CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901062

Structure and Bonding in Neutral and Cationic 14-Electron Gold Alkyne π Complexes

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Dedicated to Professor Yitzhak Apeloig on the occasion of his 65th birthday

Abstract: Cyclododecyne (**5**) as a prototype unstrained alkyne was coordinated to either the neutral [AuCl] fragment or to two different cationic [Au(NHC)]$^+$ entities (NHC = N-heterocyclic carbene), and the resulting complexes **6**, **8**, and **10** were characterized by X-ray crystallography and NMR spectroscopy. Since the structure of cyclododecyne in the solid state could also be obtained after in situ crystallization, a comparison was possible that provides insights into structural changes imposed on the alkyne by the different gold fragments. These data are interpreted on the basis of a DFT analysis of the bonding situation in the individual compounds, which provides insights into the very first elementary step common to many gold-catalyzed transformations.

Keywords: alkyne ligands • alkynes • carbene ligands • density functional calculations • gold

Introduction

The use of gold and platinum compounds for the selective activation of π bonds has been a major thrust of catalysis research during the last decade.[1] Gold, in particular, in its function as a soft, carbophilic, Lewis acidic transition metal, allows remarkably high degrees of molecular complexity to be built up in reactions that are operationally simple, safe, and convenient to perform. Therefore, it is finding increasing application in target-oriented synthesis.[1–3]

Despite this success story, the underlying mechanisms are not yet well understood. This is particularly true for transformations of polyunsaturated substrates such as enynes, which are believed to commence with coordination of only one of the π bonds to the catalytically active metal center.[4] Even though binding of Au^I to the alkene might be thermodynamically favored,[5] indirect evidence suggests that it is coordination to the alkyne unit that triggers the subsequent chemical transformation.[1] Pertinent experimental data to support this view, however, are scarce; even though the structures of an appreciable number of gold complexes of metal acetylides are known in the literature,[6] only very few gold complexes of regular alkynes have been isolated in pure form. In addition to the unstrained and neutral 3-hexyne(AuCl) complex **2** recently described by Dias and coworkers,[7] Shapiro and Toste characterized the dimeric species **1**, which was formed on coordination of cationic Au^I to a substrate carrying a phosphine donor tethered to an alkyne unit protected by a bulky triisopropylsilyl (TIPS) group.[8,9] The only other structurally characterized gold alkyne complexes are **3** and **4**, each incorporating a highly strained cycloalkyne as ligand.[10] Whereas **4** is a coordination polymer, **3** features a dimeric array with a trigonal gold coordination mode and is devoid of any aurophilic interactions. In this complex, pronounced backbonding helps to reduce the angular strain of the thiacycloheptyne moiety. This effect is clearly expressed in the C≡C bond length (1.259(12) Å) and the C≡C−C angles Φ (147.3(8) and 146.4(9)°), and may also explain the trigonal coordination geometry, which is unusual for Au^I but rather reminiscent of the coordination modes of Au^{III}.[10]

As part of our investigations into the elementary steps of π-acid catalysis,[11–15] we decided to study alkyne activation in more detail. Here we report the preparation and characterization of a series of 14-electron gold alkyne coordination compounds that are more similar to the actual catalytic systems because they do not invoke any tailor-made substrates and deliberately employ gold templates commonly used for

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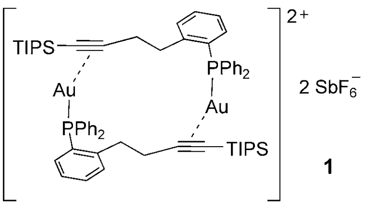
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901062.



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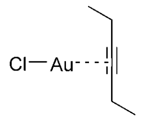

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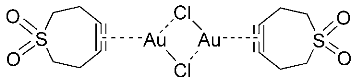

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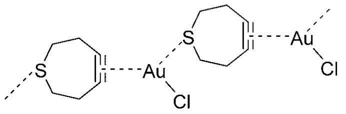

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preparative purposes. Moreover, we give first insights into the effects induced by the neutral [AuCl] unit as compared to those of two different cationic $[Au(NHC)]^+$ fragments.[16]

Results and Discussion

Starting point for our study was to choose cyclododecyne (**5**) as a supposedly unhindered and relatively unstrained substrate.[17] Even though this compound is liquid at ambient temperature, we were able to determine its structure in the solid state by in situ crystallization (m.p. −54 °C by differential scanning calorimetry). Figure 1[18] shows one of the two independent molecules in the asymmetric unit, and Scheme 1 gives pertinent distances and angles. As expected, the alkyne bond is almost straight and thus relatively unstrained.

