Gold Complexes

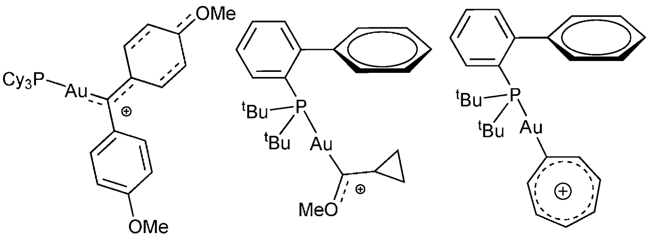
International Edition: DOI: 10.1002/anie.201412401
German Edition: DOI: 10.1002/ange.201412401

The Stabilizing Effects in Gold Carbene Complexes**

Laura Nunes dos Santos Comprido, Johannes E. M. N. Klein, Gerald Knizia, Johannes Kästner, and A. Stephen K. Hashmi**

Abstract: *Bonding and stabilizing effects in gold carbene complexes are investigated by using Kohn–Sham density functional theory (DFT) and the intrinsic bond orbital (IBO) approach. The π-stabilizing effects of organic substituents at the carbene carbon atom coordinated to the gold atom are evaluated for a series of recently isolated and characterized complexes, as well as intermediates of prototypical 1,6-enyne cyclization reactions. The results indicate that these effects are of particular importance for gold complexes especially because of the low π-backbonding contribution from the gold atom.*

There has been an ongoing debate regarding the nature of the gold–carbon bond in various intermediates in the field of gold catalysis.[1] At the heart of this discussion is the question whether these intermediates are best described as gold carbene complexes or gold-stabilized carbocations. It was only recently that gold complexes of this type could be isolated and structurally characterized, allowing further insight.[2] As these complexes mimic reactive intermediates they are often stabilized through strongly electron-donating groups, such as electron-rich arenes in **1** (Figure 1, left)[2a] or heteroatom substituents in **2** (Figure 1, middle).[2b] A somewhat different strategy was employed by Harris and Widenhoefer in the preparation of cycloheptatrienyl-substituted gold complex **3**, in which aromaticity is the origin of stabilization (Figure 1, right).[2c]



1 **2** **3**

Figure 1. Representative recent examples of gold carbene complexes.

The carbene character is often implied by depicting the bond between the gold and carbon atoms as a double bond, where one line represents σ donation and the other line represents π backdonation, while the gold atom carries a positive formal charge. Based on the structural parameters of complex **1**, Seidel and Fürstner challenged this way of depicting the bond.[2a] They observed a rather long Au−C bond (2.039(5) Å) and significantly contracted C−C bonds (1.429(7) and 1.455(6) Å) between the carbon atom coordinated at gold and the adjacent carbon atoms from the aromatic substituents in the solid state. This situation led them to conclude that there is no significant C–Au double-bond character, and hence, no pronounced π backbonding is present in complexes of this type. Instead, they suggest that the carbon atom coordinated to gold is strongly stabilized through the organic fragment as evidenced by the contraction of the C−C bonds.

Seidel and Fürstner's observations can be corroborated with experimental and computational studies on gold carbonyl complexes, which indicate that the bonding between the gold atom and the bound carbon atom is dominated by electrostatic interactions, some σ donation, and only a small amount of π backbonding.[3] This situation has also been reported for gold carbene complexes.[4]

Herein we investigate the bonding and the stabilizing effects in these complexes using Kohn–Sham density functional theory (DFT) and the intrinsic bond orbital (IBO)[5] approach to clarify and strengthen the observations and conclusions made by Seidel and Fürstner. We further extend this analysis to bonding in intermediates of 1,6-enyne cyclization reactions as a prototypical transformation catalyzed by gold.[6] Throughout we focus on the role of the organic fragments and their stabilizing effects, which have received little attention in gold catalysis to date. The stabilization of a cationic formal charge in cyclopropyl-substituted intermediates in gold catalysis has previously been alluded to by Echavarren and co-workers.[6b,7]

