polar and nonpolar faces to different extents. We have found that if the relative polarities of the various crystal faces are known, it is possible to predict the habit modification induced by a solvent of a specific nature in those systems where there are large differences in the polarity of the faces. We have demonstrated that electrostatic potential maps at closest approach distances to the various crystal faces are instructive for the study of the polarities of crystal faces. However, to understand the detailed differences

between faces of comparable nature, it is necessary to calculate the binding energy of the solvent molecules to the various faces. Studies on this line are presently underway.[51]

Communications to the Editor

Specific Rate Enhancement by Olefin Coordination in Reductive Elimination of η³-Allylpalladium Complexes

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Increasing attention has been paid to reductive elimination of allylmetal complexes as a key step in organic synthesis.[1-3] Of particular help in raising the synthetic value of the reaction of allylpalladium complexes was the unique use of some olefinic additives (e.g., maleic anhydride) not as a substrate but as a mediator.[1] We wish to report on mechanistic studies of the reaction of both η³- and η¹-allylpalladium complexes with some olefins which shed light on the origin of such unique role of the olefinic additives.

We found previously[4] that reductive elimination of η³-allyl complex **1** is greatly accelerated by some olefins (e.g., allyl chloride, maleic anhydride) (Scheme I). . Notably, this reaction was *retarded* considerably by addition of free PPh₃. Now kinetics of the reaction of **2**[5] in toluene at 0 °C could be followed cleanly[6] in the presence of added AsPh₃ [(2.2 × 10⁻⁴) – (2.2 × 10⁻³) M for the reaction of allyl chloride; 0.02–0.4 M for other olefins[7]]. Under the pseudo-first-order condition ([**2**] = 0.005–0.02 M, [olefin] = 0.05–2.46 M), the rate obeyed[8] eq 1 for the reaction

$$\text{rate} = k_{obsd}[\mathbf{2}] = [k_1[\text{olefifn}]/(k_2 + [\text{AsPh}_3])][\mathbf{2}] \quad (1)$$

$$\text{rate} = k_{obsd}[\mathbf{2}] = [k_1[\text{olefin}]/[\text{AsPh}_3]][\mathbf{2}] \quad (2)$$

of C₃H₅Cl and (*E*)-CNCH=CHCN or eq 2 for the rest.[7] In Table I are summarized the rate data for several olefins. Styrene

Scheme I

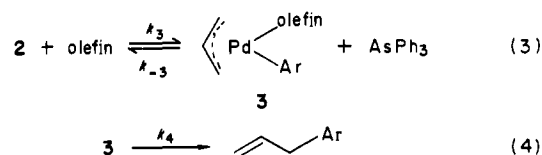Ar · C₆H₃Cl₂-2,5
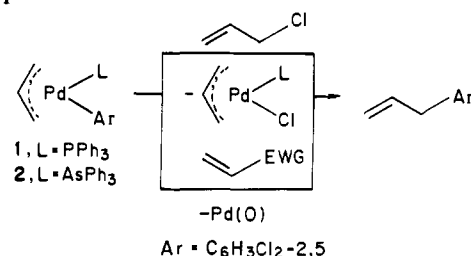
Scheme II

Table I. Rate Data[a] for Some Olefins

olefin	k_1, h⁻¹
CH₂=CHCH₂Cl[b]	2.0 × 10⁻⁴
CH₂=CHCN	2.5 × 10⁻³
CH₂=CHCOOMe	4.5 × 10⁻³
(*Z*)-MeOOCCH=CHCOOMe	1.5 × 10⁻²
(*E*)-MeOOCCH=CHCOOMe	0.24
(*E*)-NCCH=CHCN[c]	0.44

[a] In toluene at 0 °C. For rate expression, see eq 1 and 2. [b] $k_2 = 1.7 × 10^{-4}$ M. [c] $k_2 = 8.0 × 10^{-2}$ M.

and allylbenzene were not reactive enough to give accurate k_1 values.

