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Facile Cleavage of Carbon-Palladium Bonds in $C_{60}Pd_n$ with Phosphines and Phosphites. An Alternative Route to $(\eta^2\text{-}C_{60})PdL_2$ and Discovery of Fluxionarity Suggesting the Rotation of C_{60} on the PdL_2 Species in Solution

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Carbon-palladium bonds in $C_{60}Pd_n$ are easily cleaved with phosphines and phosphites to afford $C_{60}[PdL_2]_n$. The reaction with $C_{60}Pd_n$ ($n = 1.0\text{-}1.4$) offers an alternative synthetic route to $C_{60}PdL_2$. Fluxional behavior indicating rotation of C_{60} on the PdL_2 species in solution is observed on ^{13}C NMR spectra of $C_{60}PdL_2$, where L = PMe_2Ph, PPh_2Me, and $P(OMe)_3$.

Particular interest has recently focussed on fascinating physical properties and chemical reactivities of C_{60} and other spherical carbon clusters (fullerenes).1,2) Organometallic complexes of fullerenes are one of the well-investigated compounds in this area; several Group VIII transition metal complexes were synthesized and subjected to crystallographic studies showing that fullerenes are coordinated to the metal center like an olefin.3,4) Although chemical reactivities of the fullerene complexes including their catalysis are an important problem, few investigation has been carried out except pioneering work on electrochemical properties by Fagan and co-workers with nickel, palladium, and platinum compounds.5)

In our previous papers, we reported successful preparation of organopalladium polymers, $C_{60}Pd_n$ and their catalysis toward hydrogenation of olefins and acetylenes.6) In further studies to explore chemical reactivities of these polymeric compounds, we discovered that a suspension of insoluble $C_{60}Pd_n$ in toluene gave a green solution in contact with PEt_3 or PPh_3. The color of the solution is characteristic to the formation of the Fagan's complex, $(\eta^2\text{-}C_{60})ML_2$ (M = Pd, Pt), which strongly indicates that the polymeric structure of $C_{60}Pd_n$ is easily decomposed by the coordination of phosphines and phosphites to give organometallic complexes, $C_{60}[PdL_2]_n$. In this paper, we wish to report application of this facile cleavage of carbon-palladium bonds in $C_{60}Pd_n$ [n = 1.0 - 1.4] with phosphines or $P(OMe)_3$ to a novel preparative method for $(\eta^2\text{-}C_{60})PdL_2$ as shown below. We also discovered fluxional behavior of the C_{60} ligand in solution in several compounds.

$$C_{60}Pd_n\ [n = 1.0 - 1.4] + 2\,L \longrightarrow (\eta^2\text{-}C_{60})PdL_2$$

L = PEt_3, PPh_3, $1/2{\cdot}Ph_2PCH_2CH_2PPh_2$ (dppe), PMe_2Ph, $PMePh_2$, $P(OMe)_3$

Table 1.[a)]

Entry	Ligand	Product	Yield % [b)]	^{31}P NMR (δ from H_3PO_4)[c)]	
1	PEt_3	$(\eta^2\text{-}C_{60})Pd(PEt_3)_2$	73	14.5	(-18.4)
2	PPh_3	$(\eta^2\text{-}C_{60})Pd(PPh_3)_2$	79	25.7[d)]	(-5.1)[d)]
3	dppe	$(\eta^2\text{-}C_{60})Pd(dppe)$	66	38.5	(-12.2)
4	PMe_2Ph	$(\eta^2\text{-}C_{60})Pd(PMe_2Ph)_2$	82	-11.7	(-44.9)
5	$PMePh_2$	$(\eta^2\text{-}C_{60})Pd(PMePh_2)_2$	72	30.1	(-26.5)
6	$P(OMe)_3$	$(\eta^2\text{-}C_{60})Pd[P(OMe)_3]_2$	72	149.4	(141.4)

a) All of the reactions were carried out in a similar manner as described in the text. b) Isolated yields after precipitation from THF-hexane. c) The spectra were measured in $CDCl_3$. In all compounds, the ^{31}P signals were observed as a sharp singlet at room temperature. The figures in parenthesis are the chemical shift (δ) of uncoordinated phosphines or phosphites in $CDCl_3$. d) lit. δ 25.4 (-4.8).[4)]

