Heterometallic binuclear complexes involving the mercury—platinum bond as a source of a platinum carbenoid in reactions with fullerene-60

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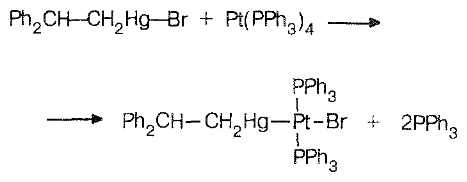
The cleavage of two σ-bonds and the formation of a metallocomplex, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, occur in a new reaction between fullerene-60 and binuclear heterometallic compounds having a mercury-platinum bond (retro-insertion promoted by C_{60}). One of these, *trans*-$Ph_2CHCH_2HgPt(PPh_3)_2Br$, **1**, which contains an electron-donating group at the mercury atom, reacts two orders of magnitude faster than *cis*-$(CF_3)_2CFHgPt(PPh_3)_2CH{=}CPh_2$, **2**, which has an electron-withdrawing substituent at mercury. An asymmetrical organomercury compound is the second product of the reaction. The reactants and products have been characterized by spectroscopic data (^1H, ^{31}P NMR, UV-VIS) and elemental analyses. Compound **2**, which is more stable to retro-insertion, gives a Pt-centered free radical upon photolysis. This was used for the free-radical functionalization of C_{60}. The platinum-fullerenyl radical *cis*-$C^{\cdot}_{60}Pt(PPh_3)_2R^2$ was identified by EPR spectroscopy.

Key words: metallocomplexes; fullerene-60; heterometallic compounds; mercury-platinum bond, retro-insertion; Pt-centered free radical; ESR, NMR, UV-VIS, spectra.

Buckminsterfullerene C_{60} is a spheroidal carbon cluster that contains 30 significantly localized double bonds and exhibits a rather strong electron affinity (2.6—2.8 eV) and a low ionization potential (7.6 eV).[1] C_{60} is known to enter such reactions as the addition of electrons and anions, carbenes and dienes, as well as of radicals and coordinationally unsaturated complexes of transition metals.[2,3] Earlier we investigated the reaction of C_{60} with the free radicals that arise in the course of the photo-induced destruction of organomercury compounds, in which the "key" atom has a magnetic moment, *viz.*, phosphorus, boron, tin, *etc.*[4,5] $(Ph_3P)_2Pd(\eta^2\text{-}C_{60})$ was prepared from $Pd(PPh_3)_4$, and its molecular structure was completely established.[6] In addition, the first optically active organometallic derivative, $[(+)DIOP]Pd(\eta^2\text{-}C_{60})$, was isolated.[7] In the course of all of these reactions, only one σ-bond of the reagent is cleaved in each elementary act, and the carbon framework of C_{60} remains unaffected.

In the present work we report a new reaction, in which the involvement of C_{60} results in the cleavage of two covalent bonds in a binuclear mercury-platinum compound. Earlier we discovered the reaction introducing the platinum carbenoid $L_2Pt(O)$ at the mercury—element bond and revealed the electron-donating character of the mercury—platinum bond.[8,9] It was suggested that such compounds could be used as donors of Pt-centered free radicals in the photo-induced functionalization of fullerenes.[4]

We investigated the bimetallic compounds R^1—Hg—$Pt(PPh_3)_2$—R^2, where $R^1 = Ph_2CHCH_2$, R^2 = Br (**1**) or $R^1 = (CF_3)_2CF$, $R^2 = Ph_2C{=}CH$ (**2**). Complex **1**, which is sensitive to sunlight like other derivatives of the alkyl series, has been obtained by us for the first time by way of redox condensation (in analogy with the previously described work[10]).



$$Ph_2CH{-}CH_2Hg{-}Br + Pt(PPh_3)_4 \longrightarrow Ph_2CH{-}CH_2Hg{-}\underset{PPh_3}{\overset{PPh_3}{Pt}}{-}Br + 2PPh_3$$

