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(11) (a) For simplicity we will generally use kcal to indicate kcal/mol. (b) Comparing the calculated energies for the processes (I) and (II) leads to an energy difference of 28.5 kcal. This small error is a measure of the internal consistency and accuracy of GVB–CI calculations.
(12) Assuming that the barrier to NH bond breaking is approximately equal to the ΔH for this process.
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A Palladium-Catalyzed Reaction of a π-Allyl Ligand with a Nucleophile. An MO Study about a Feature of the Reaction and a Ligand Effect on the Reactivity

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Abstract: A CNDO-type MO study was carried out for the reaction between OH^- and the π-allyl ligand coordinating to palladium(II), as a model reaction of various nucleophilic attacks on the π-allyl ligand. MO calculations showed the following feature of the reaction: when a nucleophile, Y, approaches the π-allyl ligand, the palladium(II) is reduced to palladium(0), and the π-allyl ligand is eliminated as an allyl derivative, $CH_2{=}CHCH_2Y$, from the palladium(0). This feature agrees with the experimental result. The reactivity regarding the OH^- nucleophilic attack increases in the order $PdCl_2(\pi\text{-}C_3H_5)^- \ll PdCl(PH_3)(\pi\text{-}C_3H_5)$ (B) $< PdCl(PH_3)(\pi\text{-}C_3H_5)$ (A) $\sim [PdCl(\pi\text{-}C_3H_5)]_2 < PdCl(CO)(\pi\text{-}C_3H_5)$ (B) $< PdCl(CO)(\pi\text{-}C_3H_5)$ (A) $< Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (B) $< Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (A), where (A) indicates an inclusion of the Pd 4dπ–CO π* π-acceptor interaction in $PdCl(CO)(\pi\text{-}C_3H_5)$ and inclusion of the Pd 4dπ–P 3dπ interaction in $PdCl(PH_3)(\pi\text{-}C_3H_5)$ and $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$, and (B) indicates exclusion of the interactions. Although the anionic ligand is unfavorable for the reaction, the neutral π-acceptor ligand is favorable. MO calculations support the proposal of Trost et al. that the nucleophilic attack of the carbanion on the π-allyl ligand is accelerated by addition of triphenylphosphine, and that the cationic complex, $Pd(PPh_3)_2(\pi\text{-}C_3H_5)^+$, is an active intermediate. It is discussed why the neutral π-acceptor ligand is favorable for the nucleophilic reaction and why the anionic ligand is unfavorable.

Introduction

It has been known that palladium complexes act as catalysts of various kinds of reactions such as the Wacker reaction, the isomerization and hydrogenation of alkenes, and nucleophilic attack on alkene and π-allyl ligands coordinating to palladium(II).[1-3] The nucleophilic attack on the ligand seems an important characteristic of the palladium catalysis, because various nucleophilic reactions of carbanion, amine, acetate anion, etc., are considered useful in the field of organic synthesis.[4-17] A nucleophilic reaction of a carbanion with the π-allyl ligand has been actively studied from the viewpoint of a formation of a new C–C bond,[4,6,10,14-17] and it has been noted that addition of a tertiary phosphine greatly accelerates the nucleophilic attack.[9,16a]

Although many experimental studies have been reported as described above, no theoretical work has been performed on such a nucleophilic reaction. The theoretical work can characterize a feature of the reaction and can elucidate why the tertiary phosphine accelerates the reaction. Knowledge about these issues seems necessary to advance the study of palladium catalysis. In this work, CNDO-type semiempirical SCF-MO calculations were carried out on some π-allylpalladium complexes, $PdCl_2(\pi\text{-}C_3H_5)^-$, $PdClL(\pi\text{-}C_3H_5)$ (L = CO or PH_3), $[PdCl(\pi\text{-}C_3H_5)]_2$, and $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$, and on a reaction between the OH^- and the π-allyl ligand in the above complexes. Although the OH^- has not been known to react with the π-allyl ligand to form allyl alcohol, the OH^- is considered here as a model of a usual nucleophile such as phenoxide, acetate, carbanion, etc. The purpose of this work is twofold; first, to elucidate how the electronic structure of the palladium complex is changed by the nucleophilic attack;

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second, to investigate the ligand effect on the reactivity, especially to elucidate why the tertiary phosphine accelerates the nucleophilic attack.

MO Calculations

A CNDO-type semiempirical SCF-MO method, described elsewhere,[18-20] was employed. This MO method gives successful results regarding electronic structures, stereochemistry, and electronic spectra of transition-metal complexes.[18-20] Parameters of the Pd and P atoms used here are described in the Appendix.

The quantity E_{AB} was used as a bond index,[21,22] and is defined as an energetic contribution of the AB bond to the total energy as follows:[18-20]

$$E_{AB} = E_{AB}{}^{(1)} + E_{AB}{}^{(2)} + E_{AB}{}^{(3)} = 2\sum_r^{A} \sum_s^{B} P_{rs}H_{rs} - 0.5 \sum_r^{A}\sum_s^{B} P_{rs}{}^2\gamma_{rs} + \sum_r^{A} \sum_s^{B}(P_{rr} - N_r)(P_{ss} - N_S)\gamma_{rs}$$

A large negative E_{AB} value indicates a strong bond between the A and the B atoms. The $E_{AB}{}^{(1)} + E_{AB}{}^{(2)}$ $(=E_{AB}{}^{(1)+(2)})$ approximately represents the strength of the covalent interaction, while $E_{AB}{}^{(3)}$ represents the strength of the electrostatic interaction.

The π back-donative interaction (the Pd 4dπ-CO π* and the Pd 4dπ-P 3dπ) is considered to play an important role in the coordination of the carbonyl and the phosphine ligands. In this work, the effect of such a π back-donative interaction was examined as follows: the overlaps between the Pd 4dπ and the C and O $2p_\pi$ orbitals were neglected in some MO calculations both of $PdCl(CO)(\pi\text{-}C_3H_5)$ and $PdCl(CO)(\pi\text{-}C_3H_5) \leftarrow OH^-$, while these overlaps were explicitly included in other calculations.[23a] Also, the 3dπ orbitals of the P atom were excluded from the basis set in some MO calculations on both of the π-allylpalladium complexes including the PH_3 ligand and their reaction systems, while these 3d's were included in other calculations.[23b] MO calculations including the π back-donative interaction were termed A and those excluding them were B in this work.

A technique, called configuration analysis, was employed in order to investigate how the electronic structure of π-allylpalladium complexes is changed by a nucleophilic attack of the OH^-. Since this technique has been described elsewhere,[24] it is briefly described here. A Slater determinant Ψ of a reaction system, π-allylpalladium complex + OH^-, is represented by a linear combination of configuration interaction (CI) wave functions as follows:

$$\Psi = C_0\Phi_0 + \sum_i^{\text{occ}} \sum_l^{\text{unocc}} C_{i\to l}\Phi_{i\to l} + \sum_k^{\text{occ}} \sum_j^{\text{unocc}} C_{k\to j}\Phi_{k\to j} + \sum_i^{\text{occ}} \sum_j^{\text{unocc}} C_{i\to j}\Phi_{i\to j} + \sum_k^{\text{occ}} \sum_l^{\text{unocc}} C_{k\to l}\Phi_{k\to l} + \ldots$$

where the Ψ is constructed from MOs ψ of the whole reaction system and the $\Phi_{i\to j}$, etc., is constructed from MOs ϕ_m of the π-allylpalladium complex and $\phi_n{}'$ of the OH^- anion. The i and k mean occupied MOs of the π-allylpalladium complex and those of the OH^-, respectively, while the l and j mean unoccupied MOs of the π-allylpalladium complex and those of the OH^-, respectively. See ref 24 for a more detailed description. The coefficients $C_{i\to j}$, etc., are obtained from MO expansion coefficients a_{mj} and b_{nj}:

$$\psi_j = \sum_m a_{mj}\phi_m + \sum_n b_{nj}\phi_n{}'$$

where the Σ_m and Σ_n mean a summation on MOs of the π-allylpalladium complex and on MOs of the OH^-, respectively. From the coefficients $C_{i\to j}$, etc., we can obtain valuable information about the electronic structure of the reaction system; for example, it can be elucidated what kinds of charge transfers between the palladium and the OH^- are caused by the OH^- attack and what kinds of polarizations are caused in the π-allylpalladium complex by the OH^- attack.

