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Nitrosyltris(triphenylphosphine)rhodium and Nitrosyltris(triphenylphosphine)cobalt as Nitrosyl Transfer Reagents

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Intermolecular transfer of the nitrosyl ligand in $RhNOP_3$ and $CoNOP_3$ to $NiCl_2P_2$, $CoClP_3$, $CoCl_2P_2$, $Co(dpe)_2(ClO_4)_2$, $FeCl_2dpe$ [$P = PPh_3$; dpe = 1,2-bis(diphenylphosphino)ethane] readily occurs at room temperature. On treating $RhNOP_3$ with trityl and silver perchlorate, the cationic species $[RhP_3(Me_2CO)]^+$ and $[Rh(NO)_2P_2]^+$ have been obtained. IR spectroscopic evidence of the formation of a nitrosyl bridge is cited.

Introduction

Very few studies have been devoted to the reactions of intermolecular transfer of the coordinated nitrosyl group compared to the large number of studies reported on intermolecular transfer of other coordinated ligands, such as halides or alkyls.

Armor [1] reported that the black cobalt nitrosyl $[Co(NH_3)_5NO]Cl_2$ does serve as an effective nitrosylating agent of Fe^{2+} and Cr^{2+}, and very recently Caulton [2] reported transfer reactions of the nitrosyl ligand in nitrosylbis(dimethylglyoximato)cobalt to several halo- and hydrido-complexes of iron, ruthenium, cobalt, rhodium and nickel. We report here the results of a study of reactions involving intermolecular transfer of the nitrosyl ligand in $Co(NO)(PPh_3)_3$ and in $Rh(NO)(PPh_3)_3$.

Experimental

All operations were carried out under pure nitrogen using Schlenk-tube techniques. The solvents were of reagent grade quality and were dried, distilled and stored under nitrogen.

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer.

Reactions of $Rh(NO)(PPh_3)_3$ (I)

With $NiCl_2(PPh_3)_2$

$Rh(NO)(PPh_3)_3$ [3] (0.502 g, 0.55 mmol) and $NiCl_2(PPh_3)_2$ [4] (0.355 g, 0.54 mmol) were dissolved in 10 ml of a 1:1 benzene–acetone mixture at 50 °C. After 2 hours the solution was cooled at 20 °C and the red-brown crystals which formed were filtered, washed with a 1:1 benzene–acetone mixture and characterized by IR spectroscopy and elemental analysis as $RhCl(PPh_3)_3$. Found: Cl, 3.9; P, 9.9. $C_{54}H_{45}ClP_3Rh$ requires: Cl, 3.8; P, 10.0.

The volume of the filtrate was reduced to 4 ml and the dark blue crystals which formed were separated by filtration, 0.28 g (80% yield), and characterized by IR (ν_{NO} = 1730 cm^{-1} in Nujol), m.p. and elemental analysis as $NiCl(NO)(PPh_3)_2$ [5]. Found: Cl, 5.3; P, 9.2; Ni, 8.8. $C_{36}H_{30}ClNOP_2Ni$ requires: Cl, 5.5; P, 9.5; Ni, 9.0.

With $CoCl_2(PPh_3)_2$

$CoCl_2(PPh_3)_2$ (0.353 g, 0.54 mmol) and *I* (0.496 g, 0.54 mmol) were stirred in 10 ml of THF for 4 hours at room temperature. The IR spectrum in Nujol of the dark green solid produced upon vacuum drying the solution showed only two strong absorption bands at 1845 and 1790 cm^{-1}, characteristic of $CoCl(NO)_2(PPh_3)_2$, in equilibrium with $[Co(NO)_2(PPh_3)_2]Cl$ [6]. Some $RhCl(PPh_3)_3$ was obtained from the benzene extract of the dry solid and characterized by its IR spectrum and m.p.

With $CoCl(PPh_3)_3$

$CoCl(PPh_3)_3$ [7] (0.479 g, 0.54 mmol) and *I* (0.500 g, 0.54 mmol) were stirred in 6 ml of benzene at room temperature. After 2 hours, the IR spectrum of the solution showed a new nitrosyl stretch at 1640 cm^{-1}, characteristic of $Co(NO)(PPh_3)_3$ [6a], and a band of reduced intensity at 1610 cm^{-1}, due to the residual $Rh(NO)(PPh_3)_3$.

