similar reaction mechanism as observed for the reaction of **3a** or **3c** with HCl, the lower nucleophilic character of the Rh atom compared to, for instance, phosphine-substituted Rh(I) complexes plays a role. Due to the coordination of the iminophosphorane entity, electron density is withdrawn from Rh by the (iminophosphoranyl)methanide ligand within the polarized metallacycle. This means that the rhodium(I) center is relatively hard in terms of HSAB. Hence, soft ligands such as CH_3X, alkynes, and CO_2 will, contrary to HCl, add sluggishly or not at all to the Rh center. So, alkynes and CO are not being activated for insertion and CH_3X will undergo direct, less specific reactions with the ligands instead of giving rise to a metal-mediated methylation (which is usually more specific).

The fact that molecules like CO, CO_2, olefins, and alkynes fail to insert into the Rh–C or Rh–N bonds indicates that the Rh–N–P–C ring is a very stable entity and that no insertion reactions take place, although upon insertion a lowering of the ring strain would occur. Insertion reactions are inhibited due to the low propensity of **3** to bind a fifth ligand that needs π back-bonding from the metal and/or the reluctance to undergo dissociation of one of the ligand atoms in the coordination plane of square-planar **3**. Furthermore the inertness of **3a,c** toward CO_2 shows that coordination of the iminophosphorane group brings about a substantial decrease in its typical reactivity, i.e. no aza-Wittig reaction with CO_2 takes place (eq 4). This result emphasizes the stability of the four-membered Rh–N–P–C ring.

Conclusions

Intramolecular coordination of an iminophosphorane group stabilizes a M(I)–C(sp^3) bond (M = Rh, Ir) in complexes of the type $[M(CH_2PPh_2{=}N\text{-}p\text{-tol})L_2]$. In these complexes the (iminophosphoranyl)methanide ligand is coordinated in a σ-N,σ-C chelating mode, giving rise to a stable four-membered M–N–P–C ring. Reaction of the rhodium (iminophosphoranyl)methanide complexes with HCl proceeds via oxidative addition at the hard Rh(I) center and subsequent migration of the hydrogen atom to either the C or the N atom of the N,C-chelated ligand.

Acknowledgment. We thank Prof. K. Vrieze for his interest in this work, J. M. Ernsting for recording the ^{103}Rh NMR spectra, and Johnson-Matthey Technology Centre (Reading, U.K.) for a loan of $RhCl_3$.

Supplementary Material Available: Tables of hydrogen coordinates and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (5 pages); a table of structure factors (38 pages). Ordering information is given on any current masthead page.

The Carbon–Carbon Bond-Forming Step In Catalytic Cross-Coupling: Migration or Elimination?

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Two alternative pathways for reductive elimination of adjacent sp^3 and sp^2 carbon substituents from palladium have been examined by the extended Hückel method, with *cis*-$(PH_3)Pd(CH_3)CH{=}CH_2$ as a model. A brief comparison with the nickel analogue has been made. In the first set of calculations, concomitant lengthening of both Pd–C bonds was permitted to proceed synchronously, leading to an isolated molecule of propene and to $(PH_3)_2Pd$. This conventional pathway for reductive elimination, which demonstrated behavior very similar to that calculated previously by the extended Hückel method for *cis*-$(PH_3)Pd(CH_3)_2$, was compared with an alternative in which cleavage of the Pd–CH_3 bond is more advanced and occurs with synchronous migration to the C_α carbon of the vinyl group. The intermediate produced in this way can form an η^2-propene complex by geometric reorganization. When calculations for the two energy surfaces are compared, the migration pathway is favored. It is particularly advantageous when the P–Pd–P angle is permitted to relax as reaction proceeds. Comparison is made with experimental evidence, and the calculations are in accord with the observed ease of elimination from square-planar 16e aryl or vinyl complexes.

Introduction

Cross-coupling reactions between an organic electrophile and an organometallic nucleophile have played a significant role in synthesis.[1] The catalyst is most frequently a Pd or Ni phosphine complex, with 1,1′-bis(diphenylphosphino)ferrocene the preferred ligand.[2] X-ray analysis of its square-planar complexes[3] reveals a cis chelate with a bite angle of 99°, very similar to the typical angle in *cis*-$(PPh_3)_2M$ square-planar complexes [98°].[4] The catalytic reaction has most generality when the electrophilic entity is unsaturated; vinyl, aryl, and allyl halides have all

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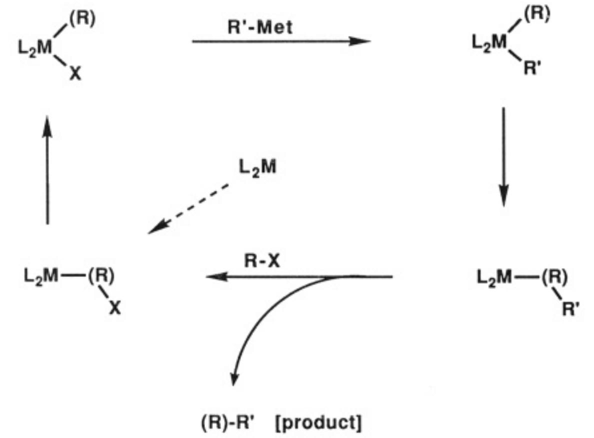
Scheme I



been successfully employed.

