Ligand Design

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Cyclopropenylylidene-Stabilized Diaryl and Dialkyl Phosphenium Cations: Applications in Homogeneous Gold Catalysis**

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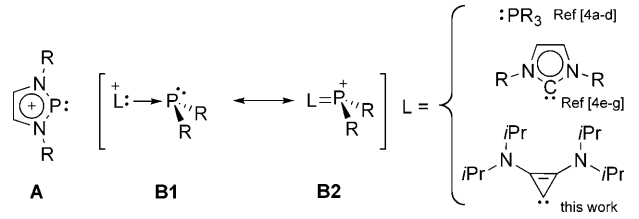
Phosphenium cations of the general formula $[R_2P{:}]^+$ are isolobal with singlet carbenes and can likewise be stabilized by donation of electron density into their empty orbital.[1] This goal is often reached either by embedding the phosphorous atom into a heterocyclic scaffold[2,3] as in **A** or by reaction with bases of a different nature to form the corresponding Lewis adducts **B** (Scheme 1).[4] In both cases, the presence of

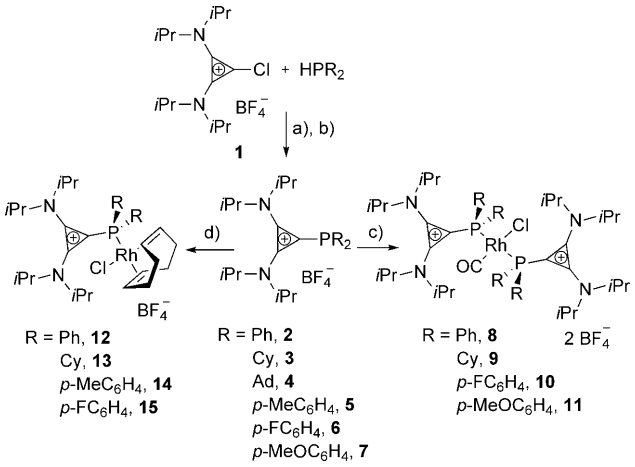


Scheme 1. Representative structures of N-heterocyclic phosphenium cations **A** and the conceivable resonance extremes of the phosphenium-base adducts **B1** and **B2**.

an unshared pair of electrons on the phosphorous atom makes the use of these compounds as ligands plausible; however, their intrinsic positive charge renders them poor σ donors and strong π acceptors.[5,6] Specifically, in **B**-type adducts the ground-state structure is dominated by resonance extreme **B2** when L is a phosphine, and therefore, transition-metal coordination complexes derived from these compounds are extremely scarce.[7] Even in the cases in which L is an N-heterocyclic carbene (NHC), the coordination properties of the resulting adducts are only comparable to those exhibited by the strongly π-accepting phosphites.[8]

However, we imagined we could generate phosphenium adducts in which resonance form **B1** might have a decisive contribution to the ground state by selecting an internal ligand L that is a stronger σ donor and an even poorer π acceptor than NHCs. This approach should provide systems with phosphine-like coordination behavior while keeping a positive charge that confers them the physicochemical properties of salts. Phosphines containing charged functionalities have already demonstrated their suitability in several chemical processes; the hydroformylation of olefins is one remarkable example.[9] Note, however, that in those phosphines, the charged groups are invariably appended to the periphery of the compound and are not directly attached to the phosphorous atom as in the present case.[10]

To put our design concept into practice, we considered 1,2-bis(diisopropylamino)cyclopropenyl-3-ylidene as an internal carbene ligand that fulfils the necessary electronic requirements.[11] The preparation of cyclopropenylylidene-stabilized phosphenium cations **2**–**7** was achieved in good to excellent yields after direct condensation of the readily available chlorocyclopropenium salt **1**[12] with a range of secondary phosphines and subsequent anion exchange. This synthetic strategy allowed the preparation of the desired salts on a multigram scale as white, air-stable solids (see Scheme 2 and the Supporting Information).



