

NMR and Kinetic Studies on Phosphine-Induced Coupling of (η^3 -Methallyl)(acetylacetonato)palladium and -platinum: Uniquely Facile C-C Bond Formation with an (η^3 -Allyl)platinum Complex

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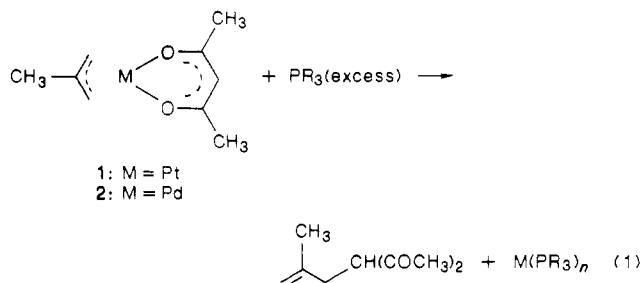
Low-temperature ^1H NMR measurements on a mixture of $\text{M}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{acac})$ (1, $\text{M} = \text{Pt}$; 2, $\text{M} = \text{Pd}$) and 2 equiv of PPh_3 or 1 equiv of $(Z)\text{-Ph}_2\text{PCH}=\text{CHPh}_2$ in dichloromethane gave unambiguous evidence for the formation of the ion pair $[\text{M}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PR}_3)_2]^+[\text{CH}(\text{COMe})_2]^-$. On warming these solutions to room temperature, the formation of moderate to good yields of the C-C coupling product $\text{CH}_2=\text{CMeCH}_2\text{CH}(\text{COMe})_2$ and zerovalent metal-phosphine complexes occurred. The kinetics of this process were examined by means of UV-visible spectroscopy to give evidence for almost exclusive participation of $[\text{M}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PR}_3)_2]^+[\text{CH}(\text{COMe})_2]^-$ ($\text{M} = \text{Pt}$, $\text{PR}_3 = \text{PPh}_3$; $\text{M} = \text{Pd}$, $\text{PR}_3 = 1/2\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) in the rate-determining step. The collapse of these ion pairs to the product was estimated to be faster in benzene than that in dichloromethane, the latter in turn having been found to be faster than that in acetonitrile/THF. The platinum analogue 1 reacted more slowly than the palladium analogue 2, but the rate difference was not so remarkable as was the case in the reductive elimination of dialkylmetal complexes of these two metals. The origin of this unique metal effect found in the reaction of 1 and 2 is discussed in terms of the nature of the η^3 -allyl-metal bonding.

Introduction

Increasing attention has been paid to both synthetic applications and mechanistic understanding of metal-catalyzed C-C coupling using allylic electrophiles and stabilized carbanions.¹ Some stereochemical studies on catalytic as well as stoichiometric coupling reactions of palladium complexes suggested a reaction scheme involving attack of the carbanion at the allylic carbon from the side opposite to the palladium atom.² On the basis of the stoichiometric alkylation reactions employing a bis(phosphine)(η^3 -allyl)palladium cation, several groups suggested a key role of the phosphine ligand coordination in facilitating the C-C bond formation.^{2a,3}

Addition of the phosphine ligands was also shown to be a key in accomplishing an apparently intramolecular C-C coupling of (η^3 -allyl)(β -diketonato)palladium complexes, and the stereochemical analysis of this reaction again was consistent with the external attack of the carbanion.⁴ A similar coupling also occurred with considerable ease in the reaction of (η^1 -allyl)platinum complexes $\text{Pt}(\eta^1\text{-allyl})(\text{acac})(\text{PPh}_3)$ ($\text{acac} = \text{acetylacetonato}$) with PPh_3 .⁵ Later we confirmed that $\text{Pt}(\eta^3\text{-allyl})(\text{acac})$ also underwent similar C-C coupling on treatment with excess PR_3 . We felt the high reactivity of these platinum derivatives somewhat surprising, since platinum alkyl complexes are usually much less reactive with respect to the reductive C-C coupling reaction⁶ than the corresponding palladium alkyl

complexes. As the examination of the metal effect is one of the key approaches to a better understanding of the metal-mediated C-C coupling reactions, the high reactivity of the allylplatinum complexes may provide a rare opportunity to gain a general insight into the C-C coupling step of the allylmetal complexes. Here we wish to describe ^1H NMR spectral and kinetic analyses of the reaction of (η^3 -methallyl)(acetylacetonato)platinum and -palladium with tertiary phosphines (eq 1).