Olefin complexes of the type $(Ph_3P)_2Pt(\eta^2\text{-olen})$, where olen = *trans*-styblene, ethylene, may also be successfully used instead of $Pt(PPh_3)_4$. This substance readily forms crystals. The molecular formula of **1** was confirmed by elemental analysis. The structure of **1** was characterized by ^{31}P NMR (CH_2Cl_2), δ: 28.7 c, $^1J_{P-Pt}$ = 3120 Hz. This spectrum indicates the *trans*-disposition of the PPh_3 ligands in the square-planar coordination sphere of platinum. This is a typical disposition for the majority of products resulting from the insertion of the carbenoid $Pt(PPh_3)_4$ species into a mercury—halogen bond. As follows from the ^1H NMR spectrum, the diphenylethyl group in **1** is attached to the mercury atom. The X-ray structural study[11] confirmed the existence of the Hg—Pt bond in the camphenyl analog of **1**. Compound **2**, *viz.*, *cis*-$(CF_3)_2CFHgPt(PPh_3)_2(CH{=}CPh_2)$, which was ob-

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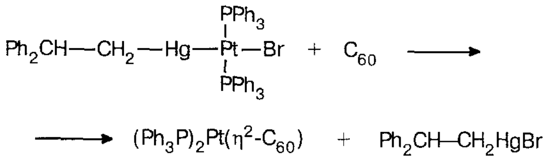
tained previously,[12] contains a σ-electron-withdrawing perfluoroalkyl group, which decreases the electron density at the Hg—Pt bond. Therefore, compound **2** is more stable than **1**. The structure of **2** was confirmed by X-ray structural analysis.*

In compound **2** the bond lengths and bond angles are typical for organic derivatives of tetracoordinated platinum and doubly coordinated mercury. This molecule contains a $Pt(PPh_3)_2R$ fragment, where the PPh_3 ligands are in the *cis*-position. The distance between the Hg and Pt atoms is 2.564(1) Å, which falls within the usual interval for single Hg—Pt bond lengths. We studied the reactions of **1** and **2** with C_{60}. When a solution of **1** in CH_2Cl_2 is treared with a solution of C_{60} in toluene at a 1:1 molar ratio, the violet- purple color of the solution caused by the specific adsorption of C_{60} in the 520—590 nm interval, turned green after 1 h. Simultaneously, the ^{31}P NMR spectrum showed a signal at 26.9 ppm, $^1J_{P-Pt}$ = 3939 Hz, instead of the signal of **1** at δ 28.7 ppm, $^1J_{P-Pt}$ = 3120 Hz. In the case of C_{60} derivatives, a green color is characteristic for the addition of one atom of a zero-valent transition metal to the double bond.[6,7,13] After slow crystallization of the reaction mixture, brown crystals (or dark green in the finely dispersed state) were isolated. They were identified as $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ (**3**) whose structure has been described previously.[13]

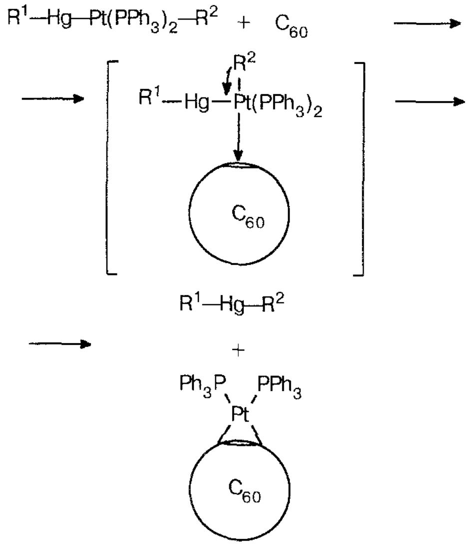


$$\mathrm{Ph_2CH{-}CH_2{-}Hg{-}}\underset{\mathrm{PPh_3}}{\overset{\mathrm{PPh_3}}{\mathrm{Pt}}}\mathrm{{-}Br} + \mathrm{C_{60}} \longrightarrow \mathrm{(Ph_3P)_2Pt(\eta^2\text{-}C_{60})} + \mathrm{Ph_2CH{-}CH_2HgBr}$$

