Journal of Organometallic Chemistry, 88 (1975) 237—248

ISOCYANATE, UREA AND AMIDE COMPLEXES FROM THE REACTIONS OF ORGANIC AZIDES WITH LOW OXIDATION STATE COMPLEXES OF TRANSITION METALS

S. CENINI, M. PIZZOTTI, F. PORTA and G. LA MONICA

Istituto di Chimica Generale, C.N.R. Center, Via G. Venezian 21, 20133 Milano (Italy)

(Received October 30th, 1974)

Summary

The reactions of organic azides RN_3 (R = p-$CH_3C_6H_4SO_2$, p-$CH_3C_6H_4CO$, C_6H_5CO, 2-carbonylfuran) with $Ru(CO)_3(PPh_3)_2$ in benzene have been studied. Isocyanate, $Ru(CO)_2(PPh_3)_2(RNCO)$, urea, $Ru(CO)_2(PPh_3)_2(RNCONR)$ or amide, $Ru(CO)_2(PPh_3)_2(NHR)_2$, derivatives were obtained, depending on the reaction conditions and on the nature of R. The urea complex (R = p-$CH_3C_6H_4SO_2$) was also obtained by the oxidative addition of *N,N'*-ditoluene-*p*-sulphonyl urea or toluene-*p*-sulphonyl isocyanate to $Ru(CO)_3(PPh_3)_2$. The isocyanate derivative with R = C_6H_5CO was found to be protonated by fluoboric acid to give the corresponding carbamoyl complex, $[Ru(CO)_2(PPh_3)_2(CONHR)]^+BF_4^-$ which on treatment with LiCl gave the non-ionic derivative, $[Ru(CO)(PPh_3)_2(CONHR)Cl]_n$. Analogous reactions were studied with the complexes $Ru_3(CO)_9L_3$ (L = CO, PPh_3), but the only characterizable product was the monomeric $Ru(CO)_2L_2$-(RNCONR) (L = PPh_3, R = p-$CH_3C_6H_4SO_2$). Attempted cycloaddition reactions in benzene of the azides to coordinated ligands L other than carbon monoxide, such as CS_2, PhNCS, alkenes, in the complexes $Pt(PPh_3)_2L$ or SO_2 in $Pt(PPh_3)_3$-SO_2 were unsuccesful. Only in protic solvents was a clean reaction observed (L = CH_2=CHCN), leading to the known complex $Pt(PPh_3)_2(N_3)(NHR)$ (R = p-$CH_3C_6H_4SO_2$). Similarly, the complexes Pd(L—L)(dba) (L—L = 2,2'-bipyridyl, *o*-phenanthroline, dba = dibenzylideneacetone), on treatment with RN_3 in ethanol gave the new amide derivatives, Pd(L—L)(X)(NHR), (X = NHR, R = p-$CH_3C_6H_4SO_2$; X = N_3, R = p-$CH_3C_6H_4CO$).

Introduction

Organic azides are known to react with low oxidation state transition metal complexes to give a variety of products, their nature being primarily determined by the solvent employed and by the character of the organic residue of the azide [1, 2]. Recently we succeeded in isolating isocyanate [2], or monomeric urea derivatives [1] by cycloaddition reactions of organic azides to coordinated carbon monoxide. We report here further studies on this type of reaction and on our attempts to achieve cycloaddition of organic azides to coordinated ligands other than carbon monoxide.

In the reactions we studied, we did not observe the formation of nitrene derivatives, a type of product formed from fluorinated azides [3]. Electron-withdrawing substituents in the organic group of the azide thus seem necessary for stabilization of the nitrene intermediate, which otherwise gives place to a concerted reaction with other ligands bound to the metal, such as carbon monoxide.

Results

Reactions with $Ru(CO)_3(PPh_3)_2$ and $Ru_3(CO)_9(PPh_3)_3$

Treatment of $Ru(CO)_3(PPh_3)_2$ with toluene-*p*-sulphonyl azide in benzene at 0·5° gave an isocyanate complex (I) (Table 1):

$$Ru(CO)_3(PPh_3)_2 + RSO_2N_3 \rightarrow Ru(CO)_2(PPh_3)_2(RSO_2NCO) + N_2 \qquad (1)$$

