Zerovalent Platinum Chemistry. Part IX.* Reduction of Dichlorobis(phosphine)platinum(II) by Hydrazine

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The isolation and characterisation of N_2H-bridged complexes formed during hydrazine reduction of *cis*-$[Pt(PR_3)_2Cl_2]$ are reported. Factors affecting the stability of these new N_2H complexes have been studied together with reactivity towards nucleophiles, hydrogen, and carbon monoxide.

REDUCTION of transition-metal complexes by hydrazine has been largely used in the synthesis of low-valent or hydridotransition-metal complexes.[1-4] This kind of reduction has afforded a large number of new complexes, particularly with tertiary phosphine ligands. However contradictory results have been reported, namely in the reduction of some platinum(II)–phosphine complexes. Malatesta and his co-workers [2] synthesised by hydrazine reduction in alcohol zerovalent tertiary phosphine–platinum complexes, whilst Chatt and Shaw [1] reported in similar reaction conditions the synthesis of hydridoplatinum(II)–tertiary phosphine compounds. Moreover with some phosphine complexes of noble metals [5-7] nitrene derivatives and related products have been formed by reactions with hydrazine.

It appears therefore that several factors, as yet unknown, play a role in defining the final reaction products; this suggests a rather complex and multi-step reaction path. This is not unexpected since it is known that heterogeneous decomposition of hydrazine to nitrogen and hydrogen proceeds by a multi-step process.[8] No detailed investigation of the hydrazine reduction of metal complexes has been reported until now with the exception of an investigation of the reduction of ruthenium(III)– and osmium(III)–tertiary phosphine complexes.[9] We report here a study of the hydrazine reduction of complexes of formula *cis*-$[Pt(PR_3)_2Cl_2]$ which has already been the subject of a preliminary communication.[10]

RESULTS

Reduction of cis-$[Pt(PR_3)_2Cl_2]$.—The reduction of *cis*-$[Pt(PPh_3)_2Cl_2]$ by hydrazine has been used to synthesize $[Pt(PPh_3)_3]$,[2] $[Pt(PPh_3)_2L]$ [11] (where L is an alkyne or an activated olefin), and *trans*-$[Pt(PPh_3)_2(H)Cl]$.[1] These reactions have been carried out in alcohol in the presence of an excess of hydrazine at temperatures higher than 40 °C. Gas evolution has been claimed in any case.

We have carried out the reduction of an ethanol suspension of *cis*-$[Pt(PPh_3)_2Cl_2]$ by adding slowly, at room temperature or lower, an alcoholic dilute solution of hydrazine which can be anhydrous or even slightly aqueous. After addition of *ca.* 5 mol equiv. of hydrazine per mol equiv. of platinum complex a yellow clear solution is obtained together with very little gas evolution. White crystals of the hydrido-complex separate after *ca.* 2 h; addition of a large excess of hydrazine and a longer reaction time produces the zerovalent species. Even at this stage of the reduction gas evolution of less than 1 mol equiv. of gas per mol equiv. of the reduced platinum complex was observed. The formation of a solution is in accord with the likely presence of an ionic intermediate, formed before the hydrido-species; this intermediate was stable enough under our reaction conditions to be isolated.

On cooling the yellow alcoholic solution at −80 °C a white crystalline material corresponding to $N_2H_4\cdot HCl$ separates. After removal of this by filtration at the same temperature, and evaporation of the clear yellow filtrate to dryness, a yellow powder was obtained the analysis for which was close to that calculated for $[Pt(PPh_3)_2N_2H_xCl]_y$ (see Experimental section); attempted recrystallisation of this led to its ready decomposition. Thus addition of benzene to the yellow solution gave rapid nitrogen evolution and the formation of *trans*-$[Pt(PPh_3)_2(H)Cl]$.

Since the absence of any Pt–Cl stretching frequency in the far-i.r. spectrum of this yellow material suggested an ionic structure for it, in order to obtain crystalline material we added to its yellow alcoholic solution large anions of poor nucleophilic character (*e.g.* BPh_4^-, BF_4^-, PF_6^-, or ClO_4^-). Pale cream crystals separated which were recrystallised to yield pure and stable ionic compounds for which analyses corresponding to $[Pt(PPh_3)_2N_2H_x]Y$ (Table 1) (Y = BPh_4, BF_4, or ClO_4) were obtained. The stability of these compounds in solution seems to be related to the nucleophilicity of the counter-ion, *e.g.* $BPh_4^- > BF_4^- > ClO_4^- > PF_6^-$. Decomposition slowly takes place in dimethylformamide (DMF) solution at 60 °C yielding in each case the corresponding cationic hydrido-complex $[Pt(PPh_3)_2(H)(DMF)]^+$. Even the solid complexes decompose with nitrogen evolution at *ca.* 160 °C, to yield deep red solids which we could not characterise.

Conductivity measurements (Table 1) suggested a dimeric structure which has been confirmed by an *X*-ray crystallographic investigation on the BPh_4 species.[10] It appears that two platinum atoms are doubly bridged by a single nitrogen atom from two N–N species. The nitrogen–

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* Part VIII, S. Cenini, R. Ugo, G. La Monica, and S. D. Robinson, *Inorg. Chim. Acta*, 1972, **6**, 182.

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[2] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

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[7] J. T. Moelwyn-Hughes and A. W. B. Garner, *Chem. Comm.*, 1969, 1309.

[8] K. Otto and M. Shelef in ' Catalysis,' ed. J. W. Hightower, North Holland–American Elsevier, 1973, vol. 1, p. 305 and refs. therein.

[9] J. Chatt, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 854.

[10] G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Comm.*, 1967, 739.

[11] J. L. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, 1969, **8**, 259.

