Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 5125–5132
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structural aspects of M-allyl (M = Ir, Rh) complexes

Akella Sivaramakrishna, Emma Hager, Feng Zheng, Hong Su, Gregory S. Smith, John R. Moss *

Department of Chemistry, University of Cape Town, Rondebosch 7701, Cape Town, South Africa

Received 10 May 2007; received in revised form 23 July 2007; accepted 23 July 2007
Available online 8 August 2007

Abstract

The synthesis, characterization and chemistry of novel η^3-allyl metal complexes (M = Ir, Rh) are described. The structures of compounds $(C_5Me_4H)Ir(PPh_3)Cl_2$ (**1**), $(C_5Me_4H)Ir(PPh_3)(\eta^3$-1-methylallyl)Br (**3a**), $(C_5Me_4H)Ir(\eta^4$-1,3,5-hexatriene) (**8**), and $(C_5Me_5)Rh(\eta^3$-1-ethylallyl)Br (**5d**) have been determined by X-ray crystallography. Structural comparisons among these complexes are discussed. It is found that the neutral metal allylic complex [Cp*IrCl(η^3-methylallyl)] (**5**) ionizes in polar solvents to give [Cp*Ir(η^3-methylallyl)]$^+$Cl$^-$ (**6**) and reaches equilibrium (**5** $\rightleftharpoons$ **6**) at room temperature. Addition of tertiary phosphine ligands to neutral complexes such as [Cp*Ir(η^3-methylallyl)Cl], results in the formation of stable ionic phosphine adducts. Factors such as solvent, length of carbon chain, temperature and light are discussed with respect to the formation, stability and structure of the allyl complexes.

Keywords: Metal-(η^3-allyl) complexes; Transmetalation reactions; Ligand addition reactions; Structure comparison; Thermolysis studies

1. Introduction

Transition metal η^3-allyl compounds display a rich chemistry [1] and are widely encountered both as synthetic reagents and in catalysis. There has also been much interest shown in elucidating the structures and stereodynamic behaviour of η^3-allyl metal complexes in solution [2]. Investigations on potential applications of these types of complexes in asymmetric synthesis as well as in heterogeneous catalysis have been carried out [3]. For example, tris(allyl)rhodium complexes with a variety of metal oxide supports have been reported as catalysts [4]. η^3-Allyl palladium complexes have been studied extensively, partly because of the extremely useful palladium-catalyzed reactions of nucleophiles with allylic substrates [5]. It has also been shown that the bulky ligand substituents can cause modifications to the structure and solution behaviour of the stable allylic metal complexes [6]. The reactivity of rhodium and iridium allylic complexes with various substrates as reactants has been reported [7]. The catalytic asymmetric hydrogenation of α-functionalized ketones using chiral Ru(II)-allyl complexes has also been reported [8]. A good knowledge of the structural aspects of these compounds is important in understanding the reactivity patterns in detail. The present work describes the synthesis, structural characterization and reactivity of some allylic iridium(III) and rhodium(III) complexes.

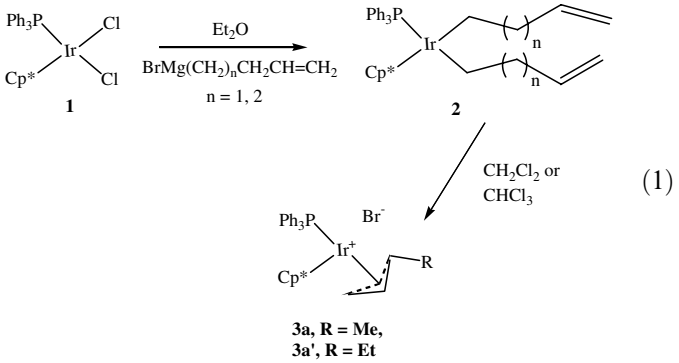
2. Results and discussion

Our original efforts were aimed at preparing and characterizing a series of iridium and rhodium alkenyl compounds with an M–C σ-bond and a pendant alkene group. However, some of the products of the reactions of **1** with 1-alkenyl Grignard reagents were shown to be the metal allyl complexes. It has been found that the compound **2** is air-sensitive in the solid state and decomposes rapidly in solution, particularly in chlorinated solvents (Eq. (1)) [9]. The analogous reaction involving the rhodium precursor with 1-alkenyl Grignard reagent showed that the PPh_3 ligand was eliminated from the metal sphere (as

* Corresponding author. Tel.: +27 21 650 2535; fax: +27 21 689 7499.
E-mail address: John.Moss@uct.ac.za (J.R. Moss).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.07.053

indicated by ^{31}P NMR) in solution as the allylic structure formation was more predominant.



Grignard reagents with short alkenyl chains (viz $BrMgCH_2CH{=}CH_2$ and $BrMgCH_2CH_2CH{=}CH_2$) gave metal–allyl halides in good yields on reaction with $[Cp^*MX_2]_2$ (where M = Ir, Rh) as shown in Scheme 1. These unexpected (η^3-allyl-metal) complexes, **5a–d** are obtained by an irreversible rearrangement of the initially formed M-alkenyl complexes. It was found that the neutral allylic complex, **5** and the cationic allylic complex, **6** are in equilibrium in solution. The formation of **5b** (M = Ir) in the solid state was identified by X-ray crystal structural analysis. But we could not solve this structure completely as there are errors associated with the space group identification. We also find that ionization becomes more favored as the size of the halide ligand increases (i.e. $I^- > Br^- > Cl^-$) (Scheme 1, where $Cp^*Ir = (C_5Me_4H)Ir$ and $Cp^*Rh = (C_5Me_5)Rh$).

