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Homogeneous Catalysis

Titanium-Mediated Catalytic Hydrogenation of Monocyclic and Polycyclic Arenes

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Abstract: Two electron-reduction of the Ti^{IV} guanidinate complex $(Im^{Dipp}N)(^{Xyket}guan)TiCl_2$ gives $(\eta^6\text{-}Im^{Dipp}N)(^{xyket}guan)Ti$ (**1**$^{\mathbf{intra}}$) and $(Im^{Dipp}N)(^{Xyket}guan)Ti(\eta^6\text{-}C_6H_6)$ (**1**$^{\mathbf{inter}}$) ($^{Xyket}guan = [(tBuC{=}N)C(NXylyl)_2]^-$, Xylyl = 2,5-dimethylphenyl) in the absence or presence of benzene, respectively. These complexes have been found to hydrogenate monocyclic and polycyclic arenes under relatively mild conditions (150 psi, 80 °C)—the first example of catalytic, homogeneous arene hydrogenation with TON > 1 by a Group IV system.

The precious metal-based homogeneous catalytic hydrogenation of substituted and polycyclic arenes has been an intensive area of study as these systems offer greater flexibility and stereochemical control over heterogeneous processes.[1] This is nicely exemplified by the Rhodium-CAAC system developed in recent years by the Glorius group.[2] Their platform catalyzes the hydrogenation of a wide range of aromatic substrates including heteroarenes as well as borylated, fluorinated, and silylated aromatics to give all *cis*-hydrogenated heterocycles and substituted cycloalkanes.[2] While these late-metal systems are effective, it does bring into focus the question of sustainability, ethical sourcing, and the toxicity of precious metals.[3] To this end, forays into the development of base metal arene hydrogenation catalysts warrants investigation, particularly with respect to abundant and non-toxic early metals such as titanium.[1b]

Despite the intrinsic limitations of early- and 3d-transition metals to mimic precious-metal type reactivity, a handful of homogeneous systems are known.[1a,4] The earliest example reported by Muetterties et al., shows the hydrogenation of a variety of aromatics to cycloalkanes using the tris(phosphite) cobalt catalyst $(\eta^3\text{-}C_3H_5)Co[P(OCH_3)_3]_3$ (1 mol %) at room temperature in the presence of 15 psi of H_2; however, while exhibiting broad substrate tolerance, the catalyst performance is low.[5] This work was later followed by Rothwell and co-workers who developed mixed hydrido-aryloxide supported Group V tantalum and niobium catalysts capable of hydrogenating benzene and polycyclic aromatics at high H_2 pressures (1200 psi) and moderate temperatures (80–100 °C).[1b,6] Later, Fryzuk and co-workers disclosed a series of niobium cyclohexadienyl complexes, which catalyze the room temperature hydrogenation of benzene with 500 psi of H_2, reaching 225 turnover numbers (TON). Yet, treatment of toluene under the same conditions led to only 2 % conversion to methylcyclohexane.[7]

More recently, Chirik et al. developed the pyridine(diimine) molybdenum catalyst $(4\text{-}tBu\text{-}^{iPr}BDI)Mo(CH_2SiMe_3)_2$ that is able to hydrogenate benzene, toluene, and *o*-xylene upon heating at 60 °C for 24 h with a catalyst loading of 5 mol % under 59 psi of H_2. Higher hydrogen pressures (470 psi), longer reaction times (48 h), and higher catalyst loadings (10 mol %) were necessary to access other more sterically hindered substituted arenes, but the catalyst is poisoned by heteroarenes such as pyridine.[8]

Muetterties and co-workers also reported the only example of a homogeneous Group IV arene hydrogenation catalyst.[9] The Ti^{II}-arene complex $Ti(\eta^6\text{-}C_6\text{-}H_5Me)Al_2Cl_8$ was shown to catalyze the conversion of benzene to cyclohexane when heated to 125 °C in the presence of an H_2 atmosphere. However, conversion was low with no turnover due to evident decomposition of the catalyst at the elevated working temperatures. Very recently, a hybrid zirconium system, which combines characteristics of both homogeneous and heterogeneous catalytic systems, benzylated $Cp^*Zr(H)Bz_3$ supported on sulfated zirconia, was found able to catalyze the all-*cis* hydrogenation of alkyl substituted and polycyclic arenes to cyclohexanes at room temperature under 102 psi of H_2.[10]

