

1. Alkyl Shifts between Transition Metals and Coordinated Main Group Atoms

by J.V. Ortiz, Zdeněk Havlas and Roald Hoffmann*

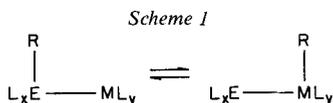
Department of Chemistry, Cornell University, Ithaca, New York 14853

(29.VIII.83)

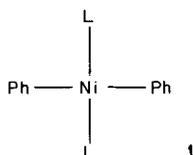
Summary

This work considers the theoretical aspects of the shift of an alkyl (or aryl) group from a coordinated phosphine to the 16-electron d^8 transition metal to which it is coordinated. This rearrangement at first seems to resemble an anionic [1,2]-sigmatropic shift. But a detailed analysis of the relatively low barrier calculated for the reaction shows how all traces of the forbiddenness of the reaction have vanished. Phenyl migration should be still more facile. We also analyze in some detail the possible pathways of alkyl halide addition to a phenyl-Pt complex. An alkyl migration, now from metal to coordinated C-atom, could possibly intervene in this process.

Introduction. – This work was stimulated by two seemingly disparate, yet in the end related, experimental findings or mechanistic hypotheses. They both involve an organometallic reaction in which an alkyl or aryl group migrates, or does so potentially between a transition metal and an attached main group ligand (*Scheme 1*).

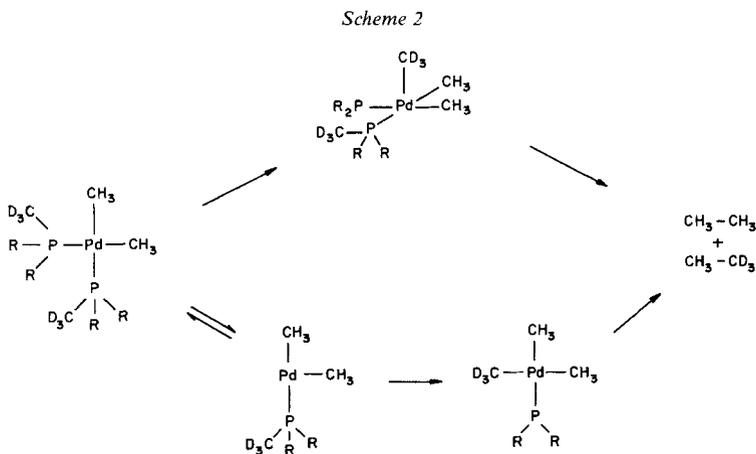


In several studies of reductive elimination, products have been found which originate partially or entirely from phosphine ligands. Complexes of Pd, Ni or Co, zerovalent or divalent, are known to catalyze the couplings between olefins and aryl phosphines, producing aryl alkenes [1]. Two mechanisms have been proposed for migration of aryl from phosphine toward the metal: a shift of aryl from the metal-bonded phosphine or an oxidative addition of arylphosphine. The reaction is followed by reductive elimination of hydrocarbons. Oxidative addition of Ph_3P to zerovalent Ni- or Pd-complexes has been studied in more detail by *Fahey & Mahan* [2], but direct formation of the crucial intermediate **1** was not observed.

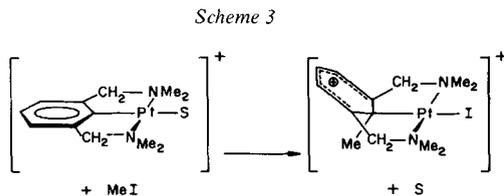


Several reactions producing dimers, trimers or other complicated structures with aryl bridges or terminal aryls are known [3]. The only sources of aryls are the phosphine ligands. These reactions must involve P-C bond fission and metal-aryl bond formation.

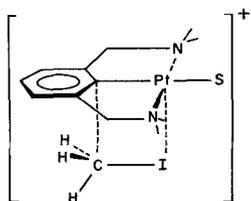
Gillie & Stille [4], in the course of a study of 1,1-reductive elimination, recently uncovered an interesting side-reaction in which an alkyl group bonded to Pd-atom and another alkyl on a ligated phosphine are eliminated (*Scheme 2*). Two of several possible mechanisms for this reaction are shown.



It would seem at first sight that the recent finding by *van Koten et al.* of the remarkable addition of MeI to a constrained phenyl-Pt complex [5] [6] (*Scheme 3*) is not related to the previous reactions. But let us examine the mechanism of this reaction in some detail.

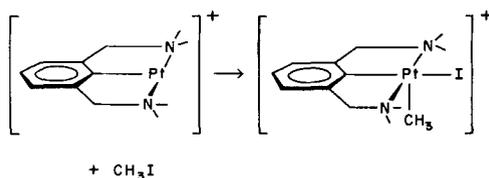


The arms of the *N,N'*-2,6-bis(dimethylaminomethyl)phenyl ligand prevent a simple reductive elimination of a methylated aryl from the Pt-center and stabilize the coordinated hexadienyl cation, which, but for the amine anchors, would be considered a frozen intermediate. Does the MeI add across the C-Pt bond in a concerted manner *via* the 4-center transition state **2**, or is the initial step an oxidative addition of MeI on the Pt-center alone (*Scheme 4*)?



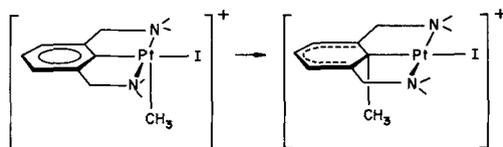
2

Scheme 4



A subsequent methyl migration from Pt to aryl-C-atom (*Scheme 5*) could complete the reaction. It is this final step, a hypothetical metal to ligand alkyl migration which provides the conceptual link with the earlier reactions.