Scheme 2. Reagents and conditions (product yields in parentheses): a) phosphine (2 equiv), THF, reflux, 24 h; b) $NaBF_4$ (excess); **2** (90%); **3** (86%), **4** (79%); **5** (96%); **6** (76%); **7** (80%); c) $[\{RhCl(CO)_2\}_2]$ (0.25 equiv), THF; **8** (93%); **9** (91%); **10** (quant.); **11** (quant.); d) $[\{RhCl(cod)\}_2]$ (0.5 equiv), CH_2Cl_2; **12** (96%); **13** (88%); **14** (98%); **15** (97%). Cy = cyclohexyl, Ad = adamantyl, cod = 1,5-cyclooctadiene.

The comparison of the C–P bonds in the X-ray structure of **2** (Figure 1) is especially informative. The C1–P1 bond is only slightly shorter than the two C–P single bonds connecting the phosphorous atom with the phenyl rings but is significantly longer than typical C–P double bonds.[13] These

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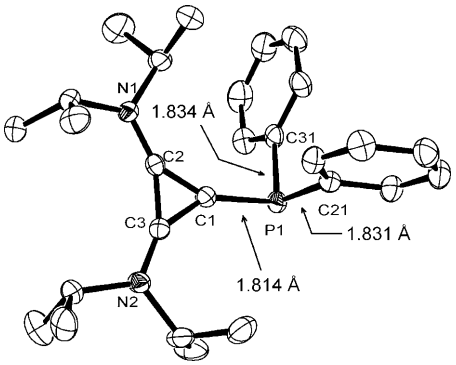
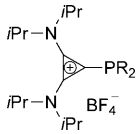
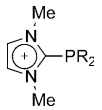


Figure 1. Crystal structure of **2.** Hydrogen atoms and the BF_4 anion are omitted for clarity; ellipsoids are set at 50% probability.[16]

data reveal that, in line with our expectations, back donation from the phosphorous atom to the cyclopropenyl ring is marginal.

The donor ability of the new phosphenium adducts was then evaluated by analysis of the CO stretching frequencies for complexes **8**–**11** (Table 1). These data suggest that adducts

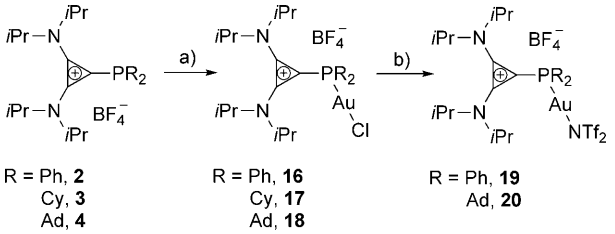
Table 1: Carbonyl stretching frequencies in complexes $[RhCl(CO)L_2](BF_4)_2$ (**8**–**11**) in the solid state and electrochemical redox potential of the corresponding complexes $[RhCl(cod)L](BF_4)$ (**12**–**15**). The values for commonly used phosphorus ligands are also included for comparison.

	Ligand	R	$\tilde{\nu}_{CO}$[a] $[RhCl(CO)L_2](BF_4)_2$	$E_{1/2}$[b] $[RhCl(cod)L]BF_4$
1		Ph	1971	0.955
2		Cy	1968	0.911
3		*p*-$MeOC_6H_4$	1969	n.d.[c]
4		*p*-FC_6H_4	1976	0.964
5		*p*-MeC_6H_4	1969	0.915
6		Ph	2003[d]	–
7	$(MeO)_3P$		2011[d]	–
8	Ph_3P		1979[e]	0.955
9	Cy_3P		1943[e]	0.917

[a] Values in cm^{-1}. [b] Calibrated versus ferrocene/ferrocenium ($E_{1/2}$ = 0.46 V), Bu_4NPF_6 (0.1 M) in CH_2Cl_2. [c] Not determined. [d] See reference [8b]. [e] See reference [13].

2–**7** have a donor capacity that even surpasses triarylphosphines (entries 1–5 and 8). In sharp contrast, analogous compounds containing NHCs as internal ligands showed phosphite-type behavior (entries 6 and 7).[14] Electrochemical results are also in agreement with this conclusion. The oxidation potentials $E_{1/2}$ of the rhodium complexes **12**–**15**, determined by cyclic voltammetry, are all in the same range as those measured for the analogous triphenyl- and tricyclohexylphosphine derivatives.[15] This finding supports the notion that the electron density donated by phosphines and phosphenium adducts **2**–**7** to the metal center is quite similar, even though the latter are cationic ligands.

