The Barrier to Rotation in Platinum Acetylene and Olefin Complexes

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Abstract: Noniterative semiempirical one-electron molecular orbital calculations have been performed on several configurations of the following platinum acetylene and olefin complexes: $(PH_3)_2Pt(CH_3C{\equiv}CCH_3)$, $(PH_3)_2Pt(H_2C{=}CH_2)$, and *trans*-$(NH_3)Cl_2Pt(H_2C{=}CH_2)$. The energy increases monotonically from a minimum at the square-planar form to a maximum at the pseudotetrahedral form for both olefin and acetylene complexes of zerovalent platinum; it then decreases monotonically to the square-planar form. For the divalent complexes a barrier interposes, which indicates that some bond breaking occurs as rotation progresses. The barrier is greater for acetylene than olefin zerovalent complexes and greater for zerovalent than divalent complexes. The results indicate that the hydridization of the central metal in the Dewar–Chatt–Duncanson model should be modified to dp^2 for zerovalent complexes and to d^2p^2 for divalent complexes. The relative stabilities and chemical properties of systems related to these models are discussed and explained in terms of the new hybridization schemes.

Because of their catalytic properties, the chemical and physical properties of numerous acetylene and olefin complexes of both Pt(II) and Pt(0) have been extensively investigated.[2–5] The abundance of experimental data facilitates the unification and systematization of the chemistry of these systems through the use of a theoretical model.

The X-ray crystal structures of the zerovalent olefin and acetylene complexes indicate a slight distortion from a square-planar structure.[6–8] The plane containing the platinum and two carbon atoms forms a dihedral angle of 6–14° with the plane containing the platinum and the other two donor atoms of the ligands. A change in oxidation state produces a change in geometry—the crystal structures[9–11] of divalent olefin and acetylene complexes indicate a dihedral angle of 90° (Figure 1).

The proton nmr spectra of solutions of zerovalent complexes containing unsymmetrical acetylenes and phosphines show coupling to two nonequivalent phosphorus atoms. This indicates that the square-planar form is maintained even in solution[12–14] On the other hand, the nmr spectra of Rh(I) and Pt(II) olefin complexes indicate that rotation of the organic moiety occurs at room temperature, even in the solid state,[15,16] with a barrier to rotation of 6–14 kcal.[17–20] At low temperatures the most stable rotamer, the pseudotetrahedral form, can be frozen out.

The rotational studies for the divalent olefin complexes, in conjunction with the X-ray crystal structures of zerovalent complexes, have led to speculation that similar rotation might be observed for the olefin or acetylene in zerovalent complexes.[21]

The Dewar–Chatt–Duncanson (DCD) description of bonding in Zeise's salt analogs is now well accepted.[22,23] The bonding in the acetylene and olefin complexes of zerovalent metals, however, has only recently been explained.[13,24,25] By changing the hybridization of the central metal in the DCD scheme from sp^2 to dp^2, the chemical properties and the bonding in zerovalent complexes of acetylenes and olefins were explained.[24,25]

The molecular orbital calculations which led to construction of the dp^2 hybridization scheme were performed[24,25] only for the square-planar (dihedral angle $\theta = 0° 0'$) and pseudotetrahedral (dihedral angle $\theta = 90° 0'$) configurations. The square-planar form was calculated to be the more stable configuration for both the zerovalent olefin and acetylene complexes. The energy difference between the two configurational extrema was greater for the acetylene complexes than for olefin complexes. Since no intermediate configurations were calculated, no conclusion regarding any interposing barrier between the two forms could be made.

We have now calculated the energies of various configurations (dihedral angles $\theta = 0° 0', 22° 30', 45° 0', 67° 30'$, and $90° 0'$) for the model compounds $(PH_3)_2Pt$-

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(1) Author to whom correspondence should be addressed.

(2) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968), and references contained therein.

(3) R. Jones, *Chem. Rev.*, **68**, 785 (1968), and references contained therein.

(4) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968), and references contained therein.

(5) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).

(6) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, **7**, 9 (1968).

(7) C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 798 (1968).

(8) C. Panattoni and R. Graziani, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 310.

(9) J. N. Dempsey and N. C. Baenziger, *J. Amer. Chem. Soc.*, **77**, 4984 (1955).

