)

$-0.979X - 0.055Y - 0.195Z + 2.223 = 0$

N(1)	1.24	O(5)	0.17	C(4)	1.21
N(2)	−1.24	C(3)	1.31	C(6)	−1.24
C(2)	−0.12	C(1)	−1.23	O(4)	2.00
C(5)	0.00	O(3)	2.25	O(6)	−2.00
O(2)	−0.20	O(1)	−2.03		

(d) Plane through N(1), N(2), and the Midpoint of Fe(1)–Fe(2)

$0.127X + 0.503Y - 0.855Z - 0.615 = 0$

Fe(1)	−1.20	O(5)	3.62	C(1)	−1.64
Fe(2)	1.20	C(3)	−1.67	C(6)	1.73
C(2)	−2.59	C(4)	1.70	O(1)	−1.72
C(5)	2.65	O(3)	−1.86	O(6)	1.98
O(2)	−3.67	O(4)	1.97		

Table V. Mass Spectrum of $[H_2NFe(CO)_3]_2$

m/e	Ion	Rel abundance
312	$Fe_2(CO)_6N_2H_4^+$	35
284	$Fe_2(CO)_5N_2H_4^+$	29
256	$Fe_2(CO)_4N_2H_4^+$	6
228	$Fe_2(CO)_3N_2H_4^+$	22
200	$Fe_2(CO)_2N_2H_4^+$	17
172	$Fe_2(CO)N_2H_4^+$	36
156	$Fe_2(CO)_6N_2H_4^{2+}$	4
144	$Fe_2N_2H_4^+$	100
143	$Fe_2N_2H_3^+$	3
142	$Fe_2N_2H_2^+$	6
140	$Fe_2N_2^+$	3
128	$Fe_2NH_2^+$	12
127	Fe_2NH^+	42
126	Fe_2N^+	34
114	$Fe_2(CO)_3N_2H_4^{2+}$	3
112	Fe_2^+	11
100	$Fe_2(CO)_2N_2H_4^{2+}$	4
86	$Fe_2(CO)N_2H_4^{2+}$	6
84	FeN_2^+ (?)	22
72	$FeNH_2^+$	25
71	$FeNH^+$	4
56	Fe^+	31

together with estimated standard deviations, calculated with the Busing–Martin–Levy function and error program[23] from the full inverse matrix (containing estimated lattice parameter errors), are listed in Tables II and III. Least-squares calculations[24] of "best" molecular planes formed by certain atoms and the perpendicular distances of these and other atoms from these planes are given in Table IV.

Mass Spectral Data. The mass spectrum of $[H_2NFe(CO)_3]_2$ was obtained from the AEI MS-902 mass spectrometer located at the University of Wisconsin.[25] The operating conditions were 70-eV electron energy, 140° probe temperature, and a resolution of approximately 5000. Samples were introduced into the ion source by a direct inlet system. The relative peak intensities were estimated by measurement of the peak heights. Table V gives the *m/e* values of the various ions present relative to a value of 100 for the most abundant species, $Fe_2N_2H_4^+$.

Discussion

The configuration of the individual molecules of this dimeric complex (shown in Figure 1) ideally possesses C_{2v}-2mm symmetry.[26] Each of the two iron atoms is coordinated to two nitrogen and three carbonyl carbon atoms located at the corners of a distorted square pyramid. The dimeric molecule formally arises from the junction of the basal planes of these two pyramids along the N–N edge at a dihedral angle of 78°.[27] The resulting molecular configuration with an iron–iron distance of only 2.402 Å (esd, 0.006 Å) can be attributed to a distinct "bent" iron–iron bond.

