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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$_6$H$_5$) CHCH$_3$)]$^-$ (**2a**) and $[Cp*(CH_3CN) Ir(\eta^3$-CH$_2$C(C$_6$H$_5$)CH$_2$)]$^-$ (**2b**), in the presence of Na$_2$CO$_3$ in CH$_3$CN. 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* (η^5-C$_5$Me$_5^-$) 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$_2$CF$_3$) with *p*-xylene and cyclopropane, and $[Cp*IrCl_2]_2$ with CH$_2$=CHCH$_2$-MgCl to obtain $[Cp*(PMe_3)Ir(\eta^3$-allyl)]$^+$OTf$^-$(allyl=CH$_2$C$_6$-H$_4$CH$_3$, C$_3$H$_5$) and Cp*IrCl(η^3-C$_3$H$_5$), respectively, while Stryker[3] and Maitlis[4] used $[Cp*Ir(S)_3]^2$ (S= CH$_3$CN, CH$_3$-COCH$_3$) 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, $[Cp*Ir(h^3$-C$_3$H$_4$C$_6$H$_4$(CH$_3$CN)] (**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$_6$H$_6$CH=CH$_2$)]$^+$, **3**), η^6-ethylbenzene complex ($[Cp*Ir(\eta^6$-C$_6$H$_5$C$_2$H$_5$)]$^{2+}$, **4**) and η^6-2-chloro-ethylbenzene complex ($[Cp*Ir(\eta^6$-C$_6$H$_5$CH$_2$CH$_2$Cl)]$^+$, **5a**).

Experimental

Caution. Metal-perchlorato 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 ¹³C. 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 Werstatten Weilheim/Obb. LBR conductivity meter was used for conductance measurements. Compounds, **1** ($[Cp*Ir(\eta^6$-C$_6$H$_5$Y)]$^{2+}$) were prepared by the literature method[5] *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$_6$H$_5$CH=CH$_2$](ClO$_4$)$_2$ (1a). A 0.11 gram of AgClO$_4$ (0.53 mmol) was added to CH$_3$COCH$_3$(15 mL) solution of $[Cp*IrCl_2]_2$(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$_3$COCH$_3$) by vacuum distillation to obtain beige solid. After adding CH$_2$Cl$_2$ (10 mL) to this beige solid, insoluble material(s) was removed by filtration. The filtrate was dried by vacuum distillation before recrystallization with CH$_3$CN/(C$_2$H$_5$)$_2$O to obtain beige-white microcrystals of $[Cp*Ir(\eta^6$-C$_6$H$_5$CH$_2$=CH$_2$H$_b$)](ClO$_4$)$_2$, **1a** (0.132 g, 82%). ¹H NMR (CD$_3$CN, 25 °C) δ 6.23 (d, 1H, *J* (H$_c$-H$_b$)=11 Hz, H$_c$), 6.36 (d, 1H, *J* (H$_b$-H$_a$)=17 Hz, H$_b$), 6.6 (dd, 1H, H$_a$), 2.25 (s, 15H, CH$_3$ of Cp*), 7.2-7.4 (m, 5H, C$_6$H$_5$).

$[Cp*Ir(\eta^6$-C$_6$H$_5$CH=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$_6$H$_5$CH$_b$=CH$_a$CH$_3$)](ClO$_4$)$_2$, **1b.** ¹H NMR (CD$_3$CN, 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$_6$H$_5$).

$[Cp*Ir(\eta^6$-C$_6$H$_5$C(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$_6$H$_5$C(CH$_2$)=CH](ClO$_4$)$_2$. **1c.** ¹H NMR (CD$_3$CN, 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$_6$H$_5$).

