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1-3-η-Allylpalladium(II) and Platinum(II) Complexes Containing Tris(2,6-dimethoxyphenyl)phosphine Ligand

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Neutral and cationic 1-3-η-(2-methylallyl) complexes of Pd and Pt containing tris(2,6-dimethoxyphenyl)-phosphine (abbreviated as $P(2,6)_3$), $M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)Cl\{P(2,6)_3\}$ and $[M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)\{P(2,6)_3\}]BF_4$, were prepared. The latter contained a weakly coordinated OMe group of $P(2,6)_3$ which was readily replaced by carbon monoxide to afford $[M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)(CO)\{P(2,6)_3\}]BF_4$. Owing to large steric bulk and high nucleophilicity of $P(2,6)_3$, addition of $P(2,6)_3$ to these complexes did not result in coordination of the second molecule of the phosphine to the metal atom but ready attack at the metal-bound 2-methylallyl and methoxyl carbon atoms to give the corresponding (2-methylallyl)phosphonium and methylphosphonium ions. From these reactions were isolated a neutral 1-3-η-(2-methylallyl)platinum(II) complex involving chelate coordination of a tertiary phosphine ligand which was derived from the loss of methyl of one methoxyl group in $P(2,6)_3$ and the resulting phenoxo ligand, and a cationic, binuclear Pt(I) carbonyl complex bridged by the 2-methylallyl group. Also prepared in this study were 1-3-η-(2-methylallyl)(acetylacetonato) complexes of Pd and Pt, $M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)(acac)\{P(2,6)_3\}$. In the platinum analog, the acetylacetonato ligand was suggested to coordinate to the metal in a monodentate fashion via the central carbon atom. Both complexes afforded moderate yields of $CH_2{=}CMeCH_2CH(COMe)_2$ upon treatment with carbon monoxide, while the reaction of $M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)(CO)\{P(2,6)_3\}^+$ with sodium acetylacetonate failed to give the same coupling product.

A new tertiary phosphine, tris(2,6-dimethoxyphenyl)-phosphine (abbreviated as $P(2,6)_3$) was shown to exhibit unusually high basicity and great nucleophilicity toward some organic electrophiles (e.g. alkyl halides, oxiranes).[1] This electronic property, together with its considerable steric bulk (cone angle= 184°),[1b] prompted us to examine coordination chemistry and catalytic activity of metal complexes containing $P(2,6)_3$ as a ligand. A brief synthesis of two-coordinated complexes, $[M\{P(2,6)_3\}_2]^+$ (M=Cu, Ag) has been reported before.[1b] We describe here synthesis and properties of 1-3-η-(2-methylallyl)palladium(II) and platinum(II) complexes containing $P(2,6)_3$.

Results and Discussion

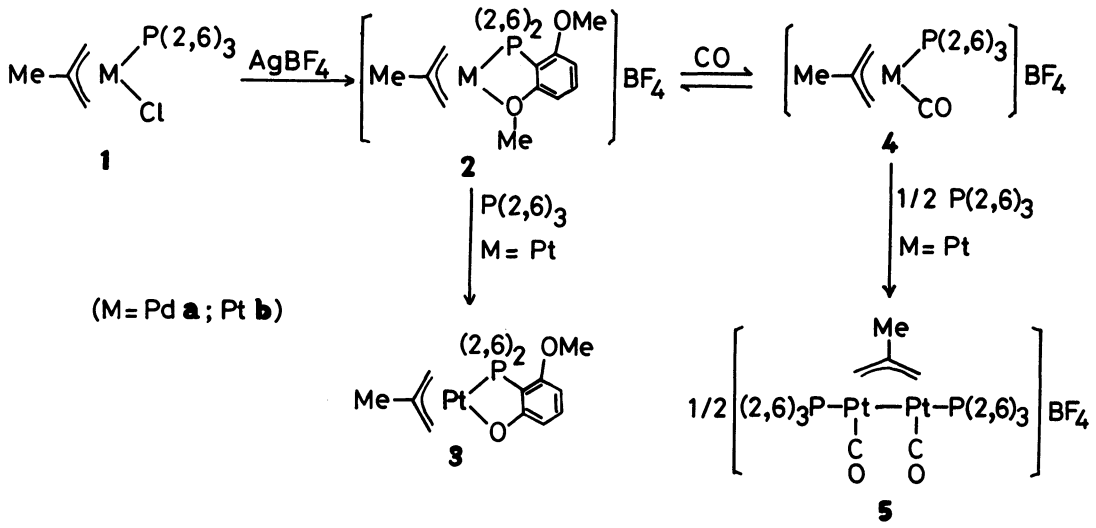
Coordination and Nucleophilic Attack of $P(2,6)_3$. Dimeric complexes, 1-3-η-(2-methylallyl)(chloro)palladium and platinum reacted with 1 molar quantity of $P(2,6)_3$ to give **1** (see Scheme 1). Treatment of **1** with $AgBF_4$ in acetone gave acetone-free cationic complexes **2**. The very large spin coupling constant between ^{195}Pt and the anti allyl proton cis to the phosphine (H^1) in the ^1H NMR spectrum of **2b** (Table 1) is consistent with coordination of the 2-OMe group having a weak trans influence to Pt.

