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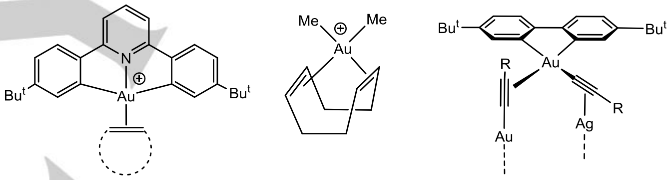
Thermally stable gold(III) alkene and alkyne complexes: Synthesis, structures, and assessment of the *trans*-influence on gold-ligand bond enthalpies

Isabelle Chambrier,[a] Luca Rocchigiani,[a] David L. Hughes,[a] Peter M. H. Budzelaar*[b] and Manfred Bochmann*[a]

Abstract: The reaction of $[(C\hat{}C)Au(OEt_2)_2]^+$ with 1,5-cyclooctadiene or norbornadiene affords the corresponding olefin complexes $[(C\hat{}C)Au(COD)]SbF_6$ and $[(C\hat{}C)Au(NBD)]SbF_6$, which are thermally stable in solution and the solid state (C^C = 4,4′-di-*t*-butylbiphenyl-2,2′-diyl). The crystal structures of these complexes have been determined. By contrast, dienones such as dibenzylideneacetone are O- rather than C=C-bonded. The reactions of $(C\hat{}C)Au(OAc^F)(L)$ (L = PMe_3 or CNxyl) with $B(C_6F_5)_3$ in the presence of bis(1-adamantyl)acetylene give the mixed-ligand alkyne complexes $[(C\hat{}C)Au(AdC{\equiv}CAd)(L)]^+$, the first complexes of their type in gold chemistry. In the presence of an excess of acetylene these compounds are thermally stable in solution and as solids. The bonding of *n*- and π-donor ligands to Au(III) fragments and the effect of the *trans* influence exerted by N- and C-donors was explored with the aid of DFT calculations. Results show that the Au-L bond enthalpies *trans* to anionic C are 35 – 60% of the enthalpies *trans* to N, with strong π-acceptors being particularly affected. In comparison with $[Me_2Au]^+$, the $[(C\hat{}C)Au]^+$ fragment is more polar and in bond enthalpy terms resembles Me_2Pt. .

Introduction

Whereas the chemistry of alkene complexes of platinum has a long history[1] and alkene complexes of gold(I) have been known since the 1970s,[2,3] π-complexes of gold(III), although often postulated as intermediates in many gold-catalysed reactions,[4] proved remarkably elusive. In 2013 we reported the first examples of π-alkene complexes of gold(III) $[(C\hat{}N\hat{}C)Au(L)]^+$ (L = ethylene, cyclopentene or norbornene) using a cyclometallated 2,6-diphenylpyridine pincer as stabilising ligand (Figure 1, structure **A**).[5] These compounds could be isolated as yellow powders and the norbornene complex was stable at room temperature, whereas the ethylene and cyclopentene complexes proved thermally labile. At about the same time Tilset *et al*. reported the synthesis of a complex of a chelating alkene, $[Me_2Au(COD)]^+OTf^-$ (**B**), which is stable below 0 °C but slowly decomposes at room temperature (COD = 1,5-cyclooctadiene). Crystals of $[Me_2Au(COD)][B(Ar^F)_4]$ suitable for X-ray diffraction could be grown at -35 °C [Ar^F = $3,5\text{-}(CF_3)_2C_6H_3$].[6] This compound is the only example of a structurally characterised π-alkene complex of gold(III), until now.



A **B** **C**

Figure 1. Previously reported gold(III) alkene and alkyne complexes

Following our recent isolation of the first examples of gold(III) alkyne complexes,[7] including the crystallographic characterisation of an alkynyl complex of type **C** (Figure 1) which uses a bis-cyclometallated biphenyl-based C^C ligand framework to provide stability (C^C = 4,4′-di-*t*-butylbiphenyl-2,2′-diyl), we decided to explore the potential of this dianionic C^C chelate ligand scaffold for the synthesis of π-alkene complexes and related reactive species. Biphenylyl ligands are attractive since they are resistant to reductive elimination, and indeed they were introduced into gold chemistry by Usón for this very reason several decades ago.[8] Here we show that this ligand framework provides access to thermally remarkably stable, crystallographically characterised Au(III) alkene adducts, as well as to new types of alkyne complexes, and explore with the aid of DFT calculations the *trans*-influence of C- and N-donor ligands on the Au-L bond energies.

Results and Discussion

The reaction of the poorly soluble compound $[(C\hat{}C)AuCl]_2$ (C^C = 4,4′-di-*tert*-butylbiphenyl-2,2′-diyl)[9] with $NBu^n{}_4Cl$ affords the

