Synthesis of a transient tropylidene substituted N-heterocyclic carbene (tropNHC): rearrangement and formation of its gold complex†

Carsten Böhler, Daniel Stein, Nicola Donati and Hansjörg Grützmacher*

Laboratory of Inorganic Chemistry, Department of Chemistry, ETH-Hönggerberg, CH-8093, Zürich, Switzerland. E-mail: gruetzmacher@inorg.chem.ethz.ch; Fax: ++41 1 632 10 90; Tel: +41 1 632 10 90

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The condensation reaction of the primary tropylidenyl amine tropamine **2** [IUPAC: (5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine] with glyoxal, OHC–CHO (**3**), leads to the corresponding 1,4-diazadiene bistropdad **4** [IUPAC: 1,4-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene] in high yield. With formaldehyde and ethereal HCl, **4** is transformed to the bistropimidazolium salt **5** [IUPAC: 1,3-bis(5*H*-dibenzo[*a*,*d*]cycloheptenyl)imidazolium chloride]. Deprotonation with KO*t*Bu in thf did not gave a stable N-heterocyclic carbene bistropNHC **6** but the imidazole derivative 2-(5*H*-dibenzo[*a*,*d*]cyclohepten-10-yl)-1-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1*H*-imidazole **9** as a product of a rearrangement. However, the unstable carbene **6** can be trapped when it is generated in the presence of [AuCl(PPh$_3$)] whereby the stable cationic mixed phosphane carbene gold complex {[1,3-bis(5*H*-dibenzo[*a*,*d*]cycloheptenyl)imidazol-2-ylidene][triphenylphosphine]gold(I)} chloride **10** is obtained which was characterised by X-ray diffraction.

Introduction

N-Heterocyclic carbenes[1,2] belong to the most strongly binding ligands for a wide range of transition metals and are intensively used in highly efficient catalytic processes.[3–6] We have reported the synthesis of the tropp ligand 1 shown below which due to its rigid concave shaped binding site proved to form very stable complexes with late transition metals.[7] Also, this ligand allows the isolation of complexes with the metal centre in an unusual low formal oxidation state. In particular, paramagnetic d^9 and anionic d^{10} valence electron configured rhodium and iridium complexes were isolated.[8,9] These may find interesting applications in bond activation chemistry.[10] It was tempting to try to mount a N-heterocyclic carbene (NHC) binding site onto the tropylidene platform in order to obtain particularly stable complexes. Here we report the first results of these efforts.

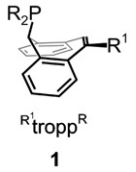

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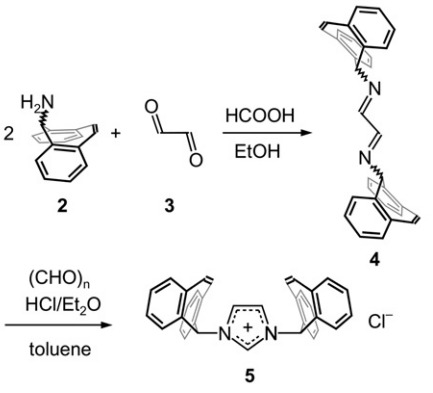
Chart 1 Representation of the tropp ligand system.

Results and discussion

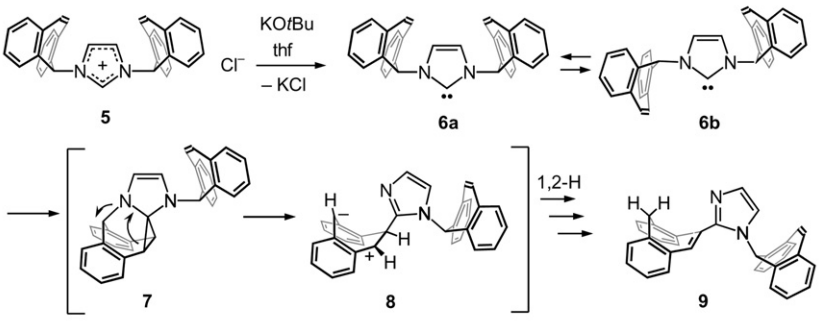
The synthesis of N-heterocyclic carbenes is most commonly achieved by deprotonation of the corresponding azolium salt.[1,2] For our purposes, we chose as the method for the azolium synthesis the three-component approach using glyoxal, a primary amine, and formaldehyde as reagents.[11] In particular, we employed the variant where 1,4-diazadiene as primary condensation product between the amine and glyoxal is isolated before reacting it further with formaldehyde.[12,13] Thus (5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine **2**[14] (dibenzotropylidenylamine = tropamin) was reacted with glyoxal **3** in ethanol in the presence of a trace of formic acid (Scheme 1).

