Inorg. Chem. **1983**, *22*, 3138-3143

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Mixed Nitrosyl–Isocyanide–Phosphine Complexes of Chromium(I) and Chromium(0): Synthesis, Characterization, and Redox Chemistry

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Received October 19, 1982

Reactions of the nitrosyl–pentakis(isocyanide) complexes $[Cr(NO)(CNR)_5]X$ (R = CMe_3, $CHMe_2$, or Me; X = PF_6 or BF_4) with monodentate tertiary phosphines PR_3 in 2-propanol result in the high-yield formation of the substitution products *trans*-$[Cr(NO)(CNR)_4(PR_3)]X$ (PR_3 = PEt_3, P-*n*-Pr_3, P-*n*-Bu_3, PMe_2Ph, or PEt_2Ph). Cyclic voltammetric studies of these 18-electron complexes reveal that they exhibit a reversible one-electron oxidation in the range $E_{1/2} = +0.26$ V to +0.39 V vs. SCE. These phosphine derivatives may be readily oxidized by nitrosonium salts NOX (X = PF_6 or BF_4) to generate the analogous 17-electron species *trans*-$[Cr(NO)(CNR)_4(PR_3)]X_2$. Treatment of $[Cr(NO)(CNCMe_3)_5]PF_6$ with the bidentate phosphine ligand 1,2-bis(diphenylphosphino)ethane (dppe) leads to the formation of *fac*-$[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$. When the 17-electron complex $[Cr(NO)(CNCMe_3)_5](PF_6)_2$ is treated with dppe, both the reduction product *fac*-$[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$ and a 17-electron fluoride abstraction product, *trans*-$[Cr(NO)(dppe)_2F]PF_6$, are isolated. The PhNC derivative $[Cr(NO)(CNPh)_5]BF_4$ and its substitution product *trans*-$[Cr(NO)(CNPh)_4(P\text{-}n\text{-}Bu_3)]BF_4$ as well as the molybdenum complex *fac*-$[Mo(NO)(CNPh)_3(dppe)]PF_6$ have also been synthesized. Complexes generated in this work have been characterized on the basis of their various spectroscopic and electrochemical properties, including ESR spectral studies on the 17-electron complexes.

Introduction

While nitrosyl complexes have long been known and their chemistry is well reviewed,[1,2] these compounds have recently been the focus of renewed interest. This is due in part to the varied bonding modes of coordinated NO,[3] as well as the involvement of these complexes in both stoichiometric and catalytic transformations of nitric oxide.[4] Our interest in nitrosyl compounds arose from reactivity studies of homoleptic chromium–isocyanide complexes in which we were successful in forming a series of Cr(0) and Cr(I) nitrosyl derivatives $[Cr(NO)(CNR)_5](PF_6)_n$ (where n = 1 or 2).[5,6] These syntheses provided us with rare examples of analogous pairs of stable 17-electron/18-electron compounds. From these parent nitrosyls we were able to generate[5] the 18-electron substitution products $[Cr(NO)(CNR)_4(amine)]PF_6$ and the 17-electron complexes $[Cr(NO)(CNR)_4X]PF_6$ (where X = Cl or Br), but in neither case could we obtain crystalline samples of the corresponding 17-electron or 18-electron species.

In view of the interest surrounding 17-electron organometallic complexes and the reactivity differences that exist between them and their 18-electron congeners, we have sought to develop this aspect of chromium–nitrosyl chemistry in order to provide examples of such complexes containing identical sets of ligands. We have now succeeded in synthesizing a series of phosphine-substituted derivatives of the type *trans*-$[Cr(NO)(CNR)_4(PR_3)]X_n$ (X = PF_6 or BF_4; n = 1 or 2) from the substitution reactions of $[Cr(NO)(CNR)_5]^{n+}$ and, furthermore, have isolated related complexes containing the bidentate $Ph_2PCH_2CH_2PPh_2$ ligand. These complexes constitute only the second such series of 17-electron/18-electron nitrosyl derivatives of the group 6 metals. The present report describes details of the synthesis of these complexes and structural assignments based upon the ESR spectral properties of the 17-electron species. Additionally, we have used the cyclic voltammetry technique to probe the redox properties of these molecules while secondary ion mass spectrometry (SIMS)[7] has provided some valuable insights into the gas-phase vs. solution-phase stabilities of these ionic species.

Experimental Section

Starting Materials. The nitrosyl–isocyanide complexes $[Cr(NO)(CNR)_5]PF_6$ and $[Cr(NO)(CNR)_5](PF_6)_2$ (where R = CMe_3 or $CHMe_2$) were prepared by our previously reported method.[5] The methyl isocyanide derivative $[Cr(NO)(CNMe)_5]BF_4$ was prepared by a different procedure. This tetrafluoroborate salt, reported here for the first time, was prepared in a manner analogous to that used to obtain the hexafluorophosphate salt $[Cr(NO)(CNMe)_5]PF_6$,[8] namely, the action of excess MeNC on the acetonitrile precursor $[Cr(NO)(NCMe)_5](BF_4)_2$.[9] Phenyl isocyanide was prepared by the literature method,[10] and the molybdenum complex $[Mo(NO)(CNPh)_5]PF_6$ was obtained by our previously reported procedure.[11] All monodentate tertiary phosphines, the bidentate phosphine 1,2-bis(diphenylphosphino)ethane (dppe), nitrosonium hexafluorophosphate, nitrosonium tetrafluoroborate, and other reagents and solvents were obtained from commercial sources and used as received.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen, and all solvents were deoxygenated prior to use by purging with N_2 gas.

In those cases where complexes were prepared by very similar procedures (see sections A–D), details of representative recipes only will be given.

A. Reactions of $[Cr(NO)(CNR)_5]PF_6$ with Tertiary Phosphines. (i) $[Cr(NO)(CNCMe_3)_4(PEt_3)]PF_6$. A quantity of $[Cr(NO)(CNCMe_3)_5]PF_6$ (0.17 g) was stirred in 9 mL of 2-propanol and heated to 65 °C. Triethylphosphine (0.10 mL) was syringed into this solution; the reaction mixture was maintained at 65 °C for 5 h. After this time, the red solution was allowed to cool slowly by packing the flask in a container of vermiculite and refrigerating overnight. The red crystals that formed were filtered off, washed with 2-propanol followed by diethyl ether, and dried in vacuo; yield 0.09 g (50%). This complex, like the other phosphine derivatives, could be recrystallized from acetone–diethyl ether or dichloromethane–diethyl ether mixtures. Anal. Calcd for $C_{26}H_{51}CrF_6N_5OP_2$: C, 46.08; H, 7.58. Found: C, 46.53; H, 7.59.