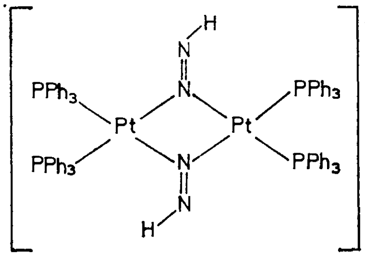
nitrogen distance suggests the presence of a dehydrodi-imide N_2H bridging ligand,[10] although the *X*-ray evidence is rather poor, owing to the easy decomposition of the crystals and the presence of some impurities which we could never eliminate completely.

TABLE 1

Analytical results and other physical data for the bridged dehydrodi-imido-complexes (required values in parentheses)

Compound	M.p./ decomp. (t/°C)	C (%)	H (%)	N (%)	Λ/cm^2 Ω^{-1} [b]
(I) $[Pt(PPh_3)_2(N_2H)]_2[BPh_4]_2 \cdot S$ [a]	151	64·2 (64·5)	4·7 (4·6)	2·3 (2·4)	64·8
(VIII) $[Pt(PPh_3)_3(N_2H)][BPh_4]$	162	68·2 (70·3)	5·2 (5·0)	2·1 (2·1)	
(II) $[Pt(PPh_3)_2(N_2H)]_2[BF_4]_2$	227	51·7 (51·7)	3·9 (3·7)	3·3 (3·4)	72·2
(IX) $[Pt(PPh_3)_3(N_2H)][BF_4]$	241	59·8 (59·0)	4·0 (4·2)	2·4 (2·6)	
(III) $[Pt(PPh_3)_2(N_2H)]_2[ClO_4]_2 \cdot S$ [a]	95	47·3 (47·6)	3·6 (3·6)	2·8 (3·0)	
(IV) $[Pt(PPh_2Me)_2(N_2H)]_2[BPh_4]_2$	124	62·8 (63·6)	5·3 (5·0)	2·5 (2·9)	52·6
(V) $[Pt(PPh_2Me)_2(N_2H)]_2[BF_4]_2$	153	43·1 (43·8)	3·7 (3·8)	3·5 (3·9)	
(VI) $[\{Pt(p\text{-tol})_3P\}_2(N_2H)]_2[BPh_4]_2 \cdot S$	113	65·3 (66·8)	5·6 (5·4)	2·1 (2·3)	
(VII) $[\{Pt(p\text{-tol})_3P\}_2(N_2H)]_2[BF_4]_2$	187	53·6 (53·0)	4·9 (4·6)	2·9 (2·9)	59·1

[a] S = CH_2Cl_2. [b] In $C_6H_5NO_2$.



We have therefore tried to evaluate the number of hydrogen atoms (*x*) probably bound to the nitrogen moiety of the platinum ion. Evidence for the presence of the N_2H ligand is given by the nearly quantitative formation of the corresponding hydridoplatinum(II) complexes with evolution of 1 mol equiv. of nitrogen either by reaction with a nucleophile or by thermal treatment. In fact the presence of some nucleophiles such as I^-, Br^-, and Cl^-, *etc.* induces the decomposition of the yellow compound to form the corresponding hydrido-complexes. In other cases (when the nucleophile X is NCO^-, NCS^-, N_3^-, $SnCl_3^-$) mixtures of the hydrido-complexes and the related $[Pt(PPh_3)_2X_2]$ compounds have been obtained.

We have also followed the thermal decomposition of $[Pt(PPh_3)_2N_2H_xCl]_y$ by thermogravimetric analysis. Gas evolution starts at *ca.* 70—80 °C and the weight loss corresponds to *ca.* 4·5—5%; this is in agreement with the evolution of 1 mol equiv. of nitrogen for each platinum atom; the residue is *trans*-$[Pt(PPh_3)_2(H)Cl]$.

I.r. spectra (Table 2) in the solid show three weak absorptions at *ca.* 3300—3200 cm^{-1} two of which must be attributed to ν_{NH}, in agreement with their shift to *ca.* 2400—2450 cm^{-1} when $N_2D_4 \cdot D_2O$ in EtOD is used as reducing agent. The absorption band at *ca.* 3290 cm^{-1} is probably a combination or overtone band, whilst absorptions at 3317 and 3276 cm^{-1} are attributed to ν_{NH}. The same absorptions were detected in CH_2Cl_2 solution.

These bands cannot be attributed to the presence of impurities of the $N_2H_5^+$ ion since this ion absorbs at lower frequencies (Table 2); moreover, it shows a bending at *ca.* 1638 cm^{-1} which is completely absent in our compounds. The separation of the two absorption bands (41 cm^{-1}) is comparable to the value observed in the deuteriated sample (*ca.* 35 cm^{-1}). This separation suggests that the two ν_{NH} absorption bands are not produced by direct coupling such as would be observed for Pt–NH–NH_2, a species which could also be formed. In fact such coupling would require a separation of *ca.* 100 cm^{-1} or more as observed, for instance, in hydrazine complexes (see Table 2).[12] Therefore it seems that the two ν_{NH} absorptions arise as a result of two different N_2H species such as would be present in a mixture with the $Pt(N_2H)_2Pt$ bridges in both *syn* and *anti* positions. The position of these bands is in agreement with the assignment to a N_2H species: in the recently reported symmetric complexes of N_2H_2 [13] and in the ionic tungsten complexes of an asymmetrically bound N_2H_2,[14] formed by protonation of the metal-bonded dinitrogen species, some reported values of ν_{NH} are in the range 3400—3250 cm^{-1}.

