VIP Ligand Effects

DOI: 10.1002/ange.200907194

Steering the Surprisingly Modular π-Acceptor Properties of N-Heterocyclic Carbenes: Implications for Gold Catalysis**

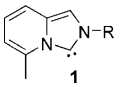
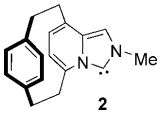
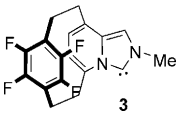
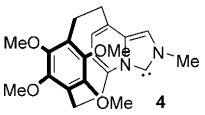
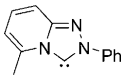
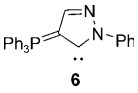
*Manuel Alcarazo, Timon Stork, Anakuthil Anoop, Walter Thiel, and Alois Fürstner**

Whereas the excellent σ-donor qualities of N-heterocyclic carbenes (NHCs) are undisputed and extensively used as an enabling feature for homogeneous catalysis, the π-acceptor properties of such ligands are usually considered weak or even negligible.[1] Only in the last decade has experimental[2] and in silico[3,4] evidence been acquired that suggests that the π acidity of NHCs deserves more serious consideration, even though this issue is still a matter of debate.[1,5] The case study outlined herein may help to clarify this aspect. Rather than relying on the interpretation of spectroscopic and structural fingerprints, we present reactivity data which demonstrate that the course of three mechanistically distinct gold-catalyzed processes can be determined solely by changing the π-acceptor properties of the ancillary NHC ligand.[6]

We previously introduced the cyclophanic NHCs **2**–**4**[7] as novel analogues of the known imidazopyridine-2-ylidene derivatives **1** (Table 1).[8] These chiral compounds exhibit interesting spectroscopic characteristics and are studied in some detail by our research group. As part of these investigations, the energies of the orbital occupied by the carbene lone pair of electrons (E_σ)[9] and of the lowest unoccupied orbital with a nonzero coefficient at the carbene center (E_π)[9] were determined by density functional theory (DFT) calculations at the BP86(RI)/TZVP level.[10,11]

The computed data revealed various salient features (Table 1): whereas the E_σ values of the parent NHC **1a** (R = Me) and its cyclophanic counterpart **2** are almost identical, the E_π value drops significantly from −0.63 eV in **1a** to −1.14 eV in **2**; moreover, the energy of the π-type acceptor orbital is highly responsive to the type of substituents present on the top layer; thus, the E_π values of the tetrafluoro- and tetramethoxy-substituted carbenes **3** and **4** are almost 0.5 eV apart. These findings are readily explained by the representation of the π acceptor orbital in Figure 1,

Table 1: Computed energies of the carbene lone-pair orbital (E_σ) and the π-acceptor orbital (E_π) for different ligands L,[9] and electrochemical redox potential ($E_{1/2}$) of the corresponding rhodium complexes of the type [L·RhCl(cod)].[a]

Compound	E_σ [eV]	E_π [eV]	$E_{1/2}$ [V]
 **1**	−4.97[b]	−0.63[b]	0.805[c]
 **2**	−5.00	−1.14	0.858
 **3**	−5.14	−1.34	0.905
 **4**	−4.86	−0.85	n.d.[d]
 **5**	−5.33	−0.97	0.955
 **6**	−4.18	−0.92	0.573

[a] Calibrated against ferrocene/ferrocenium ($E_{1/2}$ = 0.46 V), Bu_4NPF_6 (0.1 M) in CH_2Cl_2. [b] R = Me. [c] R = mesityl. [d] Not determined. cod = 1,5-cyclooctadiene.

