# Formation of transition metal carbenes using haloalkylzinc reagents

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*Received (in Cambridge, UK) 11th April 2007, Accepted 15th May 2007*
*First published as an Advance Article on the web 1st June 2007*
**DOI: 10.1039/b705459a**

**A new reaction of haloalkylzinc compounds, leading to transition metal carbenes, is described; halomethylzinc and halobenzylzinc compounds react with ruthenium and iridium complexes to form methylene and benzylidene complexes, including the Grubbs catalyst.**

Haloalkylzinc reagents are useful reagents in organic synthesis. For example, bis(iodomethyl)zinc and iodomethylzinc iodide, produced *in situ* from diiodomethane and diethylzinc, are used in the Simmons–Smith cyclopropanation reaction, which has been a subject of intensive investigations over the past five decades.[1] They are also used in homologation[2] and alkylation.[3] Haloalkylzinc compounds, stabilized by coordination of bipyridine, were isolated.[4]

We were intrigued by the possibility of employing haloalkylzinc compounds as reagents for the formation of transition metal Schrock-type carbene (alkylidene) complexes, which are widely used in synthetic chemistry.[5] For instance, catalysis of alkene metathesis reactions by Schrock molybdenum alkylidenes[6] and Grubbs ruthenium alkylidenes[7] has resulted in a multitude of synthetic applications.[8]

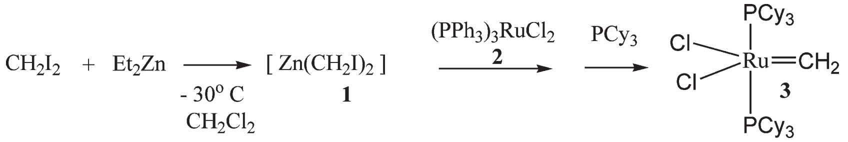
Several useful methods for the synthesis of alkylidene complexes have been described,[9] perhaps the most common one being based on diazoalkane precursors. However, this method suffers from thermal instability of the diazo precursors and in many cases, metal diazo adducts are formed rather than carbene complexes. Recently, we have developed a general method for the preparation of carbene complexes based on the use of sulfur ylides, which are prepared *in situ* from simple sulfonium salts.[10]

We have now discovered a new reaction, involving haloalkyl zinc compounds, which upon reaction with transition metal complexes lead to metal alkylidenes. Using halomethylzinc and halobenzylzinc reagents, Grubbs-type ruthenium methylidene and benzylidene complexes and an Ir-based benzylidene complex were formed.

First, we have examined the reaction of the common cyclopropanation reagent, bis(iodomethyl)zinc, with Ru(II). A slightly modified literature procedure[11] was used for the *in situ* formation of this reagent. Addition of a hexane solution of $Et_2Zn$ (2 equivalents) to a dichloromethane solution of $CH_2I_2$ (4.4 equivalents) at −30 °C followed by warming to 0 °C resulted in formation the iodomethylzinc complex **1** (Scheme 1). To this reaction mixture was added a methylene chloride solution of $(PPh_3)_3RuCl_2$ **2** (one equivalent) at −30 °C, followed by substitution of the triphenylphosphine ligands by tricyclohexylphosphine (2.5 equivalents), for stabilization of the resulting carbene complex.[10] After 2 h at room temperature, $^{31}P$ and $^1H$ NMR spectra revealed formation of the previously reported[12] complex $(PCy_3)_2Cl_2Ru{=}CH_2$ (**3**) in 80% yield.† The synthesis of this compound by the sulfur ylide method resulted in a low yield, due to the instability of the methylene sulfur ylide.[10] To our knowledge, this is the first example of the use of haloalkyl zinc reagents (or, to our knowledge, metal carbenoid precursors in general) for the preparation of a metal alkylidene complex.

Studying the applicability of the reaction for the formation of alkylidene complexes beyond methylidenes, we applied it to formation of the widely used Grubbs ruthenium benzylidene catalyst. Indeed, the reaction proceeded smoothly with the benzal chloride-derived zinc reagent. Thus, addition of $Et_2Zn$ to a methylene chloride solution of benzal chloride at −30 °C led to formation of a yellow precipitate, presumably the bis(chlorobenzyl)zinc complex **4**, which was reacted *in situ* with $(PPh_3)_3RuCl_2$. Following substitution of the triphenylphosphine ligands by tricyclohexylphosphine, complex $(PCy_3)_2RuCl_2({=}CHPh)$[12] **5** was formed in 81% yield, as indicated by $^{31}P$ NMR. Following workup, this complex was isolated in 63% yield (Scheme 2).†

The reaction of haloalkyl zinc reagents with transition metal complexes is not limited to ruthenium complexes. For instance, this reaction can be utilized for formation of an iridium benzylidene complex. While *disubstituted* alkylidene iridium complexes, *trans*-$[(PR_3)_2IrCl({=}CR'R'')]$ were synthesized,[13] and iridium methylene complexes[14] were also reported, stable[15] *mono-substituted* alkylidene iridium complexes were unknown until, recently, *trans*-$[(P^iPr_3)_2ClIr{=}CHPh]$ **7** was prepared by utilizing the sulfur ylide-based method.[10] We have now found that the zinc-reagent based reaction is also capable of direct formation of complex **7**. Thus, when the chlorobenzyl zinc reagent, generated *in situ* from $Et_2Zn$ and benzal chloride, was reacted with the *in situ* prepared $[(P^iPr_3)_2IrCl]_2$ complex **6**[10] at −30 °C, complex **7** was formed in 60% isolated yield (Scheme 2).†



