Alkyl dehydrogenation in a Rh(i) complex via an isolated agostic intermediate

CHAPLIN, Adrian B., et al.

Abstract
A well-characterised 14-electron rhodium phosphine complex, [Rh(PiPr3)3][BArF4], which contains a β-CH agostic interaction, is observed to undergo spontaneous dehydrogenation to afford [Rh(PiPr3)2(PiPr2(C3H5))[BArF4]; calculations on a model system show that while C–H activation is equally accessible from the β-CH agostic species or an alternative γ-CH agostic isomer, subsequent β-H-transfer can only be achieved along pathways originating from the β-CH agostic form.

Reference
CHAPLIN, Adrian B., et al. Alkyl dehydrogenation in a Rh(i) complex via an isolated agostic intermediate. Chemical Communications, 2009, no. 2, p. 244-246

DOI: 10.1039/b816739g
Alkyl dehydrogenation in a Rh(I) complex via an isolated agostic intermediate†

Adrian B. Chaplin,Amalia I. Poblador-Bahamonde,Hazel A. Sparkes,Judith A. K. Howard,* Stuart A. Macgregor and Andrew S. Weller*a

Received (in Cambridge, UK) 24th September 2008, Accepted 31st October 2008
First published as an Advance Article on the web 19th November 2008
DOI: 10.1039/b816739g

A well-characterised 14-electron rhodium phosphine complex, [Rh(PiPr3)3][BARF4], which contains a β-CH agostic interaction, is observed to undergo spontaneous dehydrogenation to afford [Rh(PiPr3)2](PiPr3(C6H4)][BARF4]; calculations on a model system show that while C–H activation is equally accessible from the β-CH agostic species or an alternative γ-CH agostic isomer, subsequent β-H-transfer can only be achieved along pathways originating from the β-CH agostic form.

Transition metal-mediated alkane dehydrogenation is an important methodology for the selective transformation of alkanes. The putative intermediates for such reactions are alkane sigma complexes, which then undergo successive C–H activation and β-H-elimination. For the intramolecular dehydrogenation of alkyl groups it is accepted that C–H activation is usually preceded by a M·−HC agostic interaction (Scheme 1), however, well-defined examples of such complexes that subsequently undergo alkyl dehydrogenation are, to the best of our knowledge, unknown. Indeed, as far as we are aware, there is only one example of a complex where an agostic interaction undergoes C–H activation for which both the agostic and C–H activated product have been crystallographically characterised, and only a few examples where these tautomers are directly observed in solution.

We report here the isolation of a “T-shaped” 14-electron rhodium phosphine complex, [Rh(PPiPr3)3][BARF4] (1, ArF = 3,5-C6H4(CF3)2], that contains an unusual β-CH agostic interaction from the isopropyl phosphine ligand and undergoes intramolecular dehydrogenation. We also demonstrate, using computational methods, that the β-agostic interaction in 1 is important in defining the ultimate product of the reaction: dehydrogenation (C–H activation/β-elimination) versus metallacyclobutane formation (C–H activation only) which arises from an alternative γ-agostic interaction.

Reaction of [Rh(BINOR-S)(PiPr3)][BARF4] (2) with 2 equivalents of PiPr3 in C6H6 solution results in reductive elimination of BINOR-S and the formation of I in quantitative yield by NMR spectroscopy. Alternatively, I can be formed by the addition of PiPr3 to [Rh(C6H6F)3(PiPr3)][BARF4] (3) in C6H6 solution. Complex I is highly fluxional in solution at room temperature, displaying one phosphine environment by 31P NMR spectroscopy which shows coupling to 103Rh (δ 47.1, J RhP = 173 Hz). This fluxional behaviour is not frozen out, even upon cooling to 200 K, where the 31P{1H} NMR spectrum shows a featureless hydride region at all temperatures. In the solid state (Fig. 1) the structure displays a distorted square planar geometry in which a β-CH agostic interaction from an isopropyl group occupies the fourth coordination site, showing a relatively short Rh1–C1a distance [2.494(12) Å, located Rh1–H1a 1.91(9) Å] and an acute Rh1–P1–C1a angle.

Scheme 2

Fig. 1 Complex I; ellipsoids are depicted at the 50% probability level. The anion, most H atoms and minor component (4) are omitted for clarity. Key bond lengths (Å) and angles (°): Rh1–P1, 2.249(2); Rh1–P2, 2.395(2); Rh1–P3, 2.268(2); P1–Rh1–P2, 149.91(6); P1–Rh1–P3, 104.24(6); P2–Rh1–P3, 105.47(6); Rh1–C1a, 2.494(12); Rh1–H1a, 1.91(9); Rh1–P1–C1a, 73.8(4); C1a–C2a, 1.540(13); C1a–C3a, 1.540(13).