$[Cp*Ir(\eta^6$-C$_6$H$_5$CHCH$_2$CH$_2$)](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$_6$H$_5$-CH$_2$CH$_2$H$_b$CH$_2$H$_d$](ClO$_4$)$_2$. **1d.** ¹H NMR (CD$_3$CN, 25 °C) δ 2.27-2.42 (m, 1H, H$_a$), 1.57 (dt, 2H, H,H,H$_d$), 1.10 (dt, 2H,

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

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

Synthesis of η³-allyl complexes, 2

[Cp*(CH$_3$CN)Ir(η³-CH$_2$CHCHC$_6$H$_5$)](OTf), 2a. A colorless CH$_2$CN (10 mL) solution of 1b, [Cp*Ir(η-C₆H₅CH =CHCH$_3$)](OTf), (0.1 g, 0.14 mmol) was refluxed in the presence of Na$_2$CO$_3$ (slightly dissolved) (0.04 g, 0.4 mmol) for 40 minutes during which time the reaction mixture turned yellow. Vacuum distillation of CH$_3$CN resulted in yellowish solid which was dissolved in CH$_2$Cl$_2$ (10 mL). Insoluble compounds (Na$_2$CO$_3$ and NaOTf) were removed by filtration and pale yellow micro crystals of 2a were obtained by recrystallization with CH$_2$Cl$_2$/(C$_2$H$_5$)$_2$O. The yield was 0.051 g or 64% based on [Cp*(CH$_3$CN)Ir(η-C₆H₅-C₆H₅C₆H₅C₆H₅)](OTf). 2a. ¹H NMR (CDCl$_3$, 25 °C) δ 4.25 (d, 1H, J (H_a-H_b)=11 Hz, H_a), 5.15 (m, 1H, H_b), 3.40 (d, 1H, J (H_b-H_c)=7 Hz, H_c), 2.43 (d, 1H, J (H_c-H_d=10 Hz, H_d), 2.88 (s, 3H, CH$_3$CN), 1.60 (s, 15H, CH$_3$ of Cp*), 7.2-7.4 (m, 5H, C$_6$H$_5$). ¹³C NMR (CDCl$_3$, 25 °C) δ 70 (C$_a$), 84 (C$_b$), 48 (C$_c$), 100 (Cp*), 131, 132, 134, 144 (C$_6$H$_5$), 4, 123 (CH$_3$CN). Anal. Calcd for IrC$_{22}$H$_{27}$F$_3$NO$_3$S: C, 41.63; H, 4.29; N, 2.21. Found: C, 41.29; H, 4.19; N, 2.29.

[Cp*(CH$_3$CN)Ir(η³-CH$_2$C(C$_6$H$_5$)CH$_2$](OTf), 2b. This compound was prepared in the same manner as described for 2a above. The yield was 76% based on [Cp*(CH$_3$CN)Ir(η³-CH$_{syn}$H$_{anti}$C(C$_6$H$_5$)CH$_{syn}$H$_{anti}$](OTf), 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$_3$CN), 1.60 (s, 15H, CH$_3$ of Cp*), 7.3-7.7 (m, 5H, C$_6$H$_5$).

The reaction of cyclopropylbenzene compound, [Cp*Ir(η-
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C$_6$H$_5$CHCH$_2$CH$_2$)](OTf), **(1d)** with CH$_3$CN in the presence of Na$_2$CO$_3$ gave only 2a but not 2b at all. The yield was relatively low (57%) based on 2a .

Reactions

Reactions of [Cp*Ir(η⁶-C$_6$H$_5$CH=CH$_2$] (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 CH$_2$Cl$_2$/(C$_2$H$_5$)$_2$O after the solvent (THF) was removed by vacuum distillation. The yield

NMR (CD$_3$COCD$_3$, 25 °C, see Figure 1 and 2 for signal as-
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signments) **3a** ([Cp*Ir(η³-CH$_2$CH$_2$CH$_2$CH$_2$C(CH=CH$_2$)CH$_2$-H$_a$)]ClO$_4$): δ 3.55 (dd, 1H, J (H_a-H_b)=13 Hz, J (H_a-H_b)=7 Hz, H_a), 4.56 (d, 1H, H_b), 4.02 (t, 1H, J (H_b-H_c)=7 Hz, H_c), 5.68 (t, 1H, J (H_c-H_d)=7 Hz, H_d), 5.76 (d, 1H, J (H_c-H_d)=7 Hz H_c), 6.97 (t, 1H, H_d), 5.8-6.3 (m, 3H, -CH=CH$_2$, overlapped with vinyl protons of other isomers), 2.31 (s, 15H,
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CH$_3$ of Cp*). **3b** ([Cp*Ir(η³-CH$_2$CH-CH$_2$C(CH=CH$_2$)CH$_2$CH$_2$-H$_a$)]ClO$_4$): δ 3.25 (dt (sextet like), 1H, J (H_a-H_b)=13 Hz, J (H_a-H_b)= J (H_a-H_b)=7 Hz, H_a), 4.62 (d, 1H, H_b), 4.02 (t, 1H, J (H_b-H_c)= J (H_b-H_c)=7 Hz, H_c), 4.08 (d, 1H, J (Hn'-H$_n$) =7 Hz, H_n), 5.68 (t, 1H, J (Hc-HD)=7 Hz H_d), 7.19 (d, 1H, H_d), 6.61 (dd, J (H_c- H_b)=17 Hz, J (H_a- H_c) =10 Hz, 1H, -CH$_a$=CH$_b$H$_c$), 5.8-6.3 (m, 2H, -CH=CH$_2$, overlapped with vinyl protons of other isomers), 2.33 (s, 15H, CH$_3$ of Cp*).