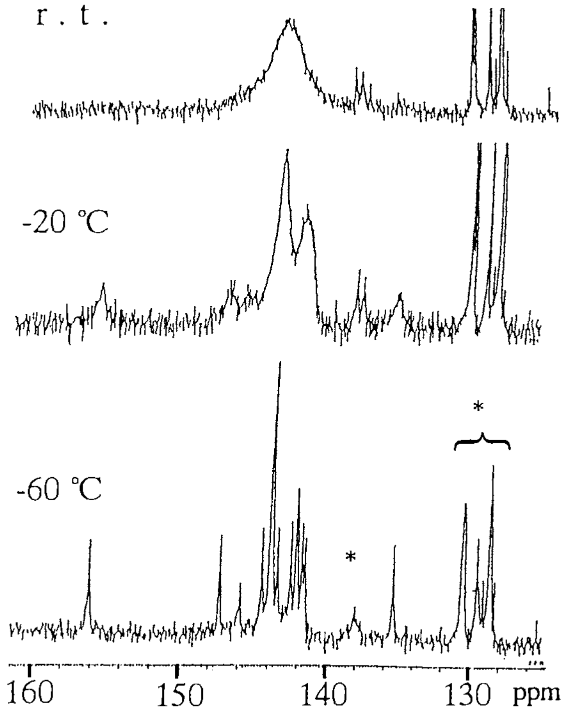
Preparation of $C_{60}Pd_n$ [n = 1.0 - 1.4; determined by elemental analysis] was made from a 2 : 1 mixture of C_{60} and $Pd_2(dba)_3 \cdot CHCl_3$ [dba = dibenzylideneacetone].[6)] Treatment of a suspension of $C_{60}Pd_n$ [n = 1.0 - 1.4] in toluene with PEt_3 (2 eq. to $C_{60}Pd_n$) gave a green solution at room temperature, from which green solids were obtained.[7)] Spectral and analytical data of the product are consistent to $(\eta^2\text{-}C_{60})Pd(PEt_3)_2$, and its cyclic voltammogaram was identical to the one in the literature.[5)] Similarly, the reaction of $C_{60}Pd_n$ [n = 1.0-1.4] with PPh_3, $Ph_2PCH_2CH_2PPh_2$ (dppe), PMe_2Ph, and PPh_2Me also gave the corresponding $(\eta^2\text{-}C_{60})PdL_2$. Trimethylphosphite also cleaved the carbon-palladium bond in $C_{60}Pd_n$ to afford $(\eta^2\text{-}C_{60})Pd[P(OMe)_3]_2$. The yields of the product and the chemical shifts of their ^{31}P NMR spectra, which showed downfield shifts compared with the uncoordinated phosphines under the same NMR conditions, are summarized in Table 1.

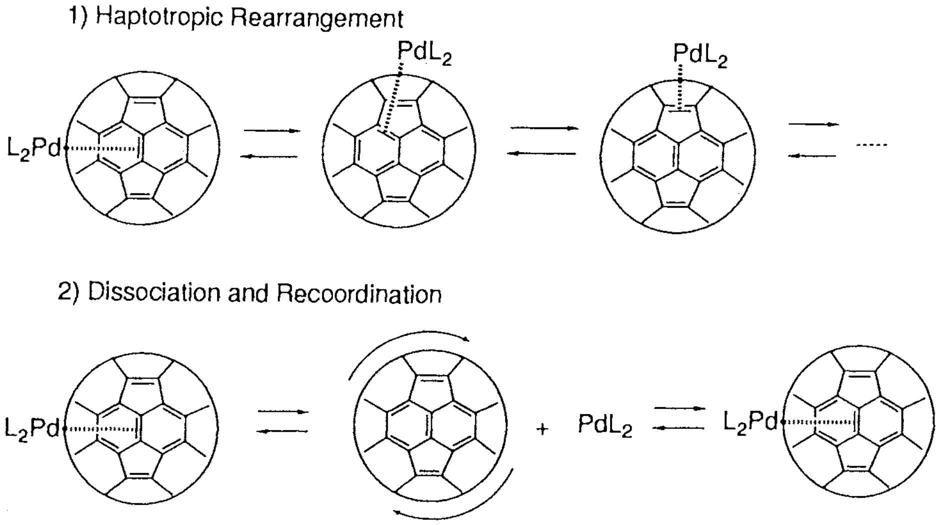
Although sharp singlets were observed for all of the complexes described above on ^{31}P NMR spectra at room temperature, well-resolved ^{13}C NMR spectra at room temperature were obtained only for the complexes with PEt_3, PPh_3, and dppe. The other three complexes showed broadening of the peaks. In a typical example, $\eta^2\text{-}C_{60}$ region of ^{13}C NMR spectrum of the PMe_2Ph complex, $(\eta^2\text{-}C_{60})Pd(PMe_2Ph)_2$, showed a broad singlet at room temperature as shown in Fig. 1. The peaks derived from PMe_2Ph in the complex are well-resolved. Variable ^{13}C NMR studies showed that all of the peaks were resolved at -60 °C, each peak was broadened and looks like five broad peaks at -20 °C, and all of the peaks were extensively broadened and coalesced to broad singlet at room temperature (Fig. 1). It was confirmed that no decomposition took place during the NMR measurement by comparison of ^1H and ^{13}C NMR spectrum before and after the measurement. Similarly, coalescence of $\eta^2\text{-}C_{60}$ region of ^{13}C NMR spectra to a broad singlet was observed in the spectrum of $(\eta^2\text{-}C_{60})Pd(PMePh_2)_2$ at 50 °C or $(\eta^2\text{-}C_{60})Pd[P(OMe)_3]_2$ at room temperature.

