Addition of Methanol to Nonactivated Internal Alkynes Catalyzed by Dichloro(diphosphine)platinum(II) Complex/Silver Salt Systems

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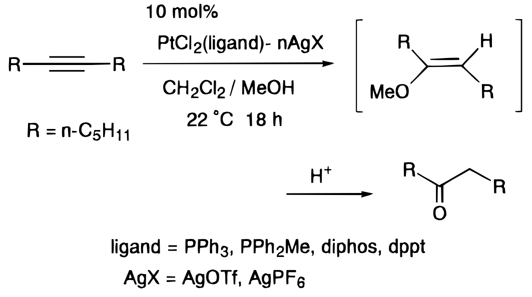
Received June 21, 1996[⊗]

Summary: Nucleophilic addition of methanol to nonactivated alkynes is catalyzed by platinum phosphine complexes derived from $PtCl_2$(ligand) [ligand = 2PPh_3, 2PPh_2Me, diphos, dppt (1,5-bis(diphenylphosphino)pentane)] and a silver salt [$AgPF_6$ or AgOTf (silver trifluoromethanesulfonate)] producing ketones in high yields. The catalytic activity is influenced by the phosphine ligand as well as by the anion and the ratio of the dichloroplatinum complex to the silver salt.

Introduction

Intermolecular addition of an alcohol to alkynes is one of the efficient routes for functionalization of a C−C triple bond.[1] Although it has been reported that intermolecular addition of alcohol to activated alkynes having electron-withdrawing groups such as an ester group is catalyzed by bases,[2] copper(I) triflate,[3] mercury(II) chloride/triethylamine,[4] palladium(II) complexes,[5] or a cuboidal $PdMoS_4$ cluster,[6] there have been only two reports on the intermolecular addition of an alcohol to nonactivated internal alkynes which have no electron-withdrawing substituents.[7]

The study of cationic palladium complexes has attracted much attention due to both enhancement of electrophilicity[8] and supply of vacant sites[9] on the metal center. Recently we have reported that dicationic platinum complexes prepared from $PtCl_2$(phosphine) (phosphine = 2PPh_3, diphosphine) and excess $AgPF_6$ catalyze the addition of an alcohol to several alkynes. Especially high catalytic activity is observed with activated alkyne such as DMAD (dimethyl acetylenedicarboxylate).[10] However during the course of our recent studies of the catalytic reaction, it was found that the real activity of the dicationic platinum complexes is obscured because a silver salt such as $AgPF_6$ by itself also showed catalytic activity in the addition of methanol to DMAD.[11] These observations prompted us to reexamine the catalyzed addition of methanol to alkynes by these platinum complexes using nonactivated alkynes to which methanol was not able to add in the presence only of silver salts. We describe here that several platinum complex systems derived from $PtCl_2$(ligand) [ligand = 2PPh_3, 2PPh_2Me, diphos, dppt (1,5-bis(diphenylphosphino)pentane)] and a silver salt [$AgPF_6$ or AgOTf (silver trifluoromethanesulfonate)] catalyze the addition of methanol to nonactivated alkynes and that the catalytic activity is influenced by the phosphine ligand as well as by the anion and the ratio of $PtCl_2$(ligand) to the silver salt.



(1)

Results and Discussion

The results of the addition of MeOH to dodec-6-yne catalyzed by several platinum species are summarized in Table 1. A mixture of dodec-6-yne (0.5 mmol) and MeOH (0.5 mL, 13 mmol) in CH_2Cl_2 (0.5 mL) was stirred at 22 °C for 18 h in the presence of a catalytic amount of the platinum species (10 mol %) prepared *in situ* from $PtCl_2$(diphos) (0.05 mmol) and AgOTf (0.05 mmol). Dodecan-6-one, the hydrolyzed product of the vinyl ether initially formed in the addition of MeOH to dodec-6-yne, was obtained in 99% yield (Table 1, run 1). The ^1H NMR spectrum of the reaction mixture did not show any sign of formation of the vinylic ether and showed only the presence of the hydrolyzed products, the respective ketones. The reaction system was so acidic that the initial products, the vinylic ethers, might be easily hydrolyzed under the reaction conditions. All platinum species derived from $PtCl_2$(diphos) and a silver salt

