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Iron Carbonyl Complexes of 2-(Phenylazo)pyridines. The First Example of a Six-Electron, Bridging 2-(Phenylazo)pyridine Ligand

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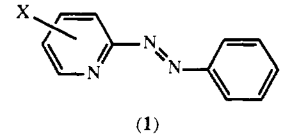
2-(Phenylazo)pyridines (**1a–c**) react with $Fe_2(CO)_9$ in THF to produce two major products, red brown $Fe(CO)_3(L\text{-}L')$ (**2a–c**) and green $Fe_2(CO)_2(L\text{-}L')_3$ (**3a–c**), where L-L′ = **1a–c**. A minor product with **3c** is the lavender nitrene-capped complex $Fe_3(CO)_9(\mu_3\text{-}N(C_6H_5))(\mu_3\text{-}N(2\text{-}(5\text{-}CF_3C_5H_4N)))$ (**4c**). **3a** also is obtained from the reaction of $Fe(\mathbf{1a})_3(PF_6)_2$ and $Na_2Fe(CO)_4$ in THF. Hence, it is proposed that the first step in the formation of **3** from $Fe_2(CO)_9$ and **1** involves the disproportionation reaction $Fe_2(CO)_9 + 3\,\mathbf{1} \rightarrow Fe(\mathbf{1})_3^{2+} + Fe(CO)_4^{2-} + 5CO$. When **3c** is chromatographed, it decomposes in part to 2-(2-phenylhydrazino)-5-(trifluoromethyl)pyridine, $(5\text{-}CF_3C_5H_3N)NHNHC_6H_5$, in which the azo bond in **1c** has been reduced to a hydrazine. Comparison of the infrared and visible spectra of **2** with those of analogous complexes of α-diimines indicates that the 2-PAP ligands are substantially better π acceptors than the α-diimines and that there is extensive mixing of the metal and ligand orbitals in the LUMO/HOMO orbitals of **2**. ^1H, ^{13}C, and ^{19}F NMR data show that the three 2-PAP ligands in **3** are inequivalent. The diiron complex **3b** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.904$ (2) Å, $b = 19.069$ (4) Å, $c = 18.606$ (2) Å, $\beta = 101.82$ (2)°, $V = 3439.4$ (15) Å^3, and $Z = 4$. The two iron atoms are in different environments. One iron atom occupies an approximate octahedral environment that consists of three pyridine nitrogen atoms and three azo nitrogen atoms from three $4\text{-}CH_3\text{-}2\text{-}PAP$ (**1b**) ligands. The second iron atom occupies a severely distorted octahedral environment that consists of two carbon monoxide carbon atoms and the four azo nitrogen atoms from two of the $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands. Two of the $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands bridge the two iron atoms with their azo linkages and serve as six-electron donors overall, while the other $4\text{-}CH_3\text{-}2\text{-}PAP$ ligand acts as a conventional nonbridging four-electron donor. The azo bond lengths of the bridging ligands are comparable to those of an N–N single bond.

Introduction

Chelating ligands with nitrogen donor atoms have been extensively used in studies of metal coordination chemistry. Among the most studied of such ligands are the α-diimines, which have in common the N=C—C=N bonding arrangement.[1,2] Recently, we, and others, have reported on the use of 2-(phenylazo)pyridine, 2-PAP (**1a**),



(1)

a, X = H; b, X = 4-CH_3; c, X = 5-CF_3

as a ligand.[3-7] In this molecule one of the imine groups of the α-diimine structure has been replaced by an azo group, thereby creating an α-azoimine structural unit. As a consequence of this structural change, 2-PAP is both a poorer σ-donor and a better π-acceptor ligand than α-diimines and is better able to stabilize complexes of metals in their lower oxidation states. This effect is evident both for metal ions[4-7] and for zerovalent metals.[3] Thus, in our studies with the group 6 metals 2-PAP readily replaced all six COs in $M(CO)_6$ (M = Cr, Mo, W) to produce air-stable zerovalent $M(2\text{-}PAP)_3$, whereas the corresponding 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) complexes are extremely air-sensitive compounds that cannot be synthesized by the direct replacement of the COs in $M(CO)_6$.

In this paper we report the results of the reactions of several 2-(phenylazo)pyridines with iron carbonyls. One reason for this study was to explore the generality of the ability of 2-PAP to stabilize zerovalent metal complexes. While metal ions of several different families have been studied with 2-PAP, the group 6 metals are the only family for which zerovalent complexes have been reported. A second interest in the iron studies was to determine whether 2-PAP would coordinate in a mode other than as a chelating four-electron σ donor, the mode found to date in all known complexes of 2-PAP. Iron is particularly well-suited to address the latter question because of the variety of iron/α-diimine complexes that are known.[2b,8-11]

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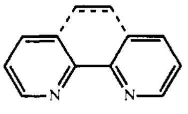
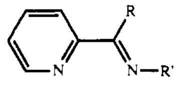
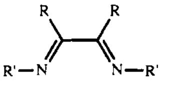
The mode of coordination of α-diimines with zerovalent iron (and other metals) depends significantly on whether both (type A), one (type B), or neither (type C) of the imine linkages is part of an aromatic ring. Principal examples of type A are the widely used ligands bpy and phen. When the C=N linkage is part of an aromatic ring, it coordinates only through the nitrogen lone pair as a two-electron donor, but when it is not part of an aromatic ring, the C=N π electrons may also take part in coordination and the imine can serve as either a two- or a four-electron donor. Thus, when they coordinate in a chelating manner, type A α-diimines act only as a four-electron donor, type B may act as either a four- or six-electron donor, and type C may act as a four-, six-, or eight-electron donor. For iron all structures are known except the eight-electron donor mode for type C, although this mode is known for ruthenium.[2] Since 2-PAP structurally is most similar to the type B α-diimines, a six-electron bonding mode seemed a reasonable possibility. We report herein that such a mode has indeed been found but in a structure that is entirely different from any yet observed in the iron/α-diimine system.



type A



type B



type C

Replacement of both imine groups of an α-diimine by nitrogen atoms generates a 1,4-tetraazadiene, RN=N—N=NR. Although 1,4-tetraazadienes are unknown in the free state, they are found as ligands in a number of transition metal compounds.[12] The only examples of iron compounds are of the type $((CH_3)_2N_4)Fe(CO)_{3-n}L_n$ (n = 0–3; L = phosphine, phosphite) with N-1,N-4 chelation of the iron by the 1,4-dimethyltetraazadiene.[13] Since $Fe(CO)_3$(α-diimine) compounds are known[8-11] and since we report herein the synthesis of complexes of the type $(2\text{-PAP})Fe(CO)_3$, comparisons of some of the properties of this set of three ligands, which are related by successive replacement of imine groups by nitrogen atoms, also can be made.

Experimental Section

General Procedures. All reactions were carried out under a dry and oxygen-free atmosphere of nitrogen using standard Schlenk techniques or a drybox. Solvents were distilled under nitrogen. Hexanes were distilled from calcium hydride, dichloromethane was distilled from P_4O_{10}, and tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Chromatography was done on a Florisil column slurry-packed with petroleum ether.

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer Model 1760 FTIR instrument. Melting points were taken on a Köfler hot-stage microscope and are uncorrected. ^1H and ^{13}C NMR spectra were obtained on an IBM/Bruker NR200 instrument at 200 and 50.3 MHz, respectively. The ^{19}F spectra were obtained at 188.3 MHz, and shifts are referenced to an external sample of $CFCl_3$ in $CDCl_3$. In the assignments that follow the primed atoms (C or H) refer to the phenyl ring of the (phenylazo)pyridine ligands. Generally, samples for NMR work were run in sealed tubes prepared on a vacuum line with $CDCl_3$ that had been dried over P_4O_{10} and degassed by several freeze/thaw cycles. CD_2Cl_2 was treated similarly. Ultraviolet–visible spectra were recorded on a Cary 17 spectrometer.

