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Reactivity of Coordinated Nucleophiles toward Cis Migration in (π-Olefin)palladium Complexes

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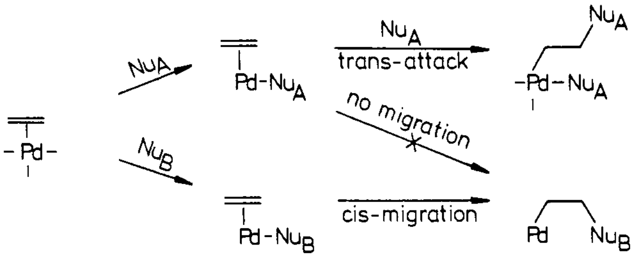
Abstract: Ab initio calculations using an effective core potential (ECP) have been performed on (π-ethene)palladium complexes with different coordinated nucleophiles, H^-, CH_3^-, OH^-, and F^-. The calculations show a weak back donation (weak π^*–d_{yz} overlap) in all complexes studied. An analysis of the reactivity of the coordinated nucleophiles toward migration to the olefin was done by estimating the bond strength and the energy of the orbital describing the palladium–nucleophile bond. The results indicate that a frontier-controlled cis migration to the olefin would be possible only for coordinated H^- and CH_3^-, whereas OH^- and F^- would be too unreactive in such a process.

Nucleophilic addition to alkenes coordinated to a transition metal is an important process for creating new carbon–carbon bonds, carbon–nitrogen bonds, and carbon–oxygen bonds. Many transition metals are known to promote such nucleophilic additions,[2] and among the metals most studied one finds palladium,[2-5] platinum,[6] and iron.[7] Theoretical treatment of transition-metal π-olefin complexes has led to a deeper understanding of the olefin activation by the metal,[8-12] and on the basis of MO calculations the reactivity of the coordinated olefin toward nucleophiles has been discussed.[9,10a]

An important question in nucleophilic addition to a coordinated alkene concerns the regio- and stereochemistry of the addition. As can be seen from Figure 1 the nucleophile can attack the coordinated alkene at four different sites, and hence four chemically different adducts may be obtained.

Because of the importance in catalysis, nucleophilic additions to (π-olefin)palladium complexes have attracted special interest.[2-5,13-17] In particular, the stereochemistry of the addition of a variety of nucleophiles to (π-olefin)palladium complexes has been studied. According to these studies one can distinguish two different classes of nucleophiles: nucleophiles that add with external trans attack (Nu_A, Scheme I) and nucleophiles that add with cis attack via an intramolecular migration from the metal to carbon (Nu_B, Scheme I).[5] Among the nucleophiles that add trans one finds water (hydroxide),[4a,5b] carboxylates,[13] alkoxides,[4c,14] amines,[15] and stabilized carbon nucleophiles,[16] and among those that add cis one finds hydride,[17a] aryl,[17a,17b] and alkyl.[17c] It has often been suggested that the main factor determining cis or trans attack would be whether the free nucleophile attacks the metal or not. However, this is an oversimplified view since most oxygen and nitrogen nucleophiles coordinate to the metal prior to the trans attack by another molecule of the nucleophile. Thus, in spite of the fact that oxygen and nitrogen nucleophiles are coordinated to the metal in (π-olefin)palladium complexes,[5b] *they do not undergo a migration from the metal to the coordinated olefin.* On the other hand nucleophiles of type B readily migrate once they are coordinated. The goal with the present study is to determine the factors governing a cis migration and to gain an understanding of the different behavior of coordinated nucleophiles of type A and B (cf. Scheme I) in (π-olefin)palladium complexes.

Scheme I



According to the theory of Fukui the energy of the frontier orbitals HOMO and LUMO are of great importance for the reactivity.[18] Many reactions, in particular cycloadditions and intramolecular rearrangements, are frontier controlled, but if the energy gap between HOMO and LUMO is large enough a reaction may become charge controlled.[19] In this paper we report SCF molecular orbital calculations on (π-olefin)palladium complexes ($Pd(H_2O)(Nu)_2$(ethene)) where Nu = H^-, CH_3^-, F^-, and OH^-. The results indicate that a frontier-controlled cis migration would be possible only for coordinated hydride and methyl, whereas coordinated fluoride and hydroxide would be too unreactive in such a process.

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(1) (a) Royal Institute of Technology. (b) University of Stockholm.

(2) Bäckvall, J. E. In "Reaction of Coordinated Ligands"; Braterman, P. S., Ed.; Plenum Press: New York, in press.

