Journal of Organometallic Chemistry xxx (2015) 1–8

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Chiral [2.2]paracyclophane-based NAC- and NHC-gold(I) complexes

Verena Göker [a], Simon Robert Kohl [a], Frank Rominger [a], Georg Meyer-Eppler [b], Lucia Volbach [b], Gregor Schnakenburg [c], Arne Lützen [b], A. Stephen K. Hashmi [a, d, *]

[a] Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
[b] Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
[c] Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
[d] Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form
4 March 2015
Accepted 10 March 2015
Available online xxx

Dedicated to Prof. Hubert Schmidbaur on the occasion of his 80th birthday.

Keywords:
Alkenes
Alkynes
Furans
Gold
Isonitriles
Carbene ligands

ABSTRACT

From enantiomerically pure, planar chiral [2.2]paracyclophane amines a series of nitrogen acyclic carbenegold(I) complexes and nitrogen heterocyclic carbenegold(I) complexes are prepared by a modular template synthesis using isonitriles and amines. These chiral catalysts are tested in two reactions, the enantiotopos-selective furanyne cyclization and the enantioselective enyne cyclization. While excellent conversions could be achieved with these new catalysts, the enantioselectivities in only some cases are in the range of best known catalysts for these conversion.

Introduction

In both the inorganic and the organometallic chemistry of gold the ligands play a pivotal role [1,2]. Metal complexes containing paracyclophanes (PCPs) as ligands are already known [3–6]. Their application as chiral catalysts is of significant interest as they possess planar chirality. Gold complexes based on PCP were first prepared in situ in 2011 by Michelet et al. [7]. These complexes were used for the domino cyclization/nucleophile addition reactions of enynes in the presence of water, methanol, or electron-rich aromatic derivatives, but the results concerning this reaction using the famous PhanePhos ligand were unsatisfactory. In 2012, however, Gagné published a gold-catalyzed Cope rearrangement where the highest yield and enantiomeric excess were found for the PhanePhos ligand [8]. Both these innovative first investigations in homogeneous gold catalysis were conducted with PCP-phosphane ligands. So far, only silver and rhodium NHC complexes with PCP substructure have been reported [9], until now there exist no *N*-hetereocyclic carbenegold complexes containing a PCP substituent.

We now report the synthesis and application of the first PCP-based NAC and NHC gold complexes.

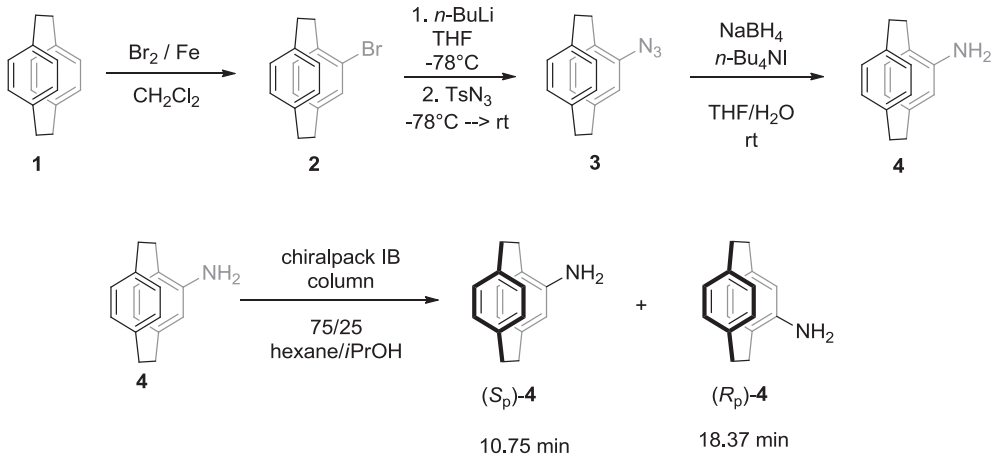
Results and discussion

Synthesis and characterization

The starting material for the synthesis of the new gold(I) complexes was the PCP-amine **4**, which was conveniently prepared in enantiomerically pure form from the achiral PCP **1** in three steps by published methods (Scheme 1) [10]: a simple electrophilic aromatic substitution provided the bromo-PCP **2**, which then was transferred into the azide **3** with *n*-BuLi and tosylazide. A reduction with sodiumborohydride delivered racemic **4**, whose enantiomers were separated via HPLC on a CHIRALPAK IB column using *n*-hexane/Isopropanol (75/25). The retention times on the analytical

* Corresponding author. Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. Tel.: +49 6221 548413; fax: +49 6221 544205.
E-mail address: hashmi@hashmi.de (A.S.K. Hashmi).

http://dx.doi.org/10.1016/j.jorganchem.2015.03.010
0022-328X/



Scheme 1. Synthesis of the enantiomerically pure amine **4**.

column were 10.75 min for the (+)-enantiomer and 18.37 min for the (−)-enantiomer. The absolute configuration of the first eluting (+)-enantiomer could then be assigned via X-ray diffraction of the corresponding hydrochloride (Fig. 1) by analysis of the Flack parameter (absolute structure parameter X = 0.04(9)) [11].

The enantiomerically pure amine then was converted into the isonitrile. The reaction of **4** with ethyl formate at reflux temperature delivered the formamide **5**, which was purified by recrystallization from acetone/pentane. **5** delivered the isonitrile (S_p)-**6** when treated with phosphorylchloride and triethylamine in THF (Scheme 2).

Finally, the synthesis of the nitrogen acyclic carbene (NAC) complex [12] was achieved by reacting the simple (Me_2S)gold(I) chloride, isonitrile (S_p)-**6**, and a secondary amine which directly lead to the desired gold complex (S_p)-**7** in an excellent yield (Scheme 3).

Different amines were tested in combination with (S_p)-**6** in order to demonstrate the broad scope of this methodology. Apart from two achiral amines, which led to the enantiomerically pure NAC-gold(I) complexes (S_p)-**8** and (S_p)-**9**, also enantiomerically pure amines were used. The latter provided NAC ligands which combined planar and central chirality on each side of the NAC. Thus, both diastereomers of **10** and complex **11** were obtained in good yields. The excess of amine had to be removed by several washings with hexane and recrystallization from DCM/hexane, which reduced the yields shown in Fig. 2.

For **11** a suitable crystal for a single crystal X-ray structure analysis could be grown. The structure of the complex is shown in Fig. 3 [11], it confirmed the absolute configuration of the paracyclophane unit and the bis(phenylethyl) amine moiety. As expected, the steric bulk of the chiral (*S*,*S*)-bisphenylethyl amine moiety positions the PCP group *syn* to the gold centre on the carbene ligand. However, the low quality of the results doesn't allow a detailed discussion. Hence, we take the results only as a proof of constitution and configuration.