It seems of particular note that the second molecule of $P(2,6)_3$ did not show any tendency to coordinate to the metal atom of **1**. Thus, when free $P(2,6)_3$ was added to a $CDCl_3$ solution of **1** at room temperature, we could observe no change in ^1H NMR spectra of **1** except for occurrence of a slow attack of $P(2,6)_3$ not on the metal atom but on the different sites, as described below. In the corresponding reaction of $M(1\text{-}3\text{-}\eta\text{-allyl})Cl(PPh_3)$ with PPh_3, there occurred quite ready formation of *trans*-$M(\sigma\text{-allyl})Cl(PPh_3)_2$ or $[M(1\text{-}3\text{-}\eta\text{-allyl})(PPh_3)_2]Cl$.[2] The mixture of **1a** and $P(2,6)_3$ in $CDCl_3$ caused formation of $[P(CH_3)(2,6)_3]Cl$ and $[P(CH_2CMe{=}CH_2)(2,6)_3]Cl$ (each ca. 10%) when kept to stand at room temperature for 12 h. **1b** and $P(2,6)_3$ afforded $[P(CH_3)(2,6)_3]Cl$ still more slowly.

The reaction of $P(2,6)_3$ with **2b** occurred much faster to give $[P(CH_3)(2,6)_3]BF_4$ and a neutral complex **3**. The corresponding reaction of **2a** resulted in rapid, high-yield formation of a mixture of $[P(CH_3)(2,6)_3]BF_4$ and $[P(CH_2CMe{=}CH_2)(2,6)_3]BF_4$ (ca. 1 : 1), but isolation of any palladium-containing product was not successful. Again there was no tendency of the coordination of two molecules of $P(2,6)_3$ to the metal atom in the cationic complexes.

The ready phosphonium ion formation in the reaction of $P(2,6)_3$ with **1** and **2** may have been induced by both steric and electronic causes. The large size of $P(2,6)_3$ would make coordination of two molecules of this ligand highly unfavorable. In addition, its high nucleophilicity facilitates attack at the carbon atom of the OMe and 2-methylallyl groups bound to the metal, with particular ease in the case of the cationic complexes. The methyl abstraction by $P(2,6)_3$ from the OMe group of the coordinated $P(2,6)_3$ ligand in **1** would have occurred via transient coordination of the OMe group to the metal. A quite similar result has been observed in the reaction of MCl_2L_2 (L=PhCN, 1/2COD; M=Pd, Pt) with $P(2,6)_3$ in unsuccessful attempts to prepare $MCl_2\{P(2,6)_3\}_2$.[3]

2 reacted with carbon monoxide to form **4**. **4a** is fairly stable in the solid state for a cationic carbonyl complex of Pd,[4] but reverts to **2a** in $CDCl_3$ in the absence of carbon monoxide. The lower ν(CO) value (2075 cm^{-1}) of **4b** than that[5] (2120 cm^{-1}) of $[Pt(1\text{-}3\text{-}\eta\text{-}$



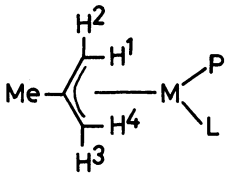
Scheme 1.

