

Synthesis and Structural Characterization of N-Heterocyclic Carbene Gold(I) Complexes

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A series of *N*-heterocyclic carbene Au(NHC)Cl complexes (NHC = IMes (**1**), SIMes (**2**), IPr (**3**), SIPr (**4**), IPrMe (**5**), IMe (**6**), ICy (**7**), IAd (**8**), ITPh (**9**)) have been synthesized either through reaction of the corresponding imidazol-2-ylidene carbene with [Au(SMe₂)Cl] or by transmetalation of the respective Ag(I)–NHC complex in the presence of 1 equiv of [Au(SMe₂)Cl]. All of the gold(I) complexes [Au(IMes)Cl] (**10**), [Au(SIMes)Cl] (**11**), [Au(IPr)Cl] (**12**), [Au(SIPr)Cl] (**13**), [Au(IPrMe)Cl] (**14**), [Au(IMe)Cl] (**15**), [Au(ICy)Cl] (**16**), [Au(IAd)Cl] (**17**), and [Au(ITPh)Cl] (**18**) have been characterized spectroscopically and structurally by X-ray diffraction. The ¹³C chemical shifts of the carbene carbon have been compared through subtraction of the corresponding imidazol-2-ylidene carbene and suggest that there is little difference in donor ability of the NHC ligands bound to gold(I). Crystal structure analysis reinforces this notion, with no obvious change in Au–C(NHC) bond length on going from saturated and unsaturated NHC ligands. For complexes **14**, **17**, and **18** Au⋯H–C interactions were observed from the sidearm substituents on the NHC ligand. Furthermore, the triazolium complex **18** also contains Au⋯Au interactions as well as head-to-tail π – π stacking of the phenyl sidearm substituent from neighboring molecules.

The development of *N*-heterocyclic carbene (NHC) metal complexes has now become a well-established area of research.¹ As a result, a large variety of metal–NHC complexes are known, many of which have been successfully used in catalytic applications.² Interestingly, most studies focusing on catalysts incorporating NHC ligands have revolved around the platinum metal groups. In numerous instances simple substitution reaction routes involving replacement of phosphines by NHC ligands lead to higher catalytic activity as well as improved thermal stability of the resulting organometallic complex. The working hypothesis is that NHCs are more powerfully σ -donating than the closely related phosphine ligands, forming stronger bonds to transition metals and thereby also leading to electron-rich metal centers.³ Recently we reported a detailed steric and electronic investigation of the NHC and phosphine ligand classes involving the square-planar complex (L)–Ni(CO)₃, which allowed a direct comparison of the two ligand families and also led to the experimental determination of Ni–C(NHC) bond energies.^{4,5} In contrast to the wealth of information available for such late-

transition-metal NHC compounds, the chemistry of linear two-coordinate coinage-metal–NHC compounds in general, and gold(I)–NHC complexes in particular, has remained relatively unexplored.^{6–9} Complexes of the general formula Au(NHC)(X) (X = halide) are especially scarce, and this prompted us to develop reliable synthetic methods for the preparation of such monocarbene–gold(I) compounds. This was initiated to provide a better understanding of the (NHC)Au^I solid-state and solution behavior and to explore their reaction chemistry. It should be noted that gold complexes have received considerable attention in medicinal chemistry, where they display interesting antitumor and antimicrobial activity.¹⁰ Moreover, Au(I) complexes often exhibit interesting photophysical properties by displaying strongly luminescent behavior.¹¹ Finally, the use of Au complexes in homogeneous catalysis has undergone a renaissance as of late and spectacular achievