Journal of Organometallic Chemistry, 64 (1974) 245—254

NEW SYNTHETIC ROUTES TO MONO-, DI- AND TRI-CARBONYL HALIDO COMPLEXES OF RHENIUM(I) AND RHENIUM(III) WITH TERTIARY PHOSPHINE

J. CHATT, J.R. DILWORTH, H.P. GUNZ and G.J. LEIGH
A.R.C. Unit of Nitrogen Fixation, University of Sussex, Falmer, Brighton, BN1 9QJ (Great Britain)

(Received May 16th, 1973)

Summary

Carbonylation of tertiary phosphine complexes under reducing conditions is shown to be a reliable and direct route to rhenium mono- and poly-carbonyl complexes.

Most routes to tricarbonylhalidorhenium complexes with tertiary phosphines involve the reactions of mono- and di-tertiary phosphines with carbonyl halido complexes, which are usually difficult to prepare. Typical preparative reactions are shown below:

$$[ReCl(CO)_5] + 2PPh_3 \xrightarrow{120^\circ} fac\text{-}[ReCl(CO)_3(PPh_3)_2] + 2CO \qquad \text{(ref. 1)}$$

$$[Re(CO)_6]ClO_4 + 5PPh_3 \xrightarrow{130^\circ} trans\text{-}[ReCl(CO)_3(PPh_3)_2] + 3PPh_3O + CO_2 + 2CO\ (54\%) \qquad \text{(ref. 2)}$$

$$[ReCl(CO)_5] + Ph_2PCH_2CH_2PPh_2 \xrightarrow{80^\circ} fac\text{-}[ReCl(CO)_3(Ph_2PCH_2CH_2PPh_2)] \qquad \text{(ref. 3)}$$

Other methods involve carbonylation of tertiary phosphine halido complexes and often proceed in low yield.

$$mer\text{-}[ReCl_3(PMe_2Ph)_3] \xrightarrow[\text{Reflux}]{HCO_2H} [ReCl(CO)_3(PMe_2Ph)_2]\ (18\%) \qquad \text{(ref. 4)}$$

$$mer\text{-}[\mathrm{ReCl_3(PMe_2Ph)_3}] \xrightarrow[\substack{\mathrm{MeOCH_2CH_2OH;}\\ \mathrm{reflux}}]{\mathrm{CO,\ 1\ atm}} fac\text{-}[\mathrm{ReCl(CO)_3(PMe_2Ph)_2}]\ (43\%)$$

(ref. 4)

$$trans\text{-}[\mathrm{ReCl_4(PMe_2Ph)_2}] \xrightarrow[\substack{\mathrm{MeOCH_2CH_2OH;}\\ \mathrm{reflux}}]{\mathrm{CO,\ 1\ atm}} trans\text{-}[\mathrm{ReCl(CO)_3(PMe_2Ph)_2}]\ (15\%)$$

(ref. 4)

Mono- and dicarbonyl complexes have also been obtained by carbonylation of tertiary phosphine halido complexes or treatment of carbonyl halido complexes with mono- or di-tertiary phosphines under forcing conditions, *e.g.*:

$$[\mathrm{ReCl_3(PMe_2Ph)_3}] \xrightarrow[\mathrm{Et_2NCH_2CH_2OH}]{\mathrm{Reflux}} trans\text{-}[\mathrm{ReCl(CO)(PMe_2Ph)_4}]\ (10\%)\quad \text{(ref. 4)}$$

$$[\mathrm{ReCl_3(PMe_2Ph)_3}] \xrightarrow[\mathrm{CO,\ 1\ atm}]{\mathrm{Na/Hg/THF}} mer\text{-}cis\text{-}[\mathrm{ReCl(CO)_2(PMe_2Ph)_3}]\ (43\%)\quad \text{(ref. 4)}$$