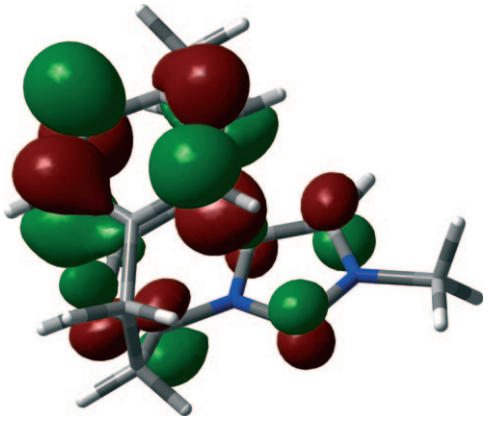


Figure 1. The π-acceptor orbital of **2**.

which shows a strong interaction between the two aromatic planes, as expected for a cyclophane skeleton.[12]

Similarly informative is the comparison between **1** and its triazo analogue **5**.[13] As expected, the energy E_π drops upon

[*] Dr. M. Alcarazo, Dipl.-Chem. T. Stork, Dr. A. Anoop, Prof. W. Thiel, Prof. A. Fürstner
Max-Planck-Institut für Kohlenforschung
45470 Mülheim/Ruhr (Germany)
Fax: (+49) 208-306-2994
E-mail: fuerstner@mpi-muelheim.mpg.de

[**] Generous financial support by the MPG and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank the NMR spectroscopy, X-ray crystallography, and chromatography departments of our institute for excellent support, K. Radkowski for the preparation of [**6**·AuCl], and Ch. Laurich, Max-Planck-Institut für Bioanorganische Chemie, Mülheim, for recording the electrochemical data.

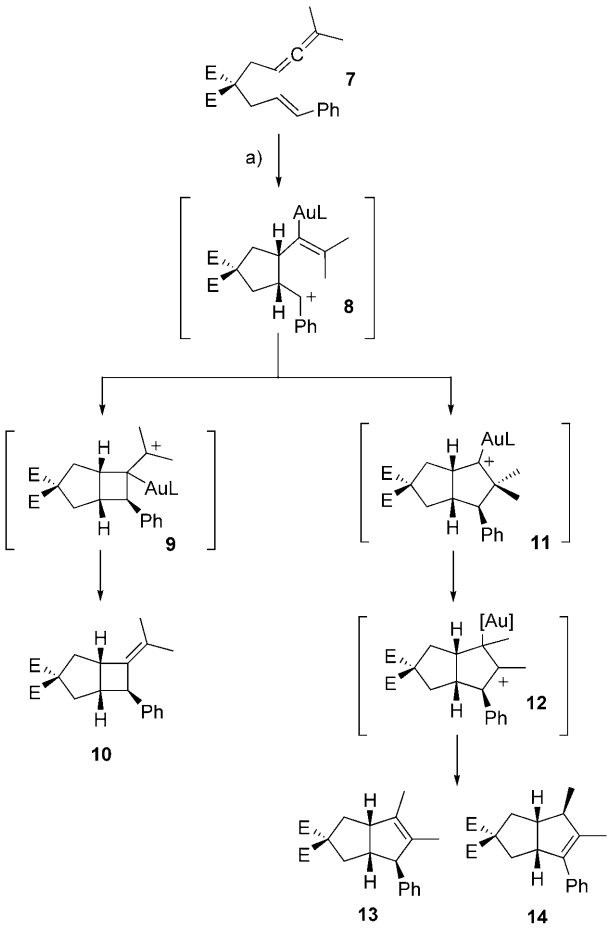
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200907194.

the formal exchange of a CH group in the backbone for N; in contrast to the cyclophanic series, however, the incorporation of the more electronegative heteroelement into the molecular frame also reduces the donor capacity of the ligand, as evident from the noticeable change in the E_σ value of **5** relative to that of **1a** (R = Me).[14] In contrast, the formal replacement of a nitrogen atom adjacent to the carbene center with an electron-releasing phosphorus ylide makes the resulting amino–ylide carbene (AYC) **6**, which is readily available in multigram quantities,[15] by far the strongest donor of all ligands in Table 1 ($E_\sigma = -4.18$ eV). The energy of its π acceptor orbital, however, is hardly affected. Specifically, the E_π value is similar to that of the triazolylidene **5** and considerably lower than that of **1a** (R = Me). This particular combination of exceptional donor *and* appreciable acceptor qualities may set AYCs apart from conventional NHCs in terms of their overall ligand properties.[16]

