

It is interesting to note the ground-state reduction potentials that have been measured for our systems. The potential for $\text{Cu}(\text{dmp})_2^+$ has been measured to be about 0.63 V vs. SHE⁸ 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 $\text{Cu}(\text{dmp})_2^+$ 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. $\text{Cu}(\text{dmp})_2^+$, 21710-12-3; *cis*-Co(IDA)₂⁻, 21718-59-2.

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Contribution from the Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cedex, France

Cationic Metal Nitrosyl Compounds. 3. Isolation and Characterization of $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{Y}^-$ (L = RCN, ROH, Me₂CO; L₂ = NBD, COD; Y⁻ = PF₆⁻, BF₄⁻, ClO₄⁻)

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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 $[\text{M}(\text{NO})_2\text{L}_2]^+$ (L = two-electron-donor ligand, M = group 8 element). Preliminary catalytic experiments have been reported⁴ and this note is related to the synthetic study and characterization of $[\text{Co}(\text{NO})_2\text{L}_2]^+$ 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 $1.3 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. 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 $[\text{Co}(\text{NO})_2\text{Cl}_2]$. $[\text{Co}(\text{NO})_2\text{Cl}_2]$ 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 $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{Y}^-$. The compounds were prepared by the same procedure for L = nitriles, acetone, and methanol.

A solution of $[\text{Co}(\text{NO})_2\text{Cl}_2]$ (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, $[\text{Co}(\text{NO})_2\text{Cl}_2]$ (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.

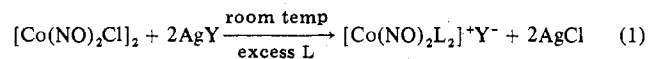
$[\text{Co}(\text{NO})_2(\text{PPh}_3)_2]^+\text{Y}^-$ (Y⁻ = PF₆⁻, BF₄⁻, ClO₄⁻). Cationic complexes (L = Me₂CO, MeOH, MeCN) were prepared according to the procedure described above. Silver chloride was removed by filtration and PPh₃ (8 mmol) was added to the solutions at room temperature. After 2 h of 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 $[\text{Co}(\text{NO})_2\text{L}_2]^+$ 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 $[\text{Co}(\text{NO})_2\text{X}]_n$ is explained by the ligand-assisted splitting of the di- μ -halo bridges. These reactions with monodentate ligands afford the monomeric species $\text{Co}(\text{NO})_2\text{LX}$. Excess ligands result in the cationic species $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{X}^-$. These complexes could be further stabilized through a metathetical exchange of the halogen anion X⁻ with a noncoordinating anion as ClO₄^{-5,7} or BPh₄^{-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



cationic complex which precipitates in an excess of hexane. Here Y⁻ = PF₆⁻, BF₄⁻, ClO₄⁻; L = acetonitrile (MeCN), benzonitrile (PhCN), acetone (Me₂CO), 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} , $\nu_{\text{C=N}}$, $\nu_{\text{C=O}}$, and ν_{OH} do not overlap with other ones so that their assignment is straightforward.

Characterization of $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{PF}_6^-$. The hexafluorophosphate anion exhibits a strong band at 830 cm⁻¹ assigned to ν_{PF} indicating that PF₆⁻ has octahedral symmetry¹² and is not coordinated.

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

Table I. Analytical Data for Cationic Compounds

Compd	Yield, %	AgCl yield, %	Mp, °C	Analysis, %							
				C		H		N		Co	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Co(NO) ₂ (MeCN) ₂] ⁺ PF ₆ ⁻	63	98	51-53	13.87	14.05	1.73	1.81	16.18	16.71	17.0	16.3
[Co(NO) ₂ (PhCN) ₂] ⁺ PF ₆ ⁻	70	95	72-74	35.74	34.51	2.13	2.38	11.91	12.00	12.5	13.3
[Co(NO) ₂ (AN) ₂] ⁺ PF ₆ ⁻	60	96	32-34	19.47	19.01	1.63	1.93	15.14	15.53	15.9	15.9
[Co(NO) ₂ NBD] ⁺ PF ₆ ⁻	65	90	130 dec	23.55	23.38	2.25	2.31	7.85	7.99	16.6	16.7
[Co(NO) ₂ COD] ⁺ PF ₆ ⁻	62	92	170 dec	25.80	25.45	3.22	3.35	7.53	7.40	15.9	15.2
[Co(NO) ₂ (PPh ₃) ₂] ⁺ ClO ₄ ⁻	90	95		58.18	57.45	4.05	4.14	3.77	3.82	7.9	8.3
[Co(NO) ₂ (PPh ₃) ₂] ⁺ PF ₆ ⁻	70	92		54.82	53.59	3.81	4.14	3.55	3.62	7.5	7.9
[Co(NO) ₂ (PPh ₃) ₂] ⁺ BF ₄ ⁻	72	80		59.17	58.58	4.10	4.20	3.83	3.87	8.1	8.1