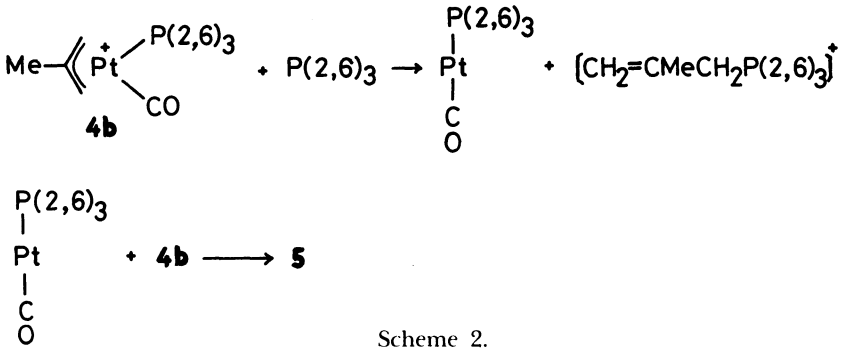
TAble 1. ^{1}H NMR Spectral Data[a] of 1-3-η-(2-Methylallyl)metal Complexes

Complex	Methallyl					P(2,6)$_3$		
	H^1	H^2	H^3	H^4	Me	OMe	3-H	4-H
1a[b]	2.46^b	2.90^b	4.07^d J_P=8	3.09^d J_P=12	1.50^s	3.57^s	6.42^{dd} J_H=8 J_P=4	7.18^t
1b	1.82^s J_{Pt}=72	2.62^b	c)	2.36^d J_P=11 J_{Pt}=34	1.49^s J_{Pt}=71	3.55^s	6.40^{dd} J_H=8 J_P=5	7.16^t
2a[b]	2.63^s	3.56^b	4.65^{bd} J_P=6	c)	2.00^s	3.75^s	6.57^{dd} J_H=8 J_P=5	7.37^t
2b	2.33^d J_P=4 J_{Pt}=112	3.20^b	4.40^b	3.40^d J_P=10 J_{Pt}=36	2.06^s J_{Pt}=79	3.82^s	6.58^{dd} J_H=8 J_{Pt}=5	7.37^t
3	1.90^s J_{Pt}=81	3.14^b	3.95^b	2.66^d J_P=10 J_{Pt}=44	1.82^s J_{Pt}=63	3.40^s 3.46^s 3.52^s	5.86^{dd} J_H=8 J_P=3 6.43^m	6.67^{bt} 7.15^m
4a	3.09^b	c)	4.80^{bd} J_P=6	3.42^d J_P=11	1.56^s	3.60^s	6.50^{dd} J_H=8 J_P=5	7.30^t
4b	2.71^b J_{Pt}=31	c)	4.68^b	3.21^d J_P=12 J_{Pt}=33	1.62^s J_{Pt}=74	3.62^s	6.57^{dd} J_H=8 J_P=5	7.38^t
6b[d]	2.07^s J_{Pt}=50	2.60^b	3.20^b	2.34^d J_P=12 J_{Pt}=42	1.60^s J_{Pt}=61	3.50^s	6.41^{dd} J_H=8 J_P=4	7.20^t

a) In $CDCl_3$ at room temperature except as noted. Chemical shifts in ppm, J in Hz. Abbreviations: s=singlet, d=doublet, t=triplet, dd=doublets of doublet, b=broad, m=multiplet. For proton numbering scheme, see below.

b) At −10°C. c) Obscured by the OMe peak. d) CH_3CO: 1.73^s (J_{Pt}=10) and 1.95^s (J_{Pt}=7). -CH<: 4.43^d (J_P=9, J_{Pt}=115).





Scheme 2.

$CH_2CMeCH_2)(CO)(PPh_3)]^+$ reflects the more basic nature of $P(2,6)_3$ than PPh_3.

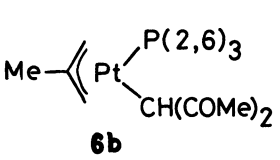
4a rapidly reacted with $P(2,6)_3$ in $CDCl_3$ containing free carbon monoxide to give almost quantitative yield of $[P(CH_2CMe{=}CH_2)(2,6)_3]BF_4$ and palladium metal. In converting **4a** to this phosphonium ion, there was no need to use equimolar amount of $P(2,6)_3$; addition of 10 mol% of $P(2,6)_3$ to **4a** caused formation of the phosphonium ion in ca. 80% yield.

