Catalytic Annulation of Heterocycles via a Novel Redox Process Involving the Imidazolium Salt N-Heterocyclic Carbene Couple

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A novel atom-efficient catalytic reaction, which converts imidazolium salts, with *N*-butenyl, *N*-substituted butenyl, and *N*-pentenyl substituents, into five- and six-membered fused-ring imidazolium and thiazolium salts has been developed. The reaction proceeds through azolium, C2−H, oxidative addition to Ni(0) followed by intramolecular insertion of the N-alkenyl double bond into the Ni hydride to give an intramolecularly bound carbene−Ni−alkyl intermediate. Reductive elimination of the linked carbene and alkyl groups gives the fused-ring azolium products and regenerates the Ni(0) catalyst. Products are potential building blocks for the synthesis of pharmaceuticals and novel ionic liquids. For example, 1,7-dimethyl-6,7-dihydro-5*H*-pyrrole[1,2-α]imidazolium bromide (**2f**), a five-membered fused-ring imidazolium salt, is formed from the catalytic ring closing of 1-butenyl-3-methylimidazolium bromide (**1f**). The reaction proceeds at moderate temperatures (50 °C) to give the products in high yield and selectivity. The catalyst was formed in situ from $Ni(COD)_2$ plus added ligand L (where L = IMes, SMes, IPr, SPr, 4,5-Me_2IPr, PPh_3, PCy_3, PCy_2(Biphenyl), P^tBu_3) in DMF.

Introduction

Since the isolation of the first free N-heterocyclic carbenes (NHC) by Arduengo and co-workers,[1] many transition-metal complexes of NHCs have been synthesized and applied in homogeneous catalysis.[2,3] NHC ligands are regarded as strong σ-donor ligands with variable π-accepting character[4–10] and are frequently compared to tertiary alkylphosphines; NHCs are able to stabilize metals in various oxidation states and support coordinatively unsaturated catalytically active intermediates. Robust catalysts have been developed for reactions, including C−C coupling reactions (Pd, Ni),[11–21] copolymerizations (Pd),[22] hydrosilylation and hydroformylation (Rh),[23–30] olefin metathesis (Ru),[31–33] and furan synthesis (Ru).[34] N-functionalized NHCs

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(1) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

(2) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309.

(3) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348–1352.

(4) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391–4394.

(5) Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, G. N. *Chem. Commun.* **1997**, 1963–1964.

(6) Niehues, M.; Erker, G.; Kehr, G.; Schwab, P.; Fröhlich, R. *Organometallics* **2002**, *21*, 2905–2911.

(7) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755–764.

(8) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640–3646.

(9) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516–3526.

(10) Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350–4358.

(11) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 2371–2375.

(12) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741–748.

(13) Caddick, S.; Cloke, F. G. N.; Clentsmith, G. K. B.; Hitchcock, P. B.; McKerrecher, D.; Titcomb, L. R.; Williams, M. R. V. *J. Organomet. Chem.* **2001**, *617−618*, 635–639.

(14) Böhm, V. P. W.; Weskamp, T.; Gstöttmayr, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602–1604.

(15) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700–706.

(16) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470–5472.

(17) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111.

(18) Navarro, O.; Marion, N.; Mei, J.; Nolan, S. P. *Chem. Eur. J.* **2006**, *12*, 5142–5148.

(19) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, *12*, 4743–4748.

(20) Organ, M. G.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Valente, C. *Chem. Eur. J.* **2006**, *12*, 4749–4755.

(21) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768–2813.

(22) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239–247.

(23) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *137*, 293–300.

(24) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217–228.

(25) Herrmann, W. A.; Goossen, L. J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 2805–2807.

(26) Enders, D.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3571–3574.

(27) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162–2168.

(28) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913–919.

(29) Chen, A. C.; Ren, L.; Decken, A.; Crudden, C. M. *Organometallics* **2000**, *19*, 3459–3461.

(30) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Gierz, V.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2008**, *27*, 224–234.

(31) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490–2493.

(32) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.

(33) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416–2419.

(34) Kucukbay, H.; Cetinkaya, B.; Guesmi, S.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2434–2439.

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Scheme 1. Imidazolium C−H/Alkene Coupling Reaction[50,51]

with P-, N-, and O-donor groups and bridged di-NHC ligands have also proved useful in catalysis.[12,35–39]

The strong M−carbene bond, which contributes to the high stability of the complexes, is one of the reasons for the success of NHCs in catalysis. However, we have reported that heterocyclic carbene complexes of Pd(II) and Ni(II) which contain alkyl, aryl, and acyl groups decompose via elimination of 2-functionalized imidazolium salts.[40–43] A combined kinetic and density functional study of the reaction (M = Pd) has confirmed that hydrocarbyl−M−carbene complexes readily undergo a concerted reductive elimination of the hydrocarbyl species to give M(0) and hydrocarbylimidazolium salts.[44] Subsequently, oxidative addition of the imidazolium cation (e.g., an ionic liquid such as [bmim][BF_4]) to low-valent M(0) (M = Ni, Pd, Pt) complexes bearing strong σ-donor ligands was reported.[45–48] The synthesis of a carbene−Pt−hydride complex, with an "abnormally" bound carbene ligand (i.e. bound at the C4/C5 position), via oxidative addition of a C2-blocked imidazolium salt to a Pt(0) center, has also been described.[49] The oxidative addition of the imidazolium salt generates in situ active carbene−M−hydride catalysts—by way of demonstration, it was subsequently found that combining the two half-reactions of oxidative addition and reductive elimination, in the presence of an alkene, establishes a unique catalytic process (Scheme 1): we previously described a catalytic azolium−alkene coupling reaction in which imidazolium salts act as substrate.[50] The reaction proceeds via a redox process involving a carbene−M−hydride intermediate. A recent combined experimental/DFT study provided insight into the detailed mechanism.[51]

Bergman and co-workers have reported the catalytic 2-substitution of N-heterocycles, including the annulation of alkenyl-substituted azoles via a rhodium-catalyzed intramolecular coupling reaction in the presence of $PCy_3 \cdot HCl$.[52–64] A Rh(I) catalyst was used to convert benzimidazoles, thiazoles, oxazoles, pyridines, and pyrimidines into 2-substituted heterocycles and fused-ring heterocyclic compounds. The proposed mechanism for this reaction consists of activation of a heterocyclic C−H bond to generate a coordinatively unsaturated Rh(I)−NHC intermediate, which was shown by X-ray crystallography to be a square-planar Rh(I) NHC/hydride complex. This species undergoes insertion of the coordinated alkene into the Rh−carbene bond, followed by elimination of the final product.[53,62]

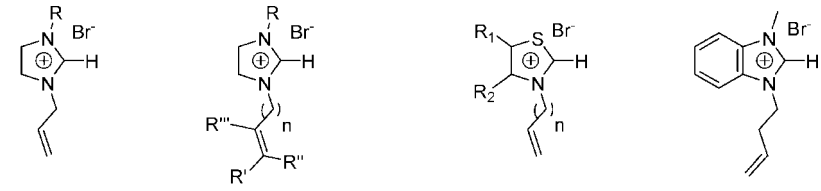
Following from our earlier studies, we anticipated that the use of *N*-vinyl or other *N*-alkenyl-substituted azolium salts in the reaction described in Scheme 1 would lead to the intramolecular formation of fused-ring or annulated heterocycles, potentially valuable as pharmaceutical "building blocks"[65,66] or possibly ionic liquid solvents.[67,68] Accordingly, we report herein the successful use of zerovalent Ni and Pd complexes with both NHC and phosphine spectator ligands (L) to produce novel fused-ring imidazolium salts. Significantly, the reaction also demonstrates the direct, in situ formation of catalytically active carbene−metal−hydride complexes.

