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Photoinduced activation of arene C–H bonds with (η^5-cyclopentadienyl)trimethylplatinum(IV): a possible role of $CpPtR_2H$

Andrei N. Vedernikov,* Sergei V. Borisoglebski, Alexei B. Solomonov and Boris N. Solomonov

Department of Chemistry, Kazan State University, 420008 Kazan, Russian Federation.
Fax: +7 8432 38 0994; e-mail: ave@ksu.ru

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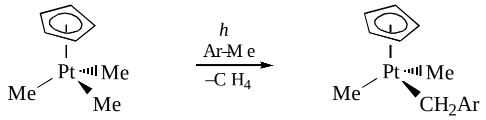
(η^5-Cyclopentadienyl)trimethylplatinum(IV) reacts with ArMe arenes rather than alkanes or benzene under heating to 150 °C in the dark or under irradiation with light at room temperature by a radical mechanism to produce (η^5-cyclopentadienyl)dimethyl(arylmethyl)platinum(IV) complexes, and the expected complex $CpPtR_2(H)$ is unstable under the reaction conditions, as found by the reduction of $CpPtMe_2I$ with complex metal hydrides.

According to recent quantum-chemical calculations,[1,2] the 16-electron cyclopentadienyl complexes of platinum(II) $[CpPt(CO)]^+$ and [CpPtCl] can undergo exothermic oxidative addition with methane to produce methyl hydrido complexes of cyclopentadienylplatinum(IV), which can be considered to be similar to platinum(IV) derivatives with *fac*-chelating ligands.[3] It has been expected that the CpPtX species are highly reactive short-lived intermediates, which can be generated by decomposition of corresponding more stable 18-electron precursors. The well-known methods for generating coordinatively unsaturated 16-electron complexes CpMX (M = Rh or Ir) involve photolysis of the dihydrides $CpMH_2(L)$ (M = Ir) or dicarbonyls $CpM(CO)_2$ or thermolysis of the hydrido complexes CpM(L)(R)H (refs. 4, 5 and 6, respectively). In this work, we attempted to obtain the platinum-containing species *via* elimination of ligands from cyclopentadienyltrimethylplatinum(IV), $CpPtMe_3$. Complexes of the general formula $CpPtR_3$ ($R_3 = Alk_3$, Alk_2R' *etc.*) are well known for R′ = alkyl or acyl[7] rather than for R′ = H.

Irradiation of solutions containing 3–5 mg of $CpPtMe_3$ and 0.5 ml of a hydrocarbon (benzene, toluene, *p*-xylene, mesitylene, *n*-pentane or cyclohexane) was performed with a 10 W high-pressure mercury lamp or a 250 W halogen lamp for 0.5–3 h using a water filter to absorb the IR component of light. The reactants were placed in sealed tubes under argon or in a vacuum. A longer time of irradiation leaded to decomposition of the starting complex and to deposition of platinum metal and platinum containing white polymer of the formula PtC_8H_{14}. The heating of the same solutions at 150 °C in the dark also leaded to decomposition of the complex. According to ^1H NMR spectroscopy data, both photoinduced and thermally induced decomposition of $CpPtMe_3$ in alkylarene solutions resulted in new cyclopentadienylplatinum(IV) derivatives, which were isolated from the reaction mixture by filtering off platinum and evaporating the solvent. Photolysis was found to be a more effective tool: the product yield was as high as 10% on a platinum basis (*cf.* 1–3% obtained by thermolysis). In the course of the reaction, new sets of typical peaks appeared in the NMR spectra at 5.0 (CpPt group, $^2J_{Pt-H} \approx 6$ Hz), 3.0 ($Pt-CH_2Ar$, $^2J_{Pt-H} \approx 99$ Hz) and 0.8–1.3 ppm (Pt–Me, $^2J_{Pt-H} \approx 83$ Hz). New absorption bands also appeared in the low-field region (7 ppm).[†] No signals were detected in the high-field region from 0 to –30 ppm; this fact indicates that no platinum hydrides are formed. New peaks were not detected in the absence of $CpPtMe_3$.

The experimental data correspond to a reaction mechanism involving the formation of dimethyl arylmethyl derivatives of cyclopentadienylplatinum(IV).



Indeed, according to mass-spectrometric data, the lipophilic residue obtained after photolysis of a $CpPtMe_3$–toluene mixture and evaporation of the solvent contained $CpPtMe_2(CH_2Ph)$ (M^+, *m/z* 380, 381, 382 and 384). Benzene was found to be inert under the reaction conditions, and the examined alkanes produced only traces of new cyclopentadienyls. The main reaction for the above substrates is decomposition of $CpPtMe_3$ to form the platinum containing polymer. The reproducibility of product yields for methylarenes was in a range of 20–30%. Traces of other unidentified compounds containing the CpPt unit were detected in toluene solutions after irradiation for a long time.