$$[\mathrm{ReI(CO)_5}] \xrightarrow[270^\circ]{\mathrm{Ph_2PCH_2CH_2PPh_2}} cis\text{-}[\mathrm{Re(CO)_2(Ph_2PCH_2CH_2PPh_2)_2}]\mathrm{I} \xrightarrow[\mathrm{EtOH}]{\mathrm{AgCl}}$$

$$cis\text{-}[\mathrm{Re(CO)_2(Ph_2PCH_2CH_2PPh_2)_2}]\mathrm{Cl} \xrightarrow[270^\circ]{\mathrm{Ph_2PCH_2CH_2PPh_2}}$$

$$[\mathrm{ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2}]\quad \text{(ref. 3)}$$

We now report that the complexes *trans*-$[\mathrm{ReX(CO)_3(PPh_3)_2}]$ (X = Cl, Br or I) can be prepared more easily and in satisfactory yields by the action of carbon monoxide at 1 atm on a suspension in refluxing toluene of $[\mathrm{ReOX_3(PPh_3)_2}]$ or $[\mathrm{ReO(OEt)X_2(PPh_3)_2}]$ in the presence of triphenylphosphine. Yields are much lower in the absence of triphenylphosphine, which is probably functioning as a reducing agent. In the presence of triphenylarsine and under similar conditions $[\mathrm{ReOCl_3(AsPh_3)_2}]$ yielded no characterisable products. The complexes prepared in this manner are summarised in Table 1.

The tricarbonyl complexes are obtained from the reaction mixture as pinkish-red or blue crystalline solids which after recrystallisation in the presence of potassium hydroxide become a very pale cream colour.

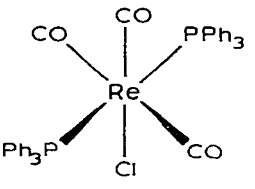
The IR spectra in the 1800 - 2100 cm^{-1} region (see Table 1) suggest the *meridional*-configuration (V) [2].

TABLE 1

RHENIUM(I) TRICARBONYL COMPLEXES

No	Complex	$\nu(\mathrm{C{\equiv}O})$ (cm^{-1})^a
(V)	*trans*-$[\mathrm{ReCl(CO)_3(PPh_3)_2}]$	2049w, 1954s, 1904s
(VI)	*trans*-$[\mathrm{ReBr(CO)_3(PPh_3)_2}]^b$	2060w, 1960s, 1910s
(VII)	*trans*-$[\mathrm{ReI(CO)_3(PPh_3)_2}]$	2040w, 1940s, 1890s
(VIII)	*trans*-$[\mathrm{ReCl(CO)_3(PPh_2Et)_2}]^b$	2060w, 1960s, 1905s

^{a}In $\mathrm{CHCl_3}$ solution, w = weak, s = strong. ^{b}Not previously reported.



(V)

The presence of three carbonyl groups was confirmed by oxidising $[ReCl(CO)_3(PPh_3)_2]$ with a large excess of dichlorine, measuring the volume of liberated gas, and then oxidising it quantitatively to carbon dioxide. Complex (V) is inert to refluxing acetonitrile, but loses one carbonyl ligand on heating under reflux in benzonitrile. The product contains no benzonitrile, is monomeric, a non-conductor in nitrobenzene and yields two moles of carbon monoxide on exhaustive chlorination, confirming the stoichiometry deduced from analysis, $[ReCl(CO)_2(PPh_3)_2]$. The IR spectrum in chloroform solution shows $\nu(C\equiv O)$ at 1840 and 1920 cm^{-1}. This same dicarbonyl has been claimed [5] as the product from the high-pressure carbonylation of $[ReOCl_3(PPh_3)_2]$ in the presence of copper powder, but our repetition of this procedure gave *trans*-$[ReCl(CO)_3(PPh_3)_2]$, from which exhaustive chlorination yielded three moles of carbon monoxide. Unfortunately, no IR spectra are contained in the original report of the dicarbonyl complex. It was also claimed therin that the products from high-pressure carbonylation of $[ReO(OEt)Br_2(PPh_3)_2]$ and $[ReO(OEt)I_2(PPh_3)_2]$ are $[ReBr(CO)_2(PPh_3)_2]$ and $[ReI(CO)(PPh_3)_2]$ respectively. Our results show that these should be reformulated as *trans*-$[ReBr(CO)_3(PPh_3)_2]$ and *trans*-$[ReI(CO)_3(PPh_3)_2]$.

