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η^3-Allyl(methyl)platinum(II) Complexes. Synthesis, Conversion into η^1-Allyl Complexes, and Electrochemical Behavior in Comparison with Thermolysis

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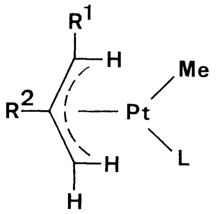
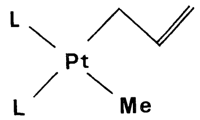
Complexes of the type [Pt(η^3-allyl)Me(L)] (**1**) (allyl=C_3H_5, 1-MeC_3H_4, or 2-MeC_3H_4; L=tertiary phosphine) as well as [Pt(η^3-C_3H_5)Bu(PPh_3)] have been synthesized and characterized by NMR (^{1}H, ^{13}C) and mass spectroscopy. By the reaction with bidentate tertiary phosphines (L–L), [Pt(η^3-C_3H_5)Me(PPh_3)] (**1b**) was converted into η^1-allyl complexes of the type [Pt(η^1-C_3H_5)Me(L–L)]. With PPh_3, *cis*-[Pt(η^1-C_3H_5)Me(PPh_3)$_2$] was isolated. The reaction of **1b** with neat 2,4-pentanedione (Hacac) afforded [Pt(acac)Me(PPh_3)]. Complexes **1** thermally decompose in the solid state and in diphenylmethane solely giving propylene and methane, but the allyl-alkyl coupling reaction to form 1-butene is promoted by the addition of maleic anhydride. A similar coupling-promoting effect was observed in the electrochemical oxidation of **1b** in THF at 23°C without additive. By taking into account the one-electron oxidation and the participation of the PPh_3 ligand in its oxidation process, a possible mechanism of this electrochemically promoted coupling is proposed.

Many unique catalytic reactions directed toward organic synthesis are possible with the use of palladium compounds,[1)] but the utility of platinum compounds as catalysts is rather limited possibly because of their relative inertness. We previously reported on the thermolytic behavior of η^3-allyl(methyl)(tertiary phosphine)palladium(II), which were synthesized as models of palladium-catalyzed allylic alkylation.[2)] The complexes were found to thermally decompose with preferential evolution of ethane rather than 1-butene, the allylic-alkylation product. However, the addition of maleic anhydride as a π-acid greatly enhanced the evolution of 1-butene, although PPh_3 and other additives had only the medium effect to promote coupling. In order to obtain further insight into the catalytic ability of metals for allyl–alkyl coupling reactions, we attempted to synthesize the corresponding platinum complexes and to compare their thermolytic behavior with that of the palladium(II) complexes. In our knowledge, such an η^3-allyl(methyl)platinum(II) complex has not been synthesized yet, although the η^3-allyl-η^1-allyl complex,[3)] allyl-platinacycles,[4)] and the allyl-aryl complexes containing phenyl[5)] and polyhalogenated phenyl[6)] have been known so far. We here report on the thermolytic and electrolytic behavior of the first isolated η^3-allyl(methyl)(tertiary phosphine)platinum(II) complexes (**1**), with emphasis placed to a novel electrochemical coupling-promoting effect. Conversion of **1** into the η^1-allyl complexes **5** is also described.



1

a: R^1=R^2=H; L=PCy_3
b: R^1=R^2=H; L=PPh_3
c: R^1=R^2=H; L=$PMePh_2$
d: R^1=R^2=H; L=PMe_2Ph
e: R^1=R^2=H; L=PBu_3
f: R^1=Me, R^2=H; L=PPh_3
g: R^1=H, R^2=Me; L=PPh_3



5

a: 2L=$Ph_2PCH_2CH_2PPh_2$ (dppe)
b: 2L=Ph_2PCH=$CHPPh_2$ (dppen)
c: L=PPh_3

Experimental

All preparations were carried out under nitrogen unless otherwise stated. Solvents and reagents were redistilled under and purged with argon, respectively. The ether solution of LiMe (0.87 mol dm^{-3}) and the hexane solution of LiBu (15.2 wt%) was used as gifted from Tosoh Akzo Corporation. The allyl complexes [Pt(C_3H_5)Cl]$_4$,[7)] [Pt(μ-Cl)(η^3-2-MeC_3H_4)]$_2$,[8)] [Pt(η^3-C_3H_5)Cl(L)],[9)] and [Pt(η^3-1-MeC_3H_4)Cl(PPh_3)][10)] were prepared by the published methods. Tertiary phosphines and other reagents were purchased and used without further purification. Standard gases were also purchased.

Synthesis of Complexes 1a—1e. To a stirred solution or suspension of [Pt(η^3-C_3H_5)Cl(L)] in toluene kept at −10 °C a stoichiometric amount of LiMe in ether was added dropwise. After being stirred for a while, the mixture was gradually warmed up to room temperature with stirring. The white precipitate formed was filtered off and evaporation was carried out in vacuo at room temperature. The residue was extracted with hexane and the extract was again evaporated to leave **1a—1e** as a colorless amorphous solid or oil.

1a: Colorless solid (77%); mp 156—157 °C (decomp);

^{1}H NMR (C_6D_6) (for proton and carbon numbering schemes, see the structure for **2**) δ=1.32 (3H, d, J_P=4.6, J_{Pt}=86.0 Hz, Pt-Me), 2.12 (1H, H^2), 2.22 (1H, H^3) (coupling constants could not be evaluated due to overlapping with the ligand signal), 3.41 (1H, dd, J_4=1.7, J_5=4.1 Hz, H^1), 3.59 (1H, m, H^4), and 4.38 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=−20.4 (d, J_P=7.3, J_{Pt}=808 Hz, Pt-Me), 51.5 (d, J_P=39.6, J_{Pt}=132 Hz, C^c), 54.1 (s, J_{Pt}=29.3 Hz, C^a), and 108.7 (s, J_{Pt}=16.2 Hz, C^b).

Found: C, 48.18; H, 7.55%. Calcd for $C_{22}H_{41}PPt$: C, 49.70; H, 7.77%.

1b: Pale yellow solid (81%); mp 138—140 °C (decomp); ^{1}H NMR (C_6D_6) δ=1.39 (3H, d, J_P=6.2, J_{Pt}=97.0 Hz, Pt-Me), 2.37 (1H, dd, J_5=10.7, J_P=10.3, J_{Pt}=63.0 Hz, H^3) (J_5 and J_P values were evaluated by application of a homodecoupling technique to the H^5 signal), 2.43 (1H, d, J_5=13.0, J_{Pt}=41.0 Hz, H^2), 3.37 (1H, dd, J_4=2.2, J_5=7.3 Hz, H^1), 3.69 (1H, m, H^4), and 4.51 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=−15.9 (d, J_P=7.3, J_{Pt}=806 Hz, Pt-Me), 50.8 (d, J_P=42.5, J_{Pt}=156 Hz, C^c), 62.2 (s, J_{Pt}=22.0 Hz, C^a), and 110.2 (d, J_P=2.9, J_{Pt}=17.6 Hz, C^b).

