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REACTIVITY OF OLEFIN AND ACETYLENE COMPLEXES OF PLATINUM(0) TOWARDS TETRACHLORO-*o*-BENZOQUINONE

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SUMMARY

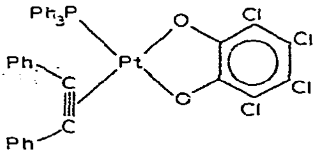
Tetrachloro-*o*-benzoquinone reacts with (diphenylacetylene)bis(triphenylphosphine)platinum(0) to give the novel platinum(II) diphenylacetylene complex, $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)(PPh_3)$, (I), which reacts with hydrogen halides to give the complexes *cis*-$PtX_2(PhC{\equiv}CPh)(PPh_3)$, ($X=Cl$ or Br). Hydrogen chloride also readily removes the tetrachloro-*o*-benzoquinone ligand from the adducts $Ni(C_6Cl_4O_2)(Ph_2PCH_2CH_2PPh_2)$ and $M(C_6Cl_4O_2)(PPh_3)_2$, ($M=Pd$ or Pt) but it has no action upon $Ir(Cl)(C_6Cl_4O_2)(CO)(PPh_3)_2$ at room temperature. The acetylene in (I) is susceptible to nucleophilic attack and reaction with diethylamine gives the vinyl adduct $Pt(C_6Cl_4O_2)(CPh{=}CPhNHEt_2)(PPh_3)$. Other reactions of (I) have also been studied. Attempts to prepare other olefin or acetylene complexes of platinum(II) by the action of tetrachloro-*o*-benzoquinone on the complexes $Pt(L)(PPh_3)_2$, ($L=PhC{\equiv}CH$, $(Et)(Me)(HO)CC{\equiv}CC(OH)(Me)(Et)$, $HOCH_2C{\equiv}CCH_2OH$, $CF_3C{\equiv}CCF_3$, $CF_2{=}CF_2$, $CF_2{=}CH_2$ or *trans*-$PhCH{=}CHPh$) are also described.

INTRODUCTION

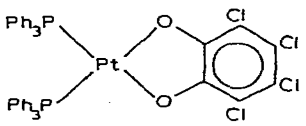
Recently Group VIII metal complexes of d^{10}, d^8 and d^6 electronic configuration *e.g.*, $Ni(CO)_4$[1,2], $Pt(PPh_3)_4$[3-5], $Pd(PPh_3)_4$[5], $M(NO)(PPh_3)_3$[6], ($M=Co$, Rh and Ir), $RhCl(PPh_3)_3$[5], *trans*-$MCl(CO)(PPh_3)_2$[5], ($M=Rh$ and Ir), $Ru(CO)_3(PPh_3)_2$[7] and $RuCl_2(PPh_3)_3$[7] have been shown to undergo both thermal and photo-induced oxidative-addition or elimination reactions with certain *o*-quinones. We have been interested[8] in the action of *o*-quinones on olefin and acetylene complexes of zerovalent platinum and other d^{10} systems and we now describe our initial studies.

RESULTS AND DISCUSSION

Tetrachloro-*o*-benzoquinone readily undergoes a novel reaction with a benzene solution of (diphenylacetylene)bis(triphenylphosphine)platinum(0) at room temperature to form a pale yellow precipitate of the complex (I). The presence of a weak, broad C≡C stretching vibration at 1961 cm^{-1} in (I) suggests the presence of an acetylene coordinated to platinum(II)[9] and this together with the formation of a quantitative yield of (II) from the reaction of (I) with triphenylphosphine provides



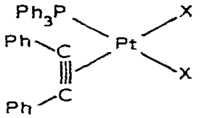
(I)



