1328 *Organometallics* 1982, *1*, 1328–1331

Homoleptic Isocyanide and Mixed Nitrosyl–Isocyanide Complexes of Chromium and Molybdenum: Secondary Ion Mass Spectrometry Studies

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Received June 7, 1982

Mass analysis of a series of homoleptic isocyanide and mixed nitrosyl–isocyanide complexes of chromium and molybdenum was undertaken by using secondary ion mass spectrometry (SIMS). Complexes of the form $[Cr(NO)(CNR)_5]PF_6$ (R = Me, $CHMe_2$, or CMe_3), $[Mo(NO)(CNR)_5]X$ (R = CMe_3, X = BF_4; R = C_6H_5, X = PF_6), and $[Cr(NO)(CNR)_5](PF_6)_2$ (R = $CHMe_2$, CMe_3, or C_6H_{11}) were investigated, as well as the substituted species $[Cr(NO)(CNCMe_3)_4(amine)]PF_6$ (amine = Me_2CHNH_2 or piperidine) and $[Cr(NO)(CNR)_4X]PF_6$ (R = $CHMe_2$, X = Cl; R = CMe_3, X = Cl or Br). The homoleptic silver isocyanide complex, $[Ag(CNCMe_3)_4]PF_6$, was also investigated. For those compounds which contain stable monocations or dications which may be readily reduced to the corresponding monocations, an informative fragmentation sequence was observed. Species for which stable monocations are unknown or not readily accessible, viz., $[Cr(CNC_6H_{11})_6](PF_6)_2$, $[Cr(CNC_6H_{11})_4(PEt_3)_2](PF_6)_2$, $[Cr(NO)(NCMe)_5](PF_6)_2$, and $[Mo(CNR)_7](PF_6)_2$ (R = Me or CMe_3), yielded SIMS spectra in which neither the molecular cation nor informative fragment ions were readily obtained. These trends are discussed in light of the redox properties of the species and the "18-electron rule".

Introduction

Our recent discovery[1] of certain nitrosyl–isocyanide complexes of chromium has led to some interesting observations with regard to their redox properties. While the 17-electron species $[Cr(NO)(CNR)_5](PF_6)_2$ (where R = $CHMe_2$, CMe_3, or C_6H_{11}) are easily isolated, their chemistry is often dominated by the ease of reduction to their 18-electron congeners. This observation no doubt reflects the moderate π acidity of the isocyanide ligands, as such a facile reduction is not observed with the acetonitrile complex $[Cr(NO)(NCMe)_5](PF_6)_2$.[2,3]

Where π-accepting capabilities exist for ligands in octahedral coordination, the formally nonbonding metal-based t_{2g} orbital set becomes bonding in character.[4] As a consequence of this π interaction, 18 electrons are required to populate all bonding molecular orbitals of the molecule. The ease with which the 17-electron complexes $[Cr(NO)(CNR)_5](PF_6)_2$ are reduced bears out the increased stability attained in an 18-electron configuration. Accordingly, the question of the gas-phase stabilities of these and related compounds arose, and characterization by secondary ion mass spectrometry (SIMS) was undertaken. The mass analysis capabilities of SIMS have previously been demonstrated for transition-metal coordination complexes,[5,6] many of which cannot be analyzed by conventional electron-impact mass spectrometry due to their low volatility or thermal instability.

Three types of compounds were chosen for investigation: (i) those compounds which contain stable (17- or 18-electron) monocations; (ii) those dications which electrochemical measurements have revealed may be readily reduced to the corresponding monocations; and (iii) species for which stable monocations are unknown or not readily accessible. The observation of molecular and fragment ions in the SIMS spectra are discussed in terms of electronic configuration and electrochemical data.

