Gold Carbenoids

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Gold Catalysis: Highly Functionalized Cyclopentadienes Prepared by Intermolecular Cyclization of Ynamides and Propargylic Carboxylates**

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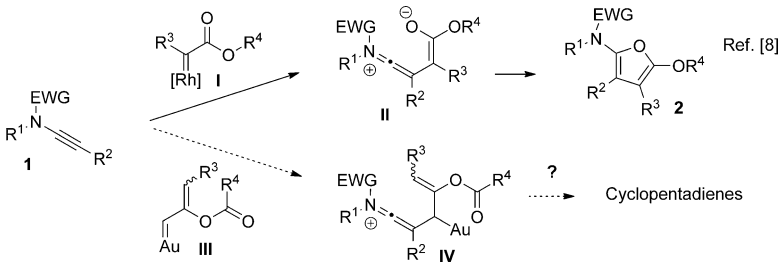
Following the first preparation of an ynamide in 1972,[1] this class of substrates remained nearly unexplored for almost thirty years. This changed tremendously at the beginning of the new millennium when a real "ynamide boom" was triggered by new synthetic methods, which enabled the synthesis of starting materials under mild conditions and with a higher functional group tolerance. Following initial work with hypervalent iodine reagents,[2] more and more copper-catalyzed ynamide syntheses have dominated the field.[3] Based on the easy availability of ynamides as starting materials, an array of useful organic transformations have been published in the recent years leading to a variety of valuable synthetic building blocks.[4] Due to the exceptional ability of gold to activate multiple bonds,[5] ynamides have also been used as substrates in gold-catalyzed reactions for a number of useful transformations.[6]

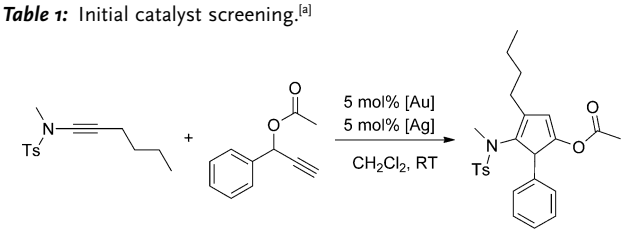
All of these reactions are initiated by the attack of a nucleophile at the π-activated triple bond of the ynamide. An exception is a gold-catalyzed dimerization of ynamides that was recently reported by Gagosz et al.[7] This exciting transformation utilizes the ambivalent nature of the ynamide. Owing to the adjacent heteroatom, an ynamide can also react as a nucleophile at its β-carbon atom. Inspired by a contribution by Li and Hsung, who reported on a synthesis of aminofurans from the reaction of ynamides with diazomalonate or phenyliodonium ylides,[8] we envisioned that gold carbenoids derived from propargylic esters would be electrophilic enough for a selective reaction in which the nucleophilic nature of ynamides could be exploited. In addition to their easy and mild access,[9] these gold carbenoids possess an additional C–C double bond, which should enable a different reaction pathway leading to highly substituted cyclopentadiene derivatives (Scheme 1).[10]

For initial experiments, we prepared ynamide **1a** according to Hsung's protocol[3d] and performed a short screening with propargylic acetate **3a** (Table 1). Even though 1,2-acetate shifts are also reported for Au^{III} compounds,[11] only a complex mixture was obtained in the case of simple $AuCl_3$ (Table 1, entry 1), while no conversion of the starting material

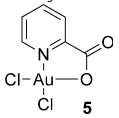
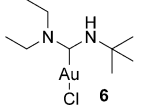


Scheme 1. Known and proposed reactions of ynamides with metal carbenoids.