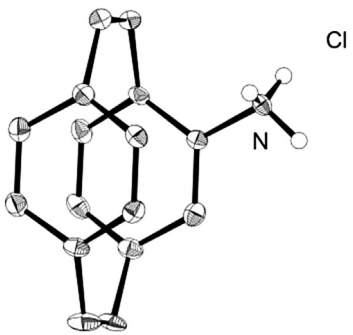


Fig. 1. Solid state molecular structure of (S_p)-**4**.

In addition to NAC-gold(I) complexes we also wanted to prepare NHC-gold(I) complexes. This was achieved by employing the functionalized amine building block **12** [13]. This amine gave the NAC complex (Sp)-**13** upon addition of the in situ-generated isonitrilegold(I) chloride. The NAC ligand in the gold complex could then be cyclized to the unsaturated NHC ligand bound to the gold centre by a condensation and elimination reaction treatment initiated by acid. In this way we were able to obtain the complexes (S_p)-**15** and (S_p)-**16**, the first one in low, the second one in high yield (Scheme 4).

Synthesis of chiral gold(I) complexes without PCP ligands

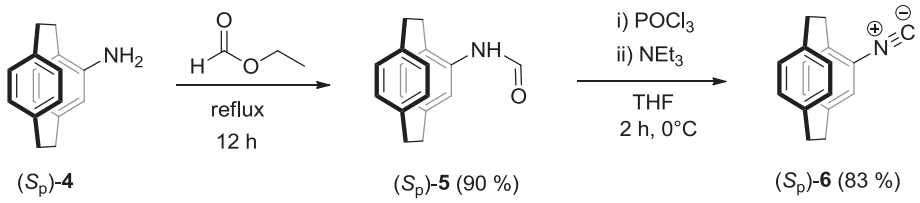
In order to evaluate the influence of the PCP ligands on the catalyst performance of the gold complexes we also prepared some other chiral gold complexes that lack the PCP moiety as reference catalysts: First (*R*)-**17** (Fig. 4) was prepared according to the usual method for the synthesis of NAC-gold(I) complexes.

As demonstrated by Gagné et al. [8], the dinuclear PCP-substituted gold complex delivers the best enantiomeric excess in Cope rearrangements. Thus, another target was the synthesis of a dinuclear NAC gold complex. From binaphtyldiamine the bis(isonitrile) was prepared by following the route described above. Subsequently, with di-*n*-propylamine and (Me_2S)gold(I) chloride the complex (S_a)-**18** was obtained in a good yield of 79% (Fig. 5).

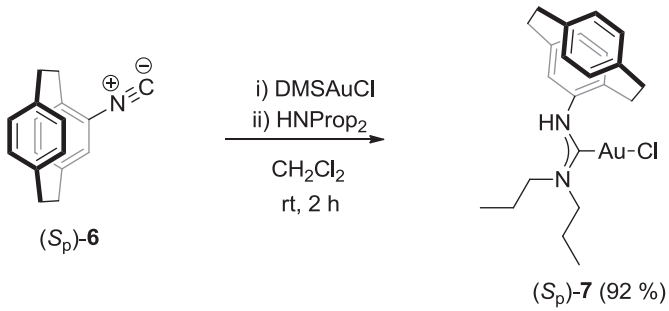
As the corresponding chiral PCP-diamine was not available, it was not possible to prepare a dinuclear PCP-substituted NAC-gold(I) complex analogue in optically pure form.

Catalytic reactions

For the investigation of the catalytic activity in enantioselective reactions two test reactions were selected. The first one is the asymmetric phenol synthesis, which has already shown to give some enantiomeric excess with phosphane ligands [14]. However, so far chiral carbene complexes have not been tested in this reaction. The substrate for this test reaction was prepared by following a previously described route [14]. Deprotonation of the 2-



Scheme 2. Synthesis of the isonitrile.



Scheme 3. Synthesis of the NAC-gold(I) complex (S_p)-**7**.

methylfuran (**19**) with *n*-BuLi and the subsequent reaction with epichlorohydrin gave the epoxide **20**. Reaction of the latter with another equivalent of lithiated **19** provided alcohol **21**, which finally was propargylated to give rise to the furanyne substrate **22** in a classical Williamson ether synthesis (Scheme 5).

Using catalyst (Sp)-**7** we first optimized the reaction conditions systematically in terms of the choice of the silver salt and the solvent (Table 1).

The best *ee* value was obtained with silver triflate in chloroform. Both transformations in DCM or in benzene (due to the melting point of benzene this reaction had to be conducted at room temperature), delivered similar *ee* values. In toluene only racemic product was obtained, in methanol no conversion was detectable. The different silver salts led to large differences in the *ee* values, silver triflate showed the highest enantiomeric excess, 17%.

After the best conditions had been identified, the reaction was conducted with both different chiral PCP-substituted gold complexes and also with the chiral gold complexes without PCP-ligand (Table 2).

(*R*)-(S_p)-**10** shows a low *ee* of 21%, whereas the other diastereomer (*S*)-(S_p)-**10** only shows 5% *ee*, an interesting matched/mismatched situation. The other catalysts also provided unsatisfactory *ee* values. The catalysis with the dinuclear (*S*)-**18** also provided only 11% *ee*. Furthermore, there was no significant difference in *ee* for PCP-substituted catalysts (Entries 1–8) and catalysts without PCP-ligand (Entries 9 and 10). Also no significant differences between the NAC- (Entries 1–6) and the corresponding NHC-ligands (Entries 7 and 8) were visible. On the other hand, the yields ranging from 87 to 97% were perfectly normal – different from the *ee* no reduction in the yield was detected.