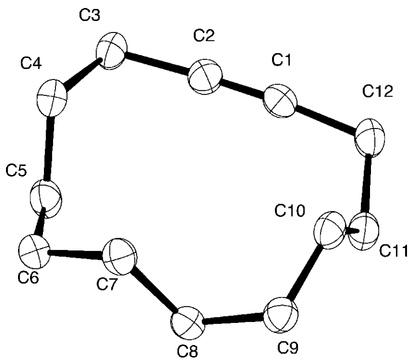
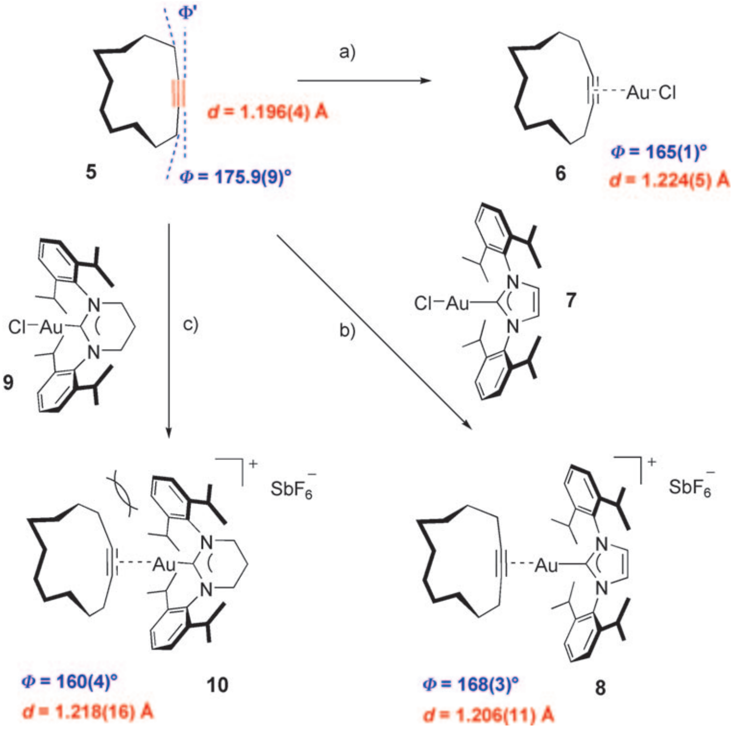


Figure 1. Structure of cyclododecyne (**5**) in the solid state at 100 K, showing the relatively linear, almost unstrained C−C≡C−C unit; note that the compound adopts a planar-chiral conformation and the crystal is a racemate.[18]



Scheme 1. Reagents and conditions: a) AuCl, CH_2Cl_2, 0 °C, 90 %; b) **7**, $AgSbF_6$, CH_2Cl_2, RT, 80 %; c) **9**, $AgSbF_6$, CH_2Cl_2, RT, 92 %; bond angles *Φ* are mean values for each compound, *d* is the C≡C bond length.

Addition of **5** to a greenish suspension of AuCl in carefully dried CH_2Cl_2 at 0 °C results in rapid (<1 min) formation of a clear and colorless solution.[19] Careful evaporation of the solvent at 0 °C, trituration of the residue with cold pentane, and crystallization of the crude product from Et_2O at −80 °C furnished complex **6** (Scheme 1) in the form of colorless crystals, which can be stored for several weeks at −50 °C but rapidly decompose at or above 0 °C even under inert atmosphere. Comparison of the structure of **6** (Figure 2) with that of the free ligand reveals that the triple bond is noticeably extended from 1.196(4) Å in **5** to 1.224(5) Å in **6**. Moreover, the two C≡C−C bond angles *Φ* are reduced from 175.9(9)° (av) in free cyclododecyne to 165(1)° (av) in **6**. The structure of **6** also features short Au···Au contacts (av 3.33(2) Å) due to the aurophilicity of Au^I (Figure 3).[20] The Cl-Au-alkyne(midpoint) angle is nevertheless almost linear (av 176(1)°), that is, the Au···Au interaction is very weak. This contrasts with the structure of **1**,

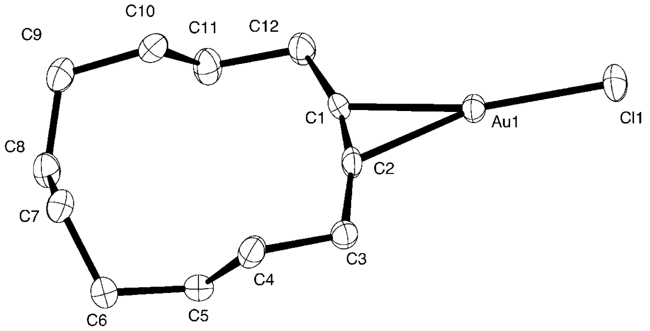


Figure 2. Structure of complex **6** in the solid state with almost linearly coordinated gold center.[18]

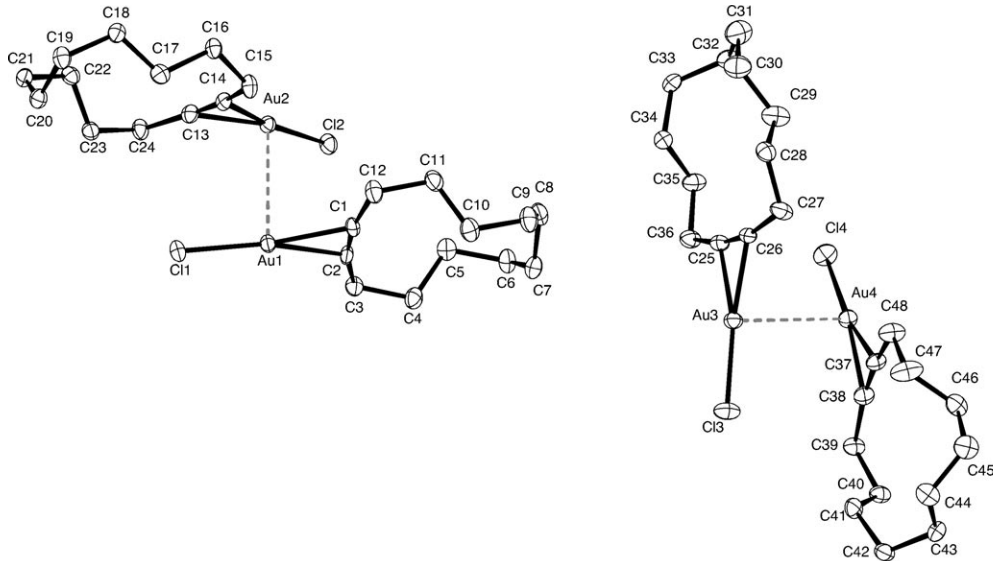


Figure 3. The four independent molecules in the crystal structure of **6**, showing the Au···Au interactions (Au1···Au2 3.318(1), Au3···Au4 3.349(1) Å).

in which the two independent P-Au-alkyne(midpoint) units are noticeably bent (173°), and the gold atoms' pointing toward dichloromethane of solvation (mean Au···Cl distance 3.66 Å) indicates possible interaction with the donating solvent, though the effect of ring strain cannot be ruled out (see Scheme S-8 in the Supporting Information).[8,18]

Since activation of the alkyne is thought to occur by withdrawal of electron density by the electrophilic gold center, it seemed appropriate to extend the study to the effects of cationic gold templates, as such species dominate contemporary gold catalysis.[1] To this end, complexes **7** and **9** carrying N-heterocyclic carbene (NHC) ligands of different ring size were prepared in good yields by established routes;[21] the structure of the previously unknown compound **9** in the solid state is shown in Figure 4.