The conversion of neutral metal allylic complexes to ionic metal complexes was observed at room temperature in the polar solvents (chloroform, dichloromethane and methanol). It is evident that the chloride and bromide ligands are not sufficiently labile to effect the dissociation of the complex in non-polar solution. For example, the ^1H NMR of **5b** (where M = Ir) revealed a significant difference in the chemical shifts of the methyl protons of tetramethylcyclopentadienyl, depending on the solvent used. In polar solvents, three different signals were observed. The spectrum of the same compound in non-polar solvent showed two signals for the methyl protons. The position of the methyl protons of tetramethylcyclopentadiene in **5b** (M = Ir) appears at δ 1.44 and 1.43 in C_6D_6 whereas in $CDCl_3$ the same compound showed peaks at 1.79, 1.83, 1.87 (1:2:1) (see Fig. 1). It was observed that the tetramethylcyclopentadienyl hydrogen shifts significantly downfield to δ 4.83 in $CDCl_3$ and in C_6D_6 appears at δ 4.15.

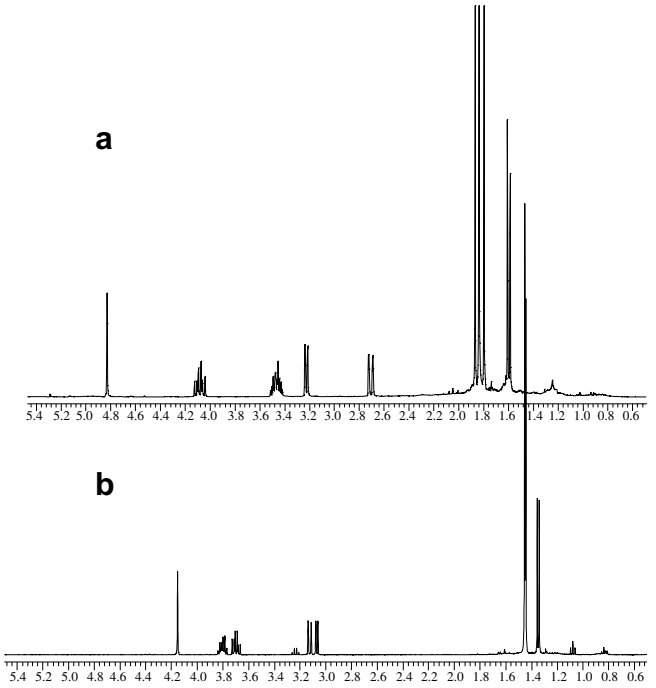
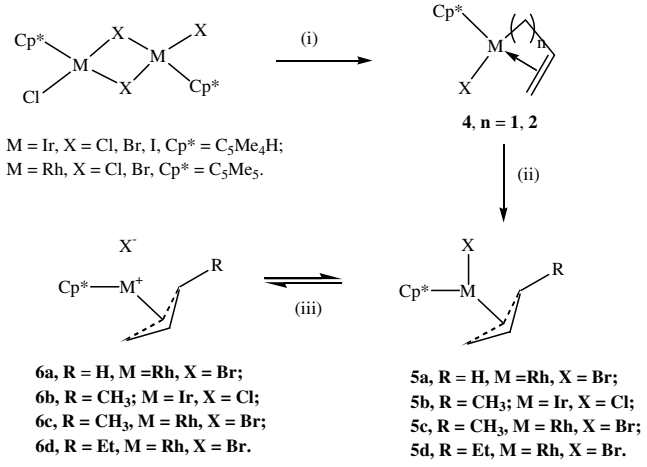
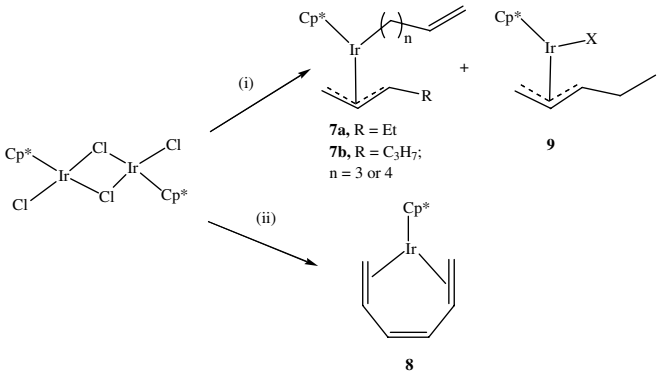


Fig. 1. (a) Compound **5b** in $CDCl_3$; (b) compound **5b** in C_6D_6.

The equilibrium dissociation increases with decreasing temperature and the position of equilibrium is readily controlled by variation of solvent polarity, temperature, and replacement of chloro-ligand by better leaving groups. These results are supported by the ^1H NMR spectra of the corresponding metal–allyl compounds.



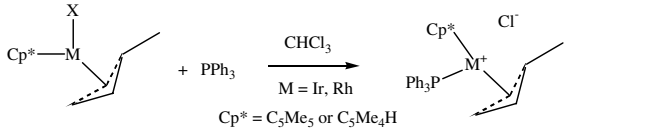
Scheme 1. (i) Et_2O, $BrMg(CH_2)_nCH{=}CH_2$ ($n = 1, 2$); (ii) benzene or toluene; (iii) $CHCl_3$ or MeOH.



Scheme 2. (i) Et_2O, $BrMg(CH_2)_nCH{=}CH_2$ ($n = 3, 4$); (ii) Et_2O, $BrMg(CH_2)_4CH{=}CH_2$, reflux at 45 °C, 5 h.

In contrast, the Grignard reagents with longer alkenyl chains gave different products at −78 °C, i.e. mainly **7**, which contains one pendant alkenyl chain along with an η^3-allylic group (Scheme 2). Reactions of $[Cp^*IrCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5 or η^5-C_5Me_4H) with $[BrMg(CH_2)_4CH{=}CH_2]$ in diethylether at 45 °C gave $[Cp^*Ir(\eta^4\text{-}C_6H_{10})]$ (**8**) as the final product formed from a reaction involving C–H activation of an alkenyl chain (Scheme 2).

