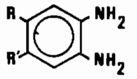
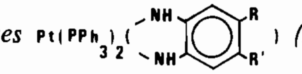
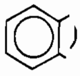
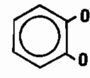
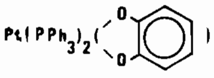
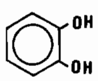
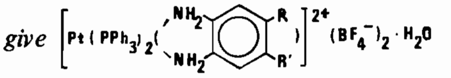
Inorganica Chimica Acta, 33 (1978) 161–166
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Reactions of Amines with Pt(PPh$_3$)$_2$O$_2$

M. PIZZOTTI, S. CENINI* and G. LA MONICA
CNR Center, Istituto di Chimica Generale, Via Venezian 21, 20133 Milan, Italy

Received June 12, 1978

By reaction of Pt(PPh$_3$)$_2$O$_2$ with  *in ethanol the complexes*  *(R = R′ = H; R = H, R′ = NO$_2$; RR′ =*  *) have been obtained. The analogous derivatives isolated from Pt(PPh$_3$)$_2$O$_2$ and the* ortho*-diamines with R = H, R′ = Me or R = R′ = Me, showed some peculiar spectroscopic properties. A related reaction has been carried out with*  *,*  *being isolated; the latter was also obtained from* cis*-Pt(PPh$_3$)$_2$Cl$_2$ and*  *in a basic medium. The platinum diamido complexes can be reversibly protonated with HBF$_4$ to give*  *. Attempted reactions of Pt(PPh$_3$)$_2$O$_2$ with NH$_3$, NH$_2$CH$_2$CH$_2$NH$_2$ and* p*-RC$_6$H$_4$NH$_2$ (R = Me, OMe, NO$_2$) did not give well characterizable products, while with Bu^t-NH$_2$ an already known cluster complex was obtained.*

Introduction

The reactions of amines with metal oxo derivatives represent a useful method for the synthesis of imido complexes [1, 2] (eq. 1):

$$L_nM(O) + RNH_2 \longrightarrow L_nM(NR) + H_2O \qquad (1)$$

and we have recently extended this reaction to sulphinylamines [3] (eq. 2):

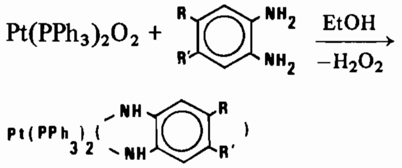
$$Re(PPh_3)_2(O)Cl_3 + ArNSO \longrightarrow Re(PPh_3)_2(NAr)Cl_3 + SO_2 \qquad (2)$$

Owing to our interest in the chemistry of imido complexes and related derivatives [2, 3] and to the reactivity of amines with transition metal complexes [4, 5], we have undertaken a study of the reactions of peroxo complexes such as M(PPh$_3$)$_2$O$_2$ (M = Pd, Pt) with a series of amines. It is known that the oxidation of primary aromatic amines with an inorganic nickel peroxide generally leads to the corresponding symmetrical azo compounds, while aliphatic amines are oxidized to the corresponding nitriles [6]. It was thus of interest to investigate whether an oxidant such as a transition metal peroxo complex could dehydrogenate in a selective way these organic molecules.

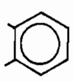
Results

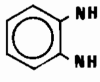
Reactions with ortho-Phenylenediamines

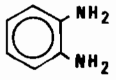
By reaction of Pt(PPh$_3$)$_2$O$_2$ in ethanol with a series of *ortho*-phenylenediamines, deeply coloured diamido derivatives of platinum have been isolated (eq. 3) (Table I):



(3)

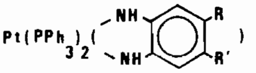
[R = R′ = H(I); R = H, R′ = NO$_2$(II); RR′ =  (III)]

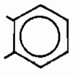
A similar reaction has been carried out between Pd(PPh$_3$)$_2$O$_2$ and  , a complex having an i.r. spectrum comparable to that of (I) being isolated. However elemental analyses were not entirely satisfactory (see Experimental).

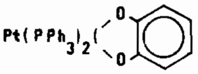
When Pt(PPh$_3$)$_3$ was reacted with  in

---

*To whom correspondence should be addressed.

TABLE I. Analytical [a] and I.r. (cm^{-1}, nujol) Data for  Complexes.

