# The reaction of diaryl derivatives of bis(triphenylphosphine)platinum(II) with [60]fullerene as a route to the platinum complex $\eta^2$-$C_{60}Pt(PPh_3)_2$

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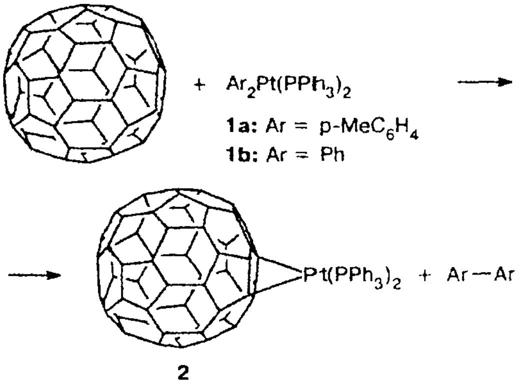
The reaction of *cis*-$Ar_2Pt(PPh_3)_2$ (Ar = *p*-$MeC_6H_4$ (**1a**) and Ar = Ph (**1b**)) with [60]fullerene in toluene afforded the metal-fullerene complex $\eta^2$-$C_{60}Pt(PPh_3)_2$ (**2**), which was isolated in the crystalline state. The reductive elimination between $C_{60}$ and **1a** or **1b** also resulted in the formation of biaryls (*p*-$MeC_6H_4)_2$ and Ph—Ph. The composition and structure of the compounds were established by $^1H$ and $^{31}P$ NMR spectroscopy, electronic absorption spectroscopy, and elemental analysis. The homolytic phosphorylation of **2** was additionally studied by the ESR method.

**Key words**: [60]fullerene, platinum(II) complexes, synthesis; platinum-fullerene complex, biaryls, NMR, electronic absorption spectra, ESR.

Exohedral complexes of [60]fullerene, $\eta^2$-$C_{60}ML_2$, containing Group 10 metals (Pt, Pd, and Ni) are the first derivatives of this polyhedral carbon cluster that were obtained in pure form. The $\eta^2$-$C_{60}ML_2$ complexes are usually formed in the reactions of [60]fullerene with coordinationally unsaturated compounds of M(0) (Pt, Pd, and Ni) stabilized by mono- and bidentate phosphine, olefinic, or phosphite ligands.[1—9] It has been established[10] recently by the study of the reactivity of fullerenes that [60]fullerene can initiate processes inverse to the oxidative addition: *retro-insertion reactions* with the formation of $\eta^2$-$C_{60}Pt(PPh_3)_2$. In the case of retro-insertion reactions, some $Pt^I$ complexes containing the mercury—platinum bond serve as the sources of carbenoid $Pt(PPh_3)_2$. The behavior of organometallic $Pt^{II}$ compounds containing the metal—carbon σ-bond with respect to fullerenes has not been considered previously.

In this work, we studied the reactions of [60]fullerene and *cis*-$Ar_2Pt(PPh_3)_2$ complexes, where Ar = $MeC_6H_4$ (**1a**) and Ph (**1b**). Platinum(II) diaryl derivatives, as known, are stable under standard conditions, exist as *cis*- and *trans*-isomers, and decompose upon thermolysis to form biaryls.[11—16] The decomposition is favored by the addition of an excess of nucleophilic ligands.[13] We studied the reactions of electrophilic [60]fullerene with complexes **1a,b** in a toluene solution under an argon atmosphere. When the colorless compound **1a** reacts with a violet-purple solution of [60]fullerene at room temperature, an intense green color of the solution appears. The change in color is due to the appearance of a new substance in the reaction mixture: its electronic absorption spectrum contains, along with other bands, bands in the 22500—22700 $cm^{-1}$ and 16500—15500 $cm^{-1}$ regions characteristic of metallocomplex derivatives of [60]fullerene.[2,5] The new compound is manifested in the $^{31}P$ NMR spectrum of the reaction mixture as a singlet with the chemical shift of 26.91 ppm and a doublet with the same shift from the isotopomer with the direct coupling constant $^1J(^{31}P,^{195}Pt)$ = 3936 Hz instead of the signals of the starting complex δ 19.7, $^1J(^{31}P,^{195}Pt)$ = 1731 Hz. These spectral parameters are characteristic of the known fullerene complex $\eta^2$-$C_{60}Pt(PPh_3)_2$ (**2**), which has been described previously.[3,10] The half-period of transformation of compound **1a** into compound **2** is 144 h at 20 °C. A similar transformation of [60]fullerene into compound **2** was observed for its reaction with compound **1b**, but in this case, due to the absence of the electron-donating substituent in the phenyl group, the reaction with the electron-withdrawing double bond of fullerene occurs more slowly.