(10) G. R. Davies, W. Hewertson, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 423 (1967).

(11) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Crystallogr.*, **13**, 149 (1960).

(12) J. H. Nelson, J. J. R. Reed, and H. B. Jonassen, unpublished results.

(13) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(14) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

(15) H. P. Fritz, K. E. Schwarzhans, and D. Sellman, *J. Organometal. Chem.*, **6**, 551 (1966).

(16) S. Maricic, C. R. Redpath, and J. A. S. Smith, *J. Chem. Soc.*, 4905 (1963).

(17) M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.*, **2**, 123 (1968).

(18) L. W. Reeves, *Can. J. Chem.*, **38**, 736 (1960).

(19) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

(20) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964); **89**, 5377 (1967).

(21) C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967).

(22) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, 79 (1951).

(23) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(24) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Commun.*, 1019 (1969).

(25) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **91**, 7005 (1969).

$(CH_3C{\equiv}CCH_3)$, $(PH_3)_2Pt(H_2C{=}CH_2)$, and *trans*-$(NH_3)Cl_2Pt(H_2C{=}CH_2)$. The results of these calculations are discussed here.

Method

The calculations were performed using the same noniterative semiempirical one-electron molecular orbital method as in the work previously reported.[24,25] The basis atomic functions are single Slater-type orbitals chosen to reproduce overlap integrals over accurate Hartree–Fock atomic orbitals for the range of interatomic distances of chemical interest.[26,27] Except for Cl, they are described in our previous papers.[24,25] For Cl, the orbitals are 3s, $n = 2$, $l = 0$, $z = 1.70$, $H_{ii} = -24.44$; 3p, $n = 2$, $l = 1$, $z = 1.38$, $H_{ii} = -13.26$. The calculations follow the method suggested by Cusachs and Cusachs.[28] As predicted,[28] the inclusion of the electrostatic potential due to neighbor atoms for relevant small molecules[29,30] leads to molecular orbitals which are much more like those of the noniterative calculation than are the results of charge self-consistent methods neglecting neighbor atom potentials. Calculations for bis(π-allyl)nickel(0)[31] further support the choice of the noniterative procedure as an economical approximation to the full calculation.

This molecular orbital method is implemented in a general program, GIVNAP, for the IBM 7044 computer, which is capable of performing charge self-consistent or noniterative calculations with and without neighbor atom potentials. The 32-K word memory of the available computer limits these calculations to not more than 120 s, p, d, and f orbitals on up to 50 atoms. The organization of the program limits it to computers with a single-precision binary word of at least 36 bits. Off-diagonal matrix elements of the effective Hamiltonian are approximated as

$$H_{ij} = (H_{ii} + H_{jj})S_{ij}(2 - |S_{ij}|)/2$$

with the usual precautions[28] to ensure invariance under rotation of the molecule with respect to the absolute coordinate system.

The localized hybridization scheme[24,25] was conconstructed to be consistent with the molecular orbital results and group theory, but was not obtained directly from the general molecular orbital approach. The hybrids were obtained by examining the ratios of coefficients of the atomic orbitals in the higher occupied molecular orbitals. For this purpose only atomic orbitals which had a coefficient of 0.25 or greater in a particular molecular orbital were considered. In molecules of very high symmetry, such as N_2 and H_2O, it is possible to discuss hybridization by transforming the general molecular orbitals to localized bond and lone-pair orbitals with a minimum of ambiguity. In molecules of low symmetry, as in the present case, the localization is so unrestricted as to become a matter of personal preference. The utility of the hybridization scheme arises in its organization and rationalization of an ample body of observed data with few assumptions, rather than in any remote relation to quantum theory.

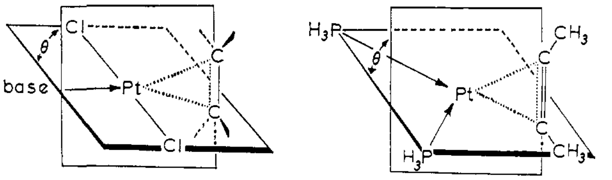

Figure 1. Definition of the dihedral angle θ for zerovalent and divalent platinum complexes.

