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Selective sp^3 C–H bond activation of alkylaromatics promoted by platinum complexes

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Abstract

Facile sp^3 C–H bond activation of toluene, *p*-xylene and mesitylene, was photochemically promoted by *trans*-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ leading to *trans*-$Pt(CH_2Ar)Br(PPh_3)_2$ quantitatively, while regioselective sp^3 C–H bond cleavage at the benzylic position of ethylbenzene and cumene readily took place to yield styrene and α-methylstyrene, respectively. A possible reaction mechanism involving radical process is discussed on the basis of isotope and radical-trap experiments.

Key words: Platinum; Benzyl; Bond activation; Radical; Photochemistry

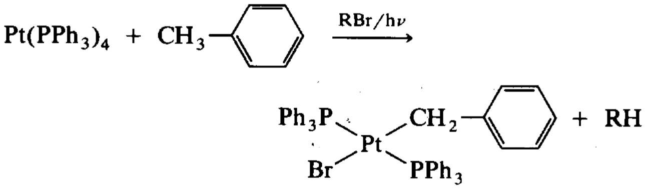
1. Introduction

The selective C–H bond activation and functionalization of saturated hydrocarbons under mild conditions are current topics in transition metal chemistry, because of their importance in developing industrial processes and functionalizing stable hydrocarbons [1]. Thermal and photochemical C–H bond activation of alkylaromatics with homogeneous transition metal complexes involving W [2a–c], Rh [2d–f], Ir [2f], Pt [2g] or Pd [2h,i] has been extensively investigated. In many cases, both sp^2 and sp^3 C–H bond scission occurs to result in the formation of aryl- and alkyl-metal complexes. Selective bond cleavage at the alkyl group is unusual except in a few examples of benzyl C–H bond scission by radical species with Ir- [3a] and Rh-porphyrin [3b] complexes. Previously, we briefly reported that the methyl C–H bond cleavage of toluene was thermally promoted by $Pt(PPh_3)_4$ in the presence of RBr (R = Me, Et, neopentyl, neohexyl or Ph) yielding benzylplatinum(II) complexes, although the reaction required a week to be completed [4].

In this report, we describe facile and selective sp^3 C–H bond activation of alkylaromatics induced by Pt^0 complexes or alkylplatinum(II) complexes under irradiation, and discuss the total features of the reaction mechanisms.

2. Results and discussion

2.1. Photochemical reaction of $Pt(PPh_3)_4$ with toluene in the presence of neohexyl bromide



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When a toluene solution of $Pt(PPh_3)_4$ containing threefold neohexyl bromide was irradiated at 20°C for 5 h, *trans*-$Pt(CH_2Ph)Br(PPh_3)_2$ (**1**) was obtained as white crystals in 84% yield affording neohexane in 94% yield [5*]. The remarkable point in this reaction is that no arene C–H bond activation to form arylplatinum species is observed throughout the reaction.

The effectiveness of other organic halides on the reactions is summarized in Table 1. The yield of **1** was

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* Reference number with asterisk indicates a note in the list of references.

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TABLE 1. Effect of R–X on the yield of **1** by photochemical C–H bond activation of toluene

R	X	**1** [b]	Other products [b]
Me	I	0	$PtMeI(PPh_3)_2$ (78%)
Et	Br	3	$PtHBr(PPh_3)_2$ (45%), ethylene
^{n}Hex	Br	8	$PtHBr(PPh_3)_2$ (78%), hexenes
Ph	Br	19	$PtPhBr(PPh_3)_2$ (63%)
Me_3CCH_2	Br	78	$PtBr_2(PPh_3)_2$ (9%)
$EtCMe_2CH_2$	Br	84	$PtBr_2(PPh_3)_2$ (4%)

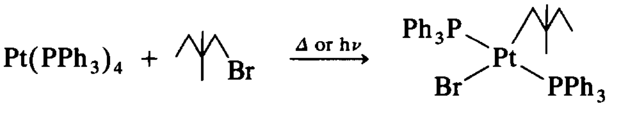
[a] Irradiated by high pressure mercury lamp equipped with a band pass filter U-350 at 20°C for 5 h. [b] Isolated yield based on $Pt(PPh_3)_4$.

unequivocally the best using neohexyl bromide. When ethyl or n-hexyl bromide was employed, *trans*-$PtHBr(PPh_3)_2$ was mainly obtained by evolving ethylene or hexenes, respectively. The poor yield of **1** in these reactions may be due to the predominant elimination of olefins from the transient alkylplatinum intermediates, prior to inducing the methyl C–H bond cleavage of toluene.