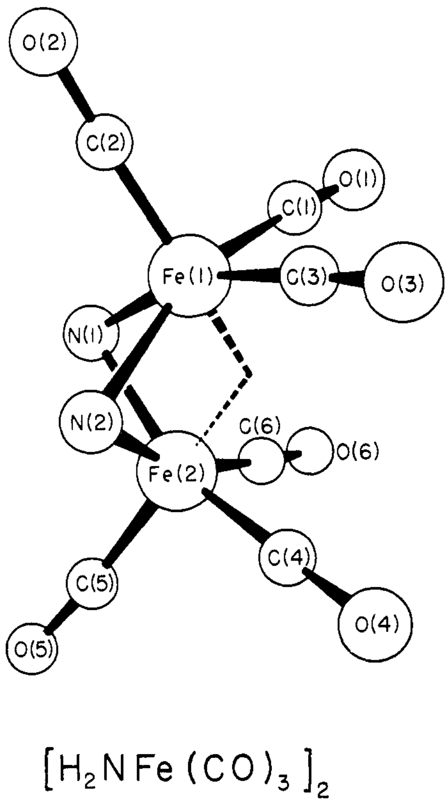

Figure 1. Molecular configuration of the $[NFe(CO)_3]_2$ skeleton of $[H_2NFe(CO)_3]_2$.

The most surprising structural feature is the *nonbonding* nitrogen–nitrogen distance of 2.50 Å (esd, 0.03 Å). Thus, the X-ray results conclusively show that this organometallic complex does not possess a HN–NH bridging group as previously proposed[6] on the basis of its presumed formula, $[HNFe(CO)_3]_2$. In order to conform to the observed diamagnetism, each of the two bridging nitrogen ligands must be coordinated to two hydrogen atoms.

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(23) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(24) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

(25) We are indebted to Mr. Alan Foust and Miss Martha Petrie of the University of Wisconsin for running the mass spectrum.

(26) Plane calculations (Table IVc and d) show that all pairs of atoms made equivalent by the two defined mirror planes are equidistant within 0.1 Å from opposite sides to these two noncrystallographic mirrors. The perpendicularity of these bilateral symmetry elements within experimental error is shown from the angle between the normals of these two planes being 90.0°. The resulting molecular twofold axis is along the line of intersection of these two vertical mirrors.

(27) All dihedral angles given in this paper are defined as angles directly between planes rather than as angles between normals to planes.

The hydrogen composition stereochemically required by the nonhydrogen molecular framework subsequently was substantiated from a mass spectrographic analysis which revealed a peak at an *m/e* of 312 due to the parent $Fe_2(CO)_6N_2H_4^+$ ion. No significant peak (other than that attributed to the substitution of ^{54}Fe for ^{56}Fe in the parent ion) was detected at an *m/e* of 310.[28] The fragmentation pattern of $[H_2NFe(CO)_3]_2$ is similar to that found for $[CH_3SFe(CO)_3]_2$ by King[29] and by Edgar, *et al.*[30] The parent $Fe_2(CO)_6N_2H_4^+$ ion undergoes the usual successive removal of carbonyl groups, but unlike the fragmentation pattern of $[CH_3SFe(CO)_3]_2$ where the ions $(CH_3S)_2Fe_2(CO)_n^+$ ($n = 1, 5$) are present in approximately the same relative abundance, the $Fe_2(CO)_nN_2H_4^+$ fragments vary from 36% for $Fe_2(CO)N_2H_4^+$ to only 6% for $Fe_2(CO)_4N_2H_4^+$. The observed stepwise loss of hydrogen atoms from the carbonyl-free $Fe_2N_2H_4^+$ ion (*m/e* 144) appears to parallel the successive demethylation found for the $(CH_3S)_2Fe_2^+$ ion in the spectrum of $[CH_3SFe(CO)_3]_2$. Peaks characteristic of the doubly charged ions $Fe_2(CO)_nN_2H_4^{2+}$ ($n = 1, 2, 3, 6$) were distinguished, but the presence of doubly charged ions with $n = 4, 5$ could not be ascertained because of the overlap of their peaks with singly charged ion peaks.

The di-μ-amido complex, $[H_2NFe(CO)_3]_2$, is electronically equivalent and structurally similar not only to the corresponding di-μ-alkylthio dimer, $[C_2H_5SFe(CO)_3]_2$, but also to two other sulfur-bridged $Fe(CO)_3$ complexes, $[C_6H_5CSFe(CO)_3]_2$[31] and $[CH_3SFe_2(CO)_6]_2S$[32] (Table VI); to the diphenylphosphorus-bridged CoC_5H_5 dimer;[8] and to six nitrogen-bridged $Fe(CO)_3$ and CoC_5H_5 dimers (Table VII, molecules I–V, VII) whose structures recently have been reported.[33–40]

