Journal of Organometallic Chemistry, 76 (1974) 355—365

SYNTHESIS AND REACTIONS OF ISOCYANATE AND CARBAMOYL COMPLEXES OF RHENIUM

G. La MONICA, S. CENINI and M. FRENI
Istituto di Chimica Generale, C.N.R. Center, Via Venezian, 21, 20133, Milano (Italy)
(Received March 12th, 1974)

Summary

$Re(CO)_2(NO)(PPh_3)_2$ reacts with aroyl azides $RCON_3$ ($R = C_6H_5$, p-$CH_3C_6H_4$) in benzene to form isocyanate complexes of formula $Re(CO)(NO)(PPh_3)_2(RCONCO)$ (I). When the reaction is carried out in protic solvents such as ethanol, carbamoyl derivatives of formula $Re(NCO)(NO)(PPh_3)_2(CONHCOR)$ (II) are obtained, which give $Re(NCO)(NO)(PPh_3)_2(CO)(NHCOR)$ when dissolved in chloroform, a terminal carbonyl ligand being formed from the carbamoyl group.

I can be transformed into II by reaction with gaseous HCl, via $[Re(CO)(NO)(PPh_3)_2\{C(OH)=NCOR\}]^+Cl^-$ followed by anion exchange with NaN_3. II reacts with mineral acids HX ($X = Cl$, BF_4) to give amide derivatives of formula $[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR)]^+ X^-$ which when $X = Cl$ can be easily transformed into $Re(NCO)(NO)(PPh_3)_2(CO)Cl$, the amide ligand being removed. Both the protonation reactions of I and II are reversible. IR and ^1H NMR data of the new compounds and the mechanisms of formation of I and II are reported and discussed.

Introduction

Recently we have undertaken a systematic study of the reactions of organic azides with low-valent transition metal complexes [1, 2]. We found that the reactions between toluene-p-sulphonyl azide and $M(CO)(NO)(PPh_3)_2$ derivatives ($M = Rh$, Ir) in benzene gave the urea complexes $M(NO)(PPh_3)_2(RNCONR)$ ($R = p$-$CH_3C_6H_4SO_2$) [1], being a cycloaddition of the nitrene residue of the azide to the coordinated carbon monoxide. A mechanism involving the formation of intermediate isocyanate derivatives, presumably via labile nitrene complexes was proposed [1], but we were unable to isolate such intermediates.

Isocyanate complexes have been previously reported for reactions of *trans*-$IrCl(CO)(PPh_3)_2$ with aroyl azides in alcohol-free solutions [3] and $Rh(PPh_3)_3Cl$

TABLE 1

ANALYTICAL DATA

Compound ($R = C_6H_5$, $R' = p\text{-}CH_3C_6H_4$)		Colour	M.p. (°C)	Analyses found/(calcd.) (%)		
				C	H	N
(Ia)	$Re(CO)(NO)(PPh_3)_2(RCONCO)$	orange	145	60.2 (59.2)	3.65 (3.82)	3.21 (3.06)
(Ib)	$Re(CO)(NO)(PPh_3)_2(R'CONCO)$	orange	165	57.9 (59.3)	4.00 (3.98)	2.67 (3.00)
(IIa)	$Re(NCO)(NO)(PPh_3)_2(CONHCOR)$	orange	184	57.23 (58.0)	3.80 (3.87)	4.34 (4.50)
(IIb)	$Re(NCO)(NO)(PPh_3)_2(CONHCOR')$	orange	207	57.87 (58.3)	4.07 (4.03)	4.39 (4.45)
(IIIa)	$Re(NCO)(NO)(PPh_3)_2(CO)(NHCOR)$	yellow	195	57.46 (58.0)	4.00 (3.87)	4.33 (4.50)
(IIIb)	$Re(NCO)(NO)(PPh_3)_2(CO)(NHCOR')$	yellow	205	57.10 (58.3)	3.92 (4.03)	4.12 (4.45)
(IVa)	$[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR)]Cl$	pale-yellow	243	55.13 (54.7)	3.59 (3.82)	4.21 (4.34)
(IVb)	$[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR')]Cl^a$	pale-yellow	250	55.8 (56.3)	3.76 (3.98)	4.17 (4.28)
(V)	$Re(NCO)(NO)(PPh_3)_2(CO)Cl$	pale-brown	250	54.6 (54.0)	3.67 (3.55)	3.19 (3.31)
(VI)	$[Re(CO)(NO)(PPh_3)_2\{C(OH)=NCOR'\}Cl]^b$	yellow	125 (dec)	55.9 (56.0)	3.80 (3.94)	2.70 (2.90)
(VII)	$[Re(CO)(NO)(PPh_3)_2(CONHCOR)]BF_4$	yellow	185	53.56 (54.0)	3.73 (3.6)	2.53 (2.8)
(VIIIa)	$[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR)]BPh_4{}^c$	pale-yellow	169	65.8 (66.2)	4.47 (4.55)	3.27 (3.36)
(VIIIb)	$[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR')]BPh_4$	yellow	140	66.2 (66.5)	4.54 (4.67)	3.18 (3.32)