The resulting 1,4-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene **4** (bistropdad) was obtained in high yield (> 90%). The compound is only sparingly soluble in most common organic solvents but can be re-crystallised from hot toluene or thf as white micro-crystals forming a cotton-like substance. In the ^{1}H NMR spectrum recorded in [D$_8$]dimethylsulfoxide (dmso), only broad signals are observed for all protons indicating a dynamic equilibrium between isomers in which the NCHCHN unit may be either bound equatorially (*exo*-isomer) or axially (*endo*-isomer) in the 5-position of the dibenzocycloheptenyl ring. Subsequently, the bistropdad **4** is reacted with a freshly prepared solution of formaldehyde in



Scheme 1 Synthesis of bistropdad **4** and bistropimidazolium **5**.

† Dedicated to Professor Walter Siebert on the occasion of his 65th birthday.



Scheme 2 Deprotonation of **5** and formation of the rearranged product **9**.

toluene and an equimolar amount of ethereal HCl (2 M). In a period over two days, the 1,3-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)imidazolium chloride **5** (bistropimidazolium) precipitates in good yield (≈80%) as a yellow powder. This compound is soluble in halogenated solvents such as methylene chloride and chloroform but little soluble in thf. In the ^{1}H and ^{13}C NMR spectra, sharp resonances are observed indicating either rapid equilibrium or—more likely—slow exchange between the *endo*- and *exo*-isomers. Steric considerations show that the *endo*-form shown in Scheme 1 should be the preferred isomer.

In view of the bulky trop-substituents at the nitrogen centres, we hoped to obtain the free N-heterocyclic bistropylidenylcarbene, bistropNHC **6**, *via* deprotonation of the imidazolium salt **5**. We used the "classical" method for this reaction,[15] *i.e.* KO*t*Bu in thf as base (Scheme 2).

Indeed, when KO*t*Bu is added to a suspension of **5** in thf, a clear solution is obtained immediately. After usual work-up and re-crystallisation from an *n*-hexane/toluene mixture, pale yellow crystals were obtained. The isolated compound **9** showed complex ^{1}H NMR and ^{13}C NMR spectra which was not compatible with the structure of the free carbene **6**. Because of extensive overlapping of the NMR signals, the exact nature of **9** was clarified by an X-ray analysis. The result of this investigation is shown in Fig. 1 below.

Instead of the carbene **6**, 2-(5*H*-dibenzo[*a*,*d*]cyclohepten-10-yl)-1-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1*H*-imidazole **9** is obtained as the major product in about 45% isolated yield. Formally this product is obtained by mutual exchange of a proton and a tropimidazole residue. We assume that this reaction proceeds *via* the mechanism depicted in Scheme 2. Starting from a conformation like **6b** where the carbene function comes into contact with the C=C double bond of the dibenzotropylidene ring, an intramolecular cyclopropanation may occur leading to the polycyclic aza-barbaralane **7**.[16] Cyclopropanations of some stable singlet carbenes, *i.e.* Bertrand-type carbenes $R_2P–C:–R^1$, are well known but have not been reported for NHC's yet.[1] The intermediate **7** may then endure a ring opening of the cyclopropane unit with concomitant C–N bond cleavage in the 5-tropylidene position leading to the zwitterionic product **8**. This intermediate finally rearranges *via* subsequent 1,2-H shifts to give the stable compound **9**. We followed the reaction of the bistropimidazolium **5** with KO*t*Bu by NMR spectroscopy but were unable to detect the free carbene with certainty.

The synthesis of N-heterocyclic carbene metal complexes using an imidazolium salt and reacting it either with a deprotonating agent in the presence of a transition metal precursor or using a sufficiently basic transition metal complex, *i.e.* transition metal alkoxides, has a long history[17,18] (see also ref. 15). We reacted [AuCl(PPh_3)] with bistropimidazolium **5** and KO*t*Bu in thf as solvent (Scheme 3).

