

Experimental and theoretical studies on the course of CO insertion into Pt–C and Pd–C bonds in neutral and cationic complexes, $[\text{MR}(\text{Cl})\{\text{P}(\text{CH}_3)_3\}_2]$ and $[\text{MR}\{\text{P}(\text{CH}_3)_3\}_2(\text{s})]^+\text{BF}_4^-$ ($\text{M} = \text{Pt}, \text{Pd}$, $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$, $\text{s} = \text{coordinated solvent}$)

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Dedicated to Martin Bennett on the occasion of his retirement in recognition of his outstanding contribution to organometallic chemistry.

Abstract

Behavior of neutral and cationic *cis*- and *trans*-monoorganoplatinum complexes has been examined and compared with that of the corresponding monoorganopalladium complexes. The *cis*- and *trans*-monoorganoplatinum complexes having two trimethylphosphine ligands, $[\text{PtR}(\text{acetone})\{\text{P}(\text{CH}_3)_3\}_2]^+\text{BF}_4^-$ ($\text{R} = \text{CH}_3$ and C_6H_5) (**4** and **5**), have been prepared by removal of the chloride ligand in neutral complexes, $[\text{PdR}(\text{Cl})\{\text{P}(\text{CH}_3)_3\}_2]$ (**2** and **3**) with one equivalent of AgBF_4 . The cationic platinum complexes retaining the *cis* configuration of the parent neutral complexes, when prepared at low temperature, were found to be isomerized into the *trans* complexes **5** above -10°C for the methyl complex **5a** and above -30°C for the phenyl complex **5b**. Treatment of the cationic complexes **4** and **5** with CO gave no CO insertion product but afforded only the CO-coordinated *trans*-monoorganoplatinum complexes. The reluctance of the organoplatinum complexes toward CO insertion stands in contrast with the ease for the CO insertion of the corresponding organopalladium complexes. For clarifying the reasons of the marked difference between the behavior of the two Group 10 metal complexes the ab initio molecular orbital calculations with the MP2 level have been performed. We have found the transition states for the *cis* to *trans* isomerization of the three-coordinated cationic monoalkylplatinum complexes and for the CO insertion into the Pt–CH₃ bond. The calculated barriers for the isomerization and CO insertion in the cationic organoplatinum complex are higher than those for the corresponding organopalladium complex in agreement with the experimental results showing the poor reactivity of the solvent-coordinated cationic organoplatinum complexes toward CO insertion compared to the organopalladium complexes. The reason for the difference in the reactivity between the palladium and platinum complexes can be ascribed to the relativistic effect of the platinum complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CO insertion; *Cis–trans* isomerization; Palladium; Platinum; Monoalkyl complexes; Ab initio calculations

1. Introduction

The CO insertion into a transition metal–carbon bond constitutes one of the most essential elementary processes in transition metal-catalyzed carbonylation of

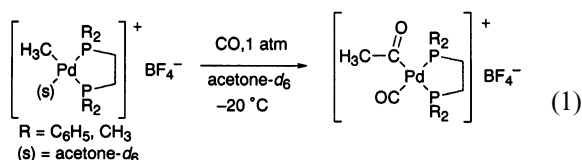
organic compounds [1–3]. Besides cobalt and rhodium complexes, palladium complexes have been utilized most extensively in the carbonylations of aryl and vinyl halides as well as of olefins. Examination of the behavior of the monoorganopalladium complexes has provided important information regarding the elementary steps in the catalytic reactions [4]. In the palladium-catalyzed carbonylation and in olefin arylation (Mi-zoroki–

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Heck process [5]) as well as in olefin polymerization [6] and copolymerization of olefin and CO [7], generation of a cationic catalytic species has been often found to enhance the catalytic activities. In our previous studies [8] as well as in the studies by others [9–12] many examples of the enhancement of the reactivities in the catalytic systems by generating cationic monoorganopalladium complexes from neutral monoorganopalladium complexes have been presented. Scheme 1 illustrates that the first order rate constant of the CO insertion process into the neutral methyl-(chloro)palladium complex is increased by 100 times by converting the neutral complex into the cationic solvent-coordinated complex by removal of the chloride ligand with AgBF_4 [8d,13].

We have also confirmed that the availability of a coordination site for the incoming substrate such as CO and olefin is quite important for the insertion process to proceed. For a monoorganopalladium complex having two monodentate tertiary phosphine ligands to undergo a concerted insertion process, the monoorganopalladium complex is required to possess a coordination site available adjacent to the hydrocarbyl ligand for the incoming substrate. In fact the reactivity of cationic organopalladium complexes having a chelating ditertiary phosphine ligand such as 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diphenylphosphino)ethane (dppe) toward CO insertion (Eq. (1)) was three times greater than that of the cationic monoorganopalladium complexes having two trimethylphosphine ligands in mutually *trans* positions [8d,13].



In spite of the obvious importance of the cationic *cis* complexes in insertion steps, few examples of *cis*-monoorganopalladium(II) bearing two monodentate phosphine ligands have been reported [14–16]. On the other hand, a variety of neutral *cis*-monoorganoplatin-

um(II) complexes, *cis*-[PtR(X)L₂], are known [17–21] and their isomerization processes have been well documented [22]. However, precedents of the CO insertion processes into neutral monoorganoplatinum complexes have been quite limited [23–25]. The results of these studies indicated that the CO insertion into the Pt–C bond is less favorable than that into the Pd–C bond. A fundamental question raised there is whether the difference in the reactivity of the organopalladium and organoplatinum complexes for the CO insertion is due to the higher barrier for the migratory CO insertion for an organoplatinum complex or due to the presence of a higher barrier for the *trans* to *cis* isomerization in the monoorganoplatinum complex. Another question is whether the CO insertion into the cationic complexes proceeds under the constraint of the square planar geometry or if there is another route through a five-coordinate intermediate.