Results and Discussion

The synthesis of mono- or disubsituted azolium salts was achieved by a simple alkylation of the corresponding imidazoles and thiazoles (Figure 1). The various imidazolium salts studied here were characterized by NMR, high-resolution electrospray MS, and/or elemental analysis.[69]

IMes acts as a powerful σ-donor ligand and has been shown to facilitate the oxidative addition reaction of imidazolium salts to Ni(0).[48] Stirring a solution of IMes and $Ni(COD)_2$ in DMF gave a purple solution that immediately changed to yellow on

(35) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.*, in press.
(36) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357–366.
(37) Peris, E.; Mata, J.; Loch, J. A.; Crabtree, R. H. *Chem. Commun.* **2001**, 201–202.
(38) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511–1514.
(39) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750–4758.
(40) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165–178.
(41) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596–1605.
(42) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 4918–4920.
(43) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617−618*, 546–560.
(44) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029–4040.
(45) McGuinness, D. S.; Cavell, K. J.; Yates, B. F. *Chem. Commun.* **2001**, 355–356.
(46) McGuinness, D. S.; Cavell, K. J.; Yates, B. F.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 8317–8328.
(47) Duin, M. A.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J. *Chem. Commun.* **2003**, 400–401.
(48) Clement, N. D.; Cavell, K. J.; Jones, C.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1277–1279.
(49) Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L.-l. *Angew. Chem., Int. Ed.* **2005**, *44*, 5282–5284.
(50) Clement, N. D.; Cavell, K. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3845–3847.
(51) Normand, A. T.; Hawkes, K. J.; Clement, N. D.; Cavell, K. J.; Yates, B. F. *Organometallics* **2007**, *26*, 5352–5363.
(52) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 13964–13965.
(53) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 3202–3203.
(54) Tan, K. L.; Vasudevan, A.; Bergman, R. G.; Ellman, J. A.; Souers, A. J. *Org. Lett.* **2003**, *5*, 2131–2134.
(55) Lewis, J. C.; Wiedemann, S. H.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 35–38.
(56) Tan, K. L.; Ellman, J. A.; Bergman, R. G. *J. Org. Chem.* **2004**, *69*, 7329–7335.
(57) Wiedemann, S. H.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 1685–1687.
(58) Thalji, R. K.; Ahrendt, K. A.; Bergman, R. G.; Ellman, J. A. *J. Org. Chem.* **2005**, *70*, 6775–6781.
(59) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 5604–5605.
(60) Lewis, J. C.; Wu, J. Y.; Bergman, R. G.; Ellman, J. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1589–1591.
(61) Wiedemann, S. H.; Ellman, J. A.; Bergman, R. G. *J. Org. Chem.* **2006**, *71*, 1969–1976.
(62) Wiedemann, S. H.; Lewis, J. C.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2006**, *128*, 2452–2462.
(63) Wilson, R. M.; Thalji, R. K.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2006**, *8*, 1745–1747.
(64) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332–5333.
(65) Roth, T.; Morningstar, M. L.; Boyer, P. L.; Hughes, S. H.; Buckheit, R. W.; Michejda, C. J. *J. Med. Chem.* **1997**, *40*, 4199–4207.
(66) Wienen, W.; Hauel, N.; Van Meel, J. C. A.; Narr, B.; Ries, U.; Entzeroth, M. *Br. J. Pharmacol.* **1993**, *110*, 245–248.
(67) Kan, H.-C.; Tseng, M.-C.; Chu, Y.-H. *Tetrahedron* **2007**, *63*, 1644–1653.
(68) Ni, B.; Garre, S.; Headley, A. D. *Tetrahedron Lett.* **2007**, *48*, 1999–2002.
(69) Some salts are extremely hygroscopic, which precluded satisfactory elemental analysis.



n=2

R'= R"= R'"= H

1a: R= Me
1b: R= Bu
1c: R= Mes
1d: R= Dipp

1f: R= Me
1g: R= ^{n}Bu
1h: R= Mes
1i: R= Dipp

1j: R= R'= R"= Me, R'"= H
1k: R= R'"= Me, R'= R"= H
1l: R= Me, R'= R'"= H, R"= Et

n=3

1p: R= Me, R'= R"= R'"= H

n=1

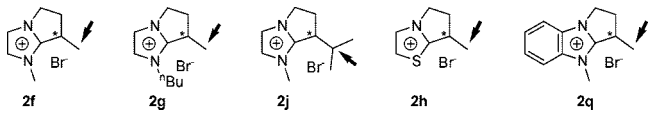
1e: R_1= R_2= H

n=2

1m: R_1= R_2= H
1n: R_1= H, R_2= Me
1o: R_1= R_2= Me

1q

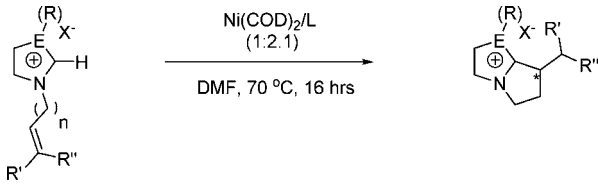
Figure 1. Imidazolium and thiazolium salts used in the catalytic reaction.



2f **2g** **2j** **2h** **2q**

Figure 2. Isolated fused-ring imidazolium salts.[70]

Scheme 2. 2-Substituted Imidazolium and Thiazolium Coupling Reaction



1a-e (n=1): no reaction
1f-o (n=2): conversion to products

addition of a DMF solution of the *N*-allyl-substituted imidazolium salt **1a**, indicating that the expected oxidative addition step had occurred. However, despite heating at 70 °C for an extended period, no product was obtained; the reaction mixture contained only unreacted **1a** (Scheme 2). The imidazolium salts **1a**−**d** and the thiazolium salt **1e** also failed to give the desired fused-ring products. However, the inclusion of a further methylene group between the nitrogen and the alkene group, giving the *N*-but-3-enyl-substituted substrates **1f**−**o**, allows the formation of five-membered fused rings. When the temperature was raised to 70 °C for 16 h, the C2-annulated products were formed. Products **2f**−**h**,**j**,**q** (Figure 2 and Table 1, entries 2, 3, 9, and 10) were isolated and fully characterized by ^{1}H and ^{13}C NMR spectroscopy, high-resolution electrospray mass spectrometry, and/or elemental analysis. The addition of 2 equiv of IMes (spectator ligand L) was necessary for effective catalytic performance, and no decomposition of the catalyst through generation of Ni metal was observed.

It is interesting to note that formation of **2f**−**h**,**q** occurs via migration of the hydride to the terminal position of the alkene, whereas **2j** is formed via hydride migration to the 2-position of the alkene. It is likely that steric factors prevent the formation of the six-membered fused-ring product in which the highly substituted carbon would be attached to the imidazole C2.

(70) Arrows indicate carbon atoms at which hydride insertion occurred.

Table 1. Catalytic Coupling Results with Different Substrates[a]

entry	substrate	conversn (%)[b]
1	**1a**−**e**	0
2	**1f**	100[c]
3	**1g**	100[c]
4	**1h**	44[c]
5	**1i**	0
6	**1m**	<5
7	**1n**	<5
8	**1o**	0
9	**1j**	100[c]
10	**1q**	88[c]

[a] Conditions: catalyst [Ni(COD)$_2$] (10 mol %), substrate 0.7 mmol, IMes 0.15 mmol, DMF (4 mL), 70 °C, 16 h. [b] Determined by ^{1}H NMR spectroscopy, average of two runs. [c] Products **2f**−**h**,**j**,**q** were isolated and characterized.