(II)

good evidence for the structure of the complex (I) in which the acetylenic bond is probably virtually perpendicular to the coordination plane as is observed in *trans*-PtCl$_2$(*p*-toluidine)(t-Bu–C≡C–t-Bu)[10]. Although the mechanism of formation of (I) is not known at present, it would appear that the *o*-quinone not only oxidatively adds to the platinum but also plays a part in the removal of one triphenylphosphine ligand, presumably as the phosphine–quinone adduct. Some evidence for this scheme is provided by the observation that equimolar quantities of the reactants give only about a 40% yield of (I) but if the ratio of quinone to platinum complex is increased to 2/1 then the yield of (I) increases to around 90%. However, attempts to displace triphenylphosphine from Pt(C$_6$Cl$_4$O$_2$)(PPh$_3$)$_2$ by treating the complex with diphenylacetylene and tetrachloro-*o*-benzoquinone in benzene at room temperature gives only unreacted Pt(C$_6$Cl$_4$O$_2$)(PPh$_3$)$_2$. When the reaction mixture is heated only *cis*-PtCl$_2$(PPh$_3$)$_2$ can be isolated.

Diphenylacetylene is not displaced from (I) by carbon monoxide at room temperature and at atmospheric pressure. The complex (I) can also be recovered unchanged when it is treated with hexafluorobut-2-yne at 65°. However, treatment of (I) with either hydrogen chloride or hydrogen bromide provides a convenient preparation of the halides (IIIa) and (IIIb). The presence of two Pt–Cl stretching vibrations at 332 and 298 cm^{-1} in the IR spectrum of (IIIa) is consistent with a *cis* arrangement of ligands about the platinum and (IIIb) probably has a similar configuration. In refluxing toluene the complex easily loses diphenylacetylene and this decomposition provides a convenient preparation of the dimer, [PtCl$_2$(PPh$_3$)]$_2$[11,12].

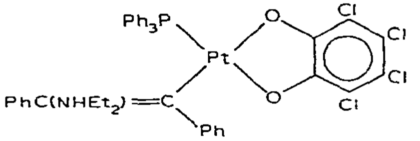


(IIIa), X=Cl;
(IIIb), X=Br

When trifluoroacetic acid is added to a solution of (I) in methylene chloride the orange solution slowly becomes pale yellow but only (I) can be isolated from the solution.

Treatment of the complex (II) with hydrogen chloride also results in displacement of the *o*-quinone which can be recovered quantitatively as tetrachlorocatechol together with *cis*-PtCl$_2$(PPh$_3$)$_2$. We also find that similar reactions take place when the square planar complexes Pd(C$_6$Cl$_4$O$_2$)(PPh$_3$)$_2$ and Ni(C$_6$Cl$_4$O$_2$)(Ph$_2$PCH$_2$-CH$_2$PPh$_2$) are treated with hydrogen chloride. However, it is interesting to note that the coordinatively saturated adduct, IrCl(C$_6$Cl$_4$O$_2$)(CO)(PPh$_3$)$_2$, does not react with hydrogen chloride at room temperature.

The reactions of (I) with protonic acids clearly illustrate how the reactivity of coordinated diphenylacetylene is affected by the oxidation state of the platinum since $Pt(PhC{\equiv}CPh)(PPh_3)_2$ readily reacts with acids to give vinyl complexes[13-15]. However, just as olefin complexes of platinum(II) *e.g.* $PtCl_2(olefin)(PR_3)$ add amines to give σ-bonded platinum–carbon derivatives, such as $PtCl_2(CH_2CH_2NHEt_2)(PPh_3)$[16], we similarly find that the acetylene in (I) is susceptible to nucleophilic attack. Thus diethylamine reacts with (I) in methylene chloride at 0° to give a white insoluble crystalline product which on the basis of elemental analysis and absence of



(IV)

a $C{\equiv}C$ stretching vibration is formulated as a 1/1 adduct, (IV). The geometry about the double bond is not known but the reaction may involve a *trans*-addition as has been observed in similar reactions of olefin platinum(II) complexes[17]. The complexes (IIIa) and (IIIb), however, do not add diethylamine under similar conditions.

