

Isocyanide Insertion Reaction of Alkyl Complexes of Iron(II)

Gianfranco Bellachioma, Giuseppe Cardaci,* and Pierfrancesco Zanazzi

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The reaction of $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{X}]$ with isocyanides gives different products according to the nature of X and isocyanides. With X = I the reaction proceeds forming ionic complexes. When the isocyanide is $\text{CNC}_6\text{H}_{11}$ the formation of $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\{\text{C}(\text{=CH}_2)\text{—NC}_6\text{H}_{11}\text{—C}(\text{=NHC}_6\text{H}_{11})\}][\text{BPh}_4]$ (**2a**) and $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CNC}_6\text{H}_{11})\{\text{C}(\text{=CH}_2)\text{—NC}_6\text{H}_{11}\text{—C}(\text{=NHC}_6\text{H}_{11})\}][\text{I}]$ (**4**) is observed. With CNCMe_3 the formation of a η^2 -iminoacyl complex $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\eta^2\text{-C}(\text{CH}_3)\text{=N—C}(\text{CH}_3)_3)][\text{BPh}_4]$ (**7a**) is obtained. The structures of **2a** and **7a** have been solved by single-crystal X-ray diffraction methods. **2a** crystallizes in the monoclinic space group $P2_1/a$ with lattice parameters $a = 20.175$ (4) Å, $b = 14.833$ (3) Å, $c = 16.052$ (3) Å, and $\beta = 106.97$ (2)°; it contains 4 molecules/cell. The structure has been solved by using 2172 observed reflections and refined to $R_w = 0.083$. Complex **7a** crystallizes in the monoclinic space group $P2_1/n$ with lattice parameters $a = 29.832$ (4) Å, $b = 12.174$ (3) Å, $c = 10.650$ (3) Å, and $\beta = 91.45$ (2)°; it contains 4 molecules/cell. The structure has been solved by using 1628 observed reflections and refined to $R_w = 0.081$. Complex **2a** shows octahedral coordination about the iron atom and contains a 1-aza-3-ferracyclobutane ring. A mechanism for its formation is proposed. Complex **7a** shows trigonal-bipyramidal coordination about the iron and an η^2 -iminoacyl structure, which is in equilibrium in solution with the methyl structure $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{—}(\text{CNC}(\text{CH}_3)_3)][\text{BPh}_4]$. The equilibrium is influenced by the anion group. With X = CN no ionization is observed. $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{CN}]$ reacts with CNCMe_3 , forming the nonionic acetyl complex $[\text{Fe}(\text{CO})(\text{PMe}_3)_2(\text{CNCMe}_3)(\text{COCH}_3)\text{CN}]$.

Introduction

The insertion reaction is one of the most important rearrangements of organic and organometallic chemistry.¹ In the last 25 years, however, only a few insertion reactions have been completely clarified. In particular, the insertion of carbon monoxide into the metal-alkyl bond has been extensively studied² since it is important in many reactions of homogeneous catalysis via transition metals, such as homologation,³ hydroformylation,⁴ the Fischer-Tropsch⁵ synthesis, etc. It is generally accepted that this reaction proceeds via migration of the alkyl group to the carbon of the carbon monoxide, coordinated to the metal in the cis position.⁶ The nature of the intermediate, which may be either an unsaturated complex or an η^2 complex coordinated via the oxygen of the acyl group,⁷ is open to question. The theoretical results are in agreement with the experimental results, but they exclude formation of the η^2 structure.⁸

The isocyanide ligand is isoelectronic with carbon monoxide⁹ and can similarly insert into a metal-alkyl bond¹⁰ with its nitrogen atom available for stabilizing the η^2 structure.⁸ A study of this insertion reaction and the structure of the intermediate¹¹ may provide further information on the insertion reaction of carbon monoxide.

After having completed the study of the insertion reactions of carbon monoxide in various alkyl complexes of iron^{12,13} $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{X}]$ (X = I, Cl, Br, NCS, CN), we started a comparable study of the insertion reaction of isocyanides in the same complexes. Preliminary results regarding the structural characterization of the complexes $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\{\text{C}(\text{=CH}_2)\text{—NC}_6\text{H}_{11}\text{—C}(\text{=NHC}_6\text{H}_{11})\}][\text{BPh}_4]$ (**2a**) and $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\eta^2\text{-CMe=N—CMe}_3)][\text{BPh}_4]$ (**7a**) were described previously.^{14,15} In this paper we give a general picture of the results.

Experimental Section

Cyclohexyl isocyanide ($\text{CNC}_6\text{H}_{11}$) and *tert*-butyl isocyanide (CNCMe_3) are commercial products (Fluka) and were used without further purification. Trimethylphosphine was prepared following the method described by Schmidbaur.¹⁶ $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{I}]$ and $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{CN}]$ were prepared as described previously.^{12,17} Benzene was dehydrated by refluxing with Na and distilled under nitrogen; tetrahydrofuran (THF) was reacted with Na and benzophenone and freshly distilled; dichloromethane was distilled from P_2O_5 ; methyl alcohol was commercial and was used without further purification.

All the reactions were carried under nitrogen. The infrared spectra were recorded on a 257 or 983 Perkin-Elmer spectrophotometer. The ¹H NMR spectra were recorded on a JEOL CHL-60 spectrophotometer using tetramethylsilane (Me_4Si) as the internal reference. The elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

* To whom correspondence should be addressed at the Dipartimento di Chimica.

Table I. Analytical Data

complex	% found			% calcd		
	C	H	N	C	H	N
2	44.2	6.59	4.55	44.25	6.94	4.49
4	49.2	7.65	5.83	49.37	7.72	5.96
4a	69.5	7.95	3.62	69.12	7.78	3.43
7a	66.9	7.45	1.99	66.98	7.40	2.06
8	40.6	6.94	4.90	39.88	6.87	4.90
9	46.2	7.63	7.32	46.41	7.79	7.22

The conductivity measurements were carried out with an Amel instrument.

Elemental analyses and IR and ¹H NMR spectra of the complexes studied are given in Tables I-III, respectively.

Preparation of the Complexes. $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\{\text{C}(\text{=CH}_2)\text{—NC}_6\text{H}_{11}\text{—C}(\text{=NHC}_6\text{H}_{11})\}][\text{I}]$ (**2**). (a) Reaction in Benzene. $\text{CNC}_6\text{H}_{11}$ (7.2 mmol) was added to a solution of 1.0 g of $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{I}]$ (2.5 mmol) in 50 mL of benzene at room temperature. Immediately the color of the solution changed from red to orange and the IR spectrum of the solution showed the formation of the intermediate $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3)\text{—}(\text{CNC}_6\text{H}_{11})\text{—C}(\text{=NHC}_6\text{H}_{11})][\text{I}]$.

- (1) Tsuji, J. In *Organic Synthesis by means of Transition Metal Complexes*; Springer-Verlag: Berlin, 1975; pp 109-143.
- (2) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299-311.
- (3) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87-145.
- (4) Bahrmann, H.; Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; pp 226-242.
- (5) Pino, P.; Piacenti, F.; Bianchi, H. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 43-231.
- (6) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103. Heinrici-Olivè, G.; Olivè, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136-141.
- (7) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30-36. Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994-3999. Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101-104.
- (8) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410-4414.
- (9) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224-7236.
- (10) Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273-1284.
- (11) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1972**, *11*, 211-214.
- (12) Yamamoto, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2653.
- (13) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196-7198.
- (14) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225-247.
- (15) Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Chem. Soc., Dalton Trans.* **1983**, 2593-2597.
- (16) Reichenbach, G.; Cardaci, G.; Bellachioma, G. *J. Chem. Soc., Dalton Trans.* **1982**, 847-850. Cardaci, G.; Reichenbach, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936-2940.
- (17) Cardaci, G.; Bellachioma, G.; Zanazzi, P. F. *Polyhedron* **1983**, 967-968.
- (18) Cardaci, G.; Bellachioma, G.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1984**, 650-651.
- (19) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149-154.
- (20) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227-234.