Found: C, 51.86; H, 4.55%. Calcd for $C_{22}H_{23}PPt$: C, 51.46; H, 4.51%.

1c: Pale yellow solid (76%); mp 48—49 °C; ^{1}H NMR (C_6D_6) δ=1.39 (3H, d, J_P=6.6, J_{Pt}=87.4 Hz, Pt-Me), 2.27 (1H, d, H^2), 2.33 (1H, t, H^3) (coupling constants could not be evaluated because of the very closely situated H^2 and H^3 signals), 3.30 (1H, dd, J_4=1.8, J_5=7.2 Hz, H^1), 3.69 (1H, m, H^4), and 4.42 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=−18.3 (d, J_P=5.9, J_{Pt}=804 Hz, Pt-Me), 50.4 (d, J_P=44.0, J_{Pt}=144 Hz, C^c), 59.4 (s, J_{Pt}=24.9 Hz, C^a), and 109.8 (s, J_{Pt}=16.1 Hz, C^b).

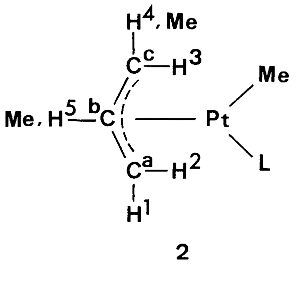
Found: C, 45.73; H, 4.77%. Calcd for $C_{17}H_{21}PPt$: C, 45.23; H, 4.69%.

1d: Brownish yellow liquid (61%); ^{1}H NMR (C_6D_6) δ=1.37 (3H, d, J_P=6.8, J_{Pt}=87.0 Hz, Pt-Me), 2.19 (1H, d, J_5=12.9, J_{Pt}=42.0, H^2), 2.30 (1H, t, J=11.0, J_{Pt}=61.0 Hz, H^3), 3.35 (1H, dd, J_4=2.2, J_5=7.3 Hz, H^1), 3.65 (1H, m, H^4), and 4.39 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=−19.5 (d, J_P=5.9, J_{Pt}=798 Hz, Pt-Me), 50.3 (d, J_P=44.0, J_{Pt}=144 Hz, C^c), 56.5 (s, J_{Pt}=28.0 Hz, C^a), and 109.7 (s, J_{Pt}=16.2 Hz, C^b).

Found: C, 36.50; H, 4.84%. Calcd for $C_{12}H_{19}PPt$: C, 37.02; H, 4.92%.

1e: Pale yellow liquid (93%); ^{1}H NMR (C_6D_6) δ=1.29 (3H, d, J_P=6.1, J_{Pt}=86.4 Hz, Pt-Me), 2.11 (1H, d, J_5=12.9, J_{Pt}=42.4 Hz, H^2), 2.22 (1H, t, J=11.0, J_{Pt}=56.0 Hz, H^3), 3.42 (1H, dd, J_4=2.2, J_5=7.2 Hz, H^1), 3.60 (1H, m, H^4), and 4.35 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=−21.2 (d, J_P=6.9, J_{Pt}=796 Hz, Pt-Me), 50.9 (d, J_P=41.1, J_{Pt}=134 Hz, C^c), 53.3 (s, J_{Pt}=20.8 Hz, C^a), and 109.1 (s, J_{Pt}=17.6 Hz, C^b).

Found: C, 42.15; H, 7.86%. Calcd for $C_{16}H_{35}PPt$: C, 42.38; H, 7.78%.



2

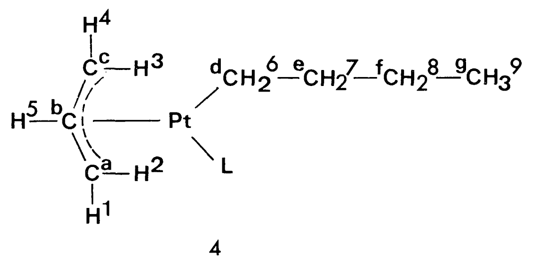
Synthesis of Complex 1f. Complex **1f** was prepared from [Pt(η^3-1-MeC$_3$H$_4$)Cl(PPh$_3$)] and LiMe by the method analogous to the preparations of **1a**—**1e**. Brownish yellow solid (71%); ^{1}H NMR (C_6D_6) (for proton and carbon numbering schemes, see the structure for **2**) δ=1.13 (3H, d, J_P=5.0, J_{Pt}=84.4 Hz, Pt-Me), 1.85 (3H, t, J_{Pt}=44.4 Hz, Me), 2.20 (1H, d, J_5=12.6, J_{Pt}=40.2 Hz, H^2), 2.83 (1H, m, J_{Pt}=67.1 Hz, H^3), 3.20 (1H, d, J_5=7.3 Hz, H^1), and 4.43 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=−5.4 (d, J_P=5.8, J_{Pt}=834 Hz, Pt-Me), 16.0 (d, J_P=4.4 Hz, Me), 56.3 (s, J_{Pt}=42.6 Hz, C^a), 64.9 (d, J_P=39.6, J_{Pt}=131 Hz, C^c), and 112.0 (s, J_{Pt}=20.5, C^b).

Synthesis of Complex 1g. To a stirred solution of [Pt(μ-Cl)(η^3-2-MeC$_3$H$_4$)]$_2$ in THF kept at −20 °C a twice molar amount of PPh$_3$ in THF was added dropwise. The solution was warmed up to room temperature resulting in a pale yellow suspension, to which an ether solution of LiMe (a three quaters equivalent based on the amount of PPh$_3$) was added dropwise with stirring. The resulting yellow solution was dried up in vacuo and the residue was treated as described above. Brownish yellow solid (30%); mp 104—107 °C (decomp); ^{1}H NMR (C_6D_6) (for proton and carbon numbering schemes, see the structure for **2**) δ=1.39 (3H, d, J_P=6.2, J_{Pt}=86.4 Hz, Pt-Me), 1.70 (3H, s, J_{Pt}=44.4 Hz, Me), 2.43 (1H, dd, J_4=2.2, J_P=11.0, J_{Pt}=64.0 Hz, H^3), 2.46 (1H, s, J_{Pt}=40.0 Hz, H^2), 3.47 (1H, d, J_4=2.9 Hz, H^1) and 3.48 (1H, m, H^4); ^{13}C NMR (C_6D_6) δ=−17.3 (s, Pt-Me), 24.6 (s, Me), 52.1 (d, J_P=44.1, J_{Pt}=164 Hz, C^c), 61.6 (s, C^a), and 123.4 (s, C^b) (coupling constants except that for C^c are unknown because of low resolution of the spectrum).

