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Nitrosoarene complexes of rhodium(III), iridium(III), copper(I) and mercury(II). Use of XPS in determining the mode of bonding to transition metals

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Abstract

Some previously synthesized nitrosoarene complexes of known coordination mode have been studied by XPS spectroscopy. New nitrosoarene complexes of Rh^{III} , Ir^{III} , Cu^{I} and Hg^{II} have been synthesized and studied by both X-ray photoelectron and IR spectroscopy. A correlation was found between the value $\Delta E_{\text{B}}(\text{O}-\text{N})$ and the bonding mode of the nitroso ligand.

Introduction

There is considerable interest in nitrosoarene ligands because of their value as nitrene precursors [1] and of their interesting mode of coordination to the metals [2].

A variety of physical spectroscopic techniques have been applied to studies of structures of the complexes formed by metals with these C-nitroso ligands; prominent amongst them is infrared spectroscopy.

It has been noted that the NO stretching frequency correlates well with the bonding mode for nitroso compounds [3]. Thus, if the NO stretching frequency increases on coordination, $\sigma(\text{O})$ coordination is present; if small decreases are found then $\sigma(\text{N})$ coordination is involved; large decreases in the NO stretching frequency ($\geq 400 \text{ cm}^{-1}$) are associated with $\pi(\text{NO})$ coordination.

It seemed to us of interest to see whether another spectroscopic technique could be applied to these structural problems, in the hope that consistent correlations would be found.

Within the past five years Batich and Donald [4] have used X-ray photoelectron spectroscopy in the study of monomeric and dimeric nitroso compounds. In conformity with valence bond (VB) and MO arguments, they showed that the N 1s peak in the dimer is shifted by about 3.4 eV to higher binding energy relative to that for the monomer, and the O 1s peak is shifted in the opposite direction by about 2 eV; thus the difference $\Delta E_B(\text{O-N})$ is about 133–134 eV for monomer and 128–129 eV for either the *cis*- or *trans*-dimer. It thus appeared probable that the interaction of either or both N and O atoms through coordination to the metal would result in the shift of binding energies (E_B) of their core levels, so providing an insight into the coordination mode. Thus we made some RNO complexes whose structure has been established by X-ray crystallography and examined their X-ray photoelectron spectra in the hope of observing correlation between $\Delta E_B(\text{O-N})$ and the bonding mode.

We also describe the preparation of some other nitrosoarene complexes and their characterization by X-ray photoelectron and IR spectroscopy. Spectroscopic parameters are considered as diagnostic indicators of the coordination mode in the absence of crystallographic information.

Experimental

Reagents

All solvents were reagent grade quality and were distilled and stored under nitrogen. $\text{Me}_2\text{NC}_6\text{H}_4\text{NO}$ and $\text{C}_6\text{H}_5\text{NO}$ were purchased from Aldrich. $\text{PdCl}_2(\text{C}_6\text{H}_5\text{NO})_2$, $\text{CoCl}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$, $\text{SnCl}_2\text{Me}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$, $\text{RhCl}(\text{NBD})(p\text{-BrC}_6\text{H}_4\text{NO})$, $\text{Pt}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$, $\text{Pd}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$ were prepared by established methods [2,5,12,3,6].

Techniques

Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer.

X-ray photoelectron spectra were obtained with a Leybold LHS-10 spectrometer using unmonochromatized Mg-K_α (1253.6 eV) radiation. The detailed spectra were recorded in the FAT (Fixed Analyser Transmission) mode with a pass energy E of 50 eV under a typical pressure of 10^{-8} mbar. Samples were examined as powders contained within an adhesive conducting tape or mounted as pellets. They were recorded at 190 K by circulating liquid nitrogen through the sample rod to avoid sublimation under vacuum and loss of ligands from the sample surface.

The spectra were collected by use of an Apple II microcomputer interfaced to the spectrometer. The data, stored as a series of data files on floppy disks, were analysed by a home-made program [7].

Preparations of the complexes

All operations were carried out under nitrogen by standard techniques.