A most probable pathway consistent with eq 1 is shown in Scheme II[9] where a steady-state approximation is applied to the intermediate **3** ($k_1 = k_3k_4/k_{-3}$, $k_2 = k_4/k_{-3}$). It may well be that in **3** allyl chloride is coordinated with Pd through the C=C bond, and oxidative addition of this substrate[4a] is included in eq 4. This is supported by the observation that addition of CH₂=CMeCH₂Cl to a mixture of **2**/AsPh₃ did not lead to the formation of CH₂=CHCH₂Cl. It seems also reasonable to assume [AsPh₃] >> k_4/k_{-3} under the conditions employed for obtaining eq 2.[7]

The trend of k_1 ($=k_3k_4/k_{-3}$) (Table I) in the main reflects the order of the electrophilic nature of the olefin.[10] Although we could

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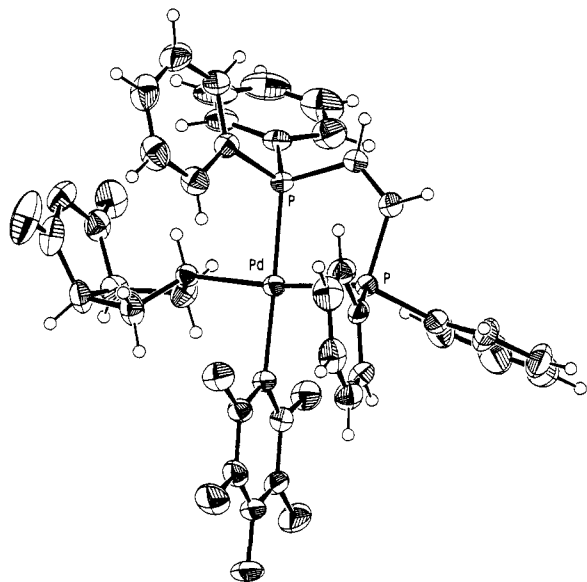
(4) (a) Kurosawa, H.; Emoto, M.; Urabe, A. *J. Chem. Soc., Chem. Commun.* **1984**, 968. (b) Numata, S.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *131*, 301.

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(6) All kinetic runs in this work were carried out similarly to those reported.[4a,5]

(7) Kinetic measurements at the lower concentrations of AsPh₃ were hampered by less satisfactory first-order dependence of the rate on [**2**] under these conditions.

(8) Conventional plots of k_{obsd} vs. [olefin] gave straight lines passing through the origin. Plots of $1/k_{obsd}$ vs. [AsPh₃] were also linear, but meaningfully large intercepts could be evaluated only in the reaction of C₃H₅Cl and (*E*)-NCCH=CHCN.

(9) Formation of no adducts between **2** and AsPh₃, as revealed by ¹H NMR spectra, strongly suggests that inverse dependence of the rate on [AsPh₃] is attributable to inhibition of a dissociative path. An alternative to Scheme II would be a rapid preequilibrium to form Pd(η³-C₃H₅)(Ar) and free AsPh₃ (K_{eq}), followed by a slow reaction of this intermediate with the olefin (k_5), also giving rise to eq 1 ($k_1 = k_5K_{eq}$, $k_2 = K_{eq}$). However, this can be excluded in view of the great difference of the k_2 values for C₃H₅Cl and (*E*)-NCCH=CHCN (see Table I).

(10) The higher electrophilicity of (*E*)- than (*Z*)-MeOOCCH=CHCOOMe was reported; Glass, R. S.; McConnell, W. W. *Organometallics* **1984**, *3*, 1630. See also Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

8254

J. Am. Chem. Soc. **1985,** *107,* 8254–8256

Figure 1. Molecular structure of **5c**. Non-hydrogen atoms are represented by thermal ellipsoids at the 30% probability level.

not separately evaluate k_4 for each olefin, this value most probably increases as the electron-withdrawing ability of olefinic substituents increases. This notion is consistent with the higher reactivity in the spontaneous reductive elimination of $Pd(\eta^3\text{-}C_3H_5)(Ar)(ER_3)$ (E = P, As) containing the more electron-withdrawing ligand (ER_3).[5] It should also be noted that the rate constant extrapolated at 0 °C from the kinetic parameters[5] for this spontaneous process of $Pd(\eta^3\text{-}C_3H_5)(Ar)[P(OPh)_3]$, the most reactive among those examined,[5] is only 1.6×10^{-2} h^{-1}. Thus, comparison of this value with k_1 in Table I may provide a good indication of signifying the effectiveness (k_4) of π-acidic olefin coordination in the C–C coupling, especially when apparently very small values of k_3/k_{-3} for each olefin[11] are taken into account.