Results and Discussion

Low-Temperature ^1H NMR Identification of Reaction Intermediate. Addition of more than 2 equiv of PPh_3 or 1 equiv of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) to 1 or 2 at room temperature in benzene or dichloromethane resulted in rapid C-C coupling of the methallyl and the acetylacetonato ligands (eq 1). Low-temperature ^1H NMR spectra were examined for a mixture of 1 or 2 and PPh_3 or $(Z)\text{-Ph}_2\text{PCH}=\text{CHPh}_2$ (dppe) in toluene- d_6 and CD_2Cl_2 . The spectral study using dppe was hampered by the multiplets of the dppe ligand. The low solubility of dppe in toluene at low temperatures also precluded the

(6) Dialkylplatinum(II) complexes do not undergo the reductive elimination under the conditions where the corresponding palladium analogues do so quite rapidly.⁷

(7) (a) Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* 1969, 2801-2808. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1981, 54, 1868-1880. (c) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* 1981, 103, 4182-4186.

(1) (a) Trost, B. M. *Acc. Chem. Res.* 1980, 13, 385-393. (b) Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 57. (c) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980.

(2) (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* 1978, 100, 3416-3426. (b) Trost, B. M.; Verhoeven, T. R. *Ibid.* 1978, 100, 3435-3443. (c) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Comm.* 1984, 107-108.

(3) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B.; Vitagliano, A. *J. Organomet. Chem.* 1987, 335, 133-142 and references cited therein.

(4) Hayashi, T.; Yamamoto, A.; Ito, Y. *J. Organomet. Chem.* 1988, 338, 261-264.

(5) Kurosawa, H. *J. Chem. Soc., Dalton Trans.* 1979, 939-943.

Table I. ¹H NMR Spectral Data^a for Complexes [M(η³-CH₂CMeCH₂)(PR₃)₂]⁺A⁻

complex			δ(methallyl)			δ(A)		
M	PR ₃	A	H-anti	H-syn	Me	Me	-CH<	
6	Pt	PPh ₃	CH(COMe) ₂	3.06 (d, J _P = 8, b)	3.43 (s)	2.01 (s, J _{Pt} = 61)	1.83 (s), 2.29 (s)	4.92 (s)
	Pt	PPh ₃	BF ₄	2.98 (d, J _P = 8, J _{Pt} = 41)	3.43 (s)	2.01 (s, J _{Pt} = 62)		
7	Pt	1/2 dppen	CH(COMe) ₂	2.78 (d, J _P = 10, J _{Pt} = 47)	4.64 (s)	2.00 (s, b)	1.76 (s), 2.19 (s)	4.85 (s)
	Pt	1/2 dppen	BF ₄	2.71 (d, J _P = 9, J _{Pt} = 45)	4.66 (s)	2.06 (s, J _{Pt} = 57)		
9	Pd	1/2 dppen	CH(COMe) ₂	3.10 (d, J _P = 11)	4.89 (br)	2.04 (s)	1.80 (s), 2.20 (s)	c
	Pd	1/2 dppen	BF ₄	3.09 (d, J _P = 11)	4.77 (d, J _P = 4)	1.96 (s)		

^aChemical shifts in ppm; *J* in Hz. Measured in CD₂Cl₂ at -40 (Pt complexes) or -70 °C (Pd complexes). ^bJ_{Pt} not resolved. ^cNot observed.

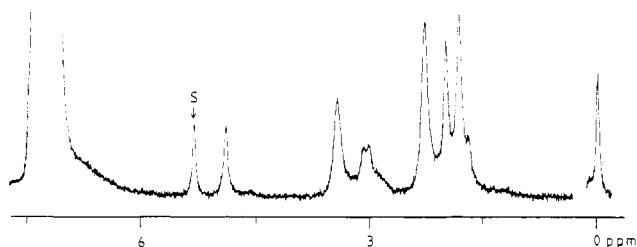
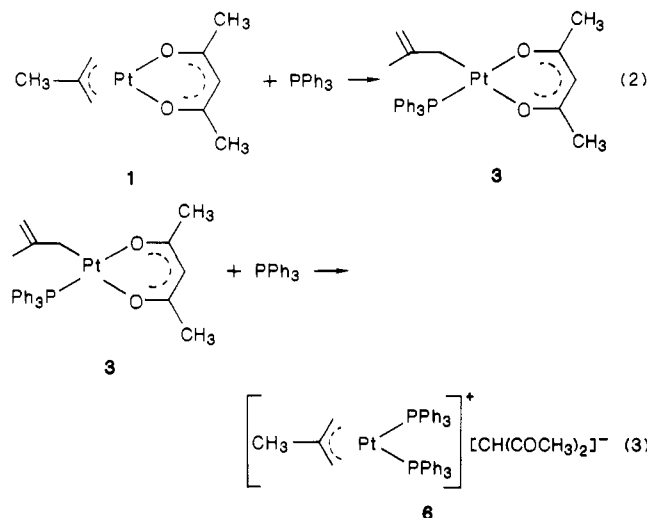