The reaction mixture becomes initially yellow at room temperature and after a short period of heating turns deep red. After usual work-up and re-crystallisation, the gold complex **10** is obtained in about 60% isolated yield as a pale red crystalline substance which is analytically pure (we assume that the reddish colour is caused by very minor amounts of an impurity). The ^{31}P NMR spectrum shows one sharp signal at 42.2 ppm which is typical for cationic bivalent gold complexes. In the ^{13}C NMR spectrum, a sharp resonance at 207.3 ppm is detected for the carbene carbon nucleus. The olefinic protons of the double bond in the tropylidene unit were not assigned and are buried under the signals of the aromatic protons. In a small tube, clear needle shaped crystals were grown which were used to further characterise compound **10** by an X-ray analysis (*vide infra*).

Molecular structures of 9 and 10

The molecular structures of compounds **9** and **10** are shown in Fig. 1 and 2, respectively. Selected bond lengths and angles for these two compounds are listed in Table 1 and Table 2. Details concerning the data collection and refinement are given in Table 3 in the experimental section.

The structure of the imidazole **9** does not show any particular features. The carbon–carbon double bonds, C4=C5, C4a=C5a, and C16=C17, show the expected lengths (1.33–1.35 Å). There is only little alternation of the bond lengths

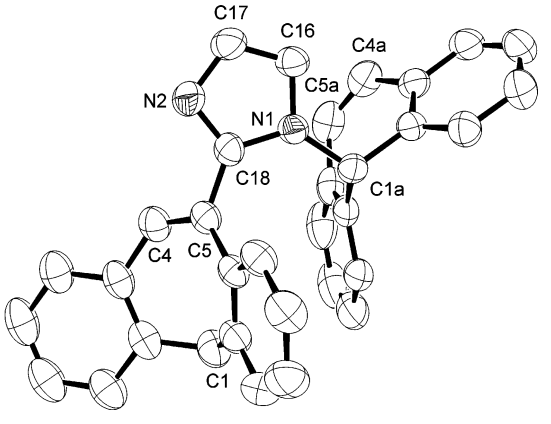
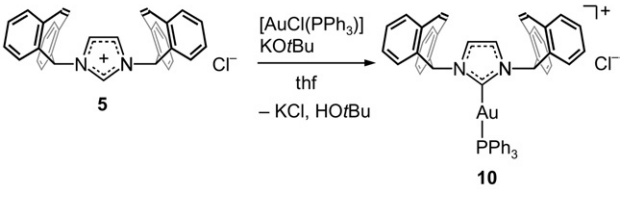


Fig. 1 ORTEP plot of the molecular structure of **9**.



Scheme 3 Synthesis of the tropNHC complex **10**.

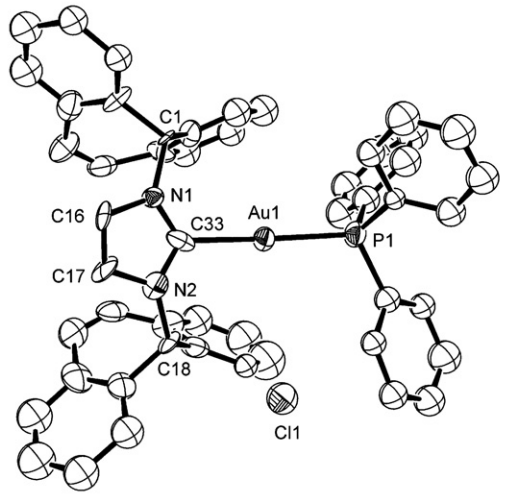


Fig. 2 ORTEP plot of the molecular structure of **10**.

in the planar imidazole ring (see entries 2–6 in Table 1). Both tropylidene units show a boat conformation and the bulky 2-(5*H*-dibenzo[*a*,*d*]cyclohepten-10-yl)-1-imidazolyl residue binds as expected in the axial position of the tropylidene unit at N1.

