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## CATALYTIC REDUCTION OF NITROSOBENZENE BY CARBON MONOXIDE USING NITROSOBENZENE COMPLEXES OF TRANSITION METALS

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### Summary

New nitrosoarene complexes of ruthenium(II), palladium(II), platinum(II) and rhodium(I) have been synthesized. Their reactions with carbon monoxide have been studied in the solid state and in ethanol suspension. The results suggest formation of a nitrene intermediate. The catalytic reduction of nitrosobenzene has been also studied; azoxybenzene and urethane are the main products in ethanol whereas azoxybenzene, phenyl isocyanate and diphenyl urea are obtained in benzene. Increase in the temperature and the carbon monoxide pressure results in increase of the yields of the carbonylated products.

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### Introduction

Nitrosoarenes are of considerable interest to chemists both because of their interesting coordination modes (side-on [1], end-on [2]) and for their potential as nitrene precursors [3] and their reactions have been extensively investigated. In contrast, the chemistry of the nitrosoarenes bonded to transition metals has been little studied and there are few examples of such complexes of transition metals, although some complexes of Fe, Co, Ni, Pd, and Pt were made some years ago [4]. Recently we reported the synthesis of some rhodium(I) and iridium(I) nitrosoarene complexes and described their reactions with carbon monoxide [5]. As a continuation of our investigation, we have extended the studies to complexes of other metals and we now report on the synthesis and the reactions of new nitrosoarene complexes of ruthenium(II), palladium(II), platinum(II) and rhodium(I).

### Results and discussion

In an earlier paper [5] we showed that the donor properties of nitrosoarene are sufficient to cleave the bridging chlorine in the  $[MCl(\text{diene})]_2$  complexes ( $M = Rh$ ,

Ir; diene = cyclooctadiene, norbornadiene), so that the corresponding nitrosoarene complexes were obtained. This procedure has now been followed to make the nitrosoarene complexes of ruthenium(II). Thus, reaction of  $[\text{RuCl}_2(\text{COD})]_n$  (COD = cyclooctadiene) with  $\text{C}_6\text{H}_5\text{NO}$  in a 1/2 molar ratio in acetone solution at room temperature gave the nitrosoareneruthenium(II) complex of formula  $\text{RuCl}_2(\text{COD})(\text{C}_6\text{H}_5\text{NO})_2$ . In an alternative procedure nitrosoareneruthenium(II) complexes were also prepared by replacement of the coordinated solvent molecules in appropriate complexes. Thus,  $\text{RuCl}_2(\text{DMSO})_2(p\text{-RC}_6\text{H}_4\text{NO})_2$  complexes (DMSO = dimethylsulfoxide; R = H, Br, Me,  $\text{N}(\text{Me})_2$ ) were synthesized by reaction of  $\text{RuCl}_2(\text{DMSO})_4$  with  $p\text{-RC}_6\text{H}_4\text{NO}$  in 1/2 molar ratio.

Similarly a new series of palladium(II) and platinum(II) complexes of formula  $\text{PdCl}_2\text{L}_2$  (L = 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{NO}$ ; 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NO}$ ;  $p\text{-MeC}_6\text{H}_4\text{NO}$ ;  $p\text{-BrC}_6\text{H}_4\text{NO}$ ) and  $\text{PtCl}_2(p\text{-MeC}_6\text{H}_4\text{NO})_2$  was prepared by replacing the  $\text{C}_6\text{H}_5\text{CN}$  ligand in  $\text{MCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  complexes. Finally, an interesting rhodium(I) complex of formula  $\text{RhCl}(\text{CO})_2(\text{C}_6\text{H}_5\text{NO})$  has been obtained by reaction of  $[\text{RhCl}(\text{CO})_2]_2$  with  $\text{C}_6\text{H}_5\text{NO}$  in benzene solution at room temperature. This compound could give useful information about the mechanism of the nitrosoarene deoxygenation by carbon monoxide (see later). The  $\nu(\text{N}-\text{O})$  frequencies for the nitroso ligand (see Experimental section), while suggesting that coordination is mostly of the end-on type, do not distinguish between donation via the nitrogen or oxygen atom. The carbonyl stretching frequencies of the  $\text{RhCl}(\text{CO})(\text{PhNO})$ , occurring at 2082 and 2020  $\text{cm}^{-1}$ , are lower than those of the starting  $[\text{RhCl}(\text{CO})_2]_2$ . The increased activation of the carbon monoxide suggests a greater  $\sigma$ -donation of the nitroso ligand compared to a bridging chlorine atom. NMR spectra were not recorded because of the low solubilities and stabilities of the compounds in common organic solvents.