A single crystal of **8** suitable for the X-ray diffraction analysis was obtained and the structure reveals trigonal planar coordination at the Ir atom. The corresponding rhodium reaction of $[Cp^*RhCl_2]_2$ with $[BrMg(CH_2)_3CH{=}CH_2]$ gave only $[Cp^*RhBr(\eta^3\text{-}C_5H_9)]$ [**5d**] and no C–H activation was observed.



5b, R = CH_3, M = Ir, X = Br;
5c, R = CH_3, M = Rh, X = Br;

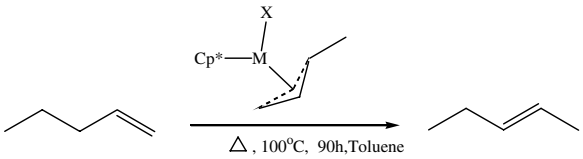
3a, R = CH_3, M = Ir, X = Br;
3b, R = CH_3, M = Rh, X = Br;

(2)

In order to expand the relatively unexplored ligand addition chemistry of these metal allyl compounds, investigations into their reactivities with various types of ligands were carried out. It was found that these stable allyl complexes, **5a–d** or **6a–d** are unreactive at 25 °C with the P, N and O (P = PPh_3, N = CH_3CN, and O = tetrahydrofuran) donor ligand systems even after several days. The stability is a likely consequence of the restricted motion of the allyl ligands as they satisfy the $18e^-$ rule and the resulting blockage of further reaction pathways. A similar trend was observed with the rhodium complexes. The synthesis of iridium and rhodium analogs demonstrated that their reactions with a variety of phosphine ligands yielded their corresponding phosphine derivatives under refluxing conditions (Eq. (2)). However, on refluxing for several hours, the neutral compound, **5b** (M = Ir) was converted to an ionic compound, **3a** (see Eq. (2)). The structure of **3a** with bromide counter anion was confirmed by X-ray structural characterization. As reported earlier [10], these η^3-allyl metal complexes with an unsymmetrical ligand environment can show different conformations such as *syn-* and *anti-*, depending on the orientation of the allyl ligand with respect to the other ligands in the complex (Chart 1).

On addition of PPh_3 to an NMR tube containing a solution of $Cp^*Rh(III)(\eta^3$-1-ethylallyl)Br (**5d**) in C_6D_6 and subsequent heating for several hours, the ^{31}P NMR spectrum shows two doublets at 47.51 ($J = 165$ Hz) and 48.09 ppm ($J = 166$ Hz) indicative of $Cp^*Rh(III)(PPh_3)$-$(\eta^3$-1-ethylallyl)Br. The appearance of 2 doublets may be due to the presence of *syn-* and *anti-* isomers. In a similar way, the formation of $Cp^*Rh(III)(\eta^3$-1-methylallyl)-(PPh_3)Br was observed when PPh_3 was added to a solution of $Cp^*Rh(III)(\eta^3$-1-methylallyl)Br[14] [**5c**] in C_6D_6.

Interestingly, these allylic metal complexes can act as alkene isomerization catalysts for the conversion of 1-alkenes to their corresponding 2-alkenes (Eq. (3)). Further studies of these reactions are under way [11].



(3)

2.1. Structural aspects

The average M–C bond distances of the metal–cyclopentadienyl rings in complexes **3a**, **8** and **5d**, are 2.2102 Å, 2.2354 Å and 2.2380 Å, respectively, somewhat longer than the corresponding distances in compound **1** (average 2.1958 Å). This might be due to the electronic effect of the central metal. The distances between the metal and the centroid of the cyclopentadienyl ring vary, depending on the nature of metal. The shortest metal-centroid distance among these complexes is found in compound **1** as 1.824(2) Å. The presence of donor ligands such as PPh_3 or alkenes has a significant effect on the metal-centroid distances (see Table 1). The positive charge on the iridium atom in compound **3a** did not induce any significant change in the metal–carbon distances of the allylic carbon atoms around the metal as compared with the neutral complex, **5d** (average distances are 2.1813 Å and 2.1643 Å for **3a** and **5d**, respectively). Strikingly, the central carbon atom in the allylic group is closest to the metal in both the complexes (**3a** and **5d**) (see Table 2). Thus, the structural features were little affected by the coordination of a bulky PPh_3 ligand to the metal centre in compound **3a**. It is interesting to note that the metal–carbon distances for compound **8** were found to be in a range 2.120–2.129 Å, which is quite close to metal–carbon sigma bond lengths. The Ir–P bonds in **1** and **3a** are almost equidistant and comparable with the literature reports [12]. The crystallographic data of all the compounds are given in Table 3 (see Figs. 2–5).

2.2. Thermal studies

Thermal decomposition of compounds **3a**, **5b** and **5d** gave a range of organic products. Unexpectedly, compound **5b** gave *n*-pentane (70%) and 1-pentene (30%) on decomposition instead of the corresponding C_4-hydrocarbon products. Similar trends were observed with the compound **3a** on decomposition. But compound **9** yielded 1-pentene (23%) and 2-pentene (25%), 2-hexene (40%) and 1,5-hexadiene (12%), which were analyzed by GC (Scheme 3). A similar decomposition trend was observed with the rhodium analog, **5d**. The methyl groups on pentamethylcyclopentadiene or tetramethylcyclopentadiene ligand may be the source for the extra carbon atom in the organic products after the decomposition. It is interesting to note that the organic product distribution on thermal

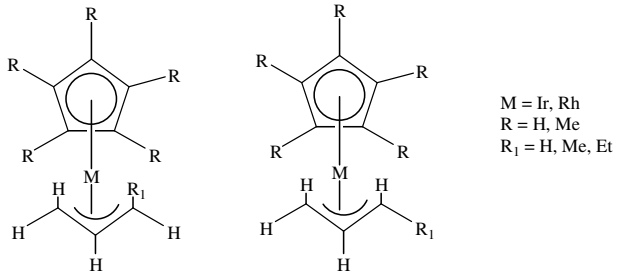


Chart 1.