When these reactions were performed without organic halide or $Pt(PPh_3)_4$ in toluene, no C–H bond activation of toluene took place either photochemically or thermally. Consequently, sp^3 C–H bond scission of toluene by $Pt(PPh_3)_4$ could be accounted for by the initial formation of an alkyl–Pt^{II} complex which might initiate sp^3 C–H bond cleavage of toluene selectively.

Previously, we reported thermal alkyl C–H bond activation of toluene using $Pt(PPh_3)_4$ in the presence of neohexyl bromide [4]. These thermal reactions took place rather inefficiently to yield **1** in 53% yield after 7 days reaction even at 50°C. $Pt(PMe_2Ph)_3$ and $Pt(PEt_3)_3$ were inactive for thermal or photochemical sp^3 C–H bond activation of toluene.

2.2. *Preparation of trans-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ from the reaction of $Pt(PPh_3)_4$ with neohexyl bromide and their use in photochemical sp^3 C–H activation of alkylaromatics: toluene, p-xylene and mesitylene*



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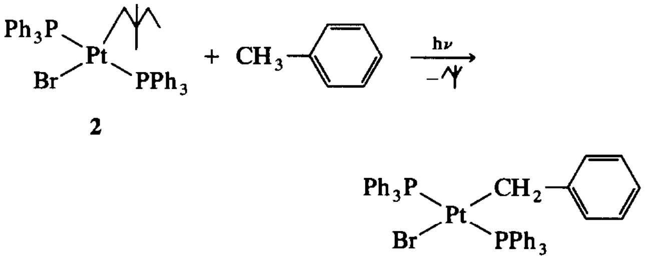
To better define mechanisms by which Pt^0 complexes induce the sp^3 C–H bond cleavage of the methyl group of toluene, we have attempted to isolate substantial reaction intermediates playing key roles for photochemical activation of alkylaromatics. When $Pt(PPh_3)_4$ was treated with neohexyl bromide in benzene with or without irradiation, light yellow crystals were isolated, and identified as *trans*-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ (**2**) (78% yield).

Interestingly, **2** has been readily and quantitatively converted to benzylplatinum(II) complexes **1** by irradiating in toluene. Toluene solution of *trans*-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ (**2**) was irradiated at 20°C. After 5 h, **1** was isolated as white crystals from the resulting light yellow suspension in 84% yield after recrystallization from toluene. The reaction solution was found to contain neohexane in 94%. When the reaction was carried out in toluene-d_8 (isotopic purity 99%), *trans*-$Pt(CD_2C_6D_5)Br(PPh_3)_2$ was obtained in 68% yield, and neohexane-d_1 (86% yield, isotopic purity 96%) was selectively generated. *p*-Xylene and mesitylene also reacted smoothly with **2** to yield the corresponding *trans*-$Pt(CH_2C_6H_4\text{-}4\text{-}Me)(PPh_3)_2$ (**3**) (83%) and *trans*-$Pt(CH_2C_6H_3\text{-}3,5\text{-}Me_2)(PPh_3)_2$ (**4**) (69%), respectively, affording a quantitative amount of neohexane as well.



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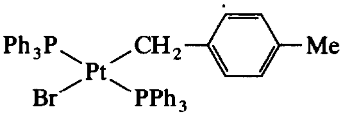

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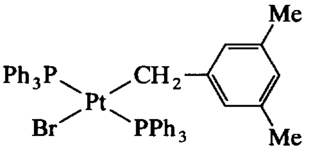

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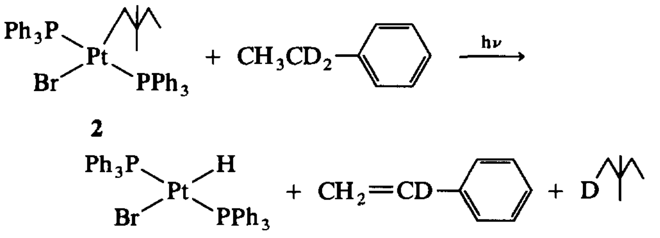
It should be noted that no trace of arylplatinum species was observed in any of the above reactions. Without irradiation, no apparent reaction occurred even at 80°C after 6 h, and the starting material **2** was quantitatively recovered.