[a] Λ_M (nitrobenzene) 11.2 (this value decreased with time). [b] Λ_M (nitrobenzene) 19.5 (unchanged with time). [c] Λ_M (nitrobenzene) 15.7 (unchanged with time).

with PhNCO [4]. The reactivity of the coordinated isocyanate ligands has not been explored. The recent synthesis in our laboratories of $Re(CO)_2(NO)(PPh_3)_2$ [5] prompted us to extend to this compound the study of the reactivity of organic azides both in protic and nonprotic solvents. We have previously shown [1, 2] that the nature of the reaction medium greatly affects the products which can be isolated when organic azides are allowed to react with transition-metal complexes. From previous studies [6, 7] in which nitrene—rhenium derivatives were easily prepared, we expected that reactions of organic azides with low-valent rhenium complexes would lead to this type of product. It is well known that organic azides are the best sources of organic nitrene intermediates. However in the previously isolated nitrene—rhenium complexes carbon monoxide was never present as a ligand and the metal was in a relatively high oxidation state. To our knowledge, the only nitrene derivatives also containing coordinated carbon monoxide are $M(CO)_2(PPh_3)_2(NR)$ (M = Ru, Os; $R = CF_3CHFCF_2$) [8a], $M(CO)(PPh_3)_2Cl(NR)$ (M = Rh, Ir; $R = CF_3CHFCF_2$) [8a] and $Ir(CO)(PPh_2Me)_2Cl(NCF_3)$ [8b], in which the fluorine substituents seem to stabilize the nitrene derivative, so preventing the formation of isocyanate by reaction with the coordinated carbon monoxide.

Results

Dicarbonylnitrosylbis(triphenylphosphine)rhenium reacts with $RCON_3$ ($R = C_6H_5$, p-$CH_3C_6H_4$) in dry benzene to give isocyanate complexes (Table 1) according to:

$$Re(CO)_2(NO)(PPh_3)_2 + RCON_3 \xrightarrow{C_6H_6} (PPh_3)_2(CO)(NO)Re(RCONCO) + N_2$$

(Ia) $R = C_6H_5$
(Ib) $R = p\text{-}CH_3C_6H_4$

In their IR spectra (Table 2) these derivatives show two strong absorption bands at 1730 and 1960 cm^{-1}, assignable to $\nu(NO)$ and $\nu(CO)$ respectively; two other bands at 1370 and 1480 (Ia) and 1360 and 1470 cm^{-1} (Ib) are present, which can be attributed to the coordinated isocyanate ligand. Two absorptions in the region 1350—1650 were reported for the known aroyl—isocyanate complexes [3], but they were assigned without further details. We did not detect any significant band in the 1600 cm^{-1} region, but only absorptions of medium-weak intensity. In the complexes here described the presence of the unchanged benzoyl residue, which excludes a rearrangement of the starting azide $RCON_3$ to RNCO, was confirmed by the isolation of the amide $RCONH_2$ during studies of the reactivities of the derivatives (see later). From our IR data, we cannot define the mode of bonding of the isocyanate ligand to the rhenium metal, although coordination to the N=C bond seems to be the most probable [3].

Complexes Ia and Ib are soluble in chloroform, in which they proved to be monomeric; (Ib) showed the methyl resonance at the usual τ value in its ^1H NMR spectrum (Table 2).