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The composition of complex **2** was confirmed by the elemental analysis data for C, H, and P of the crystalline samples isolated from the reaction mixture. According to the data of the $^{31}P$ NMR spectrum of compound **2**, the $Pt(PPh_3)_2$ group bound to fullerene has equivalent, symmetrically arranged triphenylphosphine ligands. The chemical shift of the P atoms and coupling constants of the directly bound P and Pt atoms coincide completely with the corresponding values for the reference compound $\eta^2$-$C_{60}Pt(PPh_3)_2$. The presence of the [60]fullerene cage in product **2** appears in the ESR spectrum during homolytic phosphorylation. The compound was identified in a toluene solution using $Hg[P(O)(Pr^iO)_2]_2$ as the source of phosphoryl radicals, resulting from UV irradiation in the resonator of an ESR spectrometer. In the initial moment, complex **2** reacts nonregioselectively with phosphoryl radicals to form at least five radicals, $(Ph_3P)_2Pt^{\cdot}C_{60}P(O)(Pr^iO)_2$, which differ in the HFC constants of an unpaired electron with nuclei of the $^{31}P$ atoms ($a$ = 58—68 G) and the $g$-factor values (2.001—2.003). The ESR spectrum with the parameters of the $^{\cdot}C_{60}P(O)(Pr^iO)_2$ radical ($g$ = 2.0022, $a$ = 63.4 G) was detected over 5-min irradiation due to demetallation *via* redox demercuration. We have previously obtained similar parameters.[17] Compound **2** has the characteristic electronic spectrum (Fig. 1) (toluene), $\nu_{max}/cm^{-1}$: 29700 (log ε = 4.76), 22600 (log ε = 4.05), 16550 (log ε = 3.64), 15600 (sh). The most characteristic band at 22600 $cm^{-1}$ is related to the fullerene—metal charge transfer. We have previously discussed the use of electronic absorption spectroscopy for the identification of monometallic derivatives of [60]fullerene containing Group 10 metals with phosphine ligands.[4,5,10,18]

Our experiments showed that when the temperature of the reaction mixture increased by ~80 °C, the reaction completed within 15 min, and complex **2** was formed in an almost quantitative yield (according to the $^{31}P$ NMR spectroscopic data). The reaction can be of preparative significance for synthesis of metal derivatives of fullerenes.

**Fig. 1.** *a*. Electronic absorption spectrum of the $\eta^2$-$C_{60}Pt(PPh_3)_2$ complex in toluene (ν is the wave number). *b*. fragment of the spectrum, ×10.

## Experimental

All experiments were carried out under an argon atmosphere. Solvents were dried, degassed, and distilled under an argon atmosphere. The starting complexes **1a,b** were obtained by the previously described method[16] from $p$-$MeC_6H_4MgBr$ and *cis*-$Pt(PPh_3)_2Cl_2$ and by the redox demercuration reaction[12] of $HgPh_2$ and $Pt(PPh_3)_3$, respectively. The reference compound $\eta^2$-$C_{60}Pt(PPh_3)_2$ was synthesized from the Pt(0) complex[3] and by the *retro-insertion* method.[10] Reference 4,4′-dimethylbiphenyl (**3**) was prepared from 4-methylphenylmercury bromide.[19] $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WP-200-SY and Bruker AMX-400 instruments; chemical shifts were measured relative to TMS and 1% $H_3PO_4$, respectively. Electronic spectra were recorded on a Specord UV-VIS spectrophotometer in a quartz cell. The homogeneity of compounds was monitored by TLC on Silufol UV-254 plates.

**Reaction of complex *cis*-($p$-$MeC_6H_4)_2Pt(PPh_3)_2$ (1a) with [60]fullerene.** $C_{60}$ (72.22 mg, 0.1002 mmol) and complex **1a** (90.05 mg, 0.0998 mmol) were dissolved in toluene (36 mL) with stirring in a Schlenk vessel ($V$ = 100 mL). The solution became green within 1 h at ~20 °C. The progress of the reaction was monitored by electronic absorption spectra and $^{31}P$ NMR spectra of samples of the reaction mixture. The $^{31}P$ NMR spectrum of the reaction mixture exhibited the following parameters of the starting complex **1a**: δ 19.7, $^1J_{Pt-P}$ = 1731 Hz; of product **2**: δ 27.0, $^1J_{Pt-P}$ = 3935 Hz. The conversion of **1a** was 50% over 144 h. When 80% conversion was achieved (350 h), hexane (to 100 mL) was added to the reaction mixture without stirring, and the resulting mixture was left to stand at ~20 °C. After 3 days, a crystalline precipitate with a green shade was filtered off, washed with diethyl ether and hexane, and dried *in vacuo*. Dark crystals of complex **2** (80.85 mg, 56%) were obtained. Found (%): C, 80.17; H, 2.09; P, 4.07. $C_{96}H_{30}P_2Pt$. Calculated (%): C, 80.06; H, 2.10; P, 4.30. $^{31}P\{^1H\}$ NMR (toluene), δ: 27.00 (s, $PPh_3$; $^1J_{Pt-P}$ = 3936 Hz).

