Organometallics 1993, *12*, 1725–1741

Amination of Complexed Carbon Monoxide by *N*-Nitrosamines: Syntheses and Structures of Iron Carbonyl and Nitrosyl Complexes and Applications to Heterocyclic Synthesis

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Received November 16, 1992

Nitrosamines, R_2NNO, undergo homolytic cleavage of the N–N bond on reaction with iron carbonyls to give $Fe(CO)_2(NO)_2$ and organoiron products containing the ligands R_2N, R_2NCO, and R_2NC, formally derived from amination of complexed carbon monoxide, together with amines and ureas. The major products from dimethyl- and diethylnitrosamine are $(OC)_4Fe(\mu\text{-}CNR_2)Fe(CO)_2NO$ (**4**). The ethyl derivative has been crystallographically characterized: space group *Pbca*, $a = 13.573(5)$ Å, $b = 14.675(2)$ Å, $c = 16.313(20)$ Å, $V = 3249.3$ Å^3, $Z = 8$, $R_F = 0.057$, and $R_w = 0.061$ for 1152 reflections with $I \geq 2\sigma(I)$. These nitrosyls are thermolyzed to the bridging carbyne complexes $(OC)_3Fe(\mu\text{-}CNR_2)_2Fe(CO)_3$ (**9**) and trinuclear $[(OC)_3Fe]_3(\mu_3\text{-}CNR_2)_2$ (**21**). Other products include $(OC)_3Fe[(\mu\text{-}CNR_2)(\mu\text{-}OCNR_2)]Fe(CO)_3$ (**5**), $(OC)_3Fe[(\mu\text{-}NR_2)(\mu\text{-}OCNR_2)]Fe(CO)_3$ (**6**), and $(OC)_3Fe[(\mu\text{-}NR_2)(\mu\text{-}CNR_2)]Fe(CO)_3$ (**8**). Thermolysis of the carbene complex $(Me_2N)_2CFe(CO)_4$ gives **5**, **8**, **9**, and **21**. The major product from *N*-methyl-*N*-nitrosoaniline and $Fe_2(CO)_9$ is the ortho-metalated ferracycle $C_6H_4N(CH_3)COFe(CO)_4$ (**7**), which has been crystallographically characterized: space group $P2_1/c$, $a = 6.396(1)$ Å, $b = 10.056(2)$ Å, $c = 19.025(3)$ Å, $\beta = 95.17(1)°$, $V = 1218.7(1)$ Å^3, $Z = 4$, $R_F = 0.032$, and $R_w = 0.042$ for 2008 reflections with $I \geq 3\sigma(I)$. This ferracycle, tetracarbonyl(1-methyl-3-ferra-2-oxindole), undergoes trimethylamine *N*-oxide induced alkyne insertion to yield 3,4-disubstituted (Et–, MeO_2C–) 1-methyl-2-quinolones, while photochemically induced insertion of an alkyne gives a product where the 3,4-alkene bond has been reduced, together with the carbonylation product, *N*-methylisatin. One of two isomers of $(OC)_3Fe[(\mu\text{-}N(Me)Ph)(\mu\text{-}OCN(Me)Ph)]Fe(CO)_3$ has been structurally characterized with ψ-*anti*-Ph and ψ-*anti*-Me groups: $P2_1/n$, $a = 19.919(7)$ Å, $b = 10.122(4)$ Å, $c = 22.548(9)$ Å, $\beta = 98.90(3)°$, $V = 4491(3)$ Å^3, $Z = 8$, $R_F = 0.045$, and $R_w = 0.062$ for 4648 reflections with $I \geq 3\sigma(I)$. Thionitrites, RSNO, react with $Fe_2(CO)_9$ to give $Fe(CO)_2(NO)_2$ and Roussin's red esters $[(ON)_2Fe(SR)]_2$, with $Ni(CO)_4$ to give polymeric $[RSNiNO]_x$, with $Hg[Co(CO)_4]_2$ to give $Co(CO)_3NO$ and unstable $[CH_3SCo(NO)_2]_2$, with $Mo(CO)_6$ to give a polymeric product, with $[C_5H_5Fe(CO)_2]_2$ to give a mixture of $[C_5H_5Fe(CO)SMe]_2$ and $[MeSFe(NO)_2]_2$, and with $[C_5H_5Mo(CO)_3]_2$ to give $C_5H_5Mo(CO)_2NO$. $[PhSNiNO]_x$ reacts with C_5H_5Na to give C_5H_5NiNO, while NO reacts with $[PhSNiC_5H_5]_2$ to give $[PhSNiNO]_x$ and C_5H_5NiNO. $Fe(CO)_2(NO)_2$ is synthesized by reacting ethyl nitrite with $Fe_2(CO)_9$ and from $Fe(CO)_4I_2$ and silver nitrite.

Introduction

It is established convention that ligands are classified according to the number of electrons they may donate to a metal, or metals, in an organometallic complex.[2] Thus, NO is usually considered to be a three-electron donor in a terminal or bridging mode, while X = R_2N–, RO–, RS– may function as one-electron donors in mononuclear complexes or as three-electron donors in binuclear and polynuclear complexes. We have previously investigated intramolecular competition experiments with these three-electron ligands and shown that X is the preferred bridging ligand.[3] For example, deliberate decomposition of **1** leads to complexes **2** rather than to any of the several alternative structures, e.g. **3**. Similarly, in related reactions of carbonyl complexes of Mo, W, Mn, Fe, Ru, Rh, and Ni, competition

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(2) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds: The Transition Elements*, 3rd ed.; Chapman and Hall: London, 1968; Vol. 2.

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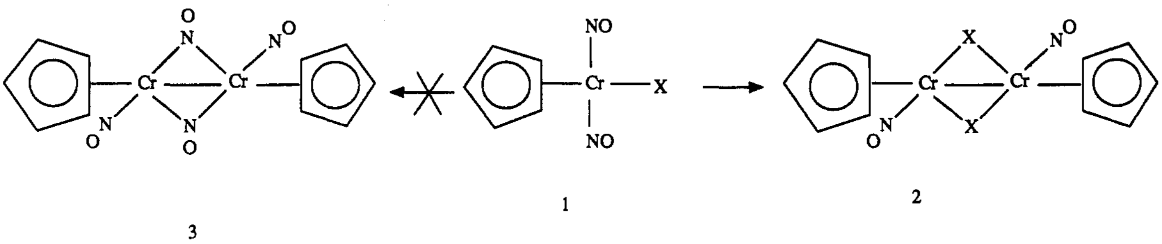
Scheme I



Scheme II

$$R_2NNO \longrightarrow R_2N\bullet + NO$$

$$RONO \longrightarrow RO\bullet + NO$$

$$RSNO \longrightarrow RS\bullet + NO$$

experiments generally produced binuclear bridging (X = SR) complexes.[4]

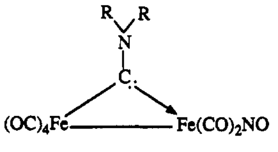
Another parallel series of investigations initiated[5] in these laboratories in the early 1960s involved the reactions between numerous different types of organo-nitrogen compounds and metal carbonyls. These yielded a wide variety of novel chemical reactions and previously unknown classes of organometallic compounds, many subsequently being structurally characterized. Thus, we were able to demonstrate that iron carbonyls can promote the cleavage of the C—N and N—N bond in diazo compounds,[5] the N=N bond in alkyl[6] and aryl azo compounds[7] and azides,[8] the N=C bond in isocyanates,[9] and the N=O bond in nitro[8] and nitroso compounds.[10] Additionally, metalation of an aromatic ring was encountered with arylimines[11] and with arylazo compounds.[7,12] This work has been developed extensively by others and is the subject of several comprehensive reviews.[13] This paper describes experiments designed to determine whether metal carbonyls could promote the homolytic cleavage of the X–NO bond of nitrosamines, nitrites, and thionitrites to produce metal nitrosyls and/or metal complexes containing the ligand X (Scheme II). While *N*-methyl-*N*-nitroso-4-toluenesulfonamide has been used quite frequently as a source of the nitrosyl ligand, there is one report[14] of diethylnitrosamine functioning as a source of a nitrosyl ligand but the fate of the diethylamino residue was not determined.

Table I. Products from Nitrosamines and $Fe_2(CO)_9$

	Me_2NNO	Et_2NNO	$PhN(Me)NO$
$Fe(CO)_2(NO)_2$	major	major	major
$(R_2NC)Fe_2(CO)_6NO$ (**4**)	major	major	trace
$(R_2NC)(R_2N)Fe_2(CO)_7$ (**5**)	some	some	nil
$(R_2N)_2Fe_2(CO)_7$ (**6**)	1 isomer	1 isomer	2–4 isomers
(R_2N minus H)$Fe(CO)_5$ (**7A**)	nil	nil	major
$(R_2NC)(R_2N)Fe_2(CO)_6$ (**8**)	trace?	trace?	nil
$(R_2NC)_2Fe_2(CO)_6$ (**9**)	artifact	artifact	nil
$(R_2NC)_2Fe_3(CO)_9$ (**21**)	artifact		

Results and Discussion

A. Reactions of Nitrosamines with Iron Carbonyls. A rich new area of chemistry was encountered when *N*-nitrosamines were reacted variously with $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$. The products resulted from the expected homolytic cleavage of the N–N bond to give NO and the radical $R_2N^\bullet$ and included organics, metal nitrosyls, and organoiron complexes possessing the bridging ligands R_2N, symmetric and asymmetric R_2NC, and R_2NCO and an aryl metalation product. The complexes $[(R_2NC)Fe_2(CO)_6NO]$ (**4**), $[(R_2NCO)(R_2NC)Fe_2(CO)_6]$ (**5**), $[(R_2NCO)(R_2N)Fe_2(CO)_6]$ (**6**), and [("R_2N minus H")$Fe(CO)_5$] (**7**) were identified from experiments using Me_2NNO, Et_2NNO, and $PhN(Me)NO$. The product range (Scheme III) from each nitrosamine is summarized in Table I.



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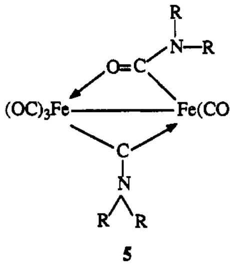

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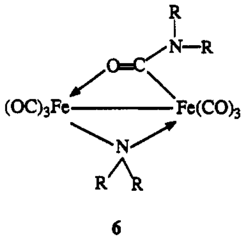

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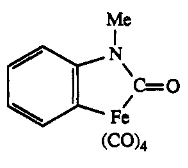

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In each case the principal product from the reaction between R_2NNO and $Fe_2(CO)_9$ was red-orange volatile $Fe(CO)_2(NO)_2$,[15] identified by IR spectroscopy and by

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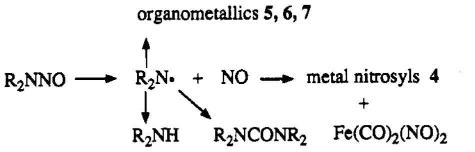
Scheme III



conversion to $(Ph_3P)_2Fe(NO)_2$[16] and $Ph_3PFe(CO)_4$.[17] This result supports the proposed homolysis of nitrosamines, since $Fe(CO)_2(NO)_2$ is also obtained when NO gas reacts with $Fe_2(CO)_9$.

The organic products from *N*-methyl-*N*-nitrosoaniline included *N*-methylaniline (42% yield), 1,3-*sym*-dimethyl-1,3-diphenylurea, and probably 1,2-dimethyl-1,2-diphenylhydrazine, while dimethylnitrosamine yielded tetramethylurea, adding support to the hypothesis of homolysis. We have previously encountered ureas and iron–urea complexes[8,9] from nitrene reactions, but we have no evidence that nitrosamines yield nitrenes.[18] Since we had already characterized some of the organometallic complexes described in this paper, we were surprised by the reports by Alper et al.[18] that pentacarbonyliron and various nitrosamines yield exclusively organic products. However, with the exception of *N*-methyl-*N*-nitrosoaniline the nitrosamines used by them were different and reaction conditions were not comparable.

Complexes 4. The principal organoiron product from the reaction between Me_2NNO and $Fe_2(CO)_9$ was diamagnetic complex 4 (R = Me), with a mass spectrometric and microanalytical formula of $C_9H_6Fe_2N_2O_7$ or $(CH_3)_2NCFe_2(CO)_6NO$. By a combination of chromatography, vacuum sublimation, and recrystallization it was isolated as air- and heat-sensitive deep maroon needles, mp 79.5 °C. IR spectroscopy revealed terminal ν(CO), terminal ν(NO), and a medium-intensity band at 1567 cm^{-1}. The mass spectrum and a singlet in the ^{13}C NMR spectrum (δ 316.16) suggested[19] that the complex contained the iron–carbyne group $Me_2NC{\equiv}Fe$, but this appeared to be inconsistent with the ^1H NMR spectrum, which exhibited a doublet CH_3 signal (δ 3.95, 3.98), and the $^{13}C\{^1H\}$ spectrum, which also showed a doublet CH_3 signal (δ 52.45, 52.79). Crystals of 4 (R = Me) were found to be twinned and unsuitable for X-ray crystallography; therefore, the corresponding ethyl derivative 4 (R = Et) was obtained from Et_2NNO and isolated as red-brown needles, mp 44 °C. The compound $(C_6H_5NCH_3)CFe_2(CO)_6NO$ was also obtained in trace quantities from the reaction of *N*-methyl-*N*-nitrosoaniline with $Fe_2(CO)_9$.

X-ray Crystal Structure of 4 (R = Et).[20] The results of a single-crystal diffraction analysis of $[(OC)_4Fe(\mu\text{-}CNEt_2)Fe(CO)_2NO]$ are presented in Figure 1 and Tables II–IV. It reveals that the molecule consists of a $CNEt_2$ unit bridging a $Fe(CO)_4$ group bonded to a $Fe(CO)_2NO$ group. The complex is thus better considered to be derived from the ylide A rather than the carbyne B. The μ-$CNEt_2$

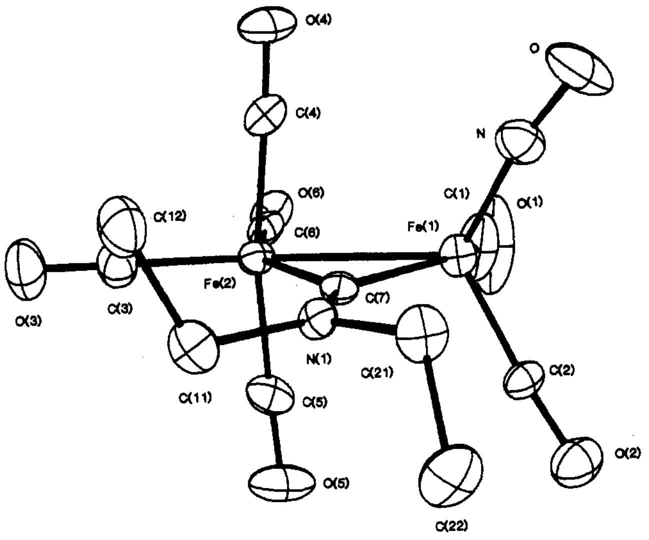


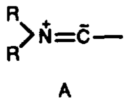
Figure 1. View of the $[(OC)_4Fe(\mu\text{-}CNEt_2)Fe(NO)(CO)_2]$ molecule (4 (R = Et)) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids enclose 50% probability levels.