(ii) $[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)]PF_6$. Yield 70%. Anal. Calcd for $C_{29}H_{57}CrF_6N_5OP_2$: C, 48.40; H, 7.98. Found: C, 48.93; H, 8.03.

(iii) $[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)]PF_6$. Yield 68%. This compound was identified by its spectroscopic and electrochemical properties

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(6) A commonly used method in the assignment of formal oxidation states is to consider coordinated NO as NO^+. In this event, the complexes $[Cr(NO)(CNR)_5](PF_6)_2$ and $[Cr(NO)(CNR)_4(PR_3)](PF_6)_2$ are *formally* Cr(I) species, while $[Cr(NO)(CNR)_5]PF_6$ and $[Cr(NO)(CNR)_4(PR_3)]PF_6$ are considered *formally* as Cr(0) complexes. As in any simple electron bookkeeping procedure, this method should in no way be construed to represent, necessarily, an accurate appraisal of the electronic structure of these complexes.

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which were very similar to those of the other phosphine derivatives of this type.

(iv) $[Cr(NO)(CNCMe_3)_4(PMe_2Ph)]PF_6$. Yield 74%. This phosphine derivative was identified by its spectroscopic and electrochemical properties.

(v) $[Cr(NO)(CNCMe_3)_4(PEt_2Ph)]PF_6$. Yield 45%. This complex was identified by its electrochemical and spectroscopic properties.

(vi) $[Cr(NO)(CNCHMe_2)_4(PEt_3)]PF_6$. Yield 84%. Anal. Calcd for $C_{22}H_{43}CrF_6N_5OP_2$: C, 42.51; H, 6.97. Found: C, 42.57; H, 6.94.

(vii) $[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Pr_3)]PF_6$. Yield 68%. Anal. Calcd for $C_{25}H_{49}CrF_6N_5OP_2$: C, 45.25; H, 7.44. Found: C, 45.37; H, 7.76.

(viii) $[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Bu_3)]PF_6$. Yield 36%. This red complex was identified by its spectroscopic and electrochemical properties.

(ix) $[Cr(NO)(CNCHMe_2)_4(PMe_2Ph)]PF_6$. Yield 64%. Anal. Calcd for $C_{24}H_{39}CrF_6N_5OP_2$: C, 44.93; H, 6.13. Found: C, 45.41; H, 6.22.

(x) $[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)]PF_6$. Yield 71%. Anal. Calcd for $C_{26}H_{43}CrF_6N_5OP_2$: C, 46.64; H, 6.47. Found: C, 47.29; H, 6.53.

B. Reactions of $[Cr(NO)(CNMe)_5]BF_4$ with Tertiary Phosphines. (i) $[Cr(NO)(CNMe)_4(PEt_3)]BF_4$. A solution of $[Cr(NO)(CNMe)_5]BF_4$ (0.30 g) in 15 mL of 2-propanol was stirred at reflux, and triethylphosphine (0.29 mL) was syringed into the reaction mixture. The reaction solution was maintained at gentle reflux for 3 h. After this time, the red solution was allowed to cool very slowly by packing the flask (while hot) in a cannister of vermiculite and refrigerating overnight. The red solid that precipitated out was filtered off, washed with 2-propanol followed by diethyl ether, and dried in vacuo; yield 0.285 g (79%). This compound was identified on the basis of its spectroscopic and electrochemical properties.

(ii) $[Cr(NO)(CNMe)_4(P\text{-}n\text{-}Bu_3)]BF_4$. Yield 48%. This red complex was identified on the basis of its spectroscopic and electrochemical properties, which were analogous to those of similar derivatives.

(iii) $[Cr(NO)(CNMe)_4(PMe_2Ph)]BF_4$. Yield 79%. Anal. Calcd for $C_{16}H_{23}BCrF_4N_5OP$: C, 40.78; H, 4.92. Found: C, 40.54; H, 4.79.

C. Preparation of Phenyl Isocyanide Derivatives. (i) $[Cr(NO)(CNPh)_5]BF_4$. The synthesis of this complex, reported here for the first time, was adapted from that reported by Lloyd and McCleverty[8] for the complexes $[Cr(NO)(CNR)_5]PF_6$ (R = Me, CMe_3, or *p*-ClC_6H_4). A quantity of the acetonitrile derivative $[Cr(NO)(NCMe)_5](BF_4)_2$ (0.60 g) and an excess of phenyl isocyanide (1.2 mL) were stirred in 25 mL of refluxing acetonitrile. After a reaction period of 3.5 h, the dark solution was cooled to room temperature and the volume reduced in vacuo. The mixture was chromatographed on silica gel with dichloromethane as eluent. After the first, minor, yellow band was discarded, a second, major, red band was collected. The volume of this solution was reduced and the mixture further chromatographed on an alumina column with acetone eluent. The first, major, red-purple band was collected and its volume reduced under N_2. A quantity of diethyl ether was added and the solution refrigerated overnight. This gave dark red-purple crystals that were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.27 g (30%). Anal. Calcd for $C_{35}H_{25}BCrF_4N_6O$: C, 61.42; H, 3.68. Found: C, 61.11; H, 3.75.

(ii) $[Cr(NO)(CNPh)_4(P\text{-}n\text{-}Bu_3)]BF_4$. To 0.10 g of $[Cr(NO)(CNPh)_5]BF_4$ dissolved in 7 mL of 2-propanol was added 0.09 mL of tri-*n*-butylphosphine. The reaction mixture was heated to 65 °C and stirred for 4 h. After reduction of its volume, the solution was chromatographed on alumina with acetone as eluent, and the first, major, red-orange band was collected. After this solution was reduced in volume and again chromatographed on alumina with dichloromethane as eluent, the first, major, yellow-orange band was collected. The volume of this solution was reduced in vacuo, and subsequent workup of this solution resulted in a yellow-orange oil that could not be induced to crystallize. The identity of this complex was established by its spectroscopic and electrochemical properties.

D. Oxidation of the Complexes $[Cr(NO)(CNR)_4(PR_3)]X$ (X = PF_6 or BF_4). (i) $[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)](PF_6)_2$. A quantity of $[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)]PF_6$ (0.140 g) was dissolved in 10 mL of acetone, and an excess of solid $NOPF_6$ (0.15 g) was added directly to the solution. The color of the solution changed immediately from red to yellow, and after the solution was stirred at room temperature for 10 min, the solution volume was reduced under vacuum, diethyl ether was added, and the mixture refrigerated. The yellow crystals of product that formed were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.154 g (92%). This complex, as well as all the oxidation products of this type, can be recrystallized from acetone–diethyl ether or dichloromethane–diethyl ether mixtures. Anal. Calcd for $C_{32}H_{63}CrF_{12}N_5OP_3$: C, 42.39; H, 7.00. Found: C, 43.08; H, 7.02.

