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Mechanisms of Reductive Eliminations in Square Planar Pd(II) Complexes: Nature of Eliminated Bonds and Role of *trans* Influence

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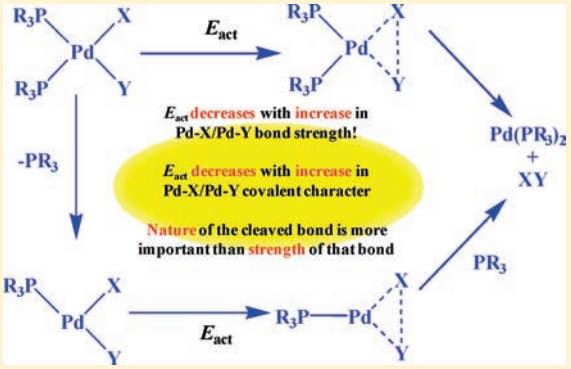
Supporting Information

ABSTRACT: The *trans* influence of various phosphine ligands (L) in direct as well as dissociative reductive elimination pathways yielding CH_3CH_3 from $Pd(CH_3)_2L_2$ and CH_3Cl from $Pd(CH_3)(Cl)L_2$ has been quantified in terms of isodesmic reaction energy, E_{trans}, using the MPWB1K level of density functional theory. In the absence of a large steric effect, E_{trans} correlated linearly with the activation barrier (E_{act}) of both direct and dissociation pathways. The minimum of molecular electrostatic potential (V_{min}) at the lone pair region of phosphine ligands has been used to assess their electron donating power. E_{trans} increased linearly with an increase in the negative V_{min} values. Further, the nature of bonds that are eliminated during reductive elimination have been analyzed in terms of AIM parameters, viz. electron density ($\rho(\mathbf{r})$), Laplacian of the electron density ($\nabla^2\rho(\mathbf{r})$), total electron energy density ($H(\mathbf{r})$), and ratio of potential and kinetic electron energy densities ($k(\mathbf{r})$). Interestingly, E_{act} correlated inversely with the strength of the eliminated metal−ligand bonds measured in terms of the bond length or the $\rho(\mathbf{r})$. Analysis of $H(\mathbf{r})$ showed that elimination of the C−C/C−Cl bond becomes more facile when the covalent character of the Pd−C/Pd−Cl bond increases. Thus, AIM details clearly showed that the strength of the eliminated bond is not the deciding factor for the reductive elimination but the nature of the bond, covalent or ionic. Further, a unified picture showing the relationship between the nature of the eliminated chemical bond and the tendency of reductive elimination is obtained from the $k(\mathbf{r})$ values: the E_{act} of both direct and dissociative mechanisms for the elimination of CH_3CH_3 and CH_3Cl decreased linearly when the sum of $k(\mathbf{r})$ at the cleaved bonds showed a more negative character. It means that the potential electron energy density dominates over the kinetic electron energy density when the bonds (Pd−C/Pd−Cl) become more covalent and the eliminated fragments attain more radical character leading to the easy formation of C−C/C−Cl bond.



INTRODUCTION

Carbon−carbon and carbon−heteroatom bond formation reactions are the most useful fundamental reactions in organic chemistry.[1] Even though nucleophilic displacement and radical additions are important ways to achieve C−C and C−heteroatom bond formations, the development of transition metal mediated catalytic reactions have attained practical importance.[2] Among such reactions, catalytic reactions of palladium complexes with ancillary phosphine ligands are given a prominent status in organic synthesis.[3−14] Reductive elimination is a key step, often the last step in catalytic cycles for the synthesis of new C−C and C−heteroatom bond.[15−19] The rate of reductive elimination depends on the steric and electronic effects of the ancillary ligands.[20−26] It is proposed that the reductive elimination reaction from square planar complexes would be proceeded through a four-coordinate (direct mechanism) or a three-coordinate transition state (dissociative mechanism).[26−32] In general, a dissociative pathway requires less activation energy than a direct pathway. However, the energy cost for the dissociation of the ancillary ligand from the four-coordinate complex often determines the feasibility of the dissociative pathway.[12,26,31] Ananikov et al.[26] theoretically investigated the C−C reductive elimination reactions in Pd(II) complexes with ancillary phosphine ligands and concluded that the steric effect of phosphine ligands has a great influence on the initial structure of square planar Pd(II) complexes, while the transition state of reductive elimination reaction is mostly affected by the electronic effect of phosphine ligands. For the bulky ancillary ligands such as PCy_3, the reductive elimination through the dissociative pathway is more favored due to the destabilization of the initial reactant complex.[26] Thus, the preferred pathway depends on the steric nature of the ancillary phosphine ligands and the extent to which the Pd−PR_3 bond is destabilized.[33] Also, the reassociation of a sterically crowded ligand to a three coordinate complex is difficult compared to a sterically less crowded ligand.[12] Recently, Ariafard and Yates[34] have investigated various factors contributing to the energy barriers of reductive elimination reactions using

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energy decomposition analysis and concluded that when bulky ancillary phosphine ligands are present, steric effect destabilizes the initial reactant complex and hence decreases the energy barrier of direct reductive elimination, whereas the steric effect showed only a marginal role in the reductive elimination from three-coordinate complexes. A computational study[35] on the reductive elimination of organic molecules from palladium(II) complexes with chelate ancillary ligands showed that the energy barriers of reductive elimination in palladium diphosphine complexes depend largely on the electronic nature of substrates and not steric effects. Very recently, Korenaga et al.[36] have studied the diphosphine electronic effects in the reductive elimination of biphenyl from *cis*-[Pt(Ph)$_2$(diphosphine)] complexes and showed good correlations between rate constant and ancillary diphosphine electronic parameters.

It is clear from the experimental and theoretical studies that the ancillary ligands with low electron donating nature will show an enhancement on the rate of reductive elimination reaction.[37] For example, the relative reactivity in C−C bond formation in L$_2$Pd(R)(R) complexes with phosphine ligands as ancillary ligands follows the order L = PCl_3 > PH_3 > PMe_3.[34] This order is inversely related with the σ-donating ability and the related *trans* influence of ancillary phosphine ligands. *Trans* influence is a well-studied phenomenon in coordination chemistry, which may be defined as the ability of a ligand to influence the ground state properties of other ligand that is present *trans* to it.[38−40] Even though *trans* influence of the ligands have a prominent effect on the rate of reductive elimination reactions,[41] systematic studies regarding the effect of *trans* ligands on the rate of C−C and C−heteroatom bond formation through reductive elimination are rare.