Table II. Infrared Spectra (cm⁻¹)

complex	solvent	$\nu_{\text{C}=\text{N}}$	ν_{CO}	ν_{COCH_3}	$\nu_{\text{C}=\text{N}}$	other bands
1	C ₆ H ₆	2160	1940	1585		
2	CH ₂ Cl ₂		2013.0		1562	$\nu_{\text{N-H}} = 3150$
	CH ₃ OH		2014		1561	$\nu_{\text{N-H}} = 3152$
	CH ₃ OD		1959.0			
			2015.0		1526.5	
			1959.0			
2a	CH ₂ Cl ₂		2020.0		1551	
	Nujol		1964.0			
			2004.0		1549	
			1953.0			
			2003.0		1551	
			1953.0			
3	C ₆ H ₆	2195.0	1970		1570	
		2165.0				
4	CH ₂ Cl ₂	2124.5	1979.5		1581.5	
	Fluorolube	2120.0	1975		1529.5	
					1573.0	
					1532.0	
					1575.0	$\nu_{\text{N-H}} =$
					1535.5	3216.5
5	C ₆ H ₆	2155	1942	1587		
	THF	2150	1940	1585		
6	CH ₂ Cl ₂	2179.0	2027.0			
			1985.0			
	Nujol	2170.0	2010.0			
			1970.0			
6a	CH ₂ Cl ₂	2170.0	2025.0			
			1985.0			
7	CH ₂ Cl ₂		2015.0		1756.0	
			1951.0			
	Nujol		2002.0		1752.0	
			1942.0			
7a	CH ₂ Cl ₂		2015.0		1753.0	
			1952.0			
8	CH ₂ Cl ₂	2190	1957	1592		
		2152				
8a	CH ₂ Cl ₂	2175	1982	1600		
		2140				
9	CH ₂ Cl ₂	2136	1959	1568		

(PMe₃)₂(CNC₆H₁₁)(COCH₃)I (1). After 2 h the formation of a light yellow microcrystalline precipitate was observed. The solution was reacted further for 48 h, and the solid was filtered out and washed with benzene. A 0.5-g sample of complex 2 was obtained (yield 34%). Complex 2 could not be recrystallized from other solvents, so the analytical measurements were performed with the crude compound. Complex 2 is ionic: equivalent conductivity $\Lambda_c = 118 \text{ S}\cdot\text{cm}^2$ for a solution 5 mM in CH₂Cl₂. It reacts with NaBPh₄ in CH₃OH to give a white-yellow microcrystalline solid, which analyzes as [Fe(CO)₂(PMe₃)₂C(=CH₂)-NC₆H₁₁-C(=NHC₆H₁₁)] [BPh₄]⁻ (2a).

The reaction in benzene was followed spectrophotometrically with IR measurements recorded in the range 2200–1500 cm⁻¹. It proceeded in successive steps, forming at least two different compounds from intermediate 1. At first the formation of a complex having the probable structure 3a was observed: it showed three IR stretching bands at 2200, 1995, and 1555 cm⁻¹. Complex 3a slowly converted into complex 3, which showed three IR stretching bands at 2200, 1970, and 1570 cm⁻¹. Following this transformation the benzene solution was dried and a red spongy solid was obtained. This solid was dissolved in CH₂Cl₂ and precipitated with *n*-hexane. A black-red viscous liquid was separated, which, after decantation and drying, became a red-yellow spongy solid. Many attempts were made to obtain complex 3 in a crystalline form. In no case, was complex 3 obtained in pure form. Even after chromatographing it over Al₂O₃ with a mixture of CH₂Cl₂/*n*-hexane as eluent or over SiO₂ with a mixture of ethyl acetate and CH₃OH as eluent, the complex could not be obtained pure. Therefore, the characterization of 3 is based on the spectroscopic features (Tables II and III) and on its chemical behavior. The relative amount of 2 with reference to the reacting complex [Fe(CO)₂(PMe₃)₂(CH₃)I] depends on the amount of CNC₆H₁₁: with a ligand/complex ratio of 2.9, the yield of 2 is 34%; with a ratio of 11.5, the yield is 3.5%.

(b) Reaction in CH₂Cl₂. The reaction proceeded as in benzene; in this solvent complexes 2 and 3 were soluble, the separation of 2 being obtained by drying the solution and extracting with benzene complex 3. The residue solid was dissolved in CH₃OH and precipitated with NaBPh₄ as 2a.

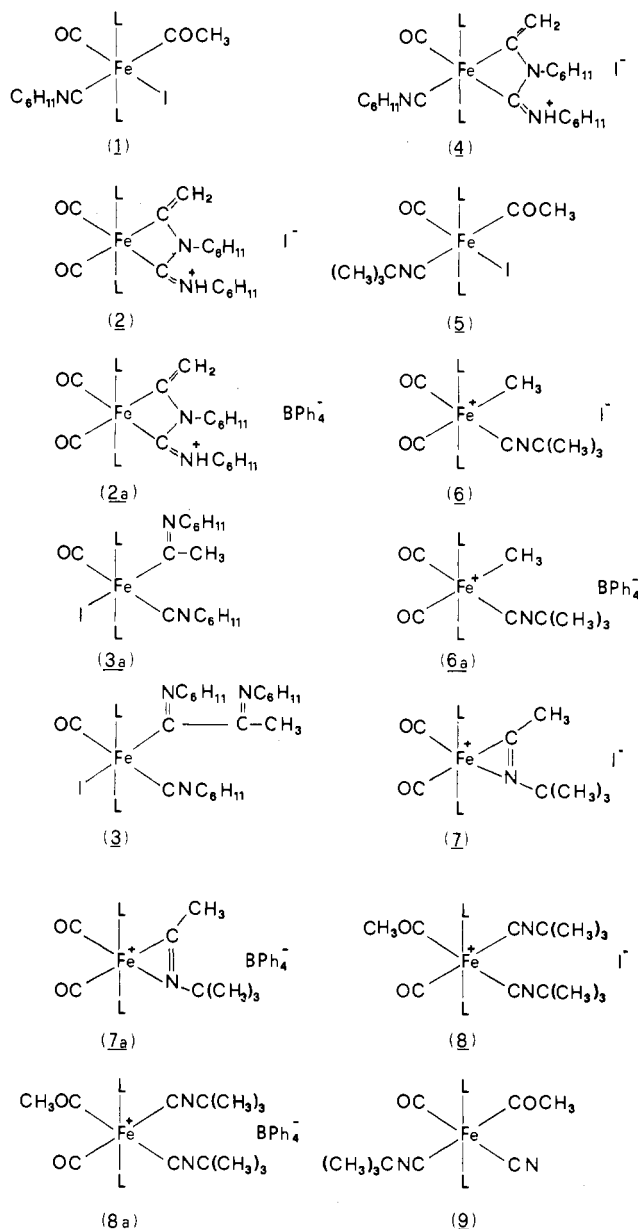


Figure 1. View of the structure of the complexes.

(c) Crystallization of Complex 2a. In no case was complex 2 crystallized. To perform a structural characterization with X-ray techniques, it was obtained as 2a, and the rate of formation in CH₃OH from complex 2 was controlled by adding a common ion: complex 2 (0.5 g) was dissolved in 150 mL of CH₃OH, containing 10 g of LiI; then 1.5 g of NaBPh₄ was added. The solution was left at -20 °C; well-formed yellow crystals were slowly precipitated over a 20-day period.

[Fe(CO)(PMe₃)₂(CNC₆H₁₁)]C(=CH₂)-NC₆H₁₁-C(=NHC₆H₁₁)]I (4). *n*-Hexane was added to the benzene solution of complex 3 up to incipient turbidity. A slow separation of yellow crystals was observed. These crystals analyze as 4 (Table I). Complex 4 is ionic: equivalent conductivity $\Lambda_c = 35 \text{ S}\cdot\text{cm}^2$ in CH₂Cl₂ at *c* 1.85 mM.

[Fe(CO)₂(PMe₃)₂(CNCMe₃)₂(COCH₃)]I (8). [Fe(CO)₂(PMe₃)₂(CH₃)I] (3.1 mmol) was added to a benzene solution of CNCMe₃ (8.8 mmol). After 20 min the formation of a yellow precipitate was observed. The reaction was complete in 5 h. The solid was filtered and 1.2 g (yield 86%) of complex 8 was obtained; mp 155–161 °C.

