Platinum(0)–[60]fullerene complexes with chelating diphosphine ligands. Syntheses and characterisation of [Pt(η^2-C_{60})(L–L)] [L–L = $Ph_2P(CH_2)_nPPh_2$, n = 2 or 3]

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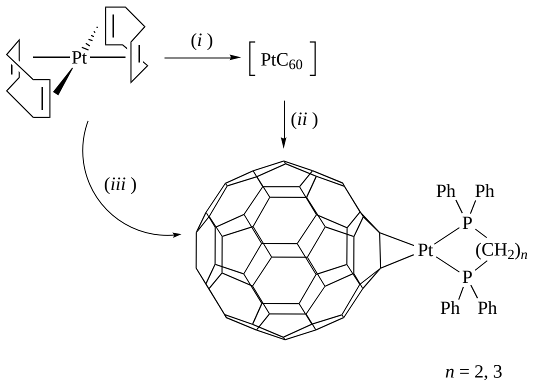
Reaction of [60]fullerene with [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) resulted in facile displacement of the cod ligand to form black-brown insoluble PtC_{60}. The reaction of a tetrahydrofuran suspension of PtC_{60} with bidentate diphosphines L−L = $Ph_2P(CH_2)_nPPh_2$ (n = 2 or 3) gave rise to cleavage of the carbon−platinum bond and formation of the [Pt(η^2-C_{60})(L−L)] complexes, which were characterised spectroscopically. The latter complexes can also be readily prepared in a one-pot synthesis by slowly adding an equimolar amount of [Pt(cod)$_2$] to a solution of [60]fullerene and the corresponding diphosphine in toluene.

Insight into the co-ordination behaviour of fullerenes was first provided by Fagan *et al.*,[1] who crystallographically established the η^2-bonding mode for [60]fullerene in [Pt(η^2-C_{60})(PPh$_3$)$_2$] and [{M(PEt$_3$)$_2$}$_6$(η^2-C_{60})] (M = Pd or Pt). Several other examples of this type of fullerene to metal co-ordination for a range of late transition metals have since been reported,[2] confirming that [60]fullerene behaves chemically like an electron-deficient alkene and that electron-rich late transition metals are particularly well suited for the preparation of π-bonded derivatives of [60]fullerene. Although most of these complexes were characterised by X-ray crystallography and ^{31}P NMR spectroscopy there is relatively little detailed information available on their ^{13}C NMR spectroscopic properties and reactivity.

In this paper we describe the reaction of [60]fullerene with [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) and the syntheses and spectroscopic characterisation of [Pt(η^2-C_{60})(L−L)] [L−L = 1,2-bis(diphenylphosphino)ethane (dppe) **1** or 1,3-bis(diphenylphosphino)propane (dppp) **2**].

Results and Discussion

When 1 equivalent of [Pt(cod)$_2$] in toluene is added to a toluene solution of [60]fullerene the cyclo-1,5-octadiene is readily displaced and PtC_{60} is obtained as a black-brown precipitate in quantitative yield. The compound is air-stable and insoluble in common organic solvents such as toluene, CH_2Cl_2 and tetrahydrofuran (thf). Based on the facts that (*a*) free cyclo-1,5-octadiene is quantitatively recovered from the filtrate and (*b*) the filtrate contains no residual unreacted [60]fullerene, it is estimated that the Pt to [60]fullerene ratio in this material is *ca.* 1:1. A similar type of reaction was described previously by Nagashima *et al.*,[3] who prepared polymeric organoplatinum compounds from [Pt(dba)$_2$] (dba = 1,5-diphenylpenta-1,4-dien-3-one) and [60]fullerene. There are however some differences. Whereas the latter reaction is reported to take *ca.* 60 h at room temperature, the reaction of [Pt(cod)$_2$] with [60]fullerene is complete in 1 h, presumably because the cod ligand is substituted more readily than the dba ligand. Furthermore, the IR spectra of the two platinum compounds differ slightly. Whether this is the result of a significant difference in the structure of the polymeric material, or caused by small amounts of insoluble impurities in the sample, could not be ascertained. Powder X-ray data could not be obtained because, like the compound reported by Nagashima *et al.*, the PtC_{60} compound is amorphous.