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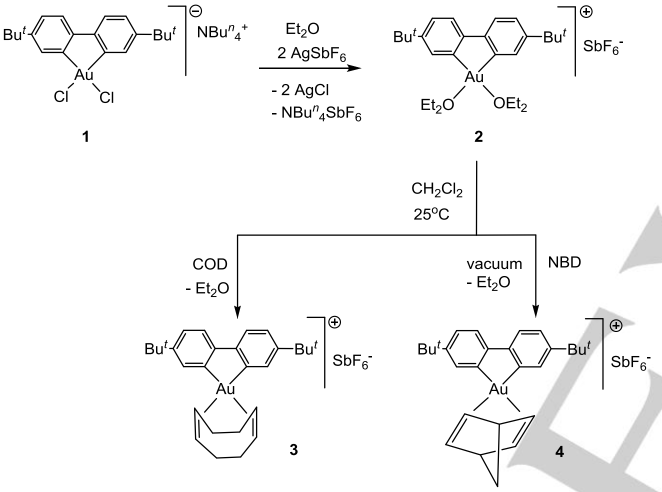
dichloro anion **1**, which is readily soluble in CH_2Cl_2 or THF. Addition of $AgSbF_6$ in dichloromethane in the presence of diethyl ether gives $[(C^\wedge C)Au(OEt_2)_2]SbF_6$ **2** which, after removal of a precipitate of $NBu^n{}_4SbF_6$ by centrifugation, can be isolated as a pale-yellow solid. The addition of 1,5-cyclooctadiene (COD) at room temperature to diethyl ether solutions of **2**, either pre-formed or generated *in-situ*, gave a colour change to yellow, accompanied by the precipitation of a yellow solid which was purified by washing with diethyl ether or hexane and isolated in 64% yield. The complex was recrystallized from dichloromethane and identified as $[(C^\wedge C)Au(COD]SbF_6$ (**3**). The addition of norbornadiene (NBD) to **2** in a similar fashion also gave a slight colour change, although in this case an ether/hexane solvent mixture was required to induce the precipitation of the alkene complex, $[(C^\wedge C)Au(NBD)]SbF_6$ (**4**). Unlike the structurally related dimethylgold complex **B**, both **3** and **4** are thermally stable under ambient conditions for indefinite periods of time.



Scheme 1 Synthesis of gold(III) alkene complexes.

The ^1H and ^{13}C NMR spectra of **3** and **4** confirm bidentate coordination of the alkenes (Table 1). The NMR data of the cyclooctadiene ligand in **3** closely correspond to those of the $[Me_2Au(COD)]^+$cation.[6] The ^1H NMR resonances for the olefinic H atoms experience only a small shift, by -1.3 and -0.83 ppm for **3** and **4**, respectively, commensurate with π-donation to the metal centre. The olefinic resonance of **4** is significantly high-frequency shifted compared to the analogous platinum complex $PtMe_2(NBD)$ [5.00 (=CH), 3.96 (CH), 1.54 (CH_2)],[10] indicative of the stronger Lewis acidity of the Au(III) cation. Whereas the olefinic ^{13}C NMR signal of the COD complex **3** is high-frequency shifted on coordination as expected, the norbornadiene complex **4** shows a low-frequency shift.

Recrystallisation of **3** and **4** from dichloromethane afforded crystals of $[(C^\wedge C)Au(COD)]SbF_6\cdot 0.125CH_2Cl_2$ and $[(C^\wedge C)Au(NBD)]SbF_6\cdot CH_2Cl_2$, respectively, which were suitable for X-ray diffraction (Figures 2 and 3). The COD ligand in **3** has (idealized) C_2 symmetry due to the constraint imposed by the ring structure, as noted earlier.[6] There are four independent cations and anions in this crystal. In the cation of Au(1), the Au-C(alkene) bond lengths differ by 0.063 Å in one C=C bond and by 0.025 Å in the other. The average C=C distance of 1.364(11) Å in **3** compares with the corresponding bond length of 1.381(12) Å in $PtMe_2(COD)$.[13] By contrast to the COD bonding, the norbornadiene ligand in **4** is bonded essentially symmetrically, with the olefinic ligand lying astride the (C^C)Au group and only small (0.005 – 0.006 Å) differences in the Au-C bond lengths. The Au-C(aryl) bond distances to the C-atoms of the C^C chelate ligand in **4** are noticeably shorter than those in **3** (average 2.022 *vs* 2.041 Å), possibly as a reflection of reduced steric interaction with the Bu^t-substituted C^C backbone and the narrower bite angle of the NBD ligand (*ca* 62° in **4** *vs* 78° in **3**). The structural parameters confirm that bonding of the alkenes occurs mainly by donation of π-electron density to the metal. Coordination of the C=C bonds to gold(III) leads to only a small elongation by 1.8% and 1.4% compared to the free COD and NBD, respectively, in line with a low degree of back-bonding by gold(III).

The lability of the ether ligands in **2** make this compound a useful synthon for complexes of weak ligands. Efforts to obtain crystals of **2** failed; however, from one such crystallisation attempt $[(C^\wedge C)Au(\mu\text{-}OH)]_2$ was obtained as a white solid, evidently due to the presence of traces of moisture (see Supporting Information). Attempts to generate $(C^\wedge C)Au^+$ complexes of ethylene or non-chelating 1-alkenes failed, due to the inability of these weak ligands to displace diethyl ether from the gold coordination sphere. The addition of a potentially chelating dienone, such as 1,5-di-*p*-tolylpenta-1,4-dien-3-one, to a solution of **2** led to an immediate colour change, and bright

Table 1. Comparison of ^1H, ^{13}C NMR (CD_2Cl_2) and structural data of gold(III) π-alkene complexes

Compound	δ ^1H, C=CH	Δδ (C=CH)	δ ^1H(CH, CH_2)	δ ^{13}C (C=C)	Δδ ^{13}C	δ ^{13}C (CH, CH_2)	r(C=C) [Å]
1,5-COD	5.57 (brs, 4H)		2.37	128.5		28.05	1.340 (3)[a]
3	6.87 (brs, 4H)	-1.3	3.31, 2.97	134.7	-6.2	28.8	1.357(11), 1.371(11)
NBD	6.8 (t, 4H, *J* = 2 Hz)		3.62 (m, 2H), 2.03 (t, 2H, *J* 1.6 Hz)	143.3		75.2, 50.3	1.3362(30)[b]
4	7.63 (t, 4H, *J* = 2.5 Hz)	-0.83	4.68 (br,2H), 2.62 (br, 2H)	133.7	9.6	85.7, 54.5	1.355(4), 1.354(4)

[a] Gas phase structure by electron diffraction, ref. [11]. [b] By microwave spectroscopy, ref. [12].