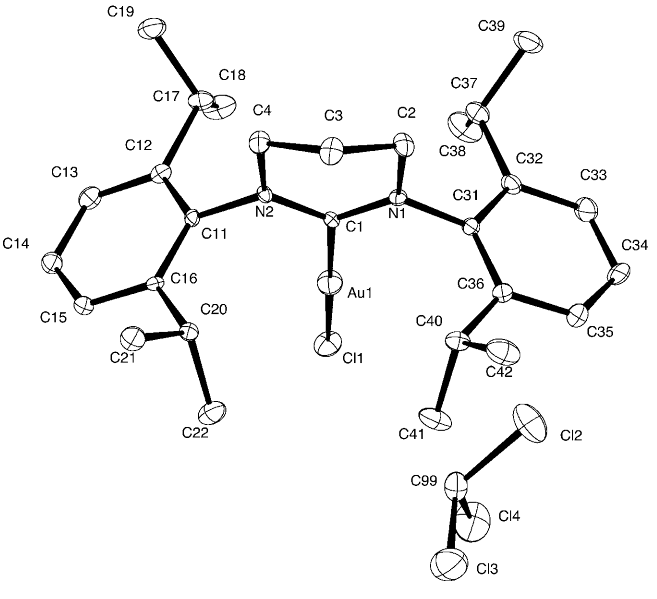


Figure 4. Structure of **9** in the solid state.[18,22]

Addition of $AgSbF_6$ to a solution of **9** and cyclododecyne in CH_2Cl_2 caused instantaneous precipitation of AgCl; careful evaporation of the resulting filtrate followed by crystallization of the crude material furnished single crystals of the desired alkyne complex **10** suitable for X-ray structure analysis. The corresponding complex **8**, bearing the imidazol-2-ylidene moiety as ancillary two-electron donor, was prepared analogously (Scheme 1). Both products are highly sensitive and slowly decompose even below −20 °C under inert conditions. Nevertheless, it was possible to obtain good X-ray diffraction data that allowed the molecular structures of **8** and **10** shown in Figure 5 and Figure 6 to be determined.

As expected, the $C\equiv C$ triple bond is again extended in both **8** and **10** relative to parent alkyne **5**, but the effect is *less* pronounced than in the neutral AuCl complex **6** (Scheme 1). One may be tempted to ascribe the slightly

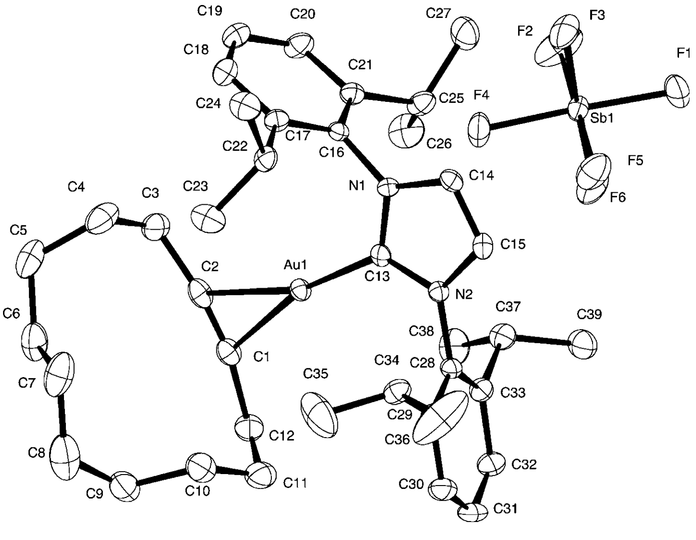


Figure 5. Structure of **8** in the solid state.[18]

