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## RHODIUM AND IRIIDIUM COMPLEXES CONTAINING NITROSOARENE LIGANDS

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### Summary

A number of new nitrosoarene complexes of rhodium(I) and iridium(I) have been prepared, and characterized by elemental analysis, IR spectroscopy and  $^1\text{H}$  NMR spectroscopy. Some reactions of the complexes have been studied.

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### Introduction

Transition metal complexes containing nitrosoarene ligands are relatively few in number. Although the  $(\text{C}_6\text{H}_5\text{NO})\text{Fe}(\text{CN})_5^{3-}$  anion has been long known [1], only a few substituted nitrosoarene complexes of iron [2], manganese, nickel, cobalt, copper [3] and palladium [4] have been described. The structure of one such complex *trans*- $\text{PdCl}_2(\text{C}_6\text{H}_5\text{NO})_2$ , was determined over a decade ago by X-ray crystallography [5]. It is known that nitrosoarenes are useful in organic synthesis because of their value as nitrene precursors, as is the case for organic azides and isocyanates [6]. Nitrene complexes have been postulated as intermediates in the metal-catalysed reactions of nitrobenzene [7].

In a programme of work on the reduction of nitro compounds [8] and on nitrosyl transfer reactions [9], we have synthesized a series of nitrosoarene complexes (suggested to be intermediates in such reactions) in order to study their reactions with carbon monoxide and tertiary phosphines and to examine the possibility of obtaining nitrene intermediates from them.

We describe below our results for rhodium(I) and iridium(I) nitrosoarene complexes.

### Results and discussion

Nitrosobenzene is a very weak base and therefore the arenenitroso complexes of metals, such as copper, cobalt and nickel, have previously been isolated only for derivatives for which the donor strength of the nitroso group was increased by a

strongly electron-donating *para*-substituent [10]. We have found that the donor properties of nitrosoarenes are sufficient to lead to cleavage of bridging chlorine in complexes of the type  $[MX(\text{diene})]_2$  ( $M = \text{Rh, Ir; X} = \text{Cl}$ ; diene = cyclooctadiene (COD), norbornadiene (NBD)) to give stable complexes. Thus complexes of formula  $MX(\text{diene})(\text{RC}_6\text{H}_4\text{NO})$  ( $M = \text{Rh, Ir; R} = \text{H, } p\text{-CH}_3, p\text{-Me}_2\text{N, } p\text{-Br, } p\text{-NO}_2$ ) were obtained when  $[MX(\text{diene})]_2$  was treated with acetone solutions of the nitroso compounds  $\text{RC}_6\text{H}_4\text{NO}$ . The complexes are soluble in acetone, benzene, chloroform, insoluble in hexane.

In contrast, the dimeric  $[\text{RhCl}(\text{COT})_2]_2$  (COT = cyclooctene) reacted with nitrosobenzene to give a product of formula  $\text{Rh}_2\text{Cl}_2(\text{COT})_3(\text{C}_6\text{H}_5\text{NO})$ . This compound is insoluble in most organic solvents and only slightly soluble in dichloromethane.

Nitrosoarene ligand could coordinate in four different ways: (a) Side-on [11] as is the case of  $M(\text{PhNO})\text{L}_2$  ( $M = \text{Pd, Pt and Ni; L} = \text{PPh}_3, t\text{-BuNC}$ ). In these complexes the N–O bond order is about 1, as evidenced from the lowering of the  $\nu(\text{N–O})$  frequency at  $973\text{--}1043\text{ cm}^{-1}$ .

(b) Through both nitrogen and oxygen atoms. There are cases in which the nitroso group bridges two metal atoms, e.g.  $[(\text{C}_6\text{H}_5\text{NO})\text{Fe}(\text{CO})_3]_2$  and  $\text{Pd}_3(\text{PhNO})_3$  as characterized by X-ray crystallography; in these complexes the  $\nu(\text{N–O})$  band appears at about  $1040\text{ cm}^{-1}$  [12].

(c) End-on through the nitrogen atom, as in the case of *trans*- $\text{PdCl}_2(\text{PhNO})_2$  whose structure was determined by X-ray crystallography [5], for this complex the  $\nu(\text{N=O})$  band appears at  $1498\text{ cm}^{-1}$ .

(d) End-on through the oxygen atom, as is the case of  $\text{CuO}_2(p\text{-MeNHC}_6\text{H}_4\text{NO})_2$  and  $\text{Ni}(\text{NO}_3)_2(p\text{-NH}_2\text{C}_6\text{H}_4\text{NO})_2$  complexes; in these the  $\nu(\text{N=O})$  band appears at about  $1500\text{ cm}^{-1}$ .