Table II. Crystallographic Data for 4, 7, and 12

	4 (R = Et)	7	12
empirical formula	$C_{11}H_{10}Fe_2N_2O_7$	$C_{12}H_7FeNO_5$	$C_{21}H_{16}Fe_2N_2O_7$
fw	393.9	301.0	520.1
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/n$
a, Å	13.573(5)	6.396(1)	19.919(7)
b, Å	14.675(2)	10.056(2)	10.122(4)
c, Å	16.313(20)	19.025(3)	22.548(9)
β, deg		95.17(1)	98.90(3)
V, $Å^3$	3249(4)	1218.7(1)	4491(3)
Z	8	4	8
D_{calc}, g cm^{-3}	1.61	1.64	1.54
cryst dimens, mm	0.85 × 0.15 × 0.03	0.62 × 0.23 × 0.15	0.31 × 0.28 × 0.27
μ(Mo Kα), cm^{-1}	18.2	12.9	13.7
max θ, deg	22	27.5	26
abs factors (on *F*)	0.77–1.39	none	none
no. of unique rflns	1990	2822	8895
no. of obs rflns	1152	2008	4648
criterion for observn	$I < 2\sigma(I)$	$I < 3\sigma(I)$	$I < 3\sigma(I)$
no. of params refined	199	172	517
discrepancy factor, *R*	0.057	0.032	0.045
R_w	0.061	0.042	0.062
largest shift/esd ratio	0.08	0.03	0.05
max $\|\Delta\rho\|$, e $Å^{-3}$	1.1	0.7	1.0

Table III. Selected Bond Distances (Å) for $[(OC)_4Fe(\mu\text{-}CNEt_2)Fe(CO)_2NO]$ (4 (R = Et))

Fe(1)–Fe(2)	2.589(2)	Fe(1)–N	1.686(12)
Fe(1)–C(1)	1.766(16)	Fe(1)–C(2)	1.717(12)
Fe(1)–C(7)	1.874(11)	Fe(2)–C(3)	1.773(15)
Fe(2)–C(4)	1.814(13)	Fe(2)–C(5)	1.772(13)
Fe(2)–C(6)	1.796(13)	Fe(2)–C(7)	1.950(10)
O–N	1.171(12)	O(1)–C(1)	1.130(15)
O(2)–C(2)	1.172(12)	O(3)–C(3)	1.133(13)
O(4)–C(4)	1.107(12)	O(5)–C(5)	1.155(13)
O(6)–C(6)	1.143(13)	N(1)–C(7)	1.266(12)
N(1)–C(11)	1.463(13)	N(1)–C(21)	1.497(13)
C(11)–C(12)	1.541(17)	C(21)–C(22)	1.495(17)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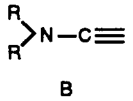
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bridging ligand completes 18-electron configurations at both metal atoms by formally donating two electrons to

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(18) Alper, H. *Organomet. Chem. Synth.* **1970**, *1*, 69. Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*, 1543. Alper proposed a possible nitrene intermediate since he found CO_2 as a reaction product between pentacarbonyliron and *N*-nitroso-*N*-phenylbenzylamine but, in contrast to this work, stated that nitric oxide was not evolved.

(19) The ^{13}C chemical shifts for carbynes R_2NC– typically fall in the range δ 310–320; see e.g.: Dalton, D. M.; Barnett, D. J.; Duggan, T. P.; Keister, J. B.; Malik, P. T.; Modi, S. P.; Shaffer, M. R.; Smesko, S. A. *Organometallics* **1985**, *4*, 1854.

(20) Inquiries concerning this structure should be addressed to K.W.M.

Table IV. Bond Angles (deg) for $[(OC)_4\overline{Fe(\mu\text{-}CNEt_2)Fe}(CO)_2(NO)]$ (4 (R = Et))

Fe(2)–Fe(1)–N	119.9(4)	Fe(2)–Fe(1)–C(1)	91.3(5)
Fe(2)–Fe(1)–C(2)	118.4(4)	Fe(2)–Fe(1)–C(7)	48.6(4)
N–Fe(1)–C(1)	106.6(8)	N–Fe(1)–C(2)	115.8(5)
N–Fe(1)–C(7)	103.3(5)	C(1)–Fe(1)–C(2)	96.3(7)
C(1)–Fe(1)–C(7)	138.7(6)	C(2)–Fe(1)–C(7)	95.6(5)
Fe(1)–Fe(2)–C(3)	155.5(5)	Fe(1)–Fe(2)–C(4)	82.6(4)
Fe(1)–Fe(2)–C(5)	87.1(5)	Fe(1)–Fe(2)–C(6)	99.8(4)
Fe(1)–Fe(2)–C(7)	46.1(4)	C(3)–Fe(2)–C(4)	93.5(6)
C(3)–Fe(2)–C(5)	94.0(6)	C(3)–Fe(2)–C(6)	104.6(6)
C(3)–Fe(2)–C(7)	109.6(5)	C(4)–Fe(2)–C(5)	168.8(6)
C(4)–Fe(2)–C(6)	92.2(6)	C(4)–Fe(2)–C(7)	85.8(5)
C(5)–Fe(2)–C(6)	93.9(6)	C(5)–Fe(2)–C(7)	83.9(5)
C(6)–Fe(2)–C(7)	145.8(5)	Fe(1)–N–O	169.5(11)
C(7)–N(1)–C(11)	124.3(9)	C(7)–N(1)–C(21)	121.0(9)
C(11)–N(1)–C(21)	114.7(9)	Fe(1)–C(1)–O(1)	177.0(17)
Fe(1)–C(2)–O(2)	174.9(10)	Fe(2)–C(3)–O(3)	179.6(17)
Fe(2)–C(4)–O(4)	176.9(12)	Fe(2)–C(5)–O(5)	177.3(12)
Fe(2)–C(6)–O(6)	179.6(13)	Fe(1)–C(7)–Fe(2)	85.2(5)
Fe(1)–C(7)–N(1)	138.5(9)	Fe(2)–C(7)–N(1)	136.2(9)
N(1)–C(11)–C(12)	112.6(10)	N(1)–C(21)–C(22)	111.4(11)

Fe(1) and one to Fe(2) (assuming the NO ligand is attached to Fe(1)). The iron carbonyl complex 9 having bridging ligand A (R = Et) was first obtained by King and Harmon[21] by reaction between $Et_2NC{\equiv}CNEt_2$ and $Fe(CO)_5$ or $Fe_3(CO)_{12}$ and has been structurally characterized by Pettersen and Cash.[22] We have also found these complexes 9 (R = Me, Et) among the reaction products from R_2NNO and $Fe_2(CO)_9$, but they are almost certainly artifacts from secondary reactions (vide infra).

Four features of the molecular structure of 4 merit discussion: the location of the single nitrosyl ligand, the bonding in the $Fe_2(\mu\text{-CNEt}_2)$ bridged diiron unit, the variation in Fe–CO bond lengths, and the Fe–Fe distance.

The conclusion that the nitrosyl is attached to Fe(1), as shown in Figure 1, is based on a consideration of bond lengths. According to a recent and authoritative survey,[23] the mean Fe–N(nitrosyl) bond length in linear Fe–NO systems (i.e. those with an Fe–N–O angle >155°) is 1.669 Å, whereas the corresponding mean for terminal Fe–C(carbonyl) bonds is 1.782 Å. With one exception the Fe–N and Fe–C(CO) distances found here are in accord with these means: the Fe(1)–N distance is 1.686(12) Å, and five of the Fe–C(CO) distances lie in the range 1.766(16)–1.814(13) Å; the exception is the Fe(1)–C(2) distance of 1.717(12) Å, which is short for an Fe–CO bond but long for an Fe–NO bond. These results are consistent with the ordered structure shown in Figure 1 if the short Fe(1)–C(2) distance is ascribed to steric and electronic factors (see below) but could also imply partial disorder of the N and C(2) sites. They are not consistent with disorder of nitrosyl over any of the other carbonyl sites on either Fe(1) or Fe(2). The structure is thus a typical, almost linear, "end-on" bonded metal nitrosyl with an Fe–N–O angle of 169.5(11)°. However, in solution the molecule exists as a mixture either of two rotamers or of two bonding isomers because two strong ν(NO) IR bands are present in petroleum ether solution (1734, 1730 cm^{-1}) and the ^1H NMR spectrum of 4 (R = Me) shows a major component (δ 2.69, 2.90) (ca. 90%) and a minor component (δ 2.86, 2.96) (ca. 10%).

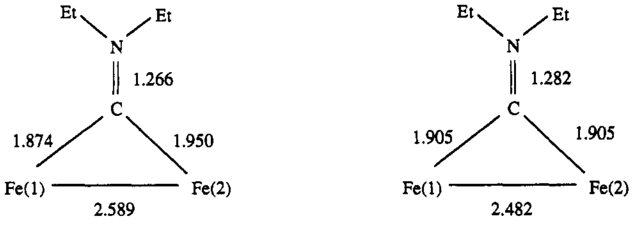

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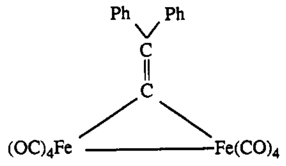
Figure 2. Comparison of bond lengths (Å) for 4 and 9[22] (R = Et).

In other $Fe_2(\mu\text{-CNR}_2)$ systems which have been structurally characterized,[22,24–27] including 9, the bridging Fe–C distances are equal, within experimental error, in each complex, though values in different complexes show some variation (from 1.85(2) to 1.927(7) Å). These Fe–C bonds are nevertheless considerably shorter than those in other bridging carbene complexes (e.g. in 10[28] the distance is 1.98(1) Å), thus reflecting the different donor–acceptor properties of the bridging ligands CNR_2 and CCR_2. In 4 the μ-$CNEt_2$ group is asymmetrically located between the iron atoms and the Fe(1)–C(7) and Fe(2)–C(7) distances, respectively 1.874(11) and 1.950(10) Å, differ significantly, with the shorter Fe–μ-$CNEt_2$ bond being that to the $Fe(CO)_2NO$ group. Also, the C(7)–N(1) bond length (1.266(12) Å) is slightly shorter than the corresponding distances of 1.279(5)–1.325(9) Å reported for other $Fe_2(\mu\text{-CNR}_2)$ systems[29] (Figure 2). Thus, in complex 4 there is a greater than unit N–C bond order (as implied in A) and consequent restricted rotation, which explains the diastereotopic R groups revealed by NMR spectroscopy. The difference in the Fe(1)–C(7) and Fe(2)–C(7) bond lengths and the relative shortness of the Fe(1)–CO bond are presumably due both to the different bonding properties of CO and NO and hence the different $d\pi_{Fe} \rightarrow p\pi^*_{CNR_2}$ back-bonding and to the greater number of π-acid ligands attached to Fe(2) compared to Fe(1). It appears that in 4 NO is perhaps functioning as a relatively good σ-donor but a poorer π-acceptor. This may be an exception to the argument developed by Jolly[30] and others, who concluded that NO was a stronger π-acceptor than CO.[31] The structure also reveals a wide variation in Fe–CO bond



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[28] Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 1282.

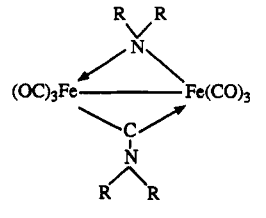
[29] For a series of μ-$CNMe_2$ carbyne complexes of osmium, Adams has shown that the C–N bond distance is very sensitive to both the nuclearity and the identity of adjacent ligands. See e.g.: Adams, R. D.; Babin, J. E. *Organometallics* **1987**, *6*, 2236; **1988**, *7*, 963, 2300.

[30] Chen, H. W.; Jolly, W. L. *Inorg. Chem.* **1978**, *18*, 2548.

[31] A description of the difficulties in assigning relative donor–acceptor properties to NO is given in a recent comprehensive review: Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293.

lengths. The shortest Fe–CO bonds are those on Fe(1), which carries the NO ligand, and furthermore the Fe–CO bond on Fe(2), trans to the Fe–Fe bond, does not show the usual shortening.[28] The Fe(1)–Fe(2) distance of 2.589(2) Å is rather longer than the Fe–Fe distances of 2.479(3)–2.565(2) Å reported for other $Fe_2(\mu\text{-}CNR_2)$ systems[22,24–27] and for $Fe_2(CO)_9$[32] but not as long as that (2.635(3) Å) in complex **10**.[28] Finally, if the necessarily irregular position of C(7) is ignored, then the coordination of Fe(1) can be viewed as trigonal bipyramidal, with Fe(2), N, and C(2) in the equatorial plane and C(1) axial. Similarly, the four CO ligands and Fe(1) occupy five vertices of a rather distorted octahedron about Fe(2).

Complexes 5. Dimethylnitrosamine and diethylnitrosamine yielded complexes **5** as the second most significant product, but we did not detect **5** among the reaction products from *N*-methyl-*N*-nitrosoaniline. Using freshly activated, neutral alumina, orange **5** eluted after red-brown **4**, but with "aged" alumina, the separation was poor and the order of elution could be reversed. The structures of the orange complexes **5** (R = Me, Et) were determined by conventional methods because we were unable to obtain good crystals of either due to solution instability. Mass spectrometry indicated the gross molecular formula $(R_2N)_2Fe_2(C)(CO)_7$. At low mass spectrometric inlet temperatures the mass spectra showed the stepwise loss of six CO groups, leaving the residue $[(R_2N)_2Fe_2(C)(CO)]^+$ as the base peak. At higher inlet temperatures the fragment $[R_2NCO]^+$ was the base peak, an observation in keeping with the work of Kaesz et al.[33] with a triruthenium complex having a bridging carbamoyl group, R_2NCO. Although the mass spectra also showed ions apparently consistent with the presence of **8**, we were able to isolate these materials subsequently and to show that these complexes were not contaminating **5**.



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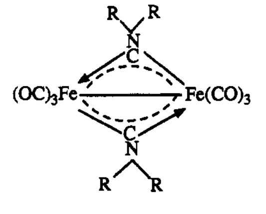
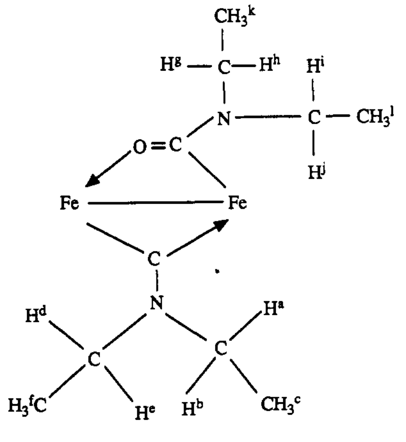


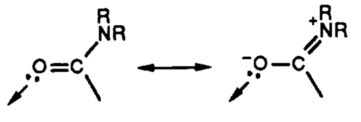
9

The ^{13}C NMR spectrum of each complex **5** revealed the presence of four different R groups and the bridging group R_2NC (R = Me, δ 328; R = Et, δ 325). The carbamoyl carbonyl, R_2NCO, exhibited a resonance signal among the metal carbonyls,[34] seven separate peaks appearing in the range δ 210.2–215.9 at 283 K. However, the structure exhibited fluxional behavior with carbonyl site exchange occurring with increasing temperature; three of the carbonyl peaks coalesce at 313 K, while there were indications (despite solution decomposition) that all six carbonyls exchange at 353 K. The ^1H NMR spectrum of the methyl complex corresponded to the ^{13}C NMR spectrum and showed four magnetically distinct methyl groups, but the striking ^1H NMR spectrum of the ethyl derivative was the most interesting feature of these complexes. Not only did it show four magnetically distinct ethyl groups but it also revealed an unprecedented situation where all eight methylene protons were diastereotopic and each appeared as an overlapping doublet of quartets with the geminal coupling $^2J_{HH}$ being 16.8 Hz and the vicinal coupling $^3J_{HH}$ being 8.4 Hz. This 250-MHz spectrum is reproduced in Figure 3 together with the related 400-MHz COSY 45 spectrum (Figure 4), which shows the proton couplings that we have used in the assignments shown in **11**. It should be noted that the assignments of H^c and H^f to the respective triplets (and hence a, b, d, and e) are arbitrary. The implication of diastereotopic methylene groups (g–j) is that there must be an element of restricted rotation about the corresponding N–C bonds and therefore the amide (carbamoyl) group C has a significant contribution from the resonance structure D. This is supported by the appearance of the weak ν(C–O) infrared peak at 1562 cm⁻¹.