We also report a facile two-stage synthesis of mono- and dicarbonylrhenium(I) complexes from a *N*-benzoylhydrazido(3-)-*O*,*N*′-rhenium(V) complex [6] (I) (Scheme 1). The preparative routes are summarised in Scheme 1, and the products detailed in Table 2.

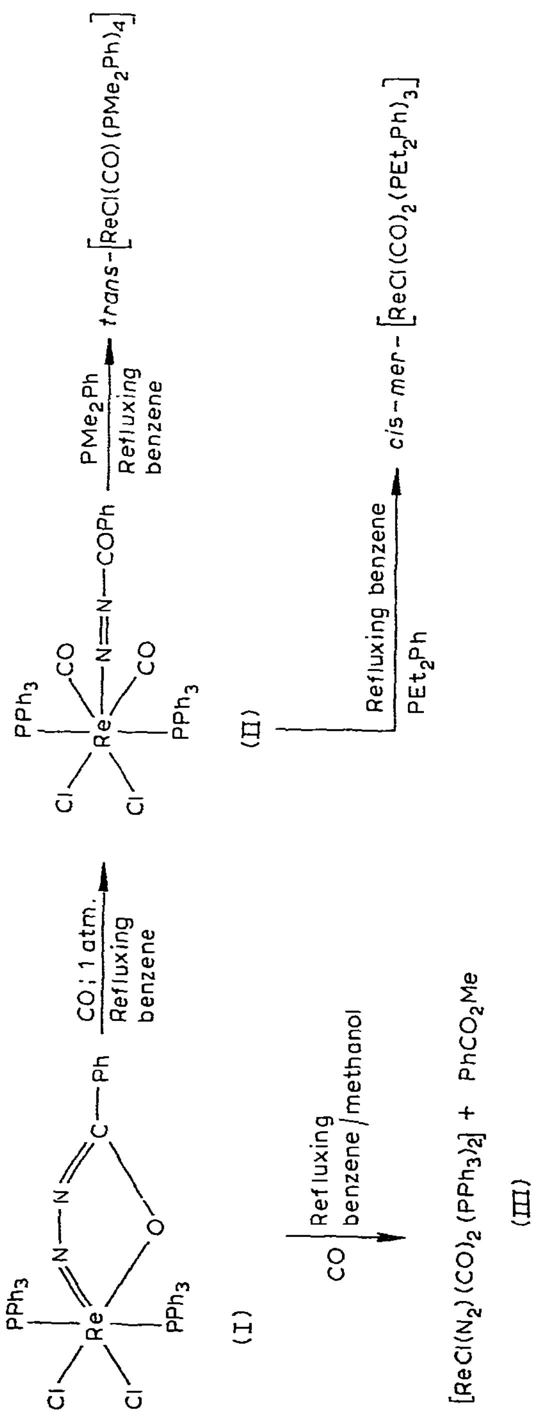
TABLE 2

RHENIUM(I) AND RHENIUM(II) MONO- AND DI-CARBONYL COMPLEXES

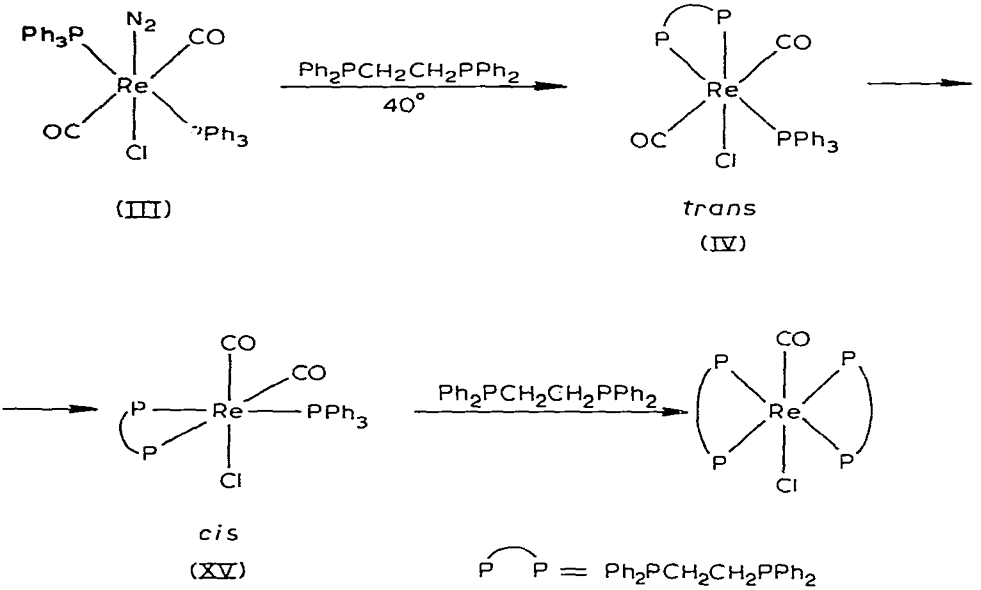
No	Complex	$\nu(C\equiv O)$ (cm^{-1}) (in $CHCl_3$ solution)
(IX)	$[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$	1820s
(X)	$[ReCl(CO)(Ph_2PCH=CHPPh_2)_2]$	1840s[a]
(XI)	$[ReCl(CO)\{Ph_2P(CH_2)_3PPh_2\}_2]$	1790s
(XII)	$[ReCl(CO)(Ph_2AsCH_2CH_2AsPh_2)_2]$	1805s
(XIII)	$[ReCl(CO)(PMe_2Ph)_4]$	1790s
(XIV)	$[ReCl(CO)_2\{CH_3C(CH_2PPh_2)_3\}]$	1895s, 1920s
(XV)	*cis*-$[ReCl(CO)_2(Ph_2PCH_2CH_2PPh_2)(PPh_3)]$[b]	1860s, 1910s
(XVI)	$[ReCl(CO)_2(PPh_3)_2]$	1840s, 1920s
(XVII)	$[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]FeCl_4$	1890s
(XVIII)	$[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]Br_3$	1890s
