

Catalytic dehydroaromatization of *n*-alkanes by pincer-ligated iridium complexes

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Aromatic hydrocarbons are among the most important building blocks in the chemical industry. Benzene, toluene and xylenes are obtained from the high temperature thermolysis of alkanes. Higher alkylaromatics are generally derived from arene-olefin coupling, which gives branched products—that is, secondary alkyl arenes—with olefins higher than ethylene. The dehydrogenation of acyclic alkanes to give alkylaromatics can be achieved using heterogeneous catalysts at high temperatures, but with low yields and low selectivity. We present here the first catalytic conversion of *n*-alkanes to alkylaromatics using homogeneous or molecular catalysts—specifically ‘pincer’-ligated iridium complexes—and olefinic hydrogen acceptors. For example, the reaction of *n*-octane affords up to 86% yield of aromatic product, primarily *o*-xylene and secondarily ethylbenzene. In the case of *n*-decane and *n*-dodecane, the resulting alkylarenes are exclusively unbranched (that is, *n*-alkyl-substituted), with selectivity for the corresponding *o*-(*n*-alkyl)toluene.

Three of the ‘seven basic building blocks of the chemical industry’ are aromatic molecules—the so-called BTX family: benzene, toluene and xylene¹. These compounds are currently obtained by reforming petroleum feedstocks. As oil reserves diminish and the world’s fuel supply shifts from gasoline to diesel², aromatics will be in increasingly short supply. Higher alkyl benzenes are commercially produced on a scale of around 60 billion pounds a year by arene-olefin coupling^{3–8}. *n*-alkanes represent a potential feedstock that is economically attractive compared with both arenes and olefins, and will probably become more so with the increasing use of the Fischer-Tropsch process (reductive oligomerization of CO and H₂)^{9,10}.

The catalytic dehydroaromatization of higher *n*-alkanes (carbon number > 6) has been reported using a variety of heterogeneous catalysts including metals, metal oxides and zeolites at high temperatures (typically 500–700 °C). Such reactions generally give low yields of aromatics and substantial quantities of non-aromatic compounds with fewer than six carbons owing to ‘cracking’. The aromatics themselves generally consist of a complex mixture, including a significant fraction with carbon numbers lower than the alkane feedstock. Toluene—generally the member of the BTX triad in least demand—is frequently the most abundant product of such mixtures, presumably reflecting facile cleavage of the weak benzylic C–C bond^{11–23}.

The products of aromatic alkylation with linear olefins, although often referred to as ‘linear alkylbenzenes’, are not ‘linear’ in the usual sense; that is, they are not *n*-alkyl derivatives. The aryl group is a substituent at an internal position of an *n*-alkane chain (for example, the 2-position when 1-alkenes are used as the olefinic reagent in the absence of prior isomerization); in this sense these molecules are branched. To our knowledge there are no existing atom-efficient large-scale routes to *n*-alkyl arenes. Current routes use coupling methods that typically start with aryl halides, or Friedel-Crafts acylation and Clemenson reduction²⁴, although the development of methods for anti-Markovnikov alkylation of non-functionalized arenes is currently a goal under intense pursuit^{24–28}.

Functionalized products derived from *n*-alkyl arenes could have advantages over branched species, such as superior properties for micelle formation as well as greater thermal stability owing to the fact that the benzylic position is less substituted^{29,30}.

In the present work we describe the first examples of dehydroaromatization of acyclic alkanes using molecular transition metal-based catalysts. The catalysts operate under relatively mild conditions to give aromatics including *n*-alkyl arenes in the case of *n*-alkanes of eight or more carbons—a conversion that is unprecedented for higher *n*-alkanes. In contrast to heterogeneous systems, molecular (or single-site) catalysts afford opportunities for catalyst tuning to affect activity or selectivity through either empirical or mechanism-based approaches. The disadvantage of molecular catalysts is generally the problem of catalyst/product separation, but we have recently reported that catalysts of this type can be efficiently supported on solids such as alumina^{31,32}; this should mitigate separation problems.