[Fe(CO)₂(PMe₃)₂(η²-CMe=N-CMe₃)] [BPh₄]⁻ (7a). [Fe(CO)₂(PMe₃)₂(CH₃)I] (0.95 mmol) was added to a benzene solution of 0.07 g (0.81 mmol) of CNCMe₃. Formation of complex 5 was observed immediately. Various attempts at the separation of 5 were unsuccessful since in the solid state it transforms into isomers 6 and 7. The characterization of 5 was supported on the basis of spectroscopic evidence (see Tables II and III). The benzene solution of 5 was dried, and the mixture of geometrical isomers 6 and 7 was obtained in the solid state. These complexes, 6 and 7, were not separated via fractional crystallization, but

Table III. ¹H NMR Spectra

complex	solvent	τ (M, I)	J , Hz	assign
2	CDCl ₃	8.44 (t, 18)		PMe ₃
		8.21 (b, 20)		C ₆ H ₁₁ NC
		6.64 (b, 2)		C ₆ H ₁₁ NC
		5.88 (q, 1)		CH ₂ =C
		4.88 (q, 1)		CH ₂ =C
2a	CD ₂ Cl ₂	8.53 (t, 18)	4.2 (J_{Me-P})	PMe ₃
		8.20 (b, 20)		C ₆ H ₁₁ NC
		6.59 (b, 2)		C ₆ H ₁₁ NC
		5.73 (q, 1)	2.2	CH ₂ =C
		4.86 (q, 1)	2.8	CH ₂ =C
3	CDCl ₃	8.52 (t)		PMe ₃
		8.30 (b)		C ₆ H ₁₁ NC
		7.62 (s)		CH ₃
4	CD ₂ Cl ₂	8.64 (t)	4.2	PMe ₃
		8.0–8.5 (b) } (48)		C ₆ H ₁₁ NC
		5.91 (m, 1)		CH ₂ =C
5	C ₆ D ₆	5.10 (m, 1)		CH ₂ =C
		8.50 (t, 18)	4.0	PMe ₃
		8.82 (s, 9)		C(CH ₃) ₃ NC
6a	CD ₂ Cl ₂	7.65 (s, 3)		COCH ₃
		9.94 (t, 3)	7.8	CH ₃ Fe
		8.35 (t, 18)	4.0	PMe ₃
7a	CD ₂ Cl ₂	8.55 (t, 18)	4.2	PMe ₃
		8.50 (s, 9)		C(CH ₃) ₃
		7.04 (t, 3)	2.4	CH ₃ C
8	CD ₃ CN	8.40 (b, 36)		PMe ₃ + CMe ₃ NC
		7.65 (s, 3)		COCH ₃
		8.38 (s, 18)		CMe ₃ NC
8a	CD ₂ Cl ₂	8.30 (t, 18)	4.0	PMe ₃
		7.50 (s, 3)		COCH ₃
		8.45–8.62 (b, 29)		PMe ₃ + C ₆ H ₁₁ NC
9	CD ₂ Cl ₂	7.60 (s, 3)		COCH ₃

by following a different path. The mixture of **6** and **7** was dissolved in CH₃OH and precipitated as a mixture of **6a** and **7a**. The IR and ¹H NMR spectra of the mixture indicated that no dynamic equilibrium between isomers **6a** and **7a** was present in the temperature range 0–40 °C. Isomer **7a** was then obtained pure via crystallization of the mixture from a THF/*n*-hexane solution. The solid mixture of **6a** and **7a** was dissolved in THF, and *n*-hexane was added up to the beginning of the crystallization. The solution was kept at –15 °C, and the formation of good crystals of **7a** was observed. Next, fractions of **7a** were obtained, and in solution, the ratio **6a**/**7a** was shifted toward complex **6a**. Despite this, complex **7a** was obtained pure during the crystallization.

The reaction between [Fe(CO)₂(PMe₃)₂(CH₃)I] and CNCMe₃ (ratio 1/1) proceeded in THF as in benzene. In this case, too, the formation in solution of complex **5** was observed. Complexes **6** and **7** precipitated from this solution in the equilibrium ratio. The solid mixture of **6** and **7** was dissolved in THF to give complex **5**.

[Fe(CO)(PMe₃)₂(CNCMe₃)(COCH₃)(CN)] (**9**). A solution of 0.2 g of [Fe(CO)₂(PMe₃)₂(CH₃)(CN)] in CH₂Cl₂ was added to 5 mL of a solution of 0.13 M CNCMe₃ at room temperature. The reaction was complete in a few minutes, the formation of complex **9** being observed. Complex **9** was crystallized from the solution by addition of *n*-hexane. Decarbonylation of complex **9** was not observed after 35 h of refluxing under bubbling with nitrogen.

Reaction between *cis,trans*-[Fe(CO)₂(PMe₃)₂(COCH₃)I] and CNC₆H₁₁. *cis,trans*-[Fe(CO)₂(PMe₃)₂(COCH₃)I] (1.2 mmol) was added to a benzene solution of CNC₆H₁₁ (3.7 mmol). The reaction proceeded as with the methyl complex but with a much slower reaction rate. The formation of the precipitate **2** was observed. The benzene solution showed the formation of complex **1**, which then gave complexes **3a** and **3**. Separation of the complexes was performed as described previously.

Isotopic Exchange with CH₃OD. Complex **2** was dissolved in CH₃OD. The ¹H NMR spectrum, which was taken at various times, showed the characteristic bands of complex **2**. The bands assigned to the C=CH₂ group (Table III) disappeared slowly, and no other exchange was observed. The IR spectrum of complex **2** (Table II), taken in CH₃OD, showed a strong decrease of the frequency of the C=N band from 1561 to 1526.5 cm⁻¹ and the disappearance of the band at 3152 cm⁻¹, assigned to the N—H stretching band.

Collection of X-ray Diffraction Data

[Fe(CO)₂(PMe₃)₂][C(=CH₂)—NC₆H₁₁—C(=NHC₆H₁₁)] [BPPh₄] (**2a**). A white-yellow crystal of **2a** was used for the determination of cell

parameters and subsequent data collection. The crystal was mounted on a glass fiber with epoxy and transferred to the diffractometer. Crystal survey, unit cell dimension determination, and data collection were performed at room temperature on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite-mono-chromatized Mo K α radiation ($\lambda = 0.71069$ Å). The observed systematic absences are consistent with the monoclinic space group *P2₁/a*. Cell dimensions were determined from a least-squares refinement based on the setting angles of 25 reflections with 2θ ranging between 17 and 25°.

The intensities were collected up to $2\theta = 40^\circ$. A total of 4120 independent reflections were measured, of which 1948 having $I \leq 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement. Three standard reflections, measured periodically, showed no apparent variation in intensity during data collection. The linear absorption coefficient for Mo K α radiation is $\mu = 4.02$ cm⁻¹. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North et al.,¹⁸ the transmission factors were in the range 0.99–0.81.

The structure was solved by direct methods and refined by the full-matrix least-squares method with the SHELX-76 package of programs.¹⁹ The phenyl groups were constrained to perfect hexagons (C—C = 1.395 Å) and refined as rigid groups, with individual isotropic thermal parameters assigned to each C atom. The hydrogen atoms (with exception of those of the methyl groups) were included at the calculated positions (C—H = 1.08 Å) with an overall isotropic parameter $U = 0.09$ Å². Anisotropic thermal parameters were refined for Fe, P, O, and N atoms and for the carbon atoms linked to the iron. The refinement converged at $R(\text{unweighted}) = 0.077$ and $R(\text{weighted}) = 0.083$ for 231 parameters and 2172 observed reflections ($R_w = (\sum_w(|F_o| - |F_c|)^2)^{1/2} / (\sum_w F_o^2)^{1/2}$; $w = (\sigma^2(F_o) + 0.0005F_o^2)^{-1}$).

[Fe(CO)₂(PMe₃)₂(η^2 -C(CH₃)=N—C(CH₃)₃)] [BPPh₄] (**7a**). A white-yellow crystal of **7a** was mounted on the diffractometer and handled as complex **2a**. The cell dimensions and the space group (monoclinic *P2₁/n*) were obtained as for complex **2a**.

The intensities were collected and treated as described for **2a**. A total of 3835 independent reflections were measured, of which 2207 having $I \leq 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement; the transmission factors were in the range 0.99–0.92.

The structure was solved by direct methods and refined by the full-matrix least-squares method with the SHELX-76 package of programs,¹⁹ with the same constraints employed for complex **2a**. The isotropic common thermal parameters of H atoms were refined to $U = 0.14$ Å². Anisotropic thermal parameters were refined for Fe and P atoms. The refinement converged at $R(\text{unweighted}) = 0.075$ and $R(\text{weighted}) = 0.081$ for 149 parameters and 1628 observed reflections ($w = (\sigma^2(F_o) + 0.030F_o^2)^{-1}$).

The atomic scattering factors for both **2a** and **7a** were taken from ref 19 for P, O, N, C, B, and H and from ref 20 for Fe; a correction for anomalous dispersion was included. Complete listings of final positional parameters are provided in Table IV (complex **2a**) and Table V (complex **7a**). A summary of crystal and intensity collection data is given in Table VI.