Results and Discussion

The total energies are presented in Table I (sum of the orbital energies as an approximation), and the variation of energy with configuration is shown in Figure 2.

Table I. Total Energies of Platinum Acetylene and Olefin Complexes as a Function of Dihedral Angle

Molecule	Dihedral angle	Total energy,[a] eV	ΔE,[b] eV
$(PH_3)_2Pt(CH_3C{\equiv}CCH_3)$	0° 0′	−739.7	
	22° 30′	−739.2	
	45° 0′	−738.4	
	67° 30′	−737.1	
	90° 0′	−736.1	3.6
$(PH_3)_2Pt(H_2C{=}CH_2)$	0° 0′	−591.8	
	22° 30′	−591.4	
	45° 0′	−590.6	3.3
	67° 30′	−589.3	
	90° 0′	−588.5	
$(NH_3)Cl_2Pt(H_2C{=}CH_2)$	0° 0′	−719.6	
	22° 30′	−719.5	
	45° 0′	−719.9	
	67° 30′	−720.4	
	90° 0′	−720.7	1.1

[a] Uncertain by ±2.0 eV. [b] ΔE = energy difference between 0° 0′ and 90° 0′ configurations.

The energy curves for both the olefin and acetylene zerovalent complexes are very similar. The energy increases monotonically from a minimum at the square-planar form to a maximum at the pseudotetrahedral form, and then decreases monotonically again to the square-planar form. The absence of double minima, one at the square-planar form and one at the pseudotetrahedral form, seems to indicate that no barrier to rotation is interposed, and that upon rotation a continuous rehybridization[32] of the orbitals participating in π bonding occurs rather than bond breaking.

For the divalent case, on the other hand, a double minimum is obtained with a configuration of maximum energy at $\theta = 22°\ 30'$ and with minima at $\theta = 0°\ 0'$ and $\theta = 90°\ 0'$. This seems to indicate that some bond breaking occurs as rotation from the square-planar form progresses to the pseudotetrahedral form.

The calculations thus predict that the most stable configuration is the square-planar form for the zerovalent complexes and the pseudotetrahedral form for the

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(26) L. C. Cusachs, D. G. Carroll, B. L. Trus, and S. P. McGlynn, *Int. J. Quantum Chem.*, **1S**, 159 (1967).

(27) L. C. Cusachs and J. H. Corrington in "Sigma Molecular Orbital Theory," O. Sinanoğlu and K. Wiberg, Ed., Yale University Press, New Haven, Conn., 1969.

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

(29) J. H. Corrington and L. C. Cusachs, *Int. J. Quantum Chem.*, **3S**, 207 (1969).

(30) K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *ibid.*, in press.

(31) K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, unpublished calculations.

(32) F. A. Cotton, private communication.