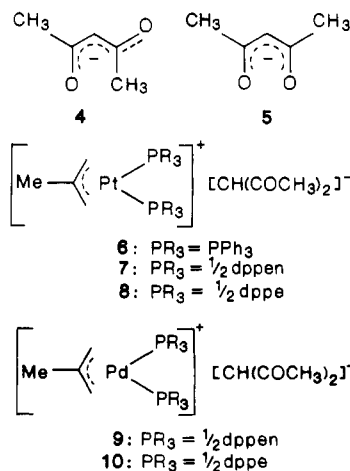
Figure 1. 100-MHz ¹H NMR spectrum of a mixture of 1 (0.13 M) and PPh₃ (0.26 M) in CD₂Cl₂ at -40 °C. S denotes the solvent resonance.

spectral analysis of the system containing this ligand in toluene-*d*₈.



The ¹H NMR spectrum of a CD₂Cl₂ solution containing 1 and PPh₃ (mole ratio, 1:2) at -40 °C is shown in Figure 1. The same spectrum was obtained when PPh₃ was added to an equivalent amount of 3, which in turn had been confirmed to be formed quantitatively from an equimolar mixture of 1 and PPh₃ (eq 2). Figure 1 reveals the presence of a single methallylmetallic species whose ligand proton signals are very similar to those of a cationic η³-methallyl complex, [Pt(η³-CH₂CMeCH₂)(PPh₃)₂]⁺BF₄⁻ (see Table I). In addition, the methyl proton resonances of the acetylacetonato ligand appeared as two singlets of equal intensity at δ 1.83 and 2.29. Their chemical shifts are very close to those⁸ (δ 1.89, 2.27) observed at low temperatures for one of the conformational isomers of the acetylacetonato anion, namely, 4. Moreover, this conformer was shown⁸ to dominate over another isomer 5 when a counteranion makes no coordination bonds with the oxygen atoms of the anion. It seems now evident that the spectral pattern of Figure 1 is in good agreement with the almost quantitative formation of the ion pair [Pt-

(η³-CH₂CMeCH₂)(PPh₃)₂]⁺[CH(COCH₃)₂]⁻ (6) (eq 3) in which there is no significant coordination bond between the platinum and the oxygen or the carbon atoms of the acetylacetonato anion. A slight difference in the chemical shifts of the allyl protons between the present intermediate and the authentic cationic complex would be due to a different degree of the ion-pair formation.



Quite similar spectral aspects to Figure 1 were observed in the CD₂Cl₂ solution of 1 and dppen and that of 2 and dppen (Table I), even though the latter system showed the weak resonances associated with the unreacted 2. These spectra are consistent with the formation of the ion pairs 7 and 9, respectively. There was observed no essential change of the spectral pattern when excess amounts of PPh₃ and dppen (P/M ≥ 4) were added to 6 and 9, respectively, except for the disappearance of the resonances due to 2 in the latter case. However, there was observed considerable line broadening upon addition of excess free dppen to 7, suggesting coordination of more than 2 equiv of dppen to platinum. There is a possibility that (η¹-allyl)platinum species is formed in this case as in the reported formation of [Pt(η¹-CH₂CMe=CH₂)(dppe)(PMe₂Ph)]⁺.^{9a} The spectra of a CD₂Cl₂ solution of 2 and excess PPh₃ showed very broad resonances even down to -90 °C. This broadening would be attributed to rapid exchange processes including η³-η¹-allyl equilibration and intermolecular allyl and phosphine exchange,⁹ but no satisfactory analysis of these spectra could be carried out.

The spectral aspects of a toluene-*d*₈ solution containing 1 (0.04 M) and 2 equiv of PPh₃ were different from those in CD₂Cl₂ shown above. The spectrum showed the presence of only a species coordinated with one molecule of PPh₃, namely, 3, formed according to eq 2. Similar NMR experiments employing higher concentrations of PPh₃ were

(9) (a) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1975**, *14*, 1518-1526. (b) Vrieze, K. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; p 441. (c) Hegedus, L. S.; Akermark, B.; Olsen, D. J.; Anderson, O. P.; Zetterberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 697-704.