(XIX)	$[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]I_3$	1870s
(XX)	$[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)]PF_6$	1890s
(XXI)	$[ReCl(CO)(PMe_2Ph)_4]FeCl_4$	1860s[a]
(XXII)	$[ReCl(CO)_2\{CH_3C(CH_2PPh_2)_3\}]Br_3$[b]	1990s, 2040s

[a] Recorded as Nujol mulls. [b] Not isolated analytically pure.

SCHEME 1


Cl
Cl
Re
PPh3
PPh3
N
N
C
O
Ph
(I)
CO; 1 atm.
Refluxing benzene
Cl
Cl
Re
PPh3
PPh3
CO
CO
N=N—COPh
(II)
PMe2Ph
Refluxing benzene
trans-[ReCl(CO)(PMe2Ph)4]
Refluxing benzene
PEt2Ph
cis-mer-[ReCl(CO)2(PEt2Ph)3]
CO
Refluxing benzene/methanol
[ReCl(N2)(CO)2(PPh3)2] + PhCO2Me
(III)

Complex (I) is converted to the dicarbonyl benzoylazo complex (II) by a stream of carbon monoxide in refluxing benzene during 15 min. Complex (II) then reacts readily with mono- and di-tertiary phosphines to give rhenium(I) mono- and dicarbonyl complexes. This reaction probably proceeds via $[ReCl(CO)_2(N_2)(PPh_3)_2]$ (III) [7] which has been shown to react with $Ph_2PCH_2CH_2PPh_2$ in three stages [8]:



(III)

trans
(IV)

cis
(XV)

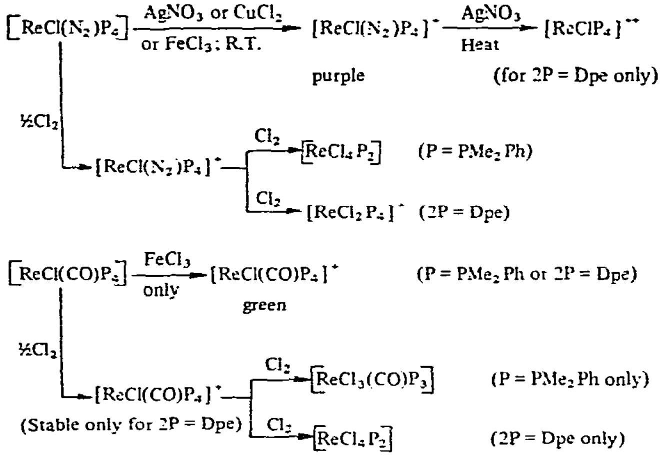
P⌒P = $Ph_2PCH_2CH_2PPh_2$

The *trans*-dicarbonyl (IV), though observable, cannot be isolated, as it rapidly isomerises to the *cis*-isomer (XIV) which is obtained from the reaction mixture. It was not possible to prepare *cis*-$[ReCl(CO)_2(Ph_2PCH_2CH_2PPh_2)(PPh_3)]$ from $[ReCl(CO)_3(PPh_3)_2]$ and the diphosphine, only $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$ was isolated. However, the complexes *cis*-$[ReCl(CO)_2\{Ph_2P(CH_2)_3PPh_2\}(PPh_3)]$ and *cis*-$[ReCl(CO)_2(Ph_2PCH_2PPh_2)(PPh_3)]$ are isolable from reaction of the tricarbonyl with the appropriate diphosphine.

The dicarbonyl complex $[ReCl(CO)_2(PEt_2Ph)_3]$ is obtained by the reaction of (II) or (III) with diethylphenylphosphine. Under similar conditions dimethylphenylphosphine yields $[ReCl(CO)(PMe_2Ph)_4]$ (Scheme 1). Somewhat better yields of $[ReCl(CO)(PMe_2Ph)_4]$ are, however, derived from the carbonylation at 1 atm of the product of the reaction of complex (I) with dimethylphenylphosphine in refluxing benzyl alcohol [9]. The complex *mer-cis*-$[ReCl(CO)_2(PMe_2Ph)_3]$ can be obtained by carbonylation of $[ReCl(CO)(PMe_2Ph)_4]$ in refluxing benzene.

The reactions of the rhenium(I) monocarbonyl complexes with oxidising agents are summarised in Scheme 2 together with reactions of the analogous rhenium(I) dinitrogen complexes [10]. No oxidation reactions were observed for tricarbonyl complexes other than those involving total loss of carbon monoxide.

SCHEME 2



Dpe = $Ph_2PCH_2CH_2PPh_2$ or other ditertiary phosphines

The cationic tetrakisphosphine rhenium(II) complexes are generally less stable thermally than their bis(diphosphine) analogues. Also, carbonyl derivatives are less easily oxidised and more readily reduced than their dinitrogen analogues. Thus $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]Br_3$ is reduced by sodium tetraphenylborate to $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$ whereas $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]Br_3$ undergoes simple anion exchange. The reaction of $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$ with halogens is different from that of the analogous bis-o-phenylenebisdimethylarsine (Diars) complexes which yield seven-coordinate cations under similar conditions [11].