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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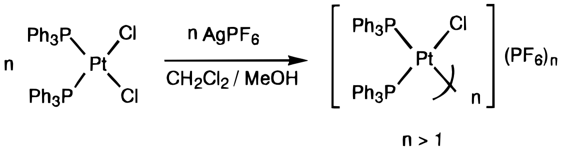
Table 1. Reaction of Dodec-6-yne with Methanol Catalyzed by Pt(II)−Ag Systems[a]

run	catalyst system	dodecan-6-one yield/%[b]
1	$PtCl_2$(diphos) − 1AgOTf	99
2	$PtCl_2$(diphos) − 3AgOTf	83
3	$PtCl_2$(diphos) − 1$AgPF_6$	89
4	$PtCl_2$(diphos) − 3$AgPF_6$	79
5	$PtCl_2(PPh_3)_2$ − 1AgOTf	95
6	$PtCl_2(PPh_3)_2$ − 3AgOTf	3
7	$PtCl_2(PPh_3)_2$ − 1$AgPF_6$	6
8	$PtCl_2(PPh_3)_2$ − 3$AgPF_6$	18

[a] Dodec-6-yne (5.0 mmol) was treated with a platinum complex (0.5 mmol) and *n* silver salts (*n* = 1, 0.5 mmol; *n* = 3, 1.5 mmol) in CH_2Cl_2 (0.5 mL) and MeOH (0.5 mL) at 22 °C for 18 h. [b] Yield was determined by GLC using a Shimazu capillary column, CBP1-M25-025.

showed similarly high activity under these conditions regardless of the anion and the amount of silver salt employed (run 1−4). On the other hand, the catalytic activity of the platinum species derived from *cis*-$PtCl_2(PPh_3)_2$ varied considerably depending on the anion and the amount of the silver salt. When *cis*-$PtCl_2(PPh_3)_2$ and AgOTf were employed as a precursor of the platinum species, the catalyst system obtained by using 1 equiv of AgOTf showed high catalytic activity (run 5), whereas an excess of AgOTf reduced the catalytic activity drastically (run 6). When $AgPF_6$ was employed as the silver salt, low activities always were observed regardless of the amount of the silver salt (runs 7, 8). The catalytic system prepared from a diphosphine complex, $PtCl_2$(dppt) [dppt = 1,5-bis(diphenylphosphino)pentane], and silver salts showed activity similar to that of the $PtCl_2$(diphos) system; dodecan-6-one was obtained in yields of 93% (with 1 equiv of AgOTf), 91% (with 3 equiv of AgOTf), 75% (with 1 equiv of $AgPF_6$), and 90% (with 3 equiv of $AgPF_6$). The activity of the $PtCl_2(PPh_2Me)_2$−silver salt system showed similar tendency to that of $PtCl_2(PPh_3)_2$ system; dodec-6-one was obtained in yields of 97% (with 1 equiv of AgOTf), 32% (with 3 equiv of AgOTf), 33% (with 1 equiv of $AgPF_6$), and 11% (with 3 equiv of $AgPF_6$).

To explore the reason of the different reactivities depending on the anion of the silver salts employed in the *cis*-$PtCl_2(PPh_3)_2$ systems, the following stoichiometric reactions were carried out. Reaction of *cis*-$PtCl_2(PPh_3)_2$ with 1 equiv of $AgPF_6$ in the presence of 3 equiv of dodec-6-yne at 22 °C in CH_2Cl_2 and MeOH (1:1) yielded a colorless precipitate. Elemental analysis of the white solid obtained after removal of AgCl from the precipitate suggested the formation of a chloride-bridged oligomer complex, $[(Ph_3P)_2PtCl]_n(PF_6)_n$ ($n > 1$) (eq 2).