Found: C, 53.88; H, 4.83%. Calcd for $C_{23}H_{25}PPt$: C, 52.38; H, 4.78%.

Synthesis of [Pt(η^3-C$_3$H$_5$)Bu(PPh$_3$)] (3). Complex **3** was prepared from [Pt(η^3-C$_3$H$_5$)Cl(PPh$_3$)] and LiBu by the method analogous to the preparations of **1a**—**1e**. Brownish yellow solid (34%); mp 82—84 °C (decomp); ^{1}H NMR (C_6D_6) (for proton and carbon numbering schemes, see the structure **4**) δ=0.99 (3H, t, J_8=7.3 Hz, H^9), 1.47 (2H, m, H^8) (application of a homodecoupling technique for this signal reduced the multiplicity of the H^9-triplet to a singlet), 2.06 (4H, m, H^6 and H^7), 2.43 (1H, d, J_5=13.7, J_{Pt}=41 Hz, H^2), 2.47 (1H, t, J_5=J_P=10.7 Hz, H^3), 3.36 (1H, dd, J_4=2.0, J_5=7.3 Hz, H^1), 3.68 (1H, m, H^4), and 4.60 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=10.4 (d, J_P=4.4, J_{Pt}=774 Hz, C^d), 14.5 (s, C^g), 29.1 (s, J_{Pt}=50.6 Hz, C^e), 39.0 (s, J_{Pt}=11.8 Hz, C^f), 51.6 (d, J_P=43, J_{Pt}=187 Hz, C^c), 61.7 (s, C^a), and 110.0 (s, C^b).

Found: C, 54.33; H, 5.25%. Calcd for $C_{25}H_{29}PPt$: C, 54.05; H, 5.26%.



4

Conversion of 1b into η^1-Allyl Complexes 5a—5c. Synthesis of 5a. Complex **1b** (0.941 mmol) and dppe (0.941 mmol) were placed in a flask kept at −60 °C. Toluene

(20 cm^3) precooled to −50 °C was added to the flask and the mixture was warmed up to room temperature over an 1 h interval with stirring, during which the pale yellow suspension changed to a yellow solution. The solvent was removed in vacuo, the residue was extracted with ether, and then the extract was concentrated. On addition of hexane, a white precipitate was deposited, which was filtered, washed with hexane, and dried in vacuo. Colorless solid (62%); mp 146—149 °C (decomp); IR (Nujol) 1601 cm^{-1} (C=C); ^{1}H NMR (C_6D_6) (for proton and carbon numbering schemes, see the structure for **6**) δ=1.48 (3H, t, $J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=7.3$, $J_{\mathrm{Pt}}=69.6$ Hz, Me), 3.07 (2H, q, $J_5=J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=9.3$, $J_{\mathrm{Pt}}=99.4$ Hz, Pt–CH$_2$) 4.68 (1H, dt, $J_5=9.8$, $J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=2.9$, $J_{\mathrm{Pt}}=27.3$ Hz, H^1), 4.87 (1H, d, $J_5=16.6$, $J_{\mathrm{P}}\simeq0$, $J_{\mathrm{Pt}}=27.8$ Hz, H^2), and 6.59 (1H, m, H^5); ^{13}C NMR (C_5D_6) δ=4.24 (dd, $J_{\mathrm{P,trans}}=96.9$, $J_{\mathrm{P,cis}}=7.2$, $J_{\mathrm{Pt}}=616$ Hz, Me), 27.42 (dd, $J_{\mathrm{P,trans}}=89.5$, $J_{\mathrm{P,cis}}=4.4$, $J_{\mathrm{Pt}}=549$ Hz, C^a), 104.4 (d, $J_{\mathrm{P,trans}}=7.4$, $J_{\mathrm{Pt}}=61.6$ Hz, C^c), and 146.8 (d, $J_{\mathrm{P,trans}}=7.4$, $J_{\mathrm{Pt}}=64.6$ Hz, C^b).

Found: C, 55.08; H, 4.94%. Calcd for $C_{30}H_{32}P_2Pt$: C, 55.47; H, 4.97%.

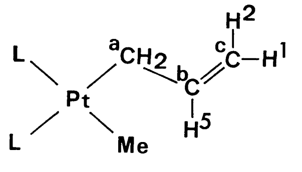
Synthesis of 5b. To a solution of **1b** (0.292 mmol) in toluene (5 cm^3) kept at −30 °C a toluene (10 cm^3) solution of dppen (0.290 mmol) precooled to −30 °C was added dropwise with stirring. The solution became turbid at the initial stage of addition and turned again homogeneous finally. The resulting solution was warmed up to room temperature and stirred for further 30 min. After the solvent was removed in vacuo, the residue was extracted with ether and the extract was evaporated to dryness to leave a pale yellow solid, which was washed with a large amount of hexane and dried in vacuo. Pale yellow solid (59%); mp 143—145 °C (decomp); IR (Nujol) 1607 cm^{-1} (C=C); ^{1}H NMR (C_6D_6) δ=1.53 (3H, t, $J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=7.3$, $J_{\mathrm{Pt}}=70.3$ Hz, Me), 3.05 (2H, q, $J_5=J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=9.1$, $J_{\mathrm{Pt}}=100$ Hz, Pt–CH$_2$), 4.66 (1H, dt, $J_5=9.8$, $J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=2.9$, $J_{\mathrm{Pt}}=28.3$ Hz, H^1), 4.96 (1H, dt, $J_5=16.9$, $J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=3.2$, $J_{\mathrm{Pt}}=28.8$ Hz, H^2), and 6.56 (1H, m, H^5); ^{13}C NMR (C_6D_6) δ=3.53 (dd, $J_{\mathrm{P,trans}}=98.3$, $J_{\mathrm{P,cis}}=5.9$, $J_{\mathrm{Pt}}=640$ Hz, Me), 26.12 (d, $J_{\mathrm{P,trans}}=92.4$, $J_{\mathrm{Pt}}=555$ Hz, C^a), 105.0 (d, $J_{\mathrm{P,trans}}=7.4$, $J_{\mathrm{Pt}}=66.0$ Hz, C^c), and 146.6 (d, $J_{\mathrm{P,trans}}=7.3$, $J_{\mathrm{Pt}}=61.6$ Hz, C^b).

Found: C, 56.12; H, 4.71%. Calcd for $C_{30}H_{30}P_2Pt$: C, 55.64; H, 4.67%.