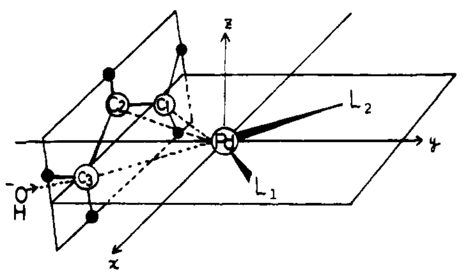


Figure 1. Coordinate system of the π-allylpalladium complexes and the course of the OH^- attack on the π-allyl ligand L_1, L_2 = Cl, CO, or PH_3. L_1 = Cl and L_2 = CO or PH_3 in $PdClL(\pi\text{-}C_3H_5)$ (L = CO or PH_3).

Geometries

The geometry of $[PdCl(\pi\text{-}C_3H_5)]_2$ was taken from an X-ray study.[25] The geometry of $PdCl_2(\pi\text{-}C_3H_5)^-$ was assumed to be similar to that of the $PdCl_2(\pi\text{-}C_3H_5)$ part of $[PdCl(\pi\text{-}C_3H_5)]_2$, because no X-ray study has been reported. The geometries of $PdCl(PH_3)(\pi\text{-}C_3H_5)$ and $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ were assumed as follows. The Pd-P bond length was taken to be 2.30 Å from an X-ray study.[26] The other parts, $PdCl(\pi\text{-}C_3H_5)$ of the former and $Pd(\pi\text{-}C_3H_5)$ of the latter, were taken to be similar to the corresponding part of $[PdCl(\pi\text{-}C_3H_5)]_2$. The geometry of $PdCl(CO)(\pi\text{-}C_3H_5)$ was assumed as follows. The Pd-CO bond length was arbitrarily taken to be 1.82 Å by considering the Pt-CO bond length of $PtCl_3(CO)^-$,[27] for no X-ray data had been reported about the Pd-CO bond length, as far as the authors were aware. The $PdCl(\pi\text{-}C_3H_5)$ part was taken to be similar to that of $[PdCl(\pi\text{-}C_3H_5)]_2$. The ClPdCl′, ClPdP, and PPdP′ angles of the above complexes were assumed to be the same as the ClPdCl′ angle of $[PdCl(\pi\text{-}C_3H_5)]_2$, because no X-ray data has been reported on these angles. This assumption does not seem unreasonable, for the ClPdCl′ angle of $[PdCl(\pi\text{-}C_3H_5)]_2$ is nearly equal to 90°.

The nucleophilic attack of the OH^- anion was investigated as a model reaction of various nucleophiles, as described in the Introduction. Trost et al. and Åkermark et al. have reported that nucleophiles such as the carbanion and the amine directly attack the π-allyl ligand on the face opposite to the palladium.[12,16b,28] Although Numata and Kurosawa have reported another reaction path in which the aryl anion first coordinates to the palladium(II) and then attacks the π-allyl ligand,[29] the present reaction path was taken to be similar to that proposed by Trost et al. and Åkermark et al.; the OH^- directly attacks the π-allyl ligand from the side opposite to the palladium, and the lone-pair orbital of the OH^- is perpendicular to the face of the π-allyl ligand, as is depicted in Figure 1.

Results and Discussion

Electronic Structures of π-Allylpalladium Complexes. First, the electronic structures and the coordinate bonding nature of π-allylpalladium complexes will be briefly examined. The electron distribution and the relative binding energy, ΔE_b, are given in Table 1 (see ref 30 for the definition of ΔE_b). The following characteristics are found: (1) the electron densities of the C_1 and C_3 atoms are remarkably reduced by the π-allyl coordination. (2) The nπ orbital of the π-allyl ligand denotes a large amount of electrons to the palladium(II), while the π orbital denotes a small amount of electrons and the π* orbital receives extremely small amounts of electrons (see Scheme I for π, nπ, etc., and see $\Delta q(\pi)$, $\Delta q(\pi^*)$, etc., in Table 1). The electron donation from nπ becomes large as the LUMO of $PdCl_2$, $PdClL^+$ (L = CO or PH_3), and $Pd(PH_3)_2{}^{2+}$ becomes

Table I. Electron Distribution of π-Allylpalladium Complexes

		C_1	C_2	C_3	$\Delta q(n\pi)$[a]	$\Delta q(\pi)$[a]	$\Delta q(\pi^*)$[b]	ΔE_b[c]	ϵ_{LUMO}[d]
$C_3H_5^-$		4.519	3.895	4.519					
$PdCl_2(\pi\text{-}C_3H_5)^-$		4.353	3.925	4.353	0.481	0.093	0.028	0.0	−5.18
$PdCl(PH_3)(\pi\text{-}C_3H_5)$	(B)	4.315	3.931	4.268	0.661	0.099	0.028	4.5	−9.85
	(A)	4.296	3.938	4.253	0.713	0.102	0.029	5.1	−10.22
$[PdCl(\pi\text{-}C_3H_5)]_2$		4.267	3.943	4.267	0.737	0.102	0.028	5.3	−10.29
$PdCl(CO)(\pi\text{-}C_3H_5)$	(B)	4.285	3.940	4.240	0.746	0.099	0.028	5.7	−11.11
	(A)	4.263	3.950	4.225	0.798	0.100	0.030	6.0	−11.31
$Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$	(B)	4.221	3.940	4.221	0.864	0.105	0.029	9.7	−14.70
	(A)	4.187	3.953	4.187	0.972	0.110	0.031	10.9	−15.39

[a] $\Delta q(n\pi)$ and $\Delta q(\pi)$ are decreases in the electron numbers of the $n\pi$ and π orbitals caused by the coordination; $\Delta q(n\pi)$ = [electron numbers on the $n\pi$ orbital of the free π-allyl ligand] − [electron numbers on the same orbital in the complex], and $\Delta q(\pi)$ is similarly defined. [b] $\Delta q(\pi^*)$ is an increase in the electron number on the π^* orbital caused by the coordination; $\Delta q(\pi^*)$ = [electron numbers on the π^* orbital in the complex] − [electron numbers on the π^* orbital in the free ligand]. [c] The relative binding energy; the binding energy of $PdCl_2(\pi\text{-}C_3H_5)^-$ was taken to be the standard (eV). See ref 30. [d] The LUMO orbital energy of $PdCl_2$, $PdCl(PH_3)^+$, $Pd_2Cl_2(\pi\text{-}C_3H_5)^-$, etc. (eV).