Although the gross configurations of these nitrogen-, sulfur-, and phosphorus-bridged dimers are the same, a comparison of their detailed structural features reveals highly significant differences characteristic of the different bridging atoms. The most remarkable observation is that the molecular shape is essentially invariant for a given bridging atom except for certain sterically predictable variations. To a first approximation, however, it can be concluded that the substitution of a first-row nonmetallic atom for a second-row atom does not appreciably alter the particular *basic* molecular geometry of these homologous complexes. Hence, the structural resemblance of $[H_2NFe(CO)_3]_2$ and the other nitrogen-bridged dimers to $[C_2H_5SFe(CO)_3]_2$ and $[(C_6H_5)_2PCoC_5H_5]_2$ is in harmony with a separate metal–metal single-bond interaction for each of these complexes; a strong, distinct cobalt–cobalt bond was proposed[8] for the phosphorus-bridged CoC_5H_5 dimer in order to account for the radical difference between its molecular configuration and that of $[(C_6H_5)_2PNiC_5H_5]_2$.

The over-all similarity of the $[NFe(CO)_3]_2$ framework in $[H_2NFe(CO)_3]_2$ with the $[SFe(CO)_3]_2$ framework found in $[C_2H_5SFe(CO)_3]_2$,[5] $[C_6H_5CSFe(CO)_3]_2$,[31] and $[CH_3SFe_2(CO)_6]_2S$[32] rather than with the S–S bonded framework in the disulfide complex $[SFe(CO)_3]_2$[6] is shown from a comparison of the X–Fe–X angles given in Table VI. The average N–Fe–N angle of 78° in $[H_2NFe(CO)_3]_2$ parallels the average S–Fe–S angle of range 77–81° in the former three sulfur complexes (as opposed to an average S–Fe–S angle of only 53.5° in $[SFe(CO)_3]_2$) and thereby emphasizes that the replacement of the two bridging RS ligands in $[C_2H_5SFe(CO)_3]_2$ by the two sterically uninhibited NH_2 ligands does not appreciably change the bridging angles subtended at the iron atoms. The significantly smaller N–Fe–N angle of 73° in μ-(N,N′-dehydrosemidinato)-bis(tricarbonyliron) (molecule I in Table VII) must be attributed to the chelated linkage of the nitrogen atoms which are constrained by the stereochemistry of the *o*-dehydrosemidine skeleton in its coordination with the two $Fe(CO)_3$ groups.[41] The still smaller analogous angles subtended at the metal atoms in μ-diphenylureylene-bis(tricarbonyliron) (III) (N–Fe–N angle, 65°)[36] and μ-(di-*t*-butylureylene)-bis(cyclopentadienylcobalt) (VII) (N–Co–N angle, 66°)[39] no doubt are a consequence of the more severe angular distortion imposed on the two nitrogen atoms due to their linkage by a bridging carbonyl group.

Another conspicuous trend indicated in Table VI is the somewhat larger average Fe–N–Fe bridging angle of 74.4° (esd, 0.5°) in $[H_2NFe(CO)_3]_2$ compared to the average Fe–S–Fe angles (of range 67–69°) in the three structurally similar alkylthio-bridged iron carbonyl complexes; even the corresponding average angle in μ-dithio-$[SFe(CO)_3]_2$ is only 70°. This significantly larger Fe–N–Fe angle in $[H_2NFe(CO)_3]_2$ is in excellent agreement with the average Fe–N–Fe angles found in $(C_6H_5NC_6H_4NH)Fe_2(CO)_6$ (I) (72.5°)[37] and $(C_6H_5NCONC_6H_5)Fe_2(CO)_6$ (III) (74°),[36] and with the

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(28) The naturally occurring isotopes or iron, carbon, and oxygen and their relative abundances are listed by King[29] who discusses the influence of such isotopes on the observed ion peaks in the mass spectra of organosulfur derivatives of metal carbonyls.

(29) R. B. King, *J. Am. Chem. Soc.*, **90**, 1429 (1968).

(30) K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc.*, 379 (1967).

(31) H. P. Weber and R. F. Bryant, *ibid.*, 182 (1967).

(32) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

(33) P. E. Baikie and O. S. Mills, *Chem. Commun.*, 707 (1966).

(34) P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, 1, 55 (1967).