There is general agreement on the broader features of the reaction mechanism.[5] Whatever the initial state of the catalytic palladium or nickel complex, it is reduced in situ to the Pd(0) (or Ni(0):) state, producing a species that reacts with the organic electrophile. When this is a vinyl halide, the initial product is an η^2-olefin complex that subsequently undergoes an internal rearrangement to form an η^1-vinyl η^1-halide complex (Scheme I). With aryl halides this internal insertion product can be formed directly. Subsequent reaction of the resulting complex with the organometallic nucleophile, which is normally a Grignard or organozinc reagent, gives an intermediate with the two components now directly bound to the catalyst by covalent M–C single bonds. In the final step of the catalytic cycle the new C–C bond is formed.

There is some divergence of pathway in this final step, depending on the nature of the metal-bound fragments. For the η^3-allyl case, the lowest energy pathway accessible is migration of alkyl to the allylic terminus and this occurs much more readily in 18e Ni biphosphine complexes than in their 16e counterparts; related Pd complexes are substantially less thermolabile.[6] For η^1-dialkyl complexes, direct elimination from a square-planar 16e intermediate is unfavorable. The preferred route may require dissociation of a phosphine ligand,[7] association of an electrophilic olefin,[8] or oxidative addition of MeI prior to reaction.[9] A third case, where one or both of the reacting groups is sp^2-bonded to the metal, constitutes the commonest example in organic synthesis. Although there can be mechanistic complications involving transmetalation and cis–trans isomerization when bis(monophosphine)palladium catalysts are employed, the elimination step is straightforward for cis-adjacent Ph and Me.[10] In preformed Pd complexes of 1,1′-bis(diphenylphosphino)ferrocene, the η^1-benzyl complex **1** can be prepared in situ and decays to the cross-coupled product **2** at −20 °C.[11] Again, the mechanism involves decay of a 16e square-planar species without external intervention.

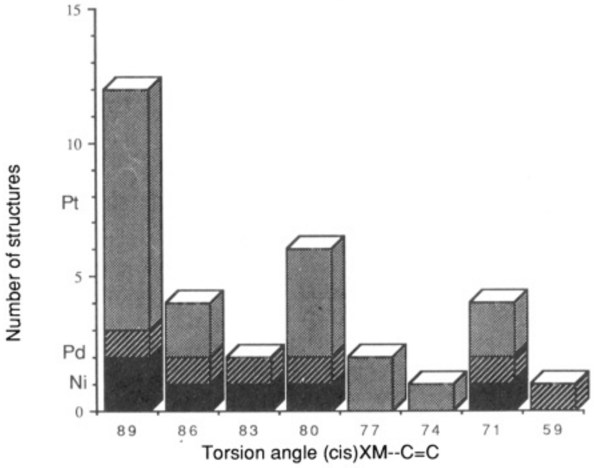
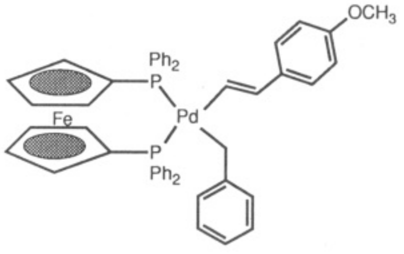
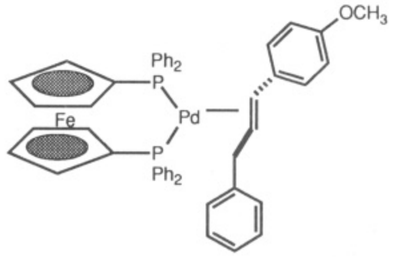


Figure 1. Torsion angles for vinyl groups of square-planar Ni, Pd, and Pt complexes derived from the CSSR data base.



1



2

The balance of experimental evidence suggests that elimination of two adjacent sp^3 organyls is much more difficult than comparable cases where one or both are sp^2. Since the hybridization change (sp^3–sp^2) causes strengthening rather than weakening of the metal–carbon bond,[12] the difference in thermal lability reflects a divergence of mechanism. Making the analogy with previous theoretical studies on the transformation $CpIr(PMe_3)(C_2H_4) \rightarrow CpIr(PMe_3)(\eta^1\text{-}C_2H_3)H$,[13] which is best described as a hydride migration from iridium to carbon, we have carried out extended Hückel calculations[14] on elimination pathways available to the model 16e compound *cis*-$(PH_3)_2Pd(CH_3)CH{=}CH_2$. In particular, a direct comparison has been made between the dissociative route (both Pd–C bonds breaking synchronously) and the migration route. This latter mechanism involves Me migration to the vinyl group, prior to molecular reorganization and formation of an η^2-propene complex.

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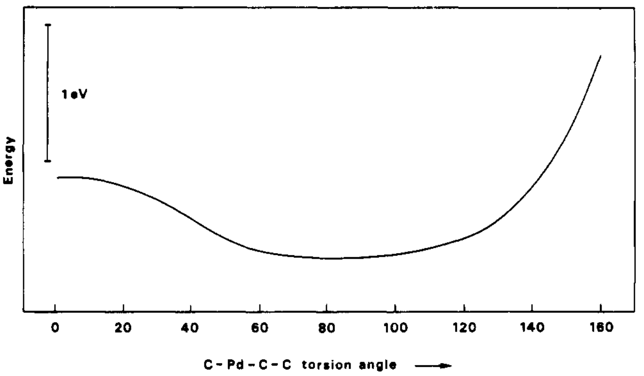

Figure 2. Calculated values for Pd–vinyl torsion angles.