Experimental Section

Materials. The compounds $[Cr(CNC_6H_{11})_6](PF_6)_2$ and $[Cr(CNC_6H_{11})_4(PEt_3)_2](PF_6)_2$ were synthesized by a previously reported method.[7] The action of nitric oxide on homoleptic isocyanide species afforded the paramagnetic complexes $[Cr(NO)(CNR)_5](PF_6)_2$ (R = $CHMe_2$, CMe_3, or C_6H_{11}) and subsequent reduction with zinc metal yielded the 18-electron complexes $[Cr(NO)(CNR)_5]PF_6$.[1] This method was not a viable route to the MeNC derivative $[Cr(NO)(CNMe)_5]PF_6$, which we obtained by an alternate procedure.[8] The substituted compounds $[Cr(NO)(CNCMe_3)_4(amine)]PF_6$ (amine = Me_2CHNH_2 or piperidine) and $[Cr(NO)(CNR)_4X]PF_6$ (R = $CHMe_2$, X = Cl; R = CMe_3, X = Cl or Br) were available from an earlier study.[1] The syntheses of the molybdenum compounds $[Mo(CNR)_7](PF_6)_2$ (R = Me or CMe_3)[9] and $[Mo(NO)(CNR)_5]X$ (R = CMe_3, X = BF_4;[10] R = C_6H_5, X = PF_6[11]) have also been reported.

The silver isocyanide complex $[Ag(CNCMe_3)_4]PF_6$ was prepared by a method analogous to that of Sacco,[12] viz., reaction of a mixture of $AgNO_3$, KPF_6, and *tert*-butyl isocyanide in an ethanol medium at room temperature for 4 h. The product, obtained upon solvent evaporation, was extracted into CH_2Cl_2, filtered to remove any residual KPF_6, and precipitated from solution by the addition of petroleum ether.

Instrumentation. SIMS spectra were obtained on a Riber Instrument (Model SQ 156L) in the positive ion mode by using an energy selector, a quadrupole mass filter, a Channeltron electron multiplier, and pulse-counting electronics. An argon ion beam was used at 4 keV with a primary ion current typically 10^{-10} A or less and was focused to a beam size of 0.1 cm^2. This fulfills

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(1) Wigley, D. E.; Walton, R. A., *Organometallics* **1982**, *1*, 0000.

(2) The acetonitrile complex $[Cr(NO)(NCMe)_5](PF_6)_2$ undergoes an irreversible electrochemical one-electron reduction at ca. −0.6 V vs. a calomel electrode in acetonitrile solution, with $[Et_4N]ClO_4$ as supporting electrolyte. See ref 3.

(3) Clamp, S.; Connelly, N. G.; Taylor, G. E.; Louttit, T. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2162.

(4) Mitchell, P. R.; Parish, R. V. *J. Chem. Educ.* **1969**, *46*, 811.

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(11) Klendworth, D. D.; Welters, W. W., III; Walton, R. A. *Organometallics* **1982**, *1*, 336.

(12) Sacco, A. *Gazz. Chim. Ital.* **1955**, *85*, 989.

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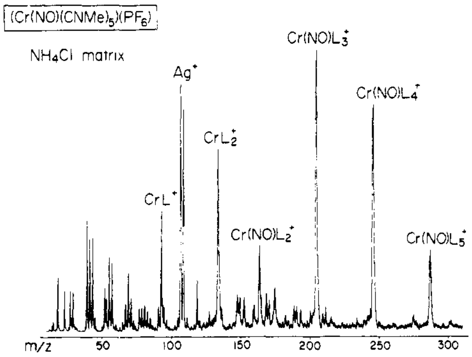

Figure 1. SIMS spectrum of the monocationic 18-electron species [Cr(NO)(CNMe)$_5$]PF$_6$ (L = MeNC).

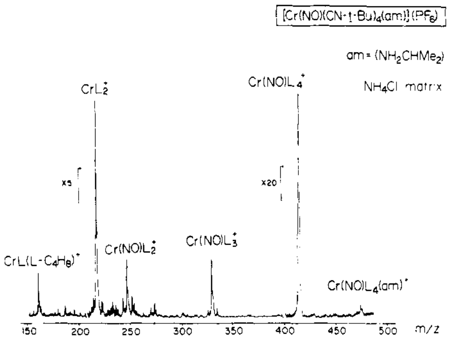

Figure 2. SIMS spectrum of the 18-electron complex [Cr(NO)(CNCMe$_3$)$_4$(NH$_2$CHMe$_2$)]PF$_6$ (L = Me$_3$CNC).

the static SIMS requirement,[13] ensuring that individual surface molecules are not subject to multiple primary ion impacts. Main chamber pressure during analysis was 1 × 10^{-8} torr or less. Samples were admixed with an excess of ammonium chloride[14] and were burnished directly onto an abrasively cleaned 1-cm^2 silver foil. No charge compensation was necessary in any of the experiments.

