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Catalytic Hydrogenation Using Abnormal N-Heterocyclic Carbene Palladium Complexes: Catalytic Scope and Mechanistic Insights

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Palladium complexes containing abnormally bound C4-bound dicarbene ligands have been exploited for catalytic alkene hydrogenation. Comparison to normally C2-bound homologues indicates that the carbene bonding mode critically influences the catalytic activity. Good catalytic performance in the hydrogenation of *cis*-disubstituted olefins and non-isomerizable terminal olefins under mild conditions (RT, 0.1 MPa H_2) only occurs when the carbene is abnormally bound to the palladium center. Detailed mechanistic investigations using dynamic light scattering in connection with time-dependent analysis of conversions, and also performance of substoichiometric catalytic experiments provide evidence that the catalysis is heterogeneous and that the abnormally bound carbene ligand has the role of an activator.

Introduction

The metal-catalyzed hydrogenation of unsaturated substrates has long been a classic domain of transition metal complexes comprising phosphine ligands.[1] N-heterocyclic carbene (NHC) ligands,[2] once considered as substitutes of phosphines,[3] have been considerably less successful in hydrogenation catalysis.[4] This limitation of NHC complexes may be due in part to the propensity of the carbene ligand to undergo reductive elimination reactions,[5] despite the fact that the M–C_{NHC} bond is generally considered to have high covalent character and thus to be relatively strong. Reductive elimination pathways are particularly relevant in catalytic transformations involving intermediates that comprise metal-bound hydrides,[6,7] alkyl,[8] or aryl groups.[9]

We recently discovered that abnormal dicarbene palladium complexes, that is, NHC-type ligands that coordinate to the metal center abnormally through the imidazolylidene C4 or C5 rather than the normal C2 position,[10] provide catalyst precursors for the hydrogenation of olefins.[11] The abnormal bonding mode was assumed to be essential for this catalytic activity,[12] since C4-bound NHCs are considerably stronger donors than their normal counterparts.[10,13] This enhanced donor ability provides access to new reactivity pathways. Specifically, the high electron density imparted to the metal center is surmised to facilitate oxidative addition reactions,[14] which are a key step in the metal-mediated activation of H_2.[15]

Herein we report on our investigation of the scope, limitation, and, specifically, on the mode of action of the dicarbene palladium complexes **1**–**4** (Figure 1). These studies lend further support that oxidative H_2 addition is a limiting factor for catalyst activation, thus emphasizing the relevance of using strongly donating abnormal carbene ligands in catalyst design. Furthermore, evidence is provided that the hydrogenation is heterogeneous, thus indicating that the carbene ligand plays a

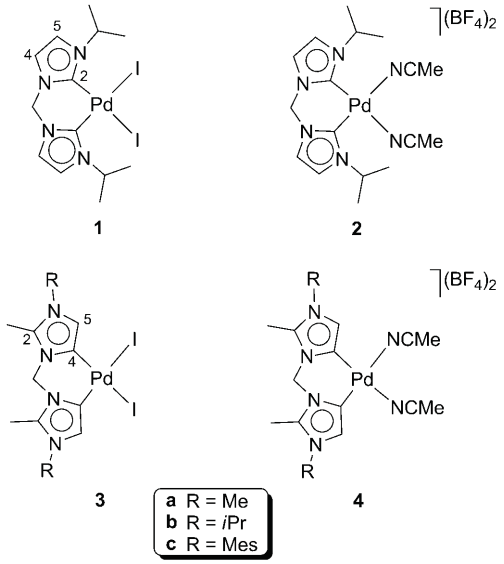

Figure 1. C2-bound dicarbene complexes **1** and **2** and the abnormal C4-bound carbene homologues **3** and **4**.

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role as activator, but not as spectator ligand in the catalytically active species.