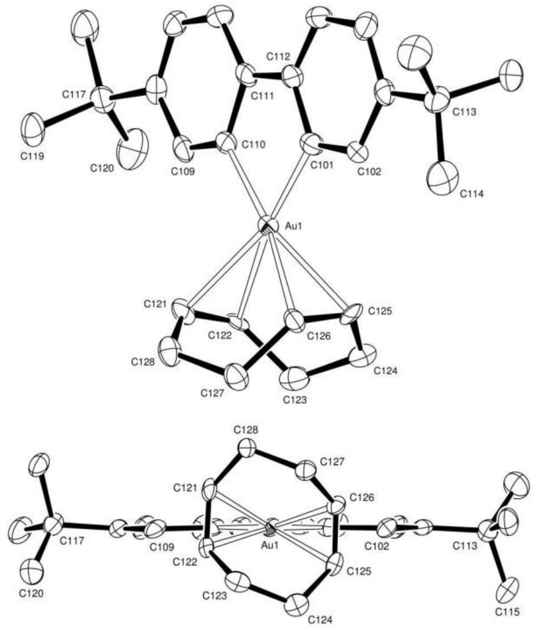


Figure 2. Top view (top) and side view (bottom) of one of the four independent cations of **3**$^+$. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [°]: Au1-C101 2.032(8), Au1-C110 2.049(7), Au1-C121 2.347(7), Au1-C122 2.410(7), Au1-C125 2.371(7), Au1-C126 2.396(7), C121-C122 1.357(11), C125-C126 1.371(11); C101-Au1-C110 81.0(3), C121-Au1-C126 77.7(3), C125-Au1-C122 78.2(3).

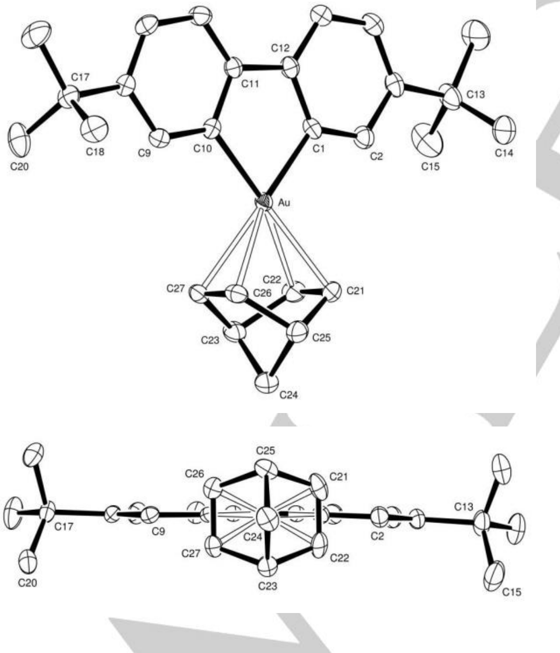


Figure 3. Top view (top) and side view (bottom) of the structure of **4**$^+$. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [°]: Au-C10 2.027(2), Au-C1 2.017(2), Au-C21 2.370(3), Au-C22 2.364(2), Au-C26 2.375(3), Au-C27 2.370(2), C(21)-C(22) 1.355(4), C(26)-C(27) 1.354(4). C1-Au-C10 80.70(10), C21-Au-C26 62.14(10), C22-Au-C27 62.43(9), C22-C23-C27 105.3(2).

orange crystals of [(C^C)Au(dienone)$_2$]SbF$_6$ (**5**) were isolated, which show a C=O stretching frequency at 1593 cm^{-1}. The crystal structure of **5** confirmed that the donor ligands are O-bonded (Figure 4), in contrast to the dienone C=C coordination in the well-known Pd$_2$(dibenzylideneacetone)$_3$ complex.[14] In the crystal, the asymmetric unit contains two cations, two anions and two 'solvent' molecules (which have not been fully identified). The two cations are very similar and related by a pseudo-centre of symmetry; each has a pseudo-twofold symmetry axis which divides the C^C ligand in two and relates (approximately) the two ketone ligands. The two cations are aligned so that the gold atom of one lies *ca* 3.64 Å over the ring of C(6-11) of the other (see Supporting Information).