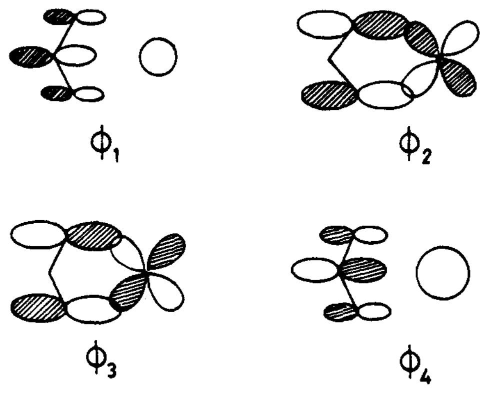
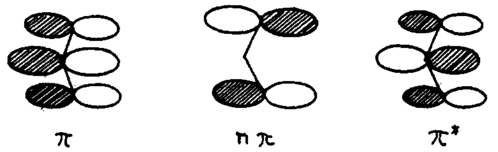


Figure 2. Important interactions between the Pd and the π-allyl ligand. The ϕ_1 and ϕ_2 are occupied, while the ϕ_3 and ϕ_4 are unoccupied.

stable. The LUMO is mainly composed of the Pd $4d_{xy}$. (3) The ΔE_b value becomes large, as the electron donation from the $n\pi$ orbital increases. The results (2) and (3) suggest that the π-allyl coordination is mainly due to the electron donation from its $n\pi$ orbital to the Pd $4d_{xy}$ orbital, while the π-allyl coordination is somewhat enhanced by the electron donation from the π orbital to the Pd. The result (1) is attributed to the electron donation from the $n\pi$ orbital; since the $n\pi$ orbital is composed of the $2p_\pi$ orbitals on the C_1 and C_3, the electron donation from the $n\pi$ remarkably reduces the electron densities of the C_1 and C_3 atoms.

Some important orbitals of π-allylpalladium complex, $\phi_1 \sim \phi_4$, are schematically shown in Figure 2. The ϕ_1 corresponds to electron donation from the π orbital to the Pd. The ϕ_1 mixes considerably with the σ MO of the π-allyl ligand obeying the same symmetry. The ϕ_2 corresponds to electron donation from the $n\pi$ to the Pd. This ϕ_2 contributes mainly to the coordinate bond. In unoccupied levels, two orbitals are noted; in the ϕ_3 the $n\pi$ orbital interacts antibondingly with the Pd $4d_{xy}$, and in the ϕ_4 the π^* orbital interacts antibondingly with the Pd 5s. These $\phi_1 \sim \phi_4$ are expected to be changed by the nucleophilic attack, which alters the electronic structure and the coordinate bonding nature of π-allylpalladium complexes.

Scheme I



Reactivity of Various π-Allylpalladium Complexes to a Nucleophilic Attack. MO calculations were performed on the reaction systems between the π-allylpalladium complex and the OH^-. It must be determined which carbon atom of the π-allyl ligand receives nucleophilic attack. The present MO calculations suggest that the C_2 attack would be less possible than the C_1 and C_3 attacks, because the total energy of the C_2-attack system is less stable than the total energies of the C_1- and C_3-attack systems; for example, the former is less stable than the latter by ca. 0.5 eV in $PdCl(CO)(\pi\text{-}C_3H_5) \leftarrow OH^-$ (A) at C-O = 2.0 Å. Experiments also show that the C_2 attack does not occur, because no product derived from the C_2 attack has been found. Thus, the C_2 attack was excluded from the present consideration. No experimental observation elucidates which of the two, the C_1 or C_3 attack, occurs in $PdClL(\pi\text{-}C_3H_5)$ (L = CO or PH_3). Although the total energy of the C_3 attack is calculated to be slightly more stable than the total energy of the C_1 attack, the difference in total energy between the C_1 and C_3 attacks is too small to be meaningful. The C_1 attack cannot be ruled out completely, and both possibilities were examined here. But the electronic structure and the bonding nature of the C_1-attack system are essentially the same as those of the C_3-attack system. The results of the C_3 attack are mainly listed in tables and mainly discussed, because the C_3 attack is slightly more stable than the C_1 attack, and a similar discussion can be presented for the C_1 attack. Some results of the C_1 attack are given in tables.

The total energy change due to the OH^- attack is shown in Figure 3, where the total energy change, ΔE_t, is defined as follows: ΔE_t = [the total energy of the reaction system, π-allylpalladium complex + OH^-] − [the total energy of the π-allylpalladium complex] − [the total energy of the OH^-]. It should be noted that only one reaction system, $PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$, is destabilized by the OH^- attack at $R_{C_3\text{-}O}$ = 3.0–2.0 Å, and that others are stabilized by the OH^- attack. Because no geometrical optimization was carried out, the ΔE_t values themselves are not very meaningful. However, their relative values are expected to reflect the relative reactivity of π-allylpalladium complex. Furthermore, the ΔE_t values do not cross with each other, going from $R_{C_3\text{-}O}$ = 2.0 Å to $R_{C_3\text{-}O}$ = 1.5 Å. Thus, the relative reactivity may be discussed by using the ΔE_t value at either $R_{C_3\text{-}O}$ = 2.0 or 1.5 Å.

A comparison of ΔE_t at $R_{C_3\text{-}O}$ = 2.0 Å reveals that reactivity increases in the following order: $PdCl_2(\pi\text{-}C_3H_5)^-$ (1.3 eV) < $PdCl(PH_3)(\pi\text{-}C_3H_5)$ (B) (−1.8 eV) < $PdCl(PH_3)(\pi\text{-}C_3H_5)$ (A) (−2.2 eV) ~ $[PdCl(\pi\text{-}C_3H_5)]_2$ (−2.2 eV) < $PdCl(CO)(\pi\text{-}C_3H_5)$ (B) (−2.4 eV) < $PdCl(CO)(\pi\text{-}C_3H_5)$ (A) (−2.8 eV) < $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (B) (−5.0 eV) < $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (A) (−5.9 eV), where the values in parentheses represent the ΔE_t values at $R_{C\text{-}O}$ = 2.0 Å and both the C_1 and C_3 attacks give almost the same stabilization energy in $PdClL(\pi\text{-}C_3H_5) \leftarrow OH^-$ (L = CO or PH_3). The above result indicates that the nucleophilic attack is accelerated by the presence of a neutral ligand, and that a neutral π-acceptor ligand, such as PH_3 (A) or CO (A), is more favorable for the

Table II. Electron Distribution and Bond Strength of the Reaction System π-Allylpalladium Complex + OH^-

	$Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (A)			$Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (B)			$PdCl(PH_3)(\pi\text{-}C_3H_5)$ (A)[a]			$PdCl_2(\pi\text{-}C_3H_5)^-$		
$R_{C\text{-}O}$	∞	2.0	1.5	∞	2.0	1.5	∞	2.0	1.5	∞	2.0	1.5
					Electron Density							
Pd	9.96	10.22	10.30	9.99	10.30	10.48	9.86	10.11	10.26	9.77	9.96	10.13
Pd $4d_{xy}$	1.13	1.63	1.84	1.04	1.45	1.73	0.94	1.34	1.68	0.75	0.98	1.26
C_1	4.19	4.14	4.18	4.22	4.18	4.19	4.30	4.23	4.22	4.35	4.31	4.31
C_2	3.95	3.96	3.95	3.94	3.95	3.98	3.94	3.97	4.01	3.93	3.95	4.12
C_3	4.19	3.94	3.88	4.22	3.95	3.84	4.25	3.94	3.83	4.35	4.03	3.81
L_1[b]	7.71	7.87	7.95	7.64	7.72	7.76	7.50	7.60	7.65	7.55	7.63	7.68
L_2[c]	7.71	7.88	7.95	7.64	7.73	7.76	7.75	7.91	8.05	7.55	7.64	7.67
					Bond Strength Described by E_{AB} (eV)							
$E_{C_1\text{-}C_2}$	−27.3	−28.5	−29.5	−27.3	−28.0	−28.8	−27.3	−27.7	−28.6	−27.5	−27.0	−26.3
$E_{C_2\text{-}C_3}$	−27.3	−25.6	−23.5	−27.3	−26.0	−23.7	−27.5	−26.3	−23.9	−27.5	−27.2	−24.7
$E_{Pd\text{-}C_1}$	−9.0	−7.7	−6.9	−9.2	−8.2	−7.4	−9.5	−8.5	−7.6	−9.4	−9.4	−9.2
$E_{Pd\text{-}C_2}$	−6.6	−6.8	−6.9	−6.6	−6.9	−7.2	−6.6	−6.9	−7.2	−6.5	−6.8	−7.6
$E_{Pd\text{-}C_3}$	−9.0	−7.1	−5.9	−9.2	−7.7	−6.4	−9.3	−7.9	−6.3	−9.4	−8.5	−6.8
$E_{Pd\text{-}L_1}$	−13.3	−13.4	−13.6	−12.4	−11.7	−11.4	−11.8	−10.2	−9.1	−12.2	−11.0	−9.9
$E_{Pd\text{-}L_2}$	−13.3	−13.3	−13.4	−12.4	−11.8	−11.6	−13.4	−13.6	−14.1	−12.2	−10.9	−9.9
$E_{C\text{-}O}$		−5.1	−15.5		−4.3	−15.3		−3.8	−15.2		−1.9	−14.0