Results and Discussion

For this series of homoleptic and substituted isocyanide complexes, the molecular cation and a characteristic fragmentation sequence were readily observed only for the first two types of compounds investigated, viz., (i) species which exist as stable monocations with 17- or 18-electron configurations and (ii) species in which such a configuration is readily accessible. As dipositive ions are rarely observed in SIMS analyses[15] such species must possess a viable pathway to a stable monocation in order to be observed in the mass analysis. Hence, the 18-electron species [Cr(NO)(CNR)$_5$]PF$_6$ (where R = Me, CHMe$_2$, or CMe$_3$) (Figure 1), [Cr(NO)(CNCMe$_3$)$_4$(amine)]PF$_6$ (where amine = Me$_2$CHNH$_2$ or piperidine) (Figure 2), [Mo(NO)(CNCMe$_3$)$_5$]BF$_4$ (Figure 3), and [Mo(NO)(CNC$_6$H$_5$)$_5$]PF$_6$ and the 17-electron dicationic species [Cr(NO)(CNR)$_5$](PF$_6$)$_2$ (where R = CHMe$_2$, CMe$_3$, or C$_6$H$_{11}$) (Figure 4) which are easily reduced electrochemically and chemically to the corresponding monocationic 18-electron systems,[1,16] as well as the stable, monocationic 17-electron [Cr(NO)(CNR)$_4$X]PF$_6$ (where R = CHMe$_2$, X = Cl; R = CMe$_3$, X = Cl or Br) (Figures 5 and 6) all give a wealth of structural information in their SIMS spectra. Particularly noteworthy is the observation that the [Cr(NO)(CNR)$_5$](PF$_6$)$_2$ and [Cr(NO)(CNR)$_5$]PF$_6$ species give essentially identical SIMS spectra. The third group of compounds chosen for study, the dicationic species [Cr(CNC$_6$H$_{11}$)$_6$](PF$_6$)$_2$ and [Cr(CNC$_6$H$_{11}$)$_4$(PEt$_3$)$_2$](PF$_6$)$_2$, formally possessing 16-electron configurations, the acetonitrile complex [Cr(NO)(NCMe)$_5$](PF$_6$)$_2$, a 17-electron system, and the 18-electron [Mo(CNR)$_7$](PF$_6$)$_2$ (where R = Me or CMe$_3$) do not have stable monocationic counterparts[3,7,17] and consequently, under our experimental conditions, yielded SIMS spectra devoid of the molecular cation and characteristic fragment ions.