(35) M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *Chem. Commun.*, 1106 (1967).

(36) (a) J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *ibid.*, 1149 (1967); (b) J. Piron, P. Piret, and M. Van Meerssche, *Bull. Soc. Chim. Belges*, **76**, 505 (1967).

(37) D. Bright and O. S. Mills, *ibid.*, 245 (1967).

(38) P. E. Baikie and O. S. Mills, *ibid.*, 1228 (1967).

(39) Y. Matsu-ura, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, T. Yoshida, and S. Otsuka, *ibid.*, 1122 (1967).

(40) A comparison of the structural features of the other nitrogen-containing organometallic complexes with those of $[H_2NFe(CO)_3]_2$ and the sulfur- and phosphorus-bridged analogs is somewhat limited at the present time since detailed structural information with atomic parameters has been published for only two of the nitrogen-bridged systems (*viz.* ref 34 and 36b).

(41) Baikie and Mills[34] pointed out that the nitrogen arrangement in μ-N,N′-dehydrosemidinato-bis(tricarbonyliron) is a preferred state since the N–C–C angles subtended at the *o*-dehydrosemidine ring are reduced from the sp^2 value of 120° to the observed value of 110° which corresponds to a shorter nonbonding N···N distance in the complex than in the free ligand. This angular distortion of the nitrogen atoms toward each other, however, leads both to the smaller average N–Fe–N angle and a shorter nonbonding N···N distance of 2.4 Å which is 0.1 Å less than that in $[H_2NFe(CO)_3]_2$. A rationalization for this directional deformation of the *o*-dehydrosemidine nitrogen atoms away from the presumably unconstrained nitrogen positions of the Fe_2N_2 system in $[H_2NFe(CO)_3]_2$ is that such an angular distortion results in *larger* and more nearly tetrahedral Fe–N–C ring angles (range 106–110°) and thereby relieves steric repulsion of the nonbonding nitrogen ligands. Hence, the N–Fe–N angles of the Fe_2N_2 fragment are influenced to a considerable extent by the stereochemical disposition of the ligands attached to the nitrogen atoms. It is noteworthy that a smaller but similar ring distortion of the bridging stilbene residue occurs in the μ-(*cis*-stilbene-α,β-dithiolato)-bis(tricarbonyliron) complex, $[C_6H_5CSFe(CO)_3]_2$,[31] such that the observed S–C–C ring angles possess an average value of 115°.

Co–N–Co angle measured in (t-BuNCONBu-t)(Co-C_5H_5)$_2$ (VII) (74.6°).[39] These unexpectedly close values for the Fe–N–Fe and Co–N–Co angles also are not different from the average Co–P–Co angle of 72.5° found in the analogous complex $[(C_6H_5)_2PCoC_5H_5]_2$ (Table VI).[8] Although greater angular deformation toward more acute bridging M–X–M angles might be expected for the bridging SR and PR_2 groups relative to the bridging NR_2 group due to their higher polarizabilities, the inseparability of the coalescent effects of the bridging atoms and direct metal–metal interaction on the resulting molecular geometry prohibits any meaningful rationalization of the dissimilarities of these nitrogen- and sulfur-bridging angles *per se*;[42] from a formalistic standpoint the larger Fe–N–Fe angles compensate to some extent for the resulting decrease in Fe–Fe distance due to substitution of the much smaller nitrogen ligands in place of the sulfur ligands.

