DOI: 10.1002/ange.200800541

Gold Catalyst for Diboration

Gold(0) Nanoparticles for Selective Catalytic Diboration**

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It has been claimed that homogeneous transition-metal catalysis can be used to make the production of fine chemicals sustainable,[1] and the amount of unwanted by-products is already being efficiently reduced in large-scale production. In particular, some of the recently described new strategies for generating products with increased functional-group complexity through catalytic organoborane chemistry[2] would substantially reduce the number of steps required in extended syntheses.[3] Chemo-, regio-, and stereoselective catalytic C−B bond formation allows access to highly selective functionalized molecules.[4] In this process, the choice of the catalyst in the metal-mediated B−B addition reaction to unsaturated molecules is of fundamental importance. Pt and Rh complexes are known to be active catalytic systems;[5] however, selective transformation was also achieved with gold complexes.[6] Homogeneous catalysis by gold has become a hot topic in organometallic chemistry,[7] but despite the clean diboration reaction observed by Marder et al.,[6] the catalytic activity and stability are lower than desired.

Inspired by these preliminary results and in an attempt to achieve clean, efficient diboration of alkenes, we report here on the enhanced catalytic activity of ligand-protected gold when it is prepared as very small particles. We first prepared a gold(I) complex modified with 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) from $(Me_2S)AuCl$ and 0.5 equiv of binap.[8] $[(binap)Au_2Cl_2]$ (**1**) was converted to $[(binap)Au_2I_2]$ (**2**) by ion exchange with an excess of KI in THF.[9] Crystals of **2** suitable for X-ray diffraction were obtained by precipitation with hexane, and the crystallographic data confirmed the dinuclearity of the complex (Figure 1). The bond lengths and angles are similar to those reported for $[(Tolbinap)Au_2Cl_2]$,[10] except for the Au–halide distance, which is 0.26 Å longer in **2** indicating that the Au−I bond is weak.

When the gold(I) complexes **1** and **2** were used as catalyst precursors in the diboration of styrene (Scheme 1), they were inactive even after 72 h at room temperature. The 1,2-bis(boronate)styrene product was obtained in only 6% yield even at higher temperatures (THF at reflux) (Table 1, entry 1). The addition of a base such as NaOAc and an excess of the diboron reagent was critical for total conversion of the substrate to give the desired diboron product within 2 h at room temperature (Table 1, entries 2–4). No asymmetric induction was observed when the ligand used was (*R*)-binap. While the chemoselectivity (diborated products versus hydroborated by-products formed from previous dehydrogenative borylation) was not affected, the reaction required 3 equiv of B_2cat_2 and 1 equiv of base to reach completion (Table 1, entries 4–6). The fact that the Au−I bond in **2** is more labile than the Au−Cl bond in **1** may explain the higher catalytic activity (Table 1, entry 7). The gold species in presence of other bases, such as NaOH or $CsCO_3$, proved to be less chemoselective towards the 1,2-bis(boronate)styrene product (Table 1, entries 8 and 9).

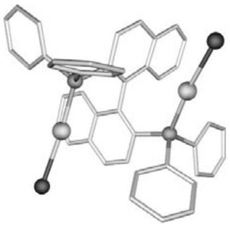
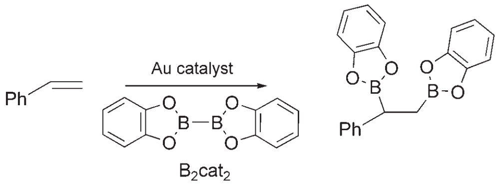


Figure 1. X-ray crystal structure of **2**. Selected distances [Å] and angles [°]: Au–P 2.257, Au–I 2.549; P-Au-I 172.20.



Scheme 1. Diboration of styrene in the presence of a gold catalyst.