**Scheme 1**

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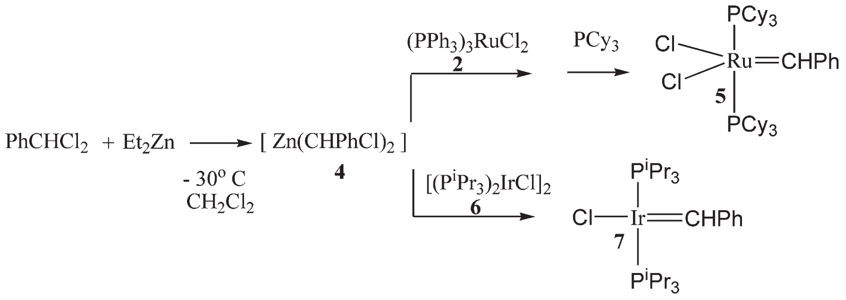
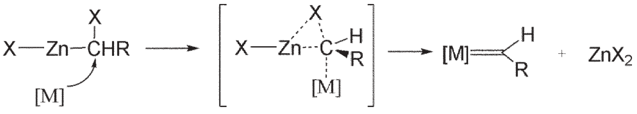


Scheme 2



Scheme 3

Theoretical studies showed that haloalkyl zinc reagents undergo the cyclopropanation reaction through a methylene transfer mechanism, in which the methylene unit (with no participation of Zn) interacts directly with the olefin.[16] In the present case, most probably, the metal center of the transition metal complex behaves as a nucleophile and attacks the methylene (or benzylidene) group, with concomitant transfer of the halide to zinc, resulting in formation of $ZnX_2$ and the carbene complex (Scheme 3).

To summarize, a new reaction, involving haloorganozinc carbenoid donors and transition metal complexes, leading to alkylidene complexes, has been discovered. While the scope of this reaction has not been fully explored yet, we have already observed that this facile and synthetically simple reaction can be utilized for formation of methylene and benzylidene complexes of ruthenium and iridium, including the Grubbs catalyst.

## Notes and references

† *Synthesis* of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ **5**.

A pre-cooled to −30 °C methylene chloride solution (3 ml) of benzal chloride (20 μl, 0.157 mmol) was treated with a −30 °C 1 M hexane solution of $Et_2Zn$ (91 μl, 0.091 mmol). After 30 min, the solution was warmed to 0 °C and stirred until a yellow–brown precipitate of the complex **4** appeared. Then 1.5 ml of a cold dichloromethane solution of $(PPh_3)_3RuCl_2$ (35 mg, 0.037 mmol) were added. After 1 h at −30 °C, cold $PCy_3$ (25 mg, 0.091 mmol) in 1 ml of $CH_2Cl_2$ was added and the reaction was warmed to room temperature and stirred for 1 h. The solvent was evaporated, the purple solid was washed with methanol (3 × 5 ml) and dried under vacuum to give 19 mg (0.023 mmol, 63% yield) of complex **5**, $(PCy_3)_2RuCl_2({=}CHPh)$.[12] Spectral data were identical to those reported in the literature.

*Synthesis* of $(PCy_3)_2Cl_2Ru{=}CH_2$ **3**.

To a methylene chloride (1.5 ml) solution of methylene iodide (11 μl, 0.137 mmol) at −30 °C was added a 1 M solution of $Et_2Zn$ in hexane (62 μl, 0.062 mmol) pre-cooled to −30 °C. After 15 min at −30 °C, the reaction vessel was warmed to 0 °C and a white precipitate of iodomethylzinc complex **1** appeared. The mixture was cooled again to −30 °C and 1.5 ml of a cold dichloromethane solution of $(PPh_3)_3RuCl_2$ (30 mg, 0.031 mmol) was added. After 30 min at −30 °C, $PCy_3$ (21 mg, 0.078 mmol) in 1 ml of $CH_2Cl_2$ was added and the reaction was kept for an additional 10 min at −30 °C, followed by warming up to room temperature. After 2 h, $^{31}P$ and $^{1}H$ NMR spectra revealed formation of the known[12] complex $(PCy_3)_3(Cl)_2Ru{=}CH_2$ **3** in 80% yield. Due to the instability of complex **3**, its isolation in pure form was not possible, and the yield was determined by $^{31}P$ NMR using triphenylphosphine oxide as an internal standard. Spectral data were identical to those reported in the literature.

*Synthesis* of $(P^iPr_3)_2ClIr{=}CHPh$ **7**.

To a pentane (7 ml) suspension of $[(COE)_2IrCl]_2$ (82 mg, 0.091 mmol) was added 58 mg (0.364 mmol) of $P^iPr_3$. The reaction mixture was stirred for 20 min at r.t. to give an orange solution of $[(P^iPr_3)_2IrCl]_2$ complex **6**, then its volume was reduced to 2 ml. Prepared *in situ* as described in preparation of **5** (benzal chloride 52 μl, 0.405 mmol and $Et_2Zn$ 235 μl, 0.235 mmol), chlorobenzylzinc complex **4** in 2 ml of $CH_2Cl_2$ was treated with a solution of **6** pre-cooled to −30 °C. After 30 min at −30 °C, 5 ml of cold pentane were added and a light-green precipitate was obtained. After decantation of the liquid, the precipitate was washed with pentane and the product complex **7** was extracted with toluene. Removal of solvent by vacuum, gave 69 mg (0.109 mmol, 60% yield) of the known[10] complex **7**. Spectral data were identical to those reported in the literature.

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