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Synthesis of palladium(0) and -(II) complexes with chelating bis(*N*-heterocyclic carbene) ligands and their application in semihydrogenation†

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A transmetallation route, using silver(I) precursors, to several zero- and di-valent palladium complexes with chelating bis(*N*-heterocyclic carbene) ligands bearing various N-substituents has been established. The resulting complexes have been characterized by NMR and mass spectroscopy. In addition, the structure of a representative compound, [Pd^0(bis-(Mes)NHC)(η^2-ma)] (**3a**), was confirmed by X-ray crystal structure determination. In contrast to the transfer semihydrogenation, in which only low activity was observed, complex **3a** showed activity (TOF = 49 mol_{sub} mol_{cat}^{-1} h^{-1}) and selectivity comparable to its monodentate counterparts in the semihydrogenation of 1-phenyl-1-propyne with molecular hydrogen.

Introduction

Following the success of their monodentate analogues, chelating bis(*N*-heterocyclic carbenes) (bis-NHCs) have become popular ligands in transition metal catalysis.[1,2] Because of the chelate effect these bis-NHCs lead to metal complexes with higher stability compared to their monodentate (bis-)NHC counterparts (Fig. 1).[1] In addition to the advantages regarding stability, bis-NHCs are good candidates for the fine-tuning of catalytic properties by altering the wingtips, backbone and linker,[3] the first of which is explored in this contribution. The influence of the linker length is briefly studied as well.

Bis-NHCs have been coordinated to many transition metals: ruthenium,[4] rhodium,[3,5] iridium,[6] palladium,[7] platinum,[8,9] and more recently also the first row metals such as nickel[10–12] and iron.[13,14] We are interested in the properties and reactivity of low-valent late transition metal complexes, notably electron rich zero-valent palladium NHC complexes, as these often play a vital role in the catalytic cycles of many reactions.[15–18] Although a lot of research has been devoted to bis-carbene Pd^{II}(halide)$_2$ complexes, usually obtained by treating a bisimidazolium salt with $Pd(OAc)_2$ at elevated temperatures,[7,19–23] we are not aware of any previous reports on chelate [Pd^0(bis-NHC)L] or [Pd^{II}(bis-NHC)(η^3-C_3H_5)]Cl complexes. Moreover, reports on zero-valent d^{10} metal complexes bearing a chelating bis-NHC ligand have not appeared in the literature at all.

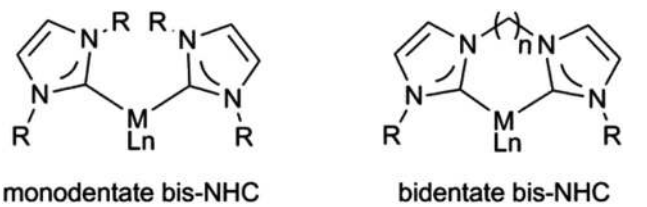

Fig. 1 General structure of the monodentate bis-NHC and bidentate bis-NHC complexes.

Results

Synthesis of bisimidazolium salts

The synthesis of bisimidazolium salts, **1**, has been documented; reacting a mono-substituted imidazole with 0.5 equivalent of dihaloalkane in several solvents at elevated temperatures gives the hygroscopic bisimidazolium salts in decent yields (Scheme 1).[24,25] However, yields are dramatically improved for the methylene linked bisimidazolium salts (**1a,c–e**) by heating the corresponding imidazole in an excess of dibromomethane, following a procedure by Lee *et al.*[23]

Silver and palladium complexes

Direct complexation by reacting the bisimidazolium salts with KOtBu in the presence of Pd^0 and Pd^{II} precursors ([Pd(*t*BuDAB)(η^2-ma)] (*t*BuDAB = 1,4-Di-*tert*-butyl-1,4-diaza-1,3-butadiene, ma = maleic anhydride), [Pd(dvtms)]$_2$ (dvtms = divinyltetramethylsiloxane) or [Pd(η^3-C_3H_5)μ-Cl]$_2$), failed to

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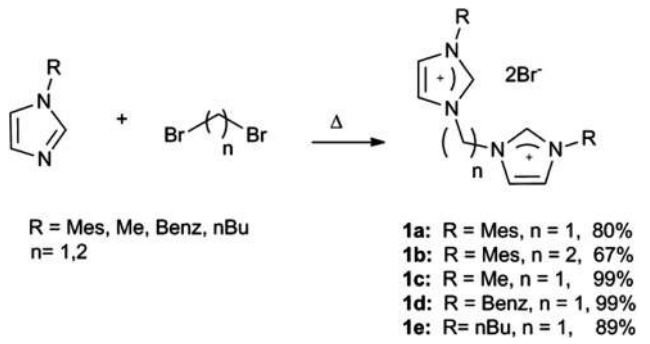