Table 1: Initial catalyst screening.[a]



1a 3a 4a

Entry	Catalyst	Yield [%]
1	$AuCl_3$	complex mixture
2	 5	–
3	$Ph_3PAuCl/AgNTf_2$	4
4	$Ph_3PAuCl/AgSbF_6$	2
5	 6 / $AgNTf_2$ /$AgNTf_2$	13
6	**6**/$AgSbF_6$	8
7	$SPhosAuCl/AgNTf_2$	23
8	$SPhosAuCl/AgSbF_6$	33
9	$IPrAuCl/AgNTf_2$	58
10	$IPrAuCl/AgSbF_6$	32
11	$AgNTf_2$	–

[a] SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, Tf = triflate, Ts = tosyl.

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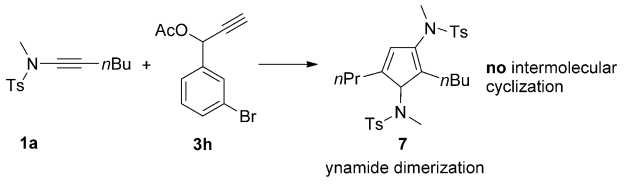
was observed for the pyridine carboxylate Au^{III} complex **5**.[12] Triphenylphosphanegold(I) chloride activated by either $AgNTf_2$ or $AgSbF_6$ gave only traces of product (Table 1, entries 3 and 4). First promising results were obtained using NAC (NAC = nitrogen acyclic carbene) complex **6** activated with $AgNTf_2$ but still only a 13% yield of product was detected (Table 1, entry 5). The yield significantly increased when the SPhos ligand was used (Table 1, entries 7 and 8). But by far the best results were obtained with the commercially available [IPrAuCl] (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), which delivered good yields in combination with $AgNTf_2$ as a halide scavenger (Table 1, entry 9). In these reaction with the IPr ligand a strong influence of the counterion was observed. The yield increased from 32% to 58% when SbF_6^- was used instead of NTf_2^-. The control experiment with only silver triflimide resulted in no conversion (Table 1, entry 11).

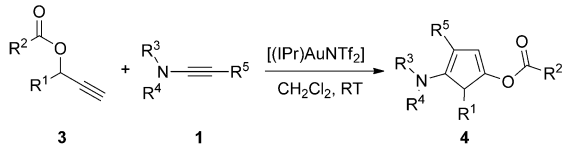
After this short optimization process we performed the conversion on a preparative scale. A product was obtained in 53% yield which indeed combined the two starting materials in a completely atom-economical[13] fashion. Based on NMR analysis using two-dimensional NMR techniques (HMBC, HSQC) we determined the product to be the desired highly functionalized cyclopentadiene derivative **4a** (Table 2, entry 1). Final proof was provided by an X-ray crystal structure analysis of compound **4a**.[14]

To evaluate the scope and limitations of this transformation, we synthesized a series of starting ynamides and reacted them with different propargylic carboxylates under the optimized conditions. The first experiments were conducted with ynamide **1a** and a series of differently substituted propargylic acetates. Substrates with *para*-substituted phenyl groups in the propargylic position showed similar reactivity (Table 2, entries 2–4, 30–56%), but unfortunately the yield dropped significantly when the aromatic moiety had a *meta*-methoxy group (Table 2, entry 5, 17%). In this case the methoxy group at the arene has no mesomeric effect on the π system of the alkyne. An even more deactivated system with an electron-withdrawing bromo substituent in *meta*-position did not lead to the desired product (Scheme 2). Instead dimerization of the ynamide was observed. Interestingly, this ynamide-dimerization product was only observed if no reactions with the acetate precursors took place. This indicates that whenever the carbenoid is formed, a fast reaction suppresses the competing reaction pathway or the major part of the catalyst is not available for ynamide dimerization as it is incorporated in the gold carbenoid. This is



Scheme 2. Dimerization as competing pathway.