11

5 (R=Et); carbonyl groups omitted



C D

Complexes 6. The three nitrosoamines Me_2NNO, Et_2NNO, and PhN(Me)NO all yielded complexes **6** as very minor products. In each case they were the least polar compounds, eluting as the first band, or bands (vide infra, PhNMe derivatives), from chromatography columns and sufficient material for characterization was obtained only after combining the products from several experiments. The methyl derivative **6** (R = Me) was a bright orange solid which melted below room temperature. This material was analyzed as $(Me_2N)_2Fe_2(CO)_7$, but the stepwise loss of six CO ligands in the mass spectrum showed that it was $(Me_2N)(Me_2NCO)Fe_2(CO)_6$. Both the ^1H and ^{13}C NMR spectra indicated the presence of four magnetically distinct methyl groups, while for the derivative **6** (R = Et) all four ethyl groups are diastereotopic and exhibited eight $-CH_2-CH_3$ complex multiplets analogous to **5** (R = Et). For both complexes **6** (R = Me, Et) the carbamoyl carbon (R_2NCO) resonance could not be distinguished from the iron carbonyl (Fe–CO) signals in the range δ 210–217 and

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[32] Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.

[33] Kaesz, H.; Szostak, R. *J. Organomet. Chem.* **1980**, *191*, 243.

[34] ^{13}C NMR carbamoyl R_2NCO resonances have been reported[33,35] in the range δ 203–239 ppm.

[35] Chisholm, M. H.; Hammon, C. E.; Huffmann, J. C. *Organometallics* **1987**, *6*, 210.

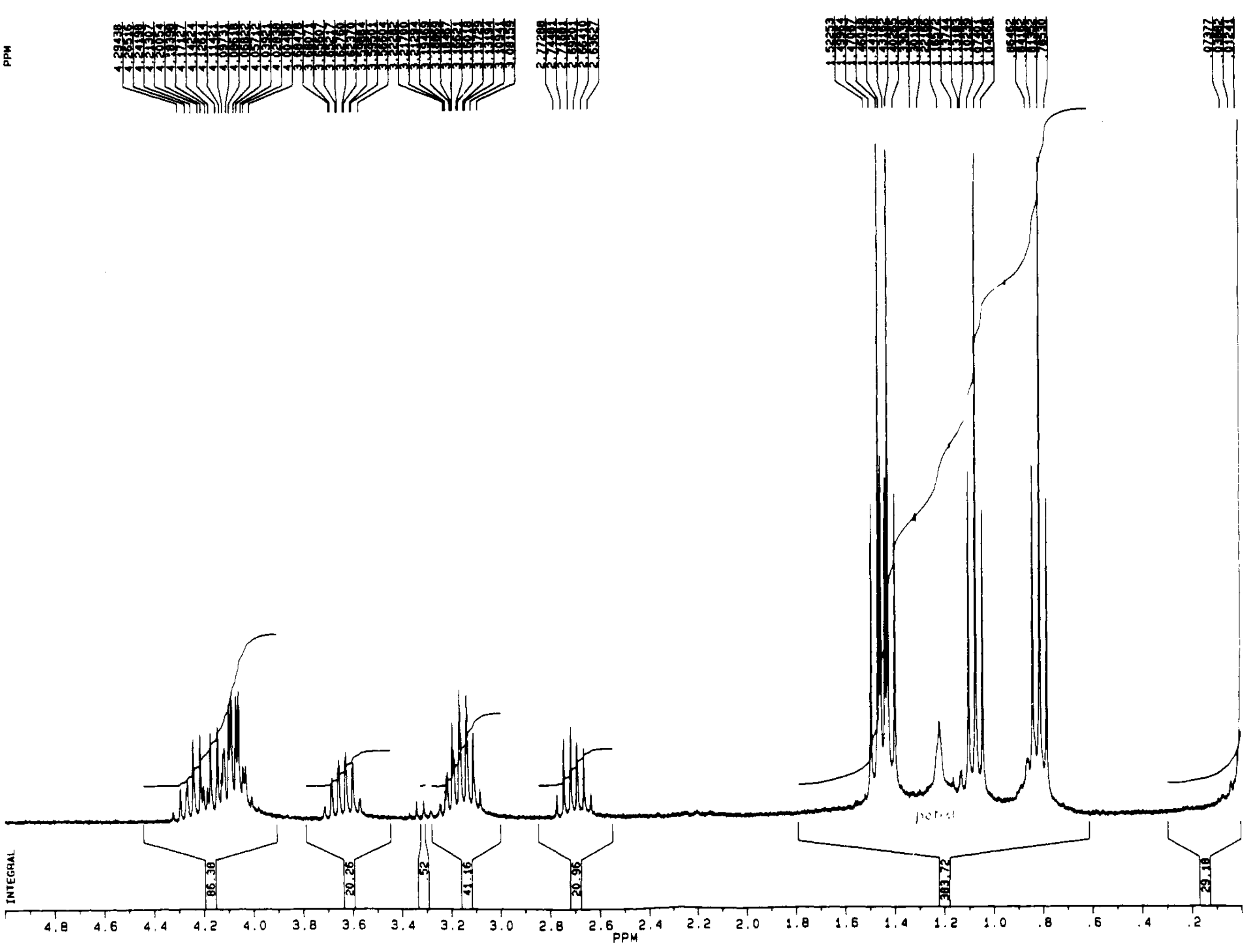

Figure 3. ^{1}H NMR spectrum of **5** (R = Et).

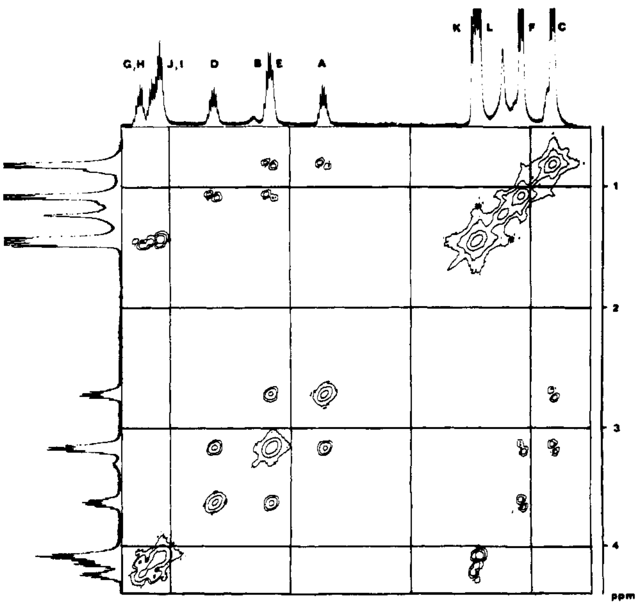

Figure 4. COSY 45 400-MHz ^{1}H NMR spectrum of **5** (R = Et).

we had insufficient material to undertake variable-temperature NMR studies of these complexes. The methyl derivative **6** was relatively unstable, and after some weeks samples which had been stored below 0 °C had decomposed partially to tetramethylurea. From the reaction between *N*-methyl-*N*-nitrosoaniline and $Fe_2(CO)_9$ two isomeric substances, $(PhNMe)_2Fe_2(CO)_7$, were obtained as red-orange crystals, mp 71–73 and 96–98 °C, while the ^{1}H and ^{13}C NMR spectra suggested the presence of at least one and probably two more isomers, which could not be separated in a pure state. As well as the expected ^{13}C NMR signals for the PhNMe residues and four signals for each complex in the region δ 206–222 for the six Fe–CO groups, the higher melting isomer had a signal at δ 169 and the lower melting isomer had a corresponding signal at δ 162. These are assigned to the carbamoyl >N—*C*═O carbons. Although these resonances show a significant shift from the values for the corresponding derivatives **6** (R = Me, Et), this is expected because of the different inductive/resonance effects of the C_6H_5 and alkyl groups, but they are still within the expected range[36] for an amide group.

An X-ray crystallographic analysis of the higher melting isomer **6** (R, R = Me, Ph) showed that it possessed the structure **12** with two $Fe(CO)_3$ units bridged by amido and carbamoyl groups. The former ligand bridges symmetrically via N, while the latter forms a bidentate bridge through C and O. An iron–iron bond completes the hexacoordinate environment about each metal atom. If the Ph(Me)N-amido group is described in terms of an *anti*-phenyl group, then we presume that the isomer with mp 71–73 °C has the structure **13** with the amido substituents reversed and possesses a *syn*-phenyl group.

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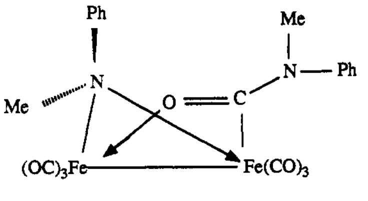
[36] *Organic Spectroscopy*, 3rd ed.; Kemp, W., Ed.; Macmillan: London, 1991. All classes of amides show a signal in the range δ 162–179 ppm.



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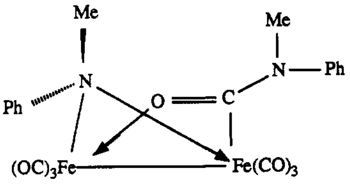

13

The crystallographic data also indicate restricted rotation about the Ph(Me)N—C=O carbamoyl bond (vide infra); thus, the possibility exists for additional isomers having *ψ-anti-* and *ψ-syn*-phenyl carbamoyl groups. We attempted to promote isomerization of these species in refluxing benzene, by analogy with other[4] isomerizations, but the complexes were thermally sensitive and largely decomposed.

X-ray Crystal Structure of 6 (R, R = Me, Ph).[37] The results of a single-crystal diffraction analysis of $(OC)_3Fe[(\mu\text{-}N(CH_3)C_6H_5)(\mu\text{-}OCN(CH_3)C_6H_5)]Fe(CO)_3$ (12) are presented in Figure 5 and Tables II, V, and VI.

The unit cell contains two crystallographically independent molecules whose structures are nearly identical, displaying only minor differences in some peripheral angles. The largest of these differences is one of 10° in the torsional angle about the N(carbamoyl)–C(phenyl) bond. In this discussion, all quoted distances and angles are values averaged over the two molecules; esd's are those of an individual measurement.

Structural details of the bridging system are much as expected for a bis(tricarbonyliron) species with a monoatomic and a diatomic bridge, where the bridging atoms are C, N, or O. Specifically, the Fe–Fe distance of 2.469(1.4) Å is of the magnitude that has been associated[38] with such a bridging arrangement. Both ligands bridge symmetrically, with mean distances Fe–N = 2.010(5) Å, Fe–C = 1.980(4) Å, and Fe–O = 1.972 (4) Å.

The closest analog to the bridging carbamoyl group in 12 is found in a bis(tricarbonyliron) dimer with Me_2NCO and $AsMe_2$ bridges reported by Vahrenkamp et al.[39] The configurations of the diatomic bridging groups in these two compounds are identical in all major respects. Specifically, the C–O and C–N distances of 1.271(6) and 1.343(7) Å, respectively, are both indicative or substantial double-bond character. This is consistent with the near-planarity of the C and N atoms (deviation from plane defined by three bonded atoms 0.015 and 0.041 Å, respectively). The Fe–O–C–Fe linkage is planar to within 0.04 Å.

Although bridging amido and dialkylamido groups are well-known in transition-metal chemistry, the only previous structurally documented example of a bis(tricarbonyliron) species with a simple NH_2 or NR_2 bridge is the dimer $[H_2NFe(CO)_3]_2$, reported by Dahl, Costello, and King in 1968.[40] Distances and angles involving the amido bridges are similar to those we observe for 12, but the

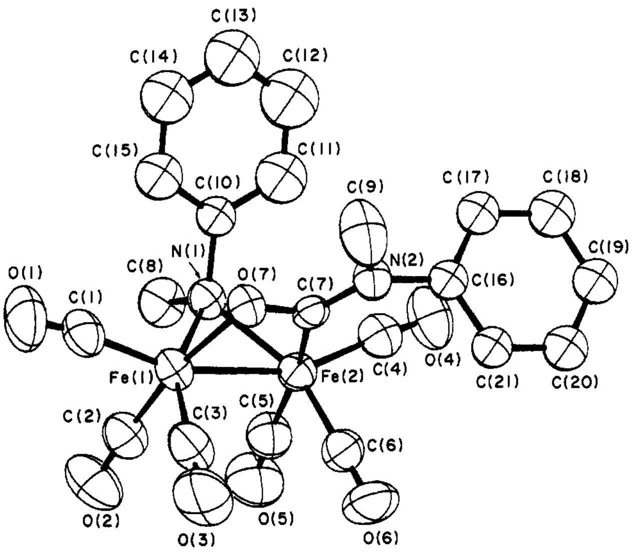

Figure 5. View of isomer 12 showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table V. Selected Bond Distances (Å) for 12

molecule 1		molecule 2	
Fe(1)–Fe(2)	2.461(1.4)	Fe(51)–Fe(52)	2.477(1.4)
Fe(1)–C(1)	1.846(8)	Fe(51)–C(51)	1.827(8)
Fe(1)–C(2)	1.775(7)	Fe(51)–C(52)	1.760(8)
Fe(1)–C(3)	1.798(8)	Fe(51)–C(53)	1.789(6)
Fe(1)–N(1)	2.007(5)	Fe(51)–N(51)	2.003(5)
Fe(1)–O(7)	1.978(4)	Fe(51)–O(57)	1.966(4)
Fe(2)–C(4)	1.815(7)	Fe(52)–C(54)	1.817(7)
Fe(2)–C(5)	1.807(7)	Fe(52)–C(55)	1.806(7)
Fe(2)–C(6)	1.767(7)	Fe(52)–C(56)	1.791(7)
Fe(2)–C(7)	1.983(5)	Fe(52)–C(57)	1.976(5)
Fe(2)–N(1)	2.015(5)	Fe(52)–N(51)	2.015(5)
C(7)–O(7)	1.276(6)	C(57)–O(57)	1.266(6)
C(7)–N(2)	1.340(7)	C(57)–N(52)	1.346(7)