TABLE 2

Relevant i.r. and ^1H n.m.r. data for $[Pt(PR_3)_2(N_2H)]_2^{2+}$ species

Compound	ν_{NH}(w)	$\nu_{N=N}$(?)	ν_{anion}(vs)	τ_{NH}
(I)	3317,[a] 3276	1578		
	3313,[b] 3278	1577		
(VIII)	3321,[c] 3280	1580		
(II)	3352,[c] 3268	1582	1056	8·17, 8·37 [d]
(IX)	3358,[a] 3275	1586	1055	
(III)	3346,[c] 3270	1584	1083	
(IV)	3324,[c] 3270	1576		
(V)	3330,[c] 3257	1583	1053	
(VI)	n.d.,[e] 3265	1582		
(VII)	n.d.,[e] 3258	1588	1055	8·27 [f]
N_2H_4 [g]	3350, 3325 3314, 3280			
$N_2H_5^+$ [h]	3261, 3150			
$[Rh(PPh_3)(N_2H_4)_2Cl]$ [i]	3292, 3165, 3059			
$[Hg(N_2H_4)_2Cl_2]$ [g]	3230, 3130, 2985			

[a] KBr Mull. [b] CH_2Cl_2 Solution. [c] Nujol mull. [d] In CD_2Cl_2. [e] Not well detected. [f] τ_{CH_3} At 7·69. [g] K. Broderson, *Z. anorg. Chem.*, 1957, **290**, 241. [h] J. C. Decius and D. P. Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 2436. [i] W. Rieber, Thesis, München University, 1973.

An absorption band of medium intensity at *ca.* 1580 cm^{-1} may be tentatively assigned to a N=N stretching frequency; this band does not shift appreciably after deuteriation.

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[12] W. Rieber, Thesis, München University, 1974; K. Broderson, *Z. anorg. Chem.*, 1957, **290**, 24.

[13] D. Sellmann, *J. Organometallic Chem.*, 1972, **44**, C46; D. Sellmann, A. Brandl, and R. Endell, *ibid.*, 1973, **49**, C22; D. Sellman, A. Brandl, and R. Endell, *Angew. Chem. Internat. Edn.*, 1973, **12**, 1019.

[14] J. Chatt, G. H. Heath, and R. L. Richards, *J.C.S. Chem. Comm.*, 1972, 1010.

A ^{15}N investigation[13] of *cis*-N_2H_2 bonded to two $Cr(CO)_5$ moieties has assigned $\nu_{N=N}$ to absorption at 1415 cm^{-1}. We failed to observe any change or shift in the i.r. spectrum of a deuteriated sample with the exception of the disappearance of a medium band at *ca.* 880 cm^{-1} which could be assigned to δ_{NNH}.[12]

The ^1H n.m.r. spectrum (CD_2Cl_2, room temperature) of (II) shows the presence of two broad and overlapping peaks at τ 8·17 and 8·37 (in one case only one) (Table 2). Upon addition of a small amount of CF_3CO_2H the signals disappeared, as expected in the case of NH groups. A very broad and very weak signal centred at *ca.* τ 6·8 was always observed; this signal also disappeared upon addition of CF_3CO_2H. Peaks due to the NH group of a metal-bonded di-imine N_2H_2 have been reported at τ 6·5 for $[WCl_2(dppe)_2(N_2H_2)]$[14] and at τ $-4{\cdot}2$ for $[(cp)Mn(CO)_2(N_2H_2)]$[13] (with $[^2H_6]$acetone as solvent). The high τ values that we have observed, are in agreement with the rather basic character of the N_2H bridge in the platinum compounds since, in the absence of nucleophiles, we have observed that the ion $[Pt_2(PPh_3)_4(N_2H_2)]^{2+}$ may be easily protonated by HBF_4 (see later) as the related $[Pt(PPh_3)_3N_2Ar]^+$ species.[15] On the other hand no deuteriation takes place when this ion is treated with a mixture of D_2O–$CDCl_3$ for more than 8 months at room temperature; this is in agreement with the very low acidic character of the N–H bond. In contrast it has been reported[14] that the observed proton shift of N_2H_2 complexes of W and Mo is very sensitive to protonic impurities in the n.m.r. solvent, indicating an exchange process.

Upon protonation of (I) we observed the shift of the NH stretching frequencies to 3183 and 3108 cm^{-1} respectively, whilst the previously supposed N ∷ N stretching frequency shifts only at 1570 cm^{-1}, a value in disagreement with the previous assignment to $\nu_{N=N}$. The protonated species is not particularly stable since when warmed the initial greenish yellow material turns white, to give a nearly insoluble compound, the analysis of which indicates its formulation as $[Pt_2(PPh_3)_4(N_2H_4)][BF_4]_4$. This latter compound is probably formed by disproportionation of the intermediate N_2H_2 ligand obtained by protonation of the initial N_2H-bridged species. Disproportionation of N_2H_2 to form N_2H_4 and N_2 is known for the free N_2H_2 species.[16] Besides protonation, in the presence of strong nucleophiles, X, or HX acids, *trans*-bis(triphenylphosphine)hydridoplatinum species are obtained in high yields (X = Cl, Br, or I).

Studies on the Stoicheiometry of the Reduction of cis-$[Pt(PR_3)_2Cl_2]$.—Different stoicheiometries for the hydrazine reduction of platinum(II) complexes have been suggested.[1-4] The present work may contribute to a better definition of the stoicheiometry and, consequently, of a possible mechanism. The first step of the reduction proceeds probably with the following stoicheiometry:

$$\textit{cis}\text{-}[Pt(PPh_3)_2Cl_2] + 2N_2H_4 \longrightarrow 1/2[Pt(PPh_3)_2N_2H_3)]_2Cl_2 + N_2H_5Cl \longrightarrow 1/2[Pt(PPh_3)_2(N_2H)]_2Cl_2 + H_2$$

Evidence for the intermediate formation of a hydrazido-complex will be reported later in discussing reactivity.