Results and discussion

The use of pincer-ligated iridium catalysts for alkane dehydrogenation³³ has been extensively developed and studied since the initial report of transfer-dehydrogenation by Kaska and Jensen^{34–36}. It has been found that hydrogen acceptors are not necessarily required, although alkene yields are limited in the absence of acceptors³⁷. The substitution of phosphino-*t*-butyl groups by *i*-propyl groups has been reported to increase activity^{38,39}. In the course of investigating the dehydrogenation of *n*-alkanes catalysed by *i*-propylphosphino-substituted pincer complexes, we have unexpectedly observed the formation of small quantities of benzene (2.3% yield) from *n*-hexane when using norbornene as the acceptor⁴⁰. We now report a much more extensive and general investigation of *n*-alkane aromatization using pincer-iridium catalysts.

Attempts to achieve dehydroaromatization using the *t*-butyl-substituted catalyst precursors (^{*t*}BuPCP)IrH_{*n*} (*n* = 2, 4 or a mixture thereof) gave negligible yields of aromatic product. Initial

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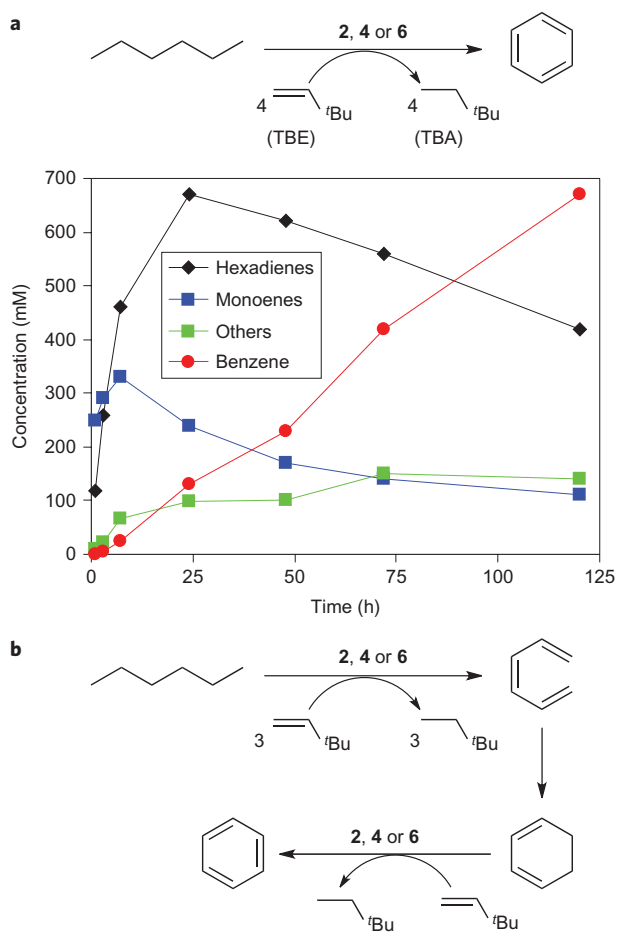


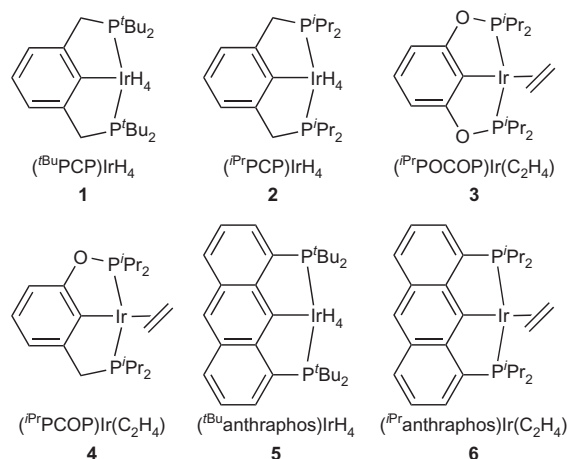
Figure 1 | Dehydroaromatization of *n*-hexane catalysed by iridium pincer complexes 2, 4 or 6. **a**, Overall reaction stoichiometry and products versus time for dehydroaromatization catalysed by 4. Conditions: [4] = 5 mM; [*n*-hexane] = 1.53 M; [TBE] = 6.13 M; 165 °C. See Supplementary Information for full data for product and reactant concentrations obtained with catalysts 2, 4 and 6. **b**, Proposed pathway for the dehydroaromatization.