Table VI. Bond Angles (deg) for 12

molecule 1		molecule 2	
C(1)–Fe(1)–C(2)	92.1(3)	C(51)–Fe(51)–C(52)	94.7(4)
C(1)–Fe(1)–C(3)	98.3(3)	C(51)–Fe(51)–C(53)	96.2(3)
C(1)–Fe(1)–N(1)	109.1(3)	C(51)–Fe(51)–N(51)	108.6(2)
C(1)–Fe(1)–O(7)	98.2(2)	C(51)–Fe(51)–O(57)	94.9(3)
C(2)–Fe(1)–C(3)	87.9(3)	C(52)–Fe(51)–C(53)	89.8(3)
C(2)–Fe(1)–O(7)	169.4(2)	C(52)–Fe(51)–O(57)	170.1(3)
C(2)–Fe(1)–N(1)	95.4(2)	C(52)–Fe(51)–N(51)	94.7(3)
C(3)–Fe(1)–O(7).	88.1(2)	C(53)–Fe(51)–O(57)	86.9(2)
C(3)–Fe(1)–N(1)	152.2(3)	C(53)–Fe(51)–N(51)	154.3(2)
N(1)–Fe(1)–O(7)	83.6(2)	N(51)–Fe(51)–O(57)	84.4(2)
C(4)–Fe(2)–C(5)	92.0(3)	C(54)–Fe(52)–C(55)	91.4(3)
C(4)–Fe(2)–C(6)	99.4(3)	C(54)–Fe(52)–C(56)	99.1(3)
C(4)–Fe(2)–C(7)	99.9(2)	C(54)–Fe(52)–C(57)	100.1(2)
C(4)–Fe(2)–N(1)	108.7(2)	C(54)–Fe(52)–N(51)	108.5(2)
C(5)–Fe(2)–C(6)	89.3(3)	C(55)–Fe(52)–C(56)	88.4(3)
C(5)–Fe(2)–C(7)	168.1(3)	C(55)–Fe(52)–C(57)	168.2(3)
C(5)–Fe(2)–N(1)	94.1(2)	C(55)–Fe(52)–N(51)	94.9(3)
C(6)–Fe(2)–C(7)	87.9(2)	C(56)–Fe(52)–C(57)	87.5(2)
C(6)–Fe(2)–N(1)	151.6(2)	C(56)–Fe(52)–N(51)	152.1(2)
C(7)–Fe(2)–N(1)	83.0(2)	C(57)–Fe(52)–N(51)	83.6(2)
O(7)–C(7)–N(2)	116.0(5)	O(57)–C(57)–N(52)	115.8(6)
Fe(2)–C(7)–O(7)	111.2(4)	Fe(52)–C(57)–O(57)	112.2(4)
Fe(2)–C(7)–N(2)	132.8(4)	Fe(52)–C(57)–N(52)	131.9(4)
Fe(1)–N(1)–Fe(2)	75.4(2)	Fe(51)–N(51)–Fe(52)	76.1(2)
Fe(1)–O(7)–C(7)	103.5(3)	Fe(51)–O(57)–C(57)	103.4(3)

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[37] Inquiries concerning this structure should be addressed to R.J.D.

[38] Gambino, O.; Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1984**, *84*, 51.

[39] Keller, E.; Trenkle, A.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 441.

[40] Dahl, L. F.; Costello, W. R.; King, R. B. *J. Am. Chem. Soc.* **1968**, *90*, 5422.

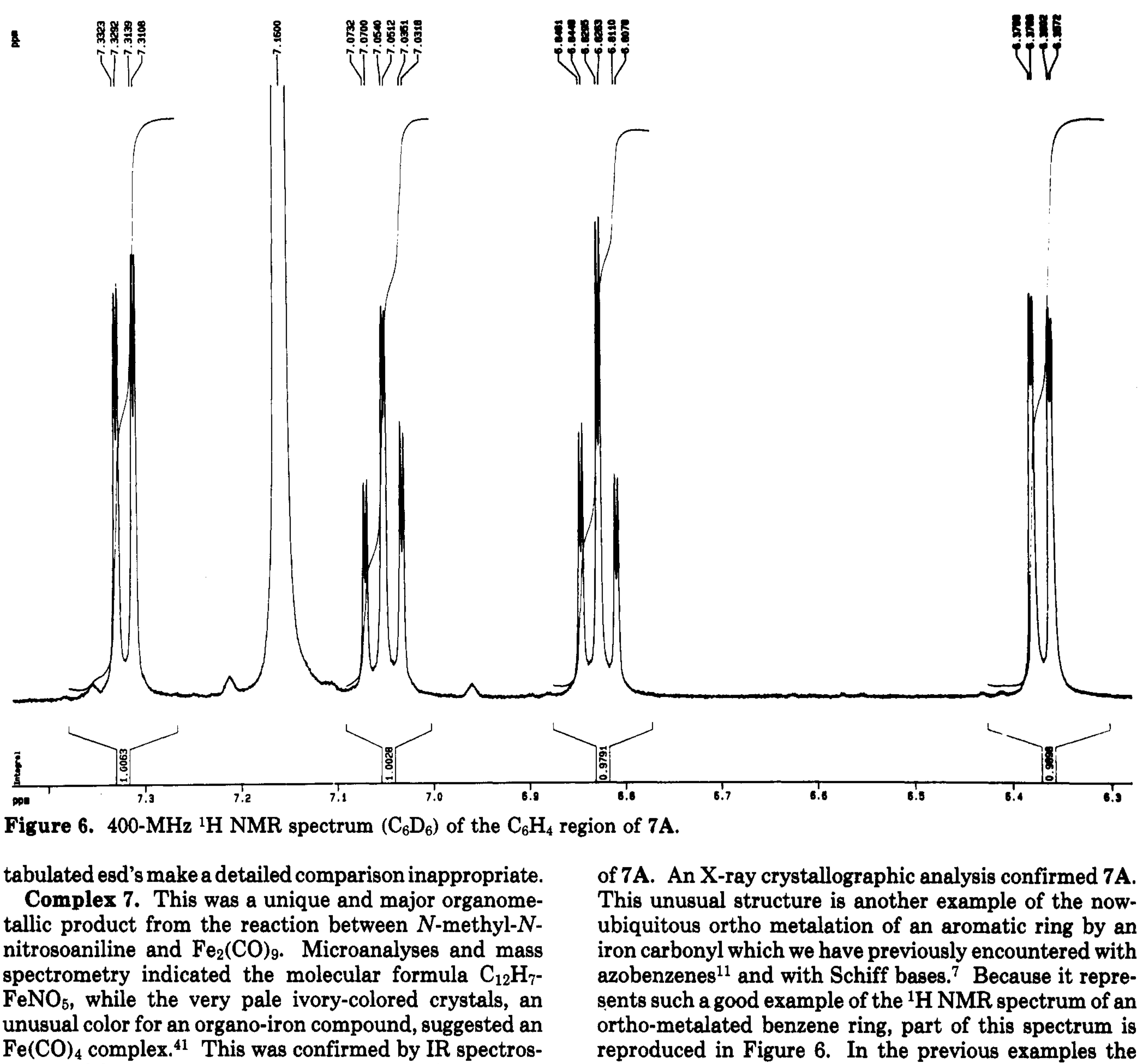
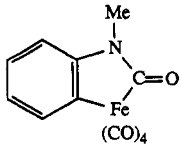


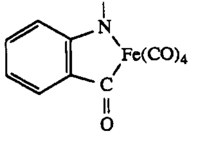
Figure 6. 400-MHz ^1H NMR spectrum (C_6D_6) of the C_6H_4 region of 7A.

tabulated esd's make a detailed comparison inappropriate.

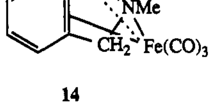
Complex 7. This was a unique and major organometallic product from the reaction between *N*-methyl-*N*-nitrosoaniline and $Fe_2(CO)_9$. Microanalyses and mass spectrometry indicated the molecular formula $C_{12}H_7FeNO_5$, while the very pale ivory-colored crystals, an unusual color for an organo-iron compound, suggested an $Fe(CO)_4$ complex.[41] This was confirmed by IR spectroscopy (ν(CO) 2190, 2062, 2042, and 2010 cm^{-1}). The ^1H NMR spectrum showed a well-resolved multiplet around δ 7, indicative of a 1,2-disubstituted C_6H_4 group, and a sharp N–CH_3 singlet. From the above data and the presence of an IR >C=O band at 1650 cm^{-1} it was not possible to differentiate unambiguously between possible structures 7A and 7B, although the mass spectrum showed an intense ion corresponding to $[CH_3NC_6H_4Fe]^+$ in favor of 7A. An X-ray crystallographic analysis confirmed 7A. This unusual structure is another example of the now-ubiquitous ortho metalation of an aromatic ring by an iron carbonyl which we have previously encountered with azobenzenes[11] and with Schiff bases.[7] Because it represents such a good example of the ^1H NMR spectrum of an ortho-metalated benzene ring, part of this spectrum is reproduced in Figure 6. In the previous examples the products were diiron (e.g. 14) or triiron complexes which we assumed had been formed via an intermediate mononuclear $Fe(CO)_4$ complex (e.g. 15) which could not be detected. In contrast, we have been unable to convert 7A into diiron species by thermal or photochemical methods, presumably because of the unfavorable geometry of the nitrogen lone pair. However, this complex appears to offer potential as an intermediate in organic synthesis (see part B below).



7A



7B



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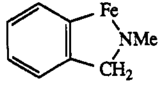

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X-ray Crystal Structure of 7A.[37] The results of a single-crystal diffraction analysis of $[\overline{C_6H_4N(CH_3)COFe}(CO)_4]$ (7A) are presented in Figure 7 and Tables I, VII and VIII. The tetracarbonyliron group is bound to the chelating ligand in a distorted-octahedral configuration. The largest distortions are reflected in the C(3)–Fe–C(4) angle of 162.69(12)° and the ring bite angle of 81.50(11)°.

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(41) The complexes $(CO)_4\overline{FeC(O)CHRCHRC}(O)$[42] ($\nu$(CO) 2111, 2056, 2052, 2028 cm^{-1}) and $(CO)_4\overline{FeCF_2CF{=}CFC}F_2$ (ν(CO) 2153, 2097, 2092, 2076, 1752 cm^{-1})[43] are colorless when pure.

(42) Case, J. R.; Clarkson, R.; Jones, E. R. H.; Whiting, M. C. *Proc. Chem. Soc., London* **1959**, 150.

(43) Hunt, R. L.; Roundhill, D. M.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 982.

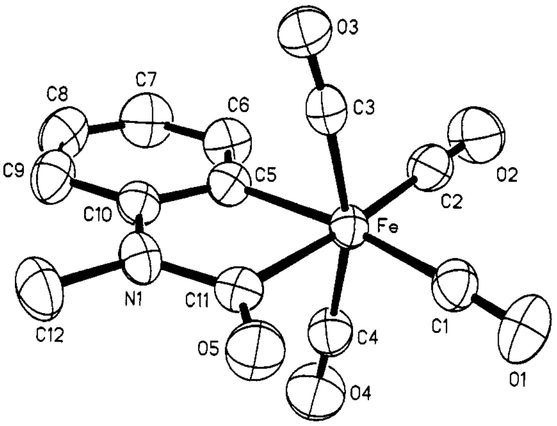


Figure 7. Molecular structure of 7. Hydrogen atoms are omitted for clarity.

Table VII. Selected Bond Distances (Å) for 7A

Fe–C(1)	1.843(3)	Fe–C(11)	2.034(3)
Fe–C(2)	1.839(3)	C(11)–O(5)	1.213(3)
Fe–C(3)	1.836(3)	C(10)–N(1)	1.406(3)
Fe–C(4)	1.801(3)	C(11)–N(1)	1.373(3)
Fe–C(5)	2.014(3)	C(12)–N(1)	1.463(3)

Table VIII. Bond Angles (deg) for 7A

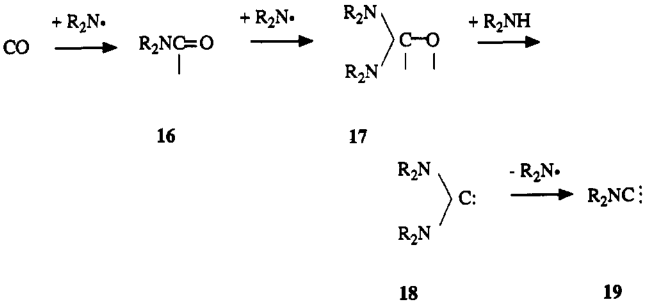
C(1)–Fe–C(2)	95.20(13)	C(4)–Fe–C(11)	86.32(12)
C(1)–Fe–C(3)	96.84(12)	C(5)–Fe–C(11)	81.50(11)
C(1)–Fe–C(4)	95.51(13)	Fe–C(5)–C(6)	128.90(23)
C(1)–Fe–C(5)	170.31(12)	Fe–C(5)–C(10)	112.69(19)
C(1)–Fe–C(11)	88.98(11)	N(1)–C(10)–C(9)	122.28(26)
C(2)–Fe–C(3)	94.62(12)	N(1)–C(10)–C(5)	115.88(23)
C(2)–Fe–C(4)	96.29(13)	O(5)–C(11)–N(1)	122.73(25)
C(2)–Fe–C(5)	94.40(12)	O(5)–C(11)–Fe	124.88(21)
C(2)–Fe–C(11)	174.83(12)	N(1)–C(11)–Fe	112.30(18)
C(3)–Fe–C(4)	162.69(12)	C(10)–N(1)–C(11)	117.08(21)
C(3)–Fe–C(5)	83.63(11)	C(10)–N(1)–C(12)	122.64(23)
C(3)–Fe–C(11)	81.83(11)	C(11)–N(1)–C(12)	120.27(24)
C(4)–Fe–C(5)	82.17(12)		

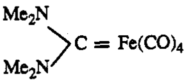
The carbon and nitrogen atoms of the chelate ring are coplanar within 0.010 Å; the iron atom is displaced from this plane by 0.167 Å. The dihedral angle of the C_3N chelate plane with that of the phenyl carbon atoms is 3.6°.

As expected, the amido nitrogen atom is planar,[44] deviating by only 0.008 Å from the plane of its three bonded atoms. The N–C(phenyl) and N–C(carbonyl) distances of 1.406(3) and 1.373(3) Å, respectively, are both indicative of the presence of some multiple-bond character; these distances are comparable to those found in related molecules where the phenyl ring and the amide linkage are nearly coplanar (e.g. acetanilide[45]).