Unless otherwise specified, chemicals were obtained from commercial sources and used as received. 2-(Phenylazo)pyridine (2-PAP, **1a**) and 4-methyl-2-(phenylazo)pyridine ($4\text{-}CH_3\text{-}2\text{-PAP}$, **1b**) were synthesized as described in the literature.[14]

Preparation of 5-(Trifluoromethyl)-2-(phenylazo)pyridine ($5\text{-}CF_3\text{-}2\text{-PAP}$, 1c). The synthesis of $5\text{-}CF_3\text{-}2\text{-PAP}$ followed that described for 2-PAP, using 5.0 g of 5-(trifluoromethyl)-2-pyridinamine and 3.5 g of nitrosobenzene as reactants.[14] However, instead of chromatography of the crude product on alumina, it was recrystallized directly from hexanes. The yield was 5.8 g (23 mmol, 75%), mp 85–86 °C. Anal. Calcd for $C_{12}H_8F_3N_3$: C, 57.38; H, 3.21; N, 16.73. Found: C, 57.29; H, 3.24; N, 16.72. ^1H NMR ($CDCl_3$, δ): 8.98 (m, 1 H, H6), 8.12 (dd, 1 H, H4), 8.0–8.1 (m, 2 H, H2' and H6'), 7.88 (dd, 1 H, H3), 7.5–7.6 (m, 3 H, H3', H4', and H5'). ^{13}C NMR ($CDCl_3$, δ): 162.6 (C2), 152.1 (C1'), 146.6 (qt, $^3J_{CF}$ = 4.0 Hz, C6), 135.7 (qt, $^3J_{CF}$ = 3.4 Hz, C4), 132.9 (C4'), 129.2 (C3' and C5'), 127.5 (qt, $^2J_{CF}$ = 33.4 Hz, C5), 123.8 (C2' and C6'), 123.1 (qt, $^1J_{CF}$ = 272.5 Hz, CF_3), 114.4 (C3).

Synthesis of $Fe(CO)_3(L\text{-}L')$ (2) and $Fe_2(CO)_2(2\text{-PAP})_3$ (3). A mixture of 4.4 mmol of $Fe_2(CO)_9$ and 4.2 mmol of **1** was stirred overnight in 60 mL of THF at room temperature, and then the solvent was removed under vacuum. The red-brown solid was treated with 10–15 mL of hexanes to dissolve the red $Fe(CO)_3(L\text{-}L')$ product, and the solution was passed through a 2- × 5-cm column of Celite. This process was repeated until the color of the wash solution changed from red to light green. The combined washings were reduced in volume under vacuum and cooled to −78 °C. When crystallization was complete, the remaining solution was removed and the crystals were washed several times with cold hexanes. Finally, the crystals were dried by pumping under vacuum while the sample was allowed to warm slowly to ambient temperature. The yield of $Fe(CO)_3(2\text{-PAP})$ (**2a**) was 22%, mp 61–63 °C. Anal. Calcd for $C_{14}H_9FeN_3O_3$: C, 52.04; H, 2.81; N, 13.00. Found: C, 51.59; H, 3.01; N, 12.94. ^1H NMR ($CDCl_3$, δ): 9.06 (d, 1 H, H6), 8.01 (d, 1 H, H3), 7.6–7.7 (m, 2 H, H2' and H6'), 7.53 (ddd, 1 H, H4), 7.4–7.5 (m, 3 H, H3', H4', and H5'), 6.90 (ddd, 1 H, H5). ^{13}C NMR ($CDCl_3$, δ): 210.6 (CO), 161.1 and 160.5 (C2 and C1'), 151.5 (C6), 132.7 (C4), 128.5 (C3' and C5'), 127.5 (C4'), 123.7 (C2' and C6'), 121.6 (C3), 114.9 (C5). The yield of $Fe(CO)_3(4\text{-}CH_3\text{-}2\text{-PAP})$ (**2b**) was 43%, mp 98–99 °C. Anal. Calcd for $C_{15}H_{11}FeN_3O_3$: C, 53.44; H, 3.29; N, 12.46. Found: C, 53.60; H, 3.30; N, 12.39. ^1H NMR ($CDCl_3$, δ): 8.90 (d, 1 H, H6), 7.82 (s, 1 H, H3), 7.5–7.7 (m, 2 H, H2' and H6'), 7.3–7.4 (m, 3 H, H3', H4', and H5'), 6.75 (dd, 1 H, H5), 2.42 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 210.8 (CO), 161.5 and 160.5 (C2 and C1'), 150.6 (C6), 144.3 (C4), 128.4 (C3' and C5'), 127.4 (C4'), 123.6 (C2' and C6'), 120.8 (C3), 117.3 (C5), 20.9 (CH_3). The yield of $Fe(CO)_3(5\text{-}CF_3\text{-}2\text{-PAP})$ (**2c**) was 51%, mp 101 °C. Anal. Calcd for $C_{15}H_8F_3FeN_3O_3$: C, 46.07; H, 2.06; N, 10.74. Found: C, 46.18; H, 2.11; N, 10.81. ^1H NMR ($CDCl_3$, δ): 9.26 (s, 1 H, H6), 8.01 (m, 1 H, H3), 7.62 (d, 1 H, H4), 7.6–7.7 (m, 2 H, H2' and H6'), 7.4–7.5 (m, 3 H, H3', H4', and H5'). ^{13}C NMR ($CDCl_3$, δ): 209.4 (CO), 160.4 (C2 and C1'), 144.9 (qt, $^3J_{CF}$ = 4.0 Hz, C6), 128.7 (C4), 128.6 (C3' and C5'), 128.0 (C4'), 123.6 (C2' and C6'), 123.6 (qt, $^1J_{CF}$ = 269.5 Hz, CF_3), 121.3 (C3), 117.8 (qt, $^2J_{CF}$ = 33.5 Hz, C5). Because $Fe(CO)_3(2\text{-PAP})$ does not crystallize well, the yield is relatively low. If, instead, the hexanes are removed and the residual solid is sublimed at 55–60 °C and 10^{-3} Torr, an improved yield of 46% is obtained.

The dark green solid remaining after the hexanes treatment was taken up in CH_2Cl_2, and the solution was filtered through the same Celite column. To the filtrate was added 2–3 times its volume of hexanes, and the volume of the mixture was reduced under vacuum, during which the more volatile CH_2Cl_2 was

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preferentially removed and green crystals precipitated. When crystallization was essentially complete, as judged by the light green color of the solution, the remaining solvent was removed by cannula. The crystals were washed several times with hexanes and then dried under vacuum. Crystals always included some incorporation of CH_2Cl_2, which was evident in the ^1H NMR spectrum as well as in the elemental analysis. The yield of $Fe_2(CO)_2(2\text{-PAP})_3\cdot{}^1/_8CH_2Cl_2$ (**3a**$\cdot{}^1/_8CH_2Cl_2$) was 10%. Anal. Calcd: C, 57.95; H, 3.77; N, 17.32. Found: C, 57.63; H, 3.93; N, 17.21. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1969 s, 1899 m. ^{13}C NMR ($CDCl_3$, δ): 212.3, 211.1, 178.6, 177.2, 168.4, 160.5, 159.7, 159.0, 149.5, 147.9, 147.3, 146.2, 137.9, 137.1, 136.9, 129.3, 128.5, 128.3, 128.2, 127.3, 127.0, 123.2, 123.0, 122.6, 121.9, 120.8, 120.2, 120.0, 119.6, 117.4, 114.7, 114.5, 114.4, 114.2. The yield of $Fe_2(CO)_2(4\text{-}CH_3\text{-}2\text{-PAP})_3\cdot{}^1/_8CH_2Cl_2$ (**3b**$\cdot{}^1/_8CH_2Cl_2$) was 43%. Anal. Calcd: C, 59.47; H, 4.35; N, 16.37. Found: C, 59.41; H, 4.37; N, 16.31. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1966 s, 1897 m. ^{13}C NMR ($CDCl_3$, δ): 212.6, 211.3, 178.5, 177.1, 168.4, 160.9, 160.0, 159.2, 149.5, 148.9, 148.7, 148.6, 147.1, 146.6, 129.2, 128.4, 128.2, 128.1, 127.1, 126.9, 123.3, 123.2, 122.7, 122.6, 120.5, 120.3, 119.9, 119.8, 117.5, 116.9, 116.5, 114.3, 114.0, 21.3, 21.0, 20.8.

