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Synthesis and Properties of Hydrazino Amino Acyclic Carbenes of Gold(I), Platinum(II), Palladium(II) and Rhodium(III)

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Dedicated to Assoc. Prof. Uno Mäeorg.

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Abstract: The nucleophilic addition of protected and substituted hydrazine derivatives to isonitrile complexes of gold(I), platinum(II), palladium(II) and rhodium(III) provides the corresponding hydrazino amino acyclic carbene complexes. These are characterized by their spectroscopic data, four different X-ray single crystal structure analyses and their catalytic activity in the gold(I)-catalyzed cycloisomerization of *N*-propargylcarboxamides to alkylideneoxazolines is investigated.

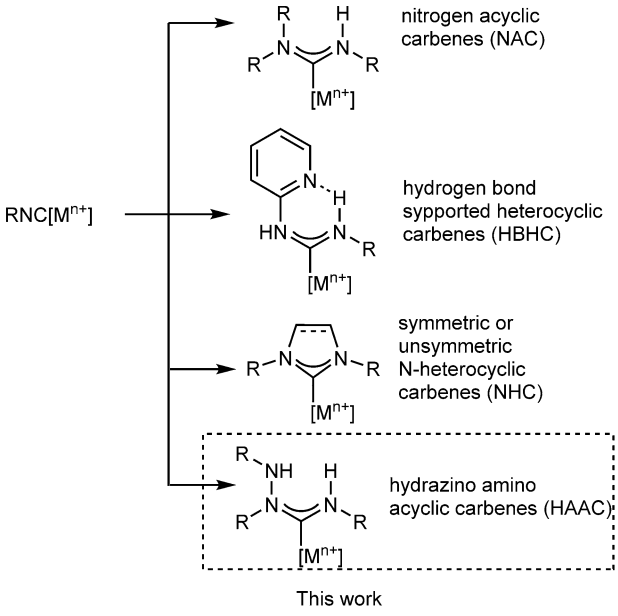
Keywords: carbene ligands; cyclization; gold; homogeneous catalysis; hydrazines

Introduction

Numerous reports on N-heterocyclic carbenes (NHC) have attracted significant attention, as these compounds perform exceedingly well as ligands in organometallic chemistry.[1] Besides the remarkable stability of the obtained NHC complexes, the easy tunability of their properties has contributed to the success of this class of ligands. More recently, nitrogen acyclic carbenes (NAC, also known as acyclic diamino carbenes, ADC) and hydrogen-bond supported heterocyclic carbenes (HBHC) have been used in catalysis, too.[2] These carbene ligands open up the possibility to further vary the electronic and steric properties of the carbene ligands as they do not possess the rigid cyclic backbone of the NHC ligands.[3] Based on pioneering work of Crociani, Bonatti and Minghetti,[4] an easy and high-yielding synthesis of transition metal-NAC and transition metal-NHC complexes, which makes use of the reactivity of coordinated isonitriles was recently developed (Scheme 1).[5,6]

In contrast to the approaches mentioned above, hydrazines have received much less attention as ligands than they have received as target molecules in synthesis, especially if compared to amines.[7]

Two possible reasons for this trend stand out: the hydrazine's ability to act as a ligand with transition metals and therefore deactivate the catalysts and its potential to reduce metals.[8] Even more rarely, have hydrazines been used as part of the ligands.[9]



Scheme 1. Different carbene complexes obtained from metal-bound isocyanides.

In spite of the reports of Chugaev, who already in 1915 published the formation of a bridged carbene from the reaction of hydrazine and a bisisocyanide complex of platinum,[10] only few reports on the use of hydrazines as part of a ligand can be found. Recently, the synthesis of a chiral hydrazino-NHC from imidazolium derivatives was reported, however this multistep synthesis with unstable intermediates is not very suitable for a systematic synthesis of the metal complexes.[11] Furthermore, hydrazones, *p*-nitrophenylhydrazine and acylhydrazine were also reported to add to palladium isonitrile complexes to yield acyclic carbene complexes.[12]

While a free persistent amino hydrazino carbene has been reported by the Bertrand group,[13] we here report on the synthesis of **H**ydrazino **A**mino **A**cyclic **C**arbene (HAAC) complexes of gold, palladium, platinum and rhodium, *via* the nucleophilic addition of a selection of substituted hydrazines to metal-coordinated isonitriles. This constitutes the first report of such a ligand being employed on gold, platinum or rhodium.