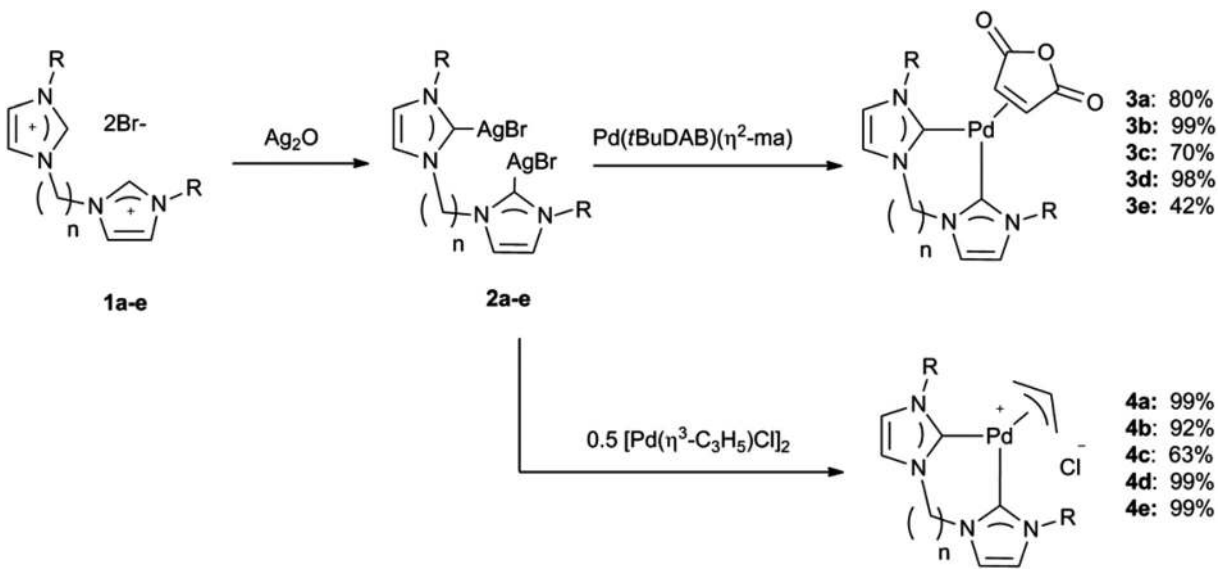
Scheme 1 General synthesis of bisimidazolium salts. Mes = 2,4,6-trimethylphenyl.

give the palladium complexes in satisfactory yields. Instead, a carbene transfer route *via* Ag(I) complexes was applied, which was first adopted for the synthesis of zero-valent palladium complexes in 2009[26] and showed excellent yields for chelate bis-NHC Pd^{II} complexes.[12,27]

The silver(I) complexes, **2**, were obtained by reacting the corresponding bisimidazolium dibromide salts (**1a–e**) with Ag_2O at room temperature in dichloromethane (R = Mes) or methanol (R = Me, Benz, *n*Bu) (Scheme 2) according to literature procedures.[28,29] Complete conversion can be monitored by the disappearance of the imidazolium-H peak around 9–10 ppm in the ^{1}H NMR spectrum and the appearance of a ^{13}C–Ag(I) resonance around 180 ppm in ^{13}C NMR. The silver complex from the mesityl bisimidazolium salt forms oligo- and polymeric structures as was shown by Wanniarachchi *et al.*,[28] while other substituents lead to dimeric complexes.[30] The reaction mixtures containing the silver(I) bis-carbene complexes were filtered over Celite, concentrated and used in the subsequent reaction without further purification.

Transmetallation of the Ag(I)NHC precursors, by reacting **2a–e** with one equivalent of [Pd(*t*BuDAB)(η^2-ma)] relative to the bis-carbene ligand in dichloromethane at room temperature, provided a convenient route to the corresponding zero-valent palladium maleic anhydride complexes (42–99% yield) (Scheme 2). The lower yields for the complexes with alkyl N-substituents (**3c** and **3e**) can be explained by the instability of their Ag(I) precursors, demonstrated by Quezada *et al.*,[30] as well as the low stability of the complexes themselves (*vide infra*).

The resulting complexes, **3**, were characterized by NMR spectroscopy and mass spectroscopy (FAB^+). It is reported that the mode of coordination (chelating or bridging) of bis-carbenes is dictated by a combination of linker, N-substituents, counter ion and reaction conditions.[22,31] It has even been doubted whether chelated methylene linked bis-NHC ligands would be able to support a zero-valent palladium center.[32] However, we observed formation of only the chelate species for all wingtip substituents and for both linker lengths, as was concluded from the NMR-spectra. In the ^{1}H NMR spectra, the signals of the methylene linker hydrogens are split in two doublets with a geminal coupling of approximately 13 Hz (Table 1). This observation can be attributed to the complexes' rigid boat structure, having a plane of symmetry bisecting the bis-carbene ligand and maleic anhydride in all cases. For **3b** (n = 2) the same rigidity was observed in the ^{1}H NMR spectrum, having two doublets of doublets assigned to the ethylene-linker hydrogens. The ^{1}H NMR spectrum of **3e** exhibits diastereotopic hydrogens for the *n*Bu groups displaying their non-equivalence as was observed before for similar complexes.[5,31] The *ortho*-methyl groups and *meta*-hydrogens on the mesityl (**3a**) group both give rise to two singlets in ^{1}H NMR as well. The $^{13}C_{NHC}$–Pd^0 resonances all fall in the expected range (187–191 ppm) corresponding to shifts of monodentate bis-carbene $Pd^0(\eta^2$-ma) equivalents (185–189 ppm),[33,34] and slightly upfield compared to their mono-carbene analogue (193 ppm).[35]



Scheme 2 Synthesis of the [Pd^0(bis-NHC)(η^2-ma)] **3** and [Pd^{II}(bis-NHC)(η^3-C_3H_5)]Cl **4** complexes *via* the silver complexes.