When $Re(CO)_2(NO)(PPh_3)_2$ was treated with aroyl azides in protic solvents, carbamoyl derivatives II (Table 1) could be isolated, according to:

TABLE 2

SPECTROSCOPIC DATA

Compound	IR absorption bands (nujol, cm^{-1})					^{1}H NMR spectra (CDCl$_3$)
	ν(NH)	ν(NCO)	ν(CO)	ν(NO)	other peaks	
Ia	—	—	1960	1730	1480; 1370	
Ib	—	—	1960	1730	1470; 1370	τ(CH$_3$) 7.67
IIa	3160	2240	—	1690	1575; 1530	
IIb	3160	2240	—	1690	1570; 1520	τ(CH$_3$) 7.62
IIIa	3370	2240	2010	1700	1610; 1570; 1420	
IIIb	3380	2240	2010	1700	1610; 1560; 1415	τ(CH$_3$) 7.75; τ(NH) 5.2
IVa	3330	2230	2010	1755	1650; 1530	
IVb	3330	2220	2000	1755	1660; 1520	
V	—	2260	2000	1730	—	
VI[a]	—	—	1980	1785	1540; 1520	
VII	3180	—	2020	1785	1615; 1550; 1520	
VIIIa	3400; 3300	2230	2010	1750	1640; 1525	
VIIIb	3360	2240	2030	1740	1660; 1535	

[a] ν(OH) 3420. This compound shows several bands in the region 1600—1690 cm^{-1}. For its formulation see text.

$$\mathrm{Re(CO)_2(NO)(PPh_3)_2 + 2RCON_3 \xrightarrow{C_2H_5OH} Re(NCO)(NO)(PPh_3)_2(CONHCOR)}$$

$$\mathrm{+\ 2\,N_2 + 2\,RCOOC_2H_5}$$

(IIa) R = C_6H_5
(IIb) R = p-$CH_3C_6H_4$

IR and NMR data (Table 2) of these non-ionic complexes were in agreement with their formulations. The ν(NH) (ca. 3150 cm^{-1}) is particularly low and lies in the region where phthalimide, in which the same CONHCO group is present, absorbs. Besides the ν(NCO) and ν(NO) bands, compounds (IIa) and (IIb) show two absorptions in the 1500—1600 cm^{-1} region which can be attributed to the carbamoyl group in accordance with the assignments reported for known carbamoyl complexes [9a, 9b]. Isomerisation of II takes place in solution, in which a terminal carbonyl ligand is generated from the carbamoyl group:

$$\mathrm{Re(NCO)(NO)(PPh_3)_2(CONHCOR) \xrightarrow{CHCl_3} Re(NCO)(NO)(PPh_3)_2(CO)(NHCOR)}$$

(II)

(IIIa) R = C_6H_5
(IIIb) R = p-$CH_3C_6H_4$

This transformation can easily be followed by IR and ^{1}H NMR spectroscopy. In compounds III ν(CO) was detected at ca. 2000 cm^{-1}, while ν(NO) and ν(NH) occur at higher wave-numbers compared with II. Two absorptions at 1570 and 1600 (IIIa) and 1560 and 1600 cm^{-1} (IIIb) are attributable to the coordinated NHCOR group. Compound IIIb clearly showed a signal due to the NH group in the NMR spectrum, which was not observed in IIb during its transformation. However in the latter case the NH group should be rather acidic and its resonance probably lies under the absorption due to phosphines. In comparison, phthalimide shows the NH group resonance at around τ 0 in deuteroacetone.

The conversion of II into III, involving carbon monoxide abstraction from the carbamoyl moiety, had been observed previously by treating carbamoyl derivatives of transition metals with hydrochloric acid [9a], for example:

$$\begin{aligned} &cis\text{-}M(CO)_4(NH_2CH_3)(CONHCH_3) + 2HCl \rightarrow [M(CO)_5(NH_2CH_3)]^+Cl^- \\ &(M = Mn, Re) \qquad\qquad\qquad\qquad\qquad\qquad + [CH_3NH_3]^+Cl^- \end{aligned}$$

and other examples of this type of reaction have been reported recently for other transition metal carbamoyl complexes [10]. II reacts with HCl in an analogous way to these manganese and rhenium complexes to give ionic derivatives IV:

$$Re(NCO)(NO)(PPh_3)_2(CONHCOR) \underset{N(C_2H_5)_3}{\overset{HCl}{\rightleftarrows}}$$

$$[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR)]^+Cl^- \quad \begin{matrix} (IVa)\ R = C_6H_5 \\ (IVb)\ R = p\text{-}CH_3C_6H_4 \end{matrix}$$

However in our case the amide derived from the carbamoyl ligand is still coordinated to the metal. The reaction is reversible and by treating IV with bases such as triethylamine, the original carbamoyl complexes could be recovered. This observation is in agreement with the acidic nature of the hydrogen of *N*-bonded coordinated amides [11].