Synthesis of 5c. To a solution of **1b** (0.263 mmol) in toluene (5 cm^3) kept at −40 °C a toluene (10 cm^3) solution of PPh$_3$ (0.263 mmol) precooled to −30 °C was added slowly with stirring. When the solution was warmed gradually, a white precipitate began to form at about −25 °C. The yellow suspension thus obtained was stirred for further 20 min and cooled again to −50 °C. The supernatant liquid was removed by filtration, the residue was washed twice with cold (−50 °C) toluene and hexane (ca. 20 °C), successively, and then dried in vacuo. White solid (67%), mp 163 °C; IR (Nujol) 1600 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ=0.55 (3H, t, $J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=7.6$, $J_{\mathrm{Pt}}=67.4$ Hz, Me), 2.18 (2H, q, $J_5=J_{\mathrm{P,trans}}=J_{\mathrm{P,cis}}=9.5$, $J_{\mathrm{Pt}}=94.8$ Hz, CH$_2$), 4.30 (2H, m, H^1 and H^2), and 5.84 (1H, m, H^5); ^{13}C NMR (CDCl$_3$) δ=11.19 (dd, $J_{\mathrm{P,trans}}=93.0$, $J_{\mathrm{P,cis}}=7.9$, $J_{\mathrm{Pt}}=636$ Hz, Me), 31.11 (d, $J_{\mathrm{P,trans}}=87.5$, $J_{\mathrm{Pt}}=560$ Hz, C^a), 104.0 (d, $J_{\mathrm{P,trans}}=6.40$, $J_{\mathrm{Pt}}=69.9$ Hz, C^c), and 145.2 (d, $J_{\mathrm{P,trans}}=7.9$, $J_{\mathrm{Pt}}=63.4$ Hz, C^b).

Found: C, 60.95; H, 4.90%. Calcd for $C_{40}H_{38}P_2Pt$: C, 61.93; H, 4.94%.

The Reaction of 1b with 2,4-Pentanedione. Complex **1b** (0.39 mmol) was dissolved in 2,4-pentanedione (Hacac) (20 cm^3) and the resulting solution was stirred overnight. Concentration and the addition of hexane gave a white precipitate of [Pt(acac)Me(PPh$_3$)] (**7**), which was filtered, washed with hexane, and dried in vacuo. GLPC analysis of the gaseous components liberated during the reaction qualitatively confirmed the evolution of propylene exclusively. White powder (68%); mp 204—208 (decomp); ^{1}H NMR (CDCl$_3$) δ=0.65 (3H, d, $J_{\mathrm{P}}=2.4$, $J_{\mathrm{Pt}}=75.0$ Hz, Pt–Me), 1.62 (3H, s, acac-Me$_{\mathrm{cis-P}}$), 1.96 (3H, s, acac-Me$_{\mathrm{trans-P}}$), 5.34 (1H, s, acac-CH); ^{13}C NMR (CDCl$_3$) δ=−18.0 (d, $J_{\mathrm{P}}=9.2$, $J_{\mathrm{Pt}}=721$ Hz, Pt–Me),27.6 (d, $J_{\mathrm{P}}=5.6$ Hz, acac-Me$_{\mathrm{trans-P}}$), 28.0 (s, acac-Me$_{\mathrm{cis-P}}$), 101.2 (s, acac-CH), and 184, 186 (s, acac-CO).



6

Found: C, 50.03; H, 4.40%. Calcd for $C_{24}H_{25}O_2PPt$:C, 50.44; H, 4.41%.

Thermolysis. A solid or solution sample was placed in a Schlenk tube and degassed several times by the freeze-pump-thaw method. A standard gas of a constant volume was introduced to the tube through a manometer, and then the sample was thermolyzed and the gases liberated were analyzed by GLPC. Propane was used as an internal standard and diphenylmethane as a solvent. The area of a gas chromatographic peak in comparison with that of a standard was used for quantitative purpose. The area was corrected for the relative solubility of a particular gas to propane in the employed solvent. A Yanaco G-180 gas chromatograph was employed for the gas analysis. Porapak Q (80—100 mesh, 2 m) or TCP C-22 (60—80 mesh, 8 m) was also used as packings.

Electrochemical Apparatus and Procedures. Voltammetric experiments were carried out in a standard three-electrode cell using a glassy carbon as working, a platinum rod as counter, and Ag/AgCl as reference electrodes, respectively. Controlled-potential electrolysis and coulometric experiments were performed in a specially designed cell equipped with the double junction connecting working and reference electrodes. A glassy carbon, a platinum rod (separated by an ungrazed tube), and $\mathrm{Pt/(I_3^-+I^-)}$ were used as working, counter, and reference electrodes, respectively. Use of the $\mathrm{Pt/(I_4^-+I^-)}$ electrode is recommended for the high potential stability for variation of electric current and the small hysteresis effect on a thermal change.[11] A Yanaco polarographic analyzer Model P1100 was employed as the voltammetric unit.

For these electrochemical experiments, THF was used as a solvent and $(\mathrm{Bu_4N})^+(\mathrm{PF_6})^-$ (hereafter abbreviated as TBAHFP) as a supporting electrolyte. The $\mathrm{Pt/(I_3^-+I^-)}$ reference electrode was constructed by mixing two acetonitrile solutions of I$_2$ (0.05 mol dm^{-3}) and NaI (0.1 mol dm^{-3}) in the volume ratio of 1:1 and placing a platinum rod in the resulting solution. All experiments were performed under argon at 23 °C. GLPC analysis of the gaseous components liberated on electrolysis was carried out using the same instrument and columns as described above. In this case, the gaseous components liberated on electlolysis were collected in a gas sampler and analyzed. Instead of propane, argon was used as an internal standard and the treatment for quantitative purpose was the same as that done in the thermolysis experiments.

Measurements. IR (Nujor or neat) spectra were recorded on a Jasco DS-701G spectrometer. Proton (400 MHz) and carbon-13 (100.5 MHz) NMR spectra were recorded on a JEOL JNM GX-400 instrument, both with $SiMe_4$ as internal standard. Mass spectra were measured with a JEOL JMS-D300 spectrometer (electron-impact type) by means of the direct injection method at an ionization potential of 30 eV. Melting points were determined on a Yanaco melting point apparatus Model MP-21.

Results and Discussion

Synthesis and Characterization of η^3-Allyl(methyl)platinum(II) Complexes. Complexes of the type [Pt(η^3-allyl)Me(L)] (**1a**—**1f**) were first synthesized by the method analogous to that for the corresponding palladium(II) complexes, i.e., the reaction of [Pt(η^3-allyl)Cl(L)] with LiMe in toluene at −10 °C (Eq. 1).

$$[\mathrm{Pt}(\eta^3\text{-allyl})\mathrm{Cl(L)}] + \mathrm{LiMe} \longrightarrow [\mathrm{Pt}(\eta^3\text{-allyl})\mathrm{Me(L)}] + \mathrm{LiCl} \qquad (1)$$

The basically same method was employed for the synthesis of **1g**, but in this case $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}2\text{-}MeC_3H_4)_2]$ was used as a starting material, and the mononuclear complex formed by the reaction with PPh_3 in THF was subjected to further reaction in situ. Recently, Clark et al.[5] reported their experimental results on the reaction between $[Pt(\eta^3\text{-}C_3H_5)Cl(PMePh_2)]$ and $SnMe_4$ in the 1:4 molar ratio in $CDCl_3$. When the reaction mixture was kept in the dark for 2 weeks, they identified, on the basis of its ^1H NMR, the formation of complex **1c** as one of the reaction products. However, the complex was not attempted to isolate.