Table 1
Distances between metal and the centroid of the Cp ring

Compound	Distance between metal and the centroid of the Cp ring (Å)
1	1.824(2)
3a	1.873(3)
8	1.883(2)
5d	1.845(5)

Table 2
Selected metal–carbon bond distances of metal–allyl complexes

3a (ionic) (Å) [Iridium(III) complex]	**5d** (neutral) (Å) [Rhodium(III) complex]
M–C_1 = 2.199(6)	M–C_{11} = 2.179(12)
M–C_2 = 2.095(8)	M–C_{12} = 2.090(2)
M–C_3 = 2.250(7)	M–C_{13} = 2.224(13)

decomposition depends on the nature of the metal, whether it is iridium or rhodium.

3. Conclusions

In summary, the isolation and structural characterization of thermally stable η^3-allyl halide complexes of iridium and rhodium has been accomplished. Results showed that, in some cases, an equilibrium between neutral and ionic complexes is observed, depending on the nature of solvent. Evidence from NMR and X-ray crystallography suggests that the C_5Me_5 or C_5Me_4H ligands cause relatively little perturbation in the essential metal–allyl geometry. The high thermal stability of the metal–allyl complexes is a likely consequence of the restricted motion of the allyl ligands (as they satisfy the $18e^-$ rule) and the resulting blocking of decomposition pathways. The interplay of steric, electronic and chelating effects is evident in the reactions of phosphine ligands with (allyl)chloro metal compounds. These allylic complexes may react with suitable substrates, resulting in the formation of functionalized organic products (on decompositions). Further investigations on the influence of these factors with various metal–allyl complexes will be carried out.

4. Experimental

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. $[(C_5Me_5)IrCl_2]_2$, $[(C_5Me_4H)IrCl_2]_2$, $(C_5Me_5)IrCl_2(PPh_3)$, $(C_5Me_4H)IrCl_2(PPh_3)$, $[(C_5Me_5)$-

Table 3
Crystal data and structure refinements

Complexes	**1**	**3a**	**8**	**5d**
Empirical formula	$C_{27}H_{28}Cl_2IrP \cdot 1.5C_6H_6$	$C_{37}H_{41}BrIrP \cdot H_2O$	$C_{15}H_{21}Ir$	$C_{15}H_{24}BrRh$
Formula weight	763.73	806.79	393.52	387.16
Data collection temperature (K)	113(2)	173(2)	113(2)	113(2)
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1$	Monoclinic, $P2_1/m$	Monoclinic, $P2_1/n$
a (Å)	8.5748(1)	9.8695(1)	5.9072(2)	8.4782(1)
b (Å)	17.3081(2)	17.8877(3)	13.6058(5)	14.0621(2)
c (Å)	21.6573(3)	9.9133(2)	8.3837(3)	12.8601(2)
α (°)	90	90	90	90
β (°)	92.5010(10)	112.386(1)	100.656(1)	90.438(1)
γ (°)	90	90	90	90
Volume (Å^3)	3211.17(7)	1618.23(5)	662.20(4)	1533.15(4)
Z, Calculated density (Mg m^{-3})	4, 1.580	2, 1.656	2, 1.974	4, 1.677
Absorption coefficient μ (mm^{-1})	4.398	5.437	10.053	3.699
$F(000)$	1516	800	376	776
Reflections collected/unique [R_{int}]	68 574/6285 [0.0623]	36 236/6117 [0.0718]	9211/1572 [0.1011]	35 506/2887 [0.0687]
Data/restraints/parameters	6285/0/366	6117/7/370	1572/6/79	2887/2/156
Goodness-of-fit on F^2	1.080	1.040	1.047	1.193
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0235$, $wR_2 = 0.0416$	$R_1 = 0.0289$, $wR_2 = 0.0511$	$R_1 = 0.0273$, $wR_2 = 0.0490$	$R_1 = 0.0744$, $wR_2 = 0.1890$
R indices (all data)	$R_1 = 0.0360$, $wR_2 = 0.0450$	$R_1 = 0.0392$, $wR_2 = 0.0538$	$R_1 = 0.0383$, $wR_2 = 0.0517$	$R_1 = 0.0818$, $wR_2 = 0.1921$
Extinction coefficient	0.00108(8)	0.0020(2)	0.0017(8)	0.0064(9)
Absolute structure parameter	n/a	0.004(6)	n/a	n/a
Largest difference in peak and hole (e Å^{-3})	1.466 and −0.613	0.987 and −0.754	2.268 and −1.397	3.452 and −1.346

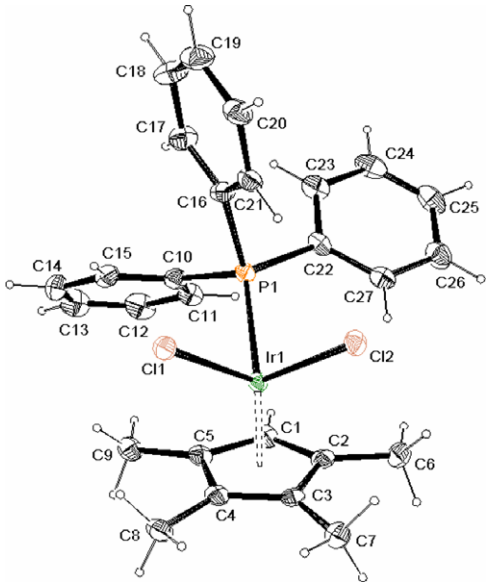


Fig. 2. Molecular structure of **1**, showing the atom-numbering scheme. One and half benzene solvent molecules are omitted. Ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Ir(1)–P(1) 2.3007(8); Ir(1)–Cl(1) 2.3939(7); Ir(1)–Cl(2) 2.4196(7); Ir(1)–C(1) 2.149(3). Selected bond angles (°): P(1)–Ir(1)–C(1) 95.35(9); P(1)–Ir(1)–Cl(1) 88.46(3); P(1)–Ir(1)–Cl(2) 93.96(3).