In the case of $5\text{-}CF_3\text{-}2\text{-PAP}$ the diiron product obtained did not give a satisfactory elemental analysis. Using cyclohexane in place of hexanes in the workup gave a better defined product but with some cyclohexane incorporation, which was verified in the ^1H NMR spectrum as well as by analysis. The yield of $Fe_2(CO)_2(5\text{-}CF_3\text{-}2\text{-PAP})_3\cdot{}^1/_2C_6H_{12}$ (**3c**$\cdot{}^1/_2C_6H_{12}$) was 18%. Anal. Calcd: C, 51.12; H, 3.14; N, 13.08. Found: C, 51.80; H, 3.25; N, 13.00. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1984 s, 1919 m. ^{13}C NMR ($CDCl_3$, δ): 210.8, 209.3, 180.1, 178.2, 169.7, 159.8, 158.6, 157.6, 145.7 (m), 134.7 (m), 133.8 (m), 129.8, 129.6, 128.8, 128.5, 127.4, 124.5, 123.2, 123.1, 121.8, 120.4, 119.8, 118.8, 118.3, 116.5, 114.6, 114.4. Low solubility prevented confident detection of some of the carbon signals that are split by coupling to the CF_3 fluorine atoms.

All of the diiron compounds show gradual decomposition and loss of color in the 150–160 °C range.

Reduction of $5\text{-}CF_3\text{-}2\text{-PAP}$ to the Hydrazine. A mixture of 2.00 mmol of $Fe_2(CO)_9$ and 2.00 mmol of **1c** was stirred 18 h in 100 mL of THF at room temperature, and then the solvent was removed under vacuum. The residue was applied to a 2.5- × 45-cm chromatography column using a minimum amount of a CH_2Cl_2/petroleum ether mixture. Elution provided four bands: (1) a small quantity of green $Fe_3(CO)_{12}$ with petroleum ether; (2) a red band of **2c** with 1:3 CH_2Cl_2/petroleum ether; (3) a yellow band of unreacted **1c** with 3:2 CH_2Cl_2/petroleum ether; (4) a green band with pure CH_2Cl_2. Removal of solvent from the second band gave a 45% yield of analytically pure **2c**.

The fourth band was shown by ^1H NMR spectroscopy of the green solid left after solvent removal to be impure **3c**. Further attempts at purification by repeated chromatography gradually resulted in the formation of a mixture of green and white solids. The white solid was sublimed at 60–70 °C and was recrystallized from CH_2Cl_2/hexanes. The yield was 136 mg of 2-(2-phenylhydrazino)-5-(trifluoromethyl)pyridine, $(5\text{-}CF_3C_5H_3N)NHNHC_6H_5$, mp 115–117 °C. Anal. Calcd for $C_{12}H_{10}F_3N_3$: C, 56.91; H, 3.98; N, 16.59. Found: C, 57.20; H, 4.00; N, 16.77. ^1H NMR ($CDCl_3$, δ): 8.38 (s, 1 H, H6), 7.67 (d, 1 H, H4), 7.20–7.30 (m, 2 H, H2′ and H6′), 6.8–7.0 (m, 4 H, H3, H3′, H4′, and H5′), 6.67 (s, br, 1 H, NH), 5.84 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, δ): 162.4 (C1), 147.2 (C1′), 145.8 (qt, $^3J_{C-F}$ = 4.5 Hz, C6), 135.3 (qt, $^3J_{C-F}$ = 3.5 Hz, C4), 129.4 (C3′ and C5′), 124.1 (qt, $^1J_{C-F}$ = 271 Hz, CF_3), 120.9 (C4′), 117.8 (qt, $^2J_{C-F}$ = 33 Hz, C5), 112.4 (C2′ and C6′), 105.3 (C3). NMR solutions left in air gradually oxidized to give the spectrum of $5\text{-}CF_3\text{-}2\text{-PAP}$.

Chromatography of the mixtures from the 2-PAP and $4\text{-}CH_3\text{-}2\text{-PAP}$ reactions is less satisfactory. Although the red band of **2a** or **2b** can be eluted, decomposition is evident by the development of a blue-green color on the Florisil as the band traverses the column. However, the product that is collected after solvent removal is analytically pure and is obtained in yields of 30–40%. Both green compounds **3a** and **3b** decompose entirely on the column, but no reduced ligand could be found in the eluent.

Synthesis of $Fe_3(CO)_9(\mu_3\text{-}NC_6H_5)(\mu_3\text{-}N(2\text{-}(5\text{-}CF_3C_5H_4N)))$ (4c). A mixture of 4.35 mmol of $Fe_2(CO)_9$ and 1.35 mmol of **1c** was stirred in 100 mL of THF at room temperature and the reaction monitored by infrared spectroscopy until the carbonyl band at 2070 cm^{-1} was judged to have reached its maximum (about 1.5 h). The solvent was removed, and the solid residue was chromatographed on a 2- × 40-cm column. Six bands were observed. Green $Fe_3(CO)_{12}$ was eluted with petroleum ether as was the second, lavender band. Next a 1:19 CH_2Cl_2/petroleum ether solvent mixture provided a yellow band, which yielded too little material to characterize. The remaining three bands of red **2c**, yellow **1c**, and green **3c** were eluted as described above. Because the lavender product was present in such low yield, the material from several runs was combined, rechromatographed, and crystallized from hexanes at −78 °C. The yield of **4c** is 51 mg (0.076 mmol, 0.9% based on **1c**); decomposition occurs gradually above ~110 °C. Anal. Calcd for $C_{21}H_8F_3Fe_3N_3O_9$: C, 37.60; H, 1.20; N, 6.26. Found: C, 37.55; H, 1.20; N, 6.16. IR (hexane, cm^{-1}): ν(CO) 2089 vw, 2059 vs, 2040 vs, 2019 vs, 2007 m, 2000 vw, 1983 m, 1974 mw. ^1H NMR ($CDCl_3$, δ): 8.42 (s, 1 H, H6), 7.72 (dd, 1 H, H4), 7.2–6.9 (m, 6 H, H3 and C_6H_5). ^{13}C ($CDCl_3$, δ): 211.9, 209.0, 202.6, 201.9 (CO), 178.8 (C2), 169.0 (C1′), 144.8 (qt, $^3J_{C-F}$ = 3.5 Hz, C6), 134.6 (qt, $^3J_{C-F}$ = 3.5 Hz, C4), 128.4 (C3′ and C5′), 125.5 (C4′), 123.4 (qt, $^1J_{C-F}$ = 270 Hz, CF_3), 122.8 (qt, $^2J_{C-F}$ = 33 Hz, C5), 122.7 (C2′ and C6′), 115.8 (C3).

Synthesis of $Fe(CO)_2(L\text{-}L')P(C_6H_5)_3$. Method A. A mixture of 0.64 mmol of **2** and 0.60 mmol of triphenylphosphine was refluxed in 50 mL of hexanes until the infrared spectrum indicated that the starting tricarbonyl complex was completely consumed (2–6 days). The solvent was removed, the solid residue was dissolved in a minimum amount of CH_2Cl_2, and the solution was filtered through a short Celite column. Several times the solution volume of hexanes was added, the solution volume was reduced under vacuum, and the solution was cooled at −78 °C. When crystallization was complete, the liquid was removed. The solid was washed several times with cold hexanes and then pumped dry while it slowly warmed to room temperature. Yields given below are for method A.

Method B. A mixture of 305 mg (0.78 mmol) of **2c**, 205 mg (0.78 mmol) of $P(C_6H_5)_3$, and 86 mg (0.78 mmol) of $ON(CH_3)_3\cdot 2H_2O$ was stirred in 100 mL of THF, and the reaction was monitored periodically by infrared spectroscopy. Additional equivalents of $ON(CH_3)_3\cdot 2H_2O$ were added after 4 and 6 h. Reaction was complete after 11 h, at which time the solvent was removed. The solid residue was worked up as in method A. Yields for method B were notably lower than for method A.