With $[Co(dpe)_2](ClO_4)_2$

$[Co(dpe)_2](ClO_4)_2$ [8] (0.685 g, 0.65 mmol) and *I* (0.597 g, 0.65 mmol) were stirred in 10 ml of a 1:1 benzene–acetone mixture for 10 hours at room

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temperature. Dark brown crystals slowly separated from the filtered solution upon standing and were characterized by IR (ν_{NO} = 1805 and 1855 cm^{-1} in Nujol) and elemental analysis as $[Co(NO)_2(dpe)]ClO_4 \cdot C_6H_6$. Found: C, 57.4; H, 4.2; Cl, 5.1; P, 8.9; Co, 8.2. $C_{32}H_{30}ClN_2O_6P_2Co$ requires: C, 55.3; H, 4.4; Cl, 5.1; P, 8.9; Co, 8.5.

With $FeCl_2dp$

i) $FeCl_2dp$ [2] (0.285 g, 0.54 mmol) and *I* (0.500 g, 0.54 mmol) were stirred in 10 ml of a 1:1 benzene–acetone mixture for 18 hours at room temperature. The filtrate from the unreacted $FeCl_2dp$, slowly produced thin green crystals in very low yields.

The IR spectrum in Nujol of the product, which is very sensitive to air and humidity, showed a strong absorption band at 1800 cm^{-1}. No successful purification of this solid was achieved.

ii) $FeCl_2dp$ (0.200 g, 0.38 mmol) and *I* (0.350 g, 0.38 mmol) were stirred in 10 ml of THF for 14 hours at room temperature. The IR spectrum (Nujol) of the solid obtained upon vacuum drying the mixture showed absorption bands at 1710, 1670, 1610 and 1585 cm^{-1}.

Addition of methanol to the benzene extract of the solid produced brown crystals of $Fe(NO)_2dp$ [9], characterized by IR (ν_{NO} = 1710 and 1670 cm^{-1} in Nujol). The IR spectrum in Nujol of the residue insoluble in benzene showed an absorption band at 1610 cm^{-1}, but no successful purification of this product was achieved.

With $[Ph_3C]ClO_4$

To 0.921 g (1 mmol) of *I* in 10 ml of acetone at room temperature was added 0.320 g (0.97 mmol) of $[Ph_3C]ClO_4$.

The solution color changes in a few minutes from an initial deep red to dark red-brown. Upon standing for several days a small amount of orange crystals formed. The filtered product was characterized by IR (ν_{CO} = 1715 and 1670 cm^{-1} in Nujol) and elemental analysis as $[Rh(CH_3COCH_3)(PPh_3)_3]ClO_4 \cdot CH_3COCH_3$ [10].

Anal. Calcd for $C_{60}H_{57}ClO_6P_3Rh$: C, 65.2; H, 5.2; Cl, 3.2; P, 8.4. Found: C, 64.5; H, 5.0; Cl, 3.1; P, 8.2.

Addition of pentane to the filtrate produced a crystalline solid which exhibited an IR spectrum characteristic of a mixture of the above compound and $[Rh(NO)_2(PPh_3)_2]ClO_4$.

Careful recrystallization from dichloromethane/ethanol produced black crystals, characterized by IR (ν_{NO} = 1765 and 1715 cm^{-1} in Nujol) and elemental analysis as $[Rh(NO)_2(PPh_3)_2]ClO_4$ [11].

Found: Cl, 4.6; P, 7.7. $C_{36}H_{30}ClN_2O_6P_2Rh$ requires: Cl, 4.5; P, 7.9.

With $[Rh(PPh_3)_3]ClO_4 \cdot CH_2Cl_2$

To 0.230 g (0.25 mmol) of *I* in 5 ml of dichloromethane was added 0.270 g (0.25 mmol) of $[Rh(PPh_3)_3]ClO_4 \cdot CH_2Cl_2$ [12] at room temperature. After 10 minutes the IR spectrum of the solution showed a strong absorption band at 1520 cm^{-1}, while the absorption band at 1615 cm^{-1} of the starting nitrosyl completely disappeared. The IR spectrum of the brown solid, produced upon removing under vacuum the solvent, showed only one absorption band at 1520 cm^{-1}, ascribable to the coordinate nitrosyl.