Bivalent gold carbene complexes with N-heterocyclic carbene ligands are known and several structures of neutral and cationic derivatives have been determined.[19–25]

Quantum chemical calculations revealed that the carbene ligand is especially strongly bound to gold [ClM(NHC) → ClM + NHC; D_e(M = Cu) = 67.4, D_e(M = Ag) = 56.5, D_e(M = Au) = 82.8 kcal mol^{-1}].[26] Complex **10** is a further example of a cationic bivalent gold NHC complex (Au···Cl 4.707 Å), however, to our knowledge the first example of a mixed phosphane, NHC gold complex. The Au–C33 distance [2.111(7) Å] is slightly but significantly longer than the bond lengths which were observed in other cationic bis(carbene) complexes of gold, $[Au(NHC)_2]^+$ (Au–C: 1.99–2.027 Å).[19,20,22] The P–Au–C angle (173.8°) deviates from the expected linear arrangement and the plane of the NHC ligand forms an angle of about 15° with the C33–Au axis. Also the sum of the bond angles around the carbene carbon atom C33 is at 356.4° smaller than the expected 360°. All these data reflect the rather high steric congestion within complex **10** although the elongated Au–C distance may be also due to the *trans*-influence of the PPh_3 ligand. Despite this steric encumbrance, we found in preliminary experiments that complex **10** is remarkably stable. Reaction with strong acids (CF_3COOH or H_2SO_4) or oxidants (H_2O_2) did not lead to a displacement of the PPh_3 group which we attempted to enforce an interaction of the gold centre with the olefinic units of the tropylidene rings. In the solid state structure of complex **10**, these are both turned away from the metal centre and point to the same side of the NHC ring.

Conclusion

The condensation reaction of tropamine **2** with glyoxal **3** led to the corresponding 1,4-diazadiene bistropdad **4** in high yield which could be successfully converted to the imidazolium salt bis(tropimidazolium) **5**. With KO*t*Bu in thf, **5** can be deprotonated to yield the N-heterocyclic carbene bistropNHC **6** as an instable intermediate. Although **6** could not be observed with certainty, its formation seems highly likely. *Via* an initial intra-molecular cyclopropanation reaction to an aza-barbarlane, it rearranges to the stable 1*H*-imidazole derivative **9** which was isolated in moderate yield. Furthermore, we succeeded in the synthesis of a gold bistropNHC complex **10** which expands the class of functionalised carbene[15] complexes. Our efforts will focus on the synthesis of metal complexes in which the bistropNHC **6** serves as a chelating ligand offering a strongly σ-donating moiety (*i.e.* the carbene centre) and π-accepting functions (*i.e.* the olefin units of the trop units). Only recently a related mixed carbene olefin ligand was prepared by a dehydrogenation reaction with a N-cyclohexyl substituted carbene iridium complex.[27]

Experimental

General techniques

The syntheses with air- and moisture sensitive compounds were performed in carefully dried glassware under an argon atmosphere which was passed through the Oxisorb®-gas purification system of Messer-Griesheim to remove the last traces of oxygen and moisture. Solvents in these reactions were dried and purified using standard procedures and were freshly distilled under argon from sodium (toluene), sodium/benzophenone (ether, thf), or from sodium/diglyme/benzophenone (hexane) or calcium hydride (CH_2Cl_2) prior to use. Air sensitive compounds were handled in a glove box (Braun MB 150 B-G system). NMR spectra were recorded using the AMX-500, Avance DRX-400, Avance DPX-300, or Avance DPX-250 systems. The chemical shifts are given as dimensionless δ values and were referenced against tetramethylsilane (tms) for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F NMR spectra. Coupling constants *J* are given in Hertz [Hz] and as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t, q, sept, or m for singlets, doublets, triplets, quartets, septets, or multiplets, respectively. Quaternary carbons are indicated as C_{quart}, aromatic as C_{ar}, alkylic as C_{alk} and broad signals as br.

IR spectra were measured with the ATR-technique on a Perkin-Elmer-2000 FT-IR-spectrometer in the range from 4000 cm^{-1} to 550 cm^{-1} using a KBr beamsplitter. The UV/Vis spectra were measured with the UV/Vis/NIR Lambda 19 spectrometer in 0.5 cm quartz cuvettes. Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode. Melting points were determined in sealed capillaries in an apparatus by fabricated by Büchi according to Dr. Tottoli and are uncorrected.

