Carbenes

DOI: 10.1002/anie.201305311

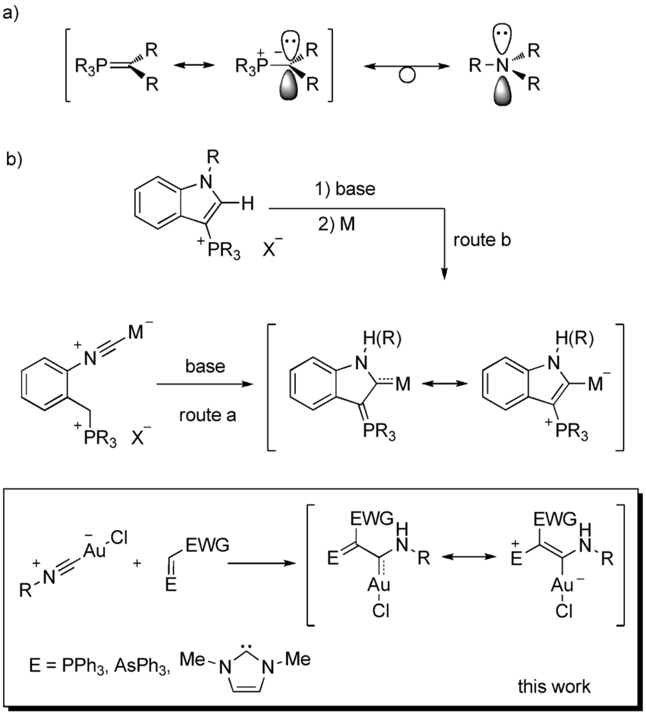
Synthesis and Reactivity of Metal Complexes with Acyclic (Amino)-(Ylide)Carbene Ligands**

*Elisa González-Fernández, Jörg Rust, and Manuel Alcarazo**

Dedicated to Professor José M. Lassaletta

The widespread use reached by N-heterocyclic carbenes (NHCs) as ancillary ligands for transition-metal catalysis is a consequence of two main factors: 1) their very strong σ-electron releasing ability and 2) their relative stability, which relies on the effective donation of electron density from both nitrogen lone pairs to the formally empty orbital at the carbene center.[1] However, nitrogen atoms are not unique for this task and other entities having an electron pair located in an orbital of appropriate symmetry might also serve the same purpose. Thus, formal replacement of one or even both nitrogen atoms by other main-group elements, such as O, S, or P, has proven to be a very efficient tool to modify the donor properties and reactivity of NHCs.[2] For this particular task, ylides can also be seen as suitable nitrogen surrogates owing to the non-shared electron pair on the formally negatively charged carbon atom (Scheme 1 a). Moreover, the lower electronegativity of carbon when compared with nitrogen should make the resulting carbenes particularly good electron-releasing ligands.

In fact, metal complexes containing such (amino)-(ylide)carbene (AYC) ligands have been known for a long time[3] although it was only recently that they have found applications in catalysis.[4] Their synthesis follows two main routes: basic treatment of the corresponding transition-metal complexes of isocyanide units bearing a phosphonium moiety (Scheme 1 b top, route a)[3a–c] or by deprotonation of the parent heterocyclic precursor (Scheme 1 b top, route b).[5] However, these two methods invariably deliver cyclic AYC metal complexes while their acyclic analogues remain unknown.[6] Considering the fundamental differences in geometrical and electronic properties between cyclic and acyclic carbenes,[7] we decided to investigate whether acyclic (amino)(ylide)carbene (AAYC) metal complexes could also be prepared. Outlined below is a synthetic entry that allows the preparation of AAYC gold complexes from P-ylides, As-ylides and interestingly, also from electron-rich olefins, such as enamines or ene-1,1-diamines (Scheme 1 b bottom). Their structural characterization and a preliminary study of their reactivity towards transmetalation are also described.



