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C–H activation by Grignard reagents: vinyl plus methylene coupling on iridium[1]

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Abstract

Reaction of $[(\eta^5\text{-}C_5Me_5)Ir(CH{=}CH_2)(Br)(Me_2SO)]$ **2**, with MeMgBr (two equivalents) gave $[(\eta^5C_5Me_5)Ir(CH{=}CH_2)(Me)(Me_2SO)]$ **3**, but with a large excess of MeMgBr (> six equivalents) the product was the η^3-allylic complex, $[(\eta^5\text{-}C_5Me_5)Ir(\eta^3\text{-}CH_2CH{=}CH_2)Br]$ **5**. Complex **5** was also obtained from $[(\eta^5\text{-}C_5Me_5)Ir(CH{=}CH_2)(Me)(Me_2SO)]$ **3**, on reaction with a variety of Grignard reagents, RMgBr (R = Me, Et, Ph). A key step is therefore the loss of H. The mechanisms are discussed. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

We have recently become interested in some special types of carbon–carbon coupling reactions, those involving a vinyl and a methylene. This has arisen from considerations of a new route for the chain propagation step in the Fischer–Tropsch reaction in which surface methylenes couple to surface alkenyls [1]. We have successfully modelled such processes on the dirhodium complex $[\{(C_5Me_5Rh)(\mu\text{-}CH_2)\}_2(CH{=}CH_2)_2]$ where the methylene and the vinyl couple to form an allyl under the influence of a mild oxidiser (Ag^+) [2]. Closely related reactions that possibly also involve vinyl plus methylene coupling have been described by Floriani et al. [3] on a diruthenium complex, by Werner [4] and Hill [5] and their co-workers on mononuclear ruthenium complexes.

We here describe a reaction of methyl and vinyl attached to a mono-iridium centre to give an allyl, we suggest it also involves methylene as an intermediate.

2. Results and discussion

Reaction of $[(C_5Me_5)IrBr_2(Me_2SO)]$ **1**, made from $[(C_5Me_5)IrBr_2]_2$ and dimethyl sulfoxide (Me_2SO) in dry THF, with two to three equivalents of vinylmagnesium bromide at low temperature gave first the monovinyl iridium bromide complex $[(C_5Me_5)Ir(CH{=}CH_2)(Me_2SO)(Br)]$ **2**. Treatment of $[(C_5Me_5)IrBr_2(Me_2SO)]$ **1**, with a large excess (four to six equivalents) of vinylmagnesium bromide gave the divinyl iridium complex $[(\eta^5\text{-}C_5Me_5)Ir(CH{=}CH_2)_2(Me_2SO)]$, in a 90% yield. The presence of a strong band in the IR at 1080 cm^{-1} is consistent with the presence of S-bonded Me_2SO ligands.

Reaction of the monovinyl iridium bromide complex with two equivalents of MeMgBr in THF gave the methyl–vinyl iridium complex $[(\eta^5\text{-}C_5Me_5)Ir(CH{=}CH_2)(Me)(Me_2SO)]$ **3**, in a 75–80% yield. While many of the related di-organo iridium complexes decomposed on reaction with CO, the methyl vinyl complex simply formed the carbonyl $[(\eta^5\text{-}C_5Me_5)Ir(Me)(CH{=}CH_2)(CO)]$ **4**, by displacement of Me_2SO on pressuring with CO (6 atm, 24 h, 20°C) (Scheme 1).

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[1] Dedicated to our dear friend, Professor Akira Nakamura, with best wishes.