(8) Raban, M.; Noe, E. A.; Yamamoto, G. *J. Am. Chem. Soc.* **1977**, *99*, 6527-6531.

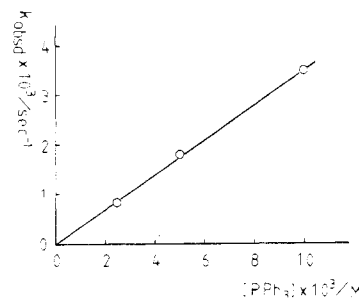


Figure 2. Plot of k_{obsd} vs $[\text{PPh}_3]$ for the reaction of **1** with PPh_3 in benzene at 25 °C. Initial concentration of **1** was 3×10^{-4} M.

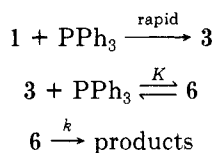
precluded by its limited solubility. We suggest that the formation of the ion pair **6** from **3** and PPh_3 according to eq 3 is by far less favorable in toluene than in dichloromethane. Previously, we also found¹⁰ that, in the reaction system composed of $\text{Pt}(\eta^3\text{-allyl})(\text{Cl})$ (allyl = CH_2CHCH_2 , CH_2CHCHMe) and 2 equiv PPh_3 , the ionic dissociation of Cl^- which is dominant in chloroform is almost completely suppressed in benzene.

Relative Rates of Eq 1. GLC analyses showed that the product yield of eq 1 was generally high ($\geq 90\%$) when the initial concentration of **1** or **2** was higher than 10^{-1} M. However, the product yield dropped considerably when the initial concentration was lower, especially in the case of the platinum complex in dichloromethane.¹¹ The course of the reaction of eq 1 was followed in the presence of sufficiently excess amounts of the phosphines except for the case of the reaction of **1** with an equivalent amount of dppe (see later).

The rate of the reaction of **1** with PPh_3 in benzene was determined by UV-visible spectroscopy by observing increase of the absorption at 350 nm due to the complex $\text{Pt}(\text{PPh}_3)_3$.¹² The reaction was first-order in the concentration of **1** up to ca. the first half-life. As shown in Table II and Figure 2, the pseudo-first-order rate constant (k_{obsd}) was dependent on the concentration of PPh_3 . At a given concentration of PPh_3 , the reactions of both **1** and **3** gave identical k_{obsd} values (see Table II). For the reaction of **1** with PPh_3 in dichloromethane, the initial rate was estimated also by UV spectra. As shown in Table II, the rate was almost independent of the amount of PPh_3 added.

We propose that the apparently different rate trends observed for the reactions of **1** in benzene and dichloromethane are accommodated by a common mechanism (Scheme I) that involves the rapid preequilibrium forming the ion pair **6**, followed by the nucleophilic attack⁴ of the $\text{CH}(\text{COMe})_2^-$ ion on the $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)_2]^+$ ion as the rate-determining step. It is the largely different K values (Scheme I) in two solvents that account for the different dependency of the rate on the concentration of PPh_3 in the two solvents.

Scheme I



(10) Kurosawa, H.; Yoshida, G. *J. Organomet. Chem.* **1976**, *120*, 297-311.

(11) For example, the proceeding of the reaction in dichloromethane appeared to cease at the level of ca. 50% and 30% conversion when 10^{-3} and 10^{-4} M concentrations of **1** were reacted with higher than 5 equiv of PPh_3 . The reaction of **1** with dppe was still slower; 5×10^{-3} M of **1** and an equiv of dppe in dichloromethane gave only a 25% product yield.

(12) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669-2676.