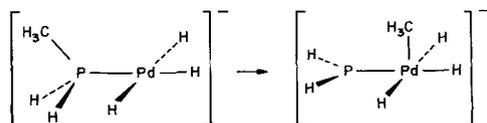
Scheme 5



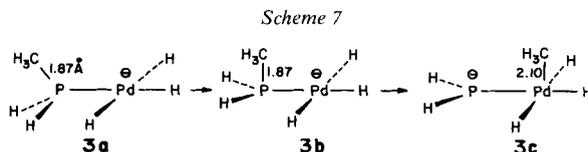
We begin our analysis with an extended *Hückel* and frontier orbital study of the migration of an alkyl or hydrogen between a transition metal and a coordinated main group ligand.

Migration of Methyl from Phosphorus to Palladium. – The model reaction which we first investigated is shown in *Scheme 6*. The reactant is a 16-electron square planar d⁸-complex of Pd(II), the product a 16-electron square pyramidal complex of Pd(IV). Monodentate phosphido ligands such as we postulate in the product are relatively uncommon, but not unknown [7].

Scheme 6



Since the extended *Hückel* method is not reliable for distances, we did not calculate a complete reaction path for the previous reaction, but instead considered a two-stage hypothetical reaction coordinate (*Scheme 7*). The first stage, costing some 0.6 eV in our calculations (see *Appendix* for computational details) was a deformation of the phosphine ligand from a tetrahedral geometry to one in which the P-CH₃ bond is perpendicular to the H₂P-PdH₃-plane. The second stage is a linear transit from **3b** to **3c**, the actual migration.



The calculated barrier for this reaction (*Fig. 1*) is 23 kcal/mol. The *Walsh* diagram for the reaction is shown in *Fig. 2*. The reactant is a typical square-planar d⁸-complex. Its four higher levels are quite well localized on the metal, and are made up of Pd *xy*, *xz*, *yz* and *z*². Phosphorus-to-carbon bonding is concentrated in a lower lying σ -orbital near -15 eV, orbital number 19. The product is a coordinatively unsaturated 16-electron ML₅-complex. The electronic structure of such molecules is well-known [8]. There is a relatively low-lying hybrid orbital pointing away from the ML₅ near -10 eV. The higher occupied orbitals are *xz*, *yz*, and *xy*. The *z*²-orbital is now involved in σ -bonding to the methyl group, No. 15, and the phosphido lone pair lies below it in energy.

The reaction seems a smooth one, with no great hills in specific orbitals, such as might come about in symmetry-forbidden reactions with real or avoided crossings. The overlap populations also evolve smoothly (*Fig. 3*).

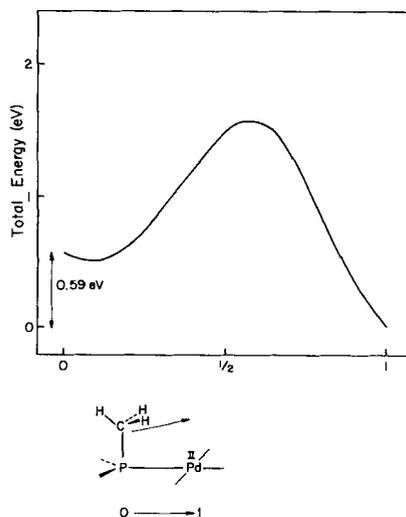


Fig. 1. Potential energy curve for methyl migration in a model $\text{H}_2\text{P}(\text{CH}_3)\text{PdH}_3^-$

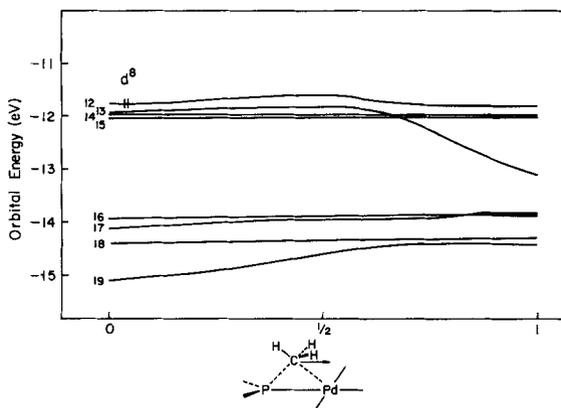


Fig. 2. The evolution of the frontier levels during methyl migration in $H_2P(CH_3)PdH_3^-$

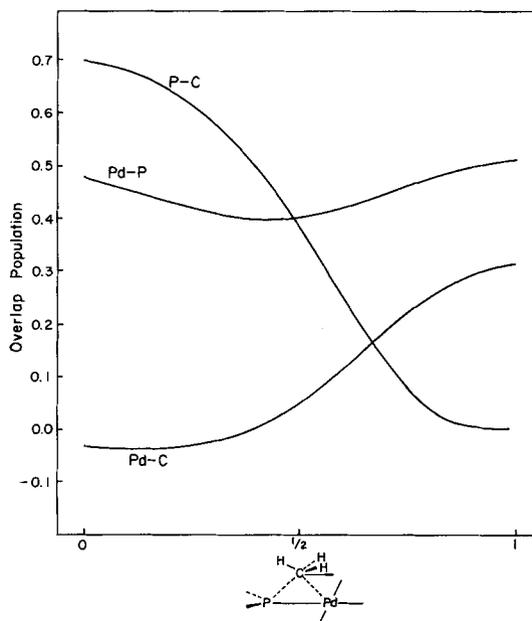
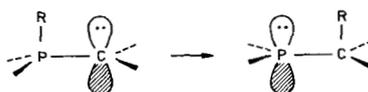
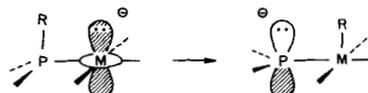