Electrochemical results (Table 1) support the conclusions drawn from the computational data. Thus, the oxidation potential $E_{1/2}$ of the corresponding rhodium complexes [LRhCl(cod)] (L = **1**–**6**) closely follows the trends observed for the computed data.[17] Specifically, a second aromatic layer spanned over the basal imidazopyridine-2-ylidene plane of **1** decreases the net electron density at the metal and hence increases $E_{1/2}$ to a considerable extent. This finding is in excellent accord with the notion that the π acidity of **2** is enhanced relative to that of **1**, whereas the σ-donor qualities of **1** and **2** are similar; the electrochemical and computational results are also in agreement in that fluorination of the "lid" augments this effect. The incorporation of an extra nitrogen atom into the basal plane (in **5**) has similar consequences, whereas the electron-releasing capacity of the AYC **6** considerably lowers the redox potential of the corresponding rhodium complex.

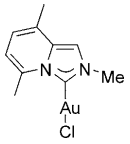
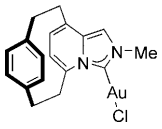
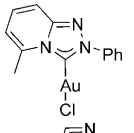
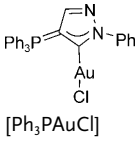
In contrast to the prevailing perception of carbene ligands,[1] these results suggest that the energy of their π acceptor orbital can be tuned readily by as much as 0.6 eV while keeping the donor capacity almost constant. We conceived that this remarkable electronic leeway should provide a handle to control the reactivity of metal–NHC-based catalysts. Therefore, a set of new NHC–gold complexes[18,19] was prepared and applied to the cycloisomerization of eneallene **7** (Scheme 1 and Table 2).[20] This transformation was chosen because intermediate **8**, which is initially formed upon coordination of $[LAu]^+$ to the allene group, may evolve along two different pathways. An electron-rich gold template could stabilize an adjacent cation and therefore favor the formal [3+2] pathway via intermediate **11**; in contrast, a more electron-deficient catalyst might favor the formation of intermediate **9**, in which the carbenium center is not directly bound to gold, and hence ultimately deliver the known alkylidenecyclobutane **10** by a formal [2+2] cycloaddition.[20]

In line with our expectations, complex [**1b**·AuCl] and its cyclophanic cousin [**2**·AuCl] (Figure 2) showed strikingly different behavior in the cycloisomerization of **7** (Table 2). Thus, [**1b**·AuCl], which contains the stronger net donor, exclusively furnished the [3+2] adduct (as a mixture of the two double-bond isomers **13** and **14**), whereas [**2**·AuCl], with



Scheme 1. Control over the cycloaddition of eneallene **7** through adjustment of the π-acceptor properties of the carbene ligand L bound to Au^+: a) [LAuCl] (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2, −5 °C (see Table 2; E = COOMe).

Table 2: Cycloisomerization of eneallene **7** catalyzed by different gold complexes.[a]

Entry	Precatalyst	**10**/**13** + **14**	Yield [%]
1	 [**1b**·AuCl]	0:62 + 38	63
2	 [**2**·AuCl]	100:0	71
3	 [**5**·AuCl]	85:10 + 5	87
4	 [**6**·AuCl]	100:0	94
5	$[Ph_3PAuCl]$	50:32 + 18	83[23]

[a] Reaction conditions: [LAuCl] (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2, −5 °C.