The influence of the substitution on the second nitrogen atom is apparent in the results summarized in Table 1. When the R group in the 3-position of **1f** was changed to mesityl (Mes), conversion to the fused-ring product decreased to 44% (Table 1, entry 4). Furthermore, when the diisopropylphenyl (dipp)-substituted imidazolium salt **1i** was employed, no conversion was observed at all. This follows the expected reactivity pattern (methyl ≈ butyl > Mes > dipp) where steric bulk of the N substituent plays a part in the reaction efficacy.

The *N*-but-3-enyl-substituted thiazolium salts **1m**−**o** were also investigated as substrates for the fused-ring catalytic reaction. Less than 5% conversion was noted for substrates **1m**,**n** (entries 6 and 7); some decomposition of the catalyst was observed. However, 3-(3-butenyl)-4,5-dimethylthiazolium bromide (**1o**) showed 50% conversion to the annulated product (Table 1, entry 8), as determined by ^{1}H NMR of the mixture (the product was isolated and characterized). The poor conversion of **1m**,**n** may be due to an interaction of the S atom and the Ni catalyst, which is hindered by the presence of the methyl group in the 4-position of **1o**.[71]

The effect of different spectator ligands was investigated using the cyclization of **1f** to **2f** as the test reaction. A variety of NHC ligands and phosphines were investigated (Figure 3), and the results are recorded in Table 2.

NHC ligands bearing a 2,6-diisopropylphenyl ring (Dipp) on both nitrogens (i.e. IPr, SPr, Me$_2$IPr) were found to give better

(71) Graham, D. C.; Cavell, K. J.; Yates, B. F. *Dalton Trans.* **2007**, 4650–4658.

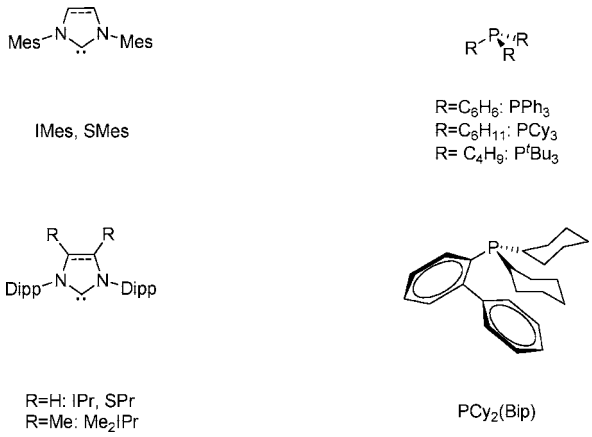


Figure 3. Spectator ligands tested in the reaction.

Table 2. Catalytic Coupling Results with Different Supporting Ligands[a]

entry	cat. loading (%)	ligand	conversn (%)[b]
1	5	IMes	78
2	5	SMes	89
3	5	IPr	100
4	2[c,d]	IPr	100
5	1[e]	IPr	traces
6	5	SPr	100
7	5	Me_2IPr	100
8	5	PPh_3	30
9	5	PCy_3	94
10	5	PCy_2(Bip)	100
11	2[c,d]	PCy_2(Bip)	traces
9	5	$PtBu_3$	35

[a] Conditions: $Ni(COD)_2$ (x mol %), substrate (**1f**) 0.7 mmol, supporting ligand (2.1x mol %), DMF (4 mL), 50 °C, 60 min. [b] Determined by ^{1}H NMR spectroscopy, average of two runs. [c] 3.5 mmol of substrate. [d] Reaction time was 20 h. [e] 7.0 mmol of substrate.

results than those with 2,4,6-trimethylphenyl (IMes and SMes). It would thus seem that, in the case of NHCs, the higher bulk of the former is beneficial for the reaction, which in turn suggests that reductive elimination or olefin insertion is the rate-determining step. For phosphines, a balance between bulk and electron-donating ability seems necessary, as neither PPh_3 (least basic and least bulky phosphine) nor $PtBu_3$ (most basic and most bulky phosphine) is very effective in promoting the reaction. This balance would seem to be achieved with the Buchwald ligand PCy_2(Bip). These results suggest a different mechanism for phosphines compared to carbenes as spectator ligands (e.g. involving phosphine dissociation equilibria).

Lower loadings of $Ni(COD)_2$ were also investigated; for the best catalysts, loadings of 2−5% enable complete conversion

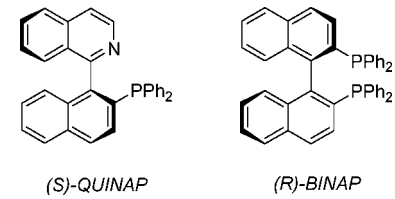


Figure 4. Chiral bidentate ligands tested in the cyclization of **1f**.

in as little as 1 h at 50 °C (Table 2, entries 3, 4, 6, 7, and 10). Considering that complete conversion was obtained with relatively low Ni loadings and IPr as the spectator ligand (Table 2, entries 3 and 4), it was initially surprising that catalyst loading could not be lowered further. When the loading was lowered to 1%, very little conversion was observed (Table 2, entry 5; the same situation occurs in the case of PCy_2(Bip), entry 11), suggesting that catalyst deactivation is occurring when substrate concentration is significantly higher than that of the catalyst. It is possible that at low loadings the active catalyst is repressed by coordination of a second alkenylimidazolium to the metal center.[73]

The annulated imidazolium salt **2g** is a low -melting oily solid and hence could be considered to be an ionic liquid (IL), and with the appropriate anion many other examples of these annulated products may behave as IL solvents. Bicyclic imidazolium salts structurally close to **2f** have been reported recently by Chu and co-workers. These salts were shown to have interesting stability profiles in basic media in comparison to commonly used ILs such as [bmim][NTf_2], due to the absence of hydrogen at the C2 position of the imidazole ring.[67] Because in our case the annulated imidazolium salts possess a chiral center, an asymmetric version of our reaction would provide a valuable catalytic route to chiral ILs. Therefore, two chiral bidentate ligands ((*S*)-QUINAP and (*R*)-BINAP, Figure 4) were tested in this reaction.

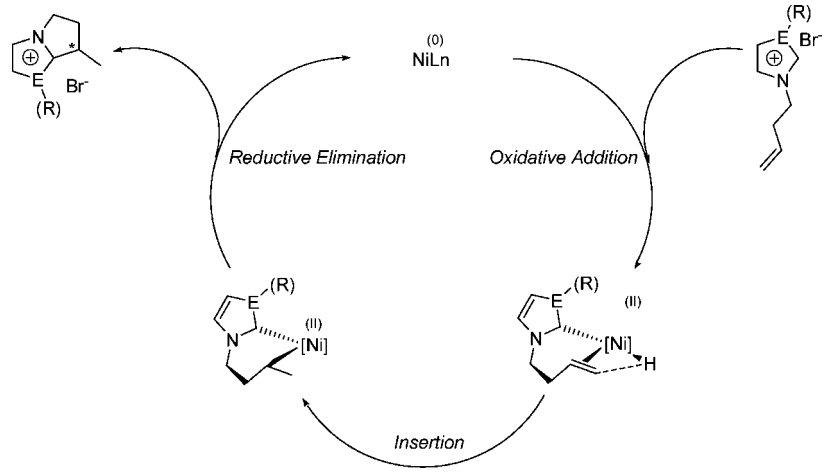
No conversion to the annulated product **2f** was observed, even at elevated temperatures. However, significant quantities (24% at 90 °C for (*S*)-QUINAP, 18% for (*R*)-BINAP) of olefin isomerization products **1f′**,**f″** were generated (Scheme 4; *Z* and *E* isomers were obtained as a 50/50 mixture (see ^{1}H NMR spectrum in the Supporting Information). It is apparent that the chelating ligands shut down the final reductive elimination step in the catalytic cycle (Scheme 3). The Ni center remains in the +II oxidation state and thus behaves as a simple isomerization catalyst. We are now investigating the use of chiral monodentate NHCs and phosphines to generate enantioenriched annulated azolium salts.