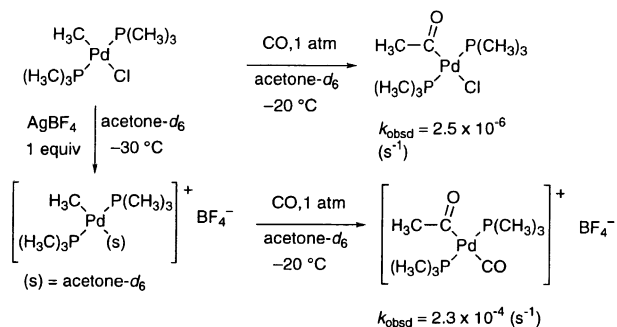
In the present paper we wish to present the results of our attempts addressed to the above questions through experimental as well as *ab initio* molecular orbital theoretical studies.

2. Results and discussion

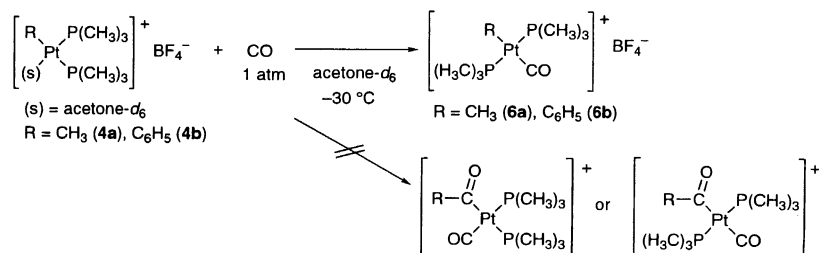
2.1. Synthesis and isomerization behavior of cationic organoplatinum(II) complexes having two monodentate tertiary phosphines

Although there are ample examples of cationic *cis*-monoalkylplatinum complexes having bidentate phosphine ligands [26] as well as the cationic *trans* complexes, *trans*-[PtRL₂]⁺ [27], less studies have been made on properties of the *cis* cationic organoplatinum complexes having monodentate phosphine ligands [28–30]. Such cationic three-coordinated monoalkylplatinum complexes, *cis*-[PtRL₂]⁺, have been proposed as key intermediates in CO insertion [31], olefin insertion [32], β -hydrogen elimination [28], and *cis*–*trans* isomerization [21]. For example, there are studies reporting that the isomerization of neutral *cis* complexes occurs via cationic three-coordinate platinum species with dissociation of an anionic ligand of the neutral complexes in a protic solvent [33,34] and some cationic *cis* methanol-coordinated complexes can be formed by protonolysis of *cis*-dialkylplatinum complexes [27,28].

We prepared first the neutral *cis*-monoorganoplatinum complexes **2** by treating *cis*-diorganoplatinum complexes **1** with an equimolar amount of HCl in ether at -78°C . The *cis* complexes **2** were isomerized into the *trans* complexes **3** by warming under reflux condition [35] (Eq. (2)). The cationic *cis*-organoplatinum complexes **4a** and **4b** were generated by treatment of the neutral monoorganoplatinum



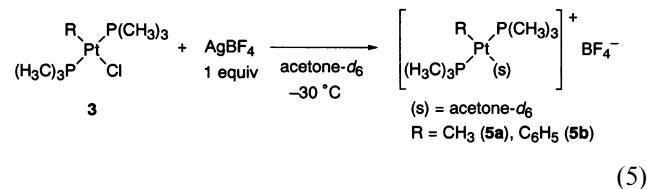
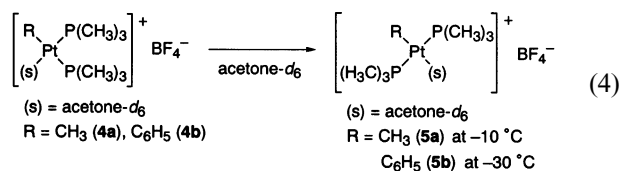
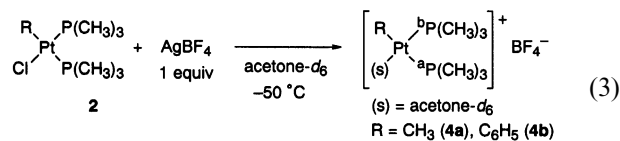
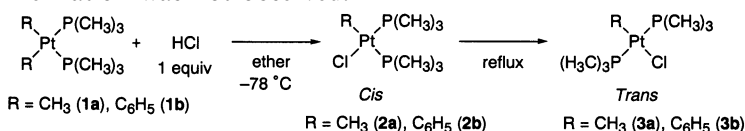
Scheme 1.



Scheme 2.

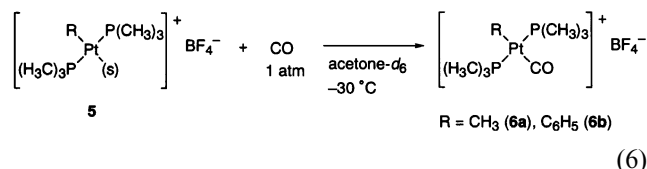
chloride complexes *cis*-[PtR(Cl){P(CH₃)₃}₂] (R = CH₃ and C₆H₅) (**2a** and **2b**) with an equivalent each of AgBF₄ in acetone at –50°C as shown in Eq. (3). The cationic *cis* complexes **4** were found to retain the *cis* configurations of the starting neutral complexes **2** below –30°C as confirmed by observation of the AB pattern signals of their trimethylphosphine ligands with a ²J_{PP} coupling constant (14.7 Hz) in the ³¹P-NMR spectra. The low ¹J_{Pt–aP} coupling constants (1687 and 1632 Hz for **4a** and **4b**) are typical of phosphorus atoms in ^aPMe₃ *trans* to the carbon atom in platinum complexes, while the values ¹J_{Pt–bP} = 4140 and 4132 Hz are consistent with the presence of a very weak *trans* donor ligand, acetone. The cationic *cis* complexes **4**, thus obtained, are thermally unstable in solution. Following the reaction course with ¹H- and ³¹P-NMR indicated that the complexes **4a** and **4b** are isomerized readily at –10 and –30°C, respectively, to the corresponding *trans* complexes **5a** and **5b** (Eq. (4)). The cationic *trans*-monoorganoplatinum complexes **5a** and **5b** were independently obtained by treatment of the neutral *trans*-organoplatinum chloride complexes **3a** and **3b** with an equimolar amount of AgBF₄ in acetone at –30°C (Eq. (5)).