Results and discussion

Structural aspects

Complexes **1**–**4** were prepared according to known procedures.[11,16] The solvento complexes **2** and **4a**–**c** were analyzed by X-ray diffraction (Figure 2, Table 1). Comparison of the structural parameters reveals only small differences between the normal complex **2** and the abnormal analogues **4a**–**c**. The Pd–C bond lengths are all similar and fit in the 1.96–2.00 Å range typical of Pd–C_{NHC} bond lengths.[8,17] The heterocyclic C–C bonds are only marginally longer in the C4-bound carbenes **4** than in the normal NHC analogue. The bite angles C1–Pd–C7 are larger in complexes **4** than in **2**, although the N-substituents seem to exert a stronger influence than the carbene bonding mode. Probably the largest structural difference consists of the dihedral angle between the palladium coordination plane and the heterocycles. In the abnormal carbene complexes **4**, this angle is small (12–36°), indicating a relatively flat boat-type conformation of the six-membered metallacycle. In the normal carbene complex, the heterocycles are twisted out of the palladium coordination plane by about 42°, presumably as a direct consequence of the presence of *ortho* substituents at the carbene. Large twists likely shield the z coordination axis at palladium and may thus influence the reactivity. Notably, in solution the metallacycle is flexible in **4** (singlet of NCH_2N group at room temperature),[11] whereas in **2** a rigid conformation is preserved, even at 80 °C, as evident from the AB pattern for the methylene protons.[16a]

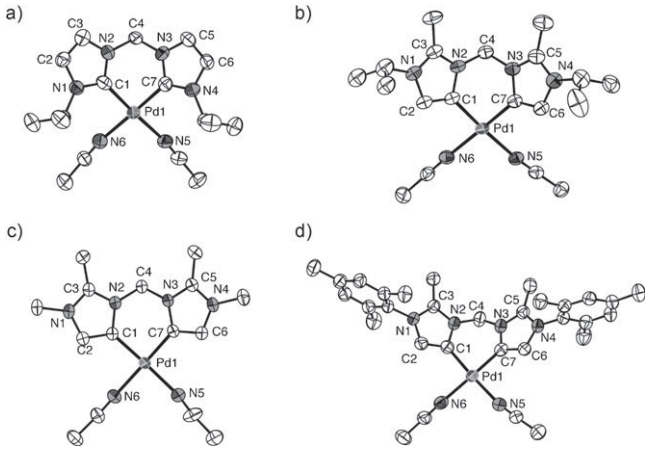


Figure 2. ORTEP representation of complexes **2** (a), **4a** (b), **4b** (c), and **4c** (d). Thermal ellipsoids are calculated at 50% probability level; hydrogen atoms and cocrystallized solvent molecules are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) in complexes **2**, **4a**, **4b**, **4c**.

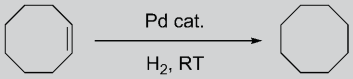
	2	**4a**	**4b**	**4c**
Pd1–C1	1.987(9)	1.973(4)	1.981(4)	1.964(4)
Pd1–C7	1.994(9)	1.974(4)	1.973(4)	1.975(4)
Pd1–N5	2.098(9)	2.097(4)	2.071(3)	2.068(4)
Pd1–N6	2.076(8)	2.074(4)	2.072(4)	2.065(4)
C_{imi}–C_{imi} [a]	1.341(14)	1.358(6)	1.356(6)	1.362(5)
C'_{imi}–C'_{imi} [b]	1.325(13)	1.362(6)	1.358(6)	1.347(5)
C1-Pd1-C7	84.1(4)	88.92(18)	85.75(17)	88.03(15)
N5-Pd1-N6	85.6(3)	89.36(18)	92.11(14)	91.67(13)
N2-C1-Pd1-C7	42.7(9)	12.6(4)	34.7(3)	22.5(3)
C1-Pd1-C7-N3	41.3(8)	15.7(4)	35.9(3)	25.7(3)

[a] C_{imi}–C_{imi} is C2–C3 for **2** and C1–C2 for **4**; [b] C'_{imi}–C'_{imi} is C5–C6 for **2** and C6–C7 for **4**.

