Cross-metathesis between ethane and toluene catalyzed by [(≡SiO)₂TaH]: the first example of a cross-metathesis reaction between an alkane and an aromatic†

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The silica-supported tantalum hydride [(≡SiO)₂TaH] 1 catalyzes at moderate temperature (150–250 °C) the cross-metathesis reaction between toluene and ethane, to form mainly ethylbenzene and xylenes.

We have previously reported that the silica-supported tantalum hydride[1] [(≡SiO)₂TaH] **1** catalyzes a new reaction of alkane metathesis which transforms any acyclic alkane into a mixture of higher and lower homologues (eqn. (1)).[2]

$$2\, C_nH_{2n+2} \rightarrow C_{n+i}H_{2(n+i)+2} + C_{n-i}H_{2(n-i)+2} \qquad (1)$$
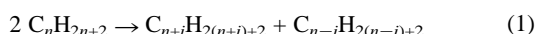
where $i = 1, 2,\ldots n - 1$, but with $i = 1$ generally favoured.

This reaction proceeds *via* both cleavage and formation of the (sp³)C–(sp³)C bonds of any acyclic paraffin. Herein we report the cross metathesis reaction between ethane and toluene which leads to the simultaneous formation of ethylbenzene and xylenes (eqn.(2)).
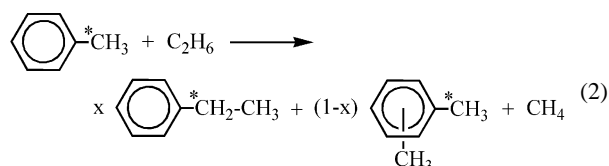
In the case of ethylbenzene, the reaction proceeds *via* a cross σ-bond metathesis between the (sp³)C–H bond of the aromatic methyl and the (sp³)C–(sp³)C bond of ethane; in the case of xylenes, it occurs *via* a cross σ-bond metathesis between the (sp²)C–H bonds of the aromatic ring and the (sp³)C–(sp³)C of ethane. To our knowledge, although σ-bond metathesis is known between molecular lutetium,[3] thorium[4] or scandium[5] hydrides, alkyls or aryls and alkanes or aromatics, it is the first example of such catalytic cross metathesis reactions.

The following experiment illustrates these two new catalytic reactions. When a (3.7/97.6) molar mixture of toluene and ethane was heated in the presence of **1** (50 mg; 5 wt% Ta), at 250 °C, under atmospheric pressure in a batch reactor (300 ml), besides methane, propane and butanes arising from the self-metathesis of ethane,[2] ethylbenzene but also the various xylenes were produced.‡ Ethylbenzene and xylenes can arise from the cross-metathesis between toluene and ethane (eqn. (2)) but also from the self metathesis of toluene (eqn. (3)) although they have not been evidenced during blank experiments
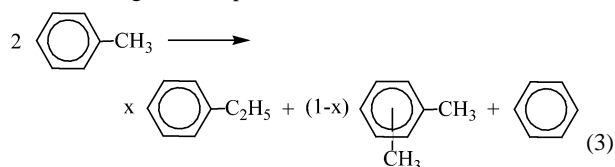

In order to further discriminate between the two hypotheses (eqn. (2) or eqn. (3)), 100% α-¹³C enriched toluene was allowed to react with ethane at 250 °C, in the presence of **1**. Under these conditions, ethylbenzene was obtained, mainly ¹³C-mono-labeled in the α-position (92%), while xylenes were 98% ¹³C-mono-labeled.[6] Thus, ethylbenzene and xylenes turn out to form mainly through the cross-metathesis process depicted in eqn. (2).

Regarding the possible mechanism, both reactions begin by a C–H bond activation with liberation of molecular hydrogen. This activation step involves a competition between the two reagents, *e.g.* ethane and toluene, as well as between the two types of CH bonds in the toluene molecule, *e.g.* in the methyl group or on the aromatic ring (Scheme 1).

This leads to a mixture of tantalum–ethyl [(≡SiO)₂Ta-C₂H₅], –benzyl [(≡SiO)₂Ta-CH₂C₆H₅] or –methylphenyl [(≡SiO)₂Ta–C₆H₄CH₃] complexes which have been effectively identified by ¹³C CP MAS NMR.[7] In a second step, these complexes would then undergo mainly the reaction with a molecule of ethane to liberate propane, ethylbenzene or xylenes respectively and form a tantalum–methyl intermediate; during this step, the kinetic of the reaction with ethane of the three intermediates will govern the final selectivity of the different products. The last step common to all cycles is the displacement of the methyl group from tantalum by either an ethane or a toluene molecule to regenerate the key intermediates: the tantalum–ethyl, –benzyl or –methylphenyl complexes.

