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The PdO catalysed reaction between $Re(CO)_5X$ (X = Cl, Br, I) and L (L = Group 15 donor ligand). Synthesis of $Re(CO)_4LX$

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Abstract

Previously there has been no high yielding synthesis of $Re(CO)_4LX$ (L = Group 15 donor ligand, X = Cl, Br, I). We here show that the PdO-catalysed reaction between $Re(CO)_5X$ and L gives $Re(CO)_4LX$ in > 75% yield when L has a cone angle less than 150°. The new complexes have been fully characterised by IR and ^1H NMR spectroscopy.

Introduction

A commonly encountered problem in the CO substitution chemistry of metal carbonyl complexes is the lack of specificity using the traditional thermal and photochemical procedures. For instance, attempts to substitute one CO ligand in $M_x(CO)_yL_z$ by L′ can lead to M–M bond cleavage [1], replacement of L [2], or replacement of more than one CO group [3]. Alternative strategies are thus required to achieve product control and the avoidance of undesired products [4].

In this publication we report on the use of catalysts to achieve this objective for the reaction:

$$Re(CO)_5I + L \rightarrow cis\text{-}Re(CO)_4LI + CO$$

(L = Group 15 donor ligand)

The use of catalysts to achieve specific CO substitution in metal carbonyl complexes has been well documented for reactions in which the incoming ligand is an isonitrile ligand [4], but few reports have appeared for L = Group 15 donor ligand [5]. Attempts to achieve CO substitution by L on $Re(CO)_5X$ (X = Cl, Br, I) have been reported in the literature and success has been achieved using thermal [6–10], photochemical [11,12] and BH_4^- [13] induced procedures. Although in many instances $Re(CO)_4LX$ was detected during the reaction by spectroscopic techniques [14,15], in nearly all reports *disubstitution* occurs to give $Re(CO)_3L_2X$ [16] as the isolated product. The usual strategy for the synthesis of $Re(CO)_4LX$ starts from metal dimer complexes and involves cleavage of the dimer by L. For instance, cleavage of the halide bridged dimer $[Re(CO)_4X]_2$ by L occurs under mild conditions to give exclusively $Re(CO)_4LX$ [16–18]. Cleavage of $[Re(CO)_4L]_2$ with X_2 [9,19–22], $Re_2(CO)_6L_2X_2$ ($L = PPh_2(CH_2)_2CN$) with CO [23], $Re_2Cl_4(PEt_3)_4$ with CO [24] or $Re_2(CO)_{10}$ with L in CCl_4 [25] also gives the required $Re(CO)_4LX$ products. In the former case both *cis* and *trans* isomers can by synthesized, the products obtained being determined by the nature of L, the solvent etc. [9,19,20,22].

Experimental

$Re(CO)_5X$ (X = Cl, Br, I) was prepared by published procedures [26]. $K_2[PtCl_4]$ was purchased from Ega Chemicals, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $K_2[PdCl_4]$ from Strem Chemicals. The remaining catalysts were purchased from Engelhardt and used as obtained. Ligands were obtained from various sources. All reactions were carried out in distilled solvents under nitrogen. Column chromatography was performed on silica gel (Merck 60F, 70–230 mesh) and thin layer chromatography (TLC) on silica plates (Merck 60F, 0.2 mm thickness). Infrared spectra were recorded on a Bruker FT-IR IFS 85 spectrometer and NMR spectra on a Bruker AC 200 NMR spectrometer. A Köffler Hot-Stage apparatus was used for melting point determinations. Photolysis was performed using a 450W Hanovia lamp. Microanalyses were performed by the Microanalytical Laboratories, CSIR, Pretoria.

Preparation of $Re(CO)_4LI$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, $P(O^iPr)_3$, $P(OMe)Ph_2$, $P(O\text{-}o\text{-}Tol)_3$)

$Re(CO)_5I$ (0.150 g, 0.33 mmol) was added to benzene (20 ml) and the solution was heated to 43° C. L (1.1 equiv.) was then added to the solution, followed by PdO catalyst (5 mg). After an initial induction period of a few minutes, effervescence was noted to occur. The reaction was monitored by TLC (eluent: hexane/benzene) and IR spectroscopy and generally found to be complete within 30 min. The cooled solution was filtered through cellulose and pumped to dryness to yield pale yellow crystalline products. Products containing $L = PMePh_2$, $P(OEt)_3$, $P(OMe)_2Ph$, $P(O^iPr)_3$, $P(OMe)Ph_2$ and $P(O\text{-}o\text{-}Tol)_3$ were dissolved in a minimum amount of benzene and subjected to column chromatography (silica; eluent: hexane/benzene). After removal of the solvent, white to pale yellow materials were obtained. Recrystallisation, when necessary, was achieved from hexane/benzene mixtures. The products were characterised by IR and NMR spectroscopy (Table 1) and elemental analyses (Table 2).