Table II. Rate Data for Eq 1 at 25 °C^a

complex	solvent	phosphine	$10^3(\text{concn}),$		$10^3 k_{\text{obsd}}, \text{ s}^{-1}$	$10^7(\text{init rate}), \text{ M s}^{-1}$
			PR_3	M		
1	benzene	PPh_3	2.5	0.83 (0.86) ^b		
			5.0	1.8 (1.6) ^b		
			10.0	3.5 (3.0) ^b		
1	CH_2Cl_2	PPh_3	0.91			4.0
			1.2			4.5
			2.4			4.9
			4.8			5.0
1	CH_2Cl_2	dppe	5.0			1.5 ^c
			2	CH_2Cl_2		dppe
6.0	1.0					
9.0	0.94					
2	MeCN/THF (3/1) ^d	dppe	3.0		0.27	
6.0			0.18			
9.0			0.26			
12.0			0.22			

^aInitial concentration of **1** or **2** was 3×10^{-4} M except as noted. ^bThe values in parentheses are from the reaction of **3**. ^cInitial concentration of **1** was 5.0×10^{-3} M. ^dBy volume.

As the formation of **3** from **1** and PPh_3 is always rapid and quantitative, the rate expression according to Scheme I in the presence of sufficiently excess amounts of PPh_3 would be

$$\text{rate} = \{kK[\text{PPh}_3]/(K[\text{PPh}_3] + 1)\}[\text{Pt-allyl}] \quad (4)$$

In dichloromethane solution, almost 100% of the allylplatinum species would exist in the form of **6** (see NMR evidence shown above). In other words, $K[\text{PPh}_3] \gg 1$ can be assumed here, and hence eq 4 becomes

$$\text{rate} = k[\text{Pt-allyl}]$$

which is consistent with the observed rate being independent of the PPh_3 concentration. On the other hand, in benzene the equilibrium between the complexes **3** and **6** would lie far on the side of complex **3** (see NMR evidence), so that $K[\text{PPh}_3] \ll 1$ would be appropriate here. Then, eq 4 is reduced to

$$\text{rate} = kK[\text{PPh}_3][\text{Pt-allyl}]$$

as was indeed found.

The slope of Figure 2 ($0.35 \text{ M}^{-1} \text{ s}^{-1}$) corresponds to kK . In order to be consistent with the assumption $K[\text{PPh}_3] \ll 1$, K must be much smaller than 10^2 M^{-1} since the kinetic trend exhibiting the linear dependency on $[\text{PPh}_3]$ was observed up to as high as $[\text{PPh}_3] = 10^{-2} \text{ M}$. Now we can estimate the lowest limit for k as $k \gg 3 \times 10^{-3} \text{ s}^{-1}$. Thus, this k value in benzene may well be sufficiently larger than the corresponding value in dichloromethane ($1.5 \times 10^{-3} \text{ s}^{-1}$) which was estimated from the initial rate by assuming the first-order rate law with respect to the concentration of Pt-allyl.

We next estimated, by the GLC method, the initial rate of the probable collapse of the ion pair **8**, which was generated by mixing **1** and dppe in dichloromethane, as $1.5 \times 10^{-7} \text{ M s}^{-1}$ at 25 °C ($[\text{I}]_0 = [\text{dppe}] = 5 \times 10^{-3} \text{ M}$). The rate was determined only in the presence of an equivalent amount of dppe because of a probable occurrence of additional complex equilibria in this system.

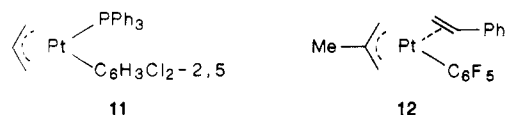
It was not possible to follow the course of the rapid reaction of **2** with PPh_3 . We could examine the kinetics of the reaction of **2** with dppe in dichloromethane. The first-order rate constant for this reaction was not affected by the amount of dppe added (see Table I). This result, together with the ^1H NMR evidence described before, suggests that the profile for the reaction of **2** with dppe is essentially similar to Scheme I. That is, a rapid preequilibrium converts most of the allylpalladium species into the ion pair **10**, which subsequently collapses into the product in the rate-determining step.

The coupling reaction caused by adding dppe to **2** in benzene solution was too rapid to be followed spectroscopically. The value of k_{obsd} for the reaction of **2** with dppe in acetonitrile-THF (3:1 by volume) was ca. $1/4$ of that in dichloromethane (Table II). These results suggest that in order for the C-C coupling to occur efficiently an almost solvent-free, tight ion-pair formation must be realized between $[M(\eta^3\text{-allyl})(\text{PR}_3)_2]^+$ and $\text{CH}(\text{COMe})_2^-$ ions. Part of the reasons for the low product yields in the case of the reaction of **1** at the low concentrations would be that a considerable portion of the ion-pair $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PR}_3)_2]^+[\text{CH}(\text{COMe})_2]^-$ dissociates at these concentrations.

The Effect of the Metal Atom on Allylic Alkylation.

