

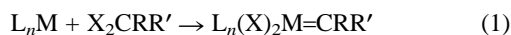
The first double oxidative addition of CH₂Cl₂ to a metal complex: facile synthesis of [Ru(CH₂)Cl₂{P(C₆H₁₁)₃}₂]

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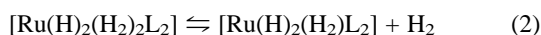
[Ru(H)₂(H₂)₂L₂] [L = P(C₆H₁₁)₃] serves as a formal source of zerovalent 'RuL₂', and undergoes unprecedented oxidative addition of both C–Cl bonds of CH₂Cl₂ to a single metal center, providing a convenient synthesis of the alkene metathesis catalyst [Ru(CH₂)Cl₂L₂].

Ruthenium carbenes of the form [Ru(CRR')Cl₂L₂] (L = phosphine) play a central role in alkene metathesis methodology in organic chemistry. The original form¹ of the ruthenium catalyst has now been simplified,² but access to carbene complexes remains less than rational: α-elimination from an alkyl complex or use of a diazoalkane reagent are the primary synthetic methodologies.



gem-Dihalogeno compounds are formally attractive as a source of a carbene ligand [eqn. (1)], but converting this idea into reality has been elusive. Eqn. (1) makes clear that L_nM must be a 14-valence electron species, or its equivalent, and the scarcity of such species accounts for the rarity of eqn. (1). Eqn. (1) might be expected to proceed stepwise, with an X–M–CRR'X intermediate, and indeed, there are numerous examples of halogenomethyl ligands that have been formed from CX₂RR'.³ However, a double oxidation addition of an R₂CX₂ sp³ carbon is unprecedented. Set against this background, we report here the first oxidative addition of both C–Cl bonds of a *gem*-dihalide to a single metal center, where all constituents of R₂CX₂ become attached to a single metal in the product,⁴ and an example where this occurs in high yield to produce the simplest of ruthenium alkene metathesis catalysts, [Ru(CH₂)Cl₂L₂], with L = P(C₆H₁₁)₃.

Reaction† of [Ru(H)₂(H₂)₂L₂] [L = P(C₆H₁₁)₃] with CH₂Cl₂ in pentane or benzene under argon occurs over 3 h at 25 °C (1 : 4 mol ratio) or 15 min at 60 °C (1 : 1.5 mole ratio) to give the known molecule [RuCl₂(CH₂)L₂],^{2b} characterized by ¹H, ¹³C and ³¹P NMR spectroscopies. The ¹H NMR signal of the carbene ligand is the most unique spectroscopic feature, appearing at δ 19.4. If the reaction is carried out with CD₂Cl₂, [RuCl₂(CD₂)L₂] is the only isotopomer produced (¹H and ²H NMR assay),‡ showing that there is no scrambling of the metal- and carbon-derived hydrogen. This reaction is remarkable because it involves a four-electron reduction of CH₂Cl₂ (to Cl[–] and what is formally CH₂^{2–}). It thus depends upon [Ru(H)₂(H₂)₂L₂] being a formal source of uncharged RuL₂ (*i.e.* zerovalent Ru), by virtue of reductive elimination of hydride from Ru^{II}, as H₂. When this reaction is repeated in a closed NMR tube, we see (³¹P{¹H} NMR) no growth and decay of any intermediate. Since there is no evidence for production of CH₃Cl or CH₄, this reaction is an unprecedented oxidative addition of both C–Cl bonds of CH₂Cl₂ to a single metal center. This reaction proceeds more slowly in an NMR tube under 1 atm argon, than in a well agitated, round-bottom flask with a considerable head-space, a fact we attribute to the accumulation of H₂, which shifts eqn. (2) to the left and thus decreases the amount of unsaturated [Ru(H)₂(H₂)L₂], which is apparently the necessary reaction partner for CH₂Cl₂.⁵



This idea of competitive inhibition by H₂ is supported by the fact that, if [Ru(H)₂(H₂)₂L₂] is stirred with CH₂Cl₂ (1 : 4) at 25 °C under 1 atm H₂ in pentane, there is no reaction over 3 h. The reaction is thus not outer-sphere electron transfer from [Ru(H)₂(H₂)₂L₂], and a 16-electron complex is the reactive species.

Since [RuH₃ClL₂]⁶ is also produced in <15% yield in this reaction, we considered that HCl {which we independently verified could convert [Ru(H)₂(H₂)₂L₂] to [RuH₃(Cl)L₂]} might participate in the reaction which forms the carbene complex. However, when the reaction of [Ru(H)₂(H₂)₂L₂] with CH₂Cl₂ is executed in the presence of NEt₃ (1 : 4 : 2 mole ratio), the carbene product and yield are unchanged, as is (qualitatively) the rate. No [NH₄Et₃]Cl precipitates. This gives support for the idea that H₂ is the fate of all metal-bound H, that [RuH₃(Cl)L₂] is produced in a side reaction, and that a 'ClRuCH₂Cl' species mediates the reaction. However, any such species must react further to give carbene product faster than it reacts with NEt₃, to quaternize the amine (giving 'ClRuCH₂–NEt₃⁺' and Cl[–]); chloromethyl ligands readily react with nucleophiles.^{3a}

The idea of multiple oxidative addition to [Ru(H)₂(H₂)₂L₂], and the idea that facile multiple losses of H₂ from this molecule permits it to serve as a formal equivalent of zerovalent 'RuL₂' deserves further exploration.

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Footnotes and References

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† [RuCl₂(=CH₂){P(C₆H₁₁)₃}₂] (method A): To a suspension of [RuH₂(H₂)₂{P(C₆H₁₁)₃}₂]⁷ (100 mg, 0.15 mmol) in pentane (7 ml) was added CH₂Cl₂ (38 μl, 0.60 mmol) *via* a syringe. The resulting suspension was stirred at room temp. for 3 h. During this time, the suspension changed from white to brown–red. The red solid obtained by filtration was washed with pentane and dried *in vacuo*. Yield: 70 mg (63%). Alternatively (method B), the reaction could be carried out heating at 60 °C for 15 min, starting from [RuH₂(H₂)₂{P(C₆H₁₁)₃}₂] (100 mg, 0.15 mmol) and CH₂Cl₂ (14.4 μl, 0.22 mmol) in pentane (5 ml). Yield: 75 mg (67%). All the spectroscopic data are consistent with those reported previously.^{2b} When the crude suspension was dried *in vacuo* and dissolved in C₆D₆, ¹H and ³¹P NMR show the presence of [RuH₃Cl{P(C₆H₁₁)₃}₂],⁶ in addition to [RuCl₂(=CH₂){P(C₆H₁₁)₃}₂], in a yield of <15%. This was shown independently to be formed by the action of H₂ on [Ru(CH₂)Cl₂{P(C₆H₁₁)₃}₂].

‡ [RuCl₂(=CD₂){P(C₆H₁₁)₃}₂]: this compound was prepared analogously as described for [RuCl₂(=CH₂){P(C₆H₁₁)₃}₂] (method A) by starting from [RuH₂(H₂)₂{P(C₆H₁₁)₃}₂] (50 mg, 0.075 mmol) and CD₂Cl₂ (19 μl, 0.30 mmol). ²H NMR (61 MHz, C₆H₆): δ 19.40 (s, Ru=CD₂).

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