attempts to catalyse dehydroaromatization using the isopropyl analogue ($i^{\text{Pr}}\text{PCP}$)IrH₄ ($i^{\text{Pr}}\text{PCP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-}[\text{CH}_2\text{P}(i\text{-C}_3\text{H}_7)_2]_2$) (2) gave results far superior to ($i^{\text{Bu}}\text{PCP}$)IrH₄. As this difference was presumably attributable to steric factors we investigated the corresponding POCOP ($i^{\text{Pr}}\text{POCOP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-}(\text{OP}(i\text{-Pr})_2)_2$) derivative. Note that computationally generated models (using density functional theory) reveal that POCOP complexes are sterically less demanding than the PCP analogues⁴¹. ($i^{\text{Pr}}\text{POCOP}$)Ir precursors (for example, ($i^{\text{Pr}}\text{POCOP}$)Ir($\eta^2\text{-C}_2\text{H}_4$)) were found to be less effective for dehydroaromatization than ($i^{\text{Pr}}\text{PCP}$)IrH₄. However, the ‘hybrid’ phosphine/phosphinite catalyst ($i^{\text{Pr}}\text{PCOP}$)Ir($\eta^2\text{-C}_2\text{H}_4$) (4) gave very good initial results and was used, along with ($i^{\text{Pr}}\text{PCP}$)IrH₄, throughout this investigation.

Haenel has reported that the ‘anthraphos’ catalyst ($i^{\text{Bu}}\text{anthraphos}$)IrH₄ is thermally more robust than the simple $i^{\text{Bu}}\text{PCP}$ derivative⁴². With this in mind we have also studied the ($i^{\text{Pr}}\text{anthraphos}$)Ir-derived catalyst⁴³ for dehydroaromatization. In this case the ethylene complex ($i^{\text{Pr}}\text{anthraphos}$)Ir($\eta^2\text{-C}_2\text{H}_4$) (6) was used as the catalyst precursor in analogy with our dehydrogenation studies using ($i^{\text{Bu}}\text{POCOP}$)Ir($\eta^2\text{-C}_2\text{H}_4$) and related (pincer)Ir($\eta^2\text{-C}_2\text{H}_4$) complexes.

The stoichiometry of *n*-alkane aromatization requires the loss of four equivalents of H₂. Accordingly, most of the experiments conducted in this study made use of four equivalents of an olefinic

hydrogen acceptor. Attempts to achieve dehydroaromatization with the same catalysts, but without any acceptor (by allowing H₂ to escape from a refluxing solution³⁷), have thus far been unsuccessful.



Aromatization of *n*-hexane. Heating solutions of *n*-hexane (1.53 M), *t*-butylethylene (TBE; 6.13 M) and catalyst 2, 4 or 6 (5 mM) at 165 °C initially resulted in the formation of acyclic C₆ olefins (hexenes and hexadienes) and commensurate quantities of hydrogenated TBE (2,2-dimethylbutane or ‘*t*-butylethane’, TBA). Continued heating resulted in the formation of benzene (Fig. 1a). After 120 h, catalyst 4 gave the highest yield of benzene, 670 mM (44%). No products lighter than C₆ were observed by gas chromatography (see Supplementary Information for full details).

