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Nitrosylrhodium (^{14}NO and ^{15}NO) Compounds Containing Triphenylphosphine

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Synopsis. The oxidation states of the NO group and the geometries for the nitrosylrhodium compounds were investigated on the basis of the ^{15}N-isotopic shifts of the N–O stretching vibrations and the frequencies of the Rh–NO stretching ones. $RhCl(NO_2)(NO)(PPh_3)_2$ was found to react with NO to give $RhCl(NO_2)_2(PPh_3)_2$.

It has been reported that the oxidation states of the metal atom and the NO group in transition-metal nitrosyl complexes significantly influence the isotopic shifts of the vibrational bands due to the metal–N–O skeleton upon ^{15}NO-substitution, and control the region where these bands are observed.[1–3] Such a view may be connected with the concept of "Stereochemical Control of Valence": that the geometry of NO group is determined by the stereochemistry of the ligands attached to the metal.[4]

On the basis of these facts, the authors measured the isotopic shifts of the following nitrosylrhodium compounds: $Rh(NO)(PPh_3)_3$ (PPh_3=triphenylphosphine), $RhX_2(NO)(PPh_3)_2$, and $RhX(NO_2)(NO)(PPh_3)_2$ (X=Cl and Br), which have been the subject of great interest as homogeneous catalysts of olefin hydrogenation.[5]

Experimental

Syntheses. The examined compounds were prepared in accordance with Ref. 6—8. One of the starting materials, rhodium(III) bromide, was prepared from $RhCl_3 \cdot 3H_2O$ by heating it with concentrated hydrobromic acid on a boiling water bath to dryness. The ^{15}NO-complexes were prepared in a vacuum line by the use of *ca.* 5 mmol of ^{15}NO (^{15}N atom %=95.5—96.8) on the same scale as that used for preparing the ^{14}NO-complexes. The elementary analyses and IR spectra showed that the desired products were obtained. All of these compounds were diamagnetic.

$RhCl(NO_2)_2(PPh_3)_2$: A 6-mmol portion of NO was trapped in a reaction vessel containing 1 mmol of $RhCl(PPh_3)_3$ in 70 ml of chlorobenzene by cooling with liquid nitrogen. Then the solid solution was melted under running water and was allowed to stand for more than 2 days, changing from dark red to yellow through green. The yellow solution was condensed to less than 5 ml by the use of liquid nitrogen to give a yellow product. Yield, 150—300 mg. Found: C, 56.98; H, 3.95; N, 3.71; Cl, 4.82%. Calcd for $RhCl(NO_2)_2(PPh_3)_2$: C, 57.29; H, 3.98; N, 3.71; Cl, 4.70%. χ_g (at 291 K)$=-0.46\times10^{-6}$ (cgs).

Measurements. The magnetic susceptibility was measured by the Gouy method at room temperature. The IR spectra were measured in the region 200—4000 cm^{-1} as Nujol and hexachlorobutadiene mulls using JASCO DS-402 G and JASCO model IR-F infrared spectrophotometers. The reproducibility was about ±0.5 cm^{-1} in the region 200—2400 cm^{-1}. The Raman spectra of the powdered samples were measured in the region 100—700 cm^{-1} on a Narumi 750 Z-1200 double monochrometer equipped with a He-Ne laser.

Results and Discussion

From the comparison of the observed isotopic shifts with the calculated ones, the following rules were established:[1–3] the observed isotopic shift of the N–O stretching vibration for NO$^+$ complex is 36—44 cm^{-1}, while that for the NO$^-$ one is 25—28 cm^{-1}; the metal-NO bending vibration is observed in the region 450—650 cm^{-1}, and its isotopic shift is 10—15 cm^{-1} for both NO$^+$ and NO$^-$ complexes; the metal-NO stretching vibration for the NO$^+$ complex is observed in the region 500—650 cm^{-1}, while that for the NO$^-$ one is seen in the region *ca.* 300 cm^{-1}, and their isotopic shifts are 2—6 cm^{-1}. The bands due to the RhNO group were assigned on this basis.

The wave numbers, isotopic shifts, and assignments of IR and Raman bands for the examined compounds are shown in Table 1.

The N–O stretching vibration of $Rh(NO)(PPh_3)_3$ was observed at 1610 cm^{-1} and shifted downwards by 49 cm^{-1} upon ^{15}NO-substitution. In the region where skeletal vibrations due to metal-NO groups have been usually observed, only a weak absorption band at 410 cm^{-1} shifted downwards by 18 cm^{-1}. This band may be assigned to the Rh–NO bending vibration. Another skeletal vibration, the Rh–NO stretching one, may be considered to overlap with the strong bands due to the coordinated PPh_3 groups. The Raman bands in the region 200—700 cm^{-1} showed no isotopic shifts. The isotopic shift of the N–O stretching vibration supports the view that the oxidation state of the NO group is I, and that of the rhodium atom, −I. The concept of "Stereochemical Control of Valence" will support the view that this compound is not a square planar one with a strongly bent RhNO group but a tetrahedral one with a linear RhNO one, if this compound is a NO$^+$ one,[4]