Preparation of $Re(CO)_4LX$ ($X = I$, Br, Cl; $L = PMePh_2$, $P(OMe)_3$)

$Re(CO)_5X$ (0.150 g, 0.33 mmol) was dissolved in THF (25 ml) at 43° C. L (1 : 1 equiv.) was added, followed by PdO catalyst (5 mg). IR spectroscopy and TLC (eluent: benzene/hexane) were used to monitor the reaction. Upon completion of the reaction the solution was filtered through cellulose. After removal of the solvent, white or pale yellow materials were obtained and were characterised as reported in Table 1.

Table 1

IR and NMR spectroscopic data for the *cis*- and *trans*-$Re(CO)_4LI$ derivatives (X = Cl, Br, I)

Complex	IR [a,b]					NMR [c,d]	
	(CO)					CH_3	other [e]
$Re(CO)_4(PMe_3)I$	2099m	2007sh	2001s	1945m		1.00 [d, 9H, CH_3, J(PH) 9]	-
$Re(CO)_4(PMe_2Ph)I$	2101m	2010sh	2003s	1946m		1.49 [d, 6H, CH_3, J(PH) 9]	6.94–7.10
$Re(CO)_4(PMePh_2)I$	2101m	2012sh	2001s	1945m		2.01 [d, 3H, CH_3, J(PH) 9]	7.26–7.36
$Re(CO)_4(PPh_3)I$	2103m	2018sh	2001s	1949m		-	6.90–6.99, 7.55–7.65
$Re(CO)_4(PMe_2Ph)Br$	2105m	2014sh	2001s	1941m		1.42 [d, 6H, CH_3, J(PH) 9]	6.94–7.07
$Re(CO)_4(PMe_2Ph)Cl$	2105w	2014sh	2001s	1937m		1.37 [d, 6H, CH_3, J(PH) 9]	6.94–7.07
$Re(CO)_4[P(OMe)_3]I$	2108m	2027sh	2008s	1964m	1956m	3.15 [d, 9H, CH_3, J(PH) 11]	-
$Re(CO)_4[P(OEt)_3]I$	2107m	2024sh	2005m	1968m	1951m	0.97 [t, 9H, CH_3] 3.79 [dq, 6H, CH_2, J(PH) 7]	 -
$Re(CO)_4[P(OMe)_2Ph]I$	2105m	2022sh	2010s	1962sh	1951m	3.12 [d, 6H, CH_3, J(PH) 12]	6.98–7.04, 7.48–7.58
$Re(CO)_4[P(O^iPr)_3]I$	2105m	2022m	2001s	1964m	1960m	1.10 [d, 18H, CH_3, J(PH) 6]	4.62–4.70 [m, 3H, CH]
$Re(CO)_4[P(OMe)Ph_2]I$	2103m	2028m	2005s	1962m	1954m	2.98 [d, 3H, CH_3, J(PH) 13]	6.96–7.02, 7.61–7.67
$Re(CO)_4[P(O\text{-}o\text{-}Tol)_3]I$	2111m	2030sh	2005s	1962m	1954m	2.28 [s, 9H, CH_3]	6.75–6.84, 7.37–7.42
$Re(CO)_4[P(OMe)_3]Br$	2113m	2028sh	2009s	1966m	1949m	3.23 [d, 9H, CH_3, J(PH) 11]	-
$Re(CO)_4[P(OMe)_3]Cl$	2113w	2026sh	2009s	1954s	1949s	3.21 [d, 9H, CH_3, J(PH) 11]	-
$Re(CO)_4(PMe_2Ph)Cl$ [f]	2108w	1994s [g]					
$Re(CO)_4(PMe_2Ph)Br$ [f]	2105w	1990s [h]					
$Re(CO)_4(PMe_2Ph)I$ [f]	2100w	1985s [h]					
$Re(CO)_4(PPh_3)Br$ [f]	2105w	1995vs [i]					

[a] Run in C_6H_6. [b] s = strong, sh = shoulder, m = medium. [c] Run in C_6D_6 relative to TMS. [d] s = singlet, d = doublet, t = triplet, dq = doublet of quartets. [e] Complex multiplet. [f] *trans*-Complexes run in $CHCl_3$. [g] See Ref. 19. [h] See Ref. 20. [i] See Ref. 9.