This system was further investigated in a continuous flow reactor. When a (3.7/97.6) mixture of toluene and ethane (flow rate of 3 ml min⁻¹) was passed over a catalytic bed of [(≡SiO)₂TaH] **1** (420 mg; 4.6 wt% Ta) at 250 °C, methane, propane and butanes
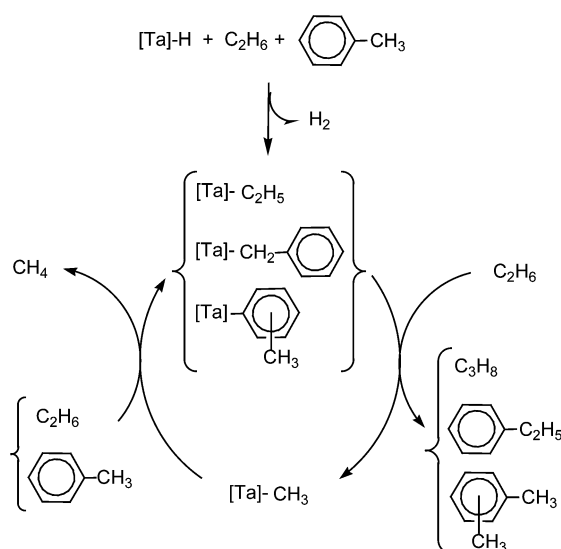
Scheme 1 Reaction scheme of the cross-metathesis between toluene and ethane.

† Electronic supplementary information (ESI) available: experimental details; Fig. 1: Effect of partial pressures on the TON of toluene and ethane. See http://www.rsc.org/suppdata/cc/b4/b403166k/

Table 1 Number of turnovers (TON) of ethane and toluene, selectivities of products obtained after 60 h during the cross-metathesis reaction between toluene and ethane catalysed by ($\equiv$SiO)$_2$TaH (420 mg) at 250 °C, under various conditions of pressure in a dynamic reactor (flow rate: 3 ml min^{-1})

| | Partial pressures/kPa | | Nb of turnovers[a] | | Selectivity (%) | | | | | | |
Entry	Ethane	Toluene	Ethane	Toluene	CH$_4$	C$_3$H$_8$	C$_4$H$_{10}$	PhH	PhEt	Xyl[b]	PhPr
1	97.6	3.7	21.8	2.6	38.5	37	2.7	0.5	15	2.5	3.6
2[c]	"	4.25	16.8	6.9	45	16.4	0.5	7.7	16.3	0.6	0.2[d]
3	5×10^2	3.7	48	3.2	45	44	4.4	0	4.8	0.5	1.2
4	10^3	"	177	2.97	51	41.5	4.6	0.04	1.6	0.4	0.3
5	25×10^2	"	198	1.22	53	41	4.4	0.04	0.5	0.13	0.02
6	10^3	41.3	53	4.9	43	42.8	4.7	0.3	6.7	0.8	1.25
7	25×10^2	71.9	85	8.25	44.5	43	3.7	0.55	6.8	0.7	1.2

(PhH = benzene, PhEt = ethylbenzene; Xyl. = xylenes; PhPr = propylbenzenes);[a] Mol/mol of Ta. [b] Generally p-Xyl $\gg$ m-Xyl > o-Xyl. [c] Reaction performed in the presence of 10% vol.of H$_2$ in ethane. [d] Saturated products as cyclohexane (2.5%) and methylcyclohexane (10.5%) were also present.

were again produced as well as ethylbenzene and xylenes but also *n*- and *iso*-propylbenzenes, resulting reasonably from a double methyl addition to the CH$_3$ group of toluene (Table 1, entry 1).[8] The conversions of ethane and toluene decreased during the first period of time on stream to reach after 60 h in a pseudo steady state, values of 0.05 and 0.25% respectively. According to the number of turnovers (TON), the reaction proves slightly catalytic affording after 100 h a production of 1.7 mol of ethylbenzene per mol of Ta.

When 10% of H$_2$ was introduced in the gas flow under 101.3 kPa at 250 °C (Table 1, entry 2), the deactivation was reduced suggesting that this process may involve the dehydrogenation of some surface species towards unsaturated ones.[9] Indeed at the steady state, the turnover frequencies (TOF) of ethane {0.13 h^{-1} (with H$_2$) instead of 0.049 h^{-1} (without H$_2$)} and toluene {0.07 h^{-1} (with H$_2$) instead of 0.013 h^{-1} (without H$_2$} were improved. Therefore, in the presence of H$_2$, a better TON of toluene and a better production of ethylbenzene (3.3 mol per mol of Ta) were obtained.[10] However, a certain amount of methylcyclohexane (10.5%), benzene (7.7%) and cyclohexane (2.5%) was also observed, resulting from hydrogenation and/or hydrogenolysis processes.

