ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Zerovalent [Pd(NHC)(Alkene)$_{1,2}$] Complexes Bearing Expanded-Ring N-Heterocyclic Carbene Ligands in Transfer Hydrogenation of Alkynes

Peter Hauwert,[†,⊥] Jay J. Dunsford,[‡,#] Dorette S. Tromp,[†] Jan J. Weigand,[§] Martin Lutz,[∥] Kingsley J. Cavell,*[,‡] and Cornelis J. Elsevier*[,†]

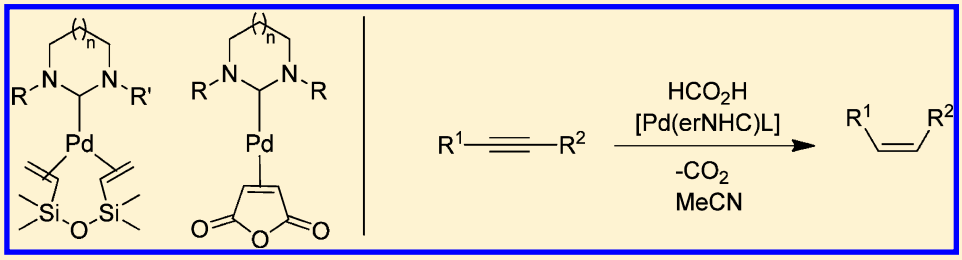
[†]Molecular Inorganic Chemistry, Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, Postbus 94157, 1090 GD Amsterdam, The Netherlands

[‡]School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

[§]Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, 48149 Münster, Germany

[∥]Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Supporting Information



ABSTRACT: In search of more active catalysts for the transfer hydrogenation of alkynes, a series of [Pd(NHC)(MA)$_{1,2}$] (**8**−**14**) and [Pd(NHC)(dvtms)] complexes (**1**−**7**), in which the NHC ancillary ligands are expanded-ring N-heterocyclic carbenes (erNHC's), have been prepared. These very bulky, strong σ-donor ligands impart a highly constrained geometry on the complexes and in some cases enable the isolation of coordinatively and electronically unsaturated complexes (**10** and **14**). Their strong σ-donor character is reflected in a decrease in IR stretching frequency for the C═O bond of the maleic anhydride ligands (**8**−**14**) in comparison to their five-membered counterparts. Significantly enhanced catalytic activity in the transfer hydrogenation of 1-phenyl-1-propyne is observed using [Pd(erNHC)(dvtms)] complexes (**1**−**7**) as precatalysts. The catalysts show high initial selectivity toward (*Z*)-alkene. However, double-bond isomerization and over-reduction to the corresponding alkane occur when all the alkyne substrate is consumed; this feature reflects the very high efficiency of these catalysts in the transfer hydrogenation of alkynes as well as alkenes.

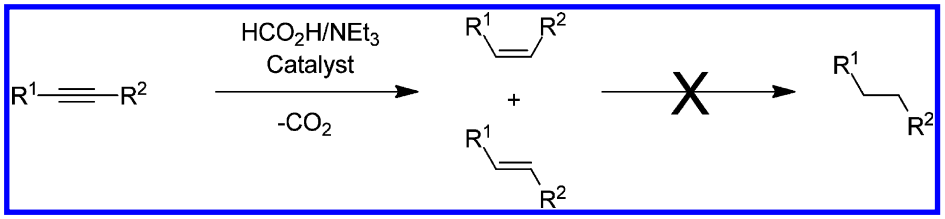
INTRODUCTION

Catalytic transfer hydrogenation is an effective tool for the reduction of carbonyl compounds, using alcohols or ammonium formate as hydrogen donors and Ru(II), Ir(I), or Rh(I) complexes as catalysts.[1] Notably, a plethora of transfer hydrogenation reactions involving ketones and imines have been reported, since polar double bonds are easily reduced.[2−5] In contrast, transfer hydrogenation of carbon−carbon multiple bonds has been scarcely reported, as it is far more difficult to achieve.[1b,5−8] While several homogeneous catalytic systems are known for transfer hydrogenation of alkenes, only three have been reported for transfer semihydrogenation of alkynes to give alkenes (Scheme 1).[7,9] Especially α-arylalkynes have proven to be difficult substrates, in both transfer hydrogenation and hydrogenation using dihydrogen.[8,9]

Semihydrogenation of alkynes is traditionally performed with Lindlar's catalyst and dihydrogen, which requires a rather elaborate experimental setup and strict monitoring of the hydrogen uptake to prevent over-reduction. Also, unsolicited partial *Z*/*E* isomerization, double-bond shifts, and problems with reproducibility occur.[10] Only very few homogeneous palladium catalysts are known to catalyze the desirable, selective semihydrogenation of alkynes to (*Z*)-alkenes. So far, only [Pd(Ar-Bian)(η^2-alkene)] complexes, containing a bis-(arylimino)acenaphthene ligand utilizing molecular hydrogen, and [Pd(NHC)L$_n$] (L = alkene, solvent; n = 1, 2), containing an N-heterocyclic carbene ligand employing transfer hydrogenation, have been reported to effectively hydrogenate a variety of alkynes to the (*Z*)-alkenes with good to excellent chemo- and stereoselectivity.[8,9]

Received: October 3, 2012
Published: December 19, 2012

Scheme 1. Transfer Semihydrogenation of Alkynes, Using Triethylammonium Formate as Hydrogen Donor

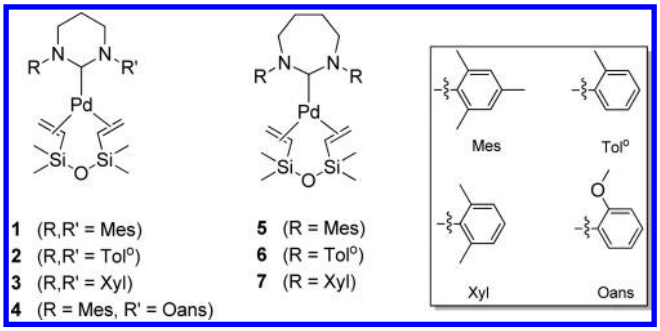


Recently, the mechanism for the fully stereo- and chemoselective transfer hydrogenation of alkynes to *cis*-alkenes employing [Pd(IMes)(MA)(solvent)] complexes and triethylammonium formate as the hydrogen donor has been elucidated, along with an explanation for the high chemospecificity for alkynes over alkenes.[11] It was found that the electron density on the metal center positively correlates with the reaction rate and inversely correlates with chemoselectivity. For alkynes with electron-releasing substituents, such as bis(4-methoxyphenyl)acetylene, the chemoselectivity is high but the reaction rate is lower in comparison with that for aliphatic or other aromatic alkynes. We have ascribed this behavior to the lower affinity of electron-rich alkynes for coordination to electron-rich Pd(0)−NHC complexes.[12] In light of this, we decided to investigate the impact of strongly donating and sterically demanding ligands such as expanded-ring N-heterocyclic carbenes (erNHC's) on the conversion of electron-rich and/or sterically hindered substrates.

The application of N-heterocyclic carbenes (NHC's) as ligands for homogeneous catalysts[13] has led to enhanced opportunities,[14] and their use in the past decade has grown exponentially, in parallel with an improved understanding of the strong donor ability and metal−ligand bond character of this class of ligand.[14e,15,16,17] This has led to several new sets of carbene architectures, such as remote and abnormal NHC's,[18] acyclic carbenes,[15f,19] bioxazoline-based NHC's,[20] and benzannulated NHC's.[21] A very recent addition to the NHC ligand armory has been the development of a series of expanded-ring NHC's with large σ-donor capacity and substantial steric demands due to an inherent increase in the N−C_{NHC}−N bond angle.[22] The simplicity and high modularity of the synthetic route allow facile adjustment of donating capacity and steric influence through variation of heterocycle ring size and N substituents. Additional donor functionalities can also be introduced on the N substituents[22b,23] or on the backbone,[24] and this methodology has led to a variety of novel erNHC complexes with metals such as Rh,[22a,b,24] Ir,[23,24c] Pt,[25] Ag,[26] Pd,[27] Ru,[28] Ni,[29] Cu,[26b,30] and Au.[22c,31] Recently, the list was extended to include complexes of zerovalent palladium, [Pd(erNHC)(dvtms)] (Scheme 2), which were found to generate highly active catalysts for Mizoroki−Heck cross-coupling.[27c] Iridium complexes bearing erNHC ligands have also recently been shown to be extremely effective catalysts for the transfer hydrogenation of ketones with iPrOH as the source of hydrogen.[23]

Building on our previous hydrogenation and synthetic studies, we report here the synthesis and full characterization of novel [Pd(erNHC)$(MA)_{1,2}$] complexes, along with the X-ray crystal structure of an air-stable 14-electron Pd(0) species, and probe their suitability as catalysts in the selective transfer hydrogenation of alkynes to *cis*-alkenes.