By precipitation of the N_2H-bridged platinum ion with $Na[BPh_4]$ and subsequent titration of excess of hydrazine with KIO_3, we have found that, at this stage of the reaction, *ca.* 2 mol equiv. of hydrazine had reacted per mol equiv. of the initial platinum complex. We have often observed a slightly higher amount of reacted hydrazine, probably because of some catalytic decomposition. Moreover, the mass spectroscopic analysis of the small amounts of gas evolved at this stage of the reaction were shown to be hydrogen; we never detected the presence of ammonia either by mass spectroscopy or gas chromatography. In general, we could never obtain an exact stoicheiometric balance of the evolved gas (1 mol equiv. of hydrogen for each mol equiv. of the platinum complex) but this could be due to the solubility in alcohol of hydrogen.

The second step could correspond to nucleophilic attack of the chloride ion on the platinum dehydrodi-imide complex:

$$1/2[Pt(PPh_3)_2(N_2H)]_2Cl_2 \longrightarrow [Pt(PPh_3)_2(H)Cl] + N_2$$

Although this has been already proved to take place with chloride as nucleophile, the very small amount of gas evolved during the hydrazine reduction to form hydrides and the absence of nitrogen in the evolved gas does not support this reaction. We cannot therefore at present offer a satisfactory explanation for the further subsequent formation of the hydrido-compounds. The final step, producing a zero-valent platinum triphenylphosphine complex, is probably related to the basic properties of hydrazine. We have, in fact, observed in the presence of an excess of hydrazine the following reaction:

$$\textit{trans}\text{-}[Pt(PPh_3)_2(H)Cl] + N_2H_4 \longrightarrow [Pt(PPh_3)_2] + N_2H_5Cl$$

The yellow very unstable precipitate formed by reduction with an excess of hydrazine has an analysis consistent with its formulation as $[Pt(PPh_3)_2]$[17] (or as a mixture of $[Pt(PPh_3)_2]$ and $[Pt(PPh_3)_3]$) when it is filtered off as soon as precipitation occurs. In agreement with this formulation this material readily reacts with ethylene in methanol suspension to form the ethylene complex $[Pt(PPh_3)_2(CH_2{=}CH_2)]$.[17] When the former reaction mixture is set aside only the $[Pt(PPh_3)_3]$ species is isolated; this does not react with ethylene.

It appears therefore that the unstable $[Pt(PPh_3)_2]$ species disproportionates quickly to $[Pt(PPh_3)_3]$ and other alcohol-soluble species which we could not characterise. The rapidity with which this occurs may explain the great difficulty in obtaining reproducible syntheses of this yellow, probably monomeric compound,[17] the existence of which has been questioned.[18] Evidence in support of its existence has been forthcoming from the synthesis and *X*-ray characterisation of $[Pd\{P(cyclohexyl)_3\}_2]$ and other zero-valent palladium two-co-ordinate complexes.[19,20]

Effect of Solvents and Phosphines on Hydrazine Reduction.—We have observed that although the presence of water does not appreciably affect the reaction products and rates, the type of alcohol used as solvent is important. Thus, when methanol is used in place of ethanol an increase of *ca.* 100 times the total reaction rate is observed. The

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[20] K. Kudo, M. Hidai, T. Murayama, and Y. Uchida, *Chem. Comm.*, 1970, 469.

following qualitative reactivity sequence has been observed: MeOH > EtOH > Pr^iOH > Bu^nOH > Bu^tOH > $(CH_2OH)_2$. The reaction does not take place in pure hydrazine. In benzene, rapid gas evolution occurs and although a yellow intermediate colour is observed, only hydrido-compounds have been isolated as reaction products. The use of phosphines of different basicity affects both the final products and reaction rates.

With triphenylphosphines which carry electronegative groups in the *para* position (*e.g.* *p*-fluoro- or *p*-chloro-triphenylphosphine) the immediate formation of the zerovalent trisphosphine platinum complexes has always been observed. With more basic phosphines such as tris-*p*-tolylphosphine and methyldiphenylphosphine the intermediate dehydrodi-imide complexes can be isolated and characterised (see Tables 1 and 2). Reaction rates are comparable to that of the triphenylphosphine complex. With dimethylphenylphosphine we have been unable to isolate the intermediate dehydrodi-imide complex in a pure state. Upon crystallisation of the crude reaction product from aqueous acetone complete decomposition takes place and the ionic hydride $[Pt(PMe_2Ph)_2(H)(H_2O)][BPh_4]$ is always obtained (see Table 3). With chelating ligands such as αα′-bipyridyl and 1,2-bis(diphenylphosphino)ethane a reaction occurs but the dehydrodi-imide species has not been isolated. With αα′-bipyridyl (bipy) the ionic compound $[Pt(N_2H_4)_2(bipy)]Cl_2$ is first formed, which, in the presence of an excess of water, reacts further to give metallic platinum with gas evolution.

TABLE 3

Relevant analytical (required values in parentheses) and i.r. data (in cm^{-1}) of some new hydrido-complexes

	Compound	M.p. (t/°C)	C (%)	H (%)	N (%)	ν_{Pt-H} And δ_{Pt-H}
(X)	$[Pt(PPh_3)_2(H)DMF][BPh_4]$ [a]	101	66·8 (67·9)	5·4 (5·2)	1·4 (1·3)	2038 and 834m
(XI)	$[Pt(PPh_3)_2(H)DMF][BF_4]$ [b]	177	52·9 (53·1)	4·5 (4·4)	1·4 (1·6)	2035 and 847m
(XII)	$[Pt(PPhMe_2)_2(H)(H_2O)][BPh_4]$ [c]	89	58·9 (59·3)	5·6 (5·5)		2060m

[a] $\nu_{C=O}$ 1657ms. [b] $\nu_{C=O}$ 1652ms. [c] ν_{OH} 3440m, br.