Results and Discussion

Synthesis

As a first test reaction a *tert*-butylisonitrilegold(I) complex was reacted with $BocNHNH_2$. In comparison to aliphatic amines, hydrazines proved to be less reactive and significantly longer reaction times were observed. As shown in Figure 1, the typical conditions used for amines, 0.1 M solution of the isonitrile complex in DCM in combination with 4 equiv. of $BocNHNH_2$ reached only 80% conversion after 11 days at room temperature.

When the temperature was raised to 45 °C, the reaction proceeded more readily, 90% conversion was achieved after 5 days, but the isolated yield was only 54%. However, in more concentrated solution (0.5 M) full conversion and 80% yield of HAAC was obtained in only 2.5 days at room temperature.

An investigation of the scope by varying the isonitrile precursors in combination with $BocNHNH_2$ revealed that the reaction proceeds equally well with aromatic and aliphatic isonitrile complexes. Sterically bulky isonitrile substituents were also tolerated well (**1a**, **1b** and **1f** *vs.* **1c**, Table 1). All of the obtained HAAC complexes are stable in non-acidic solution, allowing an easy purification by silica gel chromatography. However, they decompose rather rapidly in the presence of traces of acid (e.g., in $CDCl_3$ solution, thus the NMR characterization was done in CD_2Cl_2 or DMSO-d_6).

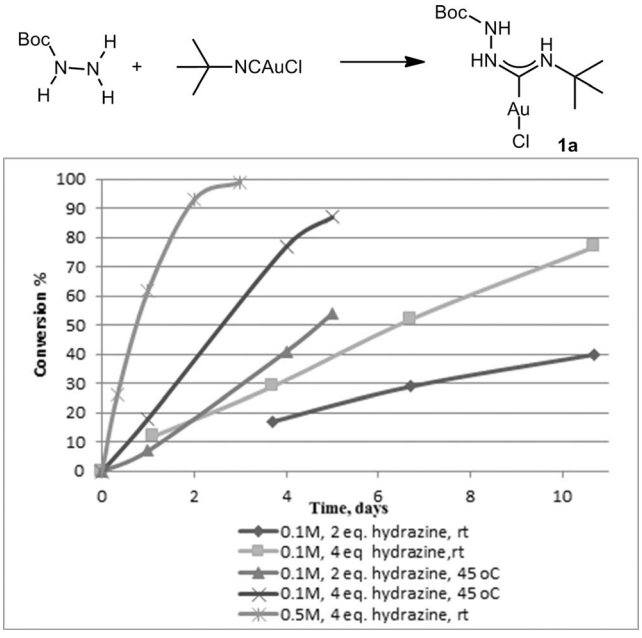
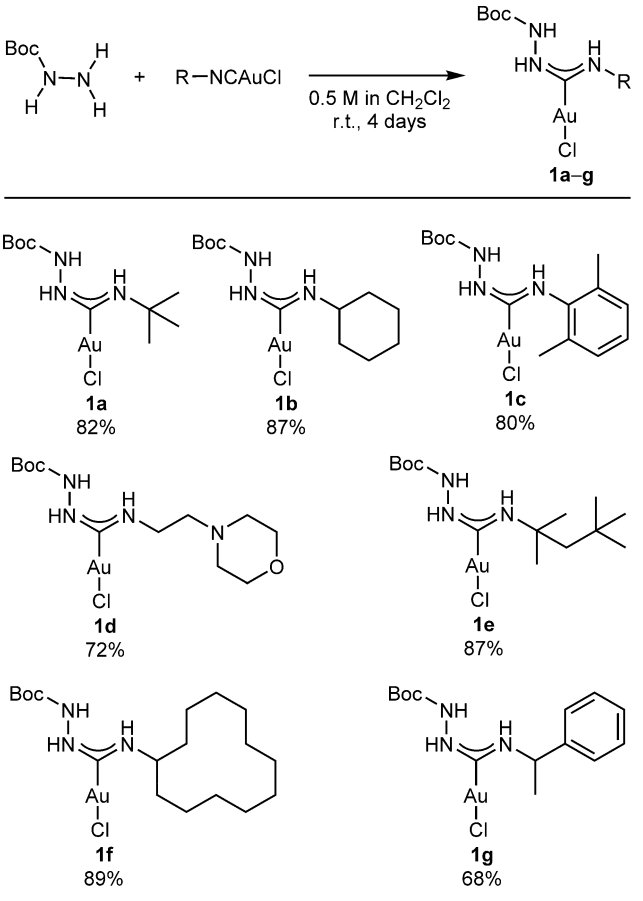


