

## THE CLASSIFICATION OF TRIGONAL BIPYRAMIDAL PLATINUM(II), RHODIUM(I) AND IRIIDIUM(I) OLEFIN COMPLEXES

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(Received February 6th, 1981)

### Summary

It is shown that trigonal bipyramidal platinum(II), rhodium(I) and iridium(I) olefin complexes are better classified with the platinum(0) complex  $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$  as class T olefin complexes than with the square-planar platinum(II) complexes such as  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$  which fall in class S. The underlying reasons for this are considered to be electronic rather than steric as was previously suggested.

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In 1972 we suggested that metal-olefin complexes could be divided into two main classes, class S and T [1,2]. Class S complexes were similar in their general properties to the square-planar platinum(II) complex  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$  and class T complexes were similar to the trigonal platinum(0) complex  $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ . It was further suggested that axial ligands could be added without affecting the classification so that octahedral metal-olefin complexes would belong to class S whereas trigonal bipyramidal metal-olefin complexes would belong to class T. The typical properties of class S and T complexes are shown in Table 1.

Since 1972 many new olefin complexes have been prepared whose properties fit this classification which is based on geometric considerations, and indeed as far as we are aware no complexes containing a single mono-olefin bound to a trigonal, square-planar, trigonal bipyramidal or octahedral metal ion whose properties do not fit those in the Table have been reported. Of particular interest in this connection are the trigonal bipyramidal complexes of platinum(II), rhodium(I) and iridium(I), since these complexes provide a good test of the proposed classification. If the geometry of the complex and hence the symmetries of the associated orbitals is indeed the underlying criterion then these complexes should have properties typical of class T olefin complexes. However, if other factors including the number of *d* electrons contributed by the metal ion, are very important then these *d*<sup>8</sup> complexes should show a closer resem-

blance to the  $d^8$   $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$  than to the  $d^{10}$   $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ .

A number of trigonal bipyramidal platinum(II)-olefin complexes of the type  $[\text{PtCl}_2(\text{NN})(\text{olefin})]$  where NN is a bidentate nitrogen donor have been described [3–6]. In all of these the olefin lies in the trigonal plane which also contains the bidentate ligand. The crystal structures show that in the solid state the olefinic double bond lies in the trigonal plane and the C=C double bond is lengthened considerably on coordination [4–6]. Both are properties typical of class T as opposed to class S metal-olefin complexes. In  $[\text{PtCl}_2(\text{PhCH}=\text{CH}_2) \cdot (\text{tBuN}=\text{CHCH}=\text{N}^t\text{Bu})]$  the phenyl ring is bent back out of the plane of the double-bond away from platinum by  $27^\circ$ , again a value more typical of class T than class S olefin complexes. Furthermore the  $^1\text{H}$  NMR spectrum of  $[\text{PtCl}_2\text{-}\{(R,S)\text{-}N,N'\text{-dimethyl-}N,N'\text{-bis}(\alpha\text{-methylbenzyl})\text{-}1,2\text{-ethane diamine}\}(\text{C}_2\text{H}_4)]$  in  $\text{CDCl}_3$  shows rotation of the ethylene about the platinum(II)-ethylene bond is hindered at room temperature [5], which is typical of a class T olefin complex.

Trigonal bipyramidal  $[\text{Rh}(\text{C}_2\text{H}_4)_3(\text{CH}_3\text{CN})_2]\text{BF}_4$  has axial acetonitrile ligands. The three ethylene ligands lie in the trigonal plane with their double-bonds coplanar with the trigonal plane [7,8], as expected for a class T complex. The negligible C=C bond lengthening (C=C in the complex =  $1.36(3)$  Å) is consistent with the presence of three ethylene ligands competing with each other. Trigonal bipyramidal iridium(I) complexes include  $[\text{IrBr}(\text{CO})\{(\text{NC})_2\text{C}=\text{C}(\text{CN})_2\}(\text{PPh}_3)_2]$ ,  $[\text{IrH}(\text{CO})\{\text{trans-NCCH}=\text{CHCN}\}(\text{PPh}_3)_2]$  [9],  $[\text{IrCl}(\text{C}_2\text{H}_4)_4]$  [10],  $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)] \cdot 1.5 \text{ C}_6\text{H}_5\text{CH}_3$  [11] and  $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P}^i\text{Pr}_2\text{-C}_3\text{H}_6)(\text{P}^i\text{Pr}_3)]$  [11]. The latter two complexes have one axial tertiary phosphine. The metallated phosphines have axial Ir-C bonds with the phosphorus atoms lying in the trigonal plane. As expected for class T complexes the ethylene molecules lie in the trigonal plane and have rather long C=C bonds of 1.45 and 1.43 Å respectively [11]. Similarly, the first two complexes involve olefinic ligands that lie in the trigonal plane and which have rather long C=C bonds of 1.506(15) and 1.431(20) Å for the tetracyanoethylene and fumaronitrile complexes, respectively [9].

