Synthesis and Reactions of Amido-complexes of Rhenium(I): Isolation of New Carbamate Derivatives †

By **Girolamo La Monica,* Sergio Ceinini, Francesca Porta,** and **Maddalena Pizzotti,** Istituto di Chimica Generale, Via Venezian 21, 20133 Milano, Italy

On reaction of $[Re(CO)_2H(PPh_3)_3]$ with aroyl azides, $RCON_3$ (R = Ph or C_6H_4Me-*p*), amido-complexes of rhenium(I), $[Re(CO)_2(NHCOR)(PPh_3)_2]$, may be isolated. I.r. data and the chemical behaviour of these new complexes suggest that the carbonyl group of the organic ligand is also involved in the co-ordination to the metal. Reactions of these complexes with neutral ligands (L) give $[Re(CO)_2L(NHCOR)(PPh_3)_2]$ (L = CO or NBu^nH_2), while secondary amines NR'_2H (R' = Et or Pr^n) react only in the presence of carbon dioxide and lead to the formation of carbamate derivatives $[Re(CO)_2(O_2CNR'_2)(PPh_3)_2]$. Analogous dithiocarbamate derivatives have been isolated by using CS_2 instead of CO_2. The amido-complexes also readily react with carboxylic acids, $R''CO_2H$, to give carboxylato-derivatives $[Re(CO)_2(O_2CR'')(PPh_3)_2]$ (R'' = H, Me, $ClCH_2$, Et, or Ph), while with mineral acids HX (X = Cl or BF_4) ionic amido-complexes $[Re(CO)_n(NH_2COR)(PPh_3)_2]X$ (n = 2 or 3; $R = C_6H_4Me$-*p*) have been obtained. The formate $[Re(CO)_2(O_2CH)(PPh_3)_2]$ has also been obtained from the reaction of CO_2 with $[Re(CO)_2H(PPh_3)_3]$.

As a continuation of our studies on the reactions of covalent azides, RN_3, with transition-metal complexes in low oxidation states,[1] we have extended our investigations to the reactions of these organic molecules with the rhenium monohydride $[Re(CO)_2H(PPh_3)_3]$. A previous study of this type of reaction showed that amido-complexes of platinum(II) can be readily obtained by this route.[2] We report here the synthesis and reactivity of the new rhenium amido-complexes, $[Re(CO)_2(NHCOR)(PPh_3)_2]$ (R = Ph or C_6H_4Me-*p*).

RESULTS AND DISCUSSION

On reaction of $[Re(CO)_2H(PPh_3)_3]$ with aroyl azides in benzene at 40—50 °C amido-complexes of Re were obtained (Table 1) [equation (1)]. Complexes (I) were obtained in *ca.* 50—55% yields. Rhenium by-products were shown to be present in the reaction mixture but they could not be identified. Moreover, aroylamides, $RCONH_2$, were also detected. These facts suggest a concomitant but unknown reaction path. The same reaction did not proceed with $[Re(CO)_3H(PPh_3)_2]$, even when a very reactive azide such as toluene-*p*-sulphonyl azide[3] was used. This is probably due either to the less basic character of rhenium in this complex[1] or to the fact that $[Re(CO)_2H(PPh_3)_3]$ has one phosphine ligand

$$[Re(CO)_2H(PPh_3)_3] + 2RCON_3 \xrightarrow[C_6H_6]{40\text{—}50\ ^\circ C} [Re(CO)_2(NHCOR)(PPh_3)_2] + [PPh_3(NCOR)] + 2N_2 \quad (1)$$

(Ia) $R = Ph$; (Ib) $R = C_6H_4Me$-*p*

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[1] S. Cenini and G. La Monica, *Inorg. Chim. Acta Rev.*, 1976, **18**, 279.

[2] W. Beck and M. Bauder, *Chem. Ber.*, 1970, **103**, 583.

[3] W. Beck, W. Rieber, S. Cenini, F. Porta, and G. La Monica, *J.C.S. Dalton*, 1974, 298.

which is easily displaced as the phosphine adduct $[PPh_3(NCOR)]$.