X-Ray analyses (Table 3)

The structures of **9** and **10** were measured on a Siemens SMART PLATFORM with CCD Detector, solved using direct methods and refined against the full matrix (*versus* F^2) with SHELXTL (Version 5.0).[28] Heavy-atoms were treated anisotropically, carbon atoms were treated isotropically.

Table 1 Selected bond lengths [Å] and angles [°] for **9**

N(1)–C(1A)	1.488(2)	C(4A)–C(5A)	1.332(2)	N(1)–C(18)–C(5)	126.4(1)
N(1)–C(16)	1.378(2)	C(4)–C(5)	1.354(2)	N(1)–C(1A)–C(7A)	113.6(1)
N(1)–C(18)	1.375(2)	C(18)–N(1)–C(16)	106.2(1)	N(1)–C(1A)–C(2A)	111.2(1)
C(16)–C(17)	1.337(2)	C(18)–N(1)–C(1A)	128.8(1)	C(18)–N(2)–C(17)	105.2(1)
N(2)–C(17)	1.377(2)	C(16)–N(1)–C(1A)	124.9(1)	C(17)–C(16)–N(1A)	106.7(1)
N(2)–C(18)	1.33(2)	N(2)–C(18)–N(1A)	110.9(1)	C(16)–C(17)–N(2)	110.9(1)
C(18)–C(5)	1.489(2)	N(2)–C(18)–C(5)	122.7(1)		

Table 2 Selected bond lengths [Å] and angles [°] for **10**

Au(1)–P(1)	2.299(2)	P(1)–Au(1)–C(33)	173.8(2)	N(1)–C(16)–C(17)	106.8(8)
Au(1)–C(33)	2.111(7)	Au(1)–C(33)–N(1)	124.0(5)	C(16)–C(17)–N2	108.9(6)
C(33)–N(1)	1.307(9)	Au(1)–C(33)–N(2)	122.6(4)	C(17)–N(2)–C(18)	124.1(5)
C(33)–N(2)	1.292(8)	N(1)–C(33)–N(2)	109.9(6)	C(18)–N(2)–C(33)	129.1(6)
N(1)–C(1)	1.514(7)	C(33)–N(1)–C(16)	108.0(5)	C(17)–N(2)–C(33)	106.3(6)
N(2)–C(18)	1.461(8)	C(33)–N(1)–C(1)	126.5(5)		
C(16)–C(17)	1.270(9)	C(16)–N(1)–C(1)	125.1(5)		

Hydrogen atoms were refined on calculated positions using the riding model. Non-coordinating solvent molecules were refined with isotropic temperature factors. An absorption correction was not applied.

CCDC reference numbers 183943 (**9**) and 183942 (**10**). See http://www.rsc.org/suppdata/nj/b2/b203670c/ for crystallographic data in CIF or other electronic format.

Syntheses

1,4-(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene (bistropdad) (4). 10.0 g (5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine **2** (48 mmol) were dissolved in 100 ml ethanol and 2.6 ml (23 mmol) of glyoxal **3** and some few drops of formic acid were added. The resulting white suspension was stirred for 12 hours and then filtered. The white solid was washed with cold methanol and re-crystallised from hot toluene or thf to furnish 9.5 g (91%) of the product **4** which was obtained as white cotton-like substance. M.p.: 209–210 °C. ^{1}H NMR ([D$_6$]dmso): $\delta = 5.79$ (s br, 2 H, CHN=), 6.98 (s br, 4 H, =C*H*), 7.20–7.36 (m, 16 H, CH_{ar}), 7.45 (s br, 2 H, N=C*H*). Due to the poor solubility no ^{13}C NMR was recorded. MS [EI, m/z (%)]: 437 (10, [M + H]), 436 (33, M), 245 (6), 191 (100, trop), 178 (20). IR (ν in cm^{-1}): 3023 w, 1628 m (N=C), 1597 w, 1483 m, 1434 m, 1354 m, 1158 w, 1033 m, 949 w, 894 m, 797 s, 786 s, 771 s, 736 s, 647 m, 611 m. Elemental analysis for $C_{32}H_{24}N_2$ (436.55): calc. C 88.04, H 5.54, N 6.42; found: C 88.09, H 5.51, N 6.40%.

