

MONOSUBSTITUTED COMPLEXES OF NITRATOPENTACARBONYL-RHENIUM(I)

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SUMMARY

The complexes *cis*- and *trans*- $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ have been prepared and separated by chromatography. Structures have been assigned by means of infrared spectral measurements and on this basis unidentate nitrate coordination is proposed in both complexes. Isomerisation and further substitution reactions of the complexes are discussed.

INTRODUCTION

Although the halogenopentacarbonyl complexes of manganese and rhenium react with donor ligands in inert solvents at high temperatures to form complexes of the type $\text{M}(\text{CO})_3\text{L}_2\text{X}^1$, monosubstituted derivatives of the type $\text{M}(\text{CO})_4\text{LX}$ have been isolated by changing the reaction conditions. Thus the reaction of $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) with triphenylphosphine or triphenylarsine in chloroform at room temperature yields $\text{Mn}(\text{CO})_4(\text{MPh}_3)\text{X}$ ($\text{M} = \text{P}$ or As)². Similarly nitratopentacarbonylmanganese(I) yields $\text{Mn}(\text{CO})_3(\text{MPh}_3)_2\text{NO}_3$ on reaction with MPh_3 ($\text{M} = \text{P}$ or As) at high temperature in nitromethane, while $\text{Mn}(\text{CO})_4(\text{MPh}_3)\text{NO}_3$ is formed by mixing stoichiometric quantities of MPh_3 and $\text{Mn}(\text{CO})_5\text{NO}_3$ in chloroform at 20°³.

The reaction between nitratopentacarbonylrhenium(I) and PPh_3 or AsPh_3 in stoichiometric amounts has been studied⁴. No reaction is observed at 0° or 20°, while from the reaction at higher temperatures the only product isolated is *cis*-(I)- $\text{Re}(\text{CO})_3(\text{MPh}_3)_2\text{NO}_3$ (see Fig. 1). The question therefore arises as to whether the isolation of these exclusively disubstituted derivatives is due to the relatively forcing

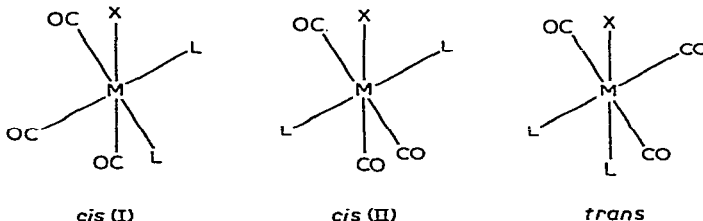


Fig. 1. Structural isomers of $\text{M}(\text{CO})_3\text{L}_2\text{X}$.

conditions required to initiate reaction or to the instability of the monosubstituted complexes. In order to resolve this point, a new route to the monosubstituted complexes has been employed.

EXPERIMENTAL

$[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ was prepared by the method of Jolly and Stone⁵.

Reaction of $[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ with N_2O_4

$[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ (0.6 g, 0.535 mmoles) was treated with N_2O_4 (5 ml) at 0° in a dry flask vented to the atmosphere by a phosphorus pentoxide guard tube. The solid dissolved immediately and gas evolution was observed. After stirring for three hours, excess N_2O_4 and volatile reaction products were removed under vacuum, leaving a brown oil. On covering the oil with hexane and standing for 24 h at 0° , a brown waxy solid was formed. This was chromatographed on a 4×30 cm neutral alumina column. Benzene/ethyl acetate (3/1) eluted a yellow band (A), a brown band (B) was eluted with methanol. Most of the solvent was removed from solution (A) under vacuum, addition of hexane gave a yellow crystalline solid (0.2 g, 30%, m.p. (darkens $157\text{--}160^\circ$) 164° dec.). (Found: C, 42.3; H, 2.3; N, 2.2. $\text{C}_{22}\text{H}_{15}\text{NO}_7\text{PRE}$ calcd.: C, 42.44; H, 2.41; N, 2.25%.) Similar treatment of solution (B) followed by cooling at 0° gave a brown microcrystalline solid (0.3 g, 45%, m.p. 164° dec.). (Found: C, 42.6; H, 2.5; N, 2.4. $\text{C}_{22}\text{H}_{15}\text{NO}_7\text{PRE}$ calcd.: C, 42.44; H, 2.41; N, 2.25%.)