Scheme 2. Expanded Ring NHC Pd(0) Complexes of the General Formula [Pd(erNHC)(dvtms)] (1−7), Previously Employed in Mizoroki−Heck Cross-Coupling[27c]



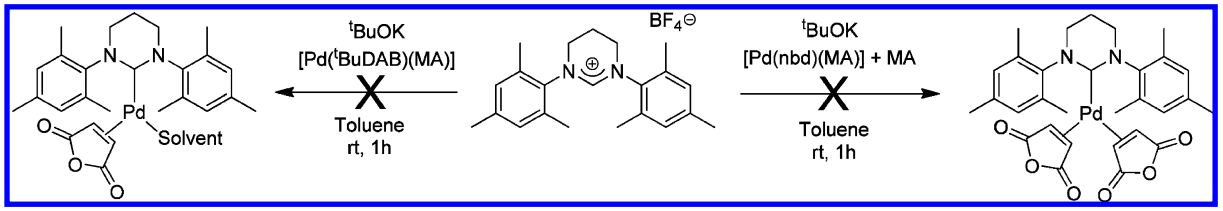
RESULTS AND DISCUSSION

In order to explore the steric and electronic effects of exchanging IMes by erNHC's, a series of six- and seven-membered amidinium salts bearing 2-methylphenyl (Tol°), 2,4,6-trimethylphenyl (Mes), 2,6-diisopropylphenyl (DIPP), and 4-methylphenyl (Tol^p) N-aryl substituents were prepared, following previously reported procedures.[26a] Initially, attempts were made to prepare complexes of the general formula [Pd(erNHC)$(MA)_2$], following the approach employed for the previously reported IMes-based derivatives:[32] i.e., by in situ generation of the free carbene followed by addition of [Pd(*t*BuDAB)(MA)] in toluene (Scheme 3).[32] However, no reaction was observed, and after addition of an extra 1 equiv of maleic anhydride to the solution the Pd(0) precursor was recovered in more than 90% yield. As the N−C_{NHC}−N bond angle in erNHC's is notably larger than in the five-membered derivatives (IMes, 101°; 6-Mes, 114°; 7-Mes, 116°),[33,26a] the N substituents are thrust in toward the carbene carbon, hindering the approach of the sterically encumbered [Pd(*t*BuDAB)(MA)] precursor. When the less hindered Pd(0) precursor [Pd(nbd)(MA)][34] was employed, a reaction was observed upon addition of the in situ generated free carbene (Scheme 3). However, ^{1}H and $^{13}C\{^1H\}$ NMR data for the isolated product demonstrated the presence of substantial amounts of unidentifiable byproducts; therefore, an alternate approach was necessary.

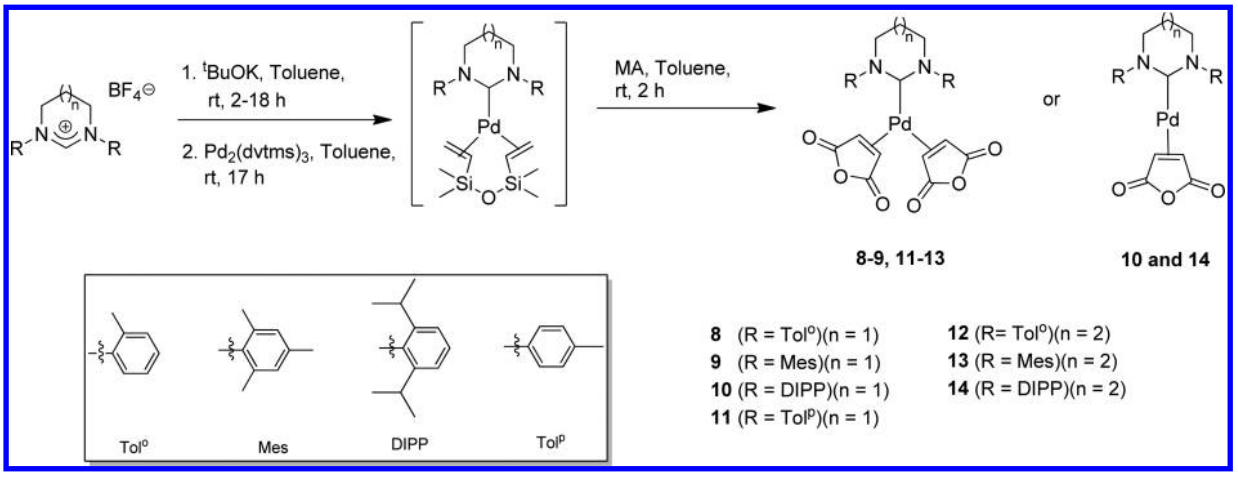
In search of a suitable alternate approach for the synthesis of [Pd(erNHC)$(MA)_2$] complexes, the previously described [Pd(erNHC)(dvtms)] complexes (Scheme 2)[27c] were employed as well-defined Pd(0) parent precursors in a coligand displacement protocol. The addition of 2 equiv of maleic anhydride to a toluene suspension of the [Pd(erNHC)(dvtms)] complexes resulted in the formation of the corresponding [Pd(erNHC)$(MA)_{1,2}$] complexes **8**−**14** (Scheme 4). The complexes were isolated in low to moderate yields, depending on the steric demand of the NHC ligand. This is reflected in the low yield of **11** (~5%) and an inability to isolate the [Pd(7-Tol^p)$(MA)_2$] complex. Coligand displacement could also be achieved through the in situ generation of

dx.doi.org/10.1021/om300930w | *Organometallics* 2013, 32, 131−140

Scheme 3. Attempted Synthesis of [Pd(erNHC)(MA)$_2$] Complexes from [Pd(^{t}BuDAB)(MA)] and [Pd(nbd)(MA)]



Scheme 4. Synthesis of [Pd(erNHC)(MA)$_{1,2}$] Complexes 8−14 via Coligand Exchange from Parent [Pd(erNHC)(dvtms)] Complexes



the parent [Pd(erNHC)(dvtms)] complexes followed by maleic anhydride addition, obviating the need for isolation of the parent [Pd(erNHC)(dvtms)] complex (see the Experimental Section for details). All complexes after their formation were found to be air-stable in the solid state. Complexes **8**−**11** bearing six-membered NHC ligands are also stable in solution, whereas complexes **12**−**14** with seven-membered NHC ligands slowly decompose in halogenated solvents, as previously noted.[27c] To the best of our knowledge, this is the first reported example of [Pd(NHC)(dvtms)] complexes[35] being employed in coligand exchange reactions involving replacement of dvtms to generate new NHC organometallic complexes (Scheme 4).[36]

Late-transition-metal complexes bearing erNHC's have been noted to exhibit N−C$_{NHC}$−N resonances which are shifted significantly to higher frequency compared with those of five-membered-ring derivatives; these range from 204 to 209 ppm for complexes of 6-NHCs (**8**−**11**) and 215−226 ppm for complexes of 7-NHCs (**12**−**14**) (Table 1). Interestingly, in the related [Pd(erNHC)(dvtms)] complexes **1**−**7** this signal occurs at even higher frequency: for example, 226 and 247 ppm for **1** (6-Mes) and **5** (7-Mes), respectively.[27c] The shift to lower frequency for complexes containing maleic anhydride coligands indicates that there is possibly an increase in π back-donation from palladium to maleic anhydride.[37] In complex **8**, bearing N-Tol° substituents, the maleic anhydride signals appear as sharp doublets at 4.05 and 3.64 ppm, respectively, while for the seven-membered analogue **12** only one sharp singlet is observed at 5.05 ppm. Interestingly, the methylene groups in the backbone of the carbene are all found to be inequivalent. For compounds **9** and **13**, bearing mesityl substituents, the maleic anhydride resonances appear as a broad singlet, similar to the case for the related [Pd(IMes)(MA)$_2$] complex.[11] For compounds **8**, **9**, and **11**−**13** the erNHC and maleic anhydride coligands are present in a 1:2 ratio, whereas the integrals of compounds **10** and **14** indicate a 1:1 ratio. Seemingly, the 2,6-diisopropylphenyl (DIPP) substituents are so sterically demanding that coordination of only one maleic anhydride is possible. This feature is observed not only in the integrals of the peaks in ^{1}H NMR but also in the high-frequency shift of the maleic anhydride alkene resonance by 0.8 and 20 ppm in ^{1}H and ^{13}C{^{1}H} NMR, respectively. The structures of these 14-electron Pd(0) complexes have been confirmed by single-crystal X-ray structure determination of complex **14**, [Pd(7-DIPP)(MA)] (Figure 4).

Table 1. ^{1}H and ^{13}C{^{1}H} NMR and FT-IR Data for [Pd(erNHC)(MA)$_{1,2}$] Complexes 8−14

entry	complex	^{13}C (N$_{NHC}$), ppm	^{1}H/^{13}C (alkene), ppm	ν(CO), cm^{-1}
1	**8**	207.2	4.05/65.8	1813, 1753
2	**9**	209.0	3.79/68.0	1847, 1777
3	**10**	206.8	2.90/48.2	1798, 1730
4	**11**	204.7	3.78/65.5	*c*
5	**12**	*a*	5.08/62.9	1773, 1733
6	**13**	226.3	3.83/68.9	1779, 1711
7	**14**	214.9	2.81/28.1	1794, 1726
8	[Pd(IMes)(MA)$_2$]	193.1[b]	3.53/64.7[b]	1816, 1761

[a]Not observed. [b]Spectra measured at −50 °C; values from ref 9a. [c]Not determined.