Table II. Characteristic Stretching Frequencies of Cationic Dinitrosylcobalt and Neutral Dinitrosyliron Compounds (Nujol Mull)

No.	Compd	ν_{NO} , cm ⁻¹	ν_{CN} , cm ⁻¹	ν_{CO} , cm ⁻¹	ν_{OH} , cm ⁻¹
1	[Co(NO) ₂ Cl] ₂	1860	1790		
2	[Co(NO) ₂ (MeCN) ₂] ⁺ PF ₆ ⁻	1910	1820	2320, 2290 ^a	
3	[Co(NO) ₂ (PhCN) ₂] ⁺ PF ₆ ⁻	1900	1810	2260 ^a	
4	[Co(NO) ₂ (Me ₂ CO) ₂] ⁺ PF ₆ ⁻	1890	1800		1680 ^b
5	[Co(NO) ₂ (MeOH) ₂] ⁺ PF ₆ ⁻	1895	1805		3550 ^c
6	[Co(NO) ₂ (AN) ₂] ⁺ PF ₆ ⁻	1910	1810	2260 ^a	
7	[Co(NO) ₂ NBD] ⁺ PF ₆ ⁻	1925	1840		
8	[Co(NO) ₂ COD] ⁺ PF ₆ ⁻	1910	1840		
9	[Co(NO) ₂ TMEDA] ⁺ PF ₆ ^{-d}	1876	1818		
10	[Co(NO) ₂ en] ⁺ ClO ₄ ^{-e}	1873	1785		
11	[Co(NO) ₂ (PPh ₃) ₂] ⁺ ClO ₄ ^{-f}	1848	1796		
12	Fe(NO) ₂ (CO) ₂	1810	1766		
13	Fe(NO) ₂ (PPh ₃) ₂	1723	1679		
14	[Co(NO) ₂ (MeCN) ₂] ⁺ BF ₄ ⁻	1910	1815	2330, 2300 ^a	
15	[Co(NO) ₂ (MeCN) ₂] ⁺ ClO ₄ ⁻	1900	1815	2320, 2290 ^a	
16	[Co(NO) ₂ (PhCN) ₂] ⁺ BF ₄ ⁻	1905	1815	2275 ^b	
17	[Co(NO) ₂ (PhCN) ₂] ⁺ ClO ₄ ⁻	1905	1815	2775 ^b	

^a Free MeCN 2255 cm⁻¹, free PhCN 2220 cm⁻¹, free acrylonitrile 2220 cm⁻¹. ^b Free Me₂CO 1715 cm⁻¹. ^c Free MeOH 3643 cm⁻¹. ^d TMEDA = *N,N,N',N'*-tetramethylethylenediamine; data from ref 9. ^e en = ethylenediamine; data from ref 5. ^f Data from ref 6. ^g Data from ref 27.

Nevertheless the quantitative yield of silver chloride and isolation of [Co(NO)₂(PPh₃)₂]⁺PF₆⁻ according to reactions 2 and 3 corroborate the presence of the cationic complex.

