(3) The increasing tendency of these molecules to be stable without CO bridges as the group is descended appears to be a significant structural principle. It is reflected also in the fact that while $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ have bridging CO groups,[18] $Ir_4(CO)_{12}$ which has an otherwise similar structure, with a tetrahedron of metal atoms, has no bridging CO's[18] in the crystalline phase.

(4) On the basis of the principle enunciated in (3), we might expect that $(\pi\text{-Cp})_2Os_2(CO)_4$, which incidently appears not to be isomorphous with its Fe and Ru analogs,[19] may have a nonbridged structure under all or nearly all conditions.[20]

Experimental Section

$(\pi\text{-Cp})_2Fe_2(CO)_4$ was kindly given to us by Professor A. Davison. It was further recrystallized from mixtures of ethyl

---

(18) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(19) E. O. Fischer and A. Vogler, *Z. Naturforsch.* **17b**, 421 (1962).

(20) Note Added in Proof.—We have been informed by R. D. Fischer, K. Noack, and A. Vogler of the Technische Hochschule, Munich and Cyanamid European Research Institute that they have also carried out similar studies on these molecules and reached the same major conclusions. Their studies included experimental work on the osmium compound which directly demonstrates the correctness of our tentative conclusion (4).

acetate and heptane immediately before use, affording beautiful, well-formed crystals.

$(\pi\text{-Cp})_2Ru_2(CO)_4$ was prepared according to Fischer and Vogler.[19] It also was given final purification by recrystallization from ethyl acetate–heptane mixtures, whence excellent crystals were again obtained.

Infrared Spectra.—These were recorded using a Perkin-Elmer 521 spectrograph, under conditions of 1-cm^{-1} resolution and using gaseous CO as calibrant. The solutions were studied with and without compensation in 1-mm standard liquid cells.

The overtone and combination spectra were recorded, using both Perkin-Elmer 521 and Cary Model 14 spectrographs, in 10-cm quartz cells. In the region below 3800 cm^{-1} the spectra were recorded without compensation and the base line was subtracted by running a spectrum, under the same conditions, with the same cell plus the solvent. Owing to the strong absorption of the quartz windows around 3600 cm^{-1}, the quality of the spectra in that range was reduced.

All of the spectra were recorded with freshly prepared solutions of recently recrystallized samples—all in the absence of light. It was noted, as pointed out by Noack,[3] that the solutions were sensitive to the beam of the spectrograph and were slowly decomposed by it. To avoid contamination of the solutions with decomposition product, the samples were allowed to stay in the beam path for only very short periods of time; hence different samples were used to record the different bands. Also some very weak bands, which increased their intensity when the samples were exposed to light, were not taken to be genuine.

π Coordination of Unsaturated Bonds Containing Heteroatoms. II. Iron Carbonyl Complexes of Azomethine Analogs of 1,3-Dienes. Preparation and Nature of the Coordination Bondings

By SEI OTSUKA, T. YOSHIDA, and A. NAKAMURA

The following mononuclear iron carbonyl complexes were prepared: (cinnamaldehydeanil)iron tricarbonyl (**1**), (crotonaldehyde-*n*-butylimine)iron tricarbonyl (**2**), (cinnamaldehydeanil)(triphenylphosphine)iron dicarbonyl (**3**), (diacetylanil)iron tricarbonyl (**4**), and (diacetyl-*n*-butylimine)iron tricarbonyl (**5**). On the basis of the nmr spectra, it was inferred that the coordination of the enimine ligands in **1**, **2**, and **3** may be of π-1,3-diene type, analogous to butadiene iron tricarbonyl, while the α-diimine in **4** and **5** coordinates through its nitrogen lone pairs forming a chelate ring similar to the well-known α-diimine Fe(II) chelate complexes. Attempted preparations of (π-benzalazine)- or (π-acetalazine)iron carbonyl complexes were unsuccessful.

Introduction

Although numerous π-olefin complexes are known, the possibility for this type of π coordination, *i.e.*, "side-on coordination," is very limited for a double bond containing oxygen, nitrogen, or a like atom. For simple molecules or anions such as carbon monoxide, cyanide, etc., their coordination bondings to metal are well recognized to involve π bonding generally in synergic interaction with the σ-type bonding, but they are not "side-on"; instead, they are of, say, "linear type." So far only a few examples have been reported where the "side-on" π coordination is claimed, *viz.*, coordination of the C=O group in $(CH_2\text{=}CH\text{—}CH\text{=}O)_2Mo(CO)_2$[1a] or $[CH_2\text{=}CH\text{—}C(CH_3)\text{=}O]_3W$,[1b] the

−N=N− group in cyclopentadienyl-*o*-(phenylazo)phenylnickel,[2a] and the −C≡N group in $(R_2N\text{—}C\text{≡}N)_2Ni_2(CO)_2$.[2b] We have recently reported[3] a successful preparation of keteniminediiron hexacarbonyl complexes whose spectral data corroborated participation of both C=C and C=N double bonds in the coordination of the cumulated double bonds.
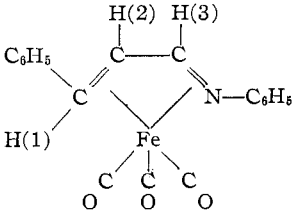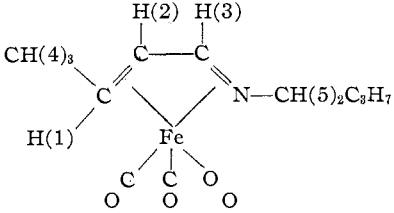
Our present interest is to see if π coordination of this type is possible for conjugated diene systems containing

(1) (a) D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965); (b) R. B. King and A. Fronzaglia, *Chem. Commun.*, 274 (1966).