After precipitation of complex **2**, the mother liquor was concentrated, and the residue was dried *in vacuo* and dissolved in $CD_2Cl_2$ (1.5 mL). 4,4′-Dimethylbiphenyl (**3**) (13.4 mg, 92.5% with respect to the consumed starting material) was identified in the solution. The amount of **3** was estimated by $^1H$ NMR. Hexamethylbenzene (HMB) (3.8 mg, 0.0234 mmol) was added to the solution as the standard, and integral intensities of signals of methyl groups of product **3** (δ 2.41) and HMB (δ 2.24) were compared. $^1H$ NMR ($CD_2Cl_2$—HMB), δ: 2.41 (s, 6 H, $CH_3$); 7.26 and 7.51 (both AA′BB′, 8 H, $CH_{arom}$, $J_{AB}$ = 8 Hz). $^1H$ NMR ($CCl_4$), δ: 2.35 (s, 6 H, $CH_3$); 7.25 and 7.51 (both AA′BB′, 8 H, $CH_{arom}$, $J_{AB}$ = 8.1 Hz).

**Reaction of *cis*-($p$-$MeC_6H_4)_2Pt(PPh_3)_2$ (1a) with [60]fullerene upon heating.** [60]Fullerene (14.0 mg, 0.0194 mmol), complex **1a** (18.78 mg, 0.0208 mmol), and toluene (7 mL) were placed in an ampoule, which was sealed *in vacuo* and heated for 15 min at the boiling temperature of heptane (98.4 °C). The reaction mixture was analyzed by $^{31}P$ NMR spectroscopy. The following $^{31}P$ NMR spectrum of complex **2** was observed in toluene, δ: 27.00 (s, $PPh_3$; $^1J_{Pt-P}$ = 3937 Hz). After crystallization from a toluene—hexane mixture, compound **2** was obtained (17.41 mg, 62%).

**Reaction of *cis*-$(C_6H_5)_2Pt(PPh_3)_2$ (1b) with [60]fullerene.** $C_{60}$ (59.90 mg, 0.0831 mmol) and complex **1b** (72.36 mg, 0.0828 mmol) were dissolved in toluene (30 mL) with stirring (the initial concentrations of the reagents were similar to those in the previous experiment) and stored at ~20 °C. According to the $^{31}P$ NMR data, after 4 days, the ratio of the starting compound **1b** (δ 19.93) to the reaction product **2** (δ 26.96) in the reaction mixture was 1 : 0.22. The conversion was 27% within 5 days. When 90% conversion of complex **1b** was achieved, the reaction product **2** was isolated by crystallization at –20 °C from a toluene—hexane mixture. Dark (with a green shade) crystals of **2** were obtained (69.9 mg, 58%). Found (%): C, 80.07; H, 2.24; P, 4.04. $C_{96}H_{30}P_2Pt$. Calculated (%): C, 80.06; H, 2.10; P, 4.30. $^{31}P\{^1H\}$ NMR (toluene), δ: 27.00 (s, $PPh_3$; $^1J_{Pt-P}$ = 3936 Hz).

After separation of **2**, the mother liquor was kept at –12 °C for 3 days, a colorless precipitate **1b** with an admixture of **2** was filtered off, and the solvents were removed *in vacuo*. Biphenyl was extracted from the residue with $Et_2O$ (5 mL) followed by chromatographic purification on a Silufol plate. The compound was identified by TLC using the reference compound: $R_f$ = 0.24 (Silufol UV-254, hexane as the eluent). $^1H$ NMR ($CD_3COCD_3$), δ: AA'BB'C system, 7.26 (1 H, *p*-$CH_{arom}$), 7.37 (2 H, *m*-$CH_{arom}$), 7.55 (2 H, *o*-$CH_{arom}$).

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