DOI: 10.1002/adsc.201100287

# Evaluation of the Electronic Properties of a Carbodiphosphorane through Gold Catalysis

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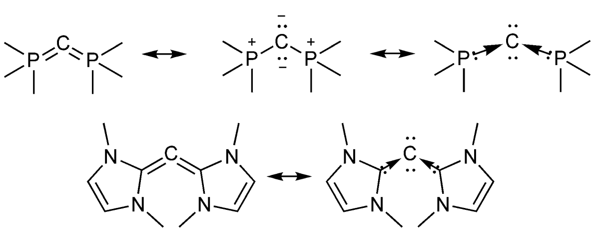
Received: April 16, 2011; Published online: August 4, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adcs.201100287.

**Abstract:** Carbodiphosphoranes [$C(PR_3)_2$] are divalent carbon(0) derivatives which can be used as ligands to form either $M \leftarrow C(PR_3)_2$ or $(M)_2 \leftarrow C(PR_3)_2$ species. They were computationally predicted to be even stronger electron donors than N-heterocyclic carbenes. We have introduced hexaphenylcarbodiphosphorane [$C(PPh_3)_2$] for the first time in gold catalysis in order to validate this prediction by experimentation. Its mono- and digold complexes were compared to tris(2,4-di-*tert*-butylphenyl) phosphite, triphenylphosphine, and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene in representative gold(I)-catalyzed transformations. The advantages and limitations of these ligands are discussed.

**Keywords:** carbenoids; carbodiphosphoranes; gold; ligand effects; phosphane ligands

Tuning the stereo-electronic properties of catalyst ligands is a critical feature to ensure a higher activity and to control the selectivity of a given reaction. One emblematic example of the impact of the ligand's nature on selectivity is the olefin metathesis catalyzed by Grubbs first generation Ru-phosphine complexes *versus* second generation NHC-based catalysts.[1] A wide array of ligands is available to chemists nowadays, including phosphites, phosphines, NHCs, CAACs, NACs, and many others.[2] Due to their π-acceptor capabilities, phosphites are weaker electron donors to metals than phosphines. On the other hand, NHCs, which display a pseudo-filled *p* orbital, are stronger donors than phosphines.[3] Beyond NHCs, more powerful σ-donors with even reduced π-acceptor character have been designed.[2] Among these, carbodiphosphoranes and carbodicarbenes, also referred to as *carbones* or *bent allenes*, feature a carbon(0) atom with two lone pairs of electrons (Scheme 1).[4] The first member of this family was hexaphenylcarbodiphosphorane [$C(PPh_3)_2$], reported in 1961.[5] Its ability to serve as ligand was shown in 1973 after the characterization of [$W(CO)_5\{C(PPh_3)_2\}$].[6] In the same paper, $C(PPh_3)_2$ was also described as $Ph_3P$-stabilized carbon(0) with two lone pairs, suggesting that such a ligand could bear two metals. The proof of concept was demonstrated in 1976, with the synthesis of [$(AuMe)_2\{\mu\text{-}C(PMe_3)_2\}$].[7] Until 2006, a few more carbodiphosphorane-complexes of rhenium,[8] rhodium,[9] nickel,[10] palladium,[9] platinum,[11] copper,[12,13] and silver[12,13] were described, as well as the mono- and digold species [$AuCl\{C(PPh_3)_2\}$] and [$(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}$].[12,14] A computational analysis of $C(PPh_3)_2$ reported in 2006,[15] and the theoretical prediction of carbodicarbenes in 2007,[16] created a renewed interest for the coordination chemistry at carbon(0), and various complexes of lithium,[17] boron,[18] ruthenium,[19] rhodium,[20,21] iridium,[21] palladium,[9] copper,[22] silver,[23] and gold[22,24] were synthesized. New theoretical studies aimed at understanding the bonding situation and predicting the reactivity of carbon(0) derivatives were reported simultaneously.[25] All of this experimental and theoretical work converged toward the idea that *carbones* are stronger donors than NHCs. Yet, to the best of our knowledge, these ligands have been tested in catalysis only once,[22] and



Scheme 1. Resonance forms of carbodiphosphoranes and carbodicarbenes.