(3) (a) Henry, P. M. "Palladium-Catalyzed Oxidation of Hydrocarbons"; D. Reidel: Dordrecht, 1980. (b) Henry, P. M. *Adv. Organomet. Chem.* **1975**, *13*, 363. (c) Jira, R.; Freiesleben, W. *Organomet. React.* **1972**, *3*, 1.

(4) (a) Stille, J. K.; Divakaruni, R. *J. Organomet. Chem.* **1979**., *169*, 239. (b) Stille, J. K.; James, D. E. *Ibid.* **1976**, *108*, 401. (c) James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1806. (d) Hegedus, L. S.; Williams, R. E.; McGuire, M. A.; Hayashi, T. *Ibid.* **1980**, *102*, 4973.

(5) (a) Bäckvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335. Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

(6) (a) Panunzi, A.; De Renzi, A.; Palumbo, R.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3879. (b) Panunzi, A.; De Renzi, A.; Paiaro, G. *Ibid.* **1970**, *92*, 3488. (c) Ambuehl, J.; Pregosin, P.-S.; Venanzi, L. M.; Consiglio, G.; Bachechi, F.; Zambonelli, L. *J. Organomet. Chem.*, **1979**, *181*, 255.

(7) (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426. (c) Roberts, B. W.; Ross, M.; Wong, J. *J. Chem. Soc., Chem. Commun.* **1980**, 428.

(8) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(9) Åkermark, B.; Almemark, M.; Almlöf, J.; Bäckvall, J. E.; Roos, B.; Støgård, Å. *J. Am. Chem. Soc.* **1977**, *99*, 4617.

(10) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *Ibid.* **1979**, *101*, 3801.

(11) (a) Rösch, N.; Messmer, R. P.; Johnson, K. *J. Am. Chem. Soc.* **1974**, *96*, 3855. (b) Hay, P. J. *Ibid.* **1981**, *103*, 1390. (c) Basch, H. *J. Chem. Phys.* **1972**, *56*, 441.

(12) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339.

(13) (a) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 1494. (b) Andell, O. S.; Bäckvall, J. E. *J. Organomet. Chem.* **1983**, *244*, 401.

(14) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996.

(15) Åkermark, B.; Bäckvall, J. E.; Siiralla-Hansên, K.; Sjöberg, K.; Zetterberg, K. *Tetrahedron Lett.* **1974**, 1363.

(16) Kurosawa, H.; Asada, N. *Tetrahedron Lett.* **1979**, *255*.

(17) (a) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 673. (b) Segnitz, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1973**, 698. (c) Murahashi, S. I.; Yamamura, M.; Mita, N. *J. Org. Chem.* **1977**, *42*, 2870.

(18) (a) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (b) Fukui, K. *J. Chem. Phys.* **1957**, *27*, 1247. (c) Fukui, K. In "Molecular Orbitals in Chemistry, Physics, and Biology"; Löwdin, P. O., Pullman, P., Eds.; Academic Press: New York, 1964; p 513. (d) Fukui, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: Heidelberg, 1970.

(19) (a) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 2. (b) "Chemical Reactivity and Reaction Paths"; Klopman, G., Ed.; Wiley: New York, 1974. (c) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976.

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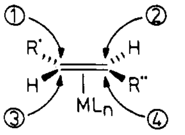


Figure 1. Different sites for nucleophilic attack.

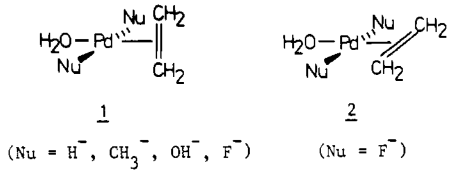
Details of Calculations

Hartree–Fock SCF molecular orbital calculations were carried out on complexes **1** and **2** using basis sets of double-ζ quality or better. All calculations are ab initio except that an effective core potential (ECP) is used to replace the noble gas core of the heavier elements. For the present investigation both the SCF and ECP approximations are expected to be highly accurate and will be discussed in more detail in this section where also the computational details and the model chosen for the complexes will be presented.