It is known that broadening and coalescence of the ^{13}C NMR peaks in organometallic complexes bound to aromatic or polyene ligands are explained by the haptotropic rearrangement,[8)] in which organometallic species are moving on delocalized π-electrons of the ligands in NMR time scale. Thus, this fluxional behavior described above can be interpreted as moving of the PdL_2 species on the surface of C_{60} or rotation of C_{60} on the PdL_2 species. The rapid rotation of C_{60} even in the solid states is an important feature of C_{60}.9) The present result apparently indicates that the rotation of C_{60} is also possible in the coordination compounds.

Two reaction pathways shown below can be proposed as the rotation mechanism; one is through the haptotropic rearrangement of PdL_2 species among the carbon-carbon double bonds in C_{60}, another is *via* reversible dissociation of C_{60} from the complex. The following evidence may support the dissociation mechanism as a favorable reaction pathway. First, local scrambling of the signals was not observed in the variable temperature NMR data. Second, Fagan and coworkers showed that dissociation of ML_2 species from $C_{60}ML_2$ (M = Ni, Pd, Pt) in solution was detected electrochemically, and the rate of the dissociation became slower on cooling the solution below 0 °C.4)

Fig. 1. VT-^{13}C NMR spectra (67.8 MHz) of (η^2-C_{60})Pd(PMe_2Ph)$_2$ in $CDCl_3$ [* = PMe_2Ph].





In summary, facile cleavage of $C_{60}Pd_n$ with phosphines and phosphites has provided a novel synthetic route to (η^2-C_{60})PdL_2. Besides the results described above, we have already obtained preliminary results that (η^2-C_{70})PdL_2 and (η^2-C_{60})PtL_2 can also be prepared from the polymeric precursors, $C_{70}Pd_n$ and $C_{60}Pt_n$, respectively. Utility of this preparative route is that complexes with a variety of L can be prepared, providing an interesting entry for further studies on chemical reactivities of this type of compounds. In fact, temperatures, at which fluxional behavior described above are observed, are apparently dependent on L in (η^2-C_{60})PdL_2. If the coalescence temperature reflects the facility of dissociation of C_{60} from the complex, the variable temperature NMR studies of (η^2-C_{60})ML_2 with various L would provide systematic information on the affinity of ML_2 species to C_{60}.

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7) In a typical example, $C_{60}Pd_{1.34}$ (200 mg, 0.23 mmol) suspended in toluene (70 ml) was treated with PEt_3 (68.5 μl, 0.46 mmol) at room temperature under a nitrogen atmosphere. After stirring overnight, the solution was filtered and the filtrate was concentrated under a reduced pressure. The crude product was purified by precipitation from a mixture of THF and hexane (187 mg, 73%). Despite some ambiguity on the peaks with close chemical shifts, ^{13}C NMR spectrum of C_{60} region consisting of less than 17 peaks suggests the most symmetrical structure, in which $Pd(PEt_3)_2$ species is bonded across the fusion of two six membered rings.$^{3,4)}$ mp 207-209 °C (dec). ^1H NMR (270 MHz; $CDCl_3$) δ 1.25 (dt, J_{PH} = 15.4 Hz, J_{HH} = 7.7 Hz), 1.94 (dq, $J_{PH} = J_{HH}$ = 7.7 Hz). ^{13}C NMR (125 MHz; $CDCl_3$) δ 8.8, 18.4, 135.1, 141.5, 141.7, 142.0, 142.2, 142.4, 143.6, 143.9 (4 peaks), 144.0, 144.6, 146.0, 147.2, 156.8 (2 peaks). IR (KBr, cm^{-1}) 526 (vs), 578 (w), 624 (w), 735 (w), 754 (m), 764 (m), 1031 (s), 1183 (w), 1237 (w), 1373 (w), 1415 (m), 1479 (w). Anal. Found: C, 80.98; H, 2.74%. Calcd for $C_{72}H_{30}P_2Pd$: C, 81.33, H, 2.84%. The cyclic voltammogram (THF, 0.2 M $TBAPF_6$, 0.2 V / sec provides reversible reduction waves at -1.16, -1.69, and -2.26 V (ferrocene internal reference) and an irreversible oxidation wave at +0.20 V. (lit.$^{5)}$ -1.18, -1.69, -2.23, and +0.20 V)

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