IR spectra of IV (Table 2) show absorption bands which are consistent with the assigned formulations. In particular, a band at around 1650 cm^{-1} is present which can be assigned to ν(CO) of the coordinated amide. This band lies ca. 50 cm^{-1} higher compared with III and ca. 15 cm^{-1} lower compared with the free amide. The band associated with NH_2 bending is lowered by about 100 cm^{-1} upon coordination and is in agreement with the results for other amide complexes [12].

Although in IV the coordination of the amide through nitrogen is more likely, especially in view of their easy reaction with bases, the IR evidence does not conclusively support this type of coordination [12].

The presence of aroyl amides as ligands has been confirmed in these derivatives by stirring a benzene suspension of IVb for 24 h. From the resulting clear solution, $Re(NCO)(NO)(PPh_3)_2(CO)Cl$ (V) was isolated, together with an organic material which was shown to be $CH_3C_6H_4CONH_2$ by comparison with an authentic sample. Free amide and V were always obtained directly when the protonation reaction of II was carried out in a carbon monoxide atmosphere in various solvents. On the other hand III did not show any reaction with mineral acids under a variety of experimental conditions. Thus the formation of complexes having amides as ligands was achieved only when carbamoyl derivatives were used as starting material while complexes where the Re—NHCOR moiety is present, did not show any tendency to undergo protonation reactions.

The reactivity of Ib with HCl was also studied. By carrying out the reaction with hydrogen chloride in an ethereal suspension, the coordinated isocyanate ligand was shown to be protonated and an ionic derivative VI (Table 1) was formed:

$$(PPh_3)_2(CO)(NO)Re(RCONCO) \underset{N(C_2H_5)_3}{\overset{HCl}{\rightleftharpoons}}$$

$$[(PPh_3)_2(CO)(NO)Re\{(C(OH){=}NCOR)\}]^+Cl^- \text{ (VI)}R = p\text{-}CH_3C_6H_4$$

The carbamoyl and nitrosyl absorptions in VI (Table 2) are at higher wavenumbers than in Ib as expected, a cationic complex being formed. Ia behaves as Ib when treated with HCl (IR evidence), but the complex obtained was not fully characterized.

VI showed a number of bands in the 1500—1650 cm^{-1} region which makes the assignment of the various bending and stretching modes predicted for this type of derivative difficult. Moreover a broad absorption at ca. 3420 cm^{-1} is present. The latter could be ascribed to ν(OH) of the coordinated organic moiety. Our formulation of compound VI presumes that in this case the protonation involves oxygen and not nitrogen of the isocyanate ligand. This is supported by the fact that if Re—CONHCOR was formed ν(NH) would be much lower (see above) than that observed. Moreover VI showed marked differences in the 1500—1600 cm^{-1} region compared with the analogous carbamoyl derivatives isolated (see compounds II). This type of derivative should correspond to the intermediate proposed during the formation of carbamoyl complexes by hydroxide addition to coordinated isocyanide ligands [10].

The protonation reaction was found to be reversible: with bases such as triethylamine with an ether suspension the starting isocyanate complexes could be recovered, and VI spontaneously loses hydrochloric acid in chloroform. In fact during attempted determinations of the ^{1}H NMR spectrum of VI, only τ(CH$_3$) due to Ib was observed and the starting isocyanate complex could be obtained from the chloroform solution.

The transformation was also followed by IR spectroscopy in CHCl$_3$ solution, when the NO absorption of the protonated species VI initially present at 1780 cm^{-1} slowly disappeared while a new band at 1730 cm^{-1}, coincident with that of Ib, gradually appeared. In nitrobenzene solution compound VI showed a molar conductivity typical of a 1/1 electrolyte, which does not change over 24 h. When HBF$_4$ was used as the protonating agent a compound analysing as VI, but with BF_4^- instead of Cl^-, was obtained but with an IR spectrum somewhat different from that of VI. In particular a band at ca. 3180 cm^{-1} was observed while the 1500—1600 cm^{-1} region was very similar to that observed for II (see above). This seems to indicate that with HBF$_4$ protonation of nitrogen rather than oxygen of the isocyanate ligand occurs leading to the carbamoyl derivative of formula $[(PPh_3)_2(CO)(NO)Re(CONHCOC_6H_5)]^+BF_4^-$ (VII). The behaviour with the two acids might be attributed to the different stabilizing effects of the anions in the solid state, since treatment of VII with LiCl in an alcoholic suspension gives the compound corresponding to VI, with R = C_6H_5.