The increased Lewis basicity of the erNHC's relative to their five-membered counterparts is also reflected in the IR spectra; increased back-donation into the π^* orbital of the maleic anhydride decreases the strength of the C═O bond. Indeed, for complexes of erNHC's C═O stretching frequencies of the maleic anhydride carbonyls occur at wavenumbers significantly lower than those for [Pd(IMes)(MA)$_2$] (Table 1),[32] and the

dx.doi.org/10.1021/om300930w | Organometallics 2013, 32, 131−140

shift to lower wavenumbers increases with an increase in heterocycle ring size from six- to seven-membered rings. However, for a set of complexes with a single ring size, the C=O stretching frequencies for maleic anhydride shift to higher wavenumbers with increasing steric bulk of the aryl substituents (Tol^p < Tol^o < Mes). As the steric bulk around the palladium center increases, the Pd–alkene bond distances increase, resulting in less efficient π back-donation. However, for complexes with DIPP substituents (**10** and **14**) carbonyl stretching frequencies are significantly lower. This observation may be rationalized on the basis that in the mono(maleic anhydride) complexes (**10** and **14**) the metal donates more electron density per alkene, and the single alkene can now approach the metal center more closely.

Solid-State Analysis. The solid-state structures of complexes **8**, **9**, **11**, and **14** were determined by single-crystal X-ray diffraction: **8**, **9**, and **11** (Figures 1–3) are confirmed as

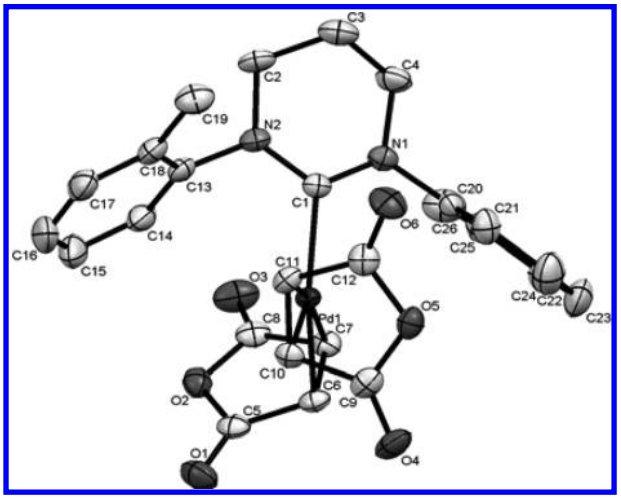


Figure 1. X-ray structure of [Pd(6-Tol^o)$(MA)_2$] (**8**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogens have been omitted for clarity.

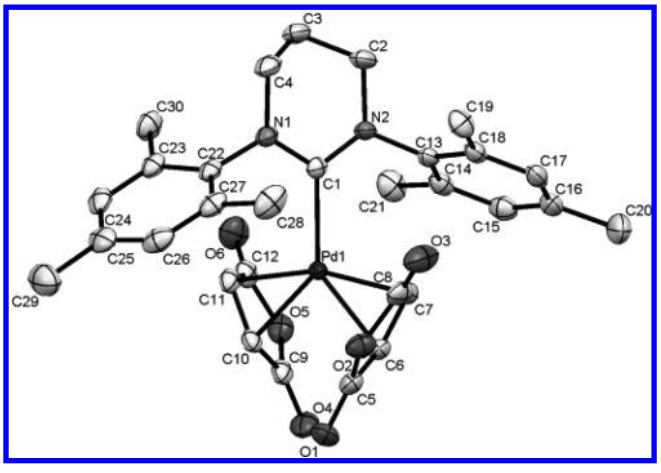


Figure 2. X-ray structure of [Pd(6-Mes)$(MA)_2$] (**9**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogens and solvent molecules have been omitted for clarity.

16-electron [Pd(NHC)$(MA)_2$] complexes, and **14** is a coordinatively unsaturated 14-electron [Pd(NHC)(MA)] complex (Figure 4). Selected bond lengths, bond angles, and dihedral angles are provided in Table 2.

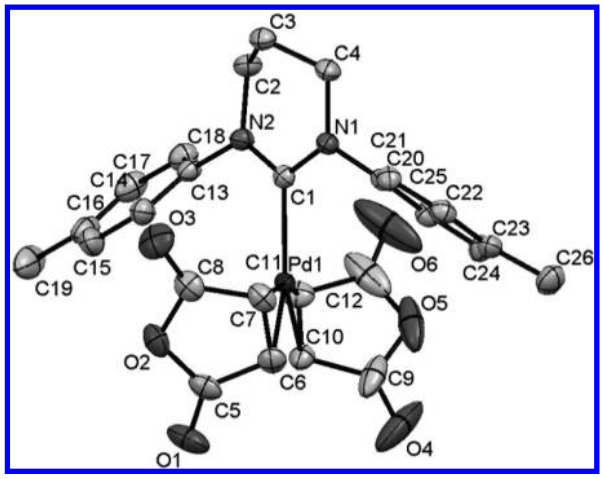


Figure 3. X-ray structure of [Pd(6-Tol^p)$(MA)_2$] (**11**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogens have been omitted for clarity.

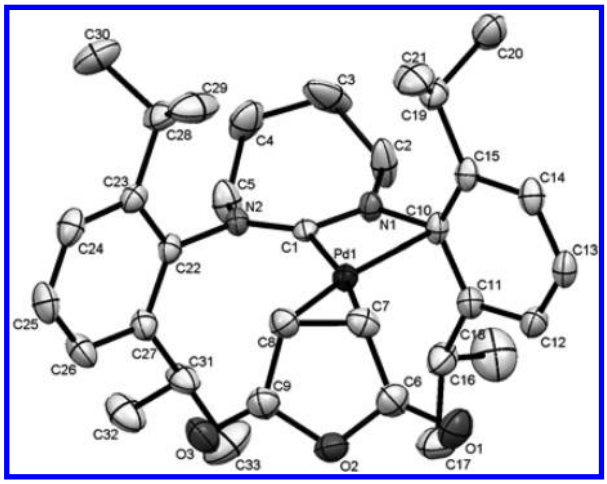


Figure 4. X-ray structure of [Pd(6-DIPP)(MA)] (**14**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogens have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Pd(erNHC)$(MA)_{1,2}$] Complexes 8, 9, 11, and 14

	8	9	11	14
Pd–C_{NHC}	2.113(2)	2.138(2)	2.1109(15)	2.086(3)
Pd–C=$C_{centroid}$	2.018, 2.020	2.039, 2.037	1.971	2.0274(12), 2.0214(12)
N–C_{NHC}–N	118.2	115.8(2)	117.17(14)	120.7(2)
tilt angle θ^a	63.2(3), 63.0(3)	55.0(3), 59.0(3)	54.45(19), 60.58(19)	2.1(3)
twist angle φ^b	70.5(4) 69.7(4)	76.6(4), 71.5(4)	56.89(17), 64.57(17)	88.9(4), 87.5(3)

[a]The tilt angle θ is defined as the angle between the carbene N–C_{NHC}–N plane and the Pd–alkene coordination plane. [b]The twist angle φ is defined as the angle between the carbene N–C_{NHC}–N plane and the plane of the aromatic ring.

As previously noted in earlier studies, we could not isolate either the 2,6-diisopropylphenyl (DIPP)- or 2,6-diethylphenyl (DEP)-substituted analogues of the [Pd(erNHC)(dvtms)] complexes.[27c] It is evident that the combination of chelating dvtms coligand and erNHC's with these large substituents is too sterically demanding. dvtms is a relatively bulky, bidentate ligand, and employing just one of its alkene moieties would not

dx.doi.org/10.1021/om300930w | *Organometallics* 2013, 32, 131–140

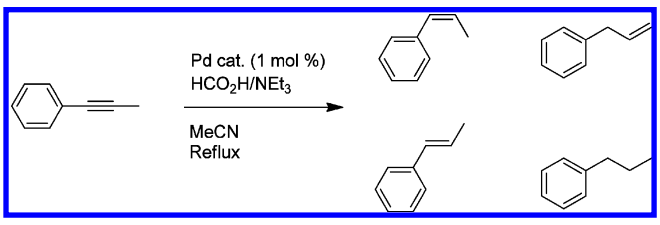
provide sufficient electron-withdrawing capacity to stabilize the coordinatively unsaturated geometry dictated by these bulky substituents. Maleic anhydride is less sterically demanding and is a better electron acceptor, providing sufficient stabilization for the 14e [Pd(7-DIPP)(MA)] species **14** (Figure 4).