The unexpected enhanced catalytic activity was related to the appearance of a reddish solid before the oxidative workup, the characterization of which concluded with the

Table 1: Gold-mediated catalytic diboration of styrene with B_2cat_2.[a]

Entry	Catalyst precursor	Base	B_2cat_2 [equiv]	*t* [h]	Conv. [%][b]	Prod. sel. [%][b]
1[c]	**1**	–	1.1	72	6	99
2	**2**	NaOAc	1.1	2	13	99
3	**2**	NaOAc	2	2	89	99
4	**2**	NaOAc	3	2	100	99
5	**2**	NaOAc[d]	3	2	63	99
6	**2**	–	3	0	2	–
7	**1**	NaOAc	3	15	75	99
8[e]	**2**	NaOH	3	2	100	84
9[e]	**2**	$CsCO_3$	3	2	100	65

[a] Standard conditions: substrate/base/Au complex 1:1:0.0125, THF, room temperature. [b] Conversion and selectivity calculated by ^1H NMR spectroscopy. [c] Reaction conducted at reflux. [d] Substrate/base 1:0.5 [e] Branched and linear hydroborated by-products were observed.

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[**] This work was supported by CTQ2007-60442/BQU and Consolider Ingenio2010 CSD-0003.

Supporting information for this article (including all experimental details) is available on the WWW under http://www.angewandte.org or from the author.

formation of binap-stabilized gold nanoparticles in situ. XRD measurements were made and the X-ray diffractogram revealed the presence of metallic Au^0 (Figure 2a). Using the fundamental parameters approach convolution algorithm[11] implemented in the program TOPAS 3.1, we calculated the crystallite size from the net integral breadth of the peaks.[12] The gold nanoparticles were estimated to have a mean crystallite size of 10.5 ± 0.3 nm. The core size and size distribution of binap–gold nanoparticles were examined by transition electron microscopy (TEM), and the image shows disperse nanoparticles 6.9 ± 3.0 nm in diameter, (Figure 2b,c). We assume that Au^I in $[(binap)Au_2I_2]$ is reduced to Au^0 by B_2cat_2, because a previous study reported that PPh_3-stabilized gold nanoparticles can be obtained by reducing $[PPh_3AuCl]$ with diborane B_2X_4.[13] It should be pointed out that in our case the less reactive B_2cat_2 was able to reduce Au^I to Au^0. The resulting by-product was identified by ^{11}B NMR spectroscopy as IBcat (29.9 ppm); two further signals at 13.6 ppm are assumed to be due to the adduct $NaOAc{\cdot}B_2cat_2$,[14] and that at 20.5 ppm is attributed to B_2cat_3.

