Reactions of Toluene-*p*-sulphonyl Azide and Isocyanate with Low Valent Transition-metal Complexes

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The reactions of toluene-*p*-sulphonyl azide (RN_3) with the complexes $Pd(PPh_3)_3CO$ and $M(NO)(CO)(PPh_3)_2$ (M = Rh or Ir) in benzene yield urea derivatives of the type $Pd(PPh_3)_2(RNCONR)$ and $M(NO)(PPh_3)_2(RNCONR)$ ($R = p\text{-}CH_3C_6H_4SO_2$). From $Pt(PPh_3)_n(CO)_{4-n}$ (n = 2 or 3) and RN_3 however a more complex compound $(PPh_3)_2Pt(R_2N_4CO)$ is obtained, whilst the platinum ureylene complex $Pt(PPh_3)_2(RNCONR)$ can be synthesized by oxidative addition of *NN'*-ditoluene-*p*-sulphonyl urea to $Pt(PPh_3)_4$. The urea complexes have also been prepared by treatment of $M(PPh_3)_4$ (M = Pd or Pt) and $M(NO)(PPh_3)_3$ (M = Rh or Ir) with toluene-*p*-sulphonyl isocyanate. Similarly $RhCl(PPh_3)_2(RNCONR)$ has been isolated from the reactions of $Rh(PPh_3)_3Cl$ with RNCO or RNHCONHR. In protic solvents such as alcohols R'OH (R' = Me, Et, or Pr^n) the reactions of RN_3 with complexes $Pt(PPh_3)_n(CO)_{4-n}$ (n = 2 or 3) lead to different products, as expected. For n = 2, the bis-alkoxycarbonyl derivative *trans*-$Pt(PPh_3)_2(CO_2R')_2$ has been isolated, whereas for n = 3, $Pt(PPh_3)_2N_3(-\underset{\underset{R}{|}}{N}-COOR')$ is the main product.

Treatment of the hydride complex $RhH(Ph_2PCH_2CH_2PPh_2)_2$ with toluene-*p*-sulphonyl azide gives a dimeric complex, probably with a di-imide bridge $(Ph_2PCH_2CH_2PPh_2)_2Rh(RNNR)Rh(Ph_2PCH_2CH_2PPh_2)_2$.

As a continuation of our investigations on the reactions of organic azides with d^{10} complexes such as $Pt(PPh_3)_3$,[1] or formally d^{10} derivatives such as $M(NO)(PPh_3)_3$ (M = Rh or Ir),[2] we have now studied the reactions of d^{10} carbonylphosphine complexes and other substrates with toluene-*p*-sulphonyl azide, and of the corresponding phosphine complexes with toluene-*p*-sulphonyl isocyanate, which in most cases lead to the same compounds.

The interaction of carbonyl derivatives different from those here investigated with organic azides has already been studied. The reaction of methyl and phenyl azides with iron carbonyls gives a number of complexes,[3]

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[1] W. Beck, M. Bauder, G. La Monica, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1971, 113.

[2] G. La Monica, P. Sandrini, F. Zingales, and S. Cenini, *J. Organometallic Chem.*, 1973, **50**, 287.

[3] M. Dekker and G. R. Knox, *Chem. Comm.*, 1967, 1243.

the main product from MeN_3 and $Fe_2(CO)_9$ is μ-dimethylureylene-bis(tricarbonyliron), $[(MeN)_2CO]Fe_2(CO)_6$, the structure of which has been elucidated by *X*-ray diffraction.[4] Similarly the product of the reaction between dodecacarbonyltri-iron and phenyl isocyanate [5] or azidobenzene has been shown to be the μ-diphenylureylene-bis(tricarbonyliron) derivative [6,7] and not the hexacarbonylbis(phenylisocyanate) complex, as it was originally proposed.[5] A complex of similar structure has been considered to be a probable intermediate in the reduction of nitrobenzene to aniline and 2,2′-diphenylurea catalysed by $Ru_3(CO)_{12}$.[8] Urea derivatives have also been obtained from $Fe_2(CO)_9$ [9] or $Co_2(CO)_8$ [10] with organic azides. On the other hand, reactions of *trans*-$IrCl(CO)(PPh_3)_2$ with aroyl azides yield aroyl isocyanate complexes in alcohol-free solutions,[11] presumably *via* labile nitrene complexes. For these derivatives co-ordination through the $-N{=}C$ double bond of the isocyanate was proposed. In fact the thermal decomposition of aryl azides in the presence of carbon monoxide yields aryl isocyanates and urea derivatives,[12] and these reactions are believed to proceed through the formation of intermediate nitrenes.[12,13] Stable nitrene–carbonyl derivatives have been obtained from the reactions of $M(CO)_3(PPh_3)_2$ (M = Ru or Os) with 1,1,2,3,3,3-hexafluoropropyl azide,[14] or of *trans*-$IrCl(CO)(PPh_3)_2$ with hexafluoroazomethane,[15] the strongly electron withdrawing fluoroalkyl groups stabilizing the fluoroalkylimido-complexes. Isocyanide complexes have been obtained from the reactions between phenyl isothiocyanate and $Fe_3(CO)_{12}$ or $Mo(CO)_6$,[5] whereas $Pt(PPh_3)_3$ yields an isothiocyanate complex with co-ordination of the isothiocyanate *via* the $-C{=}S$ double bond.[16] In the products from alkyl or aryl isothiocyanates with $Rh(PPh_3)_3Cl$, both π-bonded and donor co-ordinated isothiocyanates are present.[16] An analogous derivative has been recently obtained from $Rh(PPh_3)_3Cl$ and PhNCO.[17]