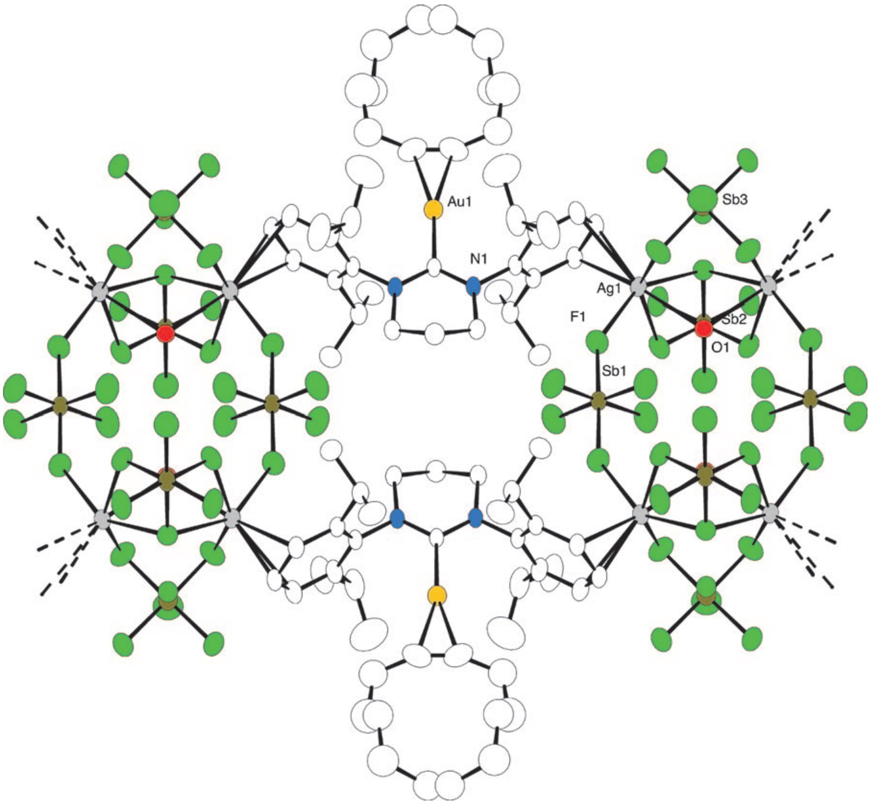


Figure 6. Solid-state structure of **10**, which cocrystallized with two equivalents of $AgSbF_6$; the silver cations engage in η coordination with the aromatic rings of the *N*-aryl groups of the NHC ligand.[18] Color code: white: C; blue: N; gray: Ag; yellow: Au; light green: F; green-brown: Sb; red: O of cocrystallized H_2O.

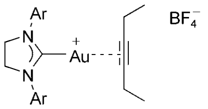
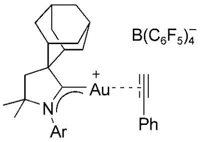
longer C1−C2 bond in **10**, as compared with **8**, to the somewhat stronger donor capacity of the six-membered NHC.[22] Although this explanation is consistent with the notion that N-heterocyclic carbenes with enlarged rings are stronger donors than the parent imidazol-2-ylidenes,[23,24] care must be taken not to overinterpret the data in view of the experimental error bars. Interestingly, however, the degree of deshielding of the alkyne sp C atom on complexation to the different gold fragments, as reflected in the ^{13}C chemical shifts (Table 1), seems to corroborate the view that **10** carries the slightly more electron donating ancillary ligand.[22]

Significant differences between the two NHC complexes, however, are observed in the degree of bending of the alkyne moiety. Whereas a rather weak flow of electron density between the ligand and the cationic gold fragment in **8** entails little change, the corresponding bond angles Φ in **10** deviate considerably from linearity (160(4)°). This effect, however, is unlikely to be electronic in nature but rather caused by the shape of the six-membered NHC, which directs the bulky *N*-aryl substituents more toward the alkyne and hence forces the ligand to adopt a rather distorted conformation (Scheme 1).

The structure of **10** in the solid state also deserves comment, since the complex cocrystallized with two molar equivalents of $AgSbF_6$. These escorting silver cations are by no means innocent, but coordinate to the π system of the *N*-aryl group of the NHC in a η fashion. Overall, this results in the intricate bonding pattern shown in Figure 6.[18]

For further analysis, we calculated the bonding situation in the different complexes using density functional theory at the BP86/def2-TZVP level. The computed distances and angles (Table 2) reproduce the experimental trends very well, except for the observed high degree of bending of the alkyne in **10**, which, however, is likely steric in origin; the crystal structure of **10** contains two equivalents of $AgSbF_6$ (see above), which are not included in the calculations. Second-order perturbation analysis in the natural bond order (NBO) framework shows that the orbital interaction energies for $\pi(C{\equiv}C)\rightarrow\sigma^*$(AuL) donation are on the order of 70–100 kcal mol^{-1} and thus 3–4 times larger than those for $d(Au)\rightarrow\pi(C{\equiv}C)^*$ backdonation, which lie in the range of 20–30 kcal mol^{-1} (Table 2).

Table 1. ^{13}C NMR shifts of the alkyne carbon atoms of the new gold-alkyne complexes and those of gold alkyne NHC complexes known in the literature.[7,25,26]

Compound	δ_C [ppm] in CD_2Cl_2
cyclododecyne (**5**)	81.7
2	86.4
6	85.9
8	88.0
10	86.6
	87.7[a]
	71/95[a,b]

[a] Ar = 2,6-diisopropylphenyl. [b] The supporting information to ref. [26] reports shifts of 71.7 and 93.8 ppm.

Hence, consistent with previous theoretical results,[7,8] $\pi\rightarrow\sigma^*$ donation clearly dominates over $d\rightarrow\pi^*$ backdonation in all cases investigated, and thus explains the highly electrophilic character of the alkyne within the coordination sphere of any chosen Au^I fragment. Interestingly, [AuCl] is not only the strongest donor, but also the strongest acceptor. The fact that both bonding interactions are more pronounced

Table 2. Computed structural parameters, natural bond order orbital (NBO) interaction energies [kcal mol^{-1}], and partial charges from NBO analysis; experimental data are given in brackets for comparison.

