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Oxidative addition of a C−H σ bond to $M(PH_3)_2$ (M = Pd or Pt). An *ab initio* molecular orbital study on the chelate phosphine effect†

Shigeyoshi Sakaki,* Bishajit Biswas and Manabu Sugimoto

Department of Applied Chemistry and Biochemistry, Faculty of Engineering,
Kumamoto University, Kurokami, Kumamoto 860, Japan

All the reactants, transition states and products of the oxidative addition of a C−H σ bond to $M(PH_3)_2$ (M = Pd or Pt) were optimized at the second-order Møller-Plesset perturbation (MP2) level and the energy changes in the reaction were evaluated by *ab initio* molecular orbital/MP4, SD-CI (single- and double-excitation configuration interaction) and CCD (coupled cluster with double substitutions) methods. In the model complexes of a monodentate phosphine this reaction requires a considerably high activation energy (E_a), 30 and 37 kcal mol^{-1} for M = Pt and Pd (MP4SDQ values), respectively. However, this reaction proceeds with a much lower activation energy when two PH_3 ligands are positioned so as to mimic a chelate phosphine, *e.g.* a diphosphinomethane; for instance, E_a = 20.0 and 3.8 kcal mol^{-1} for M = Pd and Pt, respectively. This significant effect of a chelate phosphine is discussed in detail from the point of view of the frontier orbital, electronic reorganization and distortion energies of $M(PH_3)_2$.

It has been believed for a long time that palladium(0) complexes are unfavourable for oxidative addition since the palladium d electrons have a low energy (palladium adopts the d^{10} electron configuration as its ground state). Oxidative addition of a C−H σ bond to $Pd(PH_3)_2$ was previously calculated to be impossible (*i.e.* reductive elimination, which is the reverse reaction of oxidative addition, occurred with no barrier), but the same reaction with $Pt(PH_3)_2$ was calculated to occur with an activation barrier of about 21–30 kcal mol^{-1}.[1,2] However, C−H oxidative addition to a palladium(0) complex has been experimentally proposed in the palladium-catalysed C−C bond formation of allene.[3] This seems surprising, considering the previous computational results.[1,2] In this regard, a different mechanism has recently been proposed for a similar reaction,[4] in which nucleophilic attack of Pd^0 on a saturated carbon atom is considered as a key step in the formation of a palladium(II) hydride complex. From a detailed inspection of these experiments[3,4] there appears to be two important factors: the use of a chelate phosphine and the presence of an electron-withdrawing group on the carbon atom.[3,4] Certainly, the chelate phosphine was proposed to enhance the reactivity of the platinum complex for the oxidative addition,[5] and the electron-withdrawing group is considered to stabilize the palladium(II)–alkyl bond.[6] Detailed investigation of these two factors is of considerable importance for an understanding of the catalysis of palladium.

Here we investigate the chelate phosphine effects on the C−H oxidative addition to $Pd(PH_3)_2$ and $Pt(PH_3)_2$ [equation (1)]

$$M(PH_3)_2 + H{-}CH_3 \longrightarrow cis\text{-}[MH(CH_3)(PH_3)_2] \qquad M = \text{Pd or Pt} \quad (1)$$

by *ab initio* molecular orbital/Møller-Plesset (MP4), SD-CI (single- and double-excitation configuration interaction) and CCD (coupled cluster with double substitutions) methods. The two main motivations of this work were to elucidate how much and why the chelate phosphine facilitates the C−H oxidative addition and to clarify whether or not the palladium(0) complex of a chelate phosphine can undergo C−H oxidative addition.

Computational Details

The geometries of the reactants, transition state and product were optimized at the MP2 level with the energy-gradient technique. The transition state was determined by calculating a Hessian matrix. In the geometry optimization effective core potentials (ECPs) were used to replace core electrons of P (up to 2p electrons),[7] Pd (up to 3d electrons) and Pt (up to 4f electrons),[8] where split-valence-type basis sets (21/21/1) (exponent of d polarization function is 0.34[9]),[7] (311/311/31) and (311/311/21)[8] were employed for the valence electrons of P, Pd and Pt, respectively; MIDI-3*[9] and (31)[10] sets were used for C and H, respectively. The d ($\zeta = 0.60$) and p ($\zeta = 1.0$) polarization functions were added to C and an active H atom, that is the coordinated hydride and the hydrogen atom which becomes the hydride ligand. This basis set system is called BS-I in this paper.

The MP4SDQ, SD-CI and CCD calculations were carried out on the MP2-optimized geometries. More flexible contracted basis sets, (311/311/211) and (311/311/111), were adopted for the valence electrons of Pd and Pt, respectively, while the ECPs used were the same as those employed for geometry optimization. The sets (721/41/1)[10] and (31/1)[10] were used for C and H atoms, respectively, without any modification of the ECP and basis set for P. This basis set system is called BS-II.

