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# Electrospray Tandem Mass Spectrometry of Nitrido and Imido Complexes

**Tai-Chu Lau* and Zhibiao Wu**

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong

**Jiangyao Wang,[†] K. W. Michael Siu,* and Roger Guevremont**

Institute for Environmental Research and Technology, National Research Council of Canada, Montreal Road,
Ottawa, Ontario, Canada K1A OR6

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The chemistry of transition metal complexes containing oxo, nitrido, imido, alkylidene, and alkylidyne ligands, in which there are metal−ligand multiple bonds, is under intense scrutiny.[1] We demonstrated recently that highly oxidizing metal−oxo ions can be readily extracted from solution with minimal fragmentation using the electrospray technique.[2] In this communication, we report results of a similar study with some ionic nitrido and imido complexes. We also report results of a preliminary examination of the relative intrinsic metal−ligand bond strengths in these complexes as revealed by their gas-phase fragmentation via collision-induced dissociation (CID) conducted in a triple-quadrupole mass spectrometer. The ionic complexes were delivered to the gas phase by means of electrospraying millimolar solutions of the complexes in water, methanol, acetone, acetonitrile, or mixtures of these solvents. The following ionic complexes were examined in this work: $K[OsO_3N]$,[3] $[(n\text{-}C_4H_9)_4N]_2[OsNCl_4]$,[4] $[OsN(terpy)Cl_2]ClO_4$ (terpy = 2,2′:6′,2″-terpyridine),[5] $[OsN(NH_3)_4Cl]Cl_2$,[6] $[(n\text{-}C_4H_9)_4N]_4[RuNCl_4]$,[4] *trans*-$[ReN(dppe)_2Cl]ClO_4$ (dppe = 1,2-bis(diphenylphosphino)ethane),[7] $[N(PPh_3)_2][Cr(NBu^t)(mnt)_2]$ (mnt = maleonitriledithiolato),[8] and $[Cr(NBu^t)_2(bpy)_2](PF_6)_2$ (bpy = 2,2′-bipyridine).[9] Their electrospray mass spectral data are shown in Table 1. Experiments were performed on a SCIEX TAGA Model 6000E triple quadrupole mass spectrometer, which has an upper limit of *m/z* ∼ 1400. Details of the setup and procedures are described elsewhere.[14] The *m/z* values listed are those of the most abundant peaks within the ions' respective isotopic distributions. In all cases, the complex ions were the most abundant ions in the electrospray mass spectra of solutions of these complexes, and the agreement between the experimental and calculated isotopic distribution patterns was excellent (Figure 1). Fragmentation under our conventional lens setting (OR−RO ∼ 10 V) was negligible except in the case of $[Cr(NBu^t)_2(bpy)_2](PF_6)_2$, where the ion $[Cr(NBu^t)(bpy)_2]^{2+}$ was observed in addition to the expected complex ion $[Cr(NBu^t)_2(bpy)_2]^{2+}$. When the potential difference in the lens region (OR−RO) was reduced to 1 V, the relative intensity of the former to the latter ion decreases to almost zero, thus indicating that $[Cr(NBu^t)(bpy)_2]^{2+}$ was a fragment ion of $[Cr(NBu^t)_2(bpy)_2]^{2+}$ and not an impurity

**Table 1.** Electrospray Mass Spectral Data for Nitrido and Imido Complexes[a]

| compound | ion (*m/z*) |
|---|---|
| $K[OsO_3N]$[b,d] | $[OsO_3N]^-$ (254) |
| $[(n\text{-}C_4H_9)_4N][OsNCl_4]$[b,e] | $[OsNCl_4]^-$ (348) |
| $[OsN(terpy)Cl_2]ClO_4$[c,f] | $[OsN(terpy)Cl_2]^+$ (509) |
| $[OsN(NH_3)_4Cl]Cl_2$[c,g] | $[OsN(NH_3)_4Cl]^{2+}$ (154.5)<br>$[OsN(NH_3)_4Cl]^{2+}\cdot xH_2O$ ($x$ = 1−6) |
| $[(n\text{-}C_4H_9)_4N][RuNCl_4]$[b,e] | $[RuNCl_4]^-$ (258) |
| *trans*-$[ReN(dppe)_2Cl]ClO_4$[c,f] | $[ReN(dppe)_2Cl]^+$ (1033) |
| $[N(PPh_3)_2][Cr(NBu^t)(mnt)_2]$[b,f] | $[Cr(NBu^t)(mnt)_2]^-$ (403) |
| $[Cr(NBu^t)(bpy)_2](PF_6)_2$[c,f] | $[Cr(NBu^t)_2(bpy)_2]^{2+}$ (253)<br>$[Cr(NBu^t)(bpy)_2]^{2+}$ (217.5) |

[a] Solutions were ca. 1 mmol $dm^{-3}$. [b] Spectrum collected in the negative-ion mode. [c] Spectrum collected in the positive-ion mode. [d] Spectrum obtained in 50/50 water/acetone. [e] Spectrum obtained in acetonitrile. [f] Spectrum obtained in acetone. [g] Spectrum obtained in 50/50 water/methanol.