The geometries of the complexes were first optimized using the TPSS[8] functional in combination with Grimme's D3 dispersion correction using Becke–Johnson damping.[9] The def2-TZVPP[10] basis set and the conductor-like screening model (COSMO)[11] simulating solvation effects of CH_2Cl_2

---

[*] M. Chem. L. Nunes dos Santos Comprido, Prof. Dr. A. S. K. Hashmi
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: hashmi@hashmi.de

Dr. J. E. M. N. Klein,[+] Prof. Dr. J. Kästner
Institut für Theoretische Chemie
Universität Stuttgart
Pfaffenwaldring 55, 70569 Stuttgart (Germany)
E-mail: kaestner@theochem.uni-stuttgart.de

Prof. Dr. G. Knizia
Department of Chemistry
Pennsylvania State University (USA)

Prof. Dr. A. S. K. Hashmi
Chemistry Department, Faculty of Science
King Abdulaziz University, Jeddah 21589, Saudi Arabia

[+] Present address: Department of Chemistry
University of Minnesota; Minneapolis (USA)

[**] L.N.d.S.C. is grateful to the DAAD for a PhD fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201412401.

($\varepsilon = 8.51$),[12] a commonly used solvent in the field of gold catalysis, were used in all calculations (for full computational details see the Supporting Information).

The structural parameters obtained are in good agreement with the experimental values. We subsequently turned our attention to the analysis of the bonding using the IBO method. The IBO method is a novel approach to analyze chemical bonding. Based on a simple mathematical criterion, a set of local orbitals (the IBOs) is determined, which exactly represents the computed Kohn–Sham wave function—without any approximation, pre-defined bonding motives, or empirical input. Nevertheless, the IBOs generally depict occupied orbitals in an intuitive way and allow for a direct interpretation of chemical bonding. The method allows for the assignment of charges to individual atoms, without any free parameters. The electrons in the doubly occupied IBOs are assigned proportionally to the individual atoms, allowing further quantitative interpretation of bonding.

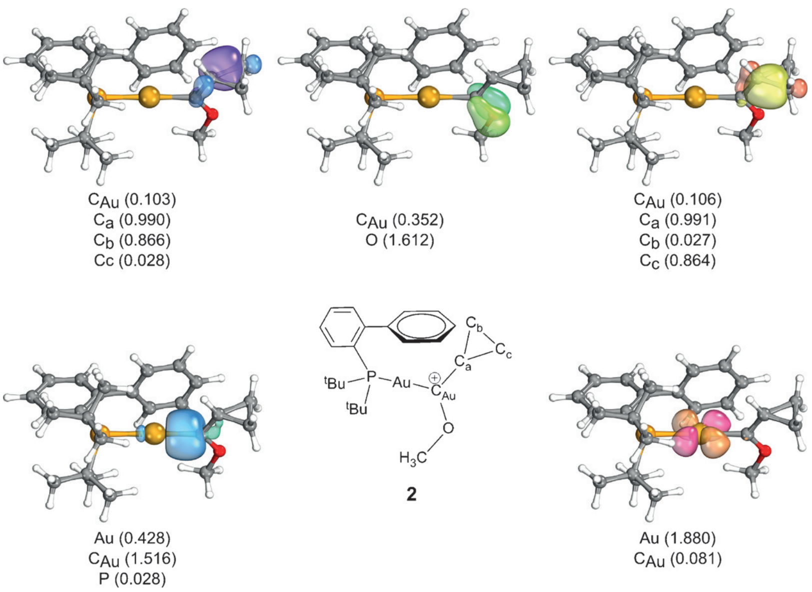


Figure 3. C_{Au}-stabilizing IBOs of complex **2**. Numbers in parentheses indicate the fraction of electrons of the doubly occupied orbital assigned to the individual atoms.