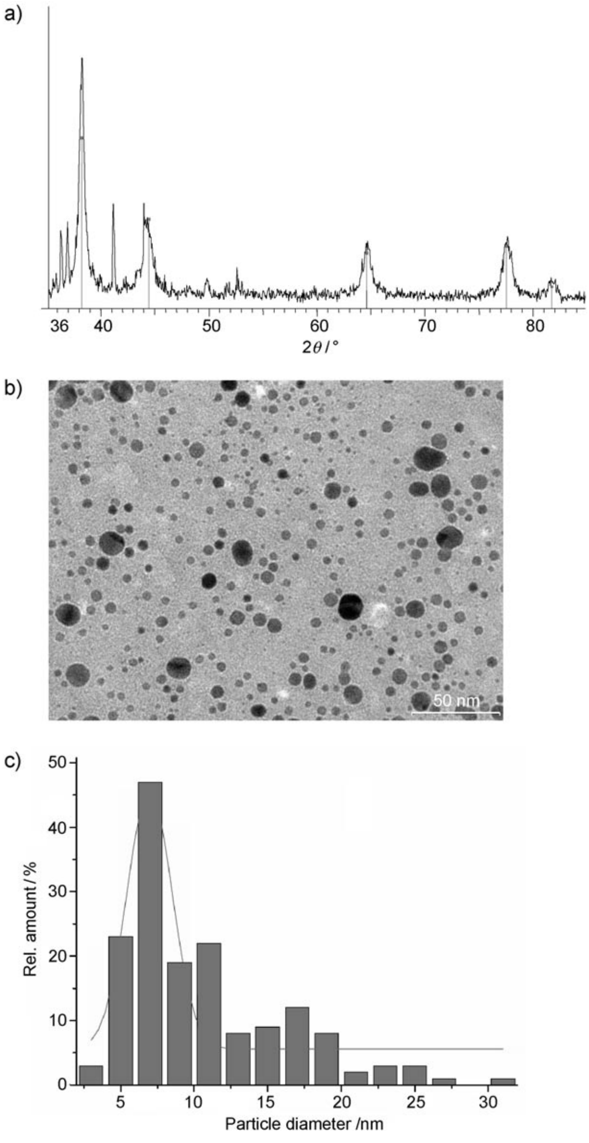


Figure 2. Characterization of the binap-stabilized gold nanoparticles generated in situ. a) X-ray diffractogram (with vertical markers for standard Au^0) , b) TEM micrograph (500000× enlargement), c) core size distribution.

Interestingly, the recovered reddish solid characterized as binap-stabilized gold nanoparticles was reused in a new catalytic diboration reaction of styrene. The conversion and total chemoselectivity towards the diborated product were high (Table 2, entry 1). This shows that the catalytic system is very stable and that it can be recycled. To distinguish between the catalytic activity of the nanoparticles and that of the plausible active metal complex leached from the nanoparticle, we performed a catalytic reaction in which an excess of Hg was added to the solution of complex **2**; substantial inhibition of the catalytic system was observed (Table 2, entry 2). Despite the ability of Hg^0 to poison heterogeneous metal-particle catalysts, the experiment is not definitive by itself.[15] Pure binap–gold nanoparticles with a small diameter (1.7 ± 0.3 nm) were synthesized following the Fujihara protocol,[16] from $HAuCl_4$ and binap in the presence of $NaBH_4$, and used in the catalytic diboration reaction. The activity and chemoselectivity observed (Table 2, entry 3) were similar to those of the binap-stabilized gold nanoparticles generated in situ.

Table 2: Catalytic diboration of styrene with gold nanoparticles (NPs) and B_2cat_2.[a]

Entry	Catalytic system	Conv. [%][b]	Prod. sel. [%][b]
1	binap–gold NPs recovered	82	99
2[c]	complex **2**	–	–
3	binap–gold NPs[d]	90	99
4	dppe–gold NPs generated in situ	91	99
5	L-glutathione–gold NPs	94	99

[a] Standard conditions: substrate/NaOAc/Au complex 1:1:0.0125, 3 equiv of B_2cat_2, THF, room temperature, 2 h. [b] Conversion and selectivity calculated by ^1H NMR spectroscopy. [c] Excess Hg added. [d] NPs were synthesized from $HAuCl_4$ and binap in the presence of $NaBH_4$ following the Fujihara protocol (see Ref. [16]).

The role of the binap ligand is controversial. Chiroptical activity of (*R*)-binap–gold nanoparticles has been reported by Fujihara et al.,[16] although the nanoparticles were not tested as catalysts in any asymmetric transformation. The lack of asymmetric induction by (*R*)-binap–gold NPs might be related to the postulated mechanism for the reaction. Therefore, we decided to perform the catalysis with the analogous achiral catalytic system $[(dppe)Au_2Cl_2]$ (**3**) (dppe = 1,2-bis(diphenylphosphino)ethane), which was prepared from $[(Me_2S)AuCl]$ and 0.5 equiv of dppe. The singlet in the ^{31}P NMR spectrum (31.5 ppm in $CDCl_3$) provided evidence that the dimeric complex formed is the same as that prepared previously from $NaAuCl_4$/thiodiglycol/dppe.[17] When complex **3** was used as the catalyst precursor in the diboration of styrene, the catalytic activity (Table 2, entry 4) was identical to that of **2**. Again the in situ formation of gold NPs stabilized by dppe was confirmed by XRD measurements, and the X-ray diffractogram revealed the presence of metallic Au^0. This suggests that these bidentate ligands ((*R*)-binap and dppe) mainly play a stabilizing role in nanoparticle formation. Gold nanoparticles stabilized by chiral thiol ligands seem to be an alternative catalytic system.[18] To this end, we chose L-glutathione to stabilize gold NPs and followed the synthetic process reported for L-glutathione–M NPs (M = Au, Pt).[19] Thus $HAuCl_4$ was treated with L-glutathione and the metal was reduced to Au^0 in the presence of $NaBH_4$. Whereas the ^1H NMR spectrum indicated that the particles were spectroscopically pure, the X-ray diffractogram revealed the presence of metallic Au^0, and the TEM image with particle size distribution mainly indicated a population of particles about 2.8 ± 1.4 nm in diameter. When we tested the catalytic activity of the L-glutathione–gold NPs in the diboration of styrene, we observed that the conversion and chemoselectivity remained very high (Table 2, entry 5) but that the enantioselectivity was nil.

