

Iridium(III) Complexes of η^6 -Arenes with Olefinic and Cyclopropyl Substituents: Facile Conversion to η^3 -henylallyl Complexes

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Olefinic and cyclopropyl group substituted arenes (C_6H_5Y) react with $[Cp^*Ir(CH_3COCH_3)_3]A_2$ ($A=ClO_4^-, OTf^-$) to give η^6 -arene complexes, $[Cp^*Ir(\eta^6-C_6H_5Y)]^{2+}$ (**1a**: $Y=-CH=CH_2$ (**a**), $-CH=CHCH_3$ (**b**), $-C(CH_3)=CH_2$ (**c**), $-CH-CH_2-CH_2$ (**d**)). Complex **1b-1d** are readily converted into η^3 -allyl complexes, $[Cp^*(CH_3CN)Ir(\eta^3-CH(C_6H_5)CHCH_2)]^+$ (**2a**) and $[Cp^*(CH_3CN)Ir(\eta^3-CH_2C(C_6H_5)CH_2)]^+$ (**2b**), in the presence of Na_2CO_3 in CH_3CN . The η^6 -styrene complex, **1a** reacts with $NaBH_4$ to give η^5 -cyclohexadienyl complex, $[Cp^*Ir(\eta^5-C_6H_6-CH=CH_2)]^+$ (**3**), while with H_2 it gives η^6 -ethylbenzene complex $[Cp^*Ir(\eta^6-C_6H_5CH_2CH_3)]^{2+}$ (**4**). Complex **1a** and **1c** react with HCl to give $[Cp^*Ir(\eta^6-C_6H_5CH_2CH_2Cl)]^{2+}$ (**5a**) and $[Cp^*Ir(\eta^6-C_6H_5CH(CH_3)CH_2Cl)]^{2+}$ (**5b**), respectively.

Introduction

Cp^* ($\eta^5-C_5Me_5^-$) containing cationic η^3 -allyl iridium(III) complexes, $[Cp^*Ir(\eta^3-allyl)(L)]^+$ have been prepared in the course of C-H bond activation.¹⁻⁴ Bergman^{1,2} reported reactions of $Cp^*(PMe_3)Ir(CH_3)(OTf)$ ($OTf=OSO_2CF_3$) with *p*-xylene and cyclopropane, and $[Cp^*IrCl_2]$ with $CH_2=CHCH_2MgCl$ to obtain $[Cp^*(PMe_3)Ir(\eta^3-allyl)]^+OTf^-$ ($allyl=CH_2C_6H_4CH_3$, C_3H_5) and $Cp^*IrCl(\eta^3-C_3H_5)$, respectively, while Stryker³ and Maitlis⁴ used $[Cp^*Ir(S)_3]^{2+}$ ($S=CH_3CN$, CH_3COCH_3) to react with olefins to produce $[Cp^*Ir(olefin)(\eta^3-allyl)]^+$. During our investigation on the reactions of η^6 -arenes coordinated to iridium(III), we observed facile conversion of olefinic and cyclopropyl group substituted η^6 -arene compounds of iridium(III), $[Cp^*Ir(\eta^6-C_6H_5Y)]^{2+}$ (**1**, $Y=-CH=CHCH_3$ (**b**), $-C(CH_3)=CH_2$ (**c**), $-CH-CH_2-CH_2$ (**d**)) to η^3 -allyl iridium(III) compounds, $[Cp^*Ir(\eta^3-C_3H_5C_6H_5(CH_3CN))]^+$ (**2**). We have also observed somewhat interesting reactivities of complex **1a** toward $NaBH_4$, H_2 and HCl giving η^5 -cyclohexadienyl complexes ($[Cp^*Ir(\eta^5-C_6H_6CH=CH_2)]^+$, **3**), η^6 -ethylbenzene complex ($[Cp^*Ir(\eta^6-C_6H_5CH_2CH_3)]^{2+}$, **4**) and η^6 -2-chloro-ethylbenzene complex ($[Cp^*Ir(\eta^6-C_6H_5CH_2CH_2Cl)]^{2+}$, **5a**).

Experimental

Caution. Metal-perchlorate complexes and perchlorates are potentially explosive. Extensive precautions should be taken in handling those compounds.