Catalytic hydrogenation

The catalytic activity of complexes **1**–**4** was evaluated in the hydrogenation of cyclooctene (coe) at 30 °C under 0.1 MPa H_2. The solvento complexes **2** and **4** showed appreciable activity whereas the iodide analogues **1** and **3** were essentially inactive. Remarkably, in polar and weakly coordinating solvents, such as alcohols, abnormal complex **4b** was a significantly more active hydrogenation catalyst than the normal analogue **2** (Table 2, entries 1 and 2). Solvent screening showed that the most efficient solvent was EtOH, in which the hydrogenation of coe was complete in less than 5 h. Conversions were very low in nonpolar solvents such as toluene, even after 24 h, presumably due to the low solubility of the complexes (Table 2, entries 3–5). In strongly coordinating solvents such as DMSO, DMF, or MeCN, no conversion was detected (Table 2, entries 6–8; see below). Lowering the catalyst loading to 0.1% gave slower conversion (74% after 4.5 h; Table 2, entry 10), and catalytic activity essentially ceased upon further lowering of the concentration of **4b** to a 10,000:1 substrate/catalyst ratio (entry 11). Catalytic runs performed in C_2D_5OD did not reveal

Table 2. Catalytic activity of **4a** and **2** for cyclooctene hydrogenation.[a]



Entry	Solvent	*t* [h]	Catalyst loading [mol%][b]	Conversion [%][c] Cat. **2**	Cat. **4b**
1	MeOH	8	1	24	78 (100)
2	EtOH	4.5	1	19	100
3	THF	8	1	9	50 (100)
4	CH_2Cl_2	8	1	0	30 (100)
5	toluene	8	1	0	0 (34)
6	DMF	24	1	n.d.	0
7	MeCN	24	1	n.d.	0
8	DMSO	24	1	n.d.	0
9	EtOH	2.5	3	n.d.	100
10	EtOH	4.5	0.1	n.d.	74
11	EtOH	72	0.01	n.d.	< 5

[a] Conditions: Cyclooctene (2.0 mmol), EtOH (6 mL), H_2 (101 325 Pa), 30 °C; [b] relative to cyclooctene; [c] determined by GC; n.d. = not determined, conversion after 24 h given in parentheses.

any significant incorporation of deuterium in coa (GC-MS), indicating H_2 as the primary source of hydrogen.

Time-dependent monitoring of the reaction under standard conditions (1 mol% catalyst loading, EtOH) indicated that the abnormal complexes **4a** and **4c** were slightly less active than **4b** (Figure 3). Most strikingly, a long induction period (>1 h)

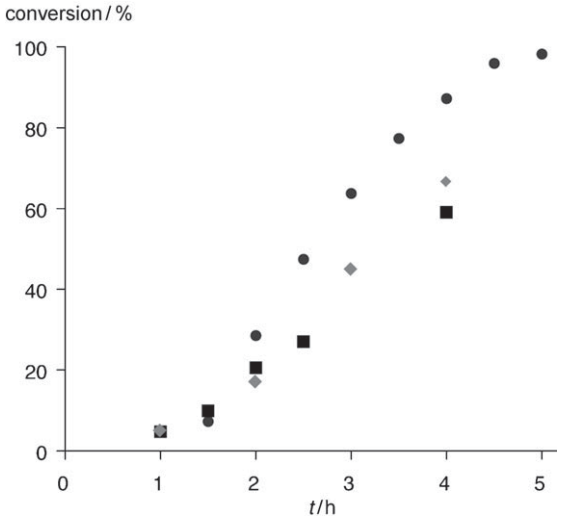


Figure 3. Time-conversion profile for cyclooctene hydrogenation using complexes **4a** (■), **4b** (●), and **4c** (◆).

was required for all three complexes. The length of this induction period is strongly dependent on the reaction temperature. At 22 °C instead of 30 °C, the induction was extended to nearly 2 h.[18] At elevated temperatures (55 °C), induction was significantly shorter (<20 min). However, the temperature raise came at the expense of the overall rate and considerably longer times were required to achieve complete substrate conversion.

Substrate screening

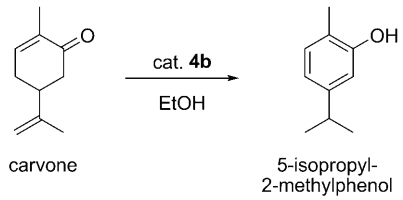
The scope of complex **4b** in the hydrogenation of double bonds was evaluated for various alkenes and also for unsaturated substrates with different functional groups (Table 3). The compiled results indicate a strong dependence of the catalytic activity on the nature of the olefin. The activity is reminiscent of that of Wilkinson's catalyst, with monosubstituted and terminal olefins being reduced most easily (Table 3, entries 1 and 2), followed by *cis*-olefins (entry 3), whereas *trans* olefins required much longer reaction times (entry 4). Trisubstituted olefins like 1-methylcyclohexene were also converted, albeit only slowly (26 h; Table 3, entry 5). Induction times were needed in each case as no conversion took place during the first hour. The induction time for *trans*-stilbene was very long (>7 h), yet it was significantly reduced when 5 mol% coe was added at the beginning of the reaction. Under these modified conditions, hydrogenation was complete after slightly more than 4 h.