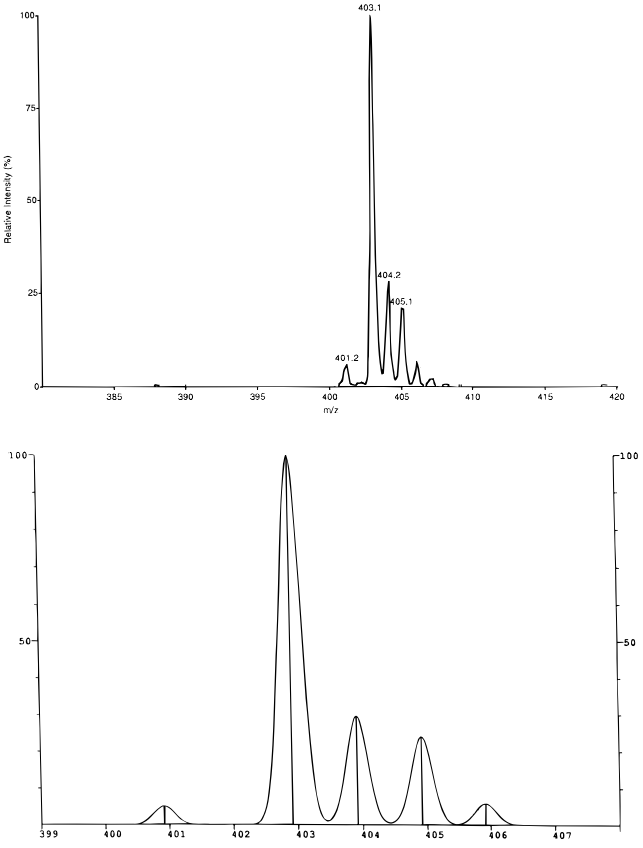

**Figure 1.** $[Cr(NBu^t)(mnt)_2]^-$: upper panel, electrospray mass spectrum of $[N(PPh_3)_2][CrNBu^t)(mnt)_2]$ in acetone; lower panel, calculated isotopic distribution of $[Cr(NBu^t)(mnt)_2]^-$.

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[†] Present address: Department of Cell and Molecular Pharmacology, Medical University of South Carolina, Charlston, SC 29425.

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**Table 2.** Fragment Ions of Nitrido and Imido ions[a]

| precursor ion ($m/z$)[b] | fragment ions ($m/z$, rel abund/%) | $E_{cm}$/eV[c] |
|---|---|---|
| $[Os(O)_3N]^-$ (254) | $[OsO_2N]^-$ (238. 0.2), $[OsO_2]^-$ (224, 1) | 5.4 |
| $[OsNCl_4]^-$ (348) | $[OsNCl_3]^-$ (311, 4.7) | 4.1 |
| $[OsN(terpy)Cl_2]^+$ (509) | $[OsN(terpy)Cl]^+$ (474, 9.4)<br>$[OsN(terpy)]^+$ (439, 0.5) | 2.9 |
| $[OsN(NH_3)_4Cl]^{2+}$ (154.5) | $[OsN(NH_3)_3Cl]^{2+}$ (146, 9)<br>$[OsN(NH_3)_4]^{2+}$ (137, 7)<br>$[OsN(NH_3)_3]^{2+}$ (128, 5) | 8.2 |
| $[RuNCl_4]^-$ (258) | $[RuNCl_3]^-$ (223, 25)<br>$[RuNCl_2]^-$ (188, 1) | 5.7 |
| $[ReN(dppe)_2Cl]^+$ (1033) | $[ReN(dppe)Cl]^+$ (633, 3) | 1.5 |
| $[Cr(NBu^t)(mnt)_2]^-$ (403) | $[Cr(mnt)_2]^-$ (332, 80) | 3.6 |
| $[Cr(NBu^t)_2(bpy)_2]^{2+}$ (253) | $[Cr(NBu^t)(bpy)_2]^{2+}$ (218, 70)<br>$[Cr(bpy)_2]^{2+}$ (183, 55)[d] | 5.5 |