Next we examined the reaction of η^1-allyl complexes $\mathbf{4}$[12] with olefins. Spontaneous reductive elimination of **4a** proceeded more slowly than that of **1** to give a good yield of the coupling product. However, allyl chloride and dimethyl maleate did not accelerate this reaction or alter the reaction course (see below). Reductive elimination of other Pd complexes that contain only η^1-bound organic ligands (e.g., $PdMe_2L_2$) has also been shown to be unaffected by π-acidic olefins.[13] With the more acidic olefin, i.e., maleic anhydride, **4** underwent a different reaction course in CH_2Cl_2 at 0 °C to result in rapid formation of comparable amounts of propene and complexes $\mathbf{5}$,[14] the first Pd-containing, formal [2 + 3] cycloadducts[15] (eq 5).

5 b,c (30–60%)

a, L_2 = $Ph_2PCH_2CH_2PPh_2$; Ar = $C_6H_3Cl_2$-2,5

b, L_2 = $Ph_2PCH_2CH_2PPh_2$; Ar = C_6F_5

c, L_2 = $Ph_2PCH=CHPPh_2$; Ar = C_6F_5

Only one isomeric cycloadduct was obtained, as revealed by ^{1}H NMR analysis of reaction mixtures. The structure of **5c** was determined by X-ray crystallography (Figure 1).[16] The mutually trans orientation of the metal and the carbonyl substituents with respect to the C$_5$ ring is opposite to the cis orientation in the [2 + 4] cycloadduct of $Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2$ and maleic anhydride.[17,18]

The results described in this study demonstrated for the first time that formation of a four-coordinated olefin complex is a prerequisite to the facile reductive elimination of ally complexes of Pd. This is in sharp contrast to reductive elimination from five-coordinated organo(olefin)nickel(II) complexes.[13b,20] The present study also suggests that the allyl–Pd bond should be subjected to highly π-acidic olefins preferably in the η^3-bound form, at least prior to the formation of the active intermediate.[21]

Supplementary Material Available: Table of fractional atomic coordinates and temperature factors for **5c** (3 pages). Ordering information is given on any current masthead page.

(16) Crystal data: $C_{39}H_{29}F_5O_3P_2Pd$, M_r = 809.0, triclinic, space group $P\bar{1}$, a = 9.526 (3) Å, b = 14.218 (5) Å, c = 14.122 (5) Å, α = 70.47 (3)°, β = 96.48 (3)°, γ = 92.64 (3)°, Z = 2, D_c = 1.500 g cm^{-3}, μ(Mo Kα) = 6.66 cm^{-1}. Intensity data were collected by the θ–2θ scan technique with a 2θ value up to 54° on a Rigaku automated, four-circle diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method and refined anisotropically by block-diagonal least-squares procedure. The final R factor is 0.054 for 6277 ($F_o > 3\sigma(F_o)$) reflections.

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(18) Equation 5 may have proceeded via direct attack of maleic anhydride at the C=C bond,[15] or initial coordination of this olefin to Pd, followed by its insertion into the Pd–C bond.[19] The precise pathway that is consistent with the observed stereochemistry is currently under investigation.

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(21) Efficient coupling of palladium(η^3-allyl)$_2$ induced by olefins[1b,c] may have proceeded via conversion of palladium(η^3-allyl)$_2$(olefin) to an intermediate of type palladium(η^3-allyl)(η^1-allyl)(olefin).

An Asymmetric Simmons–Smith Reaction

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Herein we report a new method of asymmetric cyclopropanation[1] that we believe has considerable potential in organic synthesis. The new process, outlined in Scheme I, appears to offer special advantages including high efficiency, procedural simplicty, predictable chirality of the product, and mildness of the reaction conditions.

When an α,β-unsaturated acetal dissolved in hydrocarbon was treated with excess methylene iodide and diethylzinc,[2] the corresponding cyclopropane was obtained in a reasonable yield with high diastereoselectivity. The acetal group was readily transformed to the aldehyde (p-TsOH–H$_2$O) or to the ester (ozonolysis).[3] Several examples of this new process are given in Table I. Since both (R,R)- and (S,S)-tartaric acid esters are readily available in optically pure form,[4] this method allows the synthesis of both

(11) We failed to detect **3** by ^{1}H NMR spectra during olefin-promoted reductive elimination.

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(14) Characterized by elemental analysis and ^{1}H NMR spectra.

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