We performed the simplest tests to reveal the reaction mechanism. The addition of 5 mg of hydroquinone to the reaction mixtures completely inhibited the photoinduced reactions. The average yields of products obtained under photolysis of $CpPtMe_3$ in $[^2H_8]$toluene were lower than those in toluene by 1–1.5 orders of magnitude. Photolysis of $CpPtMe_3$ in toluene mixtures with cyclohexane, *p*-xylene or mesitylene gave following results. Alkanes remained inert, and polymethylbenzenes competed for the metal complex. Photolysis of $CpPtMe_3$ in the presence of iodine leaded to $[PtMe_3I]_4$ and, in a moderate yield, cyclopentadienyldimethyliodoplatinum(IV), $CpPtMe_2I$, which was identified in the reaction mixture by spectroscopy.[‡]

Photolysis of $CpPtMe_3$ in a toluene mixture with *p*-xylene (50 vol%) gave benzyl and *p*-methylbenzyl derivatives in the 1:1.5 ratio. The ratio between benzyl and 2,3-dimethylbenzyl complexes obtained in a mixture of toluene and mesitylene (1:1, v/v) was 1:2.5. Taking into account the difference in molar concentrations of active C–H bonds in the mixtures of substrates (1:1.7 and 1:2.3, respectively), we can conclude that there is no considerable difference in the reactivity of benzylic C–H bonds of these substrates. At the same time, the hydrogen kinetic isotope effect of the reaction is sufficiently high; this fact allowed us to conclude that the cleavage of benzylic C–H bonds is the rate-determining step. Taking into account the low reactivity of methylarenes towards $CpPtMe_3$, the inertness of alkanes containing stronger C–H bonds seems to be in agreement with the above explanation.

An analysis of the substrate selectivity and regioselectivity of the reaction and an analogy with the published data[8] concerning the photoinduced activation of arene C–H bonds with organic platinum(II) complexes allowed us to suggest a radical mechanism of the metathesis of hydrocarbon C–H bonds and metal complex Pt–C bonds as follows:

[†] $CpPtMe_2(3,5-Me_2C_6H_3CH_2)$: ^1H NMR (250 MHz, 20 °C, $CDCl_3$) δ: 1.01 (s, 6H, Pt–Me, $^2J_{Pt-H}$ 83.4 Hz), 2.30 (s, 6H, 3,5-Me), 2.89 (s, 2H, $Pt-CH_2$, $^2J_{Pt-H}$ 98.8 Hz), 5.38 (s, 5H, C_5H_5, $^2J_{Pt-H}$ 6.6 Hz), 6.82 (s, 1H, *p*-C–H), 6.98 (s, 2H, *o*-C–H).

$CpPtMe_2(4-MeC_6H_4CH_2)$: ^1H NMR (250 MHz, 20 °C, $CDCl_3$) δ: 1.00 (s, 6H, Pt–Me, $^2J_{Pt-H}$ 83.4 Hz), 2.25 (s, 3H, 4-Me), 2.93 (s, 2H, $Pt-CH_2$, $^2J_{Pt-H}$ 98.8 Hz), 5.38 (s, 5H, C_5H_5, $^2J_{Pt-H}$ 6.2 Hz), 6.9–7.1 (m, C_6H_4).

$CpPtMe_2(CH_2Ph)$: ^1H NMR (250 MHz, 20 °C, $CDCl_3$) δ: 1.02 (s, 6H, Pt–Me, $^2J_{Pt-H}$ 83.2 Hz), 2.96 (s, 2H, $Pt-CH_2$, $^2J_{Pt-H}$ 98.4 Hz), 5.37 (s, 5H, C_5H_5, $^2J_{Pt-H}$ 6.4 Hz), 7.10–7.24 (m, 5H, Ph).

[‡] $CpPtMe_2I$: ^1H NMR (250 MHz, 20 °C, C_6D_6) δ: 2.07 (s, 6H, Pt–Me, $^2J_{Pt-H}$ 84.4 Hz), 5.04 (s, 5H, C_5H_5, $^2J_{Pt-H}$ 12.4 Hz).

$$\mathrm{CpPtMe_3 \longrightarrow [CpPtMe_2]^{\cdot} + Me^{\cdot}};$$

$$\mathrm{[CpPtMe_2]^{\cdot}Me^{\cdot} + Me{-}Ar \longrightarrow [CpPtMe_2]^{\cdot}(CH_2Ar)^{\cdot} + CH_4};$$

$$\mathrm{[CpPtMe_2]^{\cdot}(CH_2Ar)^{\cdot} \longrightarrow [CpPtMe_2(CH_2Ar)]}$$

or

$$\mathrm{[CpPtMe_2]^{\cdot}R^{\cdot} \longrightarrow [CpPtMe] + MeR};$$

$$\mathrm{[CpPtMe] + RH \longrightarrow CpPtMe(R)H}$$

and

$$n\mathrm{CpPtMe_3} \xrightarrow{h\nu} \mathrm{[PtC_8H_{14}]}_n.$$

Iodine is able to scavenge the $[\mathrm{CpPtMe_2}]^{\cdot}$ radical to form $\mathrm{CpPtMe_2I}$.

