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Metal Nitrosyl Complexes. I. Cyclobutadieneiron Nitrosyl Derivatives[1]

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Air-stable yellow-orange crystalline complexes of cyclobutadieneiron dicarbonyl nitrosyl hexafluorophosphate, $[R_4C_4Fe(CO)_2NO]^+PF_6^-$ (R = H, CH_3, Ph), have been prepared by the reaction of $R_4C_4Fe(CO)_3$ and $NO^+PF_6^-$. These complexes undergo facile monocarbonyl substitution reactions with various σ-donor ligands (L) to afford complexes of the type $[R_4C_4Fe(CO)(NO)L]^+PF_6^-$ (R = H, L = Ph_3P, Ph_3As, Ph_3Sb; R = Ph, L = Ph_3P, Ph_3As). A dicarbonyl substitution product of the type $[Ph_4C_4Fe(NO)[(PhO)_3P]_2]^+PF_6^-$ has also been isolated.

Introduction

Metal complexes of cyclobutadiene and substituted cyclobutadienes have been reported with carbonyl,[2] halide,[2] hydride,[3a] phosphine,[2] trifluoromethylthio,[3b] σ-phenyl,[4] and various π ligands.[2] The preparation of the parent[5] and numerous partially[6] and fully[7] substituted cyclobutadieneiron tricarbonyl complexes is well documented. However, little attention has been given to the study of its inorganic aspects. Except for $Me_4C_4Fe(CO)_2(CF_3)_2CO$,[8] $C_4H_4Fe(CO)_2(MeOOCCH{=}CHCOOMe)$,[9] $C_4H_4Fe(C_6H_6NCOOEt)$,[10] $C_8H_6Fe(CO)_2(Ph_3P)$,[5] and $Ph_4C_4Fe(CO)_2(Ph_3P)$,[11] no other cyclobutadieneiron derivatives are known. This work describes the preparation of cyclobutadieneiron nitrosyl complexes—the first known cyclobutadienemetal nitrosyl complexes.

Experimental Section

The preparation of the cyclobutadieneiron nitrosyl complexes is described below. All melting points are uncorrected (Table I). Infrared spectra (Table II) were taken in KBr pellets and recorded on a Perkin-Elmer 225 grating spectrometer. Each spectrum was calibrated using the 1601- or 1944-cm^{-1} band of a polystyrene film. Proton nmr spectra (Table II) were run in acetone-d_6 solution with TMS as an internal standard on a Varian T-60 or a Jeol JNM-MH-100 spectrometer. Mossbauer spectra (Table II) were obtained at liquid nitrogen temperature. The IS values are given with respect to the center of a room-temperature spectrum of NBS SRM metallic iron, which was also used to effect the velocity calibration. Conductometric measurements were carried out on nitromethane solutions using a YSI Model 31 conductivity bridge. The cell constant was determined by the use of a standard aqueous solution of KCl. The molar conductance at infinite dilution (λ_0) of each compound (Table II) was obtained by extrapolations from the λ–$\sqrt{C}$ curve on the basis of at least five different concentrations in the range, 10^{-2}–10^{-4} *M* at 26°. The slopes (Table II) were computed from the curves of $(\lambda_0 - \lambda)/\sqrt{C}$. At low concentrations (~10^{-4} *M*) appropriate corrections for the conductance of the solvent were employed.

Nitrogen atmosphere was routinely provided for the following operations: (i) carrying out reactions, (ii) admitting evacuated vessels, and (iii) handling filtered solutions of organometallic compounds.

The reagents $C_4H_4Fe(CO)_3$ (**1**; R = H),[12] $(CH_3)_4C_4Fe(CO)_3$ (**1**; R = CH_3),[13] and $Ph_4C_4Fe(CO)_3$[14] (**1**; R = Ph) were prepared by known procedures. Nitrosonium hexafluorophosphate was purchased from PCR Inc., Gainesville, Fla.

