

THE OXIDATIVE ADDITION REACTION OF SOME PLATINUM ACETYLENE COMPLEXES

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SUMMARY

Complexes of the type $(PPh_3)_2Pt(\text{acetylene})$ have been prepared using a variety of mono- and disubstituted acetylenes. Values for the lowering of the IR stretching frequency of the triple bond on coordination have been obtained, and the variation compared down the series of acetylenes. The oxidative addition of strong protonic acids (HX) to these complexes has also been studied, the product being $(PPh_3)_2PtX_2$ rather than $(PPh_3)_2Pt(H)X$, which is one found with $(PPh_3)_4Pt$ and $(PPh_3)_2Pt$ (ethylene) with HX. A possible explanation for this change in the course of the reaction is given.

Acetylene complexes of bis(triphenylphosphine)platinum were first reported by Chatt¹ and subsequently by other workers²⁻⁴. Recently much interest has been shown in developing models to describe the bonding in these and other transition metal acetylene complexes⁵⁻⁷. In the course of our work we have prepared several new acetylene complexes of this species, which when considered with the previously known complexes form a series of complexes for both monosubstituted acetylenes and the corresponding disubstituted acetylene (Table 1). The strength of bonding

TABLE 1

INFRARED DATA FOR $(PPh_3)_2Pt(\text{ACETYLENE})$ COMPLEXES

Complex	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})	$\Delta\nu(\text{C}\equiv\text{C})$ (cm^{-1})	Complex	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})
$(PPh_3)_2Pt(\text{HC}\equiv\text{C}-\text{CH}_2\text{OH})(\text{I})$	1705	425	$(PPh_3)_2Pt(\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})(\text{VI})^a$	1780
$(PPh_3)_2Pt(\text{HC}\equiv\text{C}-\text{CH}_2\text{OMe})(\text{II})^a$	1708	422	$(PPh_3)_2Pt(\text{MeOCH}_2\text{C}\equiv\text{CCH}_2\text{OMe})(\text{VII})^a$	1808
$(PPh_3)_2Pt(\text{HC}\equiv\text{C}-\text{CMe}_2(\text{OH}))(\text{III})^4$	1684	430	$(PPh_3)_2Pt((\text{HO})\text{Me}_2\text{CC}=\text{CCMe}_2(\text{OH}))(\text{VIII})^a$	1745
$(PPh_3)_2Pt(\text{HC}\equiv\text{CC}_6\text{H}_5)(\text{IV})^1$	1684	436	$(PPh_3)_2Pt(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)(\text{IX})^1$	1740
$(PPh_3)_2Pt(\text{HC}\equiv\text{C}-\text{CF}_3)(\text{V})^3$	1705	446	$(PPh_3)_2Pt(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{X})^2$	1775
$(PPh_3)_2Pt(\text{HC}\equiv\text{C}-\text{CO}_2\text{H})(\text{XI})^a$	1710	412		

^a This work.

has been inferred from the magnitude of the lowering of the triple bond stretch [$\Delta\nu(\text{C}\equiv\text{C})$] on coordination^{5,6}, and from evidence of displacement reactions this strength has been found to qualitatively decrease in the order $\text{C}_2(\text{C}_6\text{H}_5)_2 > \text{C}_2(\text{H})\text{-C}_6\text{H}_5 > \text{C}_2(\text{Alkyl})_2 > \text{C}(\text{H})\text{Alkyl}$ ¹. The situation is reversed however when one considers kinetics of the reaction of $(\text{PPh}_3)_2\text{Pt}$ with acetylenes where the relative rates follow the opposite order of reactivity for substituted acetylenes⁸. Comparison of the values of $\Delta\nu(\text{C}\equiv\text{C})$ in Table 1 for the series of monosubstituted acetylenes shows that the stability of the complexes follows the order $\text{CF}_3 > \text{Ph} > \text{Alkyl}$, but that the difference in the values of $\Delta\nu(\text{C}\equiv\text{C})$ over the whole series is extremely small and the variation in the bond strength is probably insignificant.

The corresponding complexes with the disubstituted acetylenes show a value of $\nu(\text{C}\equiv\text{C})$ about 70 cm^{-1} higher than the monosubstituted acetylene complexes. The value of $\nu(\text{C}\equiv\text{C})$ for an uncoordinated disubstituted acetylene however is about 100 cm^{-1} higher than a monosubstituted acetylene and so the value of $\Delta\nu(\text{C}\equiv\text{C})$ for the disubstituted acetylene complexes will be somewhat higher than is found for the monosubstituted acetylene ones, although once more the difference in the relative stabilities is only small.

We have found that these acetylenes are readily displaced by strong protonic acids at room temperature giving olefins. These acids will react with tetrakis(triphenylphosphine)platinum⁹ or bis(triphenylphosphine)ethyleneplatinum¹⁰ to give the platinum hydride. With these acetylene complexes however the product of the reaction of an acid HX is not the hydride $(\text{PPh}_3)_2\text{Pt}(\text{H})\text{X}$ but complexes of stoichiometry $(\text{PPh}_3)_2\text{PtX}_2$. This has been observed when $\text{X}=\text{Cl}$, giving *cis* $(\text{PPh}_3)_2\text{PtCl}_2$ [m.p. 310° , $\nu(\text{Pt}-\text{Cl})$ 315, 294 cm^{-1}] in 70% yield, and has been confirmed with complexes (II), (IV), (VI) and (VII)*. A similar reaction occurs by reacting HBr and CF_3COOH with $(\text{PPh}_3)_2\text{Pt}(2\text{-butyne})$ giving *cis* $(\text{PPh}_3)_2\text{PtBr}_2$ [m.p. $>300^\circ$, $\nu(\text{Pt}-\text{Br})$ 204 cm^{-1}] and $(\text{PPh}_3)_2\text{Pt}(\text{COOCF}_3)_2$ ¹¹ [confirmed by analysis, $\nu(\text{C}=\text{O})$ 1710 cm^{-1} , $\nu(\text{C}-\text{F})$ 1142, 1170, 1200 cm^{-1}] respectively. In each of these cases also, $(\text{PPh}_3)_4\text{Pt}$ gives the hydride¹⁰. Picric acid also reacts with both $(\text{PPh}_3)_4\text{Pt}$ and complex (VI), giving a hydride in the first case, and the dipicrate in the second.