	Cyclododecyne (**5**)	**6**	**8**	**10**
d(C1≡C2) [Å]	1.216	1.256	1.246	1.247
	[1.196(4)]	[1.224(5)]	[1.206(11)]	[1.218(16)]
Φ[a] [°]	174.9	164.2	163.1	166.4
	[175.9(9)]	[165(1)]	[168(3)]	[160(4)]
Φ'[a] [°]	174.8	162.0	167.4	167.0
	[175.9(9)]	[165(1)]	[168(3)]	[160(4)]
$\pi\rightarrow\sigma^*$		100.1	77.4	69.7
$d\rightarrow\pi^*$		27.2	19.8	20.3
difference[b]		72.9	57.6	49.4
q(AuL)[c]		0.00	0.88	0.90

[a] The experimental values are mean bond angles. [b] Reflects the different strengths of donation from the π(C≡C) NBO to the σ*(AuL) NBO and backdonation from the d(Au) NBO to the π*(C≡C) NBO. [c] Group charges on AuL, where L is Cl in **6** and the NHC ligand in **8** and **10**; note that **8** and **10** are cations; the group charges on the alkyne are thus 0.00 in **6**, 0.12 in **8**, and 0.10 in **10**.

than in the cationic counterparts is reflected in the tighter contact between the gold atom and the triple bond (the distance between the midpoint of the alkyne and the gold center is only 2.064(3) Å in **6** but 2.142(5) Å in **8**; for a comparison of relevant structural data of all known Au^{I} alkyne complexes characterized by X-ray crystallography, see Table 3). Somewhat surprisingly, the computed NBO charges indicate that there is essentially no net flow of electrons between the two fragments in **6**, since AuCl and cyclododecyne remain almost neutral. In cationic complexes **8** and **10**, net electron donation from the alkyne ligand occurs which is slightly larger in the case of the five-membered NHC ligand (0.12 vs. 0.10).

Table 3. Structural data of all currently known Au^{I} alkyne complexes characterized by X-ray crystallography, excluding acetylides.[6]

Complex	d(C≡C) [Å]	d(Au···AM[a]) [Å]	av Φ [°]	Ref.
1	1.221(8)	2.159(13)	167.2(6)	[8]
2	1.224(6)	2.074(9)	165(5)	[7]
3	1.259(12)	1.967(15)	146.8(8)	[10]
4	1.244(11)	1.980(15)	146.5(7)	[10]
6	1.224(5)	2.064(3)	165(1)	–[b]
8	1.206(11)	2.142(5)	168(3)	–[b]
10	1.218(16)	2.14(1)	160(4)	–[b]

[a] AM = alkyne midpoint. [b] This work.

We also computed the binding energies of the complexes from the difference between the total energies of the constituent molecules (alkyne and AuL) and those of the corresponding complexes (Table 4). For the complexes with AuCl, we find B3LYP binding energies of 146.5 kJ mol^{-1} (35.0 kcal mol^{-1}) for acetylene and 157.0 kJ mol^{-1} (37.5 kcal mol^{-1}) for cyclododecyne, which are consistent with previously published B3LYP values for acetylene (142.8 kJ mol^{-1}), propyne (151.4 kJ mol^{-1}),[27] and 3-hexyne (157 kJ mol^{-1}).[7] Clearly, the computed binding energies increase with increasing donor strength of the alkyne. For the cationic complexes, we obtain values of 165.7 kJ mol^{-1} (39.6 kcal mol^{-1}) for **8** and 138.4 kJ mol^{-1} (33.1 kcal mol^{-1}) for **10**. The weaker donor–acceptor interaction and the larger steric strain (see above) both contribute to the lower binding energy of **10** compared with **8**.

Table 4. Bond dissociation energies [kcal mol^{-1}].

Complex	BP86		B3LYP
	ΔE	ΔG	ΔE
6	44.58	33.26	37.52
8	43.82	27.59	39.60
10	37.30	24.66	33.08
(acetylene)AuCl	42.65	33.81	35.01

Conclusions

A series of neutral and cationic 14-electron Au^{I} complexes has been obtained in which the gold atoms are free from extraneous donors in the crystal. Among the two NHC complexes investigated, we observe that the five-membered imidazol-2-ylidene ligand in **8** allows for more electron withdrawal from the alkyne than its six-membered homologue in **10**. Moreover, the net energetic effect of π(C≡C)→Au donation and Au→π(C≡C)* backdonation is computed to be larger in **8** than in **10**. This suggests that the use of a classical Arduengo carbene[23,28] as ancillary ligand for cationic Au^{I} combines strong π→Au acceptor properties with weak Au→π* donation, which may be the reason for the rapidly growing number of applications of such catalysts in the preparative context.[1,21,29] This conclusion must also be seen in the light of the NBO analysis of the dimeric phosphine complex **1**,[8] which indicates that donation of π-electron density to the gold atom as well as backdonation from the metal center are both less pronounced than in the NHC complexes presented herein.

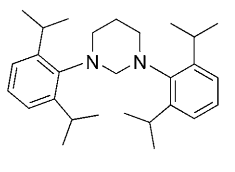
Experimental Section

General: All reactions were carried out under Ar in flame-dried glassware. Solvents were purified by distillation over the indicated drying agents prior to use and were transferred under Ar: Et_2O, 1,2-dimethoxyethane (Mg/anthracene), CH_2Cl_2, $CHCl_3$, (CaH_2), pentane (Na/K), MeOH (Mg). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, or AV 400 spectrometers in the solvents indicated. The solvent signals were used as references, and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C = 77.23$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H = 7.27$ ppm; CD_2Cl_2: $\delta_C = 53.8$ ppm; residual $CHDCl_2$ in CD_2Cl_2: $\delta_H = 5.32$ ppm). IR: Magna IR750 (Nicolet) or Spectrum One (Perkin–Elmer) spectrometer. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. Cyclododecyne was purified by distillation over $LiAlH_4$ prior to use.

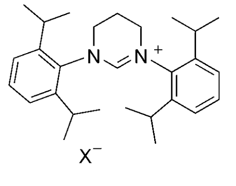
Complex 6: Cyclododecyne (318 mg, 1.936 mmol) was added to a cold (0 °C) suspension of AuCl (225 mg, 0.968 mmol) in CH_2Cl_2 (1 mL) and the resulting clear solution was stirred for 5 min before all volatile materials were evaporated at this temperature with the aid of a gentle stream of argon. The residue was triturated three times with cold (−78 °C) pentane and dried under Ar to give complex **6** as a colorless powder (345 mg, 90 %). Single crystals were grown by cooling a saturated solution in Et_2O from −10 °C to −80 °C over 24 h. The resulting crystals can be stored at −50 °C under Ar for weeks but decompose rapidly at above 0 °C. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 2.72$ (t, $J = 5.5$ Hz, 4 H), 1.72–1.65 (m, 4 H), 1.56–1.49 (m, 4 H), 1.45–1.39 ppm (m, 8 H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 85.9$, 26.8, 25.9, 25.8, 24.8, 21.5 ppm.