Table 3. Screening of different substrates using **4b** as a catalyst.[a]

Entry	Substrate	*t* [h]	Conversion [%]
1	styrene	2.5 (±0.7)	>98
2	α-methylstyrene	2.9 (±1)	>98
3	cyclooctene	4.5 (±0.1)	>98
4	*trans*-stilbene	14/4[b]	>98
5	methylcyclohexene	26	>98
6	benzaldehyde	8	>95
7	nitrobenzene	5 (±0.1)	>98
8	phenylacetylene	24	>98
9	benzonitrile	24	<2

[a] Conditions unless otherwise stated: Complex **4b** (0.02 mmol), substrate (2.0 mmol), EtOH (6 mL), H_2 (101 325 Pa), 30 °C; [b] coe (0.1 mmol) added as promoter.

Allylbenzene constituted a special case, because its hydrogenation to propylbenzene was preceded by an isomerization process including the formation of β-methylstyrene by double-bond migration. Selective formation of the *trans*-olefin intermediate was indicated by the large coupling constant $^3J(H,H) = 16.1$ Hz of the doublet at $\delta = 6.40$ in the ^{1}H NMR spectrum. Similar isomerization processes also took place with more complex substrates, such as carvone (Scheme 1). Under standard hydrogenation conditions, complex **4b** induced a double-bond isomerization to yield 5-isopropyl-2-methylphenol[19] without further reaction.



Scheme 1. Isomerization of carvone catalyzed by **4b**.

Functional groups were reduced with varying degrees of success. Upon hydrogenation of benzaldehyde under standard conditions, various side products were detected when the reaction was carried out in EtOH. In THF, hydrogenation proceeded much more cleanly and afforded the expected benzyl alcohol and toluene. After 8 h, a 3:1 product distribution was detected by GC-MS (95% conversion; Table 3, entry 6). This ratio also remained constant upon extending the reaction time to several days, indicating that benzyl alcohol and toluene were formed concomitantly via independent pathways rather than consecutively. Hence, benzyl alcohol does not constitute an intermediate for the full reduction of benzaldehyde to toluene. Although we currently have no rationale for the catalytic C–O bond cleavage required to form toluene, optimization of this hydrogenation process may prove interesting for synthetic purposes.

Nitrobenzene was transformed cleanly into aniline (Table 3, entry 7), and phenylacetylene gave a mixture of phenylacetylene, styrene, and ethylbenzene in 0.49:0.48:0.03 ratio after

5 h. Semihydrogenation was not selective and after prolonged reaction times, ethylbenzene was the only product (Table 3, entry 8). Benzonitrile was not hydrogenated at all and the starting material was recovered (Table 3, entry 9).

Mechanistic investigations

To obtain mechanistic insights, we sought to prepare an activated precatalyst containing the substrate olefin in the palladium coordination sphere. Attempts to synthesize a complex with coordinated coe have to date proved unsuccessful. However, olefin coordination was achieved when potentially chelating 1,5-cyclooctadiene (cod) was stirred with the neutral complex **3b** in the presence of $AgBF_4$. Formation of complex **5** was confirmed by X-ray diffraction analysis of crystals that were grown in the presence of excess cod (Figure 4).