The results on the isomerization behavior of monoorganoplatinum complexes having two monodentate phosphine ligands indicate that the *cis* to *trans* isomerization takes place readily in the cationic organoplatinum complexes while the *trans* to *cis* isomerization was not observed.



2.2. Reaction of cationic organoplatinum complexes with CO

Treatment of the cationic *trans* complexes **5** with atmospheric pressure of CO afforded CO-coordinated *trans* complexes [PtR(CO){P(CH₃)₃}₂]⁺BF₄[–] (R = CH₃; **6a**, C₆H₅; **6b**) at room temperature without forming any acyl complexes produced by CO insertion into the Pt–C bond (Eq. (6)). The cationic *cis* complexes **4** did not undergo the CO insertion but simply isomerized rapidly to the *trans* carbonyl complexes **6** even at –50°C, despite that they have an available coordination site *cis* to the methyl or phenyl group (Scheme 2).

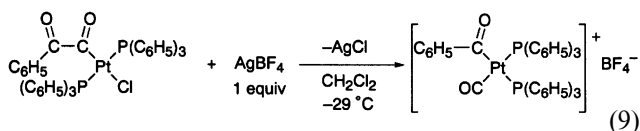
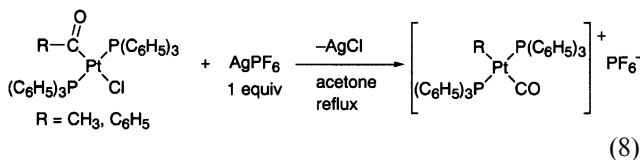
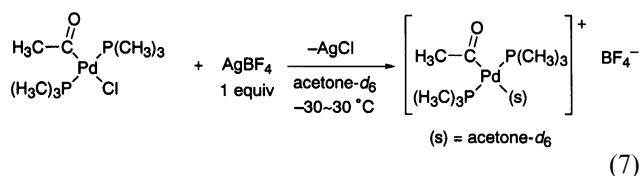


The CO insertion into the Pt–C bond of the cationic complexes **4** and **5** bearing two trimethylphosphine

ligands was not observed even under 11 atm of CO at 50°C in acetone, whereas CO insertion into cationic phenylplatinum complex with a bidentate phosphine ligand was confirmed [26c]. In this case, retaining the *cis* configuration with the bidentate ligand hinders the isomerization, keeping the site *cis* to the phenyl ligand available for the CO ligand to allow the migratory insertion.

In contrast to the cationic monoorganoplatinum system that is reluctant to undergo the CO insertion, the

monomethylpalladium complex, $trans$ -[PdCH₃-(acetone){P(CH₃)₃}₂]⁺BF₄[−], undergoes ready CO insertion to form the CO-coordinated acetyl complex, $trans$ -[Pd{CH₃C(O)}(CO){P(CH₃)₃}₂]⁺BF₄[−] (7), under atmospheric CO at −20°C (Scheme 1). The cationic solvent-coordinated acetylplatinum complex, $trans$ -[Pt{CH₃C(O)}(acetone){P(CH₃)₃}₂]⁺BF₄[−], can be also prepared from the neutral acetylplatinum complex, $trans$ -[Pt{CH₃C(O)}(Cl){P(CH₃)₃}₂], with one equivalent of AgBF₄ without causing the decarbonylation of the acetyl ligand (Eq. (7)). On the contrary, decarbonylation of the neutral acylplatinum complexes, $trans$ -[Pt{RC(O)}(Cl){P(C₆H₅)₃}₂] (R = alkyl and aryl), was found to be promoted by AgPF₆ to give cationic monoorgano(carbonyl)platinum complexes, $trans$ -[PtR(CO){P(C₆H₅)₃}₂]⁺PF₆[−] [36] (Eq. (8)). These results imply that the cationic acetylplatinum species weakly bound with a solvent molecule are thermodynamically unstable relative to the corresponding acetylplatinum complexes. A cationic benzoylplatinum complex, cis -[Pt{C₆H₅C(O)}(CO){P(C₆H₅)₃}₂]⁺BF₄[−], on the other hand, was isolated as a stable complex in the decarbonylation of an α-keto benzoylplatinum complex [37] (Eq. (9)).

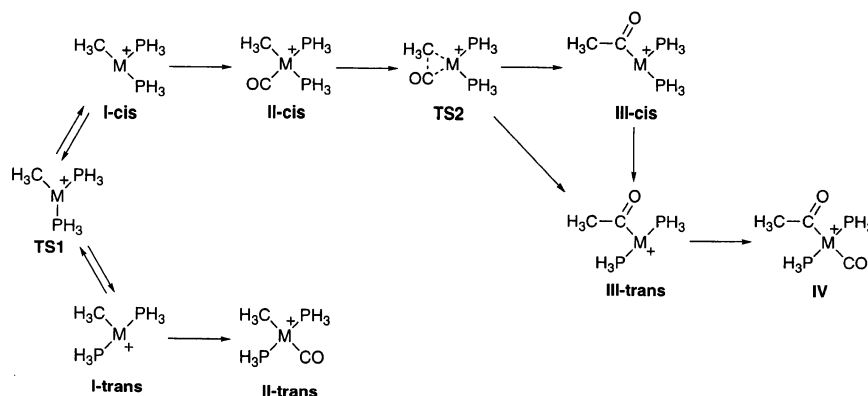


2.3. Theoretical studies on the reactions of cationic monomethyl complexes [M(CH₃)(PH₃)₂]⁺ (M = Pt and Pd) with CO

The above experimental results have shown that the cationic solvent-coordinated monoorganoplatinum complexes are inert to CO insertion in contrast to the corresponding monoorganopalladium complexes that readily undergo the CO insertion. In order to clarify the dominant factors influencing the CO insertion processes and the reason for the different behavior between the cationic organopalladium and organoplatinum complexes toward CO, we carried out ab initio molecular orbital calculation with MP2 level taking into account electron-correlation effects. The calculations were carried out using PH₃ for P(CH₃)₃. We optimized the structures of the reactants, intermediates, transition states (TSs), and products. The calculated reaction paths of the isomerization and CO insertion for the platinum and palladium complexes are shown in Scheme 3. In the left part of the Scheme 3 are shown the cis – $trans$ isomerization courses and in the right part the CO insertion courses. The optimized bond distances and bond angles are shown in Figs. 1 and 2. The potential energy profiles of the isomerization, insertion, and decarbonylation paths for palladium and platinum complexes are shown in the Figs. 3 and 4, respectively.