Encouraged by this analysis, we decided to test the potential of these compounds in catalysis and prepared a set of gold complexes in which salts **2**–**4** were used as ligands (Scheme 3). Compounds **16**–**18** were obtained as air-stable



Scheme 3. Reagents and conditions (product yields in parentheses): a) $[(Me_2S)AuCl]$ (1 equiv), CH_2Cl_2, RT, 1 h; **16** (97%); **17** (94%); **18** (95%); b) $AgNTf_2$ (1 equiv), CH_2Cl_2, 1 h; **19** (96%); **20** (88%).

white solids in excellent yields by addition of $[(Me_2S)AuCl]$ to solutions of **2**–**4** in dichloromethane. Subsequent exchange of the chloride anion for the less coordinating bis(trifluoromethanesulfonyl)imidate anion was performed, thus allowing for a convenient way to obtain isolable yet active catalysts **19** and **20** without the use of highly hygroscopic silver salts as cocatalysts (Scheme 3).[17] Moreover, crystals of **16** were obtained, and its structure was determined, thus confirming the expected connectivity (Figure 2).

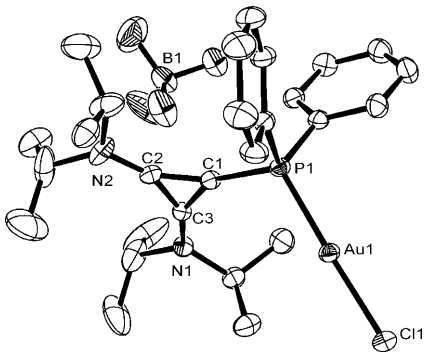
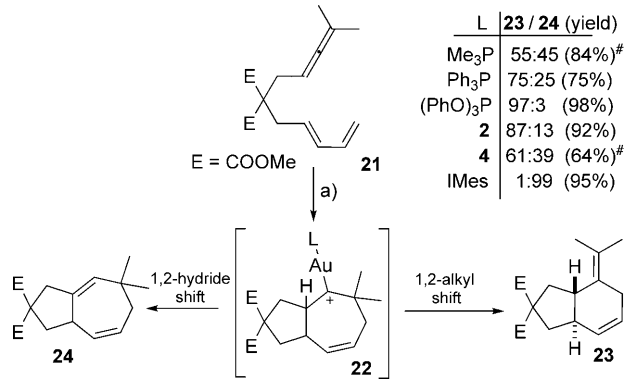


Figure 2. Crystal structure of **16**. Hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability.[16]

To compare the catalytic performance of compounds **19** and **20** with standard gold(I) phosphine complexes, the new catalysts were tested in a range of reported transformations.[18] The reaction of allene diene **21** was first chosen, because evolution of intermediate **22** is known to be extremely dependent on the global electron density at the gold atom, thus providing an additional measure for the donor properties of our ligands, now based on reactivity parameters.[19]

When π-acidic ligands L are used, the carbocationic nature of intermediate **22** is enhanced, thus promoting ring contraction by a 1,2-alkyl shift. In contrast, strongly σ-donating ligands at the gold center increase the carbene character of **22**, thus favoring the 1,2-hydride migration process. As illustrated by the examples compiled in Scheme 4,

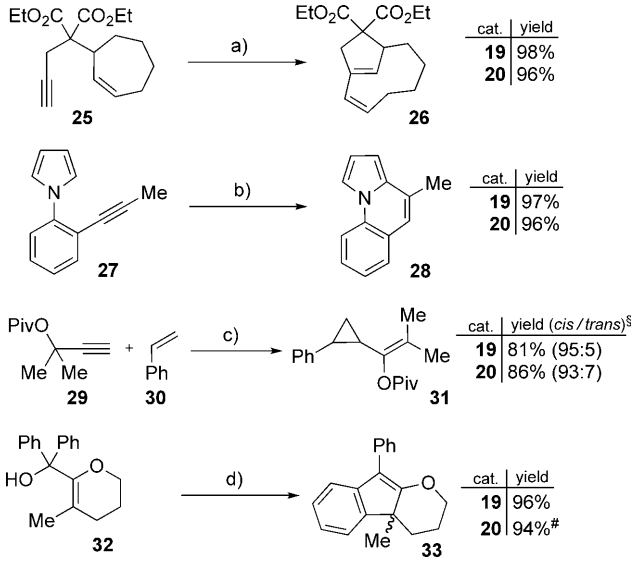


L	23 / 24 (yield)
Me_3P	55:45 (84%)#
Ph_3P	75:25 (75%)
$(PhO)_3P$	97:3 (98%)
2	87:13 (92%)
4	61:39 (64%)#
IMes	1:99 (95%)