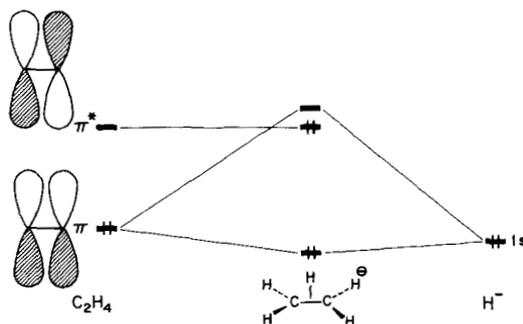
Fig. 3. Changes in selected overlap populations along the migration coordinate in $H_2P(CH_3)PdH_3^-$

Why should there be a shadow of concern in our minds about this being possibly a 'forbidden' reaction? The reason is that the alkyl migration is, in one way of looking at it, a three-center four-electron process, involving a metal z^2 -orbital. Such reactions, the

prototype of which is the [1,2]-anionic sigmatropic shift (*Scheme 8*) are forbidden. Let us examine the progression from the [1,2]-sigmatropic shift, through a related rearrangement of a phosphonium ylid (*Scheme 9*) to the reaction of interest to us (*Scheme 10*).

Scheme 8*Scheme 9**Scheme 10*

The analysis of the simple sigmatropic shift (*Scheme 8*) is well-known [9]. The easiest way to think of the transition state of this reaction is to imagine the interaction of H^- with an ethylene, as shown in (*Scheme 11*). Midway in the reaction the H^- lone pair can interact only with ethylene π and not with π^* . If one had two electrons (a cationic [1,2]-sigmatropic shift) that would be fine, but if one has four electrons the top two electrons must enter a high-lying MO.

Scheme 11

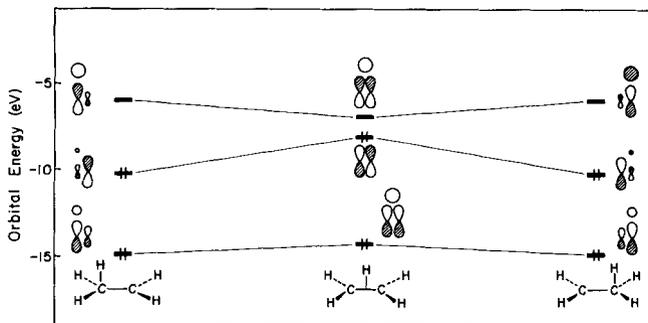


Fig. 4. Evolution of the frontier levels in H-migration in CH_3CH_2^-

As the orbitals actually evolve (Fig. 4) there is no level crossing. Nevertheless this is clearly a forbidden reaction.

In the phosphonium ylid rearrangement (Scheme 9) there is now no symmetry left even in the transition state. Nevertheless the general features of the anionic [1,2]-sigmatropic shift remain, as the Walsh diagram of Fig. 5 shows. Near the transition state the $\text{R}_2\text{P}-\text{CH}_2^+$ -fragment has orbitals much like those of ethylene, though left-right symmetry is lost. And these orbitals interact with the R^- lone pair along the lines in Scheme 11. The computed activation energy for rearrangement in our model phosphonium ylid is very high, 140 kcal/mol.

The orbitals of $\text{R}_2\text{P}-\text{PdH}_3$ are very different from those of H_2CCH_2 or $\text{R}_2\text{P}-\text{CH}_2^+$. They are shown schematically in 4. Lowest in energy is the phosphido lone pair. Above it

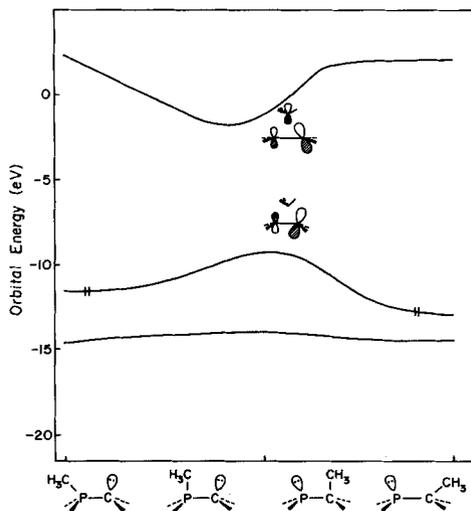
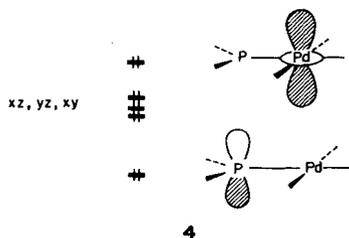


Fig. 5. Walsh diagram for methyl migration in $(\text{CH}_3)_3\text{PCH}_2$



are the Pd xz , yz , xy which are not important in the reaction, because they do not have the correct symmetry or pseudosymmetry to mix at all or much with the R^- -orbital. The metal z^2 is different – it does interact substantially. And with the given electron count neutral R_2P-PdH_3 is formally Pd(IV). Thus the z^2 -orbital is empty. An interaction diagram with R^- at the transition state (Fig. 6) shows the nice stabilizing interaction and formal electron transfer from the R^- lone pair to the z^2 . There are no orbitals at high energy in the transition state, and this is not a forbidden reaction.

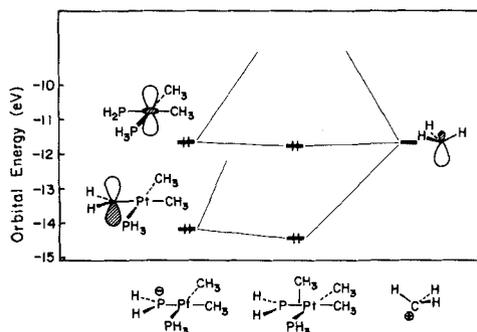
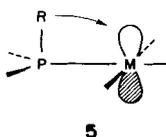


Fig. 6. Interaction diagram for the transition state region in $h_2P(CH_3)Pt(PH_3)(CH_3)_2$. The orbitals of methyl are at right.