Table 2: Synthesis of cyclopentadienes **4** under the optimized conditions.[a]



3 1 4

1a: R^3 = Me, R^4 = Ts, R^5 = *n*Bu
1b: R^3 = Me, R^4 = Ts, R^5 = *t*Bu
1c: R^3 = Bn, R^4 = Ts, R^5 = *n*Bu
1d: R^3 = Me, R^4 = Ts, R^5 = TIPS
1e: R^3 = Bn, R^4 = Ts, R^5 = TIPS
1f: R^3 = Bn, R^4 = SO_2Mes, R^5 = TIPS

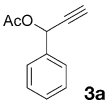
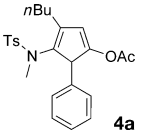
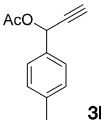
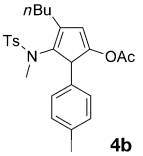
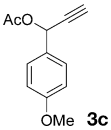
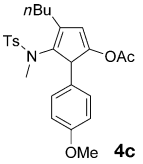
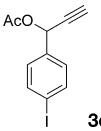
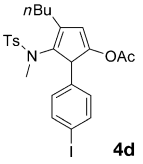
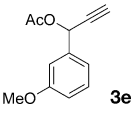
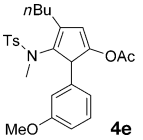
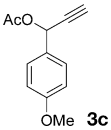
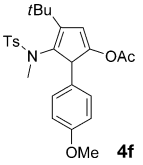
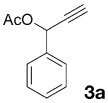
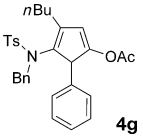
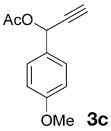
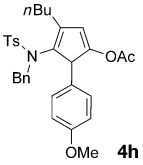
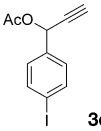
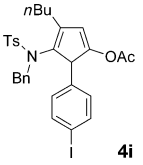
Entry	Acetate	Ynamide	Product	Yield [%]
1	 **3a**	**1a**	 **4a**	53
2	 **3b**	**1a**	 **4b**	47
3	 **3c**	**1a**	 **4c**	56
4	 **3d**	**1a**	 **4d**	30
5	 **3e**	**1a**	 **4e**	17
6	 **3c**	**1b**	 **4f**	70
7	 **3a**	**1c**	 **4g**	71
8	 **3c**	**1c**	 **4h**	82
9	 **3d**	**1c**	 **4i**	56

Table 2: (Continued)