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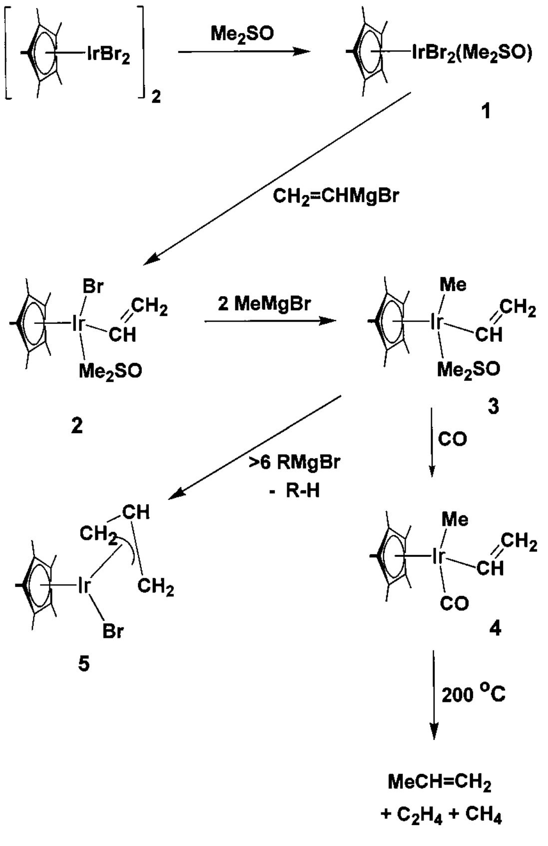
Dry thermal decomposition (200°C, 2 h, under nitrogen) of [(η^5-C_5Me_5)Ir(Me)(CH=CH_2)(CO)] **4**, gave propene, methane, and ethene; the propene formed by coupling of the methyl and the vinyl ligands was the major product (56%). There was also complete decomposition of the metal complex.

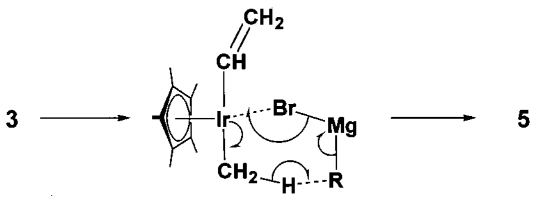
To our surprise, however, when we investigated the reaction of the monovinyl iridium bromide complex with a large excess of MeMgBr (six to ten equivalents) the product, formed in a 65–70% yield, was not [(η^5-C_5Me_5)Ir(CH=CH_2)(Me)(Me_2SO)], but the η^3-allyl bromide complex, [(C_5Me_5)Ir(η^3-CH_2CHCH_2)(Br)] **5**. This was identified by microanalysis and NMR spectroscopy, comparing the chemical shifts and coupling constants to those of closely related molecules previously synthesised [6].

Further investigation showed that if the methyl–vinyl iridium complex [(C_5Me_5)Ir(CH=CH_2)(Me)(Me_2SO)] was first prepared and isolated and then reacted with an excess of MeMgBr (six to ten equivalents), the same η^3-allyl iridium complex **5**, was obtained, and in similar yield (60–70%).

To probe the way in which [(C_5Me_5)Ir(η^3-CH_2CHCH_2)(Br)] **5**, arose a number of related reactions were carried out on [(C_5Me_5)Ir(CH=CH_2)(Me)(Me_2SO)]. The identical allylic complex **5** was also formed, and in a 60% yield, by the action of ethylmagnesium bromide on the methyl–vinyl complex **3**. The reaction of [(C_5Me_5)Ir(CH=CH_2)(Me)(Me_2SO)] with excess PhMgBr (six to ten equivalents) also gave **5**, but in somewhat lower yield (ca. 42%).



Scheme 1.



Scheme 2.

Since the allyl iridium complex **5** is accessible from a number of different Grignards, the role of the Grignard cannot be to alkylate; it must therefore be to deprotonate. There are two ways in which the reaction could occur. (a) There could first be a primary coupling of the methyl and the vinyl to give a π-propene complex which is then deprotonated to the allyl iridium complex by the Grignard acting as base in a second step. Alternatively (b) the iridium methyl could be deprotonated in a first step (a C–H bond activation of methyl by the Grignard reagent, as sketched in Scheme 2) to give an intermediate methylene complex, containing a moiety Ir=CH_2, which then couples with the vinyl.