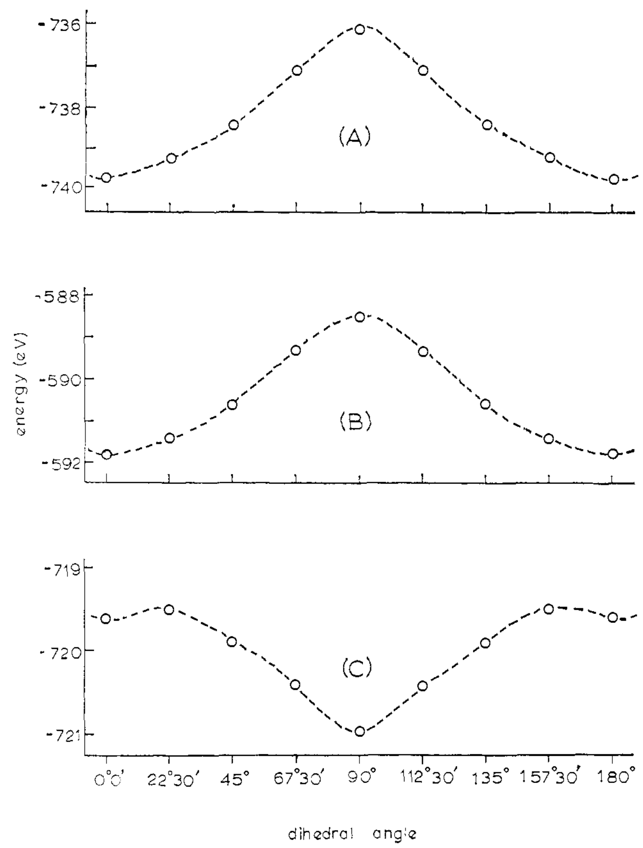

Figure 2. Total energy as a function of the dihedral angle θ for the complexes (A) $(PH_3)_2Pt(CH_3{-}C{\equiv}C{-}CH_3)$, (B) $(PH_3)_2Pt(C_2H_4)$, and (C) *trans*-$(NH_3)Pt(C_2H_4)Cl_2$. The total energies are approximated by the sum of the energies of the occupied molecular orbitals, an approximation generally satisfactory for estimating conformational barriers when the atomic charges are small, as in the case of the molecules of interest here. Owing to uncertainties in the input atomic data, the calculated total energies are uncertain by ±2.0 eV. The differences in energy are more significant.

divalent complexes, in agreement with the X-ray structures.

The energy differences between configurational extrema are also significant. Assuming the same shape for the curves, zerovalent platinum complexes of $CH_3C{\equiv}CCH_3$, $CH_3C{\equiv}CH$, $(CN)_2C{=}C(CN)_2$, and $H_2C{=}CH_2$ yield calculated energy differences of 3.6, 3.8, 2.6, and 3.3 eV, respectively, for the configurational extrema. Since the barrier to rotation should be a function of the amount of π bonding, *i.e.*, the greater the π-bonding interaction, the higher the energy barrier, these data support the thesis that π interactions in the acetylene complexes are greater than in the olefin complexes.

The nature and number of π interactions are a consequence of the dp^2 hybridization scheme and the π orbitals on the organic moiety. Both acetylenes and olefins can form in-plane π bonds, but only acetylenes can form out-of-plane π bonds. With a larger number of π interactions possible, the energy difference between configurational extrema is therefore greater for the acetylene than for the olefin complexes.

The extension of the DCD scheme to the zerovalent complexes indicated the necessity of a modification from sp^2 to dp^2 hybridization.[24,25] A similar analysis of the MO coefficients for *trans*-$(NH_3)Cl_2Pt(H_2C{=}CH_2)$ indicates this for the divalent compound as well. Since the Pt 6s orbital does not participate in bonding, the hybridization of the central metal should be changed to d^2p^2. This change permits rationalization and systematization of the properties of these complexes irrespective of oxidation state.

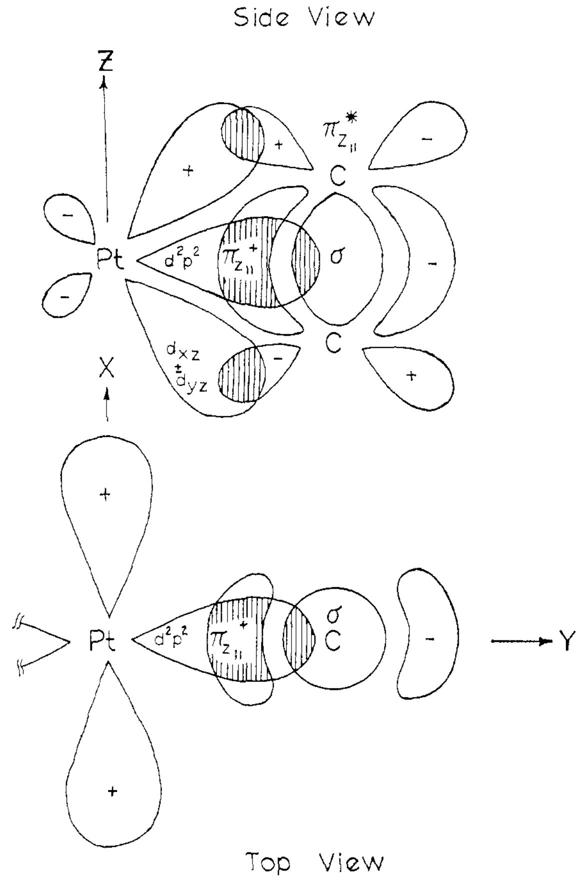

Figure 3. Orbitals participating in bonding for divalent platinum olefin complexes.