2.3.1. Cis – $trans$ isomerization of the cationic monomethyl complexes

The stable structure of cationic monomethylpalladium complex having the two phosphine ligands takes the T-shaped $trans$ and cis forms, **I-*trans*** and **I-*cis***, where the **I-*trans*** form is more stable than the **I-*cis*** form by 7.2 kcal mol^{−1} (Fig. 3). Due to the $trans$ influence of the methyl ligand the bond lengths of the Pd–P and Pt–P bonds ($trans$ to the methyl) in **I-*cis*** are longer than those of the Pd–P and Pt–P in **I-*trans***.



Scheme 3.

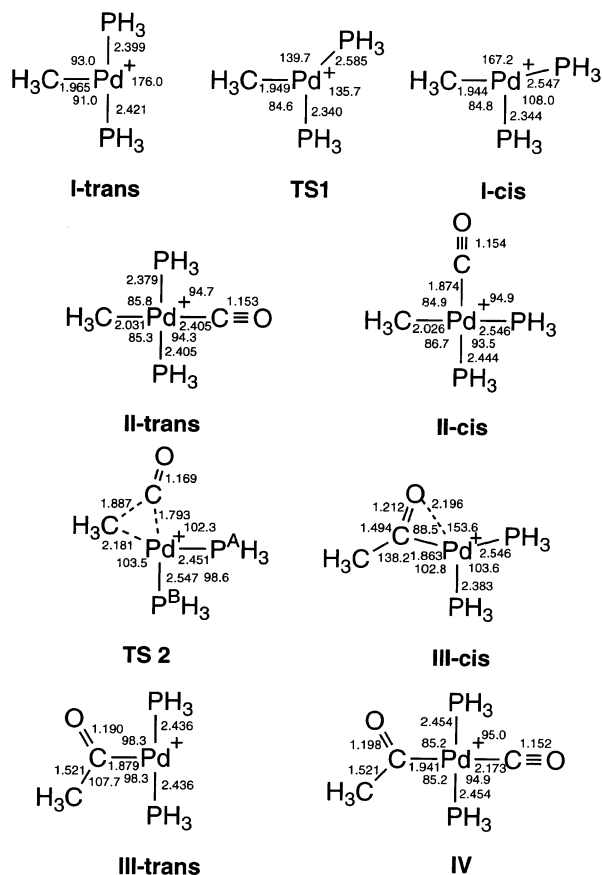


Fig. 1. Optimized geometries (in Å and °) of intermediates and transition states for CO insertion into $[\text{PdCH}_3(\text{PH}_3)_2]^+$.

The *cis* complex isomerizes to the *trans* one with swinging of the PH_3 ligand via the Y-shaped transition states. The energy of the transition state TS1 having the Y shape is $2.7 \text{ kcal mol}^{-1}$ higher than that of the *I-cis* for the palladium complex. Although a quite similar profile is found for the platinum analog, we can find the difference that the energy barrier for the *cis* to *trans* isomerization is smaller for the platinum complex than for the palladium analog and the *cis* to *trans* isomerization is more exothermic (Fig. 4).

It should be noted that for the migratory CO insertion into *I-trans* to take place the reverse process, i.e. isomerization from the *I-trans* to *I-cis* is required as the initial step. The barriers for the isomerization from the *I-trans* to *I-cis* are calculated as 14.4 and $9.9 \text{ kcal mol}^{-1}$ for the platinum and palladium complexes, respectively. The higher barrier for the isomerization in the methylplatinum complex than that for the corresponding methylpalladium complex partly accounts for the poor reactivity of the solvent-coordinated cationic organoplatinum complexes toward CO insertion.

2.3.2. CO insertion into the metal–carbon bond via four-coordinate intermediates

Stabilization of the T-shaped complexes is observed in coordination of the CO ligand with the cationic

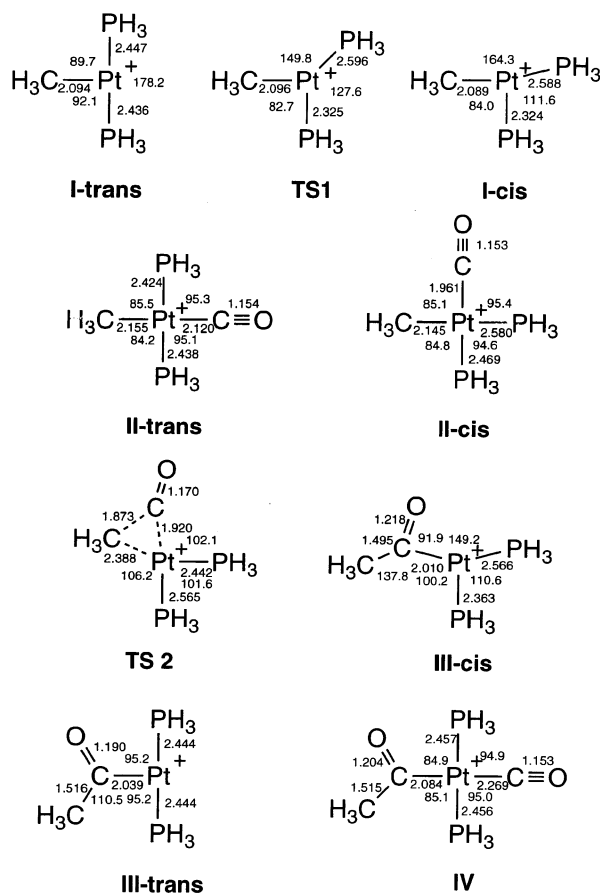


Fig. 2. Optimized geometries (in Å and °) of intermediates and transition states for CO insertion into $[\text{PtCH}_3(\text{PH}_3)_2]^+$.