In some calculations, p ($\zeta = 0.034$)[10] and s ($\zeta = 0.036$)[11] diffuse functions were added to C and H atoms, respectively, because H and CH_3 in $[MH(CH_3)(PH_3)_2]$ are formally considered to be hydride and alkyl anions. Also, the effects of an f polarization function ($\zeta = 1.472$ for Pd)[12] were investigated; such effects were previously examined in the oxidative addition of Si−H to $Pt(PH_3)_2$.[13] This is because some differences are expected to be found between the oxidative additions of Si−H and C−H: the former reaction reaches the transition state in the early stage[13] whereas the latter reaction reaches it in the late stage as will be discussed below.

In all these calculations the core orbitals were excluded from the active space. In CCD calculations a contribution from single and triple excitations was evaluated with a CCD wavefunction.[14] The GAUSSIAN 92 program[15] was used for these calculations.

The geometry of PH_3 was taken from experimental work.[16] When the model system of a chelate phosphine complex was investigated, two PH_3 ligands were positioned so as to reproduce the P−P distance of the real chelate phosphine complex (Scheme 1). In the geometry optimization the M−X, P^1−X and P^2−X distances were optimized, where X lies on the $P^1 \cdots P^2$ line. This means that each M−P distance is optimized with the P $\cdots$ P

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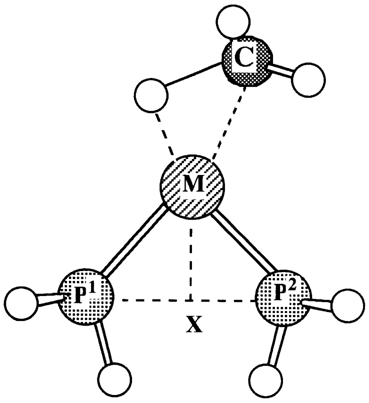
† *Non-SI units employed*: hartree ≈ 4.36 × 10^{-18} J, cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J.

Table 1 Basis-set effects at the MP2 level on the activation energy (E_a) and the reaction energy (ΔE) for C−H oxidative addition to Pd(dipe)

	BS-I	BS-II			
Pd	(311/311/31)	(311/311/211)	(311/311/211)	+4f	4f
C	MIDI3*	(721/41/1)	+diffuse	(721/41/1)	+diffuse
H_{active}	(31/1)	(31/1)	+diffuse	(31/1)	+diffuse
H_{others}	(31)	(31/1)	+diffuse	(31/1)	+diffuse
E_a/kcal mol^{-1}	18.8	18.8	20.0	18.4	19.6
ΔE/kcal mol^{-1}	8.2	8.2	9.2	8.4	9.3



Scheme 1

distance fixed. The latter was rather arbitrarily taken so as to mimic those in 1,2-bis(dicyclohexylphosphine)ethane (dcpe)[17] and bis(di-*tert*-butylphosphino)methane (dbpm)[5] complexes of Pt^{II}. The model for the former is called dipe and that for the latter dipm in this paper.

The other possible way to mimic a chelate phosphine is to take the P−M−P angle to be the same as that in the real complex. However, geometry optimization using this constraint leads to abnormally long Pt−P and Pd−P distances.‡ Thus, we did not adopt this method.

Results and Discussion

Geometry changes

Optimized geometries are shown in Figs. 1 and 2. Prior to a detailed discussion of the geometry changes we will first compare the optimized geometries of model systems with the geometries of real complexes. In [PtH(CH_3)(dipm)] the calculated Pt−P distances (2.273 and 2.256 Å) are a little bit shorter than the experimental distances (2.338 and 2.330 Å) of [PtH(CH_2CMe_3)(dbpm)],[5] but the calculated Pt−H (1.557 Å) and Pt−C (2.091 Å) distances and the P−Pt−P angle (76.8°) agree well with the experimental values,[5] R(Pt−H) = 1.58, R(Pt−C) = 2.117 Å, and P−Pt−P 74.7°. In [PtH(CH_3)(dipe)] the calculated Pt−P distances are slightly longer than that of [Pt(dfppe)$_2$] [dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$][18] probably due to the *trans* influence of H and CH_3, but slightly shorter than those in *cis*-[Pt($SiMe_2H$)$_2$(dcpe)][16] because $SiMe_2H$ exhibits a stronger *trans* influence than H and CH_3.[2] Also, the calculated P−Pt−P angle of 88° is only 2° larger than that of [Pt($SiMe_2H$)$_2$(dcpe)].[16] Since these differences are very small the present model systems are reasonable.