Interestingly, *trans*-$PtMeI(PPh_3)_2$ and *cis*-$PtPhBr(PPh_3)_2$ were found to be inactive for these reactions with or without irradiation by recovering the starting Pt complexes.

2.3. *Ethylbenzene and cumene*

Regioselective sp^3 C–H bond scission at the benzylic position took place cleanly when **2** was irradiated in ethylbenzene or cumene at 20°C for 4 h giving styrene or α-methylstyrene in 87% or 92% yield, respectively. In each reaction, there was a quantitative yield of neohexane, while *trans*-$PtHBr(PPh_3)_2$ was isolated as a white crystalline solid in 67% or 75% yield, respectively. No sp^3 C–H bond cleavage of ethylbenzene occurred without irradiation (50°C, 10 h).

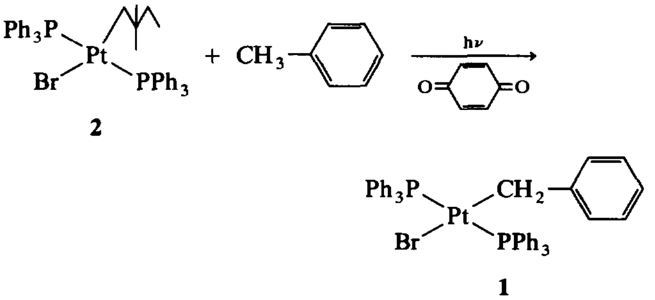
To investigate the regioselectivity of sp^3 C–H bond activation of ethylbenzene by **2**, we have prepared α,α'-dideuteroethylbenzene (isotopic purity 99%) derived by reduction of methyl benzoate with $LiAlD_4$. The treatment of **2** with deuterated ethylbenzene under the same reaction conditions stated above, resulted in the formation of styrene-d_1, neohexane-d_1 and a Pt-hydride complex as in the following scheme.



Under irradiation, the reaction of $Pt(PPh_3)_4$ with threefold $PhCH_2CH_2Br$ gave the isolable *trans*-$Pt(CH_2CH_2Ph)(PPh_3)_2$, whereas the reaction with PhCHBrMe extensively afforded styrene and *trans*-$PtHBr(PPh_3)_2$ which likely resulted from the transient *trans*-$Pt(CHMePh)Br(PPh_3)_2$. This may be compatible with the fact that the regioselective C–H bond cleavage of ethylbenzene by **1** took place at the benzylic position, although *trans*-$Pt(CHMePh)Br(PPh_3)_2$ could not be isolated.

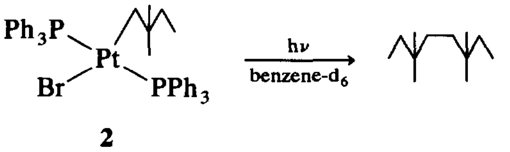
2.4. Possible mechanism of photochemical alkyl C–H bond cleavage of alkylaromatics

Basic to the understanding of these reactions is the answer to a primary question: what species abstract hydrogen from alkyl group of alkylaromatics? When **1** was irradiated in toluene-d_8 at 20°C, *trans*-$Pt(CD_2C_6D_5)Br(PPh_3)_2$ was isolated together with the formation of neohexane-d_1 selectively.



In this reaction, the isotope effect obtained from kinetic measurement at the initial stage until 35% of the starting complex **2** was converted to **1**, was estimated as $k_H/k_D = 4.6$. This may suggest that the rate determining step throughout the reaction could be virtually in the benzylic C–H bond cleavage step of toluene.

