Molecular Orbital Studies of Platinum Olefin and Acetylene Complexes: Reactions and Reaction Mechanisms

By **Kenneth S. Wheelock, John H. Nelson, J. Duncan Kelly, Hans B. Jonassen,*** and **L. Chopin Cusachs,** Richardson Chemistry Laboratories, Tulane University, New Orleans, Louisiana 70118, U.S.A.

Relative energies of platinum olefin and acetylene complexes, obtained from non-iterative semi-empirical one-electron molecular-orbital (NISEMO) calculations, are in qualitative agreement with available experimental results. Based on a synthesis of these calculations and the experimental results, mechanisms are proposed for (*a*) olefin–vinyl rearrangement, (*b*) HCl addition to π-bonded acetylene, and (*c*) π-bonded acetylene–acetylide-hydride rearrangement. This method provides a reasonable and economical approach to predicting the mechanisms and courses of reaction of fairly large molecules.

FORMALLY zero- and bi-valent platinum olefin and acetylene complexes have been studied previously using non-iterative semi-empirical one-electron molecular-orbital calculations (NISEMO). These calculations predicted relative stabilities of pseudo-tetrahedral and square-planar forms of these complexes, in both 0 and II oxidation states, which were in good agreement with experimental data.[1-3] Analysis of the calculations provided a modification of the familiar Dewar–Chatt–Duncanson model of π-bonding, and a ready systematization of the observed chemistry of these complexes. An *X*-ray photoelectron spectroscopic study of similar compounds by Cook *et al.*[4] yielded data interpreted as indicating low, almost zerovalent, oxidation states for complexes which were formally zerovalent. Atomic charges computed in the NISEMO calculations[1-3] were in basic agreement with the pattern of the experimental data. In the present paper, further computations have been performed in a study of the nature and course of reactions of formally zerovalent platinum olefin and acetylene complexes.

METHOD

The NISEMO method has been previously described in detail.[1-3] Basis functions are Slater type orbitals (STO) which have been previously tabulated.[2] Limitations of time and computer size influenced the choice of model complexes; bond lengths and geometries were abstracted from the available *X*-ray data.[5]

The use of experimental bond lengths and angles deserves comment. In a previous study of the prediction of bond angles,[6] NISEMO calculations were performed for a set of angles covering the range of interest for rotation and bending of the ligands. The orbital-energy sum, total Mulliken overlap population, and total overlap energy were computed. These quantities, as functions of the bond angles, were fitted to curves by least squares and equilibrium angles were predicted. The orbital-energy sum (OES) is the least reliable of the three quantities for the prediction of geometries. This is hardly surprising since it differs from the proper total energy in replacing core repulsion with electron-repulsion terms which are only asymptotically equal.[7] This approximation is more reasonable for the prediction of bond angles than for attempts to estimate bond distances directly. However, as all three quantities vary little with bond angle (curves are shallow even fairly far from the minima), use of standard distances is expected to be satisfactory. Unfortunately, comparisons between different complexes are very doubtful, unless the species compared are permutation isomers of the same empirical formula, and the basis set of atomic orbitals is not varied. In such a case, errors implicit in using the OES (which is readily available), in place of the total energy (which is not), may be expected to cancel in estimating differential stability.

In the present calculations we replaced PPh_3 by PH_3, since six phenyl groups alone would have exceeded the capacity of the largest computer available. Since acetylene or olefin complexes are known[8,9] to be formed after prior dissociation of the precursor phosphine complex, steric crowding around the metal atom is absent. Other calculations, supporting the replacement of PPh_3 by PH_3,[10] indicate that this will have little effect on the phosphorus–metal bond.

RESULTS AND DISCUSSION

Halogeno-olefin–Halide-Vinylide Isomerization.—Reactions of halogeno-olefins with zerovalent nickel, palladium, and platinum have recently been reviewed[5] and are summarized in equations (1)—(5) (M = Ni, Pd, or Pt; R = alkyl). For Pt and Ni, the reactions proceed (I) → (II) → (III) → (IV).[11-19] For Pd, however,

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[1] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Comm.*, 1969, 1019.

[2] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1969, **91**, 7005.

[3] K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1970, **92**, 5110.

[4] C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johanssen, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1971, **93**, 1904.