(ii) $[Cr(NO)(CNCMe_3)_4(PMe_2Ph)](PF_6)_2$. Yield 89%. The identity of this compound was established by its electrochemical and spectroscopic properties.

(iii) $[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)](PF_6)_2$. Yield 85%. Anal. Calcd for $C_{26}H_{43}CrF_{12}N_5OP_3$: C, 38.34; H, 5.32. Found: C, 38.73; H, 4.91.

(iv) $[Cr(NO)(CNMe)_4(PEt_3)](BF_4)_2$. Yield 93%. This complex was identified by its spectroscopic and electrochemical properties and by the characteristic molecular monocation and fragment ions in the SIMS spectrum of this compound.

E. Reaction of $[Cr(NO)(CNCMe_3)_5](PF_6)_n$ (*n* = 1 or 2) with 1,2-Bis(diphenylphosphino)ethane. (i) $[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$. $[Cr(NO)(CNCMe_3)_5]PF_6$ (0.15 g) and 1,2-bis(diphenylphosphino)ethane, dppe (0.19 g), were stirred in 10 mL of ethanol while the reaction mixture was heated to 65 °C. After reaction for 5 h at this temperature, the solution was cooled to room temperature and then blown to dryness under a stream of N_2. After the residue was dissolved in acetonitrile and filtered to remove excess ligand, the volume was again reduced and the solution chromatographed on silica gel with acetone as eluent. The first, major, red band was collected, reduced in volume, and then stirred in an C_2H_5OH/KPF_6 slurry for 24 h. After this time the mixture was taken to dryness under N_2, reconstituted in dichloromethane, filtered to remove excess KPF_6, and then again blown to dryness under N_2. The sample was redissolved in acetone, diethyl ether was added, and the sample was refrigerated for several days. A crop of red-brown crystals formed over this period which, after being filtered and washed with diethyl ether, were dried in vacuo; yield 0.041 g (20%). Anal. Calcd for $C_{41}H_{51}CrF_6N_4OP_3$: C, 56.29; H, 5.88. Found: C, 56.36; H, 6.17.

(ii) $[Cr(NO)(dppe)_2F]PF_6$. $[Cr(NO)(CNCMe_3)_5](PF_6)_2$ (0.30 g) and dppe (0.42 g) were heated to 65 °C in 10 mL of ethanol for a period of 4 h. The reaction solution was cooled to near room temperature, and the orange solid that formed was filtered off, washed with ethanol followed by diethyl ether, and dried in vacuo; yield 0.110 g (28%). This complex could be recrystallized from dichloromethane–diethyl ether solutions. Anal. Calcd for $C_{52}H_{48}CrF_7NOP_5$: C, 59.89; H, 4.64; F, 12.75. Found: C, 59.79; H, 4.88; F, 11.68. The red filtrate from the above reaction could be worked up in the method described in E(i) to yield a small quantity of the reduced species $[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$, which was identified by its spectroscopic and electrochemical properties.

F. $[Mo(NO)(CNPh)_3(dppe)]PF_6$. A sample of $[Mo(NO)(CNPh)_5]PF_6$ (1.0 g) was stirred in 50 mL of THF while 0.25 g of dppe was added to the solution. The reaction mixture was stirred at room temperature for 12 h, during which time the dark purple solution changed to orange-red. The volume of the solution was reduced, a hexane–diethyl ether mixture added, and the sample refrigerated to yield red crystals; yield 1.10 g (88%). This product could be recrystallized from acetone–ether mixtures. Anal. Calcd for $C_{47}H_{39}F_6MoN_4OP_3$: C, 57.68; H, 4.02. Found: C, 57.79; H, 4.10.

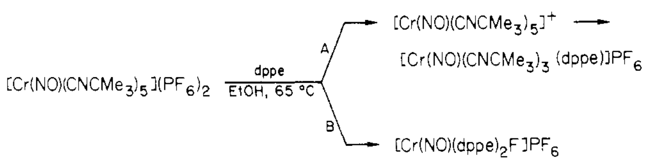
Physical Measurements. These were carried out as described previously.[5,7]

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory or by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Results and Discussion

Reactivity Studies. The reactions of monodentate tertiary phosphines with mixed nitrosyl–isocyanide complexes of chromium of the type $[Cr(NO)(CNR)_5]X$ (R = CMe_3, $CHMe_2$, or Me; X = PF_6 or BF_4) in alcohol solvents lead to the simple substitution products $[Cr(NO)(CNR)_4(PR_3)]X$ (PR_3 = PEt_3, P-*n*-Pr_3, P-*n*-Bu_3, PMe_2Ph, or PEt_2Ph). The isolation of these 18-electron complexes is critically dependent upon the choice of starting material, reaction solvent, and reaction temperature. 2-Propanol was found to be an ideal solvent, and the reaction between $[Cr(NO)(CNR)_5]X$ (X = PF_6 or BF_4) and PR_3 was found to occur over a period of 3–7 h to yield the desired species $[Cr(NO)(CNR)_4(PR_3)]X$ in 40–80% yield. These air-stable, red crystalline complexes are

Scheme I



soluble in polar organic solvents, e.g., dichloromethane and acetone, and may be recrystallized from them by the slow addition of diethyl ether. Similar reactions with the more sterically hindered, less basic phosphines $PMePh_2$ and PPh_3 did not readily yield clean substitution products.

The monosubstituted series $[Cr(NO)(CNR)_4(PR_3)]X$ (X = PF_6 or BF_4) were found to be stable in solution (dichloromethane, acetone) for much longer periods of time than the analogous amine-substituted complexes.[5] The amine complexes *trans*-$[Cr(NO)(CNR)_4(amine)]PF_6$ were found to decompose in solution to yield their pentakis(isocyanide) precursors $[Cr(NO)(CNR)_5]PF_6$.[5] This decomposition presumably proceeds via initial loss of amine ligand[5] and scavenging of an RNC ligand from a small proportion of the molecules that decompose with loss of RNC. The weakly bound nature of the amine ligand has also been observed in gas-phase studies of these compounds.[7] Contrast this behavior with the much greater solution stability and gas-phase stability (vide infra) of the phosphine-substituted derivatives. These observations are certainly not unexpected, as the π-accepting ability of the PR_3 ligands ensures a comparatively strong M–P bond. The amine ligands, on the other hand, are not capable of exhibiting π-acidic behavior toward the relatively electron-rich metal center and hence are easily lost.