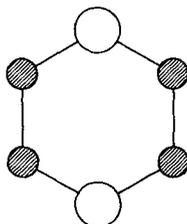
One resolution of the seeming paradox of an allowed four-electron [1,2]-sigmatropic shift is to realize that the d^8 metal center is ambiphilic – a base through its z^2 , but also an acid through its metal p_z -orbital. This dual acid-base character manifests itself in the stacking mode aggregation of some d^8 -complexes in the solid state and in solution [10].

From the viewpoint of the acid character of the metal this reaction is as much a two-electron [1,2]-sigmatropic shift, **5**, as it is a four-electron one. Actually, we find very little participation of the metal p -orbital in the interaction. The migrating C-atom does, however, become more positive in the intermediate stages of the reaction.



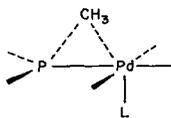
Possible Stabilization of the Reaction Pathway. – The computed activation energy for the shift of a methyl group in the simplest $\text{H}_2\text{P}(\text{CH}_3)\text{-PdH}_3^-$ -model was 23 kcal/mol. In a slightly more realistic $\text{H}_2\text{P}(\text{CH}_3)\text{-Pd}(\text{PH}_3)(\text{CH}_3)_2$ we calculate a barrier of 31 kcal/mol. These are, of course subject to the large uncertainties of the extended *Hückel* model. Can we lower the activation energy for the reaction? One possibility is to provide a π -system in the migrating group so as to strengthen bonding in the intermediate stages of the reaction. We probed this possibility with a phenyl group.

For phenyl migration, the barrier is reduced to a very low 1.6 kcal/mol when the plane of the aromatic ring is perpendicular to the Pd–P axis. (When the plane is parallel, the barrier is 43.9 kcal/mol.) One of the e_{1g} π^* -orbitals of the phenyl, **6**, indeed stabilizes the

**6**

Pd d_{z^2} -orbital in the intermediate points of the transit. The Pd–C overlap population therefore rises monotonically, unlike the case of methyl migration, where there is an initial dip in this quantity. By the latter stages of the transit, the d_{z^2} to π^* -interaction has waned; it nearly vanishes at the final point. Overlap population curves for the P–C and P–Pd interactions have nearly identical shapes for the methyl and phenyl transits. π -Stabilization of 1,2-phenyl shifts has been previously analyzed for carbanions [11]. The phenyl migration barrier that we calculate is too low, but we are confident that it in fact reflects a trend-migration of phenyl groups from coordinated phosphines to metals should be facile.

A σ -donating ligand *trans* to the shifting methyl group, **7**, mixes the Pd z - and z^2 -orbitals, making a larger lobe that has a bigger overlap than the pure z^2 -orbital with the

**7**

methyl lone pair orbital. The nodal plane cone is more open in the case of the hybrid. Metal-to-methyl bonding occurs in the earlier stages of the reaction coordinate. The calculated barrier is somewhat lower, 18 kcal/mol. Of course, the product is greatly stabilized, as it is now coordinatively saturated.

To emphasize the role of the Pd p_z -orbital and increase mixing with the z^2 -orbital, we put π -accepting ligands (carbonyls) on Pd. These ligands seem to have, according to our calculations, negligible influence on the energy surface, however.

Calculation of fragment charges shows a bigger positive charge on the methyl in the region of the reaction barrier than for the starting or final structures. One might expect then that a less electronegative migrating group might have a lower activation energy to the P-to-metal shift. Our computed potential energy curve for SiH₃-migration (*Fig. 7*) shows a much lower activation energy, in fact some ‘leaning’ of the silyl group toward the metal.

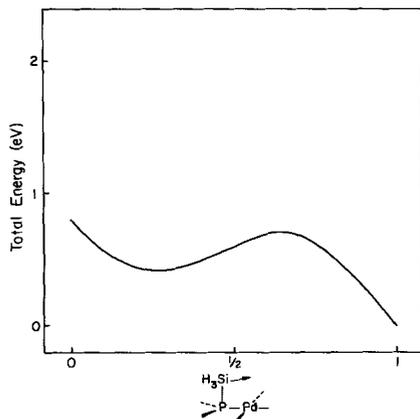


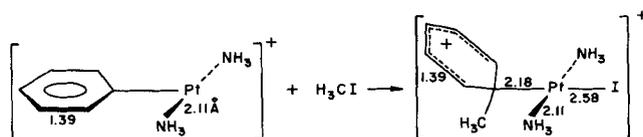
Fig. 7. Potential energy curve for silyl migration in $H_2P(SiH_3)PdH_3^-$

Abel & Sabherwa [12] have published reactions involving P–Si bond fission which can possibly be explained as SiR₃-migration. Nothing is known about the mechanism of these reactions.

In the course of the reaction there is formed a new lone pair on the phosphido group. One can think of stabilizing that lone pair by π -acceptors on P-atom. A model calculation (CN)₂PCH₃–PdH₃[–] given a small decrease of the barrier to 15 kcal/mol, with substantial product stabilization. There seem to be no phosphine ligands with π -accepting substituents, however.

The Addition of MeI to a Phenyl-Pt Complex. – We now turn to the addition of MeI to a constrained phenyl-Pt (*Scheme 3*), a reaction that could proceed in a concerted manner, or stepwise, with methyl migration from Pt to C. A somewhat simplified model of this system to be employed for the present calculations, is presented in *Scheme 12* along with some geometrical assumptions taken from X-ray crystallographic studies.