(2) (a) J. P. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963); (b) H. Bock and H. T. Dieck, *Chem. Ber.*, **99**, 213 (1966).

(3) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organometal. Chem.* (Amsterdam), in press.

TABLE I

NMR DATA

	Free ligand τ (multiplicity)		Complexed ligand τ (multiplicity, rel intens)
$C_6H_5CH=CH-CH=NC_6H_5Fe(CO)_3$ (1) in CCl_4			
H(1)	2.55, 3.00[a]		6.65 (broad, 1)
H(2)			4.35 (broad, 1)
H(3)	1.88 (quintet)		2.60, 3.30[a]
	$J_{13} = 3.3$		...
	$J_{23} = 5.4$		...
$CH_3CH=CH-CH=NC_4H_9Fe(CO)_3$ (2) in C_6H_6			
H(1)	4.41 (sextet)		8.05 (complex, 1)
H(2)	3.81 (quintet)		6.04 (quintet, 1)
H(3)	2.52 (doublet)		4.51 (doublet, 1)
H(4)	8.69 (doublet)		9.14 (doublet, 3)
H(5)	6.79 (triplet)		8.25 (triplet, 2)
	$J_{12} = 14.3$		$J_{12} = 10.0$
	$J_{23} = 7.5$		$J_{23} = 2.9$
	$J_{14} = 7.0$		
	$J_{13} = 0$		$J_{13} = 0$
$C_6H_5N=C(CH_3)-C(CH_3)=NC_6H_5Fe(CO)_3$ (4) in C_6H_6			
CH_3	8.12 (singlet)		8.72 (singlet)
$C_4H_9N=C(CH_3)-C(CH_3)=NC_4H_9Fe(CO)_3$ (5) in C_6H_6			
CH_3	7.98 (singlet)		8.76 (singlet, 3)
$N-CH_2$	6.72 (triplet)		6.21 (triplet, 2)
$[C_4H_9N=C(CH_3)-C(CH_3)=NC_4H_9]_3Fe^{II}(BF_4)_2$ (6) in $C_6H_5NO_2$			
CH_3	8.00 (singlet)		6.93 (singlet, 3)
$N-CH_2$	6.66 (triplet)		6.50[b] (broad, 1)
			5.62[b] (broad, 1)
	J_{11} (gem) = 0		...
6 in SO_2			
CH_3	...[c]		7.89[d] (singlet, 0.5)
			7.29[d] (singlet, 2.5)
$N-CH_2$	...[c]		6.33[b] (double triplet, 1)
			5.96[b] (double triplet, 1)
	...		J_{11}(gem) = 5

[a] These signals appeared in the region of phenyl protons.   [b] The reason for appearance of two signals has not been elucidated, although the same geminal coupling constant (5 cps) supports the assignment.   [c] Immeasurable owing to formation of a solid adduct with SO_2.   [d] The reason for splitting into two signals is also unknown.

the azomethine group. The following three systems were chosen because of their ready accessibility: cinnamaldehydeanil and crotonaldehyde-*n*-butylimine as an unsaturated imine (hereafter abbreviated as enimine) (–CH=CH—CH=N–), diacetylanil and diacetyl-*n*-butylimine as a diimine (–N=CR—CR=N–), and benzalazine and acetalazine as an azine system (–CH=N—N=CH–). A purpose of this paper is to present the preparation of iron carbonyl complexes containing these ligands and also of the tris(diacetyldi-*n*-butyl-imine)iron(II) complex. Their nmr and infrared spectra will be used to discuss the natures of the coordination bondings.

Experimental Section

Materials.—Triiron dodecacarbonyl,[4] diiron enneacarbonyl,[5] cinnamaldehydeanil,[6] crotonaldehydebutylimine,[7] diacetylanil,[8] diacetyl-*n*-butylimine,[7] benzalazine,[9] and acetalazine[10] were prepared by known methods.

(4) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York, N. Y., 1965, p 95.

(5) Reference 4, p 93.

(6) O. Doebner and W. Miller, *Chem. Ber.*, **16**, 1664 (1883).

(7) H. C. Barany, E. A. Braude, and M. Pianka, *J. Chem. Soc.*, 1898 (1949).

(8) H. Peckmann, *Chem. Ber.*, **21**, 1411 (1888).

(9) L. F. Audrieth and T. T. Nickles, *Inorg. Syn.*, **1**, 92 (1939).