The complexes [Cr(NO)(CNR)$_5$]PF$_6$ (Figure 1) and [Cr(NO)(CNCMe$_3$)$_4$(amine)]PF$_6$ (Figure 2) yield SIMS spectra very characteristic of the analyte. For all three monocationic, 18-electron pentakis(isocyanide) complexes, virtually identical fragmentation patterns were observed. Relative ion abundances are influenced by the primary ion current, with fragmentation increasing with increasing primary ion current. Fragmentation is seen to occur initially by the loss of isocyanide ligands. The loss of one isocyanide from the molecular cation is observed and the loss of a second yields the base peak (Figure 1). These observations are somewhat expected due to the greater π-accepting ability of the nitrosyl ligand, thereby ensuring a strong M–NO bond. While relative bond strengths are important in determining *initial* ligand loss from larger ions, the ability of the smaller ions to delocalize charge becomes a dominant factor in determining their relative abundances. This effect is seen in further fragmentation sequences. The loss of a third isocyanide ligand also occurs, but in this case, the resulting [Cr(NO)(CNR)$_2$]$^+$ ion appears in somewhat low abundance presumably due to the rapid, subsequent loss of the nitrosyl ligand to give the observed [Cr(CNR)$_2$]$^+$ ion. Loss of an isocyanide ligand from this species occurs, yielding [Cr(CNR)]$^+$; no ions corresponding to either [Cr(NO)(CNR)]$^+$ or [Cr(NO)]$^+$ were detected. This phenomenon was also observed in the SIMS spectra of the substituted species [Cr(NO)(CNCMe$_3$)$_4$(amine)]PF$_6$. Because of the facile loss of the amine ligand only a very weak molecular ion is observed (less than 1% relative abundance). Again, [Cr(NO)(CNR)]$^+$ and [Cr(NO)]$^+$ were not seen. The absence of [Cr(NO)]$^+$ contrasts with the observation of [Cr(CNR)]$^+$, a result which might reflect the ability of the larger RNC ligand to disperse charge throughout the fragment. Similarly, the greater stability of [Cr(CNR)$_2$]$^+$ as compared to the unobserved [Cr(NO)(CNR)]$^+$ can be rationalized on similar grounds, since both fragments can be considered to have been generated by selective ligand loss from the [Cr(NO)(CNR)$_2$]$^+$ ion, which itself appears in low abundance.

We next turned our attention to the dicationic species [Cr(NO)(CNR)$_5$](PF$_6$)$_2$ (where R = CHMe$_2$, CMe$_3$, or C$_6$H$_{11}$). These complexes possess facile electrochemical and chemical reduction pathways to the corresponding monocations[1,16] and hence are readily reduced by secondary electrons during the SIMS experiment. As a result, the 17-electron dicationic species yielded SIMS spectra virtually identical with their 18-electron congeners. Thus, although analysis of the dicationic complexes was undertaken, it was the 18-electron monocations that were observed; this ease of reduction is expected on the basis of the "18-electron rule".[4] The spectrum of [Cr(NO)(CNCHMe$_2$)$_5$](PF$_6$)$_2$, a representative complex of this type, is presented in Figure 4.

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[16] The cyclic voltammograms of [Cr(NO)(CNR)$_5$](PF$_6$)$_2$ (R = CHMe$_2$, CMe$_3$, or C$_6$H$_{11}$) (dichloromethane–0.2 M tetra-*n*-butylammonium hexafluorophosphate, scan rate of 200 mV/s) reveal a reduction wave at $E_{1/2}$ = +0.30 to +0.35 V vs. SCE; $E_{p,a} - E_{p,c} \simeq$ 100 mV. See ref 1.

[17] Mialki, W. S.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1380.

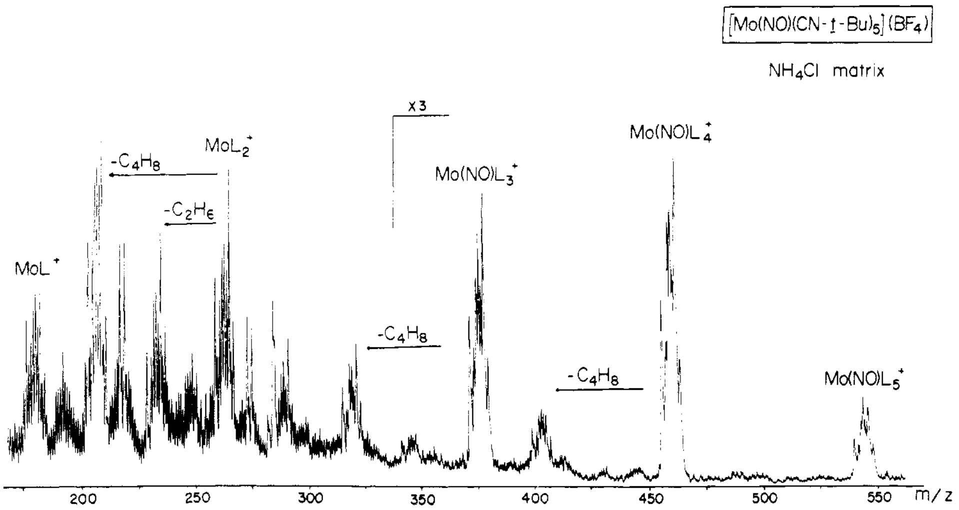

Figure 3. SIMS spectrum of the 18-electron molybdenum complex $[Mo(NO)(CNCMe_3)_5]BF_4$ (L = Me_3CNC).