TABLE 1

Analytical data

	Complex [a]	Colour	M.p. (θ_c/°C)	Analysis (%) [b] C	H	N	M [b]
(Ia)	$[Re(CO)_2(NHCOR)(PPh_3)_2]$	White	220	60.0 (60.8)	4.1 (4.05)	1.58 (1.55)	888 [c] (886)
(Ib)	$[Re(CO)_2(NHCOR')(PPh_3)_2]$	White	235	61.8 (61.2)	4.25 (4.25)	1.5 (1.55)	865 [c] (900)
(IIa)	$[Re(CO)_3(NHCOR)(PPh_3)_2]$	White	195	59.7 (60.3)	4.0 (3.95)	1.45 (1.55)	
(IIb)	$[Re(CO)_3(NHCOR')(PPh_3)_2]$	White	220	60.2 (60.8)	4.05 (4.1)	1.4 (1.5)	
(IIIa)	$[Re(CO)_2(NHCOR)(NBu^nH_2)(PPh_3)_2]$	White	180 (decomp.)	60.75 (61.2)	4.8 (4.9)	2.75 (2.9)	
(IIIb)	$[Re(CO)_2(NHCOR')(NBu^nH_2)(PPh_3)_2]$	White	176 (decomp.)	61.5 (61.6)	5.0 (5.0)	2.7 (2.85)	825 [d] (973)
(IVa)	$[Re(CO)_2(O_2CNEt_2)(PPh_3)_2]$ [e]	White	197	57.5 (58.6)	4.4 (4.55)	1.6 (1.6)	
(IVb)	$[Re(CO)_2(O_2CNPr^n{}_2)(PPh_3)_2]$	White	201	59.1 (59.3)	4.7 (4.85)	1.5 (1.55)	1 020 [c] (910)
(Va)	$[Re(CO)_2(PPh_3)_2(S_2CNEt_2)]$ [f]	Pale yellow	208	57.25 (56.4)	4.5 (4.4)	1.45 (1.55)	
(Vb)	$[Re(CO)_2(PPh_3)_2(S_2CNPr^n{}_2)]$	White	199	58.0 (57.4)	4.75 (4.7)	1.45 (1.5)	
(VI)	$[Re(CO)_2(NH_2COR')(PPh_3)_2]Cl$	Pale brown	180	59.45 (59.0)	4.15 (4.3)	1.45 (1.5)	
(VII)	$[Re(CO)_3(NH_2COR')(PPh_3)_2][BF_4]$	White	157	55.0 (55.6)	3.8 (3.85)	1.5 (1.4)	

[a] R = Ph, R′ = C_6H_4Me-*p*. [b] Calculated values are given in parentheses. [c] Determined osmometrically in $CHCl_3$. [d] Determined osmometrically in C_6H_6. [e] O, 7.55 (7.3%). [f] S, 6.65 (7.0%).

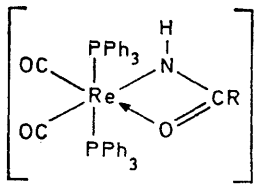
TABLE 2

Infrared [a] and n.m.r. spectral data

Complex	ν(NH)	ν(CO)	Other significant absorptions	τ(NH)	$\tau(CH_3)$
(Ia)	3 400w	1 910s, 1 830s	1 565m, 1 515m, 1 455m	4.65 [b]	
(Ib)	3 410w	1 920s, 1 835s	1 540m, 1 505m, 1 430m	4.6 [c]	7.84
(IIa)	3 390w	2 030m, 1 935s, 1 890s	1 605m, 1 565m	5.38 [b]	
(IIb)	3 390w	2 020m, 1 940s, 1 880s	1 600m, 1 560m	5.4 [b]	
(IIIa)	3 380w, 3 280w	1 910s, 1 820s	1 610m, 1 550m		
(IIIb)	3 380w, 3 290w	1 910s, 1 825s	1 610m, 1 550m	*d*	7.97 [b]
(IVa)		1 920s, 1 840s	1 545s, 1 320w		9.6 [b,e]
(IVb)		1 930s, 1 850s	1 540s, 1 320w		Complex
(Va)		1 910s, 1 840s	1 480m, 1 270m, 1 215w, 1 145mw		9.34 [c,f]
(Vb)		1 910s, 1 840s	1 485m, 1 290m, 1 230m, 1 145m		Complex
(VI)	3 330w, 3 160w	1 920s, 1 835s	1 640m, 1 620m		
(VII)	3 300w, 3 220w	2 025m, 1 950s, 1 900s	1 630m		7.7 [g]

