

Synthesis and Reactions of Organoplatinum Compounds of C₆₀, C₆₀Pt_n

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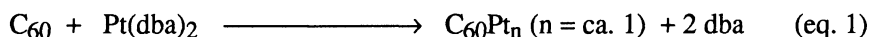
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The organoplatinum compound of C₆₀, C₆₀Pt_n (n = 1-2), was prepared either by the reaction of C₆₀ with Pt(dba)₂ or by the thermal disproportionation of C₆₀Pt_n (n = ca. 1). The C₆₀Pt_n obtained catalyzed the hydrogenation of diphenylacetylene regardless of the platinum content. Cleavage of carbon-platinum bonds of C₆₀Pt_n (n = ca. 1) was accomplished by the reactions with phosphines or phosphites, which provided general access to (η²-C₆₀)PtL₂ [L = phosphines and phosphites].

Transition metal complexes of fullerenes have contributed to the understanding of structure, electrochemical properties, and chemical reactivity of fullerenes.¹⁾ In our previous paper, we reported successful preparation of a new class of organometallic fullerene derivatives, C₆₀Pd_n, by the reaction of C₆₀ with Pd₂(dba)₃•CHCl₃ [dba = 1,5-diphenyl-1,4-pentadien-3-one].^{2a)} This compound is different from the other fullerene complexes in that the coordination of the palladium atom with C₆₀ is likely to form polymeric framework. As an interesting reactivity of this compound, we have discovered the catalytic activity in the hydrogenation of olefins and acetylenes^{2b)} or the facile cleavage of carbon-palladium bonds in C₆₀Pd_n by auxiliary ligands which provides a novel synthetic method of C₆₀PdL₂, where L = phosphines and phosphites.^{2c)} As an extension of these studies, we have been interested in synthesis and reactions of homologues of C₆₀Pd_n including different transition metals. In this paper, we wish to report successful preparation and several reactions of the platinum homologue, C₆₀Pt_n (n = ca. 1).

Preparation of C₆₀Pt_n: Preparation of C₆₀Pt_n (n = ca. 1) was accomplished by the reaction of C₆₀ with Pt(dba)₂ in toluene as shown in eq. 1.



In a typical example, a solution of C₆₀ (0.945 g, 1.31 mmol) dissolved in toluene (540 ml) was treated with a solution of Pt(dba)₂ (0.869 g, 1.31 mmol) in toluene (855 ml) at room temperature, and the solution was stirred at room temperature for 60 h to give a dark orange supernatant and black precipitates. HPLC and ¹H NMR analysis of the supernatant revealed that C₆₀ had disappeared and dba had formed. The formed black precipitates, which were not soluble in common organic solvents such as THF, CH₂Cl₂,

alcohols, or hydrocarbons, were filtered and washed with toluene (1.06 g). Concentration of the filtrate gave a dark orange solid, extraction of which with ether afforded recovered dba (612 mg, 2.62 mmol, 100% based on $\text{Pt}(\text{dba})_2$ charged). The residue was unreacted C_{60} (113 mg, 0.16 mmol). The following results strongly indicate that the precipitates can be assigned to the Pt homologue of C_{60}Pd_n , namely C_{60}Pt_n . First, almost all of the dba existing in the charged $\text{Pt}(\text{dba})_2$ was recovered from the filtrate as dba, which suggests that complete replacement of the dba ligand in $\text{Pt}(\text{dba})_2$ by C_{60} occurred during the reaction. Second, decomposition of the precipitates under a CO atmosphere gave C_{60} and Pt-black in quantitative yields, indicating that the precipitates are composed of only C_{60} and Pt.³⁾ Similar to C_{60}Pd_n ($n = \text{ca. } 1$), the IR spectrum of the precipitates showed peaks at 527 (s), 576 (w), 670 (m), 700 (s), 730 (w), 740 (m), 760 (m), 1182 (m), 1429 (w) cm^{-1} , whereas powdered X-ray analysis showing only broad weak peaks indicated that this solid is amorphous. The proportion of C_{60} to Pt in this solid was estimated to be 1 : 1.1 from the carbon content (78.2%) found in elemental analysis. Repeated experiments revealed the reproducibility of this procedure for the preparation of C_{60}Pt_n ($n = 1.2 \pm 0.2$).