Discussion

(1) **Description of the Molecular Structure of [Fe(CO)₂(PMe₃)₂][C(=CH₂)—NC₆H₁₁—C(=NHC₆H₁₁)] [BPPh₄] (**2a**).** The molecular structure of the cation of complex **2a** is shown in Figure 2. Table VII reports the salient bond distances and angles. The cation of **2a** shows an octahedral structure with two trans PMe₃ ligands (P(1)—Fe—P(2) = 176.1 (2)°) and two cis CO ligands (C(8)—Fe—C(7) = 97.4 (6)°). The last two positions are occupied by the 1-aza-3-ferracyclobutane ring. The most interesting feature of the structure of complex **2a** is the 1-aza-3-ferracyclobutane moiety. The series of N(2)—C(17)—N(1)—C(9)—C(10) atoms lie in the same plane (maximum atomic deviation from the least-squares plane is 0.04 Å). The bond distances (C(9)—C(10) = 1.364 (17), C(9)—N(1) = 1.426 (14), N(1)—C(17) = 1.347 (13), and C(17)—N(2) = 1.337 (13) Å), intermediates between single and double C—C and C—N bonds, indicate an extensive conjugation²¹

- (18) North, A. C. T.; Phillips, D. L.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **1968**, *A24*, 351–359.
 (19) Sheldrick, G. M. *SHELX, Programme for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.
 (20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

Table IV. Fractional Atomic Coordinates in Complex 2a^a

atom	x/a	y/b	z/c
Fe	0.1360 (1)	0.1354 (1)	0.6472 (1)
P(1)	0.0648 (2)	0.1965 (2)	0.5253 (2)
P(2)	0.2125 (2)	0.0720 (2)	0.7643 (2)
O(1)	0.0165 (6)	0.0581 (7)	0.6905 (7)
O(2)	0.1612 (5)	-0.0141 (8)	0.5424 (8)
N(1)	0.1998 (5)	0.2851 (6)	0.6792 (6)
N(2)	0.1181 (5)	0.3034 (7)	0.7554 (6)
C(1)	0.0048 (8)	0.1200 (11)	0.4546 (11)
C(2)	0.1045 (10)	0.2505 (15)	0.4451 (14)
C(3)	0.0074 (10)	0.2862 (13)	0.5395 (13)
C(4)	0.2586 (7)	0.1473 (9)	0.8566 (9)
C(5)	0.1774 (7)	-0.0173 (10)	0.8159 (10)
C(6)	0.2853 (7)	0.0135 (9)	0.7411 (9)
C(7)	0.0629 (8)	0.0874 (9)	0.6747 (9)
C(8)	0.1517 (8)	0.0435 (11)	0.5848 (11)
C(9)	0.2133 (7)	0.2094 (9)	0.6319 (9)
C(10)	0.2666 (8)	0.2044 (9)	0.5957 (9)
C(11)	0.2335 (6)	0.3743 (8)	0.6967 (7)
C(12)	0.3067 (6)	0.3704 (9)	0.7532 (9)
C(13)	0.3428 (7)	0.4619 (9)	0.7730 (9)
C(14)	0.3367 (7)	0.5103 (10)	0.6871 (9)
C(15)	0.2617 (7)	0.5185 (9)	0.6322 (9)
C(16)	0.2281 (7)	0.4245 (9)	0.6112 (8)
C(17)	0.1456 (6)	0.2543 (8)	0.7040 (8)
C(18)	0.0586 (6)	0.2743 (8)	0.7843 (7)
C(19)	0.0800 (6)	0.2170 (8)	0.8646 (8)
C(20)	0.0179 (7)	0.1936 (10)	0.8966 (10)
C(21)	-0.0215 (8)	0.2767 (11)	0.9072 (11)
C(22)	-0.0434 (8)	0.3342 (11)	0.8263 (10)
C(23)	0.0200 (6)	0.3602 (8)	0.7979 (8)
C(24)	-0.0573 (4)	0.3887 (5)	0.2556 (5)
C(25)	0.0111 (4)	0.3919 (5)	0.2527 (5)
C(26)	0.0608 (4)	0.4396 (5)	0.3162 (5)
C(27)	0.0421 (4)	0.4841 (5)	0.3825 (5)
C(28)	-0.0263 (4)	0.4809 (5)	0.3854 (5)
C(29)	-0.0760 (4)	0.4332 (5)	0.3220 (5)
C(30)	-0.0924 (4)	0.2441 (4)	0.1350 (5)
C(31)	-0.0353 (4)	0.1955 (4)	0.1848 (5)
C(32)	-0.0164 (4)	0.1150 (4)	0.1528 (5)
C(33)	-0.0546 (4)	0.0832 (4)	0.0711 (5)
C(34)	-0.1116 (4)	0.1318 (4)	0.0214 (5)
C(35)	-0.1305 (4)	0.2122 (4)	0.0533 (5)
C(36)	-0.1353 (4)	0.4224 (5)	0.1000 (5)
C(37)	-0.0937 (4)	0.4316 (5)	0.0447 (5)
C(38)	-0.1023 (4)	0.5057 (5)	-0.0111 (5)
C(39)	-0.1525 (4)	0.5705 (5)	-0.0114 (5)
C(40)	-0.1941 (4)	0.5613 (5)	0.0439 (5)
C(41)	-0.1854 (4)	0.4872 (5)	0.0997 (5)
C(42)	-0.1878 (4)	0.3058 (6)	0.2034 (6)
C(43)	-0.2548 (4)	0.3115 (6)	0.1465 (6)
C(44)	-0.3108 (4)	0.2793 (6)	0.1720 (6)
C(45)	-0.2999 (4)	0.2414 (6)	0.2545 (6)
C(46)	-0.2330 (4)	0.2357 (6)	0.3114 (6)
C(47)	-0.1769 (4)	0.2679 (6)	0.2859 (6)
B	-0.1187 (7)	0.3405 (9)	0.1743 (9)

^aEsd's in parentheses refer to the last digit.

along the 1-aza-3-ferracyclobutane ring. This excludes the bonding of the hydrogen atom to the N(1) atom, which should assume a tetrahedral geometry, and supports the bonding of hydrogen to the N(2) atom. The Fe-C(17) and Fe-C(9) bond distances of 1.970 (12) and 1.982 (12) Å, respectively, are typical of an iron-carbon single bond.²²

(2) Description of the Molecular Structure of [Fe(CO)₂(PMe₃)₂(η²-C(CH₃)=N-C(CH₃)₃)]BPh₄ (7a). The molecular structure of the cation of complex 7a is shown in Figure 3. Table VIII reports the salient bond distances and angles. The cation of 7a shows a trigonal-bipyramidal structure with the two apical

Table V. Fractional Atomic Coordinates in Complex 7a^a

atom	x/a	y/b	z/c
Fe	0.3725 (1)	0.2789 (2)	0.4191 (2)
P(1)	0.4102 (1)	0.1564 (3)	0.2997 (4)
P(2)	0.3364 (1)	0.3982 (3)	0.5460 (3)
O(1)	0.4518 (4)	0.2983 (9)	0.5779 (10)
O(2)	0.3268 (5)	0.0934 (11)	0.5307 (12)
N	0.3416 (4)	0.3447 (8)	0.2673 (9)
C(1)	0.3748 (6)	0.0555 (14)	0.2110 (15)
C(2)	0.4499 (6)	0.0686 (15)	0.3934 (17)
C(3)	0.4441 (6)	0.2151 (14)	0.1746 (15)
C(4)	0.3461 (5)	0.5460 (12)	0.5184 (14)
C(5)	0.2755 (5)	0.3886 (13)	0.5410 (14)
C(6)	0.3518 (6)	0.3824 (15)	0.7118 (16)
C(7)	0.4192 (5)	0.2902 (12)	0.5127 (13)
C(8)	0.3468 (6)	0.1692 (15)	0.4883 (15)
C(9)	0.3769 (5)	0.3906 (11)	0.2901 (11)
C(10)	0.4043 (5)	0.4829 (13)	0.2399 (14)
C(11)	0.3032 (5)	0.3537 (13)	0.1706 (14)
C(12)	0.3278 (6)	0.3494 (14)	0.0379 (16)
C(13)	0.2720 (6)	0.2572 (15)	0.1914 (17)
C(14)	0.2816 (6)	0.4670 (15)	0.1836 (15)
B	0.1127 (5)	0.2792 (14)	0.5985 (14)
C(15)	0.1092 (3)	0.2662 (7)	0.4431 (6)
C(16)	0.1473 (3)	0.2724 (7)	0.3703 (6)
C(17)	0.1430 (3)	0.2743 (7)	0.2396 (6)
C(18)	0.1006 (3)	0.2700 (7)	0.1816 (6)
C(19)	0.0625 (3)	0.2639 (7)	0.2543 (6)
C(20)	0.0667 (3)	0.2620 (7)	0.3851 (6)
C(21)	0.0780 (3)	0.1929 (7)	0.6726 (8)
C(22)	0.0676 (3)	0.2180 (7)	0.7964 (8)
C(23)	0.0410 (3)	0.1466 (7)	0.8649 (8)
C(24)	0.0247 (3)	0.0501 (7)	0.8096 (8)
C(25)	0.0351 (3)	0.0250 (7)	0.6859 (8)
C(26)	0.0617 (3)	0.0964 (7)	0.6174 (8)
C(27)	0.1008 (3)	0.4100 (6)	0.6255 (8)
C(28)	0.1344 (3)	0.4898 (6)	0.6251 (8)
C(29)	0.1233 (3)	0.6004 (5)	0.6386 (8)
C(30)	0.0786 (3)	0.6312 (6)	0.6524 (8)
C(31)	0.0451 (3)	0.5514 (6)	0.6528 (8)
C(32)	0.0562 (3)	0.4407 (6)	0.6393 (8)
C(33)	0.1628 (3)	0.2443 (7)	0.6628 (8)
C(34)	0.1802 (3)	0.2980 (7)	0.7677 (8)
C(35)	0.2201 (3)	0.2629 (7)	0.8255 (8)
C(36)	0.2428 (3)	0.1722 (7)	0.7783 (8)
C(37)	0.2255 (3)	0.1166 (7)	0.6733 (8)
C(38)	0.1855 (3)	0.1517 (7)	0.6155 (8)

^aEsd's in parentheses refer to the last digit.