In the divalent case, the use of the d_{xy}, $d_{x^2-y^2}$, p_x, and p_y orbitals to form the four σ bonds necessitates the staggered pseudotetrahedral form, as the orbitals which can participate in π bonding are in the xz or yx planes (see Figure 3). Consequently, the pseudotetrahedral configuration is necessary for π interaction.

A modification of the DCD schemes from sp^2 to dp^2 for the three-coordinate zerovalent complexes and from dsp^2 to d^2p^2 for the four-coordinate divalent complexes rationalizes the observed configurations found in the X-ray structures.[33] For the zerovalent complexes the square-planar form is more stable, whereas the stable

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(33) Use of d and p rather than s orbitals in constructing hybrid orbitals on the metal atom does not follow the usual assumptions, and this departure from tradition calls for explanation. The s orbital has large overlap integrals with many ligand orbitals, but is higher in energy than the ligand atomic orbitals. In the molecules it appears conspicuously in high-energy empty molecular orbitals, but mixes very little with the d orbitals, which lie deep in energy, and has very small overlap integrals with the ligands. It is possible that our results might be altered by including an inner s orbital, but it is very difficult to imagine a change large enough to lead to the classical bonding scheme. It should be stressed that the results of the molecular orbital calculation are far from encouraging a localized hybrid orbital description, but rather the scheme proposed does least violence to the all-valence calculations. Conventional localized bonding theories would predict relations among the populations of the d, s, and p orbitals making up the hybrids that are very far from being satisfied by the molecular orbitals obtained without imposing the assumption of hybridization.

divalent complexes have pseudotetrahedral stereochemistry.

The nmr spectra indicate that the square-planar form of the zerovalent complexes is maintained even in solution, whereas for the divalent complexes rotation occurs at room temperature. The smaller number of π interactions allowed in the divalent complexes decreases the metal–ligand interaction compared to the zerovalent complexes, and the barrier to rotation and/or dissociation, therefore, also decreases. If the hybridization of the metal in the divalent case were dsp^2 instead of d^2p^2, a d orbital would be available for in-plane (xy) π bonding and the same situation would obtain as for the zerovalent case. The fact that rotation is observed supports the new hybridization, and the d^2p^2 scheme rationalizes the rotation.[34]

This is dramatically underscored by the properties of the divalent acetylene complexes. Since, relative to ethylene, the π bonding and antibonding levels are energetically closer to one another in acetylene, acetylene should be both a better σ donor and π acceptor than ethylene[35] and should therefore form more stable complexes.

However, unless the acetylenes have bulky substituents or functional groups which can interact with the metal or the other ligands, the acetylene complexes of divalent platinum are not stable,[36–38] and polymerization of the acetylene occurs. This argues strongly for the conclusion that both in-plane (xy) and out-of-plane (xz or yz) π bonding are necessary to stabilize the acetylene complex. If only one of the π orbitals and its antibonding counterpart are involved, the other π orbital is destabilized in the synergic mechanism, raising it to nonbonding energy levels and causing the complex to act as a Lewis base. Consequently, unless the acetylene polymerization is sterically or chemically inhibited, the divalent acetylene complexes are not stable. When both π orbitals on the acetylene can be involved in the synergic mechanism (as in the zerovalent complexes) the problem of relative destabilization does not assert itself. In the olefin complexes this cannot occur since only one π orbital is present in the ligand. However, for these systems, the thermodynamics of the oligomerization of acetylenes to substituted benzenes must also be considered.[38–40]

Frequently the synthetic methods employed use replacement of a weaker π acid by stronger ones.[41] The stronger π acids have the π antibonding levels at lower energies; hence the strength of the synergic mechanism is increased. This is found to be the case for tetracyanoethylene.[42,43] The relative stabilities have been amply demonstrated by the smaller dissociation constants and replacement rate constants observed for the zerovalent acetylene complexes compared to the zerovalent olefin complexes.[5] These studies also demonstrated that the metal–ligand interaction in the zerovalent state is stronger than in the divalent state, and that the zerovalent metal is a better π base, as would be expected from the fact that the third ionization potential is much greater than the first.