The reaction with HBF$_4$ was also found to be reversible, the starting isocyanate complex being recovered by treatment with $N(C_2H_5)_3$. The easy deprotonation of VI and the BF_4^- carbamoyl derivative to regenerate I supports the view that they are the intermediates in the catalytic formation of organic isocyanates from CO and amines in the presence of a transition metal compound, as pointed out by Angelici [9b]. Compound VI was treated with NaN$_3$ to prepare the azide derivative but a further reaction was observed: the nucleophilic attack of N_3^- on coordinated carbon monoxide to give IIb:

$$\underset{\text{(VI)}}{[(PPh_3)_2(CO)(NO)Re\{C(OH)=NCOR\}]^+Cl^-} \xrightarrow{NaN_3} \underset{\text{(IIb)}}{(PPh_3)_2(NCO)(NO)Re(CONHCOR)}$$

$(R = p\text{-}CH_3C_6H_4)$

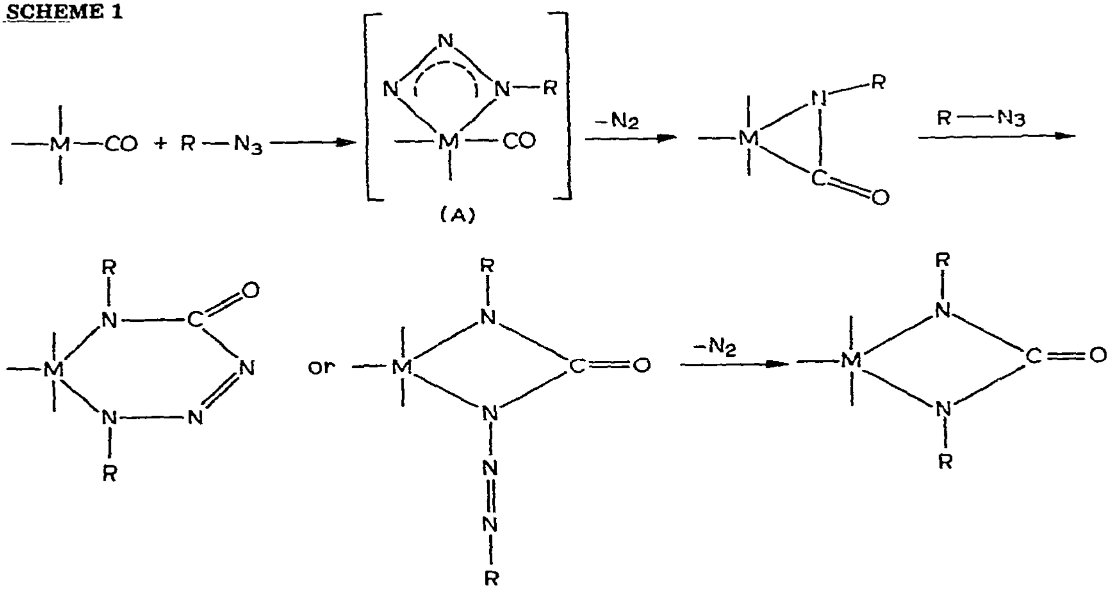
The formation of complexes containing NCO from metal carbonyls and N_3^- is a well known reaction [13, 14]. IIb is the same product as that obtained from $Re(CO)_2(NO)(PPh_3)_2$ and $RCON_3$ ($R = p\text{-}CH_3C_6H_4$) in ethanol, and this seemed to clarify the mechanism of the reactions in protic solvents. However as we will discuss later, an alternative route leading to II seems more probable.

The reaction of $Re(CO)_2(NO)(PPh_3)_2$ with toluene-*p*-sulphonyl azide at room temperature under various conditions was also investigated. This organic azide had been found to give well-characterizable derivatives in previously studied reactions [2, 15] but with our rhenium substrate we never observed the formation of derivatives containing the tolyl residue. When protic solvents were used, only the presence of the azido group in the products was detected by IR spectroscopy and the recovered materials were shown to be complex mixtures from which it was difficult to isolate well-defined compounds.