[a] Nujol and hexachlorobutadiene mulls (cm^{-1}). [b] In C_6D_6. [c] In $CDCl_3$. [d] For NH and NH_2 signals see text. [e] Triplet; $\tau(CH_2)$ 7.58 (q). [f] Triplet; $\tau(CH_2)$ 7.22 (q). [g] In C_3D_6O.

Complexes (I) are very stable, even in solution. This indirectly suggests that the organic moiety does not behave as a unidentate ligand, leaving the metal five-co-ordinate, but that the oxygen of the RCONH residue is also involved in the co-ordination.[4] This is supported both by i.r. evidence (Table 2) and by the reactions of these complexes with neutral ligands (see later). The two strong terminal-carbonyl stretching frequencies, which lie at values comparable with those of the corresponding pentane-2,4-dionate (pd) derivatives,[5] suggest a *cis* arrangement of the carbonyl groups. Thus the above configuration appears to be the most plausible. In the 1 570—1 400 cm^{-1} region more absorptions were observed but they were not easily assignable. However, no bands were present at *ca.* 1 600 cm^{-1}, which is the usual region for ν(C=O) of a unidentate amido-ligand.[2] Absorptions in this region were in fact observed for amidorhenium(I) complexes which certainly have this type of co-ordination (see later). A chelated mode of co-ordination has already been suggested for other aliphatic amido-complexes.[4,6] For complexes (I), ν(NH) and τ(NH) could be readily detected (Table 2).



The exchange reaction of compound (Ib) with D_2O gave a product which did not show the band at 3 410

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[4] G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc.* (*A*), 1970, 2550.

[5] M. Freni, P. Romiti, and D. Giusto, *J. Inorg. Nuclear Chem.* 1970, **32**, 145.

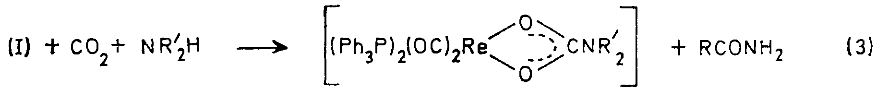
[6] J. D. Wilkins, *J. Organometallic Chem.*, 1974, **67**, 269.

cm^{-1} in its i.r. spectrum, while a new absorption at 2 525 cm^{-1} appeared, with the expected ratio between ν(NH) and ν(ND). Complexes (I) reacted with CO and butylamine to give (II) and (III) respectively (Table 1), according to equation (2). Complexes (II) showed the

$$\underset{\text{(II)}}{[\mathrm{Re(CO)_3(NHCOR)(PPh_3)_2}]} \xleftarrow{\mathrm{CO}} \mathrm{(I)} \xrightarrow{\mathrm{NBu^nH_2}} \underset{\text{(III)}}{[\mathrm{Re(CO)_2(NHCOR)(NBu^nH_2)(PPh_3)_2}]} \quad (2)$$

expected ν(CO) pattern for $[Re(CO)_3(PPh_3)_2X]$ derivatives (X = anion ligand), having the bulky phosphines in the *trans* position.[7,8] For these complexes the ketonic absorptions of the amido-ligand increased to *ca.* 1 600 cm^{-1}, a value in agreement with an unchelated mode of co-ordination. A similar shift of ν(C=O) was observed for complexes (III). The latter did not show very significant ^1H n.m.r. data, owing to the fact that they released the amine ligand in warm solutions, giving the starting complexes.