Analytical [a] and spectroscopic data

No.	Compound	Colour	M.p. (t/°C)	C	H	N	*M*	I.r. absorption bands/cm^{-1}					^{1}H N.m.r. spectra
								ν(C=O)	$\nu_{as}(SO_2)$	$\nu_{sym}(SO_2)$	ν(S–N)	ν(N=O)	$\tau(CH_3)$
(I)	$Pd(PPh_3)_2(RNCONR)$	Yellow	198—200	61·4	4·50	2·80	996·8	1678s	1312s	1141vs	913m		7·72
	(a)			59·83	4·20	2·90	930 ^{b}				855s		
	(b)			60·64	4·50	2·80	989 ^{b}						
(II)	$Pt(PPh_3)_2(RNCONR)$	White	240—242	56·40	4·08	2·57	1086	1693s	1319s	1141vs	922m		
	(a)			57·45	4·69	2·39					857s		
	(b)			55·63	3·52	2·72							
(III)	$Rh(NO)(PPh_3)_2(RNCONR)$	Yellow-orange	209—210	59·80	4·34	4·11	1022·9	1667s	1316s	1137vs	925m	1792s	
	(a)			60·40	4·20	4·10					840s		
	(b)			59·88	4·25	4·10							
(IV)	$Ir(NO)(PPh_3)_2(RNCONR)$ ^{c}	Pale yellow	252—253	55·00	3·99	3·77	1112·6	1684s	1321s	1140vs	933m	1770s	
	(a)			54·20	3·70	3·50		(1708m)			845s		
	(b)			54·81	3·70	3·65							
(V)	$Rh(PPh_3)_2Cl(RNCONR)$	Yellow	159—161	59·40	4·31	2·72	1029·4	1698s	1318s	1143s	937m		7·69—7·75 (1 : 1) ^{e}
	(a)			59·02	4·11	2·68	1040 ^{d}	(1733m)					
	(b)			58·59	4·04	2·59							
(VI)	$Pt(PPh_3)_2(R_2N_4CO)$	White	227	54·90	3·95	4·97	1113	1740s	1325s	1145s	910s		7·58—7·62 (1 : 1) ^{e}
				55·30	3·74	4·79	1215 ^{b}				855m		
(VII)	$(Ph_2PCH_2CH_2PPh_2)_4Rh_2(RNNR)$	Yellow	219—220	66·5	5·15	1·31	2136		1279s	1131s	879m		
				67·56	5·73	1·14	2100—2400 ^{f}						
(VIII)	$Pt(PPh_3)_2(CO_2Et)_2$	White	191	58·40	4·62		865	1625s					9·57(t) ^{g}
				58·84	4·41		870 ^{b}	[ν(C–O) 1020]					
(IX)	$Pt(PPh_3)_2(CO_2Me)_2$	White	193	57·20	4·40		885	1630s					7·48[J(Pt–H) *ca.* 4 Hz]
				57·20	3·90		810 ^{b}	[ν(C–O) 1025]					
(X)	$Pt(PPh_3)_2(N_3)(NRCO_2Et)$	White	226	54·80	4·20	5·50	1003	1690s	1320s	1155s	945m		7·65 (tolyl)
				55·30	4·35	5·30	1080 ^{b}	[ν(C–O) 1080]					8·65 (t) ^{h}
								[$\nu(N_3)$ 2060]					
(XI)	$Pt(PPh_3)_2(N_3)(NRCO_2Pr^n)$	White	211	55·50	4·30	5·50	1017	1680s	1315s	1160s	925m		7·70 (tolyl) ^{i}
				54·20	3·60	4·95	896 ^{b}	[ν(C–O) 1075]					
								[$\nu(N_3)$ 2050]					

[a] Calc./found; a,b: way of preparation; R = p-$CH_3C_6H_4SO_2$. [b] In $CHCl_3$. [c] Calc. for iridium 17·3, found 17·4%. [d] In benzene. [e] In $CDCl_3$. [f] In acetone (does not dissolve very well). [g] $\tau(CH_2)$ 7·07 (Complex quartet). [h] $\tau(CH_2)$ 5·95 (q). [i] In the n.m.r. spectrum the signals due to the Pr^n group appear as complex absorptions at τ 6·2, 8·35, and 9·0.