Previously, we have quantified the *trans* influence of various ligands and the contributions of *trans* influence to the bond dissociation energies of ligands in square planar Pd(II) and Pt(II) complexes by using a combination of simple isodesmic reaction approach[42,43] and atoms in molecule (AIM) analysis.[44] In the present work, the isodesmic reaction approach will be used to quantify the *trans* influence of various phosphine ligands. The term E_{trans} is used to represent the quantified values of *trans* influence. The main aim of this study is to elucidate the importance of E_{trans} on the C−C and C−Cl bond formation reactions from square planar Pd(II) complexes through the reductive elimination mechanism involving both direct and dissociative mechanisms. The electronic parameter of free phosphine ligands in these reactions is discussed in terms of molecular electrostatic potential (MESP), observed in the lone pair region of a phosphine ligand.[45] Further, the AIM analysis has been used to correlate electron density features of bond critical points to the mechanistic features of reductive elimination reactions.

COMPUTATIONAL DETAILS

All the calculations were done at the MPWB1K[46] level of the DFT method with the Gaussian03[47] suite of programs. The MPWB1K is a newly developed hybrid-meta DFT method based on the modified Perdew and Wang 1991 exchange functional (mPW or MP) by Zhao and Truhlar.[46] For Pd, the basis set Lanl2DZ[48,49] with an extra f polarization function[50] was chosen. For all the other atoms, the 6-31++G(d,p) basis set was selected, and the combined basis set for all the atoms is named as BS1. MPWB1K is chosen for this study because of its reliable performance in thermo-chemical kinetics and noncovalent interactions and also in the determination of barrier heights.[51−53] All the stationary points were confirmed by means of vibration analysis, and all the transition states were characterized by the determination of a single imaginary frequency and its relationship with nuclei motion.

The MPWB1K/6-31++G(d,p) level of theory was used to calculate the molecular electrostatic potential (MESP) of free phosphine ligands. MESP is an observable physical property of a molecule[54−56] and can be calculated using electron density, $\rho(\mathbf{r})$, with the help of eq 1, where Z_A is the charge on the nucleus A, located at $\mathbf{R_A}$.

$$V(\mathbf{r}) = \sum_{A}^{N} \frac{Z_A}{|\mathbf{r} - \mathbf{R_A}|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \quad (1)$$

The lone pair region of a free phosphine ligand is characterized by a negative MESP, indicating an electron-rich character,[45] and the MESP topology calculation is useful to identify the deepest MESP point (V_{min}) in this region.[55,45,57]

As suggested in our previous work, the quantification of the *trans* influence of various phosphine ligands (L = PH_3, PCl_3, PH_2CF_3, PH_2Et, PH_2Ph, $PMeCl_2$, PMe_3, $PHEt_2$, PEt_3, and PPh_3) has been done using isodesmic reactions of the type $[PdCl_3]^-$ + $[PdCl_2L] \rightarrow [PdCl_3L]^-$ + $[PdCl_2]$ at the MPWB1K/BS1 level of theory, and solvent corrections in water were applied through a conductor-like screening model (COSMO),[58] which is a widely used self-consistent reaction field (SCRF) method.

To calculate the topological features of electron density, atoms in molecule (AIM) analysis was done using the AIM2000 program.[59] In order to get reliable AIM parameters, the effective core potential basis set for Pd in BS1 was replaced with the all electron basis set, DGDZVP,[60,61] to generate the wave function at the MPWB1K method. AIM analysis is based on Bader's theory,[44] and for the present study, the bond critical points (bcp) of the nature (3, −1) are located for Pd−C and Pd−Cl bonds of all the reactant complexes. At the bcp, electron density ($\rho(\mathbf{r})$), Laplacian ($\nabla^2\rho(\mathbf{r})$), density of the total energy of the electron ($H(\mathbf{r})$), kinetic electron energy density ($G(\mathbf{r})$), and potential electron energy density ($V(\mathbf{r})$) were determined. These AIM parameters are powerful tools for the characterization of chemical bonds and are also used for the analysis of chemical problems involving bond breaking and bond forming reactions.[44,62−70] In many applications, $\rho(\mathbf{r})$ has been used as a measure of the strength of the bonding interaction, particularly the σ-interaction. $\nabla^2\rho(\mathbf{r})$ indicates the regions where the $\rho(\mathbf{r})$ is depleted or concentrated. For shared bonds, $\nabla^2\rho(\mathbf{r})$ is negative, while positive values are observed for interactions showing closed-shell character.[44] Apart from this, valuable information about chemical bonds is obtained from $H(\mathbf{r})$ and its two components $G(\mathbf{r})$ and $V(\mathbf{r})$, and eq 2 shows the relation between these parameters.

$$H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}) \quad (2)$$

Regions where the electrons are more localized are characterized by relatively higher $V(\mathbf{r})$ values, whereas large $G(\mathbf{r})$ values correspond to regions where the electrons move faster.[64] In general, for covalent interactions, $|V(\mathbf{r})| > G(\mathbf{r})$, and hence, the value of $H(\mathbf{r})$ is negative. For closed-shell interactions, $|V(\mathbf{r})| < G(\mathbf{r})$, and thus, $H(\mathbf{r})$ shows a positive value.[64] Equations 3 and 4 show the relation between $H(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$.

$$(\hbar^2/8m)\nabla^2\rho(\mathbf{r}) = H(\mathbf{r}) - (1/2)V(\mathbf{r}) \quad (3)$$

$$H(\mathbf{r}) = (\hbar^2/8m)\nabla^2\rho(\mathbf{r}) + (1/2)V(\mathbf{r}) \quad (4)$$

Scheme 1. Formation of CH_3-X through Direct and Dissociative Mechanisms, Where L Is Ancillary Phosphine Ligands