We also found that gold nanoparticles were better than other nanoparticles in the same group (Ag and Cu nanoparticles) for the catalytic diboration of alkenes. In fact when silver nanoparticles were synthesized following the Yang method[20] and used to add B_2cat_2 catalytically to alkenes, conversions were moderate (51 % for styrene, 47 % for indene, and 54 % for *trans*-β-methylstyrene) although the total chemoselectivity towards the desired product remained the same. Catalytic activity was lowest (26 % for styrene) for the copper nanoparticles synthesized following the Zhong method.[21] This shows that the gold catalyst has the advantages of higher activity, higher selectivity, and milder reaction conditions.[22]

The scope of the diboration catalyzed by system **2** was extended to aliphatic alkenes such as vinylcyclohexene and 3,3-dimethylbutene; the conversion was complete and the chemoselectivity quantitative (Figure 3), but no enantioselectivity was observed. The diboration of internal alkenes led to the quantitative *cis* B–B addition to *trans*-β-methylstyrene and the selective formation of *cis*-bis(boryl)cyclic moieties for endocyclic alkenes such as indene and norbornene (Figure 3). The diboration of norbornene has been reported using base-free Pt^0[23] and Rh^I complexes,[24] which provided good yields and chemoselectivities but required long reaction times and higher temperatures. Only one report has described the diboration of indene but with lower chemoselectivity (68 %).[25] These approaches open up new perspectives for synthethic pathways to 2-*exo*-3-*exo*-norbornanediol and 1,2-indanediol[26] through the oxidative workup of the bis(boronate)ester intermediates.

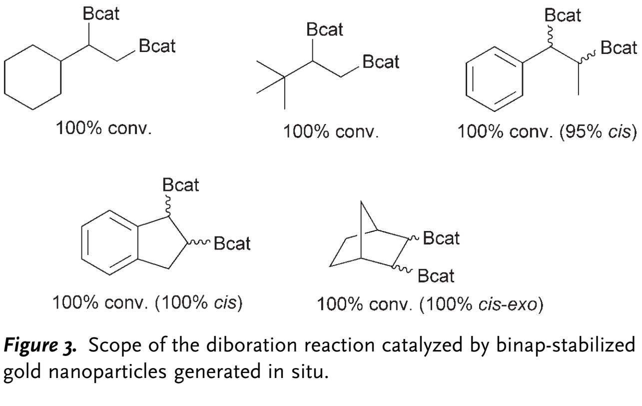
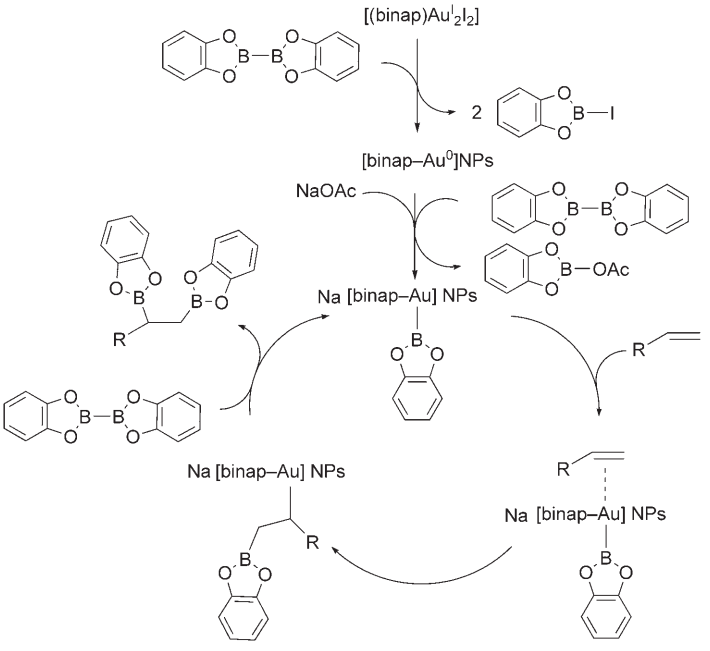