Some Aspects of Reactivity of Dehydrodi-imide Complexes.—Some reactions have been already reported. Dehydrodi-imide complexes react with a number of nucleophiles in alcohol or CH_2Cl_2 solution to evolve nitrogen and form the corresponding platinum(II) hydrides. Analogously, heating of a dimethylformamide solution of $[Pt(PPh_3)_2(N_2H)]_2[BPh_4]_2$ at 60 °C gives a deep red-orange solution, from which the cationic complex $[Pt(PPh_3)_2(H)(DMF)][BPh_4]$ has been isolated (Table 3). This complex can be recrystallised, without loss of dimethylformamide, from CH_2Cl_2–Et_2O. Reaction with an excess of PPh_3 produces a 1 : 1 adduct of formula $[Pt(PPh_3)_3N_2H]Y$ (Y = BF_4 or BPh_4). The reaction with acids HX (X = Cl, Br, or I) readily affords the *trans*-hydridoplatinum(II) complexes as described above.

We have examined the reactivity of $[Pt(PPh_3)_2(N_2H)]_2[BF_4]_2$ towards hydrogen and carbon monoxide. With hydrogen at 1 atm in methanol or ethanol a deep yellow solution is first obtained which with time becomes orange and finally red. Evaporation of solvent leaves a red platinum–phosphine compound; crystals of $N_2H_5 \cdot BF_4$ were also isolated from the reaction mixture. The red final material corresponds to the one obtained from a solution of $[Pt(PPh_3)_2(C_2H_4)]$ upon passage of nitrogen. This latter compound is generated from $[Pt(PPh_3)_2]$ formed by ethylene dissociation.[17,21] As a consequence of these observations we may propose the two following series of reactions.

$$\begin{tikzcd}
\tfrac{1}{2}[Pt(PPh_3)_2(N_2H)]_2[BF_4]_2 \arrow[r, shift left, "H_2"] \arrow[dr, "+H_2,\ -N_2,\ -HBF_4"'] & \tfrac{1}{2}[Pt(PPh_3)_2(N_2H_3)]_2[BF_4]_2 \arrow[l, shift left] \arrow[d, "H_2"] \\
 & \{[Pt(PPh_3)_2H_2]\} + N_2H_5 \cdot BF_4 \arrow[d] \\
 & [Pt(PPh_3)_2] + H_2 \arrow[d] \\
 & \text{Red material}
\end{tikzcd}$$

However we have no firm evidence that $N_2H_5 \cdot BF_4$ has been formed only by hydrogenation of the N_2H ligand, since it could also originate from hydrazido-species such as $[Pt(PPh_3)_2N_2H_3]_2^{2+}$ which always contaminates (see later) the dehydrodi-imidoplatinum complex. In fact, similar products and reaction trends have been observed upon hydrogenation of a freshly prepared solution of $[Pt(PPh_3)_2N_2H]_2^{2+}$ or an alcoholic solution of *cis*-$[Pt(PPh_3)_2Cl_2]$ reduced with hydrazine. A yellow-green solution is initially obtained when hydrazine reduction is carried out under hydrogen and a similar solution may be obtained by allowing hydrogen to react with a yellow alcoholic solution of the N_2H–platinum cation. Upon addition of an excess of BF_4^- or BPh_4^- anion to this yellow-green solution hydrogen is evolved and the N_2H–platinum cation is regenerated. These results support the presence of a hydrazido-complex in the yellow-green solution, which, since it is too unstable in the solid state to be isolated, is rapidly converted into the N_2H complex. Only subsequently we observed under hydrogen a slow change of the yellow-green solution to a deep yellow colour. ^1H N.m.r. investigation of this deep yellow alcoholic solution {formed either from the N_2H species or from the hydrazine reduced solution of $[Pt(PPh_3)_2Cl_2]$} shows no signal attributable to a Pt–H species {*e.g.* $[Pt(PPh_3)_2H_2]$}. This is not unexpected since it is known that $[PtL_nH_2]$ (n = 2 or 3) compounds are stable only when L = PEt_3 (n = 3)[22] or $P(cyclohexyl)_3$ (n = 2).[23] As a consequence this solution probably corresponds to $[Pt(PPh_3)_2]$ which is slowly transformed.

The reaction with carbon monoxide is very complex (see Schemes 1 and 2). Upon passage of carbon monoxide (1 atm) into a CH_2Cl_2 solution of $[Pt(PPh_3)_2N_2H]_2[BF_4]_2$ the colour changes to orange and carbonyl bands appear at 1995 cm^{-1} (shoulder at 2015 cm^{-1}) corresponding to the absorption of 1 mol equiv. of carbon monoxide for each platinum atom. After few minutes the major i.r. absorptions change and shift at 2070 (probably ν_{CO}) and 2170 cm^{-1} (probably ν_{Pt-H}) suggesting the intermediate formation of the known hydrido-cation *trans*-$[Pt(PPh_3)_2(H)CO]^+$ (ν_{Pt-H} at 2170 cm^{-1} and ν_{CO} at 2080 cm^{-1} respectively).[24]

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[21] F. Glockling, T. McBride, and R. J. I. Pollock, *J.C.S. Chem. Comm.*, 1973, 650.

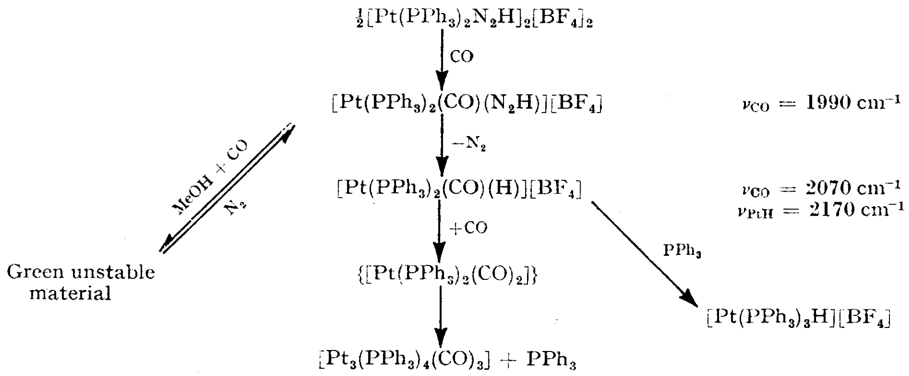
[22] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

[23] K. Kudo, M. Hidai, and Y. Uchida, *J. Organometallic Chem.*, 1973, **56**, 413.