[5] J. H. Nelson and H. B. Jonassen, *Co-ordination Chem. Rev.*, 1971, **6**, 27.

[6] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Inorg. Chem.*, 1972, **11**, 412.

[7] J. B. Florey and L. C. Cusachs, *J. Amer. Chem. Soc.*, 1972, **94**, 3040.

[8] R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319.

[9] M. Belluco, R. Crociani, R. Pietropaolo, and P. Uguagliatti, *Inorg. Chim. Acta Rev.*, 1969, **3**, 19.

[10] L. C. Cusachs and D. J. Miller, in 'Trends in Sulfur Research,' eds. T. Wiewiorowski and D. J. Miller, Amer. Chem. Soc., Washington, 1972.

[11] P. Fitton and J. E. McKeon, *Chem. Comm.*, 1968, 4.

[12] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.

[13] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1969, 2062.

[14] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *Chem. Comm.*, 1966, 502.

[15] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

[16] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1969, **18**, 199.

[17] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **14**, 201.

[18] W. J. Bland and R. D. W. Kemmitt, *Nature*, 1966, **211**, 963.

[19] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3019.

the π-complex (II) has not yet been isolated and the reactions proceed directly to the halide–vinylide complexes (III) and (IV), or the bivalent halogeno-complexes (V). In some cases, however, the bivalent halageno-complexes of Pt are formed.[20-22]

$$\underset{\text{(I)}}{[(PPh_3)_4M]} + R_2C{=}CXR \longrightarrow \underset{\text{(II)}}{[(\pi\text{-}R_2C{=}CXR)M(PPh_3)_2]} + 2PPh_3 \qquad (1)$$

$$\underset{\text{(II)}}{[(\pi\text{-}R_2C{=}CXR)M(PPh_3)_2]} \longrightarrow \underset{\text{(III)}}{cis\text{-}[(\sigma\text{-}R_2C{=}CR)MX(PPh_3)_2]} \qquad (2)$$

$$\underset{\text{(I)}}{[(PPh_3)_4M]} + R_2C{=}CXR \longrightarrow \underset{\text{(IV)}}{trans\text{-}[(\sigma\text{-}R_2C{=}CR)MX(PPh_3)_2]} + 2PPh_3 \qquad (3)$$

$$\underset{\text{(III)}}{cis\text{-}[(\sigma\text{-}R_2C{=}CR)MX(PPh_3)_2]} \rightleftharpoons \underset{\text{(IV)}}{trans\text{-}[(\sigma\text{-}R_2C{=}CR)MX(PPh_3)_2]} \qquad (4)$$

$$\underset{\text{(I)}}{[(PPh_3)_4M]} + R_2C{=}CXR \longrightarrow \underset{\text{(V)}}{cis\text{- or } trans\text{-}[(PPh_3)_2MX_2]} \qquad (5)$$

NISEMO calculations were performed only for Pt complexes and the discussion of the results is strictly limited to the applicable chemistry of Pt, and, only by inference, to that of Pd and Ni. Tables 1 and 2 summarize the calculations for the three isomeric tetrachloroethylene and five isomeric trichloroethylene complexes. The experimental results for the platinum tetrachloroethylene complexes can be summarized by

TABLE 1

NISEMO results for tetrachloroethylene complexes

Complex	Orbital energy sum/eV	Overlap population
$[(PH_3)_2Pt(\pi\text{-}C_2Cl_4)]$ (VI)	−985·91	2·80
trans-$[ClPt(PH_3)_2(\sigma\text{-}C_2Cl_3)]$ (VII)	−992·23	3·49
cis-$[ClPt(PH_3)_2(\sigma\text{-}C_2Cl_3)]$ (VIII)	−992·41	3·54

$$[Pt(PPh_3)_4] + C_2Cl_4 \xrightarrow[C_6H_6]{105\ ^\circ C} [(\pi\text{-}C_2Cl_4)Pt(PPh_3)_2] + 2PPh_3 \qquad (6)$$