The ^{31}P NMR spectra in THF of the reaction product **3** and the sample obtained by an alternative synthesis according to a known procedure,[13] are identical, *i.e.*, δ 26.9, $^1J_{P-Pt}$ = 3936 Hz. The electron absorbtion spectra of **3** recorded in toluene exhibit characteristic absorption bands at λ_{max} 445, 611, and 651 nm (ε_{max} $1.13 \cdot 10^4$, $5.22 \cdot 10^3$, and $4.08 \cdot 10^3$ $L mol^{-1} cm^{-1}$, respectively). Analogously, λ_{max} for a solution of $(Ph_3P)Pd(\eta^2\text{-}C_{60})$ in toluene (see Ref. 6) are 439, 615, and 662 nm, respectively. It is probable that the band at 445 nm is associated with the fullerene—metal charge transfer. The molecular formula of **3** was confirmed by elemental analysis. The second product isolated in a pure state from the reaction mixture was identified as 1,1-diphenyl-2-(bromomercur)ethane, Ph_2CHCH_2HgBr. Thus, it was found that in the interaction between C_{60} and a bimetallic complex of the alkyl series having a Hg—Pt bond, the latter is a source of the carbenoid $Pt(PPh_3)_2$ species. The reaction, which is the opposite of insertion, eliminates an asymmetric mercury compound. Complex **3**, in which platinum is incorporated in the three-membered metallocycle, does not undergo redox condensation with an organomercury compound, which is a reaction characteristic of compounds of Pt^0. Apparently, in solution **3** does not dissociate to $Pt(PPh_3)_2$ and C_{60}, as was believed previously.[14]

The reaction with C_{60} revealed the fact that the Hg—Pt bond of compound **2** is more stable to thermal and photolytic action than that of compound **1**. At 18—25 °C the conversion of **2** to $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ proceeds for many days. Under the experimental conditions, at a $7.2 \cdot 10^{-3}$ mol L^{-1} concentration of the reagents, the half-conversion time, estimated by monitoring the reaction by means of ^{31}P NMR spectroscopy, was 187 h. The reaction rate increases with heating. Complex **3** was isolated and identified analogously to the reaction of **1** with C_{60}.

In the reactions of **1** and **2** with C_{60}, the formation of intermediates was not observed. It is possible that the transfer of $Pt(PPh_3)_2$ involves the concerted cleavage of two covalent bonds and occurs through a penta-coordinated transition state, where C_{60} occupies the apical position at the Pt^{II} atom as an electron-withdrawing ligand. The new reaction may be called *retro-insertion promoted by* C_{60} *and accompanied by the transfer of a platinum carbenoid.*



The obtained results made it possible to use compounds of type **2** as a source of platinum-centered free radicals to be bound to C_{60}, since these organoheterometallics are the most stable to retro-insertion. The UV irradiation of a toluene solution of C_{60} and **2** (an equimolar ratio, 0.0025 *M*) at 260—290 K in the resonator of an ESR spectrometer resulted in a radical that was characterized by the interaction between an unpaired electron and two non-equivalent nuclei having spin 1/2 and the following parameters: a_1 = 30.5 G, a_2 = 3.5 G, g = 2.0013. After 15 min of irradiation, the

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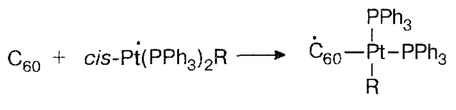
* X-ray structure analysis was performed by Yu. T. Struchkov, Yu. L. Slovokhotov, and A. V. Mironov.

initial radical disappeared, and a new one was accumulated, which was detected as an unresolved singlet with $g = 2.0022$. Photolytic destruction of compound **2** gave rise to three radicals. One of them was Pt-centered, another one was Hg-centered, and the third was the perfluoropropyl carbon-centered radical which was formed from the Hg-centered radical on elimination of mercury:

$$\mathbf{2} \xrightarrow{h\nu} \dot{\mathrm{P}}\mathrm{t(PPh_3)_2R} + \dot{\mathrm{H}}\mathrm{g[CF(CF)_2]} \longrightarrow$$
$$\longrightarrow \dot{\mathrm{C}}\mathrm{F(CF_3)_2} + \mathrm{Hg}$$