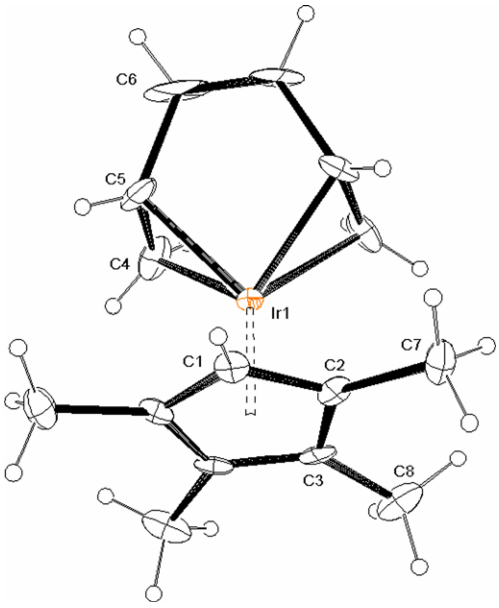


Fig. 4. Molecular structure of **8**, showing the atom-numbering scheme. Ellipsoids are drawn at 35% probability level. Selected bond lengths (Å): Ir(1)–C(1) 2.225(5); Ir(1)–C(2) 2.219(4); Ir(1)–C(3) 2.275(4); Ir(1)–C(4) 2.131(4); Ir(1)–C(5) 2.129(4). Selected bond angles (°): C(1)–Ir(1)–C(4) 135.35(14); C(1)–Ir(1)–C(5) 111.31(18).

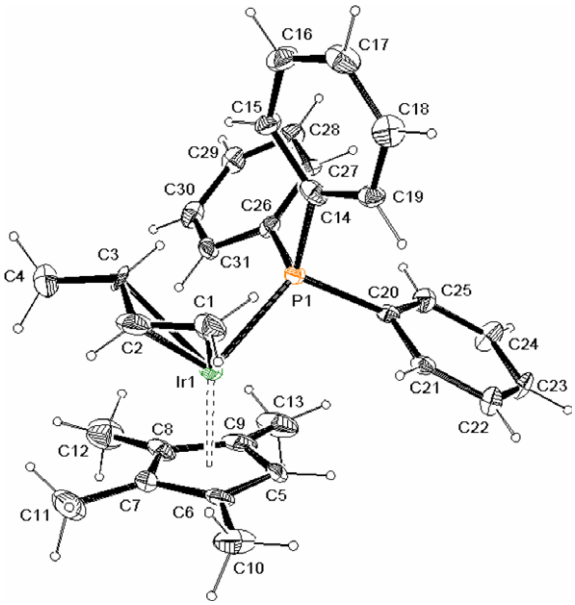


Fig. 3. Molecular structure of **3a**, showing the atom-numbering scheme. Bromide and a water molecule are omitted. Ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Ir(1)–P(1) 2.3015(14); Ir(1)–C(1) 2.199(6); Ir(1)–C(2) 2.095(8); Ir(1)–C(3) 2.250(7). Selected bond angles (°): P(1)–Ir(1)–C(5) 101.90(18); P(1)–Ir(1)–C(1) 90.32(15); P(1)–Ir(1)–C(2) 107.0(2).

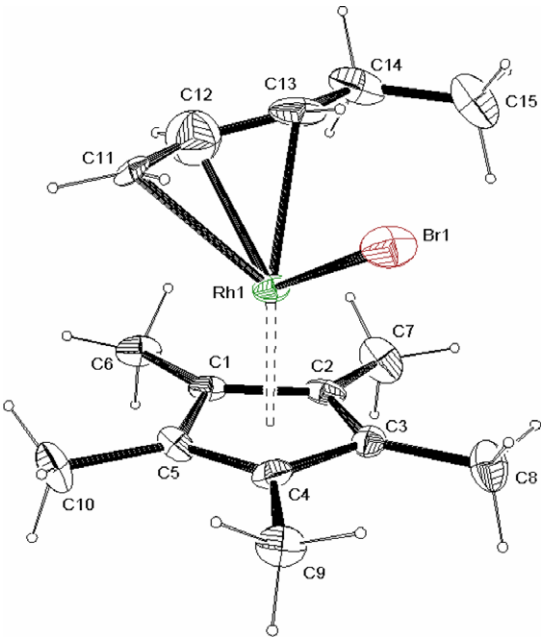
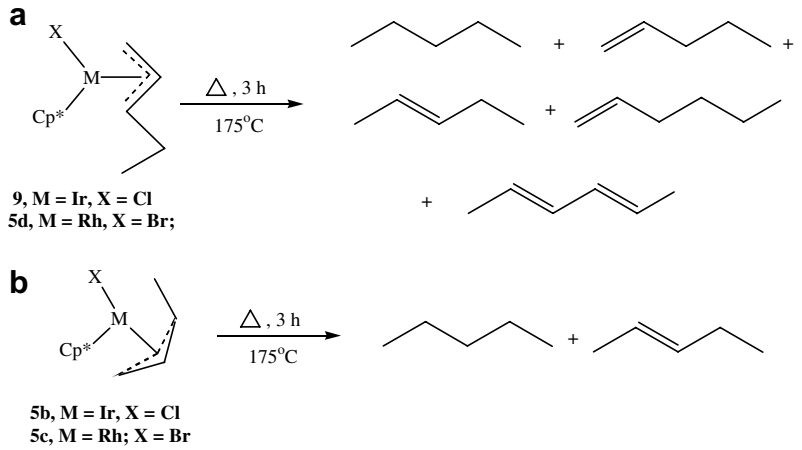