Since the geometry changes upon C−H oxidative addition were discussed previously[2] we will mainly discuss here the chelate phosphine effects on the geometry change. These are summarized as follows. (1) The Pt−CH_4 distance of the precursor complex is much shorter in the chelate phosphine model than in the monodentate phosphine model. (2) In the transition state of platinum–chelate phosphine model complexes the C−H bond to be broken is slightly shorter but the Pt−H and Pt−CH_3 distances are slightly longer than in the transition state of the platinum–monodentate phosphine model. (3) In the palladium systems the Pd−H and Pd−CH_3 distances are almost the same in both transition states of the monodentate and chelate phosphine models, while the C−H bond to be broken is slightly shorter in the chelate phosphine model. However, these differences between monodentate and chelate phosphine model complexes are rather small, and the transition-state geometries are similar in the two models. In other words, the position and geometry of CH_4 in the transition state depend only slightly on the phosphine ligand. (4) The P−M−P angle becomes slightly smaller upon going to the product from the reactant even in the chelate phosphine models. Similar results were found experimentally: the P−Pt−P angle is 89.5° in [Pt^0(dfppe)$_2$][17] but slightly smaller (85.7°) in [Pt($SiMe_2H$)$_2$(dcpe)].[16] Although the substituents on the P atom are different between dfppe and dcpe, this observed change seems consistent with the computational results presented here. Moreover, the decrease in the P−M−P angle seems reasonable in the chelate phosphine complexes since the M−P bond is longer in the product than in the reactant due to the *trans* influences of the H and CH_3 ligands in the product, which leads to a decrease in the P−M−P angle since the P · · · P distance cannot lengthen very much in the chelate phosphine.

Basis-set and correlation effects on the activation energy (E_a) and the reaction energy (ΔE)

The basis-set effects of diffuse functions on C and H atoms were first examined at the MP2 level. Effects of diffuse functions are surprisingly small, as shown in Table 1; E_a and ΔE increase by only 1.2 and 1.0 kcal mol^{-1}, respectively, upon addition of diffuse functions. Then, the effects of an f-polarization function on Pd were examined. Again, E_a and ΔE change little from those of the MP2/BS-II calculation. It is reasonably concluded that the BS-II set yields reliable E_a and ΔE values in this kind of oxidative addition.

Electron-correlation effects on E_a and ΔE are also worthy of note. As shown in Table 2, the introduction of such effects decreases E_a and the endothermicity, as previously reported in the Si−X oxidative addition to complexes of Pt^0 and Pd^0.[2,13] It is important that E_a and ΔE change little upon going from MP3 to CCD(ST4), except for SD-CI with Davidson correction.§,[19] This result suggests that a single-reference wavefunction would be useful to investigate the C−H oxidative addition to complexes of Pd and Pt.

However, the very long C−H distance in the transition state of palladium reaction systems suggests that the MC-SCF (multi configurational self-consistent field) calculation is neces-

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‡ When the P−M−P angle was taken to be 85.7° as in [Pt($SiMe_2H$)$_2$(dcpe)], the Pt−P bond *trans* to H was 2.396 Å and that *trans* to CH_3 was 2.351 Å, the Pd−P bond *trans* to H was 2.511 Å and that *trans* to CH_3 was 2.435 Å. When the angle was taken to be 74.7° as in [PtH(CH_2CMe_3)(dbpm)] the Pt−P bond *trans* to H was 2.489 Å, that *trans* to CH_3 was 2.399 Å, the Pd−P bond *trans* to H was 2.658 Å and that *trans* to CH_3 was 2.497 Å. Some of these values are too long compared to the experimental distances.[5,16,18]

§ In many cases the Davidson correction yields slightly different values in oxidative-addition reactions, suggesting that a size-consistent correction is insufficient.[13]