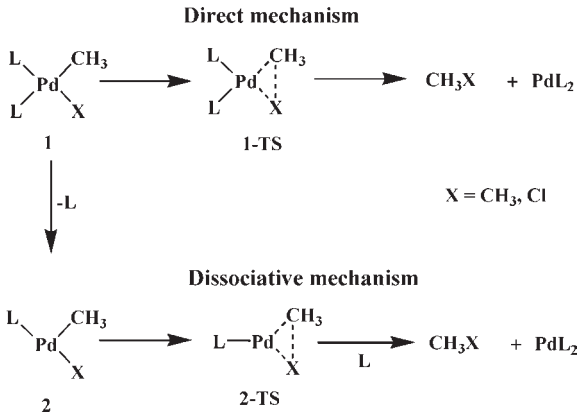

Table 1. E_{act} Values for the Reductive Elimination of CH_3CH_3 and CH_3Cl via Direct and Dissociative Mechanisms

	E_{act} for CH_3CH_3 reductive elimination (kcal mol^{-1})		E_{act} for CH_3Cl reductive elimination (kcal mol^{-1})	
ancillary ligand	direct mechanism	dissociative mechanism	direct mechanism	dissociative mechanism
PH_3	23.91	10.25	44.02	30.28
PCl_3	15.12	8.57	32.18	25.78
PH_2CF_3	21.64	8.98	41.02	26.89
PH_2Et	26.64	10.67	47.99	32.34
PH_2Ph	26.93	10.64	47.35	32.33
$PMeCl_2$	21.13	9.97	39.97	28.33
PMe_3	31.35	11.72	55.68	35.85
$PHEt_2$	28.76	10.99	52.05	34.37
PEt_3	31.66	12.15	56.07	36.40
PPh_3	26.23	11.46	46.31	34.63

The combined use of both $H(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ has been practiced as an excellent descriptor for defining the nature of chemical bonds.[71] For shared-shell interactions, $\nabla^2\rho(\mathbf{r}) < 0$, and also by definition, $V(\mathbf{r})$ is negative at the bcp. Consequently as from eq 4, $H(\mathbf{r})$ will be negative. For closed-shell interactions, $H(\mathbf{r})$ would be positive, and this occurs when $(\hbar^2/8\ m)\nabla^2\rho(\mathbf{r}) > |(1/2)V(\mathbf{r})|$. There is another possibility that $\nabla^2\rho(\mathbf{r}) > 0$ and $H(\mathbf{r}) < 0$ indicates partial ionic and partial covalent nature of the bond. Thus, pure closed-shell interactions without covalency are characterized by $H(\mathbf{r}) > 0$, whereas $H(\mathbf{r}) < 0$ includes two types of interactions, viz. closed-shell interactions with covalent character where $\nabla^2\rho(\mathbf{r}) > 0$ and shared-shell interactions where $\nabla^2\rho(\mathbf{r}) < 0$. Nakanishi et al.[71,72] characterized the shared-shell and closed-shell interactions for a better understanding of the weak to strong interactions by plotting $H(\mathbf{r})$ versus $\nabla^2\rho(\mathbf{r})$ values at the bcps and found that the ratio of $V(\mathbf{r})$ and $G(\mathbf{r})$ (denoted as $k(\mathbf{r})$; $k(\mathbf{r}) = V(\mathbf{r})/G(\mathbf{r})$) is highly useful to explain these plots. The higher magnitude of $k(\mathbf{r})$ indicates the extent of dominance of $V(\mathbf{r})$ over $G(\mathbf{r})$ values. In this study, we also determined $k(\mathbf{r})$.

RESULTS AND DISCUSSION

Reductive Elimination of CH_3CH_3 and CH_3Cl. A schematic illustration of direct and dissociative mechanisms is presented in Scheme 1 for the reductive elimination of either CH_3CH_3 or CH_3Cl from the corresponding palladium complex. We have calculated the activation energy (E_{act}) for the direct mechanism as well for the dissociative mechanism for the 10 $[Pd(CH_3)_2L_2]$ complexes and 10 $[Pd(CH_3)(Cl)L_2]$ complexes (Table 1). The E_{act} of the direct mechanism is the energy difference between **1-TS** and **1**, while E_{act} of the dissociative mechanism is the energy difference between **2** and **2-TS** (Scheme 1). Because the mechanism of these types of reactions are well understood, we do not want to elaborate more on the mechanistic aspects and suggest ref 26 to obtain more details on the reductive elimination of CH_3CH_3. However, reductive elimination of CH_3Cl is discussed for the first time. It may be noted that in the case of $[Pd(CH_3)(Cl)L_2]$ complexes, because the *trans* influence of the $-CH_3$ is higher than $-Cl$,[42,73] to follow a dissociative mechanism, the L ligand *trans* to $-CH_3$ has to always dissociate.

The highest E_{act} for both CH_3CH_3 and CH_3Cl in the direct and dissociation pathway is observed for PEt_3, whereas the lowest E_{act} is obtained for PCl_3. In the direct mechanism, the decreasing order of E_{act} values for various ancillary ligands can be written as $PEt_3 \sim PMe_3 > PHEt_2 > PH_2Et \sim PH_2Ph \sim PPh_3 > PH_3 > PMeCl_2 \sim PH_2CF_3 > PCl_3$, while for the dissociative mechanism this order can be written as $PEt_3 > PMe_3 > PPh_3 > PHEt_2 > PH_2Et \sim PH_2Ph > PH_3 > PMeCl_2 > PH_2CF_3 > PCl_3$. For the CH_3CH_3 elimination via direct mechanism, the E_{act} ranges from 15.12 to 31.66 kcal mol^{-1}, and through dissociative mechanism, the E_{act} are within a small range from 8.57 to 12.15 kcal mol^{-1}. This shows that the direct mechanism is more highly influenced by the nature of the ancillary phosphine ligand than the dissociative mechanism. For the reductive elimination of CH_3Cl, the E_{act} of the direct mechanism is in the range from 32.18 to 56.07 kcal mol^{-1}, while for the dissociative mechanism, it is from 25.78 to 36.40 kcal mol^{-1}. Thus, it is clear that irrespective of the mechanism, the reductive elimination involving a C−Cl bond formation is more difficult than that involving a C−C bond formation.