This product variation with the nature of the platinum complex could be due to the different nature of the reactive species. These acetylene complexes are quite stable in organic solvents and although the replacement of one acetylene by another occurs by initial displacement¹² this change in reactivity with acids probably occurs because the acetylene remains coordinated when the acid oxidatively adds. This would allow hydrogen transfer to the acetylene to finally yield the olefin¹³. With $(\text{PPh}_3)_4\text{Pt}$ and $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ dissociation is extensive and the reactive species is $(\text{PPh}_3)_2\text{Pt}$ ^{8,14}.

This product change in the oxidative addition only occurs however with strong acids; HCN will oxidatively add to $(\text{PPh}_3)_4\text{Pt}$ ⁹ to give the hydride and we have found that the product of the reaction of HCN with both complexes (IV) and (VI) is also the hydride, and not the dicyano complex which would be expected by analogy with the reaction of strong protonic acids.

* The reaction has been carried out in both benzene and acetone. The product in acetone always contains solvent of crystallization which cannot be removed *in vacuo* at 56° .

EXPERIMENTAL

All reactions were carried out in the absence of oxygen.

Complexes (II), (VI), (VII) and (VIII)

These were obtained by reducing *cis*-(PPh₃)₂PtCl₂ with hydrazine in the presence of the acetylene⁴.

Bis(triphenylphosphine)(3-methoxy-1-propyne)platinum (II). (Found: C, 60.4; H, 4.57. C₄₀H₃₆OP₂Pt calcd.: C, 60.8; H, 4.59 %.)

Bis(triphenylphosphine)(2-butyne-1,4-diol)platinum (VI). (Found: C, 60.1; H, 4.28. C₄₀H₃₆O₂P₂Pt calcd.: C, 59.6; H, 4.50 %.)

Bis(triphenylphosphine)(1,4-dimethoxy-2-butyne)platinum (VII). (Found: C, 60.5; H, 4.81. C₄₂H₄₀O₂P₂Pt calcd.: C, 60.5; H, 4.88 %.)

Bis(triphenylphosphine)(2,5-dimethyl-3-hexyne-2,5-diol)platinum (VIII). (Found: C, 60.8; H, 5.22. C₄₄H₄₄O₂P₂Pt calcd.: C, 61.3; H, 5.15 %.)

Bis(triphenylphosphine)(propionic acid)platinum (XI)

To a solution of tetrakis(triphenylphosphine)platinum in benzene was added an excess of propionic acid and the solution stirred under nitrogen for 2 h. The solvent was removed under reduced pressure and ether added to precipitate the complex. The complex was recrystallized from benzene and ether, washed well with ether, and dried *in vacuo*. $\nu(\text{C}\equiv\text{C})$ 1710 cm⁻¹, $\nu(\text{CO}_2\text{H})$ 1645 cm⁻¹. (Found: C, 61.7; H, 4.50. C₃₉H₃₂O₂P₂Pt calcd.: C, 59.3; H, 4.08 %.) The high analysis is caused by ether remaining in the lattice. Even when the complex is dried *in vacuo* for four days the NMR spectrum of the compound shows strong peaks due to ether. Other solvent systems cannot be used because they cause decomposition of the complex to a tar.

Tris(triphenylphosphine)hydridopicratoplatinum

To a solution of tetrakis(triphenylphosphine)platinum in benzene was added an equimolar solution of picric acid in the same solvent. The solution was stirred for 1 h, and after removal of the solvent under reduced pressure the complex was obtained from ethanol as orange crystals, $\nu(\text{Pt-H})$ 2130 cm⁻¹. (Found: C, 59.1; H, 3.89; N, 3.49. C₆₀H₄₈N₃O₇P₃Pt calcd.: C, 59.5; H, 3.99; N, 3.47 %.) The ¹H NMR (CDCl₃) shows a singlet at τ 1.04 (picryl protons) and a multiplet at τ 3.3 (triphenylphosphine protons) with the area ratio of 1/23 which confirms the stoichiometry of the complex. The compound is probably not 5-coordinate, it is more likely that the third PPh₃ is bound to the picric acid as an adduct, which is well-known for aromatics such as naphthalene.

Bis(triphenylphosphine)dipicratoplatinum

To a solution of complex (VI) dissolved in the minimum amount of benzene was added a solution of picric acid in the same solvent. After 2 h the solvent was removed and the solid remaining washed with hexane and ether. Recrystallization from benzene/ether gave the complex as yellow crystals. The complex was also prepared in a similar manner from *bis*(triphenylphosphine)(2-butyne)platinum. (Found: C, 49.0; H, 3.56; N, 6.39. C₄₈H₃₄N₆O₁₄P₂Pt calcd.: C, 49.0; H, 2.91; N, 7.14 %.)

The reactions with other protonic acids were carried out in a similar manner by bubbling the dry gas through a solution of the acetylene complex in dry degassed benzene. The complex $(PPh_3)_2PtX_2$ precipitated from the solution, was washed with benzene, and dried *in vacuo*.

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