We propose that the formation of benzene from *n*-hexane proceeds via extensive and reversible dehydrogenation and olefin isomerization (probably including both double bond migration and *cis*-*trans* isomerization) to give 1,3,5-*cis*-hexatriene. This triene undergoes a classic thermal electrocyclozation, with a first-order

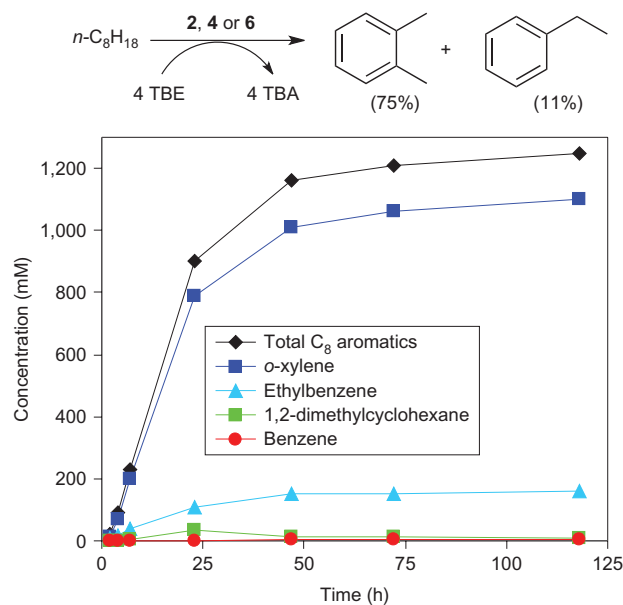


Figure 2 | Dehydroaromatization of *n*-octane catalysed by 2, 4 or 6 (with TBE as hydrogen-acceptor). Conditions: [4] = 5 mM; [*n*-octane] = 1.46 M; [TBE] = 5.84 M; 165 °C. Percentages in parentheses are yields based on *n*-octane obtained after 118 h with catalyst 4. See Supplementary Information for full data for product and reactant concentrations obtained with catalysts 2, 4 and 6 (2 mM and 5 mM catalyst concentrations).

rate constant of $2.5 \times 10^{-3} \text{ s}^{-1}$ at 165°C (ref. 44), followed by iridium-catalysed transfer-dehydrogenation (Fig. 1b). Very approximately, the maximum observed rate of benzene formation with catalysts **2** and **4** is approximately 10 mM h^{-1} . Assuming the cyclization rate of $2.5 \times 10^{-3} \text{ s}^{-1}$, a maximum steady-state concentration of the *cis*-hexatriene of approximately 1.1 mM is implied. This does not seem to be a particularly high value for a triene given that the steady-state concentration of monoenes and dienes is on the order of 0.2 M and 0.6 M , respectively.

Aromatization of higher *n*-alkanes. The reaction of *n*-octane (1.46 M) with four equivalents of TBE (5.84 M) catalysed by **2**, **4** or **6** (5 mM catalyst; 165°C) gave substantial conversion to C_8 mono-, di- and trienes⁴⁵ at early reaction times (within about 2 h; see Supplementary Information for full details). After 118 h, 95–99% of *n*-octane was consumed and the total yields of C_8 aromatics (*o*-xylene and ethylbenzene) were 48% and 86% with catalysts **2** and **4**, respectively (Fig. 2).

Yields of aromatic product are thus significantly higher than those obtained from *n*-hexane. All three catalysts are selective for formation of *o*-xylene over ethylbenzene. In particular, catalyst **4** gives a 7:1 ratio of *o*-xylene:ethylbenzene after 118 h, although at early reaction times the ratio is much lower. *m*-xylene, *p*-xylene and toluene were not observed in any of these catalytic reactions. Only small amounts of benzene (<2% of total aromatics, 0.5% in the case of catalyst **4**) were formed.

The dehydrogenation of *n*-octane to olefins is catalysed more rapidly by **2** than by **4**; however, catalyst **4** affords higher yields of aromatics. This may suggest that catalyst **4** is more active for isomerization, or that the dehydrogenation of 1,2-dimethylcyclohexadiene (the product of cyclization of 2,4,6-octatrienes) is faster with catalyst **4**. The latter scenario seems plausible as significantly higher formation of *cis*- and *trans*-dimethylcyclohexane (presumably resulting from the hydrogenation of dimethylcyclohexadiene) is observed during the reaction with catalyst **2** (see Supplementary Information for full details).