$$[ReCl(CO)(Diars)_2] \xrightarrow{Br_2} [ReBr_2(CO)(Diars)_2]Br_3$$

The products obtained from chlorination of the carbonyl and dinitrogen complexes reflect the relatively stronger binding of carbon monoxide to rhenium in its higher oxidation states. The lability of dinitrogen coordinated to rhenium(III) is shown by the formation of $[ReCl_4(PMe_2Ph)_2]$ by treatment of $[ReCl(N_2)(PMe_2Ph)_4]$ [10] with dichlorine. The carbonyl analogue forms the stable rhenium(III) complex $[ReCl_3(CO)(PMe_2Ph)_3]$.

Experimental

All preparations involving free tertiary phosphines were carried out under dinitrogen. Unless otherwise stated reagent grade solvents were used throughout. Infrared spectra were recorded on a SP 1200 Unicam spectrophotometer, molecular weights were determined on a Hitachi—Perkin—Elmer osmometer, and analyses were performed by A.G. Olney at the University of Sussex.

trans-Tricarbonylchlorobis(triphenylphosphine)rhenium(I), (V)

Oxotrichlorobis(triphenylphosphine)rhenium(V) [12] (2.0 g) and triphenylphosphine (2.0 g) were heated in toluene (150 ml) under reflux for 3 h while passing a stream of dry carbon monoxide through the solution. The pinkish-red solution was evaporated to 10 ml at 15 mmHg and the complex precipitated as a pink solid by the addition of ethanol. The complex was recrystallised as pink plates from benzene/ethanol (1.5 g, 78%). (Found: C, 56.4; H, 4.0. $C_{39}H_{30}O_3P_2ClRe$ calcd.: C, 56.4; H, 3.6%.) Recrystallisation from benzene/methanol in the presence of potassium hydroxide gave the product as pale cream crystals.

trans-Bromotricarbonylbis(triphenylphosphine)rhenium(I), (VI)

Prepared analogously to the chloro complex using $[ReO(OEt)Br_2(PPh_3)_2]$ [12] and was isolated as a pink solid. This was recrystallised as pale yellow plates from benzene/methanol in the presence of potassium hydroxide (71%) (Found: C, 54.3; H, 3.9. $C_{39}H_{30}O_3P_2BrRe$ calcd.: C, 53.6; H, 3.5%.)

trans-Tricarbonyliodobis(triphenylphosphine)rhenium(I), (VII)

Prepared analogously to the chloro complex using $[ReO(OEt)I_2(PPh_3)_2]$ [12] and was isolated as a blue solid. This was recrystallised as yellow plates from benzene/methanol in the presence of potassium hydroxide (66%). (Found: C, 51.3; H, 3.3. $C_{39}H_{30}O_3P_2IRe$ calcd.: C, 50.9; H, 3.2%.)

trans-Tricarbonylchlorobis(ethyldiphenylphosphine)rhenium(I), (VIII)

Prepared analogously to complex (V) using $[ReO(OEt)Cl_2(PPhEt_2)_2]$ [12] and was isolated as a purplish solid. This was recrystallised as above from benzene/methanol as pale yellow plates (68%). (Found: C, 49.9; H, 4.4. $C_{31}H_{30}O_3P_2ClRe$ calcd.: C, 50.5; H, 4.1%)

Carbonylchlorobis[1,2-bis(diphenylphosphino)ethane] rhenium(I), (IX)

[*N*-Benzoylhydrazido(3)-*N'*,*O*]dichlorobis(triphenylphosphine)rhenium (V) [6] (2.0 g) in benzene (60 ml) was heated under reflux for 20 min with passage of carbon monoxide through the reaction mixture. Addition of 1,2-bis(diphenylphosphino)ethane (2.0 g) to the resulting brown solution and heating under reflux for a further 30 min caused the *complex* to precipitate as a pale yellow solid. This was recrystallised as pale yellow plates from benzene/methanol (1.6 g, 70%) and had an identical IR spectrum to a sample prepared according to ref. 3. (Found: C, 61.1; H, 4.8; Cl, 3.8. $C_{53}H_{48}ClOP_4Re$ calcd.: C, 60.9; H, 4.6; Cl, 3.4%.)