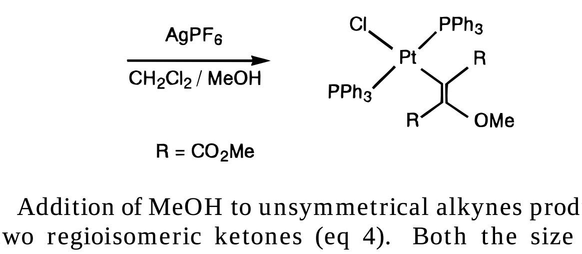
(2)

The latter was not soluble in CH_2Cl_2 and therefore did not show any catalytic activity. On the other hand, the reaction of the *cis*-$PtCl_2(PPh_3)_2$ with 1 equiv of AgOTf precipitated only AgCl, leaving the active platinum species in solution. These results indicate that a triflate anion, which has a higher coordination ability[12] but can be replaced by alkynes, prevented the formation of the insoluble platinum oligomer complex.

In order to obtain further information about the catalytically active species we have examined the ^{31}P NMR spectra of the catalyst systems. The ^{31}P NMR spectrum of the reaction mixture derived from *cis*-$PtCl_2(PPh_3)_2$ and 1 equiv of AgOTf in a mixed solvent of MeOH-d_4 and CH_2Cl_2 (1:1) showed mainly two sets of signals [δ 4.2 (d, $J_{Pt-P} = 4019$ Hz, $J_{P-P} = 18$ Hz), 19.4 (d, $J_{Pt-P} = 3962$ Hz, $J_{P-P} = 18$ Hz) and δ 9.2 (d, $J_{Pt-P} = 3554$ Hz, $J_{P-P} = 18$ Hz), 13.3 (d, $J_{Pt-P} = 4108$ Hz, $J_{P-P} = 18$ Hz)], probably due to *cis*-$(Ph_3P)_2PtCl(OTf)$ and *cis*-$[(Ph_3P)_2PtCl(MeOH)](OTf)$ or *vice versa*. Although several other singlet signals are present, the signal due to the starting dichloride $PtCl_2(PPh_3)_2$ [δ 14.8 (s, $J_{Pt-P} = 3700$ Hz)] disappeared completely.

When *cis*-$PtCl_2(PPh_3)_2$ was reacted with an excess of silver salt, the chloride ligands can be removed completely judging from the disappearance of the Pt−Cl stretch in the IR spectrum of the reaction product.[13] The ^{31}P NMR spectrum also supported the removal of the chloride ligand. For example, the ^{31}P NMR spectrum of *cis*-$PtCl_2(PPh_3)_2$−3AgOTf in MeOH-d_4 and CH_2Cl_2 (1:1) showed three signals at δ 4.8 (s, $J_{Pt-P} = 4080$ Hz), 8.2 (s, $J_{Pt-P} = 3730$ Hz), and 33.3 (s, $J_{Pt-P} = 3014$ Hz). The first two signals could be assigned to *cis*-$[Pt(PPh_3)_2(MeOH)_2](OTf)_2$ and *cis*-$Pt(PPh_3)_2(OTf)_2$ or *vice versa* and the lowest field signal to *trans*-$[Pt(PPh_3)_2(MeOH)_2]$ $(OTf)_2$ according to the coupling constants between ^{195}Pt and ^{31}P.[14]

The reason that the catalytic activity of *cis*-$PtCl_2(PPh_3)_2$−3AgX (X = PF_6 or OTf) systems, despite the soluble platinum species formed, was extremely low compared to that of the $PtCl_2$(diphos)−3AgX systems is not clear at present. It could be due to the difference of their geometry. The bidentate diphosphine ligand (diphos) can only take *cis* configuration but triphenylphosphine can also take a *trans* configuration, which may be the predominant but inactive species at the key step of the catalytic process; reaction of DMAD and MeOH with *cis*-$PtCl_2(PPh_3)_2$ and 1 equiv of $AgPF_6$ in CH_2Cl_2 gave *trans*-$PtCl(PPh_3)_2\{\eta^1$-(*E*)-$CH_3O_2CC{=}C(OMe)CO_2CH_3\}$ in 74% isolated yield (eq 3). Despite careful NMR investigation of the reaction mixture, we have not been able to obtain any positive information about the real catalytic species, so far; we could not observe an interaction of the alkyne with a platinum species, etc.



(3)

Addition of MeOH to unsymmetrical alkynes produces two regioisomeric ketones (eq 4). Both the size and electronic properties of the substituents on the alkyne influence the regioselectivity. For example, reaction of

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[13] ν(Pt−Cl): 346 cm^{-1} for $PtCl_2$(diphos); 296 and 320 cm^{-1} for *cis*-$PtCl_2(PPh_3)_2$.