Imidazolium salts with substituted-butenyl moieties on the nitrogen were also investigated as substrates (Table 3). With 1-(3-methyl-but-3-enyl)-3-methylimidazolium bromide (**1k**), 20% conversion to the fused imidazolium salt **2k** (Table 3, entry 1) was observed. This is significantly lower than the conversion observed with **1f** under the same conditions (Table 1, entry 2). The extra steric bulk probably hinders the ring fusion reaction. The longer chain alkenyl-substituted salt 1-(hex-3-enyl)-3-methylimidazolium bromide (**1l**) was reacted to yield the fused-ring product **2l** with 79% conversion (Table 3, entry 2), using IMes as the supporting ligand. Surprisingly, with SMes only

(72) The fate of Br^- during the course of the reaction (i.e. bound to Ni or in the second sphere of coordination) is not known exactly; therefore, we have voluntarily left it out of the formula. Also, a reviewer has suggested an alternative view on our proposed mechanism. It was pointed out that after the oxidative addition a nickel dicarbene complex is formed, consisting of the original carbene ligand and the carbene generated from the substrate imidazolium salt. The substrate now becomes a chelate ligand (carbene + η^2 coordination) and may provide a better ligand than the original IMes monodentate carbene ligand. In this case both carbene ligands would compete for coordination at the metal center. Therefore, the suggestion is that the original IMes ligand is eliminated as the imidazolium salt IMesHBr, and afterwards the catalytic cycle takes place with the chelating carbene as the actual ligand L. However, we feel that our previous studies[46,51] provide a sound basis for the mechanism depicted in Scheme 3. Indeed, dissociation of IMes or reductive elimination of IMesHBr is unlikely to be a favorable process, considering (a) the strong Ni−NHC BDE and (b) the very exothermic C−H oxidative addition reaction of Ni(0) to imidazolium salts. We agree that a chelating NHC−olefin ligand would form very stable species; however, we think it would not be kinetically possible.

(73) The last step of the catalytic cycle in the intermolecular version of this reaction is thought to proceed from a 14-electron Ni(II) species (see ref 46 for a detailed discussion), which facilitates reductive elimination. The coordination of an extra olefin might inhibit this step, by creating a stabilized 16-electron Ni(II) complex. Indeed, we observed a green coloration appearing in the course of the reaction at low loadings, indicating a Ni(II) species.

Scheme 3. Proposed Catalytic Cycle for the *N*-Butenyl Azolium Annulation Reaction[72]



Scheme 4. Isomerization of 1f in the Presence of Chelating Ligands

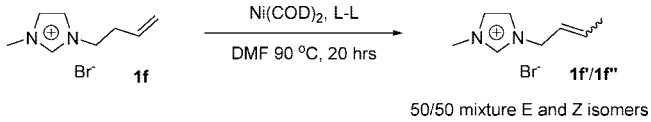
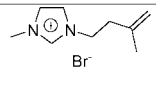
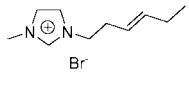
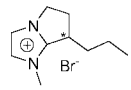
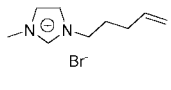


Table 3. Catalytic Coupling Results with Different Substrates[b]

Entry	Substrate	Product	Ligand	Conv. (%)[a]
1	 **1k**	 **2k**	IMes	20
2	 **1l**	 **2l**	IMes SMes	79 23†
3	 **1p**	 **2p**	IMes SMes	85 67†

[a] Determined by ^{1}H NMR spectroscopy, average of two runs. [b] Conditions: catalyst [Ni(COD)$_2$] (10 mol %), substrate 0.7 mmol, supporting ligand 0.15 mmol, DMF (4 mL), 70 °C, 16 h. A dagger next to a conversion value indicates that catalyst decomposition was observed.

23% conversion was obtained (Table 3, entry 2), and decomposition of the catalyst, giving a green solution, was observed. The formation of larger fused rings was also investigated. Thus, the reaction of **1p** afforded the desired six-membered fused ring **2p** with 85% conversion (Table 3, entry 3). As before, when SMes was used in the reaction, the conversion dropped (67%) and catalyst decomposition was observed (Table 3, entry 3). This observation highlights the fact that ligand efficiency may be substrate-dependent. Indeed, SMes is a better ligand for the annulation of **1f** than IMes, a trend opposite to that observed for **1l**,**p**.

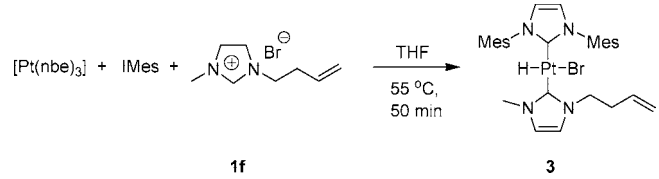
Pd catalysts were also studied in the cyclization of **1f**, albeit with significantly lower activity than the Ni systems. The combination of 5 mol % of Pd(dba)$_2$ and 2.1 equiv of IPr gave 6% coupled product at 70 °C (Table 4, entry 1), and raising the temperature to 90 °C only provided a slight increase in activity (entry 4). With IMes as spectator ligand and 10 mol % Pd(dba)$_2$ 10% conversion was obtained (entry 2), and the use of the Buchwald phosphine was unsuccessful (entry 3). Although the Pd systems are poorer catalysts than those of Ni, the fact that some reaction is occurring indicates that active carbene−Pd−hydride species are generated from Pd(0) and imidazolium salts.

Table 4. Annulation of 1f with Pd(0) Catalysts[a]

entry	ligand	temp (°C)	conversn (%)[b]
1	IPr	70	6
2	IMes	70	10[c]
3	PCy$_2$(Bip)	70	0
4	IPr	90	20

[a] Conditions: Pd(dba)$_2$ (5 mol %), substrate (**1f**) 0.7 mmol, ligand 11 mol %, DMF (4 mL), 17 h. [b] Determined by ^{1}H NMR spectroscopy, average of two runs. [c] 10 mol % of [Pd] was used.

Scheme 5. Oxidative Addition of 3a to a Pt(0) center (nbe = Norbornene)



Stoichiometric Oxidative Addition of 3a to Pt(0) and Ni(0). A THF solution of Pt(nbe)$_3$ (1 equiv) and IMes (1 equiv) was prepared in situ and added to a THF solution of salt **1f** (0.9 equiv). The reaction mixture was stirred at 55 °C for 50 min, yielding **3** (Scheme 5) as an off-white oily product. The complex was characterized by ^{1}H NMR spectroscopy. The hydride appears in the ^{1}H NMR spectrum of **3** (CD_2Cl_2) at δ −18.06 ($^1J_{Pt-H}$ = 1690 Hz). We were unsuccessful in growing crystals for X-ray diffraction.