## Reactivity

When the compounds were heated in the solid state under carbon monoxide no reaction was observed at temperatures below the decomposition points. Carbon dioxide in non stoichiometric amounts was evolved, however, when the samples were melted. We were unable to identify the residue of reaction; but in order to confirm nitrene formation the crude residue was heated with ethanol and the solution analysed by GLC. Azoxybenzene and a small amount of aniline were detected. The complex  $\text{RhCl}(\text{CO})_2(\text{PhNO})$  under the same conditions reacted in a somewhat different way:  $\text{CO}_2$  was evolved slowly at 70 °C in almost stoichiometric amount and the residue after treatment with ethanol gave aniline and a small amount of azoxybenzene. In all cases, however, the yield of organic products was about 40% with respect to the nitroso ligand in the starting compound.

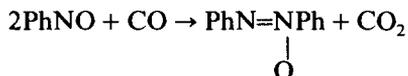
When the reaction was carried out in ethanol suspension all the tested compounds reacted similarly. Thus, milder temperature conditions (70 °C) could be used, and aniline was the main product, in a yield of about 40%. It may be noted that no influence of the substituted groups in the aromatic ring on the stability of the nitrene intermediate was observed.

The reactions described can be rationalized by assuming that the aniline is the final product from a labile nitrene intermediate. Furthermore the reaction of  $\text{RhCl}(\text{CO})_2(\text{PhNO})$  in the solid state suggests that carbon monoxide coordination is essential for nitrene formation under mild conditions. Thus, when the reaction is

carried out in suspension carbon monoxide coordination must again be involved. The formation of azoxybenzene instead of aniline observed for the reactions in the solid state and the more drastic temperature conditions required for reactions are in agreement with this view. In this case the reactions must be regarded as taking place between CO and the free nitroso species produced by the decomposition (see also Table 1, runs 1,8,9)

### Catalysis

Reactions of nitrosobenzene in the presence of a catalytic amount of some nitrosobenzene complexes have been carried out under various experimental conditions. The results, summarized in Table 1, show that in ethanol, under relatively mild temperature and pressure conditions, azoxybenzene is the main product along with small amounts of aniline and azobenzene (runs 1–6). In all the cases examined, however, varying amounts (0–30%) of unidentified mixtures of polymeric organic products were always obtained. Though the conversion of PhNO into azoxybenzene has been observed under both stoichiometric [6] and catalytic [7] conditions, the nature of the deoxygenating species has not been completely defined. In our case we observed for the runs at atmospheric pressure that the amounts of carbon monoxide used and CO<sub>2</sub> evolved were in accord with the stoichiometry of the following reaction:



The runs in Table 1 also show that RhCl(COD)(PhNO) is more effective as a catalyst than ruthenium(II) complexes. Blank runs (1,8,9) show also that the nitrosobenzene transformation is lower in absence of the catalysts.

When the catalysis was carried out under more drastic temperature and pressure conditions (runs 7–14) urethane formation, accompanied by a fall in the yield of

TABLE 1  
REACTIONS OF NITROSOBENZENE WITH CO IN ETHANOL

Run	Catalyst	Reaction time (h)	<i>T</i> (°C)	<i>P</i> (atm)	PhN(O)NPh (%)	PhNHCOOR (%)	Conversion (%)
1	–	4	75	1	12.8	–	15
2	RhCl(COD)(PhNO)	4	75	1	70	–	100
3	PdCl <sub>2</sub> (PhNO) <sub>2</sub>	4	75	1	80	–	100
4	PtCl <sub>2</sub> (PhNO) <sub>2</sub>	4	75	1	30	–	45
5	RuCl <sub>2</sub> (COD)(PhNO) <sub>2</sub>	4	75	1	60	–	65
6	RuCl <sub>2</sub> (DMSO) <sub>2</sub> (PhNO) <sub>2</sub>	4	75	1	15	–	15
7	RhCl(COD)(PhNO)	4	75	60	60	11	98
8	–	1	150	30	81	–	100
9	–	1	150	60	88	–	100
10	RhCl(COD)(PhNO)	1	150	1	68	1	100
11	RhCl(COD)(PhNO)	1	150	30	50	15	100
12	RhCl(COD)(PhNO)	1	150	60	40	30	100
13	PdCl <sub>2</sub> (PhNO) <sub>2</sub>	1	150	60	10	33	100
14	RuCl <sub>2</sub> (DMSO) <sub>2</sub> (PhNO) <sub>2</sub>	1	150	60	10	23	100