[a] Results of the C_3 attack are given. The C atom trans positioned to the PH_3 is attacked by the nucleophile. [b] $L_1 = PH_3$ cis positioned to the attacked C atom in $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$. $L_1 = Cl^-$ in $PdCl(PH_3)(\pi\text{-}C_3H_5)$. $L_1 = Cl^-$ cis positioned to the attacked C atom in $PdCl_2(\pi\text{-}C_3H_5)^-$. [c] $L_2 = PH_3$ trans positioned to the attacked C atom in $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$. $L_2 = PH_3$ in $PdCl(PH_3)(\pi\text{-}C_3H_5)$. $L_2 = Cl^-$ trans positioned to the attacked C atom.

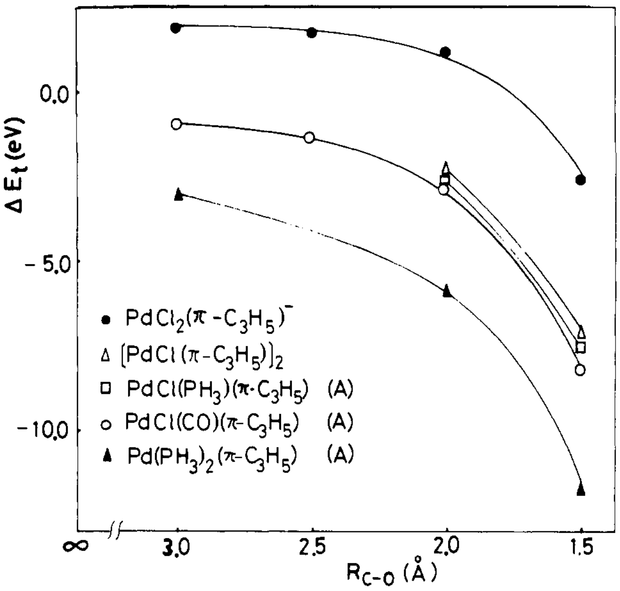
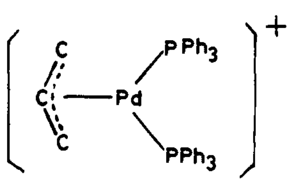


Figure 3. Total energy changes of the π-allylpalladium + OH^- reaction system. ΔE_t (eV unit). Result of the C_3 attack is presented for $PdClL(\pi\text{-}C_3H_5)$ (L = CO or PH_3).

Scheme II



reaction than a neutral ligand without π-acceptor orbital, such as PH_3 (B) and CO (B).

Trost et al. studied nucleophilic attack of a carbanion on the π-allylpalladium complex $[PdCl(\pi\text{-}C_3H_5)]_2$, and found that, although the malonate anion led to no reaction without addition of triphenylphosphine, addition of at least 4 equiv of triphenylphosphine allowed the reaction to proceed in minutes at room temperature.[9,16a] They suggested that the cationic complex shown in Scheme II is a reactive intermediate. It is interesting to examine their suggestion. Addition of 2 equiv of triphenylphosphine would yield $PdCl(PPh_3)(\pi\text{-}C_3H_5)$. According to the present MO calculations, its reactivity is almost the same as that of $[PdCl(\pi\text{-}C_3H_5)]_2$. However, addition of 4 equiv of triphenylphosphine would yield $Pd(PPh_3)_2(\pi\text{-}C_3H_5)^+$. Its reactivity was calculated to be much greater than that of $[PdCl(\pi\text{-}C_3H_5)]_2$, as described in the above. Thus, the present MO calculations support the reactive intermediate suggested by Trost et al.

On the other hand, the anionic ligand is suggested to be unfavorable for the reaction. For example, $PdCl_2(\pi\text{-}C_3H_5)^-$ is expected to be unreactive. This complex is formed from $[PdCl(\pi\text{-}C_3H_5)]_2$ by addition of KCl.[31] Thus, it can be predicted that addition of KCl depresses the nucleophilic reaction.

In conclusion, the neutral π-acceptor ligand is favorable for the nucleophilic attack. The intermediate suggested by Trost et al., $Pd(PPh_3)_2(\pi\text{-}C_3H_5)^+$, is supported by the present MO calculation.

How the Electronic Structure of π-Allylpalladium Changes Due to the OH^- Attack. Let us see how the electronic structure of the reaction system, $PdClL(\pi\text{-}C_3H_5) \leftarrow OH^-$, etc., changes during the reaction. Table II gives the electron distribution and E_{AB} values of $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+ \leftarrow OH^-$ (A) and (B), $PdCl(PH_3)_2(\pi\text{-}C_3H_5) \leftarrow OH^-$ (A), and $PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$, as examples, where the C_1 attack is omitted here, because very similar results are obtained in both the C_1 and C_3 attacks. The following characteristics are found in the former three: (1) As the OH^- approaches the π-allyl ligand and the C_3–O bond is formed, the electron density of Pd, C_2, Cl, and PH_3 increases, that of the C_3 remarkably decreases, and that of the C_1 decreases slightly. The electron density of the Pd $4d_{xy}$ increases remarkably, which increases the electron density of the Pd. (2) The absolute value of $E_{C_1\text{-}C_2}$ becomes increasingly large, while that of $E_{C_2\text{-}C_3}$ becomes increasingly small. The absolute values of $E_{Pd\text{-}C_1}$, $E_{Pd\text{-}C_3}$, and $E_{Pd\text{-}Cl}$ become increasingly small, while that of $E_{Pd\text{-}C_2}$ becomes increasingly large. The absolute value of $E_{Pd\text{-}PH_3}$ becomes slightly larger in (A), while it becomes slightly smaller in (B). (3) The sum of the absolute values, $E_{Pd\text{-}C_1}$, $E_{Pd\text{-}C_2}$, and $E_{Pd\text{-}C_3}$, becomes small. Similar results were obtained in the other reaction systems except for $PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$. In the latter reaction system, some differences were found: (1) The electron densities of the Pd and its $4d_{xy}$ orbital become large to a lesser extent than those of the other reaction systems. (2) The absolute value of $E_{C_1\text{-}C_2}$ decreases slightly, while this value in-

Table III. Coefficients of Some Important CI Wave Functions[a]

CI wave function[b]		$\phi_n \rightarrow \phi_3$	$\phi_n \rightarrow \phi_4$	$\phi_2 \rightarrow \phi_3$	$\phi_2 \rightarrow \phi_4$	$\phi_1 \rightarrow \phi_3$[c]
$PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$		0.232	0.193	−0.231	−0.121	−0.002
$PdCl(PH_3)(\pi\text{-}C_3H_5) \leftarrow OH^-$	(B)	0.327	0.200	−0.250	−0.104	−0.118
		(0.334	0.179	−0.254	−0.090	−0.131)[d]
	(A)	0.347	0.179	−0.265	−0.083	−0.138
$[PdCl(\pi\text{-}C_3H_5)]_2 \leftarrow OH^-$		0.359	0.180	−0.201	−0.091	−0.144
$PdCl(CO)(\pi\text{-}C_3H_5) \leftarrow OH^-$	(B)	0.353	0.202	−0.250	−0.092	−0.140
	(A)	0.386	0.185	−0.266	−0.068	−0.147
		(0.394	0.169	−0.272	−0.064	−0.151)[d]
$Pd(PH_3)_2(\pi\text{-}C_3H_5)^+ \leftarrow OH^-$	(B)	0.424	0.169	−0.256	−0.073	−0.160
	(A)	0.468	0.154	−0.295	−0.048	−0.172