These results clearly show that early- and 3d-transition metals can be effective as homogenous arene hydrogenation catalysts but also suggests an unrealized potential for Group IV elements, which is especially relevant as titanium is the second most earth abundant transition metal. In our laboratory, we have been endeavoring to develop such catalysts. For instance, we reported the Ti^{II} synthon $(\eta^6\text{-}Im^{Dipp}N)(^{ket}guan)Ti$ (**A**) ($^{ket}guan = [(tBuC{=}N)C(NDipp)_2]^-$; $Im^{Dipp}N^- =$ 1,3-bis(Dipp)imidazolin-2-iminato, Dipp = 2,6-diisopropylphenyl), which behaves as a transfer hydrogenation catalyst (Scheme 1 a).[11]

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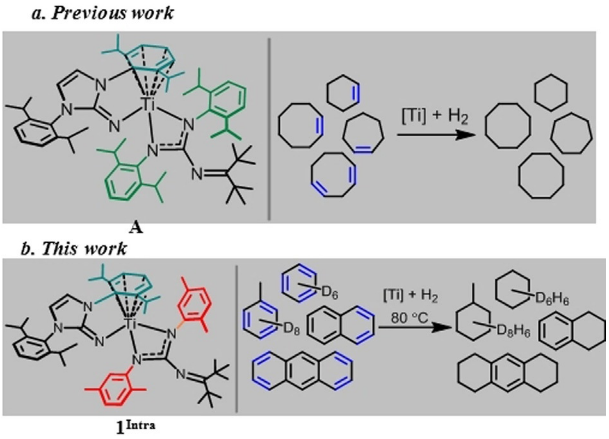
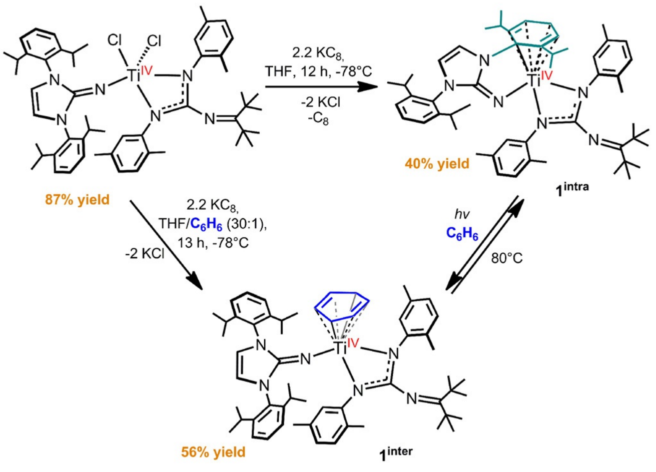


Scheme 1. Steric effects on titanium-based hydrogenation catalysis.

Compound **A** readily binds cyclic olefins to give titanium metallacycles that eliminate cycloalkanes under mild conditions (30 psi H_2 and 55 °C). A major structural feature of **A** is the two-electron reduction and coordination of a peripheral Dipp-ring to the titanium center, providing an intramolecularly masked metal species. The hydrogenation of cyclic olefins by **A** suggests the Ti-arene coordination is labile; however, no indication of other arene binding to **A** has been observed. Based on this, we have been working to modify our ligand platform to favor intermolecular over intramolecular arene binding to promote the hydrogenation of aromatic substrates, namely by reducing the steric profile of the ketimine-guanidinate ligand. Here, we report the synthesis and characterization of the new, masked titanium species (η^6-Im$^{\text{Dipp}}$N)($^{\text{Xyket}}$guan)Ti (**1**$^{\text{intra}}$) and (Im$^{\text{Dipp}}$N)($^{\text{Xyket}}$guan)Ti(η^6-C_6H_6) (**1**$^{\text{inter}}$) ($^{\text{Xyket}}$guan = [(*t*BuC=N)C(NXylyl)$_2$]$^-$, Xylyl = 2,5′-dimethylphenyl) and describe their use in the catalytic hydrogenation of monocyclic and polycyclic arenes (Scheme 1 b).