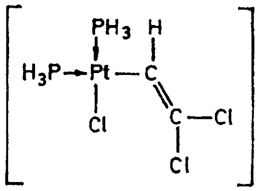
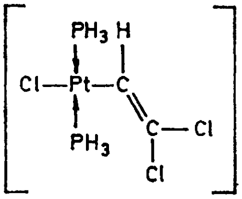
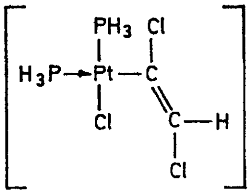
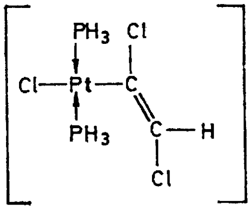
$$[(\pi\text{-}C_2Cl_4)Pt(PPh_3)_2] \xrightarrow[\text{reflux}]{\text{EtOH}} cis\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}C_2Cl_3)] \qquad (7)$$

$$cis\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}C_2Cl_3)] \xrightarrow[C_6H_6]{170\ ^\circ C} trans\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}C_2Cl_3)] \qquad (8)$$

equations (6)—(8).[12,17,18] In the absence of more definitive kinetic and thermochemical studies, these experimental results imply the order of stabilities *cis*-$[Cl(PPh_3)_2Pt(\sigma\text{-}C_2Cl_3)]$ > *trans*-$[Cl(PPh_3)_2Pt(\sigma\text{-}C_2Cl_3)]$ > $[(\pi\text{-}C_2Cl_4)Pt(PPh_3)_2]$. Table 1 shows the same order of stabilities in either the total overlap population or the OES.

TABLE 2

NISEMO results for trichloroethylene complexes

Complex		Orbital energy sum/eV	Overlap population
$[(PH_3)_2\,Pt\,(\pi\text{—}C_2HCl_3)]$	(IX)	−887·19	3·38
	(X)	−893·59	4·03
	(XI)	−893·27	3·97
	(XII)	−893·59	3·89
	(XIII)	−893·50	3·85

Experimental results for the platinum trichloroethylene complexes can be summarized by equations (9)—(12).[12,13,16] From these results a similar stability

$$[Pt(PPh_3)_4] + HC_2Cl_3 \xrightarrow[C_6H_6]{105\ ^\circ C} trans\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}HC_2Cl_2)] \qquad (9)$$

$$cis\text{-}[Cl_2Pt(PPh_3)_2] + HC_2Cl_3 \xrightarrow[N_2H_4]{\text{neat}} trans\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}HC_2Cl_2)] \qquad (10)$$

$$cis\text{-}[Cl_2Pt(PPh_3)_2] + HC_2Cl_3 \xrightarrow[\text{EtOH, }N_2H_4]{25\ ^\circ C} cis\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}HC_2Cl_2)] \qquad (11)$$

$$\begin{tikzcd} cis\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}HC_2Cl_2)] \arrow[d, bend right, "\text{EtOH, } N_2H_4\text{, heat (a)}"'] \arrow[d, bend left, "C_6H_6\text{, 110 °C (b)}"] \\ trans\text{-}[Cl(PPh_3)_2Pt(\sigma\text{-}HC_2Cl_2)] \end{tikzcd} \qquad (12)$$

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[20] D. R. Fahey, *J. Amer. Chem. Soc.*, 1970, **92**, 402.

[21] A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 4023.

[22] R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell *J. Amer. Chem. Soc.*, 1970, **92**, 1511.

series to that in the previous paragraph can be deduced, *i.e. cis-* $\geqslant$ *trans-* $>$ π-, and the data in Table 2 agree with these results. The vinyl complexes are more stable than the π-complex and the *cis*-complexes are more, but only slightly more, stable than the *trans*, which in view of the known stereochemistry of Pt^{II} is reasonable. The present experimental data do not preclude the possibility of some of the isomers produced being kinetically rather than thermodynamically preferred. Our calculations, of course, correspond to the thermodynamically more stable case.

The calculations also permit comments on the isomerization of the π-trichloroethylene complex. For tetrachloroethylene the π-halogeno-olefin–halide-vinylide rearrangement has a calculated energy change (ΔE) of $16{\cdot}41 \pm 0{\cdot}09$ eV, *cf.* $6{\cdot}24 \pm 0{\cdot}16$ eV for trichloroethylene. Previous work,[3] on the transformation between pseudo-tetrahedral and square-planar forms of the complexes, show that ΔE values of 3—7 eV are within the uncertainties of calculations taken to represent thermal accessibility. This conclusion is strongly implied here and suggests that, at room temperature, the $\pi \longrightarrow \sigma$ isomerization proceeds readily for the trichloroethylene complex.