The NMR spectra were obtained either on a Varian Gemini 200 or 300 MHz for 1H and 75 or 68 MHz for ^{13}C . A Shimadzu IR-440 was used for infrared spectral measurements. Elemental analyses were carried out at the Organic Chemistry Research Center, Sogang University, Korea. A Wiss-Tech Werstätten Weilheim/Obb. LBR conductivity meter was used for conductance measurements. Compounds, **1** ($[Cp^*Ir(\eta^6-C_6H_5Y)]^{2+}$) were prepared by the literature method⁶ via the generation of $[Cp^*Ir(CH_3COCH_3)_3]^{2+}$ in solution to which arenes were added to produce **1** (see Experimental for details). Most organic compounds were

reagent grade (from Aldrich) and used as purchased.

Synthesis of η^6 -arene complexes, **1**

$[Cp^*Ir(\eta^6-C_6H_5CH=CH_2)(ClO_4)_2]$ (1a**).** A 0.11 gram of $AgClO_4$ (0.53 mmol) was added to CH_3COCH_3 (15 mL) solution of $[Cp^*IrCl_2]$ (0.10 g, 0.13 mmol) and the resulting reaction mixture was stirred at 25 °C under N_2 for 30 minutes before the white precipitation of $AgCl$ was removed by filtration. A 0.45 gram of styrene (4.35 mmol) was added to the filtrate solution, and the pale-yellow resulting solution was stirred further for an hour before the removal of solvent (CH_3COCH_3) by vacuum distillation to obtain beige solid. After adding CH_2Cl_2 (10 mL) to this beige solid, insoluble material(s) was removed by filtration. The filtrate was dried by vacuum distillation before recrystallization with $CH_3CN/(C_6H_5)_2O$ to obtain beige-white microcrystals of $[Cp^*Ir(\eta^6-C_6H_5CH=CH_2)(ClO_4)_2]$, **1a** (0.132 g, 82%). 1H NMR (CD_3CN , 25 °C) δ 6.23 (d, 1H, $J(H_a-H_b)=11$ Hz, H_a), 6.36 (d, 1H, $J(H_b-H_c)=17$ Hz, H_b), 6.6 (dd, 1H, H_c), 2.25 (s, 15H, CH_3 of Cp^*), 7.2-7.4 (m, 5H, C_6H_5).

$[Cp^*Ir(\eta^6-C_6H_5CH=CHCH_3)(ClO_4)_2]$ (1b**).** This compound was prepared in the same manner as described for **1a** above. The yield was 80% based on $[Cp^*Ir(\eta^6-C_6H_5CH=CH_2)(ClO_4)_2]$, **1b**. 1H NMR (CD_3CN , 25 °C) δ 6.97 (dq, 1H, $J(H_a-CH_3)=3$ Hz, $J(H_a-H_b)=16$ Hz, H_a), 6.27 (d, 1H, H_b), 2.18 (d, 3H, CH_3), 2.22 (s, 15H, CH_3 of Cp^*), 7.1-7.2 (m, 5H, C_6H_5).

$[Cp^*Ir(\eta^6-C_6H_5C(CH_3)=CH_2)(ClO_4)_2]$ (1c**).** This compound was prepared in the same manner as described for **1a** above. The yield was 76% based on $[Cp^*Ir(\eta^6-C_6H_5C(CH_3)=CH_2)(ClO_4)_2]$, **1c**. 1H NMR (CD_3CN , 25 °C) δ 6.06 (m, 2H, H_a and H_b), 2.12 (m, 3H, CH_3), 2.24 (s, 15H, CH_3 of Cp^*), 7.3-7.5 (m, 5H, C_6H_5).

$[Cp^*Ir(\eta^6-C_6H_5CHCH_2CH_2)(ClO_4)_2]$ (1d**).** This compound was prepared in the same manner as described for **1a** above. The yield was 72% based on $[Cp^*Ir(\eta^6-C_6H_5-CHCH_2CH_2)(ClO_4)_2]$, **1d**. 1H NMR (CD_3CN , 25 °C) δ 2.27-2.42 (m, 1H, H_a), 1.57 (dt, 2H, H_bH_c), 1.10 (dt, 2H,

H_b, H_c), 2.20 (s, 15H, CH_3 of Cp^*), 7.1-7.2 (m, 5H, C_6H_5).