Coordination through the oxygen atom proposed on the basis of the NMR and IR spectra [10]. Because of the absence of absorption bands in the range  $950\text{--}1050\text{ cm}^{-1}$  in the IR spectra of the complexes we prepared, it is possible to rule out bonding of the nitrosoarene in the a or b mode. The presence of absorption bands in the range  $1450\text{--}1510\text{ cm}^{-1}$  indicate that these ligands coordinate end-on, but it is not possible from the IR spectra to decide whether the coordination is through the N or O atom.

## Reactivity

The reactions of nitrosoarene have been intensively investigated. In summary, the nitroso arene react (1) with deoxygenating compounds such as carbon monoxide or tertiary phosphines to give nitrene species which can then give amines, isocyanates, ureas or azoxybenzenes depending on the reaction conditions [13];

(2) with conjugated dienes in a Diels–Alder reaction to give oxazines [14];

(3) with alkenes to give oxazetidines [15].

The reactions of nitrosoarene coordinated to transition metals have been little studied. Otsuka has reported some reactions of the coordinated nitrosoarene with tertiary phosphines and with isocyanides [11], and Cenini has reported the reaction of the coordinated nitrosoarene with carbon monoxide [16]. We have examined the reactions of our complexes with tertiary phosphines, carbon monoxide and dioxygen.

TABLE 1  
REACTIONS OF  $MCl(\text{diene})(C_6H_5NO)$  WITH CO

| Complex (mmol)                         | $PhNH_2$ (mmol) | $CO_2$ (mmol) |
|----------------------------------------|-----------------|---------------|
| $RhCl(COD)(C_6H_5NO)$ (0.5)            | 0.46            | 0.47          |
| $RhCl(NBD)(C_6H_5NO)$ (0.5)            | 0.47            | 0.51          |
| $IrCl(COD)(C_6H_5NO)$ (0.4)            | 0.37            | 0.38          |
| $RhCl(COD)(C_6H_5NO)$ (0.2)            | 0.19            | 0.2           |
| $RhCl(COD)(p\text{-}BrC_6H_5NO)$ (0.1) | 0.09            | 0.1           |

Reaction with  $PPh_3$  results in displacement of the nitroso ligand. For example, the reaction of  $RhCl(COD)(PhNO)$  with a stoichiometric amount of  $PPh_3$  at room temperature gives the well known  $RhCl(COD)(PPh_3)$  and free nitrosobenzene. Under these conditions only a trace of the phosphine oxide was found, the amount increasing with increasing temperature. The nitrosoarene complexes do not react with dioxygen even in boiling benzene for 12 h. They do react with carbon monoxide to give anilines or azoxybenzenes. The reactions are shown to proceed through nitrene intermediates by the following results: (1) Heating the nitrosobenzene complexes of Rh or Ir under carbon monoxide at atmospheric pressure in ethanol [19] gives aniline and carbon dioxide in stoichiometric quantity (see Table 1); (2) Similarly in the presence of free  $PhNO$ , azoxybenzene and  $CO_2$  were quantitatively formed. (When  $PhNO$  reacts with carbon monoxide in the absence of the Rh or Ir complex the yields of azoxybenzene are very low.)

The formation of azoxybenzene can be interpreted in terms of the formation of a nitrene species which reacts further with the  $PhNO$  present according to eq. 1–3.



The formation of aniline can be attributed to the reaction of the nitrene species with the protic solvent.

## Experimental

The reactions were carried out under nitrogen. All solvents were reagent grade and were distilled and stored under nitrogen. Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer; proton NMR spectra of the complexes and ligands were recorded on a Varian XL-200 spectrometer. GLC measurements were carried out on a Varian 6000 gas chromatograph using a 1.5 m column SP-2250, and biphenyl as internal standard. Determination of  $CO_2$  by GLC were carried out on Porapak Q column using a Carlo Erba Fractovap C connected to Hewlett–Packard 3380 A integrator.  $[RhCl(COD)]_2$ ,  $[RhCl(NBD)]_2$ ,  $[IrCl(COD)]_2$ ,  $[RhCl(COT)]_2$ ,  $p\text{-}XC_6H_4NO$  ( $X = Me_2N$ , Me, H,  $NO_2$ , Br) were prepared by known methods [17,18].

### Preparation of complexes

All complexes were prepared as follows. A suspension of  $\text{RC}_6\text{H}_4\text{NO}$  and  $[\text{MCl}(\text{diene})]_2$  in 1/1 molar ratio in acetone was stirred for 2 h at room temperature. The solution was filtered, concentrated and stored at  $-30^\circ\text{C}$ . The microcrystals formed were filtered off, washed with cold acetone, and dried.