Structure of η^1 Metal Vinyls

The structure and conformation of the square-planar ground state are of critical importance in any evaluation of the reaction energy surface for elimination. A search of the CSSR crystallographic data base reveals over 100 transition-metal vinyl complexes. Of these, 32 are square-planar derivatives of Ni,[15] Pd,[16] or Pt[17] in which there are no constraints to rotation about the M–C(sp^2) bond. Examination of the torsion angle X–M- - -C–C about this bond (X is a cis-adjacent substituent in the square plane) reveals a consistent feature—the vinyl group is out of plane, tending toward orthogonality with the complexation plane. Nearly half the structures examined indicate a torsion angle insiginficantly removed from 90°, and in all but one that angle is between 70 and 90° (Figure 1). In many of these cases, this is the direct consequence of steric repulsion between the vinyl group and its adjacent ligands, but this is not universally true, and an electronic contribution is implied. A similar situation is found in square-planar η^1-acyl complexes; the rather smaller number of relevant X-ray structures indicate that the acyl group prefers to be orthogonal to the coordination plane. A simple molecular mechanics analysis indicates that this preference is steric in origin, at least in part. For sterically uncongested cases, these calculations demonstrate that the torsional potential is rather flat over the angle range 40–90°.[18]

A further feature of many η^1-vinyl complex structures is that the bond angle M—C═C is unusually wide, up to 133° with an average of 126°. Most of those cases where the angle is close to 120° possess a constraining buttressing effect between vicinal substituents on the olefin. This may reflect an increase in s character of the C_α atom through hyperconjugation of d_{z^2} with the C_α–X bond. Where X = Cl, so that this interaction is encouraged, angle widening is particularly marked.

Before any calculations on the reaction pathway were carried out, the ground-state structure of the model complex was evaluated by extended Hückel calculations.[14] When the initial geometry was set up, several features were assumed. The geometry around the Pd atom was taken to be identical with that obtained in a previous theoretical study[19] on the $(PH_3)_2Pd(CH_3)_2$ system carried out at the extended Hückel level. Further details are given in the Appendix. The torsion angle about the Pd–vinyl bond was optimized by calculation (Figure 2).

The curve depicting the change in energy is very flat in a wide range of torsion angles centered around the 70–90° interval, where most of the known structures are found, the minimum occurring for 82°. While the bonding of the vinyl group to the $Pd(PH_3)_2(CH_3)$ fragment remains the same, rotation of $-CH{=}CH_2$ away from the plane on the molecule relieves the steric repulsion between this group and the neighboring CH_3, leading to the disappearance of a four-electron destabilizing interaction. The orthogonal species was used for the calculations.

Concerted Reductive Elimination

This reaction pathway, and in particular the case $L_nM(CH_3)_2 \rightarrow L_nM + C_2H_6$, has previously been studied by a number of theoretical groups for nickel, palladium, and platinum complexes.[19-22] The case most relevant to the present work is provided by Tatsumi et al.,[19] who have carried out extended Hückel calculations on ethane elimination from $(PH_3)_2Pd(CH_3)_2$. By employing a rather restricted energy surface, but permitting increase of the P–Pd–P angle as the Pd–CH_3 bonds lengthen, they predict an energy barrier of 39 kcal mol^{-1} for the process. With a more rigorous GVB ab initio approach, Low and Goddard[21] suggest a much lower energy barrier is likely for the same elimination process, around 10–13 kcal mol^{-1}. The ease of reaction for Pd relative to Pt is associated with a greater preference for the d^{10} configuration in the former case. Some caution is required in interpreting the absolute activation energies involved, since many *cis*-P_2PdMe_2 complexes are known that are thermally stable under ambient conditions.[23] Indeed, the mechanism of ethane

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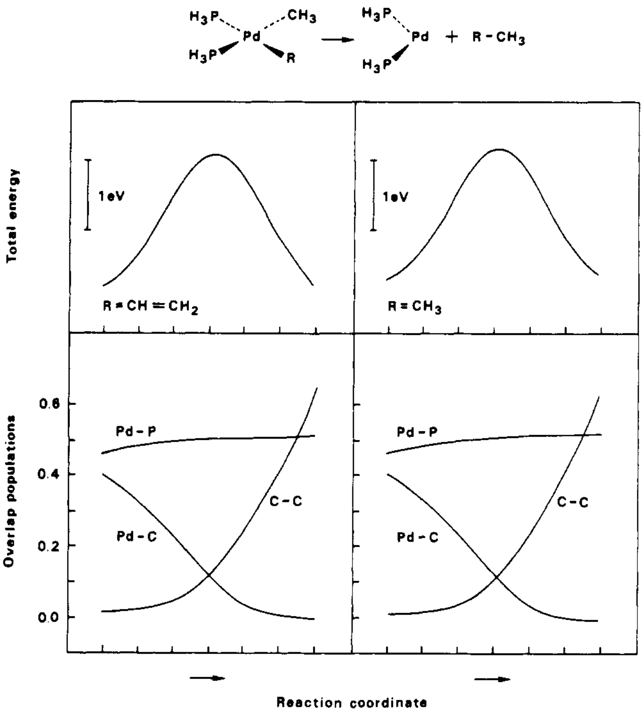

Figure 3. Energies and overlap populations calculated for the concerted-elimination process.

elimination from compounds in this class involves prior dissociation of one phosphine ligand. The main value of calculations is that they permit a comparison between the *relative* energies of different pathways. Given the substantial approximations made in the extended Hückel method, strict adherence to comparison between closely related structures is required.