In the ECP method the core orbitals are regarded as inert in the reaction studied (frozen core approximation) and the core–valence interaction is approximated by one-electron operators. The only electrons explicitly treated are the valence electrons, which allows the basis set to be reduced to a valence basis by removing the innermost core basis functions. In this work we have used essentially the method of Huzinaga[20] for the first row atoms and the frozen orbital ECP method[21] for palladium. The nodes in the valence orbitals have been retained with the exception of carbon in CH_3 and oxygen in the water ligand where the ECP parameters were taken from the literature.[22] Retaining the nodes minimizes the corrections from the ECP to the valence interactions since these are then well described by orbital interactions.[23] The inclusion of the nodal structure in the valence orbitals requires somewhat larger basis sets than if nodeless orbitals are used but has been found to be a much safer procedure. Substantial CPU time savings are still obtained, however, as exemplified by 60% reductions in the integral evaluation time on molecules such as CH_2S, SiH_4, and $[PdH_4]^{2-}$. The geometrical parameters for these systems are obtained with errors less than 0.01 Å in bond lengths and of the order of 0.1–0.2° in bond angles as compared with the all-electron results.

For Pd, the valence 4d orbitals are not well separated from the 4s, 4p core orbitals, and some care must be taken in treating this interaction. In this case, the frozen orbital ECP method[21] was chosen. Now only the innermost core orbitals (1s–3p) are parametrized while the outer core orbitals (3d–4p) are expanded in the valence basis and are used in the calculations as explicitly frozen orbitals (i.e., not varied in the calculations). These orbitals thus constitute a part of the ECP and improve the description of the large interactions between the outer core orbitals and the valence. With this ECP on Pd, atomic excitation energies and molecular orbital energies are obtained within 0.1 eV and bond lengths within 0.01 Å with reference to the corresponding all-electron calculations.[21]

The SCF approximation when applied to transition-metal compounds is often found to give results which even qualitatively deviate from those of a treatment including configuration interaction. In particular, this is the case of certain nickel compounds,[24] and the question may be raised of the reliability of the SCF method when applied to palladium compounds. However, from a theoretical point of view palladium complexes are more easily described than corresponding nickel compounds. This can be seen partly as a result of the differences in the atomic spectra of the two atoms. Pd has a $4d^{10}$ (^1S) closed-shell ground state, and the positions of the excited states are obtained in reasonable agreement with experiment at the SCF level, while for Ni the experimentally near degenerate $3d^84s^2$ (^3F) and $3d^9s$ (^3D) states are separated by 1.31 eV in this approximation.[25] The effects of correlation are larger in the Ni compounds with its tighter valence d shell, and an SCF description is often even qualitatively incorrect, while for Pd the SCF approximation has been found much more adequate.[24]



1 2

(Nu = H^-, CH_3^-, OH^-, F^-) (Nu = F^-)

Figure 2. Structures of (π-olefin)palladium complexes used in the calculations.

Table I. ECP Parameters[a] for the First-Row Atoms

atom	C[b]	O	F
Z^{eff}	4.0	6.0	7.0
B_{1s}	10.50752	25.0	39.5
A_1	0.116270	0.189915	0.253679
A_2	0.027980	0.228189	0.272529
A_3		0.017518	0.011603
α_1	671.07342	270.2276	214.01297
α_2	4.187345	28.7181	38.71898
α_3		4.7207	9.51402
state[c]	$sp^3(^3D)$	$s^2p^4(^3P)$	$s^2p^5(^2P)$

[a] For definition of the ECP parameters see ref 21. [b] The ECP parameters for carbon were taken from ref 22. [c] Atomic state for which parametrization was performed.

Table II. Valence Basis for Oxygen

2s		2p	
exponent	coeff	exponent	coeff
48.89807	−0.103875	7.75579	0.129262
8.80724	−0.244977	1.62336	0.480758
1.06314	0.495906	0.36503	1.000000
0.32268	1.000000	0.082	1.000000

The structures of the reacting complexes are not well-known experimentally, but a fair assumption is that in the initial complex palladium is four-coordinated in a square-planar geometry. In our model of the complex we have chosen structures (Figure 2) in which ethene, two molecules of the nucleophile, and an extra ligand, in all cases H_2O, are coordinated to palladium. The Pd–Nu bond distances were optimized in each case while the internal geometries of the H_2O and ethene groups, as well as their distances to palladium, were kept fixed in all calculations. This approximation should not seriously affect the overall results obtained when the nucleophiles are changed.

The basis set for palladium is 7s6p7d contracted to 4s4p4d which includes two diffuse p functions to describe the 5p orbital and one diffuse d function. Palladium was described by using the frozen orbital ECP method with ECP parameters and basis set given in ref 21.

The C–C bond distance in ethene was optimized for the Pd–ethene system with the palladium atom at a distance of 2.21 Å from the midpoint of the C–C bond. This calculation was performed by using the ECP description of Pd but at the all-electron level for ethene. For carbon the MIDI-4 basis of Tatewaki et al.[26] was used, and for hydrogen the 4s basis of Huzinaga[27] was used in a double-ζ contraction and with one p function (0.789) added for polarization. Compared with the carbon–carbon bond for the ethene molecule alone, the bond distance was increased by 0.021 Å through the interaction with palladium. This geometry and ab initio description were then kept in all subsequent calculations.