Similar to **A**, **1**$^{\text{intra}}$ is synthesized via the two-electron reduction of the Ti$^{\text{IV}}$ dihalide (Im$^{\text{Dipp}}$N)($^{\text{Xyket}}$guan)TiCl$_2$ with 2.2 equiv of KC_8 in THF solution at −78 °C (Scheme 2). Interestingly, when the reduction is carried out in the presence of a small amount of C_6H_6, benzene-capped **1**$^{\text{inter}}$ forms as the favored product (Scheme 2). Complexes **1**$^{\text{intra}}$ and **1**$^{\text{inter}}$ are highly soluble in aromatic solvents, and partially soluble in Et_2O and non-polar solvents such as hexanes and pentanes. The molecular structures of **1**$^{\text{intra}}$ and **1**$^{\text{inter}}$ were inferred from ^{1}H, ^{13}C{^{1}H}, COSY, and HSQC NMR spectral analyses (Figures S12–S19, Supporting Information (SI)) with further confirmation provided by X-ray crystallography.



Scheme 2. Synthesis and interconversion of **1**$^{\text{intra}}$ and **1**$^{\text{inter}}$.

Light-brown crystals of **1**$^{\text{intra}}$ or **1**$^{\text{inter}}$ can be grown from concentrated toluene or THF/Et_2O (10:1) solutions stored at −35 °C for four to seven days. As anticipated, the solid-state molecular structure of **1**$^{\text{intra}}$ is structurally analogous to **A** as it features η^6-coordination of a peripheral Dipp-ring to the titanium metal center; however, poor X-ray diffraction data precludes in-depth analysis of its metrical parameters (Figure S2, SI). On the other hand, the solid-state structure of **1**$^{\text{inter}}$ is well-resolved and inspection of the coordinated benzene moiety reveals clear structural distortions consistent with dearomatization and reduction to a cyclohexadienide dianion (Figure 1 and Figure S3, SI), similar to those found for the coordinated ring of **A**.[11]

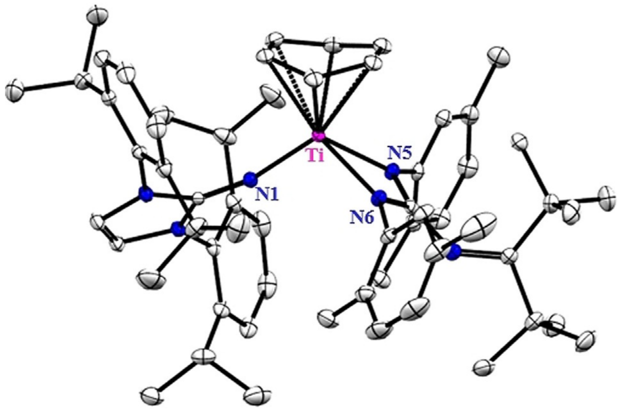


Figure 1. Solid-state molecular structure of **1**$^{\text{inter}}$.

In solution, the masking interaction of **1**$^{\text{intra}}$ is clearly maintained on the NMR timescale as the ^{1}H NMR spectra displays tell-tale resonances with a multiplet at 3.14 ppm and a triplet at 2.51 ppm, in a 2:1 ratio, attributable to the upfield-shifted signals of the dearomatized Dipp ring protons (Figure S12, SI). In contrast, the protons of the reduced benzene ring in **1**$^{\text{inter}}$ appear as a single peak at 3.97 ppm (Figure S16, SI), suggesting resonance-form delocalization and free rotation of the coordinated ring in solution.

Heating [D$_6$]benzene solutions of **1**$^{\text{intra}}$ at 80 °C for extended periods does not lead to any observable change, as indicated by ^{1}H NMR spectroscopy. Conversely, heating [D$_6$]benzene solutions of **1**$^{\text{inter}}$ at 80 °C slowly leads to the near quantitative formation of **1**$^{\text{intra}}$ over the course of two weeks (Figure S21, SI). During this time, C_6H_6 for [D$_6$]benzene exchange is observed by the rapid loss of signal intensity of the masking ring protons in the ^{1}H NMR spectrum of **1**$^{\text{inter}}$ concomitant with the appearance of a new, corresponding signal at 3.98 ppm in the

^{2}D NMR spectrum indicative of [D$_6$]benzene binding (Figure S23, Supporting Information).