The use of 2 mM of catalyst **2** or **4** gave yields of *o*-xylene and ethylbenzene only slightly lower than those obtained with 5 mM

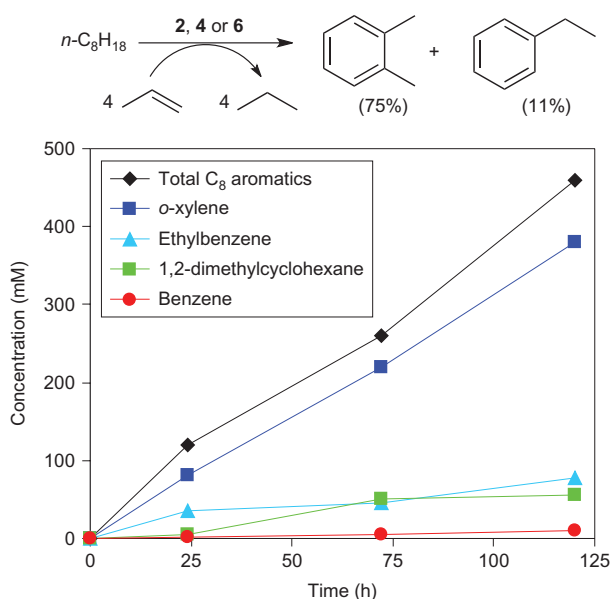


Figure 3 | Dehydroaromatization of *n*-octane catalysed by **2 with propene as hydrogen acceptor.** Conditions: [**2**] = 5 mM ; [*n*-octane] = 1.23 M ; in 0.39 ml mesitylene; $P_{\text{propene}} = 1 \text{ atm}$ (four equivalents in 60-ml reaction vessel); 165°C . See Supplementary Information for full data for product and reactant concentrations obtained with catalysts **2** and **4**.

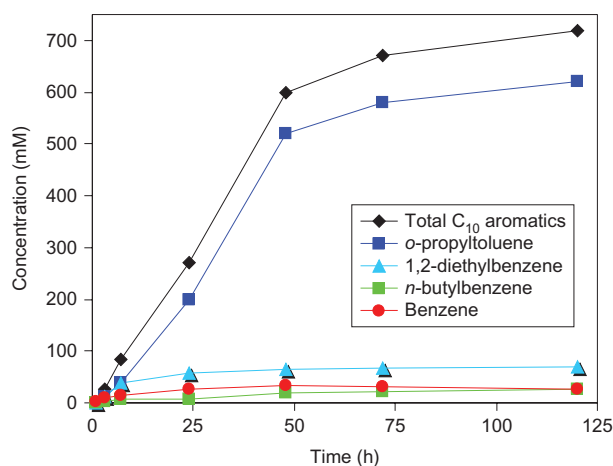
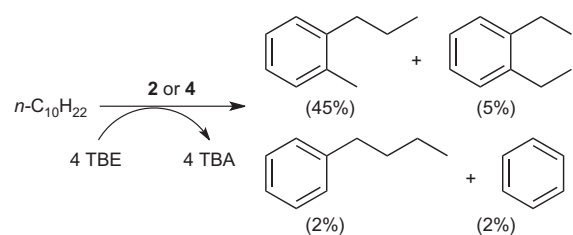


Figure 4 | Dehydroaromatization of *n*-decane catalysed by **4.** Conditions: [**4**] = 5 mM ; [*n*-decane] = 1.39 M ; [TBE] = 5.57 M ; 165°C . Percentages in parentheses are yields based on *n*-decane obtained after 120 h with catalyst **4**. See Supplementary Information for full data for product and reactant concentrations obtained with catalysts **2** and **4**.

of catalyst. The turnover numbers (moles of aromatic product per moles of catalyst) obtained for total aromatics were 330 and 580 after 118 h, for catalysts **2** and **4** respectively.