The water molecule, which was fixed at its experimental internal geometry, was described by using the ECP of Wahlgren[22] for

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(20) (a) Bonifacic, V.; Huzinaga, S. *J. Chem. Phys.* **1974**, *60*, 2779. (b) Sakai, Y., Huzinaga, S. *Ibid.* **1982**, *76*, 2537.

(21) Pettersson, L.; Wahlgren, U.; Gropen, O. *Chem. Phys.*, in press.

(22) Wahlgren, U. *Chem. Phys.* **1978**, *32*, 215.

(23) Pettersson, L.; Strömberg, A. *Chem. Phys. Lett.* in press.

(24) Brandemark, U.; Blomberg, M.; Pettersson, L.; Siegbahn, P.; Larsson, M.; to be published.

(25) (a) Bauschlicher, C. W. *Chem. Phys. Lett.* **1982**, *91*, 4. (b) Bauschlicher, C. W.; Walch, S. P.; Partridge, H. *J. Chem. Phys.* **1982**, *76*, 1033.

(26) Tatewaki, J.; Huzinaga, S. *J. Comp. Chem.* **1980**, *3*, 205.

(27) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

Table III. Calculated Pd–Nu Bond Distance and Bond Strength

	calcd, Å	exptl, Å	force const,[a] eV/Å^2
H^-	1.69		24
CH_3^-	2.21	2.02 (1)–2.16 (5)[b]	25
OH^-	1.99		47
F^-	1.96	1.96[c]	43

[a] Calculated force constant from a variation (±0.05 Å) of the Pd–Nu bond distance. [b] From ref 31. [c] From ref 32.

Table IV. Charges of Different Parts of the Complexes and the Amount of p Character of the Valence Orbitals of Palladium

$Pd(Nu)_2$-(H_2O)(ethane)	% p of Pd valence orbitals	charge			
		Pd	Nu	ethene	water
Nu = H^-	7	0.00	−0.22	0.25	0.18
Nu = CH_3^-	6	0.25	−0.34	0.24	0.18
Nu = OH^-	4	0.92	−0.73	0.33	0.20
Nu = F^-	4	0.84	−0.69	0.34	0.20

oxygen and the 3s basis of Huzinaga[27] contracted to two and scaled by 1.25 for the hydrogen. The palladium–oxygen distance was kept at a value of 2.10 Å.[28]

In the case of OH^- as nucleophile the 1s orbital of the oxygen atom was replaced by an ECP. The basis set used is the 7s3p basis of Roos–Siegbahn[29] reduced to 4s3p. The two innermost s functions were further least-squares fitted to maximize the overlap with the original 2s orbital. A diffuse p function (0.082) was added to the oxygen basis to improve the electron affinity of the hydroxide ion, which was obtained as −0.11 eV with the extra function and −2.64 eV without. This valence basis for oxygen and the ECP parameters for the first row atoms are given in Tables I and II. In the calculations the O–H bond distance was kept at 0.98 Å. The same hydrogen basis as for water was used also for the hydroxide ion, while the H^- was described by using the Huzinaga 4s basis[27] contracted to two and extended with one p function (0.789).

The 1s orbital of F^- was parametrized in an ECP. The original basis is that of Roos–Siegbahn[29] including one diffuse p function added to describe F^-. The three innermost s functions were deleted, and this reduced basis was further contracted to 3s and 3p. The atomic results for the orbital energies of F (^2P) and F^- (^1S) agree within 0.01 eV between the ECP and the all-electron calculation. The SCF electron affinity obtained is 1.38 eV for the all-electron calculation and 1.40 eV using the ECP.

Finally, the carbon atom in the methyl group was described by using the ECP of Wahlgren[22] while the hydrogen basis was the Huzinaga 4s basis[27] contracted to two. The geometry of the methyl group was taken from a separate gradient optimization on $HPdCH_3$[30] yielding a C–H distance of 1.09 Å and a H–C–H angle of 111.0°. This internal geometry was retained in all calculations.