The most notable molecular structure reported here is that of the highly coordinatively unsaturated, 14e complex **14**, in which the palladium center interacts with the ipso carbon of one of the aryl substituents (Figure 4). The 2,6-diisopropyl (DIPP) groups on the aryl ring are so sterically demanding that only one maleic anhydride is able to coordinate, rendering the complex coordinatively and electronically unsaturated. The observed interaction with the aryl substituent alleviates the electronic unsaturation, leading to a highly distorted geometry. On closer inspection it is seen that the Pd center is coordinated perpendicularly to the aryl plane (Pd−N−aryl plane angle 85°), centered directly above the ipso carbon of the aromatic ring. This interaction heavily influences the structure, as the tilt angle (θ) is very acute (2.2(3)°) in comparison to those of **8** (63°) and **9** (55−59°). This feature means that the NHC ring is (almost) in the coordination plane, while for the other complexes the carbene N−C_{NHC}−N plane is twisted away from the coordination plane (defined by the Pd(alkene)$_2$ moiety) by 63.1(4)° (**8**) and 57.0(4)° (**9**), respectively.

The structures of the six-membered ring NHC complexes **8**, **9**, and **11** reveal bond lengths and angles which are similar to literature values for erNHC's, but with slightly elongated M−C_{NHC} bond lengths of 2.09−2.14 Å. As can be seen in Figures 1−3 and the data in Table 2, the *o*-tolyl substituents are oriented with the methyl group directed away from the metal center (Figure 1), while the aromatic rings of the mesityl (Figure 2) and *p*-tolyl (Figure 3) substituents are facing the palladium center. This feature induces more effective back-bonding to the alkenes in **8**, and hence the C=C distances are somewhat longer in **8** than in **9** and **11**. Interestingly, the increased π back-donation to the alkene in **14** is not reflected in the C=C bond distance to the extent that it is in the C=O and the Pd−alkene bond distances. For other M(erNHC) complexes it has been noted that the carbene carbon exhibits pyramidal distortion, measured by the distance of C_{NHC} out of the N−Pd−N plane.[24b] For the present complexes this distortion is barely evident, the aforementioned distance ranging from 0.015 Å in **8** down to 0.007 Å for **14**.

Transfer Hydrogenation Catalysis. The catalytic performances of novel [Pd(erNHC)$(MA)_{1,2}$] complexes **8**−**14** were evaluated in the transfer hydrogenation of 1-phenyl-1-propyne (Scheme 5) and compared to that of the related five-membered analogues [Pd(5-NHC)$(MA)_2$][11] (Table 3). Furthermore, to provide additional comparisons with the [Pd(NHC)$(MA)_{1,2}$] complexes, we have also tested the previously described [Pd(erNHC)(dvtms)] complexes[27c] **1**, **2**, **4**, and **5** in transfer hydrogenation. This comparison of both NHC ring size and olefin coligand allows a number of important conclusions to be drawn, and these are discussed below.

Scheme 5. Product Distribution for the Transfer Hydrogenation of 1-Phenyl-1-propyne



When TOF (h^{-1}) values and percentage conversions after 24 h are compared for the complexes of the type [Pd(NHC)-$(MA)_{1,2}$], it is evident that increasing NHC ring size is accompanied by a significant decrease in catalytic activity (Table 3, entries 2−4 (5-, 6-, and 7-Mes) and 5−7 (5-, 6-, and 7-DIPP)). While increasing ring size leads to an increase in σ-donor capacity of the erNHC ligand, it is also accompanied by increased steric demand, which may have an impact on catalytic performance. For example, when using complex **9** (with the 6-Mes ancillary ligand) as catalyst for transfer hydrogenation of bis(4-methoxyphenyl)acetylene, under analogous conditions, no reaction was observed. The very bulky erNHC ligand is too large to allow coordination of the more bulky substrate to the palladium center, thus preventing transfer hydrogenation from occurring. It appears the enhanced σ-donor capacity of the six- and seven-membered erNHC ligands is outweighed by the increasing steric demand of the ligands. Alternatively, and consistent with the spectroscopic data above, the enhanced σ-donor capacity of the six- and seven-membered erNHC ligands results in increased back-donation to the hence more strongly bound MA coligand, which competes with the alkyne for vacant sites, thus affecting catalytic performance. Hence, the chemoselectivity for alkenes over alkanes for these catalysts remains excellent, although it is noted for several catalysts (Table 3, entries 3−6) that an increased amount of allylbenzene is formed. However, the concept of apparent "selectivity" for these catalysts is discussed in more detail in the following paragraphs.

The application of [Pd(erNHC)(dvtms)] complexes **1**−**7** as catalysts might be expected to yield improved reaction rates, as the metal center is more electron rich than in the related [Pd(erNHC)$(MA)_{1,2}$] complexes **8**−**14** (as noted from $^{13}C\{^1H\}$ NMR), and dvtms, albeit chelating, is a more weakly bound ligand. This is indeed observed: TOF (h^{-1}) values are exceptionally high, and quantitative conversion of the 1-phenyl-1-propyne substrate occurred between 45 min and 2 h (Table 3, entries 8−11). It appears that double-bond isomerization and over-reduction of the alkene also increases for these catalyst systems. Nevertheless, a consideration of plots of conversion versus time for [Pd(erNHC)(dvtms)] complexes **1**, **2**, **4**, and **5** (Figures 5 and 6 and Figures S1 and S2 in the Supporting Information) shows that double-bond isomerization and over-reduction largely occur only when all the alkyne substrate is consumed. In a mixture of alkyne substrate and alkene product, the alkyne is preferentially (and strongly) coordinated and only when all alkyne is consumed will the alkene coordinate, leading to the observed double-bond isomerization and over-reduction. Chemoselectivity is influenced by the lifetime of the [Pd(NHC)(product alkene)] species;[11] more strongly donating bulky ligands should destabilize this species, and hence, it may be expected that increasing NHC ring size should lead to lower amounts of alkane being formed.

An interesting NHC ligand, wherein one of the N-aryl substituents is an *o*-anisidyl group (Oans) (see Scheme 2, complex **4**),[27c] is thought to stabilize catalytic intermediates and improve catalytic performance. The ligand was previously applied in iridium-catalyzed transfer hydrogenation (leading to significantly enhanced activities)[22a,24a] and in palladium-catalyzed Mizoroki−Heck cross-coupling[27c] (complex **4** is

dx.doi.org/10.1021/om300930w | *Organometallics* 2013, 32, 131−140

Table 3. Transfer Hydrogenation of 1-Phenyl-1-propyne Utilizing [Pd(erNHC)(MA)$_{1,2}$] Complexes 8, 9, 10, 13, and 14 and [Pd(erNHC)(dvtms)] Complexes 1, 2, 4, and 5[a]

				selectivity (Z/E/allyl/alkyl)[c]	
entry	complex	TOF, h^{-1} [b]	conversion after 24 h, %	after 0.5 h	after 24 h
1	[Pd(6-^{o}Tol)(MA)$_2$] (**8**)	1.06	33		98/2/tr/tr
2	[Pd(IMes)(MA)$_2$]	32.4	75		97/2/0/0
3	[Pd(6-Mes)(MA)$_2$] (**9**)	4.3	46		80/3/17/1
4	[Pd(7-Mes)(MA)$_2$] (**13**)	0.32	7		85/2/11/2
5	[Pd(5-DIPP)(MA)$_2$]	47.6	100		74/9/11/7
6	[Pd(6-DIPP)(MA)] (**10**)	7.5	73		86/4/7/3
7	[Pd(7-DIPP)(MA)] (**10**)	40.84	19		94/4/1/1.4
8	[Pd(6-Mes)(dvtms)] (**1**)	72.7	~100 (2 h)	81/10/6/3	2/8/0/91
9	[Pd(7-Mes)(dvtms)] (**5**)	97.6	~100 (1 h)	86/3/2/8	1/4/0/96
10	[Pd(6-Mes/Oans)(dvtms)] (**4**)	91.1	~100 (2 h)	87/3/0/10	<1/3/0/96
11	[Pd(6-Tol^{o})(dvtms)] (**2**)	142.3	~100 (45 min)	88/3/0/9	0/2/0/98

[a]Reaction conditions: 1-phenyl-1-propyne (150 mmol), HCO_2H/NEt_3 (440/600 mmol), and catalyst (1.5 mmol) in refluxing MeCN for 24 h. [b]TOF values determined after 50% conversion or after 24 h if 50% conversion was not achieved. [c]Selectivity, conversion, and TOF (h^{-1}) determined by GC.