It is well-known that the electronic nature of phosphine ligands and the related *trans* influence play an important role in the rate of reductive eliminations.[26] To the best of our knowledge, a relationship between E_{act} of reductive eliminations and *trans* influence parameters has not been clearly addressed yet. *Trans* bond length (d) parameters have been used as a structural parameter to quantify the *trans* influence.[42] In general, short *trans* bond length indicates the weak *trans* influencing ancillary ligand, while the strong *trans* influencing ancillary ligands cause an enhancement in the *trans* bond length. All the $Pd-C_{methyl}$ bond lengths of both $[Pd(CH_3)_2L_2]$ and $[Pd(CH_3)_2L]$ complexes can be put in a small range from 2.008 to 2.077 Å, whereas the Pd−Cl bond length in both $[Pd(CH_3)(Cl)L_2]$ and $[Pd(CH_3)(Cl)L]$ show larger variation in the range from 2.268 to 2.388 Å (see Supporting Information for actual values). It means that the Pd−Cl bond is more sensitive to the *trans* influence of the phosphine ligand than the $Pd-C_{methyl}$ bond.[26] The Pd−Cl distances correlate strongly with the E_{act} (E_{act} = 417.39d − 940.24; correlation coefficient, r = 0.978 for $[Pd(CH_3)(Cl)L_2]$ complexes and E_{act} = 269.53d − 585.70; r = 0.991 for $[Pd(CH_3)(Cl)L$ complexes). On the other hand, $Pd-C_{methyl}$ distances show only poor correlation with E_{act}

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Scheme 2. Isodesmic Reactions Modeled To Quantify the *trans* Influence of the Ligand L in Pd(II) Complexes

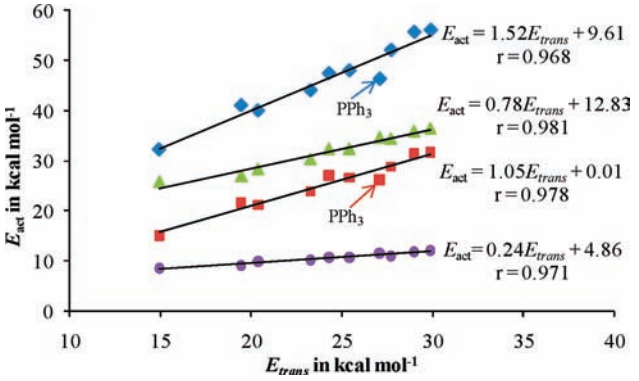

Figure 1. Correlation between E_{trans} and E_{act} values for the reductive elimination of CH_3CH_3 and CH_3Cl via direct and dissociative mechanisms (blue diamond, CH_3Cl direct; red square, CH_3CH_3 direct; green triangle, CH_3Cl dissociative; purple circle, CH_3CH_3 dissociative mechanisms).

(E_{act} = 648.24d − 1316.20; r = 0.685 for $[Pd(CH_3)_2L_2]$ complexes and E_{act} = 229.98d − 452.61; r = 0.917 for $[Pd(CH_3)_2L]$ complexes). All these correlations are given in the Supporting Information (Figure S1). Hence, we may conclude that the distance parameter is not always a good measure of the *trans* influence. However, these correlations suggest that in general a strong *trans* influencing ancillary ligand decreases the tendency of reductive elimination.

***Trans* Influence from Isodesmic Reactions.** On the basis of our previous studies,[42,43] the isodesmic reaction-based approach presented in Scheme 2 is used to quantify the *trans* influence of any ligand L. In this reaction, the reactant and product sides are nearly identical with respect to the type of metal to ligand bonds. The reactant and product sides differ mainly in the *trans* influence they experience; the product side has a *trans* influence from L on Cl^-, while reactant side is devoid of such an influence. Therefore, the energy of this reaction (designated as E_{trans}) represents a good thermodynamic measure of the *trans* influence. The reaction is endothermic as the *trans* influence weakens both Pd−L and *trans* Pd−Cl bonds in the product side. The following trend in E_{trans} values are obtained: PEt_3 (29.86) > PMe_3 (28.96) > $PHEt_2$ (27.68) > PPh_3 (27.07) > PH_2Et (25.39)> PH_2Ph (24.27) > PH_3 (23.26) > $PMeCl_2$ (20.37) > PH_2CF_3 (19.45) > PCl_3 (14.94) (values in parentheses are E_{trans} in kcal mol^{-1}). This order of *trans* influence is almost similar to the Pd−Cl bond length-based order of *trans* influence.

In Figure 1, E_{trans} is correlated with the E_{act} values of both direct and dissociation pathways. It is gratifying that the correlation coefficient, r, of all these linear plots is higher than 0.96. The slopes of the linear correlation for the CH_3Cl direct mechanism, CH_3CH_3 direct mechanism, CH_3Cl dissociative mechanism, and CH_3CH_3 dissociative mechanism are 1.52, 1.05, 0.78, and 0.24, respectively, suggesting that E_{act} of CH_3Cl the direct elimination

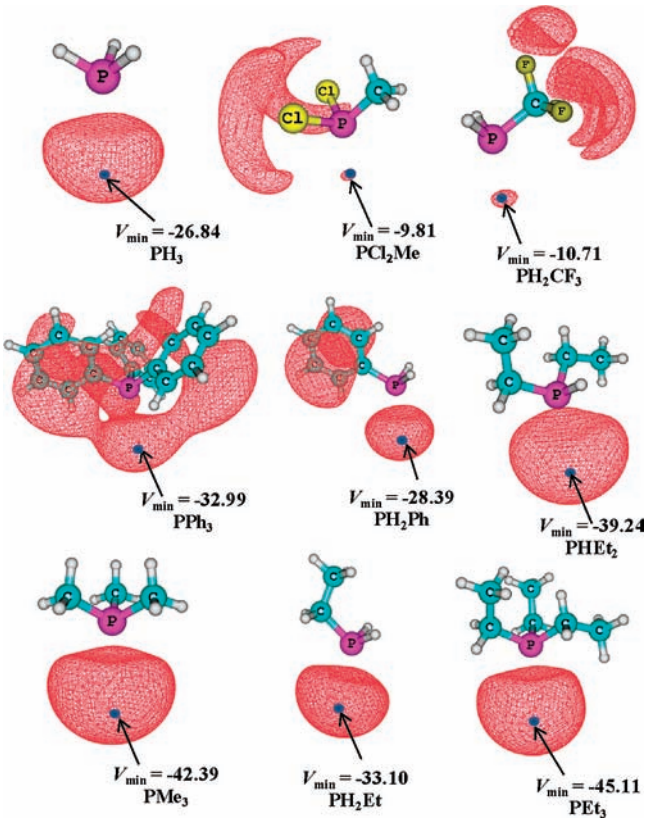

Figure 2. MESP isosurface at −9.0 kcal mol^{-1} for various phosphine ligands. The V_{min} in kcal mol^{-1} is also depicted.

is highly influenced by the *trans* influence, while this influence has less impact on the CH_3CH_3 dissociative elimination. The order of E_{act} corresponding to both the direct and dissociative mechanisms is in accordance with the E_{trans} values of ancillary phosphine ligands. The ligand PPh_3 shows some deviation from the linear plot for the direct mechanism, which can be attributed to the steric effect of this ligand.