The yield of $Fe(CO)_2(2\text{-PAP})P(C_6H_5)_3$ was 53%, mp 130–131 °C. Anal. Calcd for $C_{31}H_{24}FeN_3O_2P$: C, 66.80; H, 4.34; N, 7.53. Found: C, 66.57; H, 4.37; N, 7.51. IR (hexane): ν(CO) 1979 vs, 1924 s cm^{-1}. ^1H NMR ($CDCl_3$, δ): 8.07 (d, 1 H, H6), 7.78 (d, 1 H, H3), 6.9–7.5 (m, 21 H, $P(C_6H_5)_3$, NC_6H_5, and H4), 6.30 (t, 1 H, H5). The yield of $Fe(CO)_2(5\text{-}CF_3\text{-}2\text{-PAP})P(C_6H_5)_3$ was 48%, mp 180–182 °C. Anal. Calcd for $C_{32}H_{23}F_3FeN_3O_2P$: C, 61.46; H, 3.71; N, 6.72. Found: C, 61.38; H, 3.72; N, 6.72. IR (hexane): ν(CO) 1987 vs, 1934 s cm^{-1}. ^1H NMR ($CDCl_3$, δ): 8.20 (s, 1 H, H6), 7.75 (d, 1 H, H3), 6.9–7.5 (m, 21 H, $P(C_6H_5)_3$, NC_6H_5, and H4). The yield of $Fe(CO)_2(4\text{-}CH_3\text{-}2\text{-PAP})P(C_6H_5)_3$ was 78%, mp 107–110 °C. Anal. Calcd for $C_{32}H_{26}FeN_3O_2P$: C, 67.26; H, 4.59; N, 7.35. Found: C, 67.19; H, 4.60; N, 7.31. IR (hexane): ν(CO) 1978 vs, 1922 s cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.89 (d, 1 H, H6), 7.60 (s, 1 H, H3), 6.9–7.5 (m, 20 H, $P(C_6H_5)_3$ and NC_6H_5), 6.16 (d, 1 H, H5), 2.27 (s, 3 H, CH_3).

Reaction of $Fe(CO)_3(5\text{-}CF_3\text{-}2\text{-PAP})$ with $5\text{-}CF_3\text{-}2\text{-PAP}$ and $ON(CH_3)_3$. A mixture of 0.050 mmol each of **2c**, **1c**, and $ON(CH_3)_3\cdot 2H_2O$ in 50 mL of CH_2Cl_2 was monitored in the carbonyl stretching region of the IR. The initial features due to **2c** gradually decreased in intensity, and no new features appeared.

Synthesis of $Fe(2\text{-PAP})_3(PF_6)_2$. This synthesis was adapted from that for $Fe(2\text{-PAP})_3I_2$.[15] A mixture of 373 mg (2.10 mmol) of **1a** and 188 mg (0.68 mmol) of $FeSO_4\cdot 7H_2O$ was prepared in 20 mL of 1:1 water/ethanol to form a deep blue-violet solution. A saturated solution of KPF_6 was added dropwise (~5 mL) until precipitation was complete. The deep blue-violet solid was collected by filtration and washed with a small amount of water, and then dried at 110 °C under vacuum. The yield was 0.49 g (0.55 mmol, 80%). Anal. Calcd for $C_{33}H_{27}P_2F_{12}FeN_9$: C, 44.26; H, 3.04. Found: C, 44.16; H, 3.07.

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[15] Raghavendra, B. S.; Chakravorty, A. *Indian J. Chem.* **1976**, *14A*, 166.

Table I. Crystal Parameters and X-ray Diffraction Data for $Fe_2(CO)_2(4\text{-}CH_3\text{-}2\text{-}PAP)_3$ (3b)

formula	$C_{38}H_{33}Fe_2N_9O_2$
fw	759.4
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.904 (2)
b, Å	19.069 (4)
c, Å	18.606 (5)
β, Å	101.82 (2)
V, $Å^3$	3439.4 (15)
Z	4
λ(Mo Kα), Å	0.710 73
μ, cm^{-1}	8.90
no. of obsd rflcns	2513 ($F > 4.0\sigma(F)$)
R, R_w	0.0510, 0.0526

Table II. Carbonyl Stretching Frequencies of $Fe(CO)_3$(X-2-PAP) and $Fe(CO)_3$(α-diimine) Complexes[a]

complex	ν(CO), cm^{-1}	ref
X-2-PAP		
$Fe(CO)_3$(2-PAP) (**2a**)[b]	2047, 1984, 1972	this work
$Fe(CO)_3$(4-CH_3-2-PAP) (**2b**)[b]	2045, 1982, 1970	this work
$Fe(CO)_3$(5-CF_3-2-PAP) (**2c**)[b]	2055, 1994, 1983	this work
Type A α-Diimines		
$Fe(CO)_3$(bpy)	1996, 1927	8c
$Fe(CO)_3$(phen)	1993, 1927	8c
Type B α-Diimines		
$Fe(CO)_3$(2-py-CH═N-Bu)	2016.5, 1946	8c
$Fe(CO)_3$(2-py-C(Ph)═N-Ph)	2020, 1960, 1944	8c
Type C α-Diimines		
$Fe(CO)_3$(*p*-tol-N═CHCH═N-*p*-tol)	2038, 1976, 1965	20
$Fe(CO)_3$(*t*-Bu-N═CHCH═N-*t*-Bu)	2016, 1937	20

[a] Recorded in hexane or pentane. [b] All bands are strong.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 3b

Fe(1)–N(1)	1.959 (7)	Fe(1)–N(3)	1.856 (6)
Fe(1)–N(4)	1.968 (6)	Fe(1)–N(6)	2.007 (7)
Fe(1)–N(7)	1.944 (7)	Fe(1)–N(9)	2.028 (6)
Fe(2)–N(5)	1.982 (6)	Fe(2)–N(6)	1.984 (6)
Fe(2)–N(8)	1.986 (7)	Fe(2)–N(9)	1.976 (7)
Fe(2)–C(40)	1.747 (10)	Fe(2)–C(50)	1.724 (10)
N(2)–N(3)	1.308 (10)	N(5)–N(6)	1.438 (10)
N(8)–N(9)	1.411 (9)	C(40)–O(2)	1.163 (12)
C(50)–O(1)	1.178 (13)		
N(1)–Fe(1)–N(3)	79.5 (3)	N(1)–Fe(1)–N(4)	92.2 (3)
N(3)–Fe(1)–N(4)	92.1 (3)	N(1)–Fe(1)–N(6)	173.4 (3)
N(3)–Fe(1)–N(6)	101.5 (3)	N(4)–Fe(1)–N(6)	81.2 (3)
N(1)–Fe(1)–N(7)	96.5 (3)	N(3)–Fe(1)–N(7)	99.2 (3)
N(4)–Fe(1)–N(7)	166.8 (3)	N(6)–Fe(1)–N(7)	89.8 (3)
N(1)–Fe(1)–N(9)	100.8 (3)	N(3)–Fe(1)–N(9)	178.0 (3)
N(4)–Fe(1)–N(9)	89.9 (3)	N(6)–Fe(1)–N(9)	78.4 (3)
N(7)–Fe(1)–N(9)	78.8 (3)	N(5)–Fe(2)–N(6)	42.5 (3)
N(5)–Fe(2)–N(8)	129.6 (3)	N(6)–Fe(2)–N(8)	94.3 (3)
N(5)–Fe(2)–N(9)	96.1 (3)	N(6)–Fe(2)–N(9)	80.2 (3)
N(8)–Fe(2)–N(9)	41.7 (3)	N(5)–Fe(2)–C(40)	112.3 (3)
N(6)–Fe(2)–C(40)	153.6 (3)	N(8)–Fe(2)–C(40)	102.3 (4)
N(9)–Fe(2)–C(40)	98.6 (4)	N(5)–Fe(2)–C(50)	99.4 (4)
N(6)–Fe(2)–C(50)	99.8 (3)	N(8)–Fe(2)–C(50)	115.7 (3)
N(9)–Fe(2)–C(50)	156.8 (3)	C(40)–Fe(2)–C(50)	91.4 (4)
Fe(2)–C(40)–O(2)	174.7 (8)	Fe(2)–C(50)–O(1)	178.9 (7)