Given that a substantial proportion of catalytic cross-coupling reactions involve at least one sp^2 partner, it is surprising that theoretical calculations on such systems are lacking. The choice of reactant for our own studies is *cis*-(PH$_3$)$_2$Pd(CH=CH$_2$)CH$_3$, dictated by its simplicity and its relationship to existing calculations. Initial work involved a study of elimination along the reaction surface described by Tatsumi et al.,[19] whereby the Pd–C distance is increased from 2.05 to 3.25 Å in equal steps and the P–Pd–P and C–Pd–C bond angles concomitantly change from 90 to 150° and from 90 to 30°, respectively. The alkyl groups are allowed to reorient as the new C–C bond is formed, and the heavy atoms remain coplanar.

The energy barrier for the elimination is virtually indistinguishable from that for the related PdMe$_2$ case (ca. 1.9 eV). The changes in overlap populations are smooth (Figure 3) and follow the same patterns in both cases, although the Pd–C(vinyl) bond is stronger than the Pd–C(methyl) bond (this result is in accordance with experimentally determined bond dissociation enthalpies in the complexes $(\eta^5\text{-}C_5H_5)(PMe_3)Ir(X)_2$: 71 kcal mol^{-1} for X = vinyl, around 50 kcal mol^{-1} for R = alkyl).[24] Both Pd–C bonds in each complex weaken simultaneously as the new C–C bond is formed, while the Pd–P bonds are strengthened, due to opening of the P–Pd–P angle, which provides for the better overlap between palladium and phosphorus orbitals. The Walsh diagram for formation of CH$_3$—CH=CH$_2$ (Figure 4) does not look exactly the same as the one for formation of CH$_3$—CH$_3$,[19] as there are now two different R groups and the symmetry is lower. All levels can mix, and there are some avoided crossings. The qualitative pattern is, however, the same and the interpretation holds. The driving force for the reaction still appears to be the stabilization of the lower energy σ(P–C) bond orbital, which should correlate with the new σ(C–C) bond. Mixing of the vinyl p orbital slightly alters the picture but not the result. The destabilization of the other σ(Pd–C) bond orbital is reflected in the relatively high activation barrier.

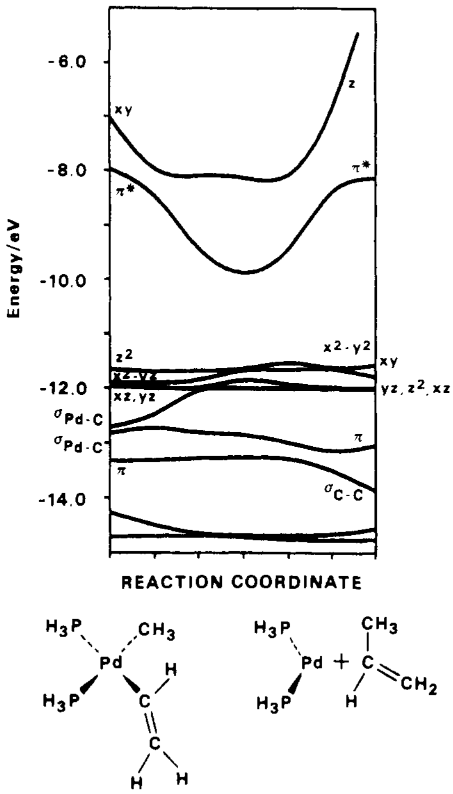

Figure 4. Walsh diagram for propene formation by the concerted-elimination pathway.

These calculations indicate that the behaviors of methyl and vinyl groups in a concerted elimination are very similar, leading to a reaction path and activation energy which is very close to that calculated for the dimethylpalladium case.

Migration Pathway

Let us now consider a mechanism in which a methyl group migrates to the vinyl α-carbon, this atom staying bonded to palladium but moving as delineated in Scheme IIa. The initial complex has its vinyl group orthogonal to the palladium square plane. During the reaction the Pd–CH$_3$ bond lengthens and the vinyl group rotates relative to the Pd–C bond so that the initially orthogonal π-bond becomes coordinated. The new C–C bond is formed with retention of configuration at the vinyl center. At the end (i.e. the right-hand side of Scheme IIa), the vinyl α-carbon lies on the line that bisects the P–Pd–P angle and is four-coordinated to Pd, the methyl carbon, the vinyl β-carbon, and the α-hydrogen, with a distorted-

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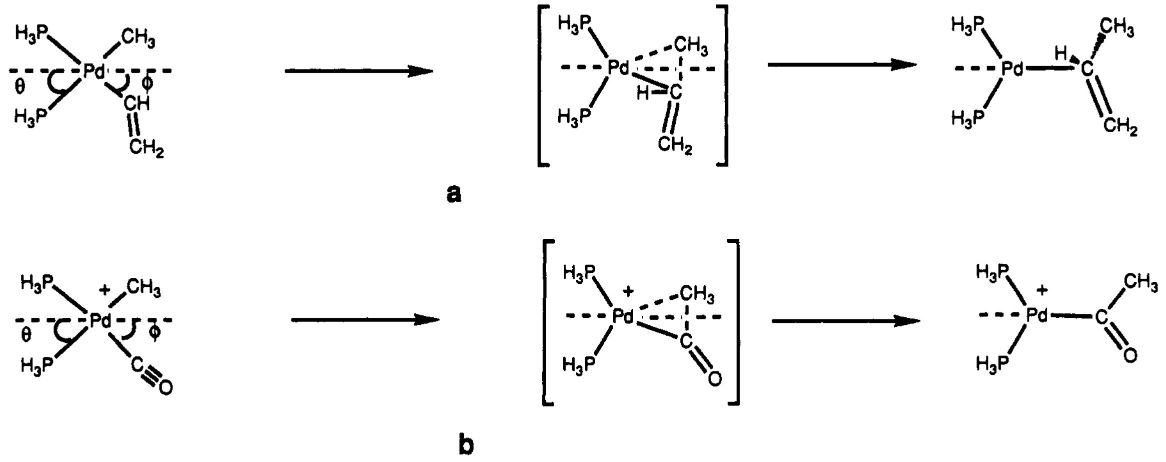
Scheme II