Molecular Electrostatic Potential Minimum (V_{min}) of Free Phosphine Ligands. The *trans* influence originates from the competition between the σ-donating ability of the *trans* ligands.[39,74,75] Efforts from our laboratory have established that the use of the minimum of the molecular electrostatic potential (MESP), observed in the lone pair region of a phosphine ligand (V_{min}), is a good parameter to assess the electronic effect of a free phosphine ligand.[45,57,76,77] To show the MESP distribution of all the phosphines, a MESP isosurface of value −9.0 kcal mol^{-1} is depicted in Figure 2, and also the V_{min} is depicted at the lone pair region. The PEt_3 ligand has the most negative V_{min} (−45.11 kcal mol^{-1}), while the least negative V_{min} (−9.81 kcal mol^{-1}) is observed for $PMeCl_2$. For the unsubstituted PH_3, the V_{min} is −26.84 kcal mol^{-1}. V_{min} reflects the impact of the electron-donating or -withdrawing effect of the P-substituent[78−80], and it is used as a good quantitative measure of the σ-donating ability.[45] A more negative V_{min} indicates a higher σ-donating ability.[45,57] In the case of PCl_3, the lone pair region of phosphorus is devoid of negative potential due to a high electron withdrawing effect from the three chloro substituents. It is gratifying that the V_{min} values show almost the same order of *trans* influence on the basis of either the *trans* Pd−Cl bond length or E_{trans} values. Further, an excellent linear correlation (r = 0.981) is obtained between V_{min}

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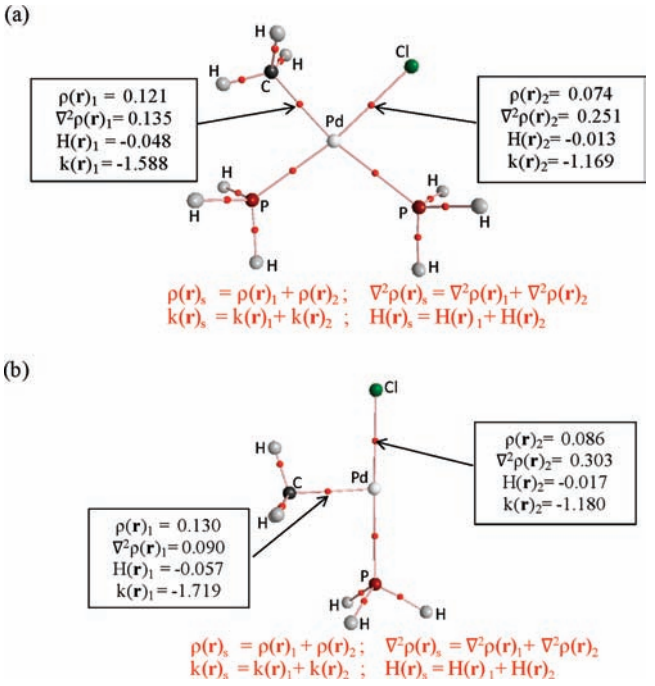

Figure 3. AIM features of representative (a) $Pd(CH_3)(Cl)L_2$ and (b) $Pd(CH_3)(Cl)L$ systems, where L = PH_3. The (3,-1) bond critical points are marked by small red circles. The $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $H(\mathbf{r})$ (all values are in au), and $k(\mathbf{r})$ at the bcp of the bonds that are cleaved during reductive elimination are marked, along with the definitions of $\rho(\mathbf{r})_s$,$\nabla^2\rho(\mathbf{r})_s$, $H(\mathbf{r})_s$, and $k(\mathbf{r})_s$.

and E_{trans} values; the corresponding equation is $E_{trans} = -0.283V_{min} + 16.69$. This reinforces that the *trans* influence of a PR_3 ligand is directly related to the electron-donating power of the ancillary ligand; more σ-donating groups must show a high *trans* influence and vice versa. Because E_{trans} and E_{act} show good linear correlation, V_{min} can also be used as a good measure of E_{act}. This also means that the reductive elimination will be inhibited substantially when the metal becomes more electron rich due to the enhancement in the electron-donating power of the phosphine ligand.[16,34,36,81]

AIM Analysis. The E_{trans} or V_{min} values along with the steric effects of ancillary phosphine ligands can be used to explain the relative changes in the E_{act} values of reductive eliminations, irrespective of the direct and dissociative mechanisms. However, these parameters are insufficient to explain the higher E_{act} values observed for CH_3Cl elimination than those for the CH_3CH_3 elimination for a particular ancillary ligand. Further, these parameters alone cannot give a satisfactory explanation to why the E_{act} of the direct mechanism shows higher values than the dissociative mechanism. It has been proposed that an increase in the σ-donating ability of the leaving groups increases the rate of reductive elimination.[81] Therefore, knowledge about the nature of the eliminating bond is also important to assess the E_{act}, and we propose to use the AIM analysis to understand this.

In Figure 3, AIM parameters, $\rho(\mathbf{r})_1$, $\nabla^2\rho(\mathbf{r})_1$, $H(\mathbf{r})_1$, and $k(\mathbf{r})_1$ for the $Pd-C_{methyl}$ bond and $\rho(\mathbf{r})_2$, $\nabla^2\rho(\mathbf{r})_2$, $H(\mathbf{r})_2$, and $k(\mathbf{r})_2$ for the Pd−Cl bond are depicted using the representative examples $Pd(CH_3)(Cl)(PH_3)_2$ and $Pd(CH_3)(Cl)(PH_3)$. Because two bonds are cleaved at the same time during the reductive elimination, the total change in the AIM parameters can be assessed by taking the sum of their individual values, and thus, the parameters $\rho(\mathbf{r})_s = \rho(\mathbf{r})_1 + \rho(\mathbf{r})_2$, $\nabla^2\rho(\mathbf{r})_s = \nabla^2\rho(\mathbf{r})_1 + \nabla^2\rho(\mathbf{r})_2$, $H(\mathbf{r})_s = H(\mathbf{r})_1 + H(\mathbf{r})_2$, and $k(\mathbf{r})_s = k(\mathbf{r})_1 + k(\mathbf{r})_2$ are also defined. The $\rho(\mathbf{r})_s$, $\nabla^2\rho(\mathbf{r})_s$, $H(\mathbf{r})_s$, and $k(\mathbf{r})_s$ values for the complexes of the type $Pd(CH_3)_2L_2$, $Pd(CH_3)_2L$, $Pd(CH_3)(Cl)L_2$, and $Pd(CH_3)(Cl)L$ are given in Tables 2, 3, 4, and 5, respectively. Detailed information of the AIM parameters for all the bonds are given in the Supporting Information.