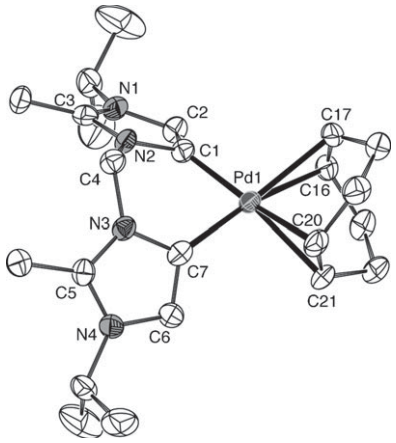
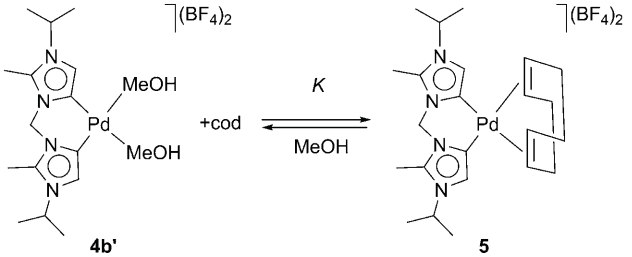


Figure 4. ORTEP representation of complex **5**. Thermal ellipsoids are calculated at 50% probability level; hydrogen atoms, noncoordinating BF_4^- anions and the cocrystallized DMSO molecules are omitted for clarity. Selected bond lengths (Å): Pd–C1 2.016(7), Pd–C7 1.989(8), Pd–C16 2.289(7), Pd–C17 2.324(7), Pd–C20 2.261(7), Pd–C21 2.295(6).

NMR spectroscopic investigation in CD_3OD revealed an equilibrium between the cod-containing complex and the bissolvento complex (Scheme 2), as indicated by the appearance of signals attributable to unbound cod. At room temperature, this equilibrium slightly favored the cod complex over the bissolvento complex (3:2 ratio, $K = 3.8$). Temperature-dependent analysis of the ratio of free and bound cod from crystalline **5**



Scheme 2. Equilibrium between bissolvento complex **4b**′ and cod-containing complex **5**.

(at an exact 1:1 ratio of cod and palladium) provided the equilibrium constant and the standard enthalpy and entropy for the olefin binding and release; $\Delta H^\circ = -22.9\ kJ\,mol^{-1}$, $\Delta S^\circ = -65.6\ J\,K^{-1}\,mol^{-1}$.[18] As catalytic experiments were carried out with monodentate olefins only, these factors need to be qualitatively corrected: The entropy term is expected to decrease and the equilibrium constant should shift further towards the solvento complex, due to the lack of chelating effects in the monodentate alkenes.

Notably, ^1H NMR spectroscopy in deuterated MeCN or DMSO showed only the bissolvento complex, that is, signals that are identical to those of complex **4b**, and quantitative amounts of free cod. Hence alcohols displaced the olefin only partially, whereas MeCN and DMSO bound too strongly to allow for olefin coordination, even when chelating cod was used. These results may provide a rationale for the inactivity of complex **4b** in olefin hydrogenation when coordinating solvents were used (*cf.* Table 1).

Further insights were gained from substoichiometric experiments with a 3:1 substrate/catalyst ratio using coe and complex **4b**. The reactions were stopped by filtration over silica after different reaction times and analyzed by NMR spectroscopy and GC-MS. No changes were detected after 10 min, and complex **4b** and all coe were still present. After 20 min, black particles were observed and ^1H NMR spectroscopy confirmed decomposition of the complex to the bisimidazolium salt (and probably an inorganic palladium salt). GC-MS measurements suggested that coe was hydrogenated to cyclooctane in 75% conversion. After 40 min, the ^1H NMR spectrum was unchanged, yet conversions reached completion according to GC-MS. These experiments suggest that the final 25% of substrate was converted at a stage when the complex was present only in trace amounts at best. Hence loss of the dicarbene ligand from complex **4b** may generate the catalytically active heterogeneous or homogeneous species.

Distinction between heterogeneous and homogeneous catalysis is far from trivial as it is difficult to exclude that traces of complex remaining in solution constitute the catalytically active species.[20] Similarly, leaching of metal atoms from a heterogeneous support may lead to homogeneous activity.[21] Such an event was excluded, however, in our case due to the results obtained from a mercury poisoning experiment.[22] Stirring of a solution of complex **4b** under hydrogen atmosphere in the presence of a large excess of mercury (> 100 equivalents) prior to the addition of coe suppressed the catalytic activity completely.