The ready occurrence of eq 1 for the platinum complex **1** provides the basis on which allylic alkylation by means of allylic acetates and stabilized carbanions has successfully been achieved with platinum catalysts.^{5,13} In view of the quite high stability of dialkylplatinum(II) complexes with respect to the reductive elimination,^{6,14} the relatively fast reaction of eq 1 for **1** seems very intriguing, particularly when we note that both the reductive elimination of dialkylplatinums and eq 1 involve the reduction of the formal oxidation state from Pt(II) to Pt(0).

The high reactivity of the (η^3 -allyl)platinum complexes is limited to only the reaction involving external nucleophilic attack, since we could observe no *intramolecular* C-C coupling of (η^3 -allyl)arylpalladium (e.g. **11**, **12**)¹⁵ under the conditions where the corresponding palladium analogues underwent the quite ready reductive elimination reaction.¹⁶ Clearly, extrusion of a Pt(0) species from the (η^1 -organo)platinum(II) complexes should meet quite a high activation barrier.



A quantitative comparison of the reactivity of (η^1 -organo)platinum vs palladium complexes has been provided only by a theoretical calculation;¹⁴ the predicted ΔH^\ddagger for the reductive elimination of $\text{PtMe}_2(\text{PH}_3)_2$ is more than 30 kcal/mol higher than that of $\text{PdMe}_2(\text{PH}_3)_2$. This energy difference corresponds to the rate ratio of ca. 10^{22} provided that the entropy term is comparable in the two metal complexes. On the other hand, the corresponding rate ratio for eq 1 with dppe should not be so enormous, even though a fully quantitative comparison may not be made from the data in Table II.

According to Low and Goddard,¹⁴ the high barrier to the reductive elimination of the (η^1 -organo)platinum complexes can be explained by assuming that there is a change of the electronic configuration on the metal atom on going from (η^1 -organo)metal(II) to zerovalent complexes and this change on the platinum atom costs a considerable energy loss.^{17a} The reaction of the (η^1 -organo)palladium com-

plexes, however, accompanies no such energy loss but rather some energy gain due to the different electronic configuration of the ground state of palladium atom from that of platinum atom.^{17a}

As already pointed out elsewhere,¹⁸ the known structural and stability trends of the allylplatinum and -palladium complexes suggest that the electronic configuration of the metal atom in (η^3 -allyl)metal(II) complexes is intrinsically different from that in the (η^1 -organo)metal(II) complexes and lies closer to that in the zerovalent complexes.^{17b} In other words, the platinum atom of the (η^3 -allyl)platinum complexes would lie higher in energy than that of the allylplatinum complexes. Consequently, the energy cost paid by the platinum atom on going from η^3 -allyl to zerovalent platinum complexes would be less than that required during the conversion from the allylplatinum(II) to zerovalent platinum complexes. On the other hand, the energy gained by the palladium atom during the reduction of the metal oxidation state would be smaller in the case of the η^3 -allyl than the alkyl complexes. Thus, the difference of the reaction exothermicity in eq 1 of the palladium and platinum complexes may be smaller than that in the reductive elimination of the dialkylpalladium and -platinum complexes.

If the difference of the activation barrier is thought to parallel that of the reaction exothermicity, then the difference of the barrier in such reactions of the (η^3 -allyl)-palladium and -platinum complexes as eq 1 would be smaller than that in the reductive elimination of the dialkylpalladium and -platinum complexes; this prediction is consistent with the present experimental results.

Experimental Section

Materials and Instruments. Complexes **1-3** and **12** were prepared according to the reported methods.^{5,16,19,20} Authentic samples of $[\text{M}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PR}_3)_2]\text{BF}_4$ for NMR data (Table I) were prepared by referring to the methods for analogous complexes.²⁰⁻²² Complex **11** was prepared from $\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Cl}(\text{PPh}_3)$ and $(\text{C}_6\text{H}_3\text{Cl}_2\text{-2,5})\text{Li}$ in a manner similar to that¹⁶ for the palladium analogue; colorless microcrystals decomposed above 160 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{23}\text{Cl}_2\text{Pt}$: C, 50.32; H, 3.60. Found: C, 50.46; H, 3.65. ¹H NMR (CDCl_3): δ 2.36 (d, $J_{\text{H}} = 13$, $J_{\text{Pt}} = 40$ Hz; anti-H cis to P), 2.56 (v br, $J_{\text{Pt}} = 58$ Hz; anti-H trans to P), 3.57 (d, $J_{\text{H}} = 7.5$ Hz; syn-H cis to P), 3.88 (br; syn-H trans to P), 4.77 (tt, $J_{\text{H}} = 13$ and 7.5, $J_{\text{Pt}} = 46$ Hz; allyl center).