RESULTS

Treatment of carbonyltris(triphenylphosphine)palladium(0) and the isoelectronic rhodium and iridium complexes $M(NO)(CO)(PPh_3)_2$ (M = Rh or Ir) with toluene-*p*-sulphonyl azide (RN_3) in dry benzene leads to the urea derivatives

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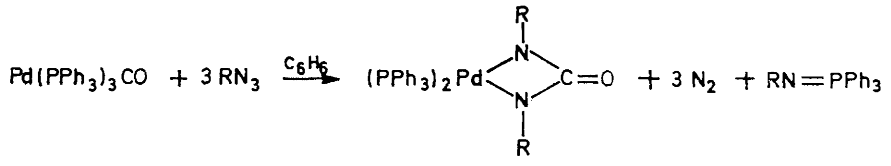
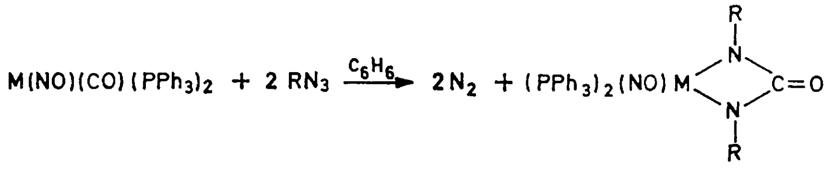
$Pd(PPh_3)_2(RNCONR)$ (I) and $M(NO)(PPh_3)_2(RNCONR)$ (III, IV) respectively (Table), according to:

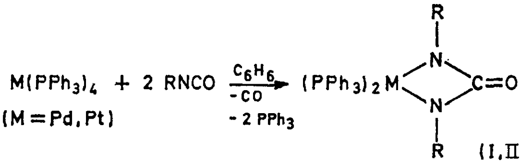


(I, M = Pd; II, M = Pt)

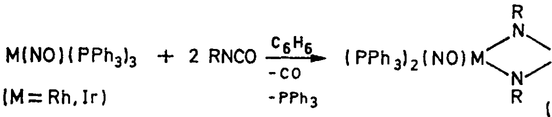


(III, M = Rh; IV, M = Ir)

$Co(NO)(CO)(PPh_3)_2$ did not show any reaction, even with liquid azide. The same complexes and the platinum analogue are obtained by reaction of tetrakis(triphenylphosphine)-palladium and -platinum, or tris(triphenylphine)nitrosyl-rhodium and -iridium, with toluene-*p*-sulphonyl isocyanate (RNCO) in dry benzene:



(I,II)



(III, IV)

In these reactions carbon monoxide is evolved, which was identified by its i.r. spectrum; the appearance of carbon dioxide which was also observed, may result from the reaction $2RNCO \longrightarrow R{-}N{=}C{=}N{-}R + CO_2$. In the i.r. spectra (Table) the complexes show strong absorption bands *ca.* 1670—1690 cm^{-1}, typical for a keto-group besides the expected bands of the $CH_3C_6H_4SO_2N$-residue. Two strong N–S absorptions are always present in the i.r. spectrum, and their separation is greater than that observed in the related tetra-azadiene complex, $Pt(PPh_3)_2(N_4R_2)$.[1,2] The absorption at lower wavelengths cannot be attributed to the aromatic *para*-substituted phenyl rings of the tosyl residue; it would be unusually intense for a bending mode. Another band at *ca.* 1200 cm^{-1} is not easy to assign. However it is also present in the i.r. spectrum of RNHCONHR, which shows moreover a ν(CO) band at 1750 cm^{-1}.

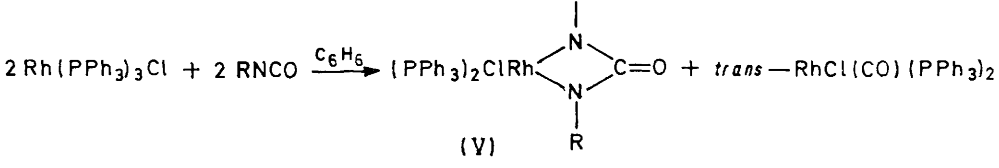
Complex (I) was soluble, and proved to be monomeric, in chloroform, with only one signal for the equivalent methyl groups in the ^1H n.m.r. spectrum (Table). The *X*-ray photoelectron spectrum of complex (II) show-Pt(4*f*5/2,7/2) core binding energies (76·9 and 73·6 respectively relative to C_{1s} 285 eV), which are comparable to those of *cis*-$Pt(PPh_3)_2Cl_2$ (77·0 and 73·7 eV respectively). This is consistent with the assumed formal oxidation state +2 in the platinum–urea complex.