AgOTf ($\text{AgOSO}_2\text{CF}_3$) can be used to prepare OTf^- salts ($[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{Y})](\text{OTf})_2$ for example) in approximately the same yields (70-80%).

Synthesis of η^3 -allyl complexes, 2

$[\text{Cp}^*(\text{CH}_3\text{CN})\text{Ir}(\eta^3\text{-CH}_2\text{CHCHC}_6\text{H}_5)](\text{OTf})_2$, 2a. A colorless CH_3CN (10 mL) solution of **1b**, $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}=\text{CHCH}_3)](\text{OTf})_2$ (0.1 g, 0.14 mmol) was refluxed in the presence of Na_2CO_3 (slightly dissolved) (0.04 g, 0.4 mmol) for 40 minutes during which time the reaction mixture turned yellow. Vacuum distillation of CH_3CN resulted in yellowish solid which was dissolved in CH_2Cl_2 (10 mL). Insoluble compounds (Na_2CO_3 and NaOTf) were removed by filtration and pale yellow micro crystals of **2a** were obtained by recrystallization with $\text{CH}_2\text{Cl}_2/(\text{C}_2\text{H}_5)_2\text{O}$. The yield was 0.051 g or 64% based on $[\text{Cp}^*(\text{CH}_3\text{CN})\text{Ir}(\eta^3\text{-C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5)](\text{OTf})_2$, **2a**. ^1H NMR (CDCl_3 , 25 °C) δ 4.25 (d, 1H, $J(\text{H}_a\text{-H}_b)=11$ Hz, H_a), 5.15 (m, 1H, H_b), 3.40 (d, 1H, $J(\text{H}_b\text{-H}_c)=7$ Hz, H_c), 2.43 (d, 1H, $J(\text{H}_b\text{-H}_c)=10$ Hz, H_c), 2.88 (s, 3H, CH_3CN), 1.60 (s, 15H, CH_3 of Cp^*), 7.2-7.4 (m, 5H, C_6H_5). ^{13}C NMR (CDCl_3 , 25 °C) δ 70 (C_a), 84 (C_b), 48 (C_c), 100 (Cp^*), 131, 132, 134, 144 (C_6H_5), 4, 123 (CH_3CN). Anal. Calcd for $\text{IrC}_{22}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_5\text{S}$: C, 41.63; H, 4.29; N, 2.21. Found: C, 41.29; H, 4.19; N, 2.29.

$[\text{Cp}^*(\text{CH}_3\text{CN})\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2)](\text{OTf})_2$, 2b. This compound was prepared in the same manner as described for **2a** above. The yield was 76% based on $[\text{Cp}^*(\text{CH}_3\text{CN})\text{Ir}(\eta^3\text{-CH}_2\text{CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2)](\text{OTf})_2$, **2b**. ^1H NMR (CDCl_3 , 25 °C) δ 4.41 (dd, 2H, $J=1.5$ and 2.0 Hz, H_{syn}), 2.30 (dd 2H, H_{anti}), 2.00 (s, 3H, CH_3CN), 1.60 (s, 15H, CH_3 of Cp^*), 7.3-7.7 (m, 5H, C_6H_5).

The reaction of cyclopropylbenzene compound, $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CHCH}_2\text{CH}_2)](\text{OTf})_2$ (**1d**) with CH_3CN in the presence of Na_2CO_3 gave only **2a** but not **2b** at all. The yield was relatively low (57%) based on **2a**.

Reactions

Reaction of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}=\text{CH}_2)](\text{ClO}_4)_2$ (1a**) with NaBH_4 .** A 0.01 g NaBH_4 (0.26 mmol) was very slowly added for an hour into a THF solution (10 mL) of **1a** (0.1 g, 0.16 mmol) at -60 °C under N_2 and the resulting reaction mixture was warmed up to 25 °C and stirred for an hour before it was filtered. Beige-white solid of **3** was obtained through recrystallization with $\text{CH}_2\text{Cl}_2/(\text{C}_2\text{H}_5)_2\text{O}$ after the solvent (THF) was removed by vacuum distillation. The yield