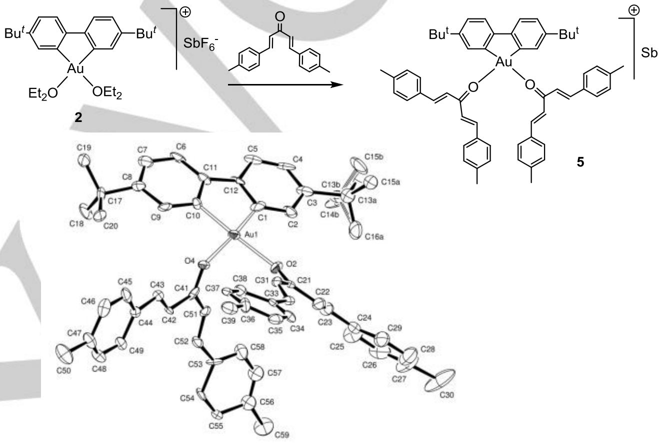
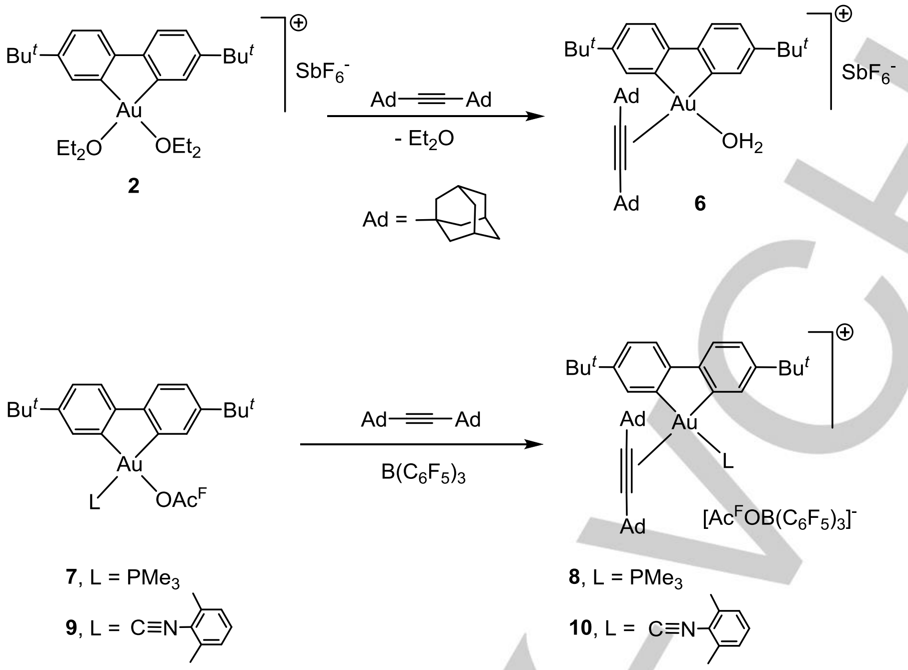


Figure 4. Synthesis and structure of the dienone complex **5**. Ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [°]: Au(1)-C(1) 1.97(3), Au(1)-C(10) 2.00(2), Au(1)-O(2) 2.142(13), Au(1)-O(4) 2.155(12), O(2)-C(21) 1.24(2), O(4)-C(41) 1.24(3), C(22)-C(23) 1.34(3); C(1)-Au(1)-C(10) 81.1(8), C(1)-Au(1)-O(2) 90.8(7), C(10)-Au(1)-O(2) 170.2(7), C(1)-Au(1)-O(4) 174.7(8).

In gold(I) complexes, alkynes have been found to be comparable in donor strength to alkenes,[15] although NMR equilibrium studies showed that alkynes such as 3-hexyne are less strongly bonded than even weakly coordinating solvents such as acetonitrile.[16] We therefore explored alkyne binding to the (C^C)Au(III) fragment.

In contrast to the inability of these gold(III) complexes to form 1-alkene complexes, the addition of two molar equivalents of bis-1-adamantyl acetylene to a solution of **2** led to the formation of a colourless microcrystalline solid which proved stable in dichloromethane solution at room temperature but slowly decomposed during crystallization attempts. The product contained one alkyne ligand per gold centre which showed NMR signals typical for coordinated alkyne, alongside the signals of free AdC≡CAd. While at room temperature the signals for the C^C ligand indicate C_2 symmetry, with only one Bu^t resonance, lowering the temperature to -30 °C showed splitting of the signals for the biphenyl backbone and two separate Bu^t signals, consistent with the formation of [(C^C)Au(AdC≡CAd)(H$_2$O)]SbF$_6$ (**6**) (Scheme 2). The product **6** was characterised in CD$_2$Cl$_2$ solution in the presence of excess acetylene; under these



Scheme 2 Synthesis of mixed-ligand gold(III) acetylene complexes

conditions it is thermally stable at room temperature for several days. Drying a sample under vacuum afforded a pale-yellow powder which showed a C≡C stretching mode in the infrared spectrum at 2120 cm^{-1}. However, removal of the excess acetylene by washing with hexane led to decomposition. The expected bis(alkyne) complex was not formed, apparently due to steric hindrance by the adamantyl substituents. The water molecule gives rise to a broad ^{1}H NMR signal at δ 6.6 ppm and is thought to be introduced during the reaction of the dihalide **1** with hygroscopic $AgSbF_6$ to generate a solution of **2** in-situ. In line with this, one crystallization attempt afforded crystallographically characterized $[(C\text{^}C)Au(OH_2)_2]SbF_6$ (see Supporting Information, Figure S1). It is noteworthy that while gold cations are known to catalyse the hydration of alkynes to ketones,[17] no such reaction was observed in the case of the aquo complex **6**, most probably due to the high steric stabilisation provided by the adamantyl substituents.

In order to avoid the introduction of traces of water with $AgSbF_6$, an alternative synthetic route was attempted by reacting the trifluoroacetate complex $(C\text{^}C)Au(OAc^F)PMe_3$ (**7**) with bis-adamantyl acetylene (Scheme 2). On addition of $B(C_6F_5)_3$ at room temperature to abstract the acetate ligand a bright yellow solution formed, which was identified spectroscopically as the alkyne complex $[(C\text{^}C)Au(AdC{\equiv}CAd)PMe_3][Ac^FOB(C_6F_5)_3]$ (**8**). Drying the product under vacuum afforded a bright yellow air-stable powder which shows the IR-active C≡C stretch at 2106 cm^{-1}. The analogous reaction of the isocyanide complex $(C\text{^}C)Au(OAc^F)(CNxyl)$ (xyl = 2,6-$Me_2C_6H_3$) (**9**) with bis-adamantyl acetylene and $B(C_6F_5)_3$ gave $[(C\text{^}C)Au(AdC{\equiv}CAd)(C{\equiv}Nxyl)][Ac^FOB(C_6F_5)_3]$ (**10**) as a bright yellow powder. The IR spectrum of the solid confirmed alkyne and isocyanide binding, with stretching modes at 2216 (C≡N) and 2114 (C≡C) cm^{-1}.