Table 2

Analytical data for the Re(CO)$_4$LI derivatives

Complex	M.p. [a] (°C)	Analysis (Found (calc.) (%))	
		C	H
Re(CO)$_4$(PMe$_3$)I	92- 94	16.50	1.61
		(16.78)	(1.81)
Re(CO)$_4$(PMe$_2$Ph)I	82- 83	25.61	1.88
		(25.59)	(1.97)
Re(CO)$_4$(PMePh$_2$)I	74- 76	32.40	1.96
		(32.65)	(2.09)
Re(CO)$_4$(PPh$_3$)I	139-141	40.13	2.24
		(38.44)	(2.20)
Re(CO)$_4$[P(OMe)$_3$]I	35- 36	14.93	1.50
		(15.31)	(1.65)
Re(CO)$_4$[P(OMe)$_2$Ph]I	98-101	24.26	1.74
		(24.21)	(1.86)
Re(CO)$_4$[P(O^{i}Pr)$_3$]I	33- 35	24.66	3.15
		(24.65)	(3.34)
Re(CO)$_4$[P(O-*o*-Tol)$_3$]I	66- 69	37.75	2.60
		(38.62)	(2.72)

[a] Uncorrected.

Results and discussion

Reaction of Re(CO)$_5$I with PMe$_2$Ph (1 : 1.1) occurs at 80 °C in benzene during 24 h (90% reaction) and yields a reaction mixture which contains Re(CO)$_5$I (10%), Re(CO)$_4$(PMe$_2$Ph)I (65%) and Re(CO)$_3$(PMe$_2$Ph)$_2$I (25%). Addition of PdO (5 mg) as catalyst to an equivalent solution of Re(CO)$_5$I and PMe$_2$Ph (1 : 1.1) at 43 °C however, results in complete disappearance of starting material within 5 min. The purified product from the reaction, *cis*-Re(CO)$_4$(PMe$_2$Ph)I, was isolated in $>95\%$ yield (Table 3). A range of other materials were also tested for catalytic activity in the above reaction and the results of this study are shown in Table 4. The influence

Table 3

Influence of steric size on the rate of reaction of Re(CO)$_5$I with L

Ligand	Reaction time [a,b] (min)	Yield (%)	θ [c] (deg)
Re(CO)$_4$(PMe$_3$)I	10	82	118
Re(CO)$_4$(PMe$_2$Ph)I	5	96	122
Re(CO)$_4$(PMePh$_2$)I	15	95	136
Re(CO)$_4$(PPh$_3$)I	31	98	145
Re(CO)$_4$[P(OMe)$_3$]I	21	98	107
Re(CO)$_4$[P(OEt)$_3$]I	14	78	109
Re(CO)$_4$[P(OMe)$_2$Ph]I	19	79	115
Re(CO)$_4$[P(O^{i}Pr)$_3$]I	49	73	130
Re(CO)$_4$[P(OMe)Ph$_2$]I	27	76	132
Re(CO)$_4$[P(O-*o*-Tol)$_3$]I	1290	81	141

[a] All reactions carried out at 43 °C. [b] Approximate values are quoted. [c] Tolman cone angle, Ref. 27.

Table 4

Screening of catalysts for their efficiency to effect the substitution of $Re(CO)_5I$ by PMe_2Ph

Catalyst	Temperature of reaction (°C)	Reaction time (min)	% Reaction
PdO	43	5	100
$[Pd(\eta\text{-}C_5H_7)Cl]_2$	43	4	100
5% Pd on $CaCO_3$	60	170	100
10% Pd on C	60	840	50
5% Pt on C [a]	60	840	40
$[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$	63	290	10
$K_2[PtCl_4]$	63	150	1
$K_2[PdCl_4]$	63	150	1
5% Ru on C	63	150	1
Blank (light)	80	4320	90
Blank (no light)	80	4320	70

[a] Moisture, sulfided

of solvent on the reaction was also studied. Reactions in THF were found to occur rapidly (5 min) while reaction in CH_3CN was slower (60 min) and in $CHCl_3$ no reaction was detected (1 h).

From the above studies it was decided to extend the reaction to other similar substrates, and to a wider range of phosphines and phosphites with PdO as catalyst (Table 3). Since $Re(CO)_5Cl$ is not very soluble in benzene, a comparative study of the reaction of $Re(CO)_5X$ (X = Cl, Br, I) with PMe_2Ph and $P(OMe)_3$ was carried out in THF (Table 5).