Complexes (I) did not react with secondary amines, NR'_2H, under an atmosphere of nitrogen. On the other hand, in the presence of even small amounts of air, a slow reaction was observed from which products having no more NHCOR moieties were obtained, the amido-residue being recovered as the corresponding free amide. Carbon dioxide was the cause of this reaction, a fast reaction occurring under an atmosphere of this gas. The products were identified as carbamate derivatives of Re^I (Table 1) [equation (3)]. Elemental analyses, and in particular oxygen analysis, are in complete agreement with this formulation. Moreover, on reaction of these complexes with mineral acids in ethanol CO_2 was evolved, while the fate of rhenium was not investigated. This remarkable reaction thus allowed the isolation of carbamate derivatives of Re^I, which to our knowledge are the first examples of carbamate derivatives of a transition metal having ligands other than NR_2 groups in the co-ordination sphere.[9,10] Moreover it is to be noted that the known carbamate derivatives all have the metal in a high oxidation state.



(IVa) R'=Et; (IVb) R'=Pr^n

Reaction (3) probably proceeds *via* the intermediate formation of the carbamic acid corresponding to the secondary amine, R'_2NCO_2H. In fact no reaction occurred between the amido-complexes and either CO_2 or NR'_2H when treated separately. This seems to exclude a previous reaction of the amido-complexes with the secondary amines giving rise to imino-derivatives, with which carbon dioxide can be inserted into the metal–nitrogen bond [equation (4)]. This is in agreement with other studies of the reaction between CO_2 and $SiMe_3(NMe_3)$ which led to $Me_3Si{-}O_2C{-}NMe_2$.[11] The reaction did not occur unless catalytic amounts of the corresponding secondary amine NMe_2H were added to the reaction medium.

The analogous reaction with CS_2 instead of CO_2, leading to dithiocarbamate complexes, $[Re(CO)_2(PPh_3)_2(S_2CNR'_2)]$, has been observed [complexes (Va; R' = Et) and (Vb; R' = Pr^n), Table 1]. More interestingly, complexes (IV) reacted with carbon disulphide at room temperature with displacement of carbon dioxide and formation of the corresponding dithiocarbamate derivatives (V).

Our formulation of the carbamate complexes as having chelated ligands is supported by i.r. evidence (Table 2). The terminal carbonyl groups absorb in the usual region for $[Re(CO)_2L(PPh_3)_2]$ species (L = pd[5] or $MeCO_2$[12]), while in the 1 550—1 330 cm^{-1} region two bands at *ca.* 1 540 and 1 320 cm^{-1} are always present. These absorptions could be assigned to the CO_2 groups of the carbamate ligands. The higher frequency band lies in the same position as ν_{asym}(C=O) of chelated carboxylato-derivatives.[12,13] On the other hand, for derivatives having unidentate carbamate moieties the $OC(O){-}NR_2$ absorptions have been observed above 1 600 cm^{-1}.[10a]

The dithiocarbamate derivatives, (V), showed medium-intensity C–N stretching absorptions at *ca.* 1 500 cm^{-1}, partially overlapping one of the bands due to the phenyl groups of the phosphines (Table 2). The occurrence of these bands in this range is usually considered as evidence of the partial double-bond character of the C–N groups.[14] Moreover, in the 900—1 000 cm^{-1} region no significant bands were detected,[15] while in the 1 100—1 300 cm^{-1} region three bands of medium–weak intensity were present; the latter seem to be related to vibrations arising from the dithiocarbamate ligand.

$$\mathrm{(I)} \underset{-\mathrm{RCONH_2}}{\overset{\mathrm{R'_2H}}{\nrightarrow}} [\mathrm{(Ph_3P)_2(OC)_2Re{-}NR'_2}] \xrightarrow{\mathrm{CO_2}} [\mathrm{(Ph_3P)_2(OC)_2Re(O_2C{-}NR'_2)}] \quad (4)$$

In the ^1H n.m.r. spectra (Table 2), the diethylcarbamate

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[7] T. Kruck and M. Noack, *Chem. Ber.*, 1964, **97**, 1693.

[8] J. Chatt, J. R. Dilworth, H. P. Gunz, and G. J. Leigh, *J. Organometallic Chem.*, 1974, **64**, 245.

[9] M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1967, **5**, 225.