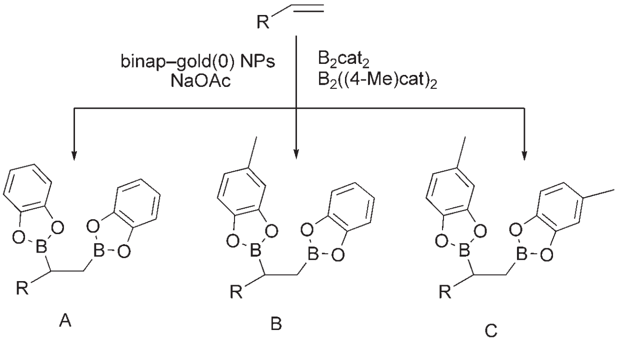
Figure 3. Scope of the diboration reaction catalyzed by binap-stabilized gold nanoparticles generated in situ.

The high chemoselectivity described with the binap-stabilized gold nanoparticles suggests that the catalytic system could be involved in a base-mediated diboration, and therefore transmetalation becomes the key step in the mechanism instead of oxidative addition (Scheme 2). The observation of the resulting by-product, IBcat, which is similar to the ClBcat observed by Baker et al.,[27] supports the B–B heterolytic cleavage. A similar mechanism based on a transmetalation sequence has been postulated for the first catalytic diboration of alkenes with palladium complexes.[14] The mechanism suggested for the gold nanoparticle mediated diboration reaction gains strong support from the crossed-addition experiment, in which B_2cat_2 and $B_2((4\text{-Me})cat)_2$[28] were simultaneously added to styrene (Scheme 3). Although the reactivity of $B_2((4\text{-Me})cat)_2$ is lower than that of B_2cat_2 (23 % of styrene converted to 1,2-bis(boronate)styrene), the formation of crossdiborated product B (about 10 %, detected by GC–MS) in conjunction with A (about 60 %) and C (about 30 %) supported this hypothesis. It should be noted that if diboration occurs by the oxidative addition of diborons to Au^0, product B should not be observed. In agreement with this transmetalation pathway, similar trends were found by Cheng et al. for the Pd^0-mediated diboration of allenes[29] and by Oshima et al. for the β-boration of esters and amides.[30] Morken et al.[31] on the other hand, described some crossover experiments that suggested that allene diboration could be initiated by the oxidative addition of diboron to Pd^0.



Scheme 2. Proposed mechanism for the reaction of an alkene with B_2Cat_2 catalyzed by binap–gold nanoparticles generated in situ.

In summary, we have reported a new gold-mediated diboration reaction, in which binap-stabilized gold(0) nanoparticles are responsible for the conversion of alkenes with complete chemoselectivity to the 1,2-bis(boronate)esters. The



Scheme 3. Crossed-addition experiment for the diboration of styrene.

formation of by-products, therefore, is significantly minimized. Of particular importance are the moderate reaction conditions (2 h and room temperature) and the substrate scope. The reaction mechanism can involve the base-assisted heterolytic cleavage of the diboron reagent and further alkene insertion and transmetalation on the catalytic system. Studies are now being made into applying chiral phosphine-stabilized gold(0) nanoparticles to the asymmetric addition of B−B to alkenes.