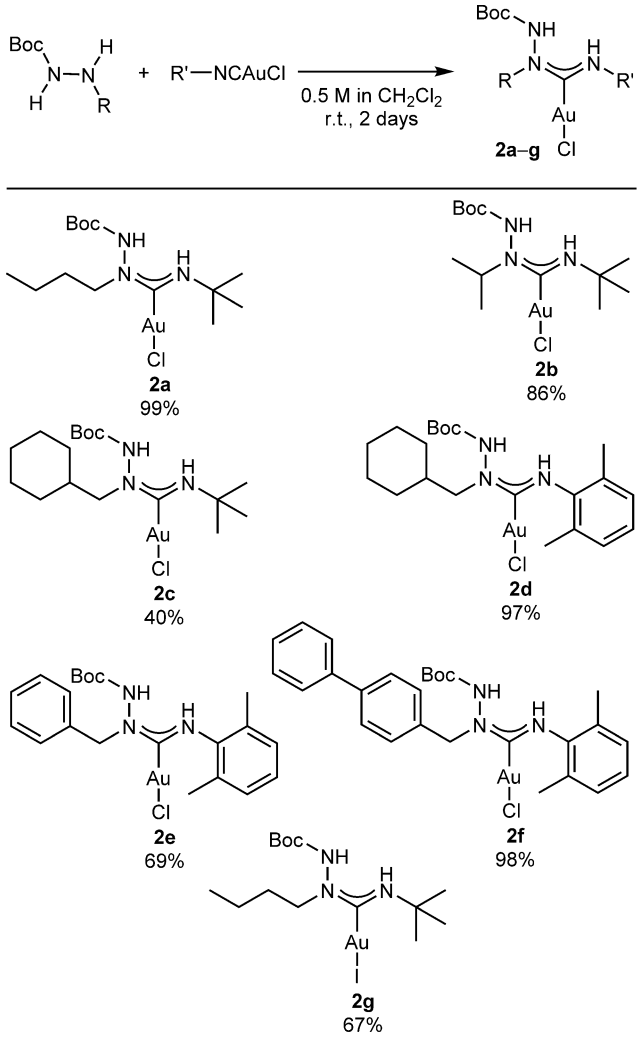
Figure 1. Conversions of *tert*-butylisonitrilegold(I) chloride in the reaction with $BocNHNH_2$ in CD_2Cl_2; mesitylene was used as internal standard (integration in the ^1H NMR spectrum).

Table 1. The scope of isonitrile complexes of gold in the reaction with $BocNHNH_2$.