† Electronic supplementary information (ESI) available: Full experimental, characterisation and crystallographic details. Energies and Cartesian coordinates of all computed species; full reference for Gaussian 03. See DOI: 10.1039/b816739g/
isolated yield). Addition of H₂ to reversible. In CH₂Cl₂ or THF dehydrogenation of did not observe a clear C–H stretch in the IR spectrum that
1
4
versus
1
5
1/2
B
1.5 h),
Fig. 3
244–246
Chem. Commun., 2009, 244–246
this journal is © the Royal Society of Chemistry 2009
View Article Online
For metallocyclophosphabutane 6γ, we were unable to locate a TS for β-H-transfer to Rh. Scans based on the Rh-βH distance led to a steady increase in energy to over 30 kcal mol⁻¹ above 6γ. TS structures were located but these were shown to be for a Rh-assisted 1,2 H shift resulting in isomerisation to 6β (E = +31.1 kcal mol⁻¹, see ESI†). For 6β, however, a number of low energy β-H-transfer pathways were characterised, two of which are shown in Fig. 4. In order to complete the dehydrogenation process a cis-dihydride must be formed upon β-H-transfer so that H₂ reductive elimination can be accessed. In Pathway 1 this is achieved by initial β-H-transfer from 6β to form trans-dihydride 7trans, (E = +16.7 kcal mol⁻¹) followed by isomerisation to 7cis. The cis-trans isomerisation TS is the highest point along Pathway 1 (E = +25.2 kcal mol⁻¹) and corresponds to a barrier of 19.6 kcal mol⁻¹ relative to 1β. Alternatively, isomerisation of square-pyramidal 6β (where H is apical) occurs prior to β-H-transfer. The lowest energy mechanism of this type, Pathway 2, proceeds via a PH₃ apical isomer (6β(PH₃), E = +8.9 kcal mol⁻¹) from which β-H-transfer leads to 7cis. The isomerisation TS is the highest point along Pathway 2 (E = +14.3 kcal mol⁻¹) equating to a barrier of only 8.7 kcal mol⁻¹ relative to 1β. A second isomerisation / β-H-transfer route via isomer 6β(PH₃) (with [PH₃] apical) was also defined, Pathway 3. This was energetically intermediated with regard to Pathways 1 and 2 with an overall barrier of 13.4 kcal mol⁻¹, the highest TS being for β-H-transfer at +19.0 kcal mol⁻¹. Full details are given in the ESI†.

To complete the dehydrogenation, reductive elimination of H₂ from 7ciss is required and a TS for this process was located at +15.1 kcal mol⁻¹. For Pathway 2 this is the highest point in the overall process, although for Pathways 1 and 3 this occurs earlier in the profile (either cis-trans isomerisation or β-H-transfer, respectively). The model products, 4′ + H₂, have a computed relative energy of +9.0 kcal mol⁻¹, although the entropy associated with H₂ dissociation means that the free energy of the products is only +2.9 kcal mol⁻¹ above 1β, consistent with the reversibility of the dehydrogenation.

In conclusion we report a “14-electron” T-shaped Rh(ı) complex with a supporting β-agostic interaction from an isopropyl phosphine that spontaneously undergoes dehydrogenation (C–H activation followed by β-H-transfer). Calculations show that while both γ- and β-agostic interactions can undergo reversible C–H activation to give metallacycle intermediates, subsequent H-transfer is only accessible when originating from the β-agostic form. Therefore only the product of C–H activation at the β-position can lead to productive dehydrogenation.

Notes and references

† Crystallographic data: 1: C₉₅H₆₂BF₃₂P,Rh, M = 1446.42, monoclinic, P2₁/n (Z = 4), a = 13.1039(6) A, b = 28.652(1) A, c = 17.9635(6) A, α = 90, β = 106.228(1), V = 6875.6(5) Å³, T = 120(2) K, 13255 unique reflections [R(int) = 0.0395]. Final R₁ = 0.0545 [I > 2σ(I)]. 2: C₉₅H₆₂BF₃₂P,Rh, M = 1444.80, monoclinic, P2₁ (Z = 6), a = 19.3219(2) A, b = 17.7922(2) A, c = 29.0443(5) Å, β = 96.6182(4). V = 9883.2(2) Å³, T = 150(2) K, 31319 unique reflections [R(int) = 0.0396]. Final R₁ = 0.0506 [I > 2σ(I)].


8 (a) D. L. Thor, Organometallics, 1998, 17, 348; (b) N. Thiraputh, D. Amorosó, A. Bell and J. D. Protasiewicz, Organometallics, 2005, 24, 4099.


17 Calculations employed Gaussian 03 with the BP86 functional. Rh and P centres were described with Stuttgart RECPs and basis sets with polarisation on P. 6-31G** basis sets were used for C and H atoms. All energies include a correction for zero-point energies. See ESI† for full details.