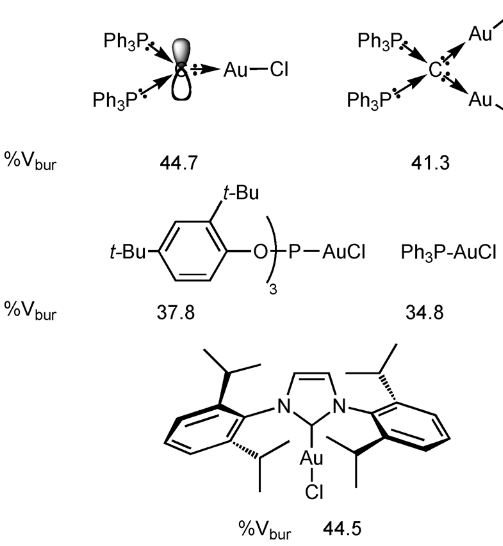
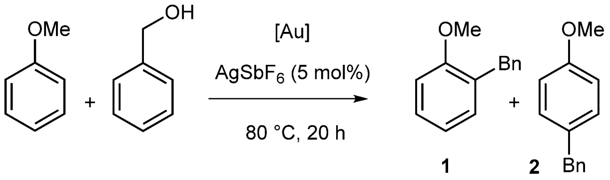


**Figure 1.** Precatalysts used in this study and $\%V_{bur}$ of the ligand when located 2 Å away from the metal.

**Table 1.** Au(I)-catalyzed benzylation of anisole.



| Entry | [Au] | Yield[a] [%] (**1**/**2**)[b] |
|---|---|---|
| 1 | $[AuCl(PPh_3)]$[c] | 96 (42/58) |
| 2 | [AuCl(IPr)][c] | 97 (43/57) |
| 3 | $[AuCl\{C(PPh_3)_2\}]$[c] | 97 (43/57) |
| 4 | $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$[d] | 95 (38/62) |

[a] Isolated yields.
[b] From $^1H$ NMR.
[c] 5 mol%.
[d] 2.5 mol%.

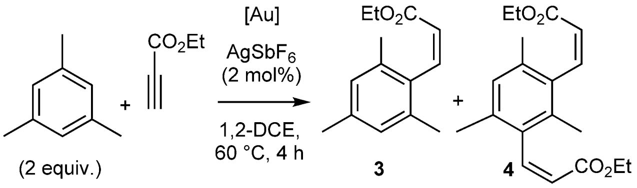
not with respect to their electronic properties. We have carried out typical gold-catalyzed transformations[26] to evaluate the donor ability of a *carbone* compared to other ligands.

The mono- and dinuclear complexes $[AuCl\{C(PPh_3)_2\}]$ and $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$ were chosen as precatalysts and their selectivity compared to $(AuCl\{P[O\text{-}(2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3\})$[27] and the commercially available $[AuCl(PPh_3)]$, and [AuCl(IPr)][28] [IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] as prototypes of phosphite, phosphine, and carbene gold complexes (Figure 1).

Hexaphenylcarbodiphosphorane $C(PPh_3)_2$[29] as well as the gold complexes $[AuCl\{C(PPh_3)_2\}]$ and $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$[14] were prepared according to literature procedures. To test the efficiency of these species, selected gold(I)-catalyzed transformations were carried out. In each case, the precatalysts were mixed with $AgSbF_6$ in a 1:1 ratio for $[AuCl\{C(PPh_3)_2\}]$ and in a 1:2 ratio with $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$ to generate the corresponding cationic and dicationic species. For the sake of comparison, the same amount of gold was maintained when using either $[AuCl\{C(PPh_3)_2\}]$ or $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$. We began our investigations by probing the oxophilicity of the carbodiphosphorane-complexes. A Friedel–Crafts reaction between anisole (used as solvent) and benzyl alcohol was carried out,[30,31] leading to *ortho*- and *para*-substitution (Table 1). In such a reaction, the nature of the ligand should have little influence on the product distribution, yet the result should be informative nonetheless on the potential of Au-*carbone* complexes to serve as catalysts. Gratifyingly, these species proved as efficient as the phosphine- and carbene-complexes, providing the benzylation products in very high yields. As expected, virtually no difference in the products ratio was observed along this series.