TABLE 2  
REACTION OF NITROSOBENZENE WITH CO IN BENZENE (reaction time 1 h)

Run	Catalyst	<i>T</i> (°C)	<i>P</i> (atm)	Conversion (%)	PhN(O)NPh (%)	PhNCO (%)	PhNHCONHPh (%)
1	RhCl(CO) <sub>2</sub> (PhNO)	150	30	100	20	15	31
2	RhCl(COD)(PhNO)	150	30	100	31	5	29
3	PdCl <sub>2</sub> (PhNO) <sub>2</sub>	150	30	100	26	44	24
4	RuCl <sub>2</sub> (COD)(PhNO) <sub>2</sub>	150	30	98	26	11	12
5	RhCl(COD)(PhNO)	150	60	98	21	15	31
6	PdCl <sub>2</sub> (PhNO) <sub>2</sub>	150	60	98	11	61	22

azoxybenzene, was observed. The yields of urethane increased with increasing carbon monoxide pressure to a maximum of about 33% at 60 atmospheres. The formation of azoxybenzene and of urethane is in agreement with participation of a nitrene intermediate. This is preferentially converted into azoxybenzene under ambient pressure by reaction with free nitrosobenzene. At higher carbon monoxide pressures isocyanate formation, followed by reaction of the latter with ethanol to give urethane, is favoured.

When the catalysed reaction was carried out in a non-protic solvent, such as benzene, higher temperatures were necessary for reaction at a satisfactory rate, and so the reactor was kept at 150°C. Table 2 lists results obtained under these conditions. Azoxybenzene, phenyl isocyanate, and diphenylurea were the main products. The phenyl isocyanate yields increase, as expected, with increasing pressure. The ability of some rhodium and iridium carbonyl complexes to catalyse the conversion of nitroso compounds into isocyanate has been observed previously [8]. We also found that the rhodium complexes were more efficient than ruthenium complexes. The catalytic activity of PdCl<sub>2</sub>(PhNO)<sub>2</sub> and the analogous PtCl<sub>2</sub>(PhNO)<sub>2</sub> were also examined. The results (runs 3,4, Table 1) show that they reacted in the same way with PdCl<sub>2</sub>(PhNO)<sub>2</sub>, the latter being more effective. It has been suggested, that the aniline necessary for diphenylurea formation is derived from nitrene in its triplet state by hydrogen abstraction from solvent [12]. We think that it is formed by decomposition of C<sub>6</sub>H<sub>5</sub>NHCOOH produced by reaction of phenyl isocyanate with traces of water. This view is supported by the fact that in ethanol under the same temperature and pressure conditions only a little aniline was obtained. Furthermore, except for the reaction involving RuCl<sub>2</sub>(COD)(PhNO)<sub>2</sub>, the yield in diphenylurea was almost independent of the catalyst.

### Experimental

The preparations of the complexes were carried out under nitrogen. All solvent were of reagent grade quality. The benzene was dried over P<sub>2</sub>O<sub>5</sub> and distilled before use. IR spectra were recorded on a Perkin-Elmer 577 Spectrophotometer; GLC measurements were carried out on a Varian 6000 gas chromatograph using a 1.5 m column SP-2250 with biphenyl as internal standard. Diphenylurea determination was carried out on Micropack-CN (25 cm) using a Varian 5000 Liquid Chromatograph connected to a 4270-Varian integrator. The GLC analysis of CO and CO<sub>2</sub> was carried out on a Porapak Q (3 m/8 in.) column using a Carlo Erba Fractovap C connected to a Hewlett-Packard 3380 A integrator.

$[\text{RuCl}_2(\text{COD})]_n$  [9],  $\text{RuCl}_2(\text{DMSO})_4$  [10],  $p\text{-RC}_6\text{H}_4\text{NO}$  ( $\text{R} = \text{Me}_2\text{N}, \text{Me}, \text{H}, \text{Br}$ ) [11] were prepared by published methods.