Discussion and conclusions

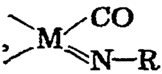
It seems to be well established that the reactions of organic azides with metal carbonyl derivatives in non-polar solvents follow the general Scheme 1.

SCHEME 1



The different types of complexes have all been isolated [1, 3], but in some cases [16] bridging urea derivatives were obtained instead of monomeric products. The intermediate (A), not isolable, should correspond to the adduct which has been postulated in azide decomposition to give nitrenes catalysed by copper and copper salts [17].

The results obtained in the protonation of $Re(CO)(NO)(PPh_3)_2(RCONCO)$ ($R = p\text{-}CH_3C_6H_4$) and subsequent anion exchange of the resulting $[Re(CO)(NO)(PPh_3)_2\{C(OH){=}NCOR\}]^+ Cl^-$ with N_3^-, seem to clarify the mechanism of formation of the carbamoyl complexes $Re(NCO)(NO)(PPh_3)_2(CONHCOR)$ in the reactions carried out in ethanol. It is reasonable to suppose that isocyanate derivatives I could be the initial products of the reactions. These complexes, by further attack by HN_3, formed from the organic azide in the ethanolic solvent, could thus be transformed into II. During HN_3 formation, the R—CO residue of the azide is converted into $RCOOC_2H_5$ by means of ethanol. However, compound Ib did not react with the azide in ethanol, and was recovered unchanged after prolonged reaction with warm ethanol.

As an alternative hypothesis, the formation of a labile nitrene complex from (A),  $>M(CO){=}N{-}R$, can be postulated which could be converted to the isocyanate complexes in benzene solution. When a protic solvent is used, the nitrene residue is protonated and the resulting M—NHR group can then insert one carbonyl ligand to give a carbamoyl complex. This is in agreement with the results previously obtained in the reaction of triphenylphosphine complexes of platinum(0) with organic azides in ethanol [15], from which $Pt(PPh_3)_2(N_3)(NHR)$ compounds were isolated. In the latter case the absence of coordinated carbonyl ligands allowed the isolation of compounds containing coordinated N_3 and NHR groups instead of NCO and CONHR substituents, as formed in the present system. From the reaction of $Pt(PPh_3)_2(CO)_2$ with sulphonyl azides in ethanol, the corresponding carbamoyl isocyanate complex was not isolated [1], while the bis-ester derivative $Pt(PPh_3)_2(COOC_2H_5)_2$ was obtained.

However, as has been found for some carbamoyl complexes [18], the $\geq$M—CONHR group can be alcoholised by ROH giving the $\geq$M—COOR system, with concomitant formation of the corresponding amines. This could also occur in the reaction of $Pt(PPh_3)_2(CO)_2$ with organic azides in alcohol, where the possible carbamoyl intermediate might be alcoholized by ethanol, but the nucleophilic attack of RO^- on an unknown cationic carbonyl intermediate can not be excluded [19, 20]. However with the carbamoyl complexes isolated in the present work, where $R = C_6H_5CO$ or $p\text{-}CH_3C_6H_4CO$ and in our experimental conditions, the derivatives are stable enough to be isolated.

Experimental

Starting materials were prepared as described in the literature. All the reactions were carried out in a nitrogen atmosphere with stirring, using well-dried solvents. IR spectra were taken on Beckman model 33 and Perkin—Elmer model 237 instruments. ^1H NMR spectra were recorded on a Varian NV-14 instrument operating at 60 MHz.

Re(CO)(NO)(PPh₃)₂(RCONCO), (Ia, R = C₆H₅; Ib, R = p-CH₃C₆H₄)

To a degassed solution (15 ml) of benzoyl azide (0.28 g) in benzene maintained at 13—15°C, $Re(CO)_2(NO)(PPh_3)_2$ (0.5 g) was slowly added and the resulting deep-red solution was stirred for 48 h. The red-orange product (Ia) was filtered off, washed with a little benzene and dried in vacuo.

The red-orange compound Ib was prepared as described for Ia using *p*-toluoyl azide.

