Homogeneous catalytic transfer dehydrogenation of alkanes with a group 10 metal center†

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Unambiguous catalytic homogeneous alkane transfer dehydrogenation was observed with a group 10 metal complex catalyst, LPt^{II}(*cyclo*-C_6H_{10})H, supported by a lipophilic dimethyl-di(4-*tert*-butyl-2-pyridyl)borate anionic ligand and *tert*-butylethene as the sacrificial hydrogen acceptor.

The alkane dehydrogenation to olefins is a viable CH bond functionalization strategy.[1–8] In particular, the well-defined homogeneous group 9,[2–7] group 7[7,8] and group 6[7] organometallic species have proven to be active in the catalytic transfer dehydrogenation (eqn (1))[2–4,8] and acceptorless dehydrogenation of alkanes (eqn (2)):[5–7]

$$RCH_2CH_2R' + R''CH{=}CH_2 \rightarrow RCH{=}CH_2R' + R''CH_2CH_3 \quad (1)$$

$$RCH_2CH_2R' \rightarrow RCH{=}CHR' + H_2 \quad (2)$$

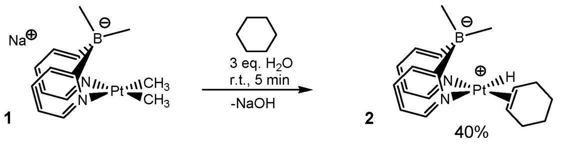
The acceptorless homogenous systems based on iridium complexes supported by rigid PCP pincer ligands developed by Goldman *et al.*[6] operate at high temperatures (150–200 °C), but are effective in achieving large turnover numbers (TON $>$ 10^3). Analogous PCP–iridium systems that utilize *tert*-butylethene (TBE) as a sacrificial hydrogen acceptor exhibit lower TONs ($<$300)[3] and operate at lower temperatures (150 °C). Introducing a platinum-based catalyst would add a group 10 metal into the arsenal of catalysts available for this important transformation. Previously, soluble platinum-based complexes have been shown to stoichiometrically dehydrogenate alkanes,[9–11] and while there has been one recent report of catalytic dehydrogenation,[12] TONs were limited to 1.1–1.3. These latter reactions were accompanied by a fast decomposition of the catalyst towards platinum black.

In the course of our recent CH activation studies in biphasic alkane–water systems with an anionic Pt^{II} complex **1** supported by dimethyl-di(2-pyridyl)borate ligand (dpb),[10] we showed that various alkanes can be stoichiometrically dehydrogenated under very mild conditions to produce Pt^{II} olefin hydride complexes, (dpb)Pt^{II}(olefin)H (see Scheme 1 for an example; **2**, olefin = *cyclo*-C_6H_{10}). The yields of these borato platinum(II) olefin hydrides, however, were limited to a low 30–40% and their reactivity was not characterized. In this communication, we disclose that the more lipophilic analogue of **2**, platinum(II) cyclohexene hydride complex **3** supported by our novel dimethyl-bis(4-*tert*-butyl-2-pyridyl)borate ligand, dpb^{tBu}, (Scheme 2) can be prepared in a virtually quantitative yield by a stoichiometric alkane dehydrogenation at room temperature and, importantly, can serve as a homogeneous catalyst for the dehydrogenation of various alkanes with TBE as a sacrificial hydrogen acceptor.

When analyzing the low efficiency of our previous dpb-based system in stoichiometric alkane dehydrogenation[10] we envisioned that it might originate from the low solubility in alkanes of the presumed Pt(IV) hydride intermediates. To solve the solubility problem we decided to introduce lipophilic *tert*-butyl groups onto the ligand scaffold (dpb^{tBu} ligand). Gratifyingly, sodium dimethylplatinate(II) complex Na[(dpb^{tBu})Pt^{II}Me$_2$], **4**, derived from our new lipophilic dimethyl-bis(4-*tert*-butyl-2-pyridyl)borate ligand, in contrast to Na[(dpb)Pt^{II}Me$_2$], **1**, proved to be soluble both in cyclohexane and *n*-pentane. In both cases, upon addition of water, a fast CH activation reaction occurred to give platinum(II) olefin hydride products in virtually quantitative yield (Scheme 2). In the case of *n*-pentane selective ($>$95%) formation of a 1-pentene derivative was observed initially when the reaction was stopped after five minutes; a 1-pentene bound complex **5** was obtained (Scheme 2).‡ Complex **5** isomerized after 1 day in cyclohexane solution towards products derived from *cis*- and *trans*-2-pentenes,§ implying that multiple reversible olefin insertion into Pt–H–β-hydride elimination reactions had occurred. A similar isomerization phenomenon was observed by Templeton *et al.*,[11] and also by Bercaw, Labinger *et al.*[13] in the activation of linear alkanes by Pt(II) complexes. Though the isolation of internal olefin complexes was reported only, it was inferred from deuterium labeling studies that initial activation took place at the terminal carbon.

