25464-08-8; $Ni(PPh_2OMe)_3(CN)_2$, 61633-89-4; $Ni(PPh(OEt)_2)_3(CN)_2$, 15282-55-0; $Ni(P(O\text{-}i\text{-}Pr)_3)_3(CN)_2$, 61633-90-7; $Ni(P(OEt)_3)_3(CN)_2$, 49756-79-8; $Ni(P(OCH_2CH_2Cl)_3)_3(CN)_2$, 61633-91-8; $(NCCN)Ni(P(O\text{-}p\text{-}tol)_3)_3$, 61634-12-6; $(NCCN)Ni(P(O\text{-}o\text{-}tol)_3)_3$, 61634-13-7; $(NCCN)Ni(PEt_3)_3$, 61665-40-5; $(NCCN)Ni(PMe_3)_3$, 61633-92-9; $Ni(PEt_3)_2(CN)_2$, 22806-42-4; $Ni(PPh_2Me)_2(CN)_2$, 61633-93-0; $Ni(PPh_2OMe)_2(CN)_2$, 61633-94-1; NCCN, 460-19-5.

References and Notes

(1) Contribution No. 2392.

(2) (a) J. D. Druliner, A. D. English, J. P. Jesson, P. Meakin, and C. A. Tolman, *J. Am. Chem. Soc.*, **98**, 2156 (1976); (b) J. Dewar and J. O. Jones, *J. Chem. Soc.*, 203 (1904).

(3) J. F. Guttenberger, *Angew. Chem.*, **79**, 1071 (1967).

(4) B. J. Argento, P. Fitton, J. E. McKeon, and E. A. Rick, *Chem. Commun.*, 1427 (1969).

(5) M. Bressan, G. Favero, B. Corain, and A. Turco, *Inorg. Nucl. Chem. Lett.*, **7**, 203 (1971).

(6) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 3994 (1968).

(7) K. J. Coskran, J. M. Jenkins, and J. G. Verkade, *J. Am. Chem. Soc.*, **90**, 5437 (1968).

(8) P. Rigo, G. Guastalla, and A. Turco, *Inorg. Chem.*, **8**, 375 (1969).

(9) E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, **91**, 526 (1969).

(10) E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, **14**, 1922 (1975).

(11) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).

(12) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

(13) We write the cyanogen-nickel(0) complex in this way to distinguish it from the Ni(II) complexes $NiL_n(CN)_2$ which contain two Ni–C bonds.

(14) Dissociative exchange of $NiL_3(CN)_2$ complexes has also been established by ^1H NMR studies by C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, **13**, 970 (1974).

(15) The intermediate reaches a maximum concentration in about 1 h at 25 °C. The UV spectrum of the intermediate shows an absorbance maximum at 390 μm ($\epsilon \sim 2 \times 10^3$).

(16) An unstable cyanogen complex of Rh(I) with IR bands at 2240 and 2090 cm^{-1} was reported in ref 5.

(17) C. A. Tolman, *Inorg. Chem.*, **10**, 1540 (1971).

(18) These complexes are so unstable and present in such low concentrations that they were not detected by ^{31}P NMR.

(19) These experiments with $Ni(CN)_2$ do not conclusively show the reversibility of reaction 2 because of complicating side reactions of cyanogen with the free ligands.

(20) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974).

(21) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

(22) L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).

(23) P. W. Jolly and K. Jonas, *Inorg. Synth.*, **15**, 30 (1974).

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A Light-Induced Redox Reaction of Bis(2,9-dimethyl-1,10-phenanthroline)copper(I)

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Many complexes of Cu(I) have rather low-lying metal-to-ligand charge-transfer excited states and might be expected to participate in some interesting photoredox chemistry. We wish to report the light-induced redox reaction we have observed when a solution containing bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu(dmp)_2^+$, and *cis*-bis(iminodiacetato)cobaltate(III), *cis*-$Co(IDA)_2^-$, is irradiated at 454 nm, which corresponds to the absorption maximum of a metal-to-ligand charge-transfer band of $Cu(dmp)_2^+$.