Table 1 Chemical shifts and multiplicity in NMR spectra of Pd^0 and Pd^{II} complexes, **3** and **4**

Complex	$C_{Carbene}$ (ppm)	Backbone-H (ppm)	Linker-H (ppm, multiplicity)
3a	187	7.38, 6.69	6.54, 5.97 (d)
3b	191	7.13, 6.93	5.29, 4.34 (dd)
3c	—[a]	7.68, 7.31	6.52, 5.71 (d)
3d	186	7.11, 6.93	5.89 (dd)
3e	184	7.10, 6.96	5.81 (dd)
4a	177	8.35, 6.99	7.46, 6.56 (d)
4b	181	7.55, 6.82	5.29–5.07 (m)[b], 3.04 (dd)
4c	175	8.11, 6.96	7.05, 6.19 (d)
4d	176	8.06, 6.93	7.52, 6.46 (bs)
4e	175	8.01, 7.04	6.82, 6.12 (bs)

[a] Not detectable, even with prolonged relaxation times. [b] Due to overlap with the signal of an allylic hydrogen the expected doublet of doublets could not be observed.

It appeared that the stability of these complexes depends on the N-substituents. Complexes **3c** and **3e** decomposed in solution and also for **3d** the formation of palladium black was observed after a couple of hours in dichloromethane. This instability has been observed for zero-valent mono-carbene palladium complexes bearing alkyl substituents as well,[36] and can be attributed to the absence of steric protection of the electron-rich metal center. The decomposition of **3c** in solution hampered the detection of the carbene signal in ^{13}C NMR spectroscopy. The complexes with the bulkier mesityl substituents, which have been used previously to ensure stability of palladium complexes bearing these ligands,[32,37,38] were stable in solution and resistant against air and moisture at room temperature for at least a week. In contrast to the findings of Riederer *et al.*,[3] we did not observe a relation between stability and linker length.

$[Pd^{II}(bis\text{-}NHC)(\eta^3\text{-}C_3H_5)]Cl$ complexes, **4**, have been synthesized *via* the same route as their zero-valent counterparts (Scheme 2). Transmetallation from the corresponding silver(I) complexes proceeded in reasonable to high yields. The resulting cationic complexes were all stable in solution and to air.

The reduced electron density on the metal of these stable palladium(II) complexes is reflected in their NMR spectra through a downfield shift of signals for the backbone hydrogens and an upfield shift for the signal of the carbene-carbon compared to the zero-valent counterparts (Table 1). In the ^{13}C NMR spectra two signals are present for the allyl group, indicating a symmetric structure for the complexes and a non-coordinating chloride anion. Again, the hydrogens of the linker give rise to two doublets in ^1H NMR spectroscopy for **4a** and **4c**, and a doublet of doublets for **4b**, indicating the inequivalence of these hydrogens and the non-fluxional behavior of the complexes at room temperature. Exceptions are complexes **4d** and **4e**, which show two broad singlets around 7.52, 6.46, 6.82 and 6.12 ppm respectively, indicating fluxionality that could be caused by a lower barrier to allyl rotation. Variable temperature 300 MHz ^1H NMR experiments showed that, according to expectation, these resonances become doublets upon cooling to −20 °C for **4e** in dichloromethane, whereas the allyl peaks broaden.

Solid state structure of 3a

X-ray quality crystals of **3a** were obtained by slow vapor diffusion of pentane into a concentrated dichloromethane solution of the complex. The X-ray crystal structure (Fig. 2a) confirms that the palladium center is coordinated to the bis-carbene in a chelating fashion. The complex adopts a planar geometry around the transition metal center, while the six-membered metallacycle, formed by the chelating bis-carbene and palladium center, shows a boat conformation (Fig. 2b). The NHCs are bent out of the metal coordination plane with dihedral angles of up to 28°. The bis-carbene bite angle of the complex is 87.50(9)°, a small deviation from the ideal angle dictated by the methylene bridge.[39]

The palladium(0)–carbene bond distances of **3a** are shorter than those of the recently reported Y-shaped $[Pd^0(bis\text{-}NHC)$-