Instruments.—Infrared spectra were measured by a Jasco Model DS-402G grating spectrophotometer and nmr spectra by a 100-Mc Model JNM 4H-100 of Japan Electron Optics Lab. Molecular weights were determined in benzene by a Mechrolab vapor pressure osmometer, Model 301A. Mass spectra were measured by a Hitachi Type RMU-7HR. Elemental analysis (C, H, N, and O) was carried out in the research laboratory of Japan Synthetic Rubber Co. Ltd., Yokkaichi City, Japan.

Preparation of Complexes.—All reactions and manipulations involving organometallic compounds were carried out under pure nitrogen. Alumina for chromatography was deoxygenated as given before.[3] Tables I and II list the nmr and infrared spectral data, respectively, for most of the following complexes.

$C_6H_5CH=CH-CH=NC_6H_5Fe(CO)_3$.   (a) Reaction of Cinnamaldehydeanil with Diiron Enneacarbonyl or with Triiron Dodecacarbonyl.—A mixture of 0.9 g (4.35 mmoles) of cinnamaldehydeanil, 1.5 g (4.13 mmoles) of diiron enneacarbonyl, and 15 ml of benzene was stirred at 40° for 2 hr. The filtered solution was concentrated under vacuum and the residue chromatographed on alumina. Elution with benzene and subsequent evaporation of the red eluate gave orange-red crystals. Recrystallization from a mixture of benzene–*n*-heptane gave 0.43 g of orange-red needles, mp 108.5–109.5° dec. *Anal.* Calcd for $C_{18}H_{13}FeNO_3$: C, 62.28; H, 3.78; N, 4.03; O, 13.84; mol wt, 347. Found: C, 62.23; H, 3.98; N, 3.75; O, 14.02; mol wt, 373. This crystalline complex is quite stable and can be kept unchanged for several months in air at room temperature.

(10) Th. Curtius and E. Zinkeisen, *J. Prakt. Chem.*, **58**, 325 (1895).

Table II

Infrared Spectral Data^a (cm^{-1})

| | | ν_{C-C}, ν_{C-N} | | |
	$\nu_{C=O}$	Free ligand	Complexed ligand	$\Delta\nu_{C-C}, \nu_{C-N}$
(1) C$_6$H$_5$CH=CH—CH=NC$_6$H$_5$Fe(CO)$_3$	2060	1621	1475	96–192
	1998	1571	1429	
	1990			
(3) C$_6$H$_5$CH=CH—CH=NC$_6$H$_5$Fe(CO)$_2$P(C$_6$H$_5$)$_3$	1928	...	1430	...
	1926		1424	
(2) CH$_3$CH=CH—CH=NC$_4$H$_9$Fe(CO)$_3$	2060	1655	1476	149–224
	1998	1625	1431	
	1984			
(4) C$_6$H$_5$N=C(CH$_3$)—C(CH$_3$)=NC$_6$H$_5$Fe(CO)$_3$	2035	1629	...	...
	1965			
(5) C$_4$H$_9$N=C(CH$_3$)—C(CH$_3$)=NC$_4$H$_9$Fe(CO)$_3$	2009	1633	1390^b	243
	1940			
(6) [C$_4$H$_9$N=C(CH$_3$)—C(CH$_3$)=NC$_4$H$_9$]$_3$Fe^{2+} ^{c}	...	1633	1521	112

^{a} Measured in Nujol mull or Nujol solution. ^{b} Unidentified. ^{c} Measured in KBr pellet.

Similarly, a mixture of 0.414 g (2 mmoles) of cinnamaldehyde-anil, 0.5 g (1 mmole) of triiron dodecacarbonyl, and 15 ml of *n*-hexane refluxed for 2 hr gave 0.08 g of the above-mentioned product.

(b) **Reaction of Cinnamaldehydeiron Tetracarbonyl[11] with Aniline.**—Aniline (0.046 g, 0.5 mmole) was added with stirring at 5° to the benzene solution (5 ml) of 0.15 g (0.5 mmole) of cinnamaldehydeiron tetracarbonyl. The reaction mixture was stirred at 45° for 3 hr. The filtered solution was concentrated under vacuum and the residue chromatographed on alumina. Elution with benzene and subsequent evaporation of the red eluate gave 0.019 g of orange-red needles, mp 106–108.5° dec.

Reaction of Cinnamaldehydeaniliron(0) Tricarbonyl with Triphenylphosphine.—A mixture of 0.05 g (0.14 mmole) of cinnamaldehydeaniliron tricarbonyl, 0.035 g (0.13 mmole) of triphenylphosphine, and 5 ml of benzene was stirred at 70–80° for 4 hr. The precipitated crystals were filtered and washed with benzene. Recrystallization from a mixture of benzene–heptane gave 0.033 g of orange needles, mp 168–172°. On the basis of elemental analysis and the molecular weight measurement, the complex product was formulated as C$_6$H$_5$—CH=CH—CH=N—C$_6$H$_5$Fe(CO)$_2$P(C$_6$H$_5$)$_3$. *Anal.* Calcd for C$_{35}$H$_{28}$FeNO$_2$P: C, 72.33; H, 4.85; O, 5.50; mol wt, 581. Found: C, 72.35; H, 5.24; O, 5.81; mol wt, 532.