These 18-electron phosphine-substituted compounds were used to synthesize the 17-electron, formally Cr(I), complexes $[Cr(NO)(CNR)_4(PR_3)]X_2$ by oxidation with solid NOX (X = PF_6 or BF_4). These reactions occur rapidly in acetone solutions at room temperature and are accompanied by the evolution of NO gas. The resulting bright yellow, air-stable, crystalline materials may be considered as simple phosphine-substituted products of the 17-electron parent complexes $[Cr(NO)(CNR)_5]X_2$ and may be compared spectroscopically to this series. The dications $[Cr(NO)(CNR)_4(PR_3)]^{2+}$ could be easily reduced back to their 1+ congeners by treatment with zinc metal, a procedure analogous to that used in the reduction of $[Cr(NO)(CNR)_5]^{2+}$ to $[Cr(NO)(CNR)_5]^+$.[5]

In the same way that monodentate phosphines react with the 18-electron complex $[Cr(NO)(CNCMe_3)_5]PF_6$ to yield the monosubstituted products $[Cr(NO)(CNCMe_3)_4(PR_3)]PF_6$, the bidentate phosphine ligand 1,2-bis(diphenylphosphino)ethane (dppe) reacts to form the product $[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$. In a more complex reaction, dppe is found to react with the oxidized, 17-electron starting material $[Cr(NO)(CNCMe_3)_5](PF_6)_2$ to yield two products as indicated in Scheme I. Pathway A of Scheme I involves the reduction of the 17-electron starting complex to the 18-electron monocation, followed by substitution to yield the same dppe complex that is formed when starting from the monocationic precursor. The small amount of $[Cr(NO)(CNCMe_3)_5]^{2+}$ that is *not* reduced during the early stages of the reaction goes on to form an orange crystalline product which we have identified as $[Cr(NO)(dppe)_2F]PF_6$ (pathway B). In this case, all the isocyanide ligands have been lost, and a fluoride ion is extracted from the PF_6^- ion. The BF_4^- salt of this complex had been reported by Connelly and co-workers[9] to be formed in the reaction between the acetonitrile derivative $[Cr(NO)(NCMe)_5](BF_4)_2$ and dppe, which gave both $[Cr(NO)(NCMe)(dppe)_2](BF_4)_2$ and the fluoride-extraction product $[Cr(NO)(dppe)_2F]BF_4$. Similar abstractions of fluoride from PF_6^- have been observed by Snow and Wimmer[12] to produce the species $[Mo(CO)_2(dppe)_2F]PF_6$.

In order to compare alkyl vs. aryl isocyanide ligands in this series of complexes, $[Cr(NO)(CNPh)_4(P\text{-}n\text{-}Bu_3)]BF_4$ was also synthesized. Although this phosphine derivative was only isolated as an oil, solution studies such as infrared spectroscopy (CH_2Cl_2 solution) and cyclic voltammetry were undertaken. The precursor to this compound was the analogous PhNC derivative, $[Cr(NO)(CNPh)_5]BF_4$, which we report here for the first time. A dppe derivative of the molybdenum complex $[Mo(NO)(CNPh)_5]PF_6$ was also synthesized in high yield by the direct action of dppe on this precursor in THF solution.

Spectroscopic and Electrochemical Studies. The mixed nitrosyl–isocyanide–phosphine complexes were studied by using several spectroscopic and electrochemical techniques. The ^1H NMR spectra of the 18-electron Cr(0) species were investigated, and in all cases, integration of the isocyanide vs. phosphine resonances confirmed the $[Cr(NO)(CNR)_4(PR_3)]^+$ stoichiometry.[13]

Infrared spectra of Nujol mulls and dichloromethane solutions of compounds prepared in this study are presented in Table I. Of particular interest are the isocyanide $\nu(C{\equiv}N)$ and nitrosyl $\nu(NO)$ modes in the regions 2050–2300 and 1600–1800 cm^{-1}, respectively. From these energies we can monitor changes in metal oxidation state as well as ligand changes. The single intense $\nu(C{\equiv}N)$ mode in the IR spectra of the $[Cr(NO)(CNR)_4(PR_3)]^+$ complex ions is consistent with a trans configuration. This ligand disposition is maintained through the oxidation process as evidenced by a single $\nu(C{\equiv}N)$ mode in the IR spectra of the dications. An interesting splitting is observed in the $\nu(C{\equiv}N)$ modes of the monocationic isopropyl isocyanide complexes in solution; this may reflect the attainment of a slight nonequivalency by the Me_2CHNC ligands. Note that isopropyl isocyanide is the least symmetrical of the alkyl isocyanide ligands used in the present investigation.

These $\nu(C{\equiv}N)$ values may be compared to the equatorial $\nu(C{\equiv}N)$ stretching modes of the parent $[Cr(NO)(CNR)_5]^+$ complexes for an indication of changes in electron distribution within these compounds. For $[Cr(NO)(CNR)_5]^+$ in the solid state, we have determined that the $\nu(C{\equiv}N)$ equatorial values are as follows: R = CMe_3, 2135 cm^{-1}; R = $CHMe_2$, 2140 cm^{-1}; R = Me, 2169 cm^{-1}.[5] In all cases, replacement of the axial RNC ligand by PR_3 lowers the $\nu(C{\equiv}N)$ equatorial energies by ca. 20–25 cm^{-1}. This observation is consistent with a transfer of electron density into the π^* levels of the equatorial RNC ligands upon replacing the axial isocyanide with a less effective π-accepting PR_3 ligand. A similar effect is observed in the $\nu(NO)$ modes of this series.

A more complex pattern of $\nu(C{\equiv}N)$ stretching modes in the dppe derivatives $[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$ and $[Mo(NO)(CNPh)_3(dppe)]PF_6$ is expected and indeed observed due to a nonequivalency of the isocyanide ligands. The energies of the $\nu(C{\equiv}N)$ and $\nu(NO)$ modes reflect the comparatively poorer π-accepting ability of the bis(phosphine) ligand relative to isocyanide ligands in the parent complexes $[Cr(NO)(CNCMe_3)_5]PF_6$[5] and $[Mo(NO)(CNPh)_5]PF_6$.[11]

Upon oxidation of the monocationic complexes to the dicationic species $[Cr(NO)(CNR)_4(PR_3)]^{2+}$, a substantial increase in the $\nu(C{\equiv}N)$ and $\nu(NO)$ energies is observed (Table I), consistent with decreased back-bonding to the π^* levels of these ligands. Both the $\nu(C{\equiv}N)$ and $\nu(NO)$ energies are shifted to higher energies by approximately 100 cm^{-1}.