Treatment of the complexes $Pt(PhC{\equiv}CH)(PPh_3)_2$, $Pt[(Et)(Me)(HO)CC{\equiv}CC(OH)(Me)(Et)](PPh_3)_2$, $Pt[HOCH_2C{\equiv}CCH_2OH](PPh_3)_2$, Pt(*trans*-$PhCH{=}CHPh)(PPh_3)_2$ and $Pt(CF_2{=}CH_2)(PPh_3)_2$ with tetrachloro-*o*-benzoquinone leads to displacement of the acetylene or olefin to give (II) and no complexes analogous to (I) can be isolated. In the reaction with $Pt(PhC{\equiv}CH)(PPh_3)_2$ a small amount of the acetylide complex, *trans*-$Pt(C{\equiv}CPh)_2(PPh_3)_2$, is formed in addition to (II). However, tetrachloro-*o*-benzoquinone has no action upon $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ and $Pt(CF_2{=}CF_2)(PPh_3)_2$ in refluxing benzene over periods of 12–16 h. Clearly the factors which control the formation of (I) must be extremely delicate. Presumably the acetylene must be able to coordinate reasonably well to platinum(II) but not too strongly or weakly to platinum(0). These factors are probably optimised with diphenylacetylene which is known to coordinate to both platinum(0) in the complex $Pt(PhC{\equiv}CPh)(PPh_3)_2$[18] and platinum(II) in the complexes $[Et_3NH][PtCl_3(PhC{\equiv}CPh)]$[19], $Pt(Acac)(Cl)(PhC{\equiv}CPh)$[20] and $[PtMe(PhC{\equiv}CPh)(AsMe_3)_2][PF_6]$[21].

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer model 225 spectrophotometer. The complexes $Pt(PhC{\equiv}CPh)(PPh_3)_2$[22], $Pt(PhC{\equiv}CH)(PPh_3)_2$[22], $Pt(HOCH_2C{\equiv}CCH_2OH)(PPh_3)_2$[23], Pt(*trans*-$PhCH{=}CHPh)(PPh_3)_2$[24], $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$[25,26], $Pt(CF_2{=}CF_2)(PPh_3)_2$[26,27], $Pt(CF_2{=}CH_2)(PPh_3)_2$[28], $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)$[29], $Pt(C_6Cl_4O_2)(PPh_3)_2$[4,5], $Pd(C_6Cl_4O_2)(PPh_3)_2$[5] and $IrCl(C_6Cl_4O_2)(CO)(PPh_3)_2$[5] were prepared as described in the literature. Analytical data, yields and melting points for all new complexes are given in Table 1.

Preparation of $Pt[(Et)(Me)(HO)CC{\equiv}CC(OH)(Me)(Et)](PPh_3)_2$

A mixture of Pt(*trans*-stilbene)$(PPh_3)_2$ (0.5 g) and 3,6-dimethyloct-4-yne-3,6-

TABLE 1

ANALYTICAL DATA FOR NEW COMPLEXES[a]

Compound	*Colour*	*Yield* (%)	*M.p.* (°C)	*Analysis found* (*calcd.*) (%)		
				C	*H*	*Cl*
$Pt[(Et)(Me)(HO)CC{\equiv}CC(OH)(Me)(Et)](PPh_3)_2$	White	60	136–138° (dec.)	61.8 (62.2)	5.23 (5.44)	
$Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)(PPh_3)$[b]	Pale yellow	90	232–234° (dec.)	51.6 (51.1)	2.78 (2.84)	16.1 (16.1)
cis-$PtCl_2(PhC{\equiv}CPh)(PPh_3)$[c]	Pale yellow	80	183–186° (dec.)	54.6 (54.4)	3.6 (3.6)	9.9 (10.0)
cis-$PtBr_2(PhC{\equiv}CPh)(PPh_3)$[d]	Yellow	87	285–287° (dec.)	48.1 (48.3)	3.2 (3.2)	[e]
$Pt(C_6Cl_4O_2)[CPh{=}C(NHEt_2)Ph](PPh_3)$	White	93	154–156° (dec.)	51.9 (52.8)	3.7 (3.7)	[f]
$Ni(C_6Cl_4O_2)(Ph_2PCH_2CH_2PPh_2)$	Dark brown	91	247–249° (dec.)	54.0 (54.7)	2.95 (2.71)	19.9 (20.2)

