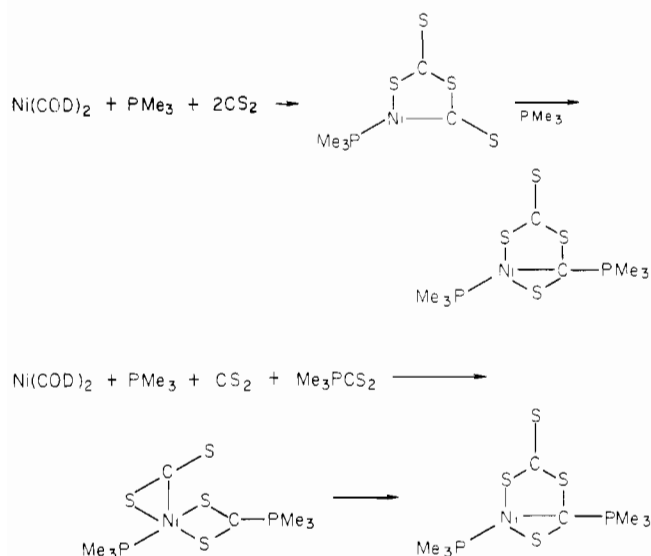


Scheme 1



Three examples of transition-metal complexes containing C₂S₄ linkages have been reported recently.^{25,32,36} But as can be deduced from Table VI, the SC(S)SC(PMe₃)S linkage in the present structure is the first example of a CS₂ condensation

linkage that has an incorporated phosphine. Two possible routes to this compound are proposed in Scheme I.

Attempts to prepare additional nickel complexes that contain R₃PCS₂ ligands were unsuccessful. Addition of R₃PCS₂ (R = Et, Bu) to preformed Ni(COD)(dppe) (from Ni(COD)₂ and dppe; dppe = 1,2-bis(diphenylphosphino)ethane) upon prolonged mixing yielded no reaction. Generation of Ni(COD)(dppe) in situ by a Zn reduction of NiCl₂(dppe) in the presence of COD⁵⁵ followed by addition of R₃PCS₂ resulted in the formation of orange compounds of unknown structure.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE80-09671) for financial support.

Registry No. [Ni(CS₂)(PPh₃)₂], 55891-51-5; [Ni(CS₂)(P(*p*-tol)₃)₂], 82999-54-0; [Ni(CS₂)(PCy₃)₂], 82999-55-1; Ni(C₂S₄PMe₃)(PMe₃), 82999-59-5; Ni(C₂S₄PEt₃)(PEt₃), 82999-60-8; Ni(COD)₂, 1295-35-8; Cy₃PCS₂, 70165-72-9; Et₃PCS₂, 3736-69-4; Me₃PCS₂, 83334-89-8; PEt₃, 554-70-1; PMe₃, 594-09-2; CS₂, 75-15-0.

Supplementary Material Available: Anisotropic thermal parameters (Table IV) and observed and calculated structure amplitudes (Table V) (22 pages). Ordering information is given on any current masthead page.

(55) Giannoccaro, P.; Sacco, A.; Vasapollo, G. *Inorg. Chim. Acta* **1979**, *37*, L455-L456.

Contribution from the Departments of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968, and The University of Houston, Houston, Texas 77030

Structure and Reactivity of M⁺[Fe(CO)₃(NO)]⁻

K. H. PANNELL,^{*1a} YU-SEN CHEN,^{1a} K. BELKNAP,^{1a} C. C. WU,^{1a} I. BERNAL,^{1b} M. W. CRESWICK,^{1b} and HSU NAN HUANG^{1a}

Received March 12, 1982

The solid and solution structures of M⁺[Fe(CO)₃(NO)]⁻ have been investigated with use of a combination of IR and NMR spectroscopy and X-ray crystallography. Ion pairing has been shown to be important, and tight ion pairs involving a cation-nitrosyl interaction have been observed. The chemical reactivity of the salt has been investigated, with MeI as a substrate, and product variations have been noted as a function of solvent and cation variations. A kinetic study of the above reaction shows relatively small rate variations as a function of ion pairing but does clearly illustrate that the solvent-separated ion pairs are more kinetically reactive. A study using the metalate system to evaluate the cation-complexing capacities of crown ethers is included. The crystal and molecular structures were determined from 3656 data (Mo Kα) for which $I > 3\sigma(I)$. The space group is $P2_1/c$. Cell constants are $a = 17.533$ (6) Å, $b = 9.202$ (17) Å, $c = 22.026$ (11) Å, and $\beta = 96.15$ (3)°, with $V = 3533.17$ Å³. The structure consists of isolated PPN cations and Fe(CO)₃(NO) anions, and while the former are fully ordered and bent (P-N-P angle 140.5 (3)°) the latter are disordered in such a way that the NO ligand occupies each of the four tetrahedral sites nearly one-fourth of the time. Thus, there is not sufficient anchoring of the anion by the cation, which would prevent lattice disorder of CO's and NO, but the disorder is not perfect. The average Fe-X (X = C, N) bond length is 1.71 Å, which is a little longer than the values found for ordered Fe-NO bonds but comparable with other cases of disordered iron carbonyl nitrosyls. The average value of the P-N bonds is 1.58 (1) Å, which is normal. The phenyl rings are well-behaved insofar as distances and angles are concerned.

Introduction

The use of transition-metal metalates as reactive intermediates in the formation of metal-carbon bonds is well established.² Detailed studies on the solution structures of these intermediates and their mode of reactivity have only recently begun to attract attention. Initial studies by Edgell and co-workers illustrated that M⁺[Co(CO)₄]⁻ existed in solution as a mixture of tight and solvent-separated ion pairs in which the former contained a cation-carbonyl oxygen interaction.³

Related cation-carbonyl oxygen interactions have been subsequently reported, e.g., [Mn(CO)₅]⁻,^{4,5} [HFe(CO)₄]⁻,⁶ and [(η⁵-C₅H₅)Mo(CO)₂(L)]⁻,⁷ while cation-ketonic carbonyl tight ion pairs have been observed in the [LFe(CO)₃COPh]⁻Li⁺ system⁸ and cation-cyanide interactions reported for [Fe(CO)₄(CN)]⁻Na⁺ and [Mo(CO)₅(CN)]⁻Na⁺.²¹ In addition to cation-carbonyl tight ion pairs, the widely used [(η⁵-C₅H₅)Fe(CO)₂]⁻ system has been shown to exhibit a further,

(1) (a) The University of Texas at El Paso. (b) The University of Houston.
 (2) For an early review of this topic, see R. B. King, *Adv. Organomet. Chem.*, **2**, 157 (1964); for a later review, see J. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).
 (3) W. F. Edgell in "Ions and Ion Pairs in Organic Reactions", Vol. 1, M. Szwarc, Ed., Wiley, New York, 1972.

(4) C. D. Pribula and T. L. Brown, *J. Organomet. Chem.*, **71**, 415 (1974).
 (5) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **94**, 3127 (1976).
 (6) M. Y. Darensbourg, D. J. Darensbourg, and H. C. L. Barros, *Inorg. Chem.*, **17**, 297 (1978).
 (7) K. H. Pannell and D. Jackson, *J. Am. Chem. Soc.*, **98**, 4443 (1976).
 (8) M. Y. Darensbourg and D. Burns, *Inorg. Chem.*, **13**, 2970 (1974).

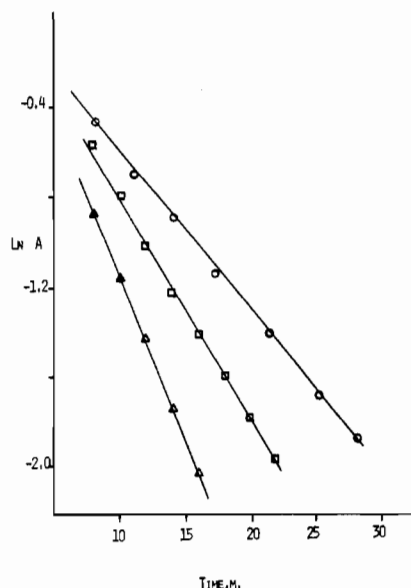


Figure 1. Plot of the natural log of the absorbance of [Fe(CO)₃(NO)]K, initially 6.15×10^{-3} mol/L, and 18-C-6, 6.15×10^{-3} mol/L, vs. time (minutes) in THF; [CH₃I] = (○) 9.2×10^{-2} mol/L, (□) 1.54×10^{-1} mol/L, (▽) 1.84×10^{-1} mol/L.

and often more predominant, tight ion-pairing mode involving a more direct cation-transition-metal atom interaction.⁷ Along with these varied solution studies, several crystal structures of transition-metal metalates have appeared and they also show a variety of ion-pair interactions, ranging from "expected" separated cation and anion salt structures for large low-charge-density cations, e.g., PPN⁺[Fe(CO)₄H]⁻ and 2[Na(crypt)]⁺[Fe(CO)₄]²⁻,^{9,10} to distinctly cation-perturbed salt structures, e.g., Na₂Fe(CO)₄·1.5dioxane.¹¹

Only two significant kinetic studies have been reported that relate to the basic chemical reaction of these metalates, i.e., formation of the transition-metal-carbon bond. Darensbourg and co-workers have reported an extensive study into the reaction of M⁺[Mn(CO)₄(L)]⁻ with various organic halides.⁵ They established that the kinetically active form of the salt was the tight-ion-paired species rather than the "anticipated" more nucleophilic separated species. The greater negative entropy of activation for the separated species was found to be the reason for this result, and arguments were presented to account for this phenomenon, including ability of the cation to polarize the metalate and substrate, thus altering dramatically the changes in coordination occurring during the reaction.

In a second study, Collman and co-workers¹² studied the reaction between Na₂Fe(CO)₄ and organic halides and found the kinetically dominant species to be the partially separated species [NaFe(CO)₄]⁻, which both is internally polarized and possesses the enhanced nucleophilicity associated with separated species.