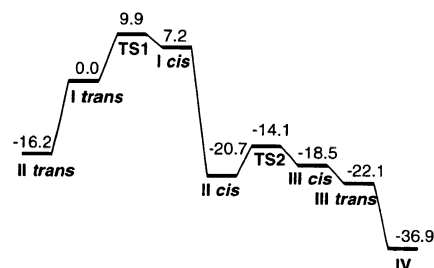


Fig. 3. Potential-energy profile of *cis-trans* isomerization and CO insertion into $[\text{PdCH}_3(\text{PH}_3)_2]^+$, in kcal mol^{-1} , relative to *I-trans*.

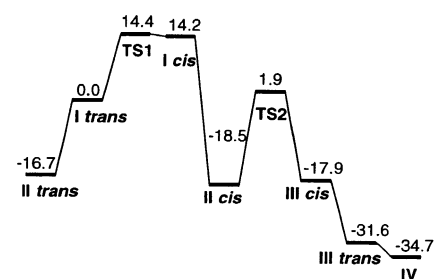


Fig. 4. Potential-energy profile of *cis-trans* isomerization and CO insertion into $[\text{PtCH}_3(\text{PH}_3)_2]^+$, in kcal mol^{-1} , relative to *I-trans*.

complexes to give **II-cis** and **II-trans** species both for the palladium and platinum analogs. The CO insertion into the Pd–CH₃ bond takes the path as shown in Scheme 3 from **II-cis** where the methyl and CO ligands are situated in mutually adjacent positions.

The Pd–CO bond in **II-cis** is considerably shorter than in the **II-trans** by 0.531 Å (Fig. 1). The short Pd–CO distance due to the smaller *trans* effect of the phosphine ligand relative to the methyl ligand may facilitate the process to approach the transition state. In the insertion transition state **TS2** the methyl group is closer to the carbonyl group with elongation of the Pd–CH₃ bond from 2.026 to 2.181 with forming CH₃–CO bond of 1.887 Å that is longer than 1.494 Å in the product **III-cis**. The increase in the ^aP–Pd–CO and ^bP–Pd–CH₃ angles of 102.3 and 103.5° in **TS2** indicates that both the methyl and the CO ligands move toward each other for the C–C bond formation. In the subsequently formed immediate insertion product **III-cis**, substantial interaction between the palladium and the oxygen atom in the acetyl group can be seen. The Pd–C–O angle of 88.5° and the Pd–O distance of 2.196 Å are close to the previous calculated values of Pd–C–O angle of 88.7° and the Pd–O distance of 2.30 Å for the η² type interaction in the acetyl complex having ethanediimine ligand [38]. Notably, the P–Pd–P angle of 103.6° in **III-cis** is greater than the value of about 84° calculated for CO insertion in a system with PH₂CH=CHPH₂ ligand [39]. The wider P–Pd–P angle may be taken as an indication that the CO insertion may be coupled with the phosphine migration to the *trans* form **III-trans**. A similar feature in the P–Pt–P angle was also observed in propene insertion in a cationic hydridoplatinum system having monodentate phosphine ligands [40]. From experimental results of an acceleration of CO insertion into cationic methylpalladium complexes in the order of dppe < dppf < dppp ≈ dppb (dppf = 1,1'-bis(diphenylphosphino)ferrocene; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane) it was argued that a large P–Pd–P angle will push the methyl group toward the coordinated CO ligand, possibly lowering the activation barrier for the ligand migration [12].

Although the comparison of the initial **II-cis** and the product **III-cis** indicates that the insertion proceeds as overall CO migration, the conformation of **TS2** may be regarded as the transition state showing a concerted migration of alkyl and CO ligands. The **III-cis** complex was found isomerized readily to **III-trans** and is further stabilized by coordination of CO to give the CO-coordinated acetyl complex **IV**. The present result is different from those in the previous theoretical studies dealing with the CO insertion into the Pd–CH₃ and Pt–CH₃ bonds in [M(CH₃)(H)(CO)(PH₃)] modeling the CO insertion into [Pd(CH₃)₂(PH₃)₂] with MP2 calculations by Koga and Morokuma [41] and from the exper-

imental studies on CO insertion into [Pd(CH₃)₂L₂] and [Pd(C₂H₅)₂L₂] complexes (L = monodentate tertiary phosphine ligands) where the product distributions are compatible with the alkyl migration processes [42]. Theoretical study by Sakaki et al. [43] on the CO insertion into [Pt(CH₃)F(CO)(PH₃)] was also compatible with the alkyl migration scheme.

The disagreement of the present result with the previous studies may reflect the difference in the complexes employed. The present study deals with the cationic monomethyl complexes having two phosphine ligands whereas the CO insertion into the neutral dialkylpalladium complexes having one phosphine ligand was studied in the previous work. In the neutral dialkyl complexes the presence of the alkyl ligand *trans* to the other alkyl ligand (modeled by H ligand) may serve to labilize the alkyl–palladium bonds by higher *trans* effect. The presence of the two phosphine ligands may also influence the course of the insertion process.

Comparison of the energy diagrams between the palladium and the platinum systems (Figs. 3 and 4) shows that the CO insertion steps from **II-cis** to **III-cis** are slightly endothermic for both palladium and platinum systems. The activation barrier of 20.4 kcal mol^{−1} from the platinum **II-cis** to **TS2** is much higher than 6.6 kcal mol^{−1} calculated for the corresponding palladium complex. The significantly higher activation barrier for the CO insertion into the methylplatinum complex than into the methylpalladium complex accounts for the poor reactivity of the cationic platinum complexes.

2.3.3. CO insertion into the metal–carbon bond via five-coordinate intermediates

Following the examination of a CO insertion course through a four-coordinate intermediate as discussed above we also examined a path through a five-coordinate intermediate. In a kinetic study concerning the carbonylation Garrou and Heck proposed a mechanism through a five-coordinate intermediate [44]. Involvement of five-coordinate species was also suggested in carbonylation with bidentate [45] and tridentate [46] ligands. However, examination of coordination course of CO to **II-trans** or **II-cis** gave no local minima corresponding to [PdCH₃(CO)₂(PH₃)₂]⁺.