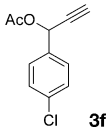
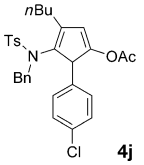
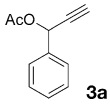
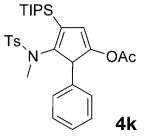
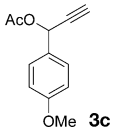
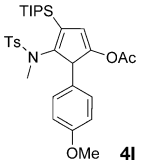
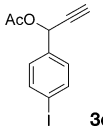
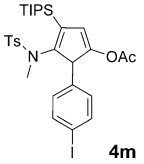
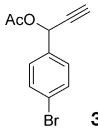
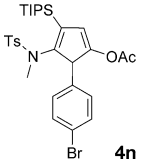
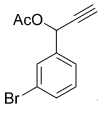
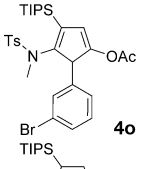
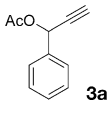
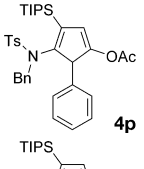
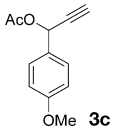
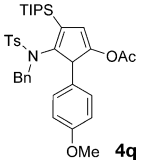
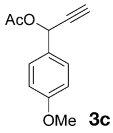
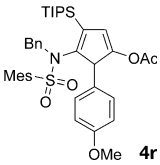
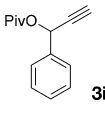
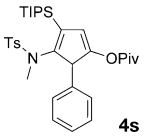
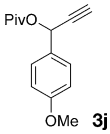
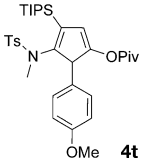
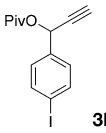
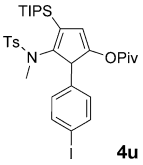
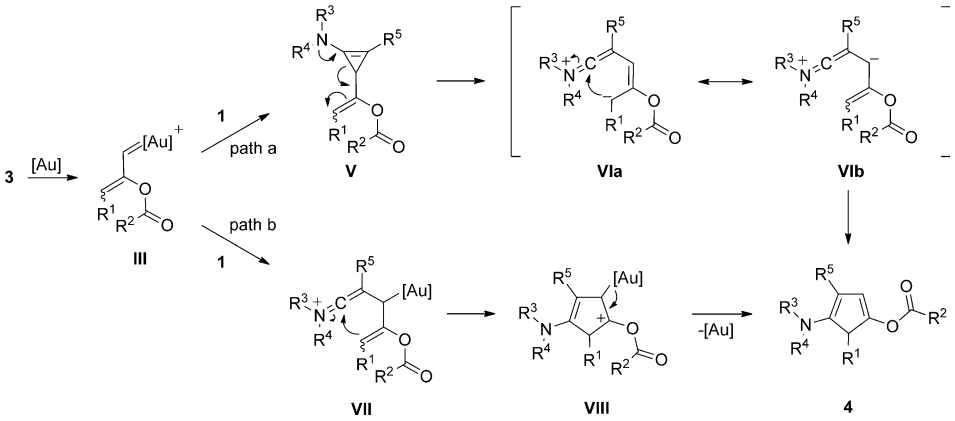
Entry	Acetate	Ynamide	Product	Yield [%]
10	 **3f**	**1c**	 **4j**	52
11	 **3a**	**1d**	 **4k**	49
12	 **3c**	**1d**	 **4l**	82
13	 **3d**	**1d**	 **4m**	72
14	 **3g**	**1d**	 **4n**	55
15	 **3h**	**1d**	 **4o**	34
16	 **3a**	**1e**	 **4p**	60
17	 **3c**	**1e**	 **4q**	74
18	 **3c**	**1f**	 **4r**	63
19	 **3i**	**1d**	 **4s**	60
20	 **3j**	**1d**	 **4t**	82

Table 2: (Continued)

Entry	Acetate	Ynamide	Product	Yield [%]
21	 **3k**	**1d**	 **4u**	67

underlined by the observation that in all other cases even if yields of the intermolecular cyclization products were not perfect, no traces of dimerization were visible in the crude ^{1}H NMR spectra. Nevertheless, substrates substituted with moieties that do not contain hydrogen atoms for a competing hydride shift led to a significant increase in yields, from 56% (Table 2, entry 3) to 70% (entry 6) for the *tert*-butyl group. It seems likely that competing pathways initiated by an initial hydride shift might also occur for the intermolecular cyclization reactions, but also simply the increased steric environment might favor the product-forming pathway.