Fryzuk and his co-workers have made a stable complex containing an Ir=CH_2 moiety and have shown that it reacts with certain olefins to give η^3-allylic hydride complexes. Deuterium labelling confirmed that the terminal CH_2 of the allyl came from the iridium–methylene and that the reaction was a methylene plus olefin [7]. In this case the olefin presumably undergoes C–H addition to the metal to give a vinyl–hydride. Interestingly, the Fryzuk reactions occurred most readily with ethene or olefins bearing electron-withdrawing substituents; propene did not react.

These observations of Fryzuk offer some support to mechanism (b) for our reaction to give **5**. Mechanism (b) is also supported by our observation that quite stringent conditions (200°C) are needed to liberate propene from the methyl–vinyl complex **4**; by contrast, methylene plus vinyl reactions appear to occur very readily. However the formation of free propene may have a quite different rate determining step than the formation of complexed propene. Thus we cannot completely exclude the possibility of mechanism (a) playing a significant role in our reaction.

We also noted that the *Z*-propenyl iridium complex [(C_5Me_5)Ir(Me_2SO)(CH=CHMe)(Br)] reacted with excess methylmagnesium bromide to give the *syn*-methylallyl iridium complex [(C_5Me_5)Ir($\eta^3$$CH_2$CHCHMe)(Br)]. This presumably again occurs via an initially formed methyl–propenyl complex. The complex

[$(C_5Me_5)Ir(Me_2SO)(CH{=}CHMe)(Br)$] was obtained from the reaction of [$(C_5Me_5)Ir(Me_2SO)Br_2$] with propenyl magnesium bromide (mainly *Z*-isomer). The geometry about the propenyl double bond was shown to be *Z*- by ^{1}H-NMR spectroscopy (*J*(H–H) 9.5 Hz).

3. Experimental

Reactions were carried out under nitrogen using standard Schlenk-line techniques. Solvents and reagents were purified and dried by standard methods and were distilled under nitrogen immediately prior to use. The complex [$\{(C_5Me_5)IrBr_2\}_2$] was prepared by the literature methods [8].

3.1. Preparation of [$(C_5Me_5)Ir(CH{=}CH_2)(Me_2SO)(Br)$]

A sample of [$\{(C_5Me_5)IrBr_2\}_2$] (0.100 g, 0.21 mmol) was dissolved in dry THF (15 ml). Dimethyl sulfoxide (Me_2SO) (0.03 ml) was added. The mixture was stirred (0.5 h) to give [$(C_5Me_5)IrBr_2(Me_2SO)$], soluble in THF. The solution was cooled down to −78°C. Vinylmagnesium bromide (0.25 ml, 1.0 M in THF (Aldrich); 0.25 mmol) was gradually added. The reaction solution was allowed to warm up to room temperature (r.t.) over 1 h. Water (0.01 ml) was carefully added to the orange solution, the reaction mixture was stirred for a further 5 min; the white precipitate was filtered off, and the solvents removed in vacuum. The resultant solid was extracted with ether (2 × 30 ml); on removal of the ether, pure yellow solid [$(C_5Me_5)Ir(CH{=}CH_2)(Me_2SO)(Br)$] (0.042 g; 90%) was obtained.

^{1}H-NMR ($CDCl_3$): 1.70 (s, 15H, C_5Me_5), 3.15 (s, 3H, Me_2SO), 3.35 (s, 3H, Me_2SO), 5.47 (dd, $J = 2$, 17 Hz, 1H, H_c), 6.38 (dd, $J = 2$, 10 Hz, 1H, H_b), 8.26 (dd, $J = 10$, 17 Hz, 1H, H_a). ^{13}C-NMR ($CDCl_3$): 10.0 (s, C_5Me_5), 42.0 (s, Me_2SO), 94.6 (s, C_5Me_5), 123.0 (s, –CH in vinyl), 138.9 (s, $=CH_2$ in vinyl).

IR (KBr): (νSO) 1109 cm^{-1} (s), 1015 cm^{-1} (s). FAB-MS (M^+, NOBA), m/z 512 (M^+, 12%). Anal. Calc. for $C_{14}H_{24}BrIrOS$: C, 32.9; H, 4.7; Br, 15.6; S, 6.2%. Found: C, 33.2; H, 4.9; Br, 15.8; S, 6.1%.