The reaction of C_{60} with $\text{Pt}(\text{dba})_2$ was slower than that with $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ as shown in Figure 1. In contrast to the fact that the preparation of C_{60}Pd_n with $n = 1 - 7$ can simply be achieved by control of the charged ratio of C_{60} to $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, the slower substitution of the dba ligand on Pt by C_{60} made it difficult to synthesize C_{60}Pt_n with higher platinum contents, even when the reaction was carried out at higher temperatures. Attempted preparation of C_{60}Pt_3 or C_{60}Pt_5 by increasing the charged ratio of $\text{Pt}(\text{dba})_2$ to C_{60} resulted in the formation of precipitates which showed a weak and broad absorption around 1600 cm^{-1} in the IR spectrum, which indicates that the solid contains some amounts of dba bonded to the platinum atoms. In fact, the solid (20 mg) obtained by the reaction of C_{60} with 3 equivalents of $\text{Pt}(\text{dba})_2$ at 50 °C was decomposed by $\text{CO}^3)$ to give a mixture of C_{60} (8 mg), platinum black (9.3 mg), and dba (0.3 mg). This suggested that the composition of the solid would be $\text{C}_{60}\text{Pt}_{3.4}(\text{dba})_{0.3}$.

The only successful route to synthesize C_{60}Pt_n with higher Pt ratio without including dba is thermal disproportionation of C_{60}Pt_n ($n = \text{ca. } 1$). In a typical example, a suspension of $\text{C}_{60}\text{Pt}_{1.3}$ (30 mg) in xylene was heated under reflux for 24 h to give a mixture of $\text{C}_{60}\text{Pt}_{2.0}$ (19 mg) and C_{60} (10 mg). This method is reproducible in the synthesis of C_{60}Pt_n ($n = 1.9 \pm 0.2$).

Catalytic hydrogenation of diphenylacetylene over C_{60}Pt_n . As previously described, hydrogenation of diphenylacetylene was achieved with a catalytic amount of C_{60}Pd_n ($n > 3$), whereas C_{60}Pd_n with $n < 3$ did not exhibit the catalytic activity.^{2a,2b)} In sharp contrast, both $\text{C}_{60}\text{Pt}_{1.2}$ prepared by the reaction of C_{60} with

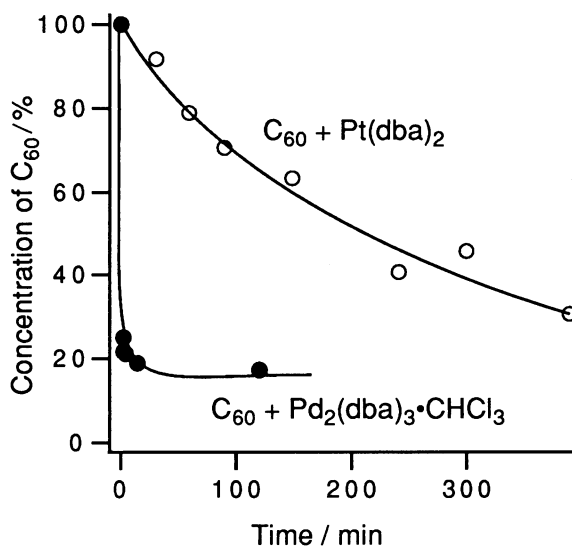
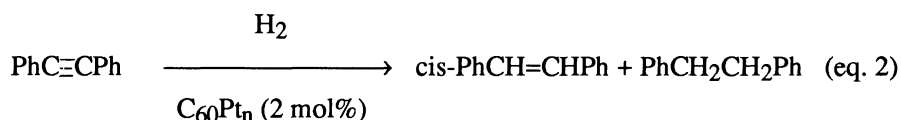


