Palladium Catalysts

Palladium–(N-Heterocyclic Carbene) Hydrogenation Catalysts**

Jeroen W. Sprengers, Jeroen Wassenaar, Nicolas D. Clement, Kingsley J. Cavell, and Cornelis J. Elsevier*

N-Heterocyclic carbenes (NHCs) have become valuable ligands in organometallic chemistry and homogeneous catalysis. In particular, palladium-NHC systems have been successfully employed in various reactions such as C-C and C-N coupling reactions, oxidations, polymerization reactions, and telomerizations.^[1] However, the important class of hydrogenation reactions has not yet been reported for palladium-NHC catalysts. Transition-metal catalysts with NHC ligands for hydrogenation have been reported for rhodium, iridium, and ruthenium^[1,2] which are suitable for hydrogenation of alkenes. It has been observed that catalytic reactions in which hydridopalladium-carbene intermediates are involved can suffer from catalyst deactivation owing to attack of the hydride on the carbene which results in reductive elimination to give the imidazolium salt.^[3] Cloke and coworkers reported complete hydrogenation of [Pd(1,3-di(tertbutyl)imidazol-2-ylidene)₂] upon its exposure to hydrogen to vield metallic palladium and 1,3-bis-tert-butylimidazolidine (Scheme 1 a).^[4] However, we recently demonstrated for the first time that hydridopalladium-NHC compounds, obtained



Scheme 1. a) Hydrogenation of $[Pd(1,3-di(tert-butyl))imidazol-2-yl-idene)_2];^[4] b) oxidative addition of imidazolium salts to <math>[Pd(1,3-di-mesitylimidazol-2-ylidene)_2]$.^[5] R = 2,4,6-trimethylphenyl.

[*] J. W. Sprengers, J. Wassenaar, Prof. Dr. C. J. Elsevier Van't Hoff Institute for Molecular Sciences University of Amsterdam Nieuwe Achtergracht 166 1018 WV Amsterdam (The Netherlands) Fax: (+31) 20-525-6456 E-mail: elsevier@science.uva.nl
N. D. Clement, Prof. Dr. K. J. Cavell Department of Chemistry, Cardiff University PO Box 912, Cardiff CF113TB Wales (UK)

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by oxidative addition of imidazolium salts to $[Pd(1,3-dimesi-tylimidazol-2-ylidene)_2]$ (Scheme 1 b),^[5] are stable, isolable entities. In that case, the large *N*-mesityl substituents prevent orbital overlap between the hydride and the carbon atom of the carbone and hence preclude the reductive elimination.

Here we report that palladium($\mathbf{0}$)-NHC catalysts that contain bulky *N*-aryl substituents are very stable under hydrogenation conditions. They catalyze the hydrogenation of 1-phenyl-1-propyne with outstanding efficiency and exquisite selectivity. In this respect, only very few homogeneous palladium catalysts are known to catalyze the desirable, selective semihydrogenation of alkynes to *Z* alkenes (Scheme 2).^[6] Problems frequently observed for this reaction



Scheme 2. Hydrogenation of alkynes catalyzed by [Pd⁰(Ar-bian)-(alkene)]. $R = CH_3$, Ph.

include inadvertent isomerization of the Z alkene to the E isomer, shift of the double bond, overreduction to the alkane, low stability of the catalyst, and low reproducibility. So far, only $[Pd(Ar-bian)(\eta^2$ alkene)] (bian = bis(arylimino)acenaphthene) complexes were reported to hydrogenate a variety of alkynes to the Z alkenes with reasonable to excellent selectivity. Unfortunately, however, the important class of arylalkynes is hydrogenated only with lower selectivity (87–92%; Scheme 2) with such a catalyst.^[6d]

Our conjecture was that palladium(0)–monocarbene compounds that contain one strongly coordinated and two labile ligands should be good catalysts for this semihydrogenation reaction, as related platinum compounds were found to be active and selective hydrosilylation catalysts.^[7] Furthermore, we have shown that platinum–NHC species formed in situ were more-active catalysts in the hydrosilylation reaction than well-defined [Pt(NHC)(η^2 -alkene)₂] complexes.^[7b] Hence, we aimed at the development of effective palladium-(0)–NHC catalysts generated in situ for the desired hydrogenation reactions. As [Pd(η^2 -ma)(η^4 -nbd)]

(ma = maleic anhydride, nbd = norbornadiene) was found to be a much more efficient palladium precursor than $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in the synthesis of a series of $[Pd(L)_2(\eta^2-ma)]$ complexes,^[8] we applied this [Pd(ma)(nbd)]complex as the source of palladium (Scheme 3).