When hydrogen is substituted for chlorine to give trichloroethylene, the OES fails to make a distinction between the four chloro(dichlorovinyl)isomers, whereas the total overlap population does. Bland and Kemmitt[13] were able to distinguish only *cis-* and *trans*-configurations around the metal atom. NISEMO calculations appear to distinguish this difference correctly and, in the total overlap population, give the best distinction between *cis-* and *trans*-structure around the unsaturated ligand. This leads to the conclusion that the complexes isolated by Bland and Kemmitt have structures (X) and (XI) (Table 2), which is reasonable since the molecular-orbital coefficients for the chloro(trichlorovinyl) complexes reveal a significant non-bonded interaction between the chlorine atom geminal to the platinum and the platinum atom itself. The same situation obtains in the chloro(dichlorovinyl) complexes of similar stereochemistry [(XII) and (XIII), Table 2]. Assuming similar transition states, a non-bonded Cl–Pt interaction will persist throughout most of the reaction path of the product when tetrachloroethylene undergoes $\pi \longrightarrow \sigma$ isomerization. This same non-bonded interaction cannot, however, occur when trichloroethylene isomerizes. Since the interaction is repulsive, as indicated by the total overlap population, the fact that the rate of $\pi \longrightarrow \sigma$ isomerization for the tetrachloroethylene complex is roughly 1 000 times slower than that for the trichloroethylene complex[16,17] can be rationalized.

Hydrogen Chloride Addition to Complexed Acetylene.—The addition of acids to platinum acetylene complexes has been investigated for both HCl[23,24] and acetic acid.[25] The mechanism postulated for the reaction of HCl with the complex $[(PPh_3)_2Pt(MeC{\equiv}CMe)]$ is given in equations (13)—(16). The various possible

$$[(Ph_3P)_2Pt(MeC{\equiv}CMe)] + HCl \longrightarrow [(PPh_3)_2Pt(MeC{\equiv}CMe)HCl] \tag{13}$$

$$[(PPh_3)_2Pt(MeC{\equiv}CMe)HCl] \longrightarrow \textit{trans}\text{-}[(PPh_3)_2PtCl(MeC{=}CHMe)] \tag{14}$$

$$\textit{trans}\text{-}[(PPh_3)_2PtCl(MeC{=}CHMe)] + HCl \longrightarrow [(PPh_3)_2Cl_2Pt(MeC{=}CHMe)H] \tag{15}$$

$$[(PPh_3)_2Cl_2Pt(MeC{=}CHMe)H] \longrightarrow \textit{cis}\text{-}[Cl_2Pt(PPh_3)_2] + \textit{trans}\text{-but-2-ene} \tag{16}$$

intermediate structures which could be involved in this reaction were calculated as a further test (Table 3). The six-co-ordinate adducts (XV)—(XVIII) have a lower average total overlap population (6·93 e) than the vinyl complexes (XIX)—(XXII) (7·8 e). These differences are significant and clearly favour the vinyl form. A driving force is suggested for formation of the latter when the 'six-co-ordinate' π-complex and the halide–vinylide are of approximately equal energy. Since controlled addition of 1 mole of acid to 1 mole of π-acetylene square-planar complex yields the vinyl complex, this tends to support the view[26-33] that the σ–π synergism is necessary. The question of whether a low-temperature reaction would yield the π-acetylene 'six-co-ordinate' adduct is thus raised.

The dp^2 hybridization scheme proposed for square-planar olefin and acetylene π-complexes does not favour the isolation of such an intermediate, since the orbitals required for bond formation on the basis of symmetry are already utilized in a σ–π synergic bond. In the xy plane of the π-acetylene complex, the d_{xz} and d_{yz} orbitals are already involved in the π-bond.[1,2] The 'six-co-ordinate' adduct would thus form along the z axis, the only z coaxial orbital available being d_{z^2}, which could form a three-centre bond. This type of bond along the z axis would be stable only if there was sufficient inertia from *polyatomic* groups along this axis to prevent rearrangement. With simple acids such as HCl this is not the case,* and the six-co-ordinate species should be only very slightly stable.