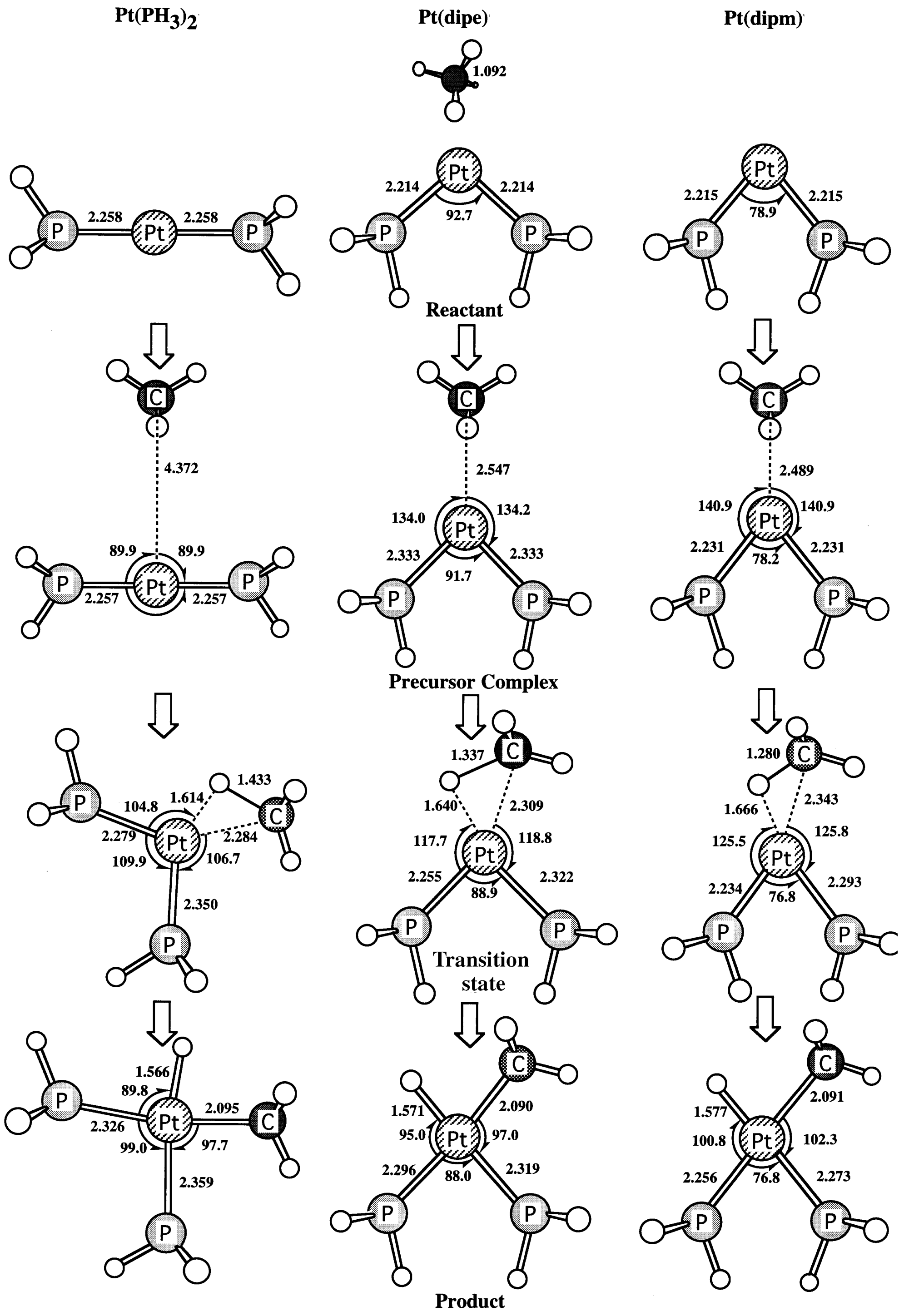

Fig. 1 Geometry changes upon C−H oxidative addition to platinum(0) complexes (bond distances in Å, angles in °): Pt(PH_3)$_2$ represents a model of a monodentate phosphine complex, Pt(dipe) a model of a diphosphinoethane complex and Pt(dipm) a model of a diphosphinomethane complex

sary to describe such transition states. Thus, CH_4 was calculated with the CAS-SCF (complete active space–self-consistent field) method (active space of eight orbitals and eight electrons), in which one of the C−H distances is lengthened very much like that in the transition state. As shown in Fig. 3, the CAS-SCF and MP4SDQ calculations yield almost the same potential-energy change, the same active space being taken in both. Moreover, the triplet instability of the Hartree–Fock wavefunction[22] was not observed in the transition state: the eigenvalue of the instability matrix is 0.046 for Pd(PH_3)$_2$, 0.050 for Pd(dipe), 0.092 for Pt(PH_3)$_2$ and 0.098 for Pt(dipe). Thus, it is reasonably concluded that the MP4SDQ/BS-II calculation on the MP2/BS-I geometry yields reliable results in the present C−H oxidative addition. Similarly, Siegbahn and co-workers[23] recently investigated C−H oxidative addition to second-row transition-metal complexes using MCPF (modified coupled-pair functional), which is a size-consistent single-reference method.

Comparisons of E_a and ΔE between model complexes of monodentate and chelate phosphines

First, we will mention the binding energy (b.e.) of the precursor complex, which is defined as the stabilization energy of the precursor complex relative to the reactants. Since its value is not very large (Table 3), the basis-set superposition error (b.s.s.e.) was taken into consideration here, which was estimated at the MP2 level using the counter-poise method.[24] Although the b.e. is negligibly small for the precursor complex of monodentate

