$C_{60}Pd_n$: The First Organometallic Polymer of Buckminsterfullerene

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The organometallic polymer, $C_{60}Pd_n$, is prepared from C_{60} and a Pd^0 precursor, and the palladium to C_{60} ratio (n) can be varied by thermal disproportionation.

Recent explosive developments of research on C_{60} and other spherical carbon clusters have provided fruitful contributions to understanding physical properties and chemical reactivities of these super aromatic molecules.[1,2] An interesting feature of C_{60} is the high reactivity of its surface towards metallic species; Fagan and coworkers reported $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ and $[(C_5Me_5Ru^+)_n(C_{60})]^{n+}$ as the first organometallic complexes including the coordination of π-electrons in C_{60} to the transition metal centre.[3] Several metallic species bound to the surface of C_{60} were also detected in the gas phase.[4] In this paper, we report an application of this particular reactivity of C_{60} with transition metal species to the synthesis of the first organometallic polymers. Thus, reaction of C_{60} with a palladium complex, $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) **1**, results in facile replacement of the dba ligand by C_{60} to form $C_{60}Pd_n$ as shown in eqn. (1).

$$C_{60} + n/2\,Pd_2(dba)_3 \cdot CHCl_3 \rightarrow C_{60}Pd_n + 3n/2\,dba + CHCl_3 \quad (1)$$

Exposure of a deep-purple benzene solution of **1** to a violet benzene solution of C_{60} furnished a dark-brown suspension. Filtration of the reaction mixture gave a black air-stable solid, which is insoluble in common organic solvents. The free dba ligand was quantitatively recovered from the filtrate. Electron probe microanalysis (EPMA) of the solid showed the composition consisting of carbon and palladium, indicating the formation of organopalladium polymer $C_{60}Pd_n$. The Pd : C_{60} ratios in $C_{60}Pd_n$ determined either by EPMA or elemental analysis were dependent on the charged ratios of C_{60} to **1** as shown in Table 1. With excess amounts of **1** to C_{60}, the Pd : C_{60} ratios in $C_{60}Pd_n$ were consistent with the ratios of charged **1** to C_{60}. In contrast, $C_{60}Pd_n$ (n = *ca.* 1) was always formed, when excess amounts of C_{60} were reacted with **1**. In this case, unreacted C_{60} was recovered from the reaction mixture, quantitatively. Fourier transform infrared (FTIR) spectra of $C_{60}Pd_n$ showed absorption at 527, 576.5 1182.5 and 1429 cm^{-1} similar to that of C_{60},[5] though the peaks were broader.

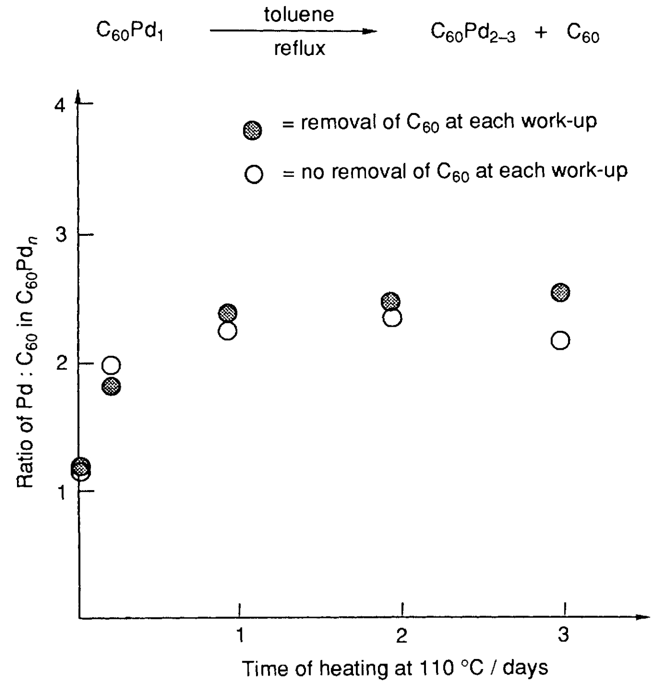

Fig. 1 Thermal recombination of Pd and C_{60} in $C_{60}Pd_n$

A suspension of the palladium polymer $C_{60}Pd_1$ in toluene was heated under reflux for several days to result in substantial increase of the Pd : C_{60} ratio in the polymer with regeneration of free C_{60}. As shown in Fig. 1, the Pd : C_{60} ratio was quickly increased to 2 : 1 within a day, and then gradually reached the ratio *ca.* 3 : 1. These results clearly suggests that thermal recombination of C_{60} and Pd induced the conversion of kinetically produced $C_{60}Pd_1$ to a thermodynamically more stable form, $C_{60}Pd_3$.