To further confirm the heterogeneous mode of action, the catalytic reaction was monitored by GC-MS and dynamic light scattering (DLS) techniques.[23] For this purpose, solutions containing the palladium complex **4a** and coe were centrifuged twice to eliminate any trace of residual particles before purging the solution with H_2 (0.1 MPa). Samples were taken at regular intervals and analyzed for conversion using GC-MS and for particle growth by DLS. In a standard run (Figure 5a), conversion was accompanied with particle growth and after 1 h, particles with hydrodynamic radius $R_H \approx 200$ nm formed. The particle size gradually increased, and microsize particles were pres-

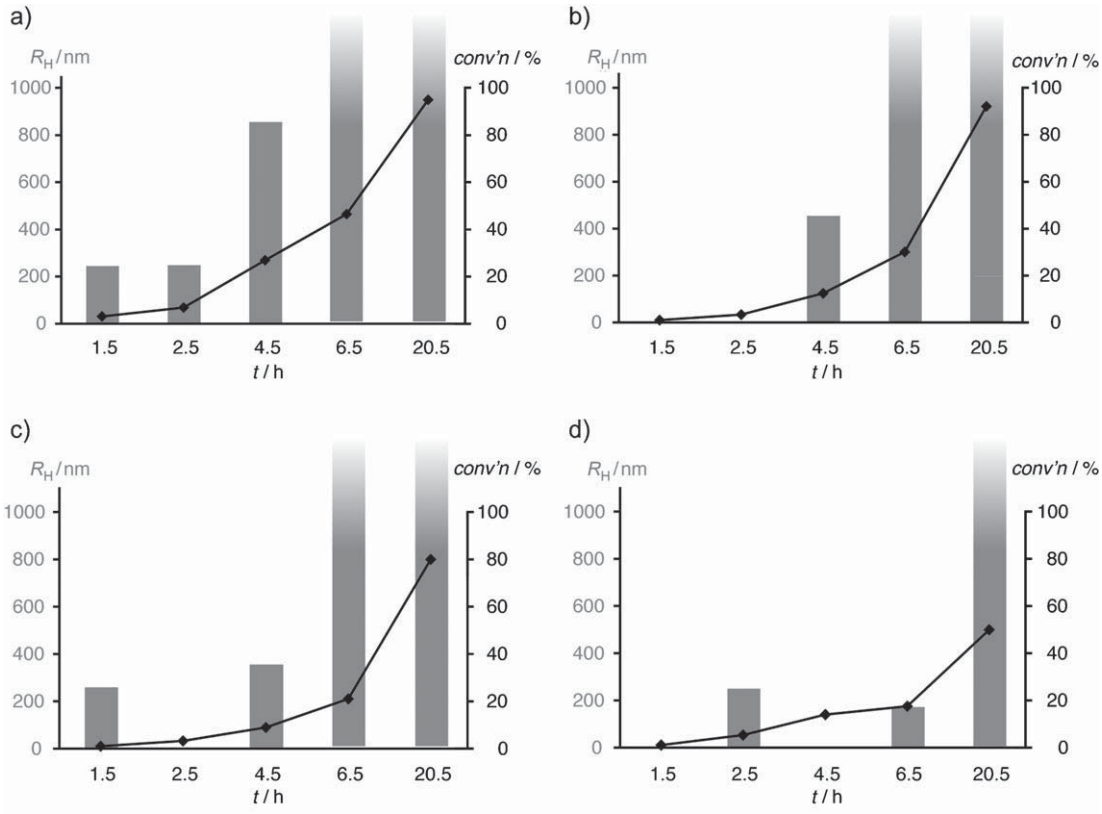


Figure 5. Correlation of particle size R_H (grey columns) and conversion (◆) for catalytic runs that were not filtered (a), and those filtered after 1 h (b), after 2 h (c), and after 4 h (d).