Complex 8: $AgSbF_6$ (55 mg, 0.161 mmol) was added to a solution of cyclododecyne (79 mg, 0.483 mmol) and **7** (100 mg, 0.161 mmol)[22] in CH_2Cl_2 (1 mL) and the resulting mixture stirred at ambient temperature for 15 min. Evaporation of the solvent with the aid of a gentle stream of Ar and trituration of the residue with cold (0 °C) pentane afforded the title complex as a colorless powder (126 mg, 80 %). Single crystals were grown by carefully layering a saturated solution of the complex in CH_2Cl_2 with pentane and storage of the resulting mixture overnight. The crystals can be stored under Ar at −20 °C but decompose within a few days at ambient temperature. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.65$–7.59 (m, 2 H), 7.51 (s, 2 H), 7.42–7.38 (m, 4 H), 2.52 (sept, $J = 6.8$ Hz, 4 H), 2.27–2.21 (m, 4 H), 1.83–1.17 (m, 16 H), 1.29 (d, $J = 6.8$ Hz, 12 H), 1.27 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 177.6$, 146.3, 133.5, 131.0, 125.1, 124.6, 88.0, 29.2, 25.8, 25.6, 24.6, 24.0, 20.9 ppm.

1,3-Bis(2,6-diisopropylphenyl)hexahydropyrimidine: An aqueous solution of formaldehyde (37 % w/w, 0.82 g, 9.94 mmol) was added to a solution of *N,N'*-bis(2,6-diisopropylphenyl)propan-1,3-diamine (3.57 g, 9.04 mmol)[30] in MeOH (20 mL) and the resulting mixture stirred at 45 °C for 16 h. All volatile materials were evaporated and the residue was dried in vacuo to give the title compound as a colorless solid (3.65 g, 99 %). M.p. 154–155 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$–7.10 (m, 6 H), 4.31 (s, 2 H), 3.73 (sept, $J = 6.9$ Hz, 4 H), 3.28 (t, $J = 5.3$ Hz, 4 H), 1.98–1.91 (m, 2 H), 1.28 (d, $J = 6.9$ Hz, 12 H), 1.23 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.4$, 144.8, 126.4, 123.8, 70.7, 50.6, 28.4, 27.4, 24.8, 24.2 ppm; IR (film): $\tilde{\nu} = 2957$, 2916, 2865, 1464, 1442, 1398, 1379, 1360, 1323, 1249, 1232, 1125, 1106, 1047, 957, 806, 760 cm^{-1}; MS (EI): *m/z* (%): 406 (32) [M^+], 405 (100); HRMS (ESI): *m/z* calcd. for $C_{28}H_{42}N_2Na$ [M^++Na]: 429.3240; found: 429.3238; elemental analysis calcd (%) for $C_{28}H_{42}N_2$: C 82.70, H 10.41, N 6.89; found: C 82.81, H 10.50, N 6.79.



1,3-Bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-1-ium halide (X = Cl, Br): *N*-Bromosuccinimide (1.15 g, 6.47 mmol) was added to a suspension of 1,3-bis(2,6-diisopropylphenyl)hexahydropyrimidine (2.63 g, 6.47 mmol) in 1,2-dimethoxyethane (15 mL) and the resulting mixture stirred for 12 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (30 mL), the organic layer was washed with water, dried over $MgSO_4$ and evaporated, and the residue purified by flash chromatography ($MeOH/CH_2Cl_2$ 1/20) to give 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide as a yellow solid (3.11 g, 99 %). M.p. 300–301 °C (decomp). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (s, 1 H), 7.41 (t, $J = 7.8$ Hz, 2 H), 7.22 (d, $J = 7.8$ Hz, 4 H), 4.21 (t, $J = 5.6$ Hz, 4 H), 3.00 (sept, $J = 6.8$ Hz, 4 H), 2.76–2.70 (m, 2 H), 1.34 (d, $J = 6.7$ Hz, 12 H), 1.20 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.8$, 145.5, 135.7, 131.1, 125.0, 48.9, 28.7, 24.7, 24.6, 19.3 ppm; IR (film): $\tilde{\nu} = 3322$, 2962, 2926, 2866, 1650, 1461, 1445, 1313, 1223, 1203, 1100, 1058, 984, 937, 809, 761, 729, 696 cm^{-1}; MS (EI): *m/z* (%): 485 (<1) [M^+], 406 (30), 405 (100), 404 (11), 389 (12); HRMS (ESI): *m/z* calcd for $C_{28}H_{41}N_2$ [M^+−Br]: 405.3264, found: 405.3261.