[10] (*a*) M. H. Chisholm and M. Extine, *J. Amer. Chem. Soc.*, 1974, **96**, 6214; (*b*) *ibid.*, 1975, **97**, 1623; (*c*) *J.C.S. Chem. Comm.*, 1975, 438.

[11] H. Breederveld, *Rec. Trav. chim.*, 1960, **79**, 1126; *ibid.*, 1962, **81**, 276.

[12] G. La Monica, S. Cenini, V. G. Albano, E. Forni, and M. Manassero, *J. Organometallic Chem.*, 1976, **112**, 297.

[13] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912.

[14] B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1969, 1668.

[15] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley–Interscience, 1970, p. 256.

and diethyldithiocarbamate derivatives, (IVa) and (Va), showed the expected signals due to the ethyl groups. The spectra of the corresponding propyl derivatives, (IVb) and (Vb), were more complex and showed the same pattern as that of the di-n-propylamine. These spectra are not simply explainable by a first-order coupling between hydrogens.

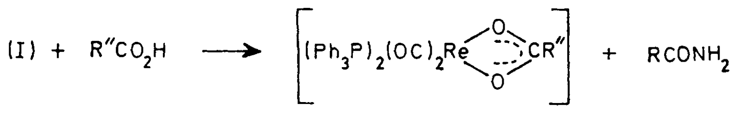
The reaction of complexes (I) with tertiary amines such as NEt_3 was also investigated; the unusual results have been reported elsewhere.[12]

TABLE 3

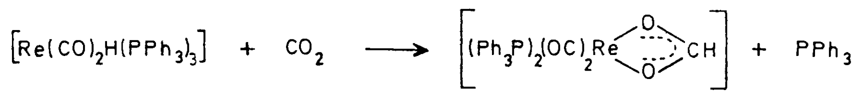
Analytical and infrared data (Nujol mull, cm^{-1}) for $[Re(CO)_2(O_2CR'')(PPh_3)_2]$ complexes [a]

R″	Colour	M.p. (θ_c/°C)	Analysis (%) [b] C	H	M [b]	ν(CO)	ν_{asym}(OCO)	ν_{sym}(OCO)
Me	White	232	58.35 (58.2)	4.1 (4.0)	840 [c] (825)	1 930s, 1 850s	1 515w	*d*
$ClCH_2$	Pale pink	214	55.6 (55.8)	3.75 (3.7)	878 [e] (859.5)	1 930s, 1 850s	1 640ms	1 440m
H	Pale yellow	193	58.4 [a] 56.95 [f] (57.7)	3.75 [a] 3.9 [f] (3.83)	834 [a,e] 797 [f] (811)	1 930s, 1 850s	1 550ms	1 360m
Et	White	198	58.7 (58.5)	4.0 (4.15)		1 930s, 1 850s	1 515m	1 450m
Ph	White	250	61.2 (61.0)	4.0 (3.95)		1 930s, 1 850s	1 505m	1 440m

[a] Obtained from the reaction of $[Re(CO)_2(NHCOR)(PPh_3)_2]$ with carboxylic acids $R''CO_2H$ (see text). [b] Calculated values are given in parentheses. [c] Determined osmometrically in $CHCl_3$. [d] Not detectable (see ref. 12). [e] Determined osmometrically in C_6H_6. [f] Obtained from the reaction of $[Re(CO)_2H(PPh_3)_2]$ with carbon dioxide.


(5)

R=Ph or C_6H_4Me-*p*; R″=$ClCH_2$, H, Ph, Me, or Et


(6)

From the reaction of complexes (I) with carboxylic acids $R''CO_2H$, derivatives having chelated carboxylato-groups were obtained [equation (5)] (see Table 3). These complexes have already been obtained by us from the reaction of $[Re(CO)_2H(PPh_3)_3]$ with the same series of carboxylic acids.[12] The formate derivative $[Re(CO)_2(O_2CH)(PPh_3)_2]$ was also obtained by the alternative route (6). This reaction involves the insertion of carbon dioxide at room temperature into the rhenium–hydrogen bond, analogously to examples using other metal hydrides.[16] In some cases this reaction has been reported to be reversible, but this was not the case for the rhenium formate derivative.

