Table I. Experimental Binding Energies of Molybdenum Complexes

	Binding energy,[a] eV						
	Mo				P	Cl	N
Molybdenum complex	$3d_{5/2}$	$3d_{3/2}$	$3p_{3/2}$	$3p_{1/2}$	$2p_{3/2}$	$2p_{3/2}$	1s
$Mo(CO)_5(P(C_6H_5)_3)$	227.6	230.8	393.5	410.9	130.6		
trans-$Mo(CO)_4(P(C_6H_5)_3)_2$	228.0	230.9	393.7	411.1	131.2		
$MoCl_2(CO)_3(P(C_6H_5)_3)_2$	229.0	232.8	395.7	413.0	131.6	198.3	
$MoCl_4(P(C_6H_5)_3)_2$	232.1	235.2	397.7	415.3	131.6	198.9	
$MoOCl_3(P(C_6H_5)_3)_2$	232.5	235.5	398.4	415.3	132.9	198.9	
$MoCl_2(NO)_2(P(C_6H_5)_3)_2$	230.5	233.4	396.5	413.7	131.6	198.5	401.6

[a] Experimental uncertainties are nominally ±0.2 eV.

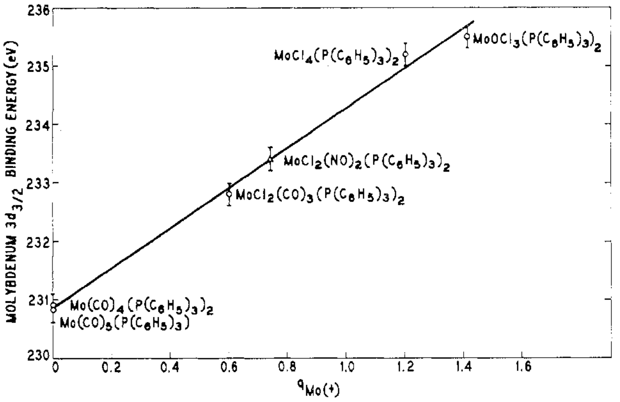

Figure 1. Correlation of $3d_{3/2}$ binding energies of molybdenum in various complexes with a charge parameter calculated as the sum of the partial ionic characters over the metal–ligand bonds.

indicate a similar electroneutrality for the CO ligand. Consequently, in our calculation of q_{Mo} we have taken $I_{P(C_6H_5)_3} = I_{CO} = 0$. Pauling electronegativities[16] have been utilized in the application of eq 2. Figure 1 shows a plot of q_{Mo}, calculated by eq 1, *vs.* the experimental Mo $3d_{3/2}$ binding energies for the first five complexes of Table I. Similar plots were obtained for the Mo $3d_{5/2}$, $3p_{3/2}$, and $3p_{1/2}$ electron binding energies.

The correlation of q_{Mo} with binding energy is quite good and can be used to assess the electron distribution in $MoCl_2(NO)_2(P(C_6H_5)_3)_2$. The observed $3d_{3/2}$ binding energy for the complex corresponds to a q_{Mo} value of 0.74+ (see Figure 1). Since the contribution of the two chlorines to q_{Mo} is 0.60+ and that of the triphenylphosphines is zero, the remaining charge (*ca.* 0.14+) on the molybdenum must be the result of a net transfer of electron density to the nitrosyl groups.[19] The nitrosyl ligands can best be described as $NO^{\delta-}$. In terms of a formal oxidation state, the molybdenum would be closest to Mo(II).

Current interpretations of the bonding of nitric oxide to transition metals associate near-linear coordination with NO^+ and a bent M-N-O linkage with NO^-. A recent single-crystal X-ray diffraction study of $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ found the Mo-N-O angles to average 161.8°.[20] These bond angles fall within the range (*vide supra*) assigned to "linear" or NO^+ nitrosyl groups. Our finding of a partial negative charge on the NO groups in the above complex indicates that nitrosyls which are nominally "linear" (NO^+) can, in fact, be net electron acceptors resulting from a strong $d\pi \rightarrow NO\ \pi^*$ interaction. The large deviation from linearity of the Mo-N-O bonds is most likely a consequence of an anisotropic distribution of electron density between the two orthogonal NO π^* orbitals.[21]

The X-ray study also found the two nitrosyl groups to be structurally equivalent in agreement with our observation of only one N 1s binding energy.