Scheme 12



The electronic structure of the reactant, $C_6H_5Pt(NH_3)_2^+$, is typical of d^8 ML_3 -fragments [13]. There are four high-lying filled orbitals, mainly metal xz , yz , xy , z^2 . One of them, xz , is involved in π -bonding with the arene. The benzene π -orbitals lie just below these metal MO's. Relatively low-lying is a hybrid of x^2-y^2 and z , pointing toward the missing fourth site in square planar coordination. These orbitals are shown in *Fig. 8*, along with those of MeI. The higher occupied MO's of the latter molecule are the expected iodide lone pairs.

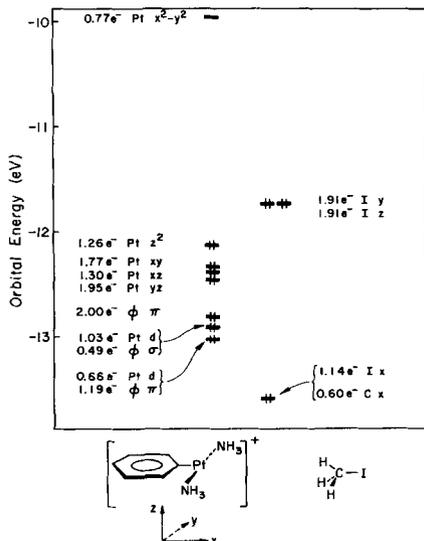
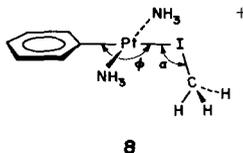


Fig. 8. Frontier orbitals of MeI and $PhPt(NH_3)_2^+$

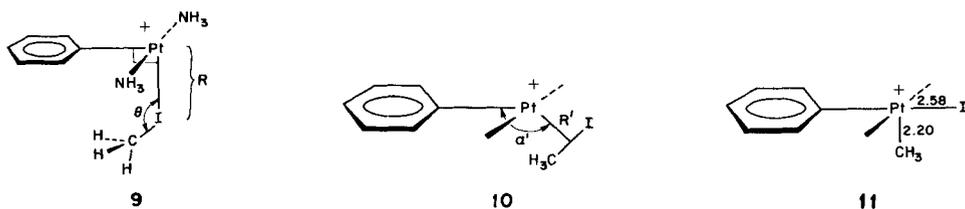
Maximizing the HOMO-LUMO donor-acceptor interaction suggests the formation of a complex where the Pt-I bond is perpendicular to the I-C bond **8**. Optimization of the Pt-I-C angle α for $R(Pt-I) = 2.5811 \text{ \AA}$ produces a minimum at $\alpha = 100^\circ$. The $(C_6H_5)(NH_3)_2Pt^+$ LUMO- H_3CI HOMO overlap population does, in fact, reach a



8

maximum at 90° , but this trend is slightly perturbed by the participation of the second HOMO (SHOMO) of MeI, the lone-pair I-orbital that lies along this fragment's C_3 -axis. SHOMO-LUMO overlap population ascends as the Pt-I-C angle increases, so the combined effect of the two interactions produces an energy minimum slightly above 90° . As might be expected from the nodal properties of the $C_6H_5(NH_3)_2Pt^+$ -fragment LUMO, ϕ , the C_2 -Pt-I angle, is computed to be 180° .

The approach of MeI along the axis perpendicular to the $C_6H_5Pt(NH_3)_2^+$ -plane (*i.e.* $\phi = 90^\circ$) is repulsive, as a result of destabilizing interactions between the I lone-pairs and Pt z^2 -orbital. Even with variations of the Pt–I–C bond angle, θ , in **9** that might suggest a connection with the aforementioned four-center reaction path, the repulsive character of the potential energy curve remains. Variation of the C_α –Pt–I angle ϕ leads smoothly back to the square planar ligand arrangement **8**.



We next began a more direct study of an oxidative addition reaction coordinate by using the midpoint of the H_3C-I bond as a focus. Let us define the C_α –Pt–midpoint of C–I bond angle as α' , defined in **10**. If α' and the Pt–midpoint distance R' are varied, the optimal α' increases slowly with R' . The minimum at $\alpha' = 150^\circ$, $R' = 2.5 \text{ \AA}$ serves as a convenient starting point for oxidative addition leading to the product structure **11**. The C_3 -axis of the methyl group is readjusted synchronously with changes in the Pt–I and Pt–C distances. *Fig. 9* shows the total energy along this reaction path, and *Fig. 10* the evolution of the overlap populations. Note the Pt–I bonding is already well-established at the beginning of the reaction. This leads us to another mode of analysis of the second stage of this reaction, namely a decomposition of the composite molecule into

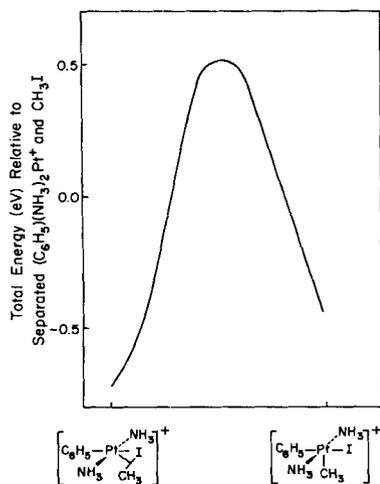


Fig. 9. Potential energy curve along a model reaction coordinate for oxidative addition of MeI to $PhPt(NH_3)_2^+$