These results suggest that the palladium atoms act as a binder of C_{60} by coordination to the π-electrons on the

Table 1 Preparation of $C_{60}Pd_n$[a]

Run	Charged ratio of Pd : C_{60}	T/°C	t/h	Yield (%)[b]	Formed ratio of Pd : C_{60} Elemental analysis	Formed ratio of Pd : C_{60} EPMA
1	1 : 2	R.t.[c]	3	29 (70)	1.27 ± 0.04	1.19 ± 0.07
2		0	6	35 (65)	1.03 ± 0.03	1.00 ± 0.02
3	1 : 1	R.t.	3	67 (27)	0.93 ± 0.04	1.26 ± 0.03
4		0	6	94	1.03 ± 0.03	1.04 ± 0.01
5	2 : 1	R.t.	3	91	2.15 ± 0.03	2.05 ± 0.35
6	3 : 1	R.t.	3	74	2.84 ± 0.10	2.64 ± 0.05
7	4 : 1	R.t.	3	97	3.57 ± 0.05	3.27 ± 0.29

[a] All reactions were carried out in benzene or toluene (entries 2 and 4) under a nitrogen atmosphere. Each experiment was carried out at least twice to confirm the reproducibility of the Pd : C_{60} ratio. [b] Figures in parentheses are yields of recovered C_{60}. [c] R.t. = room temperature.

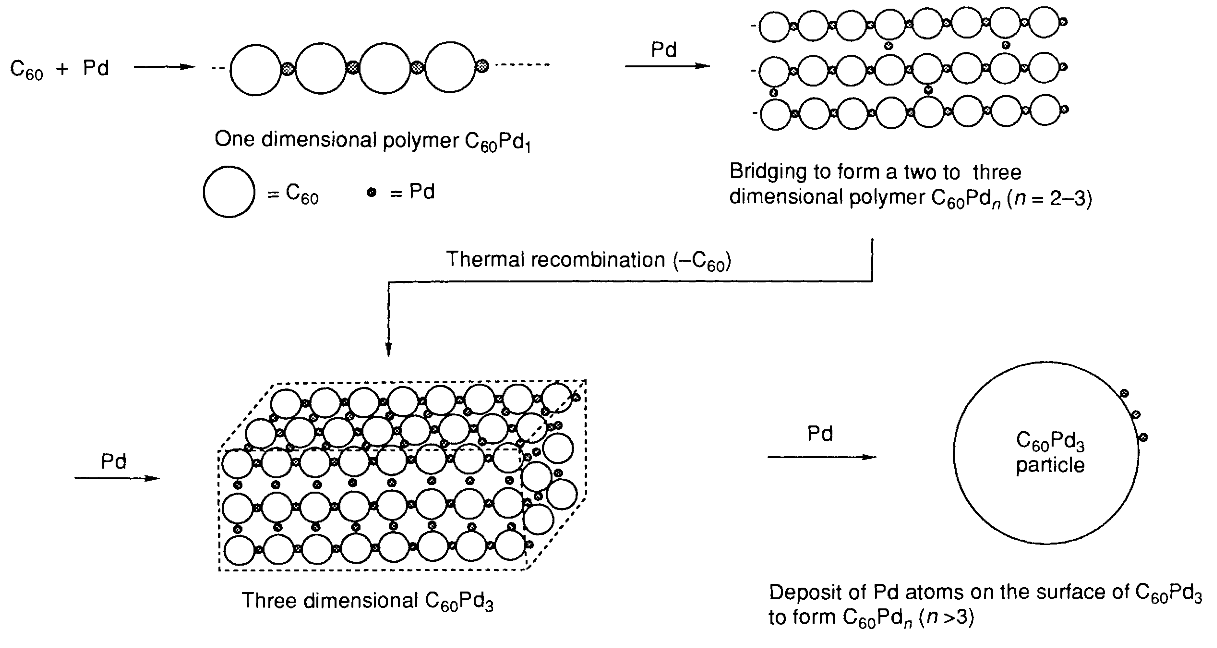

Fig. 2 Proposed mechanism for the formation of $C_{60}Pd_n$

aromatic surface; two C_{60} atoms are bound to one palladium centre analogous to a dumbbell complex $(C_{60})_2Ni^+$.[4] A proposed mechanism of the formation of $C_{60}Pd_n$ is illustrated in Fig. 2, in which a one dimensional polymer $C_{60}Pd_1$ is formed at the first stage, and then, insertion of additional palladium atoms between the polymer chains make bridges to form $C_{60}Pd_n$ ($n > 1$). The reaction of **1** with C_{60} may give $(C_{60})PdL_2$, where L = dba or solvent, as an intermediate; however, its isolation has so far been unsuccessful due to facile replacement of L by additional C_{60}. Since a C_{60} derivative, $C_{60}[Pt(PEt_3)_2]_6$, in which six platinum–phosphine species are bound to a C_{60} atom, has been reportedly characterized by Fagan and Calabrese,[6] it is reasonable that $C_{60}Pd_3$, in which each C_{60} atom is coordinated to six palladium atoms, is a thermodynamically stable form of the organometallic polymer. It is of interest that $C_{60}Pd_n$ ($n > 3$) was formed from a 4 : 1 mixture of **1** to C_{60}. In this case, an excess of palladium atoms would be deposited on the surface of $C_{60}Pd_3$. We discovered that heterogeneous hydrogenation of diphenylacetylene occurred with a catalytic amount of $C_{60}Pd_{3.5}$ in cyclohexane, whereas the catalytic activity was not observed with $C_{60}Pd_n$ ($n < 3$). This result indicates that surface palladium species exist on $C_{60}Pd_{3.5}$, but not on $C_{60}Pd_n$ ($n < 3$).

As metallic derivatives of C_{60}, alkali metal-doped C_{60} such as $C_{60}K_3$ have actively been investigated.[7] These crystalline compounds are ionic and unstable to air and water. In contrast, $C_{60}Pd_n$ is neutral, amorphous and stable to air.[8]

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