1,3-Bis(5*H*-dibenzo[*a*,*d*]cycloheptenyl)imidazolium chloride (5). 550 mg Paraformaldehyde (18 mmol) were suspended in 100 ml toluene and heated until a clear solution was obtained. After cooling to room temperature, 8.1 g bistropdad **4** (18 mmol) were added and subsequently 9 ml of an ethereal solution of HCl (18 mmol, 2 M in Et$_2$O) were added dropwise. The mixture was stirred for two day at room temperature. The yellow product precipitated and was collected by filtration. After washing with 25 mL of thf and drying in vacuum, 6.8 g (79%) of analytical pure imidazolium salt **9** were obtained. M.p.: 148–154 °C (decomp.). ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 6.45$ (d, $^3J_{HH} = 1.3$ Hz, 2 H, NC*H*), 6.64 (s br, 1 H, *H*Cl), 6.83 (s, 4 H, =C*H*), 7.15 (s, 2 H, C*H*N), 7.46 (m, 12 H, CH_{ar}), 7.85 (m, 4 H, CH_{ar}). ^{13}C NMR (CD$_2$Cl$_2$): $\delta = 68.5$ (s, 2 C, *C*HN), 121.5 (s, 2 C, N=*C*H), 130.0 (s, 4 C, *C*H$_{ar}$), 130.2 (s, 4 C, *C*H$_{ar}$), 130.5 (s, 4 C, =*C*H), 130.8 (s, 4 C, *C*H$_{ar}$), 131.5 (s, 4 C, *C*H$_{ar}$), 132.8 (s, 4 C, C_{quart}), 134.3 (s, 4 C, C_{quart}), 134.5 (s, 1 C, *C*H···Cl). MS [EI, m/z (%)]:448 (82, [M − HCl]), 191 (100, [trop]). IR (ν in cm^{-1}): 3021 w, 2389 m, 1599 w, 1495 m, 1437 m, 1109 s, 800 s, 729 s, 634 m. Elemental analysis for $C_{33}H_{25}ClN_2$ (484.17): calc. C 81.71, H 5.20, N 5.78; found: C 82.01, H 5.26, N 5.72%.

2-(5*H*-Dibenzo[*a*,*d*]cyclohepten-10-yl)-1-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1*H*-imidazole (9). 400 mg 1,3-Bis(5*H*-dibenzo[*a*,*d*]cycloheptenyl)imidazolium chloride **5** (0.89 mmol) were suspended in 15 ml thf and 200 mg KO*t*Bu (1.56 mmol, 1.75 eq) were added. The suspension was yellow in the beginning and turned into a pale brownish clear solution at the end. In order to remove some insoluble material, the solution was filtered over Celite®, the residue washed with about 10 ml of toluene and subsequently the filtrate was concentrated to about 1/3 of its starting volume under vacuum. The addition of 20 ml *n*-hexane caused precipitation of a yellow sustance which after re-crystallisation from toluene/*n*-hexane gave 175 mg (44%) small pale yellow crystals. Cubic crystals which were suitable for an X-ray analysis were obtained by layering a toluene solution with *n*-hexane. M.p.: 209–210 °C. ^{1}H NMR (C$_6$D$_6$): $\delta = 3.73$ (s, 2 H, CH_2), 6.41 (s, 1 H, C*H*N), 6.82 (s, 2 H, =C*H*), 6.89 (t, $^3J_{HH} = 6.8$ Hz, 1 H, CH_{ar}), 7.27–6.97 (m, 16 H, CH_{ar}), 7.49 (s, 1 H, CH_{ar}), 7.91 (s, 1 H, =C*H*). ^{13}C NMR (C$_6$D$_6$): $\delta = 42.3$ (s, 1 C, *C*H$_2$), 65.9 (s, 1 C, *C*HN), 121.7 (s, *C*H$_{ar}$), 126.5 (s, *C*H$_{ar}$), 127.5 (s, *C*H$_{ar}$), 128.0 (s, *C*H$_{ar}$), 128.2 (s, *C*H$_{ar}$), 128.5 (s, *C*H$_{ar}$), 128.9 (s, 2 C, =*C*H), 129.0(s, *C*H$_{ar}$), 129.5 (s, *C*H$_{ar}$), 130.1 (s, *C*H$_{ar}$),