Finally, a brief report on the reactivity of [(η⁵-C₅H₅)Fe(CO)₂]⁻ with various epoxides led to varying yields of ring-opened product that was interpreted as suggesting that the tight-ion-pair forms were the kinetically active species.¹³

It is the purpose of this paper to report the details of the crystal and solution structure of M⁺[Fe(CO)₃(NO)]⁻ and further to report the results of the reactions of this salt with

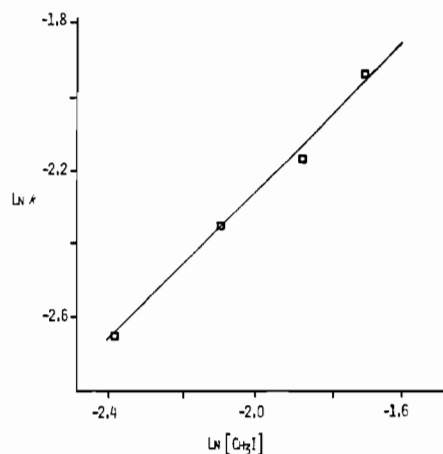


Figure 2. Natural log of the pseudo-first-order rate constant, k , vs. $\ln [\text{CH}_3\text{I}]$ (slope = 1.01 ± 0.05 , $k_2 = 0.78 \pm 0.078 \text{ M}^{-1} \text{ min}^{-1}$).

methyl iodide under a variety of conditions and report the results of a kinetic study on these reactions.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen, with use of dry oxygen-free solvents. The preparation of the [Fe(CO)₃(NO)]⁻ salts involved the published procedures of Hieber;²⁵ the PPN⁺ salt was synthesized from the Na⁺ salt by addition of 1 equiv of PPN⁺Cl⁻ to a THF solution of the Na⁺ salt. Removal of the solvent followed by recrystallization from a CH₂Cl₂-hexane mixture produced excellent yields of the described product.

Kinetic runs were performed by monitoring the disappearance of the E-mode band of the ferrate salt with use of a concentration of the appropriate salt of 5.2×10^{-3} mol/L, under pseudo-first-order conditions. A plot of $\ln [\text{Fe}(\text{CO})_3(\text{NO})\text{M}]$ vs. t was made, and some typical plots are illustrated in Figure 1. For a determination of the order of the reaction between the ferrate and MeI, pseudo-first-order rate constants were obtained with use of MeI concentrations in 10–50-fold excess. Two analyses of the resulting data were performed: a simple plot of k_{obsd} vs. [MeI], which produced a straight line that passes through the origin and hence illustrates first-order kinetics with respect to MeI, and a plot of $\log k_{\text{obsd}}$ vs. $\log [\text{MeI}]$, which yielded a straight line of slope 1, confirming the above conclusion (Figure 2).

For those reactions used for the purpose of isolation of the various reaction products, some typical reactions are described below.

Reaction of [Fe(CO)₃(NO)]⁻Na⁺ with Methyl Iodide in Diethyl Ether. To a solution of the title salt (0.4 g, 2.1×10^{-3} mol) was added an excess of MeI. The reaction mixture was stirred for 3 h, and at this time an infrared spectrum of the reaction mixture indicated no starting salt, bands being observed at 2083, 2032, 1818, 1994, 1801, and 1756 cm⁻¹. This combination of bands was shown to be exactly equivalent to a mixture (1/1) of [Fe(CO)₅] and [Fe(CO)₂(NO)₂] with use of the spectral authentic materials. To the mixture from the original reaction of the ferrate was added an excess of triphenylphosphine. The reaction mixture was allowed to stir for 7 h, and then the solvent was removed under reduced pressure, leaving an orange solid residue. This was dissolved in the minimum of hexane-CH₂Cl₂ (2/1) and placed upon a $6 \times 3/4$ in. alumina column. Elution of the column with hexane-methylene chloride yielded 0.1 g of [Fe(CO)(PPh₃)(NO)₂], identified by comparison of our infrared data with the published data.³² Further elution with CH₂Cl₂ yielded 0.04 g of [Fe(NO)₂(PPh₃)₂], identified in a similar fashion.

Reaction of [Fe(CO)₃(NO)]⁻PPN⁺ with Methyl Iodide in THF. To a solution of the title salt (0.3 g, 4.21×10^{-4} mol) was added an excess of MeI. The mixture was allowed to stir for 4 h and an infrared spectrum recorded. No starting ferrate was present, but new bands were observed: 2010, 1940, 1712, 1711, and 1680 cm⁻¹. The reaction mixture was permitted to stir for a further 15 h and a fresh spectrum recorded, indicating the presence of only two bands in the $\nu(\text{CO})$, $\nu(\text{NO})$ region, 1712 and 1772 cm⁻¹. The solvent was removed and the residue recrystallized from a CH₂Cl₂-hexane mixture to yield 0.14 g of [Fe(NO)₂(I)₂]⁻PPN⁺. This salt was identified by comparison of its infrared spectrum with that published and by comparison of its ESR spectrum with a characteristic 11-line signal.³¹

- (9) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973).
- (10) R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1104 (1977).
- (11) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976).
- (12) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 1647 (1977).
- (13) M. Nitay and M. Rosenblum, *J. Organomet. Chem.*, **136**, C23 (1977).

Reaction of $[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{Na}^+$ with Methyl Iodide and PPh_3 in THF. To a solution of the title salt (0.5 g , $2.6 \times 10^{-3} \text{ mol}$) and PPh_3 (0.7 g , $2.7 \times 10^{-3} \text{ mol}$) was added an excess of MeI . The solution was stirred for 4 h and the reaction stopped; the solvent was removed under reduced pressure to yield an orange solid. This solid was placed upon an alumina column in the minimum of hexane–methylene chloride. Elution of the orange-yellow band with a 3/1 hexane– CH_2Cl_2 solvent mixture produced a yellow solution that, upon concentration to approximately 30% of its original volume, yielded 0.27 g of $[\text{Fe}(\text{CO})_2(\text{NO})(\text{PPh}_3)(\text{COCH}_3)]$. This complex was identified by comparison of its spectral properties with the published data.³⁰

X-ray Crystallographic Analysis. The crystal selected, mounted approximately along its [110] direction, was first centered automatically, with use of 25 reflections found by the routine SEARCH and processed by the program INDEX.⁴¹ Then 25 strong high-angle reflections were centered and used with the least-squares routine (LS) to yield the orientation matrix for data collection and the cell constants listed in Table IA. The Niggli matrix was used in conjunction with tables provided by Roof⁴² to determine the crystal system and lattice symbol. Once this information was available, the details of the space group symbol were determined by searching for possible systematic absences, with use of the ZIGZAG mode in the routine DATCOL.

The diffracted intensities were collected, with use of the θ - 2θ scan technique. For each reflection, a preliminary scan was made at 5° min^{-1} and the prescan intensity (I_{pre}) and $\sigma(I_{\text{pre}})$ were calculated. If the ratio $I_{\text{pre}}/\sigma(I_{\text{pre}})$ was found to be greater than 1.9, the reflection was classified as observed. If $\sigma(I_{\text{pre}})$ was greater than 0.2, a second scan was made with its speed adjusted so as to obtain a final estimated standard deviation of less than 0.02. The maximum time allowed for the second scan was 5 min. In both scans, backgrounds were measured on each side of the peak for 25% of the total scan time. For any measured reflection, the width of the scan was calculated by the equation

$$\text{scan range} = A + B \tan \theta$$

with $A = 1.10$ and $B = 0.35$. The settings of the variable aperture were determined in the same fashion, with A and B set at 2.50 and 0.00 mm, respectively. The crystal-to-source and crystal-to-detector distances were fixed at 216 and 173 mm, respectively. So that the electronics and the stability of the crystal could be checked, two reflections, [618] and $[\bar{6}\bar{1}\bar{8}]$, were used to monitor intensity at intervals of 120 min in X-ray exposure time. During the 11 days of data collection, the intensity standards differed by no more than +1.6% of their initial intensities. The data reduction was carried out with a locally written program.⁴³

A total of 3656 independent reflections and 208 intensity standards were collected for I in a range of $4^\circ \leq 2\theta \leq 40^\circ$; 2241 reflections having $I > 3\sigma(I)$ were classified as observed. All of the observed reflections were used in the final refinement cycles with standard deviations in their intensities estimated as $\sigma^2(I) = I_{\text{tot}} + 2I_{\text{BG}}$. Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_o|$. Due to the relatively low absorption coefficient, absorption corrections were deemed unnecessary. Standard deviations in structure factor amplitudes, $\sigma(|F_o|)$, were estimated as $\sigma(|F_o|) = \sigma(I)/2Lp|F_o|$.

Solution and Refinement. The structure was solved by direct methods with use of the routines in MULTAN-74⁴⁴ and refined with use of the SHELX-76 system.⁴⁵ Neutral-atom atomic scattering factors were used on the refinements; both real and imaginary anomalous parts of the correction to the atomic scattering were applied to Fe.⁴⁶ An E map, based on 400 phases from the starting set and having the highest overall figure of merit, revealed most of the non-hydrogen atoms, and the nine missing carbons of the triphenylphosphine groups were located in subsequent difference Fourier maps. Refinement of the non-hydrogen atoms, with use of individual isotropic thermal motion, yields the agreement factors

$$R(F) = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.1059$$

$$R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0968$$

with

$$w = 1/\sigma^2(F)$$

The assignment of anisotropic thermal parameters to all non-hydrogen atoms, except the phenyl carbons, followed by further refinement lowered the agreement factors to $R(F) = 0.0766$ and $R_w(F) = 0.0676$.