CH$_3$CH=CH—CH=NC$_4$H$_9$Fe(CO)$_3$.—A mixture of 1.0 g (8 mmoles) of crotonaldehyde-*n*-butylimine, 1.4 g (4 mmoles) of diiron enneacarbonyl, and 10 ml of benzene was stirred at 40° for 3 hr. The mixture was filtered under nitrogen and concentrated under vacuum. Alumina chromatography of the residue using *n*-hexane gave a red oil. Distillation of the oil at 50° (10^{-2} mm) yielded 0.2 g of a liquid complex which was air sensitive and decomposed slowly on standing even in nitrogen at ambient temperature. *Anal.* Calcd for C$_{11}$H$_{15}$FeNO$_3$: C, 49.85; H, 5.71; N, 5.28; O, 18.11. Found: C, 50.55; H, 6.01; N, 5.31; O, 18.43.

Reaction of Crotonaldehyde-*n*-butylimineiron(0) Tricarbonyl with Triphenylphosphine.—A mixture of 46.9 mg (0.176 mmole) of crotonaldehyde-*n*-butylimineiron(0) tricarbonyl and 92.2 mg (0.352 mmole) of triphenylphosphine in 5 ml of heptane was heated at 70–80° for 3 hr. The reaction gave 61.9 mg of yellow bis(triphenylphosphine)iron tricarbonyl, mp 265–270° dec.

C$_6$H$_5$N=C(CH$_3$)—C(CH$_3$)=NC$_6$H$_5$Fe(CO)$_3$.—A mixture of 1.4 g (6 mmoles) of diacetylanil, 1.22 g of (3.4 mmoles) of diiron enneacarbonyl, and 20 ml of benzene was stirred at 40° for 3.5 hr. About 50 ml of CO was evolved. After filtration, the mixture was concentrated under vacuum. Alumina chromatography of the residue using *n*-hexane gave a red crystalline product. Recrystallization from *n*-hexane gave 0.87 g of red needles, mp 129–132° (under nitrogen). The molecular weight was measured

by mass spectra. *Anal.* Calcd for C$_{19}$H$_{16}$FeN$_2$O$_3$: C, 60.71; H, 4.29; N, 7.44; O, 12.76; mol wt, 376. Found: C, 59.99; H, 4.48; N, 7.12; O, 13.39; mol wt, 376. Diacetylaniliron(0) tricarbonyl sublimed at 70° (~5 × 10^{-3} mm). An attempted reaction of C$_6$H$_5$N=C(CH$_3$)—C(CH$_3$)=NC$_6$H$_5$Fe(CO)$_3$ with triphenylphosphine in a molar ratio of 2 at 80° for 5 hr resulted in recovery of the starting materials.

C$_4$H$_9$N=C(CH$_3$)—C(CH$_3$)=NC$_4$H$_9$Fe(CO)$_3$.—Diacetyl-*n*-butylimine (0.4 g, 2 mmoles) was added with stirring under nitrogen to the benzene (4 ml) dispersion of 0.36 g (1 mmole) of diiron enneacarbonyl at 20°. Red color immediately developed. After being stirred at 40° for 7 hr, the mixture was filtered and concentrated under vacuum. The residue was chromatographed on alumina under nitrogen. Elution with benzene–*n*-hexane (1:2) and subsequent evaporation of the red eluate gave a red oil. Distillation at 70–75° (5 × 10^{-3} mm) gave 0.08 g of a purple-red viscous oil. *Anal.* Calcd for C$_{15}$H$_{24}$FeN$_2$O$_3$: C, 53.59; H, 7.19; N, 8.33; O, 14.33. Found: C, 53.46; H, 7.54; N, 8.38; O, 14.00.

[C$_4$H$_9$N=C(CH$_3$)—C(CH$_3$)=NC$_4$H$_9$]$_3$Fe^{II}(BF$_4$)$_2$.—Diacetyl-*n*-butylimine (0.59 g, 3 mmoles) was added with stirring at room temperature to the ethanol solution (10 ml) of 0.16 g (1 mmole) of FeCl$_2$·2H$_2$O. The mixture was stirred at room temperature for 30 min. The blue-purple solution was filtered under nitrogen and concentrated under vacuum. To the residue dissolved in deaerated water was added 0.33 g (3 mmoles) of sodium tetrafluoroborate. The purple precipitate was filtered and recrystallized from methanol to give 0.18 g of purple crystals, mp 174°. *Anal.* Calcd for C$_{12}$H$_{24}$B$_2$F$_8$FeN$_2$: C, 52.76; H, 8.86; N, 10.21. Found: C, 52.22; H, 8.93; N, 9.95.

Reaction of Benzalazine with Diiron Enneacarbonyl.—A mixture of 0.35 g (1.7 mmoles) of benzalazine, 0.34 g (1 mmole) of diiron enneacarbonyl, and 10 ml of benzene was stirred at 40° for 3 hr. The filtered solution was concentrated under vacuum and the residue chromatographed on silica gel. Elution with benzene–*n*-hexane (1:10) and subsequent evaporation gave red crystals. Recrystallization from *n*-hexane gave 0.05 g of red cubic crystals, mp 83.5–84.5°. *Anal.* Calcd for C$_{20}$H$_{12}$Fe$_2$N$_2$O$_6$: C, 49.27; H, 2.48; N, 5.76; O, 19.67; mol wt, 487. Found: C, 48.76; H, 2.56; N, 5.60; O, 19.69; mol wt, 443.