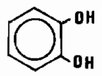
Compound	R	R'	Colour	M.p. (°C)	C[b]	H[b]	N[b]	ν_{NH}	ν_{C-N}
(I)[e,f]	H	H	deep red	>240	60.75 (60.50)	4.48 (4.80)	3.42 (3.20)	3390	1295
(II)	H	NO_2	violet	>240	57.02 (57.60)	4.39 (4.48)	4.16 (4.58)	3400	1275
(III)			brick red	>240	62.35 (63.00)	4.23 (4.34)	3.24 (3.20)	3400	1335
(IV)[c]	H	H	yellow	>240	60.88 (60.94)	4.16 (4.11)	–	–	d

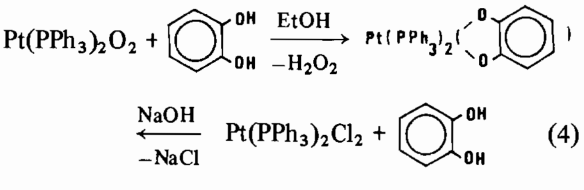
[a] Required values in parentheses. [b] Compounds (I) and (II) clathrate one mol of ethanol in the lattice, as seen by ^1H n.m.r. [c] This compound corresponds to . [d] ν_{C-O} = 1480–1270–1260. [e] λ(nm) = 378 in CHCl. [f] By rapid crystallisation from $CHCl_3$/n-hexane the complex free of solvent was obtained (found: C, 59.46; H, 4.36; N, 3.23. No signals were detected in the ^1H n.m.r. spectrum attributable to clathrated ethanol).

benzene in a nitrogen atmosphere, no reaction was observed and the platinum compound was recovered unchanged. This emphasized the role of the peroxo group in this reaction.

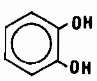
Compound (I) was shown to be diamagnetic in the solid state, monomeric in chloroform and nonelectrolyte in nitrobenzene.

Some of these derivatives chlathrate ethanol in the lattice (Table I) as seen by ^1H n.m.r. By rapid crystallisation of (I) from chloroform the corresponding solvent-free derivative was obtained.

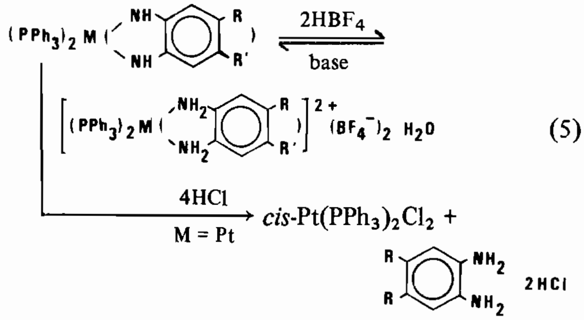
Compounds (I)–(III) show in their i.r. spectra a band at *ca.* 3400 cm^{-1} due to ν_{NH} and a band at *ca.* 1300 cm^{-1} due to ν_{C-N} (Table I), a value slightly higher than that observed in the free ligands. Even the absorptions in the visibile region were not particularly different from those observed in the free amines (Table I). A related reaction can also be conducted on  (eq. 4):



(4)

The same *ortho*-diphenol derivative (IV) was also obtained from *cis*-$Pt(PPh_3)_2Cl_2$ and  in the presence of NaOH.

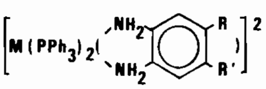
Analogous platinum derivatives have been previously obtained from $Pt(PPh_3)_3$, but by reaction with a series of substituted *ortho*-quinones [7]. Compound (I) does not react with neutral ligands such as pyridine or carbon monoxide, even in refluxing benzene or with dioxygen, while compounds (I) and (II) and the impure palladium complex can be readily protonated with an acid having an anion with poor nucleophilic character, to give the cationic complexes (V)–(VII) (Table II) (eq. 5):



(5)

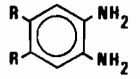
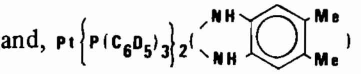
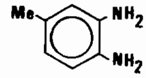
(R = R' = H; R = H, R' = Me)