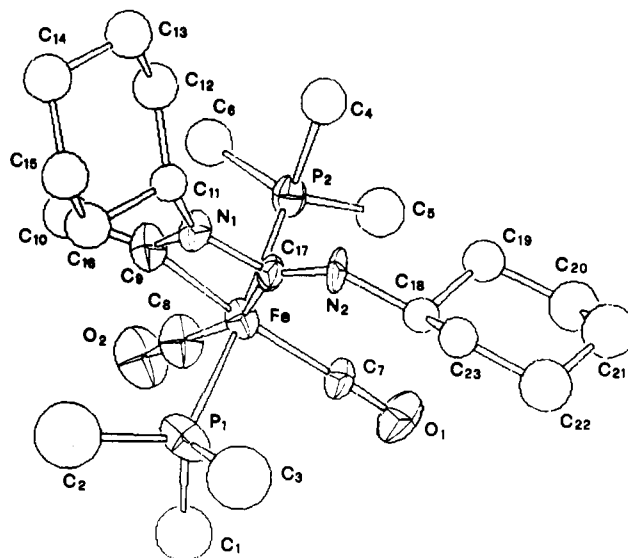


Figure 2. Molecular structure of the cation of the complex 2a.

positions occupied by two trimethylphosphine ligands. Two other cis positions are occupied by the CO ligands with an angle between them of 100.3 (7)°. The third position is occupied by an η²-

- (21) Merenyi, R. In *Advances in Organic Chemistry*; Bohme, H., Viehe, H. G., Eds.; Wiley-Interscience: New York, 1976; Vol. 9, Part I, pp 23-105.
- (22) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 2647-2648. Wagner, K. P.; Treichel, P. M.; Calabrese, J. C. *J. Organomet. Chem.* **1974**, *71*, 299-308.

Table VI. Summary of Crystal Data and Intensity Collection for Complexes **2a** and **7a**

	2a	7a
A. Crystal Data		
formula	$C_{23}H_{43}N_2O_2P_2Fe \cdot C_{24}H_{20}B$	$C_{14}H_{30}NO_2P_2Fe \cdot C_{24}H_{20}B$
cryst dimens, mm	$0.40 \times 0.25 \times 0.20$	$0.30 \times 0.25 \times 0.20$
color	white-yellow	white-yellow
cell params (errors)		
<i>a</i> , Å	20.175 (4)	29.832 (4)
<i>b</i> , Å	14.833 (3)	12.174 (3)
<i>c</i> , Å	16.052 (3)	10.650 (3)
β , deg	106.97 (2)	91.45 (2)
cryst type	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
<i>Z</i>	4	4
d_{calcd} , g/cm ³	1.179	1.045
B. Data Collection and Reduction		
diffractometer	Philips PW1100	Philips PW1100
monochromator	graphite	graphite
radiation	Mo K α ($\lambda = 0.71069$ Å)	Mo K α ($\lambda = 0.71069$ Å)
temp, °C	20	20
scan range, deg	$2\theta \leq 40$	$2\theta \leq 40$
scan method	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	1.4	1.2
scan speed, deg/s	0.05	0.05
μ , cm ⁻¹	4.02	4.7
abs cor	empirical	empirical
no. of unique data	4120	3825
no. of data with $I > 3\sigma(I)$	2172	2207
T_{min} , T_{max}	0.81, 0.99	0.92, 0.99
C. Solution and Refinement		
<i>R</i>	0.077	0.075
<i>R_w</i>	0.083	0.081

Table VII. Relevant Bond Lengths (Å) and Angles (deg) in Complex **2a**^a

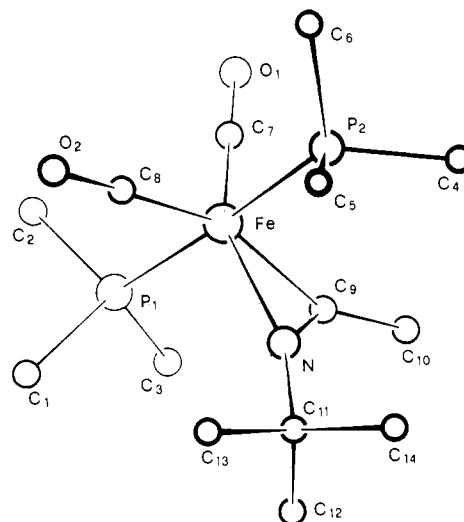
Bond Lengths			
Fe-P(1)	2.253 (4)	C(8)-O(2)	1.142 (15)
Fe-P(2)	2.259 (3)	C(9)-C(10)	1.364 (17)
Fe-C(7)	1.803 (15)	C(9)-N(1)	1.426 (14)
Fe-C(8)	1.774 (18)	N(1)-C(11)	1.476 (13)
Fe-C(9)	1.981 (12)	N(1)-C(17)	1.347 (13)
Fe-C(17)	1.970 (12)	N(2)-C(17)	1.337 (13)
C(7)-O(1)	1.127 (13)	N(2)-C(18)	1.473 (13)

Angles			
P(1)-Fe-P(2)	176.1 (2)	Fe-C(8)-O(2)	178 (1)
P(1)-Fe-C(7)	90.7 (4)	Fe-C(9)-C(10)	140 (1)
P(1)-Fe-C(8)	89.6 (5)	C(10)-C(9)-N(1)	125 (1)
P(1)-Fe-C(9)	89.7 (4)	N(1)-C(9)-Fe	95 (1)
P(1)-Fe-C(17)	89.6 (3)	C(9)-N(1)-C(11)	131 (1)
P(2)-Fe-C(7)	92.4 (4)	C(9)-N(1)-C(17)	101 (1)
P(2)-Fe-C(8)	87.6 (5)	C(11)-N(1)-C(17)	128 (1)
P(2)-Fe-C(9)	87.8 (3)	N(1)-C(11)-C(12)	114 (1)
P(2)-Fe-C(17)	92.1 (3)	N(1)-C(11)-C(16)	111 (1)
C(7)-Fe-C(8)	97.4 (6)	N(1)-C(17)-Fe	98 (1)
C(7)-Fe-C(9)	168.1 (6)	N(1)-C(17)-N(2)	121 (1)
C(7)-Fe-C(17)	102.6 (6)	Fe-C(17)-N(2)	140 (1)
C(8)-Fe-C(9)	94.5 (6)	C(17)-N(2)-C(18)	124 (1)
C(8)-Fe-C(17)	160.0 (6)	N(2)-C(18)-C(19)	117 (1)
C(9)-Fe-C(17)	65.5 (5)	N(2)-C(18)-C(23)	107 (1)
Fe-C(7)-O(1)	179 (1)		

^a Esd's in parentheses refer to the last digit.

iminoacyl bond. The Fe-N bond length (2.007 (10) Å) is consistent with the coordination of the nitrogen atom. The C(9)-N bond length of 1.211 (14) Å, which is intermediate between a triple C-N bond (1.16 Å) and a double C-N bond (1.31 Å), is shortened upon coordination of the iminoacyl group to the iron atom.