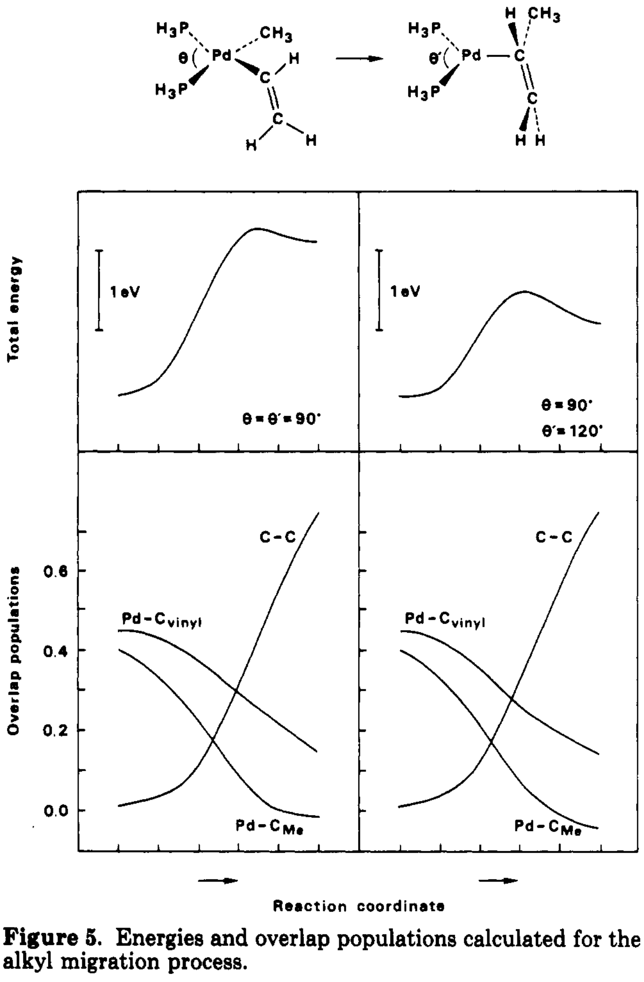


Figure 5. Energies and overlap populations calculated for the alkyl migration process.

tetrahedral environment. The angle ϕ (defined in Scheme IIa) will be 0° when the distorted, η^1-coordinated olefin is formed, so that the geometry is trigonal. During the migration, the vinyl group twists so as to maximize the bonding between C_α and palladium. The P-Pd-P angle is simultaneously allowed to increase incrementally from 90 to 120°. The change in energy for this reaction pathway is depicted in Figure 5 (right side), along with the variation of overlap poulations. The later part of the reaction involves the rearrangement of the coordinated η^1-olefin to a noncoordinated undistorted olefin plus a $Pd(PH_3)_2$ fragment. This is a downhill process with no activation energy. The sum of the energies of the two fragments is lower (ca. 0.1 eV) than the energy of the initial methylvinylpalladium complex. The alternative fate of the intermediate involving relaxation of the η^1-olefin to a conventional alkene complex was not investigated.

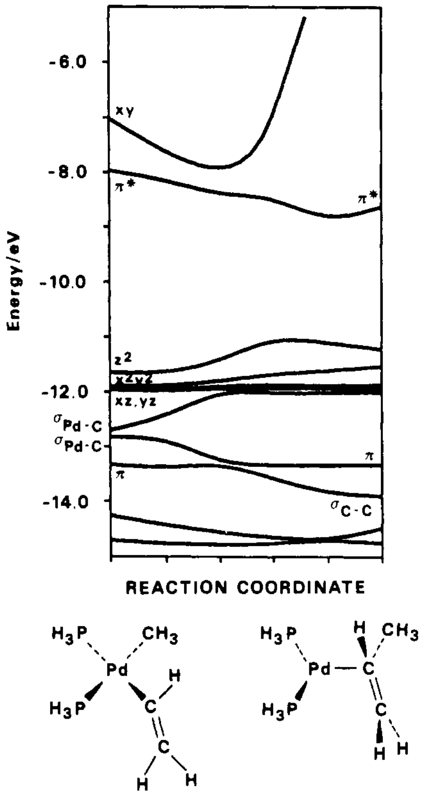


Figure 6. Walsh diagram for propene complex formation by the alkyl migration pathway.