All the newly isolated platinum complexes **1a**—**1g** are air-stable amorphous solids or oily substances and their structures are fully characterized by the ^1H and ^{13}C NMR data given in the Experimental section. Complexes **1a** and **1g** are very difficult to obtain in an analytically pure state and probably contain some impurities, but these are essentially pure on the NMR basis.

Some significant features of the ^1H and ^{13}C NMR are worthy of remark: (1) The methyl proton-platinum coupling constants (84—97 Hz) are very high relative to those (about 50—85 Hz) observed for several methylplatinum(II) complexes,[12] suggesting that the methyl group bind very strongly to the metal in the present complexes. (2) The coupling constant (40.0—42.4 Hz) of the allylic proton H^2 to ^{195}Pt is somewhat smaller than that (56.0—67.1 Hz) of H^3 to ^{195}Pt, probably reflecting stronger trans influence of the methyl than phosphine. (3) All the allylic carbons of **1a**—**1e** coupled to ^{195}Pt and the observed asymmetry in the J_{Pt} coupling constants, i.e., $J_{Pt\text{-}C^a}=20.8$—29.3, $J_{Pt\text{-}C^b}=16.1$—17.6, and $J_{Pt\text{-}C^c}=132$—156 Hz, seems to result from the contribution of asymmetric η^1–η^2 allyl bonding modes to the symmetrical η^3-allyl arrangement as was argued for the asymmetric J_{Pt} values of $[Pt\ (\eta^3\text{-}C_3H_5)Ph(P(4\text{-}FC_6H_4)_3)]$($J_{Pt\text{-}C^a}=18.0$ $J_{Pt\text{-}C^b}=12.2$, $J_{Pt\text{-}C^c}=152.3$ Hz).[5]

Interestingly, of the potentially possible four structural isomers of the η^3-1-methylallyl complex, only the syn isomer with the methyl substituent trans to P was isolated exclusively. This was identified on the basis of a comparison with chemical shift data of the unsubstituted allyl complexes and of the disappearance of a complex multiplet originally observed for H^4.

The characteristic mass spectral data for **1a**—**1e** and **1g** are given in Table 1. All the complexes exhibit their molecular-ion peaks. In contrast with the case of palladium, the fragment of ML^+ was not detected, indicating that in the platinum complexes coupling of the allyl and methyl groups to form 1-butene or 2-methyl-1-butene is difficult to occur. It is noteworthy that three particular fragments are detected, especially in the following order of intensity; $(PtL\text{-}1)^+ > Pt(allyl)L^+ > PtMeL^+$. The first fragment corresponds to loss of both the methyl radical and propylene molecule from the molecular ion. Thus the complexes tend to first lose the methyl group and then the allyl group in remaining $Pt(allyl)L^+$ abstracts a H-radical from the coordinated phosphine ligand, liberating propylene or 2-methylpropene. These characteristics are similar to those of the [Pd(η^3-allyl)Me(L)] complexes, although in the latter case somewhat different trend, i.e.,

Table 1. Characteristic Mass Spectral Data for Complexes **1a**—**1e** and **1g**[a]

Complex	M^+	$Pt(allyl)L^+$	$PtMeL^+$	$(PtL\text{-}1)^+$
1a	531(27)	516(100)	490(50)	474(307)
1b	513(19)	498(100)	472(14)	456(161)
1c	451(27)	436(100)	410(9)	394(182)
1d	389(41)	374(100)	348(15)	332(208)
1e	453(24)	448(100)	412(12)	396(175)
1g	527(15)	512(100)	472(3)	456(109)

[a] For convenience, the peak intensity (%) of the $[Pt(allyl)L]^+$ fragment is used as a base and only the most intense peak containing ^{195}Pt and ^{12}C isotopes is listed for each fragment.

Pd(allyl)L$^+$>PdL$^+$>(PdL-1)$^+$, was observed.[2]

Synthesis and Characterization of η^3-Allyl(butyl)-platinum(II) Complex. The butyl complex **3** was also synthesized from [Pt(η^3-C_3H_5)Cl(PPh_3)] and LiBu by the method analogous to the preparations of **1a**—**1f**. Complex **3** is an air-stable amorphous solid and the structure is fully characterized by the ^1H and ^{13}C NMR data given in the Experimental section.

Conversion into the η^1-Allyl(methyl)platinum(II) Complexes. On addition of tertiary phosphines, the η^3-allyl ligand in **1b** was converted into the η^1-allyl bonding and η^1-allyl(methyl)platinum(II) complexes **5a**—**5c** were isolated as air-stable solids. Although platinum is known to exhibit a most marked preference for forming η^1-allyl complexes between the nickel triad metals, examples of such a complex containing both η^1-allyl and alkyl ligands on a same central metal have never so far, to our knowledge, been known; only η^1-allyl(polyhalogenated phenyl)platinum complexes have been synthesized by Kurosawa et al.[6] All of the ^1H and ^{13}C NMR signals of **5a**—**5c** can be readily assigned to the methyl and η^1-allylic protons and carbons as shown in the Experimental section. Kurosawa et al. proposed the trans configuration for the PPh_3 ligands in complexes of the type [Pt(η^1-allyl)(aryl)(PPh_3)$_2$] on the IR spectral basis. In the present case, however, the cis configuration is unequivocally shown for **5c** on the basis of a coupling mode of the methyl carbon to phosphorus atoms, namely a doublet of doublets but not a triplet. The most striking aspect of the NMR data for these complexes is that remote coupling through five bonds to phosphorus are observed for the terminal olefinic protons of the η^1-allyl ligand as well as a four-bond coupling to phosphorus for C^3. These results, together with the high J_{Pt-CH_2} value of about 95—100 Hz, strongly suggest that in these complexes the η^1-allylic carbon is bound very strongly to platinum.

Isolation of the Methyl (2,4-pentanedionato)platinum(II) Complex. When η^3-allyl(methyl)platinum(II) complex **1b** was allowed to react with an equimolar amount of 2,4-pentanedione in benzene overnight, the starting complex was recovered. However, **1b** gradually reacted with neat 2,4-pentanedione to give the air-stable [Pt(acac)Me(PPh_3)] complex (**7**) with the evolution of propylene.