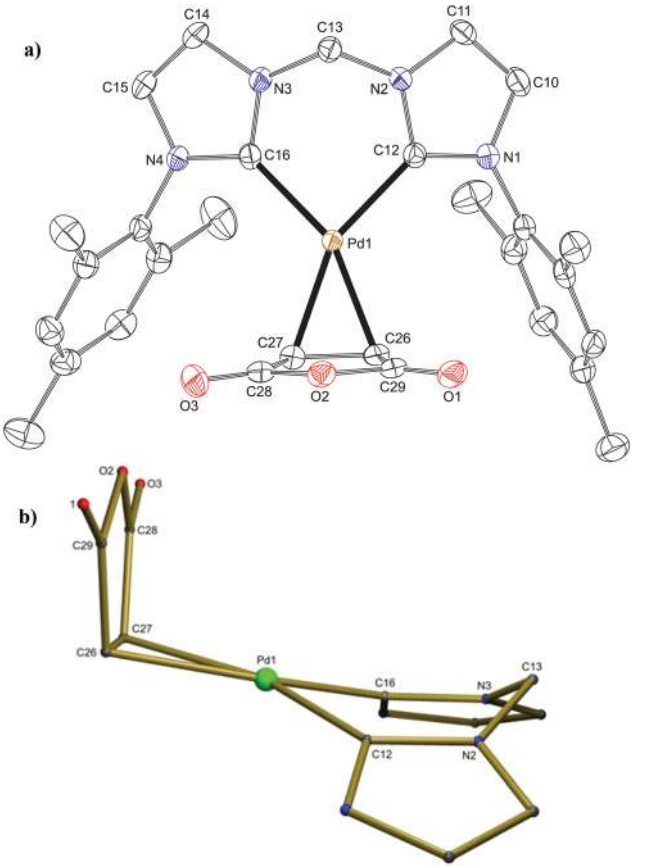


Fig. 2 (a) Molecular structure of complex **3a** in the crystal, drawn at the 50% probability level. Hydrogen atoms and dichloromethane solvent molecules are omitted for clarity. Selected bond distances (Å) and (dihedral) angles (°): Pd1–C12: 2.046(2); Pd1–C16: 2.045(2); C26–C27: 1.445(3); C16–Pd1–C12: 87.50(9); C12–Pd1–C26: 115.26(9); C27–Pd1–C16: 116.64(10); C26–Pd1–C27: 40.18(9); Pd1–C12–C16–C26–C27^N1–N2–C10–C11–C12: 27.54(12); Pd1–C12–C16–C26–C27^N3–N4–C14–C15–16: 23.64(13); Pd1–C12–C16–C26–C27^C26–C27–C28–C29–O2: 77.59(12). (b) Conformation of the six-membered metallacycle in **3a** and orientation of η^2-maleic anhydride with respect to the Pd plane. Mesityl substituents and hydrogens are omitted for clarity.

(ma)] complex containing two dissymmetric monodentate NHC ligands (2.061(2)–2.067(3) Å),[33] but are in agreement with the values of chelate heteroditopic zero-valent palladium complexes (2.0315(14)–2.045(2) Å).[26,40–42] In addition, Lee *et al.* reported unequal palladium-carbene lengths within their zero-valent monodentate bis-carbene palladium complexes in the same range (2.043(4)–2.070(3) Å).[43] The C=C double bond of the maleic anhydride, which is η^2 coordinated to the metal center and almost perpendicular to the coordination plane (Fig. 2), is elongated compared to the free alkene due to π-back bonding from the palladium(0) center.

Suitable crystals of **4a** were obtained as well, by slow vapor diffusion of pentane into a concentrated dichloromethane solution of the complex, but the structure could not be solved satisfactorily. A large number of solvent molecules were present in the crystal structure, which led to a high degree of disorder. The results did however show unequivocally that the carbene was coordinated in a bidentate fashion and that the chloride anion was not coordinated to the metal center.

Catalytic semihydrogenation of 1-phenyl-1-propyne

Palladium NHC complexes have been successfully applied in many reactions,[44–46] including the (transfer) semihydrogenation of alkynes (Scheme 3).[15,41,47] We applied complex **3a** in this reaction, using 1-phenyl-1-propyne as the substrate and formic acid as a hydrogen donor at 70 °C in acetonitrile. Unfortunately, this complex showed poor activity of only 18% conversion for this system (Table 2, entry 1). Considering the proposed mechanism for the mono-NHC analogue in which both formic acid and the alkyne coordinate to the Pd^0 center,[15] this may be explained by the presence of only one available vacant site in this system, whereas two are needed if the same mechanism would hold here.

When hydrogen gas was used as the source of hydrogen, the complex proved to be more active (Table 2, entry 2). After an induction period of approximately four hours, presumably needed for sufficient alkene dissociation or hydrogenation in order to create a vacant site, the reaction proceeded to completion within two hours (TOF = 49 mol_{sub} mol_{cat}^{-1} h^{-1}). Moreover, **3a** showed high selectivity towards the *Z*-alkene up to 80% conversion. When most of the alkyne was consumed, over-reduction to the alkane was observed (Fig. 3). The catalyst was still active when adding a new substrate after almost full conversion of the alkyne.