Direct evidence of the considerable strength of the iron–iron bond in $[H_2NFe(CO)_3]_2$ is given by its unusually short distance of 2.402 Å which is at least 0.1 Å smaller than the metal–metal distances (of range 2.51–2.56 Å) in the sulfur- and phosphorus-bridged complexes listed in Table VI. Nevertheless, this iron–iron distance and the average Fe–N distance of 1.98 Å agree exceedingly well with the corresponding distances reported in the other nitrogen-bridged dimers containing two nitrogen atoms symmetrically linked with two $Fe(CO)_3$ groups (Table VII), *viz.* $(C_6H_5NC_6H_4NH)Fe_2(CO)_6$ (I) (2.37 and 2.00 Å),[33,34] $[(p\text{-}CH_3C_6H_4)_2CNHNFe(CO)_3]_2$ (II) (2.40 and 1.99–2.02 Å),[35] $(C_6H_5NCONC_6H_5)Fe_2(CO)_6$ (III) (2.41 and 2.00 Å),[36] and $[(p\text{-}CH_3C_6H_4)_2CNFe(CO)_3]_2$ (IV) (2.403 and 1.94 Å).[37] The significantly shorter average Fe–N bond length of 1.94 Å in di-μ-(4,4′-dimethylbenzophenoniminato)-bis(tricarbonyliron) (IV) can be ascribed[37] to this complex possessing two three-coordinated trigonal-like bridging nitrogen atoms in contrast to the four-coordinated tetrahedral-like bridging nitrogen atoms contained in the other above complexes listed in Table VII.[43–45] The Fe–Fe and Fe–N distances in the Schiff-base complex $(p\text{-}CH_3C_6H_4NCH_2C_6H_4)Fe_2(CO)_6$ (V) (2.43 and 1.95–1.96 Å)[33] may be a consequence of its containing only one symmetrically bridging nitrogen atom.

The trimeric complex $\{(C_6H_5)_2CNN\}_2Fe_3(CO)_9$ (VI),[38] which contains two triply bridging iron-coordinated nitrogen atoms, also has two short Fe–Fe bonding distances of 2.43 and 2.46 Å and one nonbonding distance of 3.06 Å. Its $(RN)_2Fe_3(CO)_9$ framework is both electronically equivalent and structurally analogous to the molecular configurations of $S_2Fe_3(CO)_9$ in $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ (Fe–Fe distances: 2.58, 2.61, and 3.37 Å)[46] and $Se_2Fe_3(CO)_9$ (Fe–Fe distances: 2.64, 2.66, and 3.51 Å).[47] It is noteworthy that the corresponding Fe–Fe distances in the basic geometry of these trinuclear iron carbonyl complexes[48] are similarly influenced by the size of the bridging atoms. The dependence of the Fe–Fe bond lengths on the *particular ligand-bridged geometry* is also apparent in that the lengthening of the single-bond Fe–Fe distances by approximately 0.05 Å in the $(RN)_2Fe_3(CO)_9$ framework with reference to the average distance of 2.40 Å in the $[NFe(CO)_3]_2$ framework is also paralleled in the sulfur analogs; the average Fe–Fe bonding distance of 2.60 Å in the $S_2Fe_3(CO)_9$ molecule is 0.05–0.09 Å longer than those of range 2.51–2.55 Å in the common $[SFe(CO)_3]_2$ framework of the four iron carbonyl sulfur complexes given in Table VI. The considerable variation of 0.5 Å in the iron–iron distances observed in different polymeric organoiron complexes[49] has been charged to the different character of the orbitals involved in iron–iron bond formation, the effective iron charge, the iron coordination number, and steric and electronic factors imposed by the other iron-coordinated ligands. The Fe–Fe distances in the nitrogen-bridged complexes are the shortest recorded and no doubt are close to the lower limit possible for presumed single-bond distances. The determined Fe–Fe distance in iron metal is 2.48 Å.[50]

Although the considerably shorter Fe–Fe distances in these nitrogen-bridged $Fe(CO)_3$ dimers are mainly a consequence of the smaller metal to bridging atom distances, with no change in angular dimensions of the X_2Fe_2 bridging atom system in $[C_2H_5SFe(CO)_3]_2$ on replacement of the mercapto sulfur atoms with NH_2 ligands, the Fe–Fe distance would decrease from 2.54 to only 2.22 Å (*i.e.*, 2.54 Å × (1.98/2.26 Å)). It is obvious that the larger Fe–N–Fe angles are primarily responsible for counterbalancing the effect on the Fe–Fe bond length of the decreased size effect of the bridging atom.

The approximate constancy of the Fe–Fe distances and Fe–X–Fe angles for a given bridging X ligand is striking and lends credulence to the fact that the principal factors influencing the geometries of the Fe_2X_2 system in these $Fe(CO)_3$ dimers are the intrinsic properties of the bonded atoms themselves and only to a lesser extent properties of the environment of the other ligands attached to these bonded atoms. It is difficult to estimate the influence on the Fe–Fe bond strength caused by the change in Fe–Fe distances between these nitrogen- and sulfur-bridged dimers due to the indi-

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(42) Differences in coordination number of the bridging atoms (*i.e.*, the effects of one nonbonding and three bonding electron pairs for the sulfur atoms *vs.* four bonding electron pairs for the nitrogen and phosphorus atoms) as well as in the electronic and steric effects of the nonidentical coordinating ligands to the bridging atoms also prevent any rigorous interpretation of small variations in the corresponding molecular parameters.