If dehydrogenation of a symmetrical substrate, cyclohexane, by complex **4** is carried out in the presence of water, a single product **3** forms which is stable for at least several weeks in cyclohexane solution.

Importantly, it was possible to substitute the sacrificial olefin TBE for bound cyclohexene or pentene. In particular, the yield of **6** produced from **3** with 5 equivalents of TBE was quantitative after 30 minutes at 20 °C. Such reactivity is one of the prerequisites for a possible catalytic alkane transfer



Scheme 1 Alkane dehydrogenation with Na[(dpb)Pt^{II}Me$_2$].

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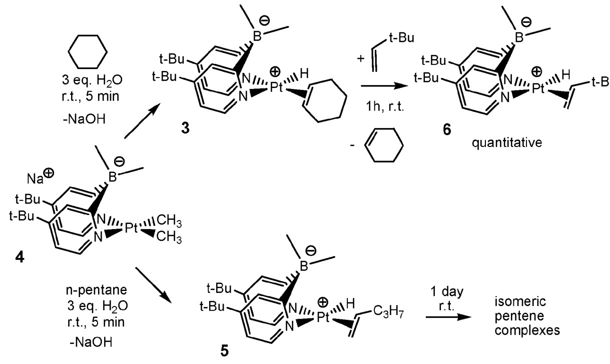
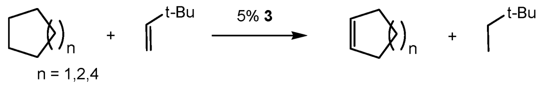


Scheme 2 New lipophilic dpb^{tBu}—complexes **3**, **4**, **5** and **6**. Alkane dehydrogenation and olefin substitution reactivity.

dehydrogenation. An alkane transfer dehydrogenation was attempted with complex **3** as the catalyst.

Experiments with TBE as the sacrificial olefin and a cycloalkane as both the substrate and the solvent showed that catalysis was already possible at 60 °C (eqn (3)):



(3)

For cyclohexane, two catalyst turnovers were achieved after 1 day of reaction time at 60 °C with two equivalents of TBE. The yield of reaction products, a cycloalkene and neohexane (NH), was determined using an NMR integration of signals of olefinic hydrogens of the cycloalkene and the hydrogen atoms of the *tert*-butyl group of neohexane, respectively, with anisole as an internal standard that was added after reaction completion.

The optimal conditions for the catalytic reaction were found eventually to be 1 day of heating at 100 °C in a closed Schlenk flask with 20 equivalents of TBE (560 mM) with regard to the catalyst (28 mM). These conditions gave higher catalyst turnover though resulted in a faster decomposition of **3** towards undetermined organometallic species after 1 day. Larger amounts of TBE led to lower TONs, with the reaction being completely suppressed when 100 equivalents of TBE were used. Similar behavior was observed by Goldman *et al.* in a (PCP)Ir-catalyzed transfer dehydrogenation of cyclooctane with TBE as a sacrificial olefin.[4] In turn, lower amounts of TBE limited the TON to the maximum amounts of TBE utilized. For instance, when 2 equivalents of TBE were used, 2 catalyst turnovers were observed.

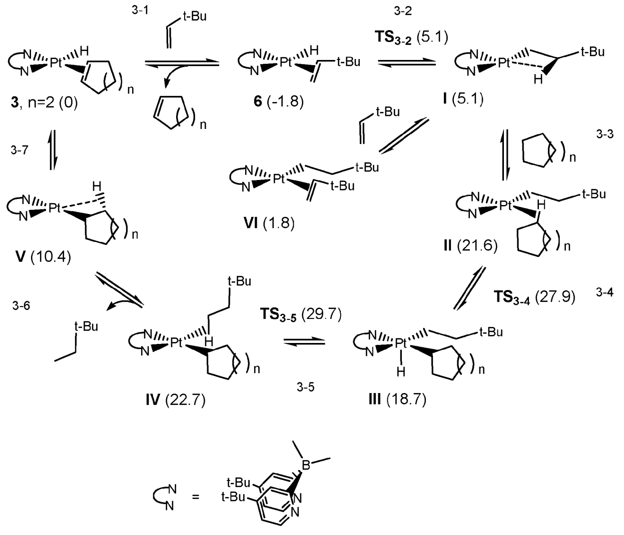
The numbers of equivalents of a cycloolefin and NH (eqn (3)) produced under these conditions are in a reasonable agreement, 7.5 and 8 ($n = 4$), 15 and 13 ($n = 2$) and 11 and 7 ($n = 1$), respectively. Formation of 1 equivalent of free cyclohexene originating from **3** was observed ($n = 1, 4$) or accounted for ($n = 2$) in all the cases.