#### Preparation of the complexes

In a typical procedure a mixture of the nitrosoarene and the complex in acetone or dichloromethane at room temperature was stirred for 20 h. After filtration the solution was concentrated then kept at  $-30^\circ\text{C}$ . The solid which separated was filtered off, washed, and dried.

$\text{RuCl}_2(\text{COD})(\text{PhNO})_2$ . Violet crystals (42% yield); dec.p. above  $85^\circ\text{C}$ . Found: C, 46.3; H, 4.35; N, 5.45; Cl, 14.7.  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{Cl}_2\text{Ru}$  calcd.: C, 48.59; H, 4.49; N, 5.67; Cl, 14.34%. IR (in Nujol): 1590(m), 1495(m), 1415(s), 1400(s), 1385(s), 1121(vs), 955(m), 880(m), 780(m)  $765(\text{s})\text{ cm}^{-1}$ .

$\text{RuCl}_2(\text{DMSO})_2(\text{PhNO})_2$ . Violet crystals (55% yield); dec.p. above  $162^\circ\text{C}$ . Found: C, 34.3; H, 4.01; N, 5.1; Cl, 13.1.  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2\text{Cl}_2\text{Ru}$  calcd.: C, 35.42; H, 4.09; N, 5.17; Cl, 13.07%. IR: 1590(m), 1405(vs), 1365(vs), 1140(vs), 1138(s), 995(m)  $880(\text{s})\text{ cm}^{-1}$ .

$\text{RuCl}_2(\text{DMSO})_2(p\text{-BrC}_6\text{H}_4\text{NO})_2$ . Violet crystals (60% yield); dec.p. above  $180^\circ\text{C}$ . Found: C, 26.0; H, 2.7; N, 3.98; Cl, 9.7; Br, 22.1.  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2\text{Br}_2\text{Cl}_2\text{Ru}$  calcd.: C, 27.44; H, 2.88; N, 4.00; Cl, 10.12; Br, 22.82%.

$\text{RuCl}_2(\text{DMSO})_2(p\text{-CH}_3\text{C}_6\text{H}_4\text{NO})_2$ . Violet crystals (62% yield); dec.p. above  $180^\circ\text{C}$ . Found: C, 36.7; H, 4.4; N, 5.0; Cl, 12.3.  $\text{C}_{18}\text{H}_{26}\text{N}_2\text{S}_2\text{O}_4\text{Cl}_2\text{Ru}$  calcd.: C, 37.89; H, 4.59; N, 4.91; Cl, 12.45%. IR: 1600(s), 1418(vs), 1350(vs), 1130(vs), 1021(s), 990(m), 925(s), 880(m),  $825(\text{m})\text{ cm}^{-1}$ .

$\text{RuCl}_2(\text{DMSO})_2(p\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})_2$ . Violet crystals (71% yield); dec.p. above  $180^\circ\text{C}$ . Found: C, 38.13; H, 4.9; N, 8.8; Cl, 11.1.  $\text{C}_{20}\text{H}_{32}\text{N}_4\text{O}_4\text{S}_2\text{Cl}_2\text{Ru}$  calcd.: C, 38.22; H, 5.09; N, 8.91; Cl, 11.29%. IR: 1600(vs), 1540(s), 1450(s), 1400(vs), 1310(s), 1150(vs), 945(s), 880(s),  $825(\text{m})\text{ cm}^{-1}$ .

$\text{PdCl}_2(p\text{-BrC}_6\text{H}_4\text{NO})_2$ . Greenish crystals (45% yield); dec.p. above  $190^\circ\text{C}$ . Found: C, 25.9; H, 1.4; N, 4.99; Br, 30.6; Cl, 12.2.  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2\text{Br}_2\text{Cl}_2\text{Pd}$  calcd.: C, 26.26; H, 1.46; N, 5.1; Br, 29.1; Cl, 12.9%. IR: 1576(s), 1490(vs), 1320(s), 1191(s), 1130(vs), 1060(m), 883(s),  $842(\text{m})\text{ cm}^{-1}$ .

$\text{PdCl}_2(p\text{-MeC}_6\text{H}_4\text{NO})_2$ . Greenish crystals (60% yield); dec.p. above  $150^\circ\text{C}$ . Found: C, 39.8; H, 3.5; N, 6.5; Cl, 16.4.  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Pd}$  calcd.: C, 40.07; H, 3.36; N, 6.68; Cl, 16.9%. IR: 1598(s), 1505(s), 1460(s), 1210(m), 1145(vs), 890(s),  $840(\text{s})\text{ cm}^{-1}$ .