[a] Ar was used as the collision gas. [b] 100% abundance. [c] The collision energy $E_{cm}$ is calculated using the equation $E_{cm} = E_{lab} \times$ mass of Ar/(mass of ion + mass of Ar) where $E_{lab}$ is the collision energy in the laboratory frame. [d] Only the two most abundant fragment ions are reported.

in the sample. The spectrum of $[OsN(NH_3)_4Cl]Cl_2$ in water/methanol exhibits hydrates of $[OsN(NH_3)_4Cl]^{2+}$; hydrates are a common feature in the electrospray mass spectra of aqueous metal salt solutions.[10]

Table 2 lists the fragment ions of selected metal−nitrido and metal−imido ions after CID. The fragmentations of $[Os(O)_3N]^-$ yielded $[Os(O)_2N]^-$, arising from the loss of an oxygen atom, as well as $[OsO_2]^-$, arising from formally the loss of NO. The absence of the ion $[OsO_3]^-$, which would have arisen from the loss of a nitrogen atom from the precursor ion, suggests that the Os≡N bond is stronger than the Os═O bond. Under comparable collision conditions, the extent of fragmentation of $[Os(O)_3N]^-$, in comparison to that of other osmium−nitrido species, was much lower; this is consistent with the fact that all the bonds in this ion are either double or triple in nature. The CID of $[OsNCl_4]^-$, $[OsN(terpy)Cl_2]^+$, and $[RuNCl_4]^-$ showed fragment ions due to the loss of chlorine atoms. More extensive fragmentation was evident in $[RuNCl_4]^-$ than in $[OsNCl_4]^-$, in apparent agreement with the expected stronger metal−ligand bonds of third-row transition metals compared to that of their lighter congeners. For $[ReN(dppe)_2Cl]^+$, the loss of the chelating ligand dppe occurs preferentially to that of chlorine; this result is surprising, especially since the chlorine is *trans* to the nitrido ligand, which is known to exert a strong *trans* effect. The collision-induced dissociations of all the nitrido ions showed little or no loss of nitrogen atoms, in accord to the triple-bond nature of the metal−nitrogen bond. Surprisingly, loss of the imido group appeared to occur readily in the two chromium−imido complexes though the metal−imido bond is also formally a triple bond[1] (Figure 2). In line with these results, facile imido transfer to phosphines has been demonstrated for an osmium[11] and a chromium imido complex[12] in solution. On the other hand, although nitrido complexes also react with phosphines,[13] complete cleavage of the metal−nitrido bond does not occur.

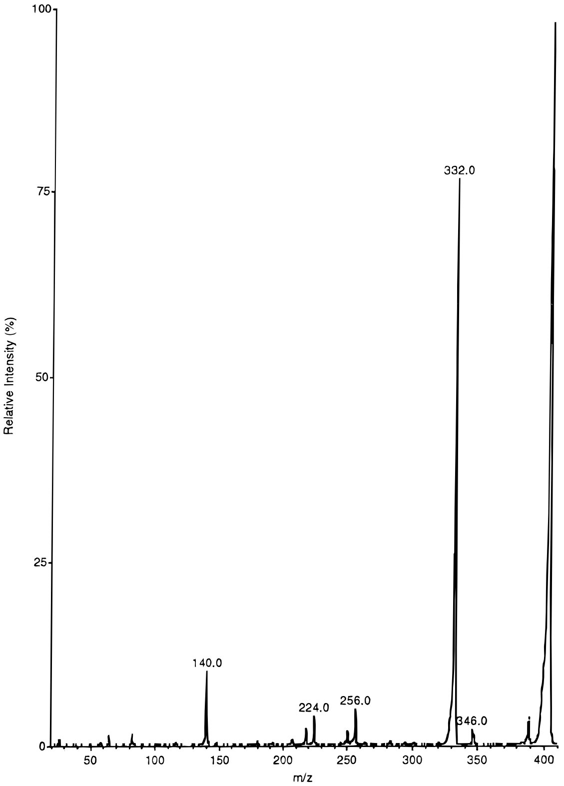

**Figure 2.** Collision-induced dissociation of $[Cr(NBu^t)(mnt)_2]^-$ ($m/z$ 403). The fragment ion at $m/z$ 332 is $[Cr(mnt)_2]^-$, arising from the loss of ($NBu^t$).

In conclusion, electrospray mass spectra of high-valent ionic metal−nitrido and −imido complexes can be readily obtained with apparently little or no sign of degradation. ESMS is thus a potentially valuable technique for characterizing and studying the reactivities of these species in solution. Systematic studies of tandem MS of complexes containing various metal−ligand multiple bonds are also in progress to probe the relative strengths of various metal−ligand bonds and to correlate with their atom-transfer reactivities in solution.

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