The last-mentioned reaction is responsible for the deposition of platinum-containing polymer, the main product of $\mathrm{CpPtMe_3}$ transformation.

The absence of platinum(IV) alkyl hydrides in the reaction mixtures suggests that either the CpPtMe species are not formed or the expected organic hydridoplatinum(IV) cyclopentadienyls CpPtMe(R)(H) are unstable under the reaction conditions.

To test the latter hypothesis, we attempted to synthesise $\mathrm{CpPtMe_2H}$. A dimethyl halogeno derivative of cyclopentadienylplatinum(IV), *e.g*., $\mathrm{CpPtMe_2I}$, can serve as a precursor in this synthesis. Cyclopentadienyldimethyliodoplatinum(IV), $\mathrm{CpPtMe_2I}$, was obtained in 25% yield by the treatment of polymeric dimethyldiiodoplatinum(IV) with cyclopentadienylthallium in absolute THF in an evacuated and sealed tube.

$$\mathrm{[PtMe_2I_2]}_n + n\mathrm{CpTl} \longrightarrow n\mathrm{CpPtMe_2I} + \mathrm{TlI}$$

The other reaction products are (η^5-Cp)$\mathrm{PtMe_2}$(η^1-Cp)[§] and $\mathrm{CpPtMe_3}$.

Cyclopentadienyldimethyliodoplatinum(IV) was treated with various hydride-ion donors (lithium aluminium hydride, lithium dibutylaluminohydride and sodium borohydride) in THF purified with the dipotassium–anthracene adduct in evacuated and sealed NMR tubes. In all cases, the reaction mixtures became colourless at room temperature, and platinum metal was deposited. Thus, it is our opinion that the $\mathrm{CpPtMe_2H}$ complex is insufficiently stable under the reaction conditions, and it cannot be detected in the room-temperature photolysis of $\mathrm{CpPtMe_3}$ solutions in hydrocarbons. A possible way of $\mathrm{CpPtMe_2H}$ decomposition may include, *e.g.*, its isomerization to the unstable planar complex (η^1-Cp)$\mathrm{PtMe_2H}$; this way of decomposition was not examined theoretically in refs. 1 and 2. Nevertheless, the corresponding cationic analogues $[\mathrm{CpPtL(Me)H}]^+$ can exhibit higher stability. Low-temperature experiments on detecting $\mathrm{CpPtMe_2H}$ and its cationic analogues are now in progress in our laboratory.

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[§] (η^5-Cp)$\mathrm{PtMe_2}$(η^1-Cp): ^{1}H NMR (250 MHz, 20 °C, $\mathrm{C_6D_6}$) δ: 1.41 (s, 6H, Pt–Me, $^2J_{\mathrm{Pt–H}}$ 82.1 Hz), 4.01 (s, 1H, CH–Pt, $^2J_{\mathrm{Pt–H}}$ 148.9 Hz), 4.93 (s, 5H, $\mathrm{C_5H_5}$, $^2J_{\mathrm{Pt–H}}$ 7.0 Hz), 6.40–6.90 (m, 4H, CH=CH).

References

1 M. D. Su and S. Y. Chu, *Organometallics*, 1997, **16**, 1621.

2 A. N. Vedernikov, G. A. Shamov and B. N. Solomonov, *Zh. Obshch. Khim.*, 1998, **68**, 709 (*Russ. J. Gen. Chem.*, 1998, **68**, 667).

3 (*a*) S. A. O'Reilly, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1996, **118**, 5684; (*b*) A. J. Canty, A. Dedieu, H. Jin, A. Milet and M. K. Richmond, *Organometallics*, 1996, **15**, 2845; (*c*) D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.*, 1997, **119**, 10235; (*d*) H. A. Jenkins, G. P. A. Yap and R. J. Puddenphatt, *Organometallics*, 1997, **16**, 1946.

4 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352.

5 J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3723.

6 W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1982, **104**, 4240.

7 A. Shaver, *Can. J. Chem.*, 1978, **56**, 228.

8 A. Miyashita, M. Hotta and Y. Saida, *J. Organometal. Chem.*, 1994, **473**, 353.

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