(a) $\text{RhCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$, $\text{RhCl}_3(\text{C}_6\text{H}_5\text{NO})_2$ and $\text{IrCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$

A solution of $\text{MCl}_3 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Rh, Ir}$) and the nitroso compounds in 1/2.5 molar ratio in ethanol was refluxed for 30 min then cooled to room temperature and

filtered. The filtrate was concentrated in vacuo, and benzene added to produce a solid, which was filtered off, washed with benzene and with diethyl ether, and then dried in vacuo.

$\text{RhCl}_3(\text{C}_6\text{H}_5\text{NO})_2$. Maroon powder (yield 68%). Decomposition point above 200°C . Anal. Found: C, 33.8; H, 2.4; Cl, 26.0; N, 6.0. $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl}_3\text{Rh}$ calcd.: C, 34.0; H, 2.38; Cl, 25.1; N, 6.62%.

$\text{RhCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$. Green powder (yield 65%). Decomposition point above 225°C . Anal. Found: C, 38.04; H, 4.2; Cl, 20.64; N, 10.5. $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2\text{Cl}_3\text{Rh}$ calcd.: C, 37.71; H, 3.96; Cl, 20.87; N, 10.99%.

$\text{IrCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$. Dark violet powder. Decomposition point above 210°C . Anal. Found: C, 32.0; H, 3.2; Cl, 18.0; N, 9.1. $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2\text{Cl}_3\text{Ir}$ calcd.: C, 32.09; H, 3.37; Cl, 17.76; N, 9.35%.

(b) $\text{RhCl}_3(\text{Me}_2\text{S})(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$

A suspension of $\text{RhCl}_3(\text{Me}_2\text{S})_3$ (300 mg, 0.76 mmol) and $p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO}$ (240 mg, 2 mmol) in diethyl ether (20 ml) was stirred at room temperature for 15 h. The precipitate was filtered off, washed with diethyl ether, and dried in vacuo (yield 90%). Decomposition point above $110\text{--}140^\circ\text{C}$. Anal. Found: C, 27.9; H, 4.1; Cl, 25.7; N, 6.1. $\text{C}_{10}\text{H}_{16}\text{N}_2\text{OSCl}_3\text{Rh}$ calcd.: C, 28.49; H, 3.83; Cl, 25.23; N, 6.65%.

(c) $\text{CuI}(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$

A suspension of CuI (200 mg, 1.04 mmol) and $p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO}$ (375 mg, 2.48 mmol) in diethyl ether (10 ml) was stirred at room temperature for 24 h. The solid formed was filtered off, washed with diethyl ether, and dried in vacuo. Green powder (yield 98%). Dec. point $155\text{--}200^\circ\text{C}$. Anal. Found: C, 27.7; H, 2.88; I, 38.0; N, 7.98. $\text{C}_8\text{H}_{10}\text{N}_2\text{OICu}$ calcd.: C, 28.21; H, 2.96; I, 37.25; N, 8.22%.

(d) $\text{HgI}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$

A mixture of HgI_2 (500 mg, 1.099 mmol) and $p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO}$ (500 mg, 3.31 mmol) in diethyl ether (10 ml) was stirred at room temperature for 24 h. The maroon powder formed was filtered off and washed with diethyl ether. (Yield 86%). Dec. point $110\text{--}120^\circ\text{C}$. Anal. Found: C, 16.0; H, 1.8; I, 42.0; N, 4.5. $\text{C}_8\text{H}_{10}\text{N}_2\text{OI}_2\text{Hg}$ calcd.: C, 15.89; H, 1.67; I, 41.98; N, 4.63%.

(e) $\text{Pt}(\text{PPh}_3)_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$

This compound was prepared by the procedure described in ref. 6 starting from $p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO}$ instead of $\text{C}_6\text{H}_5\text{NO}$.

