Geminal dehydrogenation of a C(sp^3) CH_2 group by unsaturated Ru(II) or Os(II)†

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Letter

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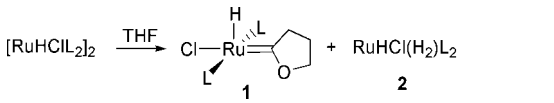
Dimeric $[RuHClL_2]_2$ ($L = PPr^i_3$), a source of the 14-electron fragment $RuHClL_2$, reacts at reflux in THF to cleanly form equimolar $L_2HClRu{=}C(CH_2)_3O$ and $RuHCl(H_2)L_2$, the products of stoichiometric geminal dehydrogenation of the α-C of THF. The same products are produced slowly at 25 °C by reaction of the transient $RuHClL_2$. Double dehydrogenation of the sp^3 α-C of THF is also effected at 25 °C by $Os(H)_3ClL_2$ if two H ligands are removed with $Bu^t(H)C{=}CH_2$.

The fragment $RuHClL_2$ ($L = PPr^i_3$), available from the dimer[1] $[RuH(\mu\text{-}Cl)L_2]_2$, has demonstrated reactivity indicative of its being electron-rich: it transforms organic molecules into π-acids, which it then coordinates to itself. For example (Scheme 1), vinyl ethers are isomerized into coordinated carbenes, aldehydes are decarbonylated to give CO, and aldimines RHC=NR′ are stripped of RH to give isonitriles CNR′.[2] In certain cases, H_2 is produced, which then binds to unreacted $RuHClL_2$ to give $RuHCl(H_2)L_2$,[3,4] another example of binding of a π-acid to $RuHClL_2$. In summary, because of the absence of π-acid ligands in $RuHClL_2$, its six d_π electrons make this a potent π-base and a reducing agent. We now find that these characteristics also make it possible to geminally dehydrogenate tetrahydrofuran at 25 °C, and we report a way to accomplish THF dehydrogenation with an osmium reagent, in spite of the absence of an isolable dimer of the 14-valence electron fragment $OsHClL_2$.

Dimeric $[RuHClL_2]_2$ reacts with excess THF to produce equimolar $RuH(H_2)ClL_2$[5,6] and the carbene complex **1**, according to eqn. (1).[7]

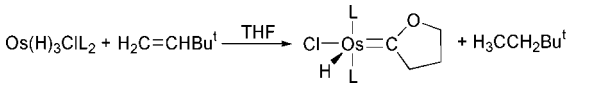


(1)

This net double C–H activation of the THF α-protons is readily achieved by heating a THF solution of $[RuHClL_2]_2$ for 3 h at 80 °C. The absence of competitive degradative loss of $RuHClL_2$ is proven by the fact that **1** and equimolar **2** are also produced over a timescale of one week at 25 °C. We propose that this reaction is initiated by oxidative addition of a THF α-C–H to yield alkyl intermediate **3**, which can lose H_2 to unreacted $[RuHClL_2]_2$ to form the observed $RuH(H_2)ClL_2$ (Scheme 2). From the undetected H_2 loss species **4**, α-H migration to Ru generates the observed carbene. An alkyl intermediate analogous to **4** was observed for the isomerization of coordinated cyclic and acyclic vinyl ethers to carbene using $[RuHClL_2]_2$ by Ru–H addition to CHR=CH(OR′), and was confirmed by ^2H labeling studies during the generation of the observed carbene products.[5,6] Since $[RuHClL_2]_2$ remains dimeric at room temperature and forms no NMR-detectable adduct in the presence of THF, mild heating is required to enhance the reaction rate. In support of that hypothesis, dehydrohalogenation[5,6] of $Ru(H)_2Cl_2L_2$ with lithium tetramethyl piperidide in THF over 12 h at room temperature gives a significant yield (15–20%) of carbene complex **1** since the initially formed $RuHClL_2$ monomer can be solvated by THF and form carbene, in competition with the observed dimerization to the other observed product, $[RuHClL_2]_2$.

Scheme 1

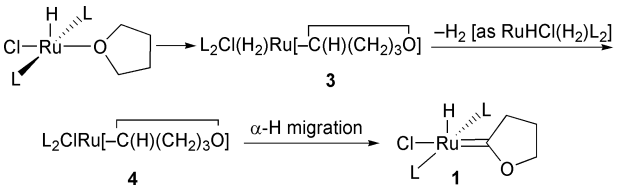
Finding an osmium analog of this chemistry confronts two facts: $OsHClL_2$ is not a known compound and the related $Os(H)_3ClL_2$[8] is a trihydride, in contrast to $Ru^{II}HCl(H_2)L_2$. The latter is no substantial impediment, since $Os(H)_3ClL_2$ reacts with *tert*-butylethylene[9,10] in THF over 2 h at 25 °C to give the carbene complex derived by double dehydrogenation at the α-C of THF [eqn. (2), 55% yield] and equimolar 2,2-dimethylbutane.[11,12]



(2)

Also formed is $OsHCl(\eta^2\text{-}H_2C{=}CHBu^t)L_2$ (30%), which is not an intermediate; it does not react further to dehydrogenate THF.