Importantly, this photochemical sp^3 C–H bond activation reaction of alkylaromatics has been considerably inhibited by the addition of threefold radical scavenger such as 1,4-benzoquinone or 9,10-dihydroanthracene. In Fig. 1, reaction of **2** with toluene was illustrated as the irradiation time-conversion curve of **2** to **1** with or without 1,4-benzoquinone. GC-MS analysis of the reaction residue suggested the formation of neohexyl adduct of 1,4-benzoquinone. These experimental facts suggest that these reactions may undergo a radical process involving photochemical homolysis of the Pt–alkyl bond which appears to be a general reaction pathway for many metal-alkyl species [3b,6]. Moreover, photochemical degradation (23°C, 8 h) of **2** in benzene-d_6 resulted in the formation of 3,3,6,6-tetramethyloctane (43%/**2**) with unidentified Pt complexes. This suggests that UV light apparently assists homolytic cleavage of a Pt–neohexyl bond of **2**.



These experimental results may be consistent with a reaction pathway involving a radical process as summarized in the following scheme [7*].

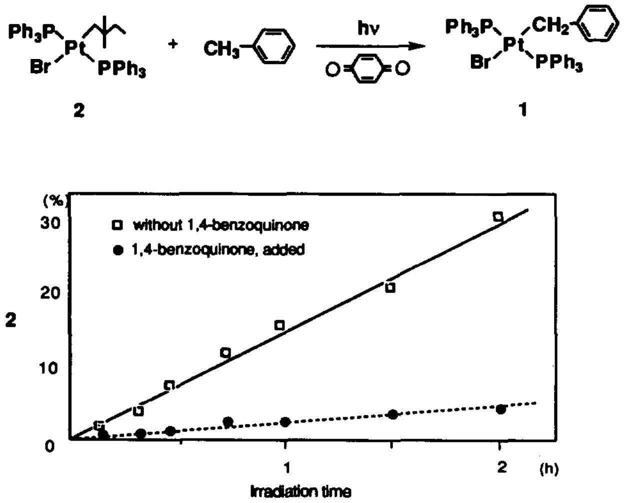
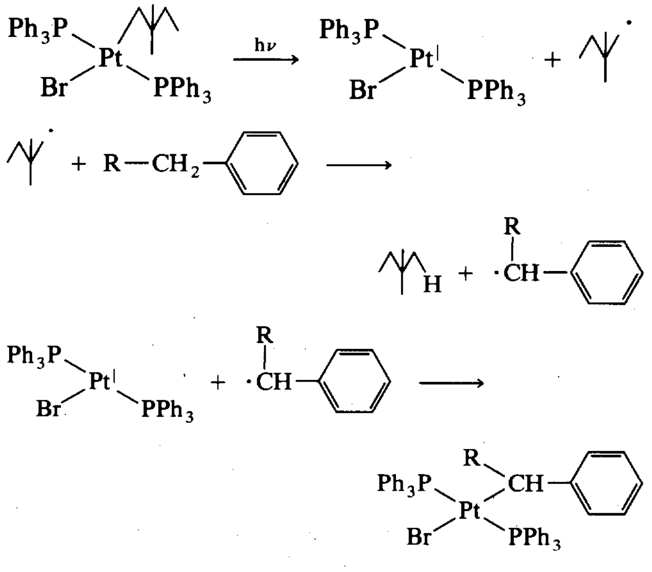


Fig. 1. Photochemical reaction of 2 with toluene with or without 1,4-benzoquinone.