(43) A tetrahedral-like, single-bond covalent N_{radius} value of 0.70 Å[44] was adopted in calculating an iron radius (Tables VI and VII) from the observed Fe–N distances for all four-coordinated bridging nitrogen atoms. For compound IV which possesses three-coordinated bridging nitrogen atoms, a trigonal-like single-bond value of 0.67 Å was assumed. This arbitrary shortening of 0.03 Å for the trigonal-like N_{radius} is assumed in analogous fashion to the similar decrease of 0.025–0.03 Å estimated[45] for the radius of a single-bond trigonal carbon atom compared to the radius of a single-bond tetrahedral carbon atom.

(44) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

(45) D. R. Lide, *Tetrahedron*, 17, 125 (1962); B. P. Stoicheff, *Tetrahedron*, 17, 135 (1962); O. Bastiansen and M. Traetteberg, *ibid.*, 17, 147 (1962).

(46) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 4, 493 (1965).

(47) L. F. Dahl and P. W. Sutton, *ibid.*, 2, 1067 (1963).

(48) Actually, the $S_2Fe_3(CO)_9$ molecule in $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ is a conformer of the molecular compound $Se_2Fe_3(CO)_9$ in which the only significant difference involves the relative orientation of the three carbonyl groups attached to the seven-coordinated apical iron atom. The two conformers are related to each other by a 30° rotation of the three carbonyl groups about the localized threefold axis of the apical $Fe(CO)_3$ fragment.

(49) For a recent tabulation of iron–iron distances, see M. R. Churchill, *Inorg. Chem.*, 6, 190 (1967).

(50) *Cf.* L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p S5.

Table VI. Comparison of Mean Geometrical Parameters of $[H_2NFe(CO)_3]_2$ with Those of Structurally and Electronically Equivalent Iron–Sulfur and Cobalt–Phosphorus Dimeric Systems[a,b]

	$[H_2NFe(CO)_3]_2$	$[C_2H_5SFe(CO)_3]_2$ (ref 5)	$[C_6H_5CSFe(CO)_3]_2$ (ref 31)	$[CH_3SFe_2(CO)_6]_2S$ (ref 32)	$[SFe(CO)_3]_2$ (ref 6)	$[(C_6H_5)_2PCoC_5H_5]_2$ (ref 8)
	Bond Distance, Å					
M–M	2.40 (0.6)	2.54 (1)	2.51 (0.5)	2.54 (0.5)	2.55 (0.2)	2.56 (1)
M–X	1.98 (1)	2.26 (0.7)	2.26 (0.3)	2.27 (0.4)	2.23 (0.2)	2.16 (0.4)
X–X′	2.50 (3)	2.93 (1)	2.88 (0.7)	2.81 (0.6) 2.82 (0.7)	2.01 (0.5)	2.88 (2)
$^1/_2$(M–M)	1.20	1.27	1.26	1.27	1.28	1.28
$\{(M\text{–}X)\text{–}X_{radius}\}^c$	1.28	1.22	1.22	1.23	1.19	1.06
	Angle, Degrees					
M–X–M′	74.4 (5)	68.3 (3)	67.4 (1)	68.8 (1)	69.9 (1)	72.5 (5)
X–M–X′	77.8 (6)	81.0 (3)	78.7 (1)	77.1 (1)	53.5 (1)	83.7 (5)
. . .[d]	78.1 (7)	95.2 (5)	91.8 (5)	88.0 (3) 88.5 (3)	79.8 (5)	105.1 (4)

[a] Where M represents the metal atom and X the metal-linked atom. [b] The values in parentheses are the esd's of the means for chemically equivalent molecular parameters. [c] The following X_{radius} values corresponding to Pauling's estimated single-bond tetrahedral-like covalent radii for atoms were utilized: N, 0.70 Å; S, 1.04 Å; P, 1.10 Å.[44] [d] Dihedral angle between the two planes in the X_2M_2 system each formed by the two bridging X atoms and one M atom.