The nitrosyl derivatives (III) and (IV) have ν(NO) at 1760—1790 cm^{-1}, a rather high value which could correspond to NO present as NO^+ with a formal oxidation state +1 for the metals, although the versatile character of this ligand does not allow definite attributions of oxidation states in the complexes.[18] For compounds (III) and (IV) a dimeric structure with one urea ligand bridging two $M(NO)(PPh_3)_2$ units is ruled out by elemental analyses; a double bridge with formation of an eight membered ring seems rather improbable. The nature of the organic ligand has been confirmed from the reactions of these urea derivatives with gaseous hydrochloric acid:

$$M(NO)(PPh_3)_2(RNCONR) + 2HCl \longrightarrow M(NO)(PPh_3)_2Cl_2 + RHNCONHR$$
(M = Rh or Ir)

$$Pd(PPh_3)_2(RNCONR) + 2HCl \longrightarrow Pd(PPh_3)_2Cl_2 + RNHCONHR$$

The anionic ligand is completely displaced with formation of *NN'*-ditoluene-*p*-sulphonylurea and the corresponding chloro-complexes. Moreover, the presence of the anionic urea ligand in these complexes has been ascertained by oxidative addition of *NN'*-ditoluene-*p*-sulphonylurea to $Pt(PPh_3)_4$, which gave a product identical to (II). An urea derivative has also been obtained from the reaction of the d^8 complex $Rh(PPh_3)_3Cl$ with toluene-*p*-sulphonyl isocyanate:



(V)

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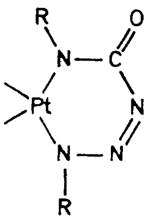
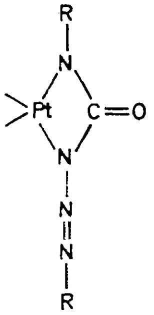
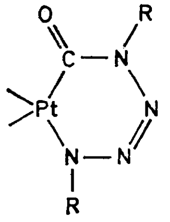
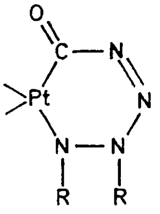
In this reaction carbon monoxide is abstracted by an excess of $Rh(PPh_3)_3Cl$, which is known to be an effective decarbonylation agent.[19-22] The same urea derivative is again formed from $Rh(PPh_3)_3Cl$ and *NN'*-ditoluene-*p*-sulphonylurea. Complex (V) shows the expected ν(CO) at 1698 cm^{-1} (Table). The appearance of two methyl signals in a 1 : 1 ratio at τ 7·69 and 7·75 in the ^1H n.m.r. spectrum of this five-co-ordinated complex is consistent with a trigonal bipyramidal structure in which the two tosyl amide groups occupy one axial and one equatorial co-ordination position around rhodium; for other structures only one methyl signal would be expected.

A product different from the expected urea derivative has been obtained from the reactions of $Pt(PPh_3)_3(CO)$, $Pt(PPh_3)_2(CO)_2$, or a mixture of both, with toluene-*p*-sulphonyl azide in dry benzene. Repeated elemental analyses correspond to the stoicheiometry $Pt(PPh_3)_2(R_2N_4CO)$ (VI). Compound (VI) which is monomeric in chloroform shows a ν(CO) band at 1740 cm^{-1}, higher than the corresponding value in the urea derivative (II). The other characteristic bands in the i.r. spectrum do not differ significantly from those of (II), and only the intensities of the two ν(NS) bands are different (Table). The ^1H n.m.r. spectrum of (VI) shows two methyl resonances in a 1 : 1 ratio at τ 7·58 and 7·62. Recrystallization from $CHCl_3$ did not change the i.r. and n.m.r. spectra significantly, only a broadening of the keto-band was observed. Decomposition with HCl afforded *cis*-$Pt(PPh_3)_2Cl_2$ together with an organic material different from RNHCONHR. This compound shows a ν(CO) band at 1705 cm^{-1}, ν(NH) at 3260 and 3100 cm^{-1}, and gave an elemental analysis in agreement with four nitrogen atoms in the organic ligand of (VI). On the basis of these data different structures seem possible:





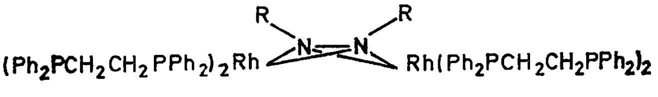




All of them would explain the presence of two different methyl signals in the n.m.r. spectrum although no bands have been found in the i.r. spectrum attributable to ν(N=N).