The electrochemical properties of complexes prepared in this study were investigated by using the cyclic voltammetry

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(13) Details of the ^1H NMR spectra may be obtained from R.A.W. upon request. For example, $[Cr(NO)(CNCHMe_2)_4(PMe_2Ph)]PF_6$: ^1H NMR (acetone-d_6) δ 4.18 (septet, $CNCHMe_2$, $J_{CH\text{-}CH_3}$ = 7 Hz), 1.39 (doublet, $CNCHMe_2$, $J_{CH_3\text{-}CH}$ = 7 Hz), 7.56 (multiplet, PMe_2Ph), 1.70 (doublet, PMe_2Ph, $J_{P\text{-}CH_3}$ = 8 Hz).

Table I. Infrared Spectra, Voltammetric Half-Wave Potentials, and Molar Conductance of Mixed Nitrosyl–Isocyanide–Phosphine Complexes of Chromium

complex	ν(NO),[a] cm^{-1}		ν(C≡N),[a] cm^{-1}		$E_{1/2}$,[c]	Λ_M[e]
	Nujol mull	CH_2Cl_2	Nujol mull	CH_2Cl_2		
$[Cr(NO)(CNCMe_3)_4(PEt_3)]PF_6$	1683 s	1678 m	2115 s	2116 s	+0.37 (75), oxidn	124
$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)]PF_6$	1675 s, 1666 s	1680 m	2115 s	2116 s	+0.38 (100), oxidn	120
$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)]PF_6$	1676 s, 1667 s	1679 m	2116 s	2115 s	+0.39 (85), oxidn	125
$[Cr(NO)(CNCMe_3)_4(PMe_2Ph)]PF_6$	1666 s, 1655 s	1681 m	2118 s	2117 s	+0.36 (80), oxidn	122
$[Cr(NO)(CNCMe_3)_4(PEt_2Ph)]PF_6$	1689 s	1681 m	2112 s	2119 s	+0.39 (80), oxidn	120
$[Cr(NO)(CNCHMe_2)_4(PEt_3)]PF_6$	1667 s	1675 m	2130 sh, 2114 s	2132 sh, 2118 s	+0.33 (80), oxidn	124
$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Pr_3)]PF_6$	1659 s	1677 m	2119 s	2130 s, 2119 s	+0.32 (85), oxidn	122
$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Bu_3)]PF_6$	1662 s	1677 m	2116 s	2130 sh, 2118 s	+0.34 (90), oxidn	118
$[Cr(NO)(CNCHMe_2)_4(PMe_2Ph)]PF_6$	1669 s	1677 m	2115 s	2130 s, 2119 s	+0.33 (80), oxidn	119
$[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)]PF_6$	1663 s	1678 m	2122 s	2131 s, 2120 s	+0.34 (80), oxidn	117
$[Cr(NO)(CNMe)_4(PEt_3)]BF_4$	1667 s	1673 m	2170 sh, 2141 s	2152 s	+0.27 (70), oxidn	124
$[Cr(NO)(CNMe)_4(P\text{-}n\text{-}Bu_3)]BF_4$	1665 s	1676 m	2144 s	2152 s	+0.28 (90), oxidn	130
$[Cr(NO)(CNMe)_4(PMe_2Ph)]BF_4$	1657 s	1673 m	2143 s	2154 s	+0.26 (80), oxidn	126
$[Cr(NO)(CNPh)_5]BF_4$	1702 s	1713 m	2201 m, 2114 s	2191 w, 2117 s	+0.65 (80), oxidn; −1.70, redn[d]	106
$[Cr(NO)(CNPh)_4(P\text{-}n\text{-}Bu_3)]BF_4$	*b*	1700 m	*b*	2100 s	+0.52 (80), oxidn	*b*
$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)](PF_6)_2$	1764 s	1779 m	2218 s	2211 m	+0.35 (80), redn	260
$[Cr(NO)(CNCMe_3)_4(PMe_2Ph)](PF_6)_2$	1796 s	1781 m	2218 s	2212 m	+0.37 (85), redn	268
$[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)](PF_6)_2$	1790 s	1780 m	2227 s	2222 m	+0.31 (80), redn	270
$[Cr(NO)(CNMe)_4(PEt_3)](BF_4)_2$	1758 s	1778 s	2256 s, 2247 s	2250 s	+0.27 (80), redn	278
$[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$	1659 s	*b*	2194 m, 2133 s, 2106 s	*b*	+0.32 (100), oxidn	120
$[Cr(NO)(dppe)_2F]PF_6$	1658 m	1671 m			−0.51 (80), redn	120
$[Mo(NO)(CNPh)_3(dppe)]PF_6$	1627 s	1655 br	2140 m, 2088 s	2145 m, 2093 w	+0.87 (75), oxidn	113

[a] Abbreviations are as follows: s, strong; m, medium; w, weak; sh, shoulder; br, broad. [b] Not measured. [c] In volts vs. SCE with a Pt bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. [d] $E_{p,c}$ reported. [e] Values in Ω^{-1} cm^2 mol^{-1}. Measured on ~10^{-3} M acetonitrile solutions of complexes, at room temperature.

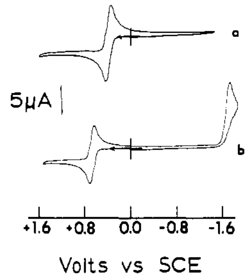

Figure 1. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane solutions of (a) $[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)]PF_6$ and (b) $[Cr(NO)(CNPh)_5]BF_4$ recorded at 200 mV/s.

technique. Voltammetric half-wave potentials vs. SCE (in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane solutions) and $E_{p,a} - E_{p,c}$ values are presented in Table I. For all phosphine-substituted compounds, a single wave is observed in the CV, representing the 17-electron/18-electron couple (Figure 1). For sweep rates (ν) between 50 and 400 mV/s, the ratio $i_p/\nu^{1/2}$ was constant and $i_{p,a}/i_{p,c} \simeq 1$ in accord with diffusion control. The potential separation between anodic and cathodic peaks, ΔE_p, was in the range 70–100 mV for a sweep rate of 200 mV/s. With our cell configuration,[14] these properties are consistent with this being a reversible electron-transfer process.

Exhaustive electrolyses of dichloromethane solutions of several $[Cr(NO)(CNR)_4(PR_3)]^{n+}$ (n = 1 or 2) complexes afforded the corresponding oxidized or reduced species. Determination of n values for representative complexes, where n is the total number of equivalents of electrons transferred in exhaustive electrolysis at constant potential, confirmed that these waves represent one-electron processes (i.e., $n = 1.0 \pm 0.1$).

The energy of the HOMO is seen not to vary to any appreciable extent as a result of phosphine substitution since the half-wave potentials are very similar to the values for the parent $[Cr(NO)(CNR)_5]^{n+}$ (n = 1 or 2) compounds.[15] Thus, while changes in the distribution of electron density throughout the entire molecule are occurring, as evidenced from the IR spectral data, this must have little effect on the HOMO energy.