Interactive hybrid fragment orbitals of [PdCH₃–(CO)(PH₃)₂]⁺ and CO to form trigonal bipyramidal structures (a) and (b) and a square planar fragment with CO to form a square pyramidal complex (c) in Chart do not show significant overlap between these fragments. A direct insertion of CO into palladium–carbon bond without coordination to the palladium center [47] as depicted in (d) is also found to be electronically inadequate. It can be concluded that the migratory insertion mechanism via four-coordinate species in *cis* form is more favorable than the other possi-

Table 1

Energy barriers for the CO insertion into the M–CH₃ bond in cationic and neutral complexes (M = Pd, Pt) (in kcal mol^{−1})

Complex	$\Delta E^\ddagger$	Complex	$\Delta E^\ddagger$
	6.6		20.4
	11.9		24.5
	15.5		25.9

Table 2

Non-relativistic (NR) and relativistic (Rel.) results of activation energy and heat of formation in the CO insertion into the Pt complex (in kcal mol^{−1})

	Reactant	TS	Product
NR	0.0	20.6	−1.5
Rel.	0.0	33.2	20.9

ble routes involving the five-coordinate transition structures for the reaction of the cationic complex with CO. The contribution of the five-coordinate intermediates for the CO insertion is considered negligible in contrast to the system bearing nitrogen donor ligands [47,48].

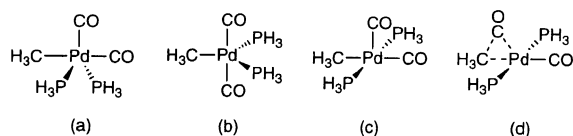


Chart 1.

2.3.4. Comparison of energy barriers for CO insertion into the Pd–CH₃ or Pt–CH₃ bond in cationic systems with those in neutral systems

The results of calculation of the energy barriers (**TS2**) for the CO insertion into the cationic and neutral methyl–palladium and platinum complexes (**II-cis**) are summarized in Table 1. The results show that the activation barriers for the CO insertion into the Pt–CH₃ bond in the cationic complexes are higher by 13.8 kcal mol^{−1} than into the Pd–CH₃ bond.

As another possible route for the CO insertion into monomethylpalladium and platinum complexes [MCH₃(Cl)(PH₃)₂] (M = Pd, Pt) remains the course involving square planar complexes [MCH₃(Cl)(CO)(PH₃)₂]

generated by replacement of one of the two PH₃ ligands by CO. Energy barriers for the CO insertion in two possible geometries with the methyl and the carbonyl ligands in mutually *cis* positions have been computed as shown in the second and third rows in Table 1. The energy barriers for CO insertions into the M–CH₃ bonds for the neutral palladium and platinum complexes were found greater than those in the corresponding cationic systems in agreement with the experimental results where the cationic complexes were found to be more susceptible to CO insertion. The higher energy barriers for CO insertion in neutral platinum systems than in the corresponding palladium systems were also computed.

2.3.5. Evaluation of relativistic effect on the CO insertion into Pt–CH₃ bond

The difference in the energetics of the palladium and platinum complexes for the CO insertion can be explained by taking relativistic effect into account as discussed by Koga and Morokuma [41]. We investigated the relativistic effect on the CO insertion into the cationic platinum complex. For this purpose, the relativistic scheme by eliminating small-components of the Dirac equation (RESC) theory [48] was employed. The RESC method is one of quasi-relativistic all-electron methods, and it is known that this method yields a satisfactory result for valence properties of heavy element compounds [48]. As the usual effective core potentials (ECPs) have already included the relativistic effect, it is difficult to compare the difference between relativistic and non-relativistic results directly. In order to discuss the relativistic and the non-relativistic results all-electron calculation was used in the RESC approach under the HF approximation. The MINI basis set was employed for platinum [49] and the optimized structures of **TS2** shown in Fig. 2 were used.

Table 2 shows the activation energy and the heat of formation in the CO migratory insertion from the platinum complex **II-cis** into **III-cis** with the non-relativistic and relativistic results. By taking the relativistic effect into account the activation energy increases by 12.6 kcal mol^{−1} and the reaction becomes 20.9 kcal mol^{−1} endothermic. The result clearly shows that the relativistic effect acts adversely to the CO insertion into the Pt–CH₃ bond to take place than into the Pd–CH₃ bond. The theoretical result is in agreement with the experimental observation. The influence of the relativistic effect conspicuously appears in the transition state of this reaction. Fig. 5 shows the difference between the relativistic and non-relativistic electron densities in the transition state. The density around the platinum atom is changed spherically by the relativistic effect due to the well-known contraction of the s atomic orbital with the relativity. Furthermore, the density difference map

shows that it becomes unfavorable to form the C–C bonding with the relativity. By considering the relativistic effect the density of the platinum side of the methyl carbon increases, whereas the density of the methyl side of the carbonyl carbon decreases. Since the relativistic effect is much larger for platinum complexes than for the palladium complexes, all the metal–carbon bonds in the platinum complexes should be stronger than in the palladium complexes. Cleavage of the strong platinum–carbon bond in the methyl(carbonyl)platinum complex in the CO insertion process will require a larger activation energy.

3. Conclusion

The overall feature of experimental results on *cis*–*trans* isomerization and CO insertion into methyl–palladium and methyl–platinum complexes having two monoteriary phosphine ligands is in agreement with the results of theoretical studies. For *trans*–methylpalladium and methylplatinum complexes having two tertiary phosphine ligands the *trans* to *cis* isomerization is required to bring the methyl and CO ligands in adjacent positions suitable for CO insertion to take place. The theoretical study reveals that the *trans* to *cis* isomerization barrier for the palladium complex is lower than that for the platinum analog. The theoretical study also indicates that the activation barrier for the CO

insertion into the Pt–CH₃ bond is significantly higher than that into the Pd–CH₃ bond in agreement with the experimental results. The feasibility of CO insertion routes involving five-coordinate intermediates having two CO ligands has been theoretically explored but was refuted as unlikely. The route involving replacement of one of the two phosphine ligands by CO in the neutral system, [MCH₃(Cl)(PH₃)₂] (M = Pd, Pt), was revealed to require higher activation barriers than the route through the cationic system, [MCH₃(CO)(PH₃)₂]⁺. The lower reactivity of the methylplatinum complex than the methylpalladium complex for CO insertion was clarified in terms of greater relativistic effect in the platinum complex with stronger Pt–CH₃ bond and less favorable transition state than in the methylpalladium complex.