3c ([Cp*Ir(η³-CH$_2$CH$_2$C(CH=CH$_2$)CH$_2$CH$_2$CH$_2$H$_a$)]ClO$_4$): δ 3.25 (dt (sextet like), 1H, J (H_x-H_y)=13 Hz, J (H_x-H_z)=(H_x-H$_z$)=7 Hz, H_x), 4.38 (d, 1H, H_z), not observed (2H, H_y and $H_{y'}$), 5.77 (t, 2H, J (H_x-H_z)=7 Hz H_z and $H_{z'}$), 6.49 (dd, 1H, J (H_x- H_b)=17 Hz, J (H_a- H_c) =10 Hz, 1H, -CH$_a$=CH$_b$H$_c$), 5.8-6.3 (m, 2H, -CH=CH$_2$, overlapped with vinyl protons of other isomers), 2.33 (s, 15H, CH$_3$ of Cp*).

Reactions of [Cp*Ir(η⁶-C$_6$H$_5$CH=CH$_2$)](ClO$_4$)$_2$ (1a) with H$_2$. A CH$_3$CN solution (20 mL) of 1a (0.2 g, 0.32
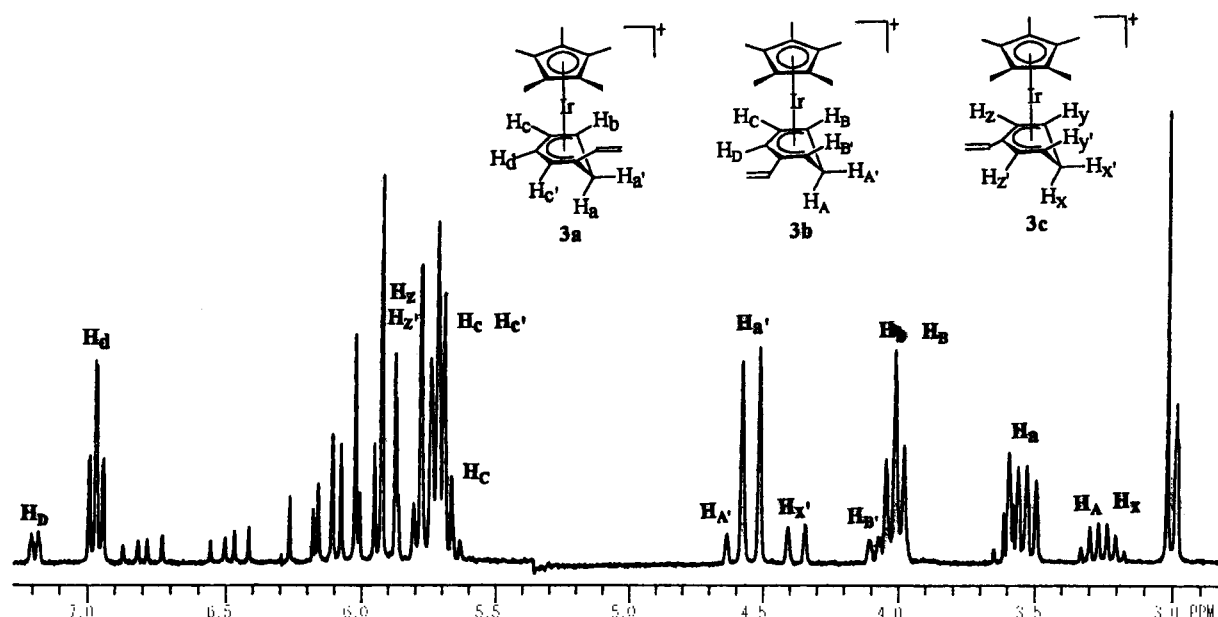