To test the carbophilicity of the carbodiphosphorane-gold complexes, the hydroarylation of ethyl propiolate by mesitylene was carried out next (Table 2).[32] While all gold complexes gave the mono-hydroarylation product as the predominant one, the dinuclear catalyst clearly outperformed the others in terms of kinetics. Because an electron-poor alkyne is used, one could expect that the most basic ligands favor the reaction. This was actually shown in the original paper where $[AuCl(PEt_3)]$ is a more active precatalyst than $[AuCl(PPh_3)]$.[32] This trend seems to be followed in our case as well, with $PPh_3 < IPr < C(PPh_3)_2$. Yet with $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$, the σ-donation of the ligand is partitioned between two metal centers. When funneled toward only one, as in $[AuCl\{C(PPh_3)_2\}]$, the reaction is slowed down, sug-

**Table 2.** Au(I)-catalyzed hydroarylation of ethyl propiolate.



| Entry | [Au] | Yield[a] [%] (**3**/**4**)[b] |
|---|---|---|
| 1 | $[AuCl(PPh_3)]$[c] | 78 (96/4) |
| 2 | [AuCl(IPr)][c] | 81 (98/2) |
| 3 | $[AuCl\{C(PPh_3)_2\}]$[c] | 30 (90/10) |
| 4 | $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$[d] | quant (95/5) |

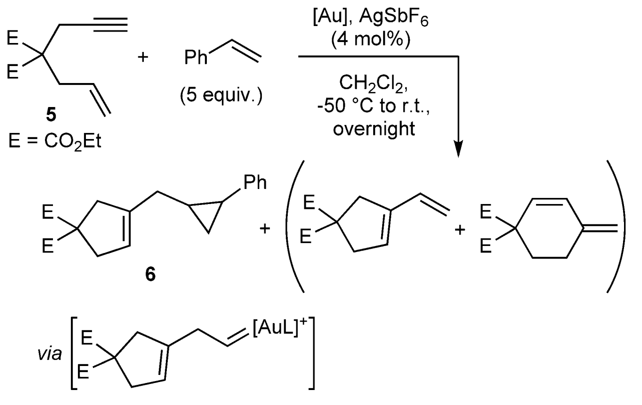
[a] Isolated yields after 4 h, also correspond to conversions (no degradation of the substrates).
[b] From $^1H$ NMR.
[c] 2 mol%.
[d] 1 mol%.

gesting a limitation due to excessive electron-enrichment. One could also argue that the metal center in $[\mathrm{Au\{C(PPh_3)_2\}}]^+$ is more sterically congested than in $[\mathrm{Au(PPh_3)}]^+$ or $[\mathrm{Au(IPr)}]^+$. To shed light on this matter, the percentage of buried volume (%$V_{\mathrm{bur}}$) was estimated for each ligand (Figure 1).[33] In fact, with a %$V_{\mathrm{bur}}$ of 44.7, $\mathrm{C(PPh_3)_2}$ surrounds the metal almost as much as IPr.[33b,34] For the dinuclear complex, because the PCP angle is more acute, an estimate of 41.3 was obtained.[35] However, the free space of the sphere will have to be occupied by two gold atoms; therefore the %$V_{\mathrm{bur}}$ of each metal center, which cannot be computed, will be obviously higher. Thus, in spite of the quite high shielding of the gold atoms, the dinuclear complex is the most active of the series, and the lower activity of $[\mathrm{AuCl\{C(PPh_3)_2\}}]$ can be explained by the reduced electrophilicity of the alkyne-gold intermediate.[36]

To gain more insights, we selected LAu(I)-catalyzed transformations for which the electronic parameters of the ligand are known to play a major role. For instance, in the intermolecular cyclopropanation of a terminal 1,6-enyne with styrene, it was noticed that a phosphite-containing precatalyst gave the best results, the transient gold-carbene being in this case more electrophilic.[27,37] Accordingly, we found that the selectivity for this process decreases as the metal becomes electron-richer (Table 3).[38] Full conversion of the starting material was reached in each case, except with $[\mathrm{AuCl\{C(PPh_3)_2\}}]$ which proved unreactive. In the crude mixtures, the expected compound **6** was observed, as well as *exo* and *endo* cycloisomers of **5**.

