The Nature of Bonding in Zerovalent Platinum–Acetylene Complexes

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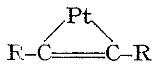
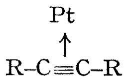
Summary Semi-empirical one-electron molecular orbital calculations on platinum acetylene and olefin complexes indicate that the Dewar–Chatt–Duncanson model can be modified and extended to include acetylenic complexes and that these complexes are best represented as three-co-ordinate complexes of zerovalent platinum.

Acetylene complexes of zerovalent platinum have presented interesting bonding problems. The suggested models[1] are represented as being of two extreme types; one a doubly σ-bonded cyclopropyl type of structure (I), and the other a dative bond involving π-orbitals on the acetylene (II).


(I)


$\overset{\overset{Pt}{\uparrow}}{R-C\equiv C-R}$
(II)

In an attempt to elucidate the bonding in acetylene complexes, semi-empirical one-electron molecular orbital calculations (see Table 1 for input parameters) using previously described methods[2] have been performed for square-planar and pseudo-tetrahedral configurations for the model compounds $(PH_3)_2Pt(CH_3C\vdots CCH_3)$ and $(PH_3)_2PtC_2(CN)_4$. Bond lengths and angles were chosen from currently available *X*-ray data.[3]

Table 1. *Overlap matched Slater type orbital (STO) parameters**†

Atom	Function	*n*	l	*zed*	VSIP
Pt	*5d*	2	2	1·61	16·54
Pt	*6s*	3	0	1·01	6·85
Pt	*6p*	4	1	0·91	1·71
C	*2s*	2	0	1·57	19·50
C	*2p*	1	1	0·88	9·90
N	*2s*	2	0	1·88	25·50
N	*2p*	1	1	1·06	12·50
P	*3s*	3	0	1·81	19·00
P	*3p*	2	1	1·08	10·04
P	*3d*	3	2	1·40	1·90
H	*1s*	1	0	1·20	13·60

* These are parameters for overlap-matched orbitals using reduced princial quantum numbers and adjusted orbital exponents to reproduce the overlap calculated from SCF functions. See ref. 2c.

† Taken from ref. 2d.

Both Mulliken and Löwdin population analyses were performed during the calculations. A Löwdin analysis indicates zerovalent platinum, whereas the Mulliken analysis indicates bivalent platinum. The results of the population analyses are only slightly sensitive to configuration (see Table 2). Hence the question arises whether to regard the compounds as three-co-ordinate platinum(0) or four-co-ordinate platinum(II).

The calculations indicate thermal accessibility for the rotation from a square-planar to a tetrahedral configuration. (See Table 3). This suggests that some of the physical properties observed for these complexes are essentially a function of configuration. Inclusion of electron-withdrawing substituents lowers the antibonding levels in the organic moiety and increases the strength of the interaction. Calculations performed for the complex (Ph_3Pt)-$[(CN)_2C{=}C(CN)_2]$ support this. Hence the experimental facts are explained by a combination of steric and electronic factors within the organic moiety, *e.g.* the low thermal barrier to rotation from one configuration to the other.

Table 2. *Charges based on population analyses*

Molecule and configuration	Atom	Löwdin	Mulliken
$(PH_3)_2Pt(CH_3C\equiv CCH_3)$ Pseudo-tetrahedral	Pt	−0·144	+1·455
	C (C≡C)	−0·054	−0·317
	C (CH_3)	+0·306	+0·299
	H (CH_3)	−0·067	−0·087
	P	+0·301	+0·352
	H (PH_3)	−0·094	−0·267
Square-planar	Pt	−0·077	+1·579
	C (C≡C)	−0·300	−0·584
	C (CH_3)	+0·263	+0·257
	H (CH_3)	−0·072	−0·093
	P	+0·587	+0·636
	H (PH_3)	−0·097	−0·273
$(PH_3)_2Pt[(CN)_2C{=}C(CN)_2]$ Pseudo-tetrahedral	Pt	+0·116	+2·167
	C (C=C)	+0·185	−0·003
	C (CN)	+0·872	+0·937
	N	−1·396	−1·634
	P	+1·069	+1·113
	H (PH_3)	−0·088	−0·266
Square-planar	Pt	+0·094	+2·172
	C (C=C)	+0·219	+0·029
	C (CN)	+0·962	+1·032
	N	−1·365	−1·606
	P	+0·818	+0·847
	H	−0·093	−0·271