4b also reacted with $P(2,6)_3$ very rapidly in 2 : 1 mole ratio to give a binuclear complex **5** and $[P(CH_2CMe{=}CH_2)(2,6)_3]BF_4$. The structure of **5** was deduced by the following spectral data. The IR spectrum showed ν(CO) bands at 2010 and 2040 cm^{-1} which are in the region expected for the Pt(I)-coordinated carbonyl ligand.[6] In the ^1H NMR spectrum, the 2-methyl proton resonance appeared as a triplet due to coupling with two equivalent ^{31}P nuclei (J_P=2.5 Hz). Furthermore, the resonances of the protons at 3- and 5-positions of $P(2,6)_3$ and the allylic syn protons appeared as double triplets ($1/2[J_P+J_P']$=2 Hz, J_H=8.5 Hz) and a triplet ($1/2[J_P+J_P']$=12 Hz), respectively, owing to virtual coupling arising from strong P-P' coupling, as observed in complexes having the P-M-M-P framework bridged by the allyl group.[7] The structure **5** should also require in ^1H NMR spectra a satellite set of the methyl signal associated with a ^{195}Pt-^{195}Pt framework which is composed of a 1 : 2 : 1 triplet with the central peak overlapping with the main peak. However, we could not observe this set due to low solubility.

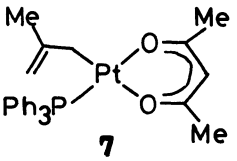
A possible route to **5** is shown in Scheme 2. The nucleophilic attack of $P(2,6)_3$ at the 2-methylallyl group of **4b** produces the phosphonium ion and $Pt(CO)\{P(2,6)_3\}$ which subsequently attacks the metal atom of another **4b** to form **5** eventually. The initial step in the corresponding reaction of **4a** with $P(2,6)_3$ may be the same as that shown in Scheme 2, but $Pd(CO)\{P(2,6)_3\}$ formed would be much less stable, releasing free $P(2,6)_3$. It seems of further interest to note that the 2-methylallyl group of **5** underwent no further nucleophilic attack of $P(2,6)_3$ even when excess $P(2,6)_3$ was added to the solution of **5**.

Preparation and Reaction of 1-3-η-(2-Methylallyl)-metal Complexes Containing $P(2,6)_3$ and Acetylacetonato Ligands. Palladium and platinum complexes of PPh_3 are known to be good catalysts for coupling reaction of allylic electrophiles and acetylacetonate anion.[8] However, the $P(2,6)_3$ complexes **1** did not show very good catalytic activity in the reaction of 2-methylallyl acetate with sodium acetylacetonate in acetone where each complex was used either by itself or in combination with free $P(2,6)_3$. Next we looked into stoichiometric reactions of 1-3-η-(2-methylallyl) complexes containing $P(2,6)_3$ with acetylacetonate anion.

The reaction of **1** with thallium acetylacetonate in benzene gave a complex of the formula, $M(C_4H_7)(acac)\{P(2,6)_3\}$ **6**. In the platinum analog, the acetylacetonato ligand may coordinate to the metal via the central carbon atom (see **6b**), as deduced by the following IR and ^1H NMR spectral data. The absence of any IR absorption at 1500—1600 cm^{-1} may exclude the chelating acetylacetonato ligand. Instead, medium to strong absorption bands appeared at 1600—1650 cm^{-1}. In the ^1H NMR spectrum of **6b** (Table 1), the methine proton of the acetylacetonato ligand resonated in the chemical shift region (δ 4.43) considerably higher than where this proton in the bidentate and monodentate oxygen-bonded ligand resonates ($\delta \geqslant$ 5.1).[9] Also, it exhibited a ^{31}P coupling of magnitude similar to those in *cis*-ML_2(acac-C)(PR_3) (M=Pd, Pt)[9] and a large ^{195}Pt coupling. Moreover, the resonance of the allylic anti proton trans to the acetylacetonato ligand showed a relatively small ^{195}Pt coupling when compared to those in **2b** and **3** containing the oxygen donor, in accord with the presence of a ligand of strong trans influence.



6b



7

It seems notable that the triphenylphosphine analog of **6b** was reported to have the structure **7** having the *O,O*-chelate and the σ-bonded 2-methylallyl group.[8c] It is not certain how the electronic effect of the phosphine ligand controls the mode of the

metal-allyl and -acetylacetonato bonding in these complexes. Adoption of the structure **6b** in the $P(2,6)_3$ analog appears reasonable in terms of the steric cause. Thus, in spite of the presence of the secondary alkyl group ($CH(COMe)_2$), **6b** would contain more room for the bulky $P(2,6)_3$ to coordinate than a structure in which PPh_3 in **7** is replaced by $P(2,6)_3$, primarily due to the smaller bite angle of the 1-3-η-allyl chelate ($\leqslant 70°$)[10] than that of the acetylacetonato chelate (90°).