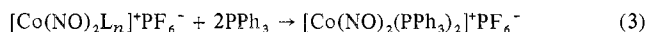
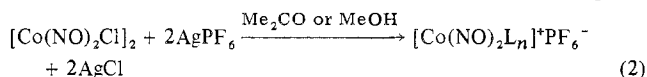


Table II reports nitrosyl stretching frequencies of the isolated compounds. A shift toward high frequencies is observed compared to the starting material [Co(NO)₂Cl]₂. According to empirical rules developed by Haymore and Ibers¹³ the observed and corrected NO stretching frequencies fall into the range above 1620 cm⁻¹ which is characteristic of linear MNO groups. X-ray experiments are undertaken to check this rule in our case. Inspection of Table II shows that the blue shift from [Co(NO)₂Cl]₂ varies according to ligands L within the range 10-65 cm⁻¹ for both symmetric and antisymmetric stretching modes. Comparison of the nitrosyl stretching frequencies for isosteric complexes of cobalt and iron shows that the main parameter in ν_{NO} shifts is the electric charge. A strong π -acceptor ligand such as carbonyl (12) does not succeed in making the electronic metal environment comparable to that of a cationic isoelectronic complex (11). Thus the bonding with nitrosyl ligands is different as rationalized by a modified molecular orbital diagram.²

The stretching frequencies $\nu_{\text{C}\equiv\text{N}}$, ν_{OH} , and $\nu_{\text{C}=\text{O}}$ of the coordinated ligands MeCN, PhCN, MeOH, and Me₂CO are reported in Table II. The shifts of $\nu_{\text{C}\equiv\text{N}}$ (complexes 2 and 3) to higher frequencies compared to the free ligands show that nitriles coordinate through the lone pair of the nitrogen atom.¹⁴ A similar ligation is observed through the oxygen atom of acetone (complex 4) and methanol (complex 5) according to the $\nu_{\text{C}=\text{O}}$ and ν_{OH} red shifts.¹⁵

The ligand acrylonitrile (AN) can coordinate through either the vinyl or the nitrile group and both types of coordination have been described.^{16,17} In the compounds Ni(AN)₂¹⁶ and Ni(AN)[P(O-*o*-tol)]₂,¹⁷ acrylonitrile is coordinated via the olefinic bond whereas in Pd(AN)₂Cl₂¹⁶ it is coordinated via the nitrile moiety. The electronic deficient character of Pd(II) has to be invoked to explain bonding with the σ -donor moiety instead of the π donor- π acceptor one. In the complex [Co(NO)₂(AN)₂]⁺PF₆⁻ (6), the nitrile stretching frequency increases and the IR spectrum exhibits characteristics of a free vinyl group ($\nu_{\text{C-H}}$ 3125, 3060, 3030 cm⁻¹; $\nu_{\text{C}=\text{O}}$ 1610 cm⁻¹; $\delta_{\text{C-H}}$ (in plane) 1410 cm⁻¹; $\delta_{\text{C-H}}$ (out of plane) 966 cm⁻¹; $\delta_{\text{C}=\text{C}}$ 685 cm⁻¹). Thus the lone pair of the nitrogen atom is involved in the metal-substrate bond pointing out the electrophilic behavior of the cationic cobalt. Coordination via the double bond may however be observed when this character is depressed by interaction of the counteranion with the cobalt cation. This is encountered with the tetraphenylborate anion in the case of acrylonitrile complexes.⁴ The magnitudes of $\nu_{\text{C}\equiv\text{N}}$ and ν_{NO} shifts for acrylonitrile and benzonitrile complexes (3 and 6) are similar showing identical electronic effects of vinyl and phenyl groups on the nitrile function.¹⁸

Compounds 7 and 8 exhibit the highest ν_{NO} frequencies. According to the Dewar^{19a}-Chatt-Duncanson^{19b} model this implies a competition of interactions between filled d_{π} metal orbitals on one hand and π^* empty nitrosyl and olefin orbitals on the other hand. The complexes contain one molecule of norbornadiene and 1,5-cyclooctadiene, respectively. The IR spectra exhibit no more olefinic $\nu_{\text{C-H}}$ (>3000 cm⁻¹) and $\delta_{\text{C-H}}$ (out of plane) (800-700 cm⁻¹). Moreover the olefin stretching mode $\nu_{\text{C}=\text{C}}$ which occurs at 1540 cm⁻¹ (NBD) and 1654 cm⁻¹ (COD) in free ligands has vanished and new weak bands appear at 1490 and 1560 cm⁻¹, respectively. Such observations have been reported for example with copper,²⁰