Next, we explored the scope with regard to different hydrazine components (Table 2). The reaction of 1-butyl-2-Boc-hydrazine with *tert*-butylisonitrilegold(I) chloride generated the corresponding HAAC complex **2a** in almost quantitative yield. In addition, based on the increased nucleophilicity, the reaction was complete within only 2 days with only 2 equivalents of the hydrazine derivative. A more sterically demanding isopropyl-substituted hydrazine reacted in a very good yield as well (**2b**). However, a β-branched substrate resulted in an incomplete conversion after 3 days at room temperature (**2c**, 54% of the starting material were recovered, this corresponds to a yield of 87% based on recovered starting material), implying an undesirable steric interaction of the isonitrile and the hydrazine. The reactivity could be restored by the use of an aryl-isonitrile complex which due to the planar sp^2-centre next to the isonitrile nitrogen is sterically less demanding. With this substrate an excellent yield was obtained (**2d**). As a consequence other ß-branched substrates were reacted with this isonitrile as well (**2e** and **2f**). In the case of benzyl-substituted hydrazine (entry 5), the low solubility of the obtained HAAC resulted in a slight drop in yield. A biphenyl moiety in hydrazine was well tolerated and the resulting HAAC was obtained in excellent yield (entry 6). In conclusion, substituted and carbamate-protected hydrazines proved to be good staring materials for the formation of the new HAAC gold(I) complexes, by employing their good nucleophilicity without the reduction of the noble metal precursor.

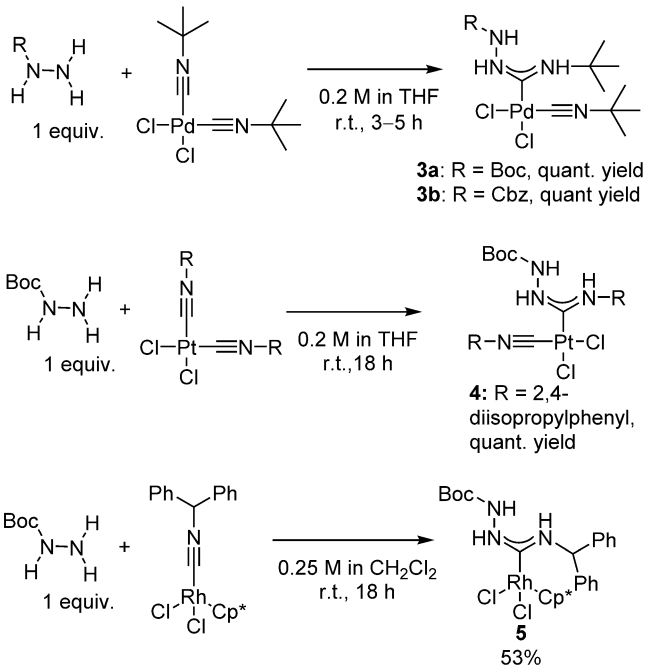
Table 2. The scope of hydrazines in the reaction with isonitrilegold halides.



Recently, it was reported that gold iodides are superior to chlorides and bromides in cycloaddition reactions of gold isonitrile complexes.[14] Therefore, we decided to test if the use of *tert*-butylisonitrilegold(I) iodide would accelerate the reaction. However in our reactions, the influence of iodide as ligand on the reaction outcome was different. For *tert*-butylisonitrilegold iodide, the reaction with $BocNHNH_2$ resulted in the formation of a golden mirror on the wall of the reaction vessel, indicating a reduction of the gold under these conditions. Reaction with isopropyl-substituted hydrazine gave low conversion and only traces of HAAC complex and the reaction with *n*-butyl-substituted hydrazine gave 67% of the desired carbene complex (entry 10, Table 2). On the other hand, when **1a** was treated with NaI in DCM, the slow formation of metallic gold was observed, which points to an intrinsically lower stability of HAACAuI complexes in comparison to the corresponding chloride complexes, which contributes to the less successful reaction outcome.

Subsequently, HAAC complexes of other transition metal were prepared by taking advantage of the developed method (Scheme 2). The reactions using dichloro-bis-isonitrilepalladium(II) complexes with $BocNHNH_2$ and $CbzNHNH_2$ resulted in quantitative yields of the new carbene complexes. Like in the case of amines as nucleophile,[6a] only one of the isonitrile ligands reacted with the hydrazine and no further cyclization leading to Chugaev-type biscarbenes was observed. In the case of palladium only 1 equiv. of hydrazine was necessary for a quantitative conversion and the reactions were completed within hours. The reaction did not tolerate a substitution on the reacting nitrogen of the hydrazine, probably due to a higher steric shielding of the metal, and only a minor conversion was detected (in the crude NMR). Palladium complexes featuring hydrazine- or *p*-nitrophenylhydrazine-based acyclic carbenes as ligands have been shown to have catalytic activity in Sonogashira cross-couplings.[15]

The tested platinum(II) complex reacted equally well, providing its corresponding HAAC-Pt complex in quantitative yield after 18 hours. The rhodium isonitrile complex $Cp^*(Ph_2CHNC)RhCl_2$ also reacted



Scheme 2. Different carbene complexes obtained from metal-bound isocyanides.

and the corresponding HAAC complex (mixture of 2 rotamers) was obtained in 53% yield after recrystallization.