Re(NCO)(NO)(PPh$_3$)$_2$(CONHCOR), (IIa, R = C$_6$H$_5$; IIb, R = p-CH$_3$C$_6$H$_4$)

To a degassed solution (50 ml) of $C_6H_5CON_3$ (1.5 g) in ethanol, $Re(CO)_2(NO)(PPh_3)_2$ (0.4 g) was added and the suspension stirred for 40 h. The insoluble orange compound IIa was filtered off, washed with benzene and then with ethyl ether and dried in vacuo.

The orange compound IIb was prepared as for IIa using *p*-toluoyl azide. The mother liquor, evaporated to dryness, gave a residue whose ^1H NMR spectrum showed signals due to the presence of the ester $CH_3C_6H_4COOC_2H_5$ as seen by comparison with that of a pure sample.

Re(NCO)(NO)(PPh$_3$)$_2$(CO)(NHCOR), (IIIa, C$_6$H$_5$; IIIb, R = p-CH$_3$C$_6$H$_4$)

A chloroform suspension of IIa was stirred for 4 h. The resulting yellow solution was evaporated to dryness and the residue treated with petroleum ether; IIIa was recovered as a yellow compound.

The yellow product IIIb was obtained using the same procedure as that described for IIIa.

[Re(NCO)(NO)(PPh$_3$)$_2$(CO)(NH$_2$COR)]$^+$Cl$^-$, (IVa R = C$_6$H$_5$; IVb, R = p-CH$_3$C$_6$H$_4$)

To an ether suspension of IIa a saturated ether solution of gaseous HCl was added with stirring. After 15 min the insoluble pale-yellow compound was filtered off, washed with ethyl ether and dried in vacuo.

The pale-yellow compound IVb was prepared as described for IVa.

Re(NCO)(NO)(PPh$_3$)$_2$(CO)Cl, (V)

To a carbon monoxide-saturated benzene solution IIa or IIb was added. A benzene solution of gaseous HCl was then added while bubbling CO. After 15 min the brown solution was evaporated to dryness and the residue treated with ethanol. The pale-brown compound was recovered as an insoluble material. The mother liquor, evaporated to dryness, contained $C_6H_5CONH_2$ or $CH_3C_6H_4CONH_2$ as shown by IR data.

Compound (V) was also obtained by stirring a benzene suspension of IVa or IVb for 48 h. The resulting solution was evaporated to dryness and the residue treated with ethyl ether (or ethanol). V was recovered as an insoluble compound. The presence of the aroyl amides was noted in the filtrate.

[Re(CO)(NO)(PPh$_3$)$_2${C(OH)=NCOC$_6$H$_4$CH$_3$}]$^+$Cl$^-$, *(VI)*

To a benzene saturated solution (10 ml) of gaseous HCl, Ib (0.25 g) was added. The yellow insoluble compound rapidly formed. It was filtered off, washed with a little benzene and dried in vacuo.

[Re(CO)(NO)(PPh$_3$)$_2$(CONHCOC$_6$H$_5$)]$^+$BF$_4^-$, (VII)

To a benzene suspension of Ia, a few drops of aqueous HBF_4 was added with stirring. After 30 min the yellow product was filtered off, washed several times with anhydrous diethyl ether and dried in vacuo.

$[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COR)]^+BPh_4^-$, (VIIIa, $R = C_6H_5$; VIIIb, $R = p\text{-}CH_3C_6H_4$)

To a saturated ethanol solution of $NaBPh_4$, IVa was added with stirring. After 1 h the pale-yellow compound VIIIa was filtered off, washed with ethanol and dried in vacuo.

The yellow compound VIIIb was similarly obtained as described for VIIIa.

Reaction of VI or VII with $N(C_2H_5)_3$

To a benzene (or ethyl ether) suspension of VI or VII, a few drops of triethylamine were added with stirring. Compound Ia or Ib respectively was rapidly formed. They were filtered off, washed with ethanol and dried in vacuo.

In the mother liquor, evaporated to dryness, the presence of $(C_2H_5)_3NH^+$ Cl^- was recognised in its IR spectrum compared with that of a pure sample.

Reaction of IVa or IVb or VIIIa or VIIIb with $N(C_2H_5)_3$

These deprotonation reactions were carried out as described for VI or VII, using ethanol as the medium. The insoluble compound was recognised as IIa or IIb depending on the starting material used. In the filtrate the triethylammonium salts $[(C_2H_5)_3NH]Cl$ or $[(C_2H_5)_3NH]BPh_4$ were identified.