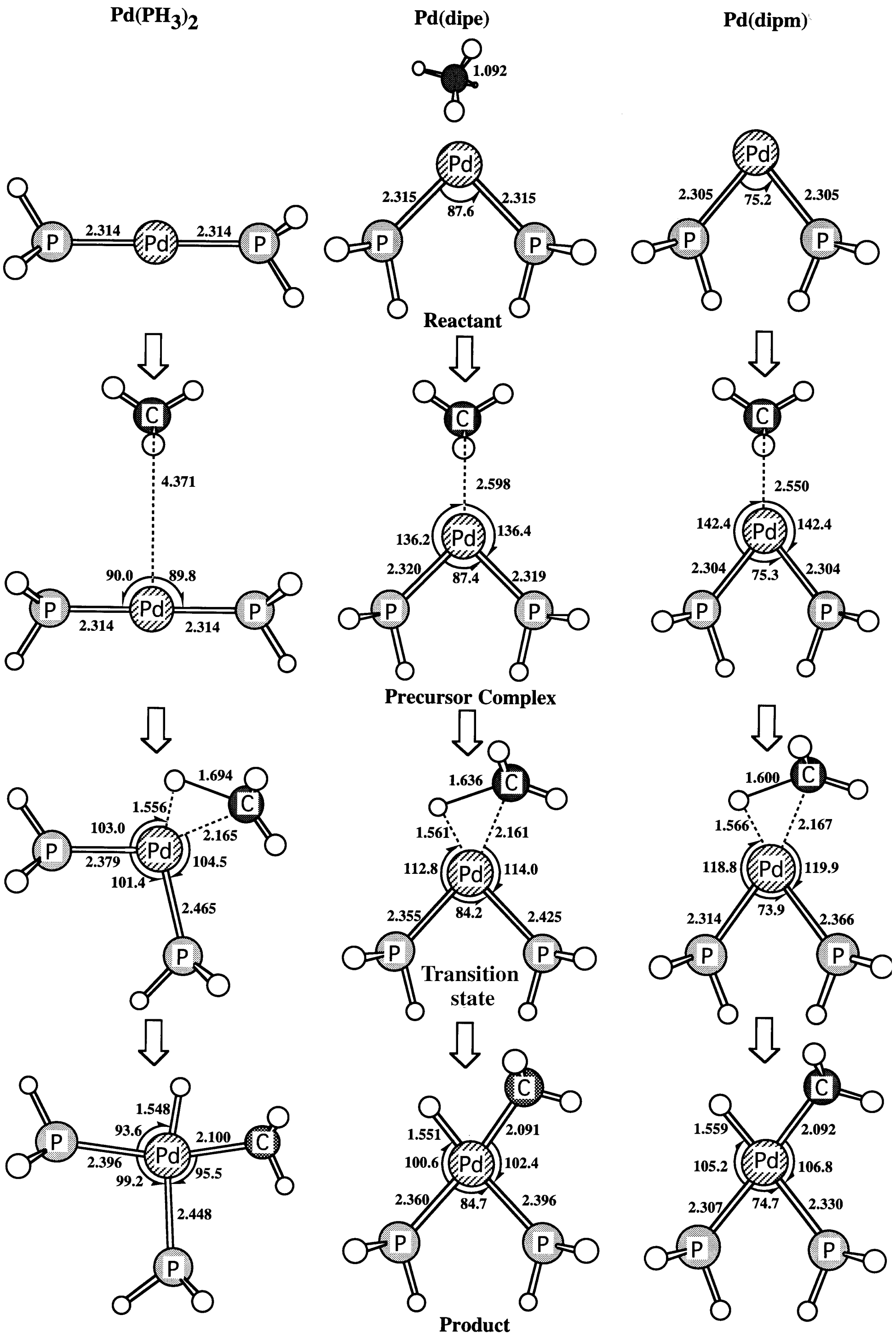

Fig. 2 Geometry changes upon C–H oxidative addition to palladium(0) complexes

phosphine models, that for chelate phosphine models is 8–12 kcal mol^{-1} before the b.s.s.e. correction and decreases by about 3 kcal mol^{-1} upon correction. Although the b.e. after correction seems small, the counter-poise method tends to overestimate the b.s.s.e., and therefore the real value is larger than 4 kcal mol^{-1}, which is much larger than that for the monodentate phosphine model complexes. The larger binding energy of the chelate phosphine model is consistent with its shorter M–CH_4 distance than in the monodentate phosphine model. Plausible reasons for this are the interaction between the dipole moment of M(chelate phosphine) and the induced dipole moment of CH_4 [note that M(dipe) and M(dipm) have a dipole moment but $M(PH_3)_2$ does not] and the smaller steric repulsion between CH_4 and phosphine.

A much more significant difference is observed in E_a and ΔE between monodentate and chelate phosphine models. In the case of the monodentate phosphine the C–H oxidative addition requires a significantly high E_a of 37 kcal mol^{-1} for Pd and 30 kcal mol^{-1} for Pt (Table 3). This suggests that the oxidative addition cannot occur thermally in the monodentate phosphine complexes of Pd^0 and Pt^0. However, the E_a value markedly decreases in the chelate phosphine models: *ca.* 4–7 kcal mol^{-1} for Pt and *ca.* 20–22 kcal mol^{-1} for Pd. If the b.s.s.e. correction is made the E_a value increases by *ca.* 3 kcal mol^{-1} (see values in parentheses in Table 3). Oxidative addition of Si–Si to $Pt(PH_3)_2$ was previously calculated to proceed with E_a = 18 kcal mol^{-1}.[3,13] The experimentally proposed Pt- and Pd-catalysed bis(silylations) of alkenes and alkynes are considered to involve Si–Si oxidative addition to complexes of Pt^0 and Pd^0.[25] Thus, it can be reasonably concluded that although complexes of Pt^0 and Pd^0

Table 2 Electron-correlation effects (kcal mol^{-1}) on the binding energy (b.e.),[a] E_a[a] and ΔE[a] in the C–H oxidative addition to Pd(mdipe); basis set BS-II

	b.e.	E_a	ΔE
HF	2.0	36.5	32.8
MP2	−7.7	18.8	8.2
MP3	−5.3	23.3	11.9
MP4DQ	−6.4	21.9	11.4
MP4SDQ	−7.7	22.1	11.7
SD-CI(D)[b]	8.2	24.6	27.8
SD-CI(DS)[c]	−3.9	21.7	12.6
SD-CI(P)[d]	−3.9	22.4	13.4
CCD	−7.6	21.4	10.5

[a] b.e. = E_t(precursor complex) − E_t(sum of reactants), $E_a = E_t$(transition state) − E_t(precursor complex), $\Delta E = E_t$(product) − E_t(sum of reactants). [b] Davidson correction[19] for higher-order excitations. [c] Davidson–Silver correction[20] for higher-order excitations. [d] Pople correction[21] for higher-order excitations.