The calculations show that the energy barrier to migration is substantially lower than that calculated for the concerted reductive elimination with similar geometrical constraints, i.e. when the P-Pd-P angle is allowed to relax in both cases. The values of the activation energy are respectively 1.3 and 1.9 eV, although for the reasons discussed above we prefer to concentrate on the differences between these values rather than the absolute values. If, however, the P-Pd-P angle is constrained to 90°, the barrier is comparable to that of the concerted mechanism (Figure 5, left side). This constraint would be the case experimentally with a rigid five-membered-ring chelating (diphosphine)palladium complex. The lower part of Figure 5 indicates how the overlap populations for Pd-C and C-C bonds change across the reaction coordinate.

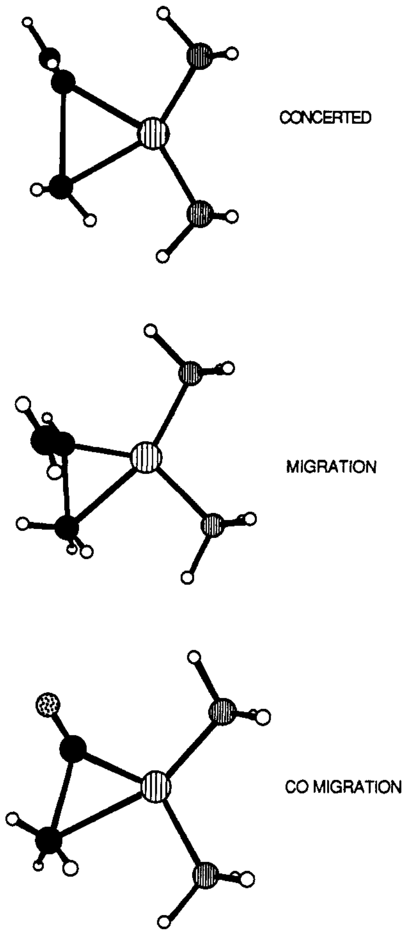


Figure 7. Transition-state structures for the three processes calculated in the paper.

The Walsh diagram shown in Figure 6 illustrates the behavior of several orbitals during the first part of the reaction for the case where methyl migration occurs with simultaneous widening of the P–Pd–P angle. Two orbitals, namely σ(C–C) and Pd(z^2), are strongly destabilized in the early part of the reaction and are thus responsible for the energy barrier.

It is fruitful to compare the transition-state structures in more detail; their geometries are displayed in Figure 7. For the concerted-elimination pathway the C–C distance for the forming bond is 2.64 Å. The vinyl group is still close to orthogonality, making a torsion angle of 74° with the Pd–P bonds. The Pd–C bonds have stretched to 2.64 and 2.65 Å, respectively. This contrasts with the migration pathway, where the new C–C bond is further developed at 2.08 Å and the Pd–CH_3 bond length is 2.57 Å. The Pd–vinyl bond length is shorter at 2.04 Å. The vinyl group remains orthogonal to the coordination plane.

When nickel replaces palladium, the calculations yield similar results, with a lower energy barrier (close to 0.25 eV).

The pathway delineated by these calculations bears a resemblance to the preferred pathway for alkyl migration to a carbonyl group. There have been several theoretical calculations on this reaction since the early studies of Hoffmann and co-workers in 1978.[25] In order to make a more direct comparison, we studied alkyl to carbonyl migration in the square-planar cationic *cis*-Pd$(PH_3)_2$Me(CO) complex and a reaction coordinate very similar to that of methyl to vinyl migration. The methyl group is allowed to move in the C–Pd–C plane toward the carbonyl carbon atom. Simultaneously, there is a rearrangement of the ligands, such that in the end the acyl complex has

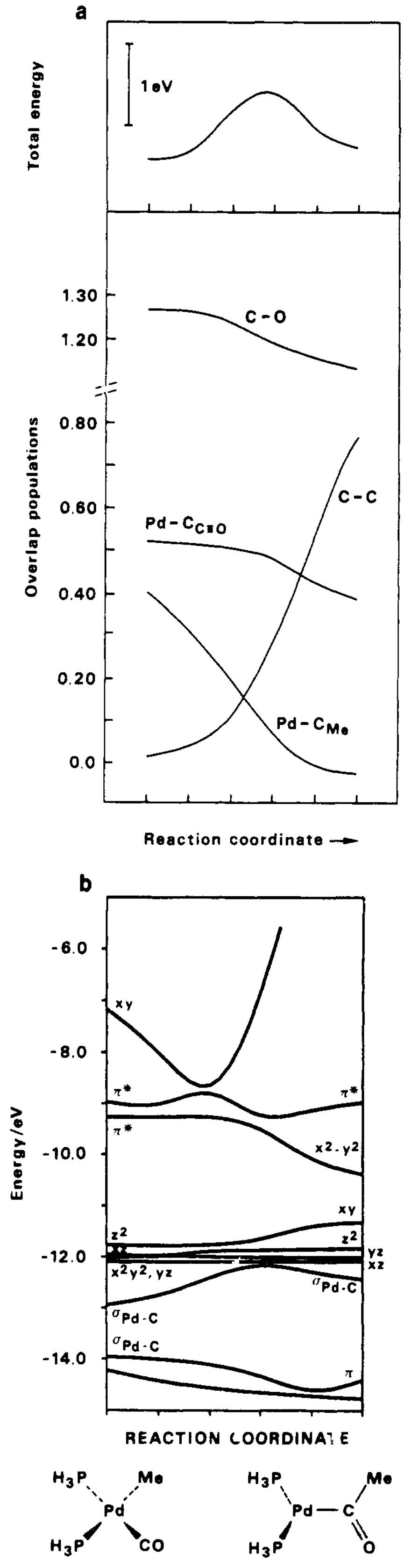


Figure 8. (a) Energies for alkyl migration to coordinated CO. (b) Walsh diagram for this process.