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

The IR spectrum of I shows two $\nu(C{\equiv}O)$ bands of equal intensity, indicating a *cis* arrangement of the carbonyl groups (Table 2). The sulphonyl group bands appear at ca. 25 cm^{-1} to lower frequencies than in the free isocyanate ligand. A band at 1020 cm^{-1} can be assigned to $\nu(N{-}S)$, although the frequency is higher than usual [1]. Another broad band, detected at 1565 cm^{-1}, was attributable to $\nu(C{=}O)$ of the coordinated isocyanate group. Compound I could not be recrystallized owing to its instability in solution and the molecular weight in chloroform was lower than that calculated. When $Ru(CO)_3(PPh_3)_2$ was treated in dry benzene at room temperature with the less reactive azides $RCON_3$ ($R = C_6H_5$, p-$CH_3C_6H_4$), a slow reaction occurred, to give the corresponding isocyanate complexes $Ru(CO)_2(PPh_3)_2(RCONCO)$ (II and III). Both complexes were obtained contaminated by a by-product, which was removed with difficulty by crystallization. In addition to the expected $\nu(C{\equiv}O)$ indicative of a *cis* arrangement of the two carbonyl groups (Table 2), these compounds show three significant bands in the 1600-1400 cm^{-1} region associated with the isocyanate ligand. The medium broad band at around 1580-1600 cm^{-1} is stronger than that observed for related rhenium isocyanate complexes [2]. In the previously studied cases, the presence of the unchanged benzoyl residue and of an isocyanate group bound to the metal was supported by chemical reactions [2]. The molecular weights and the ^{1}H NMR spectra were consistent with the formulation of these derivatives, which proved to be more stable than I. A slow reaction was also observed between $Ru(CO)_3(PPh_3)_2$ and furoyl azide. However in this case the product was soluble in the reaction medium and was identified as the amide complex (IV), $Ru(CO)_2(PPh_3)_2(NHCOR)_2$ (R = furyl). In the IR spectrum the two bands of the *cis*-carbonyl groups were observed at 2045 and 1975 cm^{-1} and $\nu(NH)$ at 3380 cm^{-1}. A strong band at 1585 cm^{-1} was assigned to $\nu(C{=}O)$

(continued on p. 241)

TABLE 1

ANALYTICAL DATA

No.	Compound[a]	Colour	Melting point (°C)	Analyses found (calcd.) (%) C	H	N	Mol. wt. or Λ_M
I	$Ru(CO)_2(PPh_3)_2(RSO_2NCO)$	white		62.2	4.3	1.7	
				(62.7)	(4.2)	(1.6)	(878)
II	$Ru(CO)_2(PPh_3)_2(R'CONCO)$	pale-yellow	148	67.1	4.4	1.7	915[b]
				(66.6)	(4.2)	(1.7)	(828)
III	$Ru(CO)_2(PPh_3)_2(RCONCO)$	white	170	66.2	4.4	1.7	716[b]
				(67.0)	(4.4)	(1.6)	(842)
IV	$Ru(CO)_2(PPh_3)_2(NHCOR'')_2$	white	190	66.2	4.4	3.1	830[c]
				(66.1)	(4.3)	(3.2)	(871)
V	$Ru(CO)_2(PPh_3)_2(RSO_2NCONSO_2R)$	white	>250	59.6	4.0	2.7	1080[c]
				(60.7)	(4.2)	(2.6)	(1047)
VI	$[Ru(CO)_2(PPh_3)_2(CONHCOR')]^+BF_4^-$	white	235	59.2	4.2	1.4	24[d]
				(60.0)	(3.9)	(1.5)	
VII	$[Ru(CO)(PPh_3)_2Cl(CONHCOR')]_n$	white	>250	64.7	4.6	1.6	[e, f]
				(64.6)	(4.6)	(1.6)	
VIII	$[Ru(CO)_2(PPh_3)_2(NH_2COR'')_2]^{2+}[BF_4^-]_2$	creamy-white	135	55.3	3.8	2.2	30.5[d]
				(55.4)	(3.8)	(2.6)	
IX	$Pd(bipy)(N_3)(NHCOR)\cdot H_2O$	yellow	193	46.3	3.7	18.3	[f]
				(47.1)	(3.9)	(18.3)	
X	$Pd(bipy)(NHSO_2R)_2$	yellow	230	47.7	3.7	9.1	576[b]
				(47.9)	(3.9)	(9.4)	(602)
XI	$Pd(phen)(NHSO_2R)_2$	yellow	235	47.8	3.6	9.1	[f]
				(47.9)	(3.9)	(9.4)	

[a] $R = p\text{-}CH_3C_6H_4$, $R' = C_6H_5$, $R'' =$ furyl. [b] Chloroform. [c] Benzene. [d] Λ_M in nitrobenzene. [e] Non-conductor in nitrobenzene. [f] Slightly soluble.