[24] H. C. Clark and H. Kurosawa, *J. Organometallic Chem.*, 1972, **36**, 399.

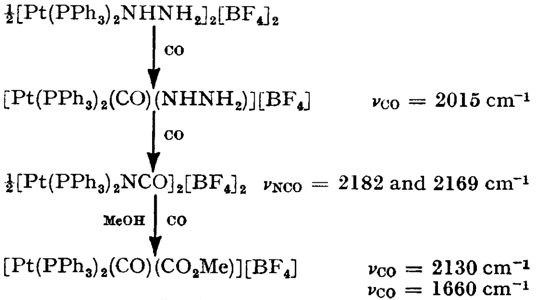
After 90 min the colour darkens to red-orange and in the i.r. spectra additional strong i.r. absorptions appear at *ca.* 1805 cm^{-1}. After a reaction time of 6 h (the solvent has to be renewed several times) only two main compounds are isolated: $[Pt(PPh_3)_3(H)][BF_4]$ [25] and an orange-red cluster carbonyl compound which has been reported as $[Pt_3(PPh_3)_4(CO)_3]$ (ν_{CO} 1854w, 1803s, and 1788s cm^{-1}) and which is known to be formed from $[Pt(PPh_3)_2(CO)_2]$.[26]

When the reaction is carried out in methanol or in CH_2Cl_2 stabilised with 1% ethanol a dark green colour appears after a few minutes (see Scheme 1). This colour corresponds to the formation of a very unstable carbonyl compound; in fact the initial yellow-orange colour can be reobtained only by passage of dry nitrogen through the solution or by addition of a small excess of triphenylphosphine. This dark green solution is characterised by i.r. absorptions at *ca.* 1710w and 1670m cm^{-1}, together with absorptions at *ca.* 1800 cm^{-1}. At the same time the initial absorption bands at 2015 and 1995 cm^{-1} observed in pure CH_2Cl_2 are very weak. This complex behaviour can be explained by a series of reactions as those reported in Scheme 1:



SCHEME 1

Small amounts of $N_2H_5{\cdot}BF_4{\cdot}0{\cdot}5H_2O$ have also been isolated. In many experiments the formation in small yields of an isocyanato-compound corresponding to $[Pt(PPh_3)_2NCO]_2[BF_4]_2$ has been observed ($\nu_{NCO} = 2181$ and 2169 cm^{-1}) [27] and in some cases this compound has also been isolated (see Experimental section). In methanol, by increasing the reaction time, we could observe its transformation into $[Pt(PPh_3)_2(CO)(CO_2R)][BF_4]$ ($R = CH_3$) which confirms that cationic isocyanatoplatinum complexes react in the presence of alcohol with carbon monoxide to give alkoxycarbonyl groups.[28] These latter data and the shoulder at 2015 cm^{-1} previously reported can be explained as in Scheme 2, on the assumption that the N_2H complexes always contain impurities of the corresponding hydrazido $NHNH_2$ complexes:



SCHEME 2

We have also observed an absorption band at *ca.* 1710 cm^{-1} which can be related to the formation of a platinum species having Pt–$NHCO_2Me$ or Pt–$CONHNH_2$ bonds.[29] However this species (which is always present in very small amounts) is rapidly transformed into the final $[Pt(PPh_3)_2(CO)(CO_2Me)]^+$ ion.

EXPERIMENTAL

All reactions were carried out under an atmosphere of pure and dry nitrogen. Reaction mixtures were worked up in the air, unless otherwise stated. Solvents were dry, purified, and saturated with N_2. Starting phosphine platinum complexes were prepared as described in the literature.[30]

I.r. spectra were obtained using a Perkin-Elmer 621 (grating) spectrophotometer and a Perkin-Elmer 137 instrument. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R10 and Varian 60 spectrometer with Me_4Si as internal standard. Conductivity data were obtained with a Phillips PR9500 instrument. M.p.s were determined on a Leitz Heiztischmikroskop. Elemental analyses were carried out in the analytical laboratory of Milan University. Quantitative determination of hydrazine was by titration with $0{\cdot}025$M-KIO_3 in concentrated hydrochloric acid solution.

Reduction of cis-$[Pt(PPh_3)_2Cl_2]$ *by Hydrazine.*—(*a*) A suspension of $[Pt(PPh_3)_2Cl_2]$ (2·5 g) in absolute ethanol (150 ml) was treated dropwise with $N_2H_4{\cdot}H_2O$ (*ca.* 300 mg) at room temperature and with stirring. After 20—30 min a yellow clear solution was obtained. Gas evolution was less than 1 mol equiv. per mol equiv. of platinum complex. After cooling of the mixture at −80 °C and removal at the same temperature of some of the $N_2H_4{\cdot}HCl$ by filtration, the resulting stable yellow solution was evaporated under high vacuum, to yield yellow material (*ca.* 1·5 g) which evolved nitrogen in the range 75—80 to 155—160 °C to give a red material. That the gas evolved was nitrogen was shown by gas chromatography. The yellow material was washed with a small amount of water; its analysis was close to that expected for $[Pt(PPh_3)_2N_2H]Cl$ (Found: C, 54·2; H, 4·2;

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[25] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.

[26] J. Chatt and P. Chini, *J. Chem. Soc.* (*A*), 1970, 1538.