While the free benzalazine showed an intense C=N stretching and out-of-plane deformations of monosubstituted benzene absorptions at 1620 and 753 and 692 cm^{-1}, respectively, the complex product showed the following infrared absorptions (provisional assignments are given in parentheses): 2070, 2034, 2000, and 1997 cm^{-1} (terminal CO stretching), 1568 cm^{-1} (very weak, C=N stretching), 755 and 752 cm^{-1} (strong, out-of-plane deformation for mono- and *ortho*-disubstituted benzene), and 690 cm^{-1} (out-of-plane deformation for monosubstituted benzene).

The nmr spectrum of the above complex showed the following resonances (the multiplicities and intensities): τ (TMS as the
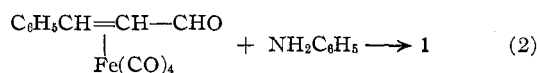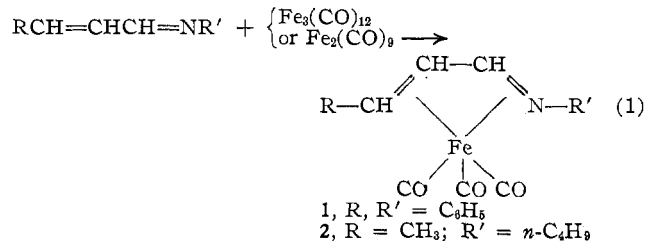
(11) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **53**, 288 (1963).

internal reference) 5.61 (singlet, 1), 2.88 (complex, 1), 2.64 (complex, 4), 2.42 (complex, 3), 2.27 (singlet, 1), 1.93 (complex doublet, 1).

An Attempted Reaction of Acetalazine with Diiron Ennea-carbonyl.—A mixture of 0.42 g (5 mmoles) of acetalazine, 0.89 g (2.4 mmoles) of diiron enneacarbonyl, and 10 ml of benzene was heated at 45° for 2 hr to give a dark brown solid. Unfortunately the instability prevented its identification.

Results

Substitution of the carbonyl ligand in diiron ennea-carbonyl or triiron dodecacarbonyl with cinnamalde-hydeanil yields a red diamagnetic crystalline complex (1). A similar reaction with crotonaldehyde-*n*-butyl-imine gives an orange-red oil (2) distillable under high vacuum. On the basis of molecular weight measurements and elemental analysis including determination of oxygen, they are formulated as $RCH{=}CH{-}CH{=}NR'{-}Fe(CO)_3$ (1, R = C$_6$H$_5$, R' = C$_6$H$_5$; 2, R = CH$_3$, R' = *n*-C$_4$H$_9$). The formulation for 1 is further supported by the preparation from cinnamaldehyde iron tetra-carbonyl[11] and aniline, 1 mole of carbon monoxide being removed during the reaction.

$$RCH{=}CHCH{=}NR' + \begin{Bmatrix} Fe_3(CO)_{12} \\ \text{or } Fe_2(CO)_9 \end{Bmatrix} \longrightarrow$$

1, R, R' = C$_6$H$_5$
2, R = CH$_3$; R' = *n*-C$_4$H$_9$

The liquid complex 2 is much more labile than 1 which can be stored unchanged for several months in air at ambient temperature. Treatment with triphenyl-phosphine of the two complexes 1 and 2 allows a qualitative comparison for the labilities of bondings between the enimine ligands and the Fe(CO)$_3$ moiety. Thus, triphenylphosphine substituted 1 mole of the carbonyl ligand in 1 yielding cinnamaldehydeanil(tri-phenylphosphine)iron dicarbonyl (3), while the aliphatic enimine ligand in 2 was readily replaced to give the known bis(triphenylphosphine)iron tricarbonyl.
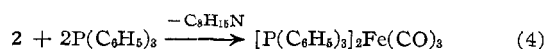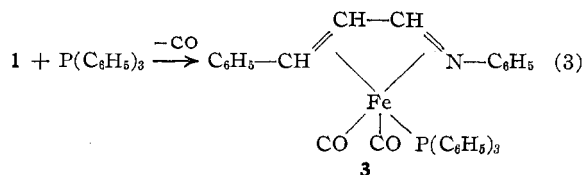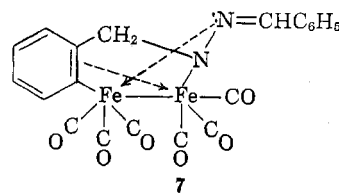
A reaction of diiron enneacarbonyl with diacetylanil and with diacetyl-*n*-butylimine produced the corresponding diimine complexes (4 and 5)

The solid complex 4 and the red liquid complex 5 are sublimable or distillable under high vacuum, indicating their considerable thermal stability. Complex 4 appears to be fairly inert, for the attempted substitution reaction with triphenylphosphine in boiling benzene resulted merely in recovery of the starting complex.