Previously we discovered that the Pt-centered radical can add to the C=C bond to give a spin-adduct in which interaction between the unpaired electron and the phosphorus nucleus of the PPh_3 ligands could be observed (see Ref. 15) . It seems likely that the doublet of doublets observed in the former radical is associated with the interaction between the unpaired electron and two phosphorus nuclei, which are not equivalent due to the *cis*-position of the PPh_3 ligands. Since the signal-to noise ratio is low, the hyperfine interaction between the unpaired electron and the ^{195}Pt nucleus could not be observed.



$$\mathrm{C_{60}} + cis\text{-}\dot{\mathrm{P}}\mathrm{t(PPh_3)_2R} \longrightarrow \dot{\mathrm{C}}_{60}\text{—}\mathrm{Pt(PPh_3)(PPh_3)(R)}$$

Apparently, the accumulation of the second broad signal (10 Gc) is associated with the repeated photoinduced addition of the $Pt(PPh_3)_2$ carbenoid according to the retro-insertion mechanism followed by the nonselective addition of the $(CF_3)_2C^{\cdot}F$ radical to $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ at different distances from the metal. An alternative variant is the intramolecular rearrangement of *cis*-$\dot{C}_{60}Pt(PPh_3)_2R$ in $[\eta^2\text{-}(R\text{—}\dot{C}_{60})]Pt(PPh_3)_2$.

We plan to continue the investigations of the retro-insertion reaction as well as the chemical properties of the free metal-fullerenyl radicals having metal—fullerene bonds of various types.

Experimental

All the syntheses were carried in an argon atmosphere. The solvents were dried, degassed, and distilled in Ar. The starting compounds, *viz*., $Pt(PPh_3)_4$, 1,1-diphenyl-2-(bromomercur)ethane, 2,2-diphenylvinyl(heptafluoroisopropyl) mercury, were prepared according to the known procedures.[16—18] The reference compound was synthesized by analogy with the earlier described procedure.[13] The $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker WP-200 SY instrument; chemical shifts are given in ppm with a 1 % solution of H_3PO_4 (^{31}P) and TMS (^1H) as the standards. Electron absorbtion spectra were obtained on a Specord UV-VIS device. ESR spectra were recorded on a Varian E-12A radiospectrometer. Photolyses of the degassed solutions were carried out in sealed quartz ampules using the focused light of a DRSh-1000 lamp.

***trans*-Bromo-(2,2-diphenylethylmercury)bis(triphenylphosphine) platinum (1).** A solution of $Pt(PPh_3)_4$ (0.87 g, 0.699 mmol) in 15 mL of toluene was added to a solution of 1,1-diphenyl-2-(bromomercur)ethane (0.32 g, 0.693 mmol). The reaction mixture was filtered through a G4 Buchner funnel. After 1 h, 60 mL of hexane was added to the solution, and it was stored in darkness at 0 °C. After 24 h, the light yellow crystalline precipitate was collected by filtration, washed with hexane, and dried *in vacuo*. 0.69 g (84 %) of bimetallic compound **1** was obtained as needles, m.p. 144 °C (with decomposition and evolution of metallic mercury). Found (%): C, 51.16; H, 3.69; Br, 6.56; Hg, 16.40. $C_{50}H_{43}BrHgP_2Pt$. Calculated (%): C, 50.82; H, 3.67; Br, 6.76; Hg, 16.98. ^1H NMR ($CDCl_3$), δ: 0.85 (d, CH_2Hg, $^3J_{H-H}$ = 8.1 Hz, $^2J_{H-Hg}$ = 110 Hz); 3.34 (t, CH, $^3J_{H-Hg}$ = 86 Hz).

