Table VI. Closest Intermolecular Contacts

Atoms	Vector between molecules	Distance, Å
H16–O8	$^1/_2 - x,\ ^1/_2 + y,\ -z$	2.57
H36–O8	$^1/_2 + x,\ ^1/_2 - y,\ z$	2.62
H23–O7	$-x,\ -y,\ -z$	2.67
H24–O9	$-x,\ -y,\ -z$	2.66
H13–O9	$^1/_2 - x,\ -y,\ ^1/_2 - z$	2.63
H35–H26	$-x,\ -y,\ -z$	2.52
H44–H26	$x,\ ^1/_2 - y,\ ^1/_2 + z$	2.53
H33–H22	$^1/_2 - x,\ -y,\ ^1/_2 - z$	2.50

trans to the P atoms have lengths of 1.822 (9) and 1.832 (9) Å while the one approximately *trans* to N is perhaps slightly shorter, 1.804 (9) Å. This might have been expected, qualitatively, on the basis of π acidity considerations, but cannot be meaningfully analyzed quantitatively.

Other bond distances and angles in this molecule are normal. Thus the C–O distances are 1.16–1.18 Å, the P–C distances are in the range 1.825–1.849 Å, and the C–C distances in the phenyl rings average 1.381 Å.

A New Bonding Model for Olefinic and Acetylenic Complexes of Transition Metals

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Abstract: Semiempirical one-electron molecular orbital calculations were performed for a series of platinum–acetylene and –olefin complexes. The results indicate that the Dewar–Chatt–Duncanson model can be modified and extended to include the acetylenic complexes. A consistent hybridization scheme, dp^2, is developed to explain the chemical and physical properties of these complexes.

Since the discovery of Zeise's salt, olefin and acetylene complexes of transition metals have presented an anomalous chemistry of great interest. Although the chemistry is well developed, a coherent theory of bonding in these complexes is still lacking. Recent attempts at explaining chemical behavior have led to invoking one argument or the other depending on the properties to be explained.

The most acute question is whether to represent the bonding in olefinic and acetylenic metal complexes as being one of two extreme types: (1) a doubly σ bonded cyclopropyl type structure, or (2) a dative bond involving π orbitals on the organic moiety.[2a] The Dewar–Chatt–Duncanson (DCD) model of bonding for olefinic complexes[2b] has successfully synthesized these two viewpoints. The model involves donation of olefin π electrons to an sp^2 metal hybrid which is synergically opposed by d back donation to the olefin π antibonding orbital.

The bonding in acetylenic complexes remains to be satisfactorily explained. The σ bond–π bond dichotomy has led to an artificial rather than an actual distinction between the two modes of bonding.[3] Thus a consistent picture of bonding for these compounds would be very useful.

Semiempirical one-electron molecular orbital calculations were therefore performed for a series of zerovalent platinum complexes in order to determine the most probable mode of bonding. The model compounds were $(PH_3)_2(CH_3C{\equiv}CCH_3)Pt$, $(PH_3)_2(CH_3C{\equiv}CH)Pt$, and $(PH_3)_2[(CN)_2C{=}C(CN)_2]Pt$, in both square-planar and pseudotetrahedral configurations.

The calculations were performed and a hybridization scheme consistent with the more general theoretical approach was derived. The scheme explains the observed physical and chemical properties and also has the virtue of an easy pictorialization.

Method

The molecular orbitals were determined as a linear combination of atomic orbitals by solution of the secular equation

$$HC = SCE \tag{1}$$

where H is the effective Hamiltonian matrix, S the overlap matrix, E the diagonal matrix of molecular orbital energies, and C the matrix of LCAO coefficients. The diagonal H matrix elements, H_{ii}, were taken as the neutral atom VSIP. The off-diagonal H matrix

$$-H_{ii} = \text{VSIP} \tag{2}$$

elements, H_{ij}, were evaluated according to Cusachs and Cusachs[4]

$$H_{ij} = {}^1/_2(H_{ii} + H_{jj})S_{ij}(2 - |S_{ij}|) \tag{3}$$

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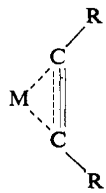
(1) NDEA predoctoral fellow.

(2) (a) R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968); (b) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18c, 79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(3) (a) J. A. Pople, *Quart. Rev.* (London), 11, 273 (1957); (b) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, 46, 3879 (1968), and references therein. It is noteworthy that these authors have concluded from mainly chemical arguments that these complexes should be regarded as platinum(0) complexes and they suggest representing them as



This in our opinion is the least misleading representation yet proposed.

(4) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, 71, 1060 (1967).