For complex **1**, two IBOs were identified which contribute similarly to the stabilization of the carbon atom coordinated to gold (C_{Au}). The π systems of the aromatic rings attached to C_{Au} are equally polarized towards C_{Au} (Figure 2, top). The carbene σ lone pair coordinated to the gold atom was also identified (Figure 2, bottom left). This IBO is largely located at C_{Au} in agreement with a coordinative bond. A similar bonding situation was observed for the lone pair of phosphorus. The IBO representing the filled d orbital at gold, aligned for potential π backbonding, is largely located at the gold atom (95%; Figure 2, bottom right) and therefore, does not appear to contribute to the stabilization of C_{Au} significantly.

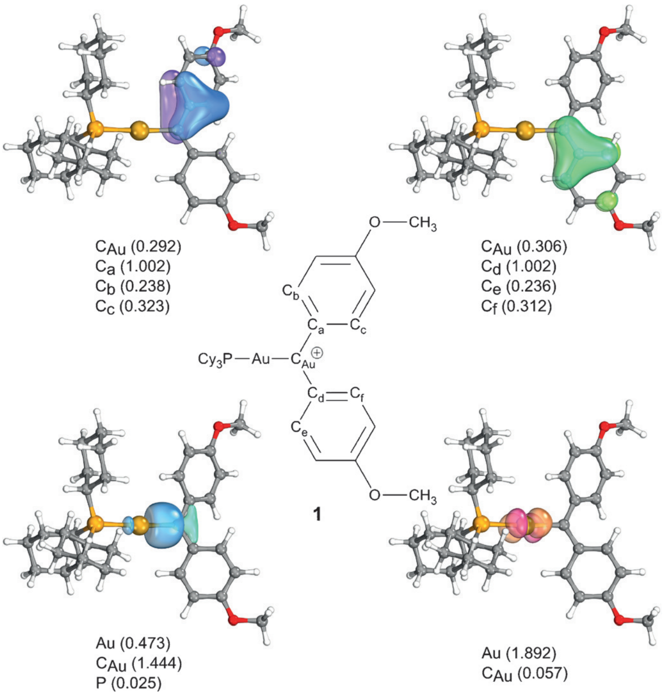


Figure 2. C_{Au}-stabilizing IBOs of complex **1**. Numbers in parentheses indicate the fraction of electrons of the doubly occupied orbital assigned to the individual atoms.

In complex **2** we identified a strong covalent stabilization which is mainly achieved through the O lone pair of the neighboring methoxy group (π stabilization; Figure 3, top middle) and thus resembles the stabilization in carbonyl compounds.[5] In addition, small contributions from the cyclopropyl banana bonds were identifiable (Figure 3, top right and left). These contributions may be attributed to partial charge delocalization into the cyclopropane ring, an anchimeric effect that Brooner and Widenhoefer also concluded made a contribution when studying complex **2** experimentally.[2b] Regarding the bonding between the gold and the carbon atom (C_{Au}), we identified the lone pair at C_{Au} as expected for a singlet carbene (Figure 3, bottom left). This lone pair is largely located at C_{Au}, consistent with coordinative bonding (σ donation). The filled d orbital that is suitably aligned for π backbonding is, however, again located largely at gold (94%; Figure 3, bottom right) suggesting little contribution to the stabilization of C_{Au}.

In complex **3**, no heteroatom substitution is present. The π stabilization of C_{Au} from the organic fragments is therefore realized in a somewhat different way, namely through aromaticity (Figure 4). The three IBOs of the six π electrons of the aromatic system are fairly equally distributed among the seven atoms. The total contributions are: C_{Au} 0.731, C_a 0.845, C_b 0.876, C_c 0.885, C_d 0.885, C_e 0.873, C_f 0.853. This distribution accounts for 99% of the six π electrons of the aromatic system. Again, the bonding between Au and C_{Au} seems to fall within the same range as for the other two complexes described above, the respective d orbital is located to 95% at gold.