This protonation reaction is reversible, and by reaction with bases the starting complexes can be readily reobtained. On the other hand, by reaction of (I) with HCl (eq. 5), *cis*-$Pt(PPh_3)_2Cl_2$ and the corresponding salt of the *ortho*-diamine were obtained. Compounds (V)–(VII) invariably contain water, as seen by elemental analyses and i.r. spectra, while ν_{NH_2} were observed at lower frequencies (Table II) with respect to ν_{NH} in the starting complexes, as is usually observed in amido and amino derivatives [5]. In these

TABLE II Analytical[a] and I r (cm^{-1}, nujol) Data for  $(BF_4^-)_2$ H_2O Complexes (M = Pd, Pt)

Compound				Colour	M p (°C)	C	H	N	Λ_M[d]	ν_{H_2O}[e]	ν_{NH_2}
	M	R	R'								
(V)	Pt	H	H	pink	>240	49 27 (49 50)	3 80 (3 92)	2 42 (2 75)	36 0	3550	3290–3190
(VI)	Pd	H	H	pink	183	54 60 (54 20)	4 33 (4 30)	3 15 (3 00)	36 4	3550	3310–3210
(VII)	Pt	H	NO_2	ochre	203	46 86 (47 30)	3 62 (3 66)	3 48 (3 94)	28 0	3520	3380–3270
(VIII)[b]	Pt	H	Me	light brown	>240	50.14 (49 70)	4 00 (4 06)	2 91 (2 70)	37 2	3550	3330–3240–3195
(IX)[c]	Pt	Me	Me	light brown	>240	51 43 (50 43)	4 06 (4 20)	2 63 (2 67)	35 0	3560	3300–3245–3190

[a] Required values in parentheses [b] τ_{Me} = 7 68 in $CDCl_3$ [c] τ_{Me} = 7 9 in CD_2Cl_2 [d] In nitrobenzene [e] Broad absorptions.

cationic complexes the band at *ca* 1300 cm^{-1} was no more observed in the i r spectrum, and it probably lies in the region where the BF_4^- absorbs This indicates that there is no carbon–nitrogen double bond character in these derivatives, as one would expect by effect of the coordination of the amine *via* the nitrogen lone pair A very peculiar fact was observed for the products obtained from the reactions of $Pt(PPh_3)_2O_2$ and  (R = H, R' = Me, R = R' = Me), which have satisfactory elemental analyses and i r spectra (see Experimental) consistent with a formulation analogous to that of compounds (I)–(III). In their ^1H n m.r spectra the methyl resonances were not detected from –6 to +25 τ in solvents such as $CDCl_3$ or CD_2Cl_2 and on changing the temperature (R = R' = Me, down to –50 °C in CD_2Cl_2) a broad peak appeared between 7 5 and 8 τ Even the homologous complex having deuterated triphenylphosphine as ligand, , did not show any signal in the ^1H n m r spectrum in CD_2Cl_2 attributable to the methyl resonances Moreover the ^{13}C n m r spectrum (R = H, R' = Me) in $CDCl_3$, showed only the peaks due to clathrated ethanol in the methyl resonances region, although the compound isolated from the still clear solution had entirely changed after one night in the n.m r tube Finally the ^1H n m r spectra of both complexes in CS_2 at room temperature showed broad and complex signals at around 8 τ On the other hand the mass spectrum (R = H, R' = Me) showed a peak due to the $Pt(PPh_3)(N_2C_7H_7)^+$ ion while compounds (VIII) and (IX), obtained from these derivatives by reaction with HBF_4 (eq 5), clearly showed in their ^1H n m r spectra the methyl resonances at *ca.* 7.8 τ in $CDCl_3$, a region where the free amines absorb Finally the reaction of the complex with R = H, R' = Me with HCl (eq 5) gave as the organic product a compound with an i r. spectrum identical to that of  2HCl , obtained from the free amine and HCl

When the same complex was left in $CDCl_3$ for one hour, it showed an i r spectrum slightly different from that of the starting material, however, even this material by reaction with HCl gave the salt of the unreacted amine Thus we cannot propose at the moment any reasonable hypothesis to explain these unusual facts

Reactions with Other Amines

The reaction of $Pt(PPh_3)_2O_2$ with amines such as $NH_2CH_2CH_2NH_2$ and p-$RC_6H_4NH_2$ (R = Me, OMe, NO_2) and with ammonia in various conditions did not give well characterizable products