We then focused on the intramolecular [4+2]cycloaddition of an arylenyne displaying an electron-rich alkene moiety (Table 4). It was shown that the cyclization of this compound is not stereoselective, and that the use of a phosphine-complex leads to the *trans* stereoisomer as major component of the mixture, whereas a phosphite-based catalyst rather furnishes the *cis* stereoisomer.[39] These results were rationalized by computing the bond distances of the putative intermediate. With a stronger donor ligand, the carbenic structure dominates, leading to the *trans* product. On the other hand, a weaker donor ligand would favor the open cationic structure. Because bond rotation is somewhat faster than nucleophilic attack of the aromatic ring, the amount of *cis* product may increase in this case. Using the described procedure for such a reaction, i.e., by carrying it out under microwave irradiation, the cyclization products were formed in high yields. As expected, the weakest *trans* selectivity was observed with the phosphite ligand

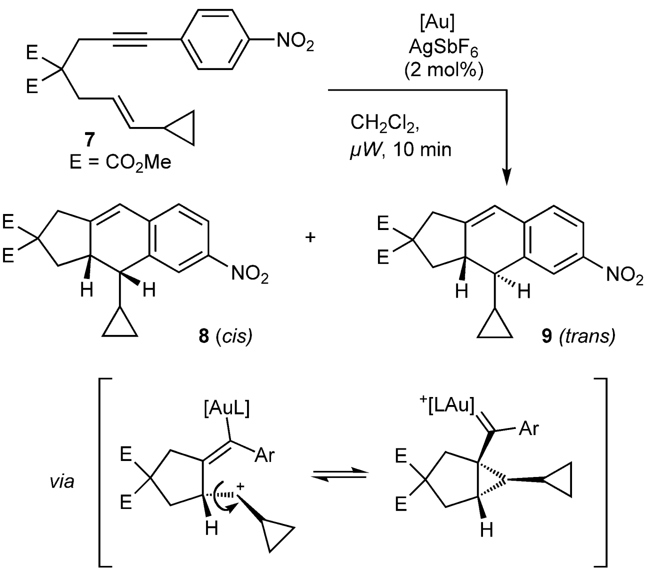
**Table 3.** Au(I)-catalyzed intermolecular cyclopropanation of a 1,6-enyne.



| Entry | [Au] | Yield of **6**[a] [%] (*cis*/*trans*)[b] |
|---|---|---|
| 1 | $[\mathrm{AuCl(P(OAr)_3)}]$[c] | 63 (2.7:1) |
| 2 | $[\mathrm{AuCl(PPh_3)}]$[c] | 57 (1.5:1) |
| 3 | $[\mathrm{AuCl(IPr)}]$[c] | 29 (1.7:1) |
| 4 | $[\mathrm{AuCl\{C(PPh_3)_2\}}]$[c] | –[e] |
| 5 | $[\mathrm{(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}}]$[d] | 19 (3.7:1) |

[a] Isolated yields (full conversion).
[b] From $^1$H NMR.
[c] 4 mol%.
[d] 2 mol%.
[e] No conversion.