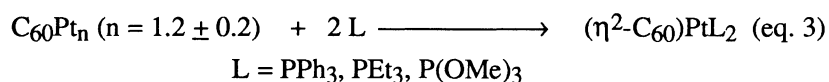
Fig. 1. Reaction profiles for the production of C_{60}M_n ($\text{M} = \text{Pd}, \text{Pt}$). The reduction rate of C_{60} in solution was monitored by HPLC [stationary phase, Develosil ODS-5; mobile phase, toluene / MeOH = 55 / 45; Detection, UV 350 nm; Internal standard, C_{70}].

Pt(dba)₂ and C₆₀Pt_{2.0} synthesized by the thermal disproportionation of C₆₀Pt_{1.2} exhibited the catalytic activity towards the hydrogenation of diphenylacetylene. Thus, a cyclohexane solution of diphenylacetylene was stirred at room temperature under a hydrogen atmosphere for 3 h in the presence of C₆₀Pt_{1.2} (2 mol% based on diphenylacetylene) to give a mixture of cis-stilbene and diphenylethane (3 : 7). The conversion of diphenylacetylene was 77%. Similar experiments with C₆₀Pt_{2.0} also gave a 3 : 7 mixture of cis-stilbene and diphenylethane with 88% conversion of diphenylacetylene.



The dramatic dependence of the hydrogenation activity of C₆₀Pd_n on the number of n stimulated us to propose that there could be two types of palladium atoms in C₆₀Pd_n; one acts as a binder of C₆₀ and does not exhibit the catalytic activity, and another exists on the surface of the particle similar to Pd / C and catalyzes the hydrogenation. In the platinum analogues, the hydrogenation proceeded even with C₆₀Pt_n (n < 3), suggesting that the catalytically active platinum species exists on the surface of the particle of C₆₀Pt_n regardless of the platinum content.

Synthesis of C₆₀PtL₂ from C₆₀Pt_n (n = ca. 1). Facile cleavage of the palladium-carbon bonds in C₆₀Pd_n by phosphines and phosphites is one of the most interesting chemical reactivity of this compounds to open a novel synthetic route to fullerene-palladium complexes with a general formula C₆₀PdL₂ (L = phosphine and phosphite). Similar reactions to cleave the carbon-platinum bonds in C₆₀Pt_n (n = ca. 1) also provides access to C₆₀PtL₂, when phosphines or phosphites are used as the auxiliary ligands. In a typical example, a suspension of C₆₀Pt_{1.2} (100 mg, 0.12 mmol) in toluene (30 mL) was treated with PPh₃ (53 mg, 0.20 mmol) at room temperature under an argon atmosphere. After stirring for 14 h, the mixture was filtered and the filtrate was concentrated. The dark green residue was recrystallized from a mixture of THF and hexane to form a dark green solid (115 mg, 75%). The spectral data⁴⁾ of the product was consistent with those of (η²-C₆₀)Pt(PPh₃)₂ and its cyclic voltammogram (0.3 mM in THF, Pt electrode, 0.2 M TBAPF₆, scan rate 0.2 V / sec) showed three reversible reduction waves identical to the reported potential values within the experimental error [obsd: -1.19, -1.80, -2.22 V; lit.⁵⁾ -1.21, -1.75, -2.23 vs. Cp₂Fe/Cp₂Fe⁺]. Using similar procedures, (η²-C₆₀)Pt(PEt₃)₂ and (η²-C₆₀)Pt[P(OMe)₃]₂ were also synthesized in 73 and 58% yield, respectively.⁴⁾