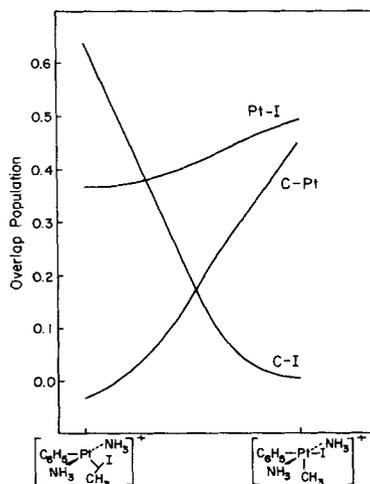
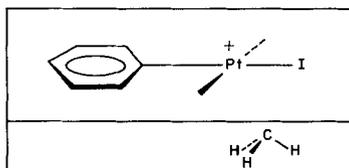


Fig. 10. Evolution of selected overlap populations along the reaction path of Fig. 9

$(C_6H_5)Pt(NH_3)_2I$ and CH_3^+ (Scheme 13). The CH_3^+ LUMO is an empty sp^3 -hybrid that rotates as the path proceeds. At first, the biggest interaction is with the HOMO of the $Ph(NH_3)_2PtI$ -fragment, primarily a lone-pair orbital on I. The CH_3^+ LUMO's interaction with the Pt z^2 -like orbital begins slowly, but rises rapidly near the middle of the path. The nodal structure of the z^2 -orbital prevents significant overlap from occurring until the C_3 -axis of the methyl is nearly aligned with the z^2 -lobe.

Scheme 13



Even larger barriers are obtained for the transit which begins from a structure such as **8**, with $\alpha = 100^\circ$. In a separate calculational experiment we tried to stabilize the product by adding a water molecule to the vacant coordination site, but this likewise was of no avail.

The final stage of the methyl's wanderings is the migration from the Pt to the phenyl C-atom. In the midst of this process, the C-ring's plane is tilted with respect to the plane of the Pt, the I⁻ and the two N-atoms. Let us imagine that this tilting to the final position of the phenyl ring precedes the migration of the methyl. Reaction coordinates for this migration (Scheme 14) produce a barrier of about 0.3 eV; the initial and final structures are within 0.1 eV of each other in total energy. The barrier is due to the factors mentioned in the previous discussion, except that the methyl has settled on an sp^3 -hybrid of the C-atom rather than on a p-orbital of the P-atom.



If the tilting of the phenyl is varied synchronously with the migration of the methyl, the barrier is eliminated. The energy curve along this reaction coordinate is in Fig. 11. In the middle of the curve, a shadow of the old barrier remains. Apparently, the wrong sign for ΔE is obtained, revealing deficiencies in the method of calculation. Many avoided crossings occur in the *Walsh* diagram since the formation and rupture of chemical bonds are spread over many molecular orbitals. Note the rate of change of certain overlap populations between atoms in Fig. 12. After the initial stages of the path, the C–C bond rapidly grows stronger. The removal of the barrier is effected by permuting the recrudescant sp^3 -hybrid at the phenyl C-atom to point toward the C_3 -axis of the methyl in the midst of the migration.

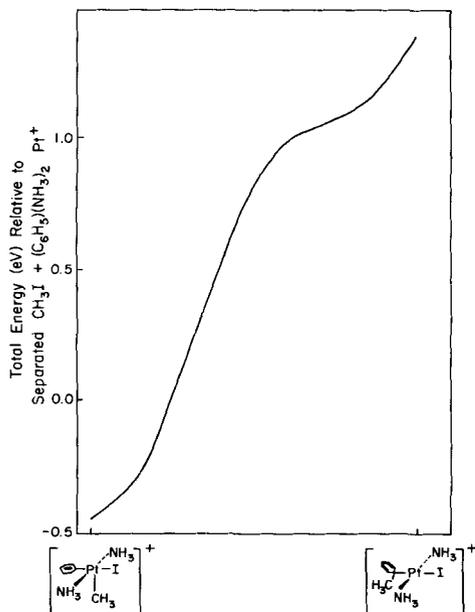


Fig. 11. Energy along a hypothetical reaction path for methyl migration from Pt to C in $\text{PhPt}(\text{CH}_3)(\text{NH}_3)_2\text{I}^+$

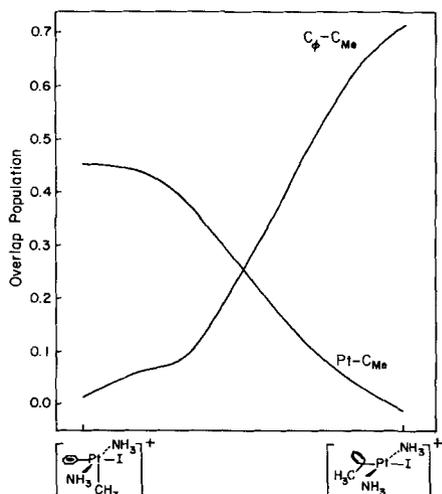
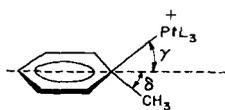


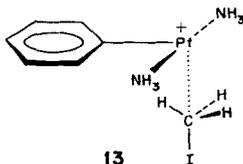
Fig. 12. Some overlap populations along the reaction coordinate of Fig. 11

Optimal arrangements of the PtL_3 - and CH_3 -groups about the sp^3 -ring C-atom have been calculated and are in qualitative agreement with the crystal structure of *van Koten's* complex. The best γ (defined in **12**) is near 60° and δ is near 30° . Potential energy curves with respect to γ and δ are rather soft, especially if the $\text{Pt}-\text{C}_\alpha-\text{C}_{\text{Me}}$ angle of 90° is returned. Distortions of 10° typically cost 0.1 eV. This may indicate that electronic structure considerations permit the length of chelating ligands to determine the geometry about the ring sp^3 -C-atom.