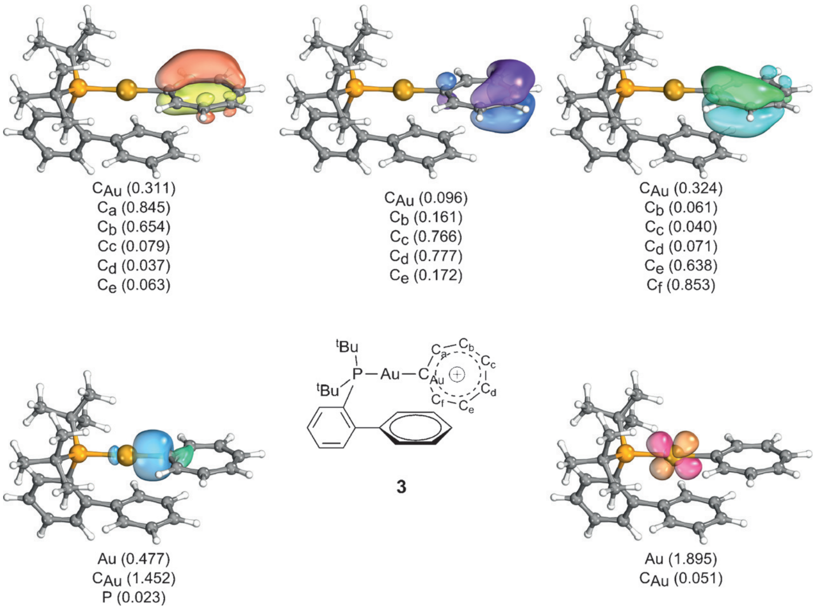


Figure 4. C_{Au}-stabilizing IBOs of complex **3**. Numbers in parentheses indicate the fraction of electrons of the doubly occupied orbital assigned to the individual atoms.

In the three complexes investigated, the stabilizing contribution to C_{Au} from π backbonding appears to be minor compared to the effects caused by the organic fragments. Despite the vastly different ligands and organic components present, the Au d orbital aligned with C_{Au} is strongly located at gold to very similar degrees (94–95%). To avoid potential bias from the localization procedure used, we also computed IBOs for complex **4**.[13] This complex was recently reported to have enhanced π backbonding. Therefore, **4** should serve as a validation of the ability of IBOs to assess this type of interaction in gold complexes. Indeed, we did observe an IBO consisting of a gold d orbital which is polarized towards C_{Au} (Figure 5, bottom right). As a result, this IBO is now only located at gold to 87%, a significantly smaller value than in complexes **1**–**3**. Furthermore, the IBOs that are observed to cause π stabilization from the aromatic rings display a reduced overlap with C_{Au} (0.191 and 0.213) compared to complex **1** (0.292 and 0.306). Nevertheless, even in complex **4** these contributions from the organic fragments clearly remain dominant over Au π backbonding.

The effects of π-stabilization have already been recognized in the early work of Fischer and co-workers, in which the presence of donating groups allowed the isolation and characterization of carbene complexes.[14] To compare the effects of π donation we also computed IBOs for the diphenylcarbene-substituted complexes **1b**, **5**, and diphenylcarbene (**6**) itself (Table 1). With decreasing π backdonation from the transition-metal center, an increase of the π donation from the phenyl groups is observed (**1b** > **4** > **5**). This effect is less pronounced in the free diphenylcarbene, in which there is increased electron density of the σ lone pair at C* owing to the absence of metal coordination.

Our assignment made is based on the partial charges of the IBOs on the individual atoms. To evaluate if this charge can be directly linked to energetic stabilization, we computed IBOs for a series of gold-substituted diphenylcarbene complexes and we found a linear correlation between the Hammett parameters (electrophilic substituent constant, σ_p^+; for details see the Supporting Information). This correlation supports our notion that IBOs allow for the assignment of the relative energetic stabilization of the gold complexes presented herein.

The comparison made in Table 1 demonstrates that π donation from the organic substituents is particularly strong for Au complexes raising the question of the influence of this effect on intermediates during catalytic transformations, especially when π-stabilizing substituents are absent.