Preparation of $[R_4C_4Fe(CO)_2NO]^+PF_6^-$ (2; R = H, CH_3, Ph). A solution of 10.0 g (51.5 mmol) of $C_4H_4Fe(CO)_3$ in 120 ml of acetonitrile was treated dropwise over a 40-min interval with a solution of 9.2 g (52.6 mmol) of nitrosonium hexafluorophosphate in 100 ml of acetonitrile. The reaction mixture was then stirred at ambient temperature for 30 min. The solvent was removed at 30° (35 mm) and the solid obtained was washed with Et_2O until the washings were colorless. The product $[C_4H_4Fe(CO)_2NO]^+PF_6^-$ (16.0 g, 92% yield) was found to be soluble in polar organic solvents such as acetone, acetonitrile, and nitromethane and insoluble in solvents such as methylene chloride, benzene, toluene, and ethyl ether. The analytically pure sample of **2**, R = H was obtained by recrystallizations from acetone solution at −78°.

$[(CH_3)_4C_4Fe(CO)_2NO]^+PF_6^-$ (2; R = CH_3) and $[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$ (2; R = Ph). The methyl and phenyl analogs **2**, R = CH_3, and **2**, R = Ph, were prepared by the same procedure described for **2**, R = H. The solubility of **2**, R = CH_3, was found to be lower than that of **2**, R = H, and the analytically pure sample could be crystallized only from acetonitrile solution. The marginal solubility of **2**, R = CH_3, in acetone-d_6 precluded obtaining a satisfactory ^1H nmr spectrum. The phenyl analog **2**, R = Ph, was found to be soluble in methylene chloride and the analytically pure sample was recrystallized from a mixture of methylene chloride and toluene.

Preparation of $[R_4C_4Fe(CO)(NO)L]^+PF_6^-$ (3; R = H, Ph; L = Ph_3P, Ph_3As, Ph_3Sb) $[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (3; R = H; L = Ph_3P). A solution of 0.65 g (1.92 mmol) of **2**, R = H, and 0.52 g (1.98 mmol) of Ph_3P in 100 ml of acetone was refluxed for a period of 2 hr. The solvent was then removed at 30° (35 mm) and the solid product obtained was washed carefully with toluene. The analytically pure sample of **3**, R = H; L = Ph_3P, was obtained by recrystallizations from a mixture of methylene chloride and hexane. The arsine and stibine derivatives **3**, R = H; L = Ph_3As, Ph_3Sb, were prepared analogously.

$[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (3; R = Ph; L = Ph_3P). A mixture of 0.35 g (0.54 mmol) of **2**, R = Ph, and 0.25 g (0.95 mmol) of Ph_3P in 50 ml of benzene was refluxed with stirring for a period of 20 hr. The reaction mixture was then allowed to reach ambient temperature and the orange precipitate formed was filtered off, washed with hexane, and dried at 0.5 mm (25°). The product $[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (0.38 g, ~80% yield) was purified by recrystallizations from a methylene chloride–hexane mixture. The complexes $[Ph_4C_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ (**3**; R = Ph; L = Ph_3As) and $\{Ph_4C_4Fe(NO)[(PhO)_3P]_2\}^+PF_6^-$ (**4**) were prepared and purified analogously. Attempts to prepare the stibine analog **3**, R = Ph; L = Ph_3Sb, by a similar procedure were unsuccessful.

Results and Discussion

It is well established that the nitrosonium cation reacts with neutral phosphine-substituted metal carbonyls ($M(CO)_xL_y$) to afford isoelectronic monocationic nitrosyl

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Table I. Cyclobutadieneiron Nitrosyl Complexes