Characterizable derivatives have not been obtained from the reactions of toluene-*p*-sulphonyl azide with $Rh(PPh_3)_3Cl$ or *trans*-$MCl(CO)(PPh_3)_2$ (M = Rh or Ir) in benzene. Only the phosphine imide $RN{=}PPh_3$ could be isolated from these reactions. No reaction was observed with the formally rhodium(I) derivative, $Rh(NO)(PPh_3)_2Cl_2$.

Previously one of us reported the reactions of organic azides with platinum hydride complexes to give amide compounds.[23] The analogous reaction of $RhH(Ph_2PCH_2CH_2PPh_2)_2$ with toluene-*p*-sulphonyl azide however resulted in the formation of a dimeric complex which we formulate as


$$(Ph_2PCH_2CH_2PPh_2)_2Rh\overset{R}{N}{=}\overset{R}{N}Rh(Ph_2PCH_2CH_2PPh_2)_2$$

(VII)

No N–H absorptions were observed in the i.r. spectrum of compound (VII). A similar iron complex was obtained by Dekker and Knox from the reaction of phenyl azide and nonacarbonyldi-iron.[3] Also, an analogous rhodium derivative having di-imide as bridging ligand was reported to be the product of the reaction between $Rh(PMe_2Ph)_3Cl_3$ and *NN'*-dibenzohydrazide.[24]

As already mentioned,[1,2] the reactions of organic azides with low valent transition metal complexes are strongly dependent on the nature of the solvent. Toluene-*p*-sulphonyl azide and $Pt(PPh_3)_2(CO)_2$ in ethanol give ***trans***-$Pt(PPh_3)_2(CO_2Et)_2$ (VIII), the azide being converted to *p*-$CH_3C_6H_4SO_2NH_2$. The presence of the ester group in compound (VIII) has been confirmed by the i.r. spectrum, which shows ν(C=O) at 1625 and ν(C–OEt) at 1020 cm^{-1}, both notably lower than the corresponding absorptions for organic esters. In the ^1H n.m.r. spectrum the expected resonances for the ethyl groups have been observed, with normal values for the coupling between protons. However τ-values for the $-CH_2$ and $-CH_3$ groups are notably at higher field ($\Delta\tau$ *ca.* 1) compared with the resonances of organic ethyl esters, and this shift is particularly useful for detecting the presence of $-CO_2R$ groups directly bound to platinum. Using methanol as solvent, the corresponding methyl ester derivative $Pt(PPh_3)_2(CO_2Me)_2$ (IX) has been obtained, which also showed the high field shift of the methyl resonance in the ^1H n.m.r. spectrum; in this case we were also able to observe a small coupling with ^{195}Pt (*J* 4 Hz). The *trans* structure of compound (VIII) which has been found also by another route [25] was confirmed by an *X*-ray structural analysis.[26]

The reaction of toluene-*p*-sulphonyl azide with $Pt(PPh_3)_3(CO)$ in ethanol is much more complex. We have isolated three different derivatives, two of them, $Pt(PPh_3)_2(NHR)_2$ and $Pt(PPh_3)_2N_3(R)$, are identical to two of the products from the reaction of $Pt(PPh_3)_3$ and RN_3 in ethanol or wet benzene.[1] This could be explained by the tendency of $Pt(PPh_3)_3(CO)$ to lose carbon monoxide giving $Pt(PPh_3)_3$.[27] The phosphine imide $RN{=}PPh_3$ is always present in the reaction mixture; another organometallic derivative obtained with difficulty in a pure state

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[26] P. L. Bellon, personal communication.

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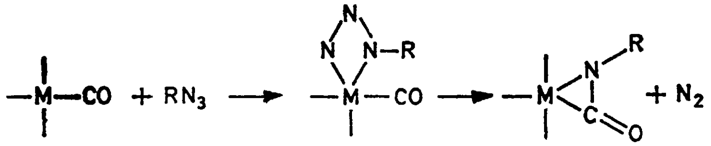
corresponds to the formula $Pt(PPh_3)_2N_3(NRCO_2Et)$ (X). Such alkoxycarbonylamido complexes of platinum, iridium, and rhodium have recently been described.[25,28] Compound (X) shows ν(N_3) at 2060, ν(C=O) at 1685, and ν(C–OEt) at 1050 cm^{-1}. The C–O stretching frequencies are higher than the corresponding values in compounds (VIII) and (IX), and close to the values expected for organic urethanes. Also, the ^{1}H n.m.r. signals lie at normal values. The nature of this product has been confirmed by reaction with hydrochloric acid. *cis*-$Pt(PPh_3)_2Cl_2$ is obtained together with an organic compound which has elemental analyses, i.r., ^{1}H n.m.r., and mass spectra consistent with the formula *p*-$CH_3C_6H_4SO_2NHCO_2Et$. We were also able to obtain the corresponding n-propanol derivative $Pt(PPh_3)_2N_3(NRCO_2Pr^n)$ (XI), although impure. The same reaction conducted in methanol leads to a mixture of compounds, among which a very insoluble material which has an i.r. spectrum identical to that found for the product of the reaction between $Pt(PPh_3)_3$ and RN_3 at 50° in ethanol with high concentrations of the reactants.[1] Owing to its insolubility, the nature of this compound could not be determined.