[a] One electron transfer type CI wave function. $R_{C\text{-}O} = 2.0$ Å. [b] See Figure 2 for π_1, π_2, etc. [c] The ϕ_1 mixes considerably with other σ MOs of the π-allyl ligand obeying the same symmetry. This value is a sum of product of C_{j3} and the $a_{\pi j}$, where the C_{j3} is the coefficient of the $\phi_j \rightarrow \phi_3$ CI wave function (j = occupied MO of the π-allylpalladium complex) and the $a_{\pi j}$ is the coefficient of the π-allyl π orbital in representing the π allylpalladium ϕ_j orbital with linear combination of MOs of π-allyl ligand and fragment $PdCl_2$, PdClL, etc. [d] Results in parentheses for the C_1 attack.

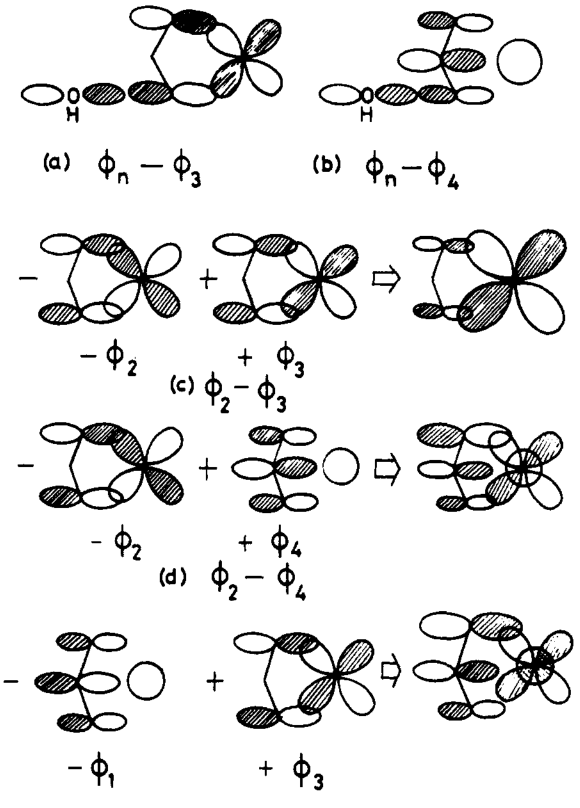
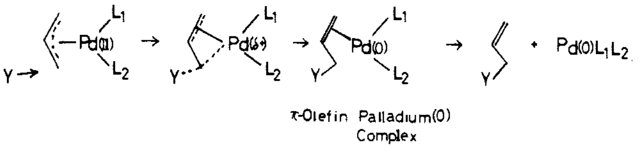


Figure 4. Schematic pictures of orbital mixings between the π-allylpalladium and the OH^-, (a) and (b), and the orbital mixing of intra-π-allylpalladium complex, (c) and (e). The plus sign means the in-phase mixing presented here, while the minus sign means the out-of-phase mixing.

creases in the other reaction systems. (3) The absolute value of $E_{Pd\text{-}C_1}$ changes little at $R_{C_3\text{-}O} = 2.0$ Å and then decreases at $R_{C_3\text{-}O} = 1.5$ Å. The sum of the absolute values, $E_{Pd\text{-}C_1}$, $E_{Pd\text{-}C_2}$, and $E_{Pd\text{-}C_3}$, also increases at $R_{C_3\text{-}O} = 2.0$ Å and then decreases at $R_{C_3\text{-}O} = 1.5$ Å.

A feature of the nucleophilic reaction is given as follows from the above results except for the reaction between $PdCl_2(\pi\text{-}C_3H_5)^-$ and OH^-. As the C_3-OH bond is formed, the palladium(II) is reduced to palladium(0). The C_1-C_2 becomes stronger and the C_2-C_3 weakens, suggesting that, while the C_2-C_3 bond becomes a C-C single bond, the C_1-C_2 becomes a C=C double bond. The Pd-C_2 bond becomes as strong as the Pd-C_1, and the Pd-C_3 bond weakens, suggesting that the π-allyl coordination changes to the C=C double bond coordination to form a π-olefin palladium(0) complex. Since the sum of the absolute values, $E_{Pd\text{-}C_1}$, $E_{Pd\text{-}C_2}$, and $E_{Pd\text{-}C_3}$, decreases, the π-olefin coordination weakens and the π-olefin group (= the product, i.e., allyl derivative) finally leaves the palladium(0). This feature, schematically shown in Scheme III, agrees with experiments;[4] the carbanion, $CH_3COCHCOOR^-$, attacks the π-allylpalladium, $[PdCl(\pi\text{-}C_3H_5)]_2$, in Me_2SO to yield $CH_2COC(CH_2CH{=}CH_2)HCOOR$, metallic palladium, and HCl.[4] It is noted in Scheme III that the π-olefin palladium(0) complex experimentally suggested as an intermediate[16a] is also supported by the present MO calculations.

Scheme III



In $PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$, the palladium(II) is reduced to palladium(0) with more difficulty than the others, both the C_2-C_3 bond and the C_1-C_2 bond weaken or obtain some single bond character, and the π-allyl group coordinates more strongly to the palladium(0). This feature disagrees with Scheme III. Again, this reaction system is suggested to be unreactive, as has been shown by the ΔE_t curve in Figure 3.