A comparison of the isoelectronic dichloro complexes $MoCl_2(CO)_3(P(C_6H_5)_3)_2$ and $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ is interesting (see Table I). Despite the larger number of potential back-bonding ligands in the CO complex, the molybdenum binding energies of the NO derivative are on the average 0.9 eV higher. This is further evidence of the greater π acidity of NO compared to CO.

The present study indicates that X-ray photoelectron spectroscopy, with suitable reference spectra for comparison, can provide information about the mode of metal-NO bonding in nitrosyl complexes. The good correlation between experimental molybdenum binding energies and an electronegativity-based calculated charge for a variety of complexes suggests that ESCA will be valuable in the study of molybdenum compounds in general.

Registry No. $Mo(CO)_5(P(C_6H_5)_3)$, 14971-42-7; *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$, 16244-53-4; $MoCl_2(CO)_3(P(C_6H_5)_3)_2$, 17250-39-4; $MoCl_4(P(C_6H_5)_3)_2$, 12103-10-5; $MoOCl_3(P(C_6H_5)_3)_2$, 12103-08-1; $MoCl_2(NO)_2(P(C_6H_5)_3)_2$, 14730-11-1.

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[19] A plot like that of Figure 1 in which $q_{Mo(+)}$ was calculated using a variable electronegativity for molybdenum (A. L. Allred, *J. Inorg. Nucl. Chem.*, 17, 215 (1961)), which largely compensates for changes in Mo-Cl and Mo-$P(C_6H_5)_3$ interactions with the Mo oxidation state, did not materially affect this result.

[20] M. O. Visscher and K. G. Caulton, *J. Amer. Chem. Soc.*, 94, 5923 (1972).

[21] S. F. A. Kettle, *Inorg. Chem.*, 4, 1661 (1965); J. H. Enemark, *ibid.*, 10, 1952 (1971).

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Preparation of Dinitrogen-Rhenium Complexes with Tertiary Arsines as Coligands. Interaction of Indium Trichloride with Rhenium(I)-Dinitrogen Species

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A number of dinitrogen complexes of rhenium-containing phosphine ligands have been reported.[1] However, no arsine-

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[1] See the following recent reviews: (a) J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1, 121 (1972); (b) A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whitely, *Chem. Rev.*, 73, 11 (1973); (c) J. E. Fergusson and J. L. Love, *Rev. Pure Appl. Chem.*, 20, 33 (1970).

containing rhenium–dinitrogen species have been reported. Indeed, only a couple of other transition metal–dinitrogen species containing arsine ligands have been cited, namely, of ruthenium[2] and molybdenum.[3,4] We wish to report in this note the preparation of $Re(arphos)_2(N_2)Cl$, as well as attempts at preparing the bis(1,2-diphenylarsino)ethane analog.

In addition a variety of metal complexes have been shown to form adducts with $ReCl(N_2)(PMe_2Ph)_4$; however BCl_3 and $AlCl_3$ when treated with $ReCl(N_2)(PMe_2Ph)_4$ evolve dinitrogen.[5-7] We have therefore studied reactions of the Lewis acid $InCl_3$ with $Re(arphos)_2(N_2)Cl$ and related phosphine analogs.

Experimental Section

Materials. Bis(1,2-diphenylphosphino)ethane (dppe), 1-diphenylphosphino-2-diphenylarsinoethane (arphos), and bis(1,2-diphenylarsino)ethane (dpae) were purchased from Strem Chemical Co. Dimethylphenylphosphine and triphenylphosphine were the generous gifts of M and T Chemical Co. Potassium perrhenate was purchased from K and K Laboratories, Inc. Anhydrous indium trichloride was purchased from Alfa Inorganics, Inc. Benzoylhydrazine was synthesized from ethyl benzoate and hydrazine hydrate in refluxing ether. *trans*-Oxotrichlorobis(triphenylphosphine)rhenium(V) and *O,N'*-benzoylhydrazido(3–)dichlorobis(triphenylphosphine)rhenium(V) were synthesized by the published procedures.[8,9]

Preparations. All complexes were prepared by the methods of Chatt and coworkers,[10] or a slight modification thereof. Reactions were carried out under a pure nitrogen atmosphere using standard inert-atmosphere techniques.