Scheme 1. a) Ylides as nitrogen substitutes in NHCs. b) Known entries into metal–cyclic AYC complexes and the synthetic route developed herein for AAYC gold complexes. AAYC: acyclic (amino)(ylide)carbene.

At first glance it seemed to us that the intermolecular nucleophilic attack of differently substituted phosphorus ylides on alkyl- or aryl isocyanide gold complexes could deliver the desired AAYC gold complexes.[8] Thus, toluene suspensions of isocyanide complexes **1** were exposed to ylides **2**. In all cases consumption of **1** was observed with concomitant formation of two new products **3** and **4** in different ratios depending on the electronic nature of the ylide employed and the substituent on the isocyanide (Table 1). Multinuclear NMR spectroscopy studies from the crude reaction mixtures indicated that the minor component **3** only gave rise signals attributable to the ylide fragment while **4** exhibited all the resonance signals expected for AAYC gold complexes, including a quite characteristic ^{31}P NMR signal at $\delta = 18$–22 ppm and a broad N-*H* peak.

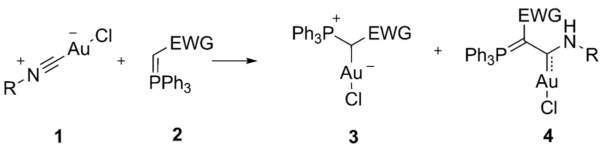
---

[*] E. González-Fernández, J. Rust, Dr. M. Alcarazo
Max-Planck-Institut für Kohlenforschung
45470 Mülheim an der Ruhr (Germany)
E-mail: alcarazo@mpi-muelheim.mpg.de

[**] Generous financial support from the Fonds der Chemischen Industrie, the European Research Council (ERC Starting Grant to M.A.) and SusChemSys (NRW-Ziel-2-Programm) is gratefully acknowledged. We also thank Prof. A. Fürstner for constant support and our NMR spectroscopy and X-ray crystallography departments for assistance.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201305311.

Table 1: Synthesis of AAYC gold complexes by nucleophilic attack of phosphorus ylides on gold isocyanide complexes.[a]

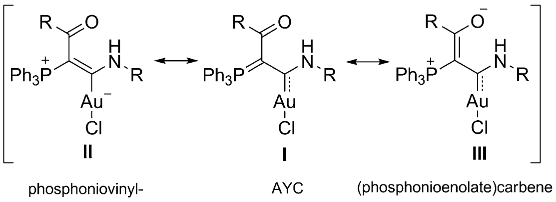


Entry	R	EWG	3:4 ratio[b]	Yield [%]
1	Ph, **1a**	COMe, **2a**	<2:98	85, **4a**
2		COOEt, **2b**	<2:98	74, **4b**
3		CN, **2c**	<2:98	88, **4c**
4		CONMe$_2$, **2d**	<2:98	81, **4d**
5		2-py, **2e**	2:98	98, **4e**
6		Ph, **2f**	76:24	5, **4f**
7	2,6-Me$_2$C$_6$H$_3$, **1b**	COMe, **2a**	<2:98	30, **4g**[c]
8		COOEt, **2b**	23:77	37, **4h**
9		CN, **2c**	26:74	25, **4i**
10		CONMe$_2$, **2d**	75:25	12, **4j**
11		2-py, **2e**	>98:2	83, **3e**

[a] EWG = electron withdrawing group. Reaction conditions: toluene, 35–50°C. [b] Determined by ^{31}P NMR spectroscopy. [c] A conversion of only 43% was achieved after 3 days.