TABLE 2

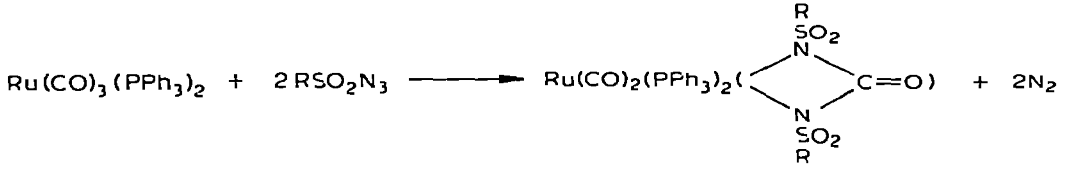
SPECTROSCOPIC DATA

No.	IR absorption bands (cm^{-1}, nujol)							^{1}H NMR spectra (CDCl$_3$)	
	ν(NH)(w)	ν(CO)(s)	ν(C=O)(m)	$\nu(SO_2)_{as}$(s)	$\nu(SO_2)_{sym}$(s)	ν(N-S)(s)	Other peaks	τ(NH)	$\tau(CH_3)$
I		2040-1975	1565	1235	1130	1020			7.6
II		2060-1950	1575				1500-1380		
III		2040-1950	1600				1480-1375		7.7
IV	3380	2045-1975	1585					5.35	^{a}
V		2050-1980	1675	1320	1140	940-870			7.70^b
VI	3170	2070-2000^c					1620-1550 1615	-0.4^d	
VII	3160	1940					1620-1560 1615		
VIII	3350	2065-2020	1650				1610-1590		
IX^{e,f}	3320		1545						
X	3280			1260	1140	925-890			7.6
XI	3280			1275	1140	935-895			

^{a} τ(CH) for the furoyl hydrogens were observed at around 3.5 and 3.8 (complex signals). ^{b} In C_6D_6. ^{c} In CH_2Cl_2. ^{d} In CD_3COCD_3. ^{e} $\nu(N_3)$ 2040. ^{f} $\nu(H_2O)$ 3520-3400.

of the furoyl residues. The presence in the complex of NH groups was confirmed by the ^1H NMR spectrum, which showed a broad resonance at τ 5.35. This abnormal reaction path with furoyl azide is probably due to adventitious moisture, which has an unusually large effect because the usual reaction is so slow. An analogous product is formed in the reaction of organic azides and $Pt(PPh_3)_4$ in wet benzene [4].

When reaction 1 was conducted at room temperature, a complex mixture of derivatives was obtained, but repeated crystallization gave low yields of a monomeric urea derivative V (eqn. 2). The IR spectrum of V shows, as for



(2)

(V, R = p-$CH_3C_6H_4$)

compounds I-IV, a *cis* arrangement of the carbonyl groups (Table 2), and the typical bands of the chelating ureylene ligand appear in the expected regions [1]. In particular the keto band at 1675 cm^{-1} was useful for detecting the presence of V in the mixture of compounds obtained from the reaction.

Compound (V) could be formed by reaction of initially formed I with the excess of azide, or by rearrangement in solution of other species [5]. Reaction of I with the azide in benzene at room temperature does in fact lead to the same mixture of derivatives, with V present in small amount.

V was also obtained by the oxidative addition to $Ru(CO)_3(PPh_3)_2$ of *N,N'*-ditoluene-*p*-sulphonyl urea in refluxing benzene or toluene-*p*-sulphonyl isocyanate at room temperature in benzene (eqn. 3). These reactions unambiguously confirm the nature of V, which was the only product isolated, and in much better yields than from reaction 2.

$$Ru(CO)_3(PPh_3)_2 + 2RSO_2NCO \xrightarrow[-2CO]{} V \xleftarrow[-CO,\,-H_2]{} Ru(CO)_3(PPh_2)_2 + RSO_2NHCONHSO_2R \qquad (3)$$

The cluster ruthenium complexes $Ru_3(CO)_9L_3$ ($L = CO, PPh_3$) show a low reactivity towards organic azides. With aroyl azides we did not observe any reaction in benzene, but with sulphonyl azides a reasonably fast reaction occurred at ca. 70°. However for $L = PPh_3$ only the monomeric ureylene complex (V) was isolated. For L = CO, a complex mixture of derivatives was obtained, and could not be separated even by column chromatography. For comparison we also studied the reaction of $Ru(CO)_3(PPh_3)_2$ with p-$CH_3C_6H_4NCO$, but even in refluxing benzene the zerovalent ruthenium complex was unchanged. These results emphasize the importance of the sulphonyl groups in stabilizing a four membered ring such as that present in compound V. Analogous urea derivatives have been previously obtained with other carbonyl complexes and toluene p-sulphonyl azide or isocyanate [1]. On the other hand the reactions of the same substrates with the less reactive azide $RCON_3$ ($R = C_6H_5$, p-$CH_3C_6H_4$) gave uncharacterizable products [6].