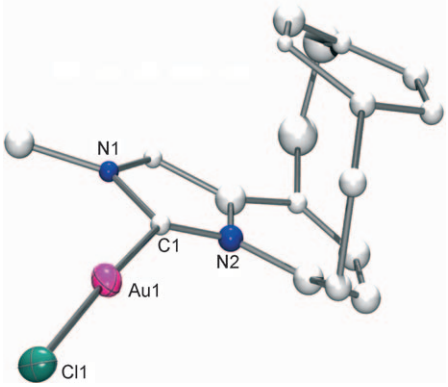


Figure 2. Molecular structure of the NHC complex [**2**·AuCl] in the solid state.[21]

the supposedly better π-acceptor ligand, gave the [2+2] adduct **10** as the only product. The constitution of the previously unknown compound **13** was confirmed by X-ray crystallography (Figure 3).[21,22] The notion that the large

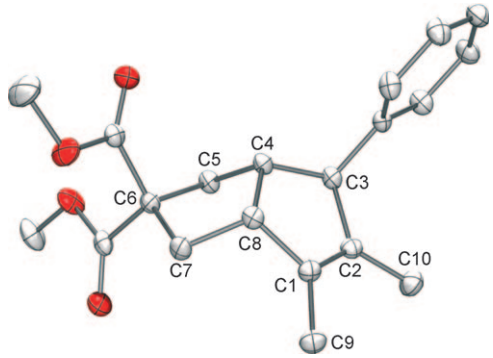


Figure 3. Structure of the [3+2] cycloadduct **13** in the solid state.[21]

difference in the acceptor quality of the ligands causes this switch from one pathway to the other is supported by the fact that complex [**5**·AuCl] (Figure 4), which contains a triazolylidene ligand, also favored the [2+2] pathway. Even the novel AYC–gold complex [**6**·AuCl] (Figure 5) gave **10** in excellent yield, probably as a result of effective intervention of the low-lying acceptor orbital of the ligand. To put these results into perspective, we performed a control experiment with

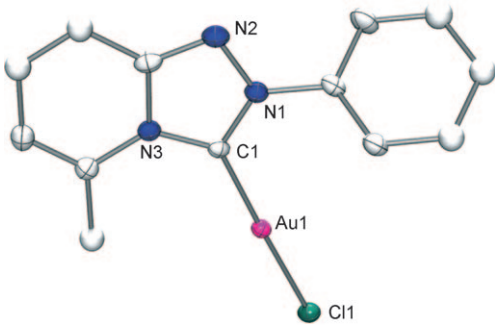


Figure 4. Molecular structure of the NHC complex [**5**·AuCl] in the solid state.[21]

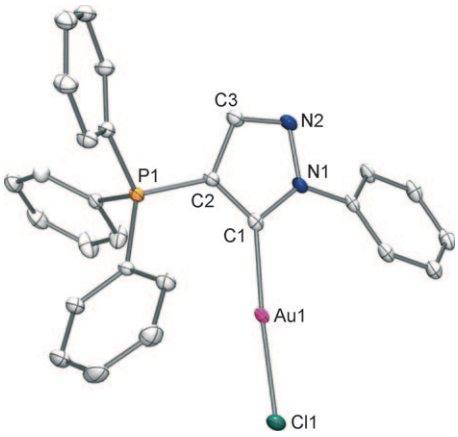
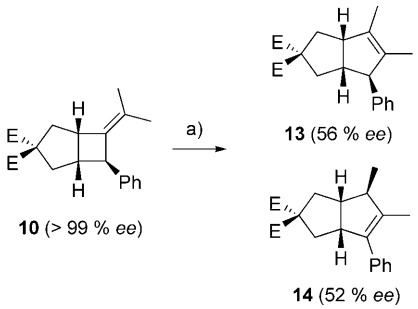


Figure 5. Molecular structure of the AYC complex [**6**·AuCl] in the solid state.[21]

[Ph_3PAuCl]: a standard precatalyst in the field of gold catalysis. This reaction delivered a mixture of products under our reaction conditions.[23]