*RhCl(COD)(C<sub>6</sub>H<sub>5</sub>NO)*. Violet crystals (yield 80%). Decomposition point above  $122^\circ\text{C}$ . Anal. Found: C, 46.54; H, 4.71; N, 3.76; Cl, 10.5.  $\text{C}_{14}\text{H}_{17}\text{NOCIRh}$  calcd.: C, 47.5; H, 5.2; N, 3.96; Cl, 10.0%. IR (in Nujol): 1600s, 1480s, 1410s, 1335w, 1185w, 1125vs, 1000w, 880w, 850s, 780m  $\text{cm}^{-1}$ .

*RhCl(NBD)(C<sub>6</sub>H<sub>5</sub>NO)*. Violet crystals (yield 60%). Decomposition above  $94^\circ\text{C}$ . Anal. Found: C, 45.9; H, 4.6; N, 3.9; Cl, 10.3.  $\text{C}_{13}\text{H}_{13}\text{NOCIRh}$  calcd.: C, 46.24; H, 3.85; N, 4.15; Cl, 10.5%. IR (in Nujol): 1589s, 1483sh, 1410vs, 1312m, 1183m, 1130vs, 870s, 772m  $\text{cm}^{-1}$ .

*IrCl(COD)(PhNO)*. Violet crystals (yield 55%). Decomposition above  $120^\circ\text{C}$ . Anal. Found: C, 38.3; H, 3.71; N, 3.4; Cl, 8.1.  $\text{C}_{14}\text{H}_{17}\text{NOCIIr}$  calcd.: C, 37.95; H, 3.85; N, 3.15; Cl, 8.0%. IR: 1585s, 1470sh, 1380vs, 1125vs, 870vs, 775m  $\text{cm}^{-1}$ .

*RhCl(COD)(p-BrC<sub>6</sub>H<sub>4</sub>NO)*. Violet crystals (yield 70%). Decomposition above  $133^\circ\text{C}$ . Anal. Found: C, 38.1; H, 3.6; N, 3.1; Cl, 8.0; Br, 18.9.  $\text{C}_{14}\text{H}_{16}\text{NOCIBrRh}$  calcd.: C, 38.8; H, 3.7; N, 3.23; Cl, 8.20; Br, 19.00%. IR: 1565s, 1460sh, 1425s, 1115vs, 1060m, 1000w, 850s  $\text{cm}^{-1}$ . Proton NMR: 7.9(d), 4.1(br), 1.8(br), 2.25(s) ppm.

*RhCl(NBD)(p-BrC<sub>6</sub>H<sub>4</sub>NO)*. Violet microcrystals (yield 62%). Decomposition above  $125^\circ\text{C}$ . Anal. Found: C, 37.3; H, 2.7; N, 3.4; Cl, 8.40; Br, 19.1.  $\text{C}_{13}\text{H}_{12}\text{NOCIBrRh}$  calcd.: C, 37.47; H, 2.88; N, 3.36; Cl, 8.51; Br, 19.9%. IR: 1565vs, 1473vs, 1432vs, 1422vs, 1300s, 1175m, 1125vs, 1060s, 1000m, 865vs, 840m  $\text{cm}^{-1}$ . Proton NMR: 8.1(d), 4.1(br), 3.9(br); 1.22(s) ppm.

*IrCl(COD)(p-BrC<sub>6</sub>H<sub>4</sub>NO)*. Violet crystals (yield 63%). Decomposition above  $137^\circ\text{C}$ . Anal. Found: C, 31.2; H, 3.2; N, 2.5; Cl, 6.5; Br, 14.6.  $\text{C}_{14}\text{H}_{16}\text{NOCIBrIr}$  calcd.: C, 32.21; H, 3.06; N, 2.68; Cl, 6.78; Br, 15.2%. IR: 1575s, 1475s, 1420s, 1125vs, 869s  $\text{cm}^{-1}$ .

*RhCl(COD)(p-MeC<sub>6</sub>H<sub>4</sub>NO)*. Violet crystals (yield 75%). Decomposition  $123\text{--}125^\circ\text{C}$ . Anal. Found: C, 48.8; H, 5.3; N, 3.7; Cl, 10.1.  $\text{C}_{15}\text{H}_{19}\text{NOCIRh}$  calcd.: C, 49.8; H, 5.2; N, 3.80; Cl, 9.8%. IR: 1595s, 1465sh, 1455s, 1420m, 1195w, 1135s, 882m, 855m  $\text{cm}^{-1}$ . Proton NMR: 7.5(br), 4.22(br), 3.5(br), 2.5(m), 1.9(m), 2.5(s) ppm.

*RhCl(NBD)(p-MeC<sub>6</sub>H<sub>4</sub>NO)*. Violet crystals (yield 80%). Decomposition above  $100^\circ\text{C}$ . Anal. Found: C, 48.1; H, 4.1; N, 3.80; Cl, 10.6.  $\text{C}_{14}\text{H}_{15}\text{NOCIRh}$  calcd.: C, 47.8; H, 4.26; N, 3.98; Cl, 10.1%. IR: 1598s, 1497 w, 1425s, 1308s, 1195m, 1135vs, 1121m, 871s ppm.