**Table 4.** Au(I)-catalyzed intramolecular [4+2]cycloaddition of an aryl-1,6-enyne.



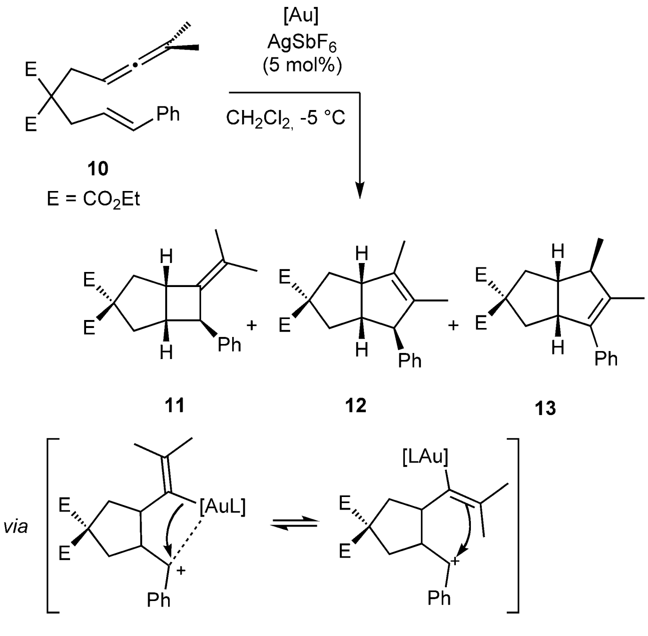
| Entry | [Au] | Yield[a] [%] (*cis*/*trans*)[b] |
|---|---|---|
| 1 | $[\mathrm{AuCl(P(OAr)_3)}]$[c] | 92 (1:1.7) |
| 2 | $[\mathrm{AuCl(PPh_3)}]$[c] | 84 (1:3.2) |
| 3 | $[\mathrm{AuCl(IPr)}]$[c] | 85 (1:4.6) |
| 4 | $[\mathrm{AuCl\{C(PPh_3)_2\}}]$[c] | 94 (1:5.7) |
| 5 | $[\mathrm{(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}}]$[c] | 90 (1:4.3) |

[a] Isolated yields.
[b] From $^1$H NMR (same ratio after purification).
[c] 2 mol%.
[d] 1 mol%.

(entry 1), and the highest with the monogold complex (entry 4).[40] This time, the digold complex proved less selective than the carbene-containing one. Nevertheless, the result obtained with the monogold species reinforces the idea that $C(PPh_3)_2$ is a stronger donor compared to IPr.

As an additional test reaction, we studied the cycloisomerization of eneallene **10**. In this type of transformation, it was shown that the ancillary ligand exerts a dramatic influence on the outcome (Table 5).[41] As described, we obtained mixtures containing the [2+2]cycloadduct **11** and the regioisomeric [3+2]cycloadducts **12** and **13**. Under the experimental reactions conditions used, we noticed an increase in the ratio of **11** as the metal becomes more electron-rich. This could be explained by a better stabilization of the carbocationic center of the vinylgold intermediate, leading to direct vinylation as previously reported in the bis-allene series.[42] Here, the selectivity for the [2+2]cycloadduct is much higher with the monogold complex. Again, the digold species was found to be less selective than the IPr complex.

**Table 5.** Au(I)-catalyzed cycloisomerization of an eneallene.



| Entry | [Au] | Yield[a] [%] (**11**/**12**/**13**)[b] |
|---|---|---|
| 1 | $[AuCl(P(OAr)_3]$[c] | 82 (1:1.6:1) |
| 2 | $[AuCl(PPh_3)]$[c] | 85 (1.8:1.4:1) |
| 3 | [AuCl(IPr)][c] | 90 (3.9:1:1) |
| 4 | $[AuCl\{C(PPh_3)_2\}]$[c] | 90 (11.7:1:1.6) |
| 5 | $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$[d] | 94 (2.9:1.2:1) |

[a] Isolated yields (> 90% conversion).

[b] From $^1H$ NMR.

[c] 5 mol%.

[d] 2.5 mol%.

In conclusion, we have shown that the gold complexes of $C(PPh_3)_2$ are valuable precatalyst for various Au(I)-catalyzed transformations. The selectivities observed strongly suggest that this ligand can be used, as predicted, as a stronger electron-donor compared to NHCs. The picture is certainly more complex when $C(PPh_3)_2$ bears two gold atoms, not only because the electron donation is partitioned between two metallic centers, but also because a dual activation mechanism can be the operative one. We are now extending our study to carbodicarbene species to get a better overview of the potential of these new gold complexes in catalysis.

## Experimental Section

Complete experimental procedures and full characterization data are given in the Supporting Information.