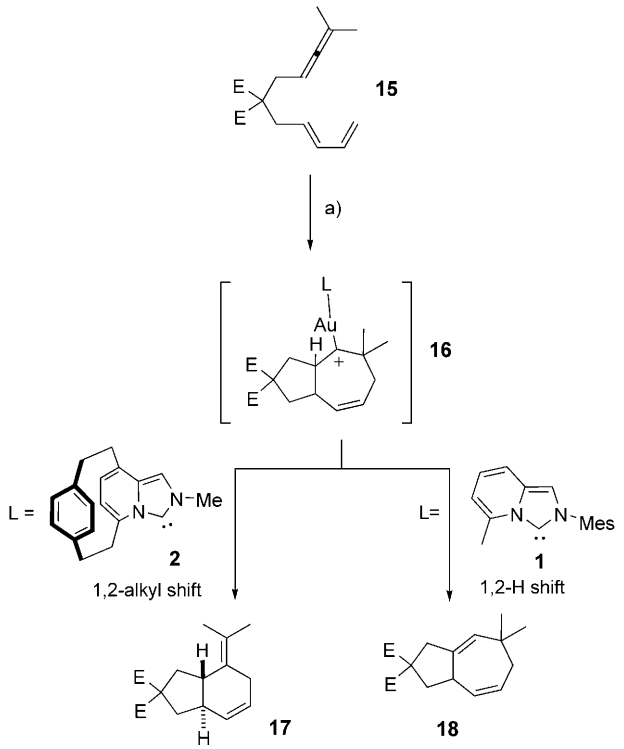
When exposed to [**1b**·AuCl], compound **10** (99% *ee*)[24] underwent rearrangement to the thermodynamically favored ring-expanded products **13**/**14** (Scheme 2). As this process is



Scheme 2. Ring expansion of **10** is accompanied by partial loss of enantiomeric purity: a) [**1b**·AuCl] (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2, −5 °C.

accompanied by a partial loss of enantiomeric purity, this result implies that recoordination of Au^+ to the double bond in **10** does not cause a conventional strain-driven Wagner–Meerwein-type rearrangement. The positive charge must be delocalized over several carbon atoms to erode the enantiomeric purity. Such a high degree of charge delocalization on the carbon framework is consistent with our current interpretation of the character of the reactive intermediates in gold catalysis.[25–27]

Importantly, other gold-catalyzed reactions, which were previously shown to be mechanistically distinct from the stepwise processes outlined above and amenable to ligand tuning, also responded to the modulation of the acceptor properties of the ancillary NHCs. Specifically, the cyclization of allene–diene **15**, which is thought to commence with a concerted cycloaddition step,[28] exclusively furnished the [4+3] adduct **18** when strong donor NHCs **1** governed the reactivity of the metal center, whereas the competing [4+2] pathway dominated with the cyclophanic counterpart **2**



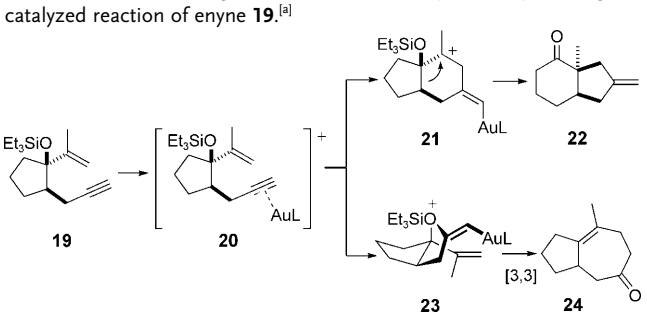
Scheme 3. Effect of NHC ligands with different π-acceptor properties on the gold-catalyzed cyclization of allene–diene **15** (E = COOMe): a) [**1**·AuCl] (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2, −5 °C, 47% (only **18**); or: [**2**·AuCl] (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2, −5 °C, 92% (**17**/**18** 72:28).