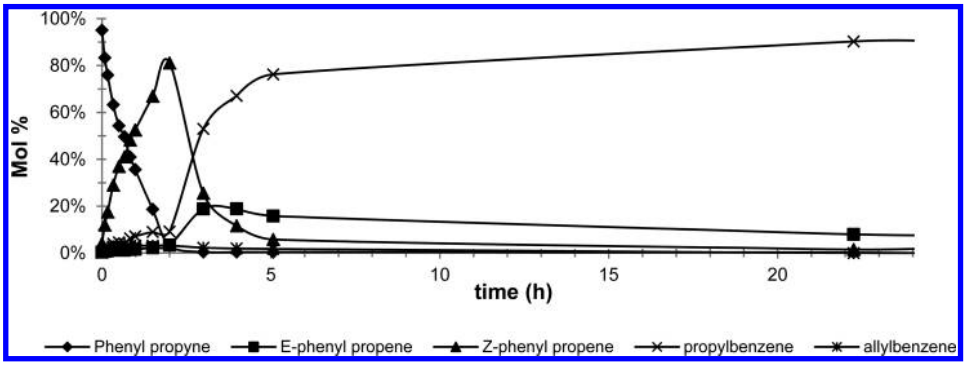


Figure 5. Transfer hydrogenation of 1-phenyl-1-propyne with [Pd(6-Mes)(dvtms)] (**1**).

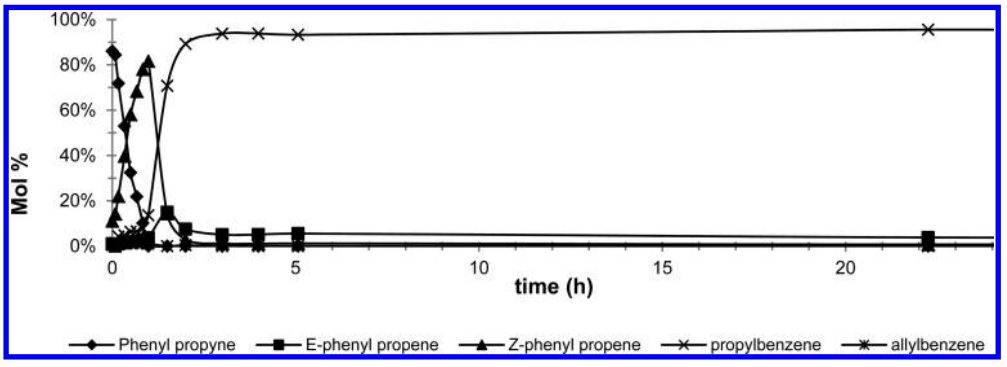


Figure 6. Transfer hydrogenation of 1-phenyl-1-propyne with [Pd(7-Mes)(dvtms)] (**5**).

highly active in Mizoroki–Heck coupling). Consequently, it was considered that the *o*-anisidyl substituent could have a similar impact on catalytic performance in the transfer hydrogenation of alkynes. Indeed, for complex **4** the reaction rate increased significantly relative to those observed for complexes **1** and **5** (over-reduction to alkanes occurred after the alkyne substrate had been consumed; see Figure S2 in the Supporting Information). However, and most interestingly, by far the most active catalyst overall was complex **2** (Scheme 2), which has the least sterically demanding N-aryl substituents (Tol^{o}); however, as previously observed, over-reduction rapidly occurs following alkyne consumption (see Figure S2 in the Supporting Information).

When complexes of the type [Pd(6-NHC)(dvtms)] (**1**, **2** and **4**) are compared, catalytic activity appears to decrease significantly as the steric bulk of the 6-NHC ligand increases (**2** > **4** > **1**; Table 3, entries 8, 10, and 11), which is consistent with the trend noted above for complexes containing MA as the coligand. However, in contrast, complex **5** (containing the bulky 7-Mes ligand) appears to be significantly more active than the analogous system **1**, with the less sterically demanding 6-Mes ancillary ligand. In fact, the complex [Pd(7-Mes)(dvtms)] (**5**) was the bulkiest system we were able to prepare. It is therefore possible that steric pressure exerted by strongly bound 7-Mes was sufficient to lead to rapid generation of the active catalyst and subsequently provide steric protection for a highly coordinatively unsaturated active species.

dx.doi.org/10.1021/om300930w | *Organometallics* 2013, 32, 131–140

Previous mechanistic studies have shown that the presence of maleic anhydride appears to have a positive influence on the chemoselectivity of the transfer hydrogenation reaction.[32] Therefore, maleic anhydride (1 equiv relative to Pd) was added to reaction mixtures containing complexes **1**−**3** and **5**−**7** (Table 4). As expected, addition of maleic anhydride led to an apparent improvement in selectivity to the (*Z*)-alkene, but with decreased activity. However, as noted above, a plot of conversion versus time (Figure 7) reveals that the addition of MA has simply slowed down the overall rate of transfer hydrogenation, including that for the conversion of alkene to alkane. Therefore, as demonstrated for all other catalysts discussed here, over-reduction of the (*Z*)-alkene to alkane only occurs after all the alkyne has been consumed, but in this case at a lower rate.

Table 4. Transfer Hydrogenation of 1-Phenyl-1-propyne with [Pd(erNHC)(dvtms)] Complexes 1−3 and 5−7 in the Presence of Maleic Anhydride[a]

entry	complex	TOF_{init}, h^{-1} [b]	conversion after 5 h, %	selectivity[b,c] (*Z*/*E*/allyl/alkyl)
1	[Pd(6-Mes)(dvtms)] (**1**)	24.3	32	79.2/2.2/17.8/0.2
2	[Pd(7-Mes)(dvtms)] (**5**)	3.4	28	90.1/2.6/5.9/1.3
3	[Pd(6-Tol°)(dvtms)] (**2**)	12.2	40	98.6/1.3/0/0.1
4	[Pd(7-Tol°)(dvtms)] (**6**)	4.3	35	98.6/1.4/0/0
5	[Pd(6-Xyl)(dvtms)] (**3**)	9.4	45	82.0/2.2/15.6/0.3
6	[Pd(7-Xyl)(dvtms)] (**7**)	9.6	35	85.8/3.4/8.8/2.0
7	[Pd(IMes)(MA)$(MeCN)_2$]	7.4	61	91.9/2.0/0/5.5

[a]Reaction conditions: 1-phenyl-1-propyne (150 mmol), HCO_2H/NEt_3 (440/600 mmol), catalyst (1.5 mmol), and maleic anhydride (1.5 mmol) in refluxing MeCN for 24 h. [b]TOF values determined after 1 h. [c]Selectivity determined at end of experiment (5 h reflux, 40 h at ambient temperature overnight, 2 h reflux).

The following experiment, which was undertaken to test overall catalyst stability, is of particular interest. During the transfer hydrogenation of 1-phenyl-1-propyne with the catalyst system {[Pd(6-Tol°)(dvtms)] + MA}, using 0.1 mol % catalyst loading, the reaction mixture was refluxed in MeCN for 5 h (at this point approximately 30% conversion of alkyne to alkene was noted; see Figure S3 in the Supporting Information). The reaction mixture was then left at ambient temperature for an additional 40 h, during which time no further hydrogenation was evident. After this period, the reaction mixture was again heated to reflux for several more hours, whereupon catalysis recommenced and continued at approximately the same rate previously noted. It is therefore evident that the active catalyst is stable for prolonged periods of time when in the presence of unreacted alkyne (or product alkene).

CONCLUSIONS

In the search for electron-rich catalysts for the transfer hydrogenation of alkynes, we have synthesized a series of novel palladium(0) complexes containing expanded-ring N-heterocyclic carbene ligands and one or two maleic anhydride coligands. The complexes were characterized using IR and NMR spectrometry, and their solid-state structures were investigated using single-crystal X-ray diffraction. The structures displayed interesting geometries; due to the increased N−C_{NHC}−N bond angles of the carbene, the complexes with very bulky 2,6-diisopropyl (DIPP) N-aryl substituents are able to incorporate only one alkene moiety, leading to electronically and coordinatively unsaturated 14-electron [Pd(erNHC)(MA)] complexes. Applying the [Pd(erNHC)(dvtms)] complexes to the transfer hydrogenation of 1-phenyl-1-propyne with triethylammonium formate/triethylamine as the hydrogen donor demonstrates that bulky, electron-rich erNHC ligands result in significantly increased activities, albeit with lower selectivities in comparison to those for traditional [Pd(5-NHC)L_n] complexes. We are currently exploring possibilities to obtain higher stereoselectivity in the hydrogenation while keeping the increased activity.