The other materials used in this study were commercially obtained and were reagent grade. Solvents for kinetic studies were spectroscopic grade and were dried and distilled in the standard methods. ¹H NMR spectra were measured on JEOL PS-100 and GSX-400 spectrometers and UV spectra on a Hitachi 200-20 spectrophotometer. GLC analyses were done with a Hitachi 164 chromatograph.

NMR Spectral Identification. In a typical procedure, an NMR tube containing **1** (0.052 mmol) and PPh_3 (0.104 mmol) was connected to a three-way stopcock and the inside was filled with nitrogen. Then the tube was dipped in a cold bath (-78 °C), and 0.4 mL of CD_2Cl_2 was added slowly. After all the solids dissolved, the solution was degassed by freeze (liquid nitrogen bath)-thaw (-78 °C bath) cycles (three times). The tube was sealed off and quickly put in a low-temperature NMR probe. The other experiments shown in Table I were carried out similarly.

Kinetic Studies. In a typical experiment, the top of a quartz cell (10 × 10 × 50 mm) was fitted with a rubber septum, and the

(13) Brown, J. M.; MacIntyre, J. E. *J. Chem. Soc., Perkin Trans. 2* 1985, 961-970.

(14) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* 1986, 108, 6115-6128.

(15) The methyl analogue $\text{Pt}(\eta^3\text{-allyl})(\text{CH}_3)(\text{PR}_3)$ was also reluctant to undergo the reductive elimination; see: Suzuki, T.; Nakamura, Y. *Abstr. Pap. Annu. Meeting Chem. Soc. Jpn.* 1988, Tokyo, 3IVB25.

(16) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* 1987, 109, 6333-6340.

(17) (a) In terms of the GVB description,¹⁴ the electronic configuration of the metal in the dialkylmetal complexes would be close to s^1d^9 which is the ground state of the platinum atom, while that in the zerovalent complexes would be close to d^{10} which is the ground state of the palladium atom. (b) The electronic configuration of the metal atom in the η^3 -allyl complexes would have less s^1d^9 and more d^{10} character than that in the dialkylmetal complexes.

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inside was filled with nitrogen by using a needle technique. A nitrogen-saturated benzene solution (3 mL) of complex 1 (4×10^{-4} M) was poured into the cell with a syringe, and the cell was kept in a constant-temperature UV compartment. From a stock solution of a given concentration of PPh_3 kept in a constant-temperature water bath was transferred a 1-mL portion into the cell quickly by using a syringe. At appropriate intervals change of the absorption at 350 nm was recorded. Plots of $\ln \{[1]_0 - [\text{Pt}(0)]\}$ vs time gave straight lines up to ca. 50% conversion. The absorption change at 400 nm gave the same rate data. The reactions of 2 were carried out similarly. The initial rates for the reaction of 1 with PPh_3 in dichloromethane were determined from the data up to ca. 15% conversion.

Yields of the coupling product $\text{CH}_2=\text{CMeCH}_2\text{CH}(\text{COMe})_2$ were

determined by GLC analysis (SE-30, 3 mm \times 2 m, 150 C; internal standard, *n*-tridecane). Initial rates of the reaction between 1 (5×10^{-3} M) and an equivalent dppe in dichloromethane were determined by observing increase of the coupling product by GLC.

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Registry No. 1, 33012-06-5; 2, 32660-97-2; 3, 71504-60-4; 6, 120906-43-6; 7, 120906-45-8; 8, 120906-46-9; 9, 120906-48-1; 10, 120906-49-2; 11, 120906-50-5; 12, 110270-78-5; $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}-\text{H}_2\text{CH}(\text{COCH}_3)_2$, 84884-24-2; $\text{Pt}(\eta^3-\text{CH}_2\text{CHCH}_2)\text{Cl}(\text{PPh}_3)_3$, 35770-09-3; $(\text{C}_6\text{H}_3\text{Cl}_2-2,5)\text{Li}$, 68099-30-9.