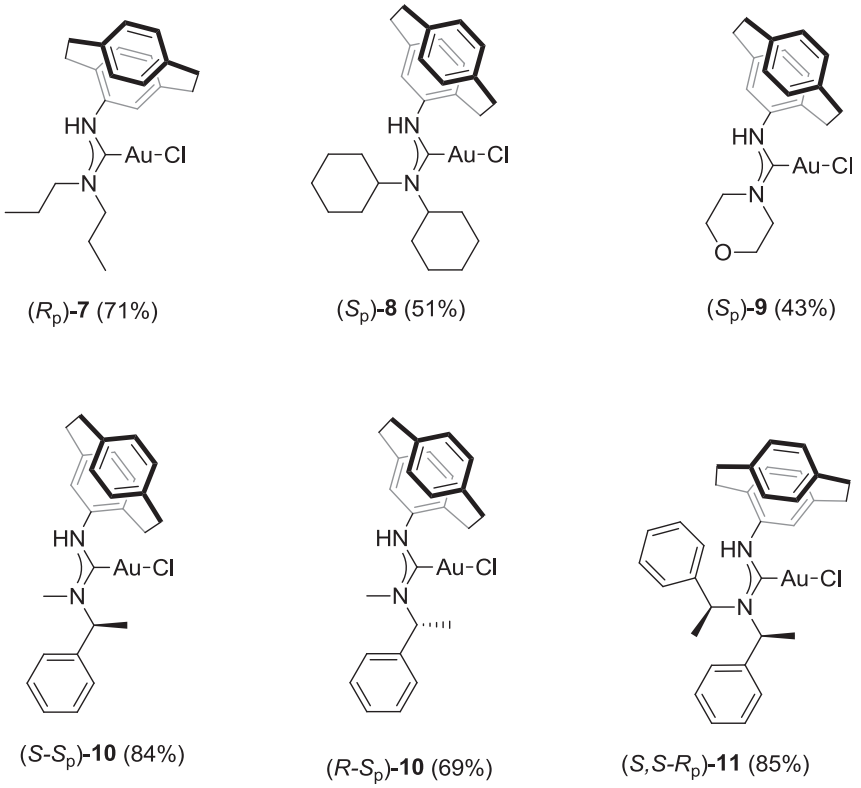


Fig. 2. NAC-gold(I) complexes containing PCP substituents.

Please cite this article in press as: V. Göker, et al., Journal of Organometallic Chemistry (2015), http://dx.doi.org/10.1016/j.jorganchem.2015.03.010

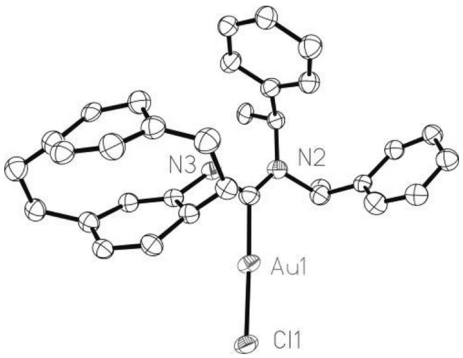


Fig. 3. Solid state molecular structure of (*S*,*S*)-(R_p)-**11**.

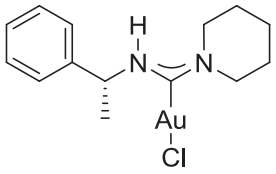
The second test reaction was the addition of methanol to an enyne substrate. With chiral NHC-gold complexes already good *ee* values have been described [15,16].

The synthesis of this substrate was done in two steps starting from **24**. Deprotonation and prenylation yielded 41% of **25**. Another deprotonation followed by propargylation provided the catalysis substrate **26** in good yield (Scheme 6) [17].

Once more the best catalysis conditions with respect to silver salt and solvent were screened. Initially the reaction was conducted in methanol only, but this gave very low *ee* values, a solvent mixture of five equivalents of methanol and a cosolvent was more suitable. Benzene was quite successful, in addition silver hexafluorophosphate was the best counter anion, 17% *ee* were obtained (Entry 3). Apart from the reaction with silver hexafluoroantimonate (Entry 7) the other silver salts gave similar *ee* values Table 3.

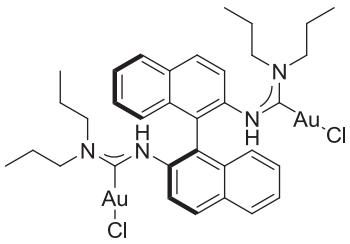
Now the different catalysts were investigated in the conversion of **26** (Table 4). Quite different *ee* values were observed. Again, like with substrate **22**, the yield of **27** was very good. The best *ee*, 52%, could be reached with the NAC-gold(I) complex (S_p)-**8** (Entry 2).

In this reaction the *ee* values obtained with NAC-ligands (Entries 1, 2, 5 and 6) were higher than those of the gold complexes with NHC-ligands (Entries 7 and 8). Similar to the conversions of test substrate **22**, a significant difference in the *ee* values obtained with (*R*)-(S_p)-**10** (Entry 5) and its diastereomer (*S*)-(S_p)-**10** (Entry 4) became visible. Surprisingly, (*S*)-**18** (Entry 10) delivered only racemic product.



(*R*)-**17** (39%)

Fig. 4. Chiral complex (*R*)-**17** lacking a PCP group.



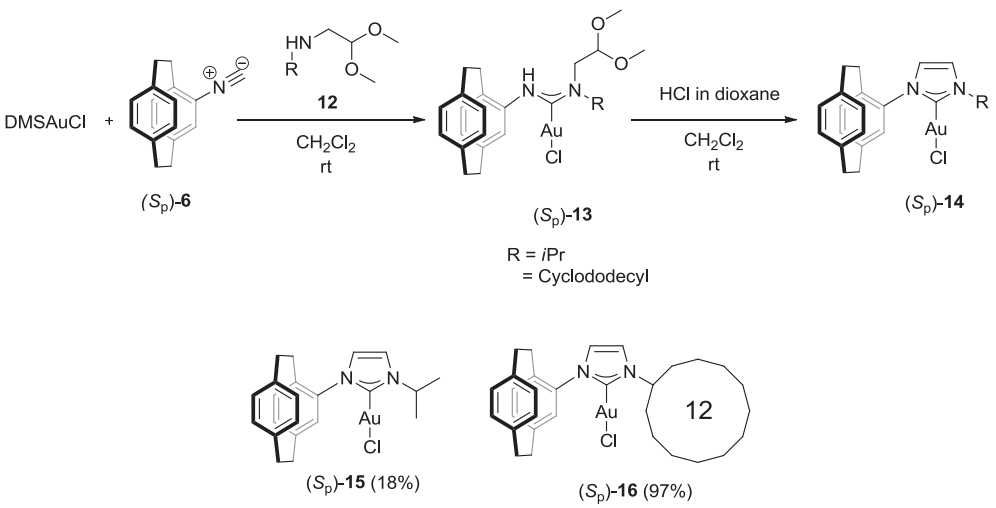
(S_a)-**18** (79%)

Fig. 5. Preparation of the dinuclear (S_a)-**18**.