$ReCl(N_2)(arphos)_2$. One gram of *O,N'*-benzoylhydrazido(3–)dichlorobis(triphenylphosphine)rhenium(V) and 2.80 g of 1-diphenylphosphine-2-diphenylarsinoethane (arphos) were refluxed in 50 ml of methanol for approximately 12 hr. The bright yellow resulting solution which also contained a yellow solid was cooled and filtered. The isolated yellow solid was boiled in 1-butanol to remove all traces of starting material (excess arphos was found to be soluble in hot 1-butanol whereas the dinitrogen complex was insoluble). The dinitrogen complex was then further purified by recrystallization from chloroform–methanol and dried *in vacuo* to yield a pale yellow product, mp 251 dec. *Anal.* Calcd for $C_{52}H_{48}ReN_2As_2P_2Cl$: C, 55.1; H, 4.27; N, 2.47. Found: C, 54.7; H, 4.36; N, 2.94.

$ReCl(N_2)(dppe)_2$ and $ReCl(N_2)(PMe_2Ph)_4$ were prepared by the published procedures,[10] which are essentially identical with that described above for $ReCl(N_2)(arphos)_2$. All attempts to prepare $ReCl(N_2)(dpae)_2$ by the analogous procedure to that employed in preparing $ReCl(N_2)(arphos)_2$ failed. In addition when 1:1 mixtures of bis(1,2-diphenylphosphino)ethane and bis(1,2-diphenylarsino)ethane were treated as above with the rhenium–benzoylhydrazido complex, only the known dinitrogen complex $ReCl(N_2)(dppe)_2$ was isolated.

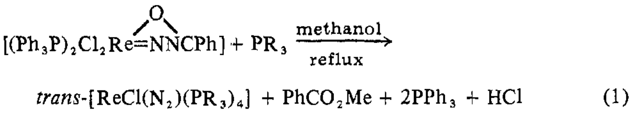
Reactions of $ReCl(N_2)(arphos)_2$ and $ReCl(N_2)(dppe)_2$ with Indium Trichloride. Anhydrous $InCl_3$ was added to a solution of $ReCl(N_2)(arphos)_2$ in chloroform under a dinitrogen atmosphere resulting in a color change of the solution from bright yellow to bright violet. An infrared spectrum of the reaction solution showed the intense band around 2050 cm^{-1} (see Figure 1) corresponding to the Re(II) cation $ReCl(N_2)(arphos)_2^+$.

Similar reactions of $InCl_3$ with $ReCl(N_2)(dppe)_2$ resulted in formation of the known $ReCl(N_2)(dppe)_2^+Cl^-$ species.[10,11] Reactions of $InCl_3$ with $ReCl(N_2)(PMe_2Ph)_4$ in chloroform led to evolution of dinitrogen with no indications in the infrared spectra of the reaction solutions (taken at various stages of the reaction) for bridging Re–N≡N–In or rhenium(II)–dinitrogen species.

Infrared Spectral Measurements. Infrared spectra were measured on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. The spectrophotometer was frequency-calibrated above 2000 cm^{-1} with carbon monoxide and below 2000 cm^{-1} with water vapor. Spectra were measured in 0.1-cm NaCl cells in Spectrograde chloroform solution. Areas under the bands were determined by use of a planimeter.