Analysis of the dark yellow residues obtained upon completion of reaction after 1 day and removal of solvent revealed the presence of a complex mixture of pyridine derivatives as determined by the multitude of aromatic signals, and a single platinum hydride in low concentration. Stopping the catalytic reaction after 6 hours revealed that the starting complex **3** was still present in the mixture. No platinum black was observed to form during the reaction. A 5% catalyst loading was found to be optimal, as higher amounts of TBE relative to the catalyst were detrimental to the yield of product. Unlike the case of a previous report by Templeton *et al.*,[12] we were unable to observe transfer dehydrogenation of oxygenated substrates, such as diethyl ether, with our system.

Based on our observations and the results of DFT-modeling of the transfer dehydrogenation of cyclohexane with TBE as a sacrificial substrate, we suggest the mechanism of the catalytic reaction presented in Scheme 3. The first step, an olefin exchange 3-1, occurs readily at room temperature. The equilibrium involving cyclohexene complex **3** is shifted toward the TBE adduct **6** already with 5 equivalents of TBE, consistent with the results of our DFT calculations that show that the reaction 3-1 is thermodynamically favorable. Subsequent TBE insertion into a Pt–H bond, reaction 3-2, leads to a β-CH agostic complex **I** and is facile ($\Delta G^{\neq}{}_{298}$ = 5.1 kcal mol^{-1}). Coordination of a cycloalkane to **I**, reaction 3-3, leads to a relatively high-energy σ-complex **II**. The cycloalkane oxidative addition 3-4 to form a Pt^{IV} dialkyl hydride **III** is followed by the reductive coupling 3-5 ($\Delta G^{\neq}{}_{298}$ = 29.7 kcal mol^{-1}) which is the reaction (3) rate determining step (RDS). Similarly, a C–H reductive elimination from a d^6 iridium(III) dialkyl hydride intermediate was suggested by Goldman *et al.* to be the RDS in a (PCP)Ir-catalyzed transfer dehydrogenation of cyclooctene with TBE as a sacrificial olefin.[4] A sequence of the subsequent neohexane dissociation 3-6 from **IV** and β-hydride elimination 3-7 from a cycloalkyl intermediate **V** leads back to the beginning of the catalytic cycle.

The key CH-agostic intermediate **I** derived from TBE might be trapped by an excess olefin present in solution to form putative alkyl olefin complex **VI**, thereby inhibiting the target dehydrogenation reaction. To suppress formation of species such as **VI**, bulkier olefins, trimethyl- and tetramethylethylene, might be useful. At the same time, olefin steric bulk might have a negative impact on the reaction steps 3-1–3-4.

In separate experiments it was found that trimethylethylene and tetramethylethylene can displace cyclohexene from **3**.



Scheme 3 Proposed mechanism of catalytic alkane transfer dehydrogenation. DFT-calculated Gibbs energies for the case of $n = 2$, ΔG^{o}_{298}, are in kcal mol^{-1} and given in parentheses.

The reactions were monitored by means of ^{1}H NMR spectroscopy at room temperature. In both cases the Pt–H signal of the new complexes was observed (δ −22.19, $^1J_{\mathrm{PtH}}$ = 1313 Hz and δ −21.89, $^1J_{\mathrm{PtH}}$ = 1280 Hz, respectively) whose intensity was a function of the initial concentrations of **3** and the olefin. These results suggest that sterics are not a crucial factor in olefin binding to the Pt atom in dpb complexes (reaction 3-1). Ready olefin substitution in borate supported Pt complexes may be the feature that enables catalysis in this system and not in others.[9,11]

To test the effect of the olefin steric bulk on the other steps of the proposed catalytic cycle we attempted to use trimethyl- and tetramethylethylene as the sacrificial olefins in the transfer dehydrogenation of cyclohexane. Trimethylethylene showed lower TONs than TBE as sacrificial olefin (2–3 TONs at the optimized conditions). An isomerization to the terminal olefin position, towards isopropyl ethylene (IPE), was evident in a large part of the remaining, unhydrogenated sacrificial olefin. Hence, the actual dihydrogen acceptor here might be IPE whereas the excessive steric bulk of trimethylethylene itself might be detrimental for the subsequent reaction steps, 3-2, 3-3 and 3-4. Finally, with tetramethylethylene, we were unable to observe clear cut cases of catalysis.

In conclusion, we were able to show an unambiguous case of alkane transfer dehydrogenation that could be carried out with a group 10 metal acting as a homogenous catalyst: complex **3**. We were able to demonstrate a facile olefin-for-olefin exchange involving platinum(II)-bound and free olefins in solution in this system, which plays a significant role in the overall catalytic success of the system. Subsequent study of the catalyst deactivation pathways might lead to a next generation, more efficient Pt-based borate systems for alkane dehydrogenation.

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Notes and references

‡ Another possible diastereomeric 1-pentene complex could not be identified because of the low fraction of other Pt$^{\mathrm{II}}$ hydrides (5% combined) present in the reaction mixtures.

§ Addition of TBE to any of these solutions resulted in the clean formation of one predominant diastereomer of complex **6**.

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