R = H, CH$_3$

3. Experimental details

3.1. General procedure

All reactions and other manipulations were carried out by standard Schlenk technique under an atmosphere of prepurified nitrogen or welding grade argon purified over BASF catalyst and a molecular sieve(4 Å) before use. Solvents were freshly distilled from Na/benzophenone ketyl under a N_2 atmosphere before use. Chemical reagents were used without further purification unless otherwise noted. $Pt(PPh_3)_4$ and $Pt(PPh_3)_3$ were prepared by the method described previously [8]. NMR spectra were recorded on 90 MHz (Jeol, FX-90Q) and 400 MHz (Bruker, AM-400 and ARX-400) FT spectrometers. Chemical shifts were reported in δ down field from tetramethylsilane for ^1H and ^{13}C spectra, and from external 85% phosphoric acid for ^{31}P spectra. Mass spectra were recorded on a Shimadzu QP-1000 and Jeol DX-303HF. GC analyses were performed on Ohkura 802F with 2-m column packed with OV-1 (7%, 1 m), SE-30 (10%, 2 m), Durapak (2 m) and Unibeads A (60/80, 2 m); and on and Shimazu GC-17A capillary column with Durabond DB5 (30 m, film thickness 1.5 mm) with a Shimazu CR-7A data processing system. Infrared spectra were recorded on a Perkin Elmer FT-IR Type 1640. Elemental analyses were performed by the Chemical Analysis Center at Saitama University and the Institute of Physical and Chemical Research. Photo-irradiation was performed by using a Ushio 500-W high pressure mercury lamp (USH-500D) equipped with a Kenko U-350 band pass filter and HA-30 heat absorption filter.

3.2. 1-Bromo-2,2-dimethylbutane; neohexyl bromide

Into a solution of acetonitrile (180 ml) containing triphenylphosphine (75.0 g, 0.286 mol) was added dropwise 16.0 ml of bromine. Into the resulting light yellow suspension, after addition of 10 ml of pyridine at 0°C, 20 ml of dry acetonitrile containing 2,2-dimethyl-1-butanol (11.0 g, 0.108 mol) was added dropwise at 0°C, and was slowly heated at 85°C for 18 h. All volatiles were collected by distillation and were dissolved in water (800 ml). Neohexyl bromide separated from the water layer, was purified by distillation to yield a colorless liquid in 53% yield (9.39 g); b.p. 129–130°C. ^1H NMR ($CDCl_3$): δ 0.84 (t, 4-CH_3, 3H); 0.98 (s, 3-CH_3, 6H); 1.38 (q, 3-CH_2, 2H); 3.29 (s, 1-CH_2, 2H).

3.3. α,α'-Dideuteroethylbenzene

Into an ether (150 ml) suspension containing $LiAlD_4$ (7.43 g, 177 mmol, isotopic purity 99%) was added dropwise an ether (20 ml) solution of methyl benzoate (13.4 g, 98.0 mmol) at 0°C. After refluxing the mixture for 72 h, α,α'-dideuterobenzyl alcohol was obtained in 75% yield (9.75 g, 73.6 mmol) after usual workup. ^1H NMR ($CDCl_3$): δ 3.65 (br, OH, 1H); 7.08 (Ph, SH). Into acetonitrile (115 ml) a solution containing PPh_3 (52.6 g, 0.201 mol) was added dropwise 13.0 ml of bromine. Into the resulting light yellow suspension after addition of 8 ml of pyridine at 0°C, 15 ml of dry acetonitrile containing α,α'-dideuterobenzyl alcohol (5.97 g, 55.2 mmol) was added dropwise initially at 0°C and warmed up to be refluxed for 14 h. After usual workup, α,α'-dideuterobenzyl bromide was obtained as a colorless liquid (5.12 g, 29.6 mmol, 53.6% yield, b.p. 35–50°C at 20 mmHg). ^1H NMR ($CDCl_3$): δ 7.16 (Ph). MS: m/z 174, 172. Into an ether (17 ml) suspension containing Mg sand (0.854 mg, 35.1 mmol) was added α,α'-dideuterobenzyl bromide (4.79 g, 27.7 mmol). The resulting Grignard reagent was added into ether (20 ml) containing $NiBr_2(dppe)$ (0.327 mg, 0.368 mmol) and CH_3I at room temperature. After refluxing the mixture for 46 h, the ether layer was separated after the addition of water (30 ml). After removing ether under reduced pressure, α,α'-dideuteroethylbenzene was obtained as a colorless liquid (1.22 g, 11.2 mmol) in 40.4% yield based on methyl benzoate, b.p., 135-157°C. ^1H NMR: δ 1.22 (s, β-CH_3, 3H); 7.05 (Ph, SH). MS: m/z 109 (M^+), 94 ($M^+ - CH_3$), 79 ($M^+ - CH_3CD_2$). Isotopic purity was calculated as 99% from the ^1H NMR spectrum.