Structure

Some of the obtained HAAC complexes could be studied by X-ray crystallography.[16] The structures of gold and rhodium complexes are shown in Figure 2 and bond lengths and angles are summarized in Table 3. Overall, carbene structural parameters are similar to those reported for NAC gold compounds.[2c] The carbene ligands are planar (the sum of angles is 359.8–360°) and the C–Au–Cl angle is very close to linearity. The bulky *N*-Boc unit is always pointing away from the carbene part to minimize steric interactions. The gold-carbene bond shows little variation, remaining between 1.98–1.99 Å (for known NACAuCl: 1.995–2.015 Å). The Au–Cl bond length is between 2.261–2.281 Å. The N2–C1–N3 angles are very similar to those reported in gold NAC complexes, N3–C1–Au and N2–C1–Au angles depend on the steric bulkiness of the substituents on the corresponding nitrogen atoms of the carbene. For instance, in the case of **2f**, the sterics are roughly similar, so are the angles. With the larger difference in the case of **1a** (BocNHNH is pointing away from the metal and therefore has less sterical impact than *t*-BuNH), the bond angles also differ significantly (7–14°). In the case of the rhodium HAAC **5**, the steric bulkiness between BocNHNH and Ph_2CHNH groups is even larger, hence the big difference in the bond angles (17°). No intramolecular hydrogen bonding between the carbonyl group of Boc and carbene NH is detected in the solid state. In the case of **1f**, and partially **1a**, it would appear that intermolecular hydrogen

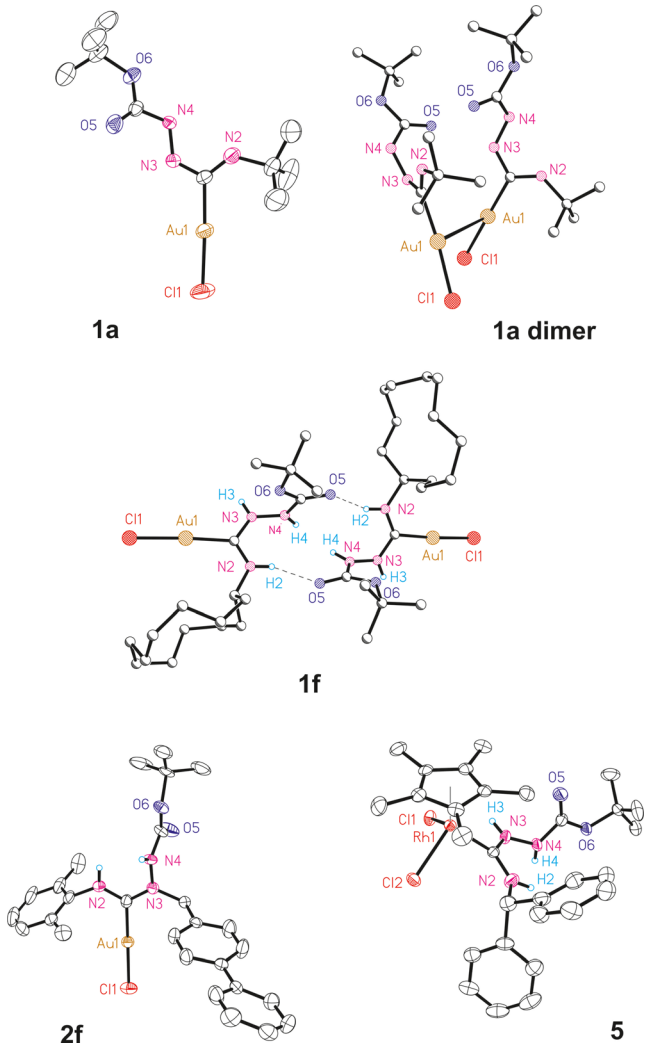


Figure 2. Solid state molecular structures of **1a**, **1f**, **2f** and **5**.