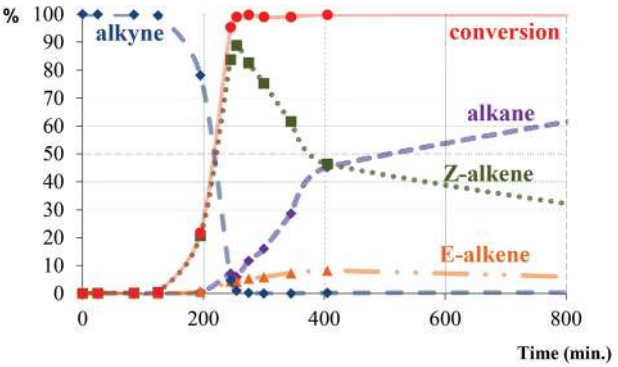
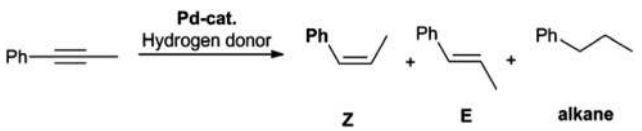


Fig. 3 Selectivity of catalyst **3a** in the semihydrogenation of 1-phenyl-1-propyne over time.

Bis-carbene complex **3a** showed good activity and selectivity in the semihydrogenation of 1-phenyl-1-propyne. However, the results were similar to previously published systems in terms of selectivity and reaction rate.[41,42,48] Catalytic tests with **4a** in both transfer and direct semihydrogenation led to disappointing results, giving no conversion at all. The reason for this lack of catalytic activity may be that the allyl group is not easily hydrogenated. Currently, we are further exploring the possible applications of these complexes.



Scheme 3 Semihydrogenation of 1-phenyl-1-propyne to products. *Z*-Alkene is preferred.

Table 2 Catalytic results of semihydrogenation of 1-phenyl-1-propyne

Entry	Cat	Hydrogen source	*T* (°C)	Time (h)	Conversion (%)	*Z*-/*E*-Alkene/alkane
1	**3a**	HCO_2H/NEt_3	70	29	18	98/2/0
2	**3a**	H_2	60	3	>99	89/4/6

(a) Reaction conditions: 2.2 mmol substrate, <1 mol% catalyst; for entry 1: 5 equiv. HCO_2H/NEt_3; for entry 2: $p(H_2)$ = 1 bar. (b) Product distribution as determined by GC at 18% and 99% conversion respectively.

Conclusion

We have described the synthesis and characterization of the first chelate bis-NHC palladium(0) and palladium(II) allyl complexes with various substituents on the wingtip position. Also the length of the linker moiety was varied. Except for the Pd^0(bis-NHC) complexes bearing alkyl substituents, the formed bis-carbene complexes were stable to air and in solution.

In contrast to their mono-carbene analogues these complexes, which lack an additional coordination site, proved to be inactive in the transfer semihydrogenation of 1-phenyl-1-propyne. On the other hand the zero-valent palladium bis-carbene complex **3a** does catalyze the reaction when molecular hydrogen (1 bar) is used and comparable activity and initial selectivity are observed as in systems using mono-carbene palladium complexes. The Pd^{II} allyl equivalent showed no conversion for the semihydrogenation under the same conditions, which can be due to the reluctance of the allyl coligand to undergo dissociative processes or reduction to the active palladium(0) species. Possibly, since they constitute in principle (re)active organometallic pre-catalysts, the current and similar new Pd(bis-NHC)(L) complexes will be

amenable to carbon–carbon and other carbon-element coupling reactions.

Experimental

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard methods.[49] All reagents were purchased from commercial suppliers and used without further purification. The following starting materials were synthesized according to literature procedures: mesitylimidazole,[50] butylimidazole,[51] the bisimidazolium dibromides[23] and [Pd(*t*BuDAB)(η²-ma)].[52] The silver(I) complexes were also prepared by following reported procedures; in MeOH for R = Me, Benz, *n*Bu[29] or dichloromethane for R = Mes.[28] The NMR spectra were recorded on Varian Mercury 300 MHz, Bruker DRX 300 and Bruker AMX 400 MHz spectrometers. Data for NMR are reported as follows: chemical shift in parts per million (δ, ppm) relative to TMS, determined by reference to residual ^{1}H and ^{13}C solvent resonances, where applicable multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), the number of hydrogens and coupling constant (Hz). Mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer and GC analyses were performed with an Interscience Trace GC Ultra instrument using an Rxi fused silica capillary column and *p*-xylene as the internal standard.

General procedure for the synthesis of bis-NHC palladium(0) maleic anhydride complexes

[Pd(*t*BuDAB)(η²-ma)] (1 equiv.) was added to a solution (0.02 M) of the corresponding silver(I) complex in dichloromethane and the mixture was stirred for 3 hours at 20 °C upon which the greyish silver salt precipitated. The mixture was filtered over a pad of Celite and concentrated to a few mL. Then pentane was added to precipitate the product, which was isolated by decanting the solvent and washed twice with pentane to yield the product.