The pale yellow (NH_3, $NH_2CH_2CH_2NH_2$) or red-violet (p-$RC_6H_4NH_2$) materials isolated did contain nitrogen, but they could not be purified In any case it is interesting that a reaction with ammonia took place and under smooth conditions (at room temperature in benzene or in ethanol), since the heterogenous oxidation of ammonia to produce NO_x (x = 1, 2) proceeds at T > 800 °C over Pt/Rh [18]

From the reaction conducted in benzene, one mol of $OPPh_3$ per mol of reacted complex was isolated, while the platinum containing product having PPh_3 as ligand (i r evidence) has an approximate ratio Pt P N of 1 1 1 Elemental analyses also showed the presence of oxygen in the complex

When Bu^t-NH_2 was employed in the reaction with $Pt(PPh_3)_2O_2$, an already known platinum cluster complex [9, 10] was isolated (eq 6)

$$Pt(PPh_3)_2O_2 \xrightarrow[EtOH/reflux]{Bu^t\text{-}NH_2} Pt_4(PPh_3)_5 \qquad (6)$$

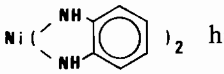
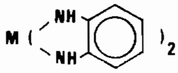
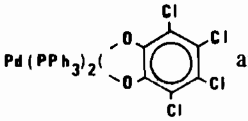
The elemental analysis does not clearly distinguish between this [9] and other alternative formulations [10], and one of us has already discussed this point [9].

In the reactions with monoamines the palladium peroxo complex generally decomposed to palladium metal, and we had no evidence for the formation of characterizable products.

Conclusions

The platinum diamido derivatives (I)–(III) can be formulated either as derivatives of the metal in the +2 oxidation state having the amide as ligand (A), or as derivatives of the zerovalent metals and of the *ortho*-benzoquinonediimine (B):

(A) (B)

Derivatives having the *ortho* [11] or *para*- [12] benzoquinonediimine as ligands are known. However the X-ray structure of  has shown only little α-diimine character [13], and polarographic measurements for  (M = Ni, Pd, Pt) are in accordance with the metals being in a +2 oxidation state [14]. Structure (A) seems the most reasonable even for compounds (I)–(III), their spectroscopic properties and chemical reactivity being in agreement with such a formulation. Polarographic measurements for compound (I) in DMF solution did not show any reduction (but also no oxidation) of the organic ligand. Furthermore, bonding parameters for  are consistent with a planar, palladium(II) hydroquinone formulation [15], and this supports an analogous structure for (IV).

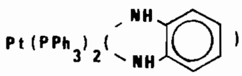
The dehydrogenation reactions of *ortho*-diamines with NiO_2 [6] or with Cu_2Cl_2 and dioxygen [16], lead to *cis, cis*-mucononitrile, probably *via* the intermediate formation of a bis-nitrene species.

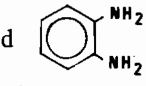
In this type of reaction, *ortho*-benzoquinonediimine is also believed to be the initial, though transient, product [14]. Under our conditions this unstable molecule is stabilized by coordination to the metal, but as the anionic amide ligand, with formation of a stable, five membered metallacycle which prevents further dehydrogenation to the bis-nitrene species.

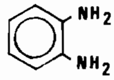
Several mechanisms can be considered for the deprotonation reaction of the *ortho*-diamines [6, 17] (eq. 3). It has been reported that the insertion reaction of organic carbonyl groups into the platinum–oxygen bond of $Pt(PPh_3)_2O_2$ requires prior coordination of the substrate to the metal [18]. Prior coordination of the amine to the metal appears to be also necessary, since the coordinatively saturated peroxo complexes $Ru(CO)_2(PPh_3)_2O_2$, $[Rh(PPh_3)_2Cl(O_2)]_2$, $IrCl(CO)(PPh_3)_2O_2$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2O_2]^+$ do not react at room temperature even with the very reactive *ortho*-diamines. The intermediate $Pt(PPh_3)_2O_2$(amine) should then collapse to the final product. However, it has been recently reported that the catalytic oxidation of PR_3 by $Pt(PR_3)_2O_2$ in protic medium proceeds *via* the displacement of species such as HO_2^- from the catalyst by a strong nucleophile like PR_3, and these species are the real oxidant of the uncomplexed PR_3 [19]. Thus only a kinetic [18] and spectroscopic [19] study could elucidate the true mechanism of the reaction of the amines reported here.