Table VII. Comparison of Derived Radii of Iron(I) and Cobalt(I) with Metal–Metal Distances for the Structurally and Electronically Equivalent Iron–Nitrogen and Cobalt–Nitrogen Complexes[a]

Nitrogen-Bridged Iron Tricarbonyl Complexes

Molecule	No.	Ref	Distance, Å Fe–Fe	Fe–N	$^1/_2$(Fe–Fe)	Fe radius, Å $\{(Fe\text{–}N)\text{–}N_{radius}\}^q$
$[H_2NFe(CO)_3]_2$		This work	2.402 (6)	1.98 (1) (av)	1.20	1.28
$(C_6H_5NC_6H_4NH)Fe_2(CO)_6$	I	33, 34	2.372 (2)	2.00 (0.6) (av)	1.185	1.30
$[(p\text{-}CH_3C_6H_4)_2CNHNFe(CO)_3]_2$	II	35	2.40	1.99–2.02	1.20	1.29–1.32
$(C_8H_5NCONC_6H_5)Fe_2(CO)_6$	III	36a	2.402 (2)	1.99–2.01 (1)	1.20	1.29–1.31
		36b	2.416 (3)	2.00 (0.4) (av)	1.21	1.30
$[(p\text{-}CH_3C_6H_4)_2CNFe(CO)_3]_2$	IV	37	2.403	1.94 (av)	1.20	1.25
$(p\text{-}CH_3C_6H_4NCH_2C_6H_4)Fe_2(CO)_6$	V	33	2.43	1.95, 1.96	1.215	1.25, 1.26
$\{(C_6H_5)_2CNN\}_2Fe_3(CO)_9$	VI	38	2.43, 2.46	1.91–1.98	1.215, 1.23	1.21–1.28

Nitrogen-Bridged Cobalt Cyclopentadienyl Complexes

	No.	Ref	Distance, Å Co–Co	Co–N	$^1/_2$(Co–Co)	Fe radius, Å $\{(Co\text{–}N)\text{–}N_{radius}\}^b$
$(t\text{-}BuNCONBu\text{-}t)(CoC_5H_5)_2$	VII	39	2.37	1.95, 1.96	1.185	1.25, 1.26

[a] The values in parentheses are the esd's of the means for chemically-equivalent molecular parameters. [b] A covalent single-bond tetrahedral-like N_{radius} of 0.70 Å was used for all compounds except IV for which a value of 0.67 Å was assumed.[43]

visibility of the effects of the bridging atoms and the presumed iron–iron single-bond interaction.

Since the Fe–X bond lengths found in these dimeric complexes also are nearly the same for a given X ligand, it was assumed that these bonds can be characterized by a set of well-defined covalent radii. Covalent radii for the iron and cobalt atoms were obtained from the determined Fe–N, Fe–S, Co–N, and Co–P distances by subtraction of the presumed single-bond covalent radii of the bridging atoms.[43–45] In Tables VI and VII a comparison is made between the corresponding calculated metal radii and one-half the metal–metal distance. One point that emerges from this comparison is that the iron radii (of range 1.25–1.32 Å) derived from the Fe–N bond lengths in the nitrogen iron carbonyl dimers are invariably larger than not only the values of one-half the Fe–Fe distances (of range 1.18–1.22 Å) in these complexes but also the covalent iron radii (of spread 1.19–1.23 Å) obtained from the Fe–S bond lengths in the sulfur iron carbonyl complexes. Unlike the SR and PR_2 bridging ligands, the bridging NR_2 groups do not have energetically available d orbitals to form multiple bonds, and hence these radii differences may be interpreted in terms of the Fe–S bonds containing some π-bonding character. Corrections of additivity of covalent radii for electronegativity differences (or partial ionic character) would lead to even longer iron radii estimated from the Fe–N bond lengths. Although no obvious explanation (other than intramolecular steric repulsion effects which cause longer than normal Fe–N bond lengths) can be made for the $^1/_2$(Fe–Fe) values being less than the empirical iron radii derived from the Fe–N bond lengths, in contrast there is excellent overlap (given above) between the $^1/_2$(Fe–Fe) values in the nitrogen dimers and the iron radii obtained from the Fe–S bond lengths. These radii are also in close agreement with the reported octahedral covalent radius of 1.23 Å for Fe(II)[44] obtained from the Fe–S distance of 2.27 Å in pyrite, FeS_2. In contrast with the reasonable radii values of 1.26 Å (av) obtained from the Co–N bond lengths in $(t\text{-}BuNCONBu\text{-}t)(CoC_5H_5)_2$ (VII) and 1.19–1.23 Å obtained from the Fe–S bond lengths in the four sulfur-bridged iron carbonyl complexes (Table VI), the ridiculously small cobalt radius of only 1.06 Å calculated from the average Co–P bond length in $[(C_6H_5)_2PCoC_5H_5]_2$ confirms the earlier conclusions[8] (drawn from a direct comparison of the Co–P and Fe–S bond lengths) that considerably greater π-bonding character exists for a bridging PR_2 ligand than for a bridging SR ligand in these complexes.