$\text{PtCl}_2(p\text{-MeC}_6\text{H}_4\text{NO})_2$ . Yellow-green crystals (43% yield); dec.p. above  $155^\circ\text{C}$ . Found: C, 32.9; H, 2.68; N, 5.5; Cl, 13.1.  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Pt}$  calcd.: C, 33.08; H, 2.78; N, 5.5; Cl, 13.9%. IR: 1598(s), 1500(m), 1450(s), 1142(vs), 895(s),  $840(\text{s})\text{ cm}^{-1}$ .

$\text{PdCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NO})_2$ . Yellow crystals (80% yield); dec.p. above  $152^\circ\text{C}$ . Found: C, 43.01; H, 4.2; N, 6.1; Cl, 16.1.  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2\text{Pd}$  calcd.: C, 42.92; H, 4.05; N, 6.25; Cl, 15.85%. IR: 1583(s), 1570(sh), 1495(s), 1452(s), 1368(s), 1371(s), 1145(vs),  $865(\text{s})\text{ cm}^{-1}$ .

$\text{PdCl}_2(2,4,6\text{-Cl}_3\text{C}_6\text{H}_2\text{NO})_2$ . Yellow crystals (81% yield); dec.p. above  $165^\circ\text{C}$ . Found: C, 23.7; H, 0.7; N, 4.52; Cl, 45.8.  $\text{C}_{12}\text{H}_4\text{N}_2\text{O}_2\text{Cl}_8\text{Pd}$  calcd.: C, 24.09; H, 0.67; N, 4.68; Cl, 47.41%. IR: 1570(s), 1560(s), 1452(s), 1440(s), 1110(vs),  $860(\text{m})\text{ cm}^{-1}$ .

$\text{RhCl}(\text{CO})_2(\text{PhNO})$ . Maroon powder (85% yield); dec.p. above  $105^\circ\text{C}$ . Found: C, 31.0; H, 1.59; N, 4.22; Cl, 11.4.  $\text{C}_8\text{H}_5\text{NO}_3\text{ClRh}$  calcd.: C, 31.87; H, 1.67; N,

4.65; Cl, 11.76%. IR: 2082(vs), 2020(vs), 1585(m), 1480(s), 1420(m), 1160(m), 1120(m), 750(s), 690(s)  $\text{cm}^{-1}$ .

#### *Reactions with carbon monoxide*

(a) *In the solid state.* A 50 ml glass reactor was charged with 0.21 g (0.7 mmol) of  $\text{RhCl}(\text{CO})_2(\text{PhNO})$  and carbon monoxide at atmospheric pressure. The reactor was heated at  $70^\circ\text{C}$  for 5 h, then the gas was analysed (0.6 mmol of  $\text{CO}_2$ ). The residue was treated with 10 ml of ethanol and the resulting solution was analysed by GLC. Aniline (0.3 mmol) was the main product.

All the other compounds were treated in the same way, the temperature being kept at  $5^\circ\text{C}$  above their decomposition points.

(b) *In ethanol.* To 0.22 g (0.73 mmol) of  $\text{RhCl}(\text{CO})_2(\text{PhNO})$  of ethanol (10 ml) was added under carbon monoxide. The reactor was heated at  $70^\circ\text{C}$  for 2 h.  $\text{CO}_2$  (0.3 mmol) and aniline (0.28 mmol) were the main products of reaction. The reactions of the other complexes were carried out in the same way.

#### *Catalysis*

(a) *At atmospheric pressure.* The reactions were carried out in a 100 ml glass reactor fitted with a thermostated jacket. In a typical experiment, 2 mmol of PhNO and 0.02 mmol of catalyst were dissolved in 10 ml of ethanol under carbon monoxide at atmospheric pressure and the mixture was stirred at the specified temperature for 4 h. At the end of the reaction the mixture was analyzed by GLC.

(b) *In an autoclave.* The reactions were carried out in a stainless steel autoclave heated by an electrical oven. In a typical experiment, a solution 2 mmol of PhNO and 0.02 mmol of catalyst, in 10 ml of benzene was introduced into the autoclave and pressurized with carbon monoxide. After heating for 1 h, the autoclave was cooled and the mixture was analyzed by GLC and by HPLC.

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