Interestingly, the reverse reaction can be achieved by photolysis of **1**^{intra} (0.044 mm) using blue LED light (365 nm) in C_6H_6 solution to generate **1**^{inter}, a conversion that can be nicely tracked through electronic absorption spectroscopy as each complex has distinctive UV/Vis spectral traces (Figure S37, SI).

Notably, the successful isolation of **1**^{inter} evidently shows that subtle ligand modifications, in this case substitution of the Dipp-guanidinate groups in **A** for less encumbering Xylyl substituents, can have a significant effect on coordination properties and molecular dynamics at the metal center. Indeed, whereas **A** is thermally unstable in solution at room temperature, leading to intramolecular C–H oxidative-addition, **1**^{intra} and **1**^{inter} are indefinitely stable in such solutions. This, combined with the interconvertibility of **1**^{intra} and **1**^{inter}, signaled to us system characteristics amenable for arene hydrogenation catalysis. This is especially true as arene capture and reduction has been proposed as an important first step in the hydrogenation process.[1b,12]

Accordingly, pressurizing solutions of **1**^{intra} in [D$_6$]benzene (0.036 mmol) with H_2 (150 psi) at 40 °C results in the formation of [D$_6$]cyclohexane—confirmed by NMR and GC/MS spectroscopies (Figures S25 and S36, SI)—as the sole hydrogenation product over the course of several hours. Examination of the ^{13}C{^{1}H} NMR spectrum of the [D$_6$]cyclohexane product (Figure S26, Supporting Information) indicates the presence of several isotopomers,[8] while the ^{2}D NMR spectrum shows no signs of H/D scrambling into the ligands (Figure S27, Supporting Information). Raising the temperature to 80 °C enhances the rate of catalysis, giving a modest turn over number of 3 after 80 h (Figure S25, Supporting Information). During this period, the onset of catalyst decomposition ($\approx$50 %) is observed along with diminished catalytic performance occurring over time. Not surprisingly, conducting the hydrogenation reaction in [D$_{12}$]cyclohexane with 20 equiv of benzene results in a significantly slower rate with TON $<$0.5 after 20 h (Figure S32, Supporting Information).

Monitoring the reaction by ^{1}H NMR spectroscopy reveals the presence of both **1**^{intra} and **1**^{inter} in solution in a relative 3:7 ratio after heating for 20 h at 80 °C. This is notable as this phenomenon is not observed in the absence of H_2 (vide supra), and the origin of the interconversion of **1**^{intra} and **1**^{inter} under these conditions is not presently known. Additionally, heating solutions of **1**^{intra} under H_2 in [D$_{12}$]cyclohexane in the absence of aromatic substrates gives no indication for the formation of hydride intermediates but begins to slowly decompose over several days under these conditions (Figure S24, Supporting Information). Nonetheless, the observation of **1**^{intra} and **1**^{inter} in these solutions indicates that each plays a pivotal role as catalyst resting states. As such, starting with **1**$^{intra/inter}$ **(1)** as the catalyst does not alter performance. Moreover, photolyzing the reactions has no effect on the outcome. Finally, hydrogenation of the coordinating Dipp-ring of **1**^{intra} is not observed but could play a role in the catalyst decomposition pathway.[6a]

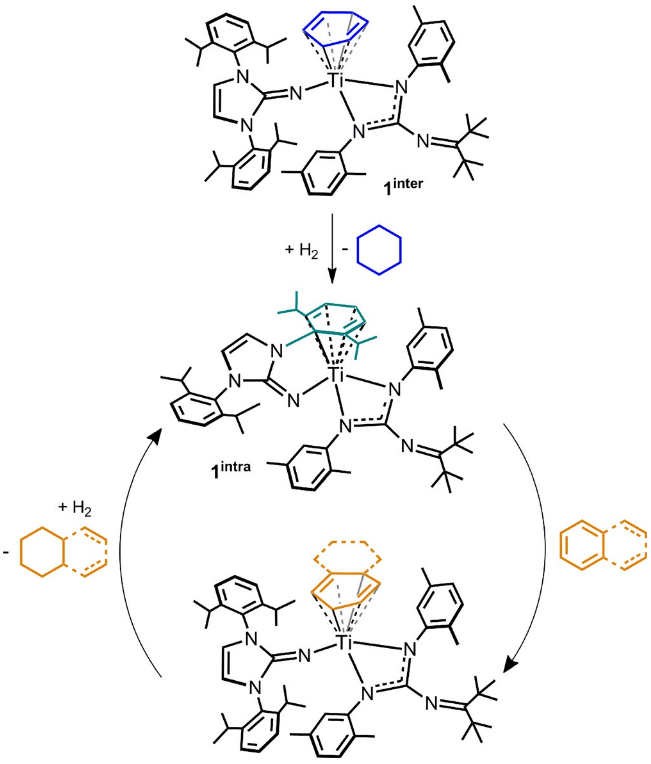
Table 1. Catalytic hydrogenation of selected unsaturated aromatics.[a]