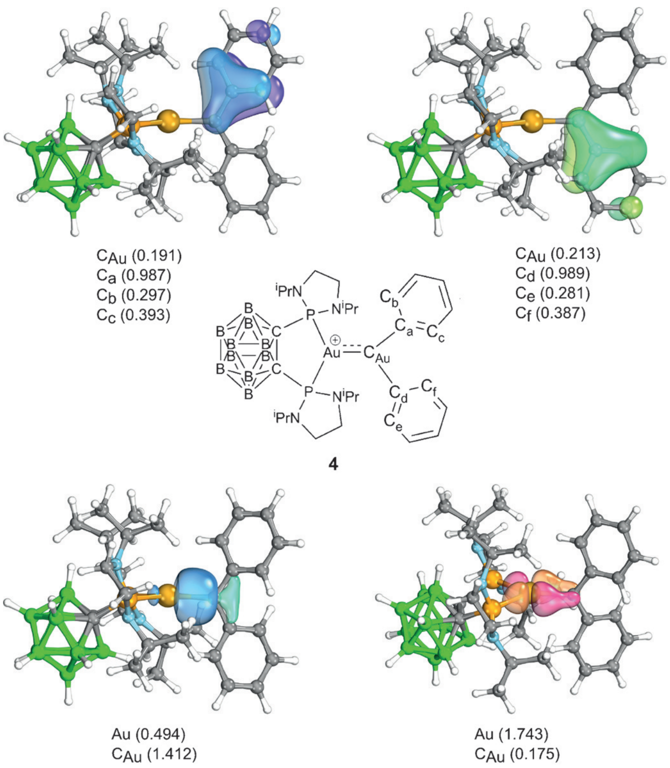
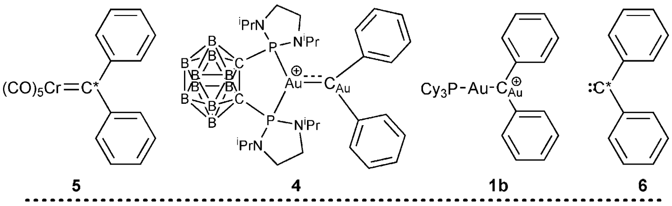
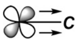
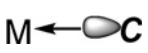
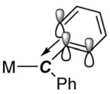


Figure 5. C_{Au}-stabilizing through π backbonding in **4**. Numbers in parentheses indicate the fraction of electrons of the doubly occupied orbital assigned to the individual atoms.

We therefore calculated IBOs for intermediates of an oxidative 1,6-enyne cyclization (Figure 6, top).[15] Knizia and Klein have recently demonstrated that IBOs can be utilized to study the electron flow in organic reactions, which is usually represented by curly arrows in mechanistic schemes.[16] This approach is therefore promising for the study of gold-catalyzed reactions,[7a,17] as bond transformations can be followed along reaction paths. For the first intermediate formed (**8**) we indeed found a bonding situation where stabilization of the

Table 1: IBO values for **1b**, **4**, **5**, and **6**.[a,b]



Complex	5	4	1b	6
π Backbonding 	0.260	0.175	0.074	–
σ Coordination at C*/C$_{Au}$ 	0.365 (1.451)	0.494 (1.412)	0.452 (1.463)	(1.806)
Sum of π donation[c] 	0.349	0.404	0.551	0.453

[a] Values indicate the fraction of electrons of the doubly occupied orbital assigned to the individual contribution. [b] For depictions of the IBOs of **1b**, **5**, and **6**, see the Supporting Information. [c] Accounts for the contribution from both Ph substituents.

form found in the isolated complexes above, is not accessible. While it could be anticipated that π backbonding may compensate, we observed little change in the IBO representing the Au d orbital. Instead stabilization is realized through the cyclopropyl substituent (Figure 6, middle). This anchimeric effect was also observed for complex **2**, albeit in a much less pronounced way. Addition of the sulfoxide in the next step makes the need for stabilization unnecessary and results in the formation of defined C–C banana bonds in the cyclopropyl moiety in structure **9** (Figure 6, bottom).