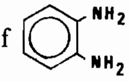
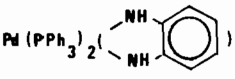
Experimental

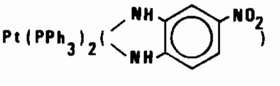
All the reactions were carried out under nitrogen at room temperature with stirring, but work-up of the reaction mixtures was carried out in air unless otherwise stated. Ethyl ether was purified from peroxides and dried over sodium; ethanol was distilled. The starting complexes were prepared as described in the literature. I.r. spectra were obtained using a Perkin–Elmer 457 instrument. ^1H n.m.r. spectra were recorded on a Varian NV-14 instrument operating at 60 MHz with Me_4Si as internal standard. Melting points were determined on a Leitz Heiztisch-mikroskop. Elemental analyses were carried out by the Analytical Laboratories of Milan University. Conductivity data were obtained with a Philips PR 9500 conductivity bridge.

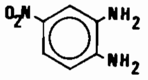
 (I)

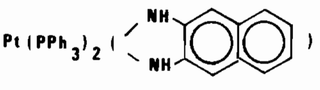
$Pt(PPh_3)_2O_2$ (0.3 g) and  (0.087 g) were mixed in ethanol (20 ml). After one hr the deep red precipitate was filtered off, washed with ethanol and ethyl ether and dried *in vacuo* (*ca.* 75% yields).

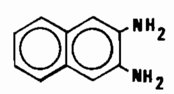
Reaction between $Pd(PPh_3)_2O_2$ and 

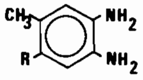
To a solution of  (0.18 g) in ethanol (10 ml) maintained at 10 °C, $Pd(PPh_3)_2O_2$ (0.5 g) was added. After one hr the green-black precipitate was filtered off under nitrogen, washed with ethanol and n-hexane degassed with nitrogen, and dried *in vacuo*. The compound was stored under nitrogen. M.p. 161 °C (found: C, 66.73; H, 4.94; N, 4.07; calcd. for  : C, 68.40; H, 4.89; N, 3.80).

 (II)

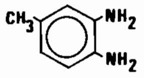
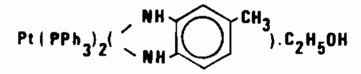
To a solution of  (0.062 g) in ethanol (13 ml), filtered under nitrogen from insoluble impurities, Pt(PPh$_3$)$_2$O$_2$ (0.15 g) was added. After one hr the violet precipitate was filtered off, washed repeatedly with ethanol and ethyl ether and dried *in vacuo*.

 (III)

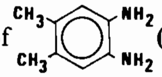
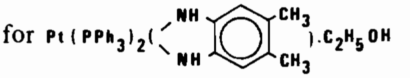
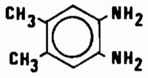
To a solution of  (0.0635 g) in ethanol (30 ml), filtered under nitrogen from insoluble impurities, Pt(PPh$_3$)$_2$O$_2$ (0.15 g) was added. After 3 hr the brick red precipitate was filtered off, washed with a little ethanol and n-hexane and dried *in vacuo*.

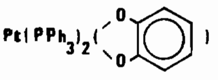
Reactions between Pt(PPh$_3$)$_2$O$_2$ and  *(R = H, CH$_3$)*

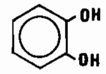
R = H

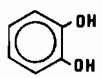
To a solution of  (0.065 g) in ethanol (15 ml), filtered under nitrogen from insoluble impurities, Pt(PPh$_3$)$_2$O$_2$ (0.2 g) was added. After 2 hr the brick red precipitate was filtered off, washed repeatedly with ethanol and dried *in vacuo*. M.p. >240 °C (found: C, 61.05; H, 4.38; N, 3.13; calcd. for  : C, 61.0; H, 4.9; N, 3.16). This compound shows ν_{NH} = 3400 cm^{-1}, ν_{C-N} = 1300 cm^{-1} and λ(nm) = 370, in CHCl$_3$.