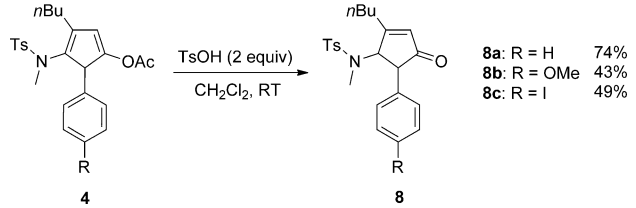
Next we changed the alkyl substituent at the ynamide nitrogen. On shifting from methyl to benzyl, no big electronic effects but rather the increased bulkiness of the benzyl group should have an effect (Table 2, entries 7–9). Indeed, the intermolecular cyclization reaction turned out to be more efficient than for the methyl-substituted ynamide. A significant increase in yields could be obtained for **3a**, **3,** and **3d** (71%, 82%, and 56%). Even propargylic carboxylate **3f** bearing an electron-deficient *p*-chlorobenzyl substituent could be transferred in acceptable yields (Table 2, entry 10, 52%). Next we tested a series of triisopropylsilyl-subtituted ynamides in combination with differently substituted propargylic acetates. For **3c** and **3d** yields were much higher than for the linear alkyl-substituted counterparts (Table 2, entries 12 and 13, 82% and 72%). This is in accordance with the previously mentioned increase in yield for substrates with moieties that are unable to undergo competing hydride-shift pathways. The only exception was **3a** which provided **4k** in only 49% yield (Table 2, entry 11). To complete the series of halogen-substituted arenes, we included bromo-substituted **3g** and **3h**. Not unexpectedly, yields for the *para*-substituted substrate (Table 2, entry 14, 55%) were higher than for the *meta*-substituted (entry 15, 34%) which can also be rationalized by increased steric interactions as well as an electronic interactions. Substrates containing two bulky groups, the triisopropylsilyl and the benzyl group, were also investigated. The obtained yields were also good to moderate (Table 2, entries 16 and 17, 60% and 74%), despite the steric demand that is evident in the solid -tate molecular structure of **4p**.[14] The even more demanding mesitylsulfonyl group in ynamide **1f** led to a decrease of the yield (Table 2, entry 18, 63%). Interestingly, a shift to the sterically more demanding pivaloyl group as the migrating carboxyl group did not significantly affect the yields, which were comparable to those with the acetyl-substituted derivatives (Table 2, entries 19–21, 60%, 82%, and 67%).



Scheme 3. Mechanistic proposal.

A short mechanistic rationale[15] for the cyclopentadiene synthesis is depicted in Scheme 3. After the initial formation of gold carbenoid **III** through 1,2-acetal shift, two mechanistic scenarios seem reasonable. Pathway a describes a cyclopropenation reaction of the electron-rich ynamide. This is an unknown reaction for gold carbenoids derived from propargylic acetates, but recently Davies and Briones reported on the cyclopropenation of internal alkynes with gold carbenoids derived from diazo acetates.[16] The next step comprises a ring opening which is triggered by the lone pairs at the nitrogen atom. The resulting zwitterionic keteniminium cation/allylic anion **VI** then undergoes ring closure to form the final product **4**. This cyclopropene to cyclopentadiene rearrangement might also be a concerted[17] or a gold-assisted process.[18] The alternative pathway b comprises a stepwise reaction in which the nucleophilic carbon atom of the ynamide attacks the electrophilic carbene carbon to deliver the keteniminum intermediate **VII**. After that, ring closure by attack of the electron-rich double bond onto the iminium carbon takes place. Elimination of the $[Au]^+$ fragment and liberation of product **4** complete the catalytic cycle.

To demonstrate the synthetic potential of the obtained cyclopentadienes, compounds of type **4** were converted under acidic conditions (Scheme 4). To our surprise cyclopentenones **8** were obtained as single products. The position of the double bond (which is not in conjugation with the benzene system) was assigned by an X-ray crystal structure analysis of compound **8a**.[14] Cyclopentenones are useful targets as they are potential intermediates for the synthesis of biologically important compounds.[19]



Scheme 4. Deprotection of cyclopentadienes to give cyclopentenones under acidic conditions.

In summary, highly substituted cyclopentadienes can be obtained through the activation of ynamides by highly electrophilic gold carbenoids. The products are formed under mild reaction conditions and with complete atom economy. This methodology opens up new possibilities to exploit the potential of ynamides in combination with gold catalysis.

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[1] Z. Janousek, J. Collard, H. G. Viehe, *Angew. Chem.* **1972**, *84*, 993 – 993; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 917 – 918.