Scheme 1 (*i*) C_{60}; (*ii*) diphosphine, thf; (*iii*) C_{60}, diphosphine, toluene

Reaction of a suspension of PtC_{60} in thf with a slight excess of the chelating phosphine (Scheme 1) yielded a green solution. The ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR and electron-impact mass spectra of the purified product confirmed the formation of [Pt(η^2-C_{60})(L−L)] (L−L = dppe **1** or dppp **2**). Compounds **1** and **2** have also been prepared by dropwise addition of a solution of [Pt(cod)$_2$] to a solution of [60]fullerene and the corresponding diphosphine in toluene. In both procedures a small excess of the diphosphine is used because the ^{31}P NMR spectra of the crude products indicate that during the course of the reaction some of the diphosphine is converted into phosphine oxide. Complexes **1** and **2** are air stable for several days in the solid state and in toluene or benzene solutions. In $CHCl_3$ and thf solutions they slowly decompose to give C_{60}, which tentatively suggests that in solution [Pt(η^2-C_{60})(L−L)] is in equilibrium with [60]fullerene and free Pt(L−L) fragments. Owing to its low solubility in both thf and $CHCl_3$, [60]fullerene precipitates, displacing the equilibrium to one side and leading to disproportionation of the organometallic complex. When PtC_{60} was used as the starting material (procedure 1) a small amount of a second brownish green product (<5%) was obtained after purification on silica gel; this is possibly a difunctionalised [{Pt(L−L)}$_2$(η^2-C_{60})] complex. Preliminary results indicate that, with [Ni(cod)$_2$] as starting material, the one-pot synthesis can also be used to obtain the corresponding [Ni(η^2-C_{60})(L−L)] complexes.

The ^{1}H NMR data for compounds **1** and **2** show multiplets for the phenyl and the CH_2 backbone protons of the diphosphine ligands. The ^{31}P-{^{1}H} NMR spectra display singlet resonances at δ 51.0 [J(PtP) = 3588 Hz] for **1** and δ 16.0

[J(PtP) = 3561 Hz] for **2** with satellites due to the coupling of ^{31}P to the spin-$\frac{1}{2}$ isotope ^{195}Pt. For the analogous [Pd(η^2-C_{60})(dppe)], δ_P 38.5.[3] The large difference between the ^{31}P chemical shift values of compound **1** and **2** reveals a strong dependence of δ_P on the size of the chelate ring, a feature generally observed for chelating diphosphines co-ordinated to transition metals.[4] The J(PtP) values for both compounds are comparable with those reported for [Pt(η^2-C_{60})(PR_3)$_2$] (R = Ph or Et),[1,3] and conventional [Pt(η^2-alkene)(PR_3)$_2$] compounds.[5]

Although several [M(η^2-C_{60})L_n] complexes have been characterised in the solid state by X-ray crystallography and in solution by both ^{1}H and ^{31}P NMR spectroscopy, it has proved to be extremely difficult to obtain completely resolved ^{13}C NMR spectra. The ^{13}C NMR spectra for [Pt(η^2-C_{60})(PR_3)$_2$] (R = Ph, Et or OMe) have been reported,[3] however no assignment of the observed resonances was given. For the analogous [Pd(η^2-C_{60})(dppe)] compound no ^{13}C NMR data were available. Owing to their C_2 symmetry the [M(η^2-C_{60})L_2] monoadducts should give rise to seventeen ^{13}C NMR lines for the cage carbon atoms, four single-intensity resonances for the eight (4 × 2) carbon atoms on the mirror planes and thirteen double-intensity resonances for the remaining 52 (13 × 4) carbon atoms. We have made several attempts to obtain the ^{13}C NMR spectra of compounds **1** and **2** using different solvents, *i.e.* [$^2H_8$]thf, $CDCl_3$ and [$^2H_8$]-toluene, however in all cases the data acquisition and assignment were hampered by the low solubility of the complexes. In CS_2, a common NMR solvent for fullerene derivatives, both complexes decompose, probably as result of ligand displacement of [60]fullerene by the stronger co-ordinating CS_2, a behaviour also observed for Pt^0(η^2-alkene) compounds.[6] The fullerene regions of the ^{13}C NMR spectra of compounds **1** and **2** show three single- and thirteen double-intensity resonances, thus accounting for 58 C_{cage} atoms. One of these [60]fullerene resonances, observed at relatively low field {δ 160 [^2J(PtC) = 28.5 Hz] and 161.5 (m) for **1** and **2** respectively} is assigned to the carbon atoms adjacent to those directly co-ordinated to platinum. The resonances of cage carbons bonded directly to platinum are expected to shift upfield, reflecting the increased shielding due to π-back donation of the metal. For Pt(η^2-alkene) compounds this upfield shift usually amounts to 20–80 ppm,[7] and for the [{Pt(PEt_3)$_2$}$_6$$C_{60}$] hexaadduct reported by Fagan *et al.*[1] the Pt–C_{cage} atoms resonate at δ 79.2. We were unable to detect the Pt–C_{cage} resonance for compounds **1** and **2**, which may be attributed to their low intensity [*cis* and *trans* J(PC) and platinum-satellites] and interference from the solvent signals. The ^{195}Pt NMR spectrum of complex **1** shows one triplet resonance [δ 5149, J(PPt) = 3589 Hz], which agrees with the values generally observed for [Pt(η^2-alkene)(PPh_3)$_2$] compounds.[5,8] Satisfactory mass spectrometric data were obtained under electron-impact conditions (70 eV, *ca.* 1.12 × 10^{-17} J), indicating high thermal stability of complexes **1** and **2**.