Consequently, imidazolinium chlorides **1a** and **1b** and imidazolium chlorides **2a–2d** were stirred with 4 equivalents



Scheme 3. Generation in situ of palladium(0)–NHC catalysts using [Pd(ma)(nbd)].

of *t*BuOK and 1 equivalent of [Pd(ma)(nbd)] in THF for 1 hour. Imidazolium chloride **2d** and the corresponding NHC generated in situ are new compounds. We then synthesized three palladium(**0**)–NHC complexes **3**, **4**, and **5**, which were also applied as catalysts. The $[Pd(NHC)(\eta^2-alkene)_2]$ complexes **3** and **5** have been reported as precatalysts for other reactions.^[9] The new complex **4** was isolated by addition of a second equivalent of maleic anhydride after the generation in situ of the palladium catalyst from **2a** and [Pd(ma)(nbd)]. This proves that palladium(**0**)–NHC species are indeed formed by the in situ approach according to Scheme **3**.

The hydrogenation was initiated by addition of the alkyne to the solution of the catalyst and then bubbling H_2 (1 bar) through the solution at 20 °C. The results of the hydrogenation of 1-phenyl-1-propyne are compiled in Table 1. Exhaustive hydrogenation to the alkane is observed when



catalysts are not stable, as is nicely demonstrated for [Pd(ma)(nbd)] (Table 1, entry 1). Immediate formation of palladium black was observed when this complex was exposed to hydrogen, and 41.8% of *n*-propylbenzene was obtained after total consumption of 1-phenyl-1-propyne. Significantly better results were obtained when NHC ligands were used. When 1,3-dimesityl-4,5-dihydroimidazolium chlo-

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Table 1: Hydrogenation of 1-phenyl-1-propyne to 1-phenyl-1-propene and n-propylbenzene.[a]

Entry	Catalyst	Yield [%] ^[b]	<i>t</i> [h]	$TOF \left[h^{-1} \right]^{[c]}$	Selectivity [%] ^[d] Z alkene:E alkene:alkane
1	[Pd(ma)(nbd)]	>99	2	100	57.0:1.2:41.8
2	$[Pd(ma)(nbd)] + 1a^{[e]}$	>99	6	18.6	90.1:2.2:7.7
3	$[Pd(dba)_{2}] + 1a^{[e]}$	>99	12	18.8	90.9:4.0:5.2
4	$[Pd(ma)(nbd)] + 1b^{[e]}$	>99	3.5	29.3	84.9:2.6:12.6
5	$[Pd(ma)(nbd)] + 2a^{[e]}$	>99	2.5	45.5	91.6:1.7:6.7
6	$[Pd(ma)(nbd)] + 2b^{[e]}$	>99	3.5	52.8	89.4:1.7:8.9
7	$[Pd(ma)(nbd)] + 2c^{[e]}$	> 99	3.5	29.0	93.6:2.9:3.5
8	$[Pd(ma)(nbd)] + 2d^{[e]}$	>99	2.75	49.9	95.0:2.0:3.0
9	3	0	-	-	_
10	4	>99	2.75	41.5	79.1:4.3:16.6
11	5	>99	2.5	46.8	76.0:6.4:17.7

[a] Catalyst (1 mol%), THF, 20 °C. [b] Yield determined by GC. [c] Turnover frequency determined at 25% conversion, defined as moles of 1-phenyl-1propyne converted per mole of catalyst per hour. [d] Selectivity determined at > 99% conversion of 1-phenyl-1-propyne. [e] Palladium precursor stirred with the imidazolium salt (1.0 equiv) and tBuOK (4 equiv) for 1 h in THF prior to addition of the substrate and initiation of hydrogenation.

ride (1a) was added to [Pd(ma)(nbd)] in the presence of tBuOK, a stable complex was obtained (entry 2). No formation of palladium black was observed when using this saturated NHC ligand, and the amount of *n*-propylbenzene produced was decreased to 7.7%. A similar selectivity was obtained when $[Pd(dba)_2]$ was applied as the precursor (entry 3), however, a very long induction time was observed. Although the turnover frequency (TOF = 18.8 h^{-1}) is almost identical to the case when [Pd(ma)(nbd)] was employed $(18.6 h^{-1})$, initially five hours are needed to obtain the active catalyst which is much longer than the 30 minutes of induction time for [Pd(ma)(nbd)]. Most likely, the alkene ligands have to dissociate or have to be hydrogenated to create vacant sites for the hydrogenation. [Pd(ma)(nbd)] is a much more labile complex than $[Pd(dba)_2]^{[8]}$ and is unquestionably a much more suitable palladium(o) precursor for many reactions. Replacement of the mesityl substituents by 2,6-diisopropylphenyl substituents (1b) results in a higher activity, but with lower selectivity.