For the zerovalent acetylene complexes, both π orbitals are involved in bonding and no relative destabilization occurs. In the divalent acetylene complexes, however, one π orbital is available to act as a Lewis base. For the olefin complexes, however, either in the zerovalent or divalent state, only one π orbital is available for the synergic mechanism, which leads to the observed relative stabilities.

The problem of defining the charge on an atom in a molecule in a chemically useful but computationally simple procedure reduces to a choice[44] between the symmetrically orthogonalized orbitals of Löwdin[45] and the analysis in the ordinary nonorthogonal basis proposed by Mulliken.[46] In the Löwdin basis, each electron occupying molecular orbital χ_m contributes a quantity of charge L_{mi}^2 to atomic orbital ϕ_i^L, where L_{mi} represents the coefficients of the Löwdin orbitals in the molecular orbitals. In the Mulliken population analysis, each electron in the molecular orbital contributes C_{mi}^2 to orbital ϕ_i, and also the quantity of charge $2C_{mi}C_{mj}S_{ij}$ to the distribution of charge described by the product of atomic orbitals $\phi_i\phi_j$, whose overlap integral is S_{ij}. When these quantities are summed over all occupied molecular orbitals, the Löwdin population is obtained in the first case and Mulliken's net orbital and overlap populations in the second. Mulliken further defined a gross population as the sum of the net orbital population and half of all overlap populations involving that orbital. When, as in the case of hydrocarbons, the atomic orbitals all have similar energies and spatial extension, the charges based on the two definitions tend to be within 0.15 electron of one another. However, as the orbitals in a molecule become dissimilar, the equal division of the overlap population in the Mulliken definition of gross population becomes progressively less realistic. Our experience, both in the present study and with many very different types of molecules, inclines us to regard the charges defined by Löwdin as the more useful both for chemical interpretation of molecular orbital calculations and for achieving charge self consistency in semiempirical procedures.

The relative amounts of π-bonding interactions are reflected in the calculated charge densities on the platinum (Table II). σ donation would tend to give the metal a partial negative charge which could be relieved by π back-donation. Thus, the more positive the charge on the platinum, the more π bonding.

The charge data in Table II show that, as expected, propyne is a better π acceptor than 2-butyne; the same is true for tetracyanoethylene relative to ethylene. Comparisons are most valid among the olefins and

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(34) Previously, Bennett argued that the original bonding scheme was too rigid as it did not allow for the observed rotation: M. A. Bennett, Second Conference of the Coordination and Metal Organic Chemistry Division of the Royal Australian Chemical Institute, Monash, Australia, May 1968.

(35) T. P. Cheeseman, A. L. Odell, and H. A. Raethel, *Chem. Commun.*, 1496 (1968).

(36) J. Chatt, R. G. Guy, and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

(37) J. Chatt, R. G. Guy, and L. A. Duncanson, *Nature*, **184**, 526 (1959).

(38) V. O. Reikshfel'd and K. L. Makovetskii, *Russ. Chem. Rev.*, **35**, 510 (1966).

(39) L. S. Meriwether, F. G. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **26**, 5163 (1961).

(40) L. S. Meriwether, M. F. Leto, F. G. Colthup, and G. W. Kennerly, *ibid.*, **27**, 3930 (1962).

(41) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

(42) W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(43) W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2**, 7 (1968).

(44) L. C. Cusachs and P. Politzer, *Chem. Phys. Lett.*, **1**, 529 (1968).

(45) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

(46) R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

Table II

Molecule	Charge on Pt	
	Mulliken	Löwdin
$(PH_3)_2Pt(CH_3C{\equiv}C{-}CH_3)$	+1.579	−0.077
$(PH_3)_2Pt(CH_3C{\equiv}C{-}H)$	+1.537	−0.067
$(PH_3)_2Pt(C_2H_4)$	+1.585	−0.044
$(PH_3)_2Pt(TCNE)$	+2.172	+0.094

acetylenes separately, as the charge density is a function of both σ and π effects. Calculations are currently in progress to assess the relative bonding contributions of olefins and acetylenes.