12

There exists an interesting alternative to mechanisms considered so far, and this is a process involving *inversion* at the methyl group. The approach of the MeI to the $\text{Pt } z^2$ -orbital is somewhat less repulsive if the CH_3 group is pointed at the metal, as indicated in **13**. Permitting the methyl H-atoms to come within 3.0 \AA raises the energy only 0.1 eV with



13

respect to the separated reactants. The LUMO of MeI is an antibonding C–I σ -orbital which is largely centered on the C-atom. This orbital's energy falls rapidly as the C–I bond length is stretched. Transmission of the methyl *via* inversion to the Pt therefore is a migration from one donor, I^- , to another, the Pt z^2 -orbital. An energy profile, shown in Fig. 13, contains a barrier of about 1.3 eV.

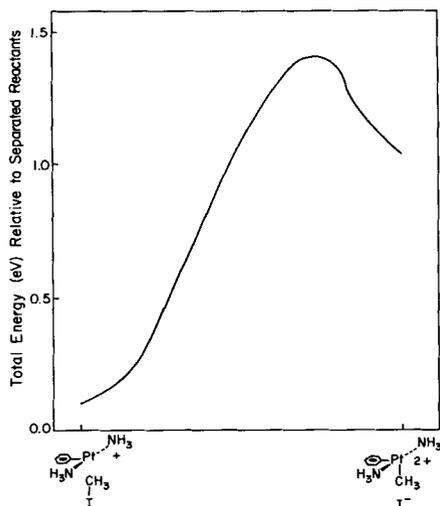


Fig. 13. Potential energy curve for a hypothetical inversion pathway of addition of MeI to $PhPt(NH_3)_2^+$

The barrier is due to the breaking of the C–I bond. The final product's energy could be greatly lowered by moving the I^- to the vacant square planar site, but the barrier is likely to remain. Moving the I^- to this site in the intermediate stages of the reaction path will not recoup much energy from Pt–I overlap until the latter energy points. At the same time, the destabilization from loss of C–I overlap will be exacerbated. Nevertheless, this mechanism is a reasonable alternative to the oxidative addition across the C–I bond, even if the initial approach is repulsive. Should the solvent molecule, omitted in most of these calculations, exhibit some reluctance to be moved aside by the I^- , this inversion pathway could be competitive.

We are grateful to *J. Stille* and *G. van Koten* for providing the stimulus for this work, and to both of them and *A. Yamamoto* for bringing several relevant references to our attention. The permanent address of *Z. Havlas* is the Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences, Prague. We thank the *National Science Foundation* for its generous support of this work through Research Grant CHE 7828048.

Appendix. – All calculations were performed by using the extended *Hückel* method [14] with weighted H_0 's [15]. The extended *Hückel* parameters used in our calculations are listed in the *Table*.

Table. Parameters Used in Extended Hückel Calculations

Orbital	H _{ii} , eV	ζ ₁	ζ ₂	C ₁ ^{a)}	C ₂ ^{a)}
Pd 5s	– 7.32	2.19			
5p	– 3.75	2.152			
4d	– 12.02	5.983	2.613	0.5535	0.6701
Pt 6s	– 9.077	2.554			
6p	– 5.475	2.535			
5d	– 12.59	6.013	2.696	0.6707	0.5844
C 2s	– 21.40	1.625			
2p	– 11.40	2.275			
P 3s	– 18.60	1.600			
3p	– 14.00	1.600			
Si 3s	– 17.30	1.383			
3p	– 9.20	1.383			
I 5s	– 17.80	2.680			
5p	– 12.00	2.320			
N 2s	– 26.00	1.950			
2p	– 13.40	1.950			
H 1s	– 13.60	1.30			

a) Contraction coefficients used in the double ζ-expansion.

Calculations on the PdH₃(PH₂)²⁻-fragment assumed Pd–H = 1.65 Å, Pd–P = 2.3 Å, P–H = 1.42 Å and H–P–Pd = 120°. The methyl shift from P to Pd linearly varied the perpendicular distance from the methyl-C-atom to the line connecting P to Pd, starting from 1.87 Å to 2.1 Å. For the PH₂CH₂CH₂⁻ calculations, the methyl-C-atom to P–C bond distance varied from 1.78 Å to 1.53 Å. The P₂P–CH₂ distance was 1.78 Å; tetrahedral angles were assumed.

For (C₆H₅)(NH₃)₂Pt⁺, C–C = 1.39 Å (regardless of tilting angle of the attached Pt(NH₃)₂-group), C–Pt = 2.183 Å, Pt–N = 2.114 Å, N–H = 1.08 Å, C–H = 1.09 Å. In structures where I⁻ is coordinated to Pt, Pt–I = 2.58 Å. For isolated MeI, or MeI coordinated through I alone, C–I = 2.05 Å. The oxidative addition of MeI across the C–I bond was studied by a linear variation of Pt–I distance, orientation of the CH₃ C_{3v}-axis, Pt–C distance, C(phenyl)–Pt–I and C(phenyl)–Pt–C(methyl). Migration of the methyl from the Pt to the phenyl group linearly varied the tilting of the Pt(NH₃)₂I-unit with respect to the phenyl plane and the perpendicular C(methyl) to C(phenyl)–Pt distance (2.2 Å to 1.55 Å). For the inversion pathway, the I–C–H angle was linearly varied from 109° to 71°. These assumptions are generally taken from [5].