(Scheme 3). This outcome is consistent with the current mechanistic interpretation:[28] π-acidic ligands remove electron density from the initial intermediate **16** and hence foster ring contraction by a 1,2-alkyl shift to a largely cationic center; in contrast, electron donation from the ancillary ligand engenders a greater "carbene" character of **16**, as expressed in preferred 1,2-H migration.[27,29]

Finally, competition between a pinacol rearrangement and a [3,3] sigmatropic rearrangement served as an additional probe (Table 3).[30] Increased π-acceptor properties of the ligand L render the initial alkyne–gold complex **20** more electrophilic and hence enable the only weakly nucleophilic silyl ether oxygen atom in enyne **19** to compete with the olefin. In accordance with this interpretation, [**2**·AuCl] and [**5**·AuCl], which contain carbenes with appreciable π-acceptor qualities, discriminate less between the nucleophilic reaction partners and hence furnished respectable amounts of product **24**; the net outcome corresponds to that observed with [Ph_3PAuCl] as the precatalyst.[30] In contrast, [**1**·AuCl] and [**6**·AuCl], which contain stronger donor ligands, clearly favored the formation of ketone **22**.[31] The fact that the AYC **6**[15] expresses its donor ability in the gold-catalyzed cyclization of enyne **19**, whereas its acceptor function prevails in the reaction with **7** corroborates the view that AYCs are more than just simple cousins of the prevalent NHCs.

In summary, the results outlined herein suggest that it can be much easier to tune the π-acceptor properties of NHCs than to alter their σ-donor qualities by similar margins. Since

Table 3: Effect of NHC ligands of different π-acceptor ability on the gold-catalyzed reaction of enyne **19**.[a]



Entry	Precatalyst	**22**/**24**	Yield [%]
1	[**1**·AuCl]	81:19	64
2	[**6**·AuCl]	88:12	80
3	[**2**·AuCl]	54:46	94
4	[**5**·AuCl]	51:49	80
5	[Ph_3PAuCl]	50:50	88[30,31]

[a] Reaction conditions: [(NHC)AuCl] (10 mol%), $AgSbF_6$ (5 mol%), *i*PrOH (1.1 equiv), CH_2Cl_2, room temperature.

the π acidity of NHCs, however, was previously often neglected or considered irrelevant, this study may help to change the perception of this important class of ancillary ligands in general.

Received: December 21, 2009
Published online: March 4, 2010

Keywords: computational chemistry · cycloaddition · gold · homogeneous catalysis · N-heterocyclic carbenes

[1] For selected reviews and monographs on NHCs, see: a) A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913–921; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; c) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; d) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239–2246; e) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815–1828; f) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; g) M. F. Lappert, *J. Organomet. Chem.* **2005**, *690*, 5467–5473; h) *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents* (Ed.: G. Bertrand), Dekker, New York, **2002**; i) *N-Heterocyclic Carbenes in Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**; j) "N-Heterocyclic Carbenes in Transition Metal Catalysis": *Topics in Organometallic Chemistry, Vol. 21* (Ed.: F. Glorius), Springer, Berlin, **2007**.

[2] a) X. Hu, Y. Tang, P. Gantzel, K. Meyer, *Organometallics* **2003**, *22*, 612–614; b) M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* **2006**, *128*, 16514–16515; c) L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, *Organometallics* **2006**, *25*, 5648–5656; d) D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042–6049; e) H. Nakai, X. Hu, L. N. Zakharov, A. L. Rheingold, K. Meyer, *Inorg. Chem.* **2004**, *43*, 855–857; f) S. Fantasia, J. L. Petersen, H. Jacobsen, L. Cavallo, S. P. Nolan, *Organometallics* **2007**, *26*, 5880–5889; g) S. Saravanakumar, A. I. Oprea, M. K. Kindermann, P. G. Jones, J. Heinicke, *Chem. Eur. J.* **2006**, *12*, 3143.

[3] H. Jacobsen, A. Correa, A. Poater, C. Costabile, L. Cavallo, *Coord. Chem. Rev.* **2009**, *253*, 687–703.