Table 3 Values (kcal mol^{-1}) of b.e., E_a and ΔE for various reaction systems at the MP4SDQ level

System	b.e.	E_a	ΔE
Pd(PH_3)$_2$	−0.7 (−0.1)*	36.9 (44.8)*	34.1
Pd(dipe)	−7.7 (−3.8)	22.1 (25.7)	11.7
Pd(dipm)	−8.9	20.0	7.7
Pt(PH_3)$_2$	−0.8 (−0.3)	29.9 (37.2)	9.9
Pt(dipe)	−9.8 (−5.7)	6.8 (8.9)	−25.7
Pt(dipm)	−12.4	3.8	−34.1

* The basis-set superposition error was corrected at the MP2 level with the counter-poise method.[24]

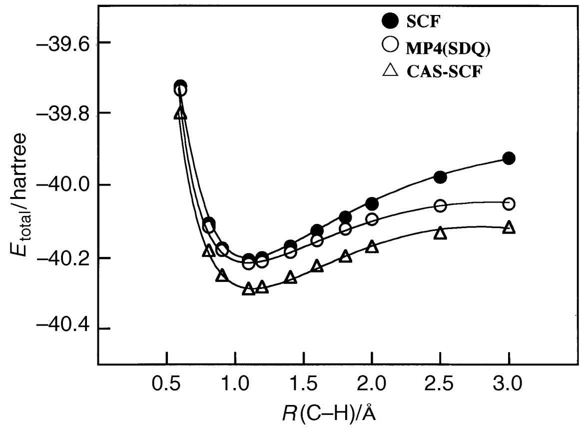

Fig. 3 Plots of total energy *vs.* C–H distance in CH_4. Eight orbitals and eight electrons are correlated in CAS-SCF and MP4SDQ calculations

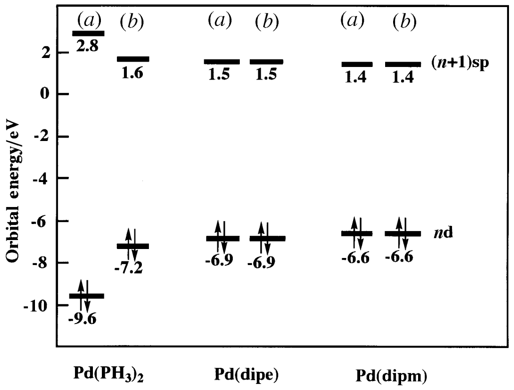

Fig. 4 The d_π and sp_σ orbital energies of M(PH_3)$_2$, M(dipe) and M(dipm): (*a*) the equilibrium structure; (*b*) the distorted structure as in the transition state

with monodentate phosphines cannot undergo C–H oxidative addition, use of a chelate phosphine instead allows the oxidative addition to occur easily in platinum(0) complexes. In the case of palladium(0) complexes the oxidative addition is certainly accelerated by the chelate phosphine, but it still requires a considerable activation energy. Thus, the introduction of a electron-withdrawing substituent would be necessary.

The important interactions in the oxidative addition are the charge transfer (c.t.) from the metal d orbital to the C–H σ^* orbital, and the reverse c.t. from the occupied C–H σ orbital to the unoccupied sp_σ orbital to the metal.[26] The chelate phosphine influences these orbital energies, as shown in Fig. 4 (the changes are similar for platinum systems). In the equilibrium structure the d_π orbital of M(dipe) and M(dipm) is at a higher energy than that of M(PH_3)$_2$, and the sp_σ orbital is at a lower energy than that of M(PH_3)$_2$. The other important feature to be noted is that the d_π orbital of M(dipe) and M(dipm) lies at a similar energy in both the reactant and transition state, while the d_π orbital of M(PH_3)$_2$ is at a much lower energy in the reactant than in the transition state. This means that M(dipe) and M(dipm) have the d_π orbital at a sufficiently high energy to undergo easily the C–H oxidative addition even in the equilibrium structure, but M(PH_3)$_2$ needs considerable distortion to raise the d_π orbital energy. This distortion is expected to yield significant destabilization energy in M(PH_3)$_2$.