In order to investigate the effect of the metal on the reactivity of the complex towards the organic reagents employed, we also studied the behaviour of $Fe(CO)_3(PPh_3)_2$ in some of the reactions above. The corresponding iron products were not formed with reagents such as p-$CH_3C_6H_4CON_3$, p-$CH_3C_6H_4$-SO_2N_3 and p-$CH_3C_6H_4SO_2NHCONHSO_2C_6H_4CH_3$-$p$. Only when the reactions were carried out in refluxing benzene and with the sulphonyl derivatives did a reaction take place, but only inorganic iron residues and the phosphine—imino adduct, $RSO_2N{=}PPh_3$, were isolated. The different behaviour of the two metals can be related to the greater basic character of $Ru(CO)_3(PPh_3)_2$ with respect to $Fe(CO)_3(PPh_3)_2$ [7]. This presumably enables the zerovalent ruthenium complex to activate the azide under mild conditions, giving intermediate nitrene derivatives which then rearrange to the products described above [2].

We have also briefly investigated the reactions of the complexes $M(CO)_3(PPh_3)_2$ (M = Fe, Ru) with the azides in protic solvents such as ethanol, which are known to influence greatly the nature of the reaction [1]. We again did not observe any reaction at room temperature for M = Fe, but the ruthenium compound gave a complex mixture of derivatives.

Reactions of the ruthenium isocyanate complexes

We have already observed that the aroyl isocyanate ligand can be readily protonated with fluoboric acid when coordinated to a metal, giving the corresponding carbamoyl complex [2]. The ruthenium carbamoyl derivative VI has been obtained in this way:

$$Ru(CO)_2(PPh_3)_2(RCONCO) + HBF_4 \rightarrow [Ru(CO)_2(PPh_3)_2(CONHCOR)]^+BF_4^- \quad (4)$$

$$(\text{VI}, R = C_6H_5)$$

The IR spectra of 1/1 electrolyte VI showed $\nu(C{\equiv}O)$ 2070 and 2000 cm^{-1} of equal intensity, shifted to higher frequencies with respect to II, as expected. $\nu(NH)$ was detected at 3170 cm^{-1}, a rather low frequency which is in accord with the presence of the CONHCO group [2]. In the 1600-1500 cm^{-1} region three significant bands were observed at 1620, 1550 and 1515 cm^{-1}. In the ^1H NMR spectrum, a signal was observed at negative values with respect to TMS; this disappeared upon treatment with D_2O and can thus be assigned to the NH group, which must be rather acidic in this complex. When the same reaction was conducted with hydrochloric acid, *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ was isolated along with benzamide. The sulphonyl isocyanate complex I gave toluene-p-sulphonamide, p-$CH_3C_6H_4SO_2NH_2$, on treatment with mineral acids. With hydrochloric acid the ruthenium moiety was recovered as *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ while with fluoboric acid a cationic hydrido ruthenium complex was detected in the mixture of products [τ(RuH) 27.6, triplet, J(P—H) 44 Hz], which were not further investigated. In no cases did we observe the formation of a carbamoyl complex, which is presumably an intermediate in these reactions and rearranges with loss of carbon monoxide. Treatment of VI with LiCl gave the new carbamoyl derivative VII, which was shown to be a non conductor in nitrobenzene:

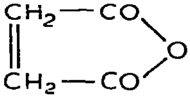
$$n\ [Ru(CO)_2(PPh_3)_2(CONHCOR)]^+BF_4^- \xrightarrow[-CO]{LiCl} [Ru(CO)(PPh_3)_2Cl(CONHCOR)]_n$$