4, R = C$_6$H$_5$
5, R = *n*-C$_4$H$_9$
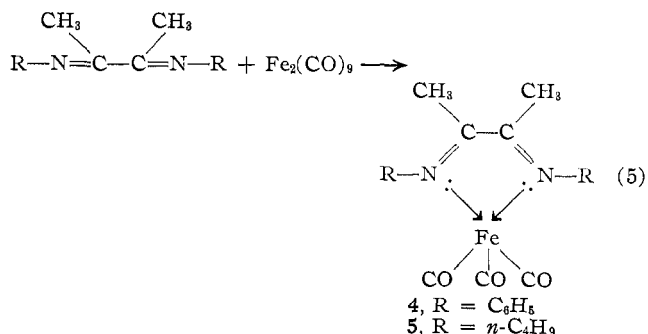
In order to add further information to the spectroscopic data of iron(0) complexes, on which the discussion of the natures of coordination bonding will be based, preparation of a diimine iron(II) complex was undertaken. Tris(diacetyldiimine)iron(II) prepared according to a known method[12] was found difficult to purify. A convenient preparation of the pure complex was the direct addition of diacetyldiimine to ferrous chloride in ethanol followed by precipitation with sodium tetrafluoroborate. Thus tris(diacetyl-*n*-butyl-imine)iron(II) tetrafluoroborate (6) was obtained in an analytically pure state as given in the Experimental Section.

An attempted preparation of a π complex involving benzalazine as a ligand from diiron enneacarbonyl gave red crystals for which the chemical composition and molecular weight corresponded to the formula (C$_6$H$_5$CH= N—N=CHC$_6$H$_5$)Fe$_2$(CO)$_6$ (7). The infrared absorptions at 755, 752, and 690 cm^{-1} suggested the presence of mono- and *ortho*-disubstituted benzene. The four absorptions of the terminal carbonyl stretchings may be ascribed to a binuclear Fe$_2$(CO)$_6$ group, as the spectra are quite similar to that of the ferrol-type complexes.[13] The two singlet nmr resonances at τ 5.61 and 2.27 may be due to methylene and methine protons adjacent to aromatic rings, respectively. These spectral data indicate that the red complex cannot be the expected π-diene type of complex. Presently the structure has not beeen settled other than that it might be a complex of the type 7 shown below, in which it is assumed that each iron ion achieves the formal closed-shell structure.

7

During preparation of this article, a brief note[14] has appeared describing an analogous complex formation from benzophenoneazine and diiron enneacarbonyl without description of the experimental evidence for the structure. To avoid the substitution reaction as seen in 7, aliphatic aldazine was applied for the preparation. However, because of the extreme instability,

(12) P. Krumholy, *J. Am. Chem. Soc.*, **75**, 2164 (1953).

(13) E. Weiss, W. Hübel, and R. Merenyi, *Chem. Ber.*, **95**, 1155 (1962).

(14) R. I. Reed, M. M. Bagga, P. L. Pauson, and F. J. Preston, *Chem. Commun.*, 543 (1965).

the purification and hence the identification of the expected π complex was not successful.

Discussion

In butadieneiron tricarbonyl, a typical π-1,3-diene-iron(0) complex, the two terminal vinylidene protons show large upfield shifts ($\Delta\tau = 4.7$ and 3.4) compared with those of the free ligand, while the upfield shift for the inner olefinic protons is very little ($\Delta\tau = 0.3$), much less than that expected from the geometry of the complex established by the X-ray studies.[15] The reasons for that can be a subject of much speculation.[16] A current view, which is in conformity with the nmr spectra, agrees[17] that, departing from sp² hybridization, the terminal carbons approach sp³ owing to their enhanced covalent bondings to Fe(0). This would imply that participation of each pπ–pπ double bond in the overlap with relevant orbitals of Fe(0) is such that the coordination cannot be considered to be of the exact (symmetrical) "side-on" type as in monoolefin complexes.

Table I indicates that in enimine complexes 1 and 2, the large upfield shifts for H(1) protons ($\Delta\tau = 3.64$–4.10) and the small upfield shift for the inner olefinic protons, H(2) and H(3), are comparable to those of the corresponding protons of butadiene in butadieneiron tricarbonyl. Note that the methyl protons, H(4), and N-methylene protons, H(5), in 2 also show upfield shift. Since the reverse shifts should be expected if the enimine nitrogen coordinates through its lone pair[18,19] and since the coordination center is the same Fe(CO)₃, the upfield shifts may be taken to indicate that these enimine ligands in 1 and 2 assume a conformation, illustrated in eq 1, analogous to that of the diene ligand in butadieneiron tricarbonyl.

