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Carbene transposition involving double dehydrogenation of an sp^3 carbon†

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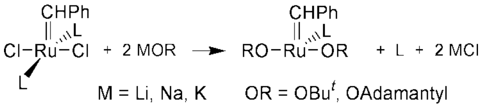
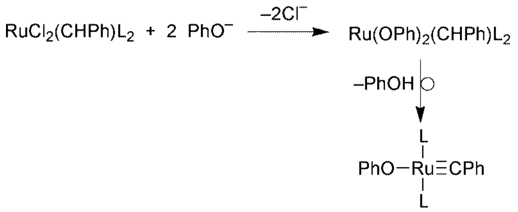
***Two* benzylic hydrogens of 2,6-$Me_2C_6H_3O^-$ coordinated to $RuCl(PCy_3)_2(CHPh)^+$ are transferred to the benzylidene ligand, liberating toluene to form a new carbene which is covalently linked to the aryloxide ligand.**

Replacement of the chloride ligand in the olefin metathesis catalyst $RuCl_2(CHR)LL'$ (L, L′ = tertiary phosphines or other neutral donors) by other pseudohalides has been actively studied, but no clear trends or dramatic improvements in reactivity have yet to emerge.[1] Two groups[2,3] have recently reported replacement of both chlorides by alkoxides on the benzylidene complex, with the result [eqn. (1)] that some combination of steric and electronic (*e.g.* π-donor) effects causes loss of one PCy_3 to give a four-coordinate species with an apparent 14-valence electron count. This species is attractive because it has an empty orbital *cis* to the carbene ligand, a feature lacking in isolable $RuCl_2(CHR)L_2$. Fluoroalkoxide analogs have also been synthesized,[2] but phenoxides behave very differently[3] [eqn. (2)], proceeding further to a benzylidyne product by liberation of phenol. We now report the wholly distinct consequence of increasing the steric bulk of the phenoxide

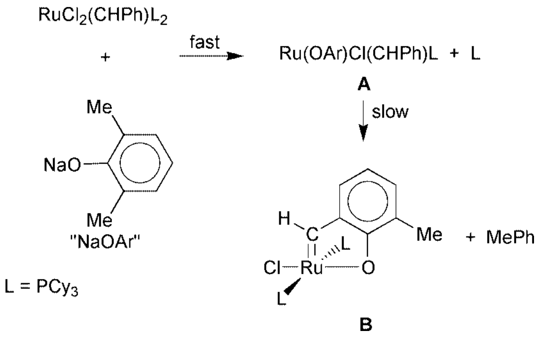


(1)



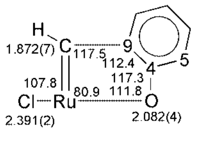
(2)

Reaction of $RuCl_2(CHPh)(PCy_3)_2$ with $NaOC_6H_3Me_2$-2,6·THF (NaOAr·THF: 1 equiv) in THF proceeds rapidly to a benzylidene complex with only one coordinated phosphine and *one* coordinated aryloxide (a second equivalent of NaOAr·THF does not replace a second Cl$^-$) [**A**, eqn. (3)]. This product is proven to have only one phosphine by the carbene proton doublet structure (16.8 ppm), as well as by the observation of free phosphine (by ^{31}P NMR). This product then evolves more slowly by transfer of two hydrogens from one *ortho*-methyl group of the aryloxide to the benzylidene carbon [**B**, eqn. (3)]. After purification on an alumina column, the product **B** clearly shows the following ^1H NMR signals: *one* aryl methyl signal, of intensity three, only *three* aryl ring chemical shifts, each of unit intensity, and a Ru=C*H*R singlet at 16.4 ppm (unit intensity). Curiously, this carbene proton signal of **B** shows no resolved multiplet structure, although unresolved broadening is evident. The formation of toluene is also observed, as is the *disappearance* of free PCy_3, in the conversion of **A** to **B**. The $^{13}C\{^1H\}$ NMR supports this assignment, showing six aromatic signals, one Ar*C*H_3 signal (16.1 ppm), diastereotopic *C*H_2 ring carbons for the PCy_3 ligands, and a broad signal at 277.7 ppm for Ru=*C*.