The peculiar spectroscopic properties of the acetate derivative, $[Re(CO)_2(O_2CMe)(PPh_3)_2]$ [ν_{asym}(C=O) and ν_{sym}(C=O) bands not clearly assignable, $\tau(CH_3)$ 9.5], prompted us to determine the *X*-ray structure.[12] The molecular configuration showed that the acetato-moiety was chelated, with the bulky phosphines in the *trans* position. A similar structure has been proposed for the other carboxylato-derivatives, on the basis of their i.r. data and reactivity with neutral ligands.[12]

The reactions of the rhenium amido-complexes with mineral acids were also studied. From these reactions rhenium complexes having the amide (NH_2COR) as ligand were isolated and characterized [(VI) and (VII), Table 1]; in some cases the products were identified only by means of their i.r. spectra [equations (7) and (8)].

$$\text{(I)} + HX \longrightarrow [Re(CO)_2(NH_2COR)(PPh_3)_2]X \quad (7)$$

$$[Re(CO)_3(NHCOR)(PPh_3)_2] + HX \longrightarrow [Re(CO)_3(NH_2COR)(PPh_3)_2]X \quad (8)$$

$$R = Ph \text{ or } C_6H_4Me\text{-}p;\ X = Cl \text{ or } BF_4$$

When the chelated amido-complexes were treated with mineral acids such as HCl and HBF_4 in non-polar solvents amide derivatives were isolated [equation (7)] which are unstable in solution. These complexes are probably ionic; however, particularly in the case of complex (VI; R = C_6H_4Me-*p*, X = Cl), an alternative non-ionic formulation cannot be excluded. This complex is soluble only in polar solvents such as ethanol, but in solution the amide ligand is lost while the rhenium moiety is transformed into $[Re(CO)_2Cl(PPh_3)_2]$. This fact prevented any conductivity measurements. The six-co-ordinate amide complex (VII; R = C_6H_4Me-*p*, X = BF_4) [equation (8)] is much more stable in solution. However, nucleophilic attack by the anion on the

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[16] M. E. Volpin and I. S. Kolomnikov, *J. Appl. Chem.*, 1973, 567 and refs. therein.

chloride derivative gave the free amide and $[Re(CO)_3Cl(PPh_3)_2]$ in solution [equation (9)]. Nitrobenzene

$$[Re(CO)_3(NH_2COR)(PPh_3)_2]Cl \longrightarrow [Re(CO)_3Cl(PPh_3)_2] + NH_2COR \quad (9)$$

solutions of this derivative gave very low molar conductivities.

Although the rhenium amido-complexes reacted with a variety of acids, the protonation did not occur when a weak acid such as water was used. The reactions with water were attempted with the aim of producing rhenium hydroxo-species, which have been recently employed as catalysts in the hydrolysis of aliphatic and aromatic nitriles to the corresponding amides.[17]

EXPERIMENTAL

Hydridorhenium complexes, $[Re(CO)_2H(PPh_3)_3]$ and $[Re(CO)_3H(PPh_3)_2]$, were prepared by literature methods. All reactions were carried out under nitrogen, using well dried solvents. The i.r. and n.m.r. spectra were recorded on Beckman model 33 and Perkin-Elmer model 237 spectrophotometers and on a Varian NV-14 instrument operating at 60 MHz, respectively.

Benzamidodicarbonylbis(triphenylphosphine)rhenium(I), $[Re(CO)_2(NHCOPh)(PPh_3)_2]$ (Ia).—To a degassed solution (100 cm^3) of $[Re(CO)_2H(PPh_3)_3]$ (1.0 g) was added benzoyl azide (0.62 g). The resulting solution was stirred for 5 h at 40—50 °C. The brownish solution was evaporated to dryness and the residue treated with ethanol. Complex (Ia) was recovered by filtration, washed with ethanol, and dried *in vacuo*. The brown ethanolic solution was evaporated to dryness. The i.r. spectrum of the residue showed the presence of the adduct $[PPh_3(NCOPh)]$ and of benzamide. Moreover, in the 1 800—2 000 cm^{-1} region several bands were present, probably attributable to a rhenium carbonyl by-product. This could not be purified, even by column chromatography.