Conclusion

A catalytic Ni(0)/Ni(II) redox reaction starting from alkenyl-substituted imidazolium salts is applicable to the construction of five- and six-membered fused-ring imidazolium, thiazolium, and benzimidazolium salts. This reaction occurs under mild conditions and represents a novel atom-efficient catalytic reaction for the formation of substituted azolium salts. Apart from its potential synthetic value (including the catalytic preparation of chiral ILs), this reaction represents a further example where azolium oxidative addition and carbene reductive elimination processes have been combined into the same catalytic cycle and illustrates the ease with which interconversion between azolium salts and N-heterocyclic carbene transition-

metal complexes occurs under mild conditions. Furthermore, the reaction provides an example of the direct, in situ formation of a catalytically active M(II)−H bond, generated from the oxidative addition of azolium salts to M(0). Such a species was observed by ^{1}H NMR spectroscopy in the case of Pt. The hydride thus formed undergoes migratory insertion with olefins to generate new products in a catalytic reaction involving an intermediate carbene complex.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed by using standard Schlenk techniques under argon or in a nitrogen glovebox. Solvents were dried by standard methods. Bis(1,5-cyclooctadiene)nickel(0),[74] 1-allyl-3-methylimidazolium bromide (**1a**),[75] 1-butyl-3-allyl-imidazolium bromide (**1b**),[76] 1-(2,3,6-trimethylphenyl)-1*H*-imidazole,[77] 1-(2,6-diisopropylphenyl)-1*H*-imidazole,[77] 3-allylthiazolium bromide (**1e**),[78] 3-(3-butenyl)-4-methylthiazolium bromide (**1n**),[79] 1-(4-pentenyl)-3-methylimidazolium bromide (**1p**),[80] *N*,*N*′-bis-(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes), *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimidazol-2-ylidene (Me_2IPr), and 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene (SMes)[81] were prepared according to published procedures. Benzothiazole was purchased from Alfa Aesar and distilled prior to use. Other commercially available compounds were used without purification.

^{1}H and ^{13}C NMR spectra were recorded at 293 K on Bruker DPX 400 or 500 spectrometers with chemical shifts (δ) referenced to internal solvent resonances and reported relative to Me_4Si. Coupling constants (*J*) are given in Hz, and NMR peaks are labeled as s = singlet, d = doublet, q = quartet, and m = multiplet. Electrospray ionization mass spectrometry (ESI/MS) was performed on a Waters LCCT Premier XE instrument. Elemental analyses were carried out by Warwick Analytical Service Ltd., Coventry, U.K. X-ray diffraction data were obtained on a Kappa Nonius CCD diffractometer equipped with an Oxford cryogenic system to maintain the crystals at 150 K. Structure solution and refinement were performed by Dr. Andreas Stasch.

General Procedure A. A mixture of N-substituted imidazole (1 mmol) and alkenyl halide (1.2 mmol) was stirred at 70 °C overnight. The reaction mixture was cooled to room temperature, and the yellow oily product or white solid thus obtained was washed several times with ethyl acetate and diethyl ether and dried under vacuum.

General Procedure B. An oven-dried Schlenk tube was charged with the N-arylimidazole (1 mmol) and alkenyl halide (1.2 mmol). THF (20 mL) was added, and the mixture was stirred at 70 °C overnight. The solvent was removed under vacuum, and diethyl ether (40 mL) was added. The off-white solid thus obtained was washed several times with diethyl ether and dried under vacuum.

Procedure for the Catalytic Coupling of Azolium Salts. A 60 mL Young Schlenk was charged with bis(cycloocta-1,5-diene)nickel(0) (10 mg, 0.037 mmol, 5 mol % in most cases) or $Pd(dba)_2$ (44 mg, 0.073 mmol, 10 mol %), a phosphine or NHC ligand (0.077 mmol, 11 mol %), and the substrate (0.73 mmol, 1 equiv) in a glovebox. DMF was then syringed into the reaction vessel under a flow of argon, and the yellow solution was heated to reaction temperature (50 °C in most cases). The solution was stirred for the required time (1 h in most cases). The solvent was then removed in vacuo and the residue dissolved in d_6-DMSO and submitted for ^{1}H NMR spectroscopy. The conversion to annulated product was calculated by comparing the integration values of *N*-Me protons of the starting material and the product (no other products were detected apart from NHC or phosphine ancillary ligand).

Oxidative Addition of 1f to Pt(0). A solution of THF (4 mL) of **1f** (91 mg, 0.27 mmol) was transferred to a mixture of $Pt(nbe)_3$ (143 mg, 0.30 mmol) and IMes (91 mg, 0.30 mmol) which was dissolved in THF (4 mL). The mixture was heated at 55 °C for 50 min. The solvent was removed under vacuum. The off-white oily product was washed several times with hexane and diethyl ether and dried under vacuum. Yield: 295 mg (0.41 mmol, 45%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −18.06 (s, 1H, M−H), 7.48 (d, 2H, Ar *H*), 7.08−6.89 (m, 6H, Ar *H*), 5.49−5.41 (m, 1H, $CH_2CH_2CH{=}CH_2$), 4.93−4.82 (m, 2H, $CH_2CH_2CH{=}CH_2$), 3.75 (t, 2H, $^3J_{HH}$ = 7.4 Hz, $CH_2CH_2CH{=}CH_2$), 3.35 (q, 2H, $^3J_{HH}$ = 6.93 Hz, $CH_2CH_2CH{=}CH_2$), 3.21 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), 2.13 (s, 12H, CH_3).

3-Allyl-1-mesitylimidazolium Bromide (1c). General procedure B was followed using 1-(2,3,6-trimethylphenyl)-1*H*-imidazole (186 mg, 1 mmol) and allyl bromide (121 mg, 1.2 mmol), giving a white solid. Yield: 280 mg (0.91 mmol, 91%). ^{1}H NMR (500.13 MHz, D_2O): δ 10.46 (s, 1H, im C2-*H*), 7.71 (s, 1H, im C4/5-*H*), 7.54 (s, 1H, C4/5-*H*), 7.21 (s, 2H, Ar *H*), 6.19−6.05 (m, 1H, $CH_2CH{=}CH_2$), 5.47 (d, 1H, $^3J_{HH}$ = 10.0 Hz, $CH_2CH{=}CHH_{cis}$), 5.40 (d, 1H, $^3J_{HH}$ = 15.0 Hz, $CH_2CH{=}CHH_{trans}$), 4.92 (d, 2H, $^3J_{HH}$ = 5.0 Hz, $CH_2CH{=}CH_2$), 2.31 (s, 3H, CH_3), 2.00 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 141.5 (im *C*2), 134.7 (Ar *C*), 130.8 ($CH_2CH{=}CH_2$), 130.2, 129.2, 124.1, 123.1 (Ar *C*), 121.4 ($CH_2CH{=}CH_2$), 51.9 ($CH_2CH{=}CH_2$), 20.2 (CH_3), 16.3 (CH_3). Anal. Calcd for $C_{15}H_{19}BrN_2$: C, 58.44; H, 6.23; N, 9.12. Found: C, 58.08; H, 6.21; N, 9.21.