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[28] W. Beck and K. v Werner, *Chem. Ber.*, 1971, **104**, 290.

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[30] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 238; B. L. Shaw and J. M. Jenkins, *J. Chem. Soc.* (*A*), 1966, 770; S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

N, 3·2. $C_{36}H_{31}ClN_2P_2Pt$ requires C, 55·1; H, 3·9; N, 3·6%). The same product was obtained when the reaction was carried out at temperatures in the range −20—20 °C. This yellow material was rather unstable when treated with non-protonic solvents (*e.g.* with benzene or chloroform), nitrogen being evolved and *trans*-$[Pt(PPh_3)_2(H)Cl]$ being formed.[1,31] The complex reacted very readily with HCl, HBr, and HI to afford *trans*-$[Pt(PPh_3)_2(H)X]$ (X = Cl, Br, or I);[1,31] with CH_3CO_2H or HNO_3 only *trans*-$[Pt(PPh_3)(H)Cl]$ was obtained.

(*b*) When the solution obtained after addition of hydrazine was left for more than 3—4 h, white crystals of *trans*-$[Pt(PPh_3)_2(H)Cl]$ were isolated (Found: C, 56·1; H, 4·35. Calc. for $C_{36}H_{31}ClP_2Pt$: C, 57·0; H, 4·4%). The hydrido-compound was obtained more easily by carrying out the reaction for a few minutes in boiling ethanol. Upon evaporation of the mother liquor further amounts of the yellow material described above were always isolated.

(*c*) To a suspension of $[Pt(PPh_3)_2Cl_2]$ (0·5 g) in ethanol (30 ml) an excess of $N_2H_4{\cdot}H_2O$ was added at *ca.* 60 °C with stirring. The addition of hydrazine was made dropwise up to the formation of a yellow clear solution at which point the solution was refluxed and a large excess of hydrazine was added. After a few minutes a pale-yellow unstable compound (dec. 160 °C in air) separated; this was quickly filtered off. The compound had an analysis consistent with its formulation as $[Pt(PPh_3)_2]$ (Found: C, 60·50—60·91; H, 4·37—4·45. Calc. for $C_{36}H_{30}P_2Pt$: C, 60·2; H, 4·2%). A suspension of this material in n-hexane or methanol reacted easily with ethylene to give $[Pt(PPh_3)_2(C_2H_4)]$ [17] which was characterised by elemental analysis and by its n.m.r. spectrum.

If the yellow compound is not filtered off as soon as precipitation occurs, a deep yellow material is slowly formed the analysis for which is consistent with its formulation as $[Pt(PPh_3)_3]$ (Found: C, 66·3; H, 4·5. Calc. for $C_{54}H_{45}P_3Pt$: C, 66·0; H, 4·6%).

Synthesis and Isolation of N_2H *Complexes*.—$[Pt(PPh_3)_2(N_2H)]_2[BPh_4]_2$ (I). To *cis*-$[Pt(PPh_3)_2Cl_2]$ (1·5 g) suspended in ethanol (60 ml) at room temperature with stirring was added hydrazine hydrate (85%; *ca.* 500 mg). The solution obtained after 40 min was cooled at −20 °C for 1 day after which the crystalline $N_2H_4{\cdot}HCl$ was filtered off. Addition of a small excess of sodium tetraphenylborate formed a cream precipitate in near quantitative yield. This was filtered off after stirring (30 min), and washed with water (40 ml), ethanol (10 ml), and ether; finally it was dried *in vacuo*. Recrystallisation from CH_2Cl_2–Et_2O yielded pale yellow crystals of complex (I) (yield 80—90%).

$[Pt(PPh_3)_2(N_2D)]_2[BPh_4]_2$ (Ia). To *cis*-$[Pt(PPh_3)_2Cl_2]$ (0·5 mmol) suspended in CH_3OD (15 ml; E. Merck-Schuschardt; 99%) under a dry atmosphere of argon $N_2D_4{\cdot}D_2O$ (400 mg) was added dropwise. Precipitation from the clear solution obtained after 15 min by addition of a solution of an excess of $NaBPh_4$ in D_2O (1 ml) at room temperature yielded a crude product, from which N_2D_5Cl could be removed by recrystallisation from $CDCl_3$–Et_2O under argon.

$[Pt(PPh_3)_2(N_2H)]_2X_2$ [X = BF_4 (II); ClO_4 (III)]. The yellow alcoholic solution containing $[Pt(PPh_3)_2(N_2H)]_2Cl_2$, prepared as described for (I), was stirred with an excess of solid $NaBF_4$, $NaClO_4$, and KPF_6, respectively, for 2 h at 0 °C. The solvent was then removed and the pale yellow residues extracted with small amounts of cold and freshly distilled CH_2Cl_2. Addition of pentane or ether yielded microcrystalline pale yellow precipitates (yield 80—90%).

In the case of X = PF_6 the complex was always contaminated with a hydride {probably $[Pt(PPh_3)_2(H)solv][PF_6]$ ν_{PtH}: *ca.* 2060 cm^{-1}} formed by decomposition. With X = ClO_4 decomposition took place in solution, when the temperature was > +10 °C.

$[PtL_2(N_2H)]_2X_2$ [L = PPh_2Me, $(p\text{-}CH_3C_6H_4)_3P$; X = BPh_4, BF_4 (IV)—(VII)]. These compounds were prepared in the same manner as described above. Yields were lower (65—70%), because of the ready decomposition of the pale yellow complexes on recrystallisation.