Fig. 5. Molecular structure of **5d**, showing the atom-numbering scheme. (ORTEP diagram; 30% probability ellipsoids). Hydrogen atoms on the alkyl chain are omitted for clarity. Selected bond lengths (Å): Rh(1)–C(11) 2.172(11); Rh(1)–C(12) 2.10(2); Rh(1)–C(13) 2.222(12); Rh(1)–C(1) 2.168(11); Rh(1)–C(2) 2.255(11). Selected bond angles (°): C(11)–Rh(1)–Br(1) 94.9(4); C(12)–Rh(1)–Br(1) 106.2(5).

$RhX_2]_2$ (X = Cl, Br), $(C_5Me_4H)Ir(PPh_3)Cl_2$ (**1**) and $(C_5Me_5)Ir(PPh_3)Cl_2$ were prepared as previously described [13]. The Grignard reagents, $BrMgCH_2CH_2CH{=}CH_2$, $BrMgCH_2CH_2CH_2CH{=}CH_2$ and $BrMgCH_2CH_2CH_2CH_2$-$CH{=}CH_2$ were prepared as per the literature procedures [14]. The solvents were commercially available and distilled from dark purple solutions of sodium/benzophenone ketyl before use. ^1H, and ^{31}P NMR spectra were recorded on a



Scheme 3. Thermal decomposition of metal (η^3-allyl) halide compounds.

Bruker DMX-400 spectrometer and all ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer instrument. The crystallographic data for all the single crystals was collected at 113 K on a Nonius Kappa CCD diffractometer using graphite- monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). GC analyses were carried out using a Varian 3900 gas chromatograph equipped with an FID and a 30 m × 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32 °C for 4 min and then to ramp to 200 °C at 10 deg/min and hold 5 min. GC–MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m × 0.25 mm Rtx-1 column (0.5 μm film thickness). The carrier gas was helium at 0.9 mL/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10 deg/min and hold 8 min.

4.1. (C_5Me_4H)Ir(III)[$(CH_2)_3CH{=}CH_2$]$_2$(PPh_3) (2)

$Cp^*Ir(PPh_3)Cl_2$ (201 mg, 0.31 mmol) in diethylether (15 mL) was cooled to −78 °C and 1.0 mL of 1-pentenyl Grignard reagent (1.30 M, 1.24 mmol) was added. The solution was brought to 0 °C and then stirred until the solution became clear. The excess Grignard reagent was removed by hydrolyzing the reaction mixture with 5 mL of saturated aqueous NH_4Cl at −78 °C. The aqueous layer was washed with 2 × 5 mL of diethylether and the organic layer was separated by a separating funnel. The solvent was removed under reduced pressure and the residue recrystallized from a diethylether/hexane mixture (2 mL:5 mL) at −10 °C for 48 h. The pale yellow crystalline solid was separated by decanting the mother liquor and dried under vacuum for several hours. For **2**; m.p. 66–68 °C (decomposition); yield 77%; ^{1}H NMR δ 6.99–8.10 (m, 15H, Ph); 5.63–5.94 (m, 2H, =CH); 4.88–5.13 (m, 4H, $=CH_2$); 4.19 (s, 1H, Cp^*-H); 0.76–2.12 (m, 12H, CH_2); $^{31}P\{^1H\}$ 25.8 (s). Anal. Calc. for compound $C_{37}H_{46}IrP$: C, 62.24; H, 6.49. Found: C, 62.14; H, 6.79%.

4.2. Cp^*Ir(III)(PPh_3)(η^3-1-methylallyl)Cl (3a)

In a Schlenk flask, PPh_3 (448 mg, 1.708 mmol) was added to **5** (690 mg, 1.708 mmol) in dichloromethane (20 mL) at room temperature. The solution was refluxed at 50 °C for 8 h. All the volatiles were removed under the high vacuum. Compound **3** was isolated from the reaction mixture using p-TLC using dichloromethane as eluent. The yellow band was extracted into dichloromethane and dried under vacuum as a yellow crystalline solid. For **3**; m.p. 98–100 °C; yield 83%; ^{1}H NMR δ 7.26–7.80 (m, 15H, Ph); 4.43 (s, 1H, Cp-H); 3.95 (m, 1H, CH); 2.95 (m, 1H, CH–CH_3); 2.20 (m, 2H, –CH_2), 1.81 (s, 12H, Cp-CH_3), 1.52 (d, 3H, CH_3); $^{31}P\{^1H\}$ 10.5 (s). Anal. Calc. for compound $C_{31}H_{35}PIrCl$: C, 55.88; H, 5.29. Found: C, 56.26; H, 5.45%. The corresponding bromo derivative, Cp^*Ir(III)(PPh_3)(η^3-1-methylallyl)Br was obtained by refluxing the compound **3a**, Cp^*Ir(III)(PPh_3)(η^3-1-methylallyl)Cl with sodium bromide for 2 h in acetone. The obtained yellow crystalline solid was recrystallized from dichloromethane to obtain single crystals suitable to the X-ray analysis. Anal. Calc. for compound $C_{31}H_{35}PIrBr$: C, 52.39; H, 4.96. Found: C, 52.66; H, 5.12%.