It is apparent that trigonal bipyramidal platinum(II), rhodium(I) and iridi-

TABLE I  
CLASSIFICATION OF OLEFIN COMPLEXES

	Class S	Class T
Model complex	$\text{K}^+[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$	$[(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)]$
Coordination number of the metal	4 or 6	3 or 5
Rotation of the olefin about metal-olefin bond?	Yes	No
Angle between axis of double bond and square-plane of metal ( $^\circ$ )	77–90	0–24
Multiple bond lengthening on coordination (Å)	~0.02	~0.15
Angle at which substituents on multiple bond bent back away from metal ( $^\circ$ )	~15	~35
Examples of metal ions giving each class of complex	$\text{Pt}^{\text{II}}, \text{Pd}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Rh}^{\text{I}}, \text{Re}^{\text{I}}, \text{Mn}^{\text{I}}$	$\text{Pt}^0, \text{Pd}^0, \text{Fe}^0, \text{Ir}^{\text{I}}, \text{W}^{\text{I}}, \text{Mo}^{\text{I}}$

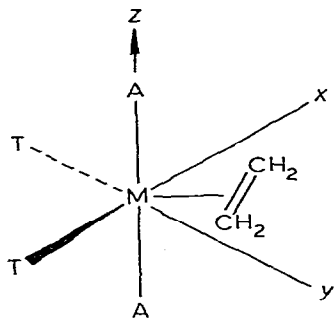


Fig. 1. Trigonal-bipyramidal metal-olefin complexes showing the  $x$ ,  $y$  and  $z$  axes as well as the axial (A) and in-plane (T) ligands.

um(I) complexes resemble  $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$  and thus fall in class T. They show distinct differences to the square-planar  $d^8$  platinum(II) complexes which typify class S. The underlying reasons behind this classification are clearly to be found in the nature of the orbitals available. In a trigonal bipyramidal geometry the metal orbitals available for the formation of M—L bonds are  $d_{z^2}$ ,  $s$ ,  $p_z$  and either  $p_x$  and  $p_y$  or  $d_{xy}$  and  $d_{x^2-y^2}$  (see Fig. 1). If the olefin lies in the trigonal plane there will be maximum opportunity for  $\pi$ -back donation from  $p_x$ ,  $p_y$  and  $d_{x^2-y^2}$  orbitals which have high electron densities due to their receiving  $\sigma$ -electron density from the other two ligands (T) in the trigonal plane. If the olefin were to lie perpendicular to the trigonal plane  $\pi$ -back donation would have to be from the  $d_{xz}$  or  $d_{yz}$  orbital hybridised with  $p_z$ . Only the  $p_z$  is receiving  $\sigma$ -electron density from the axial (A) ligands. Accordingly,  $\pi$ -back donation will be greatest when the olefin lies in the trigonal plane, as is observed. Rotation of the olefin about the metal—olefin bond should require a relatively high activation energy, as is also observed [5]. Furthermore, the formation of stable trigonal bipyramidal complexes will be favoured by the presence of strong  $\sigma$ -donor ligands (T) in the trigonal plane, as is observed [4].

It has been suggested previously [4,11] that the olefin lies in the trigonal plane for steric reasons since this minimises non-bonded interactions with the axial ligands. We believe that electronic factors are also very important since neither chloride in the platinum(II) nor acetonitrile in the rhodium(I) complexes are sterically very demanding, as is demonstrated by the fact that on heating  $[\text{PtCl}_2\{(R,S)\text{-}N,N'\text{-dimethyl-}N,N'\text{-bis}(\alpha\text{-methylbenzyl})\text{-1,2-ethanediamine}\}(\text{C}_2\text{H}_4)]$  in  $\text{CDCl}_3$  ethylene begins to rotate about the platinum(II)—ethylene bond.

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