Carbonylchlorobis[1,2-bis(diphenylphosphino)ethylene] rhenium (I), (X)

Prepared analogously to (IX) above, using 1,2-bis(diphenylphosphino)-ethylene and recrystallised from 1,2-dichloroethane/methanol as yellow plates (64%). (Found: C, 60.7; H, 4.8; Cl, 3.5. $C_{53}H_{44}ClOP_4Re$ calcd.: C, 61.1; H, 4.2; Cl, 3.4%.)

Carbonylchlorobis[1,2-bis(diphenylphosphino)propane] rhenium(I), (XI)

Prepared analogously to (IX) above, using 1,2-bis(diphenylphosphino)-propane, and recrystallised from chloroform/diethyl ether as pale cream crystals, (67%). (Found: C, 50.9; H, 4.8. $C_{55}H_{50}ClOP_4Re$ calcd.: C, 51.5; H, 4.8%.)

Chlorocarbonylbis[1,2-bis(diphenylarsino)ethane] rhenium(I), (XII)

Prepared analogously to (IX) above using 1,2-bis(diphenylarsino)ethane and recrystallised as white plates from chloroform/diethyl ether (66%). (Found: C, 51.9; H, 4.2. $C_{53}H_{48}As_4OClRe$ calcd.: C, 52.3; H, 3.9%.)

Chlorocarbonyltetrakis(dimethylphenylphosphine)rhenium(I), (XIII)

(*a*). Prepared analogously to complex (IX) using dimethylphenylphosphine, and recrystallised as white prisms from ethanol.

(*b*). [*N*-Benzoylhydrazido(3-)-*N*′,*O*] dichlorobis(triphenylphosphine)rhenium(V) (6.2 g), dimethylphenylphosphine (9.6 g) and benzyl alcohol (5 ml) were heated to 190° in an oil bath for 20 min. A stream of carbon monoxide was then passed through the cooled solution at room temperature for 2.5 h. The resulting orange-brown solution was treated with a 1/1/1 mixture of methanol, ethanol and 60 - 80 petroleum ether (150 ml) and the *complex* precipitated as a pale yellow solid. This was recrystallised as off-white prisms from benzene/methanol (2.5 g, 48%). (Found, C, 49.6; H, 5.7. $C_{33}H_{44}P_4OClRe$ calcd.: C, 49.4; H, 5.5%.)

Chlorodicarbonyl{1-(diphenylphosphino)-2,2-bis[(diphenylphosphino)methyl] propane}rhenium(I), (XIV)

Prepared analogously to complex (IX) using 1-(diphenylphosphino)-2,2-bis[(diphenylphosphino)methyl] propane and recrystallised as yellow prisms from benzene/methanol (62%). (Found: C, 57.1; H, 4.4; Cl, 4.8. $C_{43}H_{39}P_3O_2ClRe$ calcd.: C, 57.2; H, 4.3; Cl, 4.0%.)

cis-Chlorodicarbonyl[1,2-bis(diphenylphosphino)ethane] triphenylphosphine-rhenium(I), (XV)

Dicarbonylchloro(dinitrogen)bis(triphenylphosphine)rhenium(I) (1.0 g) and 1,2-bis(diphenylposphino)ethane (2.0 g) in benzene (40 ml) were stirred at 40°C for 1 h. The resulting yellow solution was evaporated at 10^{-2} mm and the complex precipitated as a yellow solid by the addition of methanol (40 ml). This was recrystallised as yellow prisms from benzene/hexane. This complex had a dipole moment of 4.4 D compared with the estimated value of 4.5 D. The *trans*-isomer could be identified in solution by IR spectroscopy [$\nu(C\equiv O)$ 1890s, 2020w cm^{-1}] but could not be isolated.