The spin–spin coupling constant J_{12} for the free crotonaldehyde-n-butylimine was found to be 14.3 cps and decreased to 10 cps in 2 (Table I). The π-coordination effect resulting in the decrease in *trans*-coupling constants has been observed in many olefin complexes of low-valent transition metals.[20,21] The coupling constant J_{23} (see Table I) also decreased from 7.5 to 2.9 cps by the coordination. A similar decrease in the coupling constant of protons of two adjacent double bonds (=CH(2)—CH(3)=) may be found in azulene and its iron carbonyl complexes.[22] In a closely related complex, π-cinnamaldehydeiron tricarbonyl, C_6H_5-CH(1)=CH(2)—CH(3)=OFe(CO)₃, Weiss, *et al.*, observed J_{23} as nearly zero.[23] On the basis of the theory of Karplus,[24] they assumed the dihedral angle of the

=CH(2) and CH(3)=O planes to be nearly perpendicular, suggesting that the carbonyl oxygen donates its lone pair to Fe(CO)₃. However, factors other than the geometrical conformation must be involved in the reduced J_{23} values.

The infrared spectra of the free enimines show two absorptions in the C=C or C=N stretching regions. These absorptions shift considerably to the lower frequency side upon coordination (Table II) indicating decrease in bond orders of the C=C and C=N bonds. However, this cannot be taken as evidence for π coordination of the C=N bond, because coordination to metal through the lone pairs on nitrogen atoms of α-diimines often causes the shift toward the same direction.[25] The infrared spectra of the two diimines and their complexes too, therefore, gave little information. An absorption at 1633 cm⁻¹ of diacetyl-n-butylimine, a strong band at 1390 cm⁻¹ of complex 5, and a band at 1521 cm⁻¹ of complex 6 may be due to the C=N stretching absorptions. Again, the absorptions of the free ligands shift to the lower frequencies by the chelate coordination. However, since the reported C=N stretching frequencies for tris(glyoxalbismethylimine) or tris(diacetylbismethylimine) complexes of Ni(II), Co(II), and Fe(II)[26] suggest that the absorptions of the free α-diimines must be assumed to shift considerably to the lower frequency side (>80 cm⁻¹) by the chelate ligation through nitrogen lone pairs to Fe(II) ion, the observed shift (112 cm⁻¹) for 6 provides no support for the π coordination of the azomethine double bonds.

The nmr spectra appear to support participation of the nitrogen lone pair in the coordination. In contrast to the enimine complex 2 in which π coordination was postulated for the diene, tris(α-diimine)iron(II) (6) showed two nmr resonances at τ 6.50 and 5.62 (in nitrobenzene) for the N-methylene protons; *i.e.*, downfield shifts ($\Delta\tau = -0.16, -1.04$). Hence, the downfield shift ($\Delta\tau = -0.51$) observed for the corresponding protons of the diimine Fe(0) complex 5 suggests the chelate coordination bonding in 5 to be of similar nature to that involved in 6; the downfield shift may be attributed to the deshielding effect caused by donation of the nitrogen lone pair to Fe(0).

While the oxidation state of the central metal in the five-membered chelate ring seems not to be able to change the shift direction of N-methylene protons of α-diimines, the methyl protons attached to the inner olefinic carbons are subject to change in the shift direction. Thus, the methyl protons of Fe(0) complex 5 showed upfield shift ($\Delta\tau = 0.88$) in contrast to the Fe(II) complex 6.

In summary, we assume π-1,3-diene coordination for the enimine ligands in 1 and 2 and σ chelation through the nitrogen lone pairs for the σ-diimine ligands in 4 and 5. The introduction of an azomethine group into a butadiene system as in cinnamaldehydeanil or croton-

(15) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960).

(16) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, 1, 4 (1964).

(17) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *ibid.*, 3, 92 (1965).

(18) B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, 2, 1023 (1963).

(19) R. B. King and M. B. Bisnette, *ibid.*, 5, 293 (1966).

(20) R. Pettit and G. Robinson, *Advan. Organometal. Chem.*, 1, 65 (1964).

(21) T. Isobe, *Bull. Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ.*, 9, 116 (1960).

(22) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 108 (1965).

(23) K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch.*, 19b, 284 (1964).

(24) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

(25) E. Bayer and G. Häfelinger, *Chem. Ber.*, 99, 1689 (1966).

(26) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 193.

aldehyde-*n*-butylimine gives rise to a slight hypso-chromic shift[7] (70–240 A) in λ_{max} of the electronic spectra. The small shift presumably implies only a slight elevation of the vacant π^* orbitals involved in the dienes; *viz.*, the dπ-accepting ability of the enimine appears not to differ significantly from that of the parent 1,3-butadiene. Nevertheless, the π-1,3-diene coordination of the enimine system seems to be re-markable when one considers the geometrical situation of the nitrogen lone pair favorable for σ donation. Fail-ure for realization of the π-diene coordination in the case of α-diimines may be understood in terms of the high-lying vacant π^* orbital (larger hypsochromic shift compared to the enimine system[7]) and of the most favorable disposition of the two lone pairs to form the chelate ring.

Reactions of Alkali Metal Derivatives of Metal Carbonyls. VIII. Preparation, Protonation, and Alkylation of Sodium Cyanopentacarbonylmetalates[1]

BY R. B. KING[2]

Sodium bis(trimethylsilyl)amide reacts with the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, or W) in benzene solution to give the white water-soluble salts $Na[M(CO)_5CN]$ (M = Cr, Mo, or W). These salts react with trimethyltin chloride to give the white trimethyltin isocyanide complexes $(CH_3)_3SnNCM(CO)_5$ (M = Cr, Mo, or W). The salts $Na[M(CO)_5CN]$ are protonated in 4 N aqueous hydrochloric acid to give the white volatile hydrogen isocyanide complexes $HNCM(CO)_5$ (M = Cr, Mo, or W).