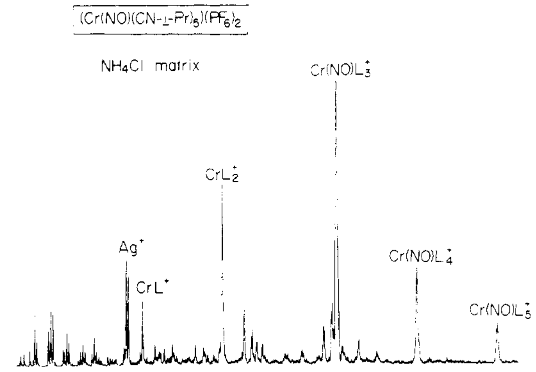

Figure 4. SIMS spectrum of the 17-electron dicationic species $[Cr(NO)(CNCHMe_2)_5](PF_6)_2$ (L = Me_2CHNC).

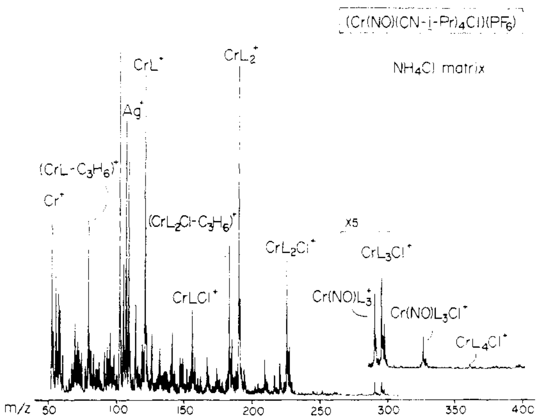

Figure 5. SIMS spectrum of the chloride-substituted, 17-electron monocationic complex $[Cr(NO)(CNCHMe_2)_4Cl]PF_6$ (L = Me_2CHNC).

The halide-substituted 17-electron species $[Cr(NO)(CNR)_4X]PF_6$ (where R = $CHMe_2$, X = Cl; R = CMe_3, X = Cl or Br) exist as stable monocations and therefore yield SIMS spectra characteristic of the analyte. As illustrated for $[Cr(NO)(CNCHMe_2)_4Cl]PF_6$ (Figure 5), the spectra are more complex than those of $[Cr(NO)(CNR)_5]^{n+}$ due to the competitive loss of nitrosyl and halide ligands, producing $[Cr(NO)(CNR)_n]^+$ (where n = 3 and 4) and $[Cr(CNR)_nCl]^+$ (n = 2–4) ions. In the case of the bromide complex $[Cr(NO)(CNCMe_3)_4Br]PF_6$, incorporation of chloride from the NH_4Cl matrix was observed as demonstrated by the appearance of $[Cr(NO)(CNCMe_3)_4Cl]^+$ in approximately the same relative abundance as $[Cr(NO)(CNCMe_3)_4Br]^+$. When NH_4NO_3 is employed as the matrix support, this incorporation is easily avoided, producing the SIMS spectrum of $[Cr(NO)(CNCMe_3)_4Br]^+$ as shown in Figure 6. In this case, the molecular ion was observed and loss of C_4H_8 from certain fragments yielded ions in high relative abundance. The peak at mass 130 was neither seen in the SIMS spectra of $[Cr(NO)(CNCMe_3)_5](PF_6)_n$ (where n = 1 or 2) nor of $[Cr(NO)(CNCMe_3)_4Cl]PF_6$ (analyzed from an NH_4NO_3 matrix) and does not contain bromide as evidenced by its monoisotopic nature. Its origin remains uncertain at present.