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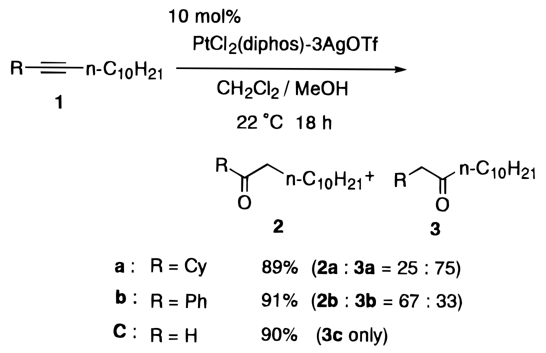

(4)

1-cyclohexyldodec-1-yne (**1a**) with MeOH in the presence of $PtCl_2$(diphos) and excess AgOTf in CH_2Cl_2 afforded a mixture of two regioisomeric ketones (**2a**:**3a** = 25:75) in 89% isolated yield. The major isomer was produced by addition of MeOH at the less hindered side of the C−C triple bond. In contrast, addition of MeOH to 1-phenyldodec-1-yne took place at the more sterically congested position α to the phenyl group.[15] When a terminal alkyne such as dodec-1-yne was employed in this reaction, MeOH added at the sterically congested site of the C−C triple bond to yield dodecan-2-one selectively.

In conclusion, we have found that cationic platinum−phosphine complexes or platinum−phosphine complexes with anions of moderate coordination ability derived from $PtCl_2$(ligand) and silver salts catalyze the addition of methanol to nonactivated alkynes affording the corresponding ketone. The catalytic activity of the platinum species depends upon the phosphorus ligand of the starting platinum complex and on the anion.

Experimental Section

All manipulations were conducted under argon atmosphere with standard Schlenk methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used after distillation. All solvents were distilled under argon prior to use, CH_2Cl_2 from CaH, MeOH from $Mg(OMe)_2$, and CH_3CN from CaH. $PtCl_2$(diphos), *cis*-$PtCl_2(PPh_3)_2$, *cis*-$PtCl_2(PPh_2Me)_2$, and $PtCl_2$(dppt) (dppt = $Ph_2P(CH_2)_5PPh_2$) were prepared according to published procedures.[16] 1-Cyclohexyldodec-1-yne (**1a**) and 1-phenyldodec-1-yne (**1b**) were prepared by similar methods to published procedures.[17,18] Column chromatography was conducted by using silica gel 60 (E. Merck 9385 230−400 mesh). The melting points were recorded on a Yanaco MP-52982 and are uncorrected. IR spectra were determined on a Hitachi 295 spectrophotometer or JASCO FT/IR-230. Mass spectra were obtained on a JEOL JMS DX-303HF spectrometer or PE-Sciex API-III plus. ^1H NMR spectra were recorded at 270.05 MHz on a JEOL GSX-270 spectrometer, and ^{31}P NMR spectra at 109.25 MHz on a JEOL GSX-270 spectrometer. Chemical shifts of ^1H NMR are expressed in ppm downfield from Me_4Si using the δ scale ($CHCl_3$ was used as an internal standard, δ 7.26), and those of ^{31}P NMR are referred to 85% H_3PO_4 as an external reference. Elemental analysis was carried out with a Yanaco MT-3.

General Procedure for Addition of MeOH to an Alkyne Catalyzed by the Systems Derived from $PtCl_2$(ligand) (Ligand = 2 Monodentate Phosphines or a Diphosphine) and a Silver Salt ($AgPF_6$ or AgOTf). To a solution of a platinum complex [$PtCl_2$(ligand), 0.05 mmol] in a mixed solvent of CH_2Cl_2 (0.5 mL) and MeOH (0.5 mL) at 22 °C was added a silver salt ($AgPF_6$ or AgOTf, 0.05 mmol or 0.15 mmol). The reaction mixture was stirred for 15 min at 22 °C, and then the alkyne (0.5 mmol) was added. After 18 h, the yield of the ketone was determined by GLC or after isolation with column chromatography.