Exposure of solutions of **1** to light brings about the deposition of metallic mercury and the formation of $Ph_2CHCH_2Pt(PPh_3)_2Br$. ^1H NMR ($CDCl_3$), δ: 1.81 (CH_2Pt, $^2J_{H-Pt}$ = 79 Hz); 3.50 (CH, $^3J_{H-Pt}$ = 33 Hz). ^{31}P NMR ($C_2H_4Cl_2$), δ: 27.1, $^1J_{P-Pt}$ = 3326 Hz.

***cis*-(2,2-Diphenylvinyl)-(heptafluoroisopropylmercury)bis(triphenylphosphine) platinum (2).** This compound was obtained according to a modified procedure[12] from 2,2-diphenylvinylheptafluoroisopropyl mercury (0.233 g, 0.424 mmol) and $Pt(PPh_3)_4$ (0.531 g, 0.427 mol) in 3.7 mL of toluene. Crystallization from 25 mL of pentane gave 0.462 g (86 %) of **2**. ^{31}P NMR (CH_2Cl_2), δ: 28.1 ($^1J_{P-Pt}$ = 2767, $^2J_{P-Hg}$ = 3390 Hz); 20.3 (J_{P-Pt} = 2103 Hz,$^2J_{P-Hg}$ = 368 Hz).

Reaction of C_{60} with *trans*-bromo-(2,2-diphenylethylmercury)bis(triphenylphosphine) platinum. Compound **1** (0.0591 g, 0.050 mmol) in 7 mL of CH_2Cl_2 and C_{60} (0.0369 g, 0.051 mmol) were mixed in an Erlenmeyer flask, toluene (5 mL) was added, and the mixture was stirred. CH_2Cl_2 being removed from the reaction mixture for 1 h. A typically green color developed, indicative of the metallated C_{60} in solution (confirmed by the ^{31}P NMR and electron absorbtion spectra). After 3 h, the solution was diluted with methanol. After a period of 5 days, the complex (dark brown crystals with an olive hue) was collected by filtration, washed with acetone and pentane, and dried *in vacuo*. 0.05079 g (70 %) of $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ (**3**) was obtained. Found (%): C, 80.13; H, 2.03; P, 4.04. $C_{96}H_{30}P_2Pt$. Calculated (%): C, 80.05; H, 2.10; P, 4.30. ^{31}P NMR (THF), δ: 26.9, $^1J_{P-Pt}$ = 3936 Hz (see Ref. 13: 27.0, $^1J_{P-Pt}$= 3936 Hz). The mother liquor and the organic washouts were combined and evaporated, and the residue was crystallized from EtOH to give 1,1-diphenyl-2-(bromomercur)ethane (0.0131 g, m.p. 127 °C). ^1H NMR ($CDCl_3$), δ: 2.67 (d, CH_2—Hg, $^3J_{H-H}$ = 8.0 Hz, $^2J_{H-Hg}$ = 183 Hz); 4.53 (t, CH, $^3J_{H-Hg}$ = 174 Hz). ^1H NMR for the starting 1,1-diphenyl-2-(bromomercur)ethane ($CDCl_3$), δ: 2.67 (d, $^3J_{H-H}$ = 8.0 Hz, $^2J_{H-Hg}$ = 183 Hz); 4.54 (t, $^3J_{H-Hg}$ = 174 Hz).

Reaction of C_{60} with *cis*-(2,2-Diphenylvinyl)-(heptafluoroisopropylmercury)bis(triphenylphosphine) platinum. Compound **2** (0.0634 g, 0.05 mmol) and C_{60} (0.0364 g, 0.05 mmol) were dissolved in toluene (7 mL). The mixture was stirred at +18 °C. The course of the reaction was monitored by means of the ^{31}P NMR spectroscopy for 16 days until the degree of conversion of **2** was 63 %. After dilution with hexane (30 mL), 0.0343 g (47 %) of $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ was isolated. Found (%): C, 80.27; H, 2.06; P, 3.94. $C_{96}H_{30}P_2Pt$. Calculated (%): C, 80.05; H, 2.10; P, 4.30. ^{31}P NMR (THF), δ: 26.9 (s, $^1J_{P-Pt}$ = 3937 Hz).

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