Results and Discussion

A reasonably extensive series of phosphine-containing terminal-dinitrogen complexes of rhenium(I) has been prepared by the degradation of the nitrogen chain in *O,N'*-benzoylhydrazido(3–)dichlorobis(triphenylphosphine)rhenium(V) (reaction 1) by Chatt and coworkers.[10]

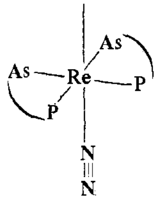


$$[(Ph_3P)_2Cl_2Re{=}NNCPh] + PR_3 \xrightarrow[\text{reflux}]{\text{methanol}} trans\text{-}[ReCl(N_2)(PR_3)_4] + PhCO_2Me + 2PPh_3 + HCl \qquad (1)$$

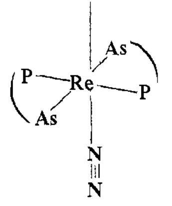
The great sensitivity of the stability of dinitrogen complexes to the electronic properties of the other ligands attached to the metal has been frequently demonstrated.[1] Only in a few instances have tertiary arsines been satisfactorily employed as coligands in dinitrogen complexes. Feltham and coworkers[2] have reported the preparation of $[RuCl(N_2)(diars)_2]PF_6$ and George and Seibold[3,4] have reported the preparations of $Mo(N_2)_2(arphos)_2$ and its very unstable dpae and diars[12] analogs.

We have found in this report that although it is possible to form readily the mixed arsine–phosphine complex $ReCl(N_2)(arphos)_2$ in good yield (>50%) *via* reaction 1; it was not possible to prepare the di(tertiary arsine) derivative $ReCl(N_2)(dpae)_2$. In fact when 1:1 mixtures of dppe and dpae were treated with the rhenium(V)–benzoylhydrazido complex, only the $ReCl(N_2)(dppe)_2$ complex was isolated with no indication for formation of the mixed arsine–phosphine complex $ReCl(N_2)(dppe)(dpae)$. These experiments further indicate the rather unexpected gross differences in stability between analogous tertiary arsine and phosphine complexes, *i.e.*, the large propensity for dinitrogen to have phosphines *vs.* arsines as coligands.[4,13] These results would also indicate that it is the presence of the phosphorus ligand in arphos that is the driving force for the formation of stable dinitrogen complexes with this ligand, *e.g.*, in $ReCl(N_2)(arphos)_2$ and $Mo(N_2)_2(arphos)_2$. This may be due to a decrease in basicity in going from phosphine to arsine ligands.

Thus far, attempts to distinguish between the two possible isomeric forms of $ReCl(N_2)(arphos)_2$ (isomers I and II) by ^{31}P



I



II

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(2) P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, 93, 84 (1971).

(3) T. A. George and C. D. Seibold, *Inorg. Nucl. Chem. Lett.*, 8, 465 (1972).

(4) T. A. George and C. D. Seibold, *Inorg. Chem.*, 12, 2544 (1973).

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(7) J. Chatt, R. C. Fay, and R. L. Richards, *J. Chem. Soc. A*, 702 (1971).

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(9) J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, *J. Chem. Soc. A*, 2631 (1971).

(10) J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 612 (1973). A diars–rhenium(I)–dinitrogen complex is reported in this paper but it was not isolated pure and fully characterized.

(11) J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Leigh, and J. R. Sanders, *Chem. Commun.*, 90 (1970).

(12) diars ≡ *o*-phenylenebis(dimethylarsine).

(13) Whether this is due to the stability of the product dinitrogen compound or to the kinetics of product formation is unknown in these cases. However, it has clearly been shown to be a thermodynamic effect in the molybdenum case.[4]

Table I. Infrared Results of ν_{N_2} in Rhenium(I)- and Rhenium(II)-Dinitrogen Species in Chloroform Solution

Compd	ν_{N_2},[a] cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	Rel intens[b] of Re(II): Re(I) species
$ReCl(N_2)(arphos)_2$	1961 (sh at 1949)	36.5	0.59
$ReCl(N_2)(arphos)_2^+$	2049	32.5	
$ReCl(N_2)(dppe)_2$	1970	29.4	0.58
$ReCl(N_2)(dppe)_2^+$	2052	30.5	

[a] Frequencies are accurate to ±2 cm^{-1}. [b] The absolute infrared intensities of the rhenium(I)–dinitrogen species are 8.95×10^4 M^{-1} cm^{-2} [D. J. Darensbourg, *Inorg. Chem.*, 11, 1436 (1972)]; therefore, the absolute infrared intensities for the rhenium(II)–dinitrogen species are about 5.3×10^4 M^{-1} cm^{-2}.