Despite the shorter Fe–Fe distances and somewhat larger Fe–N–Fe bridging angles in the nitrogen-bridged iron tricarbonyl dimers, the distortion of the square-pyramidal array of nitrogen and carbonyl carbon atoms about each iron atom in $[H_2NFe(CO)_3]_2$ amazingly resembles the distortion of the pyramidally oriented sulfur and carbonyl ligands about each iron atom in the sulfur-bridged $Fe(CO)_3$ complexes. Examination of the calculated "best" least-squares basal plane through the two nitrogen and two carbon atoms of each monomeric unit of $[H_2NFe(CO)_3]_2$ (Table IVa and b) reveals that the two iron atoms are equivalently displaced by 0.33 and 0.34 Å from their respective basal planes in the direction of their apical carbonyl groups. Similar "best" plane calculations in $[C_2H_5SFe(CO)_3]_2$, $[CH_3SFe_2(CO)_6]_2S$, and $[SFe(CO)_3]_2$ show analogous displacements of range 0.32–0.38 Å for the individual iron atoms from their sulfur–carbon basal planes toward the apical carbonyl ligands. These pyramidal deformations can be attributed to strong nonbonding intramolecular apical, equatorial C···C and C···N (or C···S) repulsions which bend the equatorial ligands inward toward the other half of the molecule.

A packing diagram of the four dimeric molecules in the unit cell is shown in Figure 2. The long intermolecular distances, all greater than 3.5 Å, indicate that the separations between molecules correspond to normal van der Waals contacts.

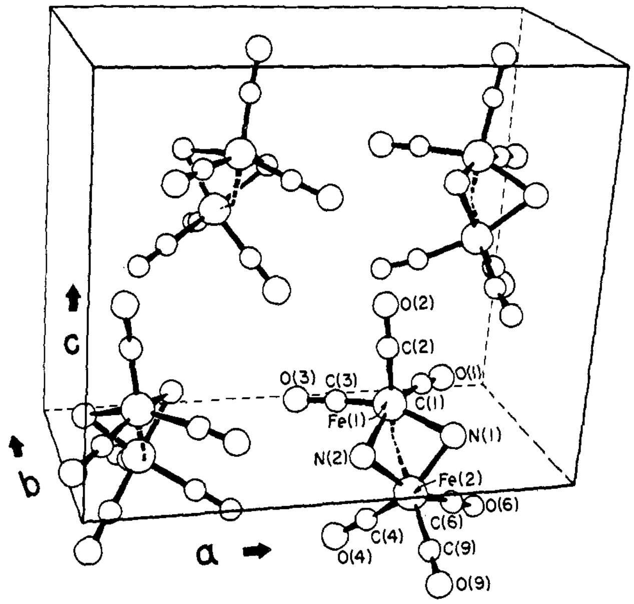

Figure 2. Packing diagram of the four $[H_2NFe(CO)_3]_2$ molecules in the orthorhombic unit cell.

Further X-ray investigations need to be done on the homologous iron carbonyl dimers containing larger sized, electronically equivalent bridging X ligands (*e.g.*, AsR_2, SeR, TeR, and I) in order to extend this appraisal concerning the stereochemical effects of different bridging atoms on the *basic* geometry of the X_2Fe_2 system containing a strong Fe–Fe bond.

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