Configuration analysis of the π-allylpalladium + OH^- reaction system was performed in order to investigate the above feature in more detail. Table III gives coefficients of some important CI wave functions, $\phi_n \rightarrow \phi_3$, $\phi_n \rightarrow \phi_4$, $\phi_2 \rightarrow \phi_3$, $\phi_2 \rightarrow \phi_4$, and $\phi_1 \rightarrow \phi_3$, where ϕ_n is the lone-pair orbital of the OH^- and the $\phi_1 \sim \phi_4$ are pictured in Figure 2. It is noted that the coefficients of $\phi_n \rightarrow \phi_3$ and $\phi_1 \rightarrow \phi_3$ CI wave functions increase with an increase in the reactivity, except for $[PdCl(\pi\text{-}C_3H_5)]_2$, and that the coefficient of the $\phi_1 \rightarrow \phi_3$ CI wave function is negligibly small in $PdCl_2(\pi\text{-}C_3H_5)^-$, the most unreactive system. These results suggest that the $\phi_n \rightarrow \phi_3$ and $\phi_1 \rightarrow \phi_3$ mixings are important. The above mixings are schematically shown in Figure 4, where the phase of ϕ_1, etc., is taken as is shown in Figure 2. The C_3-OH bonding interaction is formed by the $\phi_n \rightarrow \phi_3$ and $\phi_n \rightarrow \phi_4$ mixings, as is shown in Figures 4a and 4b. The $\phi_2 \rightarrow \phi_3$ mixing, shown in Figure 4c, lowers the electron densities of the C_1 and C_3 atoms and increases the electron density of the Pd $4d_{xy}$ orbital. This mixing also decreases the overlap between the Pd $4d_{xy}$ and the π-allyl $n\pi$ orbital. Thus, palladium(II) is reduced to palladium(0) and the coordinate bond of the π-allyl ligand is weakened by this mixing. The $\phi_2 \rightarrow \phi_4$ mixing, shown in Figure 4d, lowers the electron density of C_3, increases that of C_1, strengthens the Pd-C_1 and C_2-C_3 bonds, and weakens the Pd-C_3 and C_1-C_2 bonds. Although the C_2-C_3 bond should become a single bond and the C_1-C_2 should become a double bond after the reaction, this mixing does not cause such changes. Thus, the $\phi_2 \rightarrow \phi_4$ mixing is unfavorable for the reaction. The ϕ_1-ϕ_3 mixing, shown in Figure 4e, increases the electron density of the C_1 atom, reduces the electron density of the C_3, strengthens the C_1-C_2 bond, and weakens the C_2-C_3. Also, the Pd-C_2 bond becomes stronger than the Pd-C_1 due to this mixing. These changes agree with the overall changes of the reaction. Regarding the C_1-C_2 and C_2-C_3 bond strength, the $\phi_1 \rightarrow \phi_3$ mixing gives the result reverse to that caused by the $\phi_2 \rightarrow \phi_4$ mixing. Where the $\phi_2 \rightarrow \phi_4$ mixing is less than the $\phi_1 \rightarrow \phi_3$ one, the C_1-C_2 bond becomes strong, the C_2-C_3 becomes weak, and the reaction proceeds easily, and vice versa. A good example is the $PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$ reaction system, which is the most unreactive. As is shown in Table III, the coefficient of the $\phi_2 \rightarrow \phi_4$ CI wave function is the largest of the complexes examined, whereas the coefficient of the $\phi_1 \rightarrow \phi_3$ CI wave function is negligibly small. Consequently, as the nucleophile approaches the π-allyl ligand, the C_1-C_2 bond becomes weak and the C_2-C_3 becomes slightly weak in $PdCl_2(\pi\text{-}C_3H_5)^- \leftarrow OH^-$. Thus, the reaction is difficult in this system. In contrast to this system, the $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+ \leftarrow OH^-$ (A) reaction system has the smallest coefficient of the $\phi_2 \rightarrow \phi_4$ CI wave function and the greatest coefficient of the $\phi_1 \rightarrow \phi_3$ CI wave function. The latter system is the most reactive.

In conclusion, the changes in electronic structure are successfully explained in terms of the ϕ_n-ϕ_3, ϕ_n-ϕ_4, ϕ_1-ϕ_3, and ϕ_2-ϕ_4 mixings. The ϕ_n-ϕ_3 and ϕ_n-ϕ_4 mixings are important for the formation of the C_3-OH bond. The former mixing seems more important than the latter for the following reasons: (1) the coefficient of the former is much greater than the latter, and (2) the coefficient of the former increases with an increase in the reactivity, while the coefficient of the latter does not always increase with an increase in the reactivity. The ϕ_2-ϕ_3 and ϕ_1-ϕ_3 mixings play important roles to cause the changes in electronic structure shown in Scheme II, whereas the ϕ_2-ϕ_4 one causes unfavorable changes in the electronic structure. Thus, the ϕ_n-ϕ_3, ϕ_1-ϕ_3, and ϕ_2-ϕ_3 mixings are especially important.

Origin of the Ligand Effect. Now it has to be studied how the reactivity depends on the ligand. The reactivity is expected to depend on three factors: (1) how easily the orbital mixings occur with the nucleophilic attack, (2) whether the Pd-L bond becomes weakened or strengthened during the reaction, and (3) how much the electron density on the C atom influences the reactivity.

First, the orbital mixing will be investigated. According to a simple perturbation theory, the extent of the ϕ_n-ϕ_3 mixing is qualitatively proportional to $(\epsilon_3 - \epsilon_n)^{-1}$.[32] Generally, ϕ_3 lies at a higher energy level than ϕ_n in the reaction system. The more stable ϕ_3 is, the greater ϕ_n-ϕ_3 mixing becomes, and the stronger C_3-OH bond is formed.

In order to investigate the ϕ_2-ϕ_3 mixing in detail, the MOs of the reaction system were represented by a linear combination of MOs of the π-allylpalladium complex and MOs of the OH^-. This treatment indicates that the reaction system has only one such MO including significant mixing between ϕ_1, ϕ_2, ϕ_3, ϕ_4, and ϕ_n, and that this MO mainly results from the ϕ_n. Thus the ϕ_2-ϕ_3 mixing is a second-order one, which is induced by the ϕ_2-ϕ_n and ϕ_3-ϕ_n mixings. The extent of the ϕ_2-ϕ_3 mixing is roughly proportional to $(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$.[33] When either the ϕ_2 energy level or the ϕ_3 one approaches the ϕ_n energy level, this quantity becomes large. By considering that the stable ϕ_3 is favorable for the ϕ_3-ϕ_n mixing, the best situation is obtained when the ϕ_3 orbital lies close to the ϕ_n orbital in energy. Similarly, the ϕ_1-ϕ_3 and ϕ_2-ϕ_4 mixings are second-order ones and are roughly proportional to $(\epsilon_1 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ and $(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_4 - \epsilon_n)^{-1}$, respectively.[34] The energy levels of $\phi_1 \sim \phi_4$, greatly depend on the charge of the ligand, but the changes of the relative energy levels of $\phi_1 \sim \phi_4$ are not so much different among the complexes examined. Taking the ϕ_1, ϕ_2, ϕ_3, and ϕ_4 energy levels as the same as those of $PdCl(PH_3)(\pi\text{-}C_3H_5)$ (A), the $(\epsilon_1 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ and the $(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_4 - \epsilon_n)^{-1}$ are calibrated for various $\epsilon_3 - \epsilon_n$ values. The result is shown in Figure 5. The situation where the absolute value of $(\epsilon_1 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ is larger than that of $(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_4 - \epsilon_n)^{-1}$ is desirable, because the former mixing is favorable for the reaction but the latter is unfavorable. Again, the stable ϕ_3 orbital is desirable from the viewpoint of the ϕ_1-ϕ_3 and ϕ_2-ϕ_4 mixings.

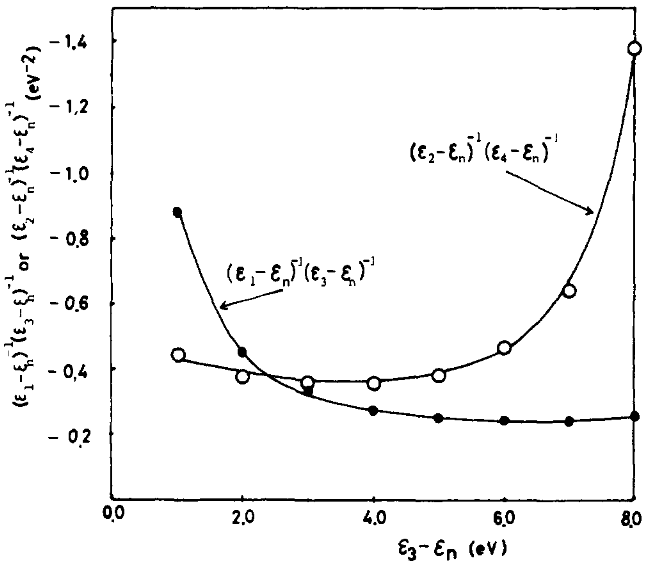


Figure 5. $(\epsilon_1 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ vs. $(\epsilon_3 - \epsilon_n)$ and $(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ vs. $(\epsilon_3 - \epsilon_n)$.

The ϕ_3 is composed of the π-allyl nπ orbital and the LUMO of the fragment, $PdCl_2$, $PdClL^+$ (L = CO or PH_3), etc. Consider two such fragments, A and A′. When the A fragment has the LUMO in a lower energy level than the A′ fragment and the A and A′ LUMOs overlap with the π-allyl nπ orbital to a similar extent, the π-allyl complex of A has ϕ_3 in a lower energy level. Since the ϕ_3 energy level becomes stable as the LUMO of $PdCl_2$, PdClL (L = CO or PH_3), etc., becomes stable (see Table I), it is sufficient for discussing the ϕ_3 energy level to examine the LUMO energy level of the $PdCl_2$, etc. The LUMO is mainly composed of the antibonding combination of the Pd $4d_{xy}$ orbital and the ligand lone-pair orbital; herewith the LUMO is called d_{xy}*.