Reaction of $Fe(2\text{-}PAP)_3(PF_6)_2$ with $Na_2Fe(CO)_4$. A mixture of 295 mg (0.330 mmol) of $Fe(2\text{-}PAP)_3(PF_6)_2$ and 114 mg (0.330 mmol) of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane in 125 mL of THF was stirred overnight at room temperature, during which time the initially brown solution became dark green. The THF was removed under vacuum, and the remaining solid was worked up as described for the reaction of **1a** with $Fe_2(CO)_9$, yielding 93 mg (0.13 mmol, 39%) of **3a**. The small quantity of **2a** was not collected.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^3) for 3b

	x	y	z	U(eq)[a]
Fe(1)	1095 (1)	8118 (1)	5396 (1)	24 (1)
Fe(2)	1959 (1)	7160 (1)	6742 (1)	27 (1)
N(1)	1632 (7)	8319 (3)	4460 (4)	25 (3)
N(2)	−388 (7)	8960 (3)	4306 (4)	26 (3)
N(3)	−300 (6)	8732 (3)	4977 (4)	22 (3)
N(4)	2 (6)	7296 (3)	4986 (4)	23 (3)
N(5)	−4 (7)	7091 (3)	6239 (4)	25 (3)
N(6)	451 (6)	7809 (4)	6300 (3)	24 (3)
N(7)	2349 (7)	8782 (4)	5982 (4)	23 (3)
N(8)	3444 (6)	7771 (4)	6520 (4)	25 (3)
N(9)	2655 (6)	7476 (3)	5874 (3)	23 (3)
O(1)	1636 (7)	7162 (3)	8257 (4)	59 (3)
O(2)	3198 (6)	5772 (3)	6935 (3)	45 (3)
C(1)	2696 (8)	8081 (4)	4154 (5)	25 (3)
C(2)	2797 (9)	8221 (4)	3453 (5)	28 (4)
C(3)	1819 (9)	8629 (4)	2995 (5)	28 (4)
C(4)	754 (9)	8890 (4)	3306 (5)	28 (4)
C(5)	694 (9)	8718 (4)	4023 (5)	22 (4)
C(6)	1877 (9)	8773 (5)	2211 (4)	41 (4)
C(7)	−1553 (8)	8934 (4)	5230 (5)	20 (3)
C(8)	−1472 (9)	9442 (4)	5760 (5)	30 (4)
C(9)	−2689 (10)	9660 (5)	5947 (5)	38 (4)
C(10)	−3943 (10)	9380 (5)	5619 (5)	37 (4)
C(11)	−3969 (10)	8858 (5)	5101 (5)	45 (4)
C(12)	−2780 (10)	8630 (5)	4898 (5)	36 (4)
C(13)	−410 (8)	7099 (5)	4283 (5)	27 (4)
C(14)	−987 (9)	6461 (5)	4096 (5)	37 (4)
C(15)	−1174 (9)	5991 (4)	4639 (6)	30 (4)
C(16)	−818 (8)	6193 (5)	5346 (6)	31 (4)
C(17)	−250 (8)	6878 (5)	5527 (5)	26 (4)
C(18)	−1785 (9)	5268 (4)	4434 (5)	48 (4)
C(19)	−249 (9)	8185 (5)	6776 (5)	30 (4)
C(20)	372 (9)	8730 (5)	7208 (5)	33 (4)
C(21)	−307 (10)	9089 (5)	7657 (5)	44 (4)
C(22)	−1661 (11)	8923 (6)	7688 (5)	51 (5)
C(23)	−2290 (10)	8378 (6)	7267 (6)	48 (4)
C(24)	−1622 (9)	8008 (4)	6804 (5)	33 (4)
C(25)	2271 (9)	9504 (5)	5966 (5)	26 (4)
C(26)	3026 (9)	9914 (5)	6488 (5)	32 (4)
C(27)	3956 (9)	9611 (5)	7077 (5)	31 (4)
C(28)	4067 (9)	8892 (5)	7094 (5)	31 (4)
C(29)	3248 (9)	8495 (5)	6531 (5)	24 (4)
C(30)	4866 (8)	10049 (5)	7651 (5)	44 (4)
C(31)	3464 (9)	7024 (5)	5516 (5)	27 (4)
C(32)	2901 (9)	6469 (5)	5102 (5)	34 (4)
C(33)	3672 (10)	6072 (5)	4700 (5)	45 (4)
C(34)	5061 (11)	6245 (6)	4736 (6)	57 (5)
C(35)	5645 (11)	6782 (6)	5181 (6)	57 (5)
C(36)	4882 (8)	7188 (5)	5572 (5)	39 (4)
C(40)	2764 (9)	6341 (5)	6861 (5)	30 (4)
C(50)	1760 (9)	7167 (4)	7641 (5)	31 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-ray Data Collection, Structure Solution, and Refinement. Crystals of **3b** were obtained from THF/pentane solution. Accurate unit cell dimensions and a crystal orientation matrix were obtained by least-squares refinement of the diffractometer setting angles of 32 high-angle reflections. The diffraction data for **3b** were collected at 143 K on a Siemens R3mV diffractometer equipped with a graphite monochromator and a LT-2 low-temperature apparatus. The intensities of three standard reflections were monitored every 97 reflections, and no significant variations in the intensities of the standards were observed; thus, the standards were treated as normal data during structure solution and refinement. The data were corrected for Lorentz and polarization effects but not for absorption. The absorption coefficient was found to be 8.9 cm^{-1}. The structure was solved by Patterson and difference Fourier methods.[16,17] Hydrogen atoms were included at their calculated positions (d_{C-H} = 0.96 Å). Although they were not refined, the hydrogen atoms were allowed to ride

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(16) Sheldrick, G. M. SHELXTL PLUS, version 4.1. Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

(17) Neutral-atom scattering factors and corrections for anomalous scattering were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

along with their bonded carbon atoms during the refinement. The largest peaks in the final difference map were in the vicinity of the iron atoms.

A summary of crystal data is found in Table I. A complete set of crystal, collection, and solution and refinement data are found in the supplementary material. Selected bond distances and angles for **3b** are found in Table III, and atomic coordinates and isotropic parameters for the non-hydrogen atoms are found in Table IV.

Results and Discussion

Synthesis. 2-(Phenylazo)pyridines (**1a–c**) react with $Fe_2(CO)_9$ in THF to produce two major products, red-brown $Fe(CO)_3(L\text{-}L')$ (**2a–c**) and green $Fe_2(CO)_2(L\text{-}L')_3$ (**3a–c**) (L-L′ = **1a–c**), which can be separated based on solubility differences. Isolation of **2a–c** by chromatography is also possible but with some loss in the cases of **2a** and **2b** due to partial decomposition on the column. However, **3a** and **3b** decompose entirely during chromatography, while **3c** does so partially and is obtained as a mixture with 2-(2-phenylhydrazino)-5-(trifluoromethyl)pyridine, $(5\text{-}CF_3C_5H_3N)NHNHC_6H_5$, in which the azo group in **1c** has been reduced to a hydrazine. In the case of the reaction of **1c** with $Fe_2(CO)_9$, chromatography also permitted the isolation of a third minor product, lavender $Fe_3(CO)_9(\mu_3\text{-}N(C_6H_5))(\mu_3\text{-}N(2\text{-}(5\text{-}CF_3C_5H_4N)))$ (**4c**).

Reactions of **1a–c** with other iron carbonyl precursors also were attempted and judged to be either less convenient or less successful. Thus, use of $Fe(CO)_5$ results in no reaction at temperatures where the products are stable, and the reaction of **1a–c** with $Fe_3(CO)_{12}$ is slow. In both instances activation with trimethylamine oxide[18] accelerates the reaction but yields a similar mixture of products. In particular, no evidence for enhanced formation of the triiron product **4c** was observed with $Fe_3(CO)_{12}$.