Substrate	Product	TON [20 h]	TOF[d] [h^{-1}]	Total TON[e] [60 h]
[D$_6$]benzene[b]	[D$_6$]cyclohexane	1.0	0.05	2.0
[D$_8$]toluene[b]	[D$_8$]methylcyclohexane	1.8	0.09	2.9
naphthalene	tetralin	4.4	0.22	7.4
anthracene	octahydroanthracene	4.6	0.23	6.5
styrene[c]	ethylbenzene	9.0	0.45	13.9[c]
pinacolborane	–			
Me$_3$SiPh	–			
anisole	–			
aniline	–			

[a] Reactions conducted using solutions of **1**^{intra} (0.036 mmol, 1.0 mL) with 20 equiv of substrate at 80 °C under H_2 (150 psi) in [D$_{12}$]cyclohexane with Fc (0.0269 mmol) as internal standard. [b] Substrate as solvent. [c] Room temperature reaction, 60 h. [d] Average turnover frequency over 20 h. [e] Averaged over three runs.

Gratifyingly, this reactivity demonstrates successful implementation of a Group 4 titanium-based system for homogeneous arene hydrogenation under relatively mild conditions. In order to determine the catalytic scope of **1**, the hydrogenation of a variety of other aromatic substrates was screened including toluene, naphthalene, anthracene, and styrene (Table 1; Scheme 3). All reactions were performed at 150 psi of H_2 at 80 °C with ferrocene as an internal standard.

Compared to [D$_6$]benzene, neat [D$_8$]toluene is more rapidly hydrogenated with nearly twice the TON over the first 20 h (Table 1; Figures S28 and S38, SI). This is surprising, as in the case of the macrocyclic phosphine amide ^{R}[P_2N_2]Nb(CH_2SiMe_3), the catalytic competency of the niobium complex drops precipitously from benzene to toluene.[7] Rothwell's niobium arene



Scheme 3. Proposed catalytic cycle.

hydrogenation catalysts also show a decrease in relative rate from benzene to toluene, though no other correlation between hydrogenation rates and sterics can be drawn from his system.[1b] However, it should be noted that, when using fewer equivalents of toluene (20 equiv) in [D_{12}]cyclohexane with **1**, the decrease in the rate of hydrogenation is pronounced (TON <0.7 after 20 h) (Figure S33, Supporting Information).

The hydrogenation of naphthalene by **1** occurs at a significantly faster initial rate than the pseudo first order [D_6]benzene or [D_8]toluene reactions, cleanly producing 1,2,3,4-tetrahydronaphthalene (i.e., tetralin) (Table 1) (Figures S29 and S39, Supporting Information). Consecutive hydrogenation of tetralin to decalin was not observed even after full consumption of the naphthalene. While Rothwell's niobium catalysts are capable of hydrogenating tetralin to decalin under 1200 psi of H_2,[1b] the same was not observed for Chirik's homogeneous molybdenum system, even when increasing the H_2 pressure from 59 to 470 psi.[8]

With respect to the hydrogenation of anthracene by **1**, its relative rate is similar to that of naphthalene and selectively forms 1,2,3,4,5,6,7,8-octahydroanthracene (Table 1) (Figures S30 and S40, Supporting Information), though it must be noted that the rate of reaction is severely limited by the poor solubility of the anthracene under the reaction conditions.