Results and Discussion

Hartree–Fock, SCF molecular orbital calculations were carried out on $Pd(H_2O)(Nu)_2$(ethene) complexes using the structures **1** and **2** shown in Figure 2. The Pd–Nu bond distances were optimized in all cases, and the values obtained agree well with known experimental values of these bonds in analogous compounds (Table III).[31,32] The strength of the Pd–Nu bond was estimated from a variation (±0.05 Å) of the bond distance, and the calculated force constants are given in Table III. The higher values of the force constant for the Pd–F and Pd–OH bonds (43 and 47 eV/Å^2) compared to the Pd–H and Pd–CH_3 bonds (24 and 25 eV/Å^2) suggest a stronger Pd–Nu bond in the former cases. The increased strength of the Pd–OH and Pd–F bonds is due to larger ionic interactions. From Table IV, which gives charges of different parts of the complexes, it can be seen that the charge on fluoride and hydroxide is approximately −0.7 compared to −0.22 and −0.34 on hydride and methyl.

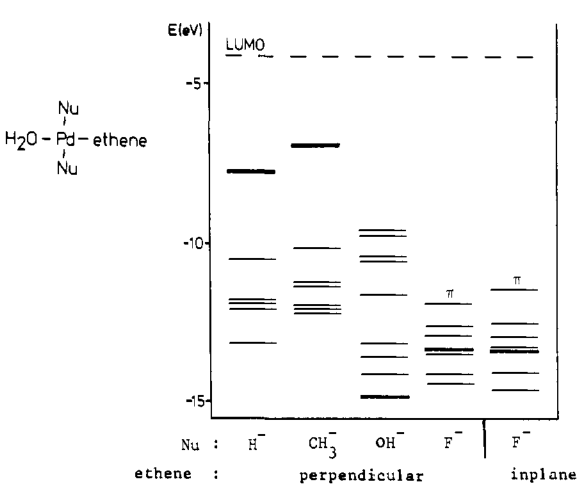

Figure 3. Orbital energies for the highest occupied molecular orbitals for complexes **1** and **2**. The Pd–Nu bond of type **4** is indicated with a thick line in each case. The Pd–Nu orbital indicated is fairly well distributed on both centers (50–70% on Nu and 30–50% on Pd, with the higher localization on the nucleophile for Nu = OH^- and F^-). In the case of Nu = OH^-, the Pd–Nu orbital mixes to some extent with a lone pair on H_2O.

The palladium–ethene bond has been studied elsewhere[11b] and will not be discussed in detail here. However, some observations need comment. Our calculations show that the mixing between the π^* orbital of ethene and the filled $4d_{yz}$ orbital of the metal, the so-called back donation, is small in all cases studied. Thus, the electron occupation in the π-back-donating orbital ($4d_{yz} + \pi^*$) is 1.88–189 on palladium and 0.09–0.10 on ethene for all the complexes studied. This is in good agreement with a previous[11b] ECP-ab initio calculation on $[PdCl_3(\text{ethene})]^-$ and with other theoretical studies on d^8 metal(II) π-olefin complexes of the nickel triad.[9-11] The barrier for rotation of ethene around the Pd–ethene axis in $PdF_2(H_2O)$(ethene) can be estimated from the calculation of the conformer **2** in which the ethene molecule is in the plane of the other ligands. The conformation **1** in which the ethene is perpendicular to the other ligands was found to be 9.2 kcal/mol more stable than the in-plane conformation **2**. This is in good agreement with the calculated[11b] barrier for $[PdCl_3(\text{ethene})]^-$ and with experimental values for the related platinum olefin complexes.[33] The barrier for rotation in square-planar platinum(II) olefin complexes, which should be slightly higher than in the corresponding palladium complexes, is in the range of 10–15 kcal/mol according to ^1H NMR coalescence studies.[33]

The barrier for rotation in $PdF_2(H_2O)$(ethene) is nicely reflected by the increase in energy of the π orbital of ethene by approximately 0.4 eV on going from the upright conformation **1** to the in-plane conformation **2** (Figure 3). It has been argued that the higher energy of the conformation **2** is mainly due to steric effects,[10b,33] which means that the filled π orbital on ethene mixes with filled ligand orbitals, leading to a destabilization. This can be seen also in our calculation, but we also see some stabilization of the upright conformation **1**, not only by a favored π^*–d_{yz} overlap, but also by a stabilization of the ethene π orbital through a better "σ-donation". The latter orbital is plotted for each conformation in Figure 4.

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[28] This distance was not optimized since water was used only as a model for a weak neutral ligand of minor importance for the overall result.

[29] Roos, B.; Siegbahn, P. *Theoret. Chim. Acta* **1970**, *17*, 209.

[30] Davstad, K., private communication.