In an attempt to change the co-ordination mode of the fullerene in [Pt(η^2-C_{60})(L–L)] and further to functionalise the fullerene cage, complex **1** was treated with several reagents. With MeI no reaction was observed after 12 h at 40 °C. Addition of $SnCl_2$ results in decomposition of **1** and liberation of [60]fullerene. The reaction of CF_3CO_2H with a toluene solution of complex **1** results in a change from green to orange-brown, however no products other than a small quantity of [60]fullerene could be isolated from the reaction mixture.

The reaction of PtC_{60} with other potential chelating phosphine ligands, *e.g.* 1,2-bis(diphenylphosphino)ferrocene (dppf), give rise to more complex product mixtures which are currently being investigated.

Experimental

General procedure

All preparations were carried out under an atmosphere of dry argon by conventional Schlenk techniques. All NMR spectra were obtained using a Bruker AMX-500 spectrometer. The solvents were carefully dried and distilled under nitrogen prior to use. Silica gel for column chromatography (Kieselgel 60, 70–230 mesh, E. Merck, Darmstadt, Germany) was dried and activated prior to use. The compound [Pt(cod)$_2$] was synthesized according to the literature procedure.[9]

Syntheses

PtC_{60}. In a typical experiment [60]fullerene (50–100 mg) in toluene (100 cm^3) was treated with an equimolar amount of [Pt(cod)$_2$] in toluene (10 cm^3). After stirring at ambient temperature for 1 h the solution was centrifuged. After decanting, the black-brown precipitate, PtC_{60}, was washed twice with toluene (30 cm^3) and dried *in vacuo*; quantitative yield. $\tilde{\nu}_{max}$/cm^{-1} (KBr): 1494m, 1459m, 1341w, 1185w, 757w, 728s, 695s, 667w, 580w, 562w, 525vs, 488m and 434m.

[Pt(η^2-C_{60})(L–L)] (L–L = dppe or dppp). *Procedure 1.* The diphosphine dppe or dppp (1.3–1.5 equivalents) was added to a suspension of PtC_{60} (30 mg, 0.033 mmol) in thf (25 cm^3) and stirred under argon at 50–60 °C for 3 h. The green solution was concentrated to *ca.* 5 cm^3 and subsequently purified by column chromatography on silica. Elution with thf–hexane (1:1) afforded an emerald-green fraction which was evaporated to dryness yielding compound **1** (32 mg, 74%) or **2** (30 mg, 68%) respectively (based on a 1:1 Pt:C_{60} ratio). Further elution with thf gave a small amount (<5%) of a brown-green compound, possibly the [{Pt(L–L)}$_2$(η^2-C_{60})] diadduct.