Methyl-1,1-di(mesitylimidazol-2-ylidene) palladium(0) maleic anhydride, 3a. Slightly yellow solid, 65 mg, 0.12 mmol, 80%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.38 (2H, d, $^3J_{HH}$ = 1.5 Hz, CH), 7.14 (2H, s, *m*-aryl-H), 6.96 (2H, d, $^3J_{HH}$ = 1.5 HZ, CH), 6.92 (2H, s, *m*-aryl-H), 6.54 (1H, d, $^2J_{HH}$ = 13.2 Hz, CH_2), 5.97 (d, $^2J_{HH}$ = 13.2 Hz, 1H, CH_2), 2.38 (6H, s, *p*-aryl-CH_3), 2.26 (2H, s, ma), 2.04 (6H, s, *o*-aryl-CH_3), 1.80 (6H, s, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2, 300 MHz): 187.0 (NCN), 173.9 (CO), 138.5 (*p*-aryl-CH), 136.7 (*i*-aryl-C), 136.2 (*o*-aryl-C), 134.9 (*o*-aryl-C), 129.0 (CH), 128.1 (CH), 121.1 (*m*-aryl-CH), 120.8 (*m*-aryl-CH), 64.1 (CH_2), 38.4 (alkene), 20.8 (*p*-aryl-CH_3), 17.6 (*o*-aryl-CH_3), 17.5 (*o*-aryl-CH_3). MS(FAB^+) for $C_{28}H_{31}N_4O_2Pd$: *m*/*z* calculated 561.1493[M − CO + H]$^+$, observed 561.1487.

Ethyl-1,1-di(mesitylimidazol-2-ylidene) palladium(0) maleic anhydride, 3b. Pale brown solid, 63 mg, 0.10 mmol, 99%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.13 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 7.04 (2H, s, *m*-aryl-H), 6.93 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 6.86 (2H, s, *m*-aryl-H), 5.29 (2H, dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 6.2 Hz, CH_2), 4.34 (2H, dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 6.2 Hz, CH_2), 2.32 (6H, s, *p*-aryl-CH_3), 2.16 (2H, s, ma), 2.13 (6H, s, *o*-aryl-CH_3), 1.81 (6H, s, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2, 300 MHz): 191.2 (NCN), 171.2 (CO), 138.3 (*p*-aryl-CH), 136.7 (*i*-aryl-C), 136.2 (*o*-aryl-C), 134.9 (*o*-aryl-C), 128.9 (CH), 128.1 (CH), 122.6 (*m*-aryl-CH), 121.0 (*m*-aryl-CH), 49.5 (CH_2), 38.2 (alkene), 20.8 (*p*-aryl-CH_3), 17.7 (*o*-aryl-CH_3), 17.6 (*o*-aryl-CH_3). MS(FAB^+) for $C_{29}H_{34}N_4O_2Pd$: *m*/*z* calculated 504.1516 [M − CO + H]$^+$, observed 504.1516.

Methyl-1,1-di(methylimidazol-2-ylidene) palladium(0) maleic anhydride, 3c. Pale yellow solid, 64 mg, 0.17 mmol, 70%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.36 (2H, s, CH), 6.97 (2H, s, CH), 6.60 (1H, d, $^2J_{HH}$ = 12.1 Hz, CH_2), 5.63 (1H, d, $^2J_{HH}$ = 12.1 Hz, CH_2), 3.82 (2H, s, ma) 3.36 (6H, s, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): 171.9 (CO), 124.5 (CH), 123.7 (CH), 64.4 (CH_2), 39.5 (alkene), 38.0 (CH_3). MS(FAB^+) for $C_9H_{12}N_4Pd$: *m*/*z* calculated 282.0100 [M − ma]$^+$, observed 282.0121.

Methyl-1,1-di(benzylimidazol-2-ylidene) palladium(0) maleic anhydride, 3d. Brown solid, 83 mg, 0.16 mmol, 98%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.41–7.26 (10H, m, aryl-H), 7.11 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 6.93 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 5.89 (2H, dd, $^2J_{HH}$ = 17 Hz, CH_2), 5.41 (2H, d, $^2J_{HH}$ = 2.7 Hz, CH_2), 3.69 (2H, s, ma). ^{13}C NMR (CD_2Cl_2, 75 MHz): 186.5 (NCN), 174.7 (CO), 138.5 (*p*-aryl-CH), 136.7 (*i*-aryl-C), 136.2 (*o*-aryl-C), 134.9 (*o*-aryl-C), 129.0 (CH), 128.1 (CH), 121.1 (*m*-aryl-CH), 120.8 (*m*-aryl-CH), 64.1 (CH_2), 39.0 (alkene), 20.8 (*p*-aryl-CH_3), 17.6 (*o*-aryl-CH_3), 17.5 (*o*-aryl-CH_3). MS(FAB^+) for $C_{24}H_{23}N_4O_2Pd$: *m*/*z* calculated 505.0865 [M − CO + H]$^+$, observed 505.0865.

Methyl-1,1-di(*n*Butylimidazol-2-ylidene) palladium(0) maleic anhydride, 3e. Pale brown solid, 35 mg, 0.08 mmol, 42%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.10 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 6.96 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 5.81 (2H, dd, $^2J_{HH}$ = 12 Hz, CH_2), 4.25–4.04 (4H, m, CH_2), 3.59 (2H, s, CH-ma), 1.85–1.65 (4H, m, CH_2), 1.40–1.22 (4H, m, CH_2), 0.91 (6H, t, $^3J_{HH}$ = 7.3 Hz, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) 183.9 (NCN), 175.0 (CO), 119.9 (CH), 119.8 (CH), 63.0 (CH_2), 51.0 (CH_2), 38.4 (alkene), 33.6 (CH_2), 19.7 (CH_2), 13.61 (CH_3). MS(FAB^+) for $C_{15}H_{24}N_4Pd$: *m*/*z* calculated 366.1042 [M − ma]$^+$, observed 366.1053.