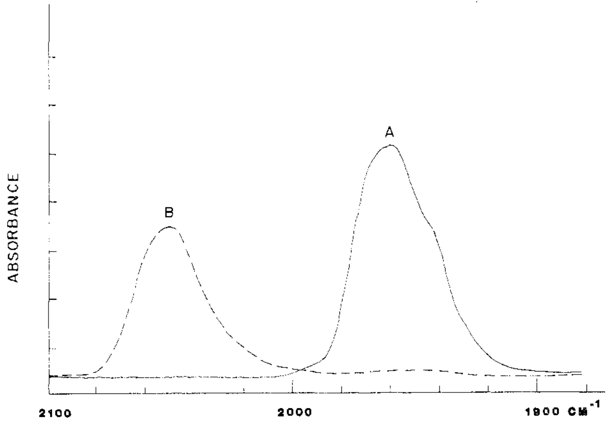

Figure 1. Infrared spectra: A (——), $ReCl(N_2)(arphos)_2$ in chloroform recorded in absorbance units; B (- - -), after addition of $InCl_3$ resulting in production of a violet solution of $ReCl(N_2)(arphos)_2^+$.

nmr have been unsuccessful due to the limited solubility of this complex in organic solvents. However, the ν_{N_2} vibration in the arphos complex shows considerable asymmetry as compared with its dppe analog (see Table I and Figure 1). This could possibly suggest a mixture of the two isomeric forms in the prepared $ReCl(N_2)(arphos)_2$ complex.

Various metal salts (*e.g.*, $CuCl_2$, $FeCl_3$, or Ag salts) or chlorine have been shown to oxidize $ReCl(N_2)(dppe)_2$ to $ReCl(N_2)(dppe)_2^+$,[10,11] whereas other metal complexes (*e.g.*, $ScCl_3$, $ZrCl_4$, $CrCl_3(THF)_3$, $MoCl_4(THF)_2$) have been found to interact with $ReCl(N_2)(PMe_2Ph)_4$ to form bridging Re–N≡N–M adducts.[5-7] Therefore, we have investigated reactions of $ReCl(N_2)(L\text{-}L)_2$ (L-L = arphos, dppe, $(PMe_2Ph)_2$) with the Lewis acid $InCl_3$ to observe whether oxidation of rhenium or terminal nitrogen adduct formation results.

When $ReCl(N_2)(arphos)_2$ or $ReCl(N_2)(dppe)_2$ was allowed to react with $InCl_3$ in the absence of oxygen, a rapid oxidation took place with the formation of the rhenium(II)-dinitrogen species $[ReCl(N_2)(arphos)_2]Cl$ and $[ReCl(N_2)(dppe)_2]Cl$, respectively. Presumably, the other product of this redox reaction is $InCl_2$ which is believed to exist as $In^+InCl_4^-$.[14] This oxidation process is to be contrasted with our results of the interaction of $(C_5H_5)Fe(CO)_2CN$ with $InCl_3$ to form an adduct through the nitrogen atom of cyanide of the type $(C_5H_5)Fe(CO)_2CN\cdot\cdot\cdot InCl_3$.[15] On the other hand, $ReCl(N_2)(PMe_2Ph)_4$ was observed to react with $InCl_3$ leading to evolution of the N_2 ligand with no solution infrared evidence for oxidation to $ReCl(N_2)(PMe_2Ph)_4^+$ or $Re{-}N{\equiv}N\cdot\cdot\cdot InCl_3$ adduct formation. This result is similar to the behavior of BCl_3 and $AlCl_3$ with $ReCl(N_2)(PMe_2Ph)_4$ as reported by Chatt and coworkers.[6]