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(25) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136. Dedieu, A.; Sakaki, S.; Strich, A.; Siegbahn, P. E. M. *Chem. Phys. Lett.* **1987**, *133*, 317. Shusterman, A. J.; Tamir, I.; Pross, A. *J. Organomet. Chem.* **1988**, *340*, 203. Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

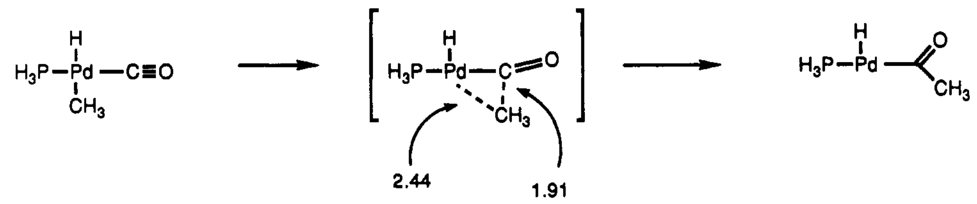


Figure 9. Transition-state structure arising from Morokuma's calculations.

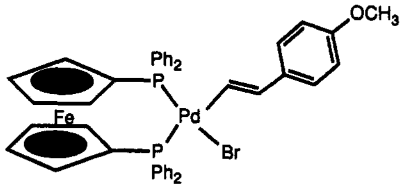
a triangular geometry. This mechanism is sketched in Scheme IIb.

The changes in energy and overlap populations are shown in Figure 8a. The new C–C bond is formed while the C–O bond weakens and the Pd–C(Me) bond breaks. The other Pd–CO bond remains relatively strong throughout the reaction. The higher σ(Pd–C) level (Walsh diagram, Figure 8b) becomes the only Pd–C bond in the final species, while the other will end as the new C–C bond (not shown in this energy window). The activation energy (0.7 eV) is smaller than that of the related methyl to vinyl migration (1.3 eV), although the Walsh diagram is similar.

Some relevant recent work is that of Morokuma et al.[25] Their calculations on the hypothetical reaction outlined in Figure 9 reveal that the transition-state region is characterized by substantial movement of CH_3 toward the acyl carbon, with concomitant weakening of the Pd–CH_3 bond. This is similar to our chosen coordinate reaction, although in our system the hydrogen atom has been replaced by PH_3. The same trends are, however, observed in the bonds. A point of interest in the present context is that the atoms involved in the migration remain in the coordination plane, while in its most stable conformation the acyl will be expected to be orthogonal to that plane.[26] This implies that migration of CH_3 is followed by rotation of the acyl group into its preferred conformation.

Relationship to Experiment

The most direct experimental comparisons with these calculations are of palladium-phenylethenyl complexes.[10,11] Thus, the rearrangement of complex 1, prepared in situ in tetrahydrofuran solution at −15 °C, goes cleanly to product 2 over a few minutes at that temperature. In contrast, when bromide 3 is reacted with arylmagnesium halides, the aryl alkenyl complex was not observed, even at −70 °C. The first observable intermediate was olefin complex 4. When the temperature was raised, partial displacement by cyclooctatetraene (present from the precursor to 3 occurred. These observations indicate that the first species formed is an η^2-olefin complex and give credence to the idea that a migration pathway is involved. In a related set of reactions carried out by Stille and Loar, mixtures of the *cis*- and *trans*-bis(phosphine) complexes 5 and 6 were prepared at low temperature. The cis isomer decomposes at low temperature (−30 °C), but the trans isomer is stable to rather higher temperatures. Its decomposition is probably preceded by trans–cis isomerization.



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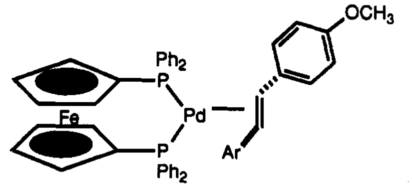

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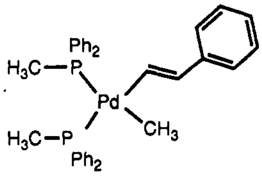

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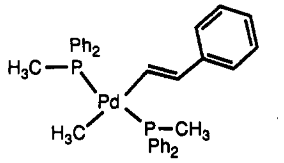

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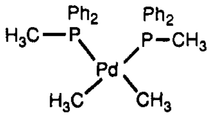
These sets of observations contrast with a substantially higher thermal stability for related cis-dialkylpalladium complexes.[7] For example, thermolysis of compound 7 occurs at an appreciable rate at 45–60 °C, but is inhibited by excess phosphine. This along with other evidence indicates that ethane is formed by prior phosphine dissociation from 7 to give a thermolabile 14e intermediate. The thermolysis of undissociated complex 7 itself must therefore be much slower, several orders of magnitude less reactive than that of complexes 1 and 5.



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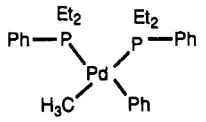
Other *cis*-dialkylpalladium complexes with at least one sp^2-bonded group also display enhanced thermal lability relative to that of the saturated complexes. A significant example is given by the recent studies of Yamomoto and co-workers[10] in which formation of toluene via complex 8 occurred under mild conditions. A pathway analogous to the migration route could be involved. If so, it would require transient formation of an η^2(1,2)-toluene complex.