Surprisingly, there is no indication of the presence of any monocyclic-hydrogenated 1,2,3,4-tetrahydroanthracene in the reaction mixture, indicating that it is immediately hydrogenated upon formation. In comparison, Rothwell's catalysts give access to both 1,2,3,4-tetrahydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene (1200 psi, 80 °C),[1b] while perhydroanthracene is the major product of Muetterties' cobalt-catalyzed reactions.[5a]

Curiously, **1** does not catalyze the aromatic hydrogenation of styrene to ethylcyclohexane under the general conditions of our experiments. Instead, it acts as an olefin hydrogenation catalyst that selectively hydrogenates styrene to ethylbenzene (TON = 9.0, 20 h) without the formation of ethylcyclohexane (Figures S31 and S41, Supporting Information). This transformation takes place at room temperature and occurs at a higher relative rate than the hydrogenation of aromatic substrates (Table 1). Upon full consumption of the styrene, formation of ethylcyclohexane from the hydrogenation of ethylbenzene is not observed even upon heating the sample at 80 °C over the course of seven days (Figure S31, Supporting Information). Similarly, starting with ethylbenzene in place of styrene results in no change after 80 h at 80 °C under H_2 (150 psi) (Figure S34, Supporting Information). In comparison, (4-*t*Bu-^{iPr}BDI)Mo(CH_2SiMe_3)$_2$ also hydrogenates styrene to ethylbenzene (59 psi), whereas higher pressures (470 psi) leads to ethylcyclohexane exclusively.[8] Regardless, when compared against **A**, **1** was found to be a superior hydrogenation catalyst as it gives significantly higher turnovers of ethylbenzene under comparable conditions (80 °C, 150 psi H_2, 18 h, and 8.0 mM in [D_{12}]cyclohexane), TON = 6 (**1**) vs. TON = 2.5 (**A**), possibly due to the more favorable steric profile of **1**.

It should be noted that, in the case of anthracene and styrene, the formation of intermediates is observed by ^{1}H NMR spectroscopy (Figures S30 and S31, Supporting Information), which we putatively assign as the catalytically active species ($Im^{Dipp}N$)(^{Xyket}guan)Ti(η^6-$C_{12}H_{14}$) and ($Im^{Dipp}N$)(^{Xyket}guan)Ti(η^2-$C_2H_3C_6H_5$), lending credence to the steps of our proposed catalytic cycle (Scheme 3). In contrast, the toluene and naphthalene analogs are not seen, suggesting that these intermediates are rapidly hydrogenated upon formation.

Finally, attempts to hydrogenate substituted arenes such as Me_3SiPh, phenyl boronic acid pinacol ester, anisole, and aniline were not met with success, either leading to no observed reactivity (Me_3SiPh) or catalyst decomposition (pinacolborane, aniline, and anisole). The decomposition of our system by *N*- and *O*-atom containing heterocycles is not surprising as we have shown our masked Ti-complexes to be potent reductants that are highly reactive towards heteroatom donors.[13] This suggests that ligand modifications will be necessary to temper the reactivity to mitigate such unwanted chemistries.

In closing, we have previously shown that our arene-masked Ti^{II} synthon (**A**) affords access to novel and distinctive late-metal type reactivity, namely transfer hydrogenation of cyclic olefins.[11] Building upon this success through subtle but judicious ligand modification, we have now reported a new platform, **1^{intra}** and **1^{inter}**, with improved thermal stability. Importantly, the steric profile of **1^{intra}** and **1^{inter}** allows for the intermolecular capture and activation of aromatic hydrocarbons at the titanium center, catalyzing the hydrogenation of monocyclic (benzene and toluene) and polycyclic (naphthalene and anthracene) arenes under relatively mild conditions (150 psi, 80 °C). Moreover, our new system also selectively hydrogenates the olefinic substituent of styrene to give ethylbenzene at room temperature. While the catalytic performance of **1^{intra}** and **1^{inter}** is admittedly modest, we present here a rare example of base-metal-mediated arene hydrogenation catalysis.[1] Our chemistry also shows that challenging chemical transformations, viz. homogenous arene hydrogenation, can be carried out using inexpensive, abundant, and non-toxic base metals such as titanium. We are continuing our efforts to optimize the catalytic outputs of **1** while targeting other late-metal type reactivity with our arene-masked titanium platforms.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arene ligands · early transition metals · homogeneous catalysis · hydrogenation · late-metal type reactivity · titanium

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