The Cl^- ligand destabilizes the d_{xy}* through both the Pd-Cl antibonding interaction and the electrostatic repulsion due to the Cl^- ligand. The neutral ligand, such as PH_3 (B) and CO (B), hardly destabilizes the d_{xy}* through the electrostatic repulsion. Thus, the d_{xy}* is destablized in $PdClL(\pi\text{-}C_3H_5)$ (L = PH_3 (B) or CO (B)) to a lesser extent than that in $PdCl_2(\pi\text{-}C_3H_5)^-$, and the d_{xy}* in $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (B) is more stable than that in $PdClL(\pi\text{-}C_3H_5)$. The neutral π-acceptor ligand, such as PH_3 (A) and CO (A), does not only cause no electrostatic repulsion but also reduces the electron density of the Pd to stabilize indirectly the d_{xy}*. Actually, an inclusion of the π back-donation decreases the electron density of the Pd, as is shown in Table I. The neutral π-acceptor ligand is most favorable from both viewpoints of the electrostatic repulsion and the electron density of the Pd. The neutral ligand without π-acceptor ability is moderately favorable from the viewpoint of the electrostatic repulsion. The anionic ligand is the worst. For example, $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (A) is the best, while $PdCl_2(\pi\text{-}C_3H_5)^-$ is the worst.

Now the second factor will be examined. Table IV gives the changes in the bond strength resulting from the nucleophilic

Table IV. Changes in Bond Strength Due to OH^- Attack[a]

		$E_{Pd-Cl}^{(1)+(2)}$	$E_{Pd-Cl}^{(3)}$	$E_{Pd-L}^{(1)+(2)}$	$E_{Pd-L}^{(3)}$	$E_{C-O}^{(1)+(2)}$	$E_{C-O}^{(3)}$
$PdCl_2(\pi\text{-}C_3H_5)^-$		0.80[b]	0.46[b]			−2.13	0.21
$PdCl(PH_3)(\pi\text{-}C_3H_5)$	(B)[c]	0.90	0.72	0.88	−0.27	−3.08	−0.26
		(1.00	0.72	0.73	−0.22	−2.90	0.0)
	(A)[c]	0.94	0.65	−0.02	−0.18	−3.49	0.35
		(1.02	0.65	−0.18	−0.05	−3.32	−0.12)
$[PdCl(\pi\text{-}C_3H_5)]_2$		1.01[d]	0.62[d]	−0.59[e]	−0.12[e]	−3.30	−0.22
$PdCl(CO)(\pi\text{-}C_3H_5)$	(B)[c]	0.90	0.70	0.60	−0.57	−3.42	−0.34
		(0.97	0.70	0.30	−0.57	−3.27	−0.09)
	(A)[c]	1.00	0.61	−0.58	−0.44	−3.74	−0.40
		(1.10	0.62	−0.72	−0.44	−3.65	−0.22)
$Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$	(B)			0.95[b]	−0.29[b]	−3.98	−0.28
	(A)			0.10[b]	−0.15[b]	−4.76	−0.31

[a] C-OH = 2.0 Å. Bond strength is described with E_{AB} value (eV). [b] The averaged value of two Pd–Cl or Pd–PH_3 bonds. [c] In parentheses: the C_1 attack. Others: the C_3 attack. [d] The averaged value of two Pd–Cl bonds which are adjacent to the π-allyl ligand attacked by the OH^-. [e] The other two Pd–Cl bonds.

attack. As palladium(II) is reduced to palladium(0) by the nucleophilic attack, the Pd–Cl electrostatic interaction weakens (see $\Delta E_{Pd-Cl}^{(3)}$) and the electron donation from the Cl^- ligand to the palladium becomes difficult (see $\Delta E_{Pd-Cl}^{(1)+(2)}$). Consequently, the Pd–Cl bond weakens, except for the Pd–Cl in $[PdCl(\pi\text{-}C_3H_5)]_2$. In the latter, the Pd–Cl bond near the π-allyl ligand attacked by the nucleophile becomes weak, whereas another Pd–Cl bond becomes strong. The Pd–Cl bond weakening is compensated and the destabilization due to the Pd–Cl bond weakening is less than that of $PdCl_2(\pi\text{-}C_3H_5)^-$. The neutral ligand, such as PH_3 (B) and CO (B), is slightly positively charged, for such a ligand donates somewhat its electrons to the palladium. When palladium is reduced to palladium(0) by the nucleophilic attack, the electrostatic interaction between the palladium and the neutral ligand becomes less weak (see $\Delta E_{Pd-L}^{(3)}$), while the σ donation from the ligand becomes difficult (see $\Delta E_{Pd-L}^{(1)+(2)}$). Eventually, the Pd–$PH_3$ (B) and Pd–CO (B) bonds moderately weaken. The Pd–PH_3 (A) and Pd–CO (A) bonds become slightly strong in $PdClL(\pi\text{-}C_3H_5)$ (L = PH_3 (A) or CO (A)) (see $\Delta E_{Pd-L}^{(1)+(2)}$ and $\Delta E_{Pd-L}^{(3)}$). When palladium(II) is reduced to palladium(0), the π back-donation from the palladium to the L ligand becomes strong to strengthen the Pd–L bond. In $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ (A), however, the Pd–PH_3 covalent interaction weakens slightly. Because this complex has two Pd–PH_3 bonds, the strengthening per a Pd–PH_3 would be less than that in $PdCl(PH_3)(\pi\text{-}C_3H_5)$. Since $\Delta E_{Pd-PH_3} + \Delta E_{Pd-PH_3'}$ of this complex is less than $\Delta E_{Pd-Cl} + \Delta E_{Pd-L}$ of other complexes, this complex receives the smallest bond weakening. Thus, from the viewpoint of the changes in the coordinate bond strength, the neutral π-acceptor ligand is most favorable, the neutral ligand without π-acceptor ability is moderately favorable, and the anionic ligand is the worst.

Finally, the effect of the electron density will be examined. Both the strength of the C–O covalent interaction and the C–O electrostatic interaction are given in Table IV. The electrostatic interaction is less than one-tenth of the total C–O interaction. The electrostatic interaction seems an unimportant factor to determine the reactivity. Thus, the reaction examined here is considered not a charge control but a frontier control.[35]

Conclusion

In this work, a reasonable feature of the reaction is obtained from MO calculations: when a nucleophile, Y, attacks the π-allyl ligand, palladium(II) is reduced to palladium(0), and the allyl derivative, $CH_2{=}CHCH_2Y$, leaves the palladium(0) via an intermediate, π-olefin palladium(0) complex. A successful discussion is presented for the reactivity of the π-allylpalladium to the nucleophile. It is suggested that $Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$ is extremely reactive, which supports the proposal of Trost et al. $PdCl_2(\pi\text{-}C_3H_5)^-$ is, on the other hand, suggested to be unreactive. The ligand effect on the reactivity is discussed from various viewpoints: (1) orbital mixing, (2) changes in the Pd–Cl and Pd–L bond strength, and (3) electron density of the C_3 atom. The former two factors are important, while the last one seems unimportant. The stable ϕ_3 orbital results in a favorable situation regarding the orbital mixing. The neutral π-acceptor ligand most stabilizes the ϕ_3 orbital energy, while the anionic ligand most destabilizes it. As palladium(II) is reduced to palladium(0) during the reaction, the coordinate bond of the neutral π-acceptor ligand becomes strong with the formation of the π back-bonding to stabilize the final state of the reaction system, while the coordinate bond of the anionic ligand becomes much weaker to destabilize the final state. From the viewpoints of the orbital mixing and the changes in the coordinate bond strength, the neutral π-acceptor ligand is most favorable for the reaction, while the anionic ligand is most unfavorable. Thus, it is theoretically elucidated why addition of a neutral π-acceptor ligand, such as triphenylphosphine, accelerates the reaction.