NMR (CD_3COCD_3 , 25 °C, see Figure 1 and 2 for signal as-

signments) **3a** ($[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_b\text{CH}_c\text{CH}_d\text{CH}_c\text{C}(\text{CH}=\text{CH}_2)\text{CH}_a\text{-H}_a)]\text{ClO}_4$): δ 3.55 (dd, 1H, $J(\text{H}_a\text{-H}_b)=13$ Hz, $J(\text{H}_a\text{-H}_c)=7$ Hz, H_a), 4.56 (d, 1H, H_c), 4.02 (t, 1H, $J(\text{H}_b\text{-H}_c)=7$ Hz, H_b), 5.68 (t, 1H, $J(\text{H}_c\text{-H}_d)=7$ Hz, H_c), 5.76 (d, 1H, $J(\text{H}_c\text{-H}_d)=7$ Hz, H_c), 6.97 (t, 1H, H_d), 5.8-6.3 (m, 3H, $-\text{CH}=\text{CH}_2$, overlapped with vinyl protons of other isomers), 2.31 (s, 15H,

CH_3 of Cp^*). **3b** ($[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_b\text{CH}_c\text{CH}_d\text{C}(\text{CH}=\text{CH}_2)\text{CH}_b\text{CH}_a\text{-H}_a)]\text{ClO}_4$): δ 3.25 (dt (sextet like), 1H, $J(\text{H}_a\text{-H}_b)=13$ Hz, $J(\text{H}_a\text{-H}_c)=7$ Hz, H_a), 4.62 (d, 1H, H_b), 4.02 (t, 1H, $J(\text{H}_b\text{-H}_c)=7$ Hz, H_b), 4.08 (d, 1H, $J(\text{H}_b\text{-H}_d)=7$ Hz, H_b), 5.68 (t, 1H, $J(\text{H}_c\text{-H}_d)=7$ Hz, H_c), 7.19 (d, 1H, H_d), 6.61 (dd, $J(\text{H}_c\text{-H}_b)=17$ Hz, $J(\text{H}_c\text{-H}_d)=10$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.8-6.3 (m, 2H, $-\text{CH}=\text{CH}_2$, overlapped with vinyl protons of other isomers), 2.33 (s, 15H, CH_3 of Cp^*).

3c ($[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_y\text{CH}_z\text{C}(\text{CH}=\text{CH}_2)\text{CH}_z\text{CH}_y\text{CH}_x\text{H}_x)]\text{ClO}_4$): δ 3.25 (dt (sextet like), 1H, $J(\text{H}_x\text{-H}_y)=13$ Hz, $J(\text{H}_x\text{-H}_z)=7$ Hz, H_x), 4.38 (d, 1H, H_y), not observed (2H, H_y and H_z), 5.77 (t, 2H, $J(\text{H}_z\text{-H}_y)=7$ Hz H_z and H_y), 6.49 (dd, 1H, $J(\text{H}_z\text{-H}_y)=17$ Hz, $J(\text{H}_z\text{-H}_x)=10$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.8-6.3 (m, 2H, $-\text{CH}=\text{CH}_2$, overlapped with vinyl protons of other isomers), 2.33 (s, 15H, CH_3 of Cp^*).

Reactions of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}=\text{CH}_2)](\text{ClO}_4)_2$ (1a**) with H_2 .** A CH_3CN solution (20 mL) of **1a** (0.2 g, 0.32