[2] a) B. Witulski, T. Stengel, *Angew. Chem.* **1998**, *110*, 495 – 498; *Angew. Chem. Int. Ed.* **1998**, *37*, 489 – 492; b) B. Witulski, M. Gössmann, *Chem. Commun.* **1999**, 1879 – 1880; c) B. Witulski, T. Stengel, *Angew. Chem.* **1999**, *111*, 2521 – 2524; *Angew. Chem. Int. Ed.* **1999**, *38*, 2426 – 2430; d) J. D. Rainier, J. E. Imbriglio, *Org. Lett.* **1999**, *1*, 2037 – 2039; e) B. Witulski, M. Gössmann, *Synlett* **2000**, 1793 – 1797; f) J. D. Rainier, J. E. Imbriglio, *J. Org. Chem.* **2000**, *65*, 7272 – 7276; g) B. Witulski, T. Stengel, J. M. Fernández-Hernández, *Chem. Commun.* **2000**, 1965 – 1966; h) B. Witulski, C. Alayrac, *Angew. Chem.* **2002**, *114*, 3415 – 3418; *Angew. Chem. Int. Ed.* **2002**, *41*, 3281 – 3284.

[3] For representative examples, see: a) M. O. Frederick, J. A. Mulder, M. R. Tracey, R. P. Hsung, J. Huang, K. C. M. Kurtz, L. Shen, C. J. Douglas, *J. Am. Chem. Soc.* **2003**, *125*, 2368 – 2369; b) J. R. Dunetz, R. L. Danheiser, *Org. Lett.* **2003**, *5*, 4011 – 4014; c) Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett.* **2004**, *6*, 1151 – 1154; d) X. Zhang, Y. Zhang, J. Huang, R. P. Hsung, K. C. M. Kurtz, J. Oppenheimer, M. E. Petersen, I. K. Sagamanova, L. Shen, M. R. Tracey, *J. Org. Chem.* **2006**, *71*, 4170 – 4177; e) A. L. Kohnen, J. R. Dunetz, R. L. Danheiser, *Org. Synth.* **2007**, *84*, 88 – 101; f) I. K. Sagamanova, K. C. M. Kurtz, R. P. Hsung, *Org. Synth.* **2007**, *84*, 359 – 367; g) K. Dooleweerdt, H. Birkedal, T. Ruhland, T. Skrydstrup, *J. Org. Chem.* **2008**, *73*, 9447 – 9450; h) T. Hamada, X. Ye, S. S. Stahl, *J. Am. Chem. Soc.* **2008**, *130*, 833 – 835; i) A. Coste, G. Karthikeyan, F. Couty, G. Evano, *Angew. Chem.* **2009**, *121*, 4445 – 4449; *Angew. Chem. Int. Ed.* **2009**, *48*, 4381 – 4385; j) A. Coste, F. Couty, G. Evano, *Org. Lett.* **2009**, *11*, 4454 – 4457.

[4] For reviews covering ynamide chemistry, see: a) C. A. Zificsak, J. A. Mulder, R. P. Hsung, C. Rameshkumar, L.-L. Wei, *Tetrahedron* **2001**, *57*, 7575 – 7606; b) K. A. DeKorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2010**, *110*, 5064 – 5106; c) G. Evano, A. Coste, K. Jouvin, *Angew. Chem.* **2010**, *122*, 2902 – 2921; *Angew. Chem. Int. Ed.* **2010**, *49*, 2840 – 2859.

[5] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064 – 8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896 – 7936; b) E. Jiménez-Núnez, A. M. Echavarren, *Chem. Commun.* **2007**, 333 – 346; c) R. Skouta, C.-J. Li, *Tetrahedron* **2008**, *64*, 4917 – 4938; d) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239 – 3265; e) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266 – 3325; f) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351 – 3378; g) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*,

1766 – 1775; h) S. Sengupta, X. Shi, *ChemCatChem* **2010**, *2*, 609 – 619; i) C. Nevado, *Chimia* **2010**, *64*, 247 – 251; j) A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657 – 1712; k) J. Xiao, X. Li, *Angew. Chem.* **2011**, *123*, 7364 – 7375; *Angew. Chem. Int. Ed.* **2011**, *50*, 7226 – 7236; l) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2012**, *41*, 2448 – 2462.