Thus, we examined the distortion energy (d.i.s.e.) and the interaction energy (i.e.), defined as the energy difference between the equilibrium and the distorted geometries in the transition state, and the stabilization energy yielded upon interaction between the distorted metal part and the distorted CH_4 part. Interestingly, the i.e. is almost the same in M(PH_3)$_2$, M(dipe) and M(dipm), as shown in Fig. 5, whereas it is much different between M = Pd and Pt. Since the d.i.s.e. of the CH_4 part is almost the same for M(PH_3)$_2$, M(dipe) and M(dipm), the difference in E_a is mostly attributed to the difference in d.i.s.e. of the metal part. It is concluded that since the d.i.s.e. of M(dipe) and M(dipm) is very small in the transition state, C–H oxidative addition to these complexes can proceed very easily with a much lower activation energy than for M(PH_3)$_2$. Why is the d.i.s.e. of M(dipe) and M(dipm) small? The reason is as follows: M(dipe) and M(dipm) adopt almost the same geometries as in the transition state due to the constraint enforced on the phosphine part in order to mimic a chelate phosphine; in other words, the geometries of M(dipe) and M(dipm) cannot be fully relaxed due to the constraint and they are restricted to be similar to those in the transition state. Thus, the d.i.s.e. of M(dipe) and M(dipm) is very small and the C–H oxidative addition to them can easily occur with a low E_a. Although significant differences are observed between Pt and Pd, discussion on the differences is omitted here since the differences were discussed in detail previously.[1]

Population changes

Several interesting features are observed in the population changes (Table 4). The hydrogen atomic population of the product is larger than in the reactant, consistent with our understanding that this reaction is oxidative addition. However, the electron population of CH_3 increases to a much lower extent than does that of the hydrogen atom. This is probably because CH_3 is somewhat negatively charged in CH_4 due to the lower electronegativity of H than that of C. These changes are common for all the reaction systems examined.

On the other hand, remarkable contrasts between monodentate and chelate phosphine models are observed in the population changes of the metal part. In [MH(CH_3)(PH_3)$_2$], the s- and d-orbital populations of Pt and Pd are considerably smaller but the p-orbital population is significantly larger than in the reactant. These changes are easily understood in terms of the hybridization change from sp (linear) to dsp^2 (square planar). In the

Table 4 Comparisons of Mulliken populations[a] between the reactants and products

	$Pt(PH_3)_2$		Pt(dipe)	
	Reactant	Product	Reactant	Product
M	18.136	18.159 (+0.023)[b]	18.025	18.145 (+0.120)[b]
s	2.446	2.148 (−0.298)	2.079	2.155 (+0.076)
p	6.088	6.565 (+0.477)	6.382	6.565 (+0.183)
d	9.602	9.446 (−0.156)	9.564	9.425 (−0.139)
H	0.854	1.000 (+0.146)	0.854	1.008 (+0.154)
CH_3	9.146	9.158 (+0.012)	9.146	9.159 (+0.013)
	$Pd(PH_3)_2$		Pd(dipe)	
M	18.116	18.117 (+0.001)[b]	18.024	18.114 (+0.090)[b]
s	2.287	2.137 (−0.150)	2.091	2.143 (+0.052)
p	6.048	6.396 (+0.348)	6.302	6.386 (+0.084)
d	9.781	9.584 (−0.197)	9.631	9.585 (−0.046)
H	0.854	0.938 (+0.084)	0.854	0.973 (+0.119)
CH_3	9.146	9.152 (+0.006)	9.146	9.152 (+0.006)

[a] At the MP2 level. The populations of M(dipm) are omitted here because they resemble those of M(dipe). [b] The difference from the population of the reactants given in parentheses.