				Elemental analyses,[b] %					
			Yield,	Calcd			Found		
Complex	Color	Mp,[a] °C	%	C	H	N	C	H	N
$[C_4H_4Fe(CO)_2NO]^+PF_6^-$ (**2**; R = H)	Yellow	>167 dec	92	21.30	1.18	4.10	21.41	1.31	4.06
$[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (**3**; R = H; L = Ph_3P)	Yellow	>171 dec	55	48.27	3.32	2.45	47.20	3.41	2.43
$[C_4H_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ (**3**; R = H; L = Ph_3As)	Yellow	>183 dec	72	44.82	3.08	2.55	44.77	3.14	2.55
$[C_4H_4Fe(CO)(NO)Ph_3Sb]^+PF_6^-$ (**3**; R = H; L = Ph_3Sb)	Yellow	>181 dec	73	41.65	2.87	2.11	41.78	3.18	2.32
$[Me_4C_4Fe(CO)_2NO]^+PF_6^-$ (**2**; R = CH_3)	Yellow	>155 dec	69	30.47	3.05	3.55	30.70	3.15	3.74
$[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$ (**2**; R = Ph)	Orange	>157 dec	64	56.10	3.12	2.18	55.10	3.12	2.04
$[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (**3**; R = Ph; L = Ph_3P)	Orange	175	80	64.30	5.17	1.59	65.00	4.17	1.41
$[Ph_4C_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ (**3**; R = Ph; L = Ph_3As)	Orange	166	68	61.30	3.80	1.52	59.50	4.23	1.39
$[Ph_4C_4Fe(NO)[(PhO)_3P]_2]^+PF_6^-$ (**4**)	Pale orange	142	21	63.60	4.14	1.06	61.90	4.14	1.18

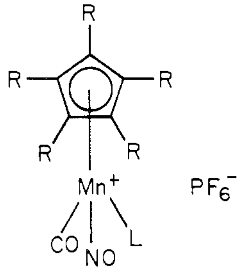
[a] Melting and decomposition points are uncorrected. [b] Additional per cent elemental analyses (calcd in parentheses): **2**, R = Ph: P, 4.59 (4.82); F, 16.90 (17.75); Fe, 9.09 (8.71). **3**, R = Ph; L = Ph_3P: Fe, 5.86 (6.38). **3**, R = Ph; L = Ph_3As: Fe, 5.67 (6.08). **4**: Fe, 4.97 (4.64).

Table II. Infrared, Proton Nmr, Mossbauer, and Conductance Data on Some Cyclobutadieneiron Nitrosyl Complexes

	Infrared,[a] cm^{-1}			Proton nmr,[b] τ		Mossbauer,[d] mm/sec		Conductance	
Complex	$\nu(CO)$	$\nu(NO)$	$\nu(PF)$	C_4H_4	C_6H_5	IS	QS	Λ_0, ohm^{-1}	Slope
$[C_4H_4Fe(CO)_2NO]^+PF_6^-$ (**2**; R = H)	2133, 2103	1882	832	3.86 s[c]		0.135	1.161	107	286
$[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (**3**; R = H; L = Ph_3P)	2075	1846	840	4.60 d	2.26 m	0.130	1.299	91	227
$[C_4H_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ (**3**; R = H; L = Ph_3As)	2065	1842	834	4.45 s	2.31 m	0.138	1.275	92	172
$[C_4H_4Fe(CO)(NO)Ph_3Sb]^+PF_6^-$ (**3**; R = H; L = Ph_3Sb)	2046	1836	833	4.35 s	2.27 m	0.148	1.203	89	117
$[Me_4C_4Fe(CO)_2NO]^+PF_6^-$ (**2**; R = CH_3)	2102, 2063	1828	838						
$[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$ (**2**; R = Ph)	2105, 2095	1853	840		2.68 m				
$[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ (**3**; R = Ph; L = Ph_3P)	2078	1819	838		2.55 m				
$[Ph_4C_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ (**3**; R = Ph; L = Ph_3As)	2060	1811	838		2.58 m				
$[Ph_4C_4Fe(NO)[(PhO)_3P]_2]^+PF_6^-$ (**4**)		1817	842		2.40 m, 2.75 m, 3.15 m				

[a] Infrared data are quoted within ±2.0-cm^{-1} accuracy. [b] Proton nmr data are given within ±0.01-ppm accuracy. Abbreviations: s, singlet; d, doublet; m, multiplet. [c] $J_{PH} \approx 2.0$ Hz. [d] The isomeric shift (IS) is given with respect to the center of a room-temperature absorption spectrum of 0.85-mil NBS SRM iron foil, which was also used for velocity calibration. The IS and QS parameters at liquid nitrogen temperature (~80 ± 2°K) are estimated to have experimental uncertainties of ±0.015 and ±0.020 mm/sec, respectively.