Table 2. Comparison of ^{13}C NMR data of gold(III) alkyne complexes

Compound	δ ^{13}C (C≡C)	Δδ ^{13}C	δ ^{13}C (CH, CH_2)
AdC≡CAd	87.6		43.5, 36.4, 29.2, 28.3
6	99.8	-12.2	42.1, 35.3, 33.2, 27.5
8	96.9	-9.3	43.1, 35.4, 34.5, 27.7
10	97.3	-9.7	43.2, 35.5, 33.9, 27.7

The alkyne coordination is further documented by the ^{13}C NMR chemical shifts (Table 2). Coordination of bis-adamantyl acetylene to the metal centre leads to deshielding and a high-frequency shift, although, as previously noted,[7] the δ and Δδ ranges of these Au(III) adducts are very similar to the values for alkyne complexes of Au(I). The chemical shift changes therefore reflect primarily the donor interaction to a Lewis acidic metal centre but are not indicative of the metal oxidation state.

The alkyne complexes reported here are significantly more thermally stable than previously reported 3-hexyne and $Bu^tC{\equiv}CMe$ complexes supported by C^N chelate ligands,[7] most probably a function of the alkyne substituents. Unfortunately attempts to grow crystals of **6**, **8** and **10** suitable for X-ray diffraction were not successful. However, the constitution of these compounds could be unequivocally established by NMR spectroscopy. These complexes represent the first examples of mixed-ligand gold alkyne complexes containing a combination of weak (alkyne) and strong donors (phosphine, isocyanide). Remarkably, there was no sign of ligand rearrangement and formation of $[(C\text{^}C)AuL_2]^+$ where L = PMe_3 or C≡NR.

Computational Studies. In order to assess the bonding of alkenes and alkynes in more detail, and also to probe the *trans*-influence of C^C vs. C^N^C ligands in these square-planar d^8 systems, we turned to density functional theory (DFT) calculations. The effect of the ancillary ligand environment was probed by comparing (C^C)Au$^+$, Me_2Au^+ and (C^N^C)Au$^+$. Simplified C^C and C^N^C ligand models were used which omitted *t*Bu substituents. Calculations included a solvent model (PCM = dichloromethane, also for geometry optimizations; see Supporting Information for additional data on checking the influence of the basis set, functional, absence of solvent model, and inclusion of the *t*Bu substituents of the C^C ligand). Although the focus of the present work is on (C^C)Au$^+$ complexes, binding to (C^N^C)Au$^+$ was included to help analyze the role of the *trans* influence on the Au-L binding energies. A range of *n*-donor (H_2O, Me_2O, Et_2O) and unsaturated ligands with strong (CO) and weak (alkenes, alkynes) acceptor properties was considered.

To understand the trends in Au-L binding energies we start with the C^N^C system of type **A** (Figure 1), where the *trans* influence due to the pyridine moiety is modest.[18] Table 3 lists binding enthalpies for a selection of simple substrates: ethers, CO, acetylenes and olefins. The enthalpies span a range of 33-53 kcal/mol, implying relatively strong binding. For the *unsubstituted* substrates the trend is CO > $CH_2{=}CH_2$ > HC≡CH > OH_2. In all cases, binding increases with *increasing* substitution of the substrate: H < Me < *t*Bu < Ad, the opposite of what would have been expected based on steric factors. The stabilization on going from [(C^N^C)Au(HC≡CH)]$^+$ to [(C^N^C)Au(MeC≡CMe)]$^+$ is remarkable: 9.2 kcal/mol, or 4.6 kcal per Me group. The geometries of these two alkyne complexes do not differ much. Of the 9.2 kcal/mol, 2.9 kcal/mol come from DFT-D3 dispersion corrections. The remainder may be related to the accumulation of positive charge at the alkyne being stabilized by alkyl substituents (+I effect). A natural population analysis (Table 4) yields a total charge on the alkyne of +0.30 *e* in [(C^N^C)Au(HC≡CH)]$^+$, increasing to +0.35 *e* in [(C^N^C)Au(MeC≡CMe)]$^+$. The increase in stabilization on going from *t*Bu to Ad is in line with the known stronger electron-donating ability of the Ad group,[19] and AdC≡CAd is the strongest-binding substrate evaluated, with a binding enthalpy that is some 17.4 kcal/mol higher than for HC≡CH.

The stabilizing effect of alkylation is smaller for alkenes ($CH_2{=}CH_2$ vs $MeCH{=}CH_2$, 2.1 kcal/mol) and even weaker for *n*-donors such as ethers (OH_2 vs OMe_2, 1.6 kcal/mol per Me group). There is no significant increase in binding energy on going from $MeCH{=}CH_2$ to *t*BuCH=CH_2. Within the group of olefin complexes, the doubly substituted and strained olefin NBE binds more strongly than even *t*BuCH=CH_2.