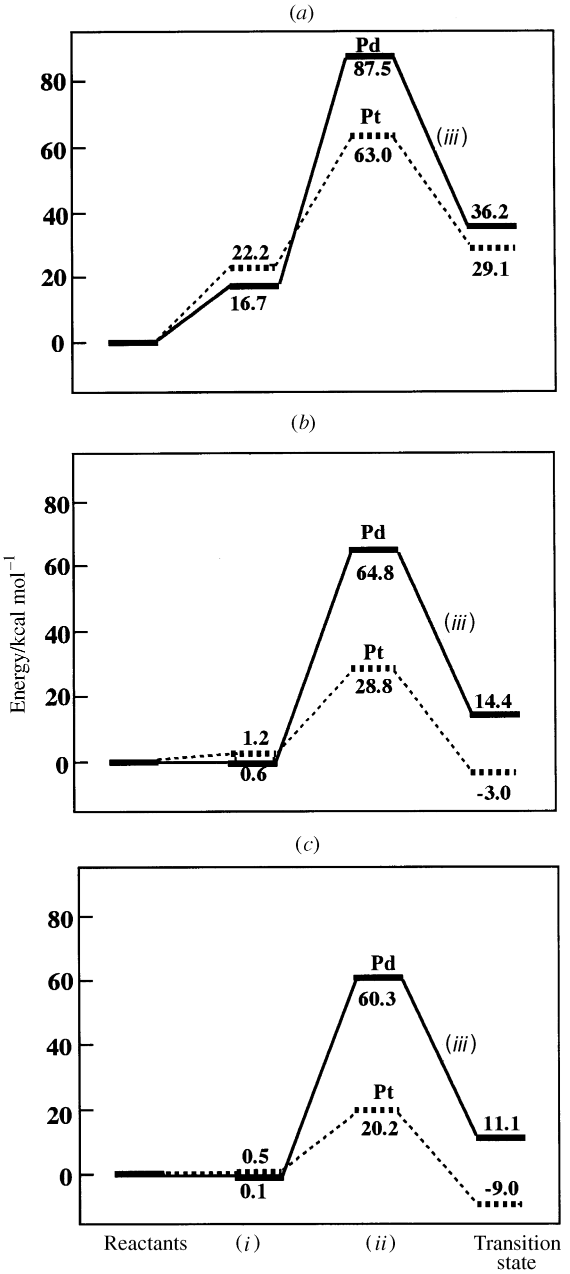

Fig. 5 Distortion and interaction energies in the transition state at the MP4SDQ level for the $M(PH_3)_2$ (*a*), M(dipe) (*b*) and M(dipm) (*c*) systems. (*i*) The distortion energy of the metal part, $E_t(ML_2)_{dist} - E(ML_2)_{eq}$; (*ii*) the distortion energy of the CH_4 part, $E_t(CH_4)_{dist} - E(CH_4)_{eq}$; (*iii*) the interaction energy, E_t(transition state) $- E_t(ML_2)_{dist} - E_t(CH_4)_{dist}$

chelate phosphine model complexes the p- and d-orbital populations alter to a much lower extent than those in the monodentate phosphine models (Table 4). Also, it should be noted that the s-orbital population does not decrease but slightly increases in the product. This is the opposite to that observed in the monodentate phosphine model. The reason for these differences is found in the electron distributions of $M(PH_3)_2$, M(dipe) and M(dipm). The s-orbital population in M(dipe) and M(dipm) is much smaller than that of $M(PH_3)_2$, while the p-orbital population of the former complexes is much larger than that of the latter. This is because two PH_3 ligands interact with one s and one p orbital in $M(PH_3)_2$ but with one s and two p orbitals in M(dipe) and M(dipm); in other words, the p orbitals of M(dipe) and M(dipm) receive considerable amounts of electrons from PH_3, and therefore PH_3 does not need to donate a lot of electrons to the s orbital. The p-orbital population of the chelate phosphine model increases in the product to a lesser extent than that of the monodentate phosphine model because the former p orbital already has considerable electron population in the reactant. The s-orbital population of the chelate phosphine model, on the other hand, slightly increases in the product because its electron population is small in the reactant and the strongly donating hydride and alkyl co-ordinate to the product.

The other result to be noted is that $[MH(CH_3)(PH_3)_2]$, $[MH(CH_3)(dipe)]$ and $[MH(CH_3)(dipm)]$ exhibit similar electron distributions. Also, the electron distributions of M(dipe) and M(dipm) resemble that of the product, but the electron distribution of $M(PH_3)_2$ is much different from that of the product. All these results indicate that the complexes of Pt^0 and Pd^0 with chelate phosphines do not need to cause a significant electronic reorganization for C–H oxidative addition, but the monodentate phosphine complex does. This is consistent with the fact that the latter model should give rise to a large d.i.s.e. energy in the transition state, but not the chelate phosphine model.

Conclusion

Oxidative addition of C–H to $M(PH_3)_2$ (M = Pd or Pt) requires a considerably high activation energy, 37 and 30 kcal mol^{-1} for M = Pd and Pt (MP4SDQ). This means that oxidative addition to these complexes cannot occur. However, the co-ordination of a chelate phosphine significantly lowers the activation energy. The C–H oxidative addition to M(dipe) proceeds with a much lower E_a of 22 and 7 kcal mol^{-1} for M = Pd and Pt, and that to M(dipm) occurs with a further lowering to 20 and 4 kcal mol^{-1} respectively, where two PH_3 are positioned so as to mimic either 1,2-bis(diphenylphosphino)ethane or bis(di-*tert*-butylphosphino)methane. These low activation energies calculated for the chelate phosphine models strongly suggest that use of a chelate phosphine facilitates C–H oxidative addition to Pt^0. Its co-ordination raises the d_π orbital in energy and lowers the sp_σ orbital. This enhances the reactivity of M(dipe) and M(dipm) for oxidative addition. From another point of view, M(dipe) and M(dipm) do not need to distort at the transition state since their geometry and electronic structure are almost the same as those in the transition state and product. This is because M(dipe) and M(dipm) cannot be fully relaxed due to the constraint placed on the phosphine part and they are forced to adopt a similar structure to that of the transition state. Thus, the distortion energy and the electronic reorganization energy in the transition state are very small for M(dipe) and M(dipm), which leads to their low E_a values. On the other hand, monodentate phosphine complexes need to undergo significant distortion in the transition state, since the geometry of the reactant can be fully relaxed and the transition-state geometry is much different. In the case of palladium(0) complexes of dipm and dipe, however, the C−H oxidative addition still requires a considerably high activation energy. Thus, not only the use of a chelate phosphine but also the introduction of an electron-withdrawing substituent at C would be necessary to perform easily the C−H oxidative addition to Pd^0. A theoretical study of the effects of electron-withdrawing substituents is in progress.

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