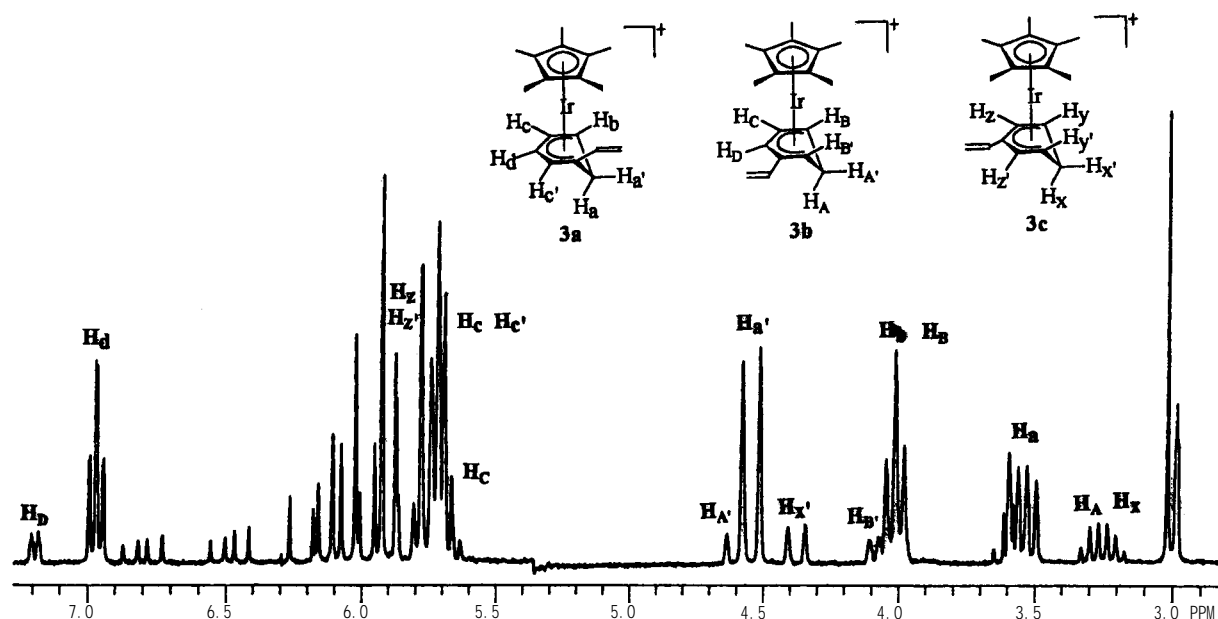


Figure 1. ^1H NMR spectrum of $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_6\text{-CH}=\text{CH}_2)](\text{ClO}_4)_3$, **3** (mixture of **3a**, **3b** and **3c**, see also Figure 2 and text for detailed assignments) in $(\text{CD}_3)_2\text{CO}$ at 25 °C at 200 MHz.

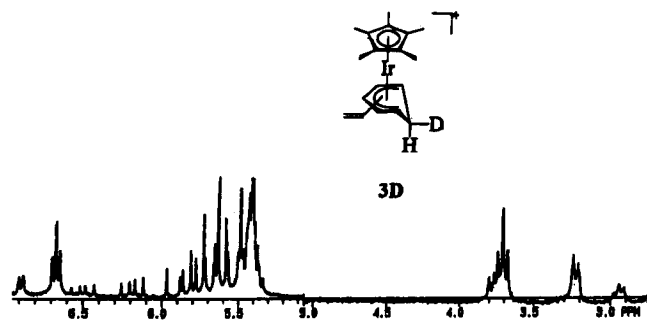


Figure 2. ^1H NMR spectrum of $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{D-CH=CH}_2)](\text{ClO}_4)$, **3D** in $(\text{CD}_3)_2\text{CO}$ at 25°C at 200 MHz.

mmol) was kept at room temperature for 2 days under H_2 (4 atm.) in a bomb reactor (Parr 1341, 360 mL). Beige-white solid of **4** ($[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_3\text{C}_2\text{H}_3)](\text{ClO}_4)_2$) (81 %) was isolated by filtration after saturation with $(\text{C}_2\text{H}_5)_2\text{O}$ (10 mL). **4**: ^1H NMR (CD_3CN , 25°C) δ 2.75 (q, 2H, $J(\text{CH}_2\text{-CH}_3)=7$ Hz, $-\text{CH}_2\text{-CH}_3$), 1.36 (t, 3H, $-\text{CH}_2\text{-CH}_3$), 7.23 (m, 5H, C_6H_3), 2.28 (s, 15H, CH_3 of Cp^*)

Reactions of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH=CH}_2)](\text{ClO}_4)_2$ (1a**) with HCl.** Dry HCl gas was bubbled into CH_3CN solution (15 mL) of **1a** for 1 minute in a 200 mL round bottom flask at 0°C and the resulting solution was stirred for 12 hours under HCl (*ca.* 1 atm.). After removing HCl and solvent by vacuum distillation, beige-white solid of **5a** ($[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl})](\text{ClO}_4)_2$, (85%)) was obtained through recrystallization with $\text{CH}_2\text{Cl}_2/(\text{C}_2\text{H}_5)_2\text{O}$. **5a**: ^1H NMR ($\text{CD}_3\text{-COCD}_3$, 25°C) δ 3.95 (t, 2H, $J(\text{CH}_2\text{-CH}_2\text{Cl})=6$ Hz, $\text{CH}_2\text{-CH}_2\text{Cl}$), 3.12 (t, 2H, $\text{CH}_2\text{CH}_2\text{Cl}$), 7.38 (m, 5H, C_6H_5), 2.31 (s, 15H, CH_3 of Cp^*).