The $\rho(\mathbf{r})_1$ values of a $Pd-C_{methyl}$ bond are in the range from 0.113 to 0.131 au, while $\rho(\mathbf{r})_2$ values of a Pd−Cl bond are in the range from 0.068 to 0.089 au. In all the systems, $\nabla^2\rho(\mathbf{r})$ values are positive (0.080−0.309 au), while the $H(\mathbf{r})$ values are negative (−0.011 to −0.057 au). The positive $\nabla^2\rho(\mathbf{r})$ indicates the ionic

Table 2. AIM Parameters $\rho(\mathbf{r})_s$,$\nabla^2\rho(\mathbf{r})_s$, $H(\mathbf{r})_s$, and $k(\mathbf{r})_s$ for $Pd(CH_3)_2L_2$ Complexes

ancillary ligands	$\rho(\mathbf{r})_s$ (au)	$\nabla^2\rho(\mathbf{r})_s$ (au)	$H(\mathbf{r})_s$ (au)	$k(\mathbf{r})_s$
PH_3	0.231	0.357	−0.086	−2.979
PCl_3	0.233	0.311	−0.090	−3.071
PH_2CF_3	0.227	0.344	−0.083	−2.983
PH_2Et	0.229	0.366	−0.083	−2.952
PH_2Ph	0.230	0.366	−0.084	−2.958
$PMeCl_2$	0.232	0.331	−0.087	−3.027
PMe_3	0.227	0.385	−0.081	−2.914
$PHEt_2$	0.230	0.373	−0.084	−2.948
PEt_3	0.226	0.387	−0.080	−2.907
PPh_3	0.231	0.360	−0.085	−2.972

Table 3. AIM Parameters $\rho(\mathbf{r})_s$,$\nabla^2\rho(\mathbf{r})_s$, $H(\mathbf{r})_s$, and $k(\mathbf{r})_s$ for $Pd(CH_3)_2L$ Complexes

ancillary ligands	$\rho(\mathbf{r})_s$ (au)	$\nabla^2\rho(\mathbf{r})$s (au)	$H(\mathbf{r})_s$ (au)	$k(\mathbf{r})_s$
PH_3	0.255	0.342	−0.104	−3.099
PCl_3	0.252	0.320	−0.103	−3.129
PH_2CF_3	0.254	0.334	−0.103	−3.109
PH_2Et	0.255	0.347	−0.103	−3.090
PH_2Ph	0.253	0.343	−0.102	−3.090
$PMeCl_2$	0.253	0.334	−0.103	−3.105
PMe_3	0.254	0.357	−0.102	−3.068
$PHEt_2$	0.254	0.351	−0.102	−3.080
PEt_3	0.253	0.358	−0.101	−3.064
PPh_3	0.254	0.347	−0.103	−3.090

Table 4. AIM Parameters $\rho(\mathbf{r})_s$,$\nabla^2\rho(\mathbf{r})_s$, $H(\mathbf{r})_s$, and $k(\mathbf{r})_s$ for $Pd(CH_3)(Cl)L_2$ Complexes

ancillary ligands	$\rho(\mathbf{r})_s$ (au)	$\nabla^2\rho(\mathbf{r})_s$ (au)	$H(\mathbf{r})_s$ (au)	$k(\mathbf{r})_s$
PH_3	0.195	0.386	−0.061	−2.756
PCl_3	0.202	0.366	−0.066	−2.851
PH_2CF_3	0.196	0.374	−0.062	−2.787
PH_2Et	0.191	0.390	−0.059	−2.731
PH_2Ph	0.192	0.394	−0.059	−2.728
$PMeCl_2$	0.198	0.366	−0.064	−2.817
PMe_3	0.187	0.398	−0.057	−2.693
$PHEt_2$	0.191	0.395	−0.059	−2.720
PEt_3	0.187	0.401	−0.056	−2.684
PPh_3	0.194	0.380	−0.061	−2.766

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Table 5. AIM Parameters $\rho(\mathbf{r})_s$, $\nabla^2\rho(\mathbf{r})_s$, $H(\mathbf{r})_s$, and $k(\mathbf{r})_s$ for $Pd(CH_3)(Cl)L$ Complexes

ancillary ligands	$\rho(\mathbf{r})_s$ (au)	$\nabla^2\rho(\mathbf{r})_s$ (au)	$H(\mathbf{r})_s$ (au)	$k(\mathbf{r})_s$
PH_3	0.216	0.393	−0.074	−2.899
PCl_3	0.216	0.389	−0.074	−2.928
PH_2CF_3	0.216	0.389	−0.074	−2.918
PH_2Et	0.214	0.395	−0.073	−2.883
PH_2Ph	0.214	0.394	−0.073	−2.886
$PMeCl_2$	0.215	0.389	−0.074	−2.919
PMe_3	0.213	0.402	−0.072	−2.852
$PHEt_2$	0.213	0.398	−0.073	−2.866
PEt_3	0.212	0.403	−0.072	−2.845
PPh_3	0.213	0.395	−0.073	−2.867