4. Experimental

4.1. General procedures

All the manipulations were performed under argon atmosphere by using Schlenk techniques. The neutral monomethyl complexes, *cis*–[PtCH₃(Cl){P(CH₃)₃}₂] (**2a**) and *trans*–[PtCH₃(Cl){P(CH₃)₃}₂] (**3a**), were synthesized by the literature method [34]. The diphenyl complex, *cis*–[Pt(C₆H₅)₂{P(CH₃)₃}₂] (**1b**) was prepared from *cis*–[PtCl₂{P(CH₃)₃}₂] with C₆H₅Li (two equivalents) according to the literature method [18a]. All the reagents were used as received from commercial suppliers. Solvents were dried, distilled, and stored under argon. ¹H- (270 MHz, referenced to SiMe₄ via residual solvent protons), ¹³C{¹H}- (67.9 MHz, referenced to SiMe₄ via the solvent resonance), and ³¹P{¹H} (109.4 MHz, referenced to 85% H₃PO₄ as an external standard) NMR were recorded on a JEOL EX-270 spectrometer. Coupling constants (*J* values) are given in hertz (Hz), and spin multiplicities are indicated as follows: d (doublet), t (triplet), m (multiplet), vt (virtual triplet), and br (broad). IR spectra were measured by a Hitachi I-2000 spectrometer. Elemental analyses were carried out using a Yanako MT-3.

4.2. Preparation of *cis*- and *trans*-phenyl(chloro)palladium complexes; *cis*–[PtC₆H₅(Cl){P(CH₃)₃}₂] and *trans*–[PtC₆H₅(Cl){P(CH₃)₃}₂] (**2b** and **3b**)

The neutral monophenylplatinum complexes were prepared using the general procedure described by Chatt [16]. Thus, an ethereal solution of dry HCl (6.0 ml, 2.48 mmol) was added to the approximately equivalent amount of *cis*–[Pd(C₆H₅)₂{P(CH₃)₃}₂] (1.216 g, 2.43 mmol) in ether at –78°C. Stirring the reaction mixture for 30 min gave a colorless solution. After evaporation

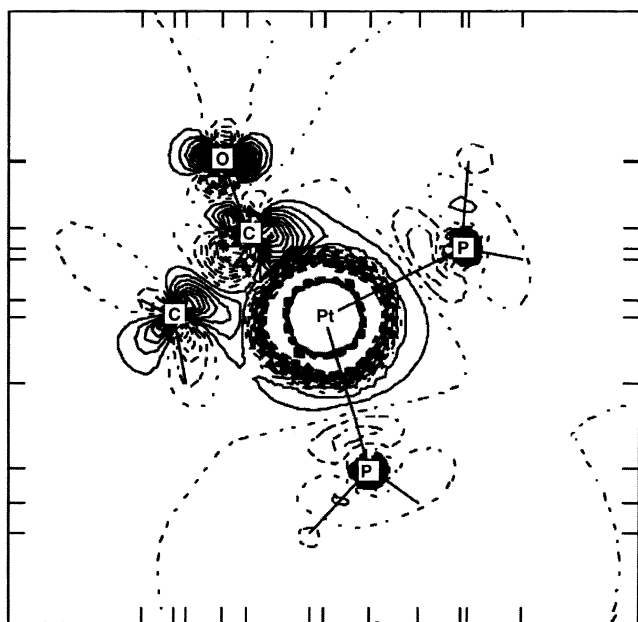


Fig. 5. Difference between the relativistic and non-relativistic densities in the transition states of the CO insertion into the methylplatinum complex (TS2). Solid lines indicate higher density of the relativistic result than that of the non-relativistic one. Lower density is represented by dashed lines.

of the solvent at -30°C , the residue was crystallized from acetone–petroleum ether to give the *cis* complex **2b** in 71% yield. The *trans* complex **3b** was obtained in 90% yield by a similar procedure under a reflux condition.

4.2.1. *cis*-[PtC₆H₅(Cl){P(CH₃)₃}₂] (**2b**)

¹H-NMR (acetone-*d*₆, -30°C) δ 6.61–7.39 (5H, PtC₆H₅, m), 1.55 (9H, P(CH₃)₃, d, ²J_{PH} = 8.8 Hz, ³J_{PtH} = 16.1 Hz), 1.43 (9H, P(CH₃)₃, d, ²J_{PH} = 11.0 Hz, ³J_{PtH} = 46.2 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -30°C) δ 19.2 (²J_{PP} = 14.6 Hz, ¹J_{PtP} = 1634 Hz), -27.3 (²J_{PP} = 14.6 Hz, ¹J_{PtP} = 4117 Hz); IR (KBr disc) $\nu_{\text{Pt-P}}$ = 408 cm⁻¹, $\nu_{\text{P-C}}$ = 950, 966 cm⁻¹; Anal. Found: C, 31.47; H, 5.11. Calc. for C₁₂H₂₃ClP₂Pt: C, 31.35; H, 5.04%.

4.2.2. *trans*-[PtC₆H₅(Cl){P(CH₃)₃}₂] (**3b**)

¹H-NMR (acetone-*d*₆, -30°C) δ 6.85–7.85 (5H, PtC₆H₅, m), 1.24 (18H, P(CH₃)₃, vt, ²J_{PH} = 4.0 Hz, ³J_{PtH} = 30.8 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -30°C) δ -13.2 (¹J_{PtP} = 2738 Hz); IR (KBr disc) $\nu_{\text{Pt-P}}$ = 501 cm⁻¹, $\nu_{\text{P-C}}$ = 956 cm⁻¹; Anal. Found: C, 31.17; H, 5.06. Calc. for C₁₂H₂₃ClP₂Pt: C, 31.35; H, 5.04%.

