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The first double oxidative addition of CH_2Cl_2 to a metal complex: facile synthesis of $[Ru(CH_2)Cl_2\{P(C_6H_{11})_3\}_2]$

Montserrat Oliván and Kenneth G. Caulton*

Department of Chemistry, Indiana University, Bloomington, IN 47405-4001, USA

$[Ru(H)_2(H_2)_2L_2]$ [L = $P(C_6H_{11})_3$] serves as a formal source of zerovalent 'RuL_2', and undergoes unprecedented oxidative addition of both C–Cl bonds of CH_2Cl_2 to a single metal center, providing a convenient synthesis of the alkene metathesis catalyst $[Ru(CH_2)Cl_2L_2]$.

Ruthenium carbenes of the form $[Ru(CRR')Cl_2L_2]$ (L = phosphine) play a central role in alkene metathesis methodology in organic chemistry. The original form[1] 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.

$$L_nM + X_2CRR' \rightarrow L_n(X)_2M{=}CRR' \qquad (1)$$

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 CX_2RR'.[3] However, a double oxidation addition of an R_2CX_2 sp^3 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 R_2CX_2 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, $[Ru(CH_2)Cl_2L_2]$, with L = $P(C_6H_{11})_3$.

Reaction† of $[Ru(H)_2(H_2)_2L_2]$ [L = $P(C_6H_{11})_3$] with CH_2Cl_2 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 $[RuCl_2(CH_2)L_2]$,[2b] characterized by ^1H, ^{13}C and ^{31}P 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 CD_2Cl_2, $[RuCl_2(CD_2)L_2]$ 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 CH_2Cl_2 (to Cl^- and what is formally CH_2^{2-}). It thus depends upon $[Ru(H)_2(H_2)_2L_2]$ being a formal source of uncharged RuL_2 (*i.e.* zerovalent Ru), by virtue of reductive elimination of hydride from Ru^{II}, as H_2. When this reaction is repeated in a closed NMR tube, we see ($^{31}P\{^1H\}$ NMR) no growth and decay of any intermediate. Since there is no evidence for production of CH_3Cl or CH_4, this reaction is an unprecedented oxidative addition of both C–Cl bonds of CH_2Cl_2 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 H_2, which shifts eqn. (2) to the left and thus decreases the amount of unsaturated $[Ru(H)_2(H_2)L_2]$, which is apparently the necessary reaction partner for CH_2Cl_2.[5]

$$[Ru(H)_2(H_2)_2L_2] \leftrightharpoons [Ru(H)_2(H_2)L_2] + H_2 \qquad (2)$$

This idea of competitive inhibition by H_2 is supported by the fact that, if $[Ru(H)_2(H_2)_2L_2]$ is stirred with CH_2Cl_2 (1 : 4) at 25 °C under 1 atm H_2 in pentane, there is no reaction over 3 h. The reaction is thus not outer-sphere electron transfer from $[Ru(H)_2(H_2)_2L_2]$, and a 16-electron complex is the reactive species.

Since $[RuH_3ClL_2]$[6] is also produced in < 15% yield in this reaction, we considered that HCl {which we independently verified could convert $[Ru(H)_2(H_2)_2L_2]$ to $[RuH_3(Cl)L_2]$} might participate in the reaction which forms the carbene complex. However, when the reaction of $[Ru(H)_2(H_2)_2L_2]$ with CH_2Cl_2 is executed in the presence of NEt_3 (1 : 4 : 2 mole ratio), the carbene product and yield are unchanged, as is (qualitatively) the rate. No $[NHEt_3]Cl$ precipitates. This gives support for the idea that H_2 is the fate of all metal-bound H, that $[RuH_3(Cl)L_2]$ is produced in a side reaction, and that a '$ClRuCH_2Cl$' species mediates the reaction. However, any such species must react further to give carbene product faster than it reacts with NEt_3, to quaternize the amine (giving '$ClRuCH_2NEt_3^+$' and Cl^-); chloromethyl ligands readily react with nucleophiles.[3a]

The idea of multiple oxidative addition to $[Ru(H)_2(H_2)_2L_2]$, and the idea that facile multiple losses of H_2 from this molecule permits it to serve as a formal equivalent of zerovalent 'RuL_2' deserves further exploration.

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Footnotes and References

* E-mail: caulton@indiana.edu

† $[RuCl_2(=CH_2)\{P(C_6H_{11})_3\}_2]$ (method A): To a suspension of $[RuH_2(H_2)_2\{P(C_6H_{11})_3\}_2]$[7] (100 mg, 0.15 mmol) in pentane (7 ml) was added CH_2Cl_2 (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 $[RuH_2(H_2)_2\{P(C_6H_{11})_3\}_2]$ (100 mg, 0.15 mmol) and CH_2Cl_2 (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 C_6D_6, ^1H and ^{31}P NMR show the presence of $[RuH_3Cl\{P(C_6H_{11})_3\}_2]$,[6] in addition to $[RuCl_2(=CH_2)\{P(C_6H_{11})_3\}_2]$, in a yield of < 15%. This was shown independently to be formed by the action of H_2 on $[Ru(CH_2)Cl_2\{P(C_6H_{11})_3\}_2]$.

‡ $[RuCl_2(=CD_2)\{P(C_6H_{11})_3\}_2]$: this compound was prepared analogously as described for $[RuCl_2(=CH_2)\{P(C_6H_{11})_3\}_2]$ (method A) by starting from $[RuH_2(H_2)_2\{P(C_6H_{11})_3\}_2]$ (50 mg, 0.075 mmol) and CD_2Cl_2 (19 μl, 0.30 mmol). ^2H NMR (61 MHz, C_6H_6): δ 19.40 (s, Ru=CD_2).

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