Treatment of $[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ (0.5 g, 0.445 mmoles) with N_2O_4 (5 ml) at 20° followed by a similar work-up procedure gave the yellow solid (0.07 g, 13%) and the brown solid (0.3 g, 54%).

Reaction of *cis*- and *trans*- $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ with triphenylphosphine

(a) *cis*- $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ (0.1 g, 0.16 mmoles) was treated with triphenylphosphine (0.05 g, 0.19 mmoles) in methanol. No reaction was observed in the cold but on refluxing the solution for two hours and then cooling to room temperature a colourless crystalline solid was precipitated. This was filtered off and dried under vacuum, (m.p. 171°) (Found: C, 54.5; H, 3.7; N, 1.8. $\text{C}_{39}\text{H}_{30}\text{NO}_6\text{PRE}$ calcd.: C, 54.61; H, 3.50; N, 1.63%.)

(b) *trans*- $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ (0.1 g, 0.16 mmoles) was treated with triphenyl phosphine (0.045 g, 0.17 mmoles) in methanol. A similar procedure to that outlined above yielded a colourless crystalline solid, (m.p. $171\text{--}172^\circ$) (Found: C, 54.5; H, 3.4; N, 1.6. $\text{C}_{39}\text{H}_{30}\text{NO}_6\text{PRE}$ calcd.: C, 54.61; H, 3.50; N, 1.63%.)

RESULTS AND DISCUSSION

Treatment of $\text{Mn}(\text{CO})_5\text{NO}_3$ with MPh_3 (M = P or As) at 20° yields exclusively *cis*- $\text{Mn}(\text{CO})_4(\text{MPh}_3)\text{NO}_3$ ⁴ and similarly treatment of $\text{Re}(\text{CO})_5\text{Br}$ with PPh_3 in boiling chloroform yields only the *cis* isomer of the monosubstituted complex, no reaction occurring below 40° ⁵. The action of bromine on $[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ in carbon tetrachloride at 0° affords a readily separable mixture of *cis*- and *trans*- $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{Br}$, however only the *cis* isomer is obtained from a similar reaction at room temperature⁵. The reaction of $[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ with N_2O_4 at 0° yields a mixture of *cis*- and *trans*-

TABLE 1

PHYSICAL DATA FOR $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ AND RELATED COMPLEXES

Compound	Colour	M.p. (°C)	IR data and assignments ^a				
			$\nu(\text{CO})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{sym}}(\text{NO}_2)$	$\nu(\text{N=O})$	$\nu(\text{ONO}_2)$
<i>cis</i> - $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$	Brown	164 dec.	2070 w ^b 2010 s 1990 s 1968 s	1520 s ^c	1265 s	995 s	790 w
<i>trans</i> - $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$	Yellow	Darkens at 157– 160 Melts at 164 dec.	2100 w ^b 2012 s	1505 s ^c	1270 s	990 s	790 s
<i>cis</i> - $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ ^d	Dark yellow		2097 m ^b 2028 s 1969 s	1565 s ^{c,e}	1540 s	1245 s	
<i>cis</i> - $\text{Re}(\text{CO})_4(\text{PPh}_4)\text{Br}$ ^f	White	146	2100 s ^g 2015 s 1998 vs 1940 s				
<i>trans</i> - $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{Br}$ ^f	White	134	2095 w ^g 1995 vs				
<i>cis</i> -(I)- $\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{NO}_3$ ^h	Colour- less	171–172	2040 s ^b 1963 s 1915 s	1475 s ^c	1268 s	996 s	798 w
<i>cis</i> -(I)- $\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{NO}_3$ ⁱ	Colour- less	171–172	2039 s ^b 1963 s 1916 s	1474 s ^c	1270 s	996 s	798 w