*RhCl(COD)(p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NO)*. Red crystals (yield 68%). Decomposition above  $150^\circ\text{C}$ . Anal. Found: C, 47.99; H, 5.6; N, 7.1; Cl, 8.8.  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{OCIRh}$  calcd.: C, 48.44; H, 5.55; N, 7.06; Cl, 8.94%. IR: 1600vs, 1535s, 1462s, 1372m, 1340vs, 1310s, 1250s, 1145vs, 855w, 835m, 740m  $\text{cm}^{-1}$ . Proton NMR: 6.9(br), 4.66(m), 3.4(m), 2.4(m), 1.86(m), 3.26(s) ppm.

*RhCl(NBD)(p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NO)*. Reddish crystals (yield 72%). Decomposition above  $181^\circ\text{C}$ . Anal. Found: C, 47.05; H, 4.8; N, 7.42; Cl, 9.2.  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{OCIRh}$  calcd.: C, 47.29; H, 4.73; N, 7.36; Cl, 9.31%. IR: 1600vs, 1550m, 1335s, 1300s, 1255s, 1150vs, 1120vs, 1070w, 935w, 875w, 835m, 740m  $\text{cm}^{-1}$ .

TABLE 2  
REACTIONS BETWEEN PhNO AND CO IN THE PRESENCE OF A Rh OR Ir CATALYST<sup>a</sup>

| Catalyst                                    | Azoxybenzene (mmol) <sup>b</sup> |
|---------------------------------------------|----------------------------------|
| RhCl(COD)(C <sub>6</sub> H <sub>5</sub> NO) | 0.9                              |
| RhCl(NBD)(C <sub>6</sub> H <sub>5</sub> NO) | 0.89                             |
| IrCl(COD)(C <sub>6</sub> H <sub>5</sub> NO) | 0.9                              |

<sup>a</sup> Reactions were carried out with 2 mmol of PhNO, 0.1 mmol of catalyst, and 10 ml of ethanol. <sup>b</sup> After 4 h at 70 °C.

*IrCl(COD)(p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NO)*. Red crystals (yield 54%). Decomposition above 140 °C. Anal. Found: C, 39.1; H, 4.61; N, 5.8; Cl, 7.3. C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>OClIr calcd.: C, 39.53; H, 4.53; N, 5.76; Cl, 7.2%. IR: 1595vs, 1532w, 1450s, 1370s, 1335s, 1305s, 1250s, 1140vs, 875m, 835m, 735m cm<sup>-1</sup>.

*RhCl(COD)(p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO)*. Marron powder (yield 30%). IR: 1590m, 1520vs, 1450sh, 1350vs, 1110s, 865m, 755w cm<sup>-1</sup>.

*Rh<sub>2</sub>Cl<sub>2</sub>(COT)<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>NO)* (COT = Cyclooctene). Dark maroon microcrystals. Decomposition above 145 °C (yield 55%). Anal. Found: C, 49.9; H, 6.5; N, 2.0; Cl, 10.1. C<sub>30</sub>H<sub>47</sub>NOCIRh<sub>2</sub> calcd.: C, 50.7; H, 6.6; N, 1.97; Cl, 10.47%. IR: 1590s, 1455vs, 1375m, 1340w, 1125vs, 878s ppm.

#### Reactions of complexes with PPh<sub>3</sub>

The procedure is exemplified by the reaction of RhCl(COD)(C<sub>6</sub>H<sub>5</sub>NO). A solution of this complex, (100 mg, 0.28 mmol) and PPh<sub>3</sub> (75 mg, 0.28 mmol) in benzene (10 ml) was stirred at room temperature for 2 h. The yellow orange RhCl(COD)(PPh<sub>3</sub>) was precipitated by adding hexane to the concentrated solution. The PhNO in the solution was determined by GLC.

#### Reactions with carbon monoxide

All reactions were carried out in a 100 ml glass-vessel reactor provided with a thermostated jacket. (a) In a typical experiment the nitrosoarene complex was dissolved in 10 ml of ethanol under carbon monoxide at atmospheric pressure and the solution was stirred at 70 °C for 4 h. After this time the CO<sub>2</sub> produced was determined by GLC and the reaction mixture was analysed by GLC (see Table 1). (b) In a typical experiment 2 mmol of PhNO and 0.1 mmol of the nitrosoarene complex were dissolved in 10 ml of ethanol under carbon monoxide at atmospheric pressure. The solution was stirred at 70 °C for 4 h. After this time the mixture was analysed by GLC (see Table 2).

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- 19 Reactions in aprotic solvent are under investigation.