Turning now to binding by (C^C)Au fragments (Table 3), we see a much decreased per-substrate binding enthalpy due to the strong *trans* influence of the Au-C(aryl) bonds. The picture for [(C^C)AuL$_2$]$^+$ compounds is also somewhat complicated by steric crowding with some of the bulkier ligands L, so it is useful to start with the *first* L binding enthalpy to the 12-electron cation [(C^C)Au]$^+$ (equ. 1):

$$[(C\text{^}C)Au]^+ + L \rightarrow [(C\text{^}C)AuL]^+ \qquad \Delta H_1 \qquad (1)$$

These values are about 2/3 of the corresponding (C^N^C)Au$^+$ values, varying from 17 to 30 kcal/mol. The parent acetylene HC≡CH is most weakly bound, but also benefits most from the +I effect of alkyl substituents, so that AdC≡CAd is again the strongest binding substrate.

Table 3. Substrate binding enthalpies[a] (298 K, kcal/mol) to [(C^N^C)Au]$^+$ and [(C^C)Au]$^+$.

	C^N^C	**C^C**			
Substrate	**ΔH_{tot}[b]**	**ΔH_1[c]**	**ΔH_2[d]**	**av. ΔH per L**	**% of CNC**
OH_2	-33.37	-20.31	-17.96	-19.1	57
OMe_2	-36.61	-21.89	-19.94	-20.9	57
OEt_2	-38.12	-22.90	-20.04	-21.5	56.3
CO	-45.52	-17.21	-14.77	-16.0	35
HC≡CH	-35.46	-16.87	-11.56	-14.2	40
MeC≡CMe	-44.61	-24.17	-19.36	-21.8	48.8
*t*BuC≡C*t*Bu	-50.17	-28.44	-11.37	-19.9	39.7
AdC≡CAd	-52.86	-30.41	-17.76	-24.1	45.6
$CH_2{=}CH_2$	-41.18	-19.02	-14.77	-16.9	41
$MeCH{=}CH_2$	-43.29	-20.92	-16.40	-18.7	43.1
*t*BuCH=CH_2	-43.65	-21.79	-14.01	-17.9	41
NBE	-46.78				

[a] TPSSH/cc-pVTZ/PCM(CH_2Cl_2)//B3LYP/SVP/PCM(CH_2Cl_2) with DFT-D3(zero damping) dispersion correction, see SI for details.
[b] Enthalpy change for the reaction [(C^N^C)Au]$^+$ + L → [(C^N^C)Au(L)]$^+$.
[c] Enthalpy change for the reaction [(C^C)Au]$^+$ + L → [(C^C)AuL]$^+$.
[d] Enthalpy change for the reaction [(C^C)AuL]$^+$ + L → [(C^C)AuL$_2$]$^+$.

Table 4. Charges from natural population analysis for [(C^N^C)AuL]$^+$ complexes.

L	Au	C^N^C	L
OMe_2	0.968	-0.235	0.266
HC≡CH	0.852	-0.150	0.299
MeC≡CMe	0.865	-0.213	0.349
NBE	0.835	-0.165	0.330
$CH_2{=}CH_2$	0.835	-0.189	0.354

The *second* L binds to the 14-electron species [(C^C)AuL]$^+$ more weakly than the first (ΔH_2 range: 11-19 kcal/mol) and steric effects become significant (equ. 2 and 3).

$$[(C\text{^}C)AuL]^+ + L \rightarrow [(C\text{^}C)AuL_2]^+ \qquad \Delta H_2 \qquad (2)$$

$$[(C\text{^}C)Au]^+ + 2\,L \rightarrow [(C\text{^}C)AuL_2]^+ \qquad \Delta H_{tot} = \Delta H_1 + \Delta H_2 \qquad (3)$$

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This is particularly evident in the acetylene series, where the second *t*BuC≡C*t*Bu binds much more weakly than either MeC≡CMe or AdC≡CAd. On going from MeC≡CMe to the *t*Bu derivative steric hindrance increases dramatically, reducing the binding energy. However, the further change from *t*Bu to Ad does not increase steric hindrance but still results in further electronic stabilization. A similar (though smaller) effect is seen in the olefin series, where the binding enthalpy is larger for $MeCH{=}CH_2$ than for either $CH_2{=}CH_2$ or *t*BuCH=CH_2. The bond enthalpy trends in C^N^C vs. C^C systems and the influence of steric repulsion in ΔH_2 are illustrated in Figure 5.

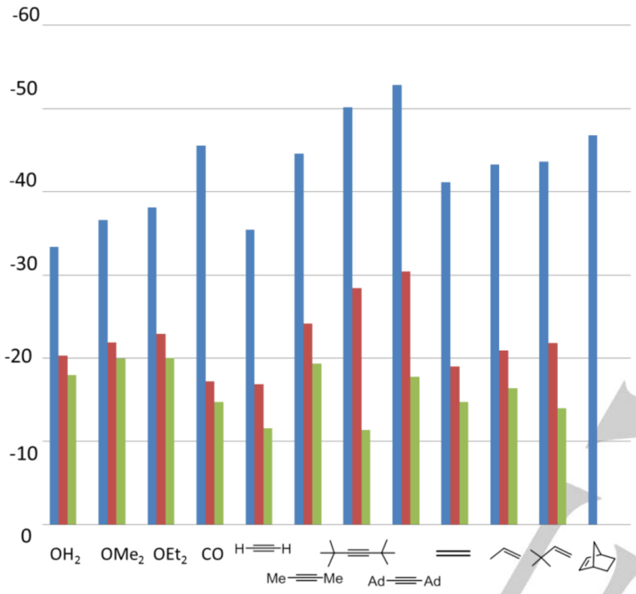
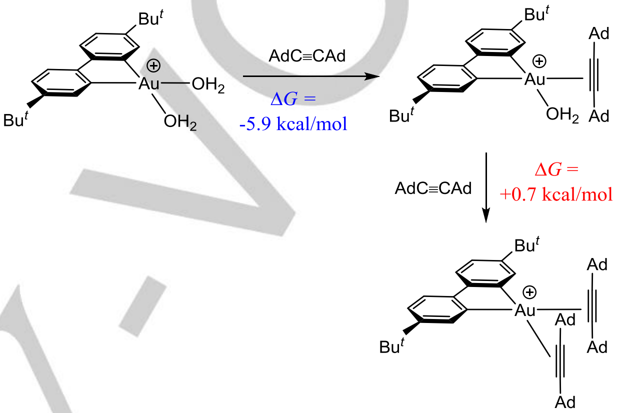