In the phenyl isocyanide derivatives on the other hand, substitution of a PhNC ligand by $P\text{-}n\text{-}Bu_3$ does cause an appreciable shift in the oxidation wave to a more negative potential (Table I). This reflects the relative ease of oxidizing $[Cr(NO)(CNPh)_4(P\text{-}n\text{-}Bu_3)]^+$ as compared to $[Cr(NO)(CNPh)_5]^+$ and is consistent with the better σ-donor/poorer π-acceptor phosphine ligand in the axial position. In addition, the $[Cr(NO)(CNPh)_5]BF_4$ complex exhibits an irreversible reduction at −1.70 V (Figure 1), reminiscent of the behavior of the analogous $[M(NO)(CNPh)_5]^+$ (M = Mo and W) series.[11] From peak currents and analogy to the Mo and W compounds, this is probably a two-electron reduction. The very negative value of $E_{p,c}$ for the reduction of $[Cr(NO)(dppe)_2F]PF_6$ demonstrates the effect of replacing all the moderately good π-accepting isocyanide ligands with the better σ-donating phosphine and halide ligands, thereby making reduction of the metal complex more difficult (Table I).

Molar conductance values (Λ_M) of ~10^{-3} M acetonitrile solutions of complexes prepared in this study are reported in Table I. For the phosphine-substituted series, Λ_M values are ca. 120 Ω^{-1} cm^2 mol^{-1} in accord with the assignment of these compound as 1:1 electrolytes.[16] The oxidized species $[Cr(NO)(CNR)_4(PR_3)]X_2$ (X = PF_6 or BF_4) exhibit values around 270 Ω^{-1} cm^2 mol^{-1}, consistent with their being 2:1 electrolytes in acetonitrile.[16]

The determination of the room-temperature magnetic moments (μ_{eff}) of the formally Cr(I), 17-electron species was

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(14) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

(15) For the series $[Cr(NO)(CNR)_5]^+$, the $E_{1/2}$ values are as follows: R = CMe_3, +0.35 V; R = $CHMe_2$, +0.33 V; R = Me, +0.27 V (ref 5). For $[Mo(NO)(CNPh)_5]^+$, $E_{1/2}$ occurs at +0.86 V as reported in ref 11.

(16) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table II. X-Band ESR Spectra of 17-Electron Mixed Nitrosyl-Isocyanide-Phosphine Complexes of Chromium

complex[a]	g_{av}[b]	$A(^{53}Cr)$, G	$A(^{14}N)$, G	$A(^{31}P)$, G
$[Cr(NO)(CNCMe_3)_4(PEt_3)]^{2+}$	1.995	18.1	4.4	21.1
$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)]^{2+}$	1.996	17.7	4.3	21.0
$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)]^{2+}$	1.994	17.7	4.4	21.0
$[Cr(NO)(CNCMe_3)_4(PMe_2Ph)]^{2+}$	1.995	17.7	4.5	22.1
$[Cr(NO)(CNCMe_3)_4(PEt_2Ph)]^{2+}$	1.996	17.6	4.4	20.9
$[Cr(NO)(CNCHMe_2)_4(PEt_3)]^{2+}$	1.994	17.9	4.3	20.9
$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Pr_3)]^{2+}$	1.994	17.7	4.4	21.1
$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Bu_3)]^{2+}$	1.994	17.5	4.3	21.1
$[Cr(NO)(CNCHMe_2)_4(PMe_2Ph)]^{2+}$	1.994	17.7	4.4	22.0
$[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)]^{2+}$	1.995	17.7	4.5	21.0
$[Cr(NO)(CNMe)_4(PEt_3)]^{2+}$	1.995	17.6	*c*	21.3
$[Cr(NO)(CNMe)_4(P\text{-}n\text{-}Bu_3)]^{2+}$	1.996	17.9	*c*	20.8
$[Cr(NO)(CNMe)_4(PMe_2Ph)]^{2+}$	1.995	17.4	*c*	22.0
$[Cr(NO)(CNPh)_5]^{2+}$	1.994	17.1	4.4	
$[Cr(NO)(CNCMe_3)_3(dppe)]^{2+}$	1.995	17.1	4.5	30.7
$[Cr(NO)(dppe)_2F]PF_6$	1.993	17.3	5.4	34.3

[a] Electrochemically generated, unless counterion is specified. [b] Measured at room temperature in CH_2Cl_2 solution. [c] See text.

undertaken on dichloromethane solutions of the complexes by the Evans method.[17,18] While the values observed (μ_{eff} = 1.3–1.5 μ_B) are lower than the spin-only value, they are quite similar to the values for the analogous $[Cr(NO)(CNR)_5](PF_6)_2$ and $[Cr(NO)(CNR)_4X]PF_6$ (X = Cl or Br) complexes[5] and are consistent with these Cr(I) complexes possessing one unpaired electron. The 18-electron complexes $[Cr(NO)(CNR)_4(PR_3)]X$ (X = PF_6 or BF_4) were, as expected, diamagnetic.

The X-band ESR spectra of the electrochemically generated 17-electron phosphine-substituted complex ions were recorded at room temperature in dichloromethane solution and are reported in Table II; identical spectra were obtained for solutions of the salts $[Cr(NO)(CNR)_4(PR_3)]X_2$. For each of the $[Cr(NO)(CNR)_4(PR_3)]^{2+}$ species, ligand hyperfine interaction with both the phosphine phosphorus ($I(^{31}P) = {}^1/_2$) and nitrosyl nitrogen ($I(^{14}N) = 1$) lead to an observed 1:1 doublet of 1:1:1 triplets with $A(^{31}P) \simeq 21$ G and $A(^{14}N) \simeq 4.4$ G at a g value of 1.99 (Figure 2a). In the case of the methyl isocyanide series $[Cr(NO)(CNMe)_4(PR_3)]^{2+}$, only a broadening of each component of the ^{31}P coupled doublet is observed as the ligand hyperfine to the nitrosyl nitrogen was not well resolved. However, some structure in the signal was apparent and suggested interaction with this nitrogen nucleus.

In addition to the ligand hyperfine interactions with ^{31}P and ^{14}N nuclei, hyperfine interaction with the active chromium nuclei ($I(^{53}Cr) = {}^3/_2$; 9.54% abundance) leads to a predicted quartet of sidebands, each of which is subject to further splittings by ligand hyperfine effects (Figure 2). In each case, $A(^{53}Cr) \simeq 17.7$ G; thus the center peaks of this quartet signal are usually obscured by the much more intense signal associated with the nonactive chromium nuclei.