The fullerene-platinum complexes, (η²-C₆₀)Pt(PPh₃)₂ and (η²-C₆₀)Pt(PEt₃)₂, were synthesized by Fagan and coworkers by the reaction of C₆₀ with either (η²-CH₂=CH₂)Pt(PPh₃)₃ or Pt(PEt₃)₄.^{1a-c,5)} The present reaction not only offers an alternative synthetic route of these compounds but also provides an versatile route to similar complexes with different ligands such as P(OMe)₃. Although elucidation of the structures and electrochemical studies of this class of compounds were reported by Fagan et al,^{1a-c,5)} exploration of their chemical reactivity requires further exploration, to which the discovery of this versatile route would contribute.⁶⁾

In summary, we have discovered a synthetic route to C₆₀Pt_n. The products are proved to be an

intriguing starting point for studies of transition metal derivatives of fullerenes including catalysis and coordination chemistry.

The authors are grateful for Grants-in-Aid for Priority Areas from the Ministry of Education, Science, and Culture of the Japanese Government (04241215 and 0533105).

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- 3) The reaction $C_{60}Pt_n$ with CO generally induced the decomposition of the compound to C_{60} and Pt metals. In a typical example, a suspension of $C_{60}Pt_{1.1}$ (20 mg) in toluene (10 ml) was stirred at room temperature under a CO pressure (20 atm) for 15 h to form a mixture of C_{60} (17 mg) and Pt (3.3 mg).
- 4) $(\eta^2-C_{60})Pt(PPh_3)_2$: 1H NMR (270 MHz, $CDCl_3$) δ 7.22-7.33 (m, 18 H), 7.52-7.59 (m, 12H). ^{31}P NMR (109 MHz, $CDCl_3$) δ 26.84 (J_{Pt-P} = 3934 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.9 (t, J_{PC} = 4.6 Hz), 129.6, 133.6 (t, J_{PC} = 6.6 Hz), 134.5, 139.9, 141.5 (two closely overlapped signals), 142.0, 142.6, 142.7, 142.8, 143.4, 143.8 (two closely overlapped signals), 143.9, 144.0, 141.1, 144.5, 146.1, 147.8, 157.4. $(\eta^2-C_{60})Pt(PEt_3)_2$: 1H NMR (270 MHz, $CDCl_3$) δ 1.28 (dt, J_{HH} = 10.8 Hz, J_{PH} = 21.6 Hz, 18H), 2.14 (dq, J_{HH} = J_{PH} = 10.8 Hz). ^{31}P NMR (109 MHz, $CDCl_3$) δ 16.90 (J_{Pt-P} = 3670 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.5 (t, J_{PC} = 12.85 Hz), 19.3 (t, J_{PC} = 14.10 Hz), 134.9, 141.1, 141.5, 141.9, 142.1, 142.7, 142.9, 143.1, 143.7, 144.1, 144.2, 144.3, 144.4, 144.8, 146.8, 147.6, 159.4. $(\eta^2-C_{60})Pt[P(OMe)_3]_2$: 1H NMR (270 MHz, $CDCl_3$) δ 3.90 (d, J_{PH} = 10.7 Hz, 18H). ^{31}P NMR (109 MHz, $CDCl_3$) δ 142.2 (J_{Pt-P} = 5886 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.2, 135.5, 141.3, 141.6, 142.0, 142.2, 142.8, 143.0, 143.2, 143.6, 143.9, 144.0, 144.4, 144.7, 144.8, 146.5, 147.1, 157.7.
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- 6) An interesting observation which we recently discovered is a difference in ^{13}C NMR spectra between $(\eta^2-C_{60})Pd[P(OMe)_3]_2$ and $(\eta^2-C_{60})Pt[P(OMe)_3]_2$. At room temperature, the signals derived from C_{60} of the palladium complex were observed as an extensively broad singlet due to the haptotropic rearrangement or dissociation of the $Pd[P(OMe)_3]_2$ species in solution. In sharp contrast, the platinum complex did not show the fluxional behavior at this temperature, suggesting that the $Pt[P(OMe)_3]_2$ species bonded more tightly to C_{60} than the palladium analogue.

(Received March 14, 1994)