General procedure for synthesis of bis-NHC palladium(II) η³-allyl chloride complexes

[Pd(η³-allyl)Cl]$_2$ (0.5 equiv.) was added to a solution (0.02 M) of the silver complex in dichloromethane and the mixture was stirred for 3 hours at room temperature upon which a greyish silver salt precipitated. The mixture was filtered over a pad of Celite and concentrated to yield the product.

Methyl-1,1-di(mesitylimidazol-2-ylidene) palladium(II) η³-allyl chloride, 4a. Off white solid, 90 mg, 0.16 mmol, 99%). ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.35 (2H, d, $^3J_{HH}$ = 2.0 Hz, CH), 7.46 (1H, d, $^2J_{HH}$ = 13 Hz, CH_2), 6.99 (2H, d, $^3J_{HH}$ = 2.0 Hz, CH), 6.92 (4H, s, *m*-aryl-H), 6.56 (1H, d, $^2J_{HH}$ = 13 Hz, CH_2), 4.65 (1H, m, allyl-CH), 2.91 (2H, dt, $^3J_{HH}$ = 7.6, $^2J_{HH}$ = 1.1 Hz, allyl-CH_2), 2.32 (6H, s, *p*-aryl-CH_3), 1.94 (6H, s, *o*-aryl-CH_3), 1.89 (6H, s, *o*-aryl-CH_3), 1.67 (2H, dt $^3J_{HH}$ = 7.6, $^2J_{HH}$ = 1.1 Hz, allyl-CH_2). ^{13}C NMR (CD_2Cl_2, 300 MHz): 176.6 (NCN), 139.9 (*p*-aryl-CH), 137.1 (*i*-aryl-C), 135.9 (*o*-aryl-C), 135.6 (*o*-aryl-C),

129.3 (*m*-aryl-CH), 124.0 (CH), 122.1 (CH), 119.2 (allyl), 63.7 (CH_2), 58.7 (allyl), 21.3 (*p*-aryl-CH_3), 18.0 (*o*-aryl-CH_3). MS-(FAB$^+$) for $C_{28}H_{34}N_4Pd$: *m*/*z* calculated 531.1751 $[M - Cl]^+$, observed 531.1757.

Ethyl-1,1-di(mesitylimidazol-2-ylidene) palladium(II) η^3-allyl chloride, 4b. Off white solid, 102 mg, 0.18 mmol, 92%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.55 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 7.03 (2H, s, *m*-aryl-H), 6.98 (2H, s, *m*-aryl-H), 6.82 (2H, d, $^3J_{HH}$ = 1.8 HZ, CH), 5.29–5.07 (3H, m, CH_2, allyl-CH overlapping), 4.07 (2H, d, $^2J_{HH}$ = 7.4 Hz, allyl-CH_2), 3.36 (2H, d, $^2J_{HH}$ = 5.4 Hz, allyl-CH_2) 3.04 (2H, dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 6.0 Hz, CH_2), 2.36 (6H, s, *p*-aryl-CH_3), 2.23 (3H, s, *o*-aryl-CH_3), 2.18 (3H, s, *o*-aryl-CH_3), 2.08 (3H, s, *o*-aryl-CH_3), 2.02 (3H, s, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2, 101 MHz): 181.7 (NCN), 139.5 (*p*-aryl-CH), 136.8 (*i*-aryl-C), 136.2 (*o*-aryl-C), 136.0 (*o*-aryl-C), 129.5 (CH), 129.4 (CH), 124.3 (*m*-aryl-CH), 122.6 (*m*-aryl-CH), 49.6 (CH_2), 21.4 (*p*-aryl-CH_3), 18.7 (*o*-aryl-CH_3), 18.6 (*o*-aryl-CH_3). MS(FAB$^+$) for $C_{29}H_{35}N_4Pd$: *m*/*z* calculated 545.1908 $[M - Cl]^+$, observed 545.1914.

Methyl-1,1-di(methylimidazol-2-ylidene) palladium(II) η^3-allyl chloride, 4c. Pale brown solid, 41 mg, 0.11 mmol, 63%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.11 (2H, s, CH), 7.05 (1H, bd, $^2J_{HH}$ = 13 Hz, CH_2), 6.96 (2H, s, CH), 6.19 (1H, bd, $^2J_{HH}$ = 13 Hz, CH_2), 5.26 (1H, m, allyl-CH), 4.18 (2H, bd, $^2J_{HH}$ = 10 Hz, allyl-CH_2), 3.75 (6H, s, CH_3), 2.85 (2H, d, $^2J_{HH}$ = 10 Hz, allyl-CH_2). ^{13}C NMR (CD_2Cl_2, 101 MHz): 175.1 (NCN), 122.9 (CH), 120.8 (CH), 119.3 (allyl), 62.4 (CH_2), 58.2 (allyl), 38.5 (CH_3). MS (FAB$^+$) for $C_{12}H_{17}N_4Pd$: *m*/*z* calculated 323.0493 $[M - Cl]^+$, observed 323.0497.