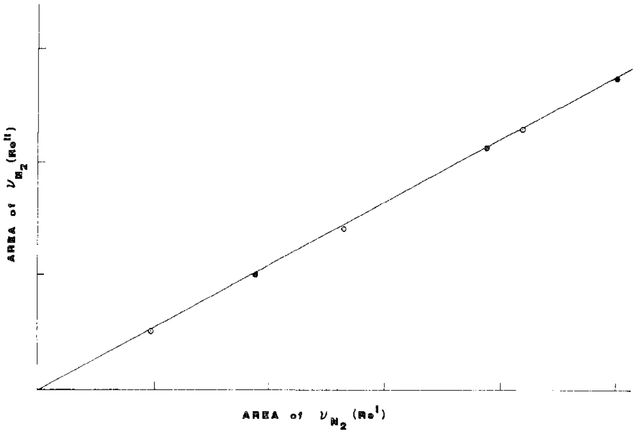

Figure 2. Plots of the area under the ν_{N_2} band in $ReCl(N_2)(arphos)_2$ or $ReCl(N_2)(dppe)_2$ at various concentrations (*e.g.*, band A in Figure 1) *vs.* the area under the ν_{N_2} band in $ReCl(N_2)(arphos)_2^+$ or $ReCl(N_2)(dppe)_2^+$ (*e.g.*, band B in Figure 1): ⊙, dppe; ●, arphos.

Figure 2 illustrates plots of the linear correlation between the area under the ν_{N_2} band of quantitatively measured samples of $ReCl(N_2)(arphos)_2$ and $ReCl(N_2)(dppe)_2$ at various concentrations and the area under the ν_{N_2} band of their $InCl_3$-oxidized species $ReCl(N_2)(arphos)_2^+$ and $ReCl(N_2)(dppe)_2^+$, respectively. These areas were obtained from a series of spectra as those illustrated in Figure 1. Table I presents quantitative infrared data for $ReCl(N_2)(arphos)_2$ and $ReCl(N_2)(dppe)_2$ and their oxidized derivatives.

It is expected from our earlier work on infrared intensities[16,17] of ν_{N_2}, as well as from the considerable body of data accumulated by others,[1] that the extent of Re-N_2 π back-bonding should decrease drastically as the metal is oxidized from Re(I) to Re(II). Concomitantly, ν_{N_2} should of course increase. As noted in Table I there is a sizable decrease in the absolute infrared intensity of the dinitrogen stretching vibration in going from the Re(I) to the Re(II) complex, specifically by a factor greater than 1.5 from 8.95×10^4 to 5.3×10^4 M^{-1} cm^{-2}.[18] This would in turn indicate that there has been a dramatic decrease in Re-N_2 π back-bonding upon oxidation of Re(I) to Re(II). Electron emission spectra from the nitrogen 1s orbitals of rhenium(I) and the analogous rhenium(II) species also support this conclusion.[19]

Acknowledgments. The authors are most grateful to Professor J. Chatt for details of the preparation of rhenium-dinitrogen complexes and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, who supported this research.

Registry No. $ReCl(N_2)(arphos)_2$, 51052-16-5; $ReCl(N_2)(arphos)_2^+Cl^-$, 51052-17-6; $ReCl(N_2)(dppe)_2$, 31817-82-0; $ReCl(N_2)(dppe)_2^+Cl^-$, 25291-83-2; $(Ph_3P)_2Cl_2Re(NNCOPh)$, 34708-18-4; $InCl_3$, 10025-82-8.

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(14) J. H. R. Clarke and R. E. Hester, *Inorg. Chem.*, 8, 1113 (1969).

(15) Unpublished results of D. J. Darensbourg. A characteristic increase of ν_{CN} by 26 cm^{-1} and of both ν_{CO} by 10 cm^{-1} in $(C_5H_5)Fe(CO)_2CN$ upon interaction with $InCl_3$ in chloroform resulted. This interaction is, as expected, somewhat weaker than that observed for interactions of $(C_5H_5)Fe(CO)_2CN$ *via* the CN ligand with $AlCl_3$ and BCl_3 as reported by D. F. Shriver and J. S. Kristoff, *Proc. Int. Conf. Coord. Chem.*, 14, 58, 1972.

(16) D. J. Darensbourg, *Inorg. Chem.*, 11, 1436 (1972).

(17) D. J. Darensbourg, *Inorg. Chem.*, 10, 2399 (1971).

(18) The absolute intensity values for the cationic dinitrogen species may be slightly underestimated and are somewhat more inaccurately determined due to small amounts of decomposition of these species in solution.

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