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* H. C. Clark, personal communication. The complexes do not appear to display any π-bonding and can be viewed as six-co-ordinate adducts which have sufficiently large and electronegative ligands that the metastable six-co-ordinate species is isolable. Five- or six-co-ordinate complexes isolated from the reaction of tetrafluoroethylene or hexafluorobut-2-yne with $[MePtXL_2]$ can be regarded in a similar fashion. This supports our view that the only z coaxial orbital available is d_{z^2}, which necessarily limits bonding most probably to a three-centre two-electron bond (preventing π-bond formation or synergism with the CF_3 group); this lack of π-bonding was predicted by one of us (K. S. W.) on the basis of *this* model.

[23] P. B. Tripathy and D. M. Roundhill, *J. Organometallic Chem.*, 1970, **24**, 247.

[24] P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1970, **92**, 3825.

[25] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Comm.*, 1969, 613.

[26] D. M. Roundhill, *Inorg. Chem.*, 1970, **9**, 254.

[27] D. M. Roundhill, *Chem. Comm.*, 1969, 567.

[28] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.

[29] H. Singer and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2516.

[30] D. M. Roundhill and H. B. Jonassen, *Chem. Comm.*, 1968, 1233.

[31] J. C. Bailar, jun., and H. Itatani, *Inorg. Chem.*, 1965, **4**, 1618

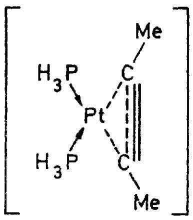
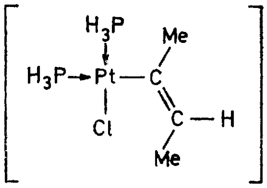
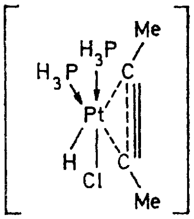
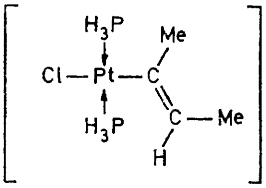
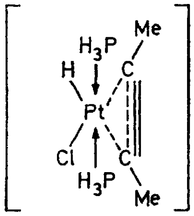
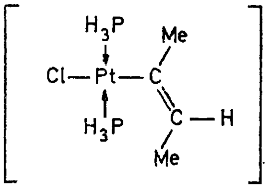
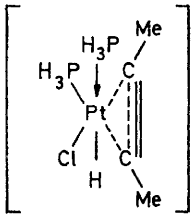
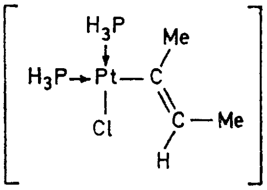
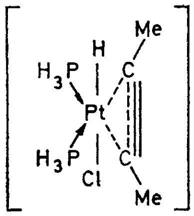
[32] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.

[33] J. H. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, 1969, **8**, 2591.

The overlap population indicates a preference for the *cis*-configuration around the unsaturation in the vinyl complex and experimental evidence confirms this.[34] The overlap population for the vinyl complexes is not altered significantly by a *cis*- or *trans*-structure around the metal, a consequence of modelling sterically complex phosphines with PH_3. The *cis*- or *trans*-structure around the unsaturation on the other hand influences these model complexes much more. Since the same basis set was used for the platinum throughout the calculation the data definitely indicate that steric effects become important. Studies of olefin and acetylene complexes with compact phosphines such as PF_3 should be very revealing.

TABLE 3

Energies of complexes derived from but-2-yne

Complex		Orbital energy sum/eV	Overlap population	Complex		Orbital energy sum/eV	Overlap population
	(XIV)	−739·65	7·98		(XIX)	−872·76	7·68
	(XV)	−873·83	6·96		(XX)	−871·25	7·93
	(XVI)	−873·81	6·78		(XXI)	−872·43	7·69
	(XVII)	−874·00	6·98		(XXII)	−871·55	7·92
				HCl		−132·21	0·68
	(XVIII)	−873·97	7·01				

Since the path involving the six-co-ordinate complex seems improbable, alternative mechanisms such as protonation and exchange of complexed acetyl-

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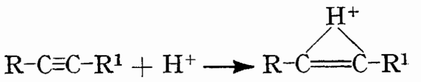
[34] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333; P. B. Tripathy, B. W. Reroe, K. Adzamli, and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1971, **93**, 4406.