At this stage, hydrogen positions were calculated ($\text{C-H} = 1.08 \text{ \AA}$) and assigned an isotropic temperature parameter. In the later stages of refinement the ideal hydrogen positions were calculated before each cycle of least squares, while the group temperature factor was allowed to refine. All four atoms bonded to the iron were refined as carbons. A final blocked least-squares refinement of all non-hydrogen positions and thermal parameters along with the overall scale factor and single hydrogen thermal parameter yielded the following final agreement factors: $R(F) = 0.0544$; $R_w(F) = 0.0489$. During the last cycle of least squares all of the parameter shifts were less than 0.11 times their respective estimated standard deviations. In a final difference Fourier map the largest residual peak appeared with a height of 0.37 e/\AA^3 . Atomic coordinates and thermal parameters are given in Table IB.

Results and Discussion

Infrared Study. The first spectroscopic analysis of salts containing the $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ species was by Hieber.¹⁴ He reported complex salts containing tris(phenanthrene) Fe^{2+} and Ni^{2+} cations, $[(\text{phen})_3\text{M}]^{2+}[\text{Fe}(\text{CO})_3(\text{NO})]^-_2$, with infrared stretching frequencies for the CO and NO ligands compatible with the assumption of local C_{3v} symmetry at the Fe anion atom, i.e.: $\nu(\text{CO})$ 1984 (A_1), 1864 (E) cm^{-1} ; $\nu(\text{NO})$ 1644 cm^{-1} (KBr). The solution spectra resulted in a similar band pattern when recorded in diglyme ($\nu(\text{CO})$ 1983, 1881 cm^{-1} ; $\nu(\text{NO})$ 1651 cm^{-1} ¹⁵), while the bands of the alkali-metal salts in Me_2SO were similar.¹⁶ These solvent systems are those with good donor character and thus might be expected to produce solutions containing only solvent-separated ion pairs. Indeed when we recorded the spectrum of the Na^+ salt in the less powerful solvent THF, we obtained the spectrum illustrated in Figure 3. The main features of this spectrum are the presence of two A_1 -mode carbonyl bands and two nitrosyl bands and considerable broadening of the E-mode band of the carbonyl groups.

Titration of transition-metal metalates with various crown ethers has proven to be a very powerful tool in elucidating ion-pairing phenomena. The crown ethers will compete most successfully with solvent and counteranion for the alkali metal and, eventually, shift the tight \rightleftharpoons separated equilibrium to crown-ether-separated ion pairs. Titration of the salt solution with 18-crown-6 results in a progressive change in the observed spectrum until finally, upon addition of 50% equivalent of the crown ether, the infrared data are interpreted as originating from a single species, with the following stretching frequencies: $\nu(\text{CO})$ 1978, 1874 cm^{-1} ; $\nu(\text{NO})$ 1646 cm^{-1} . The species removed by the titration with crown ether has the following infrared bands: $\nu(\text{CO})$ 1989, 1885 cm^{-1} ; $\nu(\text{NO})$ 1616 cm^{-1} .

Since the crown ether titration progressively removed a tight-ion-paired species and, further, this species has higher carbonyl stretching frequencies and a lower nitrosyl stretching frequency than the solvent- and/or crown-ether-separated species, it follows that the tight ion pair involves a cation–nitrosyl interaction as opposed to the more common cation–carbonyl interaction.

Thus in the moderate solvent THF, at 25 °C, the salt $\text{Na}^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ exists as a dynamic equilibrium of a tight-ion-paired species involving a sodium–nitrosyl interaction and an almost equal amount of a solvent-separated ion-pair species.

Examination of the spectra of $\text{Na}^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ in diethyl ether, a solvent in which the salt has a much lower solubility, establishes that the stretching frequency bands are more broad in general, but the data obtained are consistent with a single species: $\nu(\text{CO})$ 2001, 1904 cm^{-1} ; $\nu(\text{NO})$ 1583 cm^{-1} . The very low nitrosyl frequency and the considerably higher carbonyl frequencies are both consistent with, and argue in favor of, assigning the species to a tight ion pair. Attempts

(14) W. Hieber, *Z. Naturforsch.*, **B**, **15B**, 323 (1960).

(15) W. Beck, *Chem. Ber.*, 1214 (1961).

(16) M. Casey and A. R. Manning, *J. Chem. Soc. A*, 2258 (1970).

Table I

A. Crystallographically Important Data Collection and Data Processing Information

empirical formula	C ₃₉ H ₃₀ N ₂ O ₄ P ₂ Fe	cryst orientation	[110]
mol wt	708.475	stds for intens control (every 30 reflctns)	[618] and $\overline{[618]}$
cell const	<i>a</i> = 17.533 (6) Å <i>b</i> = 9.202 (17) Å <i>c</i> = 22.026 (11) Å <i>β</i> = 96.15 (3) ^o	scan width for each reflctn	(1.10 + 0.35 tan <i>θ</i>) ^o
unit cell vol	3533.17 Å ³	max scan time	5 min
space group	<i>P</i> 2 ₁ / <i>c</i>	prescan acceptance criterion ^a	<i>I</i> _{pre} ≥ 1.90σ(<i>I</i> _{pre})
density calcd (<i>Z</i> = 4)	1.33 g cm ⁻³	scan technique	<i>θ</i> -2 <i>θ</i>
measd	1.32 g cm ⁻³	total no. of reflctns collected ^b	3656
abs coeff (Mo Kα)	<i>γ</i> = 5.09 cm ⁻¹	no. of contributing reflctns in the last least squares ^b	2241
radiation used for data collection	Mo Kα (λ = 0.71069 Å)	no. of variables	254
scanning range for 2 <i>θ</i>	4.0 ^o ≤ 2 <i>θ</i> ≤ 40.0 ^o	weighting scheme	1/σ ² (<i>F</i>)
		final <i>R</i> (<i>F</i>) ^c	0.0544
		final <i>R</i> _w (<i>F</i>) ^d	0.0438

B. Atomic Coordinates and Thermal Parameters (×1000)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Fe	0.7628 (1)	0.8016 (2)	0.1379 (1)	72 (1)	78 (1)	68 (1)	-6 (1)	-2 (1)	7 (1)
P1	0.6630 (1)	0.2880 (2)	0.3987 (1)	36 (1)	40 (1)	38 (1)	5 (1)	3 (1)	2 (1)
P2	0.8303 (1)	0.2419 (2)	0.3949 (1)	36 (1)	37 (1)	41 (1)	3 (1)	0 (1)	-1 (1)
N	0.7487 (3)	0.3179 (6)	0.3874 (2)	19 (3)	44 (4)	45 (4)	4 (3)	4 (3)	4 (3)
X1	0.7270 (4)	0.7022 (10)	0.1938 (4)	52 (6)	81 (8)	55 (6)	-12 (6)	7 (5)	5 (6)
O1	0.7036 (3)	0.6307 (7)	0.2310 (3)	85 (5)	131 (7)	84 (5)	-15 (4)	17 (4)	19 (5)
X2	0.6865 (5)	0.8378 (10)	0.0845 (4)	84 (8)	58 (7)	95 (8)	4 (6)	-21 (6)	0 (6)
O2	0.6355 (4)	0.8622 (8)	0.0492 (4)	153 (8)	95 (6)	182 (8)	16 (6)	-88 (6)	12 (6)
X3	0.7987 (5)	0.9667 (10)	0.1675 (4)	74 (7)	62 (8)	54 (7)	-9 (6)	-3 (5)	1 (6)
O3	0.8213 (4)	1.0747 (7)	0.1869 (3)	167 (7)	81 (6)	91 (6)	-25 (5)	-9 (5)	-14 (5)
X4	0.8297 (5)	0.7000 (9)	0.1065 (4)	58 (6)	54 (7)	52 (6)	-5 (5)	10 (5)	-6 (5)
O4	0.8745 (4)	0.6285 (7)	0.0859 (3)	101 (6)	103 (6)	91 (5)	7 (5)	15 (4)	-16 (5)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²
C11	0.6136 (4)	0.4601 (7)	0.3970 (3)	36 (2)	C64	0.9688 (5)	0.3611 (9)	0.5760 (4)	69 (3)
C12	0.5457 (4)	0.4739 (8)	0.4248 (3)	49 (2)	C65	0.9817 (5)	0.2289 (10)	0.5496 (4)	81 (3)
C13	0.5064 (4)	0.6085 (8)	0.4190 (3)	59 (3)	C66	0.9395 (4)	0.1913 (9)	0.4942 (3)	67 (3)
C14	0.5349 (4)	0.7210 (9)	0.3879 (3)	64 (2)	H12	0.5242 (4)	0.3847 (8)	0.4499 (3)	80 (0)
C15	0.6005 (4)	0.7061 (9)	0.3599 (3)	62 (2)	H13	0.4533 (4)	0.6220 (8)	0.4391 (3)	80 (0)
C16	0.6407 (4)	0.5732 (8)	0.3646 (3)	51 (2)	H14	0.5052 (4)	0.8239 (9)	0.3855 (3)	80 (0)
C21	0.6133 (4)	0.1780 (8)	0.3387 (3)	42 (2)	H15	0.6212 (4)	0.7955 (9)	0.3345 (3)	80 (0)
C22	0.5339 (4)	0.1568 (8)	0.3369 (3)	55 (2)	H16	0.6926 (4)	0.5600 (8)	0.3428 (3)	80 (0)
C23	0.4965 (5)	0.0703 (8)	0.2895 (4)	70 (3)	H22	0.5021 (4)	0.2053 (8)	0.3711 (3)	80 (0)
C24	0.5366 (5)	0.0143 (9)	0.2463 (4)	71 (3)	H23	0.4357 (5)	0.0496 (8)	0.2881 (4)	80 (0)
C25	0.6137 (4)	0.0377 (9)	0.2458 (4)	68 (3)	H24	0.5068 (5)	-0.0516 (9)	0.2107 (4)	80 (0)
C26	0.6530 (4)	0.1222 (8)	0.2929 (3)	58 (2)	H25	0.6440 (4)	-0.0076 (9)	0.2101 (4)	80 (0)
C31	0.6530 (4)	0.2034 (8)	0.4714 (3)	42 (2)	H26	0.7136 (4)	0.1432 (8)	0.2933 (3)	80 (0)
C32	0.6867 (4)	0.2750 (9)	0.5231 (3)	58 (2)	H32	0.7134 (4)	0.3800 (9)	0.5192 (3)	80 (0)
C33	0.6856 (4)	0.2077 (9)	0.5800 (4)	75 (3)	H33	0.7123 (4)	0.2597 (9)	0.6208 (4)	80 (0)
C34	0.6506 (5)	0.0773 (10)	0.5838 (4)	82 (3)	H34	0.6506 (5)	0.0272 (10)	0.6281 (4)	80 (0)
C35	0.6161 (5)	0.0068 (11)	0.5345 (4)	86 (3)	H35	0.5874 (5)	-0.0954 (11)	0.5401 (4)	80 (0)
C36	0.6177 (4)	0.0680 (9)	0.4757 (4)	70 (3)	H36	0.5924 (4)	0.0122 (9)	0.4353 (4)	80 (0)
C41	0.8847 (4)	0.0444 (7)	0.3893 (3)	36 (2)	H42	0.8657 (4)	0.0409 (8)	0.2991 (3)	80 (0)
C42	0.8479 (4)	-0.0228 (8)	0.3363 (3)	45 (2)	H43	0.8587 (4)	-0.2302 (8)	0.2922 (3)	80 (0)
C43	0.8435 (4)	-0.1755 (8)	0.3326 (3)	53 (2)	H44	0.8177 (4)	-0.3722 (9)	0.3764 (3)	80 (0)
C44	0.8202 (4)	-0.2552 (9)	0.3797 (3)	56 (2)	H45	0.7802 (4)	-0.2508 (9)	0.4681 (3)	80 (0)
C45	0.7997 (4)	-0.1867 (9)	0.4317 (3)	61 (2)	H46	0.7889 (4)	0.0183 (8)	0.4777 (3)	80 (0)
C46	0.8042 (4)	-0.0357 (8)	0.4372 (3)	49 (2)	H52	0.9914 (4)	0.2294 (8)	0.3759 (3)	80 (0)
C51	0.8827 (4)	0.3107 (7)	0.3354 (3)	38 (2)	H53	0.0614 (5)	0.3172 (9)	0.2916 (4)	80 (0)
C52	0.9614 (4)	0.2862 (8)	0.3376 (3)	58 (2)	H54	0.9937 (5)	0.4459 (9)	0.2058 (4)	80 (0)
C53	1.0004 (5)	0.3352 (9)	0.2904 (4)	77 (3)	H55	0.8537 (5)	0.4868 (9)	0.1982 (4)	80 (0)
C54	0.9618 (5)	0.4074 (9)	0.2420 (4)	82 (3)	H56	0.7829 (4)	0.4023 (8)	0.2848 (3)	80 (0)
C55	0.8833 (5)	0.4321 (9)	0.2373 (4)	79 (3)	H62	0.8313 (4)	0.4945 (8)	0.4728 (3)	80 (0)
C56	0.8439 (4)	0.3833 (8)	0.2858 (3)	56 (2)	H63	0.9072 (4)	0.5608 (9)	0.5697 (3)	80 (0)
C61	0.8841 (4)	0.2866 (4)	0.4665 (3)	40 (2)	H64	1.0007 (5)	0.3898 (9)	0.6190 (4)	80 (0)
C62	0.8733 (4)	0.4194 (8)	0.4941 (3)	51 (2)	H65	1.0239 (5)	0.1550 (10)	0.5716 (4)	80 (0)
C63	0.9158 (4)	0.4567 (9)	0.5488 (3)	57 (3)	H66	0.9501 (4)	0.0889 (9)	0.4727 (3)	80 (0)