$[Re(CO)_2(NHCOC_6H_4Me\text{-}p)(PPh_3)_2]$, (Ib).—This complex was prepared as for (Ia) using *p*-toluoyl azide (0.65 g) and $[Re(CO)_2H(PPh_3)_3]$ (1.0 g). It was crystallized from chloroform–ethanol, but no variations were observed in its spectra and elemental analyses. *p*-Toluoyl amide, the phosphine adduct, and the rhenium by-product were also shown to be present.

Benzamidotricarbonylbis(triphenylphosphine)rhenium(I), $[Re(CO)_3(NHCOPh)(PPh_3)_2]$ (IIa).—Carbon monoxide was slowly bubbled through a benzene solution (60 cm^3) of (Ia) (0.1 g) for 12 h. The solution was evaporated to dryness and the residue washed with n-hexane; the white product was recovered by filtration and then dried *in vacuo*. The complex $[Re(CO)_3(NHCOC_6H_4Me\text{-}p)(PPh_3)_2]$, (IIb), was obtained using the same procedure.

Benzamidodicarbonyl(n-butylamine)bis(triphenylphosphine)rhenium(I), $[Re(CO)_2(NHCOPh)(NBu^nH_2)(PPh_3)_2]$ (IIIa).—To a suspension of (Ia) (0.1 g) in ethanol (50 cm^3) were added 15 drops of n-butylamine. The mixture was stirred for 12 h. The insoluble white complex, (IIIa), was filtered off, washed with ethanol, and dried *in vacuo*.

$[Re(CO)_2(NHCOC_6H_4Me\text{-}p)(NBu^nH_2)(PPh_3)_2]$, (IIIb).—To a benzene solution (50 cm^3) of (Ib) (0.08 g) were added 10 drops of n-butylamine with stirring. After 3 h the pale yellow solution was evaporated to dryness and the residue was treated with n-hexane. Complex (IIIb) was recovered by filtration and dried *in vacuo*.

Dicarbonyl(diethylcarbamato)bis(triphenylphosphine)rhenium(I), $[Re(CO)_2(O_2CNEt_2)(PPh_3)_2]$ (IVa).—To a benzene solution (80 cm^3) of (Ib) (0.1 g) were added a few drops of diethylamine and the resulting solution was stirred for 15 h in the air. It was then evaporated to dryness and the residue was treated with ethanol. Complex (IVa) was recovered by filtration as an insoluble product. In the filtrate, evaporated to dryness, the presence of $p\text{-}MeC_6H_4CONH_2$ was confirmed by comparison of the i.r. spectrum with that of an authentic sample. When the same reaction was conducted in a carbon dioxide atmosphere it was complete in 2 h. The complex $[Re(CO)_2(O_2CNPr^n_2)(PPh_3)_2]$, (IVb), was prepared as for (IVa).

Dicarbonyl(diethyldithiocarbamato)bis(triphenylphosphine)rhenium(I), $[Re(CO)_2(PPh_3)_2(S_2CNEt_2)]$ (Va).—(a) To a benzene solution (50 cm^3) of (Ib) (0.07 g), maintained at 45 °C, were added a few drops of CS_2 and NEt_2H with stirring. After 2.5 h the pale brown solution was evaporated to dryness and the residue was washed with ethanol. Complex (Va) was recovered by filtration, washed with ethanol, and dried *in vacuo*.

(b) The complex was also obtained by stirring a CS_2 solution of complex (IVa) for 48 h. The solution was evaporated to dryness and the residue treated with ethanol. Complex (Va) was recovered by filtration.

The complex $[Re(CO)_2(PPh_3)_2(S_2CNPr^n_2)]$, (Vb), could be prepared, as for (Va), either by reaction of (Ib) with carbon disulphide and di-n-propylamine, or by displacing CO_2 with CS_2 from (IVb).

Reactions of the Amido-complexes with HCl.—(a) $[Re(CO)_2(NH_2COC_6H_4Me\text{-}p)(PPh_3)_2]Cl$, (VI). To an n-hexane–cyclohexane (4 : 1) mixture, previously saturated with gaseous HCl, was added (Ib). The suspension was stirred for 1 h and the insoluble complex (VI) was filtered off and dried *in vacuo*. Conductivity measurements in nitrobenzene gave values attributable to approximately non-conducting solutions (see text).