EXPERIMENTAL SECTION

General Remarks. The synthesis of all complexes was carried out in dried glassware using standard Schlenk techniques under an atmosphere of purified nitrogen. Solvents were dried according to standard procedures.[38] All formamidines,[39] amidinium tetrafluoroborates,[22a,26a] [Pd(*t*BuDAB)(MA)],[40] [Pd(nbd)(MA)],[41] [Pd(IMes)$(MA)_2$],[32] and [Pd(erNHC)(dvtms)] complexes **1**−**7**[27c] were prepared according to literature procedures. Maleic anhydride was recrystallized from hot dichloromethane to remove maleic acid and stored in a Schlenk flask under nitrogen. Potassium *tert*-butoxide was evacuated overnight and stored in a Schlenk flask under nitrogen. Other compounds were ordered from commercial sources and used without further purification. Gas chromatographic analyses were run on a Carlo Erba HRGC 8000 Top instrument with a DB-5 column and *p*-xylene as internal standard. NMR spectra were recorded on a Bruker DRX300 spectrometer (^{1}H, 300.11 MHz; ^{13}C{^{1}H}, 75.47 MHz), a Bruker ARX400 spectrometer (^{1}H, 400.13 MHz; ^{13}C{^{1}H}, 100.61 MHz), a Varian Mercury 300 spectrometer (^{1}H, 300.13 MHz; ^{13}C{^{1}H}, 75.48 MHz), or a Varian Inova 500 spectrometer (^{1}H, 499.86 MHz; ^{13}C{^{1}H}, 125.70 MHz). Positive chemical shifts (ppm)

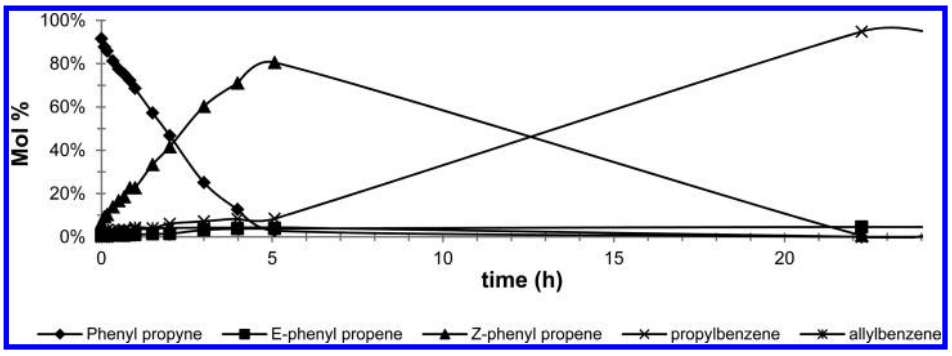


Figure 7. Transfer hydrogenation of 1-phenyl-1-propyne with {[Pd(6-Mes)(dvtms)] (**1**) + 1 equiv of maleic anhydride}.

dx.doi.org/10.1021/om300930w | *Organometallics* 2013, 32, 131−140

denoted in the ^{1}H and ^{13}C NMR data are reported relative to TMS and were determined by reference to residual ^{1}H and ^{13}C solvent resonances. IR spectra were recorded on a Shimadzu 8400s FT-IR spectrophotometer.

General Procedure for the Synthesis of [Pd(erNHC)(alkene)$_{1,2}$] Complexes 8−14 via Coligand Displacement. The [Pd(erNHC)(dvtms)] complexes (1 mmol) were suspended in toluene (20 mL) with stirring at ambient temperature. To this stirred suspension was added maleic anhydride (2 mmol) in one portion under a cone of nitrogen, resulting in a color change to orange, red, or brown, depending on the carbene N-aryl substituents. The reaction mixture was stirred for 1−2 h at room temperature, upon which a yellow to red solid precipitated. The supernatant was taken off and the solid washed in *n*-pentane, furnishing the desired complexes. For the seven-membered-ring NHC complexes **12**−**14**, it was necessary to concentrate the toluene suspension before adding pentane. The obtained crude product was then dissolved in dichloromethane and isolated by precipitation with diethyl ether or pentane. For seven-membered-ring NHC complexes it can be necessary to quickly filter the dichloromethane solution over a bed of dried Celite before precipitation, to remove Pd black.

General Procedure for the in Situ Synthesis of [Pd(erNHC)(alkene)$_{1,2}$] Complexes 8−14. The azolium tetrafluoroborate salts (1 mmol) and KO^{t}Bu (1.6 mmol) were suspended in toluene (20 mL) and stirred at room temperature for 2 h (six-membered rings) or overnight (seven-membered rings) to generate the free carbene. This solution was either filtered via a cannula or decanted over a bed of dried Celite into a dried Schlenk (the Celite was flushed with 2 × 10 mL of toluene), to remove potassium salts. The solution of Pd(dvtms) in dvtms (10.74% Pd, 1 mL, 1 mmol) was added dropwise to the free carbene solution, and this clear yellow solution was stirred overnight at room temperature, resulting in a color change to bright yellow-orange. The alkene (2 mmol) was added in one portion, resulting in a color change to orange, red, or brown, depending on the carbene N-aryl substituents. The reaction mixture was stirred for 1−2 h at room temperature, upon which a yellow to red solid precipitated. The supernatant was taken off and the solid washed in *n*-pentane, furnishing the desired complexes. For the seven-membered-ring NHC complexes **12**−**14**, it was necessary to concentrate the toluene suspension before adding pentane. The obtained crude product was then dissolved in dichloromethane and isolated by precipitation with diethyl ether or pentane. For seven-membered-ring NHC complexes it can be necessary to quickly filter the dichloromethane solution over a bed of dried Celite before precipitation, to remove Pd black.

*(1,3-Bis(2-methylphenyl)tetrahydropyrimidin-2-(1H)-ylidene)bis(η^2-maleic anhydride)palladium (**8**).* The product was obtained as a red-brown powder in 63% yield. Crystals were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.32 (d, 2H, ^3J = 7.5 Hz, *m*-$C_{Ar}H$), 7.24 (t, 2H, ^3J = 7.5 Hz, *p*-$C_{Ar}H$), 7.13 (t, 2H, ^3J = 7.2 Hz, *m*-$C_{Ar}H$), 6.79 (d, 2H, ^3J = 7.7 Hz, *o*-$C_{Ar}H$), 4.05 (d, 2H, ^3J = 4.6 Hz, HC═C), 3.79 (dt, 2H, ^3J = 12.5 Hz, 6.0 Hz, NCH_2), 3.64 (d, 2H, ^3J = 4.6 Hz, HC═C), 3.59 (m, 2H, ^3J = 6.0 Hz, NCH_2), 2.65 (s, 6H, *o*-CH_3), 2.47 (p, 2H, ^3J = 6.0 Hz, NCH_2CH_2) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 207.17 (NCN), 169.44 and 167.93 (2 C═O), 146.80 (*i*-C_{Ar}), 134.10 (*o*-C_{Ar}Me), 132.00 (*o*-$C_{Ar}H$), 129.31 and 129.06 (2 *m*-C_{Ar}), 128.17 (*p*-C_{Ar}), 65.84 and 65.45 (2 C═C), 48.20 (NCH_2), 21.34 (*o*-CH_3), 18.36 (NCH_2CH_2) ppm. IR: 1813, 1753 (C═O), 1505 (C═C→M) cm^{-1}. MS (FAB+): *m*/*z* observed 469.0759 for $C_{33}H_{37}N_2O_8Pd$ [M − MA + H]$^+$. Anal. Calcd for $C_{26}H_{24}O_6N_2Pd$: C, 55.09; H 4.27; N, 4.94. Found: C, 55.04; H, 4.27; N, 4.95.

*(1,3-Bis(2,4,6-trimethylphenyl)tetrahydropyrimidin-2-(1H)-ylidene)bis(η^2-maleic anhydride)palladium (**9**).* The product was obtained as a yellow powder in 47% yield. Crystals were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.92 (s, 4H, $C_{Ar}H$), 3.79 (br s, 4H, HC═CH), 3.49 (t, 4H, ^3J = 6.0 Hz, NCH_2), 2.41 (m, 2H, NCH_2CH_2), 2.30 (s, 12H, *o*-CH_3), 2.25 (s, 6H, *p*-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 208.97 (NCN), 168.33 (C═O), 143.54 (*i*-C_{Ar}), 139.01 (*p*-C_{Ar}), 135.58 (*o*-C_{Ar}), 130.18 (*m*-C_{Ar}), 68.04 (br s, C═C), 48.34 (NCH_2), 21.82 (NCH_2CH_2), 21.19 (*p*-CH_3), 18.17 (*o*-CH_3) ppm. IR: 1847, 1777 (C═O), 1713, 1556, 1528 (C═C→M) cm^{-1}. MS (FAB+): *m*/*z* observed 426.1300 for $C_{22}H_{28}N_2Pd$ [M − 2 MA]$^+$/497.14 for $C_{22}H_{28}N_2Pd$ [M − MA − CO + H]$^+$.

*(1,3-Bis(2,6-diisopropylphenyl)tetrahydropyrimidin-2(1H)-ylidene)(η^2-maleic anhydride)palladium (**10**).* The product was obtained as an orange powder in 29% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.26 (t, 2H ^3J = 8.0 Hz, *p*-$C_{Ar}H$), 7.16 (d, 4H, ^3J = 8.0 Hz, *m*-$C_{Ar}H$), 3.30 (t, 4H, ^3J = 6.0 Hz, NCH_2), 3.02 (septet, 4H, ^3J = 6.9 Hz, $CHMe_2$), 2.90 (s, 2H, HC═CH), 2.25 (p, 2H, ^3J = 6.6 Hz, NCH_2CH_2), 1.31 (d, 12H, ^3J = 6.9 Hz), 1.17 (d, 12H, ^3J = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 206.83 (NCN), 169.70 (C═O), 146.06 (*o*-C_{Ar}), 134.52 (*i*-C_{Ar}), 129.21 (*p*-C_{Ar}), 124.99 (*m*-C_{Ar}), 48.20 (C═C), 46.71 (NCH_2), 29.36 ($CHMe_2$), 25.32 (CH_3), 25.02 (CH_3), 21.03 (NCH_2CH_2) ppm. IR: 1798, 1730 (CO), 1552, 1512 (C═C→M) cm^{-1}. MS (FAB+): *m*/*z* observed 510.2241 for $C_{28}H_{40}N_2Pd$ [M − MA]$^+$/581.2372 for $C_{31}H_{43}N_2O_2Pd$ [M + CO + H]$^+$.