On the laboratory scale, TBE is a convenient hydrogen acceptor as it is a liquid and is resistant to isomerization. Practical large-scale applications would obviously require the use of acceptors that are low-cost and/or readily recyclable. In this context, it is worth noting that propene can be used as a hydrogen acceptor for the dehydroaromatization of *n*-octane (Fig. 3). After heating for 5 days under 1 atm propene at 165°C , 38% and 18% conversions to aromatics were obtained with catalysts **2** and **4**, respectively. Considering the very different conditions of these reactions, including the large differences in concentrations of *n*-octane and olefin acceptor in solution, and greatly different volumes of the reaction vessels (60 ml for propene versus 0.2 ml for TBE), as well as the presumably large differences in both the hydrogen-accepting and coordinating abilities of propene versus TBE, a close comparison of reaction yields is probably not meaningful.

The dehydroaromatization of *n*-decane with four equivalents of TBE resulted in surprisingly high selectivity for *o*-propyltoluene (Fig. 4). Using catalyst **2** (120 h at 165°C), 26% *o*-propyltoluene was obtained with approximately 2% each of *n*-butyl benzene and 1,2-diethylbenzene, totalling 30% aromatic products. With catalyst **4**, 52% conversion to total aromatics is obtained including 45% *o*-propyltoluene as the major dehydroaromatization product. With both catalysts, a small amount of benzene was produced—5% and 2% conversion with catalysts **2** and **4**, respectively.

The reaction of *n*-dodecane with four equivalents of TBE (Fig. 5a) yielded *o*-pentyltoluene as the major aromatic product. With catalysts **2** and **4**, 14% and 21% conversion to *o*-pentyltoluene was obtained after 120 h, respectively. In addition to *o*-pentyltoluene, *n*-hexylbenzene, 2-*n*-butylethylbenzene and 1,2-di-*n*-propylbenzene were also formed totalling 23% and 35% conversion to C_{12} -alkyl-aromatics with **2** and **4**, respectively. Alkenylaromatics