The S matrix is directly calculated using single Slater-type orbitals (STO) with principal quantum numbers and orbital exponents chosen to reproduce the overlap determined from SCF atomic orbitals as proposed by Cusachs, *et al.*[5] For extravalent orbitals where no data are available, a choice of STO parameters which seemed reasonable was made (*i.e.*, by a linear extrapolation of trends in orbital exponents and reduced principal quantum numbers, etc.). The STO parameters used are summarized in Table I.

Table I. STO Parameters

Atom	Function	n	e	z^{ed}	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

The computer program employed for solution of the secular equation first computes the matrix of the transformation between the original basis (STO) and a set of symmetrically orthogonalized, or Löwdin, orbitals. The H matrix is then transformed to the orthogonal basis and diagonalized after rotational invariance with respect to the molecular coordinate system has been achieved. The molecular orbitals are determined as linear combinations in the Löwdin basis. By a transformation to the STO basis the molecular orbitals are expressed in terms of the STO basis. Both sets of molecular orbital coefficients are used to determine orbital populations and atomic charges. Thus both Löwdin and Mulliken analyses are obtained in the same calculation.

For the purpose of deriving a pictorialization consistent with the more general molecular orbital approach, iteration to self-consistency by any definition was regarded as unnecessary. Iteration to self-consistency while altering the energies obtained does not substantially alter the molecular orbital coefficients and certainly would not affect any qualitative arguments which are mainly determined by geometry and the diffuseness of the orbitals. Iteration to charge self-consistency has been shown to be misleading and a more complete calculation including so-called madelung type terms (*e.g.*, Corrington's neighbor atom potential) usually returns the H_{ii}'s to values close to free-atom parameters and generally returns the molecular orbital coefficients to values obtained by a simple noniterative approach affecting only the energies.[6,7] Hence iteration to self-consistency would be an unnecessary refinement for the purpose of deriving a localized picture of bonding.

The bond lengths and angles used in the calculations were obtained from currently available X-ray data.[8]

Once the molecular orbitals were determined, the coefficients of each molecular orbital were examined. Atomic orbitals having a coefficient less than 0.2500 in each molecular orbital were eliminated from consideration in constructing the hybrids. The localized picture was developed to be consistent with this criterion.

Results

The Löwdin and Mulliken population analyses do not resolve the question of the oxidation state of the platinum. The Löwdin results indicate zerovalent platinum whereas the Mulliken analysis indicates platinum(II) (see Table II). This is true for all the cases studied. Thus the complexes can be regarded as zerovalent or bivalent platinum compounds, *but not both.*

Table II. Charges Based on Population Analyses

Molecule and configuration	Atom	Löwdin	Mulliken
$(PH_3)_2Pt(CH_3C{\equiv}CCH_3)$ Pseudotetrahedral	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
$(PH_3)_2Pt[(CN)_2C{=}C(CN)_2]$ Pseudotetrahedral	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 (PH_3)	−0.093	−0.271
$(PH_3)_2Pt(CH_3C_b{\equiv}C_aH)$ Pseudotetrahedral	Pt	−0.131	+1.421
	C_{1a}	+0.326	+0.077
	C_{2b}	−0.441	−0.713
	C (CH_3)	+0.310	+0.303
	P	+0.317	+0.370
	H (CH_3)	−0.055	−0.076
	H (C≡C)	+0.025	−0.006
	H (PH_3)	−0.094	−0.266
Square-planar	Pt	−0.067	+1.537
	C_a	−0.084	−0.356
	C_b	−0.548	−0.839
	C (CH_3)	+0.262	+0.256
	P	+0.622	+0.675
	H (CH_3)	−0.066	−0.087
	H (C≡C)	−0.025	−0.057
	H (PH_3)	−0.098	−0.272

Using the sum of the orbital energies as an approximation to the total energy, the two configurations of each molecule are very nearly equal in energy (see Table

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[5] (a) L. C. Cusachs, B. L. Trus, D. G. Carroll, and S. P. McGlynn, *Int. J. Quantum Chem.*, 1 (Slater Symposium Issue), 423 (1967); (b) L. C. Cusachs and J. H. Corrington in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. Wiberg, Ed., W. A. Benjamin, in press; (c) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, 43, 5160 (1965).

[6] J. H. Corrington and L. C. Cusachs, *Int. J. Quantum Chem.*, in press.

[7] (a) K. S. Wheelock, H. B. Jonassen, and L. C. Cusachs, submitted for publication; (b) L. C. Cusachs and P. Politzer, *Chem. Phys. Lett.*, 1, 529 (1968).

[8] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication, No. 11, The Chemical Society, London, 1958. See also footnotes *a–d*, Table IV.

III). In addition the tetracyanoethylene complex is shown to be more stable than the acetylene complexes.