Scheme 4. Comparison of the selectivity of different ligands in the gold-catalyzed cyclization of allene diene **21**. Reaction conditions: a) [LAuCl] (2 mol%), $AgBF_4$ (2 mol%),CH_2Cl_2, RT, 3 h (entries 1–3) or [$LAuNTf_2$] (2 mol%), CH_2Cl_2, RT, 3 h (entries 4–6). #: reaction time 9 h.

the selectivity obtained using catalysts **19** and **20** is comparable to that of phosphines, thus definitely confirming the conclusions drawn from the spectroscopic and electrochemical measurements as well as our initial working hypothesis.

The general utility of catalysts **19** and **20** was further demonstrated in a number of other synthetically useful and mechanistically distinct gold(I)-promoted processes, such as the cycloisomerization of enyne **25**,[20] the generation of pyrrolo[1,2-*a*]quinoline **28** from *ortho*-alkynylated phenylpyrrole,[21] the cyclopropanation of styrene,[22] and the unprecedented hydroxide abstraction from the dibenzylic alcohol **32**.[23] As shown in Scheme 5, the corresponding products were all isolated with good to excellent yields that in some cases surpassed those obtained with Ph_3P-derived catalysts.



cat.	yield
19	98%
20	96%

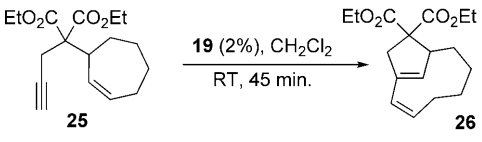
cat.	yield
19	97%
20	96%

cat.	yield (*cis*/*trans*)§
19	81% (95:5)
20	86% (93:7)

cat.	yield
19	96%
20	94%#

Scheme 5. Versatility of catalysts **19** and **20**. Reagents and conditions: a) cat. (1 mol%), CH_2Cl_2, RT, 40 min.; b) cat (2 mol%), CH_2Cl_2, RT, 5 h; c) cat. (1 mol%), CH_3NO_2, RT, 3 h. §: ratio determined by gas chromatography; d) cat. (1 mol%), CH_2Cl_2, RT, 30 min. #: reaction time 4 h; Piv = pivaloyl.

Finally, to illustrate that we can take advantage of the cationic nature of these adducts, the potential recycling of gold catalyst **19** has been studied using the cycloisomerization of enyne **25** as a model reaction. Complex **19** is insoluble in diethyl ether, whereas diene **26** can be easily dissolved in this medium. Therefore, after full conversion, the reaction solvent was removed in vacuum, and diethyl ether was added. The catalyst precipitated, and it was separated from the product by simple filtration and reused for the next cycle. As shown in Scheme 6, the test reaction could be performed up to four times with consistent excellent yields.



Run	yield#
1	98%
2	98%
3	98%
4	95%
5	76%

Scheme 6. Catalyst recycling in the cycloisomerization of enyne **25**. Reaction conditions: enyne (0.13 mmol), **19** (2.0 mol%), CH_2Cl_2 (2 mL), 45 min, RT; #: runs 1–3 yield of isolated product, runs 4, 5 yield determined by gas chromatography.

In conclusion, the synthesis of cyclopropenylylidene-stabilized phosphenium adducts has been achieved and their coordination behavior studied. In contrast to other phosphenium carbene adducts, these compounds exhibit the attributes of classical triaryl and trialkyl phosphines, even though they carry a global positive charge. Moreover, gold complexes with these ligands have been synthesized and their practical utility in catalysis was demonstrated in several mechanistically diverse transformations. Finally, taking advantage of the saline nature of our ligands, the recycling possibilities of the catalysts derived thereof were also explored.