3-Allyl-1-(2,6-diisopropylphenyl)imidazolium Bromide (1d). General procedure B was followed using 1-(2,6-diisopropylphenyl)-1*H*-imidazole (227 mg, 1 mmol) and allyl bromide (121 mg, 1.2 mmol), giving a off-white solid. Yield: 201 mg (0.60 mmol, 60%). ^{1}H NMR (500.13 MHz, D_2O): δ 9.14 (s, 1H, im C2-*H*), 7.75 (s, im C4/5-*H*), 7.67 (s, im C4/5-*H*), 7.60 (t, 1H, $^3J_{HH}$ = 7.50 Hz, Ar *H*), 7.43 (d, 2H, $^3J_{HH}$ = 5.00 Hz, Ar *H*), 6.19−6.08 (m, 1H, $CH_2CH{=}CH_2$), 5.47 (d, 1H, $^3J_{HH}$ = 10.0 Hz, $CH_2CH{=}CHH_{cis}$), 5.40 (d, 1H, $^3J_{HH}$ = 15.0 Hz, $CH_2CH{=}CHH_{trans}$), 4.93 (d, 2H, $^3J_{HH}$ = 10.0 Hz, $CH_2CH{=}CH_2$), 2.39−2.28 (m, 2H, $CH(CH_3)$), 1.11 (d, 12H, $^3J_{HH}$ = 5.0 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 145.8 (im *C*2), 136.8 (Ar *C*), 131.8 ($CH_2CH{=}CH_2$), 130.2, 125.4, 124.5, 123.3 (Ar *C*), 121.4 ($CH_2CH{=}CH_2$), 51.9 ($CH_2CH{=}CH_2$), 28.3 ($CH(CH_3)$), 23.3 (CH_3). Anal. Calcd for $C_{18}H_{25}BrN_2$: C, 61.89; H, 7.21; N, 8.02. Found: C, 61.61; H, 7.19; N, 7.84. This compound has been reported previously, but no analytical data were provided.[82]

1-Butenyl-3-methylimidazolium Bromide (1f). General procedure A was followed using 1-methylimidazole (82 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving a yellow oily product. Yield: 162 mg (0.75 mmol, 75%). Characterization data were identical with those in the literature.[83]

1-Butyl-3-(3-butenyl)imidazolium Bromide (1g). General procedure A was followed using *N*-butylimidazole (124 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving a yellow oily

(74) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5–9.
(75) Hahn, F. E.; Heidrich, B.; Pape, T.; Hepp, A.; Martin, M.; Sola, E.; Oro, L. A. *Inorg. Chim. Acta* **2006**, *359*, 4840–4846.
(76) Ohno, H.; Mizumo, T.; Yoshida, M.; Suga, T. WO 2005080347, 2005.
(77) Arduengo, A. J. I.; Gentry, F. P. J.; Taverkere, P. K.; Simmons, H. E. I. U.S. Patent 6,177,575, 2001.
(78) Schilling, C. L.; Mulvaney, J. E. *Macromolecules* **1968**, *1*, 452–455.
(79) Chen, Y. T.; Jordan, F. *J. Org. Chem.* **1991**, *56*, 5029–5038.
(80) Corberan, R.; Sanau, M.; Peris, E. *Organometallics* **2007**, *26*, 3492–3498.
(81) Anthony, J.; Arduengo, I.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534.
(82) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2002**, 482–483.
(83) Corberan, R.; Sanau, M.; Peris, E. *Organometallics* **2007**, *26*, 3492–3498.

product. Yield: 181 mg (0.70 mmol, 70%). ^{1}H NMR (500.13 MHz, D_2O): δ 8.74 (s, 1H, im C2-*H*), 7.45 (d, 2H, $^3J_{HH}$ = 5.0 Hz, im C4/5-*H*), 5.79−5.73 (m, 1H, CH_2CH_2CH=CH_2), 5.05 (d, 1H, $^3J_{HH}$ = 10.0 Hz, CH_2CH_2CH=$CH H_{cis}$), 4.98 (d, 1H, $^3J_{HH}$ = 20.0 Hz, CH_2CH_2CH=$CH H_{trans}$), 4.24 (t, 2H, $^3J_{HH}$ = 5.0 Hz, CH_2CH_2CH=CH_2), 4.15 (t, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 2.57 (q, 2H, $^3J_{HH}$ = 6.7 Hz, CH_2CH_2CH=CH_2), 1.80 (quent, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.24 (sextet, 2H, $^3J_{HH}$ = 6.7 Hz, $CH_2CH_2CH_2CH_3$), 0.87 (t, 3H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 135.2 (im *C*2), 133.3 (CH_2CH_2CH=CH_2), 122.4 (im C4/5), 118.8 (CH_2CH_2CH=CH_2), 49.3 ($CH_2CH_2CH_2CH_3$), 48.8 (CH_2CH_2CH=CH_2), 33.8 (CH_2CH_2CH=CH_2), 31.2 ($CH_2CH_2CH_2CH_3$), 18.7 ($CH_2CH_2CH_2CH_3$), 12.61 (CH_3). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 179.1541 (calcd 179.1548, dev −3.9 ppm). This compound was found to be too hygroscopic for satisfactory elemental analysis.

1-Mesityl-3-(3-butenyl)imidazolium Bromide (1h). General procedure B was followed using 1-(2,3,6-trimethylphenyl)-1*H*-imidazole (186 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving an off-white solid. Yield: 138 mg (0.43 mmol, 43%). ^{1}H NMR (500.13 MHz, D_2O): δ 8.89 (s, 1H, im C2-*H*), 7.70 (s, 1H, im C4/5-*H*), 7.49 (s, 1H, im C4/5-*H*), 7.10 (s, 2H, Ar H), 5.88−5.73 (m, 1H, CH_2CH_2CH=CH_2), 5.08 (d, 1H, $^3J_{HH}$ = 10.0 Hz, CH_2CH_2CH=$CH H_{cis}$), 5.01 (d, 1H, $^3J_{HH}$ = 20.0 Hz, CH_2CH_2CH=$CH H_{trans}$), 4.37 (t, 2H, $^3J_{HH}$ = 5.0 Hz, CH_2CH_2CH=CH_2), 2.64 (q, 2H, $^3J_{HH}$ = 5.0 Hz, CH_2CH_2CH=CH_2), 2.29 (s, 3H, CH_3), 1.96 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 141.5 (im *C*2), 136.3, 135.3 (Ar *C*), 133.1 (CH_2CH_2CH=CH_2), 130.8, 129.2, 124.1, 123.0 (Ar *C*), 119.4 (CH_2CH_2CH=CH_2), 49.1 (CH_2CH_2CH=CH_2), 33.9 (CH_2CH_2CH=CH_2), 20.2 (CH_3), 17.1 (CH_3). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 241.1706 (calcd 241.1705, dev 0.4 ppm). Anal. Calcd for $C_{16}H_{21}BrN_2$: C, 59.82; H, 6.59; N, 8.72. Found: C, 59.92; H, 6.59; N, 8.75.

1-(2,6-Diisopropylphenyl)-3-(3-butenyl)imidazolium Bromide (1i). General procedure B was followed using 1-(2,6-diisopropylphenyl)-1*H*-imidazole (227 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving a off-white solid. Yield: 94 mg (0.26 mmol, 26%). ^{1}H NMR (500.13 MHz, D_2O): δ 9.05 (s, 1H, im C2-*H*), 7.72 (s, 1H, im C4/5-*H*), 7.62 (s, 1H, im C4/5-*H*), 7.57 (t, 1H, $^3J_{HH}$ = 10.0 Hz, Ar *H*), 7.40 (d, 1H, $^3J_{HH}$ = 10.0, Ar *H*), 5.81−5.65 (m, 1H, CH_2CH_2CH=CH_2), 5.09 (d, 1H, $^3J_{HH}$ = 10.0 Hz, CH_2CH_2CH=$CH H_{cis}$), 5.01 (d, 1H, $^3J_{HH}$ = 15.0 Hz, CH_2CH_2CH=$CH H_{trans}$), 4.38 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_2CH=CH_2), 2.64 (q, 2H, $^3J_{HH}$ = 5.0 Hz, CH_2CH_2CH=CH_2), 2.34−2.23 (m, 2H, $CH(CH_3)_2$), 1.09 (d, 12H, $^3J_{HH}$ = 5.0 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 145.8 (im *C*2), 136.7, 135.4 (Ar *C*), 133.0 (CH_2CH_2CH=CH_2), 131.8, 130.3, 125.4, 124.5, 123.0 (Ar *C*), 119.4 (CH_2CH_2CH=CH_2), 49.1 (CH_2CH_2CH=CH_2), 34.0 (CH_2CH_2CH=CH_2), 28.3 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$). Anal. Calcd for $C_{19}H_{27}BrN_2$: C, 62.81; H, 7.49; N, 7.71. Found: C, 62.59; H, 7.59; N, 7.74.