^a ν Stretching modes, out of plane rock. ^b CHCl_3 solution. ^c Nujol mull. ^d See ref. 3. ^e For assignments see ref. 3. ^f See ref. 5. ^g Cyclohexane solution. ^h From $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ and PPh_3 . ⁱ From $\text{Re}(\text{CO})_5\text{NO}_3$ and PPh_3 (ref. 4).

$\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$, the former being isolated in greater amounts. In contrast to the bromination reaction however, nitration of $[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ at room temperature again yields a mixture of isomers, but at this temperature the yield of *trans* isomer is low (13%). No conditions have been found under which the formation of the *trans* isomer predominates over the *cis* form.

The structural assignment of the two isomers has been made on the basis of infrared spectral evidence (see Table 1). The yellow form of $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ shows two infrared active CO stretching bands and is thus assigned as the *trans* isomer, while the brown product shows four such bands as predicted for the *cis* form. Bands assigned to coordinated nitrate groups are also observed for both complexes, these being essentially similar in position and intensity to those observed for $\text{Re}(\text{CO})_5\text{NO}_3$ ⁶ which has been shown by X-ray structural studies to contain unidentate nitrate coordination⁷. It therefore appears that the bonding of the nitrate group to the metal in these complexes is quite different from that in $\text{Mn}(\text{CO})_4(\text{MPh}_3)\text{NO}_3$ ($\text{M} = \text{P}$ or As), for which a structure consisting of a planar, or almost planar, nitrate group bonded to the metal *via* the central nitrogen atom has been proposed³.

Isomerisation of *trans*- $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{NO}_3$ is observed when the solid is

heated to 157–160°. However isolation of the *cis* complex by this method is made extremely difficult as the latter melts (with decomposition) at 164°. Some degree of interconversion is also obtained by refluxing the *trans* isomer in chloroform solution, isomerisation being monitored by infrared spectroscopy. However, attempts to achieve complete conversion by prolonged refluxing led only to decomposition.

Both isomers readily undergo further substitution when treated with triphenylphosphine in refluxing methanol. In both cases the *cis*-(I) isomer of $\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{NO}_3$ is obtained. (See Table 1 and Fig. 1). No evidence was found for formation of either the *cis*-(II) isomer, which is formed in similar reactions of $\text{Mn}(\text{CO})_4(\text{MPh}_3)\text{NO}_3$ and MPh_3 ($\text{M} = \text{P}$ or As), or the *trans* form, either as final products or as intermediates (reactions monitored by infrared spectroscopy).

It thus appears that the non-isolation of monosubstituted derivatives from reactions of $\text{Re}(\text{CO})_5\text{NO}_3$ with MPh_3 is due to their ready conversion to *cis*-(I)- $\text{Re}(\text{CO})_3(\text{MPh}_3)_2\text{NO}_3$ rather than their inherent instability. In this context, it is noteworthy that the extreme stability of $\text{M}(\text{CO})_3\text{L}_2\text{X}$ ($\text{M} = \text{Mn}$ or Re , $\text{X} = \text{halogen}$, $\text{L} = \text{donor ligand}$) complexes has been widely observed. Thus the number of reported monosubstituted complexes is fairly restricted compared with the number of disubstituted derivatives^{1,8}. Further substitution of the disubstituted derivative is only possible under forcing conditions; *e.g.* $\text{Re}(\text{CO})_3(\text{Diars})\text{X}$ ($\text{Diars} = o\text{-phenylenebis}(\text{dimethylarsine})$, $\text{X} = \text{Cl}$, Br or I) reacts with excess Diars to give $\text{Re}(\text{CO})(\text{Diars})_2\text{X}$ only on heating to 270° in a sealed tube⁹.

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