(3) **Reactivity of $[Fe(CO)_2(PMe_3)_2(CH_3)X]$.** The molecular structure of $[Fe(CO)_2(PMe_3)_2(CH_3)X]$ contains Fe-CO, Fe-CH₃, and Fe-X bonds; thus various types of reaction with isocyanide, previously observed in the literature²³ in different complexes, are

**Figure 3.** Molecular structure of the cation of the complex **7a**.**Table VIII.** Relevant Bond Lengths (Å) and Angles (deg) in Complex **7a**^a

Bond Lengths			
Fe-P(1)	2.277 (4)	C(7)-O(1)	1.186 (14)
Fe-P(2)	2.273 (4)	C(8)-O(2)	1.194 (18)
Fe-C(7)	1.698 (15)	C(9)-C(10)	1.496 (19)
Fe-C(8)	1.715 (18)	C(9)-N	1.211 (14)
Fe-C(9)	1.940 (13)	N-C(11)	1.523 (16)
Fe-N	2.007 (10)		
Angles			
P(1)-Fe-P(2)	177.4 (2)	C(8)-Fe-C(9)	152.8 (7)
P(1)-Fe-C(7)	88.3 (5)	C(8)-Fe-N	117.2 (6)
P(1)-Fe-C(8)	87.8 (6)	C(9)-Fe-N	35.7 (4)
P(1)-Fe-C(9)	91.1 (4)	O(1)-C(7)-Fe	179.8 (4)
P(1)-Fe-N	92.0 (3)	O(2)-C(8)-Fe	175.7 (15)
P(2)-Fe-C(7)	89.6 (5)	N-C(9)-Fe	75.2 (8)
P(2)-Fe-C(8)	91.1 (6)	C(10)-C(9)-Fe	145.7 (11)
P(2)-Fe-C(9)	90.9 (4)	N-C(9)-C(10)	139.1 (13)
P(2)-Fe-N	90.6 (3)	C(11)-N-Fe	153.5 (9)
C(7)-Fe-C(8)	100.3 (7)	C(9)-N-Fe	69.1 (8)
C(7)-Fe-C(9)	106.8 (6)	C(9)-N-C(11)	137.4 (12)
C(7)-Fe-N	142.5 (6)		

^a Esd's in parentheses refer to the last digit.

possible: (a) CO substitution; (b) CO and isocyanide insertion; (c) ionization of the Fe-X bond.

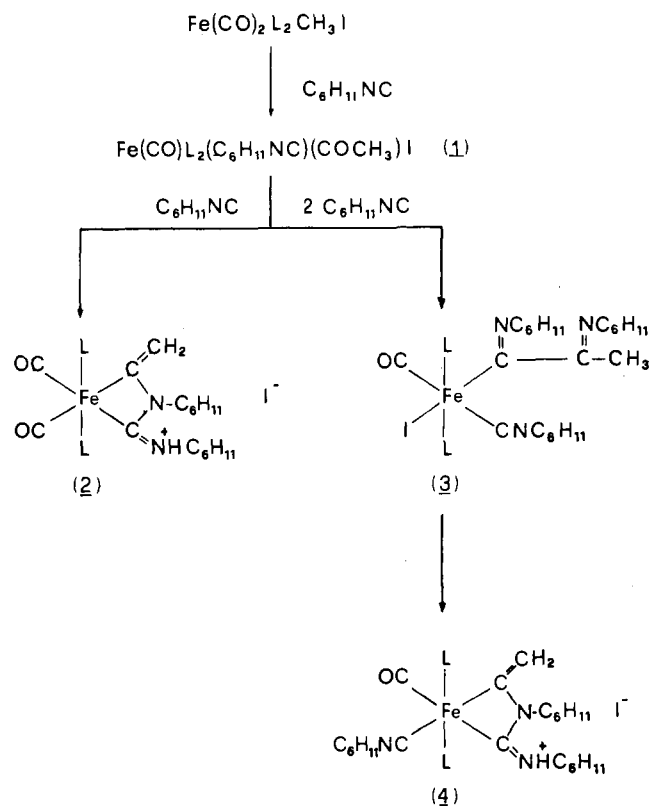
The reaction of $[Fe(CO)_2(PMe_3)_2(CH_3)X]$ and isocyanide shows only the first common step, whatever X and the isocyanides are; this step is the insertion of CO in the iron-methyl bond with formation of **1**, **5**, or **9**. The structure of these complexes was assigned by comparison with that of the phosphine derivatives $[Fe(CO)(PMe_3)_2L'(COCH_3)X]$ (L' = phosphine ligand), previously discussed.¹² The trans influence of COCH₃ stabilizes the structure with L' trans to this group. For X = CN, the ionization of the Fe-CN bond is not observed and the reaction stops at the formation of complex **9**, whereas, for the complexes with X = I, the ionization of the Fe-I bond opens new reaction paths, which vary according to the isocyanide ligand. The results are therefore discussed separately.

(a) **Reaction of $[Fe(CO)_2(PMe_3)_2(CH_3)I]$ with CNC_6H_{11} .** The picture of the observed reactions is given in Scheme I.

The structure of **2** was determined when the anion is BPh₄ (complex **2a**) by the X-ray method and is discussed elsewhere.

The observed structure is consistent with the ¹H NMR spectrum, which shows two multiplets of equal intensity at $\tau = 4.86$ and $\tau = 5.10$, assigned to the olefinic CH₂ group. The multiplet structure of these bands is due to the coupling of one hydrogen atom with the other and with the two P atoms through the iron.²⁴

Scheme I



There is no spectroscopic evidence to indicate the position of the hydrogen coordinated to the nitrogen. It is known²⁵ that the hydrogen atom in these structures is often not observable in the ¹H NMR spectra. In the IR spectrum a band at 3152 cm⁻¹ (KBr pellet) is observed, which can be assigned to the N—H stretching band.

The structure of **4** is assigned on the basis of the spectroscopic evidence. The structure is the same as that of complex **2** with a CO substituted by an isocyanide ligand. The IR spectrum shows a band at 3216.5 cm⁻¹, assigned to an N—H stretching band; a C≡N stretching band at 2121 cm⁻¹, absent in complex **2**, is assigned to a terminal isocyanide ligand; a CO stretching band at 1974 cm⁻¹ is assigned to a terminal CO ligand and the two bands at 1575 and 1535 cm⁻¹ are assigned to the C=N of the 1-aza-3-ferracyclobutane structure. The ¹H NMR spectrum shows two multiplets of equal intensity at $\tau = 5.91$ and 5.10, assigned to the C=CH₂ structure as in complex **2**.²⁶

The formation of complex **2** can be explained on the basis of Scheme II. The first step is the ionization of the Fe—I bond, followed by the insertion of isocyanide into the first ionic product **1a**, with the formation of complex **1b**. The formation of **1a** is in agreement with the ionic product **6**, observed with CNCMe₃. The fast insertion of isocyanide in complex **1a** to form complex **1b** is in agreement with the structure of complex **7**, observed with CNCMe₃. Complex **1b** reacts via intramolecular nucleophilic interaction of the lone pair of the nitrogen of the η^2 -iminoacyl group with the carbon of the cis terminal isocyanide group, giving the cyclic complex **1c**. Intermolecular nucleophilic attack on the carbon of terminal isocyanide has recently been observed in Pt complexes²⁷ and some years ago in iron complexes.²⁸ In any case, nucleophilic attack has not been observed when there is an intramolecular interaction or when there is the possibility of insertion

of isocyanide into the σ bond. Complex **1c** of Scheme II was not observed. The final product was **2**, which can be formed via hydrogen extraction with formation of the enamine group. This type of reaction is observed in organic compounds.^{29,30} In these cases, however, the equilibrium is shifted toward the iminium compounds.³¹ It has been observed that the carbon-bonded imine complex³² *trans*-[Pd(C(CH₃)=N(*p*-tolyl))Cl(PEt₃)₂] exists as two tautomers, the enamine form and the ketimine form. The enamine form is stabilized via addition across a triple bond. In complex **1b** this can occur by addition to the triple bond of the terminal isocyanide coordinated to the iron.

No direct information has been obtained on the position of the hydrogen atom. We assign it to the C=N⁺HR group on the basis of the planarity of the N=C—N—C=N moiety and of the presence of a band at 3152 cm⁻¹. The presence of a labile N—H bond is confirmed by the hydrogen–deuterium exchange, observed with CH₃OD. Complex **2**, dissolved in CH₃OD, shows a gradual decrease in the intensity of the C=CH₂ band in the ¹H NMR spectrum. This confirms a fast equilibrium between complexes **1c** and **2**, which gives scrambling of the C=CH₂ protons and of the N—H group. The IR spectrum of complex **2** in CH₃OD shows an interesting behavior. The C=N stretching band at 1561 cm⁻¹ (Table II) is lowered in energy to 1526.5 cm⁻¹ in CH₃OD. This can be explained by a fast exchange of the N—H to form an N—D group and by a mixing of the C=N stretching with the N—D bending as observed in *N*-methylacetamide³³ and polypeptide chains.³⁴

It is difficult to assign the structure of complex **3**. The course of the reaction, followed by the IR spectra, shows a stepwise formation in benzene and a nonionic structure. Complex **3** contains three CNC₆H₁₁ groups per iron atom and a terminal carbonyl group. The hypothetical structure **3** is assigned, also owing to the easy explanation of the formation of complex **4** via ionization of the Fe—I bond, deinsertion of one isocyanide group, and successive reaction steps as for the formation of the isostructural complex **2**, as indicated in Scheme III.

(b) Reaction of [Fe(CO)₂(PMe₃)₂(CH₃)I] with CNCMe₃. The products observed during the reaction of [Fe(CO)₂(PMe₃)₂(CH₃)I] and CNCMe₃ are presented in Scheme IV.