complexes of the type $[M(CO)_{x-1}L_y(NO)]^+PF_6^-$.[15,16] This type of oxidative substitution reaction has also been shown to occur with metal carbonyls containing π ligands. For example, the manganese complexes $(h^5\text{-}R_5C_5)Mn(CO)_3$ undergo facile oxidative substitution with $NO^+PF_6^-$ in CH_3CN solution to give $[(h^5\text{-}R_5C_5)Mn(CO)_2NO]^+PF_6^-$ (**5**; R = H, CH_3; L = CO) in high yield.[17,18] Similarly, the reaction of polymethylated arenechromium tricarbonyl with $NO^+PF_6^-$ in methanol-toluene mixtures was recently reported[19] to give $[(C_6Me_{6-n}H_n)Cr(CO)_2NO]^+PF_6^-$. By contrast, the above reaction when carried out in CH_3CN solution resulted in the displacement of the arene ligand and all of the carbonyl groups along with the formation of $[Cr(NO)_2(CH_3CN)_4]^{2+}[PF_6^-]_2$.[17]



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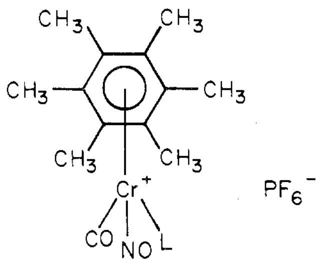

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In view of the facile oxidative displacement of the cyclobutadiene ring from $C_4H_4Fe(CO)_3$ (**1**; R = H) by relatively mild oxidizing agents such as $FeCl_3$ and $(NH_4)_2Ce(NO_3)_6$,[20] the formation of the cyclobutadieneiron nitrosyl complexes **2**, R = H, CH_3, Ph, by the action of a strong oxidizing agent such as nitrosonium hexafluorophosphate is somewhat surprising. The cyclobutadieneiron nitrosyl complexes **2**, R = H, Ph, undergo a facile thermal monocarbonyl substitution reaction with typical σ-donor ligands such as Ph_3P, Ph_3As, and Ph_3Sb. Dicarbonyl substitution was encountered only in the reaction between **2**, R = Ph, and $(PhO)_3P$ in which the product **4** was obtained in rather poor yield (21%). (See Scheme I.) Attempts to achieve carbonyl-substitution reactions with **2**, R = CH_3, and σ-donor ligands under a variety of reaction conditions were unsuccessful. In part this can be attributed to the marginal solubility of **2**, R = CH_3, in most organic solvents including acetone and acetonitrile.

The structures assigned to the new complexes are in full accord with the spectroscopic properties summarized in Table II. The infrared spectra in the 2200-1600-cm^{-1} region confirm the presence of terminal carbonyl and/or nitrosyl groups. A strong band in the 832-842-cm^{-1} region, characteristic of the hexafluorophosphate anion, supports the ionic nature of these new complexes. The electrolyte type of the parent cyclobutadiene complexes **2**, R = H, and **3**, R = H; L = Ph_3P, Ph_3As, Ph_3Sb, was determined by conductometric measurements in nitromethane

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Table III. Infrared Spectra (1600-2200 cm^{-1}) of $[(R_5C_5)Mn(CO)(NO)L]^+PF_6^-$ and $[(Me_6C_6)Cr(CO)(NO)L]^+PF_6^-$ Complexes