2,4-Pentanedione is usually present as an equilibrium mixture of keto-enol tautomers. Therefore, it behaves as an electrophile in certain cases and as a nucleophile in other cases. In the present case, however, Hacac does not act as an electrophile, because no evolution of a methane gas is recognized during the reaction. Instead, Hacac attacks on the metal center to form either one or both of the two possible intermediates represented in Eq. 2. Although the subsequent reaction seems to contain the electrophilic attack by the enol proton on the allyl terminal carbon or the methyl group, the preferential formation of the final product **7** but not the [Pt(acac)(η^1-allyl)(PPh_3)] complex might reflect the much more reactive nature of the η^1-allyl group than the methyl.

Thermolysis of the η^3-Allyl(methyl)platinum(II) Complexes. The PCy_3 and PPh_3 complexes, **1a** and **1b**, have a relatively high melting point (>138 °C), and hence the thermolysis of the solid samples **1a**—**1c** were performed under the conditions of 120 °C for 2 h in vacuo. These results are listed in Table 2, together with those obtained for [Pd(η^3-C_3H_5)Me(PPh_3)][2] for comparison. Owing to the high thermal stability of these platinum complexes, the total molar amount of the gases evolved on thermolysis are small in spite of the rather severe conditions than in the case of the palladium(II) complexes. As is seen in Table 2, the thermolysis of **1a**—**1c** in the solid state evolved propylene and methane as main organic products and no formation of 1-butene, the allylic alkylation product, was found. When the thermolysis was performed in diphenylmethane, no drastic change was recognized in the relative composition of propylene and methane (see Table 3, runs 1, 2, and 8). The propylene to methane ratio a little decreased only. These results are entirely different from those obtained for the corresponding palladium(II) complexes, in which ethane was a major organic product (see Tables

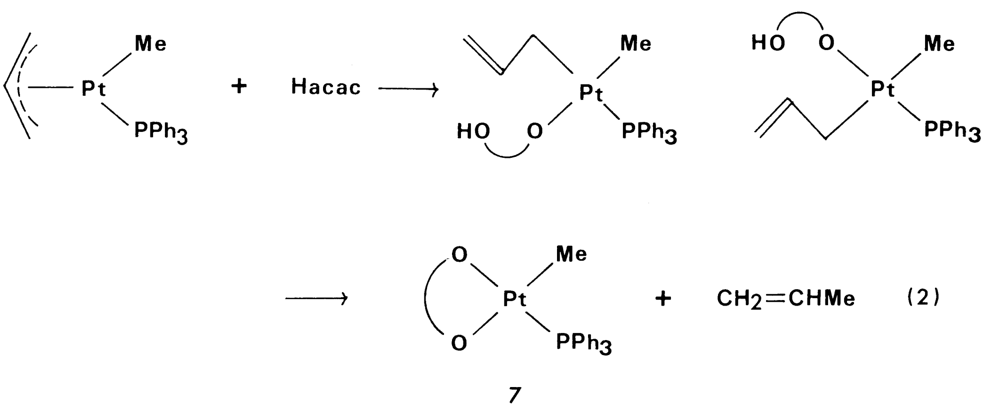


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Table 2. Gases Evolved in the Thermolysis of Complexes **1a**—**1c** in the Solid State[a]

Complex	Total mol per Pt	Evolved gas ratio				
		Methane	Ethylene	Ethane	Propylene	1-Butene
1a	0.06	14.1			85.9	
1b	0.20	21.5	1.0		77.5	
1c	0.37	18.0	1.0		80.0	1.0
Pd[b]	0.42[c]	3.2		77.5	3.3	16.1

a) Thermolysis in an evacuated tube under the conditions of 120 °C, 2 h. b) Data for $[Pd(\eta^3\text{-}C_3H_5)Me(PPh_3)]$ (100 °C, 40 min); see Ref. 2. c) In this case, the figure represents a total mol per Pd.

Table 3. Gases Evolved in the Thermolysis of Complexes **1a**—**1c** and **5a** in Solution[a]

Run	Complex	Additive[b]	Total mol per Pt	Evolved gas ratio				
				Methane	Ethylene	Ethane	Propylene	1-Butene
1	**1a**	None	0.05	30.8			69.2	
2	**1b**	None	0.17	37.4	1.1		61.5	
3	**1b**	PPh_3	0.10	5.9	0.6		93.5	
4	**1b**	Hacac	0.28	19.9	0.3		79.6	0.2
5	**1b**	st	0.08	31.8	1.2		67.0	
6	**1b**	Ph_2C_2	0.08	38.0	0.6		58.4	3.0
7	**1b**	ma	0.82	16.5	4.3		28.4	50.8
8	**1c**	None	0.11	23.9	1.5		74.6	
9	**5a**	None	0.07	9.7	0.6		84.9	4.7
10	Pd[c]	None	0.36[d]	4.2		79.7	12.9	3.2

a) Thermolysis of the sample (50 mg) in the degassed Ph_2CH_2 (1 cm^3) under the conditions of 100 °C, 2 h. b) Hacac= 2,4-pentanedione; st=stilbene; ma=maleic anhydride. An equimolar amount per complex was added. c) Data for $[Pd(\eta^3\text{-}C_3H_5)Me(PPh_3)]$ (50 °C, 1 h); see Ref. 2. d) In this case, the figure represents a total mol per Pd.

2 and 3). In the latter case, we proposed that the evolution of ethane occurs intermolecularly through the binuclear methyl-bridged intermediate $[Pd_2(\mu\text{-}Me)_2(\eta^3\text{-allyl})_2]$ formed by phosphine dissociation. The present results seem to reflect the rather substitution-inert character of these platinum complexes to prevent dissociation of phosphine.

Next we examined the effect of PPh_3 and other additives on thermolytic products. However, neither of the phosphine, olefin, acetylene, nor 2,4-pentanedione as a proton source could have an effect to cause the allyl–alkyl coupling. These results are somewhat different from the case of the palladium(II) complexes, in which the addition of phosphines and olefins also brought about the medium effect to promote coupling.[2] As described earlier, the addition of PPh_3 converts **1b** into the η^1-allyl complex **5c**. The results shown in Table 3 (runs 3 and 9) imply that in the η^1-allyl(methyl)platinum(II) complexes the allyl-metal bond is more preferentially cleaved. In contrast to these additives, the addition of maleic anhydride as a π-acid increased the total molar amount of the liberated gases and resulted in the evolution of 1-butene in the relative molar ratio of 50.0%.