To better ascertain the connectivities of these new compounds, X-ray diffraction analyses of single crystals were carried out confirming the AAYC gold complex nature of compounds **4a–j** (Figure 1 and Supporting Information). Conversely, the isolation of side products **3a–f** in pure form was not straightforward. Only crystals of **3e** could be obtained but fortunately that was enough to unambiguously determine their constitution by NMR spectroscopy and crystallography. This analysis showed **3e** to be an ylide gold complex formed by substitution of the isocyanide ligand originally on gold by ylide **2e** (Table 1, entry 11; Figure 1 and Supporting Information).[9] This "parasite" ligand-exchange process leading to the formation of **3a–f** is favored by the use of a sterically demanding isocyanide (**1b**) and, especially, by using non-stabilized ylides as nucleophiles (compare entries 6–11 of Table 1). In these cases the AAYC gold complexes **4f–j** could still be isolated in pure form, albeit poor yield, by iterative fractional crystallization.

Comparison of the X-ray structures of the AAYC gold complexes depicted in Figure 1 is highly informative. Steric clash between the triphenylphosphino and (dimethylamino)carbonyl substituents in **4j** forces a complete twist of the (dimethylamino)carbonyl substituents out of the C2-C1-N1 plane ($\Phi = 90.6°$). Hence, this fragment interaction with the carbene π system is largely cancelled and, for this reason, the C2–C3 bond (1.513 Å) is longer than expected for a normal C$_{sp^2}$–C$_{sp^2}$ single bond and better falls within the range for C$_{sp^3}$–C$_{sp^3}$ bonds.[11] As a result, the donation of electron density from the ylide carbon to the carbene center is maximized and the C1–C2 bond length is only 1.390 Å. These structural data indicate that compound **4j** should be better described as an intermediate between the mesomeric forms of gold carbene **I** and phosphoniovinyl complex **II** (Scheme 2).



Scheme 2. Conceivable resonance formulae of the AAYC gold complexes.

A very similar bonding situation can be found in complex **4f** (for its X-ray structure see the Supporting Information). In contrast in **4a**, conjugation between the carbonyl and the carbene moieties is allowed (Figure 1). The C2–C3 distance in this complex (1.451 Å) is considerably shorter than in **4j**, whereas the C1–C2 bond is elongated (1.422 Å), which confirms that the most representative mesomeric form for this compound, and other related structures, such as **4c** and **4e**, is **III** (Scheme 2).

In an attempt to generalize our synthetic route, we investigated whether other ylides might also take part in the stabilization of vicinal carbene centers. To this end, a toluene suspension of **1a** was treated with arsenic ylide **5** (Scheme 3). Again, a smooth reaction took place giving the desired AAYC gold complex **6** in moderate yield. The bond lengths (C2–C3 1.449 Å, C3–O1 1.252 Å) suggest a situation similar to that