The IR spectrum of the palladium analog **6a** was much the same as that of **6b**. However, **6a** decomposed relatively rapidly when dissolved in chloroform and dichloromethane (see below), so that the ^1H NMR spectral data were not obtained in these solvents. The spectrum in toluene-d_8 was very broad at room temperature, and the spectra at the lower temperatures (down to −70°C) indicated the presence of free $P(2,6)_3$ and Pd(1-3-η-CH_2CMeCH_2)(acac) in ca. 30% amount. However, the remaining parts of the spectra were still very broad and no definitive structural assignment could be made.

Attempts to isolate a triphenylphosphine analog of **6a** were unsuccessful owing to fast decomposition to give good yields of the coupling product, $CH_2=CMeCH_2CH(COMe)_2$ **8**. Interestingly, however, decomposition of **6a** in methanol or chloroform gave only low yields of **8** (up to ca. 30%). The ^1H NMR spectra of the CD_3OD or $CDCl_3$ solution of **6a** after being kept at room temperature for one day showed the presence of the $[P(CH_2CMe=CH_2)(2,6)_3]^+$ ion (ca. 30—50%), although the nature of its counter anion remains to be identified. **6b** is fairly stable in solutions under the similar conditions.

It was reported before[11,12] that addition of phosphine or carbonyl ligand to otherwise stable 1-3-η-allyl (acetylacetonato) complexes of Pd and Pt greatly accelerates the formation of the C-C coupling products. Adding $P(2,6)_3$ to **6a** did not result in the increase of the formation of **8**, but bubbling carbon monoxide through a $CDCl_3$ solution of **6a** somewhat raised the amount of **8** (46%). Addition of $P(2,6)_3$ to **6b** caused no change. On the contrary, it was reported[8c] that **7** reacts with PPh_3 very rapidly to give **8** in good yields. However, **6b** did afford **8** (55—60%) rapidly when carbon monoxide was bubbled through its methanol or chloroform solution. Formation of some 30% amount of the ion, $[P(CH_2CMe=CH_2)(2,6)_3]^+$ was also confirmed by ^1H NMR spectroscopy.

When thallium or sodium acetylacetonate was added to **4a** in methanol-chloroform mixture under an atmospheric pressure of carbon monoxide, immediate decomposition of **4a** occurred. However, to our surprise, **8** was obtained in only 3% yields, the major product being $[P(CH_2CMe=CH_2)(2,6)_3]BF_4$ (92%). Surprisingly again, in the reaction of **4b** and sodium acetylacetonate in methanol-dichloromethane, **8** was not obtained so efficiently as in the reaction of **6b** with carbon monoxide.

It is possible that the reaction of **6** with carbon monoxide to give **8** does not take a pathway proceeding via an ion pair, $[M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)(CO)\{P(2,6)_3\}]^+CH(COMe)_2^-$, **9**, as was often postulated in analogous reactions of platinum and palladium complexes.[8c,11b,12] One possible alternative pathway would be intramolecular reductive elimination of **8** from **6** assisted by coordination of carbon monoxide. Or it is also conceivable that the reaction of **6** with carbon monoxide does proceed via **9**, a kind of built-in ion pair, but in the reaction of **4** with sodium acetylacetonate the presence of the counter anion and cation (BF_4^-, Na^+) prohibits close contact of two reacting ions. Evidently, more works are necessary before any definitive conclusion on the mechanistic pathway is attained.

Experimental

Preparation of Complexes. **1a** and **1b** were obtained from the reaction of $[M(1\text{-}3\text{-}\eta\text{-}CH_2CMeCH_2)Cl]_2$ with $P(2,6)_3$ (1 : 1) in chloroform at 0 °C, and recrystallized from dichloromethane-hexane. As for the preparation of **2a**, an acetone solution (1 cm^3) of $AgBF_4$ (1 mmol) was added dropwise to **1a** (1 mmol) in the same solvent (100 cm^3). White precipitates of AgCl obtained immediately were filtered off, and the solution was concentrated to about a half volume by evaporation under vacuum. Hexane was added to cause precipitation of pale-yellow solids. These were recrystallized from dichloromethane-hexane. **2b** was prepared in a similar manner.