[a] Molecular weights were determined osmometrically in chloroform. [b] Mol. wt. 925 (calcd. 881). [c] Mol. wt 698 (calcd. 706). [d] Mol. wt. 780 (calcd. 795). [e] Br, 20.4 (calcd. 20.1). [f] N, 1.44 (calcd. 1.47).

diol (0.2 g) in diethylether (20 ml) was shaken for 2 h. The white cubic crystals of the product which formed were collected and dried *in vacuo*. ν(OH), 3200 cm^{-1}; ν(C≡C), 1745 cm^{-1}.

Reactions of tetrachloro-o-benzoquinone

(*a*) *With* $Pt(PhC{\equiv}CPh)(PPh_3)_2$. Tetrachloro-*o*-benzoquinone (1.6 g) in benzene (5 ml) was shaken with $Pt(PhC{\equiv}CPh)(PPh_3)_2$ (2.8 g) in benzene (40 ml). The resulting pale yellow precipitate of $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)$ (PPh_3) was collected and dried *in vacuo*. ν(C≡C) 1961 cm^{-1}.

(*b*) *With* $Pt(PhC{\equiv}CH)(PPh_3)_2$. A mixture of tetrachloro-*o*-benzoquinone (0.18 g) in benzene (5 ml) and $Pt(PhC{\equiv}CH)(PPh_3)_2$ (0.5 g) in benzene (30 ml) was allowed to stand at room temperature for 15 h. The resulting yellow precipitate was filtered off, washed with benzene, recrystallised from methylene chloride/petroleum spirit (b.p. 40–60°), and dried *in vacuo*. The product was identified as $Pt(C_6Cl_4O_2)(PPh_3)_2$ (II) by its m.p. and IR spectrum. Yield 0.3 g (25%). The filtrate was evaporated to dryness under reduced pressure to give a dark brown oil. The oil was dissolved in methylene chloride and chromatographed on Florosil to give *trans*-$Pt(C{\equiv}CPh)_2(PPh_3)_2$ (0.025 g, 3%) identified by its m.p. and IR spectrum[30].

(*c*) *With* $Pt[(Et)(Me)(HO)CC{\equiv}CC(OH)(Me)(Et)](PPh_3)_2$. Tetrachloro-*o*-benzoquinone (0.4 g) in benzene (5 ml) was shaken for 2 h with the platinum complex (0.5 g) in benzene (20 ml) to afford yellow crystals of $Pt(C_6Cl_4O_2)(PPh_3)_2$ (II), (0.48 g, 89%) which was identified by its m.p. and IR spectrum[5].

(*d*) *With* $Pt(HOCH_2C{\equiv}CCH_2OH)(PPh_3)_2$. As above to give $Pt(C_6Cl_4O_2)(PPh_3)_2$ (II), (90%).

(*e*) *With* $Pt(trans\text{-}stilbene)(PPh_3)_2$. As above to give $Pt(C_6Cl_4O_2)(PPh_3)_2$ (II), (90%).

(*f*) *With* $Pt(CF_2{=}CH_2)(PPh_3)_2$. As above to give $Pt(C_6Cl_4O_2)(PPh_3)_2$ (II), (91%).

Similar reactions with $Pt(CF_2{=}CF_2)(PPh_3)_2$ and $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ gave the unchanged starting complexes even when the benzene solutions were refluxed for 12 h.

Reactions of $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)(PPh_3)$

(*a*) *With triphenylphosphine.* $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)(PPh_3)$ (0.1 g) in chloroform (20 ml) was heated for 12 h with triphenylphosphine (0.2 g). Petroleum spirit (b.p. 100–120°) was added to the cooled solution and the solvent was removed under reduced pressure. The residue was crystallised from methylene chloride/ethanol to give $Pt(C_6Cl_4O_2)(PPh_3)_2$ (II) (0.13 g, 99%) which was identified by its m.p. and IR spectrum[5].