Reactions of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2)](\text{ClO}_4)_2$ (1c**) with HCl.** This reaction was carried out in the same way as described above for the reaction of **1a** with HCl except that the reaction time was 4 hours. ^1H NMR spectrum of the beige-white solid product shows all the signals due to **1c** (57%) and new signals (see data below) due to $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})](\text{ClO}_4)_2$, **5b** (43%). **5b**: ^1H NMR (CD_3COCD_3 , 25°C) δ 3.38 (m, 1H, $\text{CH}(\text{CH}_3)$), 3.90 (m, 2H, CH_2Cl), 1.42 (d, 3H, $J(\text{CH}_2\text{-CH}(\text{CH}_3))=7$ Hz, $\text{CH}(\text{CH}_3)$), 7.39 (m, 5H, C_6H_5), 2.31 (s, 15H, CH_3 of Cp^*).

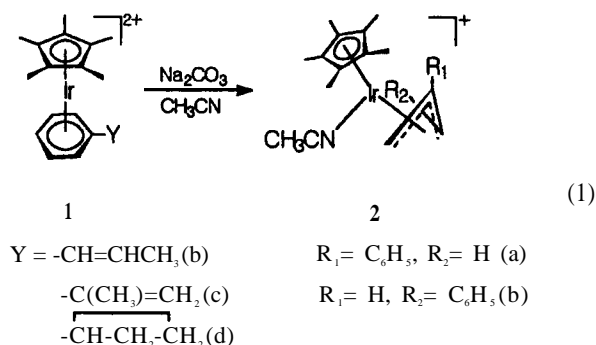
Results and Discussion

While $\text{Cp}^*\text{Ir(III)}$ complexes containing η^6 -arenes (with various substituents) and related ligands have been prepared before,⁶⁻⁹ no olefin substituted η^6 -arene containing $\text{Cp}^*\text{Ir(III)}$ complexes, to the best of our knowledge, have been reported thus far. Complex **1** ($[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{Y})]^{2+}$; $\text{Y}=-\text{CH}=\text{CH}_2$ (**a**), $-\text{CH}=\text{CH-CH}_3$ (**b**), $-\text{C}(\text{CH}_3)=\text{CH}_2$ (**c**), $-\text{CH-CH}_2\text{-CH}_2$ (**d**)) were prepared from the reactions of $[\text{Cp}^*\text{Ir}(\text{CH}_3\text{CO-CH}_3)_2]^{2+}$ with $\text{C}_6\text{H}_5\text{Y}$ in the same manner as reported previously for $[\text{Cp}^*\text{Ir}(\eta^6\text{-arene})]^{2+}$.⁶ Spectral data (see Experimental) analysis unambiguously suggests that $\text{C}_6\text{H}_5\text{Y}$ in complex **1** are coordinated to iridium through the π -system of the arene ring in η^6 -fashion as previously reported,⁶⁻⁹ but not through the π -system of the olefinic group. For example, ^1H NMR spectra of **1** show no significant shifts for the sig-

nals due to the olefinic protons of **Y** upon coordination of $\text{C}_6\text{H}_5\text{Y}$ to " Cp^*Ir " (see data in Experimental section). X-ray crystal analysis for **1a** clearly show no interaction between iridium and the olefinic group, $-\text{C}_\alpha\text{H}=\text{C}_\beta\text{H}_2$ (for example, $\text{Ir-C}_\alpha=3.38 \text{ \AA}$, $\text{Ir-C}_\beta=4.28 \text{ \AA}$).