When the reaction with $Fe_2(CO)_9$ is monitored by infrared spectroscopy in the carbonyl stretching region, the first new bands to appear are those attributable to **2**. Bands due to **3** next appear along with several bands due to an unidentified product or products, which then gradually disappear. No carbonyl bands are observed below ~1900 cm^{-1}, where the lowest band of **3** occurs. The final spectrum shows only the presence of **2** and **3**. The bands due to **4** are obscured by other features. In an attempt to understand how **3** is formed, **2** was allowed to react separately with excess **1** and with excess $Fe_2(CO)_9$. In neither case were bands due to **3** formed. With excess **1** no new carbonyl features of any type appeared, while with excess $Fe_2(CO)_9$ the same unidentified bands as in the regular reaction mixture grew and then diminished. Increasing the ratio of $Fe_2(CO)_9$/**1c** from 1:1 to 3:1 increases the yield of **4c** somewhat but does not change the proportions of **2c** and **3c**. Running the reactions at 0 °C also made no noticeable change.

A possible mechanism for the formation of **3a** for which there is experimental support involves a disproportionation reaction to give $Fe(\mathbf{1})_3^{2+}$ and $Fe(CO)_4^{2-}$ (eq 1),[19] followed

$$3\,\mathbf{1} + Fe_2(CO)_9 \rightarrow Fe(\mathbf{1})_3^{2+} + Fe(CO)_4^{2-} + 5CO \quad (1)$$

$$Fe(\mathbf{1})_3^{2+} + Fe(CO)_4^{2-} \rightarrow \mathbf{3} + 2CO \quad (2)$$

by their reaction to produce **3** (eq 2). Thus, carbonyl bands due to **3a** appear immediately in the infrared spectrum when $Na_2Fe(CO)_4$ is added to a THF solution containing $Fe(2\text{-}PAP)_3(PF_6)_2$. Relatively less **2a** is formed as is indicated by the lower intensity of its carbonyl bands. When the reaction of $Fe(2\text{-}PAP)_3^{2+}$ and $Fe(CO)_4^{2-}$ is carried out on a preparative scale, the yield of **3a** is higher than that from the reaction of **1a** with $Fe_2(CO)_9$. Nonetheless, this synthesis of **3a** is less convenient because of the prior preparation of $Fe(2\text{-}PAP)_3^{2+}$ required.

It is also possible that $Fe_2(CO)_9$ could react with $Fe(\mathbf{1})_3^{2+}$, once it is formed (eq 1), to give **3a**, along with some unknown iron(II) species (eq 3). Addition of $Fe_2(CO)_9$ to a THF solution of $Fe(2\text{-}PAP)_3(PF_6)_2$ does produce carbonyl bands due to **3a**, but they do not persist unless excess $Fe_2(CO)_9$ is present.

$$Fe(\mathbf{1})_3^{2+} + Fe_2(CO)_9 \rightarrow \mathbf{3} + 7CO + \text{“Fe(II)”} \quad (3)$$

Tricarbonyl Complexes (2). The tricarbonyl complexes **2** show three strong carbonyl stretches in the infrared at frequencies distinctly higher than the corresponding bands in the complexes of bpy, phen, and other α-diimine ligands (Table II). This parallels what was observed in the group 6 complexes of 2-PAP ligands and reflects again that these molecules are better π-acceptor and poorer σ-donor ligands than α-diimines.[3] The substituent effects of the electron-donating CH_3 group and the electron-withdrawing CF_3 group are evident in the lower and higher carbonyl frequencies of **2b** and **2c**, respectively, compared to **2a**. The greater stability of **2c** to chromatography is likely a consequence of the lower electron density on the iron atom in this complex. The strong π-acceptor nature of the 2-PAP ligand also is reflected in the reduction of $\nu(N{=}N)$ from 1412 cm^{-1} in uncoordinated **1a** to 1342 cm^{-1} in **2a**. This compares with a reduction of 128 cm^{-1} in $Cr(CO)_4(2\text{-}PAP)$ and indicates that there is less π back-bonding in the iron complex. The complexity in the 1500–1200-cm^{-1} region of their spectra prevents an unambiguous assignment of $\nu(N{=}N)$ in **2b** and **2c**.

Although 2-PAP ligands are better π acceptors than α-diimines, they are weaker than 1,4-tetraazadiene ligands. The high carbonyl frequencies of $((CH_3)_2N_4)Fe(CO)_3$ at 2068 and 1995 cm^{-1}, as well as theoretical studies, indicate that 1,4-dimethyltetraazadiene is comparable to that of two carbonyl groups.[13b]

The intense red-brown color of **2** is due to a strong absorption band in the visible region of the spectrum with λ_{max} for hexane solutions of **2a**, **2b**, and **2c** at 487, 485, and 487 nm, respectively. By analogy with the studies on the comparable α-diimine[8c,20,21] and 1,4-tetraazadiene[13b] complexes, this lowest energy electronic transition arises from a LUMO/HOMO combination that involves the mixing of the lowest ligand π^* orbital with the iron d orbitals. In the bpy and phen complexes this transition has considerable charge-transfer (CT) character and shows a strong dependence on solvent polarity.[8c] For the α-diimines this solvent effect decreases in the order type A > type B > type C, such that complexes of the type C ligand have little or no CT character or solvatochromism. The visible absorption bands in the 1,4-tetraazadiene complex $((CH_3)_2N_4)Fe(CO)_3$ also have no CT character.[13b] Likewise the 2-PAP complexes **2a–c** show virtually no solvatochromic behavior with λ_{max} values of 485, 485, and 480 nm, respectively, in the polar solvent acetone. Accordingly, there must be little or no CT character in the 2-PAP complexes, which indicates substantial mixing of metal and ligand orbitals in the HOMO and LUMO in these complexes.

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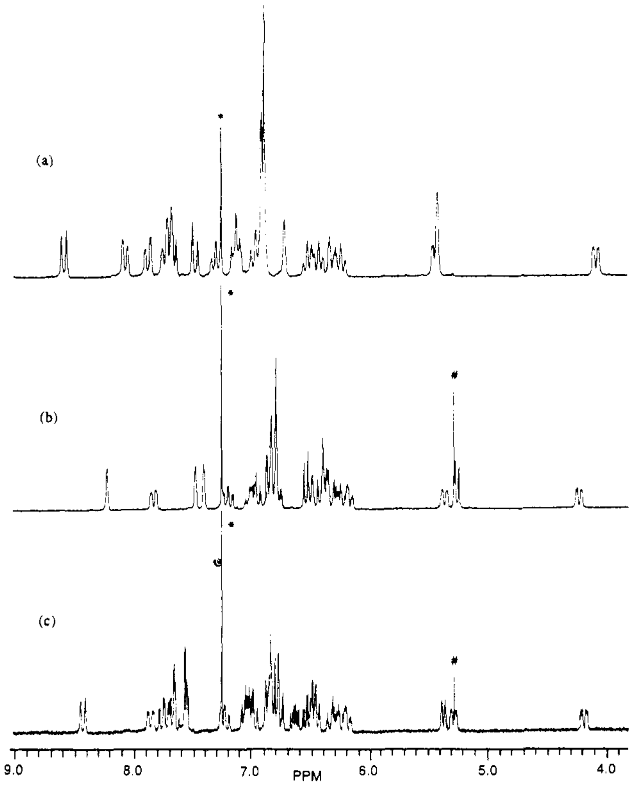

Figure 1. ^1H NMR spectra of (a) $Fe_2(CO)_2(2\text{-PAP})_3$ (**3a**), (b) $Fe_2(CO)_2(4\text{-}CH_3\text{-}2\text{-PAP})_3$ (**3b**) (the three methyl signals not shown but given in the text), and (c) $Fe_2(CO)_2(5\text{-}CF_3\text{-}2\text{-PAP})_3$ (**3c**) obtained in $CDCl_3$ at 200 MHz. The signals labeled with asterisks are due to $CHCl_3$ and those labeled with number signs are due to CH_2Cl_2.

Assignments of the ^1H and ^{13}C NMR spectra were aided by the substituents on the pyridyl ring of the 2-PAP ligands and by the carbon–fluorine coupling constants in the 5-CF_3 carbon spectra. The most likely structure for **2** is a distorted trigonal bipyramid, which has been found for type B $Fe(CO)_3(\alpha\text{-diimine})$ complexes,[22] or a distorted square pyramid, which has been found for type C $Fe(CO)_3(\alpha\text{-diimine})$ complexes[21] and the $((CH_3)_2N_4)Fe(CO)_3$ 1,4-tetraazadiene complex.[23] However, the observation of only one carbonyl peak in their ^{13}C spectra, even down to −93 °C when the spectrum of **2b** was run in CD_2Cl_2, indicates that the molecules are fluxional. $Fe(CO)_3(\alpha\text{-diimine})$ complexes of type C ligands[24] and $((CH_3)_2N_4)Fe(CO)_3$[13b] behave similarly down to at least −80 and −105 °C, respectively.