The data from the above and related studies permit the following statements to be made:

1. The reaction between $Re(CO)_5X$ and L is not catalysed by PdO when L is large i.e., the Tolman cone angle θ [27] exceeds 150°. Thus reactions with L = $P(CH_2Ph)_3$ and $P(C_6H_{11})_3$ did not proceed to any extent over 24 h in the presence of PdO.
2. The reaction between $Re(CO)_5X$ and L is dependent on a mixture of both electronic and steric effects. Thus, when the reaction rate between $Re(CO)_5I$ and a series of phosphines (PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) (series 2, Fig. 1) or phosphites ($P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$, $P(O\text{-}o\text{-}Tol)_3$) (series 1, Fig. 1) is

Table 5

The influence of X = Cl, Br, I in $Re(CO)_5X$ on the reaction with $P(OMe)_3$ or PMe_2Ph

Complex	Reaction time [a] (min)
$Re(CO)_4(PMe_2Ph)Cl$	90
$Re(CO)_4(PMe_2Ph)Br$	62
$Re(CO)_4(PMe_2Ph)I$	5
$Re(CO)_4[P(OMe)_3]Cl$	152
$Re(CO)_4[P(OMe)_3]Br$	116
$Re(CO)_4[P(OMe)_3]I$	21

[a] Reactions carried out at 43° C in THF.

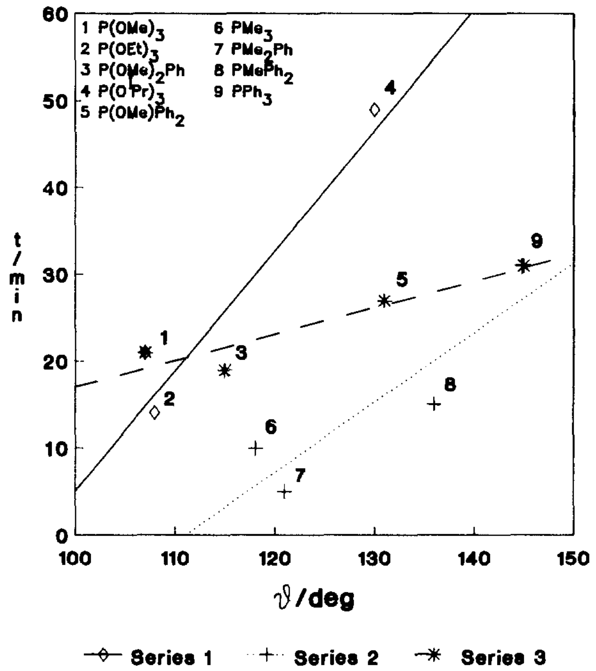

Fig. 1. Plot of Tolman cone angle versus reaction time for the PdO catalysed reaction $Re(CO)_5I + L \rightarrow Re(CO)_4LI$.

considered, a general increase in reaction time is observed with increase in cone angle. However, the two series are quite distinct implying that electronic effects are also significant. This is further highlighted for the mixed series $P(OMe)_3$, $P(OMe)_2Ph$, $P(OMe)Ph_2$, PPh_3 (series 3, Fig. 1) which reveals only a small variation in reaction time with cone angle.

3. The reaction between PMe_2Ph and $Mn(CO)_5I$ is not catalysed by PdO. The reaction time in the presence of PdO catalyst is 2.5 h (20% conversion) under reaction conditions identical to that of the catalysed reaction between $Re(CO)_5I$ and PMe_2Ph (100% conversion; 5 min).

The above results clearly establish that the mechanism for the substitution reaction is quite different to that of the thermal reaction which has been established as occurring via an S_N1 mechanism [15]. In the thermal reaction, substitution of $Mn(CO)_5X$ by L occurs 60 times more rapidly than the reaction of $Re(CO)_5X$ with L [15].

The results suggest that there is a steric threshold for the reaction [28]. Above a certain size (cone angle) no catalysis is observed. Below this value ($\theta = 150°$) electronic effects do have an influence on the reaction. The importance of the steric and electronic effects is also indicated by the influence of X on the reaction rate. The rate follows the sequence $Re(CO)_5I > Re(CO)_5Br > Re(CO)_5Cl$ for the reaction with $P(OMe)_3$ or PMe_2Ph, which is the opposite of the thermal S_N1 mechanism observed [15].