Results and discussion

(a) *Preparation of the complexes*

As previously noted [8], the donor properties of nitrosoarene are sufficiently strong to give stable complexes. Thus, $\text{RhCl}_3(\text{C}_6\text{H}_5\text{NO})_2$, $\text{RhCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$ and $\text{IrCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$ were readily prepared by reaction of halide salts of MCl_3 ($\text{M} = \text{Rh}, \text{Ir}$) with the nitroso compound in 1/2 molar ratio in ethanol. Similarly, $\text{RhCl}_3(\text{Me}_2\text{S})(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$ was obtained by replacing the Me_2S ligand in $\text{RhCl}_3(\text{Me}_2\text{S})_3$ by the nitroso ligand.

Table 1

Binding energies (eV) in the nitroso complexes

Compound	Bonding mode	$E_B(N)$	$E_B(O)$	$E_B(M)$	$\Delta E_B(O-N)$	Ref.
I $p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO}$		399.9	532.3		132.4	
II $\text{PdCl}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	$\sigma(N)$	400.2	530.6	338.2 ($\text{Pd}3d_{5/2}$)	130.4	3
III $\text{CoCl}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	$\sigma(N)$	400.3	531.1	779.8 ($\text{Co}2p_{3/2}$)	130.8	13
IV $\text{PdCl}_2(\text{C}_6\text{H}_5\text{NO})_2$	$\sigma(N)$	400.4	531.0	338.5 ($\text{Pd}3d_{5/2}$)	130.6	2
V $\text{RhCl}(\text{NBD})(p\text{-BrC}_6\text{H}_4\text{NO})$	$\sigma(N)$	402.1	532.9	308.0 ($\text{Rh}3d_{5/2}$)	130.8	3
VI $\text{IrCl}_3(\text{Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	$\sigma(N)$	400.3	530.8	62.1 ($\text{Ir}4f_{7/2}$)	130.5	this work
VII $\text{SnCl}_2\text{Me}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	$\sigma(O)$	400.1	532.1	487.0 ($\text{Sn}3d_{5/2}$)	132.0	12
VIII $\text{CuI}(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$	$\sigma(O)$	400.1	532.2	932.7 ($\text{Cu}2p_{3/2}$)	132.7	this work
IX $\text{HgI}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$	$\sigma(O)$	399.9	532.7	100.7 ($\text{Hg}4f_{7/2}$)	132.8	this work
X $\text{Pd}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$	$\pi(N,O)$	400.0	532.0	337.3 ($\text{Pd}3d_{5/2}$)	132.0	2
XI $\text{Pt}(\text{PPh}_3)_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$	$\pi(N,O)$	398.8	531.2	71.2 ($\text{Pt}4f_{7/2}$)	132.4	this work
XII $\text{Ni}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$	$\pi(N,O)$	399.4	532.0	854.5 ($\text{Ni}2p_{3/2}$)	132.6	2
XIII $\text{Pt}(\text{PPh}_3)(\text{C}_6\text{H}_5\text{NO})$	$\pi(N,O)$	400.0	532.1	72.0 ($\text{Pt}4f_{7/2}$)	132.1	6

$\text{CuI}(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$ and $\text{HgI}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$ were obtained by treating the salt of copper and mercury with the nitroso compound in diethyl ether. Despite the fact that preparation involved heterogeneous conditions, the compounds isolated were analytically pure, and were used as obtained for X-ray photoelectron spectral analysis (Table 1).

Table 2 shows the IR spectral data for the arylnitroso complexes along with the corresponding bonding mode.