The magnitude of the calculated energy barriers for the zerovalent complexes suggests that it might be possible to observe rotation in the nmr spectra at elevated temperatures. The spectra must, however, be obtained in solvents which do not react with the complexes, therefore precluding halocarbon solvents such as chloroform, with which the following oxidative addition reaction is known to occur[13]

$$L_2Pt(Ac) + XY \longrightarrow L_2XPtY + Ac$$

where L = triphenylphosphine, Ac = acetylene, X = halogen, and Y = the hydrocarbon or halocarbon fragment. Preliminary thermodynamic investigations indicate that the oxidative addition reactions occur before rotation can be observed in these solvents.[47]

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[47] J. H. Nelson and H. B. Jonassen, unpublished results.

Systematic Preparation and Characterization of *Pentahapto*cyclopentadienylcopper(I) Compounds[1]

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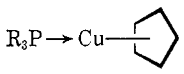
Abstract: A convenient and general method for the preparation of $(h^5\text{-}C_5H_5)(L)Cu$ compounds is described and illustrated for compounds with L = $(C_2H_5)_3P$, $(C_4H_9)_3P$, $(C_6H_5)_3P$, $(CH_3O)_3P$, and CH_3NC. The method involves reaction of the appropriate $(LCuI)_4$ or $(LCuBr)_4$ compound with C_5H_5Tl. The compounds have all been characterized by analyses, pmr, infrared and mass spectra, and, for L = $(C_6H_5)_3P$ and $(C_2H_5)_3P$, by X-ray diffraction as *pentahapto*cyclopentadienyl compounds. The compound $(h^5\text{-}C_5H_5)(CO)Cu$ has also been prepared by reaction of CuCl, C_5H_5Tl, and CO in pentane at 0°. It has a very high CO stretching frequency (2093 cm^{-1}) and decomposes rapidly at room temperature.

Recent reports have presented infrared[3] and X-ray evidence[4] to show that $C_5H_5CuPR_3$ compounds have the structure, I, in which there is a *pentahapto*-



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cyclopentadienyl ring. Our investigations were made feasible by the development of a new general procedure for the preparation of such compounds.

Previously, only the compound containing triethylphosphine was known;[5] it was prepared by the reaction of Cu_2O with cyclopentadiene and triethylphosphine. This type of reaction could, perhaps, be applied more generally, but it has practical disadvantages and a more straightforward, general route was sought.

This paper describes such a route, illustrates its application by describing in detail the preparation and characterization of the five compounds $(h^5\text{-}C_5H_5)(L)Cu$, where L = (1) $P(C_2H_5)_3$, (2) $P(C_4H_9)_3$, (3) $P(C_6H_5)_3$, (4) $P(OCH_3)_3$, and (5) $CNCH_3$, and comments briefly on the properties, relative stabilities, and bonding in these compounds. The compound $(h^5\text{-}C_5H_5)(CO)Cu$ has also been prepared by a different method. It is much less stable than the phosphine compounds.

Experimental Section

The preparation and handling of all organometallics was carried out in an atmosphere of prepurified nitrogen, since the h^5-cyclopentadienyl compounds are moderately air sensitive as solids and extremely so when in solution. All solvents were carefully dried in an appropriate manner and were freshly distilled under nitrogen prior to use. Melting points were determined in sealed, nitrogen-filled capillaries.

Considerable difficulty was encountered in obtaining satisfactory elemental analyses, especially for carbon. Best results were obtained from Scandinavian Microanalytical Laboratories, Herlev, Denmark, and Mrs. N. Alvord, of the M.I.T. Microanalytical Laboratory.

Triethylphosphineiodocopper(I),[6] tributylphosphineiodocopper(I),[7] triphenylphosphinebromocopper(I),[8] (trimethyl phosphite)iodo-

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[1] Supported by the National Science Foundation under Grant No. GP 7034X.

[2] National Science Foundation Predoctoral Fellow, 1966–1970.

[3] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

[4] (a) F. A. Cotton and J. Takats, *ibid.*, **92**, 2353 (1970); (b) L. T. J. Delbaere, D. W. McBride, and R. B. Ferguson, *Acta Crystallogr., Sect. B*, **26**, 518 (1970).

[5] (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); (b) G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967).

[6] G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, 9 (1963).