4.3. Generation of the cationic complexes (**4** and **5**) in NMR tube

To a solution containing complex **1** in acetone-*d*₆ (0.35 ml) was added a solution of one equivalent of silver salts in acetone-*d*₆ (0.10 ml) at -78°C in an NMR tube. The NMR tube was shaken ten times (white suspension of silver halide was formed immediately) and was kept until the upper layer became clear before the NMR spectrum was measured.

4.3.1. *cis*-[PtCH₃{(CD₃)₂CO}{P(CH₃)₃}₂]⁺BF₄⁻ (**4a**)

¹H-NMR (acetone-*d*₆, -50°C) δ 1.76 (9H, P(CH₃)₃, d, ²J_{PH} = 11.9 Hz, ³J_{PtH} = 53.6 Hz), 1.52 (9H, P(CH₃)₃, d, ²J_{PH} = 9.0 Hz, ³J_{PtH} = 16.9 Hz), 0.35 (3H, PtCH₃, dd, ³J_{PH} = 2.2 Hz, ³J_{PH} = 7.3 Hz, ²J_{PtH} = 46.8 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -50°C) δ -13.2 (²J_{PP} = 14.7 Hz, ¹J_{PtP} = 1687 Hz), -25.2 (²J_{PP} = 14.7 Hz, ¹J_{PtP} = 4140 Hz).

4.3.2. *cis*-[PtC₆H₅{(CD₃)₂CO}{P(CH₃)₃}₂]⁺BF₄⁻ (**4b**)

¹H-NMR (acetone-*d*₆, -50°C) δ 6.61–7.39 (5H, PtC₆H₅, m), 1.58 (9H, P(CH₃)₃, d, ²J_{PH} = 11.7 Hz, ³J_{PtH} = 16.2 Hz), 1.56 (9H, P(CH₃)₃, d, ²J_{PH} = 9.2 Hz, ³J_{PtH} = 53.5 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -50°C) δ 19.2 (²J_{PP} = 14.7 Hz, ¹J_{PtP} = 1632 Hz), -27.3 (²J_{PP} = 14.7 Hz, ¹J_{PtP} = 4132 Hz).

4.3.3. *trans*-[PtCH₃{(CD₃)₂CO}{P(CH₃)₃}₂]⁺BF₄⁻ (**5a**)

¹H-NMR (acetone-*d*₆, -30°C) δ 1.43 (18H, P(CH₃)₃, vt, ²J_{PH} = 3.6 Hz, ³J_{PtH} = 30.1 Hz), 0.66 (3H, PtCH₃, t, ³J_{PH} = 7.7 Hz, ²J_{PtH} = 89.4 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -30°C) δ -6.7 (¹J_{PtP} = 2717 Hz).

4.3.4. *trans*-[PtC₆H₅{(CD₃)₂CO}{P(CH₃)₃}₂]⁺BF₄⁻ (**5b**)

¹H-NMR (acetone-*d*₆, -30°C) δ 6.78–7.89 (5H, PtC₆H₅, m), 1.23 (18H, P(CH₃)₃, vt, ²J_{PH} = 4.0 Hz, ³J_{PtH} = 32.1 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -30°C) δ -12.7 (¹J_{PtP} = 2717 Hz).

4.4. Preparation of the cationic monoorgano(carbonyl)platinum complexes (**6**)

4.4.1. *trans*-[PtCH₃(CO){P(CH₃)₃}₂]⁺BF₄⁻ (**6a**)

A solution of AgBF₄ (271 mg, 1.39 mmol) in acetone (5 ml) was added dropwise to an acetone (10 ml) solution of *trans*-[PtCH₃(Cl){P(CH₃)₃}₂] (558 mg, 1.40 mmol) at -40°C . After the white precipitate immediately formed was removed by filtration, CO was bubbled into the colorless solution at -40°C . A small amount of Pt black was removed by filtration. The solution was evaporated to one-fourth of its original volume under reduced pressure. Ether was added into the concentrate until a white precipitate was formed. The solvent was decanted and the residue was dried in vacuo to give 451 mg (67%) of white powder. ¹H-NMR (acetone-*d*₆, -30°C) δ 1.87 (18H, P(CH₃)₃, vt, ²J_{PH} = 4.2 Hz, ³J_{PtH} = 31.5 Hz), 0.68 (3H, PtCH₃, t, ³J_{PH} = 8.8 Hz, ²J_{PtH} = 64.1 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -30°C) δ -13.6 (¹J_{PtP} = 2299 Hz); ¹³C{¹H}-NMR (acetone-*d*₆, -30°C) δ 179.4 (PtCO, br), 13.9 (P(CH₃)₃, vt, ¹J_{PC} = 10.1 Hz, ²J_{PtC} = 35.1 Hz), -2.0 (PtCH₃, t, ¹J_{PC} = 7.3 Hz); IR (KBr disc) $\nu_{\text{C-O}}$ = 2092 cm⁻¹.

4.4.2. *trans*-[PtC₆H₅(CO){P(CH₃)₃}₂]⁺BF₄⁻ (**6b**)

The phenyl complex can be obtained in 70% yield by the similar procedure. ¹H-NMR (acetone-*d*₆, -30°C) δ 7.07–7.70 (5H, PtC₆H₅, m), 1.65 (18H, P(CH₃)₃, vt, ²J_{PH} = 4.3 Hz, ³J_{PtH} = 32.3 Hz); ³¹P{¹H}-NMR (acetone-*d*₆, -30°C) δ -14.7 (¹J_{PtP} = 2321 Hz); IR (KBr disc) $\nu_{\text{C-O}}$ = 2108 cm⁻¹.

The rapid formation of the carbonyl complexes **6a** and **6b** from the cationic complexes **4** and **5** was monitored by NMR. CO gas was bubbled into the acetone-*d*₆ (0.45 ml) solution of each cationic platinum complex generated at -78°C in NMR tube as mentioned above.

4.5. Computational details

All geometries and transition states were optimized with the second-order Møller–Plesset perturbation (MP2) method in the GAUSSIAN-94 program package [50]. We have employed the standard Huzinaga–Dunning basis set [51] augmented by the polarization function for carbon and oxygen atoms, and the Hay–Wadt effective core potential (ECP) [52] are used for palladium, platinum, and phosphorus atoms.

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