4a and **4b** were prepared by passing carbon monoxide through a dichloromethane solution of **2a** or **2b** at 0 °C for 10 min. To the resulting solution was added diethyl ether to give pale-pink **4a** or colorless **4b** precipitates. **4b** was recrystallized from dichloromethane-hexane, but **4a** was used without recrystallization for analysis, spectroscopy, and further reactions. IR (Nujol): **4a** 2098 cm^{-1}; **4b** 2075 cm^{-1}.

6a and **6b** were prepared from the reaction of **1a** and **1b** with thallium acetylacetonate, respectively, in manners similar to that for obtaining **7** described before.[8c] IR (Nujol): **6a** 1610 and 1630 cm^{-1}; **6b** 1624 and 1653 cm^{-1}. The ^1H NMR spectrum of **6a** in toluene-d_8 at −30 °C showed, other than the resonances due to $P(2,6)_3$ and Pd(1-3-η-CH_2CMeCH_2)(acac),[13] broad peaks at δ=1.53, 1.89, and 3.15 and very broad, weak peaks at δ=2.4, 3.9, and 4.6.

Reaction of 2b with $P(2,6)_3$. A chloroform solution (5 cm^3) of **2b** (0.26 mmol) was added to $P(2,6)_3$ (0.26 mmol) at room temperature. The resulting pale-yellow solution was concentrated under vacuum, and hexane was added to cause precipitation of pale-yellow solids. These were extracted with benzene (100 cm^3). Benzene insoluble materials were identified as $[P(CH_3)(2,6)_3]BF_4$ by ^1H NMR spectra ($CDCl_3$). The benzene extract was passed through a short Florisil column. After adding hexane, **3** was obtained as pale-yellow solids (37%). The same reaction as well as the analogous one between **2a** and $P(2,6)_3$ in $CDCl_3$ were also followed by ^1H NMR spectroscopy.

Reaction of 4b with $P(2,6)_3$. A chloroform solution (5 cm^3) of **4b** (0.25 mmol) was added to $P(2,6)_3$ (0.13 mmol) at room temperature. After concentrating the pale-yellow solution by evaporation under vacuum, diethyl ether was added

Table 2. Analytical Data of Complexes

Complex	Mp[a]	C (%)		H (%)	
	θ_m/°C	Found	(Calcd)	Found	(Calcd)
1a[b]	160	52.24	(52.60)	5.39	(5.36)
1b[c]	172	46.38	(46.19)	4.76	(4.70)
2a	150	48.54	(48.69)	4.98	(4.96)
2b	150—153	43.02	(43.15)	4.46	(4.40)
3	168—170	48.25	(47.86)	4.78	(4.61)
4a	150	48.21	(48.46)	4.87	(4.77)
4b	200—205	43.19	(43.14)	4.28	(4.24)
5	180	43.93	(44.03)	4.17	(4.17)
6a	110	56.16	(56.38)	6.11	(5.88)
6b	150—152	49.48	(50.06)	5.38	(5.22)

a) With decomposition. b) Cl (%): 6.22 (5.55). c) Cl (%): 5.25 (4.87).

to cause precipitation of pale-yellow solids. These were dissolved in 20 cm^3 of ethanol, and this solution was kept at −30 °C overnight to give pale-yellow crystals of **5** (36%). This was further recrystallized from dichloromethane-hexane kept in a refrigerator. IR (Nujol): 2010 and 2040 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.32 (t, J_P=2.5 Hz, J_{Pt}=60 Hz, Me); 1.47 (br s, anti-H); 2.88 (br t, $1/2[J_P+J_P']$=12 Hz, syn-H); 3.51 (s, OMe); 6.45 (dt, $1/2[J_P+J_P']$=2 Hz, J_H=8.5 Hz, 3- and 5-H); 7.25 (t, J_H=8 Hz, 4-H). The stoichiometry of this reaction was also followed by ^1H NMR spectroscopy, and found very clean.

Analytical data of new complexes thus obtained are summarized in Table 2.

Reactions of Other Complexes. The reactions involving **4a** were run in deuterated solvents which had been saturated with an atmospheric pressure of carbon monoxide. The proceeding of all the reactions was followed by ^1H NMR spectroscopy. The reactions of **6**, and those of **4** with sodium acetylacetonate, were also followed by GLC analysis for the determination of the coupling product **8** (SE30, 2 m×3 mm, internal reference, tridecane).

GLC analysis was run on a Hitachi 163 gas chromatograph. ^1H NMR spectra were measured on a JEOL JNM-PS-100 spectrometer, and IR spectra on a Hitachi 215 grating spectrophotometer.

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