The addition of maleic anhydride and other π-acidic olefins is known to accelerate reductive elimination of two organic groups in the complexes $[Pd(\eta^3\text{-allyl})(aryl)(phosphine)]$.[13—15] The reaction was ascertained to proceed via the 16-electron intermediary complex formed by replacement of the phosphine ligand by olefin.[14,15] Based on the extended Hückel MO calculations for $[Pd(\eta^3\text{-}C_3H_5)Me(H_2C{=}CH_2)]$ employed as a model, Kurosawa et al.[15] concluded that the coordination of olefin in place of the phosphine lowers the activation energy for reductive elimination and its effect is brought about by elevating HOMO of the allyl–Pd–Me fragment interacting properly with the π^* orbital of in-plane coordinated olefin. We are therefore interested in examining whether the electrochemical oxidation of the present complexes can have the effect comparable to the addition of π-acidic olefins to promote coupling or not.

Voltammetric Behavior of 1b and Related Complexes. Table 4 lists the peak potential values (vs. Ag/AgCl) from cyclic voltammograms for complexes **1a**—**1c** and **5a** in the presence or absence of additive in THF. Complexes **1b** and **1c** gave an irreversible cathodic peak at a potential near the negative limit of potential window, indicating that the complexes are hard to be electrochemically reduced. On the other hand, an anodic peak appeared at about 1.0 V for all complexes of **1a**—**1c**, suggesting that the complexes are subject to oxidation rather than reduction, although the oxidation process was also irreversible. No correlation was found between anodic peak potential (E_{pa}) of the complex and basicity (pK_a) of the phosphine ligand.

Figure 1 shows the cyclic voltammograms for complex **1b**, PPh_3, and a 1:1 mixture of **1b** and PPh_3, in THF. In addition to the irreversible cathodic peak at −2.78 V and the anodic peak at 1.22 V, **1b** shows one broad anodic peak at −0.28 V and one small cathodic peak at about −1.5 V. The former can be ascribed to oxidation of the species formed by a subsequent chemical reaction of the cathodic reduction product, while the latter to reduction of the chemical species originating from the anodic oxidation product. As the anodic peak at 1.22 V and the following small peak at −1.5 V resemble those of PPh_3 in both shape and potential (see Fig. 1), we can suppose that the PPh_3 ligand participates, more or less, in the oxidation process of **1b**. Moreover, it was confirmed by controlled-potential coulometry that the oxidation process of **1b** is that of one-electron. This result also supports the participation of PPh_3 since the ligand itself is known to undergo one-electron oxidation.[16]

The shape and potential of the anodic peak of **1b** do not appreciably change by the addition of olefins like stilbene and maleic anhydride. However, the addition of PPh_3 causes the appearance of a new anodic peak at 0.85 V with the formation of $[Pt(\eta^1\text{-}C_3H_5)Me(PPh_3)_2]$ in solution. The cyclic voltammogram having two anodic peaks is also observed for **5a** and it seems to be the characteristic of the η^1-allyl complexes (for **5b**, see Table 4). Such an oxidizable property of the η^1-allyl complexes may enhance nucleophilicity of the complexes as the result of elevating their HOMO. When an equimolar mixture of **1b** and PPh_3 in THF was electrolyzed at the first anodic peak potential of 0.85 V (corresponds to 0.63 V vs. $Pt/(I_3^- + I^-)$, see Table 5, footnote c) and the resulting solution was subjected to

Table 4. Anodic and Cathodic Peak Potential Values (E_{pa} and E_{pc} vs. Ag/AgCl) from Cyclic Voltammograms for Complexes **1a**—**1c** and **5a** in the Presence or Absence of Additive[a)]

		E_{pa}	E_{pc}
		V	V
Complex			
1a		1.12	Undetected
1b		1.22	−2.78
1c		1.04	−2.78
5a		1.06, 0.65	−2.98
Complex+additive[b)]			
1b	PPh_3	1.20, 0.85	−2.78
1b[c)]	PPh_3	1.2, 0.2 br	−1.66
1b	st	1.26	−2.9 br
1b	ma	1.22	−1.14, −2.45
Additive alone[b)]			
PPh_3		1.67	Undetected
st		Undetected	−2.67
ma		Undetected	−1.14, −2.45

a) In THF at 23 °C; scan rate=0.1 V s^{-1}; [complex]=0.1 mol dm^{-3}; [TBAHFP]=0.1 mol dm^{-3}; [additive]=1.0 mmol dm^{-3}; br=broad. b) st=stilbene; ma=maleic anhydride. c) After electrolysis at 0.85 V.

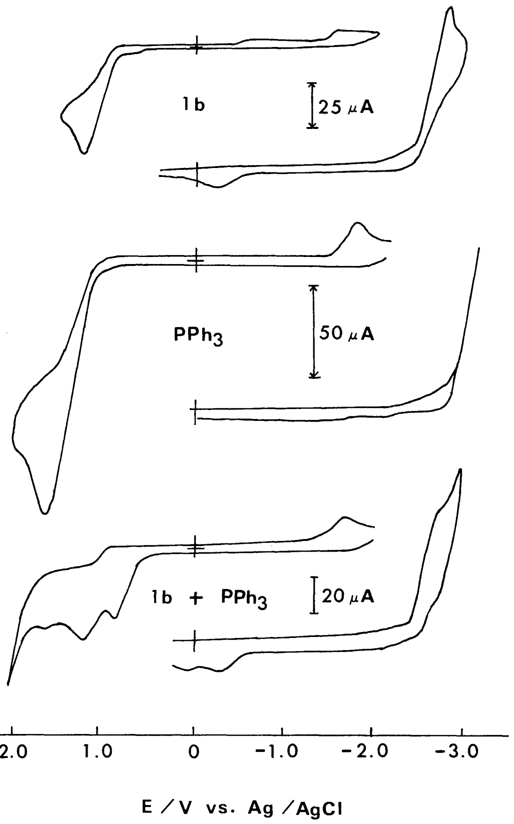
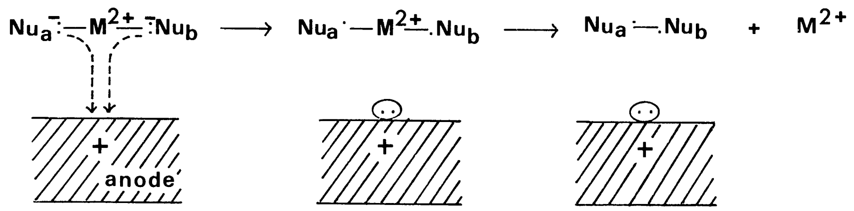


Fig. 1. Cyclic voltammograms for complex **1b**, PPh_3, and an equimolar mixture of **1b** and PPh_3, in THF; [complex]=1.0 mmol dm^{-3}; [TBAHFP]=0.1 mol dm^{-3}; scan rate=100 mV s^{-1}.