The corresponding chloride salt was obtained as a yellow solid by stirring a solution of the bromide (2.71 g, 5.59 mmol) in MeOH with DOWEX (22 Cl anion-exchange resin) for 12 h at ambient temperature and flash chromatography of the crude material ($MeOH/CH_2Cl_2$ 1/10) (2.36 g, 96 %). M.p. 326–327 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.54$ (s, 1 H), 7.41 (t, $J = 7.8$ Hz, 2 H), 7.22 (d, $J = 7.8$ Hz, 4 H), 4.20 (t, $J = 5.6$ Hz, 4 H), 3.01 (sept, $J = 6.8$ Hz, 4 H), 2.82–2.75 (m, 2 H), 1.35 (d, $J = 6.8$ Hz, 12 H), 1.20 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.8$, 145.5, 135.7, 131.1, 125.0, 49.0, 28.8, 24.7, 24.7, 19.3 ppm; IR (film): $\tilde{\nu} = 3306$, 3210, 2964, 2867, 2745, 1652, 1466, 1447, 1383, 1316, 1206, 1182, 1059, 1042, 807, 754 cm^{-1}; MS (EI): *m/z* (%): 406 (23), 405 [M^+−Cl] (84), 404 (80), 403 (60), 390 (30), 389 (100), 361 (13), 202 (32), 201 (20), 186 (33), 172 (20), 146 (21); HRMS (ESI): *m/z* calcd for $C_{28}H_{41}N_2$ [M^+−Cl]: 405.3264, found: 405.3260; elemental analysis calcd (%) for $C_{28}H_{41}ClN_2$: C 76.24, H 9.37, N 6.35; found: C 76.25, H 9.40, N 6.44.

Complex 9: Silver oxide (315 mg, 1.36 mmol) was added to a solution of 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium chloride (1.00 g, 2.27 mmol) in CH_2Cl_2 (14 mL) and the resulting mixture stirred in the dark for 4 h. The precipitate was filtered off with an HPLC filter and the filtrate treated with $AuCl{\cdot}SMe_2$ (667 mg, 2.27 mmol). After stirring for 1 h in the dark, the mixture was again filtered through an HPLC filter, the filtrate evaporated, and the residue triturated with pentane and dried in vacuo to give complex **9** as a colorless powder. Single crystals were grown from a solution in $CHCl_3$ layered with pentane. M.p. > 120 °C (decomp); ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.41$ (t, $J = 7.7$ Hz, 2 H), 7.26 (d, $J = 7.7$ Hz, 4 H), 3.46 (t, $J = 5.8$ Hz, 4 H), 3.07 (sept, $J = 6.9$ Hz, 4 H), 2.41–2.35 (m, 2 H), 1.32 (d, $J = 6.9$ Hz, 12 H), 1.32 ppm (d, $J = 6.9$ Hz, 12 H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 205.1$, 146.0, 142.9, 129.6, 125.0, 46.4, 46.4, 28.9, 25.0, 24.7, 20.6 ppm; IR (film): $\tilde{\nu} = 2962$, 2921, 2867, 1514, 1462, 1338, 1312, 1209, 1059, 1034, 995, 804, 760, 735 cm^{-1}; MS (EI): *m/z* (%): 636 (18) [M^+], 600 (11), 405 (27), 404 (100), 403 (89), 401 (23), 390 (17), 389 (58), 361 (19), 202 (15), 186 (19); HRMS (ESI): *m/z* calcd. for $C_{28}H_{40}AuClN_2$ [M^+]: 636.2545; found: 636.2539.

Complex 10: $AgSbF_6$ (53.9 mg, 0.156 mmol) was added to a solution of complex **9** (100 mg, 0.156 mmol) and cyclododecyne (25.7 mg, 0.156 mmol) in CH_2Cl_2 (2 mL) and the resulting mixture was stirred at ambient temperature for 5 min. All solid materials were filtered off and the filtrate was diluted with pentane (15 mL) to precipitate the product (144 mg, 92 %). Single crystals were grown at −78 °C from a solution in CH_2Cl_2 layered with cold pentane. They can be stored at −20 °C under Ar but decompose at ambient temperature within a few days. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.48$–7.40 (m, 2 H), 7.32–7.27 (m, 4 H), 3.64 (t, $J = 5.8$ Hz, 2 H), 3.58 (t, $J = 5.8$ Hz, 2 H), 3.07 (sept, $J = 6.8$ Hz, 2 H), 3.02 (sept, $J = 6.8$ Hz, 2 H), 2.78 (brs, 2 H), 2.48 (dq, $J = 5.8$, 11.7 Hz, 2 H), 1.75–1.66 (m, 2 H), 1.40–1.10 ppm (m, 40 H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 194.5$, 194.2, 146.7, 146.5, 146.3, 142.6, 142.6, 141.0, 140.7, 130.6, 130.4, 130.4, 125.6, 125.5, 125.3, 86.6, 48.2, 48.0, 46.5, 46.4, 29.1, 29.0, 26.2, 26.0, 25.6, 25.3, 25.3, 25.2, 24.9, 24.8, 24.8, 24.7, 24.7, 24.6, 24.5, 22.8, 20.5, 20.3, 20.0, 20.0, 19.6 ppm.

X-ray crystal structure analysis of 5: $C_{12}H_{20}$, $M_r = 164.28$ g mol^{-1}, colorless cylinder, crystal size 0.50 × 0.40 × 0.40 mm, monoclinic, space group $P2_1/c$, $a = 9.1005(7)$, $b = 13.5069(11)$, $c = 16.9276(14)$ Å, $\beta = 90.073(4)°$, $V = 2080.7(3)$ Å^3, $T = 100$ K, $Z = 8$, $\rho_{calcd} = 1.049$ g cm^{-3}, $\lambda = 1.54178$ Å, $\mu(Cu_{K\alpha}) = 0.420$ mm^{-1}, empirical absorption correction ($T_{min} = 0.18$, $T_{max} = 0.86$), Proteum X8 diffractometer, $4.19 < \theta < 68.11°$, 36475 measured reflections, 3664 independent reflections, 2927 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares techniques against F^2 to $R_1 = 0.076$ [$I > 2\sigma(I)$], $wR_2 = 0.175$; 214 parameters, H atoms riding, $S = 1.158$, residual electron density +0.3/−0.3 e Å^{-3}.