Consider now the ESR spectrum of the 17-electron complex $[Cr(NO)(dppe)_2F]PF_6$ (Figure 2c). In this spectrum we observe coupling to four equivalent, therefore equatorial, ^{31}P nuclei leading to a 1:4:6:4:1 pentet, each component of which is further split by the nitrosyl nitrogen into a 1:1:1 triplet (Figure 2). In this case, however, the hyperfine coupling constant to the ^{31}P nuclei is much different ($A(^{31}P)$ = 34.3 G) from that observed for the trans phosphine adducts ($A(^{31}P) \simeq 21$ G). This empirical difference in the cis phosphine vs. trans phosphine coupling constants allows us to suggest a structure for the adduct $[Cr(NO)(CNCMe_3)_3(dppe)]^{2+}$. The

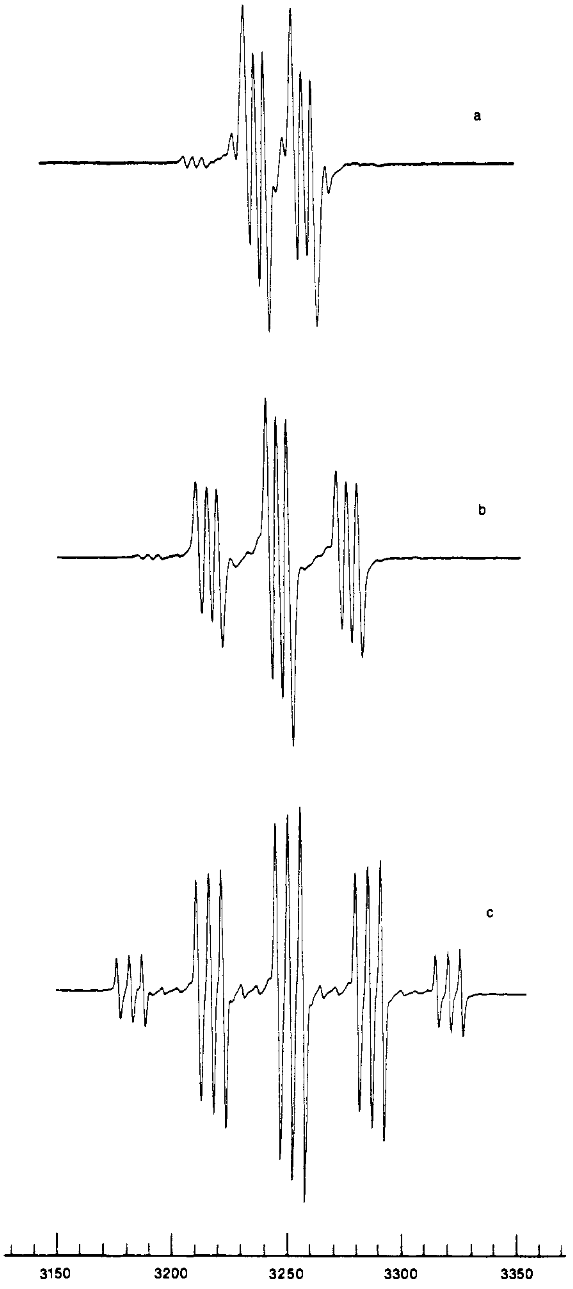

Figure 2. X-Band ESR spectra of dichloromethane solutions at room temperature containing (a) $[Cr(NO)(CNCMe_3)_4(PEt_2Ph)]^{2+}$, (b) $[Cr(NO)(CNCMe_3)_3(dppe)]^{2+}$, and (c) $[Cr(NO)(dppe)_2F]PF_6$.

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(17) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(18) Magnetic moments (μ_{eff}) in Bohr magnetons, determined on dichloromethane solutions of complexes at room temperature by the Evans method, are as follows: $[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)](PF_6)_2$, 1.26; $[Cr(NO)(CNCMe_3)_4(PMe_2Ph)](PF_6)_2$, 1.33; $[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)](PF_6)_2$, 1.41; $[Cr(NO)(CNMe)_4(PEt_3)](BF_4)_2$, 1.47; $[Cr(NO)(dppe)_2F]PF_6$, 1.36.

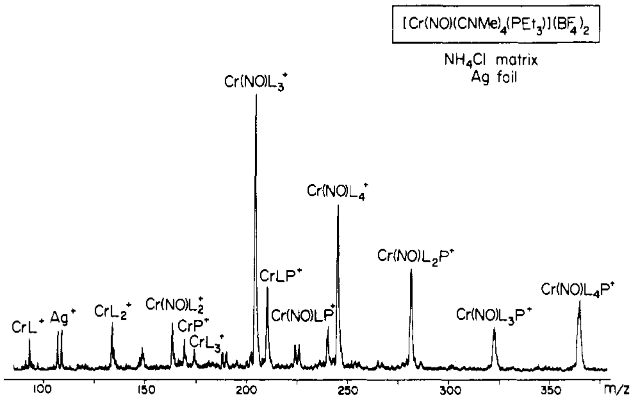

Figure 3. SIMS spectrum of the 17-electron dicationic species $[Cr(NO)(CNMe)_4(PEt_3)](BF_4)_2$ (L = MeNC; P = PEt_3).

ESR spectrum of this species (Figure 2b) is a 1:2:1 triplet ($A(^{31}P)$ = 30.7 G) of 1:1:1 triplets ($A(^{14}N)$ = 4.5 G), suggesting ligand hyperfine interaction of the spin density with two equivalent phosphorus nuclei, with a coupling constant characteristic of cis (to the nitrosyl) phosphorus nuclei. This observation is consistent with an assignment of the structure of this paramagnetic 2+ species (and presumably the parent 1+ species also) as the facial isomer, *fac*-$[Cr(NO)(CNCMe_3)_3(dppe)]^{2+}$.

The electrochemically generated molybdenum species $[Mo(NO)(CNPh)_3(dppe)]^{2+}$ also exhibits a 1:2:1 triplet ($A(^{31}P)$ = 21.2 G; g = 2.016) demonstrating an equivalency of phosphorus nuclei; we accordingly assign its structure as *fac*-$[Mo(NO)(CNPh)_3(dppe)]^{2+}$. In the case of $[Mo(NO)(CNPh)_5]^{2+}$ a signal at g = 2.015 is observed (peak-to-peak separation 10 G) but, as with the ESR spectrum of $[Mo(NO)(CNPh)_3(dppe)]^{2+}$, hyperfine coupling to the nitrosyl nitrogen was not resolved and must, accordingly, be much less than in the case of the analogous chromium systems.