Conclusion

We succeeded in the efficient preparation of a series of the first planar-chiral PCP-substituted NAC- and NHC-gold(I) complexes as well as **17**, an NAC-complex with central chirality, and the dinuclear gold(I) complex **18** with an axis of chirality. All these complexes were tested as enantioselective catalysts in two reactions, a furanyne cyclization and an enyne cyclization. With *ee* values of 21% for the NAC-complex (*R*)-(S_p)-**10** in the furanyne cyclization the results are inferior to the known results with phosphane ligands [14], with 52% for the NAC-complex (S_p)-**8** the results in the enyne cyclization are comparable to the values published for the best NHC-gold(I) complex for this reaction [15,16].

All these results show the potential of the method for the modular template synthesis of carbenegold(I) complexes. The chiral groups used in this investigation still are not ideal for the reaction types investigated.



(S_p)-**6**

(S_p)-**13**

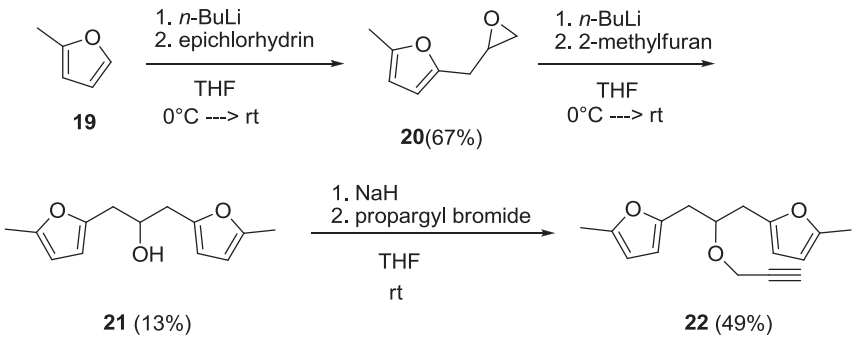
(S_p)-**14**

(S_p)-**15** (18%)

(S_p)-**16** (97%)

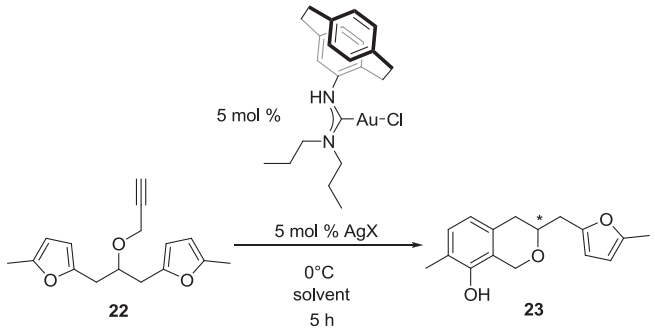
Scheme 4. Synthesis of the NHC-complexes (S_p)-**15** and (S_p)-**16**.

Please cite this article in press as: V. Göker, et al., Journal of Organometallic Chemistry (2015), http://dx.doi.org/10.1016/j.jorganchem.2015.03.010



Scheme 5. Synthesis of substrate **22** bearing two enantiotopic furyl groups for the gold-catalyzed enantioselective phenol synthesis [14].

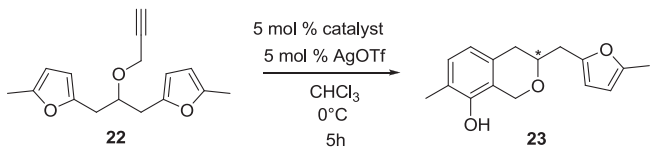
Table 1
Influence of the solvent and the counter anion on the conversion of **22**.



Entry	Catalyst	Solvent	Silver salt	Yield of **23**	*ee*
1	(S_p)-**7**	DCM	$AgPF_6$	81%	4
2	(S_p)-**7**	Chloroform	$AgPF_6$	91%	5
3[a]	(S_p)-**7**	Benzene	$AgPF_6$	71%	4
4	(S_p)-**7**	Toluene	$AgPF_6$	96%	rac
5	(S_p)-**7**	Methanol	$AgPF_6$	–	–
6	(S_p)-**7**	Chloroform	$AgSbF_6$	95%	9
7	(S_p)-**7**	Chloroform	$AgBF_4$	98%	6
8	(S_p)-**7**	Chloroform	AgOTf	99%	17
9	(S_p)-**7**	Chloroform	$AgNTf_2$	95%	3

[a] The reaction was conducted at RT.

Table 2
Catalyst screening in the gold-catalyzed cyclization of **22**.



Entry	Catalyst	Yield of **23**	*ee*
1	(R_p)-**7**	97%	7%
2	(S_p)-**8**	93%	9%
3	(S_p)-**9**	94%	9%
4	(*S*)-(S_p)-**10**	93%	5%
5	(*R*)-(S_p)-**10**	95%	21%
6	(*R*,*S*)-(R_p)-**11**	87%	2%
7	(S_p)-**15**	94%	11%
8	(S_p)-**16**	96%	5%
9	(*R*)-**17**	88%	8%
10	(*S*)-**18**	93%	11%

Experimental section

General procedures (GPs)

General procedure 1 (GP 1): synthesis of PCP-substituted NAC-gold(I) complexes

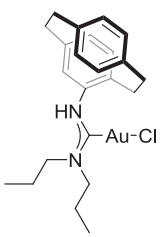
PCP-substituted NAC-gold(I) complexes were prepared according to a literature procedure [12]. One equivalent of (DMS)AuCl was dissolved in dry dichloromethane and one equivalent of PCP-isocyanide was added at room temperature. Then the mixture was stirred for 15 min. After that time 2 equivalents of the amine were added. The mixture was stirred at room temperature and protected from light for 1 h. The solution was filtered through celite and the solvent removed under reduced pressure. The solid was dissolved in DCM and pentane was added. The precipitate was collected on a frit, washed with pentane and dried in vacuum to afford the desired NAC gold complex as a colourless solid.

General procedure 2 (GP 2): synthesis of PCP-substituted NHC-gold(I) complexes

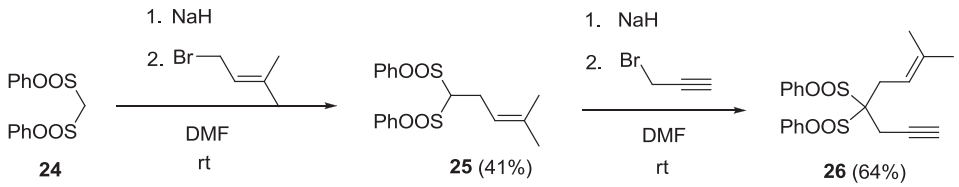
PCP-substituted NHC-gold(I) complexes were prepared according to a literature procedure. One equivalent of (SMe_2)AuCl was dissolved in dry dichloromethane and one equivalent of PCP-isocyanide was added at room temperature and stirred for 15 min. Then 2 equivalents of the amine were added. The mixture was stirred at room temperature and protected from light for 1 h. Then 14 equivalents of HCl in dioxane were added. After completion (monitored by TLC) of the reaction the mixture was filtered through Celite and the solvent removed under reduced pressure. The precipitate was dissolved in DCM and pentane was added. The solid was collected on a frit, washed with pentane and dried in vacuum to afford the desired NHC gold complex as a colourless solid.