The N–O stretching vibration of $RhX_2(NO)(PPh_3)_2$ was observed in the region *ca.* 1630 cm^{-1}; the isotopic shift was 28 cm^{-1}. The band at *ca.* 590 cm^{-1} shifted downwards by *ca.* 15 cm^{-1}, and the 339 cm^{-1} band for the bromide shifted downwards by 2 cm^{-1}. The former band can be assigned to the Rh–NO bending vibration, and the latter one to the Rh–NO stretching one. The Rh–NO stretching vibration of the chloride could not be observed because of the overlapping with the strong band due to the Rh–Cl stretching one. The Rh–Cl band was observed as a single band on both IR and Raman spectra. This suggests that the two chloride ions are in a *trans* position to each other in this compound.

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TABLE 1. WAVE NUMBERS, OBSERVED ISOTOPIC SHIFTS, AND ASSIGNMENTS OF IR AND RAMAN BANDS$^{a)}$

Assignments	$Rh(NO)(PPh_3)_3$	$RhCl_2(NO)(PPh_3)_2$	$RhBr_2(NO)(PPh_3)_2$
NO str	1610 vs (49)$^{b)}$	1632 vs (28)	1631 vs (28)
Rh-NO bend	410 w (18)	591 s (15), 598$^{c)}$ (14)	586 s (15)
Rh-P str	450 s	456 s	460 s
Rh-NO str	not obsd.	not obsd.	339 m (2)
Rh-X str		341 vs, 347$^{c)}$	271 vs

Assignments	$RhCl(NO_2)(NO)(PPh_3)_2$	$RhBr(NO_2)(NO)(PPh_3)_2$
NO str	1659 vs (29), 1632 w (28)	1653 vs (28), 1625 w (29)
Rh-NO bend or NO_2 wag	577 m, br (15); 560 s (13)	573 m (17), 554 w (14)
Rh-P str	459 m	459 s
Rh-NO str	341 m (1)	320 m (2)
Rh-X str	318 vs	280 m, br

a) The bands which are characteristic of PPh_3 and the nitro group are eliminated. b) The wave numbers in parentheses indicate the observed isotopic shifts. c) Raman band.

Abbreviations: vs = very strong; s = strong; m = medium; w = weak; br = broad; str = stretching vibration; bend = bending vibration; wag = wagging vibration.

For $RhX(NO_2)(NO)(PPh_3)_2$, two N–O stretching vibrations were observed in the region 1630—1660 cm^{-1}, and these shifted downwards by 28—29 cm^{-1}. The ^{15}N-isotopic shifts of the bands which are characteristic of the nitro group were comparable to those of $[Rh(NO_2)(NH_3)_5]Cl_2$.[9] The two bands observed in the region 550—580 cm^{-1} are considered to be assigned to the wagging vibration of the NO_2 group and the Rh–NO bending vibration. These bands, however, could not be assigned distinctly because their isotopic shifts are almost equal to each other. The 320 cm^{-1} band of the bromide shifted downwards by 2 cm^{-1}, and can be assigned to the Rh–NO stretching vibration. The 341 cm^{-1} band of the chloride is considered to be the Rh–NO stretching vibration. The oxidation state of the NO group for $RhX_2(NO)(PPh_3)_2$ and $RhX(NO_2)(NO)(PPh_3)_2$ is considered to be —I, that of the rhodium atom, III. If these compounds are NO^- ones, the concept of "Stereochemical Control of Valence" will support the view that the geometries of these five-coordinate compounds are tetragonal pyramids with an apical NO^-.[4]

It is established that the metal–NO stretching vibration for the NO^- complex is in the region *ca.* 300 cm^{-1}, as observed for the nitrosylplatinum complexes such as $M_2[PtX_5(NO)]$.[2]

For $RhCl(NO_2)_2(PPh_3)_2$, no absorption bands could be observed in the region where the N–O stretching vibration has been usually observed, but the absorption bands and their ^{15}N-isotopic shifts, which are characteristic of the coordinated nitro group, could be observed in addition to the bands due to PPh_3. The IR bands and the elementary analyses show that this new compound is $RhCl(NO_2)_2(PPh_3)_2$. The reaction of NO with a square-planar d^8 complex of rhodium, such as $RhCl(PPh_3)_3$, has been reported to give a five coordinate derivative, $RhCl(NO_2)(NO)(PPh_3)_2$.[8] It was found from this study that the nitro-nitrosyl compound further reacts with NO to give the dinitro compound, $RhCl(NO_2)_2(PPh_3)_2$. The apical NO^- ion of the nitro-nitrosyl compound is considered to react with NO to give NO_2^- ion and N_2O.

$$RhCl(NO_2)(NO)(PPh_3)_2 + 2NO \longrightarrow RhCl(NO_2)_2(PPh_3)_2 + N_2O.$$

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