Procedure 2. A solution of [Pt(cod)$_2$] (21 mg, 0.05 mmol) in toluene (10 cm^3) was slowly added to a solution of [60]fullerene (36 mg, 0.05 mmol) and the corresponding diphosphine [26 mg (dppe), 27 mg (dppp), 0.065 mmol] in toluene (30 cm^3) at ambient temperature and subsequently stirred at 50 °C for 2 h during which the solution changed from purple to green. Concentration to *ca.* 5 cm^3, followed by addition of hexane (50 cm^3) caused the product to precipitate. The crude product was redissolved in toluene and purified by chromatography over alumina. Elution with toluene and subsequent removal of the solvent afforded pure green [Pt(η^2-C_{60})(L–L)] (**1**, 55 mg, 84%; **2**, 51 mg, 77%). This procedure can also be used to prepare the previously reported [Pt(η^2-C_{60})(PR_3)$_2$] compounds[1] in good yields.

[Pt(η^2-C_{60})(dppe)]: $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3060w, 2919m, 1772w, 1715w, 1571w, 1479w, 1458m, 1435s, 1421m, 1331m, 1277w, 1253w, 1185m, 1102m, 877w, 744m, 691s (br), 580w and 526s; δ_H(500 MHz, solvent $CDCl_3$, standard $SiMe_4$) 8.00 (8 H, m, PC_6H_5), 7.45 (12 H, m, PC_6H_5) and 2.68 (4 H, m, PCH_2); δ_P(202.48 MHz, solvent $CDCl_3$, standard H_3PO_4) 51.0 [J(PtP) = 3588 Hz]; δ_C(125.76 MHz, solvent $CDCl_3$, standard $SiMe_4$) 159.99 [4 C, m, ^2J(PtC) = 28.5, J(PC) ≈ 5 (average), Pt–C–*C*], 147.76, 147.07 (2 C, s), 145.10, 144.82 (2 C, s), 144.61, 144.52, 144.23, 143.81 (2 C, s), 143.33, 143.26, 142.30, 142.20, 141.71, 141.45, 135.53 (C_{60} resonances), 132.59 [8 C, t, J(PC) ≈ 7, C_{ortho}], 132.5 [4 C, m, J(PC) ≈ 24, C_{ipso}], 130.81 (4 C, s, C_{para}), 128.88 [8 C, t, J(PC) ≈ 5, C_{meta}] and 27.77 [2 C, br t, J(PC) ≈ 49 Hz, PCH_2]; δ_{Pt}(107.35 MHz, solvent $CDCl_3$, standard [$PtCl_6$]$^{2-}$) −5149 [t, J(PPt) = 3589 Hz]; electron-impact mass spectrum *m/z* 1314 (M^+, $PtC_{86}H_{254}P_2$).

[Pt(η^2-C_{60})(dppp)]: $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3053w, 2920m, 2856m, 1571w, 1481w, 1458m, 1434s, 1420m, 1346w, 1331m, 1277w, 1237w, 1184m, 1158w, 1100m, 1063w, 966w, 913w, 831w, 793w, 745m, 693s, 665m, 586w, 579m, 560w, 527s, 512s, 496w and 481w; δ_H(500 MHz, solvent $CDCl_3$, standard $SiMe_4$) 7.91 (8 H, m), 7.35 (12 H, m, PC_6H_5), 3.05 (4 H, m, PCH_2) and 2.20 (2 H, m, PCH_2CH_2); δ_P(202.48 MHz, solvent $CDCl_3$, standard H_3PO_4) 16.0 [J(PPt) = 3561 Hz]; δ_C(125.76 MHz, solvent [$^2H_8$]thf, standard $SiMe_4$) 161.5 (4 C, m, Pt–C–*C*), 149.37, 147.94 (2 C, s), 145.85, 145.45 (2 C, s), 145.26, 145.19, 145.18, 144.69 (2 C, s), 144.08, 143.97, 143.02, 142.78, 142.49, 141.69, 135.90 (C_{60} resonances), 133.57 (16 C, m, C_{ortho} and C_{ipso}), 131.09 (4 C, s, C_{para}), 129.1 [8 C, d, J(PC) ≈ 5 Hz, C_{meta}], PCH_2 and PCH_2CH_2 not observed; electron-impact mass spectrum *m/z* 1328 (M^+, $PtC_{87}H_{26}P_2$).

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