^a In the new CAD-4 software package, this criterion is used rather than a minimum number of counts on prescan. ^b A total of 3656 reflections were collected of which 2241 having *I* > 3σ(*I*) were classified as "observed" with the remaining 1415 being omitted. ^c *R*(*F*) = Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|. ^d *R*_w(*F*) = [Σw(|*F*_o| - |*F*_c|)²/Σw|*F*_o|²]^{1/2}.

to create separated ion pairs in diethyl ether by the gradual addition of crown ethers were unsuccessful since precipitation of the salt occurred, presumably as the [Na(crown)]⁺ derivative. Use of the chelating solvent dimethoxyethane (DME) resulted in the observation of both the tight and the separated species, but their relative concentrations were such that barely 15% of the salt is in the tight-ion-paired form, again in accord

with the better coordinating capacity of the chelating solvent compared to that of THF.

A study into the variations of the stretching frequencies and relative abundances of the two ion-pair forms for the K⁺ salt was made. The results are qualitatively similar, with the major exception that in all solvents the K⁺ salt exists in the tight-ion-paired form to a greater extent than the Na⁺ salt. This

Table II. Stretching Frequencies and Relative Abundances of Tight Ion Pairs (TIP) in Various Solvents at 25 °C^a

solvent	[Fe(CO) ₃ (NOM)]		[Fe(CO) ₃ (NO)] ⁻ M ⁺		% TIP	
	$\nu(\text{CO})$ [$\nu(\text{NO})$], cm ⁻¹		$\nu(\text{CO})$ [$\nu(\text{NO})$], cm ⁻¹		Na ⁺	K ⁺
	Na ⁺	K ⁺	Na ⁺	K ⁺		
Et ₂ O	2001, 1900 [1599]	2001, 1903 [1593]	1978, 1875 [1646]	1978, 1875 [1646]	100	100
THF	1990, 1885 [1615]	1992, 1887 [1613]	1978, 1875 [1646]	1978, 1875 [1646]	48	55
DME	1988, 1882 [1618]	1989, 1885 [1623]	1978, 1877 [1647]	1979, 1877 [1647]	20	35

^a [Fe(CO)₃(NO)]⁻PPN⁺ exhibits bands at 1978, 1876, and 1645 cm⁻¹ (THF).

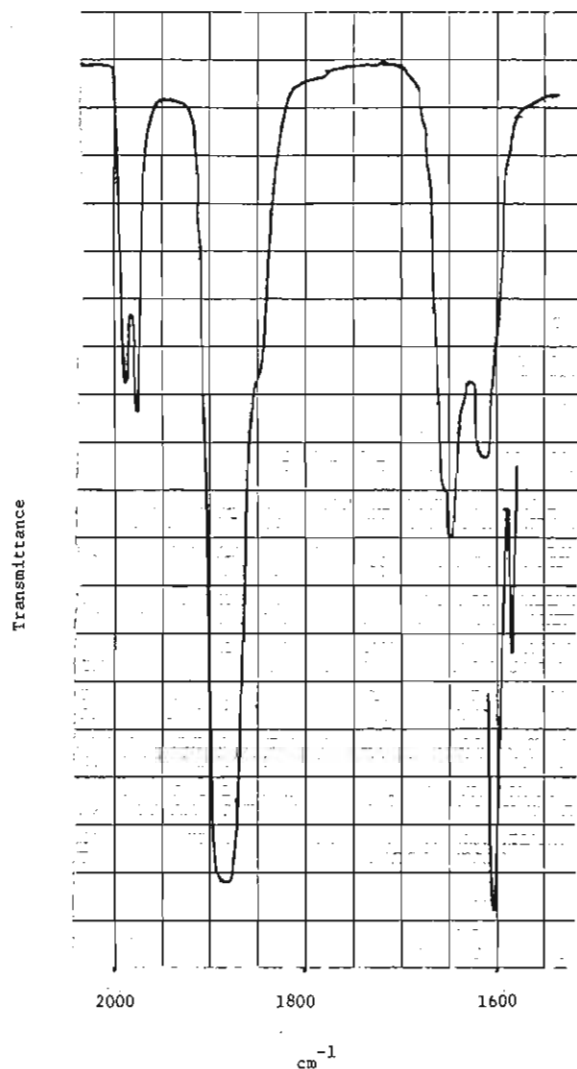


Figure 3. Infrared spectrum of Na⁺[Fe(CO)₃(NO)]⁻ in THF.

reflects the greater size of the K⁺ ion producing a lower electrostatic potential, which results in a weaker interaction with the solvent, thereby causing the cation to interact with its counteranion to a greater extent. Table II presents a summary of the infrared data outlining the stretching frequencies and relative abundances of the ion-pair forms for both the Na⁺ and the K⁺ salts in the various solvents used.

Examination of the data leads to two interesting observations.

(a) All of the carbonyl and nitrosyl frequencies for the PPN⁺, Na⁺, and K⁺ solvent- and/or crown-ether-separated ion pairs are within very narrow limits identical, i.e.: $\nu(\text{CO})$ 1978.5 ± 0.5, 1875 ± 1.0 cm⁻¹; $\nu(\text{NO})$ 1646.5 ± 0.5 cm⁻¹. This observation implies that, once the cation, Na⁺, K⁺, or PPN⁺, has effectively been separated from the anion by a small sheath of solvent, or a crown ether, it is essentially incapable of perturbing the anion sufficiently to change the internal vibrational modes of the complex anion.

Table III. Effects of Crown Ethers^a upon Ion Pairing of [Fe(CO)₃(NO)]⁻K⁺ (0.04 M) in THF

crown ether ^a	18-C-6	(NH ₂) ₂ DBC	Br ₄ DBC	(NO ₂) ₂ DBC
SIP/TIP ^b	1.2	1.0	0.97	0.93

^a 15% equivalent of each crown added; DBC = dibenzo-18-crown-6. ^b SIP/TIP ratio of separated/tight ion pair from average of CO(A) and NO infrared band intensities.