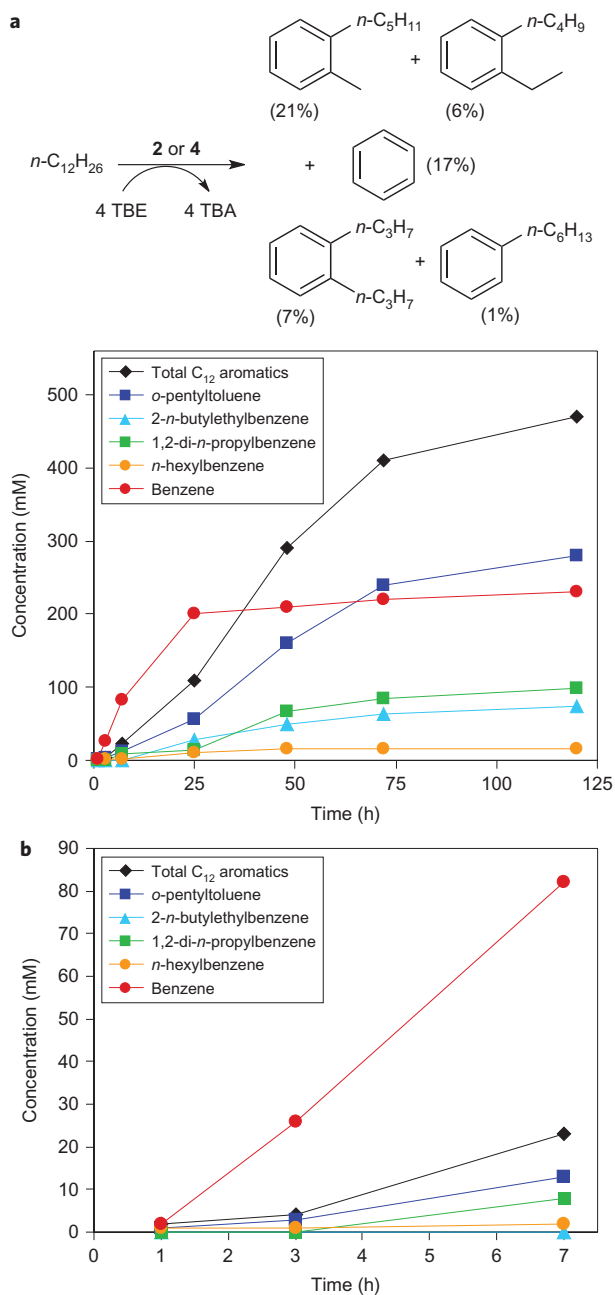


Figure 5 | Dehydroaromatization of *n*-dodecane. **a**, Conditions: [4] = 5 mM; [*n*-dodecane] = 1.33 M; [TBE] = 5.33 M; 165 °C. Percentages in parentheses are yields based on *n*-dodecane obtained after 120 h with catalyst 4. The graph shows aromatic product concentrations over the course of 120 h. **b**, Aromatic product concentrations over the first 7 h. See Supplementary Information for full data for product and reactant concentrations obtained with catalysts 2 and 4.

were not observed when four equivalents of TBE were used. However, when eight equivalents of TBE were used the major product obtained from the reaction catalysed by 4 (120 h at 165 °C) was *ortho*-(penta-di-1,3-enyl)toluene (187 mM) with a small amount of 1,5-dimethylnaphthalene (11 mM).

In addition to the C₁₂ aromatic compounds, significant conversion to benzene was obtained with catalysts 2 and 4—22% and 17% respectively after 120 h. At early reaction times (<24 to 48 h) benzene was the major aromatic product (Fig. 5b). We initially suspected that the benzene formation might result from a C–C cleavage reaction of *n*-hexylbenzene. However, when *n*-hexylbenzene was

used as the substrate for dehydrogenation under the same reaction conditions, benzene formation was not observed. Moreover, the use of *n*-hexylcyclohexane as a substrate gave only 22 mM benzene, much less than that obtained from *n*-dodecane. These observations suggest that C–C bond cleavage is not occurring after cyclization. Nevertheless it seems highly unlikely that C–C cleavage would occur selectively at the C6–C7 bond prior to cyclization. Therefore we suspect that the C–C bond cleavage occurs synchronously with formation of a six-membered ring; however any detailed mechanistic proposal would be highly speculative at this point. The mechanism of this very surprising reaction is currently under investigation.

Summary

The dehydroaromatization of *n*-alkanes has been achieved using pincer-ligated iridium catalysts with hydrogen acceptors at relatively low temperatures. This use of molecular or solution-phase catalysts for the aromatization of acyclic olefins is unprecedented. The resulting selectivity for the formation of arenes with the same carbon number as the *n*-alkane reactant is very high for *n*-hexane and *n*-octane. For *n*-decane, the aromatic products are predominantly C₁₀ but significant quantities of benzene are also formed (up to around 15% of total aromatics at high overall conversion, with much higher relative amounts at low conversion). In the reaction of *n*-dodecane, benzene is the major arene observed at low conversion whereas at high conversion the concentrations of benzene and total C₁₂ arenes are comparable. For the three C_{*n*} *n*-alkanes studied with *n* > 6, the aromatic products with C_{*n*} conserved are either the corresponding *n*-alkylbenzene or an *ortho*-substituted dialkylbenzene, consistent with no skeletal isomerization of the linear carbon chain during reaction. In particular, in all three cases the major aromatic product with C_{*n*} conserved is the corresponding *ortho*-alkyltoluene (alkyl = methyl, *n*-propyl or *n*-pentyl for C₈, C₁₀ and C₁₂ respectively).