4.3. Cp^*Rh(III)(η^3-allyl)bromide (5a)

Allylmagensium bromide (1 mmol) was added to a suspension of $[Cp^*RhBr_2]_2$ (160 mg, 0.2 mmol) in 10 cm^3 diethylether at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 3 h. Saturated NH_4Cl solution was added and the organic layer extracted with benzene and dried over anhydrous $MgSO_4$. Removal of solvent *in vacuo* furnished a solid red–brown product (110 mg, 76%). m.p. 120–122 °C (decomposition). NMR ($CDCl_3$): δ (^{1}H) = 1.78 (s, 15H), 3.14 (d, 2H$_a$,

$J = 11.7$ Hz), 3.33 (d, $2H_b$, $J = 6.8$ Hz), 3.95 (m, 1H). Anal. Calc. for compound $C_{13}H_{20}RhBr$: C, 43.5; H, 5.6. Found: C, 43.8; H, 5.5%. Mass spec. FAB: *m/z* 359 (M^+), 279 ($M^+ - Br$), 237.

4.4. $Cp^*Ir(III)(\eta^3$-1-methylallyl)Cl (**5b**)

In a Schlenk flask, $[Cp^*IrCl_2]_2$ (168 mg, 0.219 mmol) in diethylether (20 mL) was cooled to $T = -78$ °C and 1-butenyl Grignard reagent (3.4 mL of 0.26 M, 0.88 mmol) was added dropwise. The solution was brought to *ca.* 0 °C and then stirred until the solution became clear. The reaction mixture was worked up as described for compound **2** (see above). The product was obtained as pale yellow crystalline solid. For **5**: m.p. 110–112 °C; yield 85%; ^{1}H NMR δ 4.43 (s, 1H, Cp-H); 3.95 (m, 1H, CH); 2.95 (m, 1H, CH–CH_3); 2.20 (m, 2H, –CH_2), 1.81 (s, 12H, Cp-CH_3), 1.52 (d, 3H, CH_3). Anal. Calc. for compound $C_{13}H_{20}IrCl$: C, 38.65; H, 4.99. Found: C, 38.56; H, 5.08%.

4.5. $Cp^*Rh(III)(\eta^3$-1-methylallyl)bromide[14] (**5c**)

Butenylmagnesium bromide (2.5 mmol) was added to a suspension of $[Cp^*RhBr_2]_2$ (400 mg, 0.503 mmol) in 10 cm^3 diethylether at −78 °C. After stirring for 1 day the reaction was hydrolyzed with saturated NH_4Cl solution and the organic layer extracted with benzene. The solvent was removed *in vacuo* and the oily red residue recrystallized from ether/hexane. The product was isolated as orange crystals (270 mg, 72%). The complex melts with decomposition above 120 °C. NMR ($CDCl_3$): δ (^{1}H) = 1.56 (d, 3H, $J = 5.4$ Hz), 1.76 (s, 15H), 3.11 (d, 1H, $J = 11.2$ Hz), 3.14 (d, 1H, $J = 6.3$ Hz), 3.76 (m, 2H). δ (^{13}C) = 9.67 (Cp^* Me), 17.90 (CH–CH_3), 56.15 (d, $J = 10.4$ Hz, –CH_2), 70.20 (d, $J = 7.6$ Hz, CH–CH_3), 95.38 (d, $J = 6.1$ Hz, CH_2–CH_c), 97.70 (d, $J = 6.1$ Hz, Cp^* ring). Anal. Calc. for compound $C_{14}H_{22}RhBr$: C, 45.06; H, 5.90. Found: C, 45.46; H, 5.76%. Mass spec. FAB: *m/e* 373 (M^+), 293 ($M^+ - Br$), 237.

4.6. $Cp^*Rh(III)(\eta^3$-1-ethylallyl)bromide (**5d**)

Pentenylmagnesium bromide (1 mmol) was added to a suspension of $[Cp^*RhBr_2]_2$ (160 mg, 0.2 mmol) in 10 cm^3 diethylether at −78 °C. After stirring for 1 day the reaction was hydrolyzed with saturated NH_4Cl solution and the organic layer extracted with benzene. Solvent was removed *in vacuo* and the oily red product was recrystallized from dichloromethane/hexane to give orange–red crystals (116 mg, 75 %). m.p. 118–120 °C. NMR ($CDCl_3$): δ(^{1}H) = 1.16 (t, 3H, 7.3 Hz), 1.77 (s, 15H), 1.93 (m, 2H), 3.11 (d, 1H, 10.1 Hz), 3.14 (d, 1H, 6.4 Hz), 3.74 (m, 2H). δ(^{13}C) = 9.72 (s, Cp^* Me), 15.92 (s, H_3C–CH_2–), 26.12 (s, –CH_2–CH_3), 56.22 (d, $J = 11.5$ Hz, –CH–CH_2), 78.21 (d, $J = 7.6$ Hz, –H_2C–CH–), 93.47 (d, $J = 6.1$ Hz, –CH–HC-CH_2), 97.76 (d, $J = 6.1$ Hz, Cp^* ring). Anal. Calc. for compound $C_{15}H_{24}RhBr$: C, 46.55; H, 6.20. Found: C, 46.97; H, 6.03%. Mass spec. FAB: *m/e* 387 (M^+), 307 ($M^+ - Br$), 237 ($M^+ - Br$–η^3-C_5H_9–H).