[31] (a) Hosokawa, T.; Calvo, C.; Lee, H. B.; Maitlis, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 4914. (b) Forsellini, E.; Bombieri, G.; Crociani, B.; Boschi, T. *Chem. Commun.* **1970**, 1203.

[32] Müller, B.; Hoppe, R. *Mater. Res. Bull.* **1972**, *7*, 1297.

[33] (a) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1969**, *53*; **1970**, 1653. Ashley-Smith, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1776. Ashley-Smith J.; Douek, Z.; Johnson, B. F. G.; Lewis, J. *Ibid.* **1974**, 128. (b) Boucher, J.; Bosnich, B. *Inorg. Chem.* **1977**, *16*, 717. (c) Sinya, M.; Saito, J. *Ibid.* **1981**, *20*, 287.

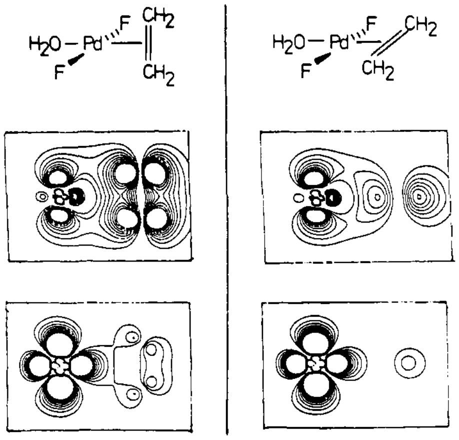


Figure 4. Electron density maps for molecular orbitals containing the symmetric Pd–ethene bond. The upper orbital is the highest occupied one in both cases (denoted with π in Figure 3).

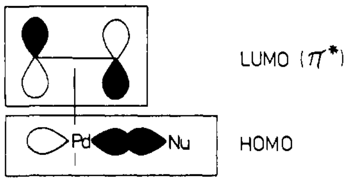
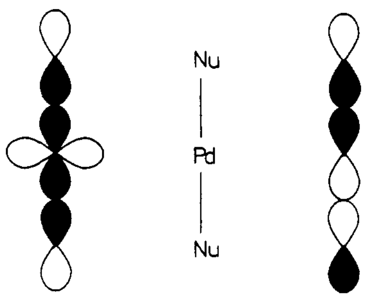


Figure 5. Frontier orbitals for a cis migration.

The energies of the molecular orbitals for the different complexes are summarized in Figure 3. The Pd–Nu bond is described by two molecular orbitals in which the valence s or 2p orbitals of the nucleophile are combined with either Pd $4d_{x^2-y^2}$ to give **3** or with Pd 5p to give **4**. The latter orbital is higher in energy.



3 4

The Pd–Nu orbital energies of type **4** are indicated in Figure 3 for all complexes, since this orbital is of importance for the reactivity of the coordinated nucleophile.

What will determine if a coordinated nucleophile will migrate to the olefin or not? It is likely that charge plays a minor role in a cis migration process, since the reaction has similarities with a (2 + 2) cycloaddition. It would therefore be expected that the reactivity of the π-olefin complexes **1** and **2** toward a cis migration is mainly determined by the frontier orbitals. The frontier orbitals involved in a cis migration are shown in Figure 5.

According to the theory of Fukui[18] one may divide the reacting system into two parts, one which contains the HOMO and one which contains the LUMO. This has been done in Figure 5, and in our case the HOMO will be the orbital describing the metal–nucleophile bond and the LUMO will be the π^* orbital. Now the reaction rate will increase with decreasing energy difference $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ provided that the steric conditions for orbital overlap remain essentially the same.[18,19] In a perturbational treatment, Klopman[19a,b] has classified reactions as frontier controlled or charge controlled. When the energy difference $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ is large, the reaction may become *charge controlled*, but when the energy gap between HOMO and LUMO is small, the reaction becomes *frontier controlled*.

The unoccupied orbitals in SCF calculations are not well described, and the calculated energy for these orbitals are generally to high. It is therefore difficult to obtain a reasonable energy value for the π^* orbital of the complexes (LUMO) from our calculations. However, we have made the assumption that the energy of the π^* orbital does not change much on complexation and therefore can be approximated with the energy of π^* of free ethene. This is a reasonable assumption since the present calculations show that the π-back donation (mixing between π^* and d_{yz}) is very small in the complexes, which is in agreement with other theoretical studies on d^8 metal(II) olefin complexes of Ni,[9] Pd,[10] and Pt.[10,11a,b] Furthermore, even if the absolute energy of the LUMO of the complexes is an approximation, its energy should not change significantly by variation of the nucleophiles. We have therefore considered LUMO to be constant throughout the whole series of complexes and set it to −4 eV, which is the weighted average of the calculated triplet and singlet excitation energies for ethene with the present basis.