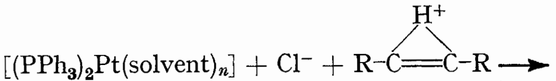
enes[5,33,35] must be considered through hydrido-complexes.

Protonation Mechanism. Equations (17)—(20) (R, R^1 = alkyl) explain the preponderance of *trans*-olefin

$$[(PPh_3)_2Pt(R{-}C{\equiv}C{-}R^1)] + n(\text{solvent}) \longrightarrow [(PPh_3)_2Pt(\text{solvent})_n] + R{-}C{\equiv}C{-}R^1 \quad (17)$$

 (18)

$$R{-}C{\equiv}C{-}R^1 + H^+ \longrightarrow R{-}\overset{H^+}{C{=}C}{-}R^1 \quad (18)$$



$$[(PPh_3)_2Pt(\text{solvent})_n] + Cl^- + R{-}\overset{H^+}{C{=}C}{-}R \longrightarrow$$

$$cis\text{- or } trans\text{-}[(PPh_3)_2PtCl(\sigma\text{-}RC_2R^1H)] \quad (19)$$

$$[(PPh_3)_2PtCl(\sigma\text{-}RC_2R^1H)] + HCl \longrightarrow cis\text{-}[Cl_2Pt(PPh_3)_2] + trans\text{-olefin} \quad (20)$$

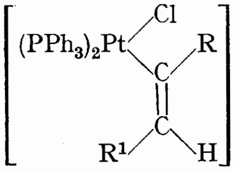
since acetylenes are well known to undergo *trans*-addition of acids. *cis*-Addition, ultimately yielding a *cis*-olefin might also be expected; however, in the presence of an excess of the acid, *cis–trans*-isomerization of the free olefin should occur, a possible explanation for the formation of minor amounts of the *cis*-product. This is particularly valid for conditions which lead to the complex *cis*-$[Cl_2Pt(PPh_3)_2]$ in these reactions.[36]

Hydride Mechanism. The experimental results can be explained by either the protonation or the hydride mechanism. The former is supported by the known exchange and dissociation of complexed acetylenes to form free acetylenes[28,35] and the familiar *trans*-addition of Brønsted acids to acetylenes to form *trans*-olefins. The hydride mechanism is supported by the known exchange of ethylene with platinum hydrido-complexes[37]

$$[(PPh_3)_2Pt(RC{\equiv}CR^1)] + n(\text{solvent}) \longrightarrow [(PPh_3)_2Pt(\text{solvent})_n] + RC{\equiv}CR^1 \quad (21)$$

$$[(PPh_3)Pt(\text{solvent})_n] + HCl \longrightarrow [(PPh_3)_2HPtCl] + n(\text{solvent}) \quad (22)$$

$$[(PPh_3)_2HPtCl] + RC{\equiv}CR^1 \longrightarrow$$

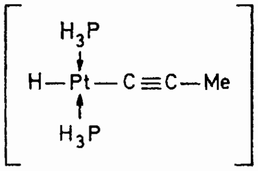
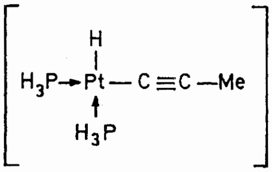
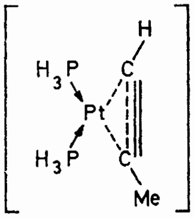
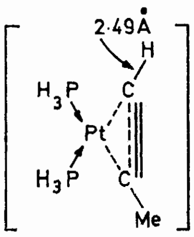
 (23)

and by the addition of acetylenes to platinum hydrido-complexes to form vinyl complexes.[38,39] Since the reaction of *trans*-β-bromostyrene with $[Pt(Ph_3P)_4]$ yields[34] *trans*-[PtBr(H–C=CHPh)$(PPh_3)_2$], platinum–carbon bond fission seems to occur either with inversion of configuration, or with initial formation of *cis*-olefins by addition of acids to zerovalent platinum acetylene complexes with subsequent isomerization to *trans*-olefins.[25] Reaction (23) should test these hypotheses.