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[1] For a general review on the synthesis and structure of phosphenium cations, see: a) A. H. Cowley, R. A. Kemp, *Chem. Rev.* **1985**, *85*, 367–382; b) D. Gudat, *Coord. Chem. Rev.* **1997**, *163*, 71–106.

[2] The stabilization of phosphenium cations inside a carbocyclic system has been also achieved: A. Schmidpeter, M. Thiele, *Angew. Chem.* **1991**, *103*, 333–335; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 308–310.

[3] For the synthesis and reactivity of N-heterocyclic phosphenium cations, see for example: a) M. K. Denk, S. Gupta, A. J. Lough, *Eur. J. Inorg. Chem.* **1999**, 41–49; b) C. A. Caputo, J. T. Price, M. C. Jennings, R. MacDonald, N. D. Jones, *Dalton Trans.* **2008**, 3461–3469; c) D. Gudat, *Acc. Chem. Res.* **2010**, *43*, 1307–1316.

[4] For adducts with phosphines, see: a) N. Burford, P. J. Ragogna, R. MacDonald, M. J. Ferguson, *J. Am. Chem. Soc.* **2003**, *125*, 14404–14410; b) N. Burford, P. J. Ragogna, *J. Chem. Soc. Dalton Trans.* **2002**, 4307–4315; c) N. Burford, P. J. Ragogna, K. Sharp, R. MacDonald, M. J. Ferguson, *Inorg. Chem.* **2005**, *44*, 9453–9460; for adducts with pyridine derivatives and other N-based

ligands, see: d) N. Burford, P. Losier, A. D. Phillips, P. J. Ragogna, T. S. Cameron, *Inorg. Chem.* **2003**, *42*, 1087 – 1091; for adducts with N-heterocyclic carbenes, see: e) N. Kuhn, J. Fahl, D. Bläser, R. Boese, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729 – 734; f) M. Azouri, J. Andrieu, M. Picquet, P. Richard, B. Hanquet, I. Tkatchenko, *Eur. J. Inorg. Chem.* **2007**, 4877 – 4883.

[5] a) H. Nakazawa, *J. Organomet. Chem.* **2000**, *611*, 349 – 363; b) N. J. Hardman, M. B. Abrams, M. A. Pribisko, T. M. Gilbert, R. L. Martin, G. J. Kubas, R. T. Baker, *Angew. Chem.* **2004**, *116*, 1989 – 1992; *Angew. Chem. Int. Ed.* **2004**, *43*, 1955 – 1958; c) C. A. Caputo, A. L. Brazeau, Z. Hynes, J. T. Price, H. M. Tounonen, N. D. Jones, *Organometallics* **2009**, *28*, 5261 – 5265.

[6] Theoretical analyses can be found in: a) H. M. Tuononen, R. Roesler, J. L. Dutton, P. J. Ragogna, *Inorg. Chem.* **2007**, *46*, 10693 – 10706; b) B. D. Ellis, P. J. Ragogna, C. L. B. MacDonald, *Inorg. Chem.* **2004**, *43*, 7857 – 7867.

[7] a) P. Le Floch, F. Mathey, *Synlett* **1991**, 743 – 744; b) H. Werner, B. Klingert, *J. Organomet. Chem.* **1981**, *218*, 395 – 407.

[8] a) J. Andrieu, M. Azouri, P. Richard, *Inorg. Chem. Commun.* **2008**, *11*, 1401 – 1404; b) M. Azouri, J. Andrieu, M. Picquet, H. Cattey, *Inorg. Chem.* **2009**, *48*, 1236 – 1242; c) S. Saleh, E. Fayad, M. Azouri, J. Hierso, J. Andrieu, M. Picquet, *Adv. Synth. Catal.* **2009**, *351*, 1621 – 1628; d) N. Debono, Y. Canac, C. Duhayon, R. Chauvin, *Eur. J. Inorg. Chem.* **2008**, 2991 – 2999; e) I. Abdellah, C. Lepetit, Y. Canac, C. Duhayon, R. Chauvin, *Chem. Eur. J.* **2010**, *16*, 13095 – 13108; f) J. J. Weigand, K. O. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* **2010**, *132*, 16321 – 16323.