It should be noted that cyclizations of this type are usually carried out with substrates that have aryl substituents. Examples with alkyl substituents are scarce.[18] We indeed noticed that in the case of aryl substitution the bonding situation changes and the formation of a cyclopropane ring is less complete and the intermediate formed still has vinyl Au character (see the Supporting Information for details). These observations are consistent with a previously suggested bonding scenario.[6b,7]

In summary, we conclude that Seidel and Fürstner's description of the bonding in gold carbene complexes currently represents the best overall classification of bonding for such species and intermediates in catalytic transformations. Furthermore, we note that the π-stabilizing effects of the organic fragment are substantial and highly depend on the organic fragment bound to the carbene carbon coordinated to the gold center, an effect that might assist in the systematic planning of experimental studies. IBO analysis represents a useful method for the elucidation of these effects based on simple DFT computations and might augment future computational studies in this field.

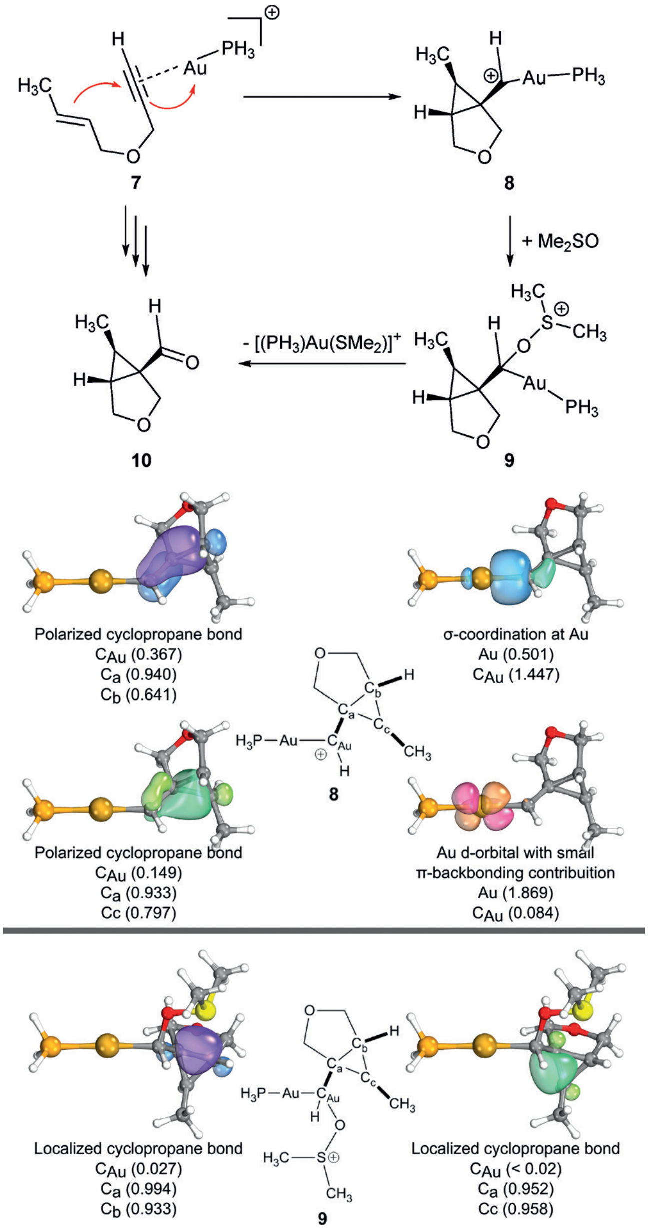


Figure 6. Pathway of 1,6-enyne cyclization and C$_{Au}$-Stabilizing through π backbonding in **8** and **9**. Numbers in parentheses indicate the fraction of electrons of the doubly occupied orbital assigned to the individual atoms.