Further insight into the mechanism of the reaction was obtained by observing the influence of O_2 and light on the reaction of $Re(CO)_5I$ with PMe_2Ph and $P(OMe)_3$. These results can be summarized as follows:

Table 6

Reaction performed in light/absence of light

Ligand	Reaction time [a] (min)	
	light	absence of light
PMe_2Ph [b]	5	12
PMe_2Ph [c]	11	33
$P(OMe)_3$ [b]	20	87
$P(OMe)_3$ [c]	40	107

[a] Reactions carried out at 43° C in C_6H_6. [b] Undegassed solvent used. [c] Degassed solvent used.

1. Reactions performed in undegassed benzene (PMe_2Ph: 5 min, 100% reaction) go more rapidly than in degassed benzene (11 min to completion) under similar reaction conditions.
2. When the above reactions were performed in foil-wrapped flasks to exclude laboratory light, the reaction rate decreased (Table 6).
3. The reaction between $Re(CO)_5I$ and PMe_2Ph is not catalysed by light (laboratory light or 450 W Hg lamp) in the absence of PdO.
4. The possible radical nature of the reaction is also shown by the effect of galvinoxyl on the reaction. Addition of galvinoxyl (0.1 molar ratio) to $Re(CO)_5I/PMe_2Ph/PdO$ results in reaction inhibition ($< 5\%$ conversion, 2 h; 75% conversion after 20 h).

As in previous studies [4,5] no definitive statement can be made regarding the actual mechanism of the reaction. However the influence of O_2, galvinoxyl, and $CHCl_3$ as solvent as well as the ligand influences on the reaction are suggestive of a radical (chain) type mechanism [5].

Product characterisation

The products $Re(CO)_4LI$, produced in the above reactions, were all characterised by a combination of IR and NMR spectroscopy as well as by element analyses. The data are entirely consistent with the formation of the *cis* isomer. Spectroscopic properties of some of the independently synthesised *trans* isomers are given in Table 1 for comparison.

The IR spectra do however show an anomalous absorption when recorded in non-polar solvents. When L = phosphine the expected [29] four absorptions for $\nu(CO)$ are detected. However for L = phosphite five absorptions are observed (see Fig. 2). This extra absorption at 1960 cm^{-1} is solvent dependent and is only observed in non-polar solvents (Table 7). This phenomenon has not been detected previously. In the only other report of the spectrum of a phosphite, $Re(CO)_4[P(O\text{-}o\text{-}Tol)_3]I$ [30], only four absorptions were reported in $CHCl_3$ as solvent.

The origin of this effect is not known. It does not relate to having different groups attached to the P atom as none of the phosphine ligands reveal the extra absorption. The appearance of the extra band is, however, observed for all the phosphites synthesised, including the mixed phosphites $P(OMe)_2Ph$ and $P(OMe)Ph_2$. Presumably the effect relates to the presence of two (or more) conformers being present in solution which are associated with the orientation of the phosphite OR groups.

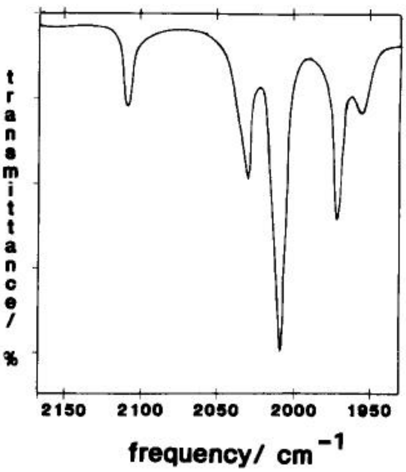

Fig. 2. Infrared spectrum of $Re(CO)_4[P(OMe)_3]I$ recorded in hexane.

Table 7

Solvent effects on the IR Spectrum of $Re(CO)_4[P(OMe)_3]I$

Solvent	Polarity index [a]	IR (CO)
C_6H_{14}	0.1	2109m, 2030m, 2009s, 1972m, 1956m
CCl_4	1.7	2109m, 2032m, 2009s, 1966m, 1958sh
Toluene	2.3	2107m, 2028m, 2007s, 1962m
CH_2Cl_2	3.4	2111m, 2026sh, 2010s, 1960m
THF	4.2	2109m, 2025sh, 2007s, 1960m
$CHCl_3$	4.4	2111m, 2029sh, 2012s, 1962m
CH_3COCH_3	5.4	2111m, 2028sh, 2010s, 1962m

[a] See Ref. 31.

Conclusions

The PdO catalysed reaction between $Re(CO)_5X$ and Group 15 donor ligands readily gives the required product $Re(CO)_4LX$ in $> 75\%$ yield. The reaction rate is influenced by solvent, light and traces of oxygen. Both electronic and steric properties associated with L influence the reaction and if the cone angle of L exceeds 150° no reaction is observed.

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