This study was next extended to include the analogous molybdenum nitrosyl–isocyanide complexes $[Mo(NO)(CNCMe_3)_5]BF_4$ (Figure 3) and $[Mo(NO)(CNC_6H_5)_5]PF_6$. The SIMS spectra of these molybdenum derivatives were, as one might expect, characteristic of 18-electron, monocationic systems. Fragmentation was somewhat more extensive than for the corresponding chromium systems in that loss of a fragment corresponding to C_4H_8 is observed from each ion in the $[Mo(NO)(CNCMe_3)_n]^+$ series (where n = 1–4). Interestingly, such ligand fragmentation has been observed in the electron-impact mass spectra of certain carbonyl–*tert*-butyl isocyanide complexes of chromium and molybdenum.[18] The intact molecular cation was observed in 20% relative abundance (for R = CMe_3) with respect to $[Mo(NO)(CNCMe_3)_4]^+$ as the base peak.

The dicationic 16-electron systems $[Cr(CNC_6H_{11})_6](PF_6)_2$ and $[Cr(CNC_6H_{11})_4(PEt_3)_2](PF_6)_2$ and the nitrile derivative $[Cr(NO)(NCMe)_5](PF_6)_2$, possessing a 17-electron configuration, do not reduce to form stable monocationic species as evidenced by electrochemical measurements[3,7] and, in accord with these observations, did not yield intact molecular cations or, under our experimental conditions, structurally diagnostic fragments in the mass spectrometer. Similar results were obtained for the molybdenum species $[Mo(CNR)_7](PF_6)_2$ (where R = Me or CMe_3). Very complex spectra devoid of the molecular cation were observed, and structurally diagnostic fragments were not readily obtained. For attainment of a cation of unit charge, viz., $[Mo(CNR)_7]^+$, a one-electron reduction to the unstable 19-electron species would have to occur. Such a process is unknown in the solution chemistry of these species,[17] and we would not expect to observe these species in the gas phase either.

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[18] Conner, J. A.; Jones, E. M.; McEwan, G. K.; Lloyd, M. K.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1246.

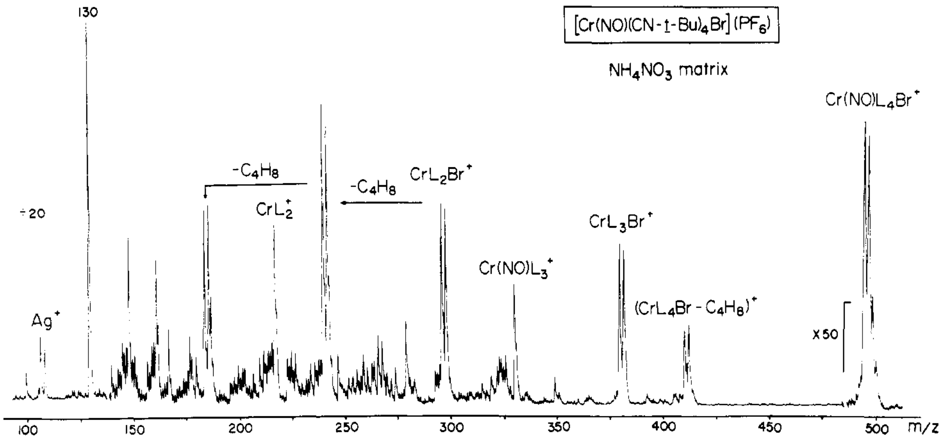

Figure 6. SIMS spectrum of the 17-electron bromide complex $[Cr(NO)(CNCMe_3)_4Br]PF_6$ analyzed from an NH_4NO_3 matrix (L = Me_3CNC).

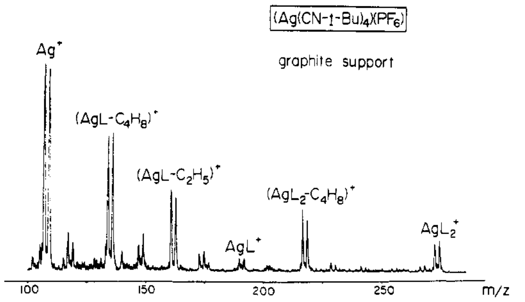

Figure 7. SIMS spectrum of the silver isocyanide complex $[Ag(CNCMe_3)_4]PF_6$ (L = Me_3CNC).