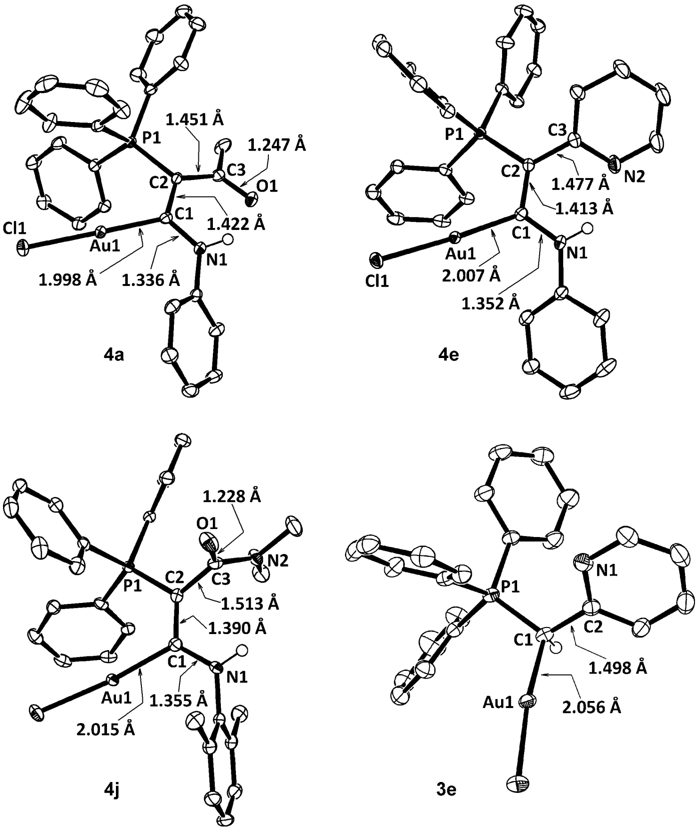
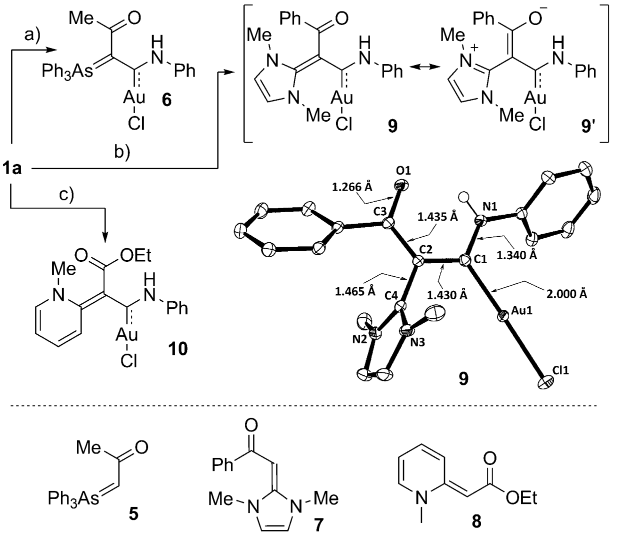


Figure 1. Crystal structures of **4a**, **4e**, **4j**, and **3e**. Solvent molecules and hydrogen atoms, except for NH and C$_{ylide}$H, are removed for clarity. Thermal ellipsoids set at 50% probability.[10]



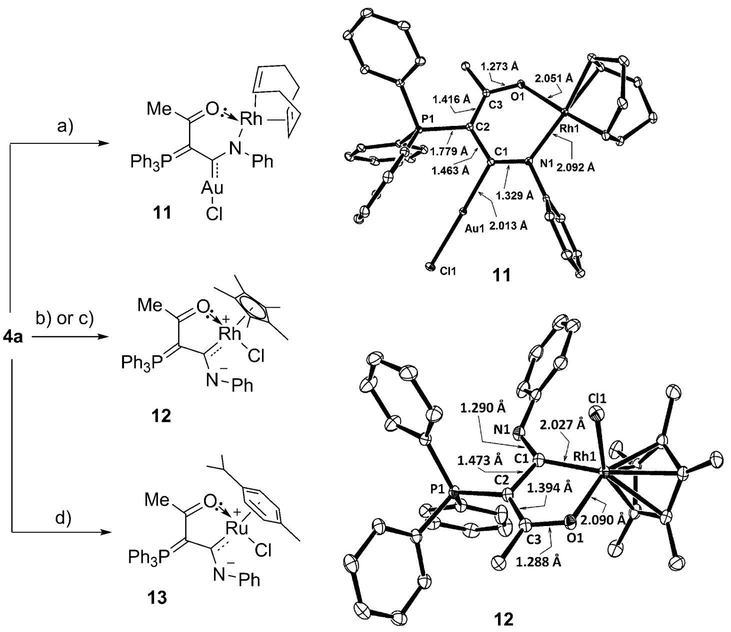
Scheme 3. Synthesis of **6**, **9**, and **10**, and crystal structure of **9** (solvent molecules and hydrogen atoms, except for NH and $C_{ylide}H$, are removed for clarity; thermal ellipsoids set at 50% probability).[10] Reagents and conditions: a) **5** (1 equiv), toluene, −10 °C, 1 day, 40%; b) **7** (1 equiv), toluene, 35 °C, 8 h, 95%; c) **8** (1 equiv), toluene, 35 °C, 1 h, 87%.

described for **4a**: the lateral Ph_3As moiety bears a partial positive charge while some electron density is delocalized along the enolate side arm.