(b) For the various tight ion pairs, the stretching frequencies for the K⁺ and Na⁺ salts are very similar in each solvent, but there are significant differences in the frequencies in differing solvents. In the very poor solvent diethyl ether, the electrostatic potential of the various cations with respect to that of the anion is dramatically enhanced. Thus, not only is the amount of tight ion pair present increased (100% in all cases) but the magnitude of the interaction is increased such that considerably more electron density appears to be funneled into the π* NO orbital, resulting in a much lower stretching frequency in this solvent (20 cm⁻¹ lower than that in THF or DME). Correspondingly, the carbonyl stretching frequencies in diethyl ether are significantly higher.

The sharp nature of the A₁-mode carbonyl stretching frequencies of the Na⁺ and K⁺ salts studied in THF suggested that this system may be a useful one for studying the selectivities and cation-complexing capacities of various crown ethers. We therefore performed a comparative study of a series of crown ethers using Na⁺- and K⁺[Fe(CO)₃(NO)]⁻. For the sodium salt it was not possible, upon addition of dibenzo-18-crown-6, to completely convert the salt to solvent-crown-ether-separated ion pairs, no matter what excess of crown ether was added, e.g., a 200% equivalent, whereas addition of a 50% equivalent of the more flexible and basic 18-C-6 resulted in complete conversion. Similarly, in DME the rigid dibenzo crown ether had no effect at all on the relative abundances of tight and separated ion pairs for the sodium salt while 18-C-6, added to a 30% equivalent, resulted in total conversion. In the case of the K⁺ salt, dibenzo-18-C-6 was effective in bringing about total conversion in both solvents upon addition of 35% and 55% equivalents, respectively, this result emphasizing the better size compatibility of the 18-crowns for K⁺, compared to that for Na⁺. In each case 18-C-6 was better at bringing about complete conversion for the K⁺ salt, a result of its greater flexibility. We included a series of substituted dibenzo-18-crown-6 ethers in this study, to observe if slight variations of basicity could be detected by the relative tight-separated abundances, and the results are included in Table III. Qualitatively, the results indicate very nicely that for a given added equivalent of the various crown ethers the transformation to separated ion pairs is in accord with the relative predicted basicity of the crowns and, thus, that such metalate systems may be useful for the rapid assessment of the cation-complexing capacities of various ionophores. It is gratifying to note that the results obtained closely agree with those obtained by more tedious extraction experiments.¹⁷

The proportion of tight- to separated-ion-paired species changes as a function of total salt concentration. Progressive

(17) K. H. Pannell, W. Yee, G. S. Lewandos, and D. C. Hambrick, *J. Am. Chem. Soc.*, **99**, 1457 (1977).

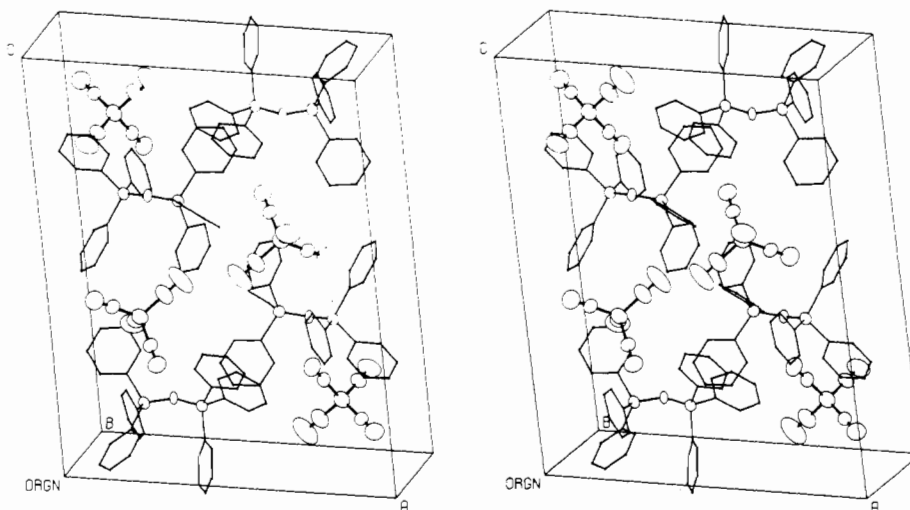


Figure 4. Packing diagram showing the contents of the unit cell. The hydrogens of the phenyl rings in the PPN cation have been omitted for clarity. Note the nearly perfect staggering of the phenyl rings across the P-N-P unit.

dilution of the salt leads to increasing the relative amount of the tight-ion-paired species, e.g., [TIP]/[SIP] \approx 1.5 at 2×10^{-2} M and 1.2 at 10^{-1} M. We have not made an exhaustive study on this aspect of the system, but the observation may best be explained in terms of the presence of aggregates of the tight and solvent-separated species which might be expected at the concentration ranges used in this study. Reasonably, it may be expected that aggregation will be more significant for the separated species, where charge separation is apparent. Since it is not possible, with infrared spectroscopy, to distinguish between monomeric or oligomeric ion pairs in this system, the increase in tight-ion-paired species observed reflects the relative decrease in oligomerization of the separated species upon dilution.

In this regard we can draw attention to another significant feature of the infrared spectra of the title salts, namely, the band shape of the nitrosyl stretching frequencies. In all cases there is a distinct high-frequency shoulder, which is more apparent in the solvent-crown-ether-separated ion pair than in the tight ion pair. Using labeled $[\text{Fe}(\text{CO})_3(^{15}\text{NO})]^-$, we have shown that these shoulders do not originate from a Fermi resonance phenomenon.⁴¹ Alternatively, the possibility that restricted rotation about a "bent" Fe-N-O linkage was responsible is ruled out by the crystal structure of the PPN⁺ salt (vide infra). We thus conclude that this shoulder represents some physical characteristic of the ion-pair aggregations noted above, and this suggestion is partially reinforced by the fact that the shoulder is more dominant in the separated-ion-pair system.

In conclusion of this section some mention of bandwidths seems appropriate. In general the A₁ modes of the CO stretches are uniformly narrow in both ion-pair forms whereas the NO bands are distinctly more broad, this being especially true for the tight-ion-paired species. Such broadness represents in reality an envelope of overlapping bands associated with structures that we lump together as tight ion pairs and separated ion pairs. More detailed analysis may well be able to discern a more definite variety of structures within each of these categories.

The preferential binding of the cation to the NO group rather than to the CO ligand is in accord with the observation that $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ interacts with various organo-lanthanide Lewis acids via adduct formation with the NO group.²⁴

NMR Studies. It was thought that a handle to the problem of oligomerization of the ion pairs may be obtained from the use of ²³Na NMR spectroscopy. This technique has proven

Table IV. ²³Na NMR Parameters (Et₂O Solvent)

$[[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{Na}]$, M	$\nu_{1/2}$, Hz	δ	$[[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{Na}]$, M	$\nu_{1/2}$, Hz	δ
2.2×10^{-1}	77.5	10.03	3.58×10^{-2}	62.7	8.69
1.47×10^{-1}	76.3	9.61	2.39×10^{-2}	59.25	8.06
1.08×10^{-1}	76.8	9.39	1.79×10^{-2}	57.5	7.72
8.67×10^{-2}	71.2	9.16	9×10^{-3}	72	6.47
7.17×10^{-2}	70.7	9.10			

$$n[\text{NaFe}(\text{CO})_3(\text{NO})]_p \rightleftharpoons [\text{NaFe}(\text{CO})_2(\text{NO})]_{np}$$

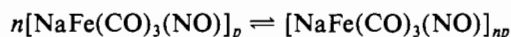
$$n = 3, 2; p = 2; K = 9-12^a$$

$$n = 6, 4; p = 4; K = 17$$

$$n = 5, 3; p = 3; K = 18-20$$

^a The authors thank Dr. A. Cornelis and Prof. P. Laszlo, Université de Liege, for the many hours of effort expended on the analysis that resulted in the above, *n*, *p*, and *K* values.

very powerful in related areas of organic and bioorganic chemistry.¹⁸ We chose to investigate the $\text{Na}^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ system in diethyl ether solution since this solvent offered us a single ion-pair form as determined by infrared spectroscopy, thus hopefully simplifying the analysis. The chemical shift and line width data as a function of salt concentration are reported in Table IV. Clear variations are apparent indicating shifting equilibrium, and on the basis of the simplest assumption



an analysis was attempted. Unfortunately, no unique result was obtained from this procedure; instead, a family of *n* and *p* values with corresponding *K* values was obtained as indicated in the table.

X-ray Crystallographic Analysis of PPN⁺[Fe(CO)₃(NO)]⁻. The structure of this salt, depicted in Figure 4, consists of approximately tetrahedral $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ anions with a bent PPN cation. The significant structural parameters are collected in Table V. The $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ anion is disordered, as is frequently the case, and our crystallographic efforts to resolve this disorder are filed as supplementary material.

The average Fe-X distance (1.71 Å) in the title compound is 0.03–0.06 Å larger than the Fe-N distances listed in Table VI for totally ordered, four-coordinate iron nitrosyls.^{19,20} The

(18) P. Laszlo, *Angew. Chem., Int. Ed. Engl.*, **8**, 284 (1978).

(19) V. G. Albano, A. Araneo, P. L. Bellon, G. Ciani, and M. Manassero, *J. Organomet. Chem.*, **67**, 413 (1974).