Introduction

Various complexes containing both metal carbonyl and metal cyanide ligands have been obtained from various metal carbonyl derivatives and the cyanide ion. Thus the anions $[M(CO)_5CN]^-$,[3,4] $[M(CO)_3(CN)_3]^{3-}$,[5] $[Mn(CO)_4(CN)_2]^-$,[6] $[C_5H_5Mo(CO)_2(CN)_2]^-$,[7] $[C_5H_5Fe(CO)(CN)_2]^-$,[7] and $[Co(CO)_2(NO)(CN)]^-$ [8] have been obtained from cyanide ion and the metal carbonyl de-rivatives $M(CO)_6$ (M = Cr, Mo, or W), $M(CO)_3$-$(NH_3)_3$ (M = Cr or Mo), $Mn(CO)_5X$, $C_5H_5Mo(CO)_3X$, $C_5H_5Fe(CO)_2X$, and $Co(CO)_3NO$, respectively.

Many of these syntheses suffer from one or more of the following disadvantages: (1) isolation of the anion as a solid salt from the methanol or water solution generally used is difficult; (2) removal of excess potassium or other alkali metal cyanide may present difficulties; (3) the reaction may not proceed to com-pletion; (4) more than one complex anion may be formed.

More recently Wannagat and Seyffert[9] described briefly an entirely different method for preparing metal carbonyl cyanide anions which does not require cyanide ion as a reagent. These workers found pentacarbonyl-iron and tetracarbonylnickel to react with sodium bis-(trimethylsilyl)amide to give the anions $[Fe(CO)_4CN]^-$ and $[Ni(CO)_3CN]^-$, respectively, apparently according to

$$M(CO)_x + NaN[Si(CH_3)_3]_2 \longrightarrow$$
$$Na[M(CO)_{x-1}(CN)]^- + [(CH_3)_3Si]_2O$$
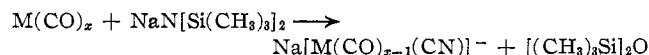
However, the sodium salts $Na[Fe(CO)_4CN]$ and $Na[Ni(CO)_3CN]$ were reported to be very sensitive to air oxidation and thus not easily handled.

Potentially more stable derivatives appeared to be the hexacoordinate salts $Na[M(CO)_5CN]$ (M = Cr, Mo, or W). These compounds were obtained as white hygroscopic precipitates in good yields by treating a benzene solution of sodium bis(trimethylsilyl)amide with the appropriate metal hexacarbonyl at room temperature.

The ready availability of the sodium salts $Na[M-(CO)_5CN]$ prompted a study of their reactions especially with various halides.[10] This resulted in the prepara-

(1) For part VII of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), in press.

(2) Department of Chemistry, University of Georgia, Athens, Ga.

(3) H. Behrens and J. Köhler, *Z. Naturforsch.*, **14b**, 463 (1959); *Z. Anorg. Allgem. Chem.*, **306**, 94 (1960).

(4) H. Behrens and H. Zizlsperger, *Z. Naturforsch.*, **16b**, 349 (1961); R. E. Maginn, U. S. Patent 3,095,436; *Chem. Abstr.*, **60**, 228h (1964).

(5) W. Hieber, W. Abeck, and H. K. Platzer, *Z. Anorg. Allgem. Chem.*, **280**, 252 (1955).

(6) R. J. Angelici, *Inorg. Chem.*, **3**, 1099 (1964).

(7) C. E. Coffey, *J. Inorg. Nucl. Chem.*, **25**, 179 (1963).

(8) R. Nast and M. Rohmer, *Z. Anorg. Allgem. Chem.*, **285**, 271 (1956); H. Behrens, E. Lindner, and H. Schindler, *Ber.*, **99**, 2399 (1966).

(9) U. Wannagat and H. Seyffert, *Angew. Chem.*, **77**, 457 (1965).

(10) When this paper was first submitted for publication, a referee pointed out some patents by R. E. Maginn describing related chemistry. The patents 3,136,797 and 3,136,799 (*Chem. Abstr.*, **61**, 7044c (1964)) describe the acylation and alkylation of the $Cr(CO)_5CN^-$ anion. The patent 3,136,-798 (*Chem. Abstr.*, **61**, 7982g (1964)) describes the protonation of $Cr(CO)_5$-CN^- salts in the presence of a bidentate ether (*e.g.*, 1,2-dimethoxyethane) to give products of the composition $[HNCCr(CO)_5]_2 \cdot$ (bidentate ether). The water solubility (in contrast to that of the $HNCM(CO)_5$ compounds described in this paper) suggests the compounds of Maginn to be bisoxonium salts $[(\text{bidentate ether}) \cdot 2H^+][Cr(CO)_5CN]_2$ containing the $Cr(CO)_5CN^-$ anion rather than true metal complexes of hydrogen isocyanide.