With a complex/ligand ratio of 1/1 in benzene, [Fe(CO)₂(PMe₃)₂(CH₃)I] yields in solution complex **5**. When the benzene is evaporated at 6 °C, complex **6** is obtained in the solid state. In solution, complex **6** is in equilibrium with complex **7**. With an excess of CNCMe₃, the formation of complex **8** is observed. Complex **5** was recognized by its IR and ¹H NMR spectra (Tables II and III). Complexes **6** and **7** were not isolated as iodide salts, since a fast equilibrium between them is established. Complex **7** was isolated as the tetraphenylborate salt **7a** and characterized by the X-ray method. Complex **7** shows two IR stretching bands and no IR band in the range 2100–2200 cm⁻¹ (C≡N stretching bands) or in the range 1500–1600 cm⁻¹ (C=N stretching bands). A band at 1750 cm⁻¹ is assigned to a C=N stretching band of the η^2 -iminoacyl structure. The ¹H NMR spectrum shows a triplet at $\tau = 7.04$ with $J = 2.4$ Hz. It is attributed to the NCH₃ protons (the splitting is due to the coupling with the phosphorus of the phosphine ligands).

Complex **8** was characterized by elemental analysis and IR and ¹H NMR spectroscopy. It shows a CO stretching band at 1982 cm⁻¹, a COCH₃ stretching band at 1600 cm⁻¹, and two stretching bands at 2175 and 2140 cm⁻¹, assigned to the C≡N of the terminal isocyanide ligands. The ¹H NMR spectrum shows a singlet at $\tau = 7.56$ due to the acetyl group.

(24) Spencer, A.; Werner, H. *J. Organomet. Chem.* **1979**, *171*, 219–228.
 (25) Olah, G. A.; Kreienbuhl, P. *J. Am. Chem. Soc.* **1967**, *89*, 4756–4759.
 (26) Grottsch, G.; Malish, W. *J. Organomet. Chem.* **1984**, *262*, C38–C42.
 (27) Herdeis, C.; Beck, W. *Chem. Ber.* **1983**, *116*, 3205–3211.
 (28) Miller, J.; Balch, A. L.; Enemark, J. H. *J. Am. Chem. Soc.* **1971**, *93*, 4613–4614.

(29) Heimgartner, H. In *Advances in Organic Chemistry*; Bohme, H., Viehe, H. G., Eds.; Wiley-Interscience: New York, 1979; Vol. 9, Part II, pp 655–731.

(30) Aubagnac, J. L.; Elguero, J.; Jacquier, R. *Bull. Soc. Chim. Fr.* **1969**, *9*, 3316–3326. Bohme, H.; Plappert, P. *Chem. Ber.* **1975**, *108*, 3574–3581.

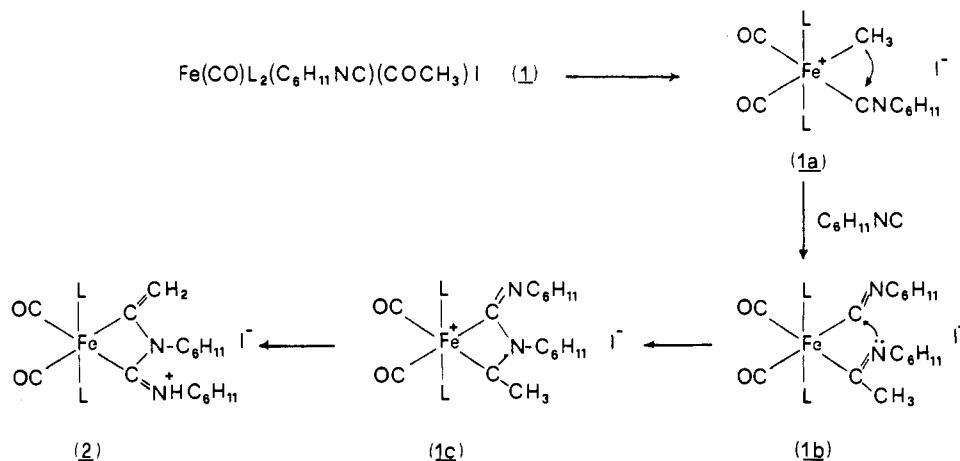
(31) Opitz, G.; Greisinger, R. *Liebigs Ann. Chem.* **1963**, *665*, 101–113.

(32) Clark, H. C.; Milne, C. R. C.; Payne, N. C. *J. Am. Chem. Soc.* **1978**, *100*, 1164–1169.

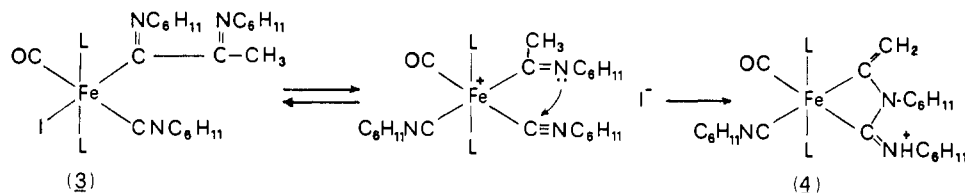
(33) Fraser, R. D. B.; Price, W. C. *Nature (London)* **1952**, *170*, 490–491.

(34) Miyazawa, T. *J. Chem. Phys.* **1960**, *32*, 1647–1652.

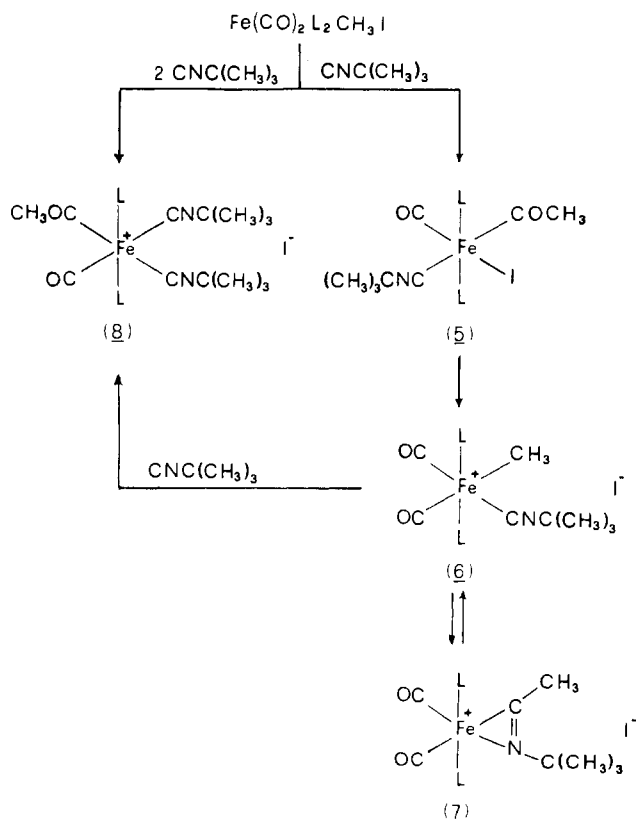
Scheme II



Scheme III



Scheme IV



The results of the reaction with CNCMe_3 show high steric hindrance; no insertion of isocyanide is observed when there is an excess of ligand; the insertion of carbon monoxide predominates in this case and the formation of complex **8** is observed. With molar ratio 1/1, the insertion of isocyanide occurs and the formation of the η^2 -iminoacyl isocyanide **7** is observed. The methyl complex **6** is in equilibrium with the η^2 -iminoacyl complex. The nature and the concentration of the anion are important for the observation of this equilibrium: with I^- , Cl^- , PF_6^- , etc., the equilibrium is observed; with BPh_4^- the two complexes are quenched and no transformation is observed. This fact allowed

us to obtain complex **7a** for an X-ray analysis. The function of the anion corresponds to the effect of the cation on the insertion of carbon monoxide into anionic systems.³⁵ We are at present carrying out a study of this effect on the insertion reaction.

The structural parameters of complex **7a** indicate an η^2 -iminoacyl structure. It can be compared with the structure of $[\text{Ru}(\eta^2\text{-C}(\text{=NR})\text{R})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = p\text{-tolyl}$),³⁶ of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^2\text{-C}(\text{CH}_3)=\text{N}-\text{C}_6\text{H}_5)]$,³⁷ and of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^2\text{-C}(\text{CH}_3)=\text{N}-\text{CH}_3)]$.³⁸ All these complexes show a C—N bond length in the range 1.211–1.30 Å, intermediate between the double and the triple CN bonds. For the four complexes reported, the variation of the C—N stretching bands is between 1654 and 1750 cm^{-1} . These frequencies are higher than those of the C=N double bond, which are found between 1500 and 1600 cm^{-1} .