REFERENCES

- [1] a) M.L.H. Green, M.J. Smith, H. Felkin & G. Swierczewski, *J. Chem. Soc., Chem. Commun.* 1971, 158; b) K. Kikukawa, T. Yamane, M. Tagaki & T. Matsuda, *J. Chem. Soc., Chem. Commun.* 1972, 965; c) T. Yamane, K. Kikukawa, M. Takagi & T. Matsuda, *Tetrahedron* 29, 955 (1973); d) R. Asano, I. Moritani, Y. Fujiwara & S. Teranishi, *Bull. Chem. Soc. Jpn.* 46, 2910 (1973); e) A. Nakamura & S. Otsuka, *Tetrahedron Lett.* 1974, 463; f) K. Kikukawa, T. Yamane, Y. Ohbe, M. Takagi & T. Matsuda, *Bull. Chem. Soc. Jpn.* 52, 1187 (1979); g) K. Kikukawa, M. Takagi & T. Matsuda, *Bull. Chem. Soc. Jpn.* 52, 1493 (1982); h) K. Kikukawa & M. Matsuda, *J. Organomet. Chem.* 235, 243 (1982).
- [2] D.R. Fahey & J.E. Mahan, *J. Am. Chem. Soc.* 98, 4499 (1976).
- [3] a) H.A. Patel, R.G. Fischer, A.J. Carty, D.V. Naik & G.J. Palenik *J. Organomet. Chem.* 60, C49 (1973); b) C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland & R. Mason, *J. Chem. Soc., Chem. Commun.* 1972, 87; c) D.R. Coulson, *Chem. Commun.* 1968, 1530; d) P. Vierling, J.G. Riess & A. Grand, *J. Am. Chem. Soc.* 193, 2466 (1981). In this study migration of phenyl from phosphoramidate to iron has been observed; e) R.

- Ugo, S. Cenini, M.F. Pilbrow, B. Deibl & G. Schneider*, *Inorg. Chim. Acta* 18, 113 (1976); f) *N.J. Taylor, P.C. Chien & J. Carty*, *J. Chem. Soc., Chem. Commun.* 1975, 448; g) *J.R. Blickensderfer & H.D. Kaesz*, *J. Am. Chem. Soc.* 97, 2681 (1975).
- [4] *A. Gillie & J.K. Stille*, *J. Am. Chem. Soc.* 102, 4933 (1980).
- [5] *D.M. Grove, G. v. Koten, J.N. Louwen, J.G. Noltes, A.L. Spek & H.J.C. Ubbels*, *J. Am. Chem. Soc.* 104, 6608 (1982).
- [6] *D.M. Grove, G. v. Koten & H.J.C. Ubbels*, *Organometallics* 1, 1366 (1982).
- [7] a) *E.L. Muetterties, J.F. Kirner, W.J. Evans, P.A. Watson, S. Abdel-Meguid, I. Tavanarepous & V.W. Day*, *Proc. Natl. Acad. Sci. USA* 75, 1056 (1978); b) *K. Issleib & E. Wenschuh*, *Chem. Ber.* 97, 715 (1964); c) *K. Issleib & E. Wenschuh*, *Z. Naturforsch. B* 17, 778 (1962); d) *K. Issleib & E. Wenschuh*, *Z. Naturforsch. B* 19, 199 (1964); e) *K. Issleib, H.O. Frohlich & E. Wenschuh*, *Chem. Ber.* 95, 2742 (1962); f) *E.W. Abel, R.A.N. McLean & I.H. Sabherwal*, *J. Chem. Soc. A* 1968, 2371; g) *P.J. Dommille, B.M. Foxman, T.J. McNeese & S.S. Wreford*, *J. Am. Chem. Soc.* 102, 4114 (1980); h) *H. Schumann & G.-M. Frisch*, *Z. Naturforsch.* 346, 748 (1979); i) *R.T. Baker, J.F. Whitney & S.S. Wreford*, *Organometallics* 2, 1049 (1983); j) *R.T. Baker, P.J. Krusic, T.H. Tulip, J.C. Calabrese & S.S. Wreford*, *J. Am. Chem. Soc.* 105, 6763 (1983); k) *S.M. Rocklage, R.R. Schrock, M.R. Churchill & H.J. Wasserman*, *Organometallics* 1, 1332 (1982); l) *L.D. Hutchins, R.T. Paine & C.F. Campana*, *J. Am. Chem. Soc.* 102, 4521 (1980); m) *V.W. Day, I. Tavanaiepour, S.S. Abdel-Meguid, J.F. Kirner, L.-Y. Goh & E.L. Muetterties*, *Inorg. Chem.* 21, 657 (1982); n) *D. Weber, E. Fluck, H.G. von Schnering & K. Peters*, *Z. Naturforsch.*, B 37, 594 (1982); o) *R.A. Jones, J.G. Lasch, N.C. Norman, B.R. Whittlesey & T.C. Wright*, *J. Am. Chem. Soc.* 105, 6184 (1983).
- [8] *M. Elian & R. Hoffmann*, *Inorg. Chem.* 14, 1058 (1975).
- [9] *R.B. Woodward & R. Hoffmann*, *J. Am. Chem. Soc.* 87, 2511 (1965).
- [10] a) 'Extended Linear Chain Compounds', Volumes 1–3, ed. J.S. Miller, Plenum, New York, 1982; b) *J.S. Miller & A.J. Epstein*, *Prog. Inorg. Chem.* 20, 1 (1976).
- [11] *H.E. Zimmerman & A. Zweig*, *J. Am. Chem. Soc.* 83, 1196 (1961).
- [12] *E.W. Abel & I.H. Sabherwal*, *J. Organomet. Chem.* 10, 491 (1967).
- [13] *T.A. Albright, P. Hofmann & R. Hoffmann*, *J. Am. Chem. Soc.* 99, 7546 (1977).
- [14] *R. Hoffmann*, *J. Chem. Phys.* 39, 1397 (1963); *R. Hoffmann & W.N. Lipscomb*, *J. Chem. Phys.* 36, 2179 (1962); *idem*, *ibid.* 37, 2872 (1962).
- [15] *J.H. Ammeter, H.-B. Bürgi, J.C. Thibeault & R. Hoffmann*, *J. Am. Chem. Soc.* 100, 3686 (1978).