Experimental Section

Preparation of Complexes. $Cu(dmp)_2BF_4$ was prepared from the 2,9-dimethyl-1,10-phenanthroline ligand (Aldrich, 99% grade) and reagent grade $CuSO_4\cdot5H_2O$ (Mallinckrodt) in an acetate-buffered 50:50 water–methanol mixture containing dissolved $NaBF_4$. After addition of ascorbic acid to effect reduction, evaporation of methanol yielded orange crystals of the complex. Analogous procedures afforded the nitrate and chloride salts of $Cu(dmp)_2^+$ as well. The purple complex K[*cis*-$Co(IDA)_2$]$\cdot1.5H_2O$ was prepared by a published method.[1] The purity of each complex was established by microanalysis. The cobalt complex was somewhat hygroscopic so that the concentration of *cis*-$Co(IDA)_2^-$ was determined from the absorbance at 562 nm. In agreement with ref 1, we found ϵ_{562} 152 M^{-1} cm^{-1} for the cobalt complex.

Table I. Quantum Yields

[*cis*-Co-(IDA)$_2^-$], mM	10^3-$\Phi_{-Cu(I)}$[a]	[*cis*-Co-(IDA)$_2^-$], mM	10^3-$\Phi_{-Cu(I)}$[a]
1.42	1.53	4.71	5.24
1.49	1.86	4.95	5.55
1.50	1.71	5.00	3.78[b]
4.71	5.86	5.00	3.99[b]
4.71	5.70	9.39	11.30
4.71	5.43	9.39	11.61

[a] Except where indicated the solvent is 30% ethanol. [b] Solvent was 80% ethylene glycol.

Preparation of Solutions. In most experiments the solvent for the photolysis experiments was a 30:70 vol/vol mixture of ethanol–water which was 0.01 M in lithium acetate and 0.01 M in acetic acid. Some experiments involved a solvent which was 80% ethylene glycol and 20% water and which was 0.01 M in acetic acid and in lithium acetate. After the cobalt and copper complexes were added, the ionic strength was adjusted to $\mu = 0.1$ by addition of $LiNO_3$ or NaCl. Two different methods for degassing the photolysis solutions were employed. In some cases the solutions were repeatedly evacuated and refilled with scrubbed N_2 gas, while in others the solutions were continuously purged with argon during the photolysis.

Apparatus. Narrow-band irradiation (13 nm) centered at 454 nm ($\sim1.8 \times 10^{16}$ photons/s) was achieved with a 1000-W xenon lamp, suitable filter, and a grating monochromator. The irradiated solutions were thermostated at 20 °C and for each cobalt concentration at least two photolyses were carried out. Absorption measurements were made on a Cary 15 spectrophotometer.

Analysis of Data. Ferrioxalate actinometry was used to measure incident light intensities.[2] The loss of Cu(I) was followed at 454 nm[3] and the appearance of Co(II) was monitored by the method of Kitson.[4] To calculate $\Phi_{-Cu(I)}$, the quantum efficiency for loss of $Cu(dmp)_2^+$, it was necessary to account for the change in the sample absorbance with time. In our experiments the reaction was pseudo first order in Co(III) so that the following differential equation described the rate of change of the absorbance due to loss of $Cu(dmp)_2^+$

$$\frac{-dA_{Cu}}{dt} = \frac{\epsilon l I_0 \Phi_{-Cu(I)}}{V}\left(\frac{A_{Cu}}{A_{Cu} + A_X}\right)(1 - 10^{-A_{Cu}}10^{-A_X})$$

In this expression A_X denotes the absorbance of other reactant and product species. The change in A_X was very small compared to the change in A_{Cu} and could be ignored. The other parameters include molar absorptivity ϵ of $Cu(dmp)_2^+$ at 454 nm, the path length l, the incident light intensity I_0, and the volume V of the photolyte solution. This equation may be integrated after separating the variables. Integrating the absorbance function over ΔA_{Cu}, the absorbance change observed in time Δt, and dividing by Δt yield $\Phi_{-Cu(I)}\epsilon l I_0/V$ from which we could extract $\Phi_{-Cu(I)}$. We used a numerical technique to integrate over A_{Cu}.