3.4. trans-Bromo(neohexyl)bis(triphenylphosphine)platinum(II) (2)

Neohexyl bromide (0.149 g, 0.903 mol) was added to 25 ml of benzene solution containing $Pt(PPh_3)_4$ (0.55 g, 0.442 mmol) under N_2. After irradiation for 8 h, the resulting yellow solution afforded a light yellow crystalline solid, after removing the ether under reduced pressure, in 77% yield (0.30 g). ^{1}H NMR ($CDCl_3$): δ 0.01 (t, CH_2CH_3, 3H); 0.26 (s, C-CH_3, 6H,), 0.40 (q, CH_2CH_3, 2H,); 1.12 (t, Pt-CH_2, J(Pt–H) = 79.0 Hz, J(P–H) = 8.6 Hz, 2H); 6.89–7.43 (m, Ph, 30H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 24.5 (s, J(Pt–P) = 3417 Hz). Anal. Found: C, 57.31; H, 5.11. $C_{42}H_{43}P_2BrPt$ calcd.: C, 57.02; H, 4.90%.

3.5. *trans-Bromo(benzyl)bis(triphenylphosphine)platinum(II) (1) from photochemical reaction of* $Pt(PPh_3)_4$ *with toluene in the presence of neohexyl bromide*

Into a toluene (10 ml) solution containing $Pt(PPh_3)_4$ (0.34 g, 0.27 mmol) was added neohexyl bromide (124.0 mg, 0.751 mmol) at room temperature. The reaction mixture was stirred and irradiated for 5 h. The resulting light yellow solution which was found to contain neohexane in 92% yield based on $Pt(PPh_3)_4$, was filtered through a celite pad. After removal of the solvent under a vacuum, the resulting white crystalline solid was recrystallized from toluene to give **1** as white crystals in 64% yield (68 mg). ^{1}H NMR ($CDCl_3$) 2.40 (t, J(Pt–H) = 91.3 Hz, J(H–P) = 8.0 Hz, Pt-CH_2, 2H); 6.44 (d, J(H–H) = 7.5 Hz, *o*-CH of CH_2–Ph, 2H); 6.73 (t, J(H–H) = 7.5 Hz, *m*-CH of CH_2–Ph, 2H); 6.64 (t, J(H–H) = 7.5 Hz, *p*-CH of CH_2–Ph, 1H); 7.11–7.81 (m, PPh_3, 30H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 17.1 (t, J(C–Pt) = 685 Hz, J(C–P) = 4.0 Hz, $PtCH_2$); 124.1 (s, 4-C of CH_2–Ph); 127.5 (s, 3-*C* of CH_2–Ph); 130.0 (s, 2-*C* of CH_2–Ph); 146.6 (s, J(C–Pt) = 47.9 Hz, 1-*C* of CH_2–Ph); 128.7, 130.4, 135.8 (m, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.9 (s, J(P–Pt) = 3265 Hz). Anal. Found: C, 58.06; H, 4.12. $C_{43}H_{37}P_2BrPt$ calcd.: C, 57.99; H, 4.19%.

3.6. *From photochemical reaction of* $Pt(CH_2CMe_2Et)Br(PPh_3)_2$ *(2) with toluene*

A toluene (10 ml) solution of neohexylplatinum complex **2** was irradiated at 20°C for 5 h, and then neohexane (94%) was found to be present in the resulting light yellow solution which was filtered through a celite pad to give a light yellow solution. Removal of toluene resulted in the formation of a white crystalline solid which was recrystallized from toluene to yield **1** in 84% yield (based on **2**).