Figure 1. ¹H NMR spectrum of [Cp*Ir(η³-C$_6$H$_5$-CH=CH$_2$)](ClO$_4$), 3 (mixture of 3a, 3b and 3c, see also Figure 2 and text for detailed assignments) in (CD$_3$)$_2$CO at 25 °C at 200 MHz.
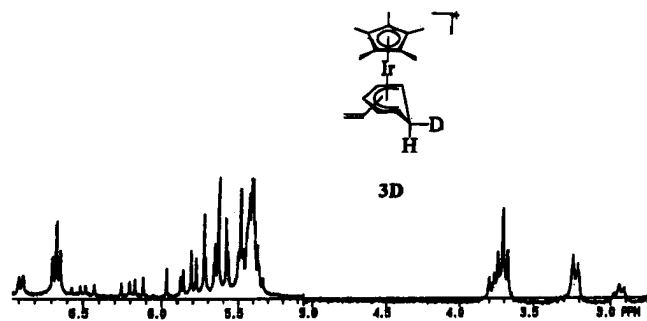
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Figure 2. ^{1}H NMR spectrum of $[Cp*Ir(\eta^6\text{-}C_6H_5D\text{-}CH\text{-}CH_2)]$ (ClO$_4$). **3D** in (CD$_3$)CO at 25 °C at 200 MHz.

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** ($[Cp*Ir(\eta^6\text{-}C_6H_5C_2H_5)](ClO_4)$) (81 %) was isolated by filtration after saturation with (C$_2$H$_5$)$_2$O (10 mL). **4** : ^{1}H NMR (CD$_3$CN, 25 °C) δ 2.75 (q, 2H, J (CH$_2$-CH$_3$)=7 Hz, -CH$_2$-CH$_3$), 1.36 (t, 3H, -CH$_2$-CH$_3$), 7.23 (m, 5H, C$_6$H$_5$), 2.28 (s, 15H, CH$_3$ of Cp*)

Reactions of [Cp*Ir(η^6-C$_6$H$_5$CH=CH$_2$)](ClO$_4$)$_2$ (1a) with HCl. Dry HCl gas was bubbled into CH$_3$CN 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** ($[Cp*Ir(\eta^6\text{-}C_6H_5CH_2CH_2Cl)](ClO_4)_2$, (85%)) was obtained through recrystallization with CH$_2$Cl$_2$/(C$_2$H$_5$)$_2$O. **5a** : ^{1}H NMR (CD$_3$-COCD$_3$, 25 °C) δ 3.95 (t, 2H, J (CH$_2$-CH$_2$Cl)=6 Hz, CH$_2$-CH$_2$Cl), 3.12 (t, 2H, CH$_2$CH$_2$Cl), 7.38 (m, 5H, C$_6$H$_5$), 2.31 (s, 15H, CH$_3$ of Cp*).

Reactions of [Cp*Ir(η^6-C$_6$H$_5$C(CH$_3$)=CH$_2$](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. ^{1}H NMR spectrum of the beige-white solid product shows all the signals due to **1c** (57%) and new signals (see data below) due to $[Cp*Ir(\eta^6\text{-}C_6H_5CH(CH_3)CH_2Cl)](ClO_4)_2$, **5b** (43%). **5b** : ^{1}H NMR (CD$_3$COCD$_3$, 25 °C) δ 3.38 (m, 1H, CH(CH$_3$)), 3.90 (m, 2H, CH$_2$Cl), 1.42 (d, 3H, J (CH$_3$-CH(CH$_3$))=7 Hz, CH(CH$_3$)), 7.39 (m, 5H, C$_6$H$_5$), 2.31 (s, 15H, CH$_3$ of Cp*).