Methyl-1,1-di(benzylimidazol-2-ylidene) palladium(II) η^3-allyl chloride, 4d. Pale yellow/brown solid, 51 mg, 0.10 mmol, 99%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.06 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 7.52 (1H, bs, CH_2), 7.45–7.25 (6H, m, aryl-H), 7.21–7.09 (4H, m, aryl-H), 6.93 (2H, d, $^3J_{HH}$ = 1.8 Hz, CH), 6.44 (1H, bs, CH_2), 5.32–5.19 (1H, m, allyl-CH), 5.29 (4H, s, CH_2), 4.05 (2H, d, $^3J_{HH}$ = 6.0 Hz, allyl-CH_2), 2.78 (2H, d, $^3J_{HH}$ = 13.3 Hz, allyl-CH_2). ^{13}C NMR (CD_2Cl_2, 101 MHz): 176.4 (NCN), 136.4 (aryl-C), 129.6 (aryl-CH), 128.9 (aryl-CH), 127.8 (aryl-CH) 123.20 (CH), 129.7 (CH), 120.2 (allyl), 63.14 (CH_2), 59.34 (allyl), 55.60 (CH_2). MS-(FAB$^+$) for $C_{24}H_{25}N_4Pd$: *m*/*z* calculated 475.1124 $[M - Cl]^+$, observed 475.1127.

Methyl-1,1-di(*n*Butylimidazol-2-ylidene) palladium(II) η^3-allyl chloride, 4e. Pale brown solid, 123 mg, 0.28 mmol, 99%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.01 (2H, d, $^3J_{HH}$ = 1.9 Hz, CH), 7.04 (2H, d, $^3J_{HH}$ = 1.9 Hz, CH), 6.12 (2H, bs, CH_2), 5.38–5.24 (1H, m, allyl-CH), 4.17 (2H, d, $^3J_{HH}$ = 7.4 Hz, allyl-CH_2), 4.09 (4H, m, CH_2), 2.86 (2H, d, $^3J_{HH}$ = 13.2 Hz, allyl-CH_2), 1.74 (2H, m, CH_2), 1.44–1.21 (4H, m, CH_2), 0.93 (6H, t, $^3J_{HH}$ = 7.4 Hz, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): 174.8 (NCN), 123.3 (CH), 122.8 (CH), 119.99 (allyl), 58.10 (allyl), 51.32 (CH_2), 40.8 (CH_2), 33.4 (CH_2), 19.7 (CH_2), 13.4 (CH_3). MS(FAB$^+$) for $C_{12}H_{17}N_4Pd$: *m*/*z* calculated 407.1434 $[M - Cl]^+$, observed 407.1432.

General procedure for catalytic transfer semihydrogenation

To a carousel vial equipped with a cross-head stirring bar and 1 mol% of catalyst, 10 mL of a stock solution (*c* = 0.15 M) of 1-phenyl-1-propyne, *p*-xylene as an internal standard, triethylamine (5 equiv.) and formic acid (5 equiv.) in MeCN were added. The mixture was stirred under nitrogen at 70 °C and monitored by GC.

General procedure for catalytic semihydrogenation with H_2

To a two-neck Schlenk equipped with a cross-head stirring bar, a balloon with hydrogen gas and 1 mol% of catalyst, 10 mL of a stock solution (*c* = 0.15 M) of 1-phenyl-1-propyne in MeCN with *p*-xylene as an internal standard was added. The mixture was stirred under H_2 pressure at 60 °C and monitored by GC.

X-ray structural determination

X-ray intensities were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å). The intensities were integrated using Saint.[53] Absorption correction and scaling was performed with SADABS.[54] The structures were solved using Direct Methods in the program SHELXS-97.[55] Least-squares refinement was performed refined with SHELXL-97[55] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps. Hydrogen atoms of the maleic anhydride ligand were refined freely with isotropic displacement parameters; all other hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[56]

Compound 3a. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane to a solution of the product in dichloromethane. $C_{29}H_{30}N_4O_3Pd\cdots0.5(CH_2Cl_2)$, Fw = 631.43, colourless needle, 0.29 × 0.07 × 0.07 mm^3, triclinic, $P\bar{1}$ (no. 2), *a* = 11.0535(6), *b* = 11.5821(7), *c* = 11.9965(6) Å, α = 101.2168(17), β = 99.4456(17), γ = 106.8020(17)°, *V* = 1401.91(13) Å^3, *Z* = 2, D_x = 1.496 g cm^{-3}, μ = 0.80 mm^{-1}. 28 028 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150(2) K. 6357 Reflections were unique (R_{int} = 0.032), of which 5611 were observed [$I > 2\sigma(I)$]. 366 Parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0315/0.0804. R_1/wR_2 [all refl.]: 0.0394/0.0845. *S* = 1.048. Residual electron density was between −1.27 and 0.90 e Å^{-3}.

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