3.2. Preparation of [$(C_5Me_5)Ir(CH{=}CH_2)(Me)(Me_2SO)$

A sample of [$(C_5Me_5)Ir(Me_2SO)(CH{=}CH_2)Br$] (0.100 g, 0.10 mmol) was dissolved in dry THF (15 ml), and the solution was cooled to −78°C. Methylmagnesium bromide (0.25 ml, 1.0 M in diethyl ether (Aldrich); 0.25 mmol) was slowly added, and the solution was allowed to warm to r.t. over 1 h. A work-up as described above gave pure yellow [$(C_5Me_5)Ir(CH{=}CH_2)(Me)(Me_2SO)$] (0.036, 80%).

^{1}H-NMR ($CDCl_3$): 1.70 (s, 15H, C_5Me_5), 0.04 (s, 3H, Me), 2.85 (s, 3H, Me_2SO), 3.00 (s, 3H, Me_2SO), 5.01 (dd, $J = 2$, 17 Hz, 1H, H_c), 6.00 (dd, $J = 2$, 10 Hz, 1H, H_b), 7.50 (dd, $J = 10$, 17 Hz, 1H, H_a). ^{13}C-NMR ($CDCl_3$): −20.1 (s, Ir–Me); 8.6 (s, C_5Me_5), 43.1 (s, Me_2SO), 43.8 (s, Me_2SO), 94.4 (s, C_5Me_5), 119.9 (s, $=CH_2$ in vinyl), 137.8 (s, –CH in vinyl). IR (KBr): (νSO) 1109 cm^{-1} (s), 1015 cm^{-1} (s). Anal. Calc. for $C_{14}H_{24}IrOS$: C, 40.2; H, 6.1; S, 7.1%. Found: C, 39.9; H, 5.9; S, 6.9%.

3.3. Formation of [$(C_5Me_5)Ir(\eta^3\text{-}CH_2CHCH_2)Br$]

3.3.1. Method 1

A sample of methylmagnesium bromide (0.4 ml, 3.0 M, in diethyl ether (Aldrich); 1.2 mmol) was slowly added to [$(C_5Me_5)Ir(Me_2SO)(CH{=}CH_2)Br$] (0.100 g, 0.20 mmol) at −78°C. The reaction solution was warmed to r.t. over l h, was stirred for 30 min and then hydrolysed and worked up to give [$(C_5Me_5)Ir(\eta^3\text{-}CH_2CHCH_2)Br$] as a yellow solid (0.060 g, 70%).

^{1}H-NMR ($CDCl_3$): 1.76 (s, 15H, C_5Me_5), 2.42 (dt, $J = 10$, 0.5 Hz, $2H_{anti}$), 3.30 (dt, $J = 6$, 0.5 Hz, $2H_{syn}$) 4.20 (m, $J = 10$, 6 Hz, $1H_{central}$). ^{13}C-NMR ($CDCl_3$): 9.1 (s, C_5Me_5), 45.4 (s, CH_2 in allyl), 80.9 (s, CH in allyl), 92.2 (s, C_5Me_5). Anal. Calc. for $C_{13}H_{20}BrIr$: C, 34.8; H, 4.5; Br, 17.6%. Found: C, 34.7; H, 4.5; Br, 17.5%.

3.3.2. Method 2

A sample of methylmagnesium bromide (0.4 ml, 3.0 M in diethyl ether (Aldrich); 1.2 mmol) was slowly added to [$(C_5Me_5)Ir(Me_2SO)(CH{=}CH_2)(Me)$] (0.100 g, 0.22 mmol) at −78°C. The reaction solution was warmed to r.t. over 1 h, was stirred for 30 min and then hydrolysed and worked up to give [$(C_5Me_5)Ir(\eta^3\text{-}CH_2CHCH_2)Br$] (0.068 g, 68%).