More interestingly, we checked if polarized C=C bonds could also participate in the stabilization of acyclic carbenes. Thus, recognizing the "carbon ylide" character of ene-1,1-diamines and some enamines,[12] **1a** was treated under the standard conditions with compounds **7** and **8**, both containing an electron-rich and strongly polarized double bond. The appearance of new ^{13}C NMR resonance signals at $\delta = 194.6$ and 189.6 ppm, which are characteristic for carbene centers coordinated to Au, supported an AAYC connectivity for **9** and **10**. This situation could be confirmed by X-ray analysis of **9**. Importantly, these results broaden the structural diversity of AAYCs that can be achieved following our synthetic procedure. Judging from the ORTEP diagram of **9** (inset of Scheme 3), the imidazolium–enolate dipolar form **9′** is dominant: the C2−C3 (1.435 Å) and the C3−O1 bond lengths (1.266 Å) are respectively the shortest and longest ones measured along the complete series of organogold complexes, whereas the C1-C2-C4-N3 torsion angle of 75.9° prevents any efficient overlap between the imidazolium cation and the carbene π system (Scheme 3).

Finally, we envisioned the possibility to prepare heterobinuclear complexes making use of the additional functional groups present at the acyclic carbene side arms. In fact, the formation of metal chelates should be favored after deprotonation of the NH unit adjacent to the carbene. Hence, treatment of a THF solution of **4a** with 1 equivalent of KOMe and 0.5 equivalents of $[\{RhCl(cod)\}_2]$ at 5 °C afforded, after work-up, a pale yellow solid (**11**) in 72% yield (Scheme 4). In solution, compound **11** features the expected ^1H and ^{13}C NMR resonance signals for both a Rh-coordinated cyclooctadiene (cod) group and a PPh_3 group while the distinctive N-H signal of **4a** has vanished. Moreover, ESI(MS) analysis showed a molecular ion signal at m/z 863 that is consistent with an structure also containing a AuCl moiety. Single crystals were grown by slow diffusion of pentane into a diluted solution of **11** in CH_2Cl_2 and X-ray diffraction analysis revealed the formation of the expected bimetallic species in which the Rh atom is coordinated through the N and the lateral carbonyl group. The Au atom remains bonded to the carbene center (see Scheme 4 for an ORTEP plot of the molecular structure of **11**).[13]

Surprisingly, this reaction is strongly influenced by the oxidation state of the incoming metal. Treatment of a dichloroethane solution of the organogold species **4a** with a harder Rh source, such as $[\{RhCp^*Cl_2\}_2]$ ($Cp^* = \eta\text{-}C_5Me_5$) and base afforded in 83% yield an orange solid that did not seem to contain Au. Multinuclear NMR analysis again showed the disappearance of the characteristic ^1H NMR N-H signal from **4a**; however, the ^{13}C NMR resonance attributable to the carbene carbon atom in **4a** was shifted to $\delta = 185.1$ ppm and interestingly, it appeared as a doublet of doublets with $J_{C,Rh} = 3.3$ Hz and $J_{C,P} = 36.2$ Hz. These data suggested a $Au \rightarrow Rh^{III}$ transmetalation of the carbene and a probable bidentate nature of the carbene ligand in the product.[14,15] Crystals were grown by diffusion of pentane into a saturated dichloromethane solution of this product and



Scheme 4. Synthesis of **11**–**13** and crystal structures of **11** and **12** (solvent molecules and hydrogen atoms are removed for clarity; thermal ellipsoids set at 50% probability).[10] Reagents and conditions: a) **4a** (1 equiv), $[\{Rh(cod)Cl\}_2]$ (0.5 equiv), KOMe (1 equiv), THF, 5 °C, 12 h; 72%; b) **4a** (1 equiv), $[\{RhCp^*Cl_2\}_2]$ (0.5 equiv), Et_3N (15 equiv), dichloroethane, 50 °C, 4 days; 83%; c) **4a** (1 equiv), $[\{RhCp^*Cl_2\}_2]$ (0.5 equiv), KOMe (0.5 equiv), THF, 5 °C, 12 h; 41%; d) **4a** (1 equiv), $[\{Ru(cym)Cl_2\}_2]$ (0.5 equiv), Et_3N (15 equiv), dichloroethane, 50 °C, 1 day; 59%. cym: *p*-cymene.