*(1,3-Bis(4-methylphenyl)tetrahydropyrimidin-2-(1H)-ylidene)bis(η^2-maleic anhydride)palladium (**11**).* This product gave difficulties in workup and could only be isolated in low yields (±5%). By concentration of the reaction mixture, addition of diethyl ether, and standing for several weeks, small yellow crystals were obtained that were suitable for crystallographic and spectroscopic analysis. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.08 (dd, 8H, ^3J = 6.x Hz, $C_{Ar}H$), 3.78 (broad, 8H, NCH_2+ HC═CH), 2.40 (quintet, 2H, NCH_2CH_2), 2.31 (s, 6H, CH_3) ppm. ^{13}C NMR (300 MHz, CD_2Cl_2): δ 204.72 (NCN), 168.13 (C═O), 145.59 (i-C_{Ar}), 138.32 (CHMe), 130.08 (o-C_{Ar}), 125.65 (m-C_{Ar}), 65.49 (C═C), 48.64 (NCH_2), 21.40 (NCH_2CH_2), 20.72 (CH_3) ppm. MS (FAB$^+$): *m*/*z* observed 441.0803 for $C_{21}H_{22}N_2O_2Pd$ [M − MA − CO + H]$^+$.

*(1,3-Bis(2-methylphenyl)-1,3-diazepan-2-ylidene)bis(η^2-maleic anhydride)palladium (**12**).* The product was obtained as a dark purple powder in 11% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.48 (d, 2H, ^3J = 6.8 Hz, *o*-$C_{Ar}H$), 7,33 (br s, 6H, *m*-$C_{Ar}H$ and *p*-$C_{Ar}H$), 5.08 (br s, 2H, HC═C), 4.26 (br s, 4H, NCH_2), 2.42 (br s, 4H, NCH_2CH_2) 2.40 (br s, 6H, *o*-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 167.86 (C═O), 142.93 (*i*-C_{Ar}), 133.58 (*o*-C_{Ar}Me), 132.32 (*o*-$C_{Ar}H$), 130.54 and 128.55 (2 *m*-C_{Ar}), 127.25 (*p*-C_{Ar}), 62.90 (C═C), 55.48 (NCH_2), 25.61 (NCH_2CH_2), 17.19 (*o*-CH_3) ppm. IR: 1773, 1733, 1654 (CO), 1490 (C═C→M) cm^{-1}. MS (FAB+): *m*/*z* observed 385.15, but product is too poorly soluble for exact mass measurement.

*(1,3-Bis(2,4,6-trimethylphenyl)-1,3-diazepan-2-ylidene)bis(η^2-maleic anhydride)palladium (**13**).* The product was obtained as a bright red powder in 45% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.02 (s, 4H, $C_{Ar}H$), 4.18 (br s, 4H, NCH_2), 3.83 (br s, 4H, HC═CH), 2.57 (br. s, 8H, *p*-CH_3), 2.47 (br s, 12H, NCH_2CH_2 + *o*-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 226.32 (NCN), 168.22 (C═O), 145.39 (*p*-C_{Ar}), 138.57 (*o*-C_{Ar}), 135.37 (*i*-C_{Ar}), 130.05 (*m*-C_{Ar}), 68.90 (C═C), 57.79 (NCH_2), 25.32 (NCH_2CH_2), 21.02 (*p*-CH_3), 18.59 (*o*-CH_3) ppm. IR: 1779, 1711 (CO), 1653, 1517, 1478 cm^{-1} (C═C→M). MS (FAB+): *m*/*z* observed 440.1443 for $C_{23}H_{30}N_2Pd$ [M − 2 MA]$^+$.

*(1,3-Bis(2,6-diisopropylphenyl)-1,3-diazepan-2-ylidene)(η^2-maleic anhydride)palladium (**14**).* The product was obtained as a brown powder in 34% yield. Crystals were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.38−7.26 (m, 6H, $C_{Ar}H$), 3.89 (br t, 4H, NCH_2), 3.26 (septet, 4H, ^3J = 6.9 Hz, $CHMe_2$), 2.81 (s, 2H, HC═CH), 2.31 (br dt, 4H, NCH_2CH_2), 1.40 (d, 12H, ^3J = 6.9 Hz), 1.29 (d, 12H, ^3J = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 214.86 (NCN), 170.01 (C═O), 144.75 (*i*-C_{Ar}), 135.59 (*o*-C_{Ar}), 128.57 (*p*-C_{Ar}), 125.23 (*m*-C_{Ar}), 55.00 (NCH_2), 48.07 (C═C), 29.66 ($CHMe_2$), 26.40 (NCH_2CH_2), 25.55 (CH_3), 24.87 (CH_3) ppm. IR: 1794, 1726 (C═O), 1509, 1458 (C═C→M) cm^{-1}. MS (FAB+): *m*/*z* observed 595.2526 for $C_{32}H_{45}N_2O_2Pd$ [M + MA − CO + H]$^+$.

General Procedure for Transfer Hydrogenation of 1-Phenyl-1-propyne. A stock solution was made of 1-phenyl-1-propyne (150 mM), *p*-xylene (150 mM), and triethylammonium formate (450 mM of HCO_2H and NEt_3) in dry MeCN, which was divided over separate reaction vessels (13 mL/reaction) and heated to 80 °C. The catalysts

(1.5 mM final concentration; ±12 mg) were weighed into an alkaloid tube and dissolved in 1 mL of MeCN before addition to the reaction vessel; for reactions in which maleic anhydride was added, this was mixed with the catalyst prior to addition of MeCN. Immediately after addition of catalyst an aliquot (0.05 mL) of the reaction mixture was taken, and this was diluted in a GC vial with 1 mL of EtOH to quench the reaction in the sample. Sampling was repeated at regular time intervals, in order to monitor the reaction by GC. Rates were determined for the initial linear part of the reaction profiles. The reaction rates varied over an order of magnitude for the various catalysts; thus, in order to compare these, TOFs at 50% conversion are depicted in Table 3.

Crystallographic Details. Suitable single crystals for all compounds were coated with Paratone-N oil, mounted using a glass fiber pin, and frozen in the cold nitrogen stream of the goniometer. X-ray diffraction data were collected on a Bruker AXS APEX CCD diffractometer equipped with a rotating anode using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with a scan width of 0.3°, and the generator setting was 50 kV and 180 mA. Diffraction data were collected over the full sphere and were corrected for absorption. Compound **11** was measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) using φ and ω scans. The data reduction was performed with the Bruker SAINT program package.[42] For further crystal and data collection details see the Supporting Information. Structure solutions were found with the SHELXS-97 package using direct methods and were refined with SHELXL-97[43] against F^2 using first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were generated with idealized geometries (compounds **8**, **9**, and **14**) or located in difference Fourier maps (compound **11**) and isotropically refined using a riding model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files providing kinetic data for the transfer hydrogenation of 1-phenyl-1-propene with complexes **2** and **4**, kinetic data for the catalyst lifetime experiment, and full crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files for this paper along with a crystal structure of [Pd(dvtms)(MA)] may also be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 900976–900979).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cavellKJ@cf.ac.uk (K.J.C.); C.J.Elsevier@uva.nl (C.J.E.).

Present Addresses

[⊥]Frames Gas Processing, Dr. A.D. Sacaharovlaan 2, 2405 WB Alphen aan den Rijn, The Netherlands.

[#]School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K..

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was funded by the National Research School Combination Catalysis in The Netherlands. We also gratefully acknowledge the EPSRC and the Cardiff Catalysis Institute for J.J.D.'s Ph.D. studentship.

■ REFERENCES

(1) (a) Klomp, D.; Hanefeld, U.; Peters, J. A. In *Handbook for Homogeneous Hydrogenation*, 1st ed.; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. *2*, p 585. (b) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226. (c) Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237. (d) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

(2) (a) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246. (b) Wu, X.; Xiao, J. *Chem. Commun.* **2007**, *35*, 2447. (c) Corberán, R.; Sanaú, M.; Peris, E. *Organometallics* **2007**, *26*, 3492. (d) Enthaler, S.; Jackstell, R.; Hagemann, B.; Junge, K.; Erre, G.; Beller, M. *J. Organomet. Chem.* **2006**, *691*, 4652.