ent after about 6 h, when conversion reached about 40 %. Filtration of identical solutions through a nanoporous membrane after 1, 2, and 4 h indicated a clear correlation between conversion and the presence of particles (Figure 5 b–d). For example, filtration after 2 h (Figure 5 c) and analysis of the reaction mixture after 2.5 h showed the efficient removal of all nanoparticles, but not of the complex, as particle formation resumed after some time. Notably, catalytic activity dropped significantly in the absence of particles, and only 6 % conversion was observed between the measurement at 2.5 h and that at 4.5 h (*cf.* 20 % conversion during the same period in the unfiltered sample, Figure 5 a). The effect is perhaps even more obvious in the run that was filtered after 4 h. Initial conversions were rather low, probably due to the absence of particles at an early stage of the reaction. After filtration of the formed particles, the catalytic reaction essentially ceased (3 % conversion between 4.5 h and 6.5 h) and only resumed once particle growth had resumed. These measurements hence suggest that formation of submicrometer size particles is essential for the catalytic activity, hence indicating a heterogeneous mechanism.

Taking all of these elements into account, a mechanism for the activity of complexes **4** is suggested that comprises the coordination of one (or two) olefins to the palladium center, which accounts for the inactivity of the neutral complexes **1** and **3**, as well as of complex **4** in strongly coordinating solvents, and the oxidative addition of dihydrogen and reductive C–H bond elimination of the imidazolium salt, leading to palladium hydride species as effective precursor for the formation of colloidal palladium.[24] Oxidative addition is obviously facilitated by the high electron density at the palladium center, imparted by the C4-bonding of the carbene ligand. Subsequent reductive elimination of C4-bound carbenes is known to be faster than that of C2-bound NHCs,[25] presumably because of the weaker bonding of abnormal carbenes. A reactivity sequence that may model this catalyst activation step was recently disclosed by reacting the palladium complexes with chlorine rather than with hydrogen.[14] Exposure of complexes similar to **4** to Cl_2 afforded instantaneously the doubly chlorinated imidazolium salt with $[PdCl_4]^{2-}$ as counterion. Substituting chlorine in this process with hydrogen would provide the protonated imidazolium salt, as observed in substoichiometric catalytic runs, and $[PdH_4]^{2-}$ as precursor for palladium nanoparticles.[26]. In agreement with this model, the dicarbene complex **2** featuring normally bound NHC ligands lacks the reactivity towards oxidative addition and reductive elimination in the presence of chlorine,[14] and is also an inefficient hydrogenation catalyst.[27] Thus, the abnormal bonding mode of the carbene in complex **4** seems to be essential to activate the catalytic species, although it is a 'suicidal' ligand that escapes from the palladium coordination sphere during the activation process.

Conclusions

Palladium complexes comprising abnormally bound dicarbene ligands are precatalysts for the hydrogenation of olefins under mild conditions (EtOH, RT, 0.1 MPa H_2, no additives such as base or coligand). Mechanistic investigations consistently indicate a heterogeneous mode of action, which is supported by ligand loss at an early stage of the reaction (as observed in substoichiometric experiments), sigmoidal reaction kinetics, long induction periods, effective catalyst poisoning by elemental mercury, and the correlation of conversion with the presence of particles. Notably, heterogenization, which is in the present case identical to catalyst activation, requires the abnormal carbene bonding mode and is presumed to involve an oxidative H_2 addition and subsequent reductive imidazolium elimination. In a broader context, this investigation may reflect the limitations of abnormal carbenes and of N-heterocyclic carbenes in general as spectator ligands in hydrogenation reactions, a field in which phosphines have to date proved much more efficient ligands.

Experimental Section

General

The synthesis of complexes **1–4** has been reported elsewhere.[11,16] All other reagents are commercially available and were used as received. NMR spectra were recorded on Bruker spectrometers at 25 °C (unless specified otherwise). Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to external $SiMe_4$. Elemental analyses were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany).

