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Synthesis and Reactions of Organoplatinum Compounds of C_{60}, $C_{60}Pt_n$

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The organoplatinum compound of C_{60}, $C_{60}Pt_n$ (n = 1-2), was prepared either by the reaction of C_{60} with $Pt(dba)_2$ or by the thermal disproportionation of $C_{60}Pt_n$ (n = ca. 1). The $C_{60}Pt_n$ obtained catalyzed the hydrogenation of diphenylacetylene regardless of the platinum content. Cleavage of carbon-platinum bonds of $C_{60}Pt_n$ (n = ca. 1) was accomplished by the reactions with phosphines or phosphites, which provided general access to $(\eta^2\text{-}C_{60})PtL_2$ [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, $C_{60}Pd_n$, by the reaction of C_{60} with $Pd_2(dba)_3 \cdot CHCl_3$ [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 C_{60} 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 $C_{60}Pd_n$ by auxiliary ligands which provides a novel synthetic method of $C_{60}PdL_2$, where L = phosphines and phosphites.$^{2c)}$ As an extension of these studies, we have been interested in synthesis and reactions of homologues of $C_{60}Pd_n$ including different transition metals. In this paper, we wish to report successful preparation and several reactions of the platinum homologue, $C_{60}Pt_n$ (n = ca. 1).

Preparation of $C_{60}Pt_n$: Preparation of $C_{60}Pt_n$ (n = ca. 1) was accomplished by the reaction of C_{60} with $Pt(dba)_2$ in toluene as shown in eq. 1.

$$C_{60} + Pt(dba)_2 \longrightarrow C_{60}Pt_n \text{ (n = ca. 1) } + 2\text{ dba} \qquad \text{(eq. 1)}$$

In a typical example, a solution of C_{60} (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 C_{60} had disappeared and dba had formed. The formed black precipitates, which were not soluble in common organic solvents such as THF, CH_2Cl_2, 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 $Pt(dba)_2$ 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 $Pt(dba)_2$ was recovered from the filtrate as dba, which suggests that complete replacement of the dba ligand in $Pt(dba)_2$ 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 = 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 $C_{60}Pt_n$ ($n = 1.2 \pm 0.2$).

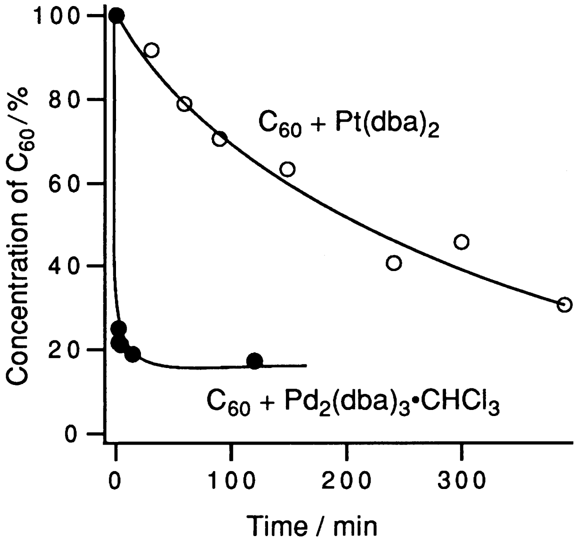

Fig. 1. Reaction profiles for the production of $C_{60}M_n$ (M = Pd, Pt). The reduction rate of C_{60} in solution was monitored by HPLC [stationary phase, Develosil ODS-5; mobile phase, toluene / MeOH = 55 / 45; Detection, UV 350 nm; Internal standard, C_{70}].

The reaction of C_{60} with $Pt(dba)_2$ was slower than that with $Pd_2(dba)_3 \cdot CHCl_3$ 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 $Pd_2(dba)_3 \cdot CHCl_3$, 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 $Pt(dba)_2$ 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 $Pt(dba)_2$ at 50 °C was decomposed by 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 $C_{60}Pt_{3.4}(dba)_{0.3}$.