(*b*) *With carbon monoxide.* Carbon monoxide was bubbled through a solution of the platinum complex (0.15 g) in methylene chloride for 15 min. Hexane was added to the solution and the solvent was slowly removed under reduced pressure to give unreacted $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)$ (PPh_3) (0.14 g, 93%).

(*c*) *With hexafluorobut-2-yne.* Excess hexafluorobut-2-yne was condensed onto a solution of the platinum complex (0.15 g) in benzene (20 ml) contained in a thick-walled glass tube cooled in liquid nitrogen. The tube was sealed, allowed to warm to room temperature, and then heated to 65° for 12 h. The tube was cooled, opened and the solution was evaporated to dryness. Recrystallisation of the orange residue afforded yellow crystals of unreacted $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)(PPh_3)$ (0.12 g, 80%).

(*d*) *With phenylacetylene.* Phenylacetylene (0.1 g) and the complex (0.2 g) in benzene (20 ml) were heated under reflux for 16 h. Removal of the benzene under reduced pressure and recrystallisation of the residue from methylene chloride/ethanol gave unreacted $Pt(C_6Cl_4O_2)(PhC{\equiv}CPh)$ (PPh_3) (0.19 g, 95%).

(*e*) *With hydrogen chloride.* Hydrogen chloride was bubbled through a solution of the complex (0.2 g) in methylene chloride (20 ml) for 10 min. During this time the deep yellow solution turned pale yellow. Addition of ethanol (10 ml) followed by slow removal of the solvent afforded pale yellow crystals of $PtCl_2(PhC{\equiv}CPh)(PPh_3)$. $\nu(C{\equiv}C)$, 1980, 1960 cm^{-1}; $\nu(PtCl)$, 332, 298 cm^{-1}.

(*f*) *With hydrogen bromide.* As above but using hydrogen bromide afforded yellow crystals of $PtBr_2(PhC{\equiv}CPh)(PPh_3)$. $\nu(C{\equiv}C)$, 1981 cm^{-1}, $\nu(PtBr)$, 228 cm^{-1}.

(*g*) *With trifluoroacetic acid.* Trifluoroacetic acid (1 ml) and the complex (0.2 g) in methylene chloride (20 ml) were stirred together at room temperature. The orange solution slowly became pale yellow but addition of petroleum spirit (b.p. 100–120°) followed by partial removal of the solvent under reduced pressure afforded yellow crystals of the unchanged platinum complex (0.18 g, 90%).

(*h*) *With diethylamine.* A solution of the complex (0.26 g) in dry methylene chloride (7 ml) at 0° was stirred under an atmosphere of nitrogen. Diethylamine (0.02 g) in dry methylene chloride (5 ml) was added dropwise to the solution over a period of 10 min and the mixture was stirred for a further 30 min. The white precipitate was filtered and collected under nitrogen and dried *in vacuo* to give white needle-shaped crystals of $Pt(C_6Cl_4O_2)[CPh{=}C(NHEt_2)Ph](PPh_3)$.

Reactions of $PtCl_2(PhC{\equiv}CPh)(PPh_3)$

(*a*) *With triphenylphosphine.* Triphenylphosphine (0.05 g) and the complex

(0.1 g) in benzene (10 ml) were heated together under reflux for 1 h. Hexane was added to the cooled solution. White crystals of *cis*-$PtCl_2(PPh_3)_2$ (0.1 g, 87%) slowly formed. This was identified by its m.p. and IR spectrum[5].

(*b*) *With diethylamine.* As in (*h*), previously, the complex (0.25 g) in dry methylene chloride (5 ml) was treated with diethylamine (0.025 g) in dry methylene chloride (5 ml). No precipitate was formed. Acetone was added and the solution was cooled to −30° for 24 h. No product separated and addition of ethanol gave unreacted starting complex.