With $AgClO_4$

i) To 0.496 g (0.54 mmol) of *I* in 8 ml of benzene at room temperature was added 0.056 g (0.27 mmol) of $AgClO_4$ dissolved in 2 ml of benzene. After a few minutes a silver mirror and a green precipitate formed. This product was extracted from the metallic silver with acetone, the solution was filtered and the filtrate taken to dryness. The IR spectrum (Nujol) of the residual solid showed a strong absorption band at 1530 cm^{-1}.

ii) To 0.650 g (0.69 mmol) of *I* in 10 ml of benzene at room temperature was added 0.290 g (1.40 mmol) of $AgClO_4$. The solid precipitated was shown by IR spectroscopy to consist of $[Rh(NO)_2(PPh_3)_2]ClO_4$ (ν_{NO} = 1765 and 1715 cm^{-1}) and metallic silver.

Reactions of $Co(NO)(PPh_3)_3$ *(II)*

With $NiCl_2(PPh_3)_2$

$Co(NO)(PPh_3)_3$ [6a] (0.500 g, 0.57 mmol) and $NiCl_2(PPh_3)_2$ (0.375 mmol) were dissolved in 10 ml of a 1:1 benzene–acetone mixture at 50 °C. After one hour the volume was reduced to 5 ml and the dark blue crystals were separated by filtration and characterized by IR as $NiCl(NO)(PPh_3)_2$. The filtrate was taken to dryness and the residual solid exhibited an IR spectrum characteristic of a mixture of $NiCl(NO)(PPh_3)_2$ and $CoCl(PPh_3)_3$, along with a small amount of *II*.

With $[Ph_3C]ClO_4$

To 0.500 g (0.57 mmol) of *II* in 10 ml of acetone at room temperature was added 0.196 g (0.57 mmol) of $[Ph_3C]ClO_4$. The volume of the solution was reduced to 4 ml, and upon standing, dark brown crystals formed. The filtered product was characterized by IR (ν_{NO} = 1793 and 1845 cm^{-1} in Nujol) and elemental analysis as $[Co(NO)_2(PPh_3)_2]ClO_4$ [6a]. Found: Cl, 5.0; P, 8.2; Co, 7.8. $C_{36}H_{30}ClN_2O_6P_2Co$ requires: Cl, 4.8; P, 8.3; Co, 7.9. No successful separation of the components of the residual solid produced by taking to dryness the filtrate was achieved.

Results and Discussion

Intermolecular transfer of the linearly bound [13] nitrosyl ligand in the four-coordinate, 18-electron complexes of rhodium and cobalt (*I* and *II*) to coordinatively unsaturated complexes of transition metals occurs very readily. With $\mathrm{NiCl_2(PPh_3)_2}$ and $\mathrm{CoCl(PPh_3)_3}$ the reaction occurs with NO/Cl interchange (eq. 1 and 2):

$$\mathrm{MNOP_3 + NiCl_2P_2 = MClP_3 + NiCl(NO)P_2} \tag{1}$$
$$(\mathrm{M = Rh, Co})$$

$$\mathrm{RhNOP_3 + CoClP_3 \rightleftharpoons Co(NO)P_3 + RhClP_3} \tag{2}$$

The rhodium nitrosyl readily reacts with $\mathrm{CoCl_2(PPh_3)_2}$ and with $\mathrm{[Co(dpe)_2](ClO_4)_2}$ to give cobalt complexes containing the $\mathrm{Co(NO)_2^+}$ moiety, and with $\mathrm{FeCl_2dpe}$ to give $\mathrm{Fe(NO)_2dpe}$ (eq. 3 and 4):

$$\mathrm{2RhNOP_3 + 2[Co(dpe)_2]^{2+} = [Co(NO)_2dpe]^+ + [Co(dpe)_2]^+ + 2[RhP_3]^+ + dpe} \tag{3}$$

$$\mathrm{2RhNOP_3 + FeCl_2dpe = Fe(NO)_2dpe + 2RhClP_3} \tag{4}$$

This latter reaction occurs with the formation of an iron–nitrosyl intermediate, which we were not able to purify. Its IR spectrum shows an absorption band at 1800 $\mathrm{cm^{-1}}$, and we tentatively assign this compound the formula Fe(NO)Cl(dpe).