1-(4-Methyl-pent-3-enyl)-3-methylimidazolium Bromide (1j). General procedure A was followed using 1-methylimidazole (82 mg, 1 mmol) and 5-bromo-2-methylpentene (196 mg, 1.2 mmol), giving a yellow oily product. Yield: 184 mg (0.75 mmol, 75%). ^{1}H NMR (500.13 MHz, D_2O): δ 8.72 (s, 1H, im C2-*H*), 7.51 (s, 1H, im C4/5-*H*), 7.44 (s, 1H, im C4/5-*H*), 5.16 (t, 1H, $^3J_{HH}$ = 8.8 Hz, CH_2CH_2CH=$C(CH_3)(CH_3)$), 4.23 (t, 2H, $^3J_{HH}$ = 6.4 Hz, CH_2CH_2CH=$C(CH_3)(CH_3)$), 3.91 (s, 3H, CH_3), 2.55 (q, 2H, $^3J_{HH}$ = 6.8 Hz, CH_2CH_2CH=$C(CH_3)(CH_3)$), 1.69 (s, 3H, CH_3), 1.42 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ 138.1 (im *C*2), 136.3 (CH_2CH_2CH=$C(CH_3)(CH_3)$), 123.7 (im *C*4/5), 122.8 (im *C*4/5), 118.6 (CH_2CH_2CH=$C(CH_3)(CH_3)$), 49.7 (CH_2CH_2CH=$C(CH_3)(CH_3)$), 36.1 (CH_3), 28.7 (CH_2CH_2CH=$C(CH_3)(CH_3)$), 25.3 (CH_2CH_2CH=$C(CH_3)(CH_3)$), 17.1 (CH_2CH_2CH=$C(CH_3)(CH_3)$). High -resolution ESI_{pos}-MS (MeCN): *m*/*z* found 165.1387 (calcd 165.1392, dev −3.0 ppm). This compound was found to be too hygroscopic to allow for satisfactory elemental analysis.

3-(3-Butenyl)thiazolium Bromide (1m). General procedure A was followed by using thiazole (85 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving a white solid. Yield: 117 mg (0.53 mmol, 53%). ^{1}H NMR (500.13 MHz, D_2O): δ 8.31 (d, 1H, $^3J_{HH}$ = 5.0 Hz, thi C4/5-*H*), 8.16 (d, 1H, $^3J_{HH}$ = 5.0, thi C4/5-*H*), 5.84−5.76 (m, 1H, CH_2CH_2CH=CH_2), 5.08 (d, 1H, $^3J_{HH}$ = 15.0 Hz, CH_2CH_2CH=$CH H_{cis}$), 4.99 (d, 1H, $^3J_{HH}$ = 20.0 Hz, CH_2CH_2CH=$CH H_{trans}$), 4.65 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_2CH=CH_2), 2.70 (q, 2H, $^3J_{HH}$ = 6.7 Hz, CH_2CH_2CH=CH_2). The proton of NHC on the thiazolium ring was not observed due to exchange with deuterium. ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 136.9 (thi *C*2), 132.6 (CH_2CH_2CH=CH_2), 125.7 (thi *C*4/5), 119.5 (CH_2CH_2CH=CH_2), 54.7 (CH_2CH_2CH=CH_2), 33.8 (CH_2CH_2CH=CH_2). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 140.0538 (calcd 140.0534, dev 2.9 ppm). Anal. Calcd for $C_7H_{10}BrNS$: C, 38.19; H, 4.58; N, 6.36; S, 14.57;Br, 36.30. Found: C, 38.13; H, 4.55; N, 6.29; S, 14.35; Br, 36.05.

3-(3-Butenyl)-4,5-dimethylthiazolium Bromide (1o). General procedure A was followed using 4,5-dimethylthiazole (113 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving a white solid. Yield: 243 mg (0.98 mmol, 98%). ^{1}H NMR (500.13 MHz, D_2O): δ 9.59 (s, 1H, thi C2-*H*), 5.85−5.80 (m, 1H, CH_2CH_2CH=CH_2), 5.11 (d, 1H, $^3J_{HH}$ = 10.0 Hz, CH_2CH_2CH=$CH H_{cis}$), 5.02 (d, 1H, $^3J_{HH}$ = 20.0 Hz, CH_2CH_2CH=$CH H_{trans}$), 4.51 (t, 2H, $^3J_{HH}$ = 5.0 Hz, CH_2CH_2CH=CH_2), 2.65 (q, 2H, $^3J_{HH}$ = 6.7 Hz, CH_2CH_2CH=CH_2), 2.53 (s, 3H, CH_3), 2.44 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 153.6 (thi *C*2), 141.9 (thi *C*4/5), 133.7 (CH_2CH_2CH=CH_2), 132.6 (thi *C*4/5), 119.6 (CH_2CH_2CH=CH_2), 52.7 (CH_2CH_2CH=CH_2), 32.9 (CH_2CH_2CH=CH_2), 11.7 (CH_3), 10.9 (CH_3). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 168.0851 (calcd 168.0847, dev 2.4 ppm). Anal. Calcd for $C_9H_{14}BrNS$: C, 43.56; H, 5.69; N, 5.64. Found: C, 43.55; H, 5.59; N, 5.57.

1-(3-Butenyl)-3-methylbenzimidazolium Bromide (1q). General procedure B was followed using 1-methylbenzimidazole (132 mg, 1 mmol) and 4-bromo-1-butene (162 mg, 1.2 mmol), giving an off-white solid. Yield: 264 mg (0.99 mmol, 99%). ^{1}H NMR (500.13 MHz, D_2O): δ 7.91−7.88 (m, 1H, Ar *H*), 7.85−7.82 (m, 1H, Ar *H*), 7.71−7.66 (m, 2H, Ar *H*), 5.88−5.76 (m, 1H, CH_2CH_2CH=CH_2), 5.02 (d, 1H, $^3J_{HH}$ = 10.00 Hz, CH_2CH_2CH=$CH H_{cis}$), 4.92 (d, 1H, $^3J_{HH}$ = 18.00 Hz, CH_2CH_2CH=$CH H_{trans}$), 4.56 (t, 2H, $^3J_{HH}$ = 6.80 Hz, CH_2CH_2CH=CH_2), 4.06 (s, 3H, NCH_3), 2.71 (q, 2H, $^3J_{HH}$ = 6.80 Hz, CH_2CH_2CH=CH_2). The proton of im C2 on the benzimidazolium ring was not observed, due to exchange with deuterium. ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 139.9 (im C_2), 133.6 (CH_2CH_2CH=CH_2), 127.2 (Ar *C*), 119.1 (CH_2CH_2CH=CH_2), 113.5, 113.3 (Ar *C*), 46.5 (CH_2CH_2CH=CH_2), 33.1 (CH_2CH_2CH=CH_2), 33.0 (NCH_3). Anal. Calcd for $C_{12}H_{15}BrN_2$: C, 53.95; H, 5.66; N, 10.49. Found: C, 53.66; H, 5.63; N, 10.44.