Mechanism of Formation of Complexes. The most striking feature of this work is the diverse range of products obtained from one reaction type; in this respect it is characteristic of many free-radical reactions. We attempted to ascertain the mechanistic pathway of formation of these products and presumed that the identified products 4–7 arise from the successive attack of $R_2N^{\bullet}$ radicals on complexed CO. Thus, the first product of such a reaction would be the carbamoyl ligand 16 found in complexes 5–7. The ligand $R_2NC\vdots$ (19) is a reduced form of the carbamoyl group, and although we have been unable to demonstrate unequivocally that any complex of R_2NCO is an intermediate in generating 19, one possible mechanism involves $R_2N^{\bullet}$ radical attack on 16 to give 17, which is unobserved as a ligand because it is reduced to give carbene 18. If the reducing agent is amine, R_2NH, a product found in significant yield in each of the nitrosamine reactions, then the secondary product of this reduction could be more radical $R_2N^{\bullet}$. Loss of radical $R_2N^{\bullet}$ from carbene 18 could generate carbyne 19. Experimental support for this hypothesis was obtained by observing the thermolytic behavior of the carbene complex 20 characterized by Petz.[46] Heating 20 in refluxing benzene yielded the four products 5, 8, 9, and 21 (R = NMe_2). Assuming the initial formation of the coordinatively unsaturated intermediate 22, then dimerization and CO loss would give 9, while trimerization and CO loss would give 21. Alternative recombination processes involving both homolysis products (Scheme V) would give 5 and 8. In some respects steps in Schemes IV and V resemble a mechanism proposed by Adams et al.[47] for the conversion of $(Me_2N)_2CH_2$ into osmium complexes of the carbene ligand $Me_2NCH{:}$ and the carbyne $Me_2NC\vdots$, except that they propose a sequence of C–H bond activations as initial steps. A similar process would also account for the production of μ-$CNMe_2$ from Me_3N.[48] Complex 8 is noteworthy since it had not been positively identified among the nitrosamine products although there was spectroscopic (^{13}C NMR) evidence for its presence. Some nitrosamine reactions also yielded small quantities of 9 and 21. However, we were able to demonstrate that these were, in fact, artifacts because thermolysis of nitrosyl 4 in refluxing benzene yielded 9 and 21 as the sole products (Scheme VI) in the approximate ratio 7:4. This reaction is unusual because it involves the cleavage of the shorter, and presumably stronger, Fe(1)–C(7) bond in 4 to give 22. *N*-Methyl-*N*-nitrosoaniline reactions yielded only a trace (mass spectrometry, IR) of 4 and none of complexes 5, 8, and 9, which contain the μ-CNR_2 ligand. This could be due to steric hindrance preventing the relatively bulky $Ph(Me)N^{\bullet}$ radical attacking 16 to give 17, although differences in the ^{13}C NMR chemical shift of the carbamoyl carbon, R_2NCO, also suggest that electronic factors may be important. Finally, while Scheme IV accounts also for the occurrence of 4, it is possible that the initial step in the particular reaction is the addition of a nitrosamine across $Fe_2(CO)_9$ rather than nitrosation of some inter-

Scheme IV





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(44) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 281.

(45) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 442.

(46) Petz, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 367.

(47) Adams, R. D.; Babin, J. E. *Organometallics* **1987**, *6*, 2236; **1988**, *7*, 963.

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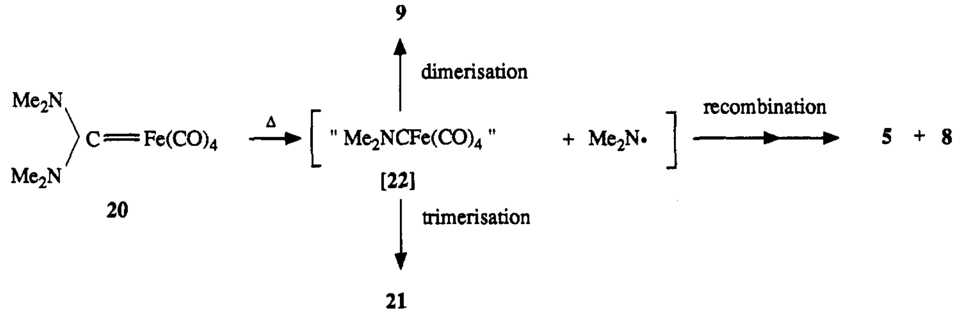
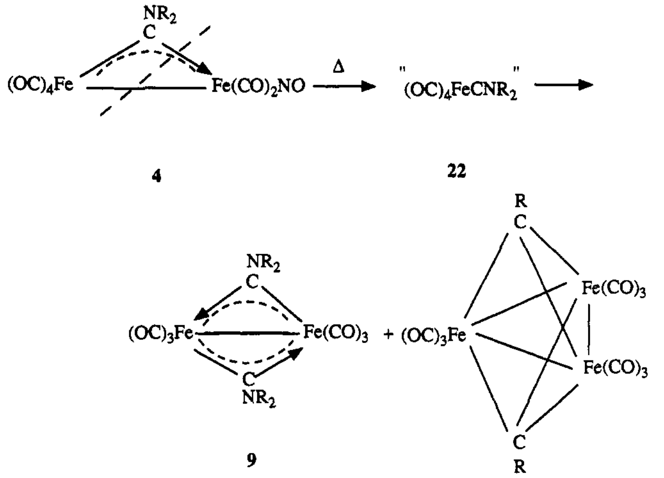
Scheme V

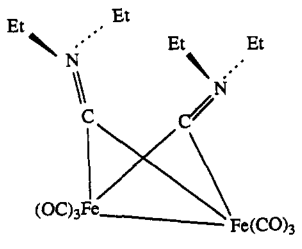


Scheme VI



mediate; low yields of the other complexes prevented any investigation of their reaction with NO.

Complexes 9 (R = Me, Et). These bright yellow compounds are thermally stable and easily purified by sublimation. Each was characterized by microanalysis, mass spectrometry, and IR and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of the methyl derivative (mp 172 °C) exhibited a single resonance at δ 2.89, while the ^{13}C NMR exhibited three signals only, corresponding to the methyl group, iron carbonyls, and tertiary carbon (δ 313.8). The properties of the known[21] ethyl derivative were similar to those reported, except that the ^{13}C NMR signal corresponding to the tertiary carbon (δ 310.3) was wrongly located previously. Also, the ^{1}H NMR spectrum shows not the reported one type of ethyl group, but two types, as would be expected from the crystallographically determined[22] geometry of the complex **9A**. Thus, the CH_2 protons are diastereotopic and exhibit the expected 12-line multiplet (an AB double doublet coupled to CH_3) shown in Figure 8.



9A

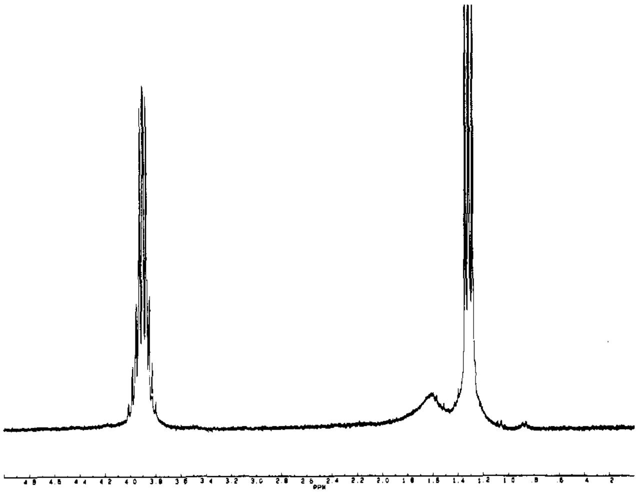


Figure 8. ^{1}H NMR spectrum of **9A** showing the 12-line multiplet for diastereotopic CH_2 groups.

Complex 8 (R = Me). The structural formula of this material, a yellow solid, was determined by a combination of mass and NMR spectrometric methods. The mass spectrum showed the expected molecular ion and fragment ions corresponding to the loss of six CO groups; while [M^+ – 5CO] was the base peak, the [M^+ – 6CO] skeleton was a prominent (82%) ion. The ^{1}H NMR spectrum showed three separate methyl signals at δ 2.19, 2.69 and 2.82 and two methyl groups exhibiting coincidence of chemical shift at δ 2.69. The ^{13}C NMR spectrum also exhibited three methyl signals together with the structurally definitive quaternary carbon signal at δ 322.4.

Complex 21 (R = NMe$_2$). Trinuclear complexes of this type have been isolated and structurally characterized previously and include R = H[49] (orange-red), R = F[49] (orange), and R = OMe[50] (red) derivatives. The dark red, beautifully crystalline derivative with R = NMe_2 was very soluble in petroleum and exhibited good solution stability. It was identified and characterized by microanalyses, mass spectrometry [M^+, $M^+ - n$CO (n = 1–9)], and IR, ^{1}H NMR (δ 2.98 s), and ^{13}C NMR (δ 52.5, CH_3; δ 212.8, CO; δ 311.8, CNR_2) spectroscopy. For other complexes of this type the μ_3-carbon exhibited a ^{13}C NMR signal in the range δ 366 (R = F) to δ 321 (R = H).

Other Reactions. Several additional reactions yielded identifiable products. Thus, photolysis of dimethylnitrosamine with $Fe(CO)_5$ yielded some $Fe(CO)_2(NO)_2$, mainly **5** (R = Me) and smaller amounts of **9** (R = Me), while refluxing dimethylnitrosamine with $Fe_3(CO)_{12}$ gave mostly **5** (R = Me) together with **6**, **8**, and **9**. The occurrence of **9** suggests that **4** was generated as an intermediate which

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[49] Lentz, D.; Michael, H. *Chem. Ber.* **1988**, *121*, 1413. Lentz, D.; Heike, M. *Chem. Ber.* **1990**, *123*, 1481.

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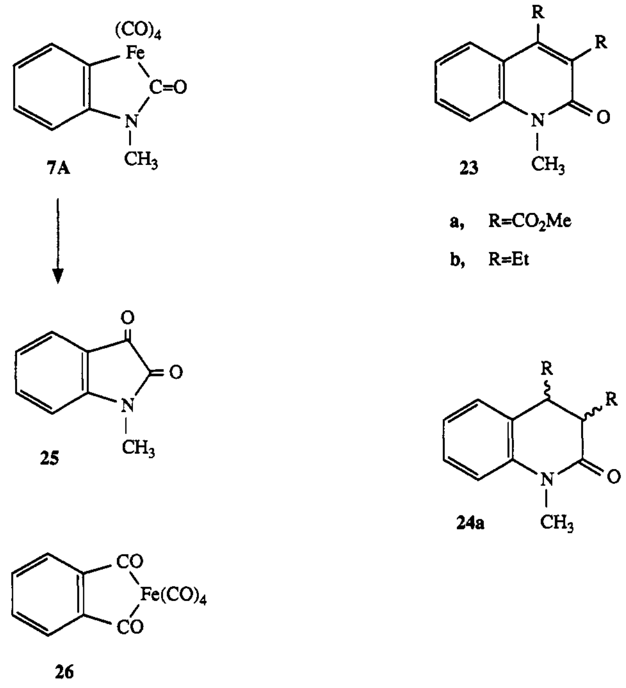
Scheme VII

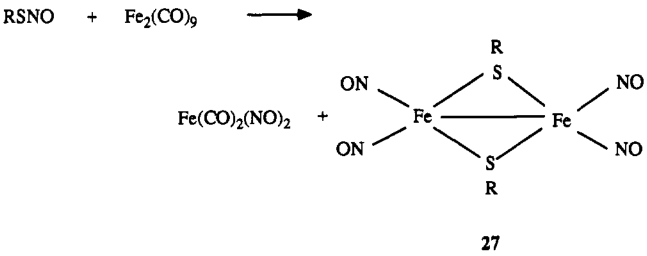


decomposed under the reaction conditions. Neither **4** (R = Et) nor **5** (R = Et) reacted further with diethylnitrosamine, but **4** (R = Et) reacted with Fe$_2$(CO)$_9$ to give **9** (R = Et).

B. Dioxindole and Quinolone Syntheses Using Ferracycle 7A. The geometry of **7A**, tetracarbonyl(1-methyl-3-ferra-2-oxindole), together with the relative accessibility of this complex, suggested that it might be a useful intermediate for heterocycle syntheses.

Some of the earliest examples of the application of transition-metal organometallics to organic synthesis involve the formation of nitrogen heterocycles by cyclocarbonylation of aromatic Schiff bases, azo compounds, oximes, and hydrazones.[51] More recently, pyridines have been generated by the CpCo(CO)$_2$-mediated cocyclization of alkynes with nitriles,[52] while alkynes with isocyanates yielded 2-pyridones.[53] In each case it is assumed[54] that an organo-cobalt intermediate[55] is involved, similar to known complexes of e.g. palladium,[56] which undergo further insertion by CO or the appropriate organic ligand. Some nonoptimized trial experiments have now shown that the organo-iron complex **7A** will undergo CO or alkyne insertion to give 2,3-dioxindoles and 2-quinolones (Scheme VII).

Scheme VIII



Complex **7A** resisted high-pressure carbonylation (90 bar, 100 °C) and reacted very slowly with dimethyl acetylenedicarboxylate in refluxing benzene, but when anhydrous trimethylamine *N*-oxide[57] was added, decarbonylation occurred rapidly at room temperature. TLC indicated the presence of a large number of products. The principal product (14%) from this reaction was the pale yellow, crystalline 2-quinolone **23a**, dimethyl 1-methyl-2-oxo-1,2-dihydroquinoline-3,4-dicarboxylate, mp 111–112 °C, identified by spectroscopic (mass, IR, ^{1}H NMR) comparison with literature values.[58] A similar product, **23b**, 1-methyl-2-oxo-3,4-diethyl-1,2-dihydroquinoline, was obtained in 18% yield from 3-hexyne.

A photochemically induced alkyne insertion into **7A** was accompanied by much decomposition to give the (*E*)- and (*Z*)-diesters **24a**, presumably formed by the in situ reduction of intermediate **23a**. A secondary product, formed by carbonyl insertion, was the orange, crystalline 1-methyl-1*H*-indole-2,3-dione (*N*-methylisatin, **25**), identified by spectroscopic comparison (mass, IR, ^{1}H NMR) with literature values.[59]

The alkyne insertions described here are similar to those resulting in 1,4-naphthoquinone syntheses from **26**,[60] but the present work is a less valuable synthetic method because of the large number of trivial byproducts.

C. Reactions of Nitrates, Nitrites, and Thionitrites with Metal Carbonyls. The reactions between alkyl thionitrites[61] and various metal carbonyl complexes were investigated briefly, but the results were unexceptional by comparison with the nitrosoamine reactions. In each case the identified products were those expected from homolytic cleavage (Scheme II).