The behavior of the η^2 -iminoacyl structures is different from that observed for the η^2 -acyl structures. In this last case, both bond lengths³⁹ and the COR stretching frequencies are intermediate between single and double bonds.⁴⁰ In the case of the η^2 -iminoacyl structures, bond lengths and C=N stretching frequencies are intermediate between those of the double C=N bond (1500–1600 cm^{-1}) and the triple bond (2100–2200 cm^{-1}). In the η^2 -iminoacyl structure, the metal transfers electron density to the double bond. On the other hand, in the η^2 -acyl structure COR transfers electron density to the metal. The reason for this is not clear, but all the isolated η^2 -iminoacyl structures show this behavior. Following the suggestion of Adams³⁷ that the structural parameters of the iminoacyl groups are similar to those of an alkyne coordinated to a metal, it is possible to assign to the $(\text{R}-\text{C}\equiv\text{N}^+-\text{R})$ moiety an alkyne-like structure and regard the coordination of this moiety to the metal as the coordination of a triple bond to a metal. The transfer of the electron density of the metal to an antibonding orbital of the ligand lowers the tri-

(35) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766–4772.

(36) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27–C29.

(37) Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41–48.

(38) Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544–6550.

(39) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297–2302.

(40) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522–523. Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46–C48.

ple-bond order of the C=N group.

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Supplementary Material Available: Tables 1S-6S, giving thermal parameters and complete listings of bond lengths and angles for **2a** and **7a** (8 pages); Tables 7S and 8S, giving observed and calculated structure factors for both complexes (23 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, 98100 Messina, Italy, and Dipartimento di Chimica, Università di Siena, 53100 Siena, Italy

Chemical Oxidation of Binuclear Rhodium(I) Complexes with Silver Salts. Synthesis, X-ray Crystal Structure, and Electrochemical Properties of the Rh₂⁴⁺ Mixed-Ligand Complex Rh₂(Form)₂(O₂CCF₃)₂(H₂O)₂·0.5C₆H₆ (Form = *N,N'*-Di-*p*-tolylformamidinate Anion)

Pasquale Piraino,*† Giuseppe Bruno,† Giuseppe Tresoldi,† Sandra Lo Schiavo,† and Piero Zanello*†

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The facile chemical oxidation of the binuclear rhodium(I) formamidinate complex [Rh(C₈H₁₂)(Form)]₂ (Form = [*p*-CH₃C₆H₄NC(H)NC₆H₄CH₃-*p*]⁻) with AgO₂CCF₃ (mole ratio 1:4) yields the mixed-ligand Rh₂⁴⁺ complex Rh₂(Form)₂(O₂CCF₃)₂(H₂O)₂. The complex reacts with Lewis bases such as pyridine, dimethyl sulfoxide, piperidine, and 4-methylimidazole to produce stable 1:2 axial adducts. The crystal structure has been determined by X-ray diffraction analysis. The green crystals are triclinic, space group *P* $\bar{1}$, with *a* = 10.467 (1) Å, *b* = 13.151 (1) Å, *c* = 15.470 (2) Å, α = 70.68 (2)°, β = 88.89 (4)°, γ = 79.16 (3)°, *V* = 1971.6 Å³, *Z* = 2, *D*_{calcd} = 1.609 g cm⁻³, *R* = 0.032, and *R*_w = 0.034. The molecule consists of two formamidinate and two trifluoroacetate groups symmetrically disposed about the Rh-Rh unit in the conventional fashion. Two water molecules are axially bonded at 2.315 (3) Å from the rhodium atoms. The striking features of the structure are the lengthening of the Rh-Rh (2.425 (1) Å) and Rh-O_{eq} (2.082 (3) Å) bond distances with respect to the analogous Rh₂(O₂CCF₃)₄(H₂O)₂·2DTBN and the cisoid arrangement of the formamidinate groups. The Rh-Rh-O_{ax} angles deviate significantly from linearity (167.9 (1) and 169.3 (1)°) as a consequence of steric interactions between the tolyl fragments and the water molecules that participate in hydrogen-bonding interactions throughout the crystal lattice. The electrochemistry in different nonaqueous solvents points out the ability of the title complex to undergo two subsequent one-electron reversible or quasi-reversible anodic processes, attributable to the Rh^IRh^{II}/Rh^{II}Rh^{III} and Rh^{II}Rh^{III}/Rh^{III}Rh^{III} charge transfers, respectively. As expected, these anodic processes are easier than in the case of the corresponding tetracarboxylato species. Of the two electrogenerable anodic products, only the mixed-valence Rh^{II}Rh^{III} derivative is fully stable, and its stability has been quantitatively evaluated and discussed also with respect to that of the other dirhodium complexes.

Introduction

Binuclear rhodium complexes containing the Rh₂⁴⁺ core have been the center of many experimental and theoretical studies.¹ For the most part, these have been directed toward complexes containing four carboxylate groups as bridging ligands. Up to now only few Rh₂⁴⁺ complexes containing mixed² or non-carboxylate bridging ligands³ have been isolated and structurally characterized. The presence of bridging ligands other than carboxylate allows a greater variation in the molecular orbital patterns and hence the chemical reactivity of the Rh₂⁴⁺ complexes. As elegantly pointed out by the electrochemical studies of Kadish, Bear, and co-workers, a dramatic variation is seen in the redox potential of the couple Rh^{II}Rh^{II}/Rh^{II}Rh^{III} as a consequence of the gradual replacement of oxygen atoms by NH groups.⁴ In some cases the Rh^{II}Rh^{III}/Rh^{III}Rh^{III} couples showed anodic behavior. Also the complex Rh₂(N₂R₂CR)₄ (R = phenyl) undergoes a quasi-reversible reduction leading to the formation of a formal Rh^{II}Rh^I derivative.^{3d}

In this paper we report the synthesis, structure analysis, and electrochemistry of the Rh₂⁴⁺ mixed-ligand complex Rh₂(Form)₂(O₂CCF₃)₂(H₂O)₂ (Form = [*p*-CH₃C₆H₄NC(H)NC₆H₄CH₃-*p*]⁻) obtained by chemical oxidation with silver trifluoroacetate of the binuclear rhodium(I) complex [Rh(C₈H₁₂)(Form)]₂. A similar synthetic route has been successfully used to prepare the Rh₂⁵⁺ complex Rh₂(Form)₃(NO₃)₂.⁵

Experimental Section

Starting Materials. [Rh(C₈H₁₂)(Form)]₂ was prepared by the literature procedure.⁶ 4-Methylimidazole (4-MeIm) and silver trifluoro-

acetate were purchased from Aldrich Chemical Co. and used as received. The supporting electrolytes tetraethylammonium perchlorate, [NEt₄]-ClO₄ (Carlo Erba), and tetrabutylammonium perchlorate, [NBu₄]-ClO₄ (Fluka), were dried in a vacuum oven at 100 °C and used without further purification. The solvents used for electrochemistry (dichloromethane, acetonitrile, acetone, tetrahydrofuran, *N,N*-dimethylformamide, dimethyl sulfoxide (Burdick and Jackson); nitromethane, benzotrifluoride (Aldrich)) were of "distilled in glass" grade and used as received.

Apparatus. Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 783 instrument. Electronic absorption spectra were run as benzene solutions on a Perkin-Elmer Lambda 5 UV-visible spectrophotometer. ESR experiments were performed on a Bruker ER 200D-SRC X-band spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan and Analytische Laboratorien Malissa and Reuter, Elbach, West Germany. The electrochemical apparatus has been described elsewhere.⁷ Potential values are referred to an aqueous saturated calomel reference

- (1) (a) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *20*, 109. (b) Boyer, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109. (c) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley-Interscience: New York, 1982; p 311.
- (2) (a) Cotton, F. A.; Thompson, S. L. *Inorg. Chim. Acta* **1984**, *81*, 193. (b) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584. (c) Chakravarty, A. R.; Cotton, F. A.; Tocher, A. D. Tocher, S. H. *Organometallics* **1985**, *4*, 8.
- (3) (a) Dennis, A. M.; Korp, J. D.; Bernal, I.; Howard, R. A.; Bear, J. L. *Inorg. Chem.* **1983**, *22*, 1522. (b) Chakravarty, A. R.; Cotton, F. A.; Tocher, A. D.; Tocher, S. H. *Inorg. Chim. Acta* **1985**, *101*, 185. (c) Barrow, A. R.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1985**, *4*, 1131. (d) Le, J. C.; Chavan, M. Y.; Chau, L. K.; Bear, J. L.; Kadish, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 7195.
- (4) Chavan, M. Y.; Zhu, T. P.; Lin, X. Q.; Ahsan, M. Q.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 4538.
- (5) Piraino, P.; Bruno, G.; Faraone, F.; Lo Schiavo, S. *Inorg. Chem.* **1985**, *24*, 4760.
- (6) Piraino, P.; Tresoldi, G.; Faraone, F. *J. Organomet. Chem.* **1982**, *224*, 305.
- (7) Zanello, P.; Leoni, P. *Can. J. Chem.* **1985**, *63*, 922.

† Università di Messina.

† Università di Siena.