[6] a) S. Couty, C. Meyer, J. Cossy, *Angew. Chem.* **2006**, *118*, 6878 – 6882; *Angew. Chem. Int. Ed.* **2006**, *45*, 6726 – 6730; b) A. S. K. Hashmi, R. Salathé, W. Frey, *Synlett* **2007**, 1763 – 1766; c) A. S. K. Hashmi, M. Rudolph, J. W. Bats, W. Frey, F. Rominger, T. Oeser, *Chem. Eur. J.* **2008**, *14*, 6672 – 6678; d) F. M. Istrate, A. K. Buzas, I. D. Jurberg, Y. Odabachian, F. Gagosz, *Org. Lett.* **2008**, *10*, 925 – 928; e) A. S. K. Hashmi, S. Pankajakshan, M. Rudolph, E. Enns, T. Bander, F. Rominger, W. Frey, *Adv. Synth. Catal.* **2009**, *351*, 2855 – 2875; f) S. Couty, C. Meyer, J. Cossy, *Tetrahedron* **2009**, *65*, 1809 – 1832; g) P. W. Davies, A. Cremonesi, L. Dumitrescu, *Angew. Chem.* **2011**, *123*, 9093 – 9097; *Angew. Chem. Int. Ed.* **2011**, *50*, 8931 – 8935; h) C. F. Xu, M. Xu, Y.-X. Jia, C.-Y. Li, *Org. Lett.* **2011**, *13*, 1556 – 1559; i) P. W. Davies, A. Cremonesi, N. Martin, *Chem. Commun.* **2011**, *47*, 379 – 381; j) R. B. Dateer, K. Pati, R.-S. Liu, *Chem. Commun.* **2012**, *48*, 7200 – 7202; k) R. B. Dateer, B. S. Shaibu, R.-S. Liu, *Angew. Chem.* **2012**, *124*, 117 – 121; *Angew. Chem. Int. Ed.* **2012**, *51*, 113 – 117.

[7] S. Kramer, Y. Odabachian, J. Overgaard, M. Rottländer, F. Gagosz, T. Skrydstrup, *Angew. Chem.* **2011**, *123*, 5196 – 5200; *Angew. Chem. Int. Ed.* **2011**, *50*, 5090 – 5094.

[8] H. Li, R. P. Hsung, *Org. Lett.* **2009**, *11*, 4462 – 4465.

[9] a) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654 – 8655; b) P. Hannen, A. Fürstner, *Chem. Commun.* **2004**, 2546 – 2547; c) M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 18002 – 18003; d) N. Marion, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 2806 – 2809; *Angew. Chem. Int. Ed.* **2007**, *46*, 2750 – 2752; e) G. Lemière, V. Gandon, K. Cariou, T. Fukuyama, A.-L. Dhimane, L. Fensterbank, M. Malacria, *Org. Lett.* **2007**, *9*, 2207 – 2209; f) D. J. Gorin, I. D. G. Watson, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 3736 – 3737; g) A. Correa, N. Marion, L. Fensterbank, M. Malacria, S. P. Nolan, L. Cavallo, *Angew. Chem.* **2008**, *120*, 730 – 733; *Angew. Chem. Int. Ed.* **2008**, *47*, 718 – 721; h) G. Li, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2008**, *130*, 3740 – 3741; i) G. Lemière, V. Gandon, K. Cariou, A. Hours, T. Fukuyama, A.-L. Dhimane, L. Fensterbank, M. Malacria, *J. Am. Chem. Soc.* **2009**, *131*, 2993 – 3006; j) Y. Wang, B. Lu, L. Zhang, *Chem. Commun.* **2010**, *46*, 9179 – 9181; k) F. Miege, C. Meyer, J. Cossy, *Beilstein J. Org. Chem.* **2011**, *7*, 717 – 734; l) C. A. Sperger, J. E. Tungen, A. Fiksdahl, *Eur. J. Org. Chem.* **2011**, 3719 – 3722.