Table V. Structural Parameters for the $[\text{Fe}(\text{XO})_4]^-$ Anion Resulting from Various Refinement Schemes with Their Estimated Standard Deviations in Parentheses

refinement technique	$U(\text{av})$ for N^a $U(\text{av})$ for O	$R(F)$ $R_w(F)$	Fe-X, X-O dist, Å				Fe-X _i -O angle, deg $i = 1-4$, deg	X _i -Fe-X _j angles, deg ^c		
			X ₁	X ₂	X ₃	X ₄		1-2 2-3	1-3 2-4	1-4 3-4
1. X ₁ -X ₄ as C's		0.0544 0.0438	1.700 (8)	1.717 (9)	1.740 (9)	1.700 (8)	178.8 (8)	106.3	110.0	108.7
			1.164 (10)	1.147 (11)	1.137 (10)	1.160 (9)	179.7 (4)	108.0	110.3	113.3
2. X ₁ as N	0.0995 (174) ^b 0.1128 (243)	0.0551 0.0461	1.748 (9)	1.726 (9)	1.753 (9)	1.706 (8)	179.2 (8)	106.3	110.0	108.8
			1.173 (8)	1.138 (8)	1.131 (8)	1.151 (8)	178.8 (7)	108.2	110.4	113.0
3. X ₂ as N	0.1237 (268) 0.1615 (364)	0.0552 0.0458	1.710 (8)	1.710 (8)	1.756 (9)	1.706 (8)	179.3 (1.0)	106.3	110.0	107.9
			1.157 (8)	1.157 (8)	1.154 (9)	1.152 (8)	178.5 (8)	108.8	110.5	113.0
4. X ₃ as N	0.1032 (171) 0.1302 (491)	0.0551 0.0459	1.719 (8)	1.719 (9)	1.784 (9)	1.707 (8)	177.9 (9)	106.3	110.2	107.9
			1.153 (8)	1.140 (8)	1.150 (9)	1.153 (8)	179.9 (2)	108.7	110.3	113.3
5. X ₄ as N	0.0899 (83) 0.1131 (20)	0.0548 0.0458	1.710 (8)	1.723 (9)	1.747 (9)	1.742 (9)	179.4 (1.0)	106.1	110.1	108.1
			1.156 (8)	1.141 (8)	1.134 (8)	1.176 (8)	178.4 (8)	108.7	110.6	113.2
						177.8 (9)				
						179.6 (7)				
						179.1 (9)				
						178.2 (8)				

^a $U(\text{av}) = (U_{11} + U_{22} + U_{33})/3$. ^b The esd stated is $\sigma(\text{mean})$. ^c Esd's are all approximately 0.4° ; i - j pairs are shown.

Table VI. Comparison of Distances (Å) and Angles (deg) for Four-Coordinate Iron Carbonyls and Nitrosyls (X = C, N)^a

compd	Fe-X dist	X-O dist	Fe-X≡O angle	X-Fe-X angle	ref
[PPN][Fe(NO)(CO) ₃]	1.700 (8)-1.740 (9) 1.714 av	1.14 (1)-1.16 (1)	178.8 (8)-179.7 (2)	106.3 (4)-113.3 (4)	this work
(Ph ₃ P)Fe(NO) ₂ Cl	1.679 (5)-1.681 (5) 1.680 av	1.136 (7)-1.163 (7)	165.5 (5)-166.4 (5)	115.6 (3)	39
Fe(NO) ₂ (CO)PPh ₃	1.690 (8)-1.732 (8) 1.709 av	1.147 (11)-1.150 (8)	177.3 (10)-178.9 (6)	113.4 (4)-117.3 (4)	19
Fe(NO) ₂ (PPh ₃) ₂ ^b	1.650 (7)	1.19 (1)	178.2 (7)	123.8 (4)	19
Na ₂ [Fe(CO) ₄]-1.5dioxane	1.738 (5)-1.745 (6)	1.162 (8)-1.175 (7)	171.0 (4)-178.7 (5)	104.2 (2)-109.7 (2)	11
[Na(crypt)] ₂ [Fe(CO) ₄]	1.74 (2)-1.81 (2)	1.13 (2)-1.20 (2)	174 (1)-179 (2)	107.3 (7)-112.2 (8)	10
K ₂ [Fe(CO) ₄] ^b	1.746 (4)	1.175 (5)	178.2 (7)	123.8 (4)	10

^a Estimated standard deviations appear in parentheses. For averaged values, $\sigma(\text{mean})$ is shown. ^b The Fe atom appears in a crystallographic special position; the Fe-X≡O groups are equivalent.

average distance is equal, within experimental error, to that reported by Albano et al.¹⁹ for the similarly disordered, neutral Fe(NO)₂(CO)PPh₃ molecule (1.709 Å).

Since the anion is disordered, any comparison of individual bond lengths and angles would be meaningless; however, several comments can be made, concerning the spread of values assumed by several bonding parameters. The range of Fe-X distances in the title compound is similar to those observed by Bau and co-workers for $[\text{Fe}(\text{CO})_4]^{2-}$ in a variety of crystal environments (see Table VI). Likewise, the X-Fe-X angles are similar, with the angles in the title compound resembling (in mean and range) those present in the $[\text{Na}(\text{cryptate})]_2-[\text{Fe}(\text{CO})_4]$ complex. The similarity, between the two compounds, insofar as a distortion from idealized tetrahedral geometry is concerned, might reflect a similarity in crystal-packing environments created by the two cations. Such deviations from tetrahedral geometry in the $[\text{Fe}(\text{CO})_4]^{2-}$ complex are the result of Coulombic attractions between carbonyl oxygens and centers of charge in adjacent cations.¹⁰ That such distortions occur in the title compound can thus be attributed more to the influence of packing forces than to the presence of the nitrosyl group. Finally, it can be seen, from comparison of Fe-X≡O angles in Table VI, that the range of these angles in the title compound is smaller than similar ranges observed for $[\text{Fe}(\text{CO})_4]^{2-}$. Additionally, the average Fe-X≡O bond

angle in the title compound is actually closer to 180° . From these two observations, we conclude that the nitrosyl group in the title compound must be linear or at least as "linear" as the carbonyls in the other complexes listed. The appearance of a linear nitrosyl group in a tetrahedral iron complex is exactly as would be predicted from the work of Enemark et al. on other metal nitrosyl complexes.²²

As shown in Table VII, the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation exhibits a geometry typical of that found in most other compounds. The two triphenylphosphine groups are skewed with respect to each other so that there is little parallel contact of the type described by Albano and others between phenyl groups on adjacent triphenylphosphines.²³ There also appears to be little parallel contact between adjacent cations. The average P-N bond length is 1.58 (1) Å while the P-N-P angle is $140.5 (3)^\circ$. These parameters agree favorably with most of those listed in Table VIII for $[(\text{Ph}_3\text{P})_2\text{N}]^+$ in several other complexes. The ability of the PPN cation to exhibit forms with P-N-P angles with variations up to 45° is unprecedented in any other molecular species, and no theories exist that can satisfactorily explain this fact. We are presently examining this problem

(20) J. Kopf and J. Schmidt, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **32B**, 275 (1975).
(21) M. Y. Darensbourg and H. C. L. Barros, *Inorg. Chem.*, **18**, 3286 (1979).

(22) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974); J. H. Enemark, R. D. Feltham, B. T. Huie, P. L. Johnson, and K. B. Swedo, *J. Am. Chem. Soc.*, **99**, 3285 (1977); K. J. Haller and J. H. Enemark, *Inorg. Chem.*, **17**, 3552 (1978).
(23) V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J. Chem. Soc., Dalton Trans.*, 175 (1972).
(24) A. E. Crease and P. Legzdins, *J. Chem. Soc., Dalton Trans.*, 1501 (1973).

Table VII. Comparison of Bond Lengths (Å) and Angles (deg) for the PPN^a Cation in Various Crystal Environments^b

assoc anion ^c	av P-N dist	av P-C dist	P-N-P angle ^d		orientation of phenyl groups ^e	ref
			obsd	calcd		
[Fe(NO)(CO) ₃] ⁻	1.580 (5)	1.81 (1)	140.5 (3)	133.2	skew	this work
[Na(Mo(CO) ₆ (NO) ₃ C ₆ H ₄ -p-OCH ₃) ₃ (μ-O) ₂] ³⁻	1.53 (1)	1.81 (2)	180.0	142.8	skew	34
[Rh ₄ (CO) ₁₁] ²⁻	1.58 (3)	1.80 (2)	139.1 (1.2)	133.2	parallel	35
	1.58 (1)	1.79 (1)	136.8 (8)	133.2	parallel	
[M ₂ (CO) ₁₆] ⁻ ·CH ₂ Cl ₂ , M = Cr	1.57 (2)	1.78	141.1 (9)	133.2	parallel	36
M = Mo	1.57 (2)	1.81	137 (1)	134.9	skew	
[Fe(CO) ₄ C ₃ H ₇] ⁻	1.58 (1)	1.80 (1)	137 (2)	134.9	skew	37
[HNi(CO) ₆] ⁻	1.549	1.792	145.9 (8)	133.2	skew	38
			175.9 (8)	138.8		

^a Bis(triphenylphosphine)nitrogen(1+) (Ph₃PNPPh₃). ^b Estimated standard deviations are in parentheses. For average values, σ(mean) is shown. ^c Charges on anions are balanced by the required number of PPN cations. ^d Angles are calculated from observed P-N distances and an assumed P...P contact distance of 2.90 Å.²¹ ^e See ref 40.

Table VIII. Kinetic Studies of Reactions between M⁺[Fe(CO)₃(NO)]⁻ and Methyl Iodide

M ⁺	solvent	temp, °C	k ₂ , M ⁻¹ min ⁻¹	activation parameters	
				ΔH, kcal mol ⁻¹	ΔS, eu
PPN ⁺	THF	0.0	0.047 ± 0.001	} 10.5 ± 1.2	26.0 ± 4.0
PPN ⁺	THF	27	0.373 ± 0.0581		
PPN ⁺	THF	42	0.671 ± 0.1		
K ⁺	THF	0.0	0.0159 ± 0.0003	} 10.3 ± 1.5	29 ± 4
K ⁺	THF	27	0.15 ± 0.006		
K ⁺	THF	42	0.241 ± 0.02		
K ⁺	THF + 18-crown-6	42	0.783 ± 0.077		
K ⁺	THF + Et ₂ O (93%)	27	0.086 ± 0.011		

and will report our findings in a future communication.