Reaction of IIa with HBF_4

To IIa suspended in ethyl ether a few drops of aqueous HBF_4 were added. After 30 min a pale-yellow compound was filtered off, washed with ethyl ether and dried in vacuo. Its IR spectrum is consistent with the formula $[Re(NCO)(NO)(PPh_3)_2(CO)(NH_2COC_6H_5)]BF_4$ (ν(NH) 3340, 3300 cm^{-1}; ν(NCO) 2220 cm^{-1}; ν(CO) 2010 cm^{-1}; ν(NO) 1760 cm^{-1}; other absorptions: 1660, 1540 cm^{-1}).

Reaction of VI with NaN_3

Solid sodium azide was added to an ethanol solution of (VI) with stirring. After 10 h the pale-orange product was filtered off, washed several times with water in order to remove the unreacted NaN_3 and NaCl, and then with a little ethanol and dried in vacuo. It was identified as $Re(NCO)(NO)(PPh_3)_2(CONHCOC_6H_4CH_3)$ (IIb), already described, by elemental analysis and its IR spectrum.

Reaction of VII with LiCl

To VII, suspended in alcohol, solid LiCl was added with stirring. After 24 h the resulting yellow solution was evaporated to dryness and the residue treated with water. The yellow insoluble product was washed several times with ethyl ether and dried in vacuo. Its IR spectrum was identical to that of $[Re(CO)(NO)(PPh_3)_2\{C(OH)=NCOC_6H_5\}]Cl$ obtained from the reaction of Ia with HCl.

Acknowledgements

We wish to thank Dr. P.C. Fantucci for recording the ^1H NMR spectra, and the Italian C.N.R. for financial support.

References

1 W. Beck, W. Rieber, S. Cenini, F. Porta and G. La Monica, J. Chem. Soc. Dalton, (1974) 298, and refs. therein.
2 G. La Monica, P. Sandrini, F. Zingales and S. Cenini, J. Organometal. Chem., 50 (1973) 287.
3 J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, J. Amer. Chem. Soc., 90 (1968) 5430.
4 I.S. Kolomnikov, Yu. D. Koreshkov, T.S. Lobeeva and M.E. Volpin, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1972) 1181.
5 G. La Monica, M. Freni and S. Cenini, J. Organometal. Chem., 71 (1974) 57.
6 J. Chatt, J.D. Garforth, N.P. Johnson and G.A. Rowe, J. Chem., Soc., (1964) 1012.
7 J. Chatt and J.R. Dilworth, J. Chem. Soc., Chem. Commun., (1972) 549.
8a M.J. McGlinchey and F.G.A. Stone, Chem. Commun., (1970) 1265.
b J. Ashley-Smith, M. Green, N. Mayne and F.G.A. Stone, Chem. Commun., (1969) 409.
9a R.J. Angelici and A.E. Kruse, J. Organometal. Chem., 22 (1970) 461.
b R.J. Angelici, Accounts Chem. Res., 5 (1972) 335.
10 P.M. Treichel and W.J. Knebel, Inorg. Chem., 11 (1972) 1285, and ref. therein.
11 R.J. Balahura and R.B. Jordan, J. Amer. Chem. Soc., 92 (1970) 1533.
12 M.F. Farona, J.G. Grasselli, H. Grossman and W.H. Ritchey, Inorg. Chim. Acta., 3 (1969) 495.
13 R.J. Angelici and L. Busetto, J. Amer. Chem. Soc., 91 (1969) 3197.
14 W. Beck, H. Werner, H. Engelmann and H.S. Smedal, Chem. Ber., 101 (1968) 2143.
15 W. Beck, M. Bauder, G. La Monica, S. Cenini and R. Ugo, J. Chem. Soc. (A), (1971) 113.
16 M. Dekker and G.R. Knox, Chem. Commun., (1967) 1243.
17 W. Lwowski (Ed.), Nitrenes, Wiley-Interscience, New York, 1970.
18 R.W. Brink and R.J. Angelici, Inorg. Chem., 12 (1973) 1062.
19 Th. Kruck and M. Noack, Chem. Ber., 97 (1964) 1693.
20 H.C. Clark, K.R. Dixon and W.J. Jacobs, J. Amer. Chem. Soc., 91 (1969) 596, 1346.