Synthesis of the carbene complexes

*((Di-n-propylamino)((S_p)-[2.2]paracyclophaneamino)methylene) gold(I) chloride (S_p)-**7**.*

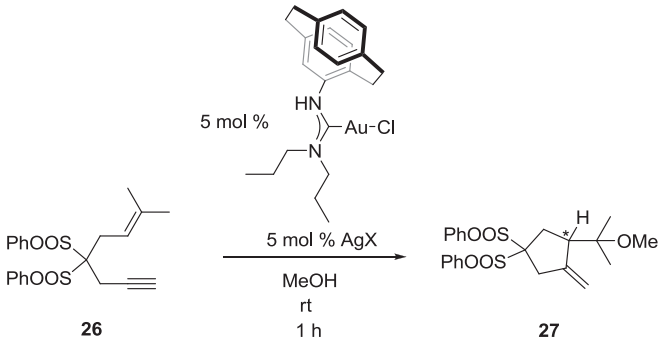


GP 1: (DMS)AuCl (50.0 mg, 170 μmol), (S_p)-4-isocyano[2.2]paracyclophane (40 mg, 170 μmol), di-*n*-propylamine (35 mg, 340 μmol), methylenechloride (3 mL), precipitation with methylenechloride/pentane, colourless solid (88 mg, 155 μmol, 92%).



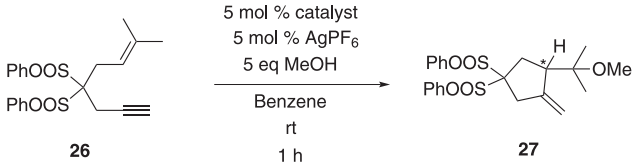
Scheme 6. Synthesis of the second test substrate **26** [17].

Table 3
Influence of the solvent and the counter ions in the test reaction with **26**.



Entry	Catalyst	Solvent	Silver salt	Yield of **27**	*ee*
1	(S_p)-**7**	Methanol	$AgPF_6$	93%	5%
2	(S_p)-**7**	DCM	$AgPF_6$	97%	11%
3	(S_p)-**7**	Chloroform	$AgPF_6$	100%	17%
4	(S_p)-**7**	Benzene	$AgPF_6$	98%	23%
5	(S_p)-**7**	Toluene	$AgPF_6$	93%	5%
6	(S_p)-**7**	Dichlorethane	$AgPF_6$	89%	4%
7	(S_p)-**7**	Benzene	$AgSbF_6$	89%	3%
8	(S_p)-**7**	Benzene	$AgBF_4$	97%	13%
9	(S_p)-**7**	Benzene	AgOTf	97%	14%
10	(S_p)-**7**	Benzene	$AgNTf_2$	96%	12%

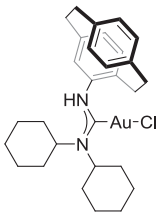
Table 4
Catalyst screening in the gold-catalyzed cyclization of **26**.



Entry	Catalyst	Yield of **27**	*ee*
1	(R_p)-**7**	97%	33%
2	(S_p)-**8**	93%	52%
3	(S_p-)-**9**	94%	7%
4	(*S*)-(S_p)-**10**	93%	3%
5	(*R*)-(S_p)-**10**	95%	36%
6	(*R*,*S*)-(R_p)-**11**	87%	11%
7	(S_p)-**15**	94%	19%
8	(S_p)-**16**	96%	8%
9	(*R*)-**17**	88%	20%
10	(*S*)-**18**	93%	1%

Mp/decomposition: 152 °C; IR (ATR): nu = 2961, 2928, 2873, 1541, 1350, 899, 748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.3 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H), 1.71-1.90 (m, 4H), 2.80–3.19 (m, 7H), 3.31–3.41 (m, 2H), 3.49–3.59 (m, 1H), 3.84–4.01 (m, 2H), 6.37 (s, 1H), 6.46–6.63 (m, 6H), 7.08 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 11.1 (q, 1C), 11.8 (q, 1C), 20.6 (t, 1C), 22.6 (t, 1C), 33.0 (t, 1C), 34.4 (t, 1C), 34.7 (t, 1C), 35.2 (t, 1C), 49.3 (t, 1C), 61.4 (t, 1C), 127.4 (d, 1C), 130.0 (d, 1C), 132.0 (d, 1C), 132.1 (d, 1C), 133.6 (d, 1C), 133.7 (d, 1C), 134.6 (s, 1C), 136.1 (d, 1C), 138.8 (s, 1C), 139.2 (s, 1C), 139.7 (s, 1C), 141.2 (s, 1C), 191.5 (s, 1C); MS [DART(+)]: *m/z* (%) = 566 (40) $[M]^+$, 434 (35), 388 (100); HR-MS [FAB (+)]: $C_{23}H_{30}N_2AuCl$ (566.92), $[C_{23}H_{30}N_2AuCl]^+$: calcd. 566.1763, found 566.1790.

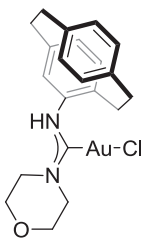
*((Dicyclohexylamino)((S$_p$)-[2.2]paracyclophaneamino)methylene) gold(I) chloride (S$_p$)-**8**.*



GP 1: DMSAuCl (63.0 mg, 214 μmol), (S_p)-4-isocyano[2.2]paracyclophane (50 mg, 214 μmol), dicyclohexylamine (77.6 mg, 428 μmol), DCM (3 mL), precipitation with DCM/Pentane, colourless solid (70 mg, 108 μmol, 51%).