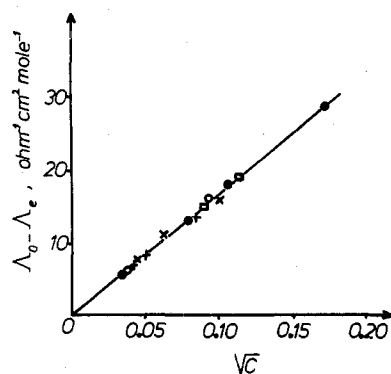


Figure 1. Plot of $\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$ for $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{PF}_6^-$ samples: L = MeCN (\bullet), AN (\circ), $\Lambda_0 = 97 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; L = COD (\times), $\Lambda_0 = 92 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; L = NBD ($+$), $\Lambda_0 = 88 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; L = PhCN (\square), $\Lambda_0 = 77 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

chromium,²¹ molybdenum,²² and nickel¹⁷ complexes: the diolefin ligands are bonded as chelates with loss of the olefinic character.

Conductometric Measurements with $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{PF}_6^-$ Complexes. Conductances have been measured in order to determine the complex electrolyte types. The best method was to carry conductometric measurements over concentrations covering the range 2×10^{-4} – 3×10^{-2} M. This method allows application of the Onsager law in the form $\Lambda_0 - \Lambda_e = Bc^{1/2}$ where the equivalent conductance Λ_e plotted against $c^{1/2}$ provides a straight line extrapolated to zero concentration to obtain Λ_0 as the intercept. The slope B is characteristic of the electrolyte and direct comparison of values obtained for different cations is available since the anion remains the same.²³ Figure 1 reports the variations of $\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$ for $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{PF}_6^-$ compounds (L = MeCN, PhCN, AN, NBD, COD). The experimental values fit very nicely with the same straight line. This result indicates that dinitrosylcobalt complexes have identical behaviors. The Λ_0 values fall within the range 77 – $97 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and the slope B is equal to 167. These data are typical of 1:1 electrolytes in nitromethane²⁴ and agree with those of other cationic nitrosylcobalt complexes.²⁵

Characterization of $[\text{Co}(\text{NO})_2\text{L}_2]^+\text{Y}^-$ (L = MeCN, PhCN, $\text{Y}^- = \text{BF}_4^-, \text{ClO}_4^-$). The tetrafluoroborate anion exhibits absorption bands centered at ca. 1000 and 525 cm^{-1} consistent with T_d symmetry.¹⁰ The perchlorate anion has similar properties with absorption maxima at 1095 and 630 cm^{-1} .²⁶ The noncoordinating interaction has not always been observed. Ibers et al.²⁷ have characterized by x-ray analysis and vibrational spectroscopy a C_{3v} symmetry of the BF_4^- moiety in the complex $\text{Cu}(\text{PPh}_3)\text{BF}_4$ denoting a Cu–FBF₃ interaction which is described as a weak coordination. A similar situation has been depicted for the compound $\text{Pt}(\text{C}_6\text{F}_5)(\text{PET}_3)\text{ClO}_4$.²⁸ Infrared and conductometric measurements lead us to assume a platinum–oxygen interaction.

Table II reports stretching frequencies of nitrosyl and nitrile groups. In comparison with data on complexes 2 and 3 no significant effect is seen to arise when the hexafluorophosphate anion is replaced by the tetrafluoroborate or perchlorate anion. Thus we can conclude that in this study the three counteranions are not coordinated.

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61506-00-1; $[\text{Co}(\text{NO})_2(\text{PPh}_3)_2]^+\text{ClO}_4^-$, 24504-01-6; $[\text{Co}(\text{NO})_2(\text{PPh}_3)_2]^+\text{PF}_6^-$, 37739-55-2; $[\text{Co}(\text{NO})_2(\text{PPh}_3)_2]^+\text{BF}_4^-$, 24507-62-8.

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Electrochemical Redox Behavior of a Series of Manganese Macrocyclic Complexes

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The redox behavior of transition metal complexes containing synthetic macrocyclic ligands has received considerable attention.¹⁻⁶ In an attempt to ascertain and characterize the various oxidation states of manganese possible when this element is coordinated with certain synthetic macrocyclic structures, we investigated the electrochemical properties of a series of manganese complexes of the type $[\text{Mn}^{\text{III}}\text{L}_2\text{X}^-$