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 = ca. 1). In a typical example, a suspension of $C_{60}Pt_{1.3}$ (30 mg) in xylene was heated under reflux for 24 h to give a mixture of $C_{60}Pt_{2.0}$ (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 $C_{60}Pt_{1.2}$ prepared by the reaction of C_{60} with

$Pt(dba)_2$ and $C_{60}Pt_{2.0}$ synthesized by the thermal disproportionation of $C_{60}Pt_{1.2}$ 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 $C_{60}Pt_{1.2}$ (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 $C_{60}Pt_{2.0}$ also gave a 3 : 7 mixture of cis-stilbene and diphenylethane with 88% conversion of diphenylacetylene.

$$\mathrm{PhC{\equiv}CPh} \xrightarrow[\mathrm{C_{60}Pt_n\ (2\ mol\%)}]{\mathrm{H_2}} \text{cis-}\mathrm{PhCH{=}CHPh} + \mathrm{PhCH_2CH_2Ph} \quad \text{(eq. 2)}$$

The dramatic dependence of the hydrogenation activity of $C_{60}Pd_n$ on the number of n stimulated us to propose that there could be two types of palladium atoms in $C_{60}Pd_n$; one acts as a binder of C_{60} 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 $C_{60}Pt_n$ ($n < 3$), suggesting that the catalytically active platinum species exists on the surface of the particle of $C_{60}Pt_n$ regardless of the platinum content.

Synthesis of $C_{60}PtL_2$ from $C_{60}Pt_n$ (n = ca. 1). Facile cleavage of the palladium-carbon bonds in $C_{60}Pd_n$ 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 $C_{60}PdL_2$ (L = phosphine and phosphite). Similar reactions to cleave the carbon-platinum bonds in $C_{60}Pt_n$ (n = ca. 1) also provides access to $C_{60}PtL_2$, when phosphines or phosphites are used as the auxiliary ligands. In a typical example, a suspension of $C_{60}Pt_{1.2}$ (100 mg, 0.12 mmol) in toluene (30 mL) was treated with PPh_3 (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 $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ and its cyclic voltammogram (0.3 mM in THF, Pt electrode, 0.2 M $TBAPF_6$, 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. Cp_2Fe/Cp_2Fe^+]. Using similar procedures, $(\eta^2\text{-}C_{60})Pt(PEt_3)_2$ and $(\eta^2\text{-}C_{60})Pt[P(OMe)_3]_2$ were also synthesized in 73 and 58% yield, respectively.4)

$$C_{60}Pt_n\ (n = 1.2 \pm 0.2) + 2\,L \xrightarrow{\qquad} (\eta^2\text{-}C_{60})PtL_2 \quad \text{(eq. 3)}$$
$$L = PPh_3,\ PEt_3,\ P(OMe)_3$$

The fullerene-platinum complexes, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ and $(\eta^2\text{-}C_{60})Pt(PEt_3)_2$, were synthesized by Fagan and coworkers by the reaction of C_{60} with either $(\eta^2\text{-}CH_2{=}CH_2)Pt(PPh_3)_3$ or $Pt(PEt_3)_4$.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 $C_{60}Pt_n$. The products are proved to be an intriguing starting point for studies of transition metal derivatives of fullerenes including catalysis and coordination chemistry.

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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) $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$: ^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 ($J_{Pt\text{-}P}$ = 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. $(\eta^2\text{-}C_{60})Pt(PEt_3)_2$: ^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 ($J_{Pt\text{-}P}$ = 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. $(\eta^2\text{-}C_{60})Pt[P(OMe)_3]_2$: ^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 ($J_{Pt\text{-}P}$ = 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 $(\eta^2\text{-}C_{60})Pd[P(OMe)_3]_2$ and $(\eta^2\text{-}C_{60})Pt[P(OMe)_3]_2$. 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.

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