Ethyl thionitrite reacted at room temperature with Fe$_2$(CO)$_9$ to give traces of Fe(CO)$_2$(NO)$_2$ and predominantly Roussin's[62] red ethyl ester **27** (R = Et); the latter was the sole product at 60 °C (Scheme VIII). Similarly methyl thionitrite reacted with Fe(CO)$_5$ at 80 °C to give the corresponding methyl derivative **27** (R = Me).[63] With Ni(CO)$_4$, ethyl thionitrite reacted rapidly to give the known polymeric (ethylthio)nickel nitrosyl[64] and methyl thionitrite gave the corresponding polymeric [MeSNiNO]$_n$. These complexes together with C$_5$H$_5$NiNO[65] (**28**) were also obtained by reaction between nitric oxide and [C$_5$H$_5$NiSR]$_2$[66] (**29**) (Scheme IX). Reaction between polymeric

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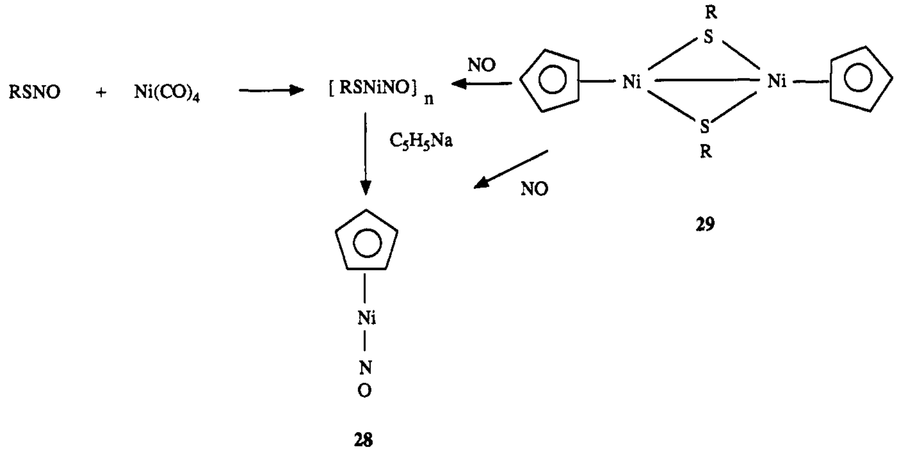
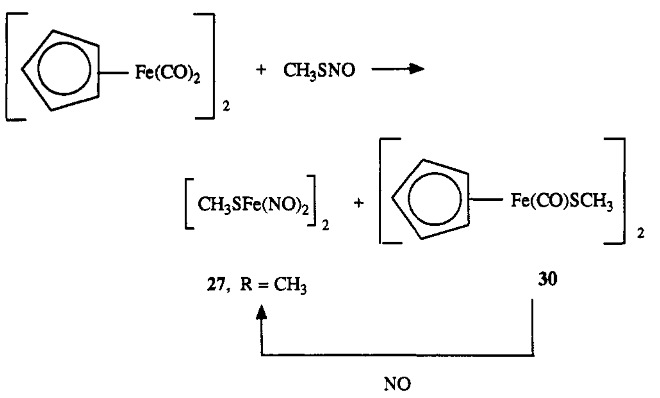
Scheme IX



Scheme X



(phenylthio)nickel nitrosyl[67] and cyclopentadienylsodium gave C_5H_5NiNO (**28**) as the only organometallic product. Methyl thionitrite also reacted smoothly with $Hg[Co(CO)_4]_2$ to give the known[68] $Co(CO)_3NO$ and a very unstable brown solid, provisionally identified as $[CH_3SCo(NO)_2]_2$ because its IR spectrum (ν(NO) 1800 s, 1760 s cm^{-1}) was very similar to those of the known[69] complexes $XCo(NO)_2$ (X = Br, SEt). A green polymeric product containing terminal nitrosyl ligands (IR ν(NO) 1770 s, 1660 s cm^{-1}) was also obtained from $Mo(CO)_6$ and may be $[(CH_3S)_2Mo(NO)_2]_n$, because the two IR peaks are in the expected region by comparison with the published[70] data for $[Mo(NO)_2Cl_2]_n$. The diiron complex $[C_5H_5Fe(CO)_2]_2$ and CH_3SNO (Scheme X) gave a mixture of $[MeSFe(NO)_2]_2$ (**27** (R = Me)) and the thermodynamically stable isomer[71] of $[C_5H_5Fe(CO)SMe]_2$ (**30**); $[MeSFe(NO)_2]_2$ was also obtained from **30** by reaction with nitric oxide. The reaction of CH_3SNO with $[C_5H_5Mo(CO)_3]_2$ was more complicated. Only the known nitrosyl $C_5H_5Mo(CO)_2NO$[72] was positively identified; the remaining blue products each exhibited two terminal nitrosyl IR frequencies but no carbonyl bands and numerous ^1H NMR methyl and cyclopentadienyl singlets. They appeared to be oligomeric and were not further investigated.

One reaction of ethyl nitrate was investigated. A very vigorous reaction ensued with $Fe_2(CO)_9$ to give the known $Fe(CO)_2(NO)_2$. Presumably a homolytic reaction occurred to give NO_2, which was reduced by carbonylation in a manner similar to the reduction of aliphatic nitro compounds.[8] Finally, it was observed that nitrite, NO_2^-, underwent a spontaneous intramolecular reduction (oxygen transfer) when $I_2Fe(CO)_4$ reacted easily with silver nitrite in anhydrous THF to give a 40% yield of $Fe(CO)_2(NO)_2$. This procedure, which is analogous to the subsequently developed use of bis(triphenylphosphine)nitrogen(1+) [PPN] nitrite,[73] does not have any preparative advantages over the conventional method.[74]

$$2AgNO_2 + I_2Fe(CO)_4 \rightarrow 2AgI + \text{“}Fe(CO)_4(NO_2)_2\text{”} \xrightarrow{-2CO_2} Fe(CO)_2(NO)_2$$

Historical Note. The work described in this paper was initiated in 1964, when we had access only to 40-MHz ^1H NMR, rudimentary mass spectroscopy, and nonautomatic X-ray crystallographic methods. Since we were unable to assign structures with any degree of confidence to most of the isolated, unstable complexes obtained in milligram quantities, the work was held in abeyance until routine ^{13}C NMR and more rapid X-ray crystallographic techniques became available to us.

Experimental Section

General Data. All experiments were conducted under an atmosphere of oxygen-free dry nitrogen. Neutral alumina was prepared by exposing active alumina to ethyl acetate for at least 10 days, washing (EtOH, H_2O), and reactivating at 150 °C for 18 h. Precoated "Polygram" silica gel (0.25 mm layer) and aluminum oxide (0.2 mm layer) TLC plates were obtained from Macherey-Nagel and Co. NMR spectra were obtained with Bruker AMX-400 and WM-250 and Perkin-Elmer R32 (90 MHz, ^1H) instruments. IR spectra were obtained with Perkin-Elmer Model 125 and 397 instruments. Mass spectra were recorded on an AEI (Kratos) MS9 mass spectrometer fitted with a Mass Spectrometry Services Solid State Console and using a GEC-905 computer system for data capture and processing.[75] Melting points were determined in sealed capillaries and are uncorrected. Pentac-

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(75) Bending, B.; Bladon, P.; Foreman, M. I.; McGregor, G.; Smith, J. Report on proceedings of 9th User Conference, MS9 and MS12 mass spectrometers, Manchester, 1973, 99.

arbonyliron (Alfa Products) was converted to enneacarbonyldiiron and dodecacarbonyltriiron by literature methods.[76] *N*-Nitrosodimethylamine, a pale yellow liquid (bp 151 °C; ^{1}H NMR (CS_2) δ 2.94 (s, 3H) 3.74 (s, 3H)), *N*-nitrosodiethylamine, a pale yellow liquid (bp 176 °C; ^{1}H NMR ($CDCl_3$) δ 1.1 (t, 3H), 1.41 (t, 3H), 3.62 (q, 2H), 4.16 (q, 2H), *J* = 8 Hz), and *N*-methyl-*N*-nitrosoaniline, a pale yellow liquid (bp 120 °C/13 Torr; ^{1}H NMR (CS_2) δ 3.29 (s, 3H), 7.3 (m, 5H); ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3H), 7.5 (m, 5H)), were prepared by textbook methods.[77] *Caution*! All operations involving the synthesis and use of these suspected carcinogenic substances were performed using gloves in a fume cupboard with an efficient extraction system. IR, ^{1}H NMR, and ^{13}C NMR data are collected in Table IX.

Reaction of *N*-Nitrosodimethylamine with Enneacarbonyldiiron. *N*-Nitrosodimethylamine (5.2 g, 5 mL, 0.07 mol) and enneacarbonyldiiron (26 g, 0.07 mol) were mixed in dry benzene (130 mL) and stirred under nitrogen at room temperature for 18 h. The mixture was filtered, the solid residue was rinsed with benzene, and the combined filtrate and washings were evaporated. Some red, volatile $Fe(CO)_2(NO)_2$ codistilled with the solvent. The residue was chromatographed on a column of neutral alumina (55 cm; B34) packed in bp 60–80 °C petroleum ether. A bright orange-red band was eluted with petroleum ether and gave a red oil (0.9 g) on evaporation. This red oil was identified as $Fe(CO)_2(NO)_2$ by IR spectroscopy[15] (ν(CO) 1831 cm^{-1}; ν(NO) 1767 cm^{-1}) and by conversion to green-black $(Ph_3P)_2Fe(NO)_2$ (mp 213 °C;[16] IR ν(NO) 1714, 1674 cm^{-1} (MeOH)) and orange-red $Ph_3PFe(CO)_4$ (mp 194 °C;[17] IR ν(CO) 2063, 1982, 1943 cm^{-1} (CS_2)).[78] Both complexes were identified further by mixed melting point and comparison of IR spectra with authentic samples.

The second band (orange-yellow) was combined with the similar band from two other experiments, rechromatographed, and evaporated to yield **6** (R = Me) as an orange oil which solidified in the freezer. MS: *m/z* 395.9349 (M^+) and $M^+ - n$CO (*n* = 1–7); base peak (100%) *m/z* 183.9155 ($M^+ -$ 6CO); calcd for $C_{11}H_{12}Fe_2N_2O_7$, M_r = 395.9343.

The third (red-brown) and fourth bands (yellow-orange) were incompletely resolved, and a quantitative separation could not be achieved. Pure **4** (R = Me) was obtained by sublimation (60 °C/0.05 Torr) followed by recrystallization to give dark red needles (petroleum ether), mp 74–75 °C. A typical experiment yielded approximately 0.87 g of pure **4** (R = Me). MS: *m/z* 365.8883 and ions corresponding to $M^+ - n$CO (*n* = 1–6) and $M^+ -$ NO; base peak $(Fe_2CNMe_2)^+$. Anal. Calcd for $C_9H_6Fe_2N_2O_7$ (M_r = 365.8874): C, 29.54; H, 1.66; N, 7.65. Found: C, 30.09; H, 1.81; N, 7.52.

The fourth band (yellow-orange) gave **5** (R = Me) as orange microcrystals, mp 129–131 °C (ether–petroleum ether, 0.17 g). MS: *m/z* 407.9339 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–7); base peak (100%) *m/z* 195.9110 ($M^+ -$ 6CO). Anal. Calcd for $C_{12}H_{12}Fe_2N_2O_7$ (M_r = 407.9343): C, 35.33; H, 2.96; N, 6.87. Found: C, 35.17; H, 2.96; N, 6.92.

Reaction of *N*-Nitrosodiethylamine and Enneacarbonyldiiron. In a typical experiment *N*-nitrosodiethylamine (6.5 g, 6.9 mL, 0.064 mol) and enneacarbonyldiiron (22.5 g, 0.062 mol) were stirred together in oxygen-free dry benzene (150 mL) at room temperature under a nitrogen atmosphere for 18 h. The solution was filtered through Kieselguhr on a glass sinter, the solvent and most of the $Fe(CO)_2(NO)_2$ were evaporated at room temperature, and the residue was chromatographed on a column (B34; 70 cm) of neutral alumina in petroleum ether (bp 60–80 °C). Five bands were developed on the column. The first band (orange-red) contained residual $Fe(CO)_2(NO)_2$ and was discarded. The second and third bands (orange) from four identical experiments were combined and rechromatographed. The second orange compound (10 mg) was identified as **6** (R = Et). MS: *m/z* 451.9977 (M^+) and $M^+ - n$CO (*n* = 1–7); calcd for $C_{15}H_{20}Fe_2N_2O_7$ M_r = 451.9969. The third band (5 mg) could not be identified. The fourth band (red-brown) yielded **4** (R = Et) as dark red needles (mp 44 °C) after recrystallization from petroleum ether (bp 40–60 °C). Yield: 0.31 g. MS: *m/z* 393.9186 (M^+) and ions corresponding to $M^+ - n$CO and $M^+ -$ NO $- n$CO (*n* = 1–6). Anal. Calcd for $C_{11}H_{10}Fe_2N_2O_7$ (M_r = 393.9187): C, 33.54; H, 2.56; N, 7.11. Found: C, 33.39; H, 2.44; N, 7.28.

After removal of solvent, the eluate from the fifth band (orange) yielded an oil (0.28 g) which was distilled (80 °C/0.05 Torr) and then crystallized from petroleum ether at −78 °C to give **5** (R = Et) as an orange solid (mp 54 °C). MS: *m/z* 463.9940 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–6); base peak *m/z* 296.0283 ($M^+ -$ 6CO) (low inlet temperature) or *m/z* 100.0763 $[(C_2H_5)_2NCO^+]$ (high inlet temperature). Anal. Calcd for $C_{16}H_{20}Fe_2N_2O_7$ (M_r = 463.9969): C, 41.41; H, 4.35; N, 6.04. Found: C, 41.43; H, 4.39; N, 6.36.

Reaction of *N*-Methyl-*N*-nitrosoaniline with Enneacarbonyldiiron. In a typical experiment *N*-methyl-*N*-nitrosoaniline (9.52 g, 8.7 mL, 0.070 mol) and enneacarbonyldiiron (26 g, 0.071 mol) were stirred under N_2 at room temperature for 60 h in dry benzene (250 mL). The reaction mixture was filtered, the residue was retained, and the filtrate was refiltered through Kieselguhr and evaporated to dryness. $Fe(CO)_2(NO)_2$ codistilled with the benzene was identified by IR spectroscopy and conversion to the triphenylphosphine derivatives described in a preceding experiment. ^{1}H NMR spectra (CS_2, C_6D_6, and $CDCl_3$), ^{13}C NMR spectra (C_6D_6, CS_2), IR spectra (liquid film, petroleum ether, $CHCl_3$), and TLC retention times were recorded on the residue after evaporation. The residue was redissolved in benzene (50 mL), and petroleum ether (bp 60–80 °C; 200 mL) was added to cause precipitation of an off-white solid which was homogeneous according to ^{1}H NMR spectroscopy. Two recrystallizations of this solid from THF/petroleum ether (bp 60–80 °C) gave very pale ivory-white rods of complex **7** (0.82 g, 8%; mp 149 °C). MS: *m/z* 300.9622 (M^+) and ions corresponding to $M^+ + 1 - n$CO and $M^+ - n$CO (*n* = 1–4); base peak (100%) *m/z* 160.9881 ($M^+ -$ 5CO). Anal. Calcd for $C_{12}H_7FeNO_5$ (M_r = 300.9673): C, 47.87; H, 2.34; N, 4.65. Found: C, 47.76; H, 2.36; N, 4.57.

The filtrate from the precipitation of **7** was concentrated and chromatographed on a column (B34, 50 cm) of neutral alumina using petroleum ether (bp 60–80 °C) as eluant. The first band (yellow-orange) gave **13** as orange-red crystals (0.23 g; mp 71–73 °C). MS: *m/z* 519.9669 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–4, 6, 7); $C_{21}H_{16}Fe_2N_2O_7$, M_r = 519.9657. The second band (yellow-orange) gave **12** as red crystals (0.072 g; mp 96–98 °C). MS: *m/z* 519.9666 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–4, 6, 7); $C_{21}H_{16}Fe_2N_2O_7$, M_r = 519.9657. The third fraction from the column consisted of an unresolved mixture of unreacted *N*-methyl-*N*-nitrosoaniline, complex **7**, which separated by crystallization, and complex **4** (R, R = Me, Ph). MS: *m/z* 399.9089 ($M^+ -$ CO) and ions corresponding to $M^+ - n$CO and $M^+ -$ NO $- n$CO (*n* = 2–6); $C_{13}H_{18}Fe_2N_2O_6$ ($M_r -$ CO) = 399.9081. Repetitive rechromatography allowed the enrichment of fractions containing pairs of ^{1}H NMR methyl signals at δ 2.31, 3.2, δ 2.82, 3.09, and δ 2.96, 3.15, but pure materials could not be isolated. The fourth fraction gave *sym*-1,3-dimethyl-1,3-diphenylurea (0.22 g; mp 101–103 °C). IR ($CHCl_3$): 1640, 1588 cm^{-1}. ^{1}H NMR (CS_2): δ 3.30 s (3H), 7.1 m (5H). MS: *m/z* 240.1251; (M^+) $C_{15}H_{16}N_2O$, M_r = 240.1262. The final fraction yielded *N*-methylaniline (3.18 g, 42%), identified by spectroscopic (IR, ^{1}H and ^{13}C NMR) comparison with an authentic sample.