Since the exact geometry of the reactive intermediate is not known, most of the calculations were made on the more stable conformation **1**, in which ethene is perpendicular to the plane of the other ligands. The energy of the orbital describing the Pd–Nu bond (HOMO) would not change much in going from **1** to the reactive complex. Different possible configurations for the reactive intermediate involved in cis hydride migration in (π-olefin)platinum hydride complexes have been discussed.[34] One of these possible intermediates is a four-coordinated complex with the olefin in the plane of the other ligands and with the hydride cis to the olefin. We have made a calculation in one case where we have used this geometry for the complex $PdF_2(H_2O)$(ethene) (**2**). The results show that the energy of the crucial orbital describing Pd–Nu bond **4** has not changed significantly (<0.3 eV) and that the change in the other orbitals is small. The major change is a destabilization of the π-ethene orbital (0.44 eV) through mixing with a lone-pair fluorine orbital, which in turn is slightly stabilized (0.14 eV).

As can be seen from Figure 3 the energy of the Pd–Nu bond orbital **4** changes drastically with different nucleophiles. For example, this orbital is high in energy for Nu = H^- and CH_3^- (−7.6 and −6.9 eV) whereas it is low in energy for Nu = OH^- and F^- (−14.8 and −13.5 eV). For the former complexes the Pd–Nu bond orbital also constitutes the HOMO of the whole system. By use of the approximate π^* energy (LUMO) of −4 eV for the complexes the energy difference ($E_{\pi^*} - E_{\text{Pd-Nu}}$) would be 3.6 and 2.9 eV for the hydride and methyl complexes, respectively, and 10.8 and 9.5 eV for the hydroxide and fluoride complexes, respectively. This indicates that only coordinated hydride and methyl would be able to undergo a frontier-controlled cis migration, whereas coordinated hydroxide and fluoride would be too unreactive in such a process. This conclusion is also in good agreement with the higher force constant calculated for the Pd–F and Pd–OH bonds compared to the Pd–H and Pd–CH_3 bonds (Table III). The weaker bonds in the latter cases would make a cis migration more probable.

Thus, a necessary condition for an intramolecular cis addition to occur is that the orbital describing the metal nucleophile bond be high enough in energy. This would in turn require that the free nucleophile has a high-energy HOMO. Often the terminology soft nucleophiles or bases has been used to classify nucleophiles or bases with high-lying available electrons, i.e., with a high-lying HOMO.[19,35] Analogously, hard nucleophiles refer to nucleophiles

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(34) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(35) (a) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581, 643. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (c) Pearson, R. G.; Songstad, J. *Ibid.* **1967**, *89*, 1827.

(36) Bäckvall, J. E.; Björkman, E. E. *J. Org. Chem.* **1980**, *45*, 2983.

(37) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135.

(38) (a) Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 485. (b) Vedejs, E.; Salomon, M. *Ibid.* **1970**, *92*, 6965.

(39) Holton, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 8083.

(40) Takahashi, H.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 2387.

(41) Wipke, W. T.; Goeke, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 4224. See also: Wieger, G.; Albelo, G.; Rettig, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 2242.

(42) Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1979**, *44*, 1189.

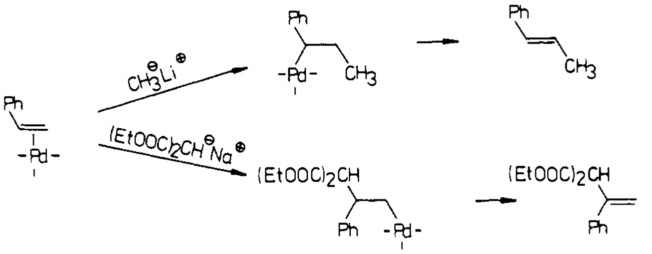
(43) Bäckvall, J. E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1980**, 943.