The illustration of a "linear" nitrosyl ligand in the title complex shows that the cation-nitrosyl interaction is essentially similar to those previously observed for cation-carbonyl ion pairs, involving the lone pair on oxygen and possibly the π-electron density of the N-O bond, in an overall slightly non-linear N-O-M⁺ interaction.

Chemical Reactivity Studies. The chemical reactivities of the title complexes are in many respects similar to those of other related transition-metal carbonylates. Protonation yields very unstable hydride species.²⁵ reactions with group 4 halides lead to the corresponding derivatives, e.g., [Fe(CO)₃(NO)-SnEt₃], [Fe(CO)₃(NO)GeCl₃], [Fe(CO)₃(NO)₂PbPh₂, etc.,²⁶ and reaction with Hg(CN)₂ leads to [Fe(CO)₃(NO)₂Hg].²⁷

The salt is also of interest due to its catalytic properties when used in conjunction with metal halides. For example, Na⁺-[Fe(CO)₃(NO)]⁻ upon reaction with [Fe(NO)₂X]₂ leads to highly reactive catalytic systems for the cyclodimerization of vinylcyclohexene,²⁸ while the salt itself is useful as a catalyst for the oxidation of *p*-xylene.²⁹ It is probable that a considerable amount of this activity stems from an early observation by Hieber that the salts are thermally unstable with respect to [Fe(CO)₂(NO)₂] and, further, that this species is important in generating the catalytically active ingredient "Fe(NO)₂".

The reactions of the salt with organic halides have been studied primarily by Pauson and co-workers.³⁰ The reaction with alkyl halides (RX) was reported to yield directly the insertion product [Fe(CO)₃(COR)(NO)] in high yield. Proof of this unusual reaction was claimed to be from the spectra and from the trapping of the complex with PPh₃ as [Fe(CO)₂(COR)(NO)(PPh₃)]. However, in the paper no spectroscopic evidence nor example of an isolated characterized

[Fe(CO)₃(COR)(NO)] complex was reported. Allylic halides reacted with the metalate to form [(η³-allyl)Fe(CO)₂(NO)]. We have reinvestigated this reaction specifically using MeI as substrate.

Under no conditions of solvent, countercation, or temperature have we been able to detect, even spectroscopically, the formation of [Fe(CO)₃(COCH₃)(NO)]. We have confirmed the formation of the corresponding phosphine complex [Fe(CO)₂(COCH₃)(PPh₃)(NO)] when the reaction between the anion and MeI is carried out in the presence of the phosphine ligand and further noted that this product is formed under all conditions of solvent and countercation. In the absence of added phosphine ligand, the first observed and characterizable complexes formed are [Fe(CO)₂(NO)₂] and [Fe(CO)₅], characterized by comparison of their IR spectra with those of authentic samples. If the reaction is permitted to reach completion in this fashion and then triphenyl phosphine is added, it is possible to isolate [Fe(CO)(PPh₃)(NO)₂] as a crystalline product. If the initial reaction is performed in diethyl ether, the formation of [Fe(CO)₅] and [Fe(CO)₂(N-O)₂] marks the end of the reaction. However, if the solvent used is THF, a further reaction may be observed. In this solvent, as noted above, there is a considerable amount of solvent-separated ion pairing; i.e., the solvent is capable of stabilizing a separate cationic species. It is clear that this capacity of the solvent generates a sufficient solubility of, e.g., the sodium (potassium) iodide formed in the initial reaction of the metalate with MeI to permit secondary reactions by the nucleophilic I⁻. Thus, we observe the secondary formation of [Fe(NO)₂I]₂ in the more polar THF, via the ability of the I⁻ to progressively displace the carbonyl ligands from [Fe(CO)₂(NO)₂]. Intermediate complexes are formed as evidenced by infrared monitoring, and these were more clearly understood upon changing the metalate cation. If the reaction between the metalate and MeI was carried out with a crown-ether-solubilized cation, e.g., (18-C-6)K⁺, or with PPN⁺, a different final product was isolated, namely, [Fe(NO)₂I]₂-M⁺.³¹

(25) W. Hieber and H. Beutner, *Z. Anorg. Allg. Chem.*, **320**, 101 (1963).

(26) M. Casey and A. R. Manning, *J. Chem. Soc. A*, 256 (1971).

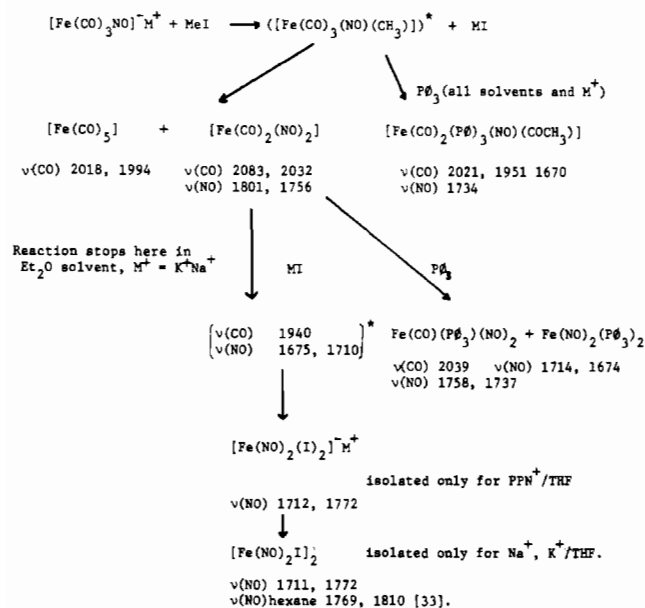
(27) R. B. King, *Inorg. Chem.*, **2**, 1275 (1963).

(28) I. Tkatchenko, *J. Organomet. Chem.*, **124**, C39 (1977).

(29) M. J. Hogsed, U.S. Patent 2 865 707 (1958); *Chem. Abstr.*, **53**, 9592d (1959).

(30) F. M. Chaudhari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 2255 (1967).

(31) N. G. Connelly and C. Gardner, *J. Chem. Soc., Dalton Trans.*, 1525 (1976).

Scheme I^a

^a IR data in THF solvent. An asterisk denotes not observed/isolated.

Clearly this paramagnetic salt is stabilized by the presence of an intrinsically stabilized cation. If the reaction between the PPN⁺ salt and MeI is monitored, a transient species between $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ and $[\text{Fe}(\text{NO})_2\text{I}_2]\text{PPN}^+$ is observed with the following stretching frequencies: $\nu(\text{CO})$ 1940 cm^{-1} ; $\nu(\text{NO})$ 1680, 1711 cm^{-1} . This may be $[\text{Fe}(\text{CO})(\text{NO})_2\text{I}]\text{M}^+$, but no isolation was possible. At a 10^{-2} M concentration of $[\text{Fe}(\text{CO})_3\text{NO}]^-$ this transient species completely disappears after ~ 16 h to leave only the isolated product $[\text{Fe}(\text{NO})_2\text{I}_2]^- \text{M}^+$.

Basolo and Morris have reported on the reactivity of $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ with ammonium halides and record infrared-characterized species similar to those above; however, they were unable to characterize or isolate any complexes. The similarity of our IR data suggests that the chemistry they observed is identical with that reported herein.³²

Overall, the reaction between $[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{M}^+$ and methyl iodide is complex and may now be outlined in Scheme I. Trace amounts of other transient carbonyl-nitrosyl-containing complexes may be observed in the THF solvent system

but in insufficient amounts to permit identification.

This system very clearly illustrates the significance of solvent and counteraction in determining the outcome of the reactions of transition-metal metalates.

Kinetic Study. We have made a kinetic investigation into the reactivity of $\text{M}^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ with methyl iodide, under conditions that ensure the salt possesses different ion-paired structures, i.e. (all at 23 °C): PPN⁺ $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ -THF (100% separated ion pairs); (18-C-6)^{K+} $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ -THF (100% separated ion pairs); ^{K+} $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ -THF (35% separated, 65% tight ion pairs); ^{K+} $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ -90% ethyl ether and 10% THF (<95% tight ion pairs).

Under all these varying conditions the rate equation for the reaction studied was $\text{rate} = k[\text{MFe}(\text{CO})_3(\text{NO})][\text{MeI}]$, i.e., first order with respect to both the metalate and methyl iodide. This rate equation is totally consistent with that previously reported for the reactions of $[\text{Mn}(\text{CO})_5]^-$ with various alkyl halides.⁵

The various second-order rate constants, along with some selected activation parameters for the reactions, are collected in Table VIII. It may be seen from these data that the variations of rate are small when compared to those noted for the different solutions of the $[\text{Mn}(\text{CO})_5]^-$ system where rate variations of an order of magnitude were observed. Nevertheless, the rate variations we observed are real and indicate that the kinetically active species in the $\text{M}^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ system is the solvent-separated ion pair in contrast to the case of the $\text{M}^+[\text{Mn}(\text{CO})_5]^-$ salt. It was argued that the reason for the kinetic activity of the tight-ion-paired species in this latter system was the need for cation assistance in the transition state en route to metal-carbon bond formation. The extra polarity provided by the tight ion pair assists the rupture of the carbon-halogen bond, thus the enhanced reactivity of the tight ion pair; cf. the less charge separated polarity of the "free" anion of a separated ion pair. A significant distinction between the manganese system and the present $[\text{Fe}(\text{CO})_3(\text{NO})]$ anion is the built-in asymmetry within the iron nitrosyl carbonyl. The presence of the nitrosyl group imparts a degree of internal charge separation for the free anionic species, and hence the extra polarity that would be produced in a transition state by the counteraction may not be as significant with respect to the overall reactivity of the salt. The activation parameters recorded in Table VIII reflect the very similar rates of the two systems studied, ^{K+} and PPN⁺. Since the percentage of ion pairs present in solution varies with temperature, there is a somewhat large percent error for the ^{K+} data. The values for ΔH and ΔS indicate that the anion is intrinsically more nucleophilic than $[\text{Mn}(\text{CO})_5]^-$, where ΔH was in the range 16–20 kcal/mol, but also that the entropy of activation is considerably larger. We cannot distinguish between the activation parameters for the PPN⁺ and ^{K+} salt reactions; the close similarity between the kinetic reactivities of the systems precludes this possibility.