Table 3. *Sum of orbital energies as an approximation to the total energy*

Molecule and configuration	Total energy (ev)*
$(PH_3)_2$ $Pt(CH_3C\equiv CCH_3)$	
Pseudo-tetrahedral	− 736
Square-planar	− 740
$(PH_3)_2$ $Pt[(CN)_2C{=}C(CN)_2]$	
Pseudo-tetrahedral	−1135
Square-planar	−1138

* The uncertainty in the approximation to the energy, due to the uncertainty in the VSIP data, implies that the configurations have essentially the same energy.

The Dewar–Chatt–Duncanson (DCD) model of bonding for olefin complexes[4] has successfully rationalized the properties of olefinic complexes. The model consists of an sp^2 metal hybrid overlapping with the olefinic π-system. Generally, the olefin has been treated as occupying only one co-ordination site. Extension to acetylenes implies that this is also the case. However, examination of the molecular orbital coefficients shows that the Pt-6*s* does not participate in bonding to the organic group in either type of compound. Thus from the calculations the only hybridization schemes also allowed by group theory are dp^2 and d^2p^2. Modification of the DCD scheme from sp^2 to dp^2 allows extension of the model to acetylene complexes. The dp^2 scheme rationalizes observed properties such as n.m.r. coupling constants, energy of rotation, kinetic effects, stabilities, and oxidative addition. The d^2p^2 scheme, on the other hand, does not rationalize all of them as satisfactorily as the dp^2 scheme, *e.g.* oxidative addition.

The desirability of a unified model is apparent; consequently modification and extension of the DCD scheme seems to be the most reasonable approach. For the acetylene complexes the dp^2 hybrid $(d_{xy} + p_x + p_y)$ overlaps with the acetylene π_{xy} and a d^2 hybrid $(d_{xz} + d_{yz})$ overlaps with the acetylene $\pi_{z\parallel}$. These two bonds are synergically opposed by $d_{x^2-y^2}$ overlap with the π_{xy} antibonding orbital and d^2 hybrid $(d_{xz} + d_{yz})$ overlaps with the $\pi_{z\parallel}$ antibonding orbital of the acetylene (Figure). Hence, the dp^2 scheme regards the acetylene as occupying only one co-ordination site. The model is consistent with all the currently observed properties of these compounds and a more complete discussion is in preparation.

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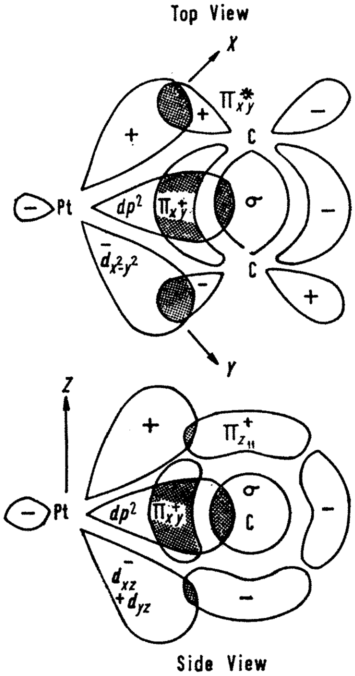

FIGURE. *Orbitals participating in bonding for metal acetylene complexes.*

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[1] See *e.g.*, R. Ugo, *Coord. Chem. Rev.*, 1968, **3**, 319; J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844, and references contained therein.

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