Complex	ν(CO)	ν(NO)	Ref
$[C_5H_5Mn(CO)_2NO]^+PF_6^-$ (**5**; R = H; L = CO)	2144, 2076	1865	*a*
$[C_5H_5Mn(CO)(NO)Ph_3P]^+PF_6^-$ (**5**; R = H; L = Ph_3P)	2028	1787	*b, c*
$[C_5H_5Mn(CO)(NO)Ph_3As]^+PF_6^-$ (**5**; R = H; L = Ph_3As)	2028	1788	*b*
$[C_5H_5Mn(CO)(NO)Ph_3Sb]^+PF_6^-$ (**5**; R = H; L = Ph_3Sb)	2029	1789	*b*
$[Me_5C_5Mn(CO)_2NO]^+PF_6^-$ (**5**; R = CH_3; L = CO)	2104, 2062	1825	*d*
$[Me_5C_5Mn(CO)(NO)Ph_3P]^+PF_6^-$ (**5**; R = CH_3; L = Ph_3P)	2021	1774	*d*
$[Me_6C_6Cr(CO)_2NO]^+$ (**6**; L = CO)	2062, 2013	1775	*e*
$[Me_6C_6Cr(CO)(NO)Ph_3P]^+PF_6^-$ (**6**; L = Ph_3P)	1980	1698	*e*

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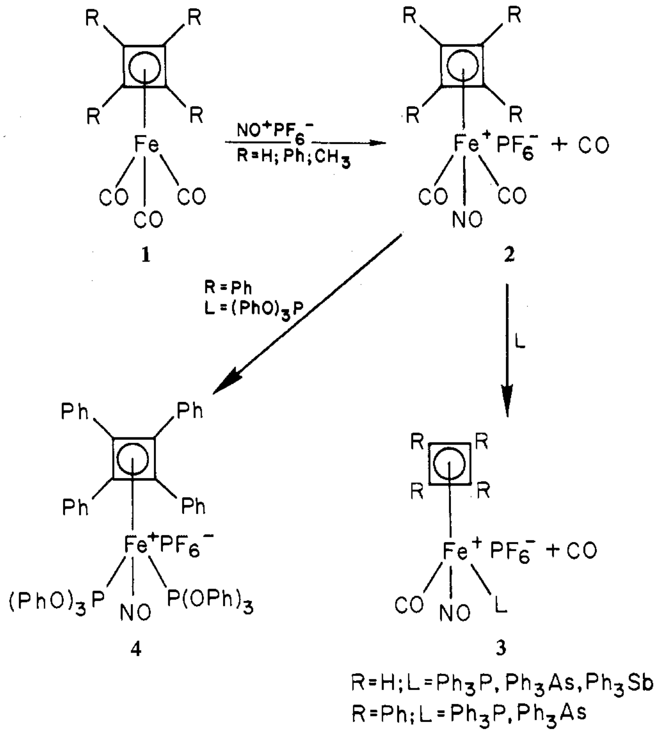
Scheme I



solution. The Λ_0 and $(\Lambda_0 - \Lambda)/\sqrt{C}$ (slope) values for the above complexes are in the range expected for a 1:1 electrolyte.[21] The slopes appear to decrease systematically with increasing molecular weight of the solute. This tendency implies stronger ion pairing and thus lower molar conductance for the heavier analogs at higher concentrations.

The proton nmr spectra of the parent cyclobutadieneiron nitrosyl complexes **2**, R = H, and **3**, R = H; L = Ph_3As, Ph_3Sb, exhibit a sharp singlet at about τ 4 arising from the equivalent protons of the ring. In the case of the phosphine analog **3**, R = H; L = Ph_3P, a doublet is observed for the C_4H_4 protons with $J_{PH} \approx 2$ Hz. The chemical shifts of the C_6H_5 protons are found in their normal region and the integration ratio of the C_4H_4 and C_6H_5 protons in **3**, R = H; L = Ph_3P, Ph_3As, Ph_3Sb, is 4:15, respectively, as expected. The presence of only one kind of iron atom in the parent cyclobutadieneiron nitrosyl complexes **2**, R = H, and **3**, R = H; L = Ph_3P, Ph_3As, Ph_3Sb, is supported by the ~80°K Mossbauer spectra which show only a single quadrupole-split doublet having line widths characteristic of a single iron site.[22]