subsequently its structure was determined by X-ray diffraction as **12** (Scheme 4). As predicted from the spectroscopic analysis, the AuCl moiety is not present in **12**, thus confirming the ability of **4a** to transfer the organic ligand. Moreover, the nitrogen atom has been deprotonated and the resulting monoanionic ligand now coordinates the $[RhCp^{*}Cl]^{+}$ moiety in a bidentate fashion through the central carbon atom and the lateral carbonyl group.

Interestingly, the same ligand-transfer reactivity was observed upon exposure of **4a** to $[\{Ru(cym)Cl_2\}_2]$ affording compound **13**. Considering that the synthesis of acyclic carbene metal complexes through the isocyanide route is basically limited to Au^{I}, Pd^{II}, and Pt^{II} isocyanide precursors,[16] this reactivity seems to offer access to complexes of different metals provided that chelation of the incoming metal is possible.

In summary, the synthesis of unprecedented AAYC Au complexes has been achieved by reaction of gold isocyanides with phosphorus or arsenic ylides. In addition, the reaction could be applied with excellent yields to "carbon ylides", such as ene-1,1-diamines and enamines. Finally, the ability of the newly prepared AAYC Au complexes to form bimetallic species and to act as ligand-transfer reagents was established by reaction with appropriate Rh or Ru sources. Whether the mono- and bimetallic complexes described herein could find applications in catalysis is under investigation.

Received: June 20, 2013

Keywords: acyclic carbenes · gold · ligand design · transmetalation · ylides

---

[1] a) J. A. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913; b) D. Bourissou, O. Guerret, F. P. Gabaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; c) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; d) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348; e) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.

[2] a) J. A. Arduengo, J. R. Goerlich, W. J. Marshall, *Liebigs Ann./Recl.* **1997**, 365; b) R. W. Alder, C. P. Butts, A. G. Orpen, *J. Am. Chem. Soc.* **1998**, *120*, 11526; c) D. Martin, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Angew. Chem.* **2005**, *117*, 1728; *Angew. Chem. Int. Ed.* **2005**, *44*, 1700; d) A. S. K. Hashmi, C. Lothschütz, K. Graf, T. Häffner, A. Schuster, F. Rominger, *Adv. Synth. Catal.* **2011**, *353*, 1407.

[3] a) G. Facchin, R. Campostrini, R. A. Michelin, *J. Organomet. Chem.* **1985**, *294*, c21–c25; b) R. A. Michelin, G. Facchin, D. Braga, P. Sabatino, *Organometallics* **1986**, *5*, 2265; c) R. A. Michelin, M. Mozzon, G. Facchin, D. Braga, P. Sabatino, *J. Chem. Soc. Dalton Trans.* **1988**, 1803; d) M. Tamm, F. E. Hahn, *Coord. Chem. Rev.* **1999**, *182*, 175.

[4] M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem.* **2010**, *122*, 2596; *Angew. Chem. Int. Ed.* **2010**, *49*, 2542.

[5] a) S. Nakafuji, J. Kobayashi, T. Kawashima, *Angew. Chem.* **2008**, *120*, 1157; *Angew. Chem. Int. Ed.* **2008**, *47*, 1141; b) M. Asay, B. Donnadieu, A. Baceiredo, M. Soleilhavoup, G. Bertrand, *Inorg. Chem.* **2008**, *47*, 3949; c) A. Fürstner, M. Alcarazo, K. Radkowski, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 8426; *Angew. Chem. Int. Ed.* **2008**, *47*, 8302; d) J. Kobayashi, S. Nakafuji, A. Yatabe, T. Kawashima, *Chem. Commun.* **2008**, 6233.

