X-RAY PHOTOELECTRON SPECTRA OF NITROGEN COMPLEXES OF RUTHENIUM

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X-ray Photoelectron Spectra of Nitrogen Complexes of Ruthenium

Sir:

The binding energies of nitrogen 1s electrons are dependent on the chemical environment of the nitrogen atoms.\(^1,2\) Consequently the chemical shifts in binding energy observed in the X-ray photoelectron spectra of nitrogen compounds give useful structural information. It has been shown that small, although significant, chemical shifts occur when nitrogen-containing ligands are coordinated to transition metal ions.\(^2\) We have now found that X-ray photoelectron spectroscopy is useful in elucidating the structures of complexes containing the Ru-N linkage. We have observed the spectrum of the coordinated dinitrogen ligand. The latter spectrum is of interest, because structural information regarding \(N_2\) complexes has previously been obtained mainly from single crystal X-ray studies\(^3-6\) and from infrared spectroscopy.


The synthesis and properties of the compounds used in this research are reported elsewhere. These compounds, \([\text{RuCl}_2(\text{das})_2]\)[PF_6]


\[\text{RuClNO(das)}_2\text{Cl}_2\] and \[\text{RuN}_3\text{Cl(das)}_2\] (das is \(\sigma\)-phenylenebis(dimethylarsine) have a trans arrangement of ligands with only a single nitrogen-containing ligand bound to the metal. The compound \([\text{C}_6\text{H}_5\text{N}_2]\)[BF_4] was prepared for comparative purposes by standard methods. All of the compounds had satisfactory analyses. The photoelectron spectra of these compounds were obtained using Mg Kα X-radiation (1253.6 eV). The kinetic energies of the photoelectrons produced were obtained using a double-focusing magnetic spectrometer of a design previously described. The resolution was limited by the band widths, which ranged from 1.4 to 2.0 eV, but the positions of the photoelectron peaks were reproducible to \(\pm\) 0.2 eV. The work function for the spectrometer material (aluminum) was assigned the value of 4.0 eV.

All of the compounds investigated gave well-defined photoelectron peaks near 400 eV. These peaks are readily identified as arising from the nitrogen 1s core electrons, because none of the other elements emit photoelectrons in this region of the spectrum. The spectrum of trans-\([\text{RuCl}_2(\text{das})_2]\)[PF_6] consists of two well-resolved photopeaks at 402.3 and 400.7 eV, with an intensity ratio of 1:1 (Table I). The observation of two photoelectron...
peaks of equal intensity in the dinitrogen complex proves that the two
nitrogen atoms are structurally nonequivalent. The photoelectron peak
of higher binding energy is tentatively assigned to the nitrogen atom
directly bound to the ruthenium. (Coordination of $N_2$ should lead to an
increase in the positive charge on the coordinated nitrogen atom, and
consequently to a higher binding energy for the nitrogen $1s$ electrons
as is observed for the coordination of ammonia.\(^2\)) However, final assign-
ment must await the observation of the photoelectron spectrum of a symmetri-
cally bridged dinitrogen complex in which both nitrogen atoms have identical
charges. Phenyl-diazonium fluoroborate, \((C_6H_5N_2)(BF_4)\), also has two peaks,
at 405.1 and 403.7 eV, with an intensity ratio of 1:1.

The ruthenium nitrosyl complex, trans-\([RuClNO(das)_2]Cl_2\), has a single
photoelectron peak at 399.8 eV, which is in the range found for other tran-
sition metal nitrosyl complexes. The complex trans-\([RuN_3Cl(das)_2]\) had been
previously identified as a dinitrogen complex because of analytical dif-
ficulties and uncertainties regarding the interpretation of the infrared
spectrum.\(^9\) The photoelectron spectrum of this material consists of two

\(\text{(9) R. D. Feltham, 157th National Meeting of the American Chemical}
\text{Society, INDR 49.}\)

\(\text{photoelectron peaks at 403.9 and 399.2 eV with relative intensities 1:2,}
\text{thus, providing the presence of the azide group. The photoelectron peaks}
\text{of sodium azide and trans-}[Co(N_3)_2(das)_{2}]\text{[ClO}_4\text{]}\text{ are also listed in Table I}
\text{for comparison.}\)
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