Table 3. Selected bond lengths and angles from **1a**, **1f**, **2f** and **5**. Averaged values are given for **1a** and **1f**.

HAAC	**1a**	**1f**	**2f**	**5**
M–C1	1.983(9)	1.98(2)	1.990(7)	2.052(4)
M–Cl	2.261(3)	2.281(7)	2.2800(18)	–
C1–N3	1.341(10)	1.34(2)	1.329(8)	1.344(5)
C1–N2	1.322(11)	1.30(2)	1.327(8)	1.315(4)
N3–N4	1.394(9)	1.38(2)	1.408(7)	1.394(4)
N2–C1–N3	116.0(8)	117.3(19)	117.3(6)	114.0(3)
N3–C1–M	117.2(6)	118.7(16)	121.8(5)	114.1(2)
N2–C1–M	126.7(7)	124.0(16)	120.8(5)	131.8(3)
C1–M–Cl	175.7(3)	176.1(7)	177.26(19)	–

bonding exists in crystals, in particular **1f** seems to have crystallized as hydrogen bonded dimer from CH_2Cl_2. **1a** has three independent molecules in the crystal and only two of them exhibit an aurophilic interaction [Au–Au bond 3.2536(5) Å].

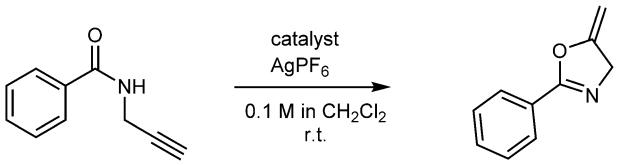
In addition, the buried volumes, based on X-ray structures, were calculated for some complexes.[17] They are 41.6% and 37.7% for **1a** and **1g**, and 36.2% for **2f**. The maps for the steric hindrance are shown in the Supporting Information. All the buried volumes are very similar. Interestingly, while **2f** has the smallest value, the hindrance provided by the ligand is more distributed along the perimeter of the coordination sphere.

Catalysis

As a next step we tested the catalytic properties of the synthesized gold(I) HAAC complexes (Table 4). The gold-catalyzed oxazoline synthesis was chosen as a test reaction, due to its reliability and well-understood mechanism.[18] All tested HAAC catalysts gave good to excellent yields, and perfect selectivity. Among the tested catalysts, HAAC **1** without any additional substitution at the nitrogen atom, led to lower reaction rates (only 10–22% of product after 3 hours). But even after longer reaction times no significant drop in catalytic activity was observed and good yields could be obtained after 2 days (entries 1–4). The more bulky catalysts **2d** and **2f** delivered higher conversions after 3 hours (entries 5 and 6) and a good stability was maintained after longer reaction times.[19] Reducing the catalytic loading of **2a** from 1 mol% to 0.5 mol% or even to 0.1 mol% resulted in slight drop in catalytic activity, although the general conversion profile looked very similar (entries 7–9). However, it should be noted that when we tried to run the reaction with the gold catalyst **2a**, that was activated with silver salt prior to the catalysis reaction, only sluggish conversions were obtained. This is probably the consequence of reduced stability of cationic gold HAAC complex. When activation with silver is performed in the absence of substrate, rapid decomposition occurs and no catalytic activity is observed. Activation in the presence of substrate however leads to conversion. That means that the substrate "stabilizes" the catalyst. With 0.1% loading there is a higher ratio between substrate and catalyst and therefore stabilization is more efficient. In the case of a copper salt instead of a silver salt for the activation,[20] no catalytic activity at all was observed.