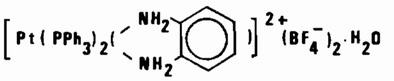
R = CH$_3$

To a solution of  (0.036 g) in ethanol (8 ml) filtered under nitrogen from insoluble impurities, Pt(PPh$_3$)$_2$O$_2$ (0.1 g) was added. After one hr the deep red precipitate was filtered off, washed repeatedly with ethanol and n-hexane and dried *in vacuo*. M.p. >240 °C (found: C, 61.07; H, 4.73; N, 3.18; calcd. for  : C, 61.4; H, 5.13; N, 3.13). This compound shows ν_{NH} = 3400 cm^{-1}, ν_{C-N} = 1300 cm^{-1} and λ(nm) = 377 in CHCl$_3$. The same procedure was used for the reaction between  and Pt{P(C$_6$D$_5$)$_3$}$_2$O$_2$.

 (IV)

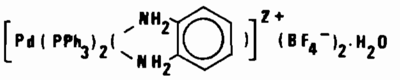
(a) To a solution of  (0.044 g) in ethanol (10 ml) Pt(PPh$_3$)$_2$O$_2$ (0.15 g) was added. After one hr the yellow product was filtered off, washed with ethanol and dried *in vacuo*.

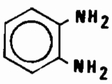
(b) To a suspension of *cis*-Pt(PPh$_3$)$_2$Cl$_2$ (0.26 g) in chloroform (20 ml), a solution of NaOH (330 mg) and  (0.073 g) in methanol (20 ml) was added. The mixture was stirred and refluxed for 30 min. The yellow precipitate was filtered off and washed with chloroform, ethanol and n-hexane. Its i.r. spectrum was identical with that of the complex prepared as described under (a).

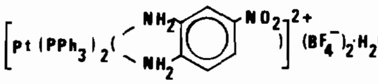
 (V)

To a suspension of (I) (0.12 g) in ethanol (5 ml), five drops of HBF$_4$ (40% solution in water) were added. The suspension immediately turned pink. After one hr the precipitate was filtered off, washed with water, ethanol, n-hexane and dried *in vacuo*.

When (V) (0.085 g) suspended in ethyl ether (10 ml) was treated with a solution of NaHCO$_3$ (0.036 g) in water (8 ml), a deep red precipitate was formed. After 3 hr it was filtered off, washed with water, then n-hexane and dried *in vacuo*. Its i.r. spectrum was identical to that of compound (I). The same reaction can also be carried out with KOH in ethanol, compound (I) being again obtained.

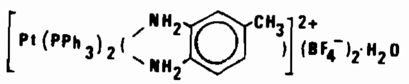
 (VI)

To a suspension of the product (0.1 g) of the reaction between Pd(PPh$_3$)$_2$O$_2$ and  in ethanol (20 ml), 20 drops of HBF$_4$ (40% sol. in water) were added. The green suspension rapidly turned pink. After one hr the precipitate was filtered off, washed with ethanol, ethyl ether, n-hexane and dried *in vacuo*. By reaction of (VI) with $NaHCO_3$ the starting material could not be reobtained.

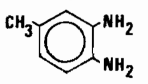


(VII)

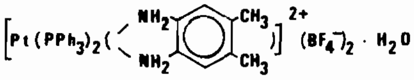
To a suspension of (II) (0.069 g) in ethanol (7 ml), 20 drops of HBF_4 (40% solution in water) were added. After 15 hr the ochre precipitate was filtered off, washed with water, ethanol, n-hexane and dried *in vacuo*. By reaction of (VII) in ethanol with a solution of $NaHCO_3$ in water for one hr, compound (II) was readily reobtained.



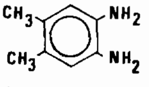
(VIII)

To a suspension of the product (0.17 g) of the reaction between $Pt(PPh_3)_2O_2$ and , in ethanol (10 ml) 4 drops of HBF_4 (40% solution in water) were added. The suspension turned immediately brown. After one hr the solution was evaporated to a small volume and on addition of ethyl ether a light brown precipitate was obtained. It was filtered off, washed with ethyl ether and dried *in vacuo*.

By reaction of (VIII) (0.18 g) in ethanol (10 ml) with a solution of $NaHCO_3$ (0.06 g) in water (10 ml), a deep red precipitate was obtained. After 3 hr it was filtered off, washed with ethanol, water, ethyl ether, n-hexane, and dried *in vacuo*. Its i.r. spectrum was identical to that of the starting material of the protonation reaction described above.