Compound (X) reacts with carbon monoxide in ethanol leading to $Pt(PPh_3)_2(NCO)(CO_2Et)$. This reaction parallels the reaction of $Pt(PPh_3)_2(X)(NHR)$ with carbon monoxide [1,28] and confirms the formulation of (X) as an amido-complex.

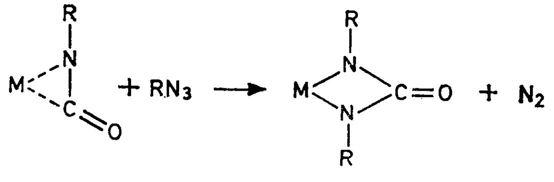
No well characterizable compounds have been obtained from the reactions in alcohol of toluene-*p*-sulphonyl azide with *trans*-$MCl(CO)(PPh_3)_2$ (M = Rh or Ir); $M(NO)(CO)(PPh_3)_2$ (M = Co, Rh, or Ir), $Pd(PPh_3)_3(CO)$, or $Rh(PPh_3)_3Cl$ complexes.

CONCLUSIONS

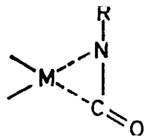
The formation of urea derivatives from the interaction of an organic azide with metal carbonyl derivatives in non-polar solvents seems a rather general reaction. The first step probably involves the



formation of intermediate isocyanate complexes which in some cases have been isolated.[11,17] The formation of isocyanato complexes with NCO$^-$-ligands both from metal carbonyls and the azide ion or from azido complexes and carbon monoxide is well established.[29,30] Further reaction with an excess of azide gives the final product:



The same complexes can be obtained directly from the organic isocyanate and the corresponding isoelectronic metal complexes where carbon monoxide is substituted by a ligand such as triphenylphosphine. In this case carbon monoxide is displaced from the second molecule of the isocyanate. The isolation of rhodium complexes where both π-bonded and donor co-ordinated isothiocyanates are present,[16] suggests that the second molecule of the isocyanate approaches the intermediate (XII)



(XII)

with the oxygen as donor site. The subsequent decarbonylation of the isocyanate seems to be facilitated in our case by the neighbouring SO_2-groups.

We have shown [1] that the carbonylation in alcohols, R′OH, of the complex obtained from the reaction of $Pt(PPh_3)_3$ with RN_3 in ethanol, leads to the ester derivatives $Pt(PPh_3)_2NCO(CO_2R')$ and RNH_2, and the possible mechanisms have been discussed.[25,28] The interactions of the platinum carbonyl complexes with RN_3 in alcohol studied here seem to be closely related reactions, since two ester groups directly bonded to platinum are formed from $Pt(PPh_3)_2(CO)_2$. The presence of the azide, which is converted into the corresponding amide, is of course necessary since a direct attack of the alcohol on $Pt(PPh_3)_2(CO)_2$ is not possible. However it is difficult to devise a simple reaction path leading to *trans*-$Pt(PPh_3)_2(CO_2R')_2$, or to $Pt(PPh_3)_2N_3(\text{-}RNCO_2R')$, obtained from $Pt(PPh_3)_3(CO)$ and RN_3.

EXPERIMENTAL

Starting materials were prepared as described in the literature. Toluene-*p*-sulphonyl isocyanate (Fluka) was distilled *in vacuo* before use. All the reactions were carried out in a nitrogen atmosphere, except for the palladium complex in the preparation (a), with stirring, using well dried solvents.

*[Bis(toluene-*p*-sulphonyl)ureylene]bis(triphenylphosphine)palladium*(II), *Compound* (*I*). (a) Toluene-*p*-sulphonyl azide (0·9 g) dissolved in nitrogen-degassed benzene (15 ml) was added to solid $Pd(PPh_3)_3(CO)$ (0·8 g) in a carbon monoxide atmosphere. A fast gas evolution was noted. The solution turned orange and a yellow compound precipitated. After 1 h the product was filtered off and washed with benzene. In the mother liquor the presence of the phosphine imide, $RN{=}PPh_3$, was observed. Compound (I) (1 g) when treated with dry diethyl ether (50 ml) saturated with gaseous hydrochloric acid, gave after 0·5 h a yellow solid which was filtered off and identified as $Pd(PPh_3)_2Cl_2$ by its i.r. spectrum. The ether was evaporated to dryness, leaving a residue which showed i.r. and ^{1}H n.m.r. spectra identical to those of RNHCONHR.