[9] a) *Applied Homogeneous Catalysis with Orgnometallic Compounds Part I + II* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1996**; b) *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1998**.

[10] a) D. M. Chisholm, J. S. McIndoe, *Dalton Trans.* **2008**, 3933 – 3945; b) for recent work on phosphines attached to imidazolium moieties through a methylene linker, see: A. Dumrath, X. Wu, H. Neumann, A. Spannenberg, R. Jackstell, M. Beller, *Angew. Chem.* **2010**, *122*, 9172 – 9176; *Angew. Chem. Int. Ed.* **2010**, *49*, 8988 – 8992; c) for the synthesis of a phosphine containing a metalated substituent, see: M. R. Axet, M. Barbazanges, M. Augé, C. Desmarets, J. Moussa, C. Ollivier, C. Aubert, L. Fensterbank, V. Gandon, M. Malacria, L. M. Chamoreau, H. Amouri, *Organometallics* **2010**, *29*, 6636 – 6638.

[11] a) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722 – 724; b) W. W. Schoeller, G. Frey, G. Bertrand, *Chem. Eur. J.* **2008**, *14*, 4711 – 4718; for the employment of this carbene to stabilize N^I and P^I centers, see: c) H. Bruns, M. Patil, J. Carreras, A. Vázquez, W. Thiel, R. Goddard, M. Alcarazo, *Angew. Chem.* **2010**, *122*, 3762 – 3766; *Angew. Chem. Int. Ed.* **2010**, *49*, 3680 – 3683; d) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638 – 5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530 – 5533.

[12] a) R. Weiss, K. G. Wagner, C. Priesner, J. Macheleid, *J. Am. Chem. Soc.* **1985**, *107*, 4491 – 4499; b) a tungsten complex containing a cyclopropenylylidene-stabilized phosphenium cation has been described, although a different synthetic protocol was used, see: N. H. T. Huy, B. Donnadieu, G. Bertrand, F. Mathey, *Chem. Asian J.* **2009**, *4*, 1225 – 1228.

[13] The carbon–phosphorous distance in an unstabilized ylide such as methylenetriphenylphosphorane ($Ph_3P{=}CH_2$) is 1.662(8) Å, see: J. C. J. Bart, *J. Chem. Soc. B* **1969**, 350 – 365.

[14] a) S. Otto, A. Rodt, *Inorg. Chim. Acta* **2004**, *357*, 1 – 10; b) D. Gusev, *Organometallics* **2009**, *28*, 763 – 770.

[15] For a similar study on [(NHC)RhCl(cod)] complexes, see: a) S. Wolf, H. Plenio, *J. Organomet. Chem.* **2009**, *694*, 1487 – 1492; b) M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem.* **2010**, *122*, 2596 – 2600; *Angew. Chem. Int. Ed.* **2010**, *49*, 2542 – 2546.

[16] CCDC 805226 (**2**) and 805225 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] N. Mézailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133 – 4136.

[18] For recent reviews on gold-promoted transformations, see: a) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326 – 3350; b) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478 – 3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410 – 3449; c) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351 – 3378.

[19] a) I. Alonso, B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós, J. L. Mascareñas, *J. Am. Chem. Soc.* **2009**, *131*, 13020 – 13030; b) P. Mauleón, R. M. Zeldin, A. Z. González, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 6348 – 6349; c) D. Benítez, E. Tkatchouk, A. Z. González, W. A. Goddard III, F. D. Toste, *Org. Lett.* **2009**, *11*, 4798 – 4801.

[20] a) B. M. Trost, M. K. Trost, *J. Am. Chem. Soc.* **1991**, *113*, 1850 – 1852; b) A. Fürstner, J. Mlynarski, M. Albert, *J. Am. Chem. Soc.* **2001**, *123*, 11863 – 11869.

[21] V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556 – 4575.

[22] M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 18002 – 18003.

[23] For a related transformation, see: P. Cordier, C. Aubert, M. Malacria, E. Lacôte, V. Gandon, *Angew. Chem.* **2009**, *121*, 8913 – 8916; *Angew. Chem. Int. Ed.* **2009**, *48*, 8757 – 8760.