Reaction of OsH_3ClL_2 with $H_2C{=}CHBu^t$ (1 : 2 molar ratio) in d_8-THF gives, after 1.5 h at 25 °C, the carbene complex with H, not D, on the metal (by ^1H NMR). Exhaustive vacuum removal of the volatiles, followed by ^2H NMR assay



Scheme 2

† Electronic supplementary information (ESI) available: complete experimental details and NMR spectra. See http://www.rsc.org/suppdata/nj/b0/b007200l/

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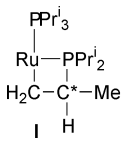
in C_6H_6 shows the absence of D on Os, but does show the three chemical shifts of the ring deuterons, in equal intensity. Because the Pr^i methyl region of the product shows 50% of these sites to be deuterium, we conclude that the primary product is $OsDCl[C(CD_2)_3O][PPr^i_3]_2$, but the 36 : 1 population ratio, together with an equilibrium isotope effect favoring D on C, not Os, leads to label redistribution from Os to Pr^i methyl in the product.

The rates of reaction of the $OsH_3ClL_2 + H_2C{=}CHBu^t$ reagent with THF and with its d_8 analog were not significantly different (each had a half-life of approximately 1.5 ± 0.2 h at 20 °C). It must therefore be that the generation of the reactive osmium species, by "dehydrogenation" of OsH_3ClL_2, is the rate-determining step. This is consistent with the fact that we can observe $OsHCl(H_2)(olefin)L_2$ upon reaction of $Os(H)_3ClL_2$ with vinyl ethers at low temperature and that its dehydrogenation is the rate-determining step to further reaction (to ultimately make a carbene complex).

When $Os(H)_3ClL_2$ reacts with equimolar *tert*-butylethylene at 20 °C in diethyl ether solvent, a 5% yield of the carbene $OsHCl[C(CH_3)(OEt)]L_2$ is obtained after 38 h. The reactive transient Os species thus dehydrogenates Et_2O, but only inefficiently in this environment. The main product (50% yield) is the olefin adduct $OsHCl[\eta^2\text{-}H_2C{=}C(H)Bu^t]L_2$, along with unreacted $Os(H)_3ClL_2$. This olefin adduct does not convert to the ether-derived carbene when dissolved in Et_2O for 24 h, indicating that it is not an intermediate in forming the carbene complex.

We have now established that reaction of $RuHCl(H_2)L_2$ with equimolar $H_2C{=}CHBu^t$ in benzene gives clean conversion to $[RuHClL_2]_2$ in <1 h at 25 °C. However, the reaction of $RuHCl(H_2)L_2$ with excess $H_2C{=}CHBu^t$ *in THF* at 25 °C over 48 h gives none of the THF-derived carbene complex **1**, but only several complexes that show the AB and AX $^{31}P\{^1H\}$ NMR patterns characteristic[13,14,15] of metallation of the phosphine Pr^i groups as in **I**; the chiral carbon and potential to bind prochiral $H_2C{=}CHBu^t$ gives rise to several possible diastereomers. Excess hydrogen-acceptor *tert*-butylethylene thus competes more effectively than THF for the available reactive ruthenium centers, and these act to dehydrogenate the products of oxidative addition of Pr^i C–H bonds to Ru. These observations in THF show that the strained ring in substructure **I** does not react with THF to produce **1**.



I

Two previous reports of geminal dehydrogenation of α-C on THF both[16,17] employ (η^3-facial ligand)Ir^{III}(Lewis base)(hydrocarbyl)$^{q+}$ species and thus appear to involve electrophilic centers. They share with $MHClL_2$ (M = Ru, Os) the d^6 configuration and the absence of π-acceptor ligands. They differ in being devoid of π-donor ligands (here Cl^-), and in being 16-, not 14-electron species. We have come to believe that the 14-electron configuration of the $MHClL_2$ fragment is effective primarily because only with the 14-electron configuration does one get an empty orbital *cis* to hydride [contrast $MHClL(phosphine)_2$, $RuHCl(PPh_3)_3$, *etc*]. The empty orbital in (η^3-facial ligand)Ir^{III}(Lewis base)(hydrocarbyl)$^{q+}$ is of course *cis* to the one-electron donor ligand. The final contrast is that the first H removed from THF is by alkyl[18] in $Cp^*Ir(PMe_3)(CH_3)^+$ and vinyl in $(Tp)Ir(C_2H_5)$(vinyl), but by H in $MHClL_2$. Finally, the observation that *all* examples involve the ether α-C suggests that this regiochemistry is controlled by preliminary O coordination of the ether.

Acknowledgements

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