Table V. Stereochemistry of Nucleophilic Addition to (π-Olefin)palladium Complexes Related to the Energy of the HOMO of the Nucleophile

nucleophile	substrate	stereochemistry (ref)	energy of HOMO
$HO^-(H_2O)$	monoolefin (ethene-d_2)	trans (4a, 5b)	low (hard)
	diolefin (1,5-cyclooctadiene)	trans (4b)	
Me_2NH, Et_2NH	monoolefin (2-butene, 1-decene-d_1)	trans (15, 36)	low (hard)
$CH_3O^-(CH_3OH)$[a]	monoolefin (2-butene, ethene-d_2)	trans (4c, 14)	low (hard)
	diolefin (bicyclopentadiene, norbornadiene 1,5-cyclooctadiene)	trans (37, 38)	
CH_3COO^-[a]	monoolefin (cyclohexene, neohexene-d_1)	trans (13)	low (hard)
	diolefin (bicyclopentadiene)	trans (38)	
$RCO\bar{C}HCOR$	monoolefin (ethene-d_2, 4-(dimethylamino)cyclopentene)	trans (16, 39)	intermediate
	diolefin (1,5-cyclooctadiene)	trans (40)	
Cl^-	diolefin (1-vinylnorbornadiene)	trans (41)	intermediate
$PhSO_2^-$	diolefin (bicyclopentadiene)	trans (42)	intermediate
Ph^-	monoolefin (cyclohexene)	cis (17a)	high (soft)
	diolefin (norbornadiene)	cis (17b)	
CH_3^-	monoolefin (styrene-d_1)	cis (17c)	high (soft)
H^-	monoolefin (cyclohexene, indirect)	cis (13a, 17a)	high (soft)

[a] The stereochemistry of oxypalladation of conjugated dienes, which is a special case, has also been studied. Oxypalladation of 1,3-cyclohexadiene occurs trans[43] whereas oxypalladation of dehydro-β-pinene (2-methylene-6,6-dimethylbicyclo[3.1.1]hept-3-ene) has recently been reported to occur cis.[44]

Scheme II



having a low-lying HOMO. Among the former nucleophiles (soft) typical examples are hydride, methyl, and cyanide, and among the latter nucleophiles (hard) typical examples are hydroxide, methoxide, and fluoride. In Table V we have summarized experimental results on stereochemical studies on nucleophilic additions to (π-olefin)palladium complexes. Some of these nucleophiles are difficult to classify as soft or hard. Take, for example, a stabilized carbon nucleophile such as diethyl malonate anion. Is this nucleophile soft or hard? Compared to the methyl anion the available electrons of dimethyl malonate are stabilized, and, therefore, the HOMO must be lower than the HOMO of the methyl anion. This would indicate that a cis migration would be less favored for a stabilized carbanion compared to methyl anion, which is also experimentally observed.[16,17c]

The nucleophiles with a low-lying HOMO usually react very efficiently in a trans-addition reaction (Scheme I), and it is therefore likely that this reaction is a charge-controlled process. The nucleophilic addition of methyllithium and diethyl sodiomalonate to a (styrene)palladium complex seems to support such as picture (Scheme II). Thus, the methyl anion attacks the carbon with the highest coefficient[45] in the LUMO (π* orbital of the double bond), whereas the diethyl malonate anion attacks the more positively charged carbon of the double bond.[17c] This is consistent with a frontier-controlled reaction in the former case and a charge-controlled reaction in the latter case. Furthermore, it was shown by using specifically deuterated styrene that the methyl anion adds cis. The results from the addition of diethyl malonate were best explained by a trans attack by the nucleophile.[17c] More recent stereochemical studies have shown that $Na^{+-}CH(COCH_3)_2$, which is related to diethyl malonate, adds trans to (π-ethene-d_2)Pd(Cp)(PPh_3).[16]

The above model is a simplified model, and many other factors may influence the ability of a coordinated nucleophile to migrate or not. However, the simplicity of the model may be useful for (i) classifying nucleophiles in nucleophilic addition to (π-olefin)palladium complexes and related organo-transition-metal complexes, (ii) giving a rough understanding of the underlying orbital interactions, and (iii) predicting the ability of a given nucleophile to undergo migration to the olefin in (π-olefin)palladium complexes and related organo-transition-metal complexes.

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Registry No. 1 (Nu = H^-), 90605-76-8; **1** (Nu = CH_3^-), 90605-77-9; **1** (Nu = OH^-), 90605-78-0; **1, 2** (Nu = F^-), 90605-79-1.

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[44] Hosokawa, T.; Imada, Y.; Murahashi, S. I. *Tetrahedron Lett.* **1982**, *23*, 3373.

[45] Because of the weak π*–d_{yz} interaction in (π-olefin)palladium complexes (vide supra), the π* orbital of the styrene double bond will be essentially unchanged on π-complex formation. In free styrene the π* orbital of the double bond (LUMO) has its largest coefficient at the terminal carbon: Eisenstein, O.; Lefour, J. M.; Nguyen Trong Anh; Hudson, R. F. *Tetrahedron* **1977**, *33*, 523.