Table 5. Gases Evolved in the Electrolysis of Complex **1b** in THF[a)]

Run	Additive[b)]	E[c)]	Total mol per Pt	Evolved gas ratio				
		V		Methane	Ethane	Propylene	1-Butene	Others[d)]
1	None	0.88	0.80	19.2	0.0	5.1	50.0	25.7
2	PPh_3	0.62	0.91	28.4	4.5	10.2	53.4	3.4
3	PPh_3	0.86	1.20	17.6	6.2	9.8	56.6	9.8
4	st	1.04	0.62	18.3	0.0	6.7	53.3	21.7
5	ma	0.98	0.31	36.0	5.6	1.3	47.9	9.2

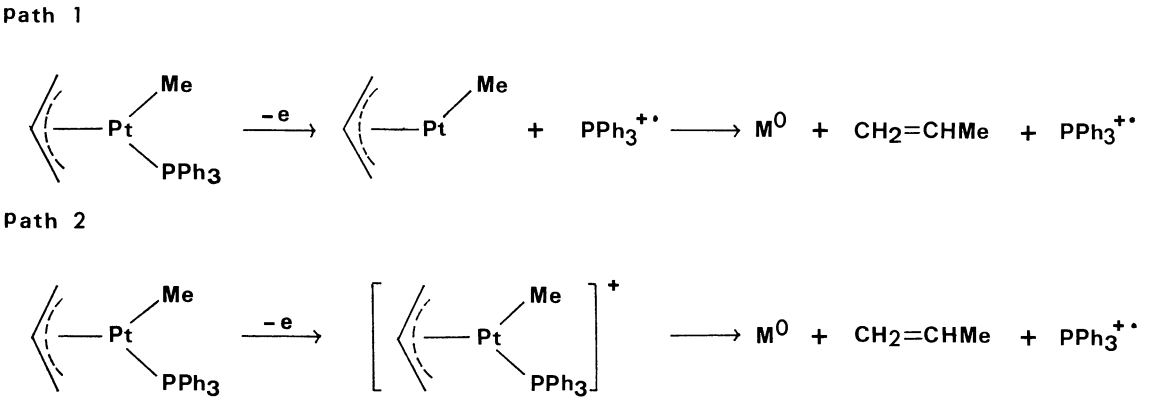
a) Electrolysis at 23 °C under argon; [complex]=3.9 mmol dm^{-3}; [TBAHFP]=0.1 mol dm^{-3}; [additive]=3.9 mmol dm^{-3}. b) st=stilbene; ma=maleic anhydride. c) Controlled-potential (vs. $Pt/(I_3^- + I^-)$) applied in electrolysis; E (vs. Ag/AgCl)=E (vs. $Pt/(I_3^- + I^-)$)+0.22 V. d) Runs 1 and 4 each includes butane as a main other species.



cyclic voltammetry, an irreversible cathodic peak appeared at −1.66 V (see Table 4). The peak potential is in accord with the reduction potential (−1.65 V) due to the chemical species originating from the electrochemical oxidation product of PPh_3 (see Fig. 1), suggesting that PPh_3 participates in the oxidation process of $[Pt(\eta^1\text{-}C_3H_5)Me(PPh_3)_2]$, too.

Electrochemical Oxidation of 1b in the Presence or Absence of Additive. Controlled-potential electrolysis of **1b** at the anodic peak potential (0.88 V vs. $Pt/(I_3^-+I^-)$) in THF at 23 °C gave 1-butene as a main organic product, indicating that the allyl–alkyl coupling reaction is largely promoted by the electrochemical oxidation of the complex (Table 5, run 1). This coupling-promoting effect is comparable to that of the addition of maleic anhydride in the thermolysis. A control experiment confirmed that the THF solution of **1b** in the presence of TBAHFP does not evolve any gases when permitted to stand for 48 h at 23 °C without electrolysis. Hence, the amount of the coupling product shown in Table 5 (run 1) is due to the net effect of electrochemical oxidation. This net effect was also observed in the electrolysis of **1b** in the presence of PPh_3 or stilbene as an additive. As is seen in Table 5 (run 5), two effects of the electrochemical oxidation and the addition of maleic anhydride are not cooperative in the electrolysis of **1b** in the presence of maleic anhydride, implying that only the addition of maleic anhydride without heating never causes coupling to form 1-butene. In fact, we confirmed that when a mixture of **1b** and maleic anhydride in THF was allowed to stand at 23 °C for 4 h under argon, any gases are not evolved.

The coupling-promoting effect of the electrolysis at an anodic peak potential can be schematically represented as shown above where Nu_a and Nu_b represent an allyl group and a methyl group, respectively, taken as nucleophiles. If electrochemical oxidation is to remove one electron from each of the Nu_a and Nu_b to anode, the Nu_a and Nu_b will become radical-like to readily form the coupling product, $Nu_a{:}Nu_b$. Thus anode is shown to function in the same manner as an electron withdrawing π-acid. When the one-electron oxidation and the participation of the PPh_3 ligand in its oxidation process are taken into account, the following two pathways are conceivable:



In path 1, the PPh_3 ligand in complex **1b** is oxidized to dissociate as a cation radical, while in path 2, the whole molecule of the complex is oxidized by the removal of one-electron from HOMO of the complex and then coupling proceeds with the simultaneous formation of the PPh_3-cation radical. Based on the fact that any indications of the promotion or the depression of coupling were not recognized by the addition of PPh_3 and stilbene, path 1 is ruled out.[17)] Therefore, we can conclude that in either case of the addition of π-acid or the electrochemical oxidation, HOMO of the complex plays an important role as a transition state for promoting coupling. The electrochemical oxidation of diorganonickel(II) complexes of the type $[NiRR'L_2]$ (R, R'=aryl or alkyl; L=tertiary phosphine) is also considered to give coupling products RR' via similar diorganonickel(III) cationic species $[NiRR'L_2]^+$.[18–20)]

A few electrochemical studies on η^3-allyl complexes have been reported so far and their attention has been focussed only on reduction reactions, i.e., cathodic electron transfer reactions.[21–23] The coupling reaction of a coordinated allyl ligand to give a hexa-1,5-diene complex has been known to occur by the chemical oxidation using silver(I) oxidant, but attempts to synthesize such a complex by electrochemical oxidation have not been done.[24]

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17) The addition of PPh_3 causes the formation of the η^1-allyl complex in solution, but, if electrochemical oxidation of the η^1-allyl complex accompanies dissociation of PPh_3 as is in path 1, the original η^3-allyl complex should be regenerated in solution. Hence, the oxidation at the anodic peak potential (0.63 V) for the η^1-allyl complex does not cause electrolytic oxidation (0.88 V) of the regenerated η^3-allyl complex and, therfore, coupling should be depressed in path 1.

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