Mp/decomposition: 141 °C; IR (ATR): nu = 3795, 3708, 3280, 2926, 2852, 2349, 1529, 1493, 1447, 895, 718 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.55 (m, 8H), 1.66–1.69 (m, 2H), 1.83–1.99 (m, 8H), 2.06–2.09 (m, 2H), 2.86–2.95 (m, 2H), 2.97–3.20 (m, 7H), 3.30–3.36 (m, 1H), 6.33 (s, 1H), 6.50–6.66 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.1 (t, 2C), 26.5 (t, 6C), 30.9 (t, 2C), 31.3 (t, 1C), 32.9 (t, 2C), 34.5 (t, 1C), 34.8 (t, 1C), 35.2 (t, 1C), 127.5 (d, 1C), 130.6 (d, 1C), 131.9 (d, 1C), 132.2 (d, 1C), 133.8 (d, 1C), 133.9 (d, 1C), 134.8 (s, 1C), 136.2 (d, 1C), 138.3 (s, 1C), 139.3 (s, 1C), 139.9 (s, 1C), 141.2 (s, 1C); MS [FAB(+)]: *m/z* (%) = 646 (69) $[M]^+$, 611 (100) $[M-Cl]^+$; HR-MS [FAB (+)]: $C_{29}H_{38}N_2AuCl$ (647.05), $[C_{29}H_{38}N_2AuCl]^+$: calcd. 646.2389, found 646.2415.

*(Morpholino((S$_p$)-[2.2]paracyclophaneamino)methylene)gold(I) chloride (S$_p$)-**9**.*

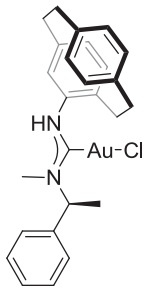


GP 1: DMSAuCl (70 mg, 238 μmol), (*S*)-4-isocyano[2.2]paracyclophane (56 mg, 238 μmol), morpholine (72 mg, 480 μmol), DCM (3 mL), precipitation with DCM/pentane, colourless solid (57 mg, 103 μmol, 43%).

Mp/decomposition: 128 °C; IR (ATR): nu = 2924, 2852, 2466, 1572, 1495, 1395, 1109, 894, 718 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): δ = 2.83–2.92 (m, 2H), 2.94–3.20 (m, 6H), 3.64–3.69 (m, 2H), 3.80–3.88 (m, 4H), 4.18–4.35 (m, 2H), 6.26 (s, 1H), 6.51 (d,

J = 7.8 Hz, 2H), 6.59–6.67 (m, 4H), 7.31 (s, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 33.0 (t, 1C), 34.2 (t, 1C), 34.6 (t, 1C), 35.0 (t, 1C), 56.7 (t, 2C), 65.6 (t, 1C), 67.2 (t, 1C), 127.3 (d, 1C), 130.1 (d, 1C), 131.8 (d, 1C), 132.3 (d, 1C), 133.6 (d, 1C), 133.8 (d, 1C), 135.7 (s, 1C), 136.1 (d, 1C), 138.5 (s, 1C), 139.5 (s, 1C), 139.7 (s, 1C), 141.7 (s, 1C), 190.4 (s, 1C); MS [FAB(+)]: *m/z* (%) = 552 (47) $[M]^+$, 517 (100) $[M-Cl]^+$; HR-MS [FAB (+)]: $C_{21}H_{24}N_2AuClO$ (552.85), $[C_{21}H_{24}N_2AuClO]^+$: calcd. 552.1243, found 552.1270.

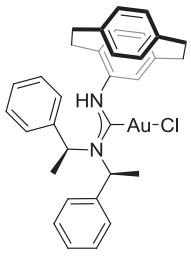
*(S_p)-((Methyl(1-phenylethyl)amino)((S)[2.2]paracyclophaneamino) methylene)gold(I) chloride (S_p)-**10**.*



GP 1: DMSAuCl (70.0 mg, 240 μmol), (S_p)-4-isocyano[2.2]paracyclophane (56 mg, 240 μmol), di-*n*-propylamine (65 mg, 480 μmol), methylenechloride (3 mL), precipitation with methylenechloride/pentane, colourless solid (120 mg, 200 μmol, 84%).

Mp: 147 °C; IR (ATR): nu = 3259, 2927, 2852, 1536, 1350, 1092, 772, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (d, J = 7.0 Hz, 3H), 2.85 (s, 3H), 2.88–3.22 (m, 7H), 3.36–3.47 (m, 1H), 6.1 (s, 1H), 6.48–6.69 (m, 7H), 7.05 (s, 1H), 7.34–7.44 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ = 16.9 (q, 1C), 29.8 (q, 1C), 33.1 (t, 1C), 34.3 (t, 1C), 34.7 (t, 1C), 35.2 (t, 1C), 66.8 (d, 1C), 125.6 (d, 1C), 126.9 (d, 1C), 127.0 (d, 1C), 127.2 (d, 1C), 128.3 (d, 1C), 128.8 (d, 1C), 128.9 (d, 1C), 130.2 (d, 1C), 132.0 (d, 1C), 132.1 (d, 1C), 133.6 (d, 1C), 133.8 (d, 1C), 136.1 (d, 1C), 138.1 (s, 1C), 138.5 (s, 1C), 139.2 (s, 1C), 139.7 (s, 1C), 141.3 (s, 1C), 142.7 (s, 1C), 192.0 (s, 1C); MS [FAB(+)]: *m/z* (%) = 600 (50) $[M]^+$, 565 (70) $[M-Cl]^+$; HR-MS [FAB (+)]: $C_{26}H_{28}N_2AuCl$ (691.06), $[C_{26}H_{28}N_2AuCl]^+$: calcd. 600.1607, found 600.1601.

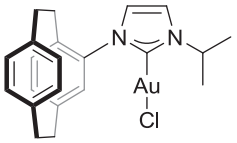
*(((S_p)-[2.2]Paracyclophaneamino)(((S)-1-phenylethyl)((S)-1-phenylethyl)amino) methylene)gold(I) chloride (R_p)-**11**.*



GP 1: DMSAuCl (63.0 mg, 214 μmol), (S_p)-4-isocyano[2.2]paracyclophane (50 mg, 214 μmol), bis-((S)-1-phenylethyl)amine (147 mg, 651 μmol), DCM (3 mL), precipitation with DCM/pentane, colourless solid (127 mg, 184 μmol, 85%).