Secondary Ion Mass Spectrometry Studies. Some of the species prepared in this study were characterized by secondary ion mass spectrometry (SIMS). Our recent SIMS study[7] of various mixed nitrosyl–isocyanide complexes allows us to predict that a characteristic fragmentation sequence should be observed for both the $[Cr(NO)(CNR)_4(PR_3)]^+$ monocations and their 17-electron dicationic counterparts $[Cr(NO)(CNR)_4(PR_3)]^{2+}$. These 2+ species possess very accessible reductions, as evidenced by cyclic voltammetric measurements (Table I), and hence are readily reduced by secondary electrons during the SIMS experiment. As a result, the 17-electron dicationic species yield SIMS spectra virtually identical with their 18-electron congeners. Thus, although analysis of the dicationic complex is undertaken, it is the 18-electron monocation and its fragment ions that are observed. The SIMS spectrum of $[Cr(NO)(CNMe)_4(PEt_3)](BF_4)_2$, a representative 17-electron complex of this type, is presented in Figure 3.

The fact that the molecular ion of this series of compounds is observed in relative abundances of at least 10% may reflect the more tightly bound nature of the phosphine ligand as compared to the amine ligands in the $[Cr(NO)(CNR)_4(amine)]^+$ series; the latter molecular ion was observed in less than 1% relative abundance due to the loss of the amine ligand.[7] We likewise note the differences of these complexes in solution, as demonstrated by the much greater stability of the phosphine-substituted complexes (vide supra).

Fragmentation of species analyzed in this study is seen to occur by two competitive processes, viz., initial loss of PR_3 ligand vs. initial loss of RNC ligand. The greater abundance of the $[Cr(NO)(CNR)_4]^+$ ions as compared to $[Cr(NO)(CNR)_3(PR_3)]^+$ indicates that initial loss of phosphine ligand is a more favored process. Both these ions may serve as precursors to the base ion $[Cr(NO)(CNR)_3]^+$, thereby accounting for its large abundance.

One interesting feature in the SIMS spectrum of the MeNC derivative is the incorporation of MeNC by the Ag foil (the sample support material) and the observation of the $[Ag(CNMe)]^+$ and $[Ag(CNMe)_2]^+$ ions (Figure 3). Incorporation of PEt_3 by Ag foil and the observation of $[Ag(PEt_3)]^+$ are also noted.

Acknowledgment. We thank the National Science Foundation for support of this work (Grant CHE82-06117). D.E.W. thanks Conoco for support in the form of a fellowship during 1982–1983. We gratefully acknowledge Dr. Janelle L. Pierce for providing the SIMS spectra and for helpful discussions. Thanks are also due Larry Arndt for providing the sample of $[Mo(NO)(CNPh)_3(dppe)]PF_6$.

Registry No. *trans*-$[Cr(NO)(CNCMe_3)_4(PEt_3)]PF_6$, 86968-57-2; *trans*-$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)]PF_6$, 86968-59-4; *trans*-$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)]PF_6$, 86968-61-8; *trans*-$[Cr(NO)(CNCMe_3)_4(PMe_2Ph)]PF_6$, 86968-63-0; *trans*-$[Cr(NO)(CNCMe_3)_4(PEt_2Ph)]PF_6$, 86968-65-2; *trans*-$[Cr(NO)(CNCHMe_2)_4(PEt_3)]PF_6$, 86968-67-4; *trans*-$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Pr_3)]PF_6$, 86968-69-6; *trans*-$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Bu_3)]PF_6$, 86968-71-0; *trans*-$[Cr(NO)(CNCHMe_2)_4(PMe_2Ph)]PF_6$, 86968-73-2; *trans*-$[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)]PF_6$, 86968-75-4; *trans*-$[Cr(NO)(CNMe)_4(PEt_3)]BF_4$, 86968-78-7; *trans*-$[Cr(NO)(CNMe)_4(P\text{-}n\text{-}Bu_3)]BF_4$, 86968-80-1; *trans*-$[Cr(NO)(CNMe)_4(PMe_2Ph)]BF_4$, 86968-82-3; *trans*-$[Cr(NO)(CNPh)_4(P\text{-}n\text{-}Bu_3)]BF_4$, 86968-86-7; *trans*-$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)](PF_6)_2$, 86968-88-9; *trans*-$[Cr(NO)(CNCMe_3)_4(PMe_2Ph)](PF_6)_2$, 86968-90-3; *trans*-$[Cr(NO)(CNCHMe_2)_4(PEt_2Ph)](PF_6)_2$, 86968-92-5; *trans*-$[Cr(NO)(CNMe)_4(PEt_3)](BF_4)_2$, 86968-94-7; *trans*-$[Cr(NO)(CNCMe_3)_4(PEt_3)]^{2+}$, 86969-00-8; *trans*-$[Cr(NO)(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)]^{2+}$, 86969-01-9; *trans*-$[Cr(NO)(CNCMe_3)_4(PEt_2Ph)]^{2+}$, 86969-02-0; *trans*-$[Cr(NO)(CNCHMe_2)_4(PEt_3)]^{2+}$, 86969-03-1; *trans*-$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Pr_3)]^{2+}$, 86969-04-2; *trans*-$[Cr(NO)(CNCHMe_2)_4(P\text{-}n\text{-}Bu_3)]^{2+}$, 86969-05-3; *trans*-$[Cr(NO)(CNCHMe_2)_4(PMe_2Ph)]^{2+}$, 86969-06-4; *trans*-$[Cr(NO)(CNMe)_4(P\text{-}n\text{-}Bu_3)]^{2+}$, 86969-07-5; *trans*-$[Cr(NO)(CNMe)_4(PMe_2Ph)]^{2+}$, 86969-08-6; *trans*-$[Cr(NO)(dppe)_2F]PF_6$, 86968-97-0; *fac*-$[Cr(NO)(CNCMe_3)_3(dppe)]PF_6$, 86968-96-9; *fac*-$[Cr(NO)(CNCMe_3)_3(dppe)]^{2+}$, 86969-10-0; $[Cr(NO)(CNCMe_3)_5]PF_6$, 51406-87-2; $[Cr(NO)(CNCMe_3)_5](PF_6)_2$, 76482-54-7; $[Cr(NO)(CNMe)_5]BF_4$, 86968-76-5; $[Cr(NO)(CNPh)_5]BF_4$, 86968-84-5; $[Cr(NO)(CNPh)_5]^{2+}$, 86969-09-7; *fac*-$[Mo(NO)(CNPh)_3(dppe)]PF_6$, 86968-99-2; *fac*-$[Mo(NO)(CNPh)_3(dppe)]^{2+}$, 86969-11-1; $[Mo(NO)(CNPh)_5]PF_6$, 78653-92-6; $[Mo(NO)(CNPh)_5]^{2+}$, 86993-44-4; $[Cr(NO)(NCMe)_5](BF_4)_2$, 75845-06-6.