Figure 5. Substrate binding enthalpies (298 K, kcal/mol) to $[(C\text{^}N\text{^}C)Au]^+$ and $[(C\text{^}C)Au]^+$, showing bonding trends for different types of *n*-donor and π-donor ligands. ■ Enthalpy change for the reaction $[(C\text{^}N\text{^}C)Au]^+ + L \rightarrow [(C\text{^}N\text{^}C)Au(L)]^+$. ■ ΔH_1 = enthalpy change for the reaction $[(C\text{^}C)Au]^+ + L \rightarrow [(C\text{^}C)AuL]^+$. ■ ΔH_2 = enthalpy change for the reaction $[(C\text{^}C)AuL]^+ + L \rightarrow [(C\text{^}C)AuL_2]^+$, illustrating the influence of steric repulsion.

Translating the above enthalpy trends to chemical behaviour is not entirely straightforward, and we will only address a few specific issues. AdC≡CAd is clearly the strongest-binding acetylene, and formation of $[(C\text{^}C)Au(AdC{\equiv}CAd)_2]^+$ from AdC≡CAd and naked $[(C\text{^}C)Au]^+$ is predicted to be favourable (ΔG = -30.3 kcal/mol). However, the bis(acetylene) complex is severely crowded, and in the presence of other ligands such as H_2O formation of a mono-acetylene mixed complex is preferred, as illustrated in Scheme 3:

This explains at least in part the non-observation of bis(AdC≡CAd)Au complexes in the presence of water or other small donors. In fact, the only bis(alkyne) or bis(alkene) complex for which formation from the $[(C\text{^}C)Au(L)(OH_2)]^+$ precursor is predicted to be exergonic is $[(C\text{^}C)Au(MeC{\equiv}CMe)_2]^+$, and that only by 0.1 kcal/mol.

Comparing the average ΔH_{av} values per L for the $[(C\text{^}C)AuL_2]^+$ system with the Au-L enthalpies in the $[(C\text{^}N\text{^}C)AuL]^+$ series (Table 3) highlights a dependence of the *trans* influence of N of C on the type of L: While the effect of an anionic C-donor weakens the Au-L bonds in all cases, simple *n*-donors such as ethers are less affected than π-donors, with an average bond enthalpy *trans* to C of about 50-60% of that *trans* to N. Ligands L which are π-donors but weak π-acceptors show ΔH_{av}(C^C) of about 40-45% that of the C^N^C system, whereas the strong π-acceptor CO is most weakened by the *trans* influence, down to 35%. These trends would make it appear less likely that C^C chelates are suitable for the stabilisation of Au(III)-CO complexes.[20]



Scheme 3. Energetics of ligand substitution by AdC≡CAd.

The formation of Au(III) diene complexes is mainly due to the chelate effect. Relative to $[(C\text{^}C)Au(OH_2)_2]^+$ di-olefin binding becomes favourable by -9.6 kcal/mol for $[(C\text{^}C)Au(COD)]^+$ and -6.0 kcal/mol for $[(C\text{^}C)Au(NBD)]^+$. The calculated free energy change for exchange of diene favours the COD complex by a margin of 4-7 kcal/mol regardless of functional, basis set, use of solvent in optimization, or simplification of the ligand. Figure 6 shows the binding enthalpy trends of OMe_2, alkynes and dienes to $(C\text{^}C)Au^+$, Me_2Au^+ and Me_2Pt fragments (for numerical values see Supporting Information, Table S1).

The results confirm the stronger binding of COD over NBD in all cases. The weaker binding of NBD relative to COD agrees with experimental observations in platinum chemistry.[21,22] However, while the enthalpies in Figure 6 show very similar trends for the three metal fragments under consideration, an analysis of charges from natural population analysis of $(C\text{^}C)Au^+$, Me_2Au^+ and Me_2Pt also show differences, such as the accumulation of negative charge on Me and only small positive change on Pt in Me_2Pt, whereas in Me_2Au^+ the methyl ligands are essentially neutral and the metal is strongly positively charged. This is illustrated in Figure 7, which shows molecular surfaces for the $[Me_2Au(NBD)]^+$ and $[(C\text{^}C)Au(NBD)]^+$ cations, colour-coded by the electrostatic potential, clearly illustrating that the C^C ligand accumulates considerably higher negative charge than the methyl ligands. This increase in negative partial charge on the C^C ligand in $(C\text{^}C)Au^+$ and more positive charges on the donor ligands and Au implies a more electron-accepting metal centre,

Table 6. Charges from natural population analysis for selected Au and Pt complexes.