Complex **1b-1d** are readily converted into η^3 -phenylallyl iridium(III) compounds, $[\text{Cp}^*(\text{CH}_3\text{CN})\text{Ir}(\eta^3\text{-CH}(\text{C}_6\text{H}_5)\text{CHCH}_2)]^+$ (**2a**) and $[\text{Cp}^*(\text{CH}_3\text{CN})\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2)]^+$ (**2b**) in refluxing CH_3CN in the presence of Na_2CO_3 (eq. 1). Formation of **2** occurs very slowly even in the absence of Na_2CO_3 . Complex **2a** is the only product from the reaction of **1d** (complex **2b** has never been observed). ^1H NMR and ^{13}C NMR spectra of **2** (see Experimental section) show all those well-established signals due to η^3 -allyl moiety¹⁰ along with those due to coordinated Cp^* and CH_3CN . Complex **2a** can also be prepared from the reaction of $[\text{Cp}^*\text{Ir}(\text{CH}_3\text{-CN})_3]^{2+}$ with $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$ in the presence of Na_2CO_3 where $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2)]^{2+}$ has never been isolated even in the absence of Na_2CO_3 . It should be mentioned that η^3 -phenylallyl complex **2a** and **2b** are also obtained from direct reactions of $[\text{Cp}^*\text{Ir}(\text{CH}_3\text{CN})_3]^{2+}$ ⁶ with $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ and $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$, respectively in the presence of Na_2CO_3 .

NOE difference spectroscopy has been used for elucidation of the relative positions of Cp^* and η^3 -allyl group in $\text{Cp}^*\text{M}(\eta^3\text{-allyl})$ species.^{11,12} The NOE measurements for **2a**¹³ show that i) β -carbon of the allyl group is toward to Cp^* group (called as *exo* form¹²) and ii) the phenyl group is also toward to Cp^* to some extent as shown by **2** in equation 1.



Cationic allyl complexes of $[\text{Cp}^*\text{Ir}(\eta^3\text{-allyl})(\text{L})]^{n+}$ ($\text{L}=\text{PR}_3$, Cl ,² olefin²⁴) have been prepared in various methods,¹⁻⁴ to which we now wish to add another way of preparing $[\text{Cp}^*\text{Ir}(\eta^3\text{-allyl})(\text{C}_6\text{H}_5)(\text{CH}_3\text{CN})]^+$ from olefin substituted η^6 -arene complexes, **1** according to eq. 1. The OTf^- salts of **1** are preferred reactants (rather than the ClO_4^- salts) for this reaction (eq. 1) since the OTf^- salts seem to give slightly higher yields of **2** than do ClO_4^- salts and are evidently safer than ClO_4^- salts.

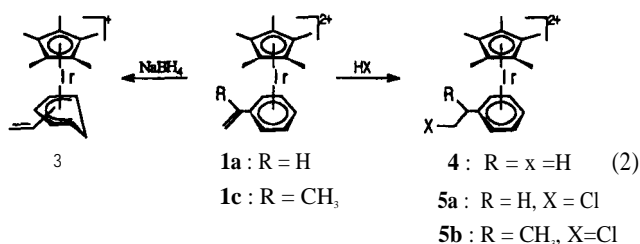
While the reaction of complex **1a** with NaBH_4 gives cyclohexadienyl complexes, $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_6(-\text{CH}=\text{CH}_2))]^+$ (**3**) (eq. 2), olefinic group hydrogenated η^6 -ethylbenzene complex, $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5(-\text{C}_2\text{H}_5))]^{2+}$ (**4**) and olefinic group HCl added η^6 -2-chloroethylbenzene complex, $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5(-\text{CH}_2\text{CH}_2\text{Cl}))]^{2+}$ (**5a**) are obtained from the reaction of **1a** with H_2 and HCl, respectively (eq. 2).

Detailed ^1H NMR spectral data for η^5 -cyclohexadienyl

metal complexes and related compounds have been reported.^{7,8,14,15} It has been well-established that H^- attacks iridium-coordinated arenes in $[Cp^*Ir(\eta^6-C_6H_5Y)]^{2+}$ ($Y=H, CH_3, t-Bu, CH_3O, Cl, OH$) to give η^5 -cyclohexadienyl metal complexes, $[Cp^*Ir(\eta^5-C_6H_5Y)]^+$.^{7,9} For example, three isomers (ortho/meta/para=46/37/17) were obtained (while no ipso isomer was observed) from the reaction of $[Cp^*Ir(\eta^6-C_6H_5C H_3)]^{2+}$.