As this is a known reaction, the results of our catalytic screening can be compared to previous catalytic systems. The same reaction with 5% $AuCl_3$ gave 95% yield after 12 hours (entry 10),[21] another publication emanating from our group reported that 2 mol% PPh_3AuNTf_2 gave 91% yield (entry 11).[22] A more exotic system reported previously by our group featuring a boronated alkyne-gold complex yielded 98% after 12 hours with a 2 mol% loading.[23] Finally, 10% of a copper salt gave only 73% of product after an overnight reaction.[24] As can be seen from Table 4, the best catalyst reported here with only 1 mol% loading gave 95% NMR yield overnight (Table 4, entry 6). As such, our system is at least as efficient as those reported before.

Table 4. Gold-catalyzed oxazole synthesis. NMR yields, using mesitylene as internal standard are shown. The HAAC catalysts were activated with $AgPF_6$ in the presence of the substrate.



Entry	Catalyst (amount)	Time	Yield
1	**1a** (1 mol%)	3 h	18%
		18 h	50%
		2 days	76%
2	**1b** (1 mol%)	3 h	10%
		18 h	56%
		2 days	83%
3	**1d** (1 mol%)	3 h	14%
		18 h	39%
		2 days	71%
4	**1e** (1 mol%)	3 h	22%
		18 h	68%
		2 days	98%
5	**2d** (1 mol%)	3 h	27%
		18 h	72%
		2 days	100%
6	**2f** (1 mol%)	3 h	50%
		18 h	95%
		2 days	100%
7	**2a** (1 mol%)	3 h	21%
		18 h	61%
		2 days	93%
8	**2a** (0.5 mol%)	3 h	24%
		2 days	92%
9	**2a** (0.1 mol%)	3 h	18%
		2 days	88%
10[a]	$AuCl_3$ (5%)	12 h	95%
11[b]	PPh_3AuNTf_2 (2%)	24 h	91%

[a] From ref.[21]
[b] From ref.[22]

Conclusions

We have developed an efficient modular synthesis of new HAAC complexes of gold(I), palladium(II), platinum(II) and rhodium(III). These simple and easy re-

actions between hydrazines and metal-isonitrile complexes proceed under mild conditions which allow the synthesis of the target compounds without reduction of the noble metal centres. The developed method serves an easy access to a novel type of ligand. The catalytic ability of the obtained complexes was demonstrated by the gold-catalyzed oxazoline synthesis that could be accomplished in remarkable yields even at low catalytic loadings.

Experimental Section

General Procedure for the Synthesis of HAAC Complexes of Gold (GP)

Isonitrilegold chloride (0.1 mmol) was dissolved in DCM (0.2 mL) and hydrazine (0.4 mmol of monosubstituted hydrazine or 0.2 mmol of disubstituted hydrazine) was added. The obtained slurry/solution was stirred until the starting gold compound was consumed (TLC). Then, the reaction mixture was directly transferred onto the column and the HAAC complex was isolated by column chromatography on silica gel using mixtures of dichloromethane and ethyl acetate as an eluent.

{[2-(*tert*-Butoxycarbonyl)hydrazinyl](*tert*-butylamino)methylene}gold(I) chloride (1a): According to the GP, the reaction was run using 33.5 mg (0.1 mmol) of *t*-butylisonitrilegold chloride and 52.8 mg (0.4 mmol) of $BocNHNH_2$ for 4 days and compound **1a** was purified using DCM:ethyl acetate 20:1 as eluent; yield: 39 mg (82%); white solid; mp 109.8 °C (dec.); R_f (DCM:ethyl acetate 20:1) = 0.18. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.55$ (s, 1H, BocNH), 7.36 (br, 1H, NH), 6.06 (br, 1H, NH), 1.59 [s, 9H, $C(CH_3)_3$], 1.49 (s, 9H, Boc); ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2): $\delta = 189.97$ (s), 154.30 (s), 84.12 (s), 54.70 (s), 31.40 (q), 28.36 (q); FT-IR (ATR): $\nu = 3166$, 3139, 2966, 1873, 1596, 1470, 1400, 1386, 1190, 1135, 1058, 966, 840, 804, 757, 610 cm^{-1}; HR-MS (FAB$^+$): $m/z = 412.2374$, calcd. for [M−Cl]: 412.2592.

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