3.3.3. Method 3

A sample of ethylmagnesium bromide (1.2 ml, 1.0 M in THF (Aldrich); 1.2 mmol) was slowly added to [$(C_5Me_5)Ir(Me_2SO)(CH{=}CH_2)(Me)$] (0.100 g, 0.22 mmol) at −78°C. The reaction solution was warmed to r.t. over 1 h, was stirred for 30 min and then hydrolysed and worked up to give [$(C_5Me_5)Ir(\eta^3\text{-}CH_2CHCH_2)Br$] (0.060 g, 60%).

3.3.4. Method 4

A sample of phenylmagnesium bromide (1.2 ml, 1.0 M in THF (Aldrich); 1.2 mmol) was slowly added to [$(C_5Me_5)Ir(Me_2SO)(CH{=}CH_2)(Me)$] (0.100 g, 0.22 mmol) at −78°C. The reaction solution was warmed to r.t. over 1 h, was stirred for 30 min and then hydrolysed and worked up to give [$(C_5Me_5)Ir(\eta^3\text{-}CH_2CHCH_2)Br$] (0.042 g, 42%).

3.4. Preparation of [(C_5Me_5)Ir(Me_2SO)(CH=CHMe)Br]

A solution of [(C_5Me_5)IrBr_2(Me_2SO)] from [(C_5Me_5)IrBr_2]$_2$ (100 mg, 0.21 mmol) and dimethyl sulfoxide (Me_2SO) (0.03 ml, 0.42 mmol) in dry THF (15 ml), was cooled to − 78°C, then propenyl magnesium bromide (0.25 ml, 1.0 M; 0.25 mmol) was added gradually. The reaction solution was warmed to r.t. over 1 h. A conventional work-up gave yellow [(C_5Me_5)Ir(CH=CHMe)(Me_2SO)(Br)] (95 mg; 90%).

^{1}H-NMR ($CDCl_3$): 1.68 (d, 5 Hz, 3H, Me); 1.72 (s, 15H, C_5Me_5); 3.08 (s, 3H, Me_2SO); 3.40 (s, 3H, Me_2SO); 6.47 (m, 9, 5 Hz, 1H, CH); 7.80 (d, 9 Hz; 1H, CH). ^{13}C-NMR ($CDCl_3$): 9.05 (s, C_5Me_5); 20.3 (s, Me); 42.5 (s, Me_2SO); 47.6 (s, Me_2SO); 94.7 (s, C_5Me_5); 129.85 (s, CH); 130.8 (s, CH). Anal. Calc. for $C_{15}H_{26}BrIrOS$: C, 34.2; H,5.0; Br, 15.2. Found: C, 34.0; H, 5.0; Br, 15.0%.

3.5. Preparation of [(C_5Me_5)Ir(η^3-$CH_2CHCHMe$)Br]

A sample of methylmagnesium bromide (0.4 ml, 3.0 M; 1.2 mmol) was slowly added to [(C_5Me_5)Ir(Me_2SO)(CH=CHMe)Br] (100 mg, 0.19 mmol) at − 78°C. The reaction solution was warmed to r.t. over 1 h, was stirred for 30 min and then hydrolysed and worked up as normal to give [(C_5Me_5)Ir(η^3-$CH_2CHCHMe$)Br] as a yellow solid (0.056 g, 64%).

^{1}H-NMR ($CDCl_3$): 1.44 (d, 6 Hz, 3H, Me_{syn}); 1.74 (s, 15H, C_5Me_5); 2.68 (dt, 10, 1 Hz, lH_{anti}); 2.97 (dd, 6, 1 Hz, lH_{syn}); 3.32 (m, lH_{central}); 3.80 (m, 10, 6 Hz, lH_{anti}). ^{13}C-NMR (CD_3COCD_3): 9.3 (s, C_5Me_5), 18.0 (s, Me); 41.3 (s, CH_2 in allyl), 54.1 (s, CH in allyl), 82.1 (s, CH in allyl); 91.5 (s, C_5Me_5). Anal. Calc. for $C_{14}H_{22}BrIr$: C, 36.4; H,4.8; Br, 17.1. Found: C, 36.1; H, 4.7; Br, 17.0.

Acknowledgements

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