Dodecan-6-one.[19] The yield was determined by GLC. GLC conditions: Simadzu capillary column, CBP1-M25-025; column temperature, 130 °C; internal standard, tetradecane; retention time, 5.0 min (dodec-6-yne), 7.3 min (dodecan-6-one), 9.5 min (tetradecane).

1-Cyclohexyldodecan-1-one (2a) and 1-cyclohexyldodecan-2-one (3a). The two compounds (**2a**:**3a** = 26:74) could not be separated with column chromatography. ^1H NMR ($CDCl_3$): δ 0.80−1.04 {m, 3H (**2a** and **3a**)}, 1.04−1.48 (m, 18H (**2a**) and 16H (**3a**)}, 1.42−1.68 {m, 4H (**2a** and **3a**)}, 1.56−1.96 {m, 6H (**2a**) and 7H (**3a**)}, 2.26 {d, J = 6.9 Hz, 2H (**3a**)}, 2.36 {t, J = 7.3 Hz, 2H (**3a**)}, 2.41 {t, J = 7.2 Hz, 2H (**2a**)}, 2.30−2.44 {m, 1H (**2a**)}. IR (neat): 2930, 2853, 1712, 1449, 1409, 1375, 1146, 721 cm^{-1}. HRMS (EI): m/z 266.2563 (M^+). Calcd for $C_{18}H_{34}O$ 266.2610.

1-Phenyldodecan-1-one (2b).[19] ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 6.7 Hz, 3H), 1.2−1.5 (m, 16H), 1.74 (tt, J = 7.4, 7.7 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 7.4−7.6 (m, 3H), 7.9−8.0 (m, 2H).

1-Phenyldodecan-2-one (3b).[20] ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 6.7 Hz, 3H), 1.1−1.4 (m, 14H), 1.4−1.6 (m, 2H), 2.43 (t, J = 7.3 Hz, 2H), 3.67 (s, 2H), 7.1−7.4 (m, 5H).

Synthesis of a Chloride-Bridged Oligomer Complex, $[(Ph_3P)_2PtCl]_n(PF_6)_n$ ($n > 1$). In a Schlenk flask was placed *cis*-$PtCl_2(PPh_3)_2$ (153 mg, 0.194 mmol) under an Ar atmosphere. To the complex were added successively at 22 °C CH_2Cl_2 (2 mL), MeOH (2 mL), and dodec-6-yne (79 mg, 0.475 mmol). $AgPF_6$ was added to the solution, and the mixture was stirred at 22 °C for 20 min. The resulting colorless precipitate was filtered and washed with CH_2Cl_2 (10 mL). To the precipitate was added a mixed solvent of nitromethane and acetonitrile (5 mL, 1:1). The insoluble, colorless solid was removed by filtration, and the filtrate was concentrated *in vacuo*. A white powder of $[(Ph_3P)_2PtCl]_n(PF_6)_n$ ($n > 1$) was obtained after recrystallization from CH_3CN-Et_2O. Mp: 251.4−254.8 °C (dec). The complex is soluble in CH_3CN and shows ^{31}P NMR signals in CD_3CN at δ −143.1 (septet, J_{P-F} = 707 Hz, 2P, PF_6), 6.0 (d, J_{Pt-P} = 3841 Hz, J_{P-P} = 18 Hz, 2P, Ph_3P), and 13.5 (d, J_{Pt-P} = 3503 Hz, J_{P-P} = 18 Hz, 2P, Ph_3P), due to a monomeric species, *cis*-$[(PPh_3)_2PtCl(CH_3CN)]^+$.[21] ^1H NMR (CD_3CN): δ 7.15−7.60 (m, 60H, arom). IR (Nujol): 1550, 1440, 1315, 1100, 1000, 880, 855, 840, 760, 750, 710, 700, 560, 555, 535, 520, 505, 320 cm^{-1}. MS (ESIMS, CH_3CN solution): m/z 796 $[PtCl(PPh_3)_2(CH_3CN)]$, 753 $[PtCl(PPh_3)_2]$, 718 $[Pt(PPh_3)_2]$. Anal. Calcd for $(C_{36}H_{30}P_3ClF_6Pt)_n$: C, 48.04; H, 3.36. Found: C, 48.18; H, 3.62.