The $\nu(CO)_{max}$ and ν(NO) in **2**, R = H, Ph, are higher than those in **3**, R = H, Ph, suggesting enhancement of the $d\pi(Fe) \rightarrow p\pi^*(CO,NO)$ back-bonding interaction in the latter as expected by substitution of a coordinated carbonyl group by a ligand of lower π acidity. The polymethylated complexes $[(h^4\text{-}Me_4C_4)Fe(CO)_2NO]^+PF_6^-$ (**2**; R = CH_3), $[(h^5\text{-}Me_5C_5)Mn(CO)_2NO]^+PF_6^-$ (**5**; R = CH_3; L = CO), and $[(h^6\text{-}Me_6C_6)Cr(CO)_2NO]^+PF_6^-$ (**6**; L = CO) are interrelated structurally. A direct comparison between their ν(CO) and ν(NO), Tables II and III, is not strictly valid since the metals, their formal oxidation states, and their d-electron configurations are different. The difference between the polymethylated complexes arises from the $(Me_nC_n)M$ unit; thus the degree of $d\pi(M) \rightarrow p\pi^*(CO,NO)$ back-bonding interactions can be related to (a) the formal oxidation state of the metal (M), (b) the nuclear charge of the metal (M), and (c) the π acidity of the Me_nC_n ligand. The atomic numbers of the metals under consideration [chromium(I) (d^5), manganese(II) (d^5), and iron(I) (d^7)] differ by a maximum of 2 units; thus the nuclear charge effect on ν(CO) and ν(NO) is likely to be negligible. The manganese atom in **5**, R = CH_3; L = CO, is formally in the 2+ (d^5) state, whereas the iron atom in **2**, R = CH_3, is formally in the 1+ (d^7) state; therefore higher ν(CO) and ν(NO) would be expected for the former. The fact that the frequencies observed for these compounds are the same (within experimental error) implies that the π acidity of the Me_4C_4 ligand is greater than that of the Me_5C_5 ligand. Similarly, comparison between the ν(CO) and ν(NO) of the parent cyclopentadienylmanganese and cyclobutadieneiron complexes (Tables II and III) reveals that with the exception of **2**, R = H, and **5**, R = H; L = CO, where the latter shows slightly higher frequencies [$\Delta\nu(CO)_{max} \approx 11$ and $\Delta\nu(NO) \approx 17$ cm^{-1}], the frequencies of the iron complexes are higher than their manganese analogs. This again supports the π-acidity order of cyclobutadiene > cyclopentadienyl. The ν(CO) and ν(NO) of the polymethylated chromium complexes **6**, L = CO, Ph_3P, are markedly lower than those of the respective manganese (**5**; R = CH_3; L = CO, Ph_3P) and iron (**2**; R = CH_3) complexes. Meaningful comparison between the frequencies of the respective manganese and chromium complexes is ruled out since in this case it is impossible to distinguish between the two above-mentioned effects (a) and (c). Conversely, comparison between the ν(CO) and ν(NO) of the chromium (**6**; L = CO) and iron (**2**; R = CH_3) complexes is in order since both metals attain the same formal oxidation state. The lower frequencies found for the chromium complex implies a π-acidity order of $Me_4C_4 > Me_6C_6$. The same conclusion can also be reached by comparing the ν(CO) and ν(NO) of the polymethylated phosphine analogs **5**, R = CH_3; L = Ph_3P, and **6**, L = Ph_3P. These results represent a most convincing illustration of the π-acceptor property of the cyclobutadiene ligand and are in full accord with previous findings.[4,23]