Keywords: alkenes · alkynes · carbene ligands · computational chemistry · gold

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10336–10340
Angew. Chem. **2015**, *127*, 10477–10481

---

[1] a) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2008**, *47*, 6754; *Angew. Chem.* **2008**, *120*, 6856; b) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482; c) A. M. Echavarren, *Nat. Chem.* **2009**, *1*, 431; d) A. Fürstner, L. Morency, *Angew. Chem. Int. Ed.* **2008**, *47*, 5030; *Angew. Chem.* **2008**, *120*, 5108.

[2] a) G. Seidel, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 4807; *Angew. Chem.* **2014**, *126*, 4907; b) R. E. M. Brooner, R. A.

Widenhoefer, *Chem. Commun.* **2014**, *50*, 2420; c) R. J. Harris, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2014**, *53*, 9369; *Angew. Chem.* **2014**, *126*, 9523; d) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642; e) G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem. Int. Ed.* **2009**, *48*, 2510; *Angew. Chem.* **2009**, *121*, 2548; f) M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, *Angew. Chem. Int. Ed.* **2014**, *53*, 9372; *Angew. Chem.* **2014**, *126*, 9526.

[3] a) H. V. R. Dias, C. Dash, M. Yousufuddin, M. A. Celik, G. Frenking, *Inorg. Chem.* **2011**, *50*, 4253; b) M. A. Celik, C. Dash, V. A. K. Adiraju, A. Das, M. Yousufuddin, G. Frenking, H. V. R. Dias, *Inorg. Chem.* **2013**, *52*, 729; c) G. Ciancaleoni, N. Scafuri, G. Bistoni, A. Macchioni, F. Tarantelli, D. Zuccaccia, L. Belpassi, *Inorg. Chem.* **2014**, *53*, 9907.

[4] a) L. Batiste, P. Chen, *J. Am. Chem. Soc.* **2014**, *136*, 9296; b) D. Marchione, L. Belpassi, G. Bistoni, A. Macchioni, F. Tarantelli, D. Zuccaccia, *Organometallics* **2014**, *33*, 4200.

[5] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834.

[6] a) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271; b) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; c) C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2004**, *43*, 2402; *Angew. Chem.* **2004**, *116*, 2456; d) C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677; e) J.-M. Mattalia, P. Nava, *J. Organomet. Chem.* **2014**, *749*, 335.

[7] a) A. Echavarren, E. Jiménez-Núñez, *Top. Catal.* **2010**, *53*, 924; b) C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2005**, *44*, 6146; *Angew. Chem.* **2005**, *117*, 6302; c) E. Jiménez-Núñez, C. K. Claverie, C. Bour, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2008**, *47*, 7892; *Angew. Chem.* **2008**, *120*, 8010; d) C. Obradors, A. M. Echavarren, *Chem. Commun.* **2014**, *50*, 16.

[8] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.

[9] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.

[10] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297; b) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

[11] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799.

[12] V. P. Pawar, *J. Chem. Eng. Data* **2006**, *51*, 882.

[13] M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 14512; *Angew. Chem.* **2014**, *126*, 14740.

[14] E. O. Fischer, *Angew. Chem.* **1974**, *86*, 651.

[15] a) C. A. Witham, P. Mauleón, N. D. Shapiro, B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 5838; b) L. Nunes dos Santos Comprido, A. S. K. Hashmi, *Isr. J. Chem.* **2013**, *53*, 883.

[16] G. Knizia, J. E. M. N. Klein, *Angew. Chem. Int. Ed.* **2015**, *54*, 5518; *Angew. Chem.* **2015**, *127*, 5609.

[17] a) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2005**, *44*, 6990; *Angew. Chem.* **2005**, *117*, 7150; b) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896; *Angew. Chem.* **2006**, *118*, 8064; c) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; d) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208; e) A. S. K. Hashmi, *Gold Bull.* **2003**, *36*, 3.

[18] C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721.

Received: December 26, 2014
Revised: February 4, 2015