(3) (a) Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2003**, *22*, 4184. (b) Samec, J. S. M.; Éll, A. H.; Åberg, J. B.; Privalov, T.; Eriksson, L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2006**, *128*, 14293. (c) Hamid, M. H. S. A.; Slatford, P. A.; Williams, J. M. J. *Adv. Synth. Catal.* **2007**, *349*, 1555.

(4) Gnanamgari, D.; Moores, A.; Rajaseelan, E.; Crabtree, R. H. *Organometallics* **2007**, *26*, 1226.

(5) Campaña, A. G.; Estévez, R. E.; Fuentes, N.; Robles, R.; Cuerva, J. M.; Buñuel, E.; Cárdenas, D.; Oltra, J. E. *Org. Lett.* **2007**, *9*, 2195.

(6) (a) Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2001**, *79*, 915. (b) Tani, K.; Iski, A.; Yamagata, T. *Chem. Commun.* **1999**, 1821.

(7) Tani, K.; Ono, N.; Okamoto, S.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1993**, 386.

(8) (a) Kluwer, A. M.; Elsevier, C. J. In *Handbook for Homogeneous Hydrogenation*, 1st ed.; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. *1*, p 375. (b) Alonso, F.; Osante, I.; Yus, M. *Tetrahedron* **2007**, *63*, 93. (c) Kluwer, A. M.; Koblenz, T. S.; Jonischkeit, T.; Woelk, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 15470. (d) van Laren, M. W. E. *Angew. Chem.* **1999**, *111*, 3926; *Angew. Chem., Int. Ed.* **1999**, *38*, 3715.

(9) (a) Sprengers, J. W.; Wassenaar, J.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J. *Angew. Chem.* **2005**, *119*, 2062; *Angew. Chem., Int. Ed.* **2005**, *44*, 2026. (b) Hauwert, P.; Maestri, G.; Sprengers, J. W.; Catellani, M.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 3223.

(10) (a) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446. (b) Molnár, A.; Sárkány, A.; Varga, M. *J. Mol. Catal. A: Chemical* **2001**, *173*, 185.

(11) Hauwert, P.; Boerleider, R.; Warsink, S.; Weigand, J. J.; Elsevier, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 16900.

(12) Schager, F.; Bonrath, W.; Pörschke, K.-R.; Kessler, M.; Krüger, C.; Seevogel, K. *Organometallics* **1997**, *16*, 4276.

(13) (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 2371. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.

(14) (a) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913. (b) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (e) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815.

(15) (a) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (b) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *1227*, 2485. (c) Gusev, D. G. *Organometallics* **2009**, *28*, 763. (d) Gusev, D. G. *Organometallics* **2009**, *28*, 6458. (e) Kelly, R. A.; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202. (f) Khramov, D. M.; Rosen, E. L.; Er, J. A.; Vu, P. D.; Lynch, V. M.; Bielawski, C. W. *Tetrahedron* **2008**, *64*, 6853. (g) Leuthausser, S.; Schwarz, D.; Plenio, H. *Chem. Eur. J.* **2007**, *13*, 7195. (h) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006. (i) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940.

(16) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.

(17) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687.

(18) Schuster, O.; Yang, L. R.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445.

(19) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed.* **1996**, *35*, 1121.
(20) (a) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195. (b) Wurtz, S.; Lohre, C.; Frohlich, R.; Bergander, K.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 8344.
(21) Hahn, F. E.; Holtgrewe, C.; Pape, T.; Martin, M.; Sola, E.; Oro, L. A. *Organometallics* **2005**, *24*, 2203.
(22) (a) Iglesias, M.; Beetstra, D. J.; Stasch, A.; Horton, P. N.; Hursthouse, M. B.; Coles, S. J.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Organometallics* **2007**, *26*, 4800. (b) Binobaid, A.; Iglesias, M.; Beetstra, D. J.; Kariuki, B.; Dervisi, A.; Fallis, I. A.; Cavell, K. J. *Dalton Trans.* **2009**, 7099. (c) Dunsford, J. J.; Cavell, K. J.; Kariuki, B. M. *Organometallics* **2012**, *31*, 4118. (d) Lu, W. Y.; Cavell, K. J; Wixey, J. S.; Kariuki, B. *Organometallics* **2011**, *30*, 5649.
(23) Binobaid, A.; Iglesias, M.; Beetstra, D.; Dervisi, A.; Fallis, I.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2010**, *2010*, 5426.
(24) (a) Iglesias, M.; Beetstra, D. J.; Cavell, K. J.; Deryisi, A.; Fallis, I. A.; Kariuki, B.; Harrington, R. W.; Clegg, W.; Horton, P. N.; Coles, S. J.; Hursthouse, M. B. *Eur. J. Inorg. Chem.* **2010**, 1604. (b) Iglesias, M.; Beetstra, D. J.; Kariuki, B.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Eur. J. Inorg. Chem.* **2009**, 1913. (c) Newman, P. D.; Cavell, K. J.; Hallett, A. J.; Kariuki, B. M. *Dalton Trans.* **2011**, *40*, 8807.
(25) Dunsford, J. J.; Cavell, K. J.; Kariuki, B. *J. Organomet. Chem.* **2011**, *696*, 188.
(26) (a) Iglesias, M.; Beetstra, D. J.; Knight, J. C.; Ooi, L. L.; Stasch, A.; Coles, S.; Male, L.; Hursthouse, M. B.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Organometallics* **2008**, *27*, 3279. (b) Kolychev, E. L.; Portnyagin, I. A.; Shuntikov, V. V.; Khrustalev, V. N.; Nechaev, M. S. *J. Organomet. Chem.* **2009**, *694*, 2454. (c) Herrmann, W. A.; Schneider, S. K.; Ofele, K.; Sakamoto, M.; Herdtweck, E. *J. Organomet. Chem.* **2004**, *689*, 2441. (d) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 1256.
(27) (a) Scarborough, C. C.; Bergant, A.; Sazama, G. T.; Guzei, I. A.; Spencer, L. C.; Stahl, S. S. *Tetrahedron* **2009**, *65*, 5084. (b) Scarborough, C. C.; Grady, M. J. W.; Guzei, I. A.; Gandhi, B. A.; Bunel, E. E.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 5269. (c) Dunsford, J. J.; Cavell, K. J. *Dalton Trans.* **2011**, *40*, 9131.
(28) Armstrong, R.; Ecott, C.; Mas-Marza, E.; Page, M. J.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2010**, *29*, 991.
(29) (a) Davies, C. J. E.; Page, M. J.; Ellul, C. E.; Mahon, M. F.; Whittlesey, M. K. *Chem. Commun.* **2010**, *46*, 5151. (b) Newman, P. D.; Cavell, K. J.; Kariuki, B. M. *Organometallics* **2010**, *29*, 2724.
(30) Newman, P. D.; Cavell, K. J.; Kariuki, B. M. *Chem. Commun.* **2012**, *48*, 6511.
(31) Hudnall, T. W.; Tennyson, A. G.; Bielawski, C. W. *Organometallics* **2010**, *29*, 4569.
(32) Sprengers, J. W.; Wassenaar, J.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2026.
(33) Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742.
(34) (a) Kluwer, A. M.; Elsevier, C. J.; Bühl, M.; Lutz, M.; Spek, A. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3501. (b) Itoh, K.; Ueda, F.; Hirai, K.; Ishii, Y. *Chem. Lett.* **1977**, 877.
(35) Jackstell, R.; Andreu, M. G.; Frisch, A.; Selvakumar, K.; Zapf, A.; Klein, H.; Spannenberg, A.; Röttger, D.; Briel, O.; Karch, R.; Beller, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 986.
(36) This coligand displacement protocol has also been utilized to access expanded-ring NHC Pd(II) complexes via oxidation of the parent [Pd(erNHC)(dvtms)] precursors; these results will be reported shortly.
(37) The ^{13}C signal of the carbene carbon in [Pd(7-Tol^{o})(MA)$_2$] could not be observed. For some of the previously reported [Pd(erNHC)(dvtms)] complexes,[36] this signal has proven to be very difficult as well, due to very slow relaxation of the carbene ^{13}C nucleus.
(38) Taylor, E. C.; Ehrhart, W. A. *J. Org. Chem.* **1963**, *28*, 1108.
(39) Kuhn, K. M.; Grubbs, R. H. *Org. Lett.* **2008**, *10*, 2075.
(40) Cavell, K. J.; Stufkens, D. J.; Vrieze, K. *Inorg. Chem. Acta* **1980**, *47*, 67.
(41) Warsink, S.; de Boer, S. Y.; Jongens, L. M.; Fu, C. F.; Liu, S. T.; Chen, J. T.; Lutz, M.; Spek, A. L.; Elsevier, C. J. *Dalton Trans.* **2009**, 7080.
(42) *SAINT 7.23A*; Bruker AXS, Madison, WI, 2006. Sheldrick, G. M. *SADABS*; Bruker AXS, Madison, WI, 2004.
(43) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Determination*; University of Göttingen, Göttingen, Germany, 1997.