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In summary, there is good evidence that palladium complexes with cis-adjacent sp^2 and sp^3 centers undergo thermal C–C bond formation more readily than their saturated counterparts. The theoretical calculations reported herein support this conclusion and offer a mechanistic interpretation consistent with available facts.

Summary and Conclusions

It needs to be stressed that not much emphasis should be placed on the absolute values calculated for activation barriers in the several mechanisms discussed. An ab initio

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[26] Ammeter, J.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 368.

Table I. Orbitals and Parameters for the Extended Hückel Calculations

orbital	$-H_{ii}$/eV	ζ_1	ζ_2	C_1	C_2
Pd 5s	7.32	2.19			
Pd 5p	3.75	2.152			
Pd 4d	12.02	5.983	2.613	0.5264	0.6373
Ni 4s	9.17	2.10			
Ni 4p	5.15	2.10			
Ni 3d	13.49	5.75	2.30	0.5798	0.5782

study[21] for the concerted reductive elimination of ethane from $(PH_3)_2Pd(CH_3)_2$ gives a much lower value for the barrier (ca. 10 kcal mol^{-1}). This is due to the difficulties of dealing reliably with bond-breaking and bond-forming processes when the extended Hückel approach is used. For these reasons, a potential surface to optimize C–C bond formation relative to Pd–C bond breaking was not explored. A different choice of the transition state might lead to a different barrier. In spite of all these considerations, it should be pointed out that the qualitative conclusions remain valid, as a 30% decrease in activation energy for the migration must indeed correspond to an easier process. There are too many degrees of freedom involved in this reaction, and a better choice of the transition state would certainly lower the barrier.

Another point to consider is the choice of method. Even in an ab initio approach, there are many limitations when one deals with heavy atoms, such as palladium, and relatively large systems. The choice of which option to apply may result in very different values, as illustrated, for instance, in the work of Morokuma.[25]

Appendix

All the calculations were of the extended Hückel type[14] with modified H_{ii}'s.[26] The basis sets for the palladium, nickel, and platinum atoms consisted of *n*s, *n*p, and (*n* – 1)d orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometry of the model $Pd(PH_3)_2RR'$ complexes was square planar with all the angles in the palladium coordination plane being 90°. The distances were taken as Pd—P = 2.30, P—H = 1.42, Pd—C(methyl) = 2.00, Pd—C(vinyl) = 2.05, C—H = 1.09, and C═C = 1.33 Å, respectively. The parameters used for the calculations were the standard ones for H, C, and P and were those reported in Table I for the metals.

Acknowledgment. N.A.C. thanks the Science and Engineering Research Council (U.K.) for postdoctoral support. M.J.C. thanks NATO for a fellowship, which permitted her to visit the laboratories of Professor R. Hoffmann at Cornell University, where most of the calculations were completed. Professor Hoffmann's interest and encouragement is greatly appreciated.

Reactions of (η^5-Ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium with Lithium Aluminum Hydride and with Organomagnesium Halides, Leading to 6-Metallocenylfulvenes

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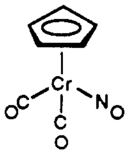
Reactions of (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (**2**) with lithium aluminum hydride and with organomagnesium halides have been investigated. Treatment of **2** with $LiAlH_4$ in THF solution followed by hydrolysis did not produce the expected product, carbinol **4**, but instead 6-ferrocenylfulvene (**5**). A reaction between **4** and $LiAlH_4$ under the same conditions likewise formed **5**. Reactions of **2** with methylmagnesium iodide produced either the normal addition product, carbinol **7**, or 6-ferrocenyl-6-methylfulvene (**8**), depending on the reaction conditions, whereas only 6-ferrocenyl-6-phenylfulvene (**9**) could be isolated from reactions between **2** and phenylmagnesium bromide. Mechanistic considerations concerning degradation of the (η^5-cyclopentadienyl)dicarbonylnitrosylchromium substituent in **2** to form 6-ferrocenylfulvenes under these conditions are discussed. Fulvenes **5**, **8**, and **9** can also be prepared conveniently and in high yield from reactions under basic conditions between cyclopentadiene and formyl-, acetyl-, or benzoylferrocene, respectively. Carbonylbis[(η^5-cyclopentadienyl)dicarbonylnitrosylchromium] (**3**) has been prepared in 26% yield from a Friedel–Crafts reaction between (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (**1**) and (η^5-(chloroformyl)cyclopentadienyl)dicarbonylnitrosylchromium in the presence of aluminum chloride.

Introduction

Recent studies in our laboratory have focused on the formation, spectral properties, structural features, and chemical reactivities of ring-substituted derivatives of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (**1**).[1]



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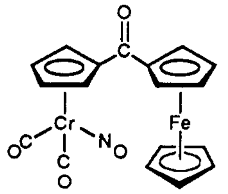

2

Acyl and carboxylic acid derivatives of **1** can be readily prepared by Friedel–Crafts acylation methods and undergo a wide variety of addition, reduction, and rearrangement

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(1) The trivial name cynichrodene has been proposed by analogy to the shortened names cymantrene and benchrotrene for (η^5-cyclopentadienyl)tricarbonylmanganese and (η^6-benzene)tricarbonylchromium, respectively.[2,3]

(2) Pittman, C. U., Jr.; Rounsefell, T. D.; Lewis, E. A.; Sheats, J. E.; Edwards, B. H.; Rausch, M. D.; Mintz, E. A. *Macromolecules* 1978, *11*, 560.

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