Mp/decomposition: 178 °C; IR (ATR): nu = 3345, 2980, 2928, 2850, 1522, 1492, 1451, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (d, J = 7.2 Hz, 3H), 2.05–2.13 (m, 1H), 2.08 (d, J = 7.2 Hz, 3H), 2.31–2.35 (m, 1H), 2.55–2.60 (m, 1H), 2.65–2.70 (m, 1H), 2.94–3.07 (m, 4H), 5.06 (q, J = 7.1 Hz, 1H), 5.53 (dd, J = 1.7 Hz, J = 7.9 Hz, 1H), 6.17 (dd, J = 1.7 Hz, J = 7.9 Hz, 1H), 6.18 (d, J = 1.6 Hz, 1H), 6.33 (dd, J = 1.7 Hz, J = 7.9 Hz, 1H), 6.36 (d, J = 7.9 Hz, 1H), 6.43 (dd, J = 1.7 Hz, J = 7.9 Hz, 1H), 6.49 (dd, J = 1.7 Hz, J = 7.9 Hz, 1H), 6.93 (d, J = 7.1 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 7.30–7.45 (m, 7H), 7.51 (d, J = 6.7 Hz, 1H), 7.72 (d, J = 7.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 17.4 (q, 1C), 17.5 (q, 1C), 31.5 (t, 1C), 34.1 (t, 1C), 34.8 (t, 1C), 35.2 (t, 1C), 52.4 (d, 1C), 69.1 (d, 1C), 125.8 (d, 1C), 127.5 (d, 1C), 128.2 (d, 2C), 129.0 (d, 1C), 129.1 (d, 2C), 129.1 (d, 1C), 129.2 (d, 1C), 129.8 (d, 2C), 131.6 (d, 1C), 131.9 (d, 1C), 132.5 (d, 1C), 133.3 (d, 1C), 133.6 (d, 1C), 134.2 (s, 1C), 135.6 (d, 1C), 137.4 (s, 1C), 138.0 (s, 1C), 139.2 (s, 1C), 139.3 (s, 1C), 139.6 (s, 1C), 140.9 (s, 1C), 192.1 (s, 1C); MS [FAB(+)]: *m/z* (%) = 690 (71) $[M]^+$, 655 (100) $[M-Cl]^+$; HR-MS [FAB (+)]: $C_{33}H_{34}N_2AuCl$ (691.06), $[C_{33}H_{34}N_2AuCl]^+$: calcd. 690.2076, found 690.2066.

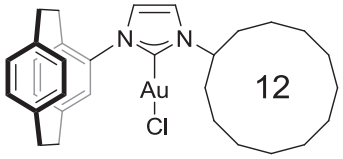
*(1-Isopropyl-3-(S_p)-[2.2]paracyclophane-1H-imidazol-2(3H)-ylidene)gold(I) chloride (S_p)-**15**.*



GP 2: DMSAuCl (45.0 mg, 152 μmol), (S_p)-4-isocyano[2.2]paracyclophane (35.5 mg, 152 μmol), *N*-(2,2-dimethoxyethyl)propan-2-amine (44.7 mg, 304 μmol), DCM (3 mL), 4 M HCl in dioxane (0.54 mL, 2.13 mmol), precipitation with DCM/pentane, colourless crystals (15 mg, 27.2 μmol, 18%).

Mp/decomposition: 140 °C, IR (ATR): nu = 3156, 3129, 2975, 2931, 2851, 1597, 1498, 1433, 1409, 1230, 843, 749, 719 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.54 (d, J = 6.7 Hz, 3H), 1.57 (d, J = 6.7 Hz, 3H), 2.91 (t, J = 6.9 Hz, 2H), 3.00–3.19 (m, 6H), 5.21–5.28 (m, 1H), 6.56–6.77 (m, 7H), 7.21 (s, 1H), 7.28 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.4 (q, 1C), 23.5 (q, 1C), 32.7 (t, 1C), 34.9 (t, 1C), 35.1 (t, 1C), 35.3 (t, 1C), 54.1 (d, 1C), 116.9 (d, 1C), 122.5 (d, 1C), 126.7 (d, 1C), 129.9 (d, 1C), 132.6 (d, 1C), 132.9 (d, 1C), 133.3 (d, 1C), 134.0 (s, 1C), 134.6 (d, 1C), 137.2 (d, 1C), 137.8 (s, 1C), 139.4 (s, 1C), 139.5 (s, 1C), 141.4 (s, 1C), 170.7 (s, 1C); MS [FAB(+)]: *m/z* (%) = 548 (30) $[M]^+$, 513 (100) $[M-Cl]^+$; HR-MS [FAB (+)]: $C_{22}H_{24}N_2AuCl$ (548.86), $[C_{22}H_{24}N_2AuCl]^+$: calcd. 548.1294, found 548.1286.

*(1-Cyclododecyl-3-(S_p)-[2.2]paracyclophane-1H-imidazol-2(3H)-ylidene)gold(I) chloride (S_p)-**16**.*



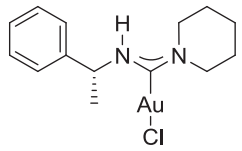
GP 2: DMSAuCl (50 mg, 170 μmol), (S_p)-4-isocyano[2.2]paracyclophane (40 mg, 170 μmol), *N*-(2,2-dimethoxyethyl)cyclododecanamine (93 mg, 340 μmol), DCM (3 mL), 4 M HCl in dioxane (0.6 mL, 2.38 mmol), precipitation with DCM/pentane, colourless solid (110 mg, 163 μmol, 97%).

Mp/decomposition: 150 °C; IR (ATR): nu = 3126, 2928, 2856, 1738, 1596, 1470, 1175, 944, 868, 719 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33–1.55 (m, 16H), 1.65–1.79 (m, 4H), 2.08–2.13 (m, 2H), 2.85–2.95 (m, 2H), 3.02–3.21 (m, 6H), 5.11–5.13 (m, 1H), 6.56–6.80 (m, 7H), 7.16 (s, 1H), 7.26 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.7 (t, 1 C), 21.8 (t, 1C), 23.1 (t, 1C), 23.2 (t, 1C), 23.4 (t, 1C), 23.5 (t, 1C), 23.6 (t, 1C), 23.7 (t, 1C), 23.8 (t, 1C), 31.21 (t, 1C), 31.24 (t, 1C), 32.8 (t, 1C), 34.9 (t, 1C), 35.1 (t, 1C), 35.3 (t, 1C), 58.6 (d, 1C), 117.8 (d, 1C), 122.2 (d, 1C), 126.7 (d, 1C), 129.9 (d, 1C), 132.6 (d,

Please cite this article in press as: V. Göker, et al., Journal of Organometallic Chemistry (2015), http://dx.doi.org/10.1016/j.jorganchem.2015.03.010

1C), 132.9 (d, 1C), 133.2 (d, 1C), 134.0 (s, 1C), 134.5 (d, 1C), 137.2 (d, 1C), 137.8 (s, 1C), 139.3 (s, 1C), 139.5 (s, 1C), 141.4 (s, 1C), 171.3 (s, 1C); MS [FAB(+)]: *m/z* (%) = 637 (30) $[M-Cl]^+$, 502 (40); HR-MS [FAB(+)]: $C_{31}H_{40}N_2AuCl$ (673.08), $[C_{31}H_{40}N_2Au]^+$: calcd. 637.2857, found 637.2864.