[4] a) X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, *Organometallics* **2004**, *23*, 755 – 764; b) D. Nemcsok, K. Wichmann, G. Frenking, *Organometallics* **2004**, *23*, 3640 – 3646; c) H. Jacobsen, A. Correa, C. Costabile, L. Cavallo, *J. Organomet. Chem.* **2006**, *691*, 4350 – 4358; d) R. Tonner, G. Heydenrych, G. Frenking, *Chem. Asian J.* **2007**, *2*, 1555 – 1567; e) U. Radius, F. M. Bickelhaupt, *Organometallics* **2008**, *27*, 3410 – 3414; f) N. S. Antonova, J. J. Carbó, J. M. Poblet, *Organometallics* **2009**, *28*, 4283 – 4287; g) R. Tonner, G. Frenking, *Organometallics* **2009**, *28*, 3901 – 3905; h) M. Lein, A. Szabó, A. Kovács, G. Frenking, *Faraday Discuss.* **2003**, *124*, 365 – 378; i) D. S. McGuinness, N. Saendig, B. F. Yates, K. J. Cavell, *J. Am. Chem. Soc.* **2001**, *123*, 4029 – 4040.

[5] It has been proposed that the carbene center of NHCs can serve as an acceptor site in interactions with the halide atoms of NHC–metal halide adducts: a) C. D. Abernethy, G. M. Codd, M. D. Spicer, M. K. Taylor, *J. Am. Chem. Soc.* **2003**, *125*, 1128 – 1129; b) P. Shukla, J. A. Johnson, D. Vidovic, A. H. Cowley, C. D. Abernethy, *Chem. Commun.* **2004**, 360 – 361.

[6] For previous reports in which changes in the catalytic activity of metal–NHC complexes were tentatively ascribed to an electronic tuning of the carbene center, see: a) N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Org. Lett.* **2005**, *7*, 1991 – 1994; b) D. M. Khramov, E. L. Rosen, J. A. V. Er, P. D. Vu, V. M. Lynch, C. W. Bielawski, *Tetrahedron* **2008**, *64*, 6853 – 6862.

[7] A. Fürstner, M. Alcarazo, H. Krause, C. W. Lehmann, *J. Am. Chem. Soc.* **2007**, *129*, 12676 – 12677.

[8] a) M. Alcarazo, S. J. Roseblade, A. R. Cowley, R. Fernández, J. M. Brown, J. M. Lassaletta, *J. Am. Chem. Soc.* **2005**, *127*, 3290 – 3291; b) S. J. Roseblade, A. Ros, D. Monge, M. Alcarazo, E. Álvarez, J. M. Lassaletta, R. Fernández, *Organometallics* **2007**, *26*, 2570 – 2578; c) C. Burstein, C. W. Lehmann, F. Glorius, *Tetrahedron* **2005**, *61*, 6207 – 6217; d) M. Nonnenmacher, D. Kunz, F. Rominger, T. Oeser, *Chem. Commun.* **2006**, 1378 – 1380; e) A. Miyashita, Y. Suzuki, M. Kobayashi, N. Kuriyama, T. Higashino, *Heterocycles* **1996**, *43*, 509 – 512; f) M. A. Schmidt, M. Movassaghi, *Tetrahedron Lett.* **2007**, *48*, 101 – 104.

[9] We also performed DFT calculations on various other cyclophanic NHCs, in addition to the examples in Table 1. In most but not all cases, the σ donor orbital is the highest occupied molecular orbital, whereas the π acceptor orbital with a nonzero coefficient at the carbene center is usually not the lowest unoccupied molecular orbital. Details will be reported in a forthcoming full paper.

[10] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822 – 8824; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297 – 3305; d) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652 – 660; e) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119 – 124; f) F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285 – 4291.

[11] The TURBOMOLE program package was used for the DFT calculations: R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165 – 169.

[12] F. Vögtle, *Cyclophane Chemistry: Synthesis, Structures, and Reactions*, Wiley, Chichester, **1993**.

[13] J. Iglesias-Sigüenza, A. Ros, E. Díez, M. Alcarazo, E. Álvarez, R. Fernández, J. M. Lassaletta, *Dalton Trans.* **2009**, 7113 – 7120.