$$(\text{VII}, R = C_6H_5)$$

The IR absorptions of the organic ligand in VII are similar to those in VI, while the single $\nu(C{\equiv}O)$ falls to 1940 cm^{-1}. This compound is possibly dimeric with bridging chlorines. Its insolubility in solvents such as benzene or chloroform prevented mol. wt. measurements. Compound VII is also produced (via abstraction of hydrochloric acid from the solvent) when the reaction between $Ru(CO)_3(PPh_3)_2$ and $RCON_3$ is conducted in chloroform instead of benzene. We also attempted to protonate the isocyanate complexes with weak acids such as ethanol. Compound I slowly gave back $Ru(CO)_3(PPh_3)_2$, while the organic moiety was transformed into toluene-*p*-sulphonamide. This reaction, which is accelerated by the presence of carbon monoxide, confirmed the nature of I and was in accord with the results obtained with stronger acids (see above). The benzoyl isocyanate complex II, did react slowly with ethanol but no characterizable products were isolated; the organic moiety is still present in the products, which also showed in the IR and ^1H NMR spectra some absorptions attributable to the presence of $COOC_2H_5$ groups [1]. Protonation of the amide complex IV with fluoroboric acid gave compound VIII, $[Ru(CO)_2(PPh_3)_2(RCONH_2)_2]^{2+}[BF_4]_2^-$. This complex with furoyl amide as ligand, was shown to be a 2/1 electrolyte in nitrobenzene. The IR spectrum showed $\nu(NH)$ 3350, $\nu(C{\equiv}O)$ 2065 and 2020 cm^{-1}, while $\nu(C{=}O)$ of the amide was detected as a strong broad band at 1650 cm^{-1}. Other minor peaks were observed at 1610 and 1590 cm^{-1}. These values are close to those observed in this type of complex [2].

Reactions with palladium and platinum complexes

Since the cycloaddition reactions of organic azides to coordinated ligands so far studied are largely limited to carbon monoxide, we also investigated the possibility of their extension to other coordinated ligands. For the complexes $Pt(PPh_3)_2L$ with $L = CS_2$ no reaction occurred with toluene-*p*-sulphonyl azide, while, for L = PhNCS and for $Pt(PPh_3)_3SO_2$ the products were shown to be complex mixtures difficult to purify, especially from the phosphineimino adduct. From the reaction in benzene with the phenylisothiocyanate complex, after repeated crystallizations and column chromatography on alumina, a product was obtained; it showed a band in the IR spectrum at 2180 cm^{-1} which can be ascribed to an isocyanide ligand bound to platinum [8]. The analysis is approximately consistent with the formula $[Pt(PPh_3)(PhNC)(RSO_2N)]_2$ ($R = p\text{-}CH_3C_6H_4$). Because of the difficulty of obtaining the compound in a pure form, it was not further investigated. Another type of ligand potentially suitable for a cycloaddition reaction are alkenes. We have studied the reactions of $Pt(PPh_3)_2L$ complexes ($L = CH_2{=}CHCN$, $\overline{OC(O)CH{=}CHC(O)}$) in different solvents. In dry benzene, or with liquid azide as solvent, the maleic anhydride derivative did not react, while for $L = CH_2{=}CHCN$ a very slow reaction was observed, but the products were not characterizable. In contrast it is known that $Pt(PPh_3)_2(CH_2{=}CH_2)$ reacts with RSO_2N_3 ($R = p\text{-}CH_3C_6H_4$), giving the tetraazadiene complex $Pt(PPh_3)_2(N_4R_2)$ with displacement of the alkene [4, 9]. Thus the reactivity of these complexes towards the azide seems to parallel the strength of the metal—alkene bond, which decreases in the order:



$> CH_2{=}CHCN \gg CH_2{=}CH_2$ (ref 10)

A clean reaction was observed in protic solvents such as ethanol ($L = CH_2{=}CHCN$) but the product was $Pt(PPh_3)_2(N_3)(NHSO_2R)$, obtained from a similar reaction with $Pt(PPh_3)_3$ [4].

Similarly, the reactions in alcohol of aroyl or sulphonyl azides with the complexes Pd(L—L)(dba) (L—L = 2,2'-bipyridyl, *o*-phenanthroline; dba = dibenzylideneacetone) gave a series of amide complexes:

$$Pd(L{-}L)(dba) \xrightarrow[-\,dba]{EtOH\,+\,RN_3} Pd(L{-}L)X(NHR) \qquad (5)$$

(IX, R = p-$CH_3C_6H_4CO$, X = N_3, L—L = 2,2'-bipyridyl)

(X, R = p-$CH_3C_6H_4SO_2$, X = NHR, L—L = 2,2'-bipyridyl)

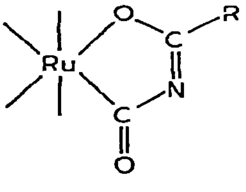
(XI, R = p-$CH_3C_6H_4SO_2$, X = NHR, L—L = *o*-phenanthroline)

The IR spectrum of compound IX revealed the presence of water, and the elemental analyses were consistent with this. A by-product obtained from both type of reactions was only very slightly soluble in solvents such as chloroform; it was not isolated in an analytically pure state but its IR spectrum [$\nu(N_3)$ 2040 cm^{-1}, broad band, absence of absorptions due to the RSO_2 or RCO residues] and the elemental analyses indicated the stoichiometry $Pd(L{-}L)(N_3)_2$. When reaction 5 was conducted in methanol instead of ethanol, the proportion of this by-product increased.