Table III. Sum of Orbital Energies as an Approximation to the Total Energy

Molecule and configuration	Total energy, eV[a]
$(PH_3)_2Pt(CH_3C{\equiv}CCH_3)$	
Pseudotetrahedral	−736
Square-planar	−740
$(PH_3)_2Pt[(CN)_2C{=}C(CN)_2]$	
Pseudotetrahedral	−1135
Square-planar	−1138
$(PH_3)_2Pt(CH_3C{\equiv}CH)$	
Pseudotetrahedral	−647
Square-planar	−650

[a] 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.

From an analysis of the molecular orbital coefficients obtained, the Pt-6s orbital does not participate in bonding to the organic group. Inclusion of data supporting this is omitted because in the case of the smallest molecule and smallest basis a matrix forty-nine square would have to be presented.

Group theory indicates that the following are suitable trigonal hybrids: sp^2, dsp, dp^2, and d^{2}p; and the following suitable square-planar hybrids: dsp^2, d^{2}p^2, d^{3}p, d^{2}sp, and dp^3, depending on the coordination assumed. From an investigation of the C_{2v} point group, these hybrids are compatible with a square-planar or pseudotetrahedral configuration. The calculations indicate that the only hybridization schemes consistent with the more general results are dp^2 or d^{2}p^2.

The DCD model for olefinic complexes has successfully rationalized their properties (*vide supra*). Generally, the olefin has been treated as occupying only one coordination site. Changing the scheme from sp^2 to dp^2 does not alter conclusions based on the model and in addition allows extension to the acetylenic complexes.

The desirability of a unified model is apparent; consequently modification and extension of the DCD scheme seem to be the most reasonable approach. Using the dp^2 hybrid scheme gives rise to a dp^2 hybrid ($d_{xy} + p_x + p_y$) overlapping with the acetylene π_{xy} and a d^2 hybrid ($d_{xz} + d_{yz}$) overlapping with the acetylene $\pi_{z_{||}}$. These two bonds are synergically opposed by $d_{x^2-y^2}$ overlap with the π_{xy} antibonding orbital and a d^2 hybrid (d_{xz}–d_{yz}) overlap with the $\pi_{z_{||}}$ antibonding orbital on the acetylene. Hence the dp^2 scheme treats the acetylene as occupying only one coordination site (see Figure 1).

It is possible to develop an explanation based on the d^{2}p^2 scheme. This alternate explanation rationalizes the energy of rotation, kinetic effects, and stabilizes as well, but does not rationalize oxidative addition and a few other properties.

Discussion and Conclusions

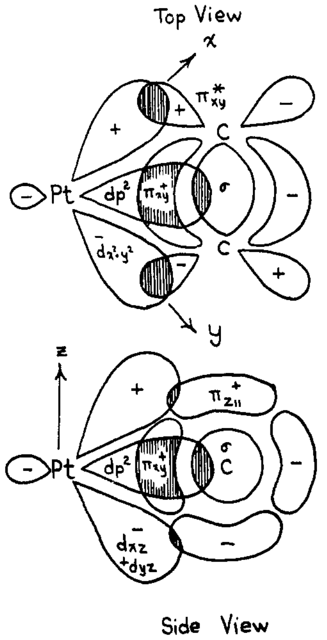

Figure 1. Orbitals participating in bonding for platinum–acetylene complexes.

The calculations while predictive do not lend themselves as easily to explanation as hybridization schemes. The calculated energies are sufficiently uncertain that the two configurations of the same compound are of essentially equal energy. This suggests that rotation of the organic moiety is thermally accessible and this is in agreement with experiments.[9,10]

As electron-withdrawing substituents are placed around the unsaturation, the strength of the interaction increases due to a lowering of the energies of the antibonding orbitals in the organic moiety which in turn increases back-bonding stabilization. This affects the stability of the various complexes and their susceptibility to substitution. Several experimental studies have confirmed this.[11,12]

The configuration of minimum energy will thus be a function of competing steric and electronic effects. The electronic stabilization is maximized in a square-planar configuration whereas the steric interaction is minimized in a pseudotetrahedral configuration.

Since both steric and electronic interactions are maximized in a square-planar configuration, it is possible to suggest a rationale for some recent nmr studies on $(PPh_3)_2Pt(C_6H_{10}(OH)C{\equiv}CH)$. At −60° the proton signal is split only by the Pt, but at room temperature the pattern is more complex. If the pseudotetrahedral configuration is responsible for the simpler spectrum at low temperature, then the room-temperature spectrum can be attributed to a thermal equilibrium between the two forms or the square-planar form. This observation tends to support the prediction of configurational rotation being thermally accessible.

The population analyses indicate platinum(0) or platinum(II) depending on the method used. Recent developments[7] have cast doubt on the Mulliken scheme

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(9) J. H. Nelson and H. B. Jonassen, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13–18, 1969, I-103.