X-ray crystal structure analysis of 6: $C_{12}H_{20}AuCl$, $M_r = 396.70$ g mol^{-1}, colorless prism, crystal size 0.13 × 0.04 × 0.02 mm, monoclinic, space group $C2/c$, $a = 54.7070(11)$ Å, $b = 11.7361(2)$, $c = 15.6081(3)$, $\beta = 97.166(1)°$, $V = 9942.9(3)$ Å^3, $T = 100$ K, $Z = 32$, $\rho_{calcd} = 2.120$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 12.014$ mm^{-1}, empirical absorption correction ($T_{min} = 0.22$, $T_{max} = 0.74$), Nonius KappaCCD diffractometer, $5.10 < \theta < 28.28°$, 128853 measured reflections, 12273 independent reflections, 9302 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares techniques against F^2 to $R_1 = 0.026$ [$I > 2\sigma(I)$], $wR_2 = 0.065$; 522 parameters, H atoms riding, $S = 1.030$, residual electron density $+1.7/-1.4$ e Å^{-3}.

X-ray crystal structure analysis of 8: $[C_{39}H_{56}AuN_2]^+[SbF_6]^-$, $M_r = 985.57$ g mol^{-1}, colorless plate, crystal size $0.14 \times 0.09 \times 0.05$ mm, orthorhombic, space group $Pna2_1$, $a = 16.1859(2)$, $b = 14.7429(2)$, $c = 34.0181(4)$ Å, $V = 8117.64(18)$ Å^3, $T = 100$ K, $Z = 8$, $\rho_{calcd} = 1.613$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 4.331$ mm^{-1}, empirical absorption correction ($T_{min} = 0.51$, $T_{max} = 0.77$), Nonius KappaCCD diffractometer, $5.86 < \theta < 33.22°$, 164022 measured reflections, 30681 independent reflections, 24434 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares techniques against F^2 to $R_1 = 0.035$ [$I > 2\sigma(I)$], $wR_2 = 0.057$; 880 parameters, absolute structure parameter $= 0.4144(19)$, H atoms riding, $S = 1.020$, residual electron density $+2.5/-1.4$ e Å^{-3}.

X-ray crystal structure analysis of 9: $C_{28}H_{40}AuClN_2 \cdot CHCl_3$, $M_r = 756.40$ g mol^{-1}, colorless plate, crystal size $0.33 \times 0.24 \times 0.18$ mm, orthorhombic, space group $P2_12_12_1$, $a = 10.6707(2)$, $b = 16.5339(4)$, $c = 17.7935(4)$ Å, $V = 3139.28(12)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd} = 1.600$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 5.047$ mm^{-1}, empirical absorption correction ($T_{min} = 0.62$, $T_{max} = 1.00$), Nonius KappaCCD diffractometer, $2.98 < \theta < 31.56°$, 10398 measured reflections, 10398 independent reflections, 10014 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares techniques against F^2 to $R_1 = 0.041$ [$I > 2\sigma(I)$], $wR_2 = 0.127$; 333 parameters, absolute structure parameter $= 0.178(7)$, H atoms riding, $S = 1.027$, residual electron density $+2.2/-1.7$ e Å^{-3}.

X-ray crystal structure analysis of 10: $[C_{40}H_{60}AuN_2]^+ \cdot 2[Ag]^+ \cdot 3[SbF_6]^- \cdot [H_2O]$, $M_r = 1706.87$ g mol^{-1}, colorless plate, crystal size $0.16 \times 0.10 \times 0.04$ mm, monoclinic, space group $C2m$, $a = 18.1953(3)$, $b = 15.7767(3)$, $c = 19.0602(3)$ Å, $\beta = 97.675(1)°$, $V = 5422.44(16)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd} = 2.091$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 4.970$ mm^{-1}, empirical absorption correction ($T_{min} = 0.42$, $T_{max} = 0.88$), Nonius KappaCCD diffractometer, $6.83 < \theta < 33.21°$, 68408 measured reflections, 10510 independent reflections, 8640 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares techniques against F^2 to $R_1 = 0.044$ [$I > 2\sigma(I)$], $wR_2 = 0.130$; 313 parameters, H atoms riding, $S = 1.045$, residual electron density $+2.9/-3.4$ e Å^{-3}.

CCDC-715728 (**5**), CCDC-715727 (**6**), CCDC-715729 (**8**), CCDC-715730 (**9**), and CCDC-715731 (**10**) 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.

Computational studies: Density functional theory (DFT) calculations were carried out with Turbomole 5.91.[31] The BP86 functional[32,33] was employed in combination with the def2-TZVP basis set.[34] The resolution-of-identity (RI) approximation was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations.[35–37] All geometries were fully optimized without symmetry constraints. The resulting structures were confirmed to be minima by force constant analysis. Single-point calculations with B3LYP[38,39]/def2-TZVP were carried out at the geometries optimized with BP86. The rigid-rotor harmonic-oscillator approximation was used to compute the zero-point vibrational energies as well as the thermal and entropic corrections needed to determine the bond-dissociation free enthalpies ΔG at 300 K. Bond dissociation energies ΔE were calculated as the energy difference between the constituent molecules (alkyne and AuL) and the complex (Table 4). Natural bond order (NBO) analysis[40,41] was carried out with Gaussian 03.[42] Coordinates [Å] and total energies [a.u.] of the structures of cyclododecyne (**5**) and complexes **6**–**10** optimized at BP86(RI)/def2-TZVP level are tabulated in the Supporting Information.

Acknowledgements

Generous financial support by the MPG and the Fonds der Chemischen Industrie (Kekulé stipend to S.F.) is gratefully acknowledged. We thank Umicore AG & Co KG, Hanau, for a gift of noble-metal salts.

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Received: April 22, 2009