	$(C^\wedge C)Au(L)_2^+$			$Me_2Au(L)_2^+$			$Me_2Pt(L)_2$		
L_2	Au	C^C	L_2	Au	Me_2	L_2	Pt	Me_2	L_2
2 OMe_2	0.899	-0.201	0.301	0.803	-0.094	0.292	0.207	-0.444	0.237
2 HC≡CH	0.769	-0.139	0.370	0.673	-0.009	0.336	0.186	-0.402	0.216
2 MeC≡CMe	0.797	-0.211	0.414	0.696	-0.074	0.377	0.211	-0.437	0.226
NBD	0.795	-0.200	0.405	0.703	-0.063	0.360	0.253	-0.441	0.189
COD	0.754	-0.228	0.474	0.659	-0.089	0.430	0.218	-0.449	0.231

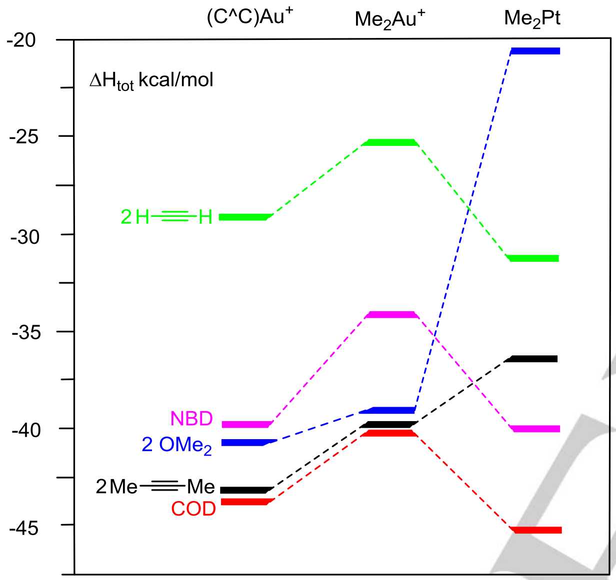


Figure 6. Comparison of total binding enthalpies (kcal/mol) of OMe_2, alkynes and dienes to $(C^\wedge C)Au^+$, Me_2Au^+ and Me_2Pt fragments (at 298 K, TPSSH/cc-pVTZ/PCM(CH2Cl2)//B3LYP/ SVP/ PCM(CH_2Cl_2) with DFT-D3(zero damping) dispersion correction).

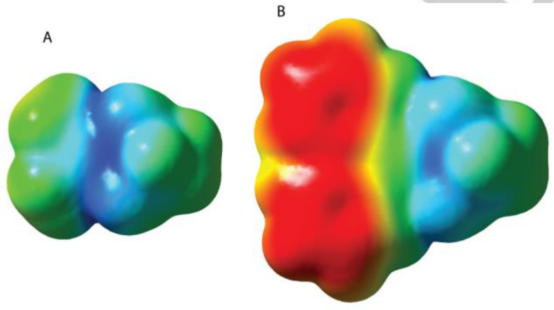


Figure 7. Colour-coded electrostatic potential (ESP) distributions on vdW surfaces defined at an electron density of 0.0004 *e*·Bohr^{-3}: (A) $[Me_2Au(NBD)]^+$; (B) $[(C^\wedge C)Au(NBD)]^+$. Colour range: red (less positive, +0.08) to blue (more positive, +0.16).

which may help explain the stronger alkene coordination and greater thermal stability of $[(C^\wedge C)AuL_2]^+$ complexes compared to the $[Me_2AuL_2]^+$ analogues.

Conclusions

The biphenylyl C^C chelate ligand has been shown to provide a convenient framework for the synthesis of gold(III) complexes with labile π-ligands, by imparting much improved thermal stability. This applies in particular to gold(III) alkyne complexes, which until very recently had been merely hypothetical species. Although the two anionic C-atoms in $[(C^\wedge C)AuL_2]^+$ cations exert a strong *trans* influence which weakens the Au-L bonds, this is alleviated to some extent by the stronger electron-withdrawing character of C^C compared to methyl ligands (as in Me_2Au^+); the resulting increase in metal Lewis acidity strengthens π-bonding. This, in effect, makes ligand binding to the $(C^\wedge C)Au^+$ fragment more akin to Me_2Pt and less like Me_2Au^+. These factors are sufficient to render alkyne and chelating alkene complexes isolable and thermally stable. The bonding of cyclooctadiene and norbornadiene to the $(C^\wedge C)Au^+$ fragment resembles the situation in (diene)$PtMe_2$, although the back-bonding is substantially less. As a computational exploration of the effect of C- vs. N-donors *trans* to L shows, different ligands are affected to different degrees, with *n*-donors showing a much smaller reduction in bond enthalpy due to the *trans* influence than strong π-acceptors like CO. The C^C ligand backbone further demonstrated its utility by enabling the synthesis of the first examples of alkyne/phosphine and alkyne/isocyanide mixed-ligand gold(III) complexes.

Experimental Section

CCDC 1839314– 1839317 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. See the Supporting Information for experimental details.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: gold • bond energy • alkene complex • alkyne complex • DFT calculation

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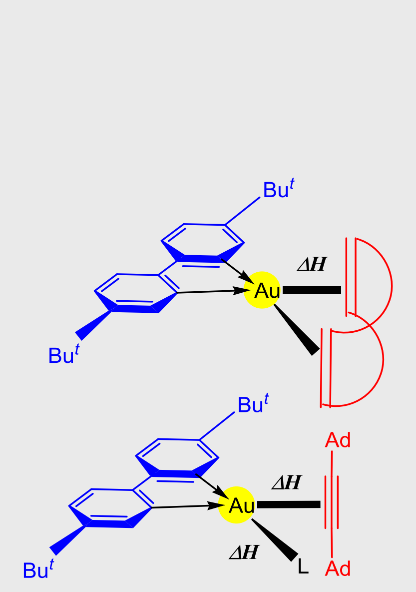

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