The IR spectrum of IX shows $\nu(N_3)$ 2040, $\nu(CO)$ 1545 and $\nu(NH)$ 3320 cm^{-1}, while for X and XI $\nu(NH)$ was observed at 3280 cm^{-1} and the absorptions of the RSO_2 group appeared in the expected positions (Table 2). These values are in accordance with those found for related platinum triphenylphosphine derivatives [4]. The compounds are only weakly soluble in common organic solvents, and we could not carry out the usual solution measurements, but the presence of the CH_3 group of the tolyl residue was clearly observed in the ^1H NMR spectrum (Table 2).

Conclusions

Cycloaddition reactions of organic azides to coordinated ligands in nonpolar solvents occur readily only with carbon monoxide. The reactions give isocyanate complexes difficult to synthesize by other means. The spectroscopic properties of the aroyl derivatives II and III, although similar to those already found for related rhenium isocyanate complexes [2], are markedly different from those observed for similar iridium derivatives [11]. In particular all but one of the bands attributable to the keto groups of the RCONCO ligands lie at unusually low frequencies. We suggest that in these cases the bonding with the metal is best represented by:



The X-ray structure of a similar metallocycle in $[Pt(PPh_3)_2(PhCONNCOPh)] \cdot C_2H_5OH$, has been recently reported [12] and coordination through the N=N double bond of the dibenzoylazo ligand was ruled out. The number of known metallocycles of this type has recently increased substantially [12]. In contrast in compound I the coordination of the sulphonyl isocyanate to the metal probably occurs via the N=C bond of the isocyanate group, since the vibrations of the SO_2 groups are not much affected by coordination to the metal.

The greater stability of II and III compared with I is also consistent with this interpretation; II and III must be considered as ruthenium(II) derivatives, while in I the value of the oxidation number is less obvious.

Experimental

Starting materials were prepared by published methods; unless otherwise stated the reactions were carried under nitrogen with stirring, but the work-up was carried out in the air. Benzene was dried over sodium and distilled immediately before use. IR spectra were recorded with a Perkin—Elmer 437 instrument. ^1H NMR spectra were recorded on a Varian NV-14 instrument operating at 60 MHz and with TMS as internal standard. Elemental analyses were carried out by the Analytical Laboratories of Milan University (Table 1). Molecular weights were obtained using a Mechrolab osmometer. Conductivity data were obtained with a Philips PR 9500 conductivity bridge.

$Ru(CO)_2(PPh_3)_2(p\text{-}CH_3C_6H_4SO_2NCO)$ (I)

To a benzene solution (10 ml) of toluene-*p*-sulphonyl azide (0.322 g) maintaned at 0-5°, was added $Ru(CO)_3(PPh_3)_2$ (0.5 g), and the resulting suspension was stirred for 4 h. The white product was filtered off from the yellow solution, washed with a little benzene, and dried in vacuo (74% yield).

$Ru(CO)_2(PPh_3)_2(C_6H_5CONCO)$ (II)

The pale yellow suspension of $Ru(CO)_3(PPh_3)_2$ (0.7 g) and benzoyl azide (0.4 g) in benzene (10 ml) was stirred for 24 h. The pale yellow precipitate was filtered off. A by-product showing a $\nu(C{\equiv}O)$ 1880 cm^{-1} was eliminated by crystallization from methylene chloride/hexane and the product was dried in vacuo (56% yield). The by-product was not unchanged starting ruthenium complex, since further treatment of the precipitate with the azide did not cause any appreciable change in the IR spectrum.

$Ru(CO)_2(PPh_3)_2(p\text{-}CH_3C_6H_4CONCO)$ (III)

This was prepared as described for II, from $Ru(CO)_3(PPh_3)_2$ (0.46 g) and toluene-*p*-benzoyl azide (0.32 g) in benzene (10 ml). The white product was crystallized three times from chloroform/hexane and dried in vacuo (33% yield), in this way a by-product showing $\nu(C{\equiv}O)$ 1885 cm^{-1} was eliminated. When this reaction was carried out in air with $Ru(CO)_3(PPh_3)_2$ (0.28 g) and toluene-*p*-benzoyl azide (0.318 g) in benzene (10 ml) for four days, a white grey material was isolated. It was crystallized repeatedly from chloroform/hexane. Its IR spectrum showed $\nu(C{\equiv}O)$ 2050 w and 1940 s cm^{-1}. The elemental analyses indicated an approximate stoichiometry $[Ru(CO)_3(PPh_3)NR]_n$ (*n* is possibly two). However this reaction was not very reproducible and the compound was not further investigated.