Results and Discussion

In a typical experiment, the initial absorbance of the $Cu(dmp)_2^+$ at 454 nm was about 1.7 and decreased smoothly upon irradiation as seen in Figure 1. In the dark the solutions showed no appreciable reaction over a time of at least several hours. Moreover, direct irradiation of solutions containing either *cis*-$Co(IDA)_2^-$ [5] or $Cu(dmp)_2^+$ [6] showed negligible photochemistry at 454 nm.

The quantum efficiency for loss of $Cu(dmp)_2^+$ increases with increasing cobalt concentration as seen in Table I. Owing to the smaller absorptivity of $Co(SCN)_4^{2-}$ and to overlap with the *cis*-$Co(IDA)_2^-$ spectrum the determination of the amount of Co(II) formed is less precise than the data for loss of Cu(I). Within the experimental error, ca. 8%, however, the formation

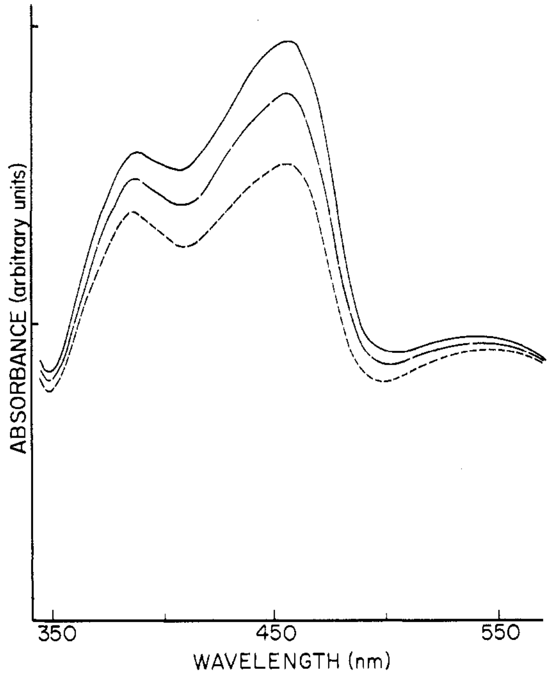

Figure 1. Absorbance spectrum of a solution decreased upon irradiation. Serial spectra are presented for irradiation times of 0 (—), 9.19 min (— —), and 19.105 min (- - -). The relative maximum at 454 nm is due to the copper complex; the other features are due to the cobalt complex.

of Co(II) and the loss of Cu(I) occurred with 1:1 stoichiometry. Duplicate Co(II) determinations were made for four different concentrations of *cis*-Co(IDA)$_2^-$. The data in Table I give a linear Stern–Volmer plot as seen in Figure 2.

To test what effect excess dmp ligand would have, we took a solution that was 5 mM in *cis*-Co(IDA)$_2^-$ and divided it into two equal parts. One was made nominally 2.5 mM in dmp and no dmp was added to the other. Identical amounts of Cu(dmp)$_2^+$ were added to both and then each solution was irradiated. The excess dmp had no measurable effect on $\Phi_{\text{-Cu(I)}}$.

To probe the influence of solvent on the reaction, we carried out some experiments in a solvent mixture consisting of 80% ethylene glycol and 20% water. This solvent is both less polar and more viscous than our aqueous ethanol solvent. It is clear from the data in Table I that, for a given concentration of cobalt, $\Phi_{\text{-Cu(I)}}$ is appreciably smaller in the more viscous solvent.

The results establish that excitation at 454 nm alters the reactivity of at least one of the reactants and induces a redox reaction. The observations do not require that an excited state of Cu(dmp)$_2^+$ be involved when the redox step occurs, but it seems clear that the singlet metal-to-ligand charge-transfer excited state is a precursor at least to reaction. (The labels singlet and triplet are convenient but not entirely satisfactory labels for the excited states, and a rigorous description would have to take account of the effects of spin–orbit coupling. We will denote the excited singlet charge-transfer state by ^{1}Cu(dmp)$_2^+$ and the corresponding triplet state by ^{3}Cu(dmp)$_2^+$.)