When for a given pressure of toluene (3.7 kPa), the pressure of ethane was progressively increased from 97.6 kPa to 2.5×10^3 kPa (Table 1, entries 1, 3, 4, 5), self-metathesis of ethane was favoured at the expense of cross-metathesis and the deactivation process was slowed down; indeed the resulting TON of ethane at 60 h, increased while that of toluene decreased as well as all the selectivities of aromatic compounds. However, the production of ethylbenzene increased slightly at 10^3 kPa (2.9 mol per mol of Ta) compared to atmospheric pressure (1.7 mol per mol of Ta). These data are consistent with the relative dependence of the surface species concentration on the partial pressures of both reagents as depicted in Scheme 1. As the pressure of ethane increases, formation of [($\equiv$SiO)$_2$Ta–CH$_2$CH$_3$] is favoured at the expense of [($\equiv$SiO)$_2$Ta–CH$_2$C$_6$H$_5$] and [($\equiv$SiO)$_2$Ta–C$_6$H$_4$CH$_3$] and thereby self-metathesis of ethane is favoured at the expense of cross-metathesis. Conversely, when the partial pressure of toluene was increased (Table 1, entries 6 and 7), the respective concentrations of [($\equiv$SiO)$_2$Ta–CH$_2$C$_6$H$_5$] and [($\equiv$SiO)$_2$Ta–C$_6$H$_4$CH$_3$] were increased. The TON of toluene increased and the self-metathesis of ethane decreased accordingly. Thus a higher yield of ethylbenzene (6 mol per mol of Ta) was obtained after 100 h under the conditions of entry 7.

In conclusion, we have shown the possibility of performing a cross-metathesis reaction between toluene and ethane catalyzed by a tantalum hydride supported on silica [($\equiv$SiO)$_2$TaH] **1** which is the first example of such a reaction; it leads to ethylbenzene and xylenes and constitutes a new example of a slightly catalytic reaction in the difficult field of C–C bond formation from alkanes where examples remain rare.[11] Moreover, the formation of xylenes

represents the first case of a metathesis reaction between an aromatic (sp^2)C–H and a (sp^3)C–(sp^3)C bond. Finally, although its performance remains modest, this reaction can be compared with the Friedel–Crafts alkylation of benzene with ethylene[12] which is currently used to manufacture ethylbenzene.

Notes and references

‡ *Analysis:* The reaction products were analyzed by GC (or GC/MS) on a Al$_2$O$_3$/KCl column: 50 m × 0.32 mm with a FID detector.

1 V. Vidal, A. Théolier, J. Thivolle-Cazat, J. M. Basset and J. Corker, *J. Am. Chem. Soc.*, 1996, **118**, 4595–4602.

2 (*a*) V. Vidal, A. Théolier, J. Thivolle-Cazat and J. M. Basset, *Science*, 1997, **276**, 99–102; (*b*) CNRS, French Patent No. 96 09033 *Chem. Abstr.* 1998, **128**, 129483a; (*c*) O. Maury, L. Lefort, V. Vidal, J. Thivolle-Cazat and J. M. Basset, *Angew. Chem. Int. Ed.*, 1999, **38**, 1952–5.

3 (*a*) P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491–3; (*b*) P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 514.

4 (*a*) C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 2214–6; (*b*) C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 425–37.

5 (*a*) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 203–19; (*b*) R. H. Crabtree, *Chem. Rev.*, 1995, **95**, 987.

6 The mass spectra gave the molecular peak for both products (*m/z* = 107) and indicated the first loss of a non-labeled CH$_3$ fragment (*m/z* = 15) for ethylbenzene instead of a mixture of labeled and non-labeled methyls for xylenes.

7 The tantalum–benzyl and –methylphenyl complexes have been evidenced by ^{13}C CP MAS NMR (300 MHz): [($\equiv$SiO)$_2$Ta–CH$_2$C$_6$H$_5$]: δ 66 (–CH$_2$–), 129 (*o,m,p*-C$_6$H$_5$) and [($\equiv$SiO)$_2$Ta–C$_6$H$_4$CH$_3$]: δ 12 (*o*-CH$_3$), 20 (*m,p*-CH$_3$), 129 (–C$_6$H$_4$); after oxidation with dry air, they lead to the corresponding oxo-alkoxo complexes: [($\equiv$SiO)$_2$Ta(= O)–OCH$_2$C$_6$H$_5$]: δ 74 (–CH$_2$–), 128 (*o,m,p*-C$_6$H$_5$), 140 (*ipso*-C$_6$H$_5$) and [($\equiv$SiO)$_2$Ta(=O)–OC$_6$H$_4$CH$_3$]: δ 17.5 (–CH$_3$), 119 (*o*-C$_6$H$_4$), 129 (*m,p*-C$_6$H$_4$), 160 (*ipso*-C$_6$H$_4$).

8 Stoichiometric studies have shown that a methyl group was more easily transferred than higher alkyls: C. Copéret, O. Maury, J. Thivolle-Cazat and J. M. Basset, *Angew. Chem. Int. Ed.*, 2001, **40**, 2331–4.

9 In the case of classical alkane metathesis, the presence of carbyne species supposed to be less or non active, could be evidenced on the used catalyst; their formation could be limited by the presence of H$_2$.

10 BASF German Patent N° 10100485/WO 02053520.

11 (*a*) R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245; (*b*) B. Rybtchinski and D. Milstein, *Angew. Chem. Int. Ed.*, 1999, **38**, 871.

12 (*a*) G. A. Olah, *Friedel–Crafts and related reactions*, Interscience, New York, 1963–1965; (*b*) K. Weissermel and H. J. Arpe, *Industrial Organic Chemistry*, VCH, Weinheim, 1993, p. 333.