Received: February 1, 2008
Published online: June 5, 2008

Keywords: catalysis · diboration · gold · nanoparticles · selectivity

[1] a) G. A. Olah, *Angew. Chem.* **2005**, *117*, 2692; *Angew. Chem. Int. Ed.* **2005**, *44*, 2636; b) N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52; *Angew. Chem. Int. Ed.* **2007**, *46*, 52.

[2] a) H. C. Brown in *Hydroboration*, Wiley-Interscience, New York, **1962**; b) H. C. Brown in *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, **1972**; c) H. C. Brown in *Organic Synthesis via Boranes*, Wiley-Interscience, New York, **1975**; d) A. Pelter, K. Smith, H. C. Brown in *Borane Reagents*, Academic Press, New York, **1988**; e) G. M. L. Cragg in *Organoboranes in Organic Synthesis*, Dekker, New York, **1973**; f) T. Onak in *Organoborane Chemistry*, Academic Press, New York, **1975**.

[3] a) J. Ramírez, V. Lillo, A. M. Segarra, E. Fernández, *Curr. Org. Chem.* **2008**, *12*, 230; b) T. Miura, M. Murakami, *Chem. Commun.* **2007**, 217.

[4] a) D. Männig, H. Nöth, *Angew. Chem.* **1985**, *97*, 854; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 878; b) I. Beletskaya, A. Pelter, *Tetrahedron* **1997**, *53*, 4957; c) M. J. Burgess, M. J. Ohlmeyer, *J. Org. Chem.* **1988**, *53*, 5178; d) I. Beletskaya, C. Morgen, *Chem. Rev.* **2006**, *106*, 2320.

[5] a) T. Ishiyama, K. Nishijima, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 7219; b) T. B. Marder, N. C. Norman, *Top. Catal.* **1998**, *5*, 63; c) V. M. Dembitsky, H. Abu Ali, M. Srebnik, *Appl. Organomet. Chem.* **2003**, *17*, 327; d) T. Ishiyama, N. Miyaura, *Chem. Rec.* **2004**, *3*, 271.

[6] R. T. Baker, P. Nguyen, T. B. Marder, S. A. Westcott, *Angew. Chem.* **1995**, *107*, 1451; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1336.

[7] A. S. K. Hashmi, *Angew. Chem.* **2005**, *117*, 7150; *Angew. Chem. Int. Ed.* **2005**, *44*, 6990.

[8] K. Angermaier, A. Sladek, H. Schmidbaur, *Z. Naturforsch. B* **1996**, *51*, 1671.

[9] D. M. Stefanescu, H. F. Yuen, D. S. Glueck, J. A. Golen, L. N. Zakharov, C. D. Incarvito, A. L. Rheingold, *Inorg. Chem.* **2003**, *42*, 8891.

[10] M. P. Muñoz, J. Adrio, J. C. Carretero, M. A Echavarren, *Organometallics* **2005**, *24*, 1293.

[11] R. W. Cheary, A. A. Coelho, *J. Appl. Crystallogr.* **1992**, *25*, 109.

[12] A. R. Stokes, A. J. C. Wilson, *Proc. Cambridge Philos. Soc.* **1942**, *38*, 313.

[13] G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. M. Calis, J. W. A. Van der Velden, *Chem. Ber.* **1981**, *114*, 3634.

[14] V. Lillo, E. Mas-Marzá, A. M. Segarra, J. J. Carbó, C. Bo, E. Fernández, *Chem. Commun.* **2007**, 3380.

[15] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317.

[16] a) M. Tamura, H. Fujihara, *J. Am. Chem. Soc.* **2003**, *125*, 15742; b) Y. Yanagimoto, Y. Negishi, H. Fujihara, T. Tsukuda, *J. Phys. Chem. B* **2006**, *110*, 116.

[17] S. J. Berners-Price, M. A. Mazid, P. J. Sadler, *J. Chem. Soc. Dalton Trans.* **1984**, 969.