(b) Photoelectron spectra

High resolution spectra were recorded in the N 1s, O 1s, C 1s binding energy regions, together with the most intense core level signals due to the metal. Binding

Table 2

IR spectral data for the complexes ^a

Complex	$\nu(\text{NO})$ (cm^{-1})	$\Delta\nu^b$ (cm^{-1})	Bonding mode
$\text{RhCl}_3(\text{C}_6\text{H}_5\text{NO})_2$	1500	-5	$\sigma(N)$
$\text{PdCl}_2(\text{C}_6\text{H}_5\text{NO})_2$	1490	-15	$\sigma(N)$
$\text{RhCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	1497	-30	$\sigma(N)$
$\text{RhCl}_3(\text{Me}_2\text{S})(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$	1525	-2	$\sigma(N)$
$\text{IrCl}_3(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	1512	-15	$\sigma(N)$
$\text{PdCl}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	1500	-27	$\sigma(N)$
$\text{PtCl}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	1499	-28	$\sigma(N)$
$\text{CoCl}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	1498	-29	$\sigma(N)$
$\text{RhCl}(\text{NBD})(p\text{-BrC}_6\text{H}_4\text{NO})$	1473	-32	$\sigma(N)$
$\text{SnCl}_2\text{Me}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$	1563	+36	$\sigma(O)$
$\text{CuI}(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$	1535	+8	$\sigma(O)$
$\text{HgI}_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$	1540	+13	$\sigma(O)$
$\text{Pt}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$	973	-532	$\pi(N,O)$
$\text{Pd}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$	1039	-466	$\pi(N,O)$
$\text{Ni}(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NO})$	1025	-480	$\pi(N,O)$

^a In nujol mulls. ^b Difference between $\nu(\text{NO})$ of the complex and the $\nu(\text{NO})$ of the free ligand.

energy values E_B are reported in Table 1, and they are referenced to the most intense C 1s peak set at 285.0 eV. The O 1s signals are quite narrow (FWHM 2 eV) and well defined; they generally show a component at about 534 eV which is attributed to traces of water condensed on the sample at the low temperature used during the recording of the spectrum. For all the nitroso compounds shown in Table 1 the expected N : O atomic stoichiometric ratio was calculated from the following relationship:

$$A_{N1s}/S_{N1s} : A_{O1s}/S_{O1s} = N : O$$

where A_{N1s} is the area of N 1s signal and A_{O1s} is the area of O 1s peak attributed to the nitroso group; S_{N1s} and S_{O1s} are the relative sensitivity factors of N 1s and O 1s core levels respectively. Wagner's empirical values [9] of the sensitivity factors were used on the basis of analyser transmission function [10] considerations.

In the case of the N 1s signal, a single main peak was always observed for both nitrosobenzene and *N,N*-dimethyl-*p*-nitroso compounds. This feature has also been reported for the free ligand by other authors [4,11], although the presence of two different peaks is predicted from CNDO calculations [4]; the observed behaviour could be ascribed to the extended conjugation existing in *N,N*-dimethyl-*p*-nitroso benzene.

When there is σ -(O) or σ -(N) coordination, this resonance is still possible, so that in the nitroso complexes only one N 1s peak is observed. Similarly, when both N and O are involved in η^2 coordination from the π -(NO) there is no significant effect on the resonance.

From inspection of the XPS data reported in Table 1 it is apparent that for all of the compounds, when there is σ -(N) coordination the value of ΔE_B (O-N) drops by 1.5–2.5 eV compared with that for the uncomplexed monomeric nitroso compound. This fall is less than that found by Batich and Donald [4] for mutual interaction of two RNO units to form *trans*- or *cis*-dimeric N₂O₂ groups. On the other hand, when there is σ -(O) coordination there is no significant change in ΔE_B (O-N) compared with the value for the monomer itself. This suggests that the O 1s binding energy is unaffected by σ -(O) coordination. Similarly, when both the N and O are involved in η^2 -coordination from the π -(NO) there is no significant change in ΔE_B (O-N).

To the best of our knowledge this is the first attempt to correlate X-ray photoelectron data for nitroso compounds with the bonding state of the ligand. We are encouraged by the general relationship observed for σ -(N) coordination, and plan to extend the study to a wider range of complexes of *C*-nitroso compounds.

Conclusions

X-ray photoelectron spectroscopy appears to be capable of providing a useful confirmation for the involvement of σ -(N) coordination between monomeric RNO to transition metals and can therefore be employed together with IR ν (NO) data in assigning coordination modes when X-ray crystallographic evidence is lacking.

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