(b) A solution of toluene-*p*-sulphonyl isocyanate (1 g) in benzene (5 ml) was added to a solution of $Pd(PPh_3)_4$ (0·7 g) in benzene (20 ml). The reaction mixture turned orange

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[28] W. Beck and K. v. Werner, *Chem. Ber.*, 1971, **104**, 2901.

[29] W. Beck, H. Werner, H. S. Smedal, and H. Engelmann, *Chem. Ber.*, 1968, **101**, 2143; *Inorg. Chim. Acta*, 1969, **3**, 331; R. J. Angelici and G. C. Faber, *Inorg. Chem.*, 1971, **10**, 514.

[30] W. Beck, W. P. Fehlhammer, P. Pöllmann, and H. Schächl, *Chem. Ber.*, 1969, **102**, 1976.

and slight gas evolution was observed. After 1 h of refluxing, a yellow precipitate was filtered off, washed with benzene (15 ml), and recrystallized from chloroform–ether.

[Bis(toluene-p-sulphonyl)ureylene]bis(triphenylphosphine)platinum(II), *Compound (II)*.—(a) Toluene-*p*-sulphonyl isocyanate (0·8 g) was dropped into a solution of $Pt(PPh_3)_4$ (0·62 g) in benzene (15 ml) at room temperature. Immediate gas evolution was observed and the solution turned colourless. After 3 h a white microcrystalline product was sucked off and washed with hot benzene. The substance is insoluble in common organic solvents.

(b) This compound was also obtained by refluxing a mixture of $Pt(PPh_3)_4$ (0·62 g) and *NN'*-bistoluene-*p*-sulphonylurea (0·4 g) in benzene (15 ml) for 24 h. Products from (a) and (b) gave identical elemental analyses and i.r. spectra.

Nitrosyl[bis(toluene-p-sulphonyl)ureylene]bis(triphenylphosphine)rhodium(II), *Compound (III)*.—(a) Solid $Rh(NO)(CO)(PPh_3)_2$ (0·3 g) was added to a solution of toluene-*p*-sulphonyl azide (0·4 g) in benzene (15 ml). After 3 h a yellow precipitate was filtered off and washed with benzene. It can be recrystallized from hot methylene chloride–n-hexane. Hydrochloric acid was bubbled through a benzene suspension (20 ml) of compound (III) (0·45 g) for 1 h. The excess of acid was removed by a stream of nitrogen. The resulting suspension was evaporated to dryness and the residue extracted with dry diethyl ether. The yellow insoluble powder was shown to be $Rh(NO)(PPh_3)_2Cl_2$ by its i.r. spectrum. The ether was evaporated to dryness giving a residue which has an elemental analysis and an i.r. spectrum corresponding to RNHCO-NHR.

(b) Toluene-*p*-sulphonyl isocyanate (1 g) was added to a solution of $Rh(NO)(PPh_3)_3$ (0·46 g) in benzene (20 ml). Moderate gas evolution was observed and a yellow substance precipitated. After refluxing for 1 h the yellow product was sucked off and washed with hot benzene (25 ml).

Nitrosyl[bis(toluene-p-sulphonyl)ureylene]bis(triphenylphosphine)iridium(II), *Compound (IV)*.—(a) Solid $Ir(NO)(CO)(PPh_3)_2$ (0·3 g) was added to a solution of toluene-*p*-sulphonyl azide (0·375 g) in benzene (15 ml). After 3 h the pale yellow to pink precipitate was filtered off and washed with benzene. It can be recrystallized from hot methylene chloride–n-hexane.

(b) The orange-red solution of $Ir(NO)(PPh_3)_3$ (0·42 g) in benzene (20 ml) was treated with toluene-*p*-sulphonyl isocyanate (1·5 g). At room temperature no reaction occurred, whereas at about 50 °C moderate gas evolution was observed. After 2 h of refluxing a pale yellow microcrystalline substance was sucked off and washed with hot benzene.

Chloro[bis(toluene-p-sulphonyl)ureylene]bis(triphenylphosphine)rhodium(III), *Compound (V)*.—(a) To a well stirred suspension of $Rh(PPh_3)_3Cl$ (0·7 g) in benzene (25 ml) toluene-*p*-sulphonyl isocyanate (1 g) was added at room temperature. After 40 h the red substance had dissolved to a yellow solution. The solvent was removed *in vacuo* to about 5 ml and ether (40 ml) added. Gradually a yellow substance crystallized, which was filtered off and washed with ether. From the mother liquor a mixture of (V) and $RhCl(CO)(PPh_3)_2$ was obtained; the two compounds were separated by fractional crystallization from hot benzene–ether.

