

**Protonation of Some Fluoro-olefin and Acetylene Complexes of Platinum and
Reactions of Some Acetylenes and Carbon Monoxide with Carboxylate
Complexes of the Type $\text{Pt}(\text{OCOR})_2(\text{PPh}_3)_2$**

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Summary Some fluoro-olefin and acetylene complexes of the type $\text{Pt}(\text{olefin})(\text{PPh}_3)_2$ and $\text{Pt}(\text{acetylene})(\text{PPh}_3)_2$ are converted by trifluoroacetic acid into alkyl and vinyl complexes, respectively; related reactions of acetylenes and carbon monoxide with $\text{Pt}(\text{OCOR})_2(\text{PPh}_3)_2$, ($\text{R} = \text{CF}_3$ or CH_3) are described.

and $\text{Rh}(\text{C}_2\text{H}_4)_2(\pi\text{-C}_5\text{H}_5)$, add hydrogen chloride to give ethyl complexes;^{1,2} similarly the fluoro-olefin complexes $\text{RhCl}(\text{C}_2\text{F}_3\text{X})(\text{PPh}_3)_2$, ($\text{X} = \text{F}, \text{Cl},$ or H) give the fluoroethyl complexes, $\text{RhCl}_2(\text{CFXCF}_2\text{H})(\text{PPh}_3)_2$.³ We now find that some platinum fluoro-olefin and acetylene complexes of the type $\text{Pt}(\text{olefin})(\text{PPh}_3)_2$ and $\text{Pt}(\text{acetylene})(\text{PPh}_3)_2$ similarly add one mole of trifluoroacetic acid.

ETHYLENE complexes of rhodium(I), *i.e.* $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{C}_2\text{H}_4)_2$

On addition of trifluoroacetic acid to a solution of

$\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$ ⁴ in methylene chloride, the ¹⁹F n.m.r. spectrum of the acetylene complex (measured at 56.4 MHz) is immediately replaced by a new signal which shows a broad multiplet at -5.0 p.p.m. and a quartet centred at -9.3 p.p.m. relative to benzotrifluoride. The quartet is further split into two smaller quartets due to coupling with ¹⁹⁵Pt, $J(\text{Pt}-\text{F}) = ca\ 130\ \text{Hz}$. This signal is consistent with the group $\text{Pt}[\text{C}(\text{CF}_3)=\text{CHCF}_3]$ ⁵ and the complex $\text{Pt}(\text{OCOCF}_3)[\text{C}(\text{CF}_3)=\text{CHCF}_3](\text{PPh}_3)_2$, (I) may be isolated from the solution. The value of about 11 Hz for $J(\text{CF}_3-\text{CF}_3)$ indicates a *cis*-arrangement of CF_3 groups.⁵ The complex $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ ⁶ also reacts with trifluoroacetic acid to give $\text{Pt}(\text{OCOCF}_3)(\text{CF}_2\text{CF}_2\text{H})(\text{PPh}_3)_2$, (II), and other platinum fluoro-olefin complexes of this type behave similarly. However, some complexes, *e.g.* $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ react further with trifluoroacetic acid to give $\text{Pt}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$, (III) and *trans*-stilbene. Vinyl and ethyl complexes similar to (I) and (II) have previously been isolated by addition of the olefin or acetylene to the complexes, $\text{PtClH}(\text{PR}_3)_2$.^{5,7}

Complexes similar to (I) may also be prepared by reaction

of some acetylenes with $\text{Pt}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$ in a variety of alcohols. Thus in both methanol and ethanol (III) reacts with diphenylacetylene to give $\text{Pt}(\text{OCOCF}_3)[\text{C}(\text{Ph})=\text{CHPh}](\text{PPh}_3)_2$, which shows bands due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ at 1700 and 1545 cm^{-1} , respectively. The reaction of hexafluorobut-2-yne with (III) in methanol is somewhat different and gives a mixture of (I) and $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$. Similarly from the reaction of tetrafluoroethylene and $\text{Pt}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$, $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ may be isolated. The products of these reactions appear to be dependent on the nature of the carboxylate group present since diphenylacetylene reacts with $\text{Pt}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$ in methanol to give $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$.

The reactions of carbon monoxide with alcoholic solutions of (III) are quite different and alkoxy-carbonyl complexes, $\text{Pt}(\text{OCOCF}_3)(\text{CO}\cdot\text{OR})(\text{PPh}_3)_2$, (R = Me or Et) are formed, which react further with solutions of lithium chloride to give the known complexes, $\text{PtCl}(\text{CO}\cdot\text{OR})(\text{PPh}_3)_2$.⁸ These reactions are analogous to the known reactions of carbon monoxide with mercuric acetate.⁹

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