$Ru(CO)_2(PPh_3)_2(NHCO\overline{-C{=}CHCH{=}C-O})_2$ (IV)

The yellow suspension of $Ru(CO)_3(PPh_3)_2$ (0.3 g) and furoyl azide (0.174 g) in benzene (10 ml) was stirred for four days. After filtration, hexane was added to the filtrate to precipitate the white complex. This was filtered off, washed with hexane and dried in vacuo.

$Ru(CO)_2(PPh_3)_2(RNCONR)$ ($R = p\text{-}CH_3C_6H_4SO_2$) (V)

(a) Benzene (15 ml) was saturated with carbon monoxide and $Ru(CO)_3(PPh_3)_2$ (0.325 g) and toluene-*p*-sulphonyl azide (0.181 g) were added. The yellow solution became colourless after 30 min. It was then left for 1.5 h under an atmosphere of carbon monoxide, then evaporated to small volume. Hexane was added and the white precipitate was filtered off, and crystallized from benzene/hexane, benzene/ethyl ether, and finally from toluene with a little hexane with cooling to —70°. The first small precipitate from each crystallization is pure product. The three portions of the compound were combined and dried in vacuo.

(b) When reaction (a) was conducted by using compound I instead of $Ru(CO)_3(PPh_3)_2$, the same mixture of products was isolated.

(c) To a suspension of $Ru(CO)_3(PPh_3)_2$ (0.2 g) in benzene (10 ml) was added a solution of toluene-*p*-sulphonyl isocyanate (0.5 ml) in benzene. The yellow solution became colourless, and after 20 h the white precipitate was filtered off, washed with hexane and dried in vacuo.

(d) To $Ru(CO)_3(PPh_3)_2$ (0.136 g) in benzene (13 ml) was added *N,N'*-di-toluene-*p*-sulphonyl urea (0.071 g). The suspension was refluxed for two days. The white precipitate was filtered off, washed with hexane and dried in vacuo. The nujoll mull spectrum showed small differencies from that of the compound isolated from the procedure above described. In particular, one of the two $\nu(C{\equiv}O)$ occurred at 1985 cm^{-1} instead of 2000 cm^{-1} (Table 2). This can be ascribed to solid state effects, since the IR spectra in solution were identical.

(e) The red-violet solution of $Ru_3(CO)_9(PPh_3)_3$ (0.2 g) and toluene-*p*-sulphonyl azide (0.06 g) in benzene (10 ml) was heated at 70-80° for 2 h. The white precipitate was filtered off, washed with a little benzene and dried in vacuo. The IR spectrum of the product showed the anomalies as described in (d), and it is noteworthy that these were observed on the two samples which were isolated from hot benzene solution.

$[Ru(CO)_2(PPh_3)_2(CONHCOC_6H_5)]^+BF_4^-$ (VI)

Compound II was suspended in ethyl ether and few drops of HBF_4 (40% in water) were added. After 1.5 h the white precipitate was filtered off, washed with ethyl ether and dried in vacuo. The Nujol mull spectrum showed two shoulders of the main $\nu(C{\equiv}O)$ absorptions. However the IR spectrum of the CH_2Cl_2 solution showed only two bands (Table 2).

When this reaction was conducted with compound III, a product with an analysis approximately consistent with the corresponding expected carbamoyl complex was obtained, but the IR spectrum showed that it was a mixture.

$[Ru(CO)(PPh_3)_2Cl(CONHCOC_6H_5)]_n$ (VII)

(a) To compound VI (0.18 g) suspended in methanol (20 ml) was added lithium chloride (0.094 g). The suspension was stirred for 6 h. The white precipitate was filtered off, washed with methanol and dried in vacuo.

(b) The same compound was obtained from the reaction of $Ru(CO)_3(PPh_3)_2$ (0.15 g) with benzoyl azide (0.09 g) in chloroform (20 ml) under an atmosphere of carbon monoxide. After 18 h the white precipitate was filtered off and washed with hexane.

$[Ru(CO)_2(PPh_3)_2(NH_2CO\text{—}\overline{C{=}CHCH{=}C\text{—}O})_2]^{2+}[BF_4^-]_2$ (VIII)

IV was suspended in ethyl ether and a few drops of HBF_4 (40% in water) were added. The suspension was stirred for 2 h, then the creamy-white product was filtered off. In some cases the product was obtained as an oil, and in this case the solution was decanted and the oil washed with ethyl ether with scratching. The solid residue was then filtered off and crystallized from chloroform/hexane.