Refluxing **2** in hexane with $P(C_6H_5)_3$ leads to replacement of one CO and the formation of $Fe(CO)_2(L\text{-}L')P(C_6H_5)_3$ (L-L′ = **1a–c**) in good yield. However, no formation of $Fe(L\text{-}L')_2CO$ was observed from the reaction of **2** with **1** either thermally or with the aid of $ON(CH_3)_3$. Hence, the iron system differs from the group 6 metal carbonyls in the extent to which 2-PAP is able to replace COs. $Fe(\alpha\text{-diimine})_2CO$ complexes are known, but they too cannot be obtained by direct reaction of the α-diimine with iron carbonyls.[11]

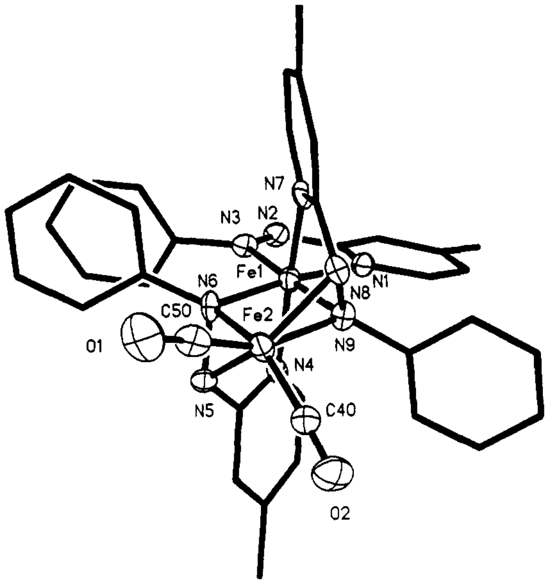

Figure 2. Computer-generated drawing of **3b** with an abbreviated atom-labeling scheme. Hydrogen atoms and thermal ellipsoids for the ring carbon atoms have been omitted for clarity.

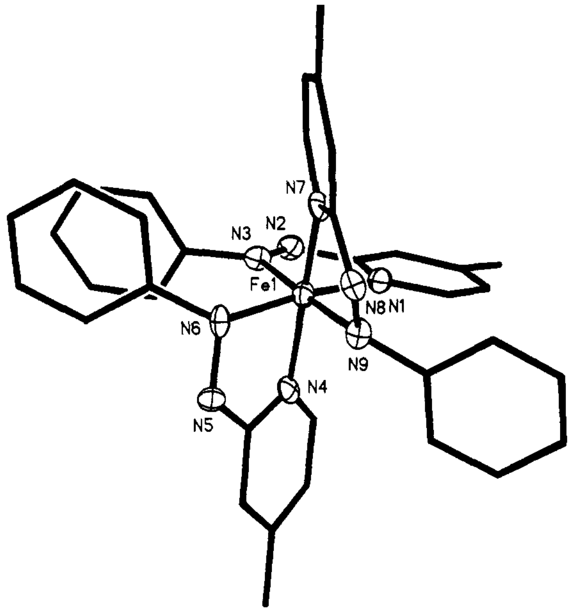

Figure 3. Drawing of the $Fe(4\text{-}CH_3\text{-}2\text{-PAP})_3$ fragment of **3b** that illustrates the approximate octahedral geometry around the one Fe atom.

Diiron Complexes (3). Assignment of the structure of **3a–c** solely on the basis of elemental analysis and spectroscopic data was not possible. The relatively high frequencies of the two carbonyl bands in the infrared are consistent with only terminal CO groups. A variety of NMR data suggests that each of the three ligands is unique. Particular support for this conclusion are the three individual methyl resonances at 2.44, 2.38, and 2.33 ppm in the proton spectrum of **3b**, which are matched by three aliphatic peaks in the carbon-13 spectrum. In addition, there are three individual ^{19}F signals at −62.23, −62.50, and −62.67 ppm in the fluorine spectrum of **3c**. The ^1H NMR spectra of **3a–c** are shown in Figure 1. On the basis of a comparison with the spectra of uncoordinated **1a–c** and with **2a–c**, the lowest field signal is assigned to H6 on a pyridyl ring. The signals below 6 ppm are at unusually high field for 2-PAP complexes and suggest a novel bonding pattern.

The molecular structure of **3b** has been determined by single-crystal X-ray diffraction, and a computer-generated drawing is shown in Figure 2. The coordination number of each iron atom is 6; however, the coordination geometry

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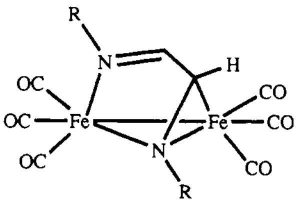
around one iron atom, Fe(1), approximates octahedral geometry, whereas that around the second iron atom, Fe(2), is severely distorted from an octahedral geometry. The complex can be considered as having resulted from the addition of the two fragments $Fe(CO)_2$ and $Fe(4\text{-}CH_3\text{-}2\text{-}PAP)_3$. The approximate geometry of the $Fe(4\text{-}CH_3\text{-}2\text{-}PAP)_3$ fragment is shown in Figure 3. Three nitrogen donor atoms, N(1), N(4), and N(7), are the pyridine nitrogen atoms of the three $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands. The remaining three nitrogen donor atoms, N(3), N(6), and N(9), are the three phenyl-bound azo nitrogen atoms of the $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands. The compound **3b** may be constructed from the $Fe(4\text{-}CH_3\text{-}2\text{-}PAP)_3$ fragment by addition of the iron atom of the $Fe(CO)_2$ fragment across the N(5)–N(6) and N(8)–N(9) double bonds of the azo linkages of two of the $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands to give the structure shown in Figure 2. This picture of the construction of **3b** is consistent with the earlier mechanistic proposal for its synthesis from the $Fe(4\text{-}CH_3\text{-}2\text{-}PAP)_3^{2+}$ and $Fe(CO)_4^{2-}$ ions (eq 2) with the $Fe(CO)_4^{2-}$ providing the equivalent of an $Fe(CO)_2^{2-}$ unit to form the neutral product. The combination of these two fragments results in two bridging six-electron-donor $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands and one nonbridging four-electron-donor $4\text{-}CH_3\text{-}2\text{-}PAP$ ligand. This is the first example of a compound in which a 2-PAP ligand has been found to serve as a six-electron donor.

The bridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands become six-electron donors by virtue of the involvement of the two π electrons of the N=N bond in coordination. The consequences of this are evident in both the N–N and Fe–N bond lengths. At 1.308 (10) Å the N–N bond length in the nonbridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligand is comparable to that of the nonbridging 2-PAP ligands in $Cr(2\text{-}PAP)_2Cl_2$,[25] $Ru(2\text{-}PAP)_2(N_3)_2$,[26] and $Ru(2\text{-}PAP)_2Cl_2$.[27] The distances between the azo nitrogen atoms N(5)–N(6) and N(8)–N(9) in the bridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands are longer at 1.438 (10) and 1.411 (9) Å, respectively, and are comparable to an N–N single bond.[28] The Fe(1)–N distances involving the two azo nitrogen atoms N(6) and N(9) of the two bridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands are 2.007 (6) and 2.028 (6) Å, respectively, while the distance between Fe(1) and the azo nitrogen N(3) of the nonbridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligand is significantly shorter at 1.856 (6) Å. We attribute these differences in the Fe–N(azo) bond lengths to differences in π bonding for the two types of $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands. Metal–nitrogen π bonding involves a d orbital on iron and the π^* orbital of the azo group. Since the bridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands no longer have an N=N bond, there is no π^* orbital with which to form a π bond with iron. Consequently, the Fe(1)–N(6) and Fe(1)–N(9) bond should have only a σ component and be longer than the Fe(1)–N(3) bond for the nonbridging ligand. Additional evidence for a π component in the Fe(1)–N(3) bond is the fact that the N(2)–N(3) bond is somewhat longer than the value of 1.24 Å for the isolated N=N bond exemplified by *trans*-azobenzene.[29] This is expected if additional electron density is being donated by the iron into the azo π^* orbital.