Although the NO group in *I* and *II* is linearly coordinated, the great electron back-donation into NO π^* orbitals, as shown by the low value of the NO IR stretch in these compounds, makes the bound nitrosyl susceptible to electrophilic attack. Therefore the above reactions most likely occur through the formation of an intermediate bridging nitrosyl $\mathrm{M(\mu\text{-}NO)M'}$, which may react according to the equations 5 to 6:

$$\mathrm{M(\mu\text{-}NO)M' = M + M'(NO)} \tag{5}$$
$$\mathrm{M(\mu\text{-}NO)M' = M^+ + |M'(NO)|^-} \tag{6}$$
$$\mathrm{M(\mu\text{-}NO)M' = M^- + |M'(NO)|^+} \tag{7}$$

Compounds *I* and *II* are fairly strong reducing agents. For instance, the rhodium nitrosyl is rapidly and quantitatively oxidized at room temperature by $\mathrm{CoClD_2(PPh_3)}$ (D = dimethylglyoximate) to give $\mathrm{RhNOCl_2(PPh_3)_2}$ [2] (eq. 8):

$$\mathrm{RhNOP_3 + 2CoClD_2P = RhNOCl_2P_2 + 2CoD_2P + P} \tag{8}$$

Therefore, the first step of the NO transfer from the rhodium–nitrosyl to the 15-electron complexes of cobalt, $\mathrm{CoCl_2P_2}$ and $\mathrm{[Co(dpe)_2]^{2+}}$, may occur through reaction [6] and not through reaction [5] or [7], which would give both the very strong reducing agents $\mathrm{Rh(PPh_3)_3}$ or $\mathrm{|Rh(PPh_3)_3|^-}$ and the fairly oxidizing species $\mathrm{Co(NO)Cl_2P_2}$ or $\mathrm{[Co(NO)(dpe)_2]^{2+}}$. Besidè $\mathrm{[Rh(PPh_3)_3]^+}$, the intermediates in this reaction should be the paramagnetic species $\mathrm{[CoCl_2(NO)P_2]^-}$ and $\mathrm{[Co(NO)(dpe)_2]^+}$, which have electronic configurations analogous to that of $\mathrm{RhCl(NO)P_3}$, the intermediate of reaction [8]. These 19-electron complexes can lose a ligand ($\mathrm{Cl^-}$ or P) to give the 17-electron species $\mathrm{CoClNOP_2}$, $\mathrm{[Co(NO)(dpe)P]^+}$ and $\mathrm{RhCl(NO)P_2}$ before undergoing the second step of the transfer reactions. Strong support for this mechanism comes from the results of the reactions of the nitrosyl complexes *I* and *II* with mild oxidizing agents such as trityl or silver perchlorate. The trityl perchlorate readily reacts at room temperature with an equimolar amount of *I* (or *II*) in benzene/acetone to give $\mathrm{[Rh(NO)_2P_2]ClO_4}$ and $\mathrm{[RhP_3(Me_2CO)]ClO_4}$ (eq. 9):

$$\mathrm{2MNOP_3 + 2Ph_3C^+ \xrightarrow{S} [M(NO)_2P_2]^+ + [MP_3S]^+ + 2Ph_3C\cdot} \tag{9}$$

S = solvent

In the case of the rhodium complex we were able to isolate and characterize both products of the reaction, while in the case of cobalt complex we could characterize only the dinitrosyl cation. The rhodium–nitrosyl complex *I* reacts with an excess of silver perchlorate to give the same cationic complexes shown in eq. 9, beside metallic silver. When the reaction is carried out whith the molar ratio Rh/Ag of 1 to 0.5, an intermediate nitrosyl complex, not yet fully characterized, is obtained. A strong absorption band at 1530 $\mathrm{cm^{-1}}$ (Nujol), shown by its IR spectrum, strongly support the presence of a bridging nitrosyl group in this product. This result suggests that the $\mathrm{[Rh(NO)(PPh_3)_3]^+}$ species produced by oxidation of *I* rapidly reacts whith *I* itself to give a stable bridging nitrosyl intermediate $\mathrm{[Rh(\mu\text{-}NO)Rh(NO)]^+}$, which by further oxidation gives the final products $\mathrm{[Rh(NO)_2]^+}$ and $\mathrm{[Rh]^+}$.

Moreover, the rapid disappearance of the nitrosyl stretching frequency at 1610 $\mathrm{cm^{-1}}$ and the concomitant appearance of a new absorption band at 1520 $\mathrm{cm^{-1}}$ on treating *I* with $\mathrm{[Rh(PPh_3)_3]ClO_4}$ in $\mathrm{CH_2Cl_2}$ clearly shows that the nitrosyl ligand in *I* readily undergoes electrophilic attack by coordinatively unsaturated nuclear species to give stable binuclear species containing a nitrosyl bridge.

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