Close examination of the 1H NMR spectrum of the product, **3** led us to suggest that it contains three isomers, **3a**

$([Cp^*Ir(\eta^5-CHCHCHCHC(CH=CH_2)CH_3)]ClO_4)$, **3b** $([Cp^*Ir(\eta^5-CHCHCHCHC(CH=CH_2)CHCH_3)]ClO_4)$ and **3c** $([Cp^*Ir(\eta^5-CHCHCHCHC(CH=CH_2)CHCHCH_3)]ClO_4)$ in the ratio 4 (**3a**) : 1 (**3b**) : 1 (**3c**) (see Figure 1).



Deutero cyclohexadienyl compounds, $[Cp^*Ir(\eta^5-C_6H_5D(-CH=CH_2))]^+$ (**3D**) were also obtained from the reaction of **1a** with $NaBD_4$. Comparing the 1H NMR spectra of the two products (**3** and **3D**) enabled us to assign the signals due to the incoming H (or D), *i.e.*, H_a' (δ 4.56 ppm, **3a**), H_b (δ 4.62 ppm, **3b**) and H_x (δ 4.38 ppm, **3c**) in Figure 1 disappear in the spectrum of **3D** in Figure 2. Differences in coupling pattern between the 1H NMR spectra of **3** and **3D** along with decoupling measurements for most signals were also useful for us to assign other signals such as those due to H_a and H_b .

It may be said that the ratio of isomers (**3a** / **3b** / **3c** = 4/1/1) in the product **3** is not the one (2:2:1) that one can predict by random attack of H on arene carbons.

It is interesting to notice that molecular hydrogen (H_2) attacks the olefinic group of **1a** to give η^5 -ethylbenzene complex, **4** leaving the coordinated arene ring intact (see eq. 2) since no such study has been previously reported. Detailed reaction pathways are yet to be investigated. The olefinic group hydrogenation of the coordinated styrene in **1a** prompted us to look into the reaction of **1** with HCl. Anti-Markovnikov addition of HCl to $-C_\alpha H=C_\beta H_2$ in **1a** to give

5a and to $-C_\alpha(CH_3)H=C_\beta H_2$ in **1c** to give **5b** (eq. 2) may suggest the initial attack of H^+ on α -carbon (unlike the attack of H on the arene ring of **1a** as described above) followed by Cl attack on β -carbon.

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References

- Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462.
- Maghee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.
- Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428.
- White, C.; Thomson, S. J.; Maitlis, P. M. *J. Chem. Soc. Dalton* **1978**, *130*, 1305.
- X-ray analysis for the crystals of $[Cp^*Ir(\eta^6-C_6H_5CH=CH_2)](ClO_4)_2$ has been determined and will be reported elsewhere.
- White, C.; Thomson, S. J.; Maitlis, P. M. *J. Chem. Soc. Dalton* **1977**, 1654.
- White, C.; Maitlis, P. M. *J. Chem. Soc. (A)*, **1971**, 3322.
- Espinete, P.; Bailey, P. M.; Downey, R. F.; Maitlis, P. M. *J. Chem. Soc. Dalton* **1980**, 1048.
- Grudy, S. L.; Maitlis, P. M. *J. Organomet. Chem.* **1984**, *272*, 265.
- $Ir(\eta^3-CH_2CHCH(C_6H_5))$ moiety has been also identified in the x-ray crystal analysis for the product ($[Ir(\eta^3-CH_2CHCH(C_6H_5)(NH=C(CH_3)(NCH_2CH_3))]^{2+}$) of the reaction of **2a** with diethylamine, which will be reported elsewhere.
- Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346.
- Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16.
- Irradiation of CH_3 (1.6 ppm) of Cp^* shows a significant enhancement in the signal due to the β -carbon bound proton, H_b (7.2%) at δ 3.40 and somewhat smaller effects in the signals due to the *endo* proton (H_c , 2.9%) bound to α -carbon of the allyl group and the phenyl protons (2.5%).
- Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. *J. Organometallics* **1988**, *8*, 286.
- Thompson, R. L.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 8961.