### Representative Procedure for the Au(I)-Catalyzed Intramolecular [4+2]Cycloaddition of 7

A 5-mL microwave sealed tube was charged with the gold(I) chloride (2 mol%, 0.0054 mmol), $AgSbF_6$ (2 mol%, 1.86 mg, 0.0054 mmol) and $CH_2Cl_2$ (1 mL). The mixture was stirred for 5 min to generate the cationic species. Then **7** (100 mg, 0.27 mmol) in $CH_2Cl_2$ (1 mL) was added and the solution was heated at 80 °C under microwave irradiation for 10 min. The mixture was passed through a short pad of silica. The solvent was evaporated and the mixture of products **8** and **9** was separated from the starting material by column chromatography (heptane/EtOAc, 94/6).

## Acknowledgements

*A. E.-H. is thankful to UPS for a PhD grant (chaire d'excellence). We also deeply thank Prof. José Vicente and Prof. Wolfgang Petz for their helpful advice for the synthesis of C-($PPh_3)_2$ and the corresponding gold complexes.*

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[34] This value was obtained from the optimized geometry of $[\mathrm{AuCl}\{\mathrm{C}(\mathrm{PPh}_3)_2\}]$ at the M06/LACVP** level of theory. Using the coordinates of the X-ray structure of $[\mathrm{H}_3\mathrm{B}\{\mathrm{C}(\mathrm{PPh}_3)_2\}]$ (see ref.[18]), we obtained a %$V_{\mathrm{bur}}$ of 46.6.

[35] This value was obtained from the optimized geometry of $[(\mathrm{AuCl})_2\{\mu\text{-}\mathrm{C}(\mathrm{PPh}_3)_2\}]$ at the M06/LACVP** level of theory. Using the coordinates of the X-ray structure (see ref.[14]), we obtained a %$V_{\mathrm{bur}}$ of 42.0.

[36] We cannot exclude the participation of the two gold atoms in the activation of the substrate; a) P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 4517; b) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733; c) D. Weber, M. R. Gagné, *Org. Lett.* **2009**, *11*, 4962; d) Y. Odabachian, X.-F. Le Goff, F. Gagosz, *Chem. Eur. J.* **2009**, *15*, 8966; e) G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.*2010, *122*, 8644; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466; f) H. Schmidbaur, A. Schier, *Organometallics* **2010**, *29*, 2.

[37] For another type of ligand-dependent gold-catalyzed cyclopropanation, see: A. Prieto, M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, P. Pérez-Galán, N. Delpont, A. M. Echavarren, *Tetrahedron* **2009**, *65*, 1790.

[38] A similar product was tested by Echavarren (see ref.[27]) with the same $[\mathrm{AuCl}(\mathrm{P}(\mathrm{OAr})_3]/\mathrm{AgSbF}_6$ catalytic system (Me groups instead of Et at the ester moieties),

giving the products in 67% isolated yield (3.3:1 *cis*:*trans* ratio).

[39] E. Jiménez-Núñez, C. K. Claverie, C. Bour, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2008**, *120*, 8010; *Angew. Chem. Int. Ed.* **2008**, *47*, 7892.

[40] The *cis:trans* selectivity is different from that reported by Echavarren with the phosphite ligand (1.7:1). However, in our case, the cationic species was generated *in situ* with $AgSbF_6$, which was not the case in ref.[39] Changes in selectivity between Au/Ag and silver-free protocols have been noted therein.

[41] a) M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem.* **2010**, *122*, 2596; *Angew. Chem. Int. Ed.* **2010**, *49*, 2542; b) M. R. Luzung, P. Mauleón, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 12402; c) H. Teller, S. Flügge, R. Goddard, A. Fürstner, *Angew. Chem.* **2010**, *122*, 1993; *Angew. Chem. Int. Ed.* **2010**, *49*, 1949.

[42] S. M. Kim, J. H. Park, Y. K. Kang, Y. K. Chung, *Angew. Chem.* **2009**, *121*, 4602; *Angew. Chem. Int. Ed.* **2009**, *48*, 4532.