Acknowledgment. The authors would like to thank Dr. Fujimoto (Kyoto University) for his kind supply of a computer program of configuration analysis. They also thank Mr. Tsuru for his help with MO calculations. MO calculations were performed with the Facom M-190 computer of the Data Processing Center at Kyushu University. This work was partially supported by a grant from the Ministry of Education (No. 435045).

Appendix

The 4d, 5s, and 5p orbitals were used as a basis for Pd, and the 3s, 3p, and 3d were used as a basis for P, while the 3s and 3p of the P were used in calculating the complex including the PH_3 (B). The MO method examined needs the valence state ionization potential, I_r, the one-center Coulomb repulsion integral, γ_{rr}, the parameters of the modified Ohno equation,[18] a_r, and the orbital exponent, ζ_r. The I_r was evaluated from atomic spectra[36a] for all orbitals of the Pd and the 3d orbital of the P, while the I_r of others was taken from previous work.[36b] The γ_{rr} are taken from the previous work[36b,c] for all orbitals of the Pd and the 3s and 3p orbitals of the P. The $\gamma_{3d,3d}$ of the P atom was theoretically calculated with the Burns exponent,[36d] and then multiplied by a scaling factor.[36c] The a_r values were determined according the procedure described in ref 18. The evaluated or estimated values follow: Pd, $I_{4d} = 8.51$, $I_{5s} = 7.25$, $I_{5p} = 3.67$, $a_{5s} = 1.52$, $a_{5p} = 2.34$ eV; P, $I_{3d} = 2.72$, $\gamma_{3d,3d} = 4.38$, $a_{3d} = 2.58$ eV. Clementi's STOs[36e] were used for all orbitals except the 4d orbital of the Pd. The double-ζ orbital was used for the 4d of the Pd.[36f]

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(23) (a) This neglect results in the neglect of both interactions between the Pd $4d\pi$ and the CO π orbital and between the Pd $4d\pi$ and the CO π^* orbital. It is, however, conceivable that the former interaction contributes little to the coordination, because both the Pd $4d\pi$ and CO π orbitals are doubley occupied. Thus, the above neglect mainly results in the neglect of the latter interaction. In fact, this neglect increases the electron density of the Pd atom and reduces the electron density of the CO ligand as is shown in Table I. (b) Strictly, it is correct that, although the basis set of the B systems include the P 3d orbitals, the overlap integrals between the Pd $4d\pi$ and the P $3d\pi$ are neglected. However, the P 3d orbitals are excluded from the basis set in the B system, because the basis set including the P 3d orbitals becomes too large and MO calculations with such a large basis set are time consuming. The exclusion of the P 3d orbitals gave the same results as those obtained when the π back-donation was excluded. Thus, the present method seems reasonable.

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(32) Strictly speaking, the extent of the ϕ_n–ϕ_3 mixing is proportional to $\beta_{3n}/(\epsilon_3 - \epsilon_n)$, where $\beta_{3n} = \sum_r \sum_s C_{3r} C_{ns} \langle r|H|s\rangle$. While the C_{ns} is constant for various reaction systems, the C_{3r} slightly depends on the kinds of π-allylpalladium complexes, and it becomes large as ϕ_3 becomes stable. As ϕ_3 becomes stable, β_{3n} slightly increases and $\epsilon_3 - \epsilon_n$ becomes small. Thus, the mixing becomes large mainly due to the $(\epsilon_3 - \epsilon_n)^{-1}$ quantity and slightly due to β_{3n}.

(33) Strictly speaking, the extent of this mixing is also proportional to $\beta_{2n}\beta_{3n}(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$, where $\beta_{2n}\beta_{3n} \simeq C_{2p}{}^{C} C_{3p}{}^{C} \langle p_\pi{}^{C}|H|p_\pi{}^{O}\rangle^2$. The product, $C_{2p}{}^{C} C_{3p}{}^{C}$, is not so much different among the complexes examined, while this value slightly increases as ϕ_3 becomes stable. Thus, the extent of the mixing is approximately proportional to $(\epsilon_3 - \epsilon_n)^{-1}(\epsilon_2 - \epsilon_n)^{-1}$.

(34) Although these mixings are, strictly speaking, proportional to $\beta_{1n}\beta_{3n}(\epsilon_1 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ and $\beta_{2n}\beta_{4n}(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_4 - \epsilon_n)^{-1}$, respectively, the $\beta_{2n}\beta_{4n}$ and $\beta_{1n}\beta_{3n}$ quantities are not so much different among the complexes. Furthermore, $\beta_{2n}\beta_{4n}$ is almost the same as $\beta_{1n}\beta_{3n}$; for example, $\beta_{2n}\beta_{4n} \simeq 0.18 C_{p_\pi}{}^{O2} \langle p_\pi{}^{C}|H|p_\pi{}^{O}\rangle^2$, and $\beta_{1n}\beta_{3n} \simeq 0.16 C_{p_\pi}{}^{O2} \langle p_\pi{}^{C}|H|p_\pi{}^{O}\rangle^2$, for $PdCl(PH_3)(\pi$-$C_3H_5)$ (A). Thus, to examine the $(\epsilon_1 - \epsilon_n)^{-1}(\epsilon_3 - \epsilon_n)^{-1}$ and $(\epsilon_2 - \epsilon_n)^{-1}(\epsilon_4 - \epsilon_n)^{-1}$ quantities is enough to investigate the relative extent of the ϕ_1–ϕ_3 and ϕ_2–ϕ_4 mixings.

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Nitrosomethane and Its Nitrone and Oxime Isomers. A Theoretical Study of 1,2- and 1,3-Intramolecular Hydrogen Shifts

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Received May 2, 1979

Abstract: Ab initio molecular orbital theory with minimal (STO-3G), split-valence (4-31G), and split-valence plus polarization (6-31G*, 6-31G**) basis sets and with electron correlation incorporated using Møller-Plesset perturbation theory terminated at second (MP2) and third (MP3) order has been used to investigate the potential-energy surface connecting nitrosomethane (**1**) and formaldoxime (**2**, **3**). The reaction path (A) for the 1,3-sigmatropic hydrogen shift leading to *syn*-formaldoxime (**2**) has been examined and the corresponding transition-state structure (**5**) has been determined. The transition state (**6**) for the subsequent isomerization of *syn*-formaldoxime (**2**) to its more stable anti isomer (**3**) has also been determined. A second reaction path (B), involving the isomerization of nitrosomethane (**1**) to *anti*-formaldoxime (**3**) by means of two successive 1,2-hydrogen shifts, is found to proceed via formaldonitrone (**4**) as an intermediate. The transition states (**7** and **8**) for the individual 1,2-hydrogen shifts have been determined. Both reaction paths A and B are found to involve high activation barriers, the rearrangement via the nitrone **4** being slightly favored. These results demonstrate the stability of nitrosomethane with respect to intramolecular rearrangement and also suggest that formaldonitrone might be amenable to experimental observation. STO-3G and 4-31G optimized structures for **1**-**8** are reported.

Introduction

Nitrosomethane is known to be less stable than its isomer formaldoxime and original attempts to isolate this molecule failed owing to its speedy isomerization to formaldoxime. More recently, however, the dimer of nitrosomethane has been prepared,[2-4] and has been shown in the gas phase to be in equilibrium with the monomer.[5] In 1968, the microwave

0002-7863/80/1502-4069$01.00/0