nature of the bond, whereas a negative $H(\mathbf{r})$ indicates the covalent nature.[82] Thus, it is clear that both the Pd−C_{methyl} and Pd−Cl bonds exhibit partial ionic and covalent characters.[82−84] The $\nabla^2\rho(\mathbf{r})$ of a Pd−Cl bond (0.241−0.309 au) is more positive than the $\nabla^2\rho(\mathbf{r})$ of a Pd−C_{methyl} bond (0.080−0.201 au), indicating a more ionic nature of the former. On the other hand, the $H(\mathbf{r})$ of a Pd−Cl bond (−0.011 to −0.018 au) is less negative than the $H(\mathbf{r})$ of a Pd−C_{methyl} bond (−0.040 to −0.057 au), suggesting a more covalent nature to the latter. Also, the $k(\mathbf{r})$ value of a Pd−C_{methyl} bond is 0.37−0.55 au more negative than that of a Pd−Cl bond, which also means that the potential electron energy density is significantly higher than the kinetic electron energy density in Pd−C_{methyl} than that of a Pd−Cl bond. The variation in the AIM parameters at the bcp of a Pd−C_{methyl}/Cl bond in the $Pd(CH_3)_2L_2$, $Pd(CH_3)_2L$, $Pd(CH_3)(Cl)L_2$, and $Pd(CH_3)(Cl)L$ complexes is mainly due to the change in electron donating ability of the ancillary ligands. There is a decrease in magnitude of the $\rho(\mathbf{r})$, $H(\mathbf{r})$, and $k(\mathbf{r})$ values at the bcp of a *trans* Pd−C_{methyl} /Cl bond when the σ-donating ability of the ancillary ligand is increased, while no such trend is observed in the case of $\nabla^2\rho(\mathbf{r})$ values. In $Pd(CH_3)_2L_2$ complexes, for the least σ-donating ancillary ligand PCl_3, the $\rho(\mathbf{r})$, H(**r**), and k(**r**) values at bcp of Pd−C_{methyl} are 0.117, −0.045, and −1.536 au, respectively, while for the highest σ-donating ancillary ligand PEt_3, these values are 0.113, −0.040, and −1.453 au, respectively. Similar observations can also be noticed for other complexes, viz. $Pd(CH_3)_2L$, Pd-$(CH_3)(Cl)L_2$,and $Pd(CH_3)(Cl)L$.

In Figure 4, the correlation between $\rho(\mathbf{r})_s$ and E_{act} is presented. In the case of direct and dissociative mechanisms of CH_3Cl elimination, E_{act} shows strong linear dependency to $\rho(\mathbf{r})_s$. However, E_{act} for CH_3CH_3 elimination shows almost no correlation with $\rho(\mathbf{r})_s$. Interestingly, a general trend is that when $\rho(\mathbf{r})_s$ decreases, E_{act} increases. Because a higher value of $\rho(\mathbf{r})_s$ indicates greater strength, one would expect more difficulty in breaking that bond. This observation is counterintuitive as a smaller value of $\rho(\mathbf{r})_s$ can be associated with a weaker bond to be cleaved, indicating lowering of the activation barrier. A very similar observation is also applicable for the correlation of the *trans* bond length versus E_{act} presented in Figure S1 of the Supporting Information: a shorter bond is activated more easily than a longer bond! This means that on the basis of the strength of the cleaved bonds assessed in terms of either bond length data or the electron density data, we cannot explain the activation process of the reductive elimination reaction.

In Figure 5, $H(\mathbf{r})_s$ values are plotted against E_{act}. These plots look very similar to the ($\rho(\mathbf{r})_s$, E_{act}) plots given in Figure 4. In

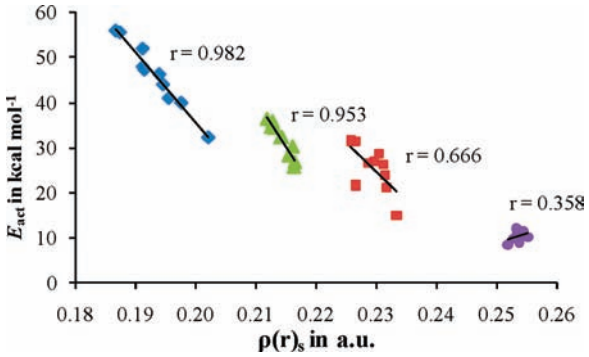

Figure 4. Correlation between $\rho(\mathbf{r})_s$ and E_{act} values (blue diamond, CH_3Cl direct; red square, CH_3CH_3 direct; green triangle, CH_3Cl dissociative; purple circle, CH_3CH_3 dissociative mechanisms).

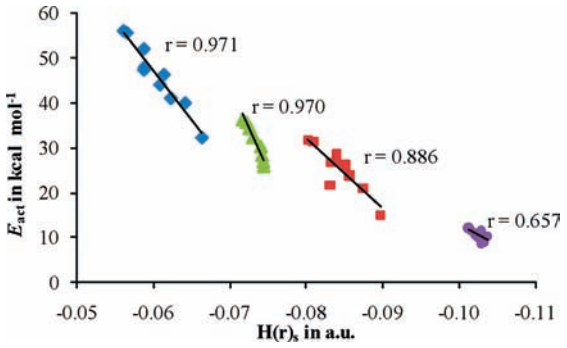

Figure 5. Correlation between $H(\mathbf{r})_s$ and E_{act} values (blue diamond, CH_3Cl direct; red square, CH_3CH_3 direct; green triangle, CH_3Cl dissociative; purple circle, CH_3CH_3 dissociative mechanisms).

general, E_{act} decreases with an increase in the negative character (covalent character) of $H(\mathbf{r})_s$. Thus, obviously there is a fundamental difference in the interpretations that we can obtain from the ($\rho(\mathbf{r})_s$, E_{act}) plots and ($H(\mathbf{r})_s$, E_{act}) plots: it is not the bond strength that matters but the nature of the cleaved bonds; the more covalent they are the easier is the reductive elimination. For instance, when a Pd−CH_3/Cl bond becomes more covalent in nature, the cleavage of a Pd−CH_3/Cl bond during the reductive elimination process leads to formation of fragments (CH_3/Cl) with more radical character, and as a result, the subsequent bond formation of CH_3-CH_3/Cl becomes easier.

The correlations of $\nabla^2\rho(\mathbf{r})_s$ versus E_{act} (Figure 6) nicely compliment the conclusion drawn from the plots of $H(\mathbf{r})_s$ versus E_{act}: the more the ionic nature of the bond to be cleaved, the higher is the activation barrier for the reductive elimination. Thus, the formation of CH_3CH_3 is quite easy compared to the formation of CH_3Cl because of the more ionic nature of the Pd−Cl bond. Even though the Pd−C_{methyl} bond is stronger than the Pd−Cl bond, the two cleaved methyl fragments with the $\bullet CH_3$ nature are easy to combine for the C−C bond formation.