***trans*-$PtCl(PPh_3)_2\{\eta^1$-(E)-$CH_3O_2CC{=}C(OMe)CO_2CH_3\}$.** To a solution of *cis*-$PtCl_2(PPh_3)_2$ (65 mg, 0.082 mmol) and dimethyl acetylenedicarboxylate (DMAD) (36 mg, 0.25 mmol) in a mixture of CH_2Cl_2 and MeOH (5 mL, 1:1) was added $AgPF_6$ (21 mg, 0.082 mmol). The reaction mixture was stirred for 20 min at 20 °C, and then the precipitated AgCl was removed by filtration. The yellow filtrate was concentrated *in vacuo*. The residual yellow semisolid was washed with two portions of ether (20 mL × 2) and then dried under reduced

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(15) Similar regioselectivities were observed in the reaction of tantalum−unsymmetrical acetylene complexes with carbonyl compounds, see: (a) Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1707. (b) Kataoka, Y.; Miyai, J.; Tezuka, M.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 6796.

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pressure to give the pure alkenylplatinum complex as a yellow powder (57 mg, 0.061 mmol) in 74% yield. Mp: 255.2−257.8 °C (dec). ^{1}H NMR ($CDCl_3$): δ 2.67 (s, 3H), 3.24 (s, 3H), 3.45 (s, 3H), 7.31−7.48 (m, 18H), 7.70−7.84 (m, 12H). ^{31}P NMR ($CDCl_3$): δ 22.2 (s, J_{Pt-P} = 2949 Hz). MS (FAB): *m*/*z* 929, 928, 987 (M^+). IR (Nujol): 1710, 1705, 1440, 1300, 1200, 1120, 1100, 1050, 1020, 750, 710, 525, 505, and 340 cm^{-1}. Anal. Calcd for $C_{43}H_{39}ClP_2O_5Pt$: C, 55.64; H, 4.23. Found: C, 55.39; H, 4.42.

^{31}P NMR Experiment [in a Mixed Solvent of MeOH-*d*$_4$ and CH_2Cl_2 (1:1)]. *cis*-$PtCl_2(PPh_3)_2$: δ 14.8 (s, J_{Pt-P} = 3700 Hz).

***cis*-$PtCl_2(PPh_3)_2$−1AgOTf:** δ 4.2 (d, J_{Pt-P} = 4019 Hz, J_{P-P} = 18 Hz), 4.9 (s, J_{Pt-P} = 4080 Hz), 8.2 (s, J_{Pt-P} = 3730 Hz), 9.2 (d, J_{Pt-P} = 3554 Hz, J_{P-P} = 18 Hz), 13.3 (d, J_{Pt-P} = 4108 Hz, J_{P-P} = 18 Hz), 15.7 (s, J_{Pt-P} = 3843 Hz), 19.4 (d, J_{Pt-P} = 3962 Hz, J_{P-P} = 18 Hz), and 33.3 (s, J_{Pt-P} = 3016 Hz).

***cis*-$PtCl_2(PPh_3)_2$−3AgOTf:** δ 4.8 (s, J_{Pt-P} = 4080 Hz), 8.2 (s, J_{Pt-P} = 3730 Hz), and 33.3 (s, J_{Pt-P} = 3014 Hz).

$PtCl_2$(diphos): δ 43.4 (s, J_{Pt-P} = 3638 Hz).

$PtCl_2$(diphos)-1AgOTf: 14.9 (d, J_{Pt-P} = 2361 Hz, J_{P-P} = 16 Hz), 18.4 (d, J_{Pt-P} = 2274 Hz, J_{P-P} = 16 Hz), 36.5 (m, J_{Pt-P} = 3947 Hz), 46.4 (m, J_{Pt-P} = 3578 Hz), 49.8 (s, J_{Pt-P} = 2315 Hz), 52.5 (s, J_{Pt-P} = 2367 Hz), 56.0 (s, J_{Pt-P} = 3016 Hz).

$PtCl_2$(diphos)−3AgOTf: 35.9 (s, J_{Pt-P} = 3620 Hz), 39.0 (s, J_{Pt-P} = 3935 Hz).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

OM9605037