$[Pt(PhMe_2P)_2(H)(H_2O)][BF_4]$ (XII). *cis*-$[Pt(PhMe_2P)_2Cl_2]$ (400 mg) was treated with $N_2H_4{\cdot}H_2O$ (85%, 250 mg) in methanol (15 ml) at 0 °C with stirring, and a small excess of solid $NaBF_4$ was added after 5 min to the deep yellow solution. The colour of the reaction mixture grew lighter and gas evolution was observed. After 15 min at 0 °C, the solvent was removed *in vacuo* and the oily residue was treated with degassed water to aid solidification; the product was then washed with ice-cold methanol (max. 2 ml), dried under reduced pressure, and recrystallised from acetone–water to yield white crystals; yield 28%.

Reaction with Nucleophiles.—(a) *Reaction with ionic nucleophiles* X (X = Cl, Br, I, SCN, or N_3). (i) Aqueous solutions of MX (M = Na or K) were added in excess to ethanolic solutions of $[PtL_2(N_2H)]_2Cl_2$ (L = PPh_3 or PPh_2Me) with stirring at room temperature. After 30 min, when gas evolution had stopped, the solvent was reduced by half, and the crude products were filtered off from the cool mixture. The hydrido-complexes $[PtL_2(H)X]$ obtained in this manner generally contained 10—20% of *cis*-$[PtL_2X_2]$; they were recrystallised twice from methanol–Et_2O or, in certain cases, from aqueous acetone; yields 45—65%.

(ii) The solutions of $[Pt(PPh_3)_2(N_2H)]_2Y_2$ (Y = BPh_4 or BF_4) (200 mg) in CH_2Cl_2 (10 ml) were stirred at room temperature for 2 h with an excess of the solid salts MX. The insoluble part, consisting of excess of MX, MY, and some $[Pt(PPh_3)_2X_2]$, was filtered off from the cool mixture and pentane was added to the filtrate until precipitation was complete (yield *ca.* 80%). The hydrido-complexes were characterised by i.r. spectroscopy and elemental analyses.

(b) *Reaction with dimethylformamide* (*DMF*). Solutions of (I) and (II), respectively, in DMF were heated to 60° until the colour had changed to red-orange. After removal of the solvent under reduced pressure red oils were obtained, which partially crystallised upon addition of Et_2O. Recrystallisation from CH_2Cl_2–Et_2O gave the complexes (X) and (XI) as pale yellow solids; yields 30—45%. Care must be taken during crystallisation in CH_2Cl_2, since partial chlorination to give $[Pt(PPh_3)_2(H)Cl]$ and $[Pt(PPh_3)_2Cl_2]$ takes place.

(c) *Reaction with triphenylphosphine*. PPh_3 (1·1 mmol) was added to saturated solutions of (I) and (II) (0·5 mmol) respectively, in pure $CHCl_3$ and the mixtures were refluxed for 15 min in the dark. After 1 h at room temperature pale yellow precipitates of (VIII) and (IX), respectively, were obtained upon slow addition of pentane to the mixtures. The products were washed with methanol and ether, and dried (yield 90—95%). These compounds could not be recrystallised.

Reaction of complex (*II*) *with* HBF_4.—Aqueous HBF_4 (35%) was added in excess to a methanolic suspension of (II) (200 mg). The i.r. spectrum of the solid changed (see Results section) quickly. The reaction mixture was refluxed;

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[31] J. Chatt, L. A. Duncanson, and B. L. Shaw, *Proc. Chem. Soc.*, 1957, 343.

after 20 min a white precipitate was obtained, which was filtered off, washed with water and methanol, and dried *in vacuo*. Recrystallisation from CH_2Cl_2 yielded colourless crystals of the product, m.p. 252 °C, the analysis for which was consistent with its formulation as $[Pt_2(PPh_3)_4N_2H_4][BF_4]_4$ (Found: C, 48·6; H, 3·7; N, 1·6. Calc. for $C_{72}H_{64}B_4F_{16}N_2P_4Pt_2$: C, 47·6; H, 3·6; N, 1·5%), Λ_M in dimethylformamide 228 cm^2 Ω^{-1}; i.r. data in cm^{-1} (KBr discs) 3222m, 3125w, 3078vw (ν_{NH}), 1604sh,br (δ_{NH}), and 968 (ν_{N-N}?).

Reaction of Complex (II) with Carbon Monoxide.—Upon passage of CO at room temperature into a solution of (II) in CH_2Cl_2 (in the absence of alcohol) the colour changed from yellow to orange (20 min) and later to red-orange (after 6 h) (the solvent must be renewed several times). Relevant i.r. changes were observed (see Results section). After 9 h the solvent was removed and the residue was extracted with dry benzene. From the soluble part (*ca.* 60% of the starting material) $[Pt_3(PPh_3)_4(CO)_3 \cdot C_6H_6]$ [26] and $[Pt(PPh_3)_3H][BF_4]$ [25] were isolated by chromatography on Al_2O_3. Both compounds were characterised by i.r. spectroscopy and elemental analyses. In the insoluble part small amounts of $N_2H_5 \cdot BF_4$ were isolated by extraction with H_2O together with some $[Pt(PPh_3)_2(NCO)]_2[BF_4]_2$ [28] which was purified by recrystallisation from CH_2Cl_2–Et_2O. The presence of alcohols (even 1% methanol in CH_2Cl_2) induced first the formation of a very unstable dark green solution (i.r. absorptions at 1800, 1710, and 1670 cm^{-1}), which became yellow-orange upon passage of nitrogen; we could not isolate the green compound. By increasing the reaction time other compounds could be detected (see Results section) spectroscopically.

Reaction of Complex (II) with Hydrogen.—Passage of hydrogen through a methanolic solution of complex (II) or a methanolic solution of *cis*-$[Pt(PPh_3)_2Cl_2]$ reduced with hydrazine gave a yellow-green colour which after 90 min changed to deep yellow. When set aside in the air, the solution became orange and finally dark red. After removal of solvent, $N_2H_5BF_4$ could be extracted from the residue with water. The red solid [27,17] was crystallised from benzene.

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