Dicarbonylchlorobis(triphenylphosphine)rhenium(I), (XVI)

trans-Tricarbonylchlorobis(triphenylphosphine)rhenium(I) (0.50 g) was heated under reflux in benzonitrile (30 ml) for 12 h. The resulting pale yellow solution was evaporated to 5 ml at 10^{-2} mm Hg and the complex precipitated as a pale cream solid by the addition of ethanol (30 ml). This was recrystallised as white needles from chloroform/ethanol and was monomeric in 1,2-dichloroethane and a non-conductor in nitrobenzene. (Found: C, 56.8; H, 3.7; Mol.wt., 940. $C_{38}H_{30}O_2P_2ClRe$ calcd.: C, 57.0; H, 3.7%. Mol.wt., 773.)

Carbonylchlorobis[1,2-bis(diphenylphosphino)ethane] rhenium(II) tetrachloroferrate (XVII)

Complex (IX) (0.1 g) and anhydrous ferric chloride (0.1 g) were heated under reflux in ethanol (10 ml) for 1 min, and cooled to give the complex as a green solid, which was recrystallised as green needles from chloroform/diethyl ether. (60 mg, 51%). (Found: C, 50.2; H, 3.9. $C_{53}H_{48}Cl_5FeOP_4Re$ calcd.: C, 51.2; H, 2.9%.) The molar conductivity of a 10^{-3} *M* nitrobenzene solution was 23.0 reciprocal ohms.

Carbonylchlorobis[1,2-bis(diphenylphosphino)ethane] rhenium(II) tribromide (XVIII)

Complex (IX) (0.1 g) in chloroform (5 ml) was exposed to bromine vapour, forming a green solution. Addition of diethyl ether (20 ml) precipitated the complex as green needles from chloroform/diethyl ether. (Found: C, 50.1; H, 4.0. $C_{53}H_{48}Br_3ClOP_4Re$ calcd.: C, 49.5; H, 3.7%.)

Carbonylchlorobis[1,2-bis(diphenylphosphino)ethane] rhenium(II) triiodide, (XIX)

Was prepared analogously using iodine. The triiodide salt was rather unstable and decomposed to complex (IX) on attempted recrystallisation.

Carbonylchlorobis[1,2-bis(diphenylphosphino)ethane] rhenium(II) hexafluorophosphate (XX)

Was prepared by addition of a saturated ethanolic solution of ammonium hexafluorophosphate to a chloroform solution of complex (XVIII) and was recrystallised as green needles from chloroform/diethyl ether. (Found: C, 52.6; H, 4.1. $C_{53}H_{48}ClF_6OP_5Re$ calcd.: C, 53.4; H, 4.0%.)

Addition of sodium tetraphenylborate to solution of complex (XVIII) caused quantitative regeneration of the rhenium(I) complex.

Carbonylchlorotetrakis(dimethylphenylphosphine)rhenium(II) tetrachloroferrate, (XXI)

(XXI) was prepared by reaction of complex (XIII) with anhydrous ferric chloride in ethanol as a purple solid, and was recrystallised from dichloromethane/hexane (Found: C, 39.7; H, 4.5. $C_{33}H_{44}Cl_5FeOP_4Re$ calcd.: C, 39.6; H, 4.4%.)

Reactions of chlorocarbonyl complexes with an excess of dichlorine

The experimental technique employing sealed tubes has been previously described [10].

(i). trans-Tricarbonylchlorobis(triphenylphosphine)rhenium(I). 87.8 mg of complex yielded 6.50 ml of carbon monoxide (91%) on treatment with dichlorine. Oxidation of this liberated gas with hot cupric oxide yielded 6.30 ml of carbon dioxide (97%).

(ii). Dicarbonylchlorobis(triphenylphosphine)rhenium(I). 109.5 mg of complex yielded 6.02 (94%) ml of carbon monoxide on treatment with excess of dichlorine.

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