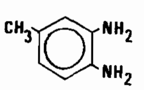
(IX)

To a suspension of the product (0.15 g) of the reaction between $Pt(PPh_3)_2O_2$ and , in ethanol (7 ml), 8 drops of HBF_4 (40% solution in water) were added. After one hr the light brown precipitate was filtered off, washed with ethyl ether, n-hexane and dried *in vacuo*.

Reaction between (I) and HCl

Dry HCl was bubbled in ethanol (15 ml) for 5 min. Solid (I) (0.08 g) was added. After one hr the white-pink precipitate was filtered off and washed with ethanol, n-hexane and dried *in vacuo*. It was shown to be *cis*-$Pt(PPh_3)_2Cl_2$ by its i.r. spectrum.

On evaporation to dryness of the mother liquor of the reaction, a product with an i.r. spectrum identical to that of *o*-$(NH_2)_2C_6H_4 \cdot 2HCl$ was obtained.

The same procedure was used for the reaction of HCl with the product of the reaction between $Pt(PPh_3)_2O_2$ and , *cis*-$Pt(PPh_3)_2Cl_2$ and the salt of the *ortho*-diamine being isolated.

Reaction between $Pt(PPh_3)_2O_2$ and Bu^t-NH_2

To $Pt(PPh_3)_2O_2$ (0.25 g) in ethanol (10 ml), Bu^t-NH_2 (5 ml) was added. The mixture was refluxed for 1.5 hr. After cooling the brown-red precipitate was filtered off and dried *in vacuo*. Found: C, 51.08; H, 3.35; N, nil. For the formulation of this product see text.

Reaction between $Pt(PPh_3)_2O_2$ and NH_3

To wet benzene (35 ml) saturated with ammonia, $Pt(PPh_3)_2O_2$ (0.3 g) was added. The solution was left in a nitrogen atmosphere for 5 hr under stirring. A small amount of undissolved material was filtered off under nitrogen and the solution was evaporated to a small volume. By addition of ethyl ether a pale brown precipitate was obtained. It was filtered off under nitrogen and washed repeatedly with ethyl ether. In the mother liquor of the reaction the presence of triphenylphosphine oxide was detected.

References

1 J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).
2 S. Cenini and G. La Monica, *Inorg. Chim. Acta, 18,* 279 (1976) and references therein.
3 G. La Monica and S. Cenini, *Inorg. Chim. Acta, 29,* 183 (1978).
4 G. La Monica, S. Cenini, F. Porta and M. Pizzotti, *J. Chem. Soc. Dalton,* 1777 (1976).
5 S. Cenini, M. Pizzotti, F. Porta and G. La Monica, *J. Organometal. Chem., 125,* 95 (1977).
6 M. V. George and K. S. Balachandran, *Chem. Rev., 75,* 491 (1975).
7 S. Cenini, R. Ugo and G. La Monica, *J. Chem. Soc. A,* 416 (1971).
8 K. Joekers, *Nitrogen,* N 50, 27 (1967).
9 R. Ugo, S. Cenini, M. F. Pilbrow, B. Deibl and G. Schneider, *Inorg. Chim. Acta, 18,* 113 (1976).
10 N. J. Taylor, P. C. Chieh and A. J. Carty, *Chem. Comm.,* 448 (1975).
11 G. Christoph and V. L. Goedken, *J. Am. Chem. Soc., 95,* 3869 (1973).
12 K. Rieder, U. Hauser, H. Siegenthaler, E. Schmidt and A. Ludi, *Inorg. Chem., 14,* 1902 (1975).
13 G. Swartz Hall and R. H. Soderberg, *Inorg. Chem., 7,* 2300 (1968).
14 A. L. Balch and R. H. Holm, *J. Am. Chem. Soc., 88,* 5201 (1966) and references therein.
15 C. G. Pierpont and H. H. Downs, *Inorg. Chem., 14,* 343 (1975).
16 J. Tsuji, H. Takayanagi and Y. Toshida, *Chem. Letters,* 147 (1976).
17 M. Hedayatullah, *Bull. Chem. Soc. France,* 2957 (1972).
18 G. M. Zanderighi, R. Ugo, A. Fusi and Y. Ben Taarit, *Inorg. Nucl. Chem. Letters, 12,* 729 (1976).
19 A. Sen and J. Halpern, *J. Am. Chem. Soc., 99,* 8337 (1977).