To investigate a four-coordinate 18-electron species, we included an analysis of the silver isocyanide complex $[Ag(CNCMe_3)_4]PF_6$. The SIMS spectrum of this compound did not reveal the molecular cation as is observed for the 18-electron chromium or molybdenum complexes. Considerable structural information, however, can be obtained through fragment ions such as $[Ag(CNCMe_3)_2]^+$ and $[Ag(CNCMe_3)]^+$ as shown in Figure 7. This complex was analyzed from a graphite support in order to minimize those interactions between the metal complex and the support which might promote fragmentation. Ligand fragmentation through the loss of C_4H_8 was also observed here. The decreased gas-phase stability of the $[Ag(CNCMe_3)_4]^+$ cation presumably reflects the tendency of Ag(I) complexes to exhibit a linear, two-coordinate structure.[19] The appearance of $[Ag(CNCMe_3)_2]^+$ as the highest mass fragment can therefore be rationalized in terms of the increased stability of the two-coordinate geometry over the tetrahedral structure of the molecular cation.

Conclusion

Prior knowledge of the redox properties of many of these homoleptic isocyanide and mixed nitrosyl–isocyanide complexes permits an understanding of why certain dicationic species are readily reduced during the SIMS experiment and characteristic ions observed, and why structurally useful fragments are not readily observed for other complexes. Mass spectra characterizing monocationic complexes or complexes which have an accessible pathway to a stable singly charged species can readily be obtained by SIMS, and this is usually a reflection of the increased stability attained in an 18-electron configuration. This study further demonstrates that metal–ligand bond strengths increase in the order Cr–amine < Cr–CNR < Cr–NO for the chromium complexes investigated.

Acknowledgment. This work was supported by the NSF-MRL Program, Grant DMR80-20249. We thank Professor R. Graham Cooks and Dr. Kenneth L. Busch for very helpful discussions and Andrew Bell for providing the silver isocyanide complex $[Ag(CNCMe_3)_4]PF_6$.

Registry No. $[Cr(NO)(CNMe)_5]PF_6$, 51406-89-4; $[Cr(NO)(CNCHMe_2)_5]PF_6$, 82583-29-7; $[Cr(NO)(CNCMe_3)_5]PF_6$, 51406-87-2; $[Mo(NO)(CNCMe_3)_5]BF_4$, 82638-72-0; $[Mo(NO)(CNC_6H_5)_5]PF_6$, 78653-92-6; $[Cr(NO)(CNCHMe_2)_5](PF_6)_2$, 82583-29-7; $[Cr(NO)(CNCMe_3)_5](PF_6)_2$, 82621-46-3; $[Cr(NO)(CNC_6H_{11})_5](PF_6)_2$, 82621-47-4; $[Cr(NO)(CNCMe_3)_4(NH_2CH_2CHMe_2)]PF_6$, 82660-16-0; $[Cr(NO)(CNCMe_3)_4(pip)]PF_6$, 82660-18-2; $[Cr(NO)(CNCHMe_2)_4Cl]PF_6$, 82660-20-6; $[Cr(NO)(CNCMe_3)_4Cl]PF_6$, 82660-22-8; $[Cr(NO)(CNCMe_3)_4Br]PF_6$, 82660-64-8; $[Ag(CNCMe_3)_4]PF_6$, 82621-49-6; $[Cr(CNC_6H_{11})_6](PF_6)_2$, 75215-58-6; $[Cr(CNC_6H_{11})_4(PEt_3)_2](PF_6)_2$, 82660-24-0; $[Cr(NO)(NCMe)_5](PF_6)_2$, 82621-51-0; $[Mo(CNMe)_7](PF_6)_2$, 66632-84-6; $[Mo(CNCMe_3)_7](PF_6)_2$, 41982-05-2.

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