Our observations are consistent, however, with the mechanistic schemes which have been developed for the tris(2,2′-bipyridine)ruthenium(II) system.[7] The lowest energy excited state in the latter system is a metal-to-ligand charge-transfer state and the emission from that level is quenched by Co(III) complexes. Net reduction of Co(III) is generally observed for these systems. The parallels that exist between the electronic structure of the ruthenium system and our Cu(I) system lead us to propose that a charge-transfer excited state of Cu(dmp)$_2^+$ may be the reactive species in our system. Two obvious ways it could react with the Co(III) complex would be (i) a dynamic mechanism in which the reaction would occur after a diffusional encounter of an excited Cu(dmp)$_2^+$ molecule and a cobalt species or (ii) a static mechanism in which an outer-sphere complex of Cu(dmp)$_2^+$ and *cis*-Co(IDA)$_2^-$ would react upon excitation of the Cu(I)-containing partner. The visible spectra of the Cu(dmp)$_2^+$ and *cis*-Co(IDA)$_2^-$ systems appear to be additive (within 4% or better) and we found no evidence for a new absorption band, which might be expected if a significant concentration of an ion-pair associate were present. The fact that the reaction is less efficient in a more viscous, less polar solvent suggests a diffusional process is involved. Moreover, in view of the relatively low charges of the ions, the polar nature of the solvent, and the ionic strength employed, the concentration of the outer-sphere complex species is expected to be small. For these reasons we suggest that the dynamic mechanism is the more likely. If so, because of the finite time interval required for an encounter, the reaction would presumably involve the triplet charge-transfer state of Cu(dmp)$_2^+$ as it is expected to be longer-lived than the singlet state.

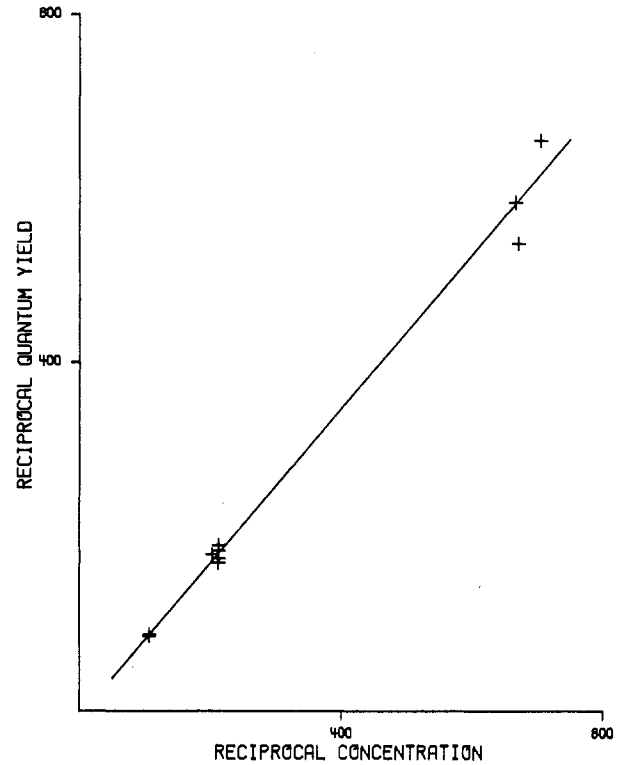

Figure 2. Dependence of $\Phi_{\text{-Cu(I)}}$ upon the concentration of *cis*-Co(IDA)$_2^-$ shown by plotting $\Phi_{\text{-Cu(I)}}^{-1}$ along the ordinate and [*cis*-Co(IDA)$_2^-$]$^{-1}$ along the abscissa where the concentration units are moles per liter. The least-squares line shown was calculated assuming the variances of the $\Phi_{\text{-Cu(I)}}$ were approximately inversely proportional to their absolute magnitude. The slope of the line was calculated to be 0.88 (0.03) and the intercept to be −6.5 (5.0).