We have briefly studied the kinetics of the reaction of PPN⁺ $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ with MeI in the presence of triphenylphosphine to yield $[\text{Fe}(\text{CO})_2(\text{P}\Phi_3)(\text{COCH}_3)(\text{NO})]$. The rate of disappearance of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ varies slightly with the increasing concentration of $\text{P}\Phi_3$. Thus, as $[\text{P}\Phi_3]$ varies up to a 6-fold excess with respect to the metalate (MeI being kept constant at a 25-fold excess), the pseudo-first-order rate constant changes from 0.1 to 0.08. This variation is in accord with the ability of $\text{P}\Phi_3$ to remove MeI from solution as the triphenylmethylphosphonium iodide as we observed by NMR spectroscopy. This effectively reduces the amount of MeI and gives rise to decrease in the rate constant.

There is no reaction between the metalate and $\text{P}\Phi_3\text{MeP}^+\text{I}^-$. The reaction of $[\text{Fe}(\text{CO})_3\text{NO}]^-$, MeI, and $\text{P}\Phi_3\text{P}$ thus exhibits

- (32) D. E. Morris and F. Basolo, *J. Am. Chem. Soc.*, **90**, 2536 (1968).
 (33) L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).
 (34) S. W. Kirtley, J. P. Chanton, R. A. Love, D. L. Tipton, T. N. Sorrell, and R. Bau, submitted for publication.
 (35) V. G. Albano, G. Ciani, A. Furrigelli, S. Martinengo, and W. M. Anker, *J. Organomet. Chem.*, **116**, 343 (1976).
 (36) L. B. Handy, J. K. Rutt, and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 7327 (1970).
 (37) G. Huttner and W. Gartzke, *Chem. Ber.*, **108**, 1373 (1975).
 (38) G. Longoni, M. Manassero, and M. Sansoni, *J. Organomet. Chem.*, **174**, C41 (1979).
 (39) M. E. Gress and R. A. Jacobson, *Inorg. Chem.*, **12**, 1746 (1973).
 (40) In complexes of $\text{P}\Phi_3\text{P}$, adjacent phenyl rings may approach each other in a fashion similar to that for layers in graphite; see, for example, ref 23 and 35.
 (41) K. H. Pannell, Yu-Sen Chen, and K. Belknap, *J. Chem. Soc., Chem. Commun.*, 362 (1977).
 (42) R. B. Roof, Jr., *Los Alamos Sci. Lab. [Rep.] LA, LA-4038* (1969).
 (43) "Reduce" by J. Korp for the Nonius CAD-4 with OS/4 Operating System, 1978.
 (44) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A* **A27**, 368 (1971).
 (45) G. Sheldrick, "Shelx-76, A System of Computing Programs", Cambridge University, Cambridge, England, 1976.
 (46) "International Tables for X-ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974, pp 72–98, 149.

kinetics identical with that of the reaction of $[\text{Fe}(\text{CO})_3\text{NO}]^-$ and MeI alone; i.e., the phosphine reacts with an intermediate in a step following the rate-determining reaction between the metalate and MeI. No reaction may be observed between the metalate and Ph_3P .⁴⁷ Using Occam's Razor, in conjunction with the very high yields of the phosphine product, we have assigned the intermediate the structure of the alkyliron complex. It is not surprising that we are unable to isolate or observe this species since it is electronically equivalent to the $[\text{Co}(\text{CO})_4\text{CH}_3]$ complex, which decomposes at temperatures in excess of -30°C .⁴⁸ We have made no attempts to discover

the fate of the alkyl group in the reactions performed in the absence of phosphine ligand.

Acknowledgment. We thank the Robert A. Welch Foundation, Houston, TX, the National Science Foundation, Washington, DC, and the Patriomonie of the University of Liege, Liege, Belgium, for support of this research.

Registry No. $[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{Na}^+$, 25875-18-7; $[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{PPN}^+$, 61003-17-6; $[\text{Fe}(\text{CO})_3(\text{NO})]^- \text{K}^+$, 25875-19-8; PPh_3 , 603-35-0; 18-C-6, 17455-13-9; $(\text{NH}_2)_2\text{DBC}$, 60016-77-5; Br_4DBC , 62667-75-8; $(\text{NO}_2)_2\text{DBC}$, 29721-41-3; MeI, 74-88-4.

Supplementary Material Available: Comments relating to the treatment of the disorder problem and a listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

(47) This comment refers to thermal reactions. If the metalate is treated with triphenylphosphine and irradiation, we have observed facile CO displacement. We are examining the new metalate formed under these conditions.

(48) W. Beck and R. E. Nitzschmann, *Chem. Ber.*, **97**, 2098 (1964).

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Role of the Trichlorostannyl Ligand in Homogeneous Catalysis. 2. Spectroscopic Studies of the Reaction of *cis*- $[\text{PtCl}_2(\text{CO})(\text{PR}_3)]$ with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$: Ligand Rearrangement Reactions in the Formation of an Olefin Hydroformylation Catalyst Precursor¹

GORDON K. ANDERSON, HOWARD C. CLARK,* and JULIAN A. DAVIES

Received February 12, 1982

The complex *cis*- $[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]$ reacts with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in acetone to yield solutions that are active in the catalytic hydroformylation of olefins. Studies by $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, $^{119}\text{Sn}\{^1\text{H}\}$, and ^{195}Pt NMR spectroscopy, including experiments utilizing ^{13}C -labeled carbon monoxide, have shown that *cis*- $[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]$ reacts with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ via a ligand rearrangement process. A cationic complex, *trans*- $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+$, and four anionic complexes, three of which are identified as $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$, *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{CO})]^-$, and *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PPh}_3)]^-$, are formed. One minor anionic product remains unidentified. Similar chemistry occurs with the analogous $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ complexes, but the rearrangement reaction occurs much more slowly with the basic PEt_3 ligand. Some conclusions concerning the mechanism of the reaction are presented; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ not only serves as a source of SnCl_2 moieties, which undergo insertion reactions, but also generates secondary cationic species, which maintain electroneutrality in the system. Attempted isolation of the ionic species leads to a further rearrangement reaction, ultimately yielding *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ as the only isolable product.

Introduction

Platinum(II) halide complexes are known to react with tin(II) chloride^{2a} to produce solutions, usually intensely colored, that are often catalytically active in the homogeneous hydrogenation^{3,4} and hydroformylation^{5,6} of olefins. It has been appreciated for some years⁷ that SnCl_2 will react with certain

transition-metal complexes containing a M-Cl bond to yield trichlorostannyl complexes, via migratory insertion reactions. Such complexes are believed to be key intermediates in the homogeneous catalytic activation of organic unsaturates. Support for these ideas has become available in recent years through the application of multinuclear magnetic resonance techniques,⁸ which allow complex systems such as the $[\text{PtCl}_2(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ catalyst precursor to be probed by ^1H , ^{31}P , $^{117,119}\text{Sn}$, and ^{195}Pt NMR methods and much structural information to be acquired concerning the species present in solution.

Extensive NMR studies by Pregosin and co-workers⁹⁻¹¹ have shown that halocarbon solutions of $[\text{PtCl}_2(\text{PR}_3)_2]$ complexes react with tin(II) chloride according to eq 1. The geometry of **1** may be either *cis* or *trans*, depending upon the nature of R, whereas **2** is always of *trans* geometry and reacts with H_2

- (1) Part 1: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.
- (2) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973: (a) p 93; (b) p 96.
- (3) Billard, C.; Clark, H. C.; Wong, C. S. IXth International Conference on Organometallic Chemistry, Dijon, France, 1979, Abstract No. C3; *J. Organomet. Chem.* **1980**, *190*, C3.
- (4) See for examples: Cramer, R. D.; Jenner, E. L.; Lindsey, R. V.; Stolberg, U. G. *J. Am. Chem. Soc.* **1963**, *85*, 1691. Tayim, H. A.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 3420. Bailar, J. C., Jr.; Itatani, H.; Crespi, M. J.; Geldard, J. *Adv. Chem. Ser.* **1967**, No. 62, 103. Bailar, J. C., Jr. *Platinum Met. Rev.* **1971**, *15*, 2. Itatani, H.; Bailar, J. C., Jr. *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 146. James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.
- (5) Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *213*, 503.
- (6) Schwager, I.; Knifton, J. F., German Patent 2 322 751, 1973. Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553. Consiglio, G.; Pino, P. *Helv. Chim. Acta* **1976**, *59*, 642. Schwager, I.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256.
- (7) Meyer, A. S.; Ayres, G. H. *J. Am. Chem. Soc.* **1955**, *77*, 2671. Davies, A. G.; Wilkinson, G.; Young, J. F. *Ibid.* **1963**, *85*, 1692.

- (8) Davies, J. A. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, in press.
- (9) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1979**, *61*, 1848.
- (10) Ostaja-Starzewski, K. A.; Pregosin, P. S.; Ruegger, H. *Inorg. Chim. Acta* **1979**, *36*, L445.
- (11) Pregosin, P. S. Biennial Inorganic Chemistry Symposium of the Chemical Institute of Canada and the American Chemical Society, Guelph, Canada, 1980.