[18] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* **1991**, 801.

[19] a) T. G. Schaaff, R. L. Whetten, *J. Phys. Chem. B* **2000**, *104*, 2630; b) S. E. Eklund, D. E. Cliffel, *Langmuir* **2004**, *20*, 6012.

[20] X. Z. Lin, X. Teng, H. Yang, *Langmuir* **2003**, *19*, 10081.

[21] D. Mott, J. Galkowski, L. Wang, J. Luo, Ch.-J. Zhong, *Langmuir* **2007**, *23*, 5740.

[22] a) G. Schmid, B. Corain, *Eur. J. Inorg. Chem.* **2003**, 3081; b) T. Ishida, M. Haruta, *Angew. Chem.* **2007**, *119*, 2; *Angew. Chem. Int. Ed.* **2007**, *46*, 2; c) for hydrosylilation: A. Corma, C. González-Arellano, M. Iglesias, F. Sánchez, *Angew. Chem.* **2007**, *119*, 7966; *Angew. Chem. Int. Ed.* **2007**, *46*, 7820; d) for CO oxidation: M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* **1989**, *115*, 301; e) J. Guzman, B. C. Gates, *J. Am. Chem. Soc.* **2004**, *126*, 2672; f) M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293; g) C. Lemire, R. Meyer, S. Shaikhutdino, H. J. Freund, *Angew. Chem.* **2004**, *116*, 121; *Angew. Chem. Int. Ed.* **2004**, *43*, 118; h) reduction of nitroarenes: A. Corma, P. Serna, *Science* **2006**, *313*, 33; i) oxidation of alcohols: L. Prati, M. Rossi, *J. Catal.* **1998**, *176*, 552; j) A. Abad, P. Concepcion, A. Corma, H. GarcIa, *Angew. Chem. Int. Ed. Angew.Chem. Int. Ed.* **2005**, *44*, 4066; k) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362; l) C−C bond formation: S. Carrettin, J. Guzmán, A. Corma, *Angew. Chem.* **2005**, *117*, 2282; *Angew. Chem. Int. Ed.* **2005**, *44*, 2242; m) A. S. K. Hashmi, L. Schwarz, J. H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285.

[23] a) T. Ishiyama, M. Yamamoto, N. Miyaura, *Chem. Commun.* **1997**, 689; b) C. N. Iverson, M. R. Smith III, *Organometallics* **1997**, *16*, 2757.

[24] C. Dai, E. G. Robbins, A. J. Scott, W. Clegg, D. S. Yufit, J. A. K. Howard, T. B. Marder, *Chem. Commun.* **1998**, 1983.

[25] J. B. Morgan, S. P. Miller, J. P. Morken, *J. Am. Chem. Soc.* **2003**, *125*, 8702.

[26] a) S. M. Grayson, B. K. Long, S. Kusomoto, B. P. Osborn, R. P. Callahan, Ch. R. Chambers, C. G. Willson, *J. Org. Chem.* **2006**, *71*, 341; b) G. J. A. Conceicao, P. P. J. S. Moran, J. A. R. Rodrigues, *Tetrahedron: Asymmetry* **2003**, *14*, 2327; c) D. E. De Vos, S. De Wildeman, B. F. Sels, P. J. Grobet, P. A. Jacob, *Angew. Chem.* **1999**, *111*, 1033; *Angew. Chem. Int. Ed.* **1999**, *38*, 980.

[27] G. Mann, K. D. John, R. T. Baker, *Org. Lett.* **2000**, *2*, 2105.

[28] N. R. Anastasi, K. M. Waltz, W. L. Weerakoon, J. F. Hartwig, *Organometallics* ***2003***, *22*, 365.

[29] F.-Y. Yang, C.-H. Cheng, *J. Am. Chem. Soc.* **2001**, *123*, 761.

[30] K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 5031.

[31] H. E. Burks, S. Liu, J. P. Morken, *J. Am. Chem. Soc.* **2007**, *129*, 8766.