[14] The particular combination of tempered donor and increased acceptor qualities of triazole-derived NHCs, as expressed in the computed data for **5**, is probably important for their overwhelming success as organocatalysts; see: D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606 – 5655.

[15] A. Fürstner, M. Alcarazo, K. Radkowski, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 8426 – 8430; *Angew. Chem. Int. Ed.* **2008**, *47*, 8302 – 8306.

[16] Literature data also suggest that AYCs can exhibit appreciable π-acceptor qualities; see: S. Nakafuji, J. Kobayashi, T. Kawashima, *Angew. Chem.* **2008**, *120*, 1157 – 1160; *Angew. Chem. Int. Ed.* **2008**, *47*, 1141 – 1144.

[17] For an electrochemical investigation of [(NHC)RhCl(cod)] complexes, see: S. Wolf, H. Plenio, *J. Organomet. Chem.* **2009**, *694*, 1487 – 1492.

[18] For details, see the Supporting Information.

[19] For a review on noble-metal–NHC complexes, see: J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561 – 3598, and references therein.

[20] M. R. Luzung, P. Mauleón, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 12402 – 12403.

[21] The anisotropic displacement parameters are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. CCDC 774776 ([**2**·AuCl]), 743804 ([**5**·AuCl]), 743802 ([**6**·AuCl]), and 743803 (**13**) 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. For crystallographic abstract, see the Supporting Information.

[22] During the course of this project, Toste and co-workers observed a related [3+2] pathway with the strongly donating ligand (*o*-biphenyl)*t*Bu_2P.[28b]

[23] We performed the cycloisomerization at −5 °C and used $AgSbF_6$ to ionize the gold precatalyst. Toste and co-workers reported that they obtained exclusively the [2+2] cycloadduct when they carried out this reaction with [Ph_3PAuCl]/$AgBF_4$ at ambient temperature.[20]

[24] For the preparation of enantiomerically pure **10**, see: H. Teller, S. Flügge, R. Goddard, A. Fürstner, *Angew. Chem.* **2010**, *122*, 1993 – 1997; *Angew. Chem. Int. Ed.* **2010**, *49*, 1949 – 1953.

[25] a) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478 – 3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410 – 3449; b) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208 – 3221.

[26] a) A. Fürstner, L. Morency, *Angew. Chem.* **2008**, *120*, 5108 – 5111; *Angew. Chem. Int. Ed.* **2008**, *47*, 5030 – 5033; b) G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.* **2009**, *121*, 2548 – 2551; *Angew. Chem. Int. Ed.* **2009**, *48*, 2510 – 2513; c) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 3254 – 3258; *Angew. Chem. Int. Ed.* **2008**, *47*, 3210 – 3214; d) S. Flügge, A. Anoop, R. Goddard, W. Thiel, A. Fürstner, *Chem. Eur. J.* **2009**, *15*, 8558 – 8565; e) M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295 – 301.

[27] D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482 – 486.

[28] 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. Benitez, E. Tkatchouk, A. Z. Gonzalez, W. A. Goddard III, F. D. Toste, *Org. Lett.* **2009**, *11*, 4798 – 4801.

[29] A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863 – 11869.

[30] a) B. Baskar, H. J. Bae, S. E. An, J. Y. Cheong, Y. H. Rhee, A. Duschek, S. F. Kirsch, *Org. Lett.* **2008**, *10*, 2605 – 2607; see also: b) H. J. Bae, B. Baskar, S. E. An, J. Y. Cheong, D. T. Thangadurai, I.-C. Hwang, Y. H. Rhee, *Angew. Chem.* **2008**, *120*, 2295 – 2298; *Angew. Chem. Int. Ed.* **2008**, *47*, 2263 – 2266.

[31] Although the switch from one pathway to the other is not complete with any of the carbene ligands tested, the use of phosphines of greatly different donor capacity does not provide rigorous control either (see Ref. [30]).