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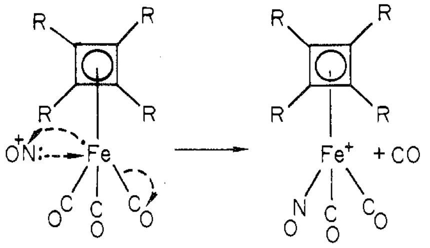
Previously, attempts to prepare cyclobutadienemetal nitrosyl complexes by a direct synthesis from cyclobutadienemetal derivatives and nitric oxide were unsuccessful.[24] Apparently, nitric oxide oxidatively displaces the cyclobutadiene ring from its complexes. These results are not unexpected since even mild oxidizing agents such as $FeCl_3$ and $(NH_4)_2Ce(NO_3)_6$ are known oxidatively to displace the cyclobutadiene ring from a relatively stable complex such as **2**, R = H.[5,20] Therefore, the preparation of cyclobutadienemetal nitrosyls should not be regarded a trivial extension of the related chemistry of cyclopentadienylmetal nitrosyl complexes. The nitrosonium ion, in spite of being a much stronger oxidizing agent than either Fe(III) or Ce(IV), does not oxidatively displace the cyclobutadiene ring under the present conditions. Unlike the reaction between **2**, R = H and Ce(IV) or Fe(III), which is believed to involve a free cyclobutadiene (singlet ground state) intermediate,[9] the reaction of the former with nitrosonium ion could best be explained in terms of a concerted oxidative substitution mechanism (eq 1). Such a process would involve an electronically and coördinatively saturated iron atom and therefore no substantial weakening of the cyclobutadiene-iron bond should occur.



1 **2** (1)

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Registry No. $[C_4H_4Fe(CO)_2NO]^+PF_6^-$, 43175-64-0; $[Me_4C_4Fe(CO)_2NO]^+PF_6^-$, 43218-57-1; $[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$, 43140-26-7; $[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$, 43140-27-8; $[C_4H_4Fe(CO)(NO)Ph_3As]^+PF_6^-$, 43140-28-9; $[C_4H_4Fe(CO)(NO)Ph_3Sb]^+PF_6^-$, 43140-29-0; $[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$, 43140-30-3; $[Ph_4C_4Fe(CO)(NO)Ph_3As]^+PF_6^-$, 43140-31-4; $[Ph_4C_4Fe(NO)[(PhO)_3P]_2]^+PF_6^-$, 43140-32-5; $C_4H_4Fe(CO)_3$, 12078-17-0; $Me_4C_4Fe(CO)_3$, 12245-09-9; $Ph_4C_4Fe(CO)_3$, 31811-56-0; $NO^+PF_6^-$, 16921-91-8; Ph_3P, 603-35-0; $(PhO)_3P$, 101-02-0.

(24) A. Efraty, unpublished results.

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Ligand Substitution at Five-Coordinate Centers. Reactions of Neutral Iron- and Cobalt-Dithiolene Complexes

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The kinetics of the substitution reactions of the five-coordinate 1,2-dithiolene complexes $M(S_2C_2Ph_2)_2X$ (M = Fe, Co; X = a phosphine or phosphite) are reported. The X group is replaced by other phosphines or phosphites by an associative mechanism with a small dissociative contribution. The iron complexes react up to an order of magnitude faster than the analogous cobalt complexes. Steric effects are important in determining the relative rates of nucleophilic substitution.

Introduction

There has been a vast amount of work on the reactions of four- and six-coordinate transition metal complexes. In general it is found that the substitution reactions of six-coordinate complexes proceed by a predominantly dissociative pathway while four-coordinate planar complexes substitute their ligands *via* an associative mechanism. Except for a few isolated cases it is not known by what mechanism(s) substitutions at five-coordinate centers occur. Whether or not generalized pathways will emerge is unknown.

Until fairly recently five-coordination was only a curiosity and so a knowledge of the reaction mechanisms of these complexes was not, perhaps, necessary. Over the past few years it has become abundantly clear, however, that coordination number 5 is widespread; hundreds of examples are now known. In fact five-coordination can now be considered commonplace. It therefore is time that some detailed knowledge of the mechanisms by which five-coordinate complexes react be made available.

A few kinetic studies of five-coordinate systems have been reported.[2-4] Most of these studies report dissociative-type mechanisms. We recently[3] reported kinetic studies of negatively charged five-coordinate iron- and cobalt-dithiolene systems

$$M(S_2C_2(CN)_2)_2PR_3^- + L \rightleftharpoons M(S_2C_2(CN)_2)_2L^- + PR_3 \qquad (1)$$

The 1,2-dithiolene ligand in reaction 1 is maleonitriledithiolate (mnt). The nucleophile, L, in (1) is either unidentate or bidentate. We found that reaction 1 proceeded by both

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