The Fe(1)–N distances involving the pyridine nitrogen atoms N(1), N(4), and N(7) are similar at 1.959 (7), 1.968 (6), and 1.944 (6) Å, respectively, suggesting that the pyridyl and azo ends of the $4\text{-}CH_3\text{-}2\text{-}PAP$ ligand act nearly independently in coordinating to a metal center. The slight differences in analogous parameters of the two similarly coordinated bridging $4\text{-}CH_3\text{-}2\text{-}PAP$ ligands might be due to crystal packing forces.

The structure exhibited by **3b** has no parallel in α-diimine/iron coordination chemistry. When type B and C α-diimines act as bridging six-electron-donor ligands, they form $Fe_2(CO)_6(\alpha\text{-diimine})$ (**5**), in which there is only one bridging α-diimine ligand, and no iron complex is known to contain both bridging and nonbridging α-diimine ligands.[2,10] The Fe–Fe bond in **5** also is considerably shorter than that in **3b**. When the α-diimine is 1,4-dicyclohexyl-1,4-diazabutadiene, **5** has an Fe–Fe length of 2.597 (1) Å,[10a] while in **3b** this distance is 3.076 Å. Consequently it is reasonable to treat **5**, but not **3b**, as having an iron–iron bond.[30] This picture is consistent with electron counting if the iron atoms in each structure are to conform to the 18-electron rule. To date, we have observed no evidence for a type **5** complex with a 2-PAP ligand.



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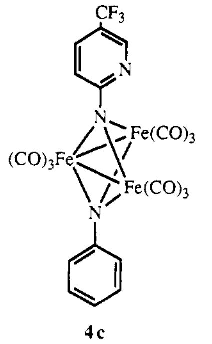
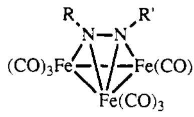
Triiron Complex (4c). The structure of **4c** is assigned on the basis of its elemental analysis and the strong similarity of its spectroscopic properties to those of the nitrene-capped cluster $Fe_3(CO)_9(\mu_3\text{-}N(C_6H_5))_2$.[31] Cleavage of the N=N bond during reaction with iron carbonyls is a major reaction pathway for azoarenes. The other major product in most cases is the *o*-semidine-ligand-containing complex $Fe_2(CO)_6(\mu\text{-}(C_6H_5)NC_6H_4NH)$.[32] The differences between **1** and azobenzene in their reactions with iron carbonyls are thus noteworthy. Recent studies on the mechanism of formation of complexes of type **4** suggest they proceed through prior formation of **6** in which the azo linkage acts as a six-electron donor.[33] The presence of the additional coordination site at the pyridine nitrogen in **1** presumably makes the formation of **6** less likely than when only the azo group is present and accounts for the very low yield of **4c**.



4c



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Supplementary Material Available: Complete details of crystal data, data collection, and solution and refinement (Table S1), complete lists of bond lengths (Table S2) and bond angles (Table S3), anisotropic thermal parameters (Table S4), and hydrogen atom coordinates and isotropic thermal parameters (Table S5), and a drawing showing the complete labeling scheme for **3b** (Figure S1) (8 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Ynol Ester Complexes of Molybdenum and Tungsten: Cleavage of the RCCO–C(O)R′ Bond and of the RCC–OC(O)R′ Bond of Ynol Ester Ligands

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Reaction of the ketenyl complexes $NEt_4[M(\eta^2\text{-}RCCO)(S_2CNR''_2)_2(CO)]$ (**3**, M = Mo, R = Ph, R″ = Et; **4**, M = W, R = Ph, R″ = Et (**a**), R = $C_6H_4CMe_3$-4, R″ = Et (**b**), R = Ph, R″ = Me (**c**)) and $K[W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(N_2C_6H_7)_2(CO)]$ (**5**) with acyl halides R′COCl (or R′COBr) affords the (ynol ester)metal complexes $[M(S_2CNR''_2)_2(CO)(\eta^2\text{-}RCCOCOR')]$ (**8**: M = Mo, R = Ph, R′ = Ph, R″ = Et) (**9**: M = W, R = Ph, R′ = Me (**a**), Ph (**b**), $CHCH_2$ (**c**), *trans*-CHCHMe (**d**), *trans*-CHCHPh (**e**), R″ = Et; R = $C_6H_4CMe_3$-4, R′ = Me (**f**), CH_2Ph (**g**), CMe_3 (**h**), R″ = Et; R = Ph, R′ = CMe_3, R″ = Me (**i**)) and $[W(N_2C_6H_7)_2(CO)(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOR')]$ (**10**: R = $C_6H_4CMe_3$-4, R′ = CMe_3 (**a**), CH_2Ph (**b**), C_6H_4-OMe-4 (**c**)). Reaction of the ynol ester complexes $[W(S_2CNEt_2)_2(CO)(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOCH_2R)]$ (R = H (**9f**), Ph (**9g**)) with dimethylamine affords the ketenyl complex $[H_2NMe_2][W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(S_2CNEt_2)_2(CO)]$. The ynol ester complexes $[W(LL)_2(CO)(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOCH_2Ph)]$ (LL = S_2CNEt_2 (**9g**), $N_2C_6H_7$ (**10b**)) react with $NaN(SiMe_3)_2$ to give the ketenyl complexes $Na[W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(LL)_2(CO)]$. Reaction of $[W(S_2CNEt_2)_2(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOCMe_3)(CO)]$ (**9h**) with $HNMe_2$ gives $[W(S_2CNEt_2)_2(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCNMe_2)(CO)]$ (**11**). Reaction of **9h** with PMe_3 gives $[W(S_2CNEt_2)_2(\eta^3\text{-}4\text{-}Me_3C\text{-}C_6H_4CCSCSNEt_2)(CO)][Me_3CO_2]$ (**12**). The reaction of **4b** with PMe_3 affords $[W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(S_2CNEt_2)(CO)(PMe_3)_2]$ (**13**). The (ynol ether)metal complexes $[M(S_2CNEt_2)_2(CO)(\eta^2\text{-}RCCOMe)]$ (**6**, M = Mo, R = Ph; **7**, M = W, R = $C_6H_4CMe_3$-4) were prepared by reaction of $NEt_4[M(\eta^2\text{-}RCCO)(S_2CNR''_2)_2(CO)]$ with $CF_3SO_3CH_3$.

Introduction

Ketenyl, or ynolate, ligands ($RCCO^-$) have become easily accessible by the coupling of alkylidyne and carbonyl ligands.[4] Kreissl and co-workers observed in 1976 the first alkylidene–carbonyl coupling in the reaction of $[W(CC_6H_4\text{-}CH_3\text{-}4)(\eta^5\text{-}C_5H_5)(CO)_2]$ with PMe_3.[5] In subsequent years additional examples of nucleophile-induced alkylidyne–carbonyl coupling reactions were described.[4] Geoffroy and co-workers reported photoinduction of alkylidyne–carbonyl coupling in the presence of donor ligands.[6] We have recently demonstrated that photogenerated ketenyl ligands may also be trapped by electrophiles.[7] Induction of alkylidyne–carbonyl coupling by electrophiles is not yet firmly established but may be involved in the formation of aluminum-substituted ynolate ligands reported by Schrock and co-workers,[8] which takes place upon reaction of a methylidyne complex with carbon monoxide in the presence of aluminum Lewis acids. The reductive coupling of two carbonyl ligands developed by Lippard and co-workers[9] also involves an alkylidyne (siloxycarbyne)–carbonyl coupling step. The formation of sulfur-substituted ketenyl ligands by coupling of thiocarbyne and carbonyl ligands was reported by Angelici and co-workers.[10]

Our knowledge of the reactivity of ketenyl ligands rests primarily on the pioneering work by Kreissl and his group.[4] Depending on the electronic requirements of the metal

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