The carbon-number selectivity (affording exclusively benzene and products with the carbon number of the reactant) has not been observed with previously reported (heterogeneous) dehydroaromatization systems. The selectivity for production of *n*-alkyltoluenes is of particular interest in view of the current lack of industrial methods for the production of *n*-alkylarenes.

Methods

All alkanes, mesitylene, and *para*-xylene were distilled under vacuum from Na/K alloy after several freeze-pump-thaw cycles and stored in an argon-atmosphere glove box. (^{Ir}PCP)IrH₄ (2) was synthesized in analogy with the procedure reported for the *para*-methoxy derivative (*p*-MeO-^{Ir}PCP)IrH₄ (ref. 40). (^{Ir}anthraphos)Ir(H)Cl was synthesized as previously reported by Grubbs and co-workers⁴³. The synthesis of (^{Ir}PCOP)Ir(η²-C₂H₄) is given in the Supplementary Information. Authentic samples of 2,4,6-octatriene⁴⁵, *o*-pentyltoluene⁴⁶ and di-*n*-propylbenzene⁴⁶ were prepared according to literature procedures. Gas chromatography-mass spectrometry (GC-MS) measurements were performed with a Varian 3900 Saturn 2100T instrument fitted with a capillary column (25 m × 0.2 mm inner diameter × 0.5 μm film thickness). Details of the gas chromatography analyses are given in the Supplementary Information.

Representative procedure for dehydroaromatization of *n*-alkanes using *tert*-butylethylene (TBE) as the H₂ acceptor. In an argon-filled glovebox, (^{Ir}PCP)IrH₄ (2.7 mg, 0.005 mmol) or (^{Ir}PCOP)Ir(η²-C₂H₄) (2.8 mg, 0.005 mmol) was dissolved in *n*-alkane (for example, hexane: 0.2 ml, 1.53 mmol); TBE (four equivalents with respect to *n*-hexane, 0.79 ml, 6.13 mmol) and mesitylene (0.01 ml, internal standard) were then added to the solution. The total solution (*n*-alkane, TBE and mesitylene) volume was 1.0 ml. Aliquots of this solution (0.1 ml each) were transferred to multiple 5 mm glass tubes. The contents were cooled under liquid nitrogen and then sealed under vacuum. These sealed tubes were heated (in parallel) in a preheated oven at 165 °C. At regular intervals, a tube was brought to room temperature and the sample was analysed by gas chromatography in comparison with authentic products. The assignments of the major products were confirmed with GC-MS.

Representative procedure for dehydroaromatization of *n*-alkanes using propylene as the H₂ acceptor. In an argon-filled glovebox, (^{Ir}PCP)IrH₄ (2.7 mg, 0.005 mmol) or (^{Ir}PCOP)Ir(η²-C₂H₄) (2.8 mg, 0.005 mmol) was dissolved in

n-octane (0.1 ml, 0.615 mmol) and mesitylene (0.39 ml, 6.47 mmol). *p*-xylene (0.01 ml, internal standard) was added. This solution (0.5 ml) was then transferred to a Schlenk flask (approximately 60 ml total volume) containing a micro stir bar fitted with a Kontes valve and an o-ring joint. The contents were cooled under liquid nitrogen and the solution was degassed via freeze-pump-thaw cycles and then brought to room temperature and charged with propylene (800 torr). The flask was then immersed in an oil bath maintained at 165 °C while the solution was stirred. After heating for 24 h, the flask was removed from the oil bath and brought to room temperature. The solution was then cooled in liquid nitrogen and the flask was evacuated and transferred to the glove box. The reaction mixture was analysed by gas chromatography. Fresh propylene was charged into the flask as above. The cycle was repeated until there was no significant change in the concentration of the products (as determined by gas chromatography).

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Author contributions

R.A., B.P., M.F., W.S., M.B. and A.S.G. conceived and designed the experiments; R.A., B.P., M.F. and C.S. performed the experiments; R.A., B.P., M.F., C.S., M.B. and A.S.G. co-wrote the paper.

Additional information

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