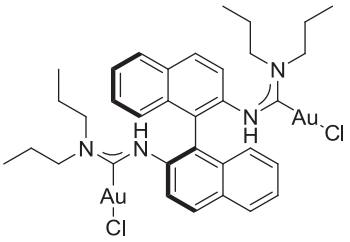
*(R)-((1-Phenylethylamino)(piperidin-1-yl)methylene)gold(I) chloride (R)-**17**.*



GP 1: DMSAuCl (50.0 mg, 169 μmol), (*R*)-(+)-methylbenzylisocyanate (22.3 mg, 169 μmol), piperidine (28.9 mg, 339 μmol), DCM (3 mL), precipitation with DCM/pentane, colourless solid (30 mg, 66.8 μmol, 39%).

Mp/decomposition: 138 °C; IR (ATR): nu = 3156, 3129, 2975, 2931, 2851, 1597, 1498, 1433, 1409, 1230, 843, 749, 719 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 1.58–1.62 (m, 2H), 1.65 (d, *J* = 6.9 Hz, 3H), 1.88–1.91 (m, 4H), 3.26–3.34 (m, 2H), 4.11–4.17 (m, 2H), 5.71 (quint, *J* = 6.9 Hz, 1H), 7.30 (sext, *J* = 4.3 Hz, 1H), 7.36 (d, *J* = 4.3 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 22.4 (t, 1C), 22.5 (q, 1C), 22.5 (t, 1C), 24.2 (t, 1C), 44.5 (t, 2C), 59.4 (d, 1C), 126.5 (d, 2C), 128.0 (d, 1C), 129.0 (d, 2C), 141.9 (s, 1C), 189.0 (s, 1C); MS [FAB(+)]: *m/z* (%) = 448 (25) $[M]^+$, 413 (100) $[M-Cl]^+$; HR-MS [FAB (+)]: $C_{14}H_{20}N_2AuCl$ (448.74), $[C_{14}H_{20}N_2AuCl]^+$: calcd. 448.0981, found 448.0975.

*(S_a)-1,1′-Binaphthylamino-2,2′-(di-n-propylamino)gold(I) chloride (S_a)-**18**.*



GP 1: DMSAuCl (49 mg, 160 μmol), (*S*)-2,2′-diisocyano-1,1′-binaphthyl (25 mg, 82 μmol), di-*n*-propylamine (33 mg, 320 μmol), DCM (3 mL), precipitation with DCM/pentane, colourless solid (56 mg, 58 μmol, 73%).

Mp/decomposition: 120 °C; IR (ATR): nu = 3259, 2927, 2852, 1536, 1495, 1263, 1092, 792, 717 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 6H), 1.22–1.30 (m, 4H), 1.57–1.68 (m, 4H), 2.56–2.70 (m, 4H), 3.51–3.60 (m, 2H), 4.11 (quint, *J* = 6.9 Hz, 2H), 6.73 (s, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 10.7 (q, 2C), 11.1 (q, 2C), 19.4 (t, 2C), 22.3 (t, 2C), 49.6 (t, 2C), 61.4 (t, 2C), 124.1 (d, 2C), 125.4 (d, 2C), 125.6 (s, 2C), 126.7 (d, 2C), 128.4 (d, 2C), 129.1 (d, 2C), 129.8 (d, 2C), 131.9 (s, 2C), 132.2 (s, 2C), 137.1 (s, 2C), 189.9 (s, 2C); MS [FAB(+)]: *m/z* (%) = 970 (20) $[M]^+$, 935 (40) $[M-Cl]^+$; HR-MS [FAB(+)]: $C_{34}H_{42}N_4AuCl_2$ (971.56), $[C_{34}H_{42}N_4AuCl]^+$: calcd. 935.2429, found 935.2408.

Acknowledgements

The authors thank Umicore AG & Co. KG for the generous donation of gold salts.

Appendix A. Supplementary material

CCDC 1051507 and 1045758 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.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.03.010.

References

[1] H. Schmidbaur, A. Grohmann, M.E. Olmos, in: H. Schmidbaur (Ed.), Gold - Progress in Chemistry, Biochemistry and Technology, Wiley, Chichester, 1999, pp. 648–745.
[2] For the discussion of this misconception, see: H. Schmidbaur Naturw. Rdsch 48 (1995) 443–451.
[3] J. Elzinga, M. Rosenblum, Organometallics 2 (1983) 1214–1219.
[4] B.F.G. Johnson, C.M. Martin, P.J. Dyson, Coord. Chem. Rev. 175 (1998) 59–89.
[5] M. Austeri, M. Enders, M. Nieger, S. Bräse, Eur. J. Org. Chem. (2013) 1667–1670.
[6] T. Focken, G. Raabe, C. Bolm, Tetrahedron Asymmetry 15 (2004) 1693–1706.
[7] A. Pradal, C.-M. Chao, M.R. Vitale, P.Y. Toullec, V. Michelet, Tetrahedron 67 (2011) 4371–4377.
[8] J. Felix, D. Weber, O. Gutierrez, D.J. Tantillo, M.R. Gagné, Nat. Chem. 4 (2012) 405–409.
[9] W. Duan, Y. Ma, F. He, L. Zhao, J. Chen, C. Song, Tetrahedron Asymmetry 24 (2013) 241–248.
[10] R.J. Seacome, M.P. Coles, J.E. Glover, P.B. Hitchcocka, G.J. Rowlands, Dalton Trans. 39 (2010) 3687–3694.
[11] CCDC 1051507 ((*S*$_p$)-**4**) and 1045758 ((*S*,*S*)-(*R*$_p$)-**11**) 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
[12] A.S.K. Hashmi, T. Hengst, C. Lothschütz, F. Rominger, Adv. Synth. Catal. 352 (2010) 1315–1337.
[13] A.S.K. Hashmi, C. Lothschütz, C. Böhling, F. Rominger, Organometallics 30 (2011) 2411–2417.
[14] (a) B. Bechem, Dissertation 2010, Universität Heidelberg; (b) Compare: A.S.K. Hashmi, M. Hamzic, F. Rominger, J.W. Bats Chem. Eur. J. 15 (2009) 13318–13322.
[15] Y. Matsumoto, K.B. Selim, H. Nakanishi, K. Yamada, Y. Yamamoto, K. Tomioka, Tetrahedron Lett. 51 (2009) 404–406.
[16] K. Yamada, Y. Matsumoto, K.B. Selim, Y. Yamamoto, K. Tomioka, Tetrahedron 68 (2012) 4159–4165.
[17] S. Clément, L. Guyard, M. Knorr, S. Dilsky, C. Strohman, M. Arroyo, J. Organomet. Chem. 692 (2007) 839–850.