***rac*-1,7-Dimethyl-6,7-dihydro-5*H*-pyrrole[1,2-α]imidazolium Bromide (2f).** ^{1}H NMR (D_2O, 500.13 MHz): δ (ppm) 7.24 (s, 2H, im C4/5-*H*), 4.28−4.23 (m, 1H, NCH_2), 4.15−4.10 (m, 1H, NCH_2), 3.77 (s, 3H,NCH_3), 3.65−3.59 (m, 1H, C*H* β to N), 2.98−2.92 (m, 1H, CH_2 γ to N, overlap with *H* anti to CH_3), 2.40−2.34 (m, 1H, CH_2 γ to N, overlap with *H* syn to CH_3), 1.39 (d, 3H, $CHCH_3$, $^3J_{HH}$ = 10.0 Hz). ^{1}H NMR chemical shifts of hydrogens on the carbon atom γ to N assigned by analogy with those of **2j** (obtained with gs-NOESY experiments).^{13}C{^{1}H} NMR (D_2O, 125.03 MHz): δ (ppm) 154.63 (im *C*2), 126.84 (im *C*4/5), 117.07 (im *C*4/5), 46.78 (NCH_2), 34.74 (NCH_3), 34.33 (CH β to N), 31.12 (CH_2 γ to N), 15.73 ($CHCH_3$). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 137.1075 (calcd 137.1079, dev −2.9 ppm).

Anal. Calcd for $C_8H_{13}N_2Br$: C, 44.26; H, 6.04; N, 12.90. Found: C, 43.92; H, 6.04; N, 12.88.

***rac*-1-Butyl-7-methyl-6,7-dihydro-5*H*-pyrrolo[1,2-α]imidazolium Bromide (2g).** ^{1}H NMR (500.13 MHz, D_2O): δ 7.36 (s, 1H, im C4/5-*H*), 7.32 (s, 1H, im C4/5-*H*), 4.33−4.26 (m, 1H, NCH_2), 4.19−4.17 (m, 1H, NCH_2, overlap with $NCH_2CH_2CH_2CH_3$), 4.11 (t, 2H, $^3J_{HH}$ = 5.40 Hz, $NCH_2CH_2CH_2CH_3$), 3.70−3.62 (m, 1H, C*H* β to N), 3.04−2.96 (m, 1H, CH_2 γ to N, overlap with residual solvent peak), 2.42−2.37 (m, 1H, CH_2 γ to N), 1.81 (p, 1H, $^3J_{HH}$ = 9.20 Hz, $NCH_2CH_2CH_2CH_3$), 1.43 (d, 3H, $CHCH_3$, $^3J_{HH}$ = 9.0 Hz), 1.34 (sextet, 2H, $^3J_{HH}$ = 8.40 Hz, $NCH_2CH_2CH_2CH_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.40 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ 154.4 (im *C*2), 121.0 (im *C*4/5), 117.7 (im *C*4/5), 49.0 ($NCH_2CH_2CH_2CH_3$), 46.9 (NCH_2), 34.1 (*C*H β to N), 31.8 ($NCH_2CH_2CH_2CH_3$), 31.1 (*C*H_2 γ to N), 19.3 ($NCH_2CH_2CH_2CH_3$), 17.2 ($CHCH_3$), 13.1 ($NCH_2CH_2CH_2CH_3$). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 179.1543 (calcd 179.1548, dev −2.8 ppm). This compound was found to be too hygroscopic for satisfactory elemental analysis.

***rac*-1-Methyl-7-isopropyl-6,7-dihydro-5*H*-pyrrolo[1,2-α]imidazolium Bromide (2j).** ^{1}H NMR (CD_2Cl_2, 500.13 MHz): δ (ppm) 7.56 (d, 1H, im C4/5-*H*, $^3J_{HH}$ = 1.9 Hz), 7.44 (d, 1H, im C4/5-*H*, $^3J_{HH}$ = 1.9 Hz), 4.27−4.33 (m, 1H, NCH_2), 4.13−4.19 (m, 1H, NCH_2), 3.88 (s, 3H, NCH_3), 3.73 (m, 1H, NCH_2), 2.78−2.87 (m, 1H, H γ to N and anti to ^{i}Pr), 2.43−2.51 (m, 1H, H γ to N and syn to ^{i}Pr), 2.26−2.36 (m, 1H, C*H*$(CH_3)_2$), 0.99 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 0.73 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.8 Hz). ^{1}H chemical shifts were assigned on the basis of a gs-NOESY experiment (see the Supporting Information). ^{13}C{^{1}H} NMR (D_2O, 125.03 MHz): δ (ppm) 153.8 (im *C*2), 127.2 (im *C*4/5), 117.3 (im *C*4/5), 47.5 (NCH_2), 42.3 (*C*H β to N), 34.8 (NCH_3), 29.2 (*C*$H(CH_3)_2$), 27.3 (*C*H_2 γ to N), 19.6 ($CH(CH_3)_2$), 16.5 ($CH(CH_3)_2$). High-resolution ESI_{pos}-MS (MeCN): *m*/*z* found 165.1385 (calcd 165.1392, dev −4.2 ppm). Anal. Calcd for $C_{10}H_{17}N_2Br$ (M_r = 245.16): C, 48.99; H, 6.99; N, 11.43. Found: C, 48.77; H, 6.95; N, 11.38.

***rac*-7-Methyl-6,7-dihydro-5*H*-pyrrolo[1,2-α]-4,5-dimethylthiazolium Bromide (2h).** ^{1}H NMR (500.13 MHz, D_2O): δ 4.55 (m, 1H, NCH_2), 4.43 (m, 1H, NCH_2), 3.94 (m, 1H, m, 1H, C*H* β to N), 3.02−2.98 (m, 1H, C*H* γ to N), 2.50 (s, 3H, CCH_3), 2.46−2.42 (m, 1H, CH_2 γ to N), 2.40 (s, 3H, CCH_3), 1.51 (d, $^3J_{HH}$ = 6.95 Hz, 3H, d, 3H, $CHCH_3$). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 175.4 (thi *C*2), 136.4, 134.7 (thi *C*4/5), 51.6 (NCH_2), 38.5 (*C*H β to N), 33.2 (*C*H_2 γ to N), 18.2 ($CHCH_3$), 11.9 (CCH_3), 10.3 (CCH_3). Anal. Calcd for $C_9H_{14}SNBr\cdot 0.5H_2O$: C, 39.28; H, 6.23; N, 5.09. Found: C, 39.03; H, 5.79; N, 4.85.

***rac*-1,7-Dimethyl-6,7-dihydro-5*H*-pyrrole[1,2-α]benzimidazolium Bromide (2q).** ^{1}H NMR (500.13 MHz, D_2O): δ 7.72 (m, 1H, Ar *H*), 7.66 (m, 1H, Ar *H*), 7.58 (m, 2H, Ar *H*), 4.51 (m, 1H, NCH_2), 4.38 (m, 1H, NCH_2), 4.01 (s, 3H, NCH_3), 3.94 (m, 1H, C*H* β to N), 3.19 (m, 1H, CH_2 γ to N), 2.58 (m, 1H, CH_2 γ to N), 1.61 (d, $^3J_{HH}$ = 6.95 Hz, 3H, d, 3H, $CHCH_3$). ^{13}C{^{1}H} NMR (125.03 MHz, D_2O): δ 160.6 (im *C*2), 136.4, 128.2, 125.9, 125.8, 112.8, 112.7 (Ar *C*), 45.1 (NCH_2), 34.1 (*C*H β to N), 31.7 (*C*H_2 γ to N), 31.4 (NCH_3), 15.9 ($CH(CH_3)_2$). Anal. Calcd for $C_{12}H_{15}N_2Br.H_2O$: C, 50.54; H, 6.01; N, 9.82. Found: C, 50.16; H, 5.83; N, 9.49.

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Supporting Information Available: A CIF file giving crystallographic data for **2f** and figures giving NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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