Table 3 Crystallographic data of compounds **9** and **10**

Compound	**9**	**10**·2CH$_2$Cl$_2$
Empirical formula	$C_{33}H_{24}N_2$	$C_{42}H_{33}AuCl_3N_2P$
Formula weight	448.54	853.40
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	tetragonal
Space group	*P*2(1)/*n*	*P*4(1)2(1)2
Unit cell dimensions/Å, °	$a = 9.773(1)$, $\alpha = 90$	$a = 14.235(1)$, $\alpha = 90$
	$b = 16.385(2)$, $\beta = 97.483(4)$	$b = 14.235(1)$, $\beta = 90$
	$c = 14.939(2)$, $\gamma = 90$	$c = 48.498(6)$, $\gamma = 90$
Volume/Å^3	2371.7(6)	9828(2)
Z	4	10
Absorption coefficient/mm^{-1}	0.073	3.266
Reflections collected	15 038	45 486
Independent reflections	4850 [*R*(int) = 0.03]	5999 [*R*(int) = 0.03]
Data/restraints/parameters	4850/0/317	5999/342/363
Method of refinement	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.029	1.210
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0382$, $wR2 = 0.0918$	$R1 = 0.0959$, $wR2 = 0.2085$
R indices (all data)	$R1 = 0.0738$, $wR2 = 0.1043$	$R1 = 0.1108$, $wR2 = 0.2145$

131.5 (s, CH_{ar}), 134.9 (s, CH_{ar}), 135.4 (s, 4 C, C_{quart}), 136.0 (s, CH_{ar}), 136.9 (s, 4 C, C_{quart}), 139.2 (s, 1 C, C_{quart}). IR (ν in cm^{-1}): 3014 w, 2358 s, 2341 s, 1601 m, 1487 m, 1434 m, 1249 m, 1125 s, 1112 s, 796 s, 752 s, 743 s, 732 s, 699 s, 648 s. Elemental analysis for $C_{33}H_{24}N_2$ (448.57): calc. C 83.35, H 5.40, N 6.24; found: C 83.28, H 5.38, N 6.29%.

[(1,3-Bis(5*H*-dibenzo[*a*,*d*]cycloheptenyl)imidazol-2-ylidene)-(triphenylphosphine)gold(I)] chloride (10). To a suspension of 878 mg of the imidazolium chloride **5** (1.8 mmol) in 60 ml thf were added 1.0 g of [AuCl(PPh_3)] (2 mmol, 1.1 eq) and 285 mg of KO*t*Bu (2.2 mmol, 1.2 eq). The yellow reaction mixture was stirred for 24 hours at room temperature and than rapidly heated to reflux temperature whereby the colour changed to deep red. After cooling to room temperature, the reaction mixture was evaporated under vacuum to dryness and the pale reddish residue was dissolved in 20 ml of CH_2Cl_2. After filtration through Celite®, the filtrate was once more evaporated, the residue dissolved in 60 ml of toluene and layered with 10 ml of *n*-hexane. After cooling for four days to −15 °C, the precipitate was separated by filtration and dried several hours under vacuum to give 1.1 g (61%) of a pale reddish powder. Crystals of **10**·$2CH_2Cl_2$ suitable for an X-ray analysis were grown in a 5 mm NMR tube from a CH_2Cl_2 solution layered with *n*-hexane. M.p.: 238–240 °C (decomp.). ^{1}H NMR ($CDCl_3$): 5.29 (s, 2 H, NC*H*=C*H*N), 6.14 (s, 2 H, NCH_{trop}), 6.82–7.74 (m, 35, H_{ar}). ^{13}C NMR ($CDCl_3$): 31.3 (2 C, NCH_{trop}), 100.1 (2 C, NC*H*=C*H*N), 128.7–134.7 (46 C_{ar}), 207.3 (C, N*C*N). ^{31}P NMR ($CDCl_3$): 42.2. IR (ν in cm^{-1}): 3012 w, 2360 s, 1495 m, 1435 s, 1308 w, 1100 s. MS [EI, m/z (%)]: 448 (15, [NHC]), 262 (76, PPh_3), 191 (66, [trop]), 101 (100, [M − 2 trop − Au]). Elemental analysis for $C_{51}H_{39}N_2AuClP$ (942.22): calc. C 64.93, H 4.17, N 2.97; found: C 64.88, H 4.10, N 3.02%.

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