4.7. $Cp^*Ir(III)(\eta^3$-1-ethylallyl)(1-pentenyl) (**7**)

In a Schlenk flask, $[Cp^*IrCl_2]_2$ (316 mg, 0.411 mmol) in diethylether (20 mL) was cooled to $T = -78$ °C and 1-pentenyl Grignard reagent (2.7 mL of 0.62 M, 1.644 mmol) was added. The solution was brought to around 0 °C and then stirred until the solution became clear. The products were isolated by p-TLC using dichloromethane as eluent. The first yellow band was found to be the compound **7**. The product was obtained as yellow oil and crystallized from *n*-hexane at −10 °C. For **7**: m.p. 66–68 °C; yield 48%; ^{1}H NMR δ 5.73–5.90 (m, 1H, =CH); 4.81–5.12 (m, 2H, $=CH_2$) 4.23 (s, 1H, Cp-H); 4.01–4.12 (m, 1H, CH); 3.35–3.51 (m, 1H, CH); 0.85–1.97 (m, 23H, –CH_2 & CH_3). Anal. Calc. for compound $C_{19}H_{31}Ir$: C, 50.52; H, 6.92. Found: C, 50.36; H, 7.08%. The second band was found to be the compound **9**. m.p. 108–112 °C (dec); ^{1}H NMR δ 4.43 (s, 1H, Cp-H); 3.95 (m, 1H, CH); 2.95 (m, 1H, CH–CH_3); 2.20 (m, 2H, –CH_2), 1.81 (s, 12H, Cp-CH_3), 1.52–1.61 (m, 2H, CH_2); 0.92–1.06 (m, 3H, CH_3). Anal. Calc. for compound $C_{14}H_{22}IrCl$: C, 40.23; H, 5.31. Found: C, 40.26; H, 5.46%.

4.8. $Cp^*Ir(I)(\eta^4$-1,3,5-hexatriene) (**8**)

In a Schlenk flask, $[Cp^*IrCl_2]_2$ (406 mg, 1.085 mmol) in diethylether (20 mL) was cooled down to $T = -78$ °C and 1-pentenyl Grignard reagent (2.8 mL of 1.34 M, 3.75 mmol) was added. The solution was brought to around 0 °C and then stirred until the solution became clear. To this, dppp (448 mg, 1.086 mmol) was added and stirred for 36 h until a clear solution is formed. The reaction mixture was worked up as described above. The product was obtained as a pale yellow crystalline solid from the *n*-hexane solution. For **8**; m.p. 80–85 °C; yield 70%; ^{1}H NMR 5.67–5.88 (m, 4H, =CH); 5.06 (s, 1H, Cp-H); 2.67-2.83 (m, 4H, $=CH_2$); 1.79–1.85 (m, 12H, Cp-CH_3). Anal. Calc. for compound $C_{15}H_{21}Ir$: C, 45.78; H, 5.38. Found: C, 45.96; H, 5.42%.

Acknowledgement

We thank AngloPlatinum Corporation, DST Centre of Excellence in Catalysis, C* Change, UCT, The UCT Chemistry EDP programme and Johnson Matthey for their support and Tanya le Roex for solving one of the crystal structures.

References

[1] (a) R. Beckhaus, Synth. Method Organomet. Inorg. Chem. 9 (2000) 1;
(b) C.N. Carlson, J.D. Smith, T.P. Hanusa, W.W. Brennessel Jr., V.G. Young, J. Organomet. Chem. 683 (2003) 191;

(c) J.B. Collman, J.R. Norton, L.S. Hegedus, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, California, 1976, pp. 881–919, and the references therein.
[2] S.K. Mandal, G.A. Nagana Gowda, S.S. Krishnamurthy, M. Nethaji, Dalton Trans. (2003) 1016, and the references therein.
[3] (a) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, D. Walter, Angew. Chem., Int. Ed. Engl. 5 (1966) 151;
(b) M.S. Eisen, T.J. Marks, J. Mol. Catal. 86 (1994) 23;
(c) M.S. Eisen, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 10358;
(d) M.S. Eisen, T.J. Marks, Organometallics 11 (1992) 3939.
[4] (a) J.M. Basset, F. Lefebvre, C. Santini, Coord. Chem. Rev. 178–180 (1998) 1703;
(b) K.D. John, K.V. Salazar, B.L. Scott, R.T. Baker, A.P. Sattelberger, Chem. Commun. (2000) 581.
[5] (a) S.K. Mandal, T.S. Venkatakrishnan, A. Sarkar, S.S. Krishnamurthy, J. Organomet. Chem. 691 (2006) 2969;
(b) Y. Ding, R. Goddard, K.-R. Poerschke, Organometallics 24 (2005) 439;
(c) P.R. Auburn, P.B. Mackenzie, B. Bosnich, J. Am. Chem. Soc. 107 (1985) 2033.
[6] C.N. Carlson, T.P. Hanusa, W.W. Brennessel, J. Am. Chem. Soc. 126 (2004) 10550.
[7] (a) K.D. John, K.V. Salazar, B.L. Scott, R.T. Baker, A.P. Sattelberger, Organometallics 20 (2001) 296;
(b) M. Green, G.J. Parker, J. Chem. Soc., Dalton Trans. (1974) 333;
(c) P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini, F. Nuti, J. Chem. Soc., Dalton Trans. (1984) 2517.
[8] F. Hapiot, F. Agbossou, C. Meliet, A. Mortreux, G.M. Rosair, A.J. Welch, New J. Chem. 21 (1997) 1161.
[9] (a) A. Sivaramakrishna, H. Clayton, C. Kauschula, J.R. Moss, Coord. Chem. Rev. 251 (2007) 1294;
(b) A. Sivaramakrishna, E. Hager, J.R. Moss, Unpublished work, 2007.
[10] (a) S. Bi, A. Ariafard, G. Jia, Z. Lin, Organometallics 24 (2005) 680;
(b) Z.-Q. Wang, M.L. Turner, A.R. Kunicki, P.M. Maitlis, J. Organomet. Chem. 488 (1995) C11–C12.
[11] A. Sivaramakrishna, I. Rogers, J.R. Moss, Unpublished work, 2007.
[12] F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
[13] (a) K.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970;
(b) W.D. Jones, F.J. Feher, Inorg. Chem. 23 (1984) 2376.
[14] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6522.