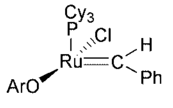


(3)

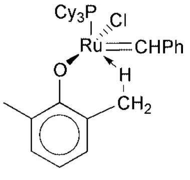
A crystal structure determination of **B** (Fig. 1)‡ confirms this remarkable transformation. The coordination geometry at Ru is the traditional square-pyramidal, but one anionic ligand is now covalently linked to the carbene ligand. As shown in **C** (distances in Å, angles in degrees), this unusual carbene/aryloxide ligand forms a planar five-membered chelate ring without substantial angular distortion at the carbene carbon. The



C



A



D

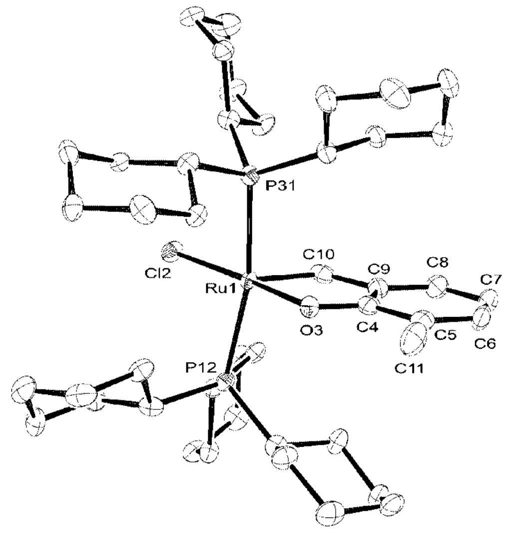


Fig. 1 ORTEP drawing of the nonhydrogen atoms of **B**. Selected distances (Å): Ru–C(10) 1.872(7), Ru–O(3) 2.082(4), Ru–Cl(2) 2.3910(17), Ru–P(12) 2.3947(19), Ru–P(31) 2.4005(19).

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† Electronic supplementary information (ESI) available: synthetic and spectroscopic data. Crystallographic data and selected bond lengths and angle for **B**. See http://www.rsc.org/suppdata/cc/b1/b102422c/

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five-membered ring interior angles sum to 539.9° (540° if planar), and the angles that suffer the greatest compression are that at aryloxide oxygen (111.8° is small for M–O–Aryl) and at Ru (compare C=Ru–O of 80.9° to C=Ru–Cl of 107.8°). There are no agostic interactions between the cyclohexyl hydrogens and the open coordination site *trans* to the carbene (shortest Ru–C 3.3 Å).

The accumulated empirical evidence[1] shows that the magnitude of the $^3J_{PH}$ value is dependent on the dihedral angle P–Ru=C–H, and thus the orientation of the carbene plane with respect to the P–Ru line can be estimated. In intermediate **A**, $^3J_{PH}$ is large enough to be readily resolved (6 Hz), consistent with calculation and experiment, which give a dihedral angle of *ca.* 0°. In **B**, where no $^3J_{PH}$ is resolved, the carbene hydrogen has a dihedral angle of 90°, consistent with earlier reports that $^3J_{PH}$ in this conformation is near zero.[1]

Numerous recent developments in olefin metathesis chemistry have been directed to appending a good leaving group to reduce the L : Ru ratio in the molecule to 1 : 1, or to attach the molecule to a polymer to facilitate separation of catalyst from product.[4] What the present report offers is the potential for more permanent (*i.e.* anion-tethered) attachment of the *initial* carbene to the molecule, which contrasts to attachment *via* a pendant neutral donor (olefin[5] or ether[6]).

The *mechanism* of the double hydrogen transfer that converts a methyl to a carbene in eqn. (3) is not yet established. However, the precedent[7] that 14-electron Ru^{II} recruits agostic interactions from sterically accessible C–H hydrogens makes **D** a likely starting point on this transformation. The driving *force* for this reaction appears to be steric in origin, since only *one* ArO$^-$ replaces chloride in the initial step of eqn. (3) and since the sterically expelled phosphine recoordinates when the bulky aryloxide and the benzylidene ligands are combined compactly into a single ligand incorporating both RO$^-$ and carbene functionalities. Toluene elimination also provides an entropic assist worth *ca.* 8 kcal mol^{-1} at 300 K.[8] The different behavior shown by tertiary alkoxides or phenoxide and by 2,6-dimethylphenoxide is certainly due to the reactivity of benzylic hydrogens.

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Notes and references

‡ *Crystal data* for $C_{47}H_{80}ClOP_2Ru$ **B**: M = 859.62, triclinic, space group $P\bar{1}$, brown/green crystals, a = 12.5352(16), b = 13.7485(18), c = 14.4562(20) Å, α = 73.591(4), β = 69.803(4), γ = 78.316(4)°, V = 2227.6(8) Å^3, Z = 2, T = −161 °C, D_C = 1.282 g cm^{-3}, μ = 5.17 cm^{-1}, $F(000)$ = 922. The final conventional R factor was 0.0503 for 6249 data and 465 parameters, $R_W(F)$ = 0.0440 and GOF = 1.21. CCDC 161342. See http://www.rsc.org/suppdata/cc/b1/b102422c/ for crystallographic data in CIF or other electronic format.

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