Phosphido Derivatives of Bis(pentamethylcyclopentadienyl)zirconium and -hafnium Complexes and the Molecular Structure of $(\eta\text{-C}_5\text{Me}_5)_2\text{Hf}(\text{H})(\text{PPh})$

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Primary and secondary phosphines react with $\text{Cp}^*_2\text{HfH}_2$ ($\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$) with extrusion of H_2 to give the phosphido derivatives $\text{Cp}^*_2\text{Hf}(\text{H})(\text{PRR}')$ (1, $\text{R} = \text{R}' = \text{Ph}$; 2, $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$; 3, $\text{R} = \text{H}$, $\text{R}' = \text{c-C}_6\text{H}_{11}$). Reactions of 1 generally proceed with elimination of PPh_2 . Thus, 1 reacts with 1 atm of H_2 , CO , and C_2H_4 to give PPh_2 and $\text{Cp}^*_2\text{HfH}_2$, $\text{Cp}^*_2\text{Hf}(\text{CO})_2$, and the metallocyclopentane $\text{Cp}^*_2\text{Hf}(\text{C}_2\text{H}_4)$, respectively. However, carbon dioxide reacts with 1 *without* loss of PPh_2 to give a product resulting from the insertion of CO_2 into the Hf-P bond, $\text{Cp}^*_2\text{Hf}(\text{H})(\text{Ph}_2\text{PCO}_2)$ (4). A second equivalent of CO_2 will insert into the Hf-H bond of 4 to cleanly give $\text{Cp}^*_2\text{Hf}(\text{HCO}_2)(\text{Ph}_2\text{PCO}_2)$ (5). Reaction of 1 equiv of LiPPh or $\text{LiPH}(\text{C}_6\text{H}_{11})$ with Cp^*_2MX_2 ($\text{M} = \text{Hf, Zr}$; $\text{X} = \text{Cl, I}$) affords the phosphido halide complexes $\text{Cp}^*_2\text{Hf}(\text{X})(\text{PHR})$ (6, $\text{X} = \text{I}$, $\text{R} = \text{Ph}$; 7, $\text{X} = \text{I}$, $\text{R} = \text{C}_6\text{H}_{11}$; 8, $\text{X} = \text{Cl}$, $\text{R} = \text{C}_6\text{H}_{11}$) and $\text{Cp}^*_2\text{Zr}(\text{Cl})[\text{PH}(\text{C}_6\text{H}_{11})]$ (9) in high yields. Orange prisms of 2 were grown from petroleum ether solution and crystallized in the orthorhombic space group *Pnma* with $Z = 4$, $a = 13.180$ (2) Å, $b = 14.157$ (2) Å, and $c = 13.191$ (2) Å. An X-ray diffraction study was carried out, and the least-squares refinement converged to $R(F) = 5.8\%$ and $R_w(F) = 6.2\%$ for 1328 unique reflections with $F_o > 5\sigma(F_o)$. The structure of 2 is disordered about a crystallographic mirror plane that contains the Cp^* ring centroids and the Hf atom. Salient metrical parameters of the structure include the following: $\text{Hf-P} = 2.549$ (8) Å; $\text{Hf-centroid} = 2.222$ (18) Å (average); centroid-Hf-centroid = 144.2 (7)°; $\text{P-Hf-centroids} = 110.8$ (6)° and 101.2 (6)°.

Introduction

The chemistry of the metallocene derivatives of the group 4 transition metals has been extensively investigated during the past 2 decades and has been comprehensively reviewed.¹⁻³ A particularly rich and well-developed area of this chemistry involves the reactions of bis(pentamethylcyclopentadienyl) complexes of the formula $\text{Cp}^*_2\text{M}(\text{X})(\text{X}')$ ($\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$; $\text{M} = \text{Zr, Hf}$; $\text{X, X}' =$ monoanionic donor ligand). We were interested in exploring the chemistry of a new class of compounds of this

type, the monophosphido derivatives of permethylzirconocene and permethylhafnocene, from two perspectives. First, although analogous complexes containing amides (i.e., $\text{Cp}^*_2\text{M}(\text{NRR}')(\text{X})$) have been previously prepared and their chemistry explored in some detail,⁴⁻⁶ the related phosphides have not been reported and we were curious whether the structures and reactivities of such complexes having "soft" PR_2 ligands would differ substantially from those possessing "hard" NR_2 (or alkoxide) donor ligands. Second, it seemed likely that steric constraints imposed by the two bulky pentamethylcyclopentadienyl ligands would strongly favor monomeric phosphido complexes that in turn might serve as useful precursors to monomeric phosphinidene (PR^2) complexes.⁷

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