[6] Carbenes stabilized by an ylide moiety and an oxygen substituent have been prepared by reaction of $[M(CO)_6]$ (M = Cr, Mo, W) with P ylides and further alkylation/silylation of the resulting intermediate; see: a) W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, W. D. Korte, *J. Am. Chem. Soc.* **1974**, *96*, 2847; b) S. Voran, H. Blau, W. Malish, U. Schubert, *J. Organomet. Chem.* **1982**, *232*, c33–c40; c) N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, I. N. Chechulina, A. S. Batsanov, Y. T. Struchkov, *J. Organomet. Chem.* **1982**, *238*, 223.

[7] a) J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333; b) L. M. Slaughter, *ACS Catal.* **2012**, *2*, 1802.

[8] For the synthesis of acyclic diamino carbenes and NHCs by nucleophilic attack to gold isocyanide complexes see for example: a) C. Bartolomé, Z. Ramiro, D. García-Cuadrado, P. Pérez-Galán, M. Raducan, C. Bour, A. M. Echavarren, P. Espinet, *Organometallics* **2010**, *29*, 951; b) A. S. K. Hashmi, C. Lothschütz, C. Böhling, F. Rominger, *Organometallics* **2011**, *30*, 2411; c) A. S. K. Hashmi, C. Lothschütz, C. Böhling, T. Hengst, C. Hubbert, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 3001; d) A. S. K. Hashmi, T. Hengst, C. Lothschütz, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 1315; e) A. S. K. Hashmi, Y. Yu, F. Rominger, *Organometallics* **2012**, *31*, 895; f) S. Handa, L. M. Slaughter, *Angew. Chem.* **2012**, *124*, 2966; *Angew. Chem. Int. Ed.* **2012**, *51*, 2912; g) R. Manzano, F. Rominger, A. S. K. Hashmi, *Organometallics* **2013**, *32*, 2199; h) M. C. Blanco-Jaimes, C. R. N. Böhling, J. M. Serrano-Becerra, A. S. K. Hashmi, *Angew. Chem.* **2013**, *125*, 8121; *Angew. Chem. Int. Ed.* **2013**, *52*, 7963.

[9] For a previous synthesis of compound **3e** see: J. Vicente, M. T. Chicote, M. C. Lagunas, *Inorg. Chem.* **1993**, *32*, 3748.

[10] CCDC 937966 (**3e**), 937968 (**4a**), 937970 (**4c**), 937969 (**4e**), 937972 (**4f**), 937967 (**4j**), 937971 (**6**), 937974 (**9**), 945351 (**11**), and 937973 (**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.

[11] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19.

[12] For general Reviews on ene-1,1-diamines see: a) W. Kantlehner, *Science of Synthesis, Vol. 24* (Ed.: A. de Meijere), Thieme, Stuttgart **2006**, p. 571; b) P. A. Keller, J. Morgan *Science of Synthesis, Vol. 24* (Ed.: A. de Meijere), Thieme, Stuttgart **2006**, p. 707.

[13] For a one-pot tandem Au/Rh-catalyzed process see: M. M. Hansmann, A. S. K. Hashmi, M. Lautens, *Org. Lett.* **2013**, *15*, 3226.

[14] Y. Shi, S. A. Blum, *Organometallics* **2011**, *30*, 1776.

[15] An NHC ligand transfer from Au to Pd has already been described: S. Liu, C. Lee, C. Fu, C. Chen, Y. Liu, C. J. Elsevier, S. Peng, J. Chen, *Organometallics* **2009**, *28*, 6957.

[16] A. S. K. Hashmi, C. Lothschütz, C. Böhling, F. Rominger, *Organometallics* **2011**, *30*, 2411. See also reference [8].