3.7. *trans-Bromo(4-methylbenzyl)bis(triphenylphosphine)platinum(II) (3)*

trans-Bromo(4-dimetylbenzyl)bis(triphenylphosphine)platinum(II) was isolated from the photochemical reaction of **2** with *p*-xylene in 83% yield as a white crystalline solid. ^{1}H NMR (CD_2Cl_2): δ 2.19 (s, CH_3, 3H); 2.39 (t, J(H–Pt) = 92.4 Hz, J(H–P) = 8.0 Hz, Pt–CH_2, 2H); 6.26 (d, J(H–H) = 7.4 Hz, 2-H, 2H); 6.60 (d, J(H–H) = 7.4 Hz, 3-H, 2H); 7.14–7.68 (m, PPh_3, 30H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 25.5 (s, J(P–Pt) = 3275 Hz). Anal. Found: C, 58.74; H, 4.42. $C_{44}H_{39}P_2BrPt$ calcd.: C, 58.41; H, 4.35%.

3.8. *trans-Bromo(3,5-dimetylbenzyl)bis(triphenylphosphine)platinum(II) (4)*

trans-Bromo(3,5-dimetylbenzyl)bis(triphenylphosphine)platinum(II) was isolated from the photochemical reaction of **2** with mesitylene in 69% yield as a white crystalline solid. ^{1}H NMR (CD_2Cl_2): δ 1.96 (s, CH_3, 6H); 2.38 (t, J(H–Pt) = 93 3 Hz, J(H–P) = 8.0 Hz, $PtCH_2$, 2H); 5.99 (s, 2-H, 2H); 6.54 (s, 4-H, 2H); 7.12–7.89 (m, PPh_3, 30H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 25.9 (s, J(P–Pt) = 3254 Hz). Anal. Found: C, 58.62; H, 4.71. $C_{45}H_{41}P_2BrPt$ calcd.: C, 58.83; H, 4.50%.

3.9. *Photochemical reaction of 2 with ethylbenzene, α,α′-dideuteroethylbenzene and cumene*

An ethylbenzene (10 ml) solution of neohexylplatinum complex **2** (19.9 mg, 0.0225 mmol) containing benzene (3.01 mg, 0.0384 mmol) as a GC internal standard, was irradiated at 20°C for 4 h. The resulting light yellow suspension was analyzed to contain neohexane (97%) and styrene (87%). Removal of all the volatiles resulted in the formation of *trans*-$PtHBr(PPh_3)_2$ as a white crystalline solid which was recrystallized from ethylbenzene in 67% yield. ^{1}H NMR ($CDCl_3$): δ 14.8 (t, J(P–H) = 12.7 Hz, J(Pt–H) = 1242 Hz, PtH, 1H); 6.5-9,1 (m. PPh_3, 30H). ^{31}P(^{1}H} ($CDCl_3$): δ 29.0 (s, J(Pt–P) = 2990 Hz). All organic compounds were identified by GC-MS and NMR analysis of the samples collected by preparative GC of the reaction solution. Photochemical reaction of **2** with α,α′-dideuteroethylbenzene or cumene was performed in essentially the same way as stated above. The reaction solution obtained from the reaction of **2** with cumene afforded α-methylstyrene (92%), neohexane (92%) and *trans*-$PtHBr(PPh_3)_2$ (75%).

3.10. *Photochemical reaction of 2 with toluene in the presence of 1,4-benzoquinone*

In a pyrex NMR tube, 1,4-benzoquinone (5.9 mg, 0.0546 mmol) and neohexylplatinum complex **2** (16.7 mg, 0.0189 mmol) were dissolved in 0.5 ml of dry toluene. Then, the NMR tube was irradiated for 2 h at 20°C, and the formation ratio of **1** to **2** dependent on the reaction time was monitored every 10–30 min by ^{31}P{^{1}H} NMR.

3.11. *Photodecomposition of 2 in benzene-d_6*

In a pyrex NMR tube, neohexylplatinum complex **2** (16.7 mg, 0.0189 mmol) was dissolved in 0.7 ml of dry benzene-d_6. Then, the NMR tube was irradiated for 8 h at 23°C, and the formation of 3,3,6,6-tetramethyloctane (43%/2) was confirmed by ^{1}H NMR and GC-MS analysis: ^{1}H NMR 0.76 (t, CH_3–CH$_2$–, 6H); 0.79 (s, C–CH$_3$, 12H); 1.07 (s, 4-CH$_2$, 4H); 1.20 (q, 2-CH$_2$, 4H). GC-MS: m/z 170 (M$^+$).

Acknowledgment

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