Synthesis of 5

1,5-Cyclooctadiene (0.54 g, 5.0 mmol) and $AgBF_4$ (0.41 g, 2.11 mmol) were added to a suspension of **4b** (0.60 g, 0.97 mmol) in THF (5 mL). The reaction mixture was stirred for 16 h under exclusion of light. After filtration through celite, the solvent was removed under reduced pressure to give **5** as a grey solid (0.59 g, 94%). Recrystallization from MeCN/Et_2O in the presence of excess cod gave an analytically pure sample. ^{1}H NMR (500 MHz, CD_3OD): $\delta = 7.34$ (s, 2H, H_{NHC}), 6.19 (s, 2H, NCH_2N), 6.19 (s, 4H, CH_{cod}), 4.60 (sept, $^3J(H,H) = 6.7$ Hz, 2H, $CHMe_2$), 2.93–2.83 (m, 4H, $CH_{2\,cod}$), 2.74 (s, 6H, $C_{NHC}CH_3$), 2.73–2.64 (m, 4H, $CH_{2\,cod}$), 1.49 ppm (d, $^3J(H,H) = 6.7$ Hz, 12H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): $\delta = 144.2$ ($C_{NHC}Me$), 135.0 ($C_{NHC}Pd$), 121.0 ($C_{NHC}H$), 120.8 (CH_{cod}), 60.9 (NCH_2N), 51.9 ($NCHMe_2$), 30.4 ($CH_{2\,cod}$), 22.4 ($CHCH_3$), 10.0 ppm (C_{NHC}-CH_3). Elemental analysis calcd. for $C_{23}H_{36}B_2F_8N_4Pd$ (648.59): C 42.59, H 5.59, N 8.64; found: C 42.43, H 5.72, N 8.71.

General procedure for alkene hydrogenation

A solution of catalyst precursor (0.013 g, 0.02 mmol) and olefin (2 mmol) in EtOH (6 mL) was saturated with H_2 for 4 min and stirred at 25 °C under an atmosphere of H_2. Samples (0.1 mL) were withdrawn at regular time intervals and filtered through a short pad of SiO_2 and analyzed by GC-MS (volatile substrates) or, after solvent evaporation, by ^{1}H NMR spectroscopy.

Stoichiometric hydrogenation

A solution of catalyst precursor (0.030 g, 0.05 mmol) and cyclooctene (0.016 g, 0.15 mmol) in EtOH (6 mL) was saturated with H_2 for 4 min and stirred at 25 °C under an atmosphere of H_2. Samples (0.1 mL) were withdrawn at regular time intervals and filtered through a short pad of SiO_2 and analyzed by GC-MS. A second aliquot (0.5 mL) was removed and precipitated by addition of Et_2O (10 mL). The brown residue was dried under vacuum and analyzed by ^{1}H NMR spectroscopy.

Dynamic light-scattering experiments

Samples were prepared by adding EtOH (6 mL) to cyclooctene (0.11 g, 1.0 mmol) and **4a** (0.013 g, 0.021 mmol). The resulting suspension was stirred at room temperature for 30 min and then centrifuged (1 h, 9000 rpm). A portion (3 mL) from the supernatant was transferred into a quartz cell and centrifuged once more (1 h, 9000 rpm). Hydrogenation was initiated by passing H_2 for 2 min through the solution, and the mixture was subsequently left under a steady H_2 atmosphere (101 325 Pa). At given time intervals, the solutions were filtered through celite and twice through a 0.45 μm filter, and then analyzed by DLS and GC-MS. The hydrodynamic radius R_H of the particles was calculated using the Stokes–Einstein relation based on average diffusion coefficients D, which were obtained from second-order cumulant analysis of the intensity correlation functions.[28]

Structure determination and refinement of the complexes

Suitable single crystals were mounted on a Stoe Mark II Imaging Plate Diffractometer System (Stoe&Cie, 2002) equipped with a graphite monochromator. Data collection was performed at −100 °C using $Mo_{K\alpha}$ radiation ($l = 0.71073$ Å). All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL-97.[29] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied using MULscanABS as implemented in PLATON03.[30] Further details on data collection and refinement parameters are collected in the Supporting Information (Table S2).

In complexes **4a**, **4b**, and **4c**, one of the two BF_4^- anions (**4a**, **4c**) or both (**4b**) were disordered. All fluorine atoms that participate in the disorder were refined with the bond distances constrained to their theoretical values and the thermal values constrained to be equal. In complex **4b**, one isopropyl group was also disordered over two positions, the participating atoms C9, C9a, C10, C10a and the corresponding riding atoms had occupancies of 0.5. Crystallographic data (excluding structure factors) for the structures **2**, **4a**, **4b**, **4c**, and **5** have been deposited with the Cambridge Crystallographic Data Centre. CCDC 782481, CCDC 782482, CCDC 782483, CCDC 782484, CCDC 782485 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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