[10] For a related rhodium-catalyzed transformation, see: J. F. Briones, J. Hansen, K. I. Hardcastle, J. Autschbach, H. M. L. Davies, *J. Am. Chem. Soc.* **2010**, *132*, 17211 – 17215.

[11] a) A. Fürstner, P. Hannen, *Chem. Commun.* **2004**, 2546 – 2547; b) A. Fürstner, P. Hannen, *Chem. Eur. J.* **2006**, *12*, 3006 – 3019; c) X. Moreau, J.-P. Goddard, M. Bernard, G. Lemiere, J. M. López-Romero, E. Mainetti, N. Marion, V. Mouriès, S. Thorimbert, L. Fensterbank, M. Malacria, *Adv. Synth. Catal.* **2008**, *350*, 43 – 48; d) T. Kusakabe, K. Kato, *Tetrahedron* **2011**, *67*, 1511 – 1517.

[12] A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph, E. Kurpejovic, *Angew. Chem.* **2004**, *116*, 6707 – 6709; *Angew. Chem. Int. Ed.* **2004**, *43*, 6545 – 6547.

[13] B. M. Trost, *Angew. Chem.* **1995**, *107*, 285 – 307; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259 – 281.

[14] CCDC 923717 (**4a**), 923718 (**4p**), and 923719 (**8a**) 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.

[15] A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360 – 5369; *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 5232 – 5241.

[16] J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc.* **2012**, *134*, 11916 – 11919.

[17] M. M. Haley, B. Biggs, W. A. Looney, R. D. Gilbertson, *Tetrahedron Lett.* **1995**, *36*, 3457 – 3460.

[18] Z.-B. Zhu, M. Shi, *Chem. Eur. J.* **2008**, *14*, 10219 – 10222.

[19] a) J. Dauvergne, A. M. Happe, S. M. Roberts, *Tetrahedron* **2004**, *60*, 2551 – 2557; b) J. Dauvergne, A. M. Happe, V. Jadhav, D. Justice, M.-C. Matos, P. J. McCormack, M. R. Pitts, S. M. Roberts, S. K. Singh, T. J. Snapea, J. Whittallc, *Tetrahedron* **2004**, *60*, 2559 – 2567; c) F. A. Davis, Y. Wu, *Org. Lett.* **2004**, *6*, 1269 – 1272; d) M. Zaja, S. Blechert, *Tetrahedron* **2004**, *60*, 9629 – 9634; e) G. K. Veits, D. R. Wenz, J. Read deAlaniz, *Angew. Chem.* **2010**, *122*, 9674 – 9677; *Angew. Chem. Int. Ed.* **2010**, *49*, 9484 – 9487; for the classical synthesis of cyclopentenones see also: f) J. Blanco-Urgoiti, L. Anorbe, L. Perez-Serrano, G. Dominguez, J. Perez-Castells, *Chem. Soc. Rev.* **2004**, *33*, 32 – 42; g) S. E. Gibson, N. Mainolfi, *Angew. Chem.* **2005**, *117*, 3082 – 3097; *Angew. Chem. Int. Ed.* **2005**, *44*, 3022 – 3037; h) M. A. Tius, *Eur. J. Org. Chem.* **2005**, 2193 – 2206; i) H. Pellissier, *Tetrahedron* **2005**, *61*, 6479 – 6517; j) A. J. Frontier, C. Collison, *Tetrahedron* **2005**, *61*, 7577 – 7606; k) T. N. Grant, C. J. Rieder, F. G. West, *Chem. Commun.* **2009**, 5676 – 5688.