The activity of the catalyst increases remarkably when reverting to unsaturated carbenes 2a and 2b (Table 1, entries 5 and 6). Relative to 1a and 1b, the high selectivities are maintained, but the TOF values nearly double to 45.5 h⁻¹ (2a) and 52.8 h^{-1} (2b). Interestingly, the reverse has been observed for hydrosilylation reactions catalyzed by platinum-(0)-NHC; there the saturated carbenes yield significantly more active catalysts than their unsaturated counterparts.^[7b] The two unsaturated carbenes that contain 2-methylphenyl and 2,6-diethylphenyl substituents (2c and 2d, entries 7 and 8) were also tested. For palladium catalysts derived from these NHC ligands, very high selectivities of 93.6% and 95.0%, respectively, towards (Z)-1-phenylpropene were observed. These results convey a significant improvement with respect to the selectivity towards Z-1-phenyl-1-propene relative to known palladium catalysts such as [Pd(2,2'-bpy)-(dmfu)]^[6d] (bpy = bipyridyl, dmfu = dimethyl fumarate;[Pd(dppe)(dmfu)]^[6d] 73%), (dppe = 1, 2-bis-(diphenylphosphino)ethane; 80%), [Pd(2-{N-(2-propyl)carbaldimino}-pyridine)(dmfu)]^[6e] (87%), [Pd(bian)(dmfu)]^[6d] (92%), and a $[Pd_2(dba)_3[P(nBu)_3]]$ system^[6c] (87%)

Z-1-phenyl-1-butene in the hydrogenation of 1-phenyl-1-butyne).

A comparison of the results obtained with the catalysts generated in situ with those for complexes 3, 4, and 5 reveals that the latter catalysts show much lower selectivities (Table 1, entries 9-11). Complex 3 does not catalyze the hydrogenation at all: it would appear that the dimethyl fumarate complexes coordinate too strongly to create vacant sites needed for catalysis. It is known that fumarates are stronger alkene ligands in platinum(o) complexes than maleic anhydride and quinones.^[10] Indeed, complexes 4 and 5 do enter the catalytic cycle owing to the weaker alkene ligands. However, during hydrogenation, considerable amounts of (E)-1-phenylpropene and alkane are observed for these catalysts. A full explanation cannot be given yet. Note that with the [Pd{1,3-(2,6-diethylphenyl)imidazol-2-ylidene}] catalyst generated in situ, complete hydrogenation can also take place, however, this process becomes significant only after all of the alkyne has been consumed.

As the new carbene 1,3-(2,6-diethylphenyl)imidazol-2vlidene (2d) shows the highest selectivity combined with good activity, this carbene ligand was applied in the hydrogenation of diphenyl acetylene and 4-octyne. Surprisingly, 4-octyne could not be hydrogenated under these conditions: less than 1% conversion was observed after 5 h. Diphenylacetylene was hydrogenated to Z-stilbene (88%), to its E isomer (5%), and 1,2-diphenylethane (7%). For comparison, [Pd(p-MeObian)(dmfu)]^[6d] yielded a selectivity of 87% towards the Z alkene and 13% towards the alkane. The electron-poor dimethyl butynedioate was selectively hydrogenated using 5 as the catalyst, with >99% conversion to dimethyl maleate (96%), dimethyl fumarate (1%), and dimethyl succinate (3%). In this case, [Pd(p-MeO-bian)(dmfu)]^[6d] induced a selectivity of 99% towards the maleate with >99% conversion.