Thermolytic Decomposition of 4. (a) R = Me. Freshly recrystallized **4** (R = Me) (0.67 g) was dissolved in dry, oxygen-free benzene (20 mL) and heated to reflux under N_2 for 16 h. TLC analysis indicated the presence of some (ca. 20%) unchanged starting material together with red and yellow products. The reaction mixture was filtered through Kieselguhr, and the filtrate was evaporated and chromatographed on neutral alumina (B24; 70 cm). The first band (bright red) yielded complex **21** (R = NMe_2) (150 mg) as dark red crystals (petroleum ether) which decomposed without melting. MS: *m/z* 531.8614 (M^+) and $M^+ - n$CO (*n* = 1–9). Anal. Calcd for $C_{15}H_{12}Fe_3N_2O_9$ (M_r = 531.8591): C, 33.87; H, 2.27; N, 5.27. Found: C, 33.76, 33.69; H,

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(76) Reference 74, pp 93, 95.

(77) *A Text Book of Practical Organic Chemistry*; Vogel, A. I., Ed.; Longmans Green: London, 1951.

(78) *Inorg. Synth.* **1966**, *8*, 186.

Table IX. Spectroscopic Data[i]

					^{1}H NMR, δ [J, Hz]		^{13}C NMR, δ (J, Hz)					IR, cm^{-1}			
compd	R	R	color	mp, °C	R	solvent	R	C	Fe–CO	other	solvent	Fe–CO	M–NO	other	solvent
4	Me	Me	red	79.5	2.69 s, 2.90 s	*a*	52.45 q, 52.79 q	316.16 s	209.65, 219.61		*a*	2082 s, 2050 vs, 2028–1980 br, s, 1968 s, 1954–1940 br, s, 1936 s	1735 s	1562 m	*c*
					3.95 s, 3.98 s	*b*						2078 vs, 2015 sh, 2000 vs, 1980 sh, 1935 s	1718 s	1568 m	*d*
4	Et	Et	red-brown	44	1.50 t (6H), 4.15 q (3H), 4.25 q (3H) [J = 8]	*b*	13.61 q, 57.97 t, 60.28 t	314.17 s	209.79, 219.95		*f*	2078 s, 2020 s, 2009 vs, 2000 vs, 1985 s, 1959 s	1734 s, 1730 s	*e*	*c*
5	Me	Me	orange	129–131	2.60 s, 3.04 s, 3.89 s, 3.96 s	*b*	33.27 q, 39.21 q, 51.45 q, 53.02 q	328.15 s	210.22, 213.02, 213.1, 213.56, 213.73, 214.59,[j] 215.96	*h*	*f*	2060 s, 2014 vs, 1989 vs, 1975 vs, 1958 vs, 1943 vs		*e*	*c*
					2.66 s, 3.10 s, 3.91 s, 4.00 s	*g*	34.10 q, 39.32 q, 51.59 q, 53.05 q		213.02, 213.47, 213.67, 214.67[j]	*h*	*a*				
					2.16 s, 2.66 s, 3.02 s (6H)	*a*									
5	Et	Et	orange-brown	53–54	0.63 t (3H), 0.82 t (3H), 0.95 t (6H), 2.36 m (1H), 2.82 m (1H), 3.06 m (1H), 3.53 m (4H), 3.68 m (1H) [^2J = 14.1; ^3J = 7.1]	*a*	13.72 q, 14.35 q, 14.42 q, 14.55 q, 39.54 t, 44.12 t, 57.96 t, 59.73 t	325.03	210.58, 213.78, 214.28, 214.58, 214.86, 216.67		*a*	2056 s, 2008 vs, 1987 vs, 1967 m, 1952 s, 1937 s		1539 w	*c*
					0.81 t (3H), 1.07 t (3H), 1.43 t (3H), 1.47 t (3H), 2.70 m (1H), 3.15 m (2H), 3.62 m (1H), 4.14 m (4H) [^2J = 16.8; ^3J = 8.4]	*b*									
6	Me	Me	orange	<20	2.67 s, 2.78 s, 3.09 s, 3.22 s	*b*	34.85 q, 39.46 q, 54.45 q, 67.02 q		210.95, 211.21, 213.09, 214.30, 217.42		*a*	2066 s, 2027 vs, 1990 vs, 1980 s, 1957 s			*c*
					2.14 s (3H), 2.47 s (3H), 2.91 s (6H)	*a*									
6	Et	Et	orange	*e*	0.92 t (3H), 1.15 t (3H), 1.17 t (3H), 1.36 t (3H), 2.3–3.6 m (8H)	*b*	13.28 q, 14.36 q, 14.40 q, 16.57 q, 40.02 t, 44.10 t, 50.27 t, 66.12 t		192.45 m	*h*	*b*	2059 s, 2015 vs, 1982 vs, 1972 vs, 1948 s			*c*
7			ivory white	149	2.84 s (3H), 6.36 dd (1H), 6.82 td (1H), 7.05 td (1H), 7.32 dd (1H)	*a*	29.39 q ($^1J_{CH}$ = 140), 111.53 dd, 123.93 dd, 128.02 dd, 132.06 s, 140.98 dd, 152.31 s ($^1J_{CH}$ = 151)		199.11, 202.45, 203.39	193.44 (C=O)	*a*	2190 m, 2062 s, 2042 vs, 2010 m		1655 m, 1639 m	*c*
					3.16 s (3H), ca. 7.0 m (4H)	*b*						2155 s, 2040 vs		1650 m	*d*
					3.25 s (3H), ca. 7.0 m (4H)	*g*									
8	Me	Me	yellow	*e*	2.19 s (3H), 2.69 s (6H), 2.82 s (3H)	*a*	51.06 q, 65.31 q, 67.07 q	322.44	ca. 198 m			2050 s, 2011 vs, 1986 sh, 1979 vs, 1969 s, 1962 vs, 1957 vs, 1949 s, 1938 m, 1920 m			*c*
9	Me	Me	bright yellow	172	2.89 s	*a*	51.87 q	313.80	215.15		*a*	2048 vs, 2041 sh, 2005 vs, 1999 sh, 1981 vs, 1972 sh, 1950 sh, 1946 vs, 1935 m, 1900 w		1548 m	*c*
					3.63 s	*b*									

Table IX (Continued)

9	Et	Et	bright yellow	102	1.34 t (12H), 3.89^{k} (8H) [^{3}J = 7]	*g*	13.86 qt, 57.56 tq	310.27	214.96		*g*	2048 vs, 2005 vs, 1981 vs, 1972 sh, 1946 vs, 1935 s, 1900 w	1548 m	*c*
12	Me	Ph	red	96–98	2.69 s (3H), 2.85 s (3H), 6.88–7.46 m (10H)	*a*	38.23 q, 58.61 q, 126.35–144.79		208.22, 209.40, 215.47	169.16 (C=O)	*a*	2070 s, 2029 vs, 1992 vs, 1985 s, 1972 w, 1958 m	*e*	*c*
13	Ph	Me	orange-red	71–73	2.21 s (3H), 3.11 s (3H), 6.86–8.01 m (10H)	*a*	30.68 q, 37.59 q, 123.68–145.10		206.62, 210.36, 215.94	162.47 (C=O)	*a*	2066 vs, 2026 vs, 1991 vs, 1982 vs, 1964 sh, m, 1960 m	*e*	*c*
21	Me_2N		dark red	dec	2.98 s	*a*	52.44 q	311.83	212.79		*a*	2015 vs, 2010 vs, 2007 sh, 1985 s, 1975 s, 1969 sh	*e*	*c*

[a] C_6D_6. [b] CS_2. [c] Petroleum ether. [d] $CHCl_3$. [e] Not recorded. [f] Toluene-d_8. [g] $CDCl_3$. [h] Not located; see text. [i] 283 K. [j] 328 K. [k] See Figure 8. [l] Abbreviations: qt, quartet of triplets; tq, triplet of quartets; td, triplet of doublets.

2.21, 2.11; N, 5.18, 5.04. The second band yielded unchanged starting material and was not cleanly separated from the third band (yellow), which gave **9** (R = Me) as yellow crystals (petroleum ether; mp 172 °C). MS: *m/z* 391.9394 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–3, 5, 6); base peak (100%) *m/z* 223.9716 (M^+ – 6CO). Anal. Calcd for $C_{12}H_{12}Fe_2N_2O_6$ (M_r = 391.9394): C, 36.78; H, 3.09; N, 7.15. Found: C, 36.43; H, 2.98; N, 7.08.

In a large-scale reaction **4** (R = Me) (2.5 g) was converted to **9** (R = Me) (0.576 g, 43% yield).

(b) R = Et. Complex **4** (R = Et) (0.583 g, 1.48 mmol) was dissolved in deoxygenated benzene (30 mL) and heated to reflux under a nitrogen atmosphere for 18 h. The reaction mixture was filtered through Kieselguhr, the solvent removed, and the residue chromatographed on flash silica using 15% ethyl acetate/85% petroleum ether. Fractions of 30 mL were collected and analyzed by TLC. Fractions 7 and 8 were combined and evaporated to give a brown solid (100 mg), which was subjected to fractional sublimation at 80 °C. Initially a red-brown sublimate (unchanged **4**) collected and was removed, and sublimation was continued at 100 °C/0.01 Torr to give a green/yellow sublimate (95 mg). This was recrystallized from petroleum ether to give shiny green-yellow crystals, mp 102 °C (lit. mp 103–105 °C). IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometric analyses identified the compound as **9** (R = Et). MS: *m/z* 448.0032 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–6); $C_{16}H_{20}Fe_2N_2O_6$, M_r = 448.0020.

Thermolytic Decomposition of 20. A freshly prepared sample of **20** (2 g) was dissolved in oxygen-free dry benzene (100 mL) and heated to reflux under N_2 for 24 h. The reaction mixture was filtered (Kieselguhr), evaporated, and chromatographed on a column (B24; 50 cm) of neutral alumina packed in petroleum ether. Four bands were developed. The first band (yellow) (48 mg) gave **8** (R = Me) as a yellow solid. MS: *m/z* 379.9393 (M^+) and ions corresponding to $M^+ - n$CO (*n* = 1–6); base peak (100%) *m/z* 239.9652 (M^+ – 5CO); $C_{11}H_{12}Fe_2N_2O_6$, M_r = 379.9394. The second, pink band gave **21** (R = NMe_2) (43 mg), identified by spectroscopic comparison with an authentic sample (see previous experiment). The third band (pale yellow) gave **9** (R = Me) (30 mg) as bright yellow crystals, identified by comparison with a previously characterized sample. The final band (yellow) gave orange crystals (13 mg) identified as **5** (R = Me) by spectroscopic comparison (IR, ^{1}H NMR, ^{13}C NMR, MS).

X-ray Analyses of 4,[20] 7A,[37] and 12.[37] All measurements were made with Mo Kα radiation (λ = 0.710 69 Å) using an Enraf-Nonius CAD4 diffractometer for **4** (Glasgow) and a Syntex/Nicolet $P2_1$ diffractometer for **7A** and **12** (Irvine). Details of the analyses are presented in Table II. The crystal of **4**, obtained from petroleum ether (bp 40–60 °C) at 0 °C, showed along the *c** needle axis unusually high mosaicity which adversely affected the quality of the analysis.

Similar methods were used for all three analyses. An empirical absorption correction[79] was applied to the data for **4**, and the data for both **4** and **12** were corrected to allow for decreases of 9% and 3.5% in intensity standards.

The structures of **4** and **7A** were solved by Patterson and difference Fourier methods, while that of **12** was derived by a combination of direct and heavy-atom techniques. All three structures were refined on $|F|$ by full-matrix least squares with $w = 1/\sigma^2(F)$ using anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms, except for methyl hydrogens in **12**, were included in fixed, idealized positions with C–H = 0.96 Å (**4**) or 0.95 Å (**7A** and **12**). In the case of **4** NO and CO were only distinguished at a late stage of the analysis: the nitrosyl site was fixed, primarily from bond length considerations (Fe–NO < Fe–CO), and the resulting model was refined satisfactorily.

Scattering factors and anomalous dispersion corrections were taken from ref 80. For **4** calculations were performed on a Gould

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(79) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(80) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974 (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands); Vol. IV.

3227 computer with the GX program system;[81] for **7A** and **12** the procedures followed have been described,[82] and further details are available in the Supplementary Material. Parameters of non-hydrogen atoms are presented in Tables III–VIII.

Reaction between 7A and Dimethyl Acetylenedicarboxylate. (a) With Trimethylamine *N*-Oxide. Complex **7A** (0.5 g, 1.66 mmol), dimethyl acetylenedicarboxylate (0.26 g, 1.82 mmol), and anhydrous trimethylamine *N*-oxide (0.12 g, 1.66 mmol) were dissolved in benzene (50 mL) and stirred under a nitrogen atmosphere at room temperature for 48 h. TLC revealed the presence of some unchanged starting material. The reaction mixture was filtered and evaporated and the residue subjected to flash chromatography on a silica gel column (B19; 30 cm) packed in petroleum ether (bp 60–80 °C). Fractions of 50 mL were collected using the following eluting solvents: fractions 1–19 (petroleum ether), 20–29 (20% ether–80% petroleum ether), 30–34 (50% ether–50% petroleum ether), 35–42 (ether), 43–50 (dichloromethane). After TLC analysis, fractions 30–50 were combined and rechromatographed on flash silica using 40% ethyl acetate–60% petroleum ether and then 100% ethyl acetate. The final fractions from this column yielded **23a** (70 mg, 14%): yellow crystals; mp 111–112 °C (lit.[58] 111–112 °C). MS: *m/z* 275.0795 (M^+) and ions corresponding to $M^+ - OCH_3$, ($M^+ - nCO_2CH_3$ (n = 1, 2), and $M^+ - 2CO_2CH_3 - CO$; $C_{14}H_{13}NO_5$, M_r = 275.0794. IR ($CHCl_3$): 1740–1710 s, br, 1643 cm^{-1} (lit. 1740, 1722, 1643 cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 3.76 s (NCH_3), 3.94 s (OCH_3), 4.00 s (OCH_3), 7.27–7.76 m (4H) (lit. δ 3.74 s, 3.93 s, 3.99 s, 7.28–7.89 m).

(b) By Photolysis Reaction. A solution of **7A** (75 mg, 0.249 mmol) and dimethyl acetylenedicarboxylate (39 mg, 0.274 mmol) in benzene (130 mL) was saturated with argon for 1 h and then irradiated with a broad-spectrum Hg lamp (Hanovia) for 4 h. The mixture was filtered and evaporated to a yellow gum, which was chromatographed on silica gel (B19, 25 cm) using petroleum ether then ether, collecting 10-mL fractions. The fractions eluted with 100% ether were combined and evaporated to give a pale yellow oil, identified as the mixed isomers **24a**. MS: *m/z* 277.0954 (M^+) and ions corresponding to $M^+ - OCH_3$, $M^+ - nCO_2CH_3$ (n = 1, 2), and $M^+ + 1 - 2CO_2CH_3 - CO$; $C_{14}H_{15}NO_5$, M_r = 277.0950. IR ($CHCl_3$): 1730, 1685, 1660 sh cm^{-1}. ^{1}H NMR ($CDCl_3$): isomer A, δ 2.34 m (1H, CHCO$_2$CH$_3$), 2.77 m (1H, CHCO$_2$CH$_3$), 3.40 s (3H, NCH$_3$), 3.70 s (3H, OCH$_3$), 3.76 s (3H, OCH$_3$), 7.02–7.13 m (2H, Ar), 7.25–7.39 m (2H, Ar); isomer B, δ 2.34 m, 2.77 m, 3.41 s, 3.69 s, 3.73 s, 7.02–7.39 m.