The plot of $k(\mathbf{r})_s$ versus the E_{act} (Figure 7) shows a unified picture of the nature of the chemical bond to the tendency of reductive elimination: irrespective of the type of reaction (elimination of either CH_3CH_3 or CH_3Cl) and the type of mechanism (direct or dissociative), all the E_{act} values can be correlated with one linear equation. In other words, when the potential electron energy density dominates over the kinetic electron energy density at the bcp, reductive elimination

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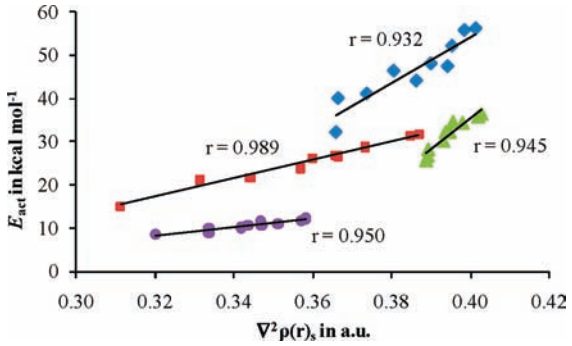

Figure 6. Correlation between $\nabla^2\rho(\mathbf{r})_s$ and E_{act} values (blue diamond, CH_3Cl direct; red square, CH_3CH_3 direct; green triangle, CH_3Cl dissociative; purple circle, CH_3CH_3 dissociative mechanisms).

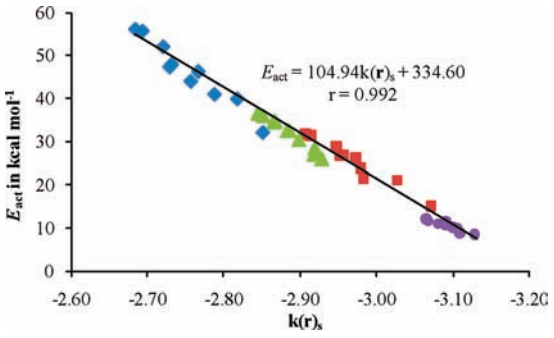

Figure 7. Correlation between $k(\mathbf{r})_s$ and E_{act} values (blue diamond, CH_3Cl direct; red square, CH_3CH_3 direct; green triangle, CH_3Cl dissociative; purple circle, CH_3CH_3 dissociative mechanisms).

becomes facile. This may show that a bond with a more covalent character has more potential electron energy density, while a bond with a more ionic character has more kinetic electron energy density and vice versa, if the covalent character of the bonds can be well estimated through $k(\mathbf{r})_s$. It can be assumed that the interplay between the covalent and ionic natures of the bonds that are cleaved during reaction is the controlling factor for the reductive elimination.

It may also be noted that $\rho(\mathbf{r})_s$ values for the less electron-donating phosphine ligand is higher, particularly for four-coordinate reactant complexes. Similar observations can also noted for $H(\mathbf{r})_s$ and $k(\mathbf{r})_s$ values. Thus, when the σ-donating ability of the ancillary ligand decreases, an increase in the strength and covalent nature of *trans* bond is observed. Also, the $\nabla^2\rho(\mathbf{r})_s$ value is found to be higher for electron-rich ancillary ligands, and this shows more ionic character to the *trans* bond when such ancillary ligands are present. The nature of ancillary ligands controls the strength and covalent nature of the *trans* Pd−C/Cl bond and also controls the activation process for the reductive elimination.

CONCLUSION

The present work has focused on the effect of ancillary phosphine ligands on C−C and C−Cl bond formation through the reductive elimination mechanism in square planar complexes of the type *cis*-$[Pd(CH_3)_2L_2]$ and *cis*-$[Pd(CH_3)(Cl)L_2]$, where L is the ancillary phosphine ligand. The results show that the E_{act} of reductive elimination reactions are directly controlled by the σ-donating ability of the ancillary phosphine ligands.[16,34,36] For bulky phosphine ligands, the steric effect was also significant. The isodesmic reaction energy-based *trans* influence parameter E_{trans} showed a strong linear relationship to V_{min} values of the ancillary phosphine ligands, suggesting that the *trans* influence is governed by the electron-donating character[73,85,86] of the phosphine ligand. Both E_{trans} and V_{min} can be used as very effective descriptors to measure the ability of the metal complex to undergo reductive elimination as both quantities showed excellent linear relationships to E_{act}. Between E_{trans} and the V_{min}, the latter is easy to compute as it involves the determination of the MESP of the free phosphine, while the former is calculated from a reaction scheme.

AIM analysis of the reactant complexes suggests that when the covalent nature of the Pd−leaving group/atom bond increases, the energy of activation for the reductive elimination decreases and vice versa. The *trans* bond length analysis or the bond strength analysis using $\rho(\mathbf{r})_s$ gives only a false impression that reductive elimination becomes easy with strong metal−ligand bonds. In fact, the correct interpretation of the reductive elimination can be obtained from the study of the ionic versus covalent nature of the bonds that are cleaved, and this important conclusion is obtained by the analysis of $\nabla^2\rho(\mathbf{r})_s$ and $H(\mathbf{r})_s$. Further, the $k(\mathbf{r})_s$ in the AIM analysis showed that the relative magnitude of the potential electron energy density and kinetic electron energy density at the bcp of the bonds that are cleaved in the reductive elimination are key factors for determining the activation energy, and using this parameter, a unified view of the process can be obtained irrespective of the type of reaction and nature of the mechanism. Further, AIM analysis showed that the strength and covalent character of the Pd−CH_3/Cl bond depend on the electronic nature of the ancillary ligands. In general, an electron-withdrawing ancillary ligand increases the strength of the *trans* bond by increasing its covalent character. Because bonds with more covalent character are more susceptible for reductive elimination than bonds with more ionic character, an electron-withdrawing ligand will promote reductive elimination reactions more than an electron-rich ligand. It may be noted that these conclusions are based on the effect of ancillary phosphine ligands on the activation of reductive elimination reactions, and no attempt has been made to generalize them for other ligands.

ASSOCIATED CONTENT

Supporting Information. Cartesian coordinates of all the geometries, energy details, AIM parameters, and additional correlation diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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