Two rather different mechanisms have been proposed to describe the intimate nature of photoredox chemistry observed with the tris(2,2′-bipyridine)ruthenium(II) system.[7] Stated in terms of our system, the proposed mechanisms involve (i) direct electron transfer from an excited Cu(dmp)$_2^+$ ion or (ii) energy transfer from an excited Cu(dmp)$_2^+$ ion to *cis*-Co(IDA)$_2^-$ which might then undergo an intramolecular redox decomposition producing radicals that *could* oxidize Cu(I) in a subsequent thermal step. The direct electron-transfer mechanism appears the more likely since the 1:1 stoichiometry we observe would be improbable in the event that ligand-based radicals were formed.

It is interesting to note the ground-state reduction potentials that have been measured for our systems. The potential for $Cu(dmp)_2^+$ has been measured to be about 0.63 V vs. SHE[8] and is relatively insensitive to solvent. From polarographic measurements the potential of *cis*-$Co(IDA)_2^-$ has been estimated to be 0.40 V vs. SHE.[9] Owing to kinetic effects the latter is probably not the thermodynamic value. We may expect that an excited-state $Cu(dmp)_2^+$ ion would be a more potent reducing agent than the ground-state ion and could readily reduce the cobalt complex.

Our results bear comparison to the work of Farr et al.,[10] in which UV irradiation of a copper(I)–olefin moiety covalently attached to a Co(III) complex resulted in a redox decomposition of the complex.

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Registry No. $Cu(dmp)_2^+$, 21710-12-3; *cis*-$Co(IDA)_2^-$, 21718-59-2.

References and Notes

(1) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969).
(2) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(3) In our solvent we find ϵ_{454} 7525 M^{-1} cm^{-1}.
(4) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).
(5) D. R. McMillin and M. T. Buckner, unpublished results.
(6) S. Sundararajan and E. L. Wehry, *J. Phys. Chem.*, **76**, 1528 (1972).
(7) A. W. Adamson, *Concepts Inorg. Photochem.*, 419–422 (1975).
(8) (a) C. J. Hawkins et al., *J. Chem. Soc.*, 2996 (1963); (b) P. Thomas et al., *Z. Chem.*, **13**, 225 (1973); (c) G. S. Patterson et al., *Bioinorg. Chem.*, **4**, 257 (1975).
(9) P. Gouzerh, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 758 (1971).
(10) J. K. Farr, L. G. Hulett, R. H. Lane, and J. K. Hurst, *J. Am. Chem. Soc.*, **97**, 2654 (1975).

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Cationic Metal Nitrosyl Compounds. 3. Isolation and Characterization of $[Co(NO)_2L_2]^+Y^-$ (L = RCN, ROH, Me_2CO; L_2 = NBD, COD; Y^- = PF_6^-, BF_4^-, ClO_4^-)

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A large variety of structural and synthetic studies devoted to nitrosyl ligand have appeared in the literature.[1,2] In contrast very few papers reported the catalytic behavior of transition metal nitrosyl.[3] To extend the understanding of the metal nitrosyl catalytic properties we are investigating cationic complexes of the type $[M(NO)_2L_2]^+$ (L = two-electron-donor ligand, M = group 8 element). Preliminary catalytic experiments have been reported[4] and this note is related to the synthetic study and characterization of $[Co(NO)_2L_2]^+$ complexes which may act as catalytic precursors.

Experimental Section

Materials and Equipment. All experiments were performed under argon. Reagent grade acetone, nitriles, alcohols, and olefins were deoxygenated, dried, and stored under argon atmosphere. Nitric oxide (purity grade >98.5%) was bubbled through a 30% NaOH solution and dried over KOH pellets before use.

Melting points were taken in sealed capillary tubes on a Büchi SMP-20 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 421 or a Beckman IR-10 spectrometer calibrated with a polystyrene film. Conductometric measurements were performed on a Tacussel CD 7N apparatus in nitromethane. The solvent conductivity was 1.3×10^{-7} Ω^{-1} cm^{-1}. Cobalt analyses were done at the Analysis Laboratory of the Institut de Catalyse and microanalyses at the Lyon Division of the Service Central de Microanalyse du CNRS.

