

Rhodium-Based Production of Aromatics

ONGOING WORK IN THE LABORATORY OF OUR RHODIUM BICENTENARY COMPETITION WINNER

We have been working towards creating new routes to arene compounds by looking at CH activation chemistry. An initial step towards this goal has now been published as a *Journal of the American Chemical Society* communication (1). The results have provided us with material for a full paper on this topic and a related reaction now published in *Chemical Communications* (2).

In initial work we looked for the cyclometallation-induced formation of M–C bonds to sp^2 carbons of aryl and vinyl groups. These were successfully achieved for a whole range of substrates. However, the reaction was only successful with iridium, not rhodium. Nevertheless rhodium is tried each time and it is likely that we will get a similar rhodium-induced reaction in the future.

The reaction shown below produces cyclometallated species for a series of substrates such as enones and aryl ketones. Attempts to insert $CH_2=CHR$ species (such as the usually particularly reactive $CH_2=CHSi(OEt)_3$) were unsuccessful, so alkynes were tried. The reaction with alkynes was remarkable, giving a double alkyne to vinylidene rearrangement, followed by an insertion into M–H to give a vinyl, followed by a second alkyne to vinylidene rearrangement and a second insertion. The resulting butadienyl proved to have a ‘ π -agostic’ structure with M...C bond lengths much longer than those of single bonds (2.5 Å was typical). No subsequent treatment, however, has so far given the required coupling.

Deuterium labelling showed that the $RC\equiv CD$ deuterium 1,2-migrates selectively to provide $RDC=C$ in the vinylidene. This occurs without

oxidative addition because that would lead to a fluxional 7-coordinate $M(H)(D)$ species or more likely to a 6-coordinate $M(H-D)$ species. Both processes are excluded because they would scramble the isotope. The 1,2-migration reaction is strictly intramolecular within each $RC\equiv CD$ group, because with $RC\equiv CD$ and $R'C\equiv CH$ both present in the same reaction mixture (crossover reaction conditions), $RDC=C$ and $R'HC=C$ are the only resulting vinylidenes.

In future work, we hope to persuade rhodium to carry out related coupling reactions, perhaps by moving to the *N*-heterocyclic carbene ligand system (L') that has been so successful in alkene metathesis and palladium coupling. Indeed we already have the required $[(cod)RhL'Cl]$ species in hand for trials.

Other work (3) includes the synthesis of rhodium and iridium(I) complexes of *N*-heterocyclic carbenes by transmetalation from the corresponding silver(I) complexes; and the involvement of rhodium in an unusual norbornadiene to nortricycyl rearrangement.

References

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- 3 A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree *Organometallics*, 2003, DOI: 10.1021/om021029+

R. H. CRABTREE

Professor Robert H. Crabtree of Yale University, U.S.A., won the Johnson Matthey Rhodium Bicentenary Competition in 2002. The competition celebrates the 200th anniversary of the discovery of rhodium in 1804 by William Hyde Wollaston.