(b) (Ia). When the same procedure was applied to complex (Ia) an insoluble pale grey material was recovered. Its i.r. spectrum showed significant bands at 3 350w, 3 180w, 1 925s, 1 835s, 1 650m, and 1 625m cm^{-1}. Although no satisfactory elemental analyses were obtained, the formulation of the product as $[Re(CO)_2(NH_2COPh)(PPh_3)_2]Cl$ is plausible.

(c) (IIb). To a saturated diethyl ether solution of gaseous HCl was added (IIb) with stirring. After 1 h a white insoluble complex was filtered off, washed with anhydrous diethyl ether, and dried *in vacuo*. The product showed significant i.r. bands at 3 240w, 2 040m, 1 960s, 1 905s, and 1 630m cm^{-1}. No reproducible analyses were obtained, but the i.r. data were consistent with the formulation $[Re(CO)_3(NH_2COC_6H_4Me\text{-}p)(PPh_3)_2]Cl$. When this product was left in ethanol solution overnight under stirring, $[Re(CO)_3Cl(PPh_3)_2]$ was recovered as insoluble material while *p*-toluamide was identified in the mother liquor.

Reactions of the Amido-complexes with HBF_4.—(a) $[Re(CO)_3(NH_2COC_6H_4Me\text{-}p)(PPh_3)_2][BF_4]$, (VII). To a benzene solution (40 cm^3) of (IIb) (0.08 g) were added a few drops of an aqueous solution of tetrafluoroboric acid. After 3 h the white complex (VII) was filtered off, washed with anhydrous diethyl ether, and dried *in vacuo*.

(b) (Ib). When the procedure described in (a) was

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[17] M. A. Bennett and T. Yoshida, *J. Amer. Chem. Soc.*, 1973, **95**, 3030.

applied to (Ib) an insoluble grey product was obtained. Its i.r. spectrum showed absorptions at 3 350w, 1 925s, 1 825s, 1 635m, and 1 555m cm^{-1}; moreover the typical band of $[BF_4]^-$ was present. No satisfactory analyses were obtained, but the i.r. spectrum seems indicative of the formation of $[Re(CO)_2(NH_2COC_6H_4Me\text{-}p)(PPh_3)_2][BF_4]$.

Reactions of $[Re(CO)_2(NHCOR)(PPh_3)_2]$ (R = Ph *or* C_6H_4Me-*p*) *with Carboxylic acids* $R''CO_2H$ (R″ = Me, $ClCH_2$, H, Et, *or* Ph).—All these reactions were carried out in ethanol at room temperature with stirring, using an excess of the organic acid. The insoluble carboxylate derivatives were filtered off, washed with ethanol, and dried *in vacuo*. The acetate derivative could also be obtained by treating complex (IIb) with acetic acid for 1 h at 50 °C in ethanol. In the mother liquor the presence of benzamide or *p*-toluamide was detected. The carboxylates were identified by their i.r. and n.m.r. spectra [12] and by elemental analyses.

Reaction of CO_2 *with* $[Re(CO)_2H(PPh_3)_3]$.—Carbon dioxide was bubbled for 7 h through a benzene solution of $[Re(CO)_2H(PPh_3)_3]$. The resulting solution was evaporated to dryness and the residue was treated with ethanol. The insoluble formate, $[Re(CO)_2(O_2CH)(PPh_3)_2]$, was filtered off, washed with ethanol, and dried *in vacuo*. It was recognised by its elemental analyses and i.r. spectrum.

Deuteriation of $[Re(CO)_2(NHCOC_6H_4Me\text{-}p)(PPh_3)_2]$.—The deuteriation was carried out in absolute benzene by stirring the complex with D_2O (1 cm^3) for 40 h. The benzene solution was evaporated to dryness and the white residue showed a band at 2 525 cm^{-1} [ν(N–D)], replacing the absorption at 3 401 cm^{-1} [ν(N–H) of the starting material].

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