Similarly no new product could be obtained using $PtBr_2(PhC{\equiv}CPh)(PPh_3)$.

(*c*) *In refluxing toluene.* (With Miss G. M. Richmond). The complex (0.05 g) was refluxed in toluene (30 ml) for 30 min. Orange crystals of $[PtCl_2(PPh_3)]_2$ (0.04 g, 80%) separated. This was identified by its m.p. and IR spectrum[11,12].

Preparation of $Ni(C_6Cl_4O_2)(Ph_2PCH_2CH_2PPh_2)$

Tetrachloro-*o*-benzoquinone (0.2 g) was added to a solution of $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)$ (0.4 g) in benzene (40 ml). An effervescence occurred and a dark coloured solution was formed. On standing for 15 h dark-brown needle-shaped crystals of $Ni(C_6Cl_4O_2)(Ph_2PCH_2CH_2PPh_2)$ were deposited. ν_{max} 1525 w, 1437 s, 1259 s, 1224 s(sh), 977 s, 808 s, 796 s, 590 s, 583 m. The complex is diamagnetic in the solid and is therefore probably square-planar.

Reactions of hydrogen chloride

(*a*) *With* $Ni(C_6Cl_4O_2)(Ph_2PCH_2CH_2PPh_2)$. Dry hydrogen chloride gas was bubbled through a solution of the nickel complex (0.2 g) in methylene chloride (10 ml). The dark solution instantly became orange. Ethanol (20 ml) was added and the mixture was evaporated to half volume under reduced pressure. On cooling to 0° orange crystals of $NiCl_2(Ph_2PCH_2CH_2PPh_2)$ separated (0.14 g, 93%). This was identified by its m.p. and IR spectrum[31]. The colourless filtrate was evaporated to half its volume, ethanol (5 ml) was added and on slow addition of water (5 ml) white needle-shaped crystals of tetrachlorocatechol separated (0.05 g, 71%) identified by its m.p. and IR spectrum.

(*b*) *With* $Pt(C_6Cl_4O_2)(PPh_3)_2$. As above, $Pt(C_6Cl_4O_2)(PPh_3)_2$ (0.19 g) and hydrogen chloride gas gave *cis*-$PtCl_2(PPh_3)_2$ (0.15 g, 96%) and tetrachlorocatechol (0.05 g, 99%).

(*c*) *With* $Pd(C_6Cl_4O_2)(PPh_3)_2$. As above, $Pd(C_6Cl_4O_2)(PPh_3)_2$ (0.2 g) and hydrogen chloride gas gave *trans*-$PdCl_2(PPh_3)_2$ (0.15 g, 94%) and tetrachlorocatechol (0.05 g, 88%).

(*d*) *With* $Ir(Cl)(C_6Cl_4O_2)(CO)(PPh_3)_2$. Hydrogen chloride gas was bubbled through a solution of $Ir(Cl)(C_6Cl_4O_2)(CO)(PPh_3)_2$ (0.2 g) in methylene chloride (15 ml) for 10 min. No colour change was observed. The orange solution was evaporated to half its volume under reduced pressure and on addition of petroleum spirit (b.p. 60–80°) the unchanged complex (0.2 g, 100%) was recovered.

Attempted reaction of $Pt(C_6Cl_4O_2)(PPh_3)_2$ *with diphenylacetylene in the presence of tetrachloro-o-benzoquinone*

$Pt(C_6Cl_4O_2)(PPh_3)_2$ (0.2 g), diphenylacetylene (0.1 g) and tetrachloro-*o*-benzoquinone (0.1 g) in benzene (20 ml) were heated under reflux for 6 h. The solution was cooled, petroleum spirit (b.p. 100–120°) was added and the solution was slowly evaporated until a pale yellow solid formed. The solid was recrystallised from methylene chloride/ethanol to give *cis*-$PtCl_2(PPh_3)_2$ (0.15 g, 84%) which was identified by its m.p. and IR spectrum[26].

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