In conclusion, the $[Pd\{1,3-(2,6-diethylphenyl))$ imidazol-2ylidene $\}]$ catalyst generated in situ is completely stable under hydrogenation conditions. The intermediately bulky NHC ligand **2d** effectively stabilizes palladium(0) species and hydridopalladium intermediates. Hence, the $[Pd\{1,3-(2,6-diethylpha))]$ diethylphenyl)imidazol-2-ylidene]] complex generated in situ is a suitable catalyst for the selective semihydrogenation of aryl-substituted alkynes to Z alkenes. The procedure for the formation of palladium(0)–NHC catalysts in situ starting from [Pd(ma)(nbd)] is very efficient. This procedure may also prove effective for the generation of catalysts for various other catalytic reactions such as C–C couplings, telomerizations, and additions of elemental hydrogen to unsaturated compounds. Further studies aimed at the elucidation of the reaction mechanism of the palladium–NHC-catalyzed semihydrogenation are in progress.

Experimental Section

All experiments were carried out using standard Schlenk-line techniques under an atmosphere of dry nitrogen. Solvents were dried according to standard procedures and distilled prior to use. **2d**: The compound was prepared in an analogous manner to that described in the literature:^[11] (9.54 g, 25.9 mmol, 51 %). ¹H NMR (300.1 MHz, [D₆]DMSO, 20 °C): $\delta = 1.11$ (t, ³*J*(H,H) = 7.4 Hz, 12 H, CH₃), 2.40 (m, 8H, CH₂), 7.44 (d, ³*J*(H,H) = 8.0 Hz, 4H, *m*-CH), 7.60 (t, ³*J*(H,H) = 8.0 Hz, 2H, *p*-CH), 8.47 (s, 2H, im-H^{4.5}), 10.06 ppm (s, 1H, im-H²); ¹³C NMR (75.5 MHz, [D₆]DMSO, 20 °C): $\delta = 15.8$ (CH₃), 24.5 (CH₂), 126.4 (im-H^{4.5}), 128.2 (*m*-CH), 132.1(*p*-CH), 132.5 (*ipso*-C), 139.5 (im-CH²), 141.0 ppm (*o*-C).

4: 1,3-Dimesitylimidazolium chloride (172 mg, 0.51 mmol) and tBuOK (0.77 mL of 1M solution in THF, 0.77 mmol) were dissolved in THF (8 mL), and the solution was stirred for 30 min at 20°C. [Pd(ma)(nbd)] (150 mg, 0.51 mmol) was added, and the dark purple mixture was stirred at 20 °C for 30 min. Maleic anhydride (50.0 mg, 0.51 mmol) was then added. The dark red solution was stirred for 2 h at 20 °C and filtered over celite, and the solvent was evaporated. The solid compound was washed with ether (4 × 10 mL) and dried in vacuo to give a red powder (157 mg, 0.26 mmol, 51 %). ¹H NMR (499.8 MHz, CD₂Cl₂, -50 °C): $\delta = 1.72$ (s, 6H, CH₃), 2.28 (s, 6H, CH₃), 2.31 (s, 6H, CH₃), 3.53 (d, ³J(H,H) = 4.6 Hz, 2H, CH=CH), 4.13 $(d, {}^{3}J(H,H) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, (Ar)CH), 7.07 (s, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = CH), 6,89 (s, 2H, CH) = 4.6 Hz, 2H, CH = 4.6 Hz, 2H, CH = 4.6 Hz, 2H, CH)$ (Ar)CH), 7.32 ppm (s, 2H, im-H^{4,5}); ¹³C NMR (125.7 MHz, CD₂Cl₂, -40 °C): $\delta = 17.4$ (CH₃), 18.2 (CH₃), 18.4 (CH₃), 64.7 (CH=CH), 68.2 (CH=CH), 124.8 (im-H^{4,5}), 129.3 (m-CH), 129.7 (m-CH), 134.5 ((Ar)C), 135.0 ((Ar)C), 135.4 ((Ar)C), 139.6 ((Ar)C), 167.6 (C=O), 167.9 (C=O), 193.1 ppm (im-CH²); IR (KBr): $\tilde{\nu} = 1816$ (C=O), 1761 cm⁻¹ (C=O).

Typical procedure for catalytic hydrogenation (in situ experiment): THF (30 mL), imidazolium chloride (0.05 mmol), [Pd(ma)-(nbd)] (0.05 mmol), and *t*BuOK (0.20 mmol) were introduced into a two-necked Schlenk tube, equipped with a septum and a stirring bar. After stirring for 1 h, the solution was filtered over Celite to remove traces of palladium black. Then the appropriate alkyne (5.0 mmol) was added through a syringe, and hydrogen gas (1 bar) was bubbled slowly through the solution by using a gas tube. Samples were removed periodically for GC analysis. The crude reaction mixtures were also analyzed by ¹H NMR spectroscopy for comparison.

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