A similar experiment with **7A** (1.0 g, 3.32 mmol) and dimethyl acetylenedicarboxylate (0.52 g, 3.65 mmol) yielded a brown gum (0.79 g), which was chromatographed on silica gel. Ether (5%)–petroleum ether (95%) eluted **7A** (0.274 g, 27% recovery). Ether (50%)–petroleum ether (50%) eluted a yellow band, which was rechromatographed using ethyl acetate (20%)–petroleum ether (80%) collecting 50-mL fractions. Fractions 37–51 yielded an orange solid, *N*-methylisatin (**25**) (22 mg), which was sublimed (60 °C/0.05 Torr). MS: *m/z* 161.0476 (M^+) and ions corresponding to $M^+ - nCO$ (n = 1, 2) and $M^+ - nCO - NCH_3$; $C_9H_7NO_2$, M_r = 161.0477. IR ($CHCl_3$): 1740 s, br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.26 s (3H, NCH_3), 6.90 d (1H), 7.13 t (1H), 7.61 m (2H) (lit.[59] δ 3.30 s, 7.10–7.29 m, 7.40–7.77 m). Complexes **24a** and **25** could not be resolved adequately by column chromatography.

Reaction between 7A and 3-Hexyne. Complex **7A** (0.5 g, 1.66 mmol), anhydrous trimethylamine *N*-oxide (0.12 g, 1.66 mmol), and 3-hexyne (0.136 g, 0.189 mL, 1.66 mmol) were stirred at room temperature with the exclusion of light for 60 h. The reaction mixture was filtered, evaporated, and chromatographed on silica gel. The first 60 fractions (50 mL each) were eluted with ethyl acetate (10%)–petroleum ether (90%). After TLC analysis, fractions 45–60 were combined to give **23b** (67 mg, 18%) as a yellow oil. MS: *m/z* 216.1338 ($M^+ + 1$) and prominent ions corresponding to M^+, $M^+ - CH_3$, $M^+ - nC_2H_5$ (n = 1, 2), and $M^+ - nC_2H_5 - CO$; $C_{14}H_{17}NO$, M_r = 215.1310. IR ($CHCl_3$): 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.19 t (3H, CH_3), 1.28 t, (3H, CH_3), 2.77 q (2H, CH_2), 2.92 q (2H, CH_2), 3.74 (s (3H, NCH_3), 7.19–7.78 m (4H, Ar).

Dicarbonyldinitrosyliron. (a) From Silver Nitrite. Tetracarbonyldiiodoiron prepared by the method reported by Hieber et al.[83] (1 g, 2.37 mmol) and silver nitrite (0.71 g, 5 mmol) in acetonitrile (20 mL) were stirred for 1 h at room temperature. The reaction mixture was concentrated carefully, but an orange-red compound codistilled with the solvent, leaving a red oil residue (400 mg, 40%) identified as dicarbonyldinitrosyliron by IR spectroscopy (ν_{max} (acetonitrile): ν(NO) 1700 (s) cm^{-1}; ν(CO) 2080 (s) 2020 (m) cm^{-1}).

(b) From Ethyl Nitrate. Ethyl nitrate (9.0 mL, 0.1 mol) and enneacarbonyldiiron (36.3 g, 0.1 mol) were mixed in benzene (100 mL) under a nitrogen atmosphere and stirred overnight, after which the initial rapid gas evolution had ceased. The dark orange-red solution was filtered and evaporated cautiously to leave a red-orange oil (4.2 g, 24%) identified as dicarbonyldinitrosyliron by IR spectroscopy and by conversion to brown-black dinitrosylbis(triphenylphosphine)iron: mp 198 °C; IR (acetonitrile) ν(NO) 1700 cm^{-1}.[16]

Reactions of Methyl Thionitrite and Ethyl Thionitrite: Syntheses. Amyl nitrite (12 g, 0.10 mol) in a three-necked flask fitted with a nitrogen inlet, a $CaCl_2$ drying tube, an alcohol thermometer, and a pressure-equalized dropping funnel, was cooled in a solid CO_2 bath. Methanethiol (11 g, 0.22 mol) was added dropwise, ensuring that the reaction temperature did not rise above −20 °C; then the mixture was left for 2 h. The apparatus was disassembled, the flask was connected to a series of three traps containing respectively anhydrous $CaCl_2$, KOH, and P_4O_{10}, and methyl thionitrite was distilled through at atmospheric temperature and reduced pressure (630 Torr) into a cold trap. The red liquid product (8.5 g, 77%) was stored over $CaCl_2$ in a refrigerator and used without further purification.

Ethyl thionitrite was prepared from ethanethiol by the above method; it was also prepared by the following procedure. Aqueous solutions of nickel(II) acetate (8.2 g) and potassium hydroxide (3.7 g) were mixed, and ethanethiol (8.2 g) was added. This mixture was stirred at room temperature for 1 h; the chocolate brown precipitate of $Ni(SEt)_2$ was filtered off and dried (18 h) over P_4O_{10} in a nitrogen atmosphere. The dried solid was dissolved in THF, and dry nitric oxide gas was passed into the stirred solution for 3 h. The green precipitate was filtered off, and the red filtrate was carefully evaporated. The residual red liquid, ethyl thionitrite, was distilled at 19 °C/95 Torr: yield 3 g (37%).

With Enneacarbonyldiiron. Ethyl thionitrite (3 g, 32.3 mmol) and enneacarbonyldiiron (1 g, 2.7 mmol) in benzene (50 mL) were heated for 4 h at 60 °C. The cooled brown reaction mixture was filtered and evaporated and the residue chromatographed on neutral alumina. A dark brown band was developed by petroleum ether (bp 30–40 °C) and eluted with ether to give black crystalline **bis(μ-ethylthio)bis(dinitrosyliron) (27 (R = Et))** (0.4 g, 40%): mp 78 °C (lit.[84] mp 78 °C, mixed mp 78 °C); IR ($CHCl_3$) ν(NO) 1780 (s), 1740 (s) cm^{-1}.

With Pentacarbonyliron. Methyl thionitrite (3 g, 32 mmol) and pentacarbonyliron (1.6 g, 2 mL, 8.2 mmol) in benzene (20 mL) were refluxed for 3 h. The dark brown reaction mixture was cooled and filtered and the solvent evaporated. The residue was chromatographed on neutral alumina using petroleum ether–ether (50:50) to give a brown band which yielded a black crystalline solid (0.81 g, 52%), identified as **bis(μ-methylthio)bis(dinitrosyliron) (27 (R = Me))** by comparison of IR spectra, melting points, and mixed melting points with those of an authentic

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sample[85] (mp 94 °C; IR ($CHCl_3$) ν(NO) 1778 (s), 1752 (s) cm^{-1}; ^1H NMR δ 3.8 (s)).

With Tetracarbonylnickel. Methyl thionitrite (3 g, 32 mmol) and tetracarbonylnickel (1.5 g, 8 mmol) in benzene (50 mL) were stirred at room temperature for 1 h. A green precipitate formed immediately. The mixture was heated to 70 °C for 1 h, cooled, and evaporated to leave green **poly((μ-methylthio)-nitrosylnickel)** (2 g, 60%): IR ν(NO) 1760 (s) cm^{-1} (Nujol) (cf. $(EtSNiNO)_x$ ν(NO) 1760 cm^{-1} (KBr)).[86]

With Bis(tetracarbonylcobalt)mercury. Methyl thionitrite (3 g, 32 mmol) and bis(tetracarbonylcobalt)mercury (1 g, 2 mmol) in benzene (50 mL) were stirred at room temperature for 16 h while the color of the reaction mixture changed to purple. The mixture was filtered and evaporated. A red compound which codistilled with the solvent was identified as **tricarbonylnitrosylcobalt** (IR ν(CO) 2100 (s), 2033 (vs) cm^{-1}; ν(NO) 1805 (s) cm^{-1}), which was converted into dicarbonylnitrosyl(triphenylphosphine)cobalt (mp 75 °C (lit.[68] mp 74–76 °C)). The residue from the evaporation was chromatographed on neutral alumina. A brown band eluted with ether gave a very unstable brown solid (IR ($CHCl_3$) ν(NO) 1800 (s), 1760 (s) cm^{-1}) which decomposed rapidly. This was tentatively identified as bis(μ-methylthio)-bis(dinitrosylcobalt) analogous to the known halogen and ethylthio compounds $[(NO)_2CoX]_2$.

With Hexacarbonylmolybdenum. Methyl thionitrite (4 g, 36 mmol) and hexacarbonylmolybdenum (1.5 g, 5.5 mmol) in benzene (50 mL) were refluxed together for 8 h. The reaction mixture changed to blue-green. The solution was filtered, leaving a black solid (1 g) which did not melt (IR (KCl) ν(NO) 1770 (s), 1660 (s) cm^{-1}). The blue filtrate was evaporated, and the unreacted hexacarbonylmolybdenum was sublimed from the residue to leave an insoluble nonmelting green powder (IR (KCl) ν(NO) 1770 (s), 1660 (s) cm^{-1}).

With $[C_5H_5Fe(CO)_2]_2$. Methyl thionitrite (3 g, 32 mmol) and $[C_5H_5Fe(CO)_2]_2$ (1 g, 2.8 mmol) in benzene were refluxed for 6 h. The reaction mixture was filtered, evaporated, and chromatographed on neutral alumina using petroleum ether (bp 40–60 °C) to yield three bands. The first band (brown) gave black crystalline **bis(μ-methylthio)bis(dinitrosyliron) (27 (R = Me))** (400 mg, 40%): mp 94 °C; IR ($CHCl_3$) ν(NO) 1774 (s), 1750 (s) cm^{-1}. The second band was unreacted starting material, and the third band gave the stable isomer[4] of **bis(μ-methylthio)bis-(carbonylcyclopentadienyliron) (30)** (70 mg): IR ($CHCl_3$) ν(CO) 1960 cm^{-1}.

With $[C_5H_5Mo(CO)_3]_2$. Methyl thionitrite (18 g, 233 mmol) and $[C_5H_5Mo(CO)_3]_2$ (5 g, 10 mmol) in benzene (100 mL) were refluxed for 18 h. The mixture was cooled, filtered, and evaporated, and the blue-violet residue was chromatographed on air-deactivated (21 h) alumina. The first, orange band eluted with petroleum ether (bp 30–40 °C) gave orange **$C_5H_5Mo(CO)_2NO$** (0.5 g, 10%): mp 85 °C; IR ($CHCl_3$) ν(CO) 2020, 1950 cm^{-1}, ν(NO) 1680 cm^{-1} (lit.[72] mp 86 °C; IR ν(CO) 2015, 1940 cm^{-1}, ν(NO) 1678 cm^{-1}). A trace yellow band (($CHCl_3$) ν(NO) 1620 (s), 1580 (s), cm^{-1}) was followed by a series of blue bands eluted with ether–dichloromethane. The first blue band gave an unidentified blue solid: mp 100 °C; IR (KCl) ν(NO) 1630, 1570 cm^{-1}; ^1H NMR δ 1.60 (s), 2.35 (s), 2.41 (s), 2.70 (s), 2.80 (s), 3.16 (s), 5.45 (s), 5.64 (s), 5.69 (s), 5.70 (s), 5.90 (s). Anal. Found: C, 27.10; H, 3.38; N, 5.06; S, 10.75. The second blue band gave a blue solid: mp >350 °C dec; IR (KCl) ν(NO) 1655, 1550 cm^{-1}; ^1H NMR δ 1.70 (s), 2.81 (s), 3.30 (s), 6.00 (s). Anal. Found: C, 12.5; H, 3.31; N, 3.62; S, 14.84. The violet zone at the top of the column was extracted (Soxhlet) with dichloromethane to give a violet solid: mp >350 °C dec; IR (KCl) ν(NO) 1630 cm^{-1}; ^1H NMR δ 1.95 (s), 2.57 (s), 2.92 (s), 3.30 (s), 5.95 (s). Anal. Found: C, 28.29; H, 3.71; N, 6.20; S, 13.65.

Reaction of Nitric Oxide with Bis(μ-phenylthio)bis-(cyclopentadienylnickel) (29, R = Ph).[66,87] Dry nitric oxide gas was bubbled through a stirred solution of bis(μ-phenylthio)-bis(cyclopentadienylnickel) (29 (R = Ph)) (3 g, 6.4 mmol) in THF (200 mL) for 90 min. The black solution rapidly became green. The solvent was evaporated to leave a dark green residue, which was extracted with pentane (100 mL). An orange solution and a green insoluble solid were obtained. Chromatography of the orange solution on neutral alumina gave **cyclopentadienylnickel nitrosyl (28)** as an orange oil (935 mg, 49%) identified by comparison (IR, ^1H NMR) with an authentic sample and diphenyl disulfide (610 mg, 87.5%) as white crystals with mp 60 °C (undepressed on mixture with an authentic sample). The green insoluble compound (1.24 g, 51%) was shown to be **poly-((phenylthio)nickel nitrosyl)** by IR spectroscopic comparison with an authentic sample.[86,88]

Reaction of (Phenylthio)nickel Nitrosyl with Cyclopentadienylsodium.[87] A suspension of (phenylthio)nickel nitrosyl (1.2 g) in THF (50 mL) was added to a solution of cyclopentadienylsodium (200 mmol) in THF (50 mL). The stirred mixture rapidly became brown. After 30 min the mixture was filtered and evaporated and the residue chromatographed on neutral alumina to give **cyclopentadienylnickel nitrosyl (28)** (720 mg, 75%) as the only organometallic product.

Reaction of Nitric Oxide with Bis(μ-methylthio)bis-(carbonylcyclopentadienyliron) (30).[87] Dry nitric oxide gas was bubbled through a solution of the stable isomer of $[C_5H_5Fe(CO)SMe]_2$ (1.54 g, 3.9 mmol) in THF (70 mL) heated to reflux for 6 h. The solvent was evaporated, and the residue was chromatographed on neutral alumina to yield **bis(μ-methylthio)-bis(dinitrosyliron) (27 (R = Me))** (460 mg, 69%) as brown crystals (mp 94 °C) and unchanged starting material (730 mg, 47% recovery).

Acknowledgment. We are indebted to Dr. P. Dennison for recording much of the NMR data. This work was supported by instrument grants from the SERC (K.W.M.) and financial assistance from the University of Glasgow (K.W.M.). We thank Professor P. L. Pauson for many helpful discussions of this work.

Supplementary Material Available: Tables of additional experimental details for the structure determination, hydrogen atom parameters, atomic displacement parameters, atomic coordinates, and equivalent isotropic displacement parameters for 4, 7A, and 12 and of interatomic distances and bond angles for 7A and 12 (25 pages). Ordering information is given on any current masthead page.

OM920724M

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