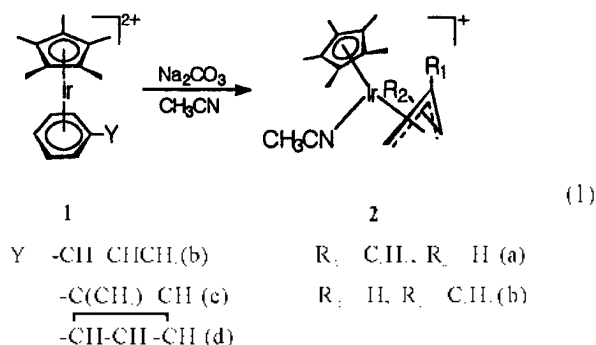## Results and Discussion

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

nals due to the olefinic protons of Y upon coordination of C$_6$H$_5$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, -C$_α$H= C$_β$H$_2$(for example, Ir-C$_α$=3.38 Å, Ir-C$_β$=4.28 Å^5).

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

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

Y		R
-CH=CHCH$_3$(b)		R$_1$ C$_6$H$_5$, R$_2$ H (a)
-C(CH$_3$)=CH$_2$ (c)		R$_1$ H, R$_2$ C$_6$H$_5$(b)
-CH-CH$_2$-CH$_3$ (d)		

(1)

Cationic allyl complexes of [Cp*Ir(η^3-allyl)(L)]$^+$ (L=PR$_3$, Cl, olefin) have been prepared in various methods, to which we now wish to add another way of preparing [Cp*Ir (η^3-allylC$_6$H$_5$)(CH$_3$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.
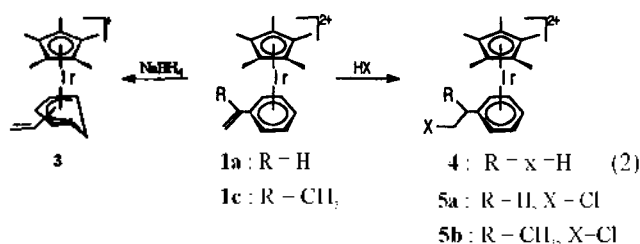
While the reaction of complex **1a** with NaBH$_4$ gives cyclohexadienyl complexes, [Cp*Ir(η^5-C$_6$H$_6$(-CH=CH$_2$))]$^+$ (3) (eq. 2), olefinic group hydrogenated η^6-ethylbenzene complex. [Cp*Ir(η^6-C$_6$H$_5$(-C$_2$H$_5$))]$^{2+}$ (4) and olefinic group HCl added η^6-2-chloroethylbenzene complex, [Cp*Ir(η^6-C$_6$H$_5$(-CH$_2$CH$_2$Cl))]$^{2+}$ (5a) are obtained from the reaction of **1a** with H$_2$ and HCl, respectively (eq. 2).

Detailed ^{1}H 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(η⁶-C₆H₅Y')]²⁺ (Y'=H, CH₃, t-Bu, CH₃O, Cl, OH) to give η⁵-cyclohexadienyl metal complexes, [Cp*Ir(η⁵-C₆H₅Y')]⁺.[29] For example, three isomers (ortho/meta/para=46/37/17) were obtained (while no ipso isomer was observed) from the reaction of [Cp*Ir(η⁶-C₆H₅C₂H₅)]²⁺.[9]

Close examination of the ¹H NMR spectrum of the product, **3** led us to suggest that it contains three isomers, **3a** ([Cp*Ir(η³-CHCHCHCHC(CH=CH₂)CH₂)]ClO₄), **3b** ([Cp*Ir (η³-CHCHCHC(CH=CH₂)CHCH₂)]ClO₄ and **3c** ([CP*Ir(η³-CHCHC(CH=CH₂)CHCHCH₂)]ClO₄) in the ratio 4 (**3a**) : 1 (**3b**) : 1 (**3c**) (see Figure 1).

3

1a : R = H
1c : R = CH₃

4 : R = x = H   (2)
5a : R = H, X = Cl
5b : R = CH₃, X=Cl

Deutero cyclohexadienyl compounds, [Cp*Ir(η⁵-C₆H₅D (-CH=CH₂))]⁺ (**3D**) were also obtained from the reaction of **1a** with NaBD₄. 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., Ha' (δ 4.56 ppm, **3a**), H_A'(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_aand 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 (H₂) attacks the olefinic group of **1a** to give η⁶-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_αH= C_βH₂ in **1a** to give

5a and to -C _α(CH₃)H=C _βH₂ 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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