Acetylene–Acetylide-Hydride Rearrangement.—Reactions of monosubstituted acetylenes with zerovalent Pt and Pd follow the same trend as that observed for halogeno-olefins.[5] For Pt, the π-complex is formed first, but can be isomerized to the acetylide–hydride, whereas for Pd the acetylide–hydride is usually obtained directly.[40] The Pt reaction yields an acetylide–hydride complex directly in one case,[30,33] however, the reaction proceeds slowly and there are preparative difficulties. The complex $[Pt(PPh_3)_4]$ reacts with β-halogeno-acetylenes to produce allenyl–halide complexes.[41] This implies that platinum complexes containing π-bonded acetylenes can rearrange to form carbon–platinum σ-bonds, and that acetylide–hydride rearrangement probably proceeds through a μ-bonded intermediate. Calculations to test this hypothesis for propyne complexes are presented in Table 4.

TABLE 4

Energies of platinum propyne complexes

Complex		Orbital energy sum/eV	Overlap population
	(XXIII)	−653·56	6·54
	(XXIV)	−653·36	6·60
	(XXV)	−650·35	6·31
	(XXV)	−653·38	5·84

The *cis*- and *trans*-acetylide–hydride complexes are very nearly equal in total overlap population. The

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[35] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1969, **46**, 3879.

[36] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.

[37] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 190.

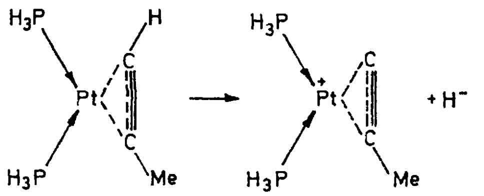
[38] H. C. Clark and W. S. Tsang, *Chem. Comm.*, 1966, 123.

[39] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 1967, **89**, 529.

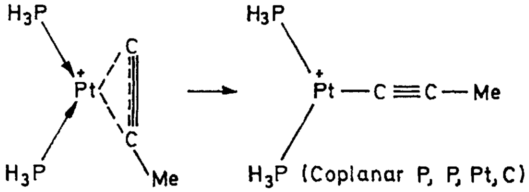
[40] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259.

[41] J. P. Collman, J. N. Cawse, and J. W. Kang, *Inorg. Chem.*, 1969, **8**, 2574.

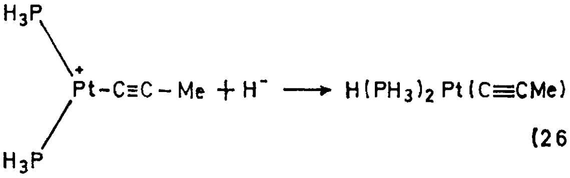
π-complex is however definitely less stable than either the *cis*- or *trans*-oxidative adduct. Two features of the distorted π-complex, which contains an elongated acetylenic C–H bond (2·49 Å), are of interest: (*a*) it is of comparable energy to the oxidative adducts, but more stable than the undistorted π-complex; and (*b*) an orbital-population analysis shows the acetylenic hydrogen to be almost completely hydridic. Thus monosubstituted π-acetylene complexes probably rearrange to the acetylide–hydride complexes *via* an S_N1 (lim.) type mechanism involving loss of hydride, rearrangement to a new cationic complex, and recombination [equations (24)—(26)]. The stereochemistry of the product in (26) has not been specified because it is not possible to exclude the *cis*-form unequivocally. Indeed, the geometry of hydride attack may be the major factor controlling the stereochemistry of the product.



(24)



(25)



(26)

The slight energy difference (0·18 eV, 4·2 kcal) between the oxidative adducts and the distorted π-complex may be significant *despite the absolute computational uncertainty*. If an excess of the monosubstituted acetylene were present, the cation could attack the free acetylene leading to the formation of a diacetylide, which indeed has been isolated.[30]

CONCLUSIONS

Although quantitative results were not attempted, the qualitative results obtained offer much promise for deducing and predicting the course of various reactions. *Ab initio* calculations for such large molecules, although quantitative, are costly, extremely laborious, and time consuming. Much of the same information may be deduced from a sequence of qualitative calculations. The NISEMO method represents an economical alternative since it allows rapid calculations, for such sequences of molecules, in sets of series which are designed to answer *qualitative questions*.

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