Synthesis of $[Co(NO)]_2Cl_2$. $[Co(NO)_2Cl]_2$ has been prepared according to the procedure described by Sacco, Rossi, and Nobile.[5] The compound was purified by sublimation with a 62% yield.

Cationic Complexes $[Co(NO)_2L_2]^+Y^-$. The compounds were prepared by the same procedure for L = nitriles, acetone, and methanol.

A solution of $[Co(NO)_2Cl]_2$ (2 mmol) in 20 mL of L was stirred under argon and 4 mmol of silver salt dissolved in 20 mL of L was added to the preceding solution at room temperature. The mixture was allowed to stand for 2 h. Silver chloride was removed by filtration and the volume of the solution reduced to 1 mL. The cationic complex precipitates by the addition of 30 mL of hexane at low temperature. The product was isolated by filtration, washed with hexane, and dried under vacuum (10^{-5} Torr) to eliminate the excess ligand and hexane.

When L was norbornadiene or 1,5-cyclooctadiene, $[Co(NO)_2Cl]_2$ (2 mmol) was dissolved in 10 mL of nitromethane and silver salt (4 mmol in 40 mL of nitromethane) was added to the cobalt solution at room temperature. Then the olefin (10 mL) was added to the mixture which was stirred for 2 h. The procedure to isolate the cationic complex was the same as that described above.

$[Co(NO)_2(PPh_3)_2]^+Y^-$ (Y^- = PF_6^-, BF_4^-, ClO_4^-). Cationic complexes (L = Me_2CO, MeOH, MeCN) were prepared according to the procedure described above. Silver chloride was removed by filtration and PPh_3 (8 mmol) was added to the solutions at room temperature. After 2 h of reaction the volume of the solutions was reduced to 1 mL. The cationic complexes were precipitated and purified as described above.

The compounds and their melting points, yields, and analyses are reported in Table I.

Results and Discussion

Cationic dinitrosyl complexes of the type $[Co(NO)_2L_2]^+$ have been reported with mono- or bidentate ligands such as triphenylphosphine,[6,7] bis(diphenylphosphino)ethane,[6] ethylenediamine,[5] phenanthroline,[8] and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[9] Their formation from halodinitrosylcobalt complexes $[Co(NO)_2X]_n$ is explained by the ligand-assisted splitting of the di-μ-halo bridges. These reactions with monodentate ligands afford the monomeric species $Co(NO)_2LX$. Excess ligands result in the cationic species $[Co(NO)_2L_2]^+X^-$. These complexes could be further stabilized through a metathetical exchange of the halogen anion X^- with a noncoordinating anion as ClO_4^- [5–7] or BPh_4^-.[5,6,9] No catalytic activity is observed with these complexes in olefin oligomerization due to the poor lability of the pnicogen ligands.[4,10,11]

In our study, reaction 1 affords quantitatively the soluble

$$[Co(NO)_2Cl]_2 + 2AgY \xrightarrow[\text{excess L}]{\text{room temp}} [Co(NO)_2L_2]^+Y^- + 2AgCl \qquad (1)$$

cationic complex which precipitates in an excess of hexane. Here Y^- = PF_6^-, BF_4^-, ClO_4^-; L = acetonitrile (MeCN), benzonitrile (PhCN), acetone (Me_2CO), methanol (MeOH), acrylonitrile (AN), norbornadiene (NBD), 1,5-cyclooctadiene (COD).

Thanks to facile exchange between L and the incoming substrate, these cationic species are catalytic precursors in the oligomerization of butadiene, norbornadiene, styrene, isoprene, and phenylacetylene.[4] Infrared spectroscopy and conductometric measurements were used to characterize these cationic complexes. The stretching frequencies ν_{NO}, $\nu_{C\equiv N}$, $\nu_{C=O}$, and ν_{OH} do not overlap with other ones so that their assignment is straightforward.

Characterization of $[Co(NO)_2L_2]^+PF_6^-$. The hexafluorophosphate anion exhibits a strong band at 830 cm^{-1} assigned to ν_{PF} indicating that PF_6^- has octahedral symmetry[12] and is not coordinated.

When L was acetone or methanol, we were unable to precipitate any compound; only a black tar was obtained.