$Pt(PPh_3)_2(R_2N_4CO)$, *Compound (VI)*. Toluene-*p*-sulphonyl azide (0·57 g) in benzene (15 ml) was added to solid $Pt(PPh_3)_2(CO)_2$ (0·45 g). Gas evolution was noted. After 3 h the white precipitate was filtered off from the reddish solution and washed with benzene. It can be recrystallized under nitrogen from chloroform–diethyl ether, giving a product which showed a slight broadening of the keto-band at 1740 cm^{-1}. The same derivative can be obtained from $Pt(PPh_3)_3(CO)$. In this case the presence of $RN{=}PPh_3$ was observed in the mother liquor.

In some preparations the precipitate was contaminated by the azadiene derivative $Pt(PPh_3)_2(N_4R_2)$, which is the product of the reaction of $Pt(PPh_3)_n$ ($n = 3$ or 4) with azide,[1] as shown by the i.r. spectrum. Also in this case crystallization from chloroform gave the pure compound. The reaction of (VI) (0·3 g) with gaseous hydrochloric acid in diethyl ether (35 ml) gave *cis*-$Pt(PPh_3)_2Cl_2$ and a white crystalline solid soluble in ether and different from RNHCONHR. This compound showed an elemental analysis consistent with four nitrogen atoms and two tosyl residues in the organic ligand of (VI) (Found: C, 47·3; H, 3·9; N, 12·7. $C_{15}H_{16}N_4O_5S_2$ requires C, 45·5; H, 4·0; N, 14·1%). This compound dissolved in water to give an acidic solution. It contained no chlorine.

μ-[Bis(toluene-p-sulphonyl)di-imide]bis(diphenylphosphinoethane)rhodium(II), *Compound (VII)*.—A solution of $RhH(Ph_2PCH_2CH_2PPh_2)_2$ (0·9 g) in benzene (25 ml) was treated with toluene-*p*-sulphonyl azide (0·4 g) at room temperature. Immediately nitrogen was evolved, and gradually a yellow substance precipitated which was filtered off after another hour of stirring, and washed with benzene. It could be recrystallized from hot benzene–light petroleum.

trans-*Bis(ethoxycarbonyl)bis(triphenylphosphine)platinum*(II), *Compound* (VIII).—Toluene-*p*-sulphonyl azide (0·6 g) dissolved in ethanol (20 ml) was added to $Pt(PPh_3)_2(CO)_2$ (0·6 g). After 5 h the white precipitate was filtered off. It was recrystallized from hot benzene–diethyl ether. In the mother liquor the presence of toluene-*p*-sulphonyl amide was detected by its i.r. spectrum.

Bis(methoxycarbonyl)bis(triphenylphosphine)platinum(II), *Compound (IX)*.—Toluene-*p*-sulphonyl azide (0·7 g) dissolved in methanol (20 ml) was added to $Pt(PPh_3)_2(CO)_2$ (0·7 g). After 5 h the white product was filtered off and crystallized from hot benzene–diethyl ether.

Azido[(ethoxycarbonyl)(toluene-p-sulphonyl)amido]bis(triphenylphosphine)platinum(II), *Compound (X)*.—Toluene-*p*-sulphonyl azide (0·9 g) in ethanol (26 ml) was added to $Pt(PPh_3)_3(CO)$ (0·9 g). After 5 h the white precipitate was filtered off and washed with benzene. It was recrystallized three times from chloroform–n-hexane. In the mother liquor the presence of $Pt(PPh_3)_2N_3(R)$ [1] and of $RN{=}PPh_3$ was observed. This reaction proved to be very complex. In more dilute solutions, and with the same ratio of the reactants, small quantities of compound (X) were obtained. The main product was $Pt(PPh_3)_3(NHR)_2$ already described,[1] together with $Pt(PPh_3)_2N_3(R)$ and $RN{=}PPh_3$. In more concentrated solutions a complex mixture of derivatives which we were unable to separate was obtained.

Compound (X) (0·1 g) when treated with dry diethyl ether (30 ml) saturated with gaseous hydrochloric acid, gave after 1 h *cis*-$Pt(PPh_3)_2Cl_2$ and a white oily organic material soluble in the ether. The elemental analyses, i.r., ^1H n.m.r., and mass spectra are consistent with the formula $RNHCO_2Et$.

Compound (X) was reacted with carbon monoxide in a suspension in ethanol for 2 days at room temperature, giving the already reported Pt$(PPh_3)_2(NCO)(CO_2Et)$.[1]

Azido[*(n-propoxycarbonyl)(toluene-*p*-sulphonyl)amido*]*-bis(triphenylphosphine)platinum*(II), *Compound* (*XI*).—Toluene-*p*-sulphonyl azide (0·85 g) in n-propanol (27 ml) was added to Pt$(PPh_3)_3$(CO) (0·85 g). After 5 h the white precipitate was filtered off. Repeated recrystallizations from chloroform–n-hexane gave a still impure product, which however showed i.r. and n.m.r. spectra consistent with its formulation.

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