(10) See, for example, (a) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964); (b) C. E. Holloway, G. H. Wiley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.*, *A*, 53 (1969); (c) S. Maricic, C. R. Redpatch, and J. A. S. Smith, *ibid*, 4905 (1963).

(11) J. P. Collmann and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

(12) (a) R. Jones, *Chem. Rev.*, **68**, 785 (1968), and references therein; (b) J. P. Collmann, *Accounts Chem. Res.*, **1**, 136 (1968); (c) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

of analysis and thus if the Löwdin scheme is preferable the compounds should be regarded as three-coordinate platinum(0) complexes. This would explain the coordinatively unsaturated behavior of the complexes and their tendency to undergo oxidative addition.

The bond lengths involved between the metal and the carbons (in those compounds determined by X-ray diffraction) vary by 0.13 Å (see Table IV). The size of the atomic radii (neutral atoms) indicates that this is an effect due primarily to the metal (Ni, 1.14 Å; Ir, 1.26 Å; Pt, 1.29 Å).[13] The metal–carbon (M–C) distance in TCNE complexes of Pt and Ir differs by only 0.04 Å, while for the TCNE and Ph_2C_2 complexes of Pt the difference is only 0.05 Å, a difference within the uncertainty of the determinations. The M–C bond length therefore seems to be the same for a given metal in analogous olefinic and acetylenic complexes.

Table IV. Metal–Carbon Bond Lengths in Metal–Olefin and –Acetylene Complexes

Compound	M–C distance, Å	Reference
$Pt(PPh_3)_2(Ph_2C_2)$	2.06	*a*
$Pt(PPh_3)_2((CN)_4C_2)$	2.11	*b*
$Ni(PPh_3)_2(C_2H_4)$	2.02	*c*
$Ir(PPh_3)_2((CN)_4C_2)(CO)Br$	2.15	*d*

[a] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, 7, 9 (1968). [b] C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 798 (1968). [c] C.D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967). [d] J. A. McGinnety and J. A. Ibers, *ibid.*, 235 (1968).

Calculations were also performed for propyne. The results of the population analyses (see Table V) show the acetylenic hydrogen to be very slightly positive in the uncomplexed acetylene whereas in the complexed acetylene it has a negative charge. This suggests an explanation for several phenomena. Under certain preparative conditions the platinum hydride acetylide complexes can be prepared from the monosubstituted acetylenes.[14] The charge analysis for the complexed acetylene is in accord with postulated mechanisms for the nickel-catalyzed oligomerization of acetylenes.[15] In addition, the small positive charge on the acetylenic hydrogen can serve as a rationale for the small acid dissociation constants observed for acetylenes.

Table V. Charges Based on Population Analyses for Methylacetylene

	$H_3C_1—C_2{\equiv}C_3—H$ Löwdin	Mulliken
$H(CH_3)$	+0.046	−0.052
C_1	+0.285	+0.317
C_2	+0.242	+0.239
C_3	−0.409	−0.442
$H(C{\equiv}C)$	+0.021	+0.041

The energy difference between configurations is a function of competing steric and electronic effects, and as a consequence the nmr spectra may show a temperature dependence based on the nonrigid stereochemistry. Likewise, substitution reactions and stabilities will be affected by the magnitude of the back-bonding stabilization. Consequently the physical properties can be explained without recourse to a localized model. However, the dp^2 scheme can be utilized as it is consistent with the general results. The fact that the dp^2 scheme can be extended from the olefinic to the acetylenic complexes suggests that this scheme might be applicable to other complexes of unsaturated molecules as well.

These phenomena can be explained either in terms of the general MO approach or the more tractable localized approach. The trigonal dp^2 hybrid is a convenient rationale for the properties of these complexes and indicates three-coordinate platinum(0) where the back-bonding scheme allows the interpretation of the electronic effects. Its relative simplicity and its consistence with the more general MO approach avoid the pitfalls of other models.

Acknowledgment. We wish to acknowledge the financial support of this work by the Esso Research Laboratories, Humble Oil and Refining Company, Baton Rouge, La.

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(13) T. Moeller, "Inorganic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1952, p 135.

(14) (a) D. M. Roundhill and H. B. Jonassen, *Chem. Commun.*, 1233 (1968); (b) J. H. Nelson, D. M. Roundhill, and H. B. Jonassen, *Inorg. Chem.*, in press.

(15) (a) L. S. Meriwether, F. G. Colthup, and G. W. Kennerly, *J. Org. Chem.*, 26, 5163 (1961); (b) L. S. Meriwether, M. F. Leto, E. G. Colthup, and G. W. Kennerly, *ibid.*, 27, 3930 (1962).