$Pd(2,2'\text{-bipyridyl})(N_3)(NHCOC_6H_4CH_3\text{-}p)\cdot H_2O$ (IX)

To Pd(bipy)(dba) (0.4 g) suspended in ethanol (20 ml) was added toluene-*p*-benzoyl azide (0.65 g). The brick-red suspension turned slowly light brown. After 5 h a grey-green precipitate was filtered off. It was extracted with chloroform and filtered. The solution was evaporated to small volume and addition of hexane gave the yellow compound. It was filtered off, washed with hexane and dried in vacuo. The green material insoluble in the chloroform showed in the IR spectrum only bands due to 2,2'-bipyridyl and to the azido group [$\nu(N_3)$ 2040 cm^{-1}]. Its analysis gave an approximate composition $Pd(bipy)(N_3)_2$. An analogous reaction was observed for the corresponding palladium-*o*-phenanthroline derivative. Since the product was less soluble in chloroform than IX, we were unable to remove completely the green by-product, and the elemental analysis were not entirely satisfactory. However, the IR spectrum was comparable to that of IX.

$Pd(2,2'\text{-bipyridyl})(NHSO_2C_6H_4CH_3\text{-}p)_2$ (X)

To Pd(bipy)(dba) (0.3 g) suspended in ethanol (20 ml) was added toluene-*p*-sulphonyl azide (0.593 g). Gas evolution was noted. After 5 h the dark green precipitate was filtered off and the yellow compound was freed from the green by-product as described for IX. The precipitate from the chloroform solution was washed repeatedly with benzene and dried in vacuo.

$Pd(o\text{-phenanthroline})(NHSO_2C_6H_4CH_3\text{-}p)_2$ (XI)

This yellow compound (28%) was obtained as described for X, by using Pd(*o*-phenanthroline)(dba) (0.53 g) and toluene-*p*-sulphonyl azide (0.608 g) in ethanol (20 ml).

Reaction of I with HCl

Compound I was added to an ether solution of gaseous HCl. The suspension was stirred for 1 h. The white product was filtered off. Its IR spectrum was identical with that of an authentic sample of *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$. The mother liquor by evaporation to dryness gave a white residue, which was shown to be $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$ by its IR spectrum.

Reaction of II with HCl

This reaction has been conducted as above described for compound I, and for 5 h. The products of the reaction were identified as *cis*-$\text{Ru(CO)}_2\text{(PPh}_3)_2\text{Cl}_2$ and $\text{C}_6\text{H}_5\text{CONH}_2$ by their IR spectra.

Reaction of I with ethanol

A suspension of compound I (0.2 g) in ethanol (25 ml) was stirred. A pale yellow precipitate slowly formed during 3-4 days. It was filtered off and identified as $\text{Ru(CO)}_3\text{(PPh}_3)_2$ by its IR spectrum in Nujol mull and in benzene [ν(C≡O) 1900 cm^{-1}]. The mother liquor was evaporated to dryness and the residue extracted with ethyl ether. Evaporation of the ether gave $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$.

Acknowledgements

We thank the Italian CNR for financial support, Dr. P. Fantucci for the ^{1}H NMR spectra, and the Accademia dei Lincei for award of a scholarship to one of us (M.P.).

References

1 W. Beck, W. Rieber, S. Cenini, F. Porta and G. La Monica, J. Chem. Soc. Dalton Trans., (1974) 298, and refs. therein.
2 G. La Monica, S. Cenini and M. Freni, J. Organometal. Chem., 76 (1974) 355.
3 M.J. McGlinchey and F.G.A. Stone, Chem. Commun., (1970) 1265.
4 W. Beck, M. Bauder, G. La Monica, S. Cenini and R. Ugo, J. Chem. Soc. A, (1971) 113.
5 M. Dekker and G.R. Knox, Chem. Commun., (1967) 1243.
6 S. Cenini, M. Pizzotti and F. Porta, unpublished results.
7 B.F.G. Johnson and J.A. Segal, J. Organometal. Chem., 31 (1971) C79.
8 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley, London, 1969.
9 G. La Monica, P. Sandrini, F. Zingales and S. Cenini, J. Organometal. Chem., 50 (1973) 287.
10 S. Cenini, R. Ugo and G. La Monica, J. Chem. Soc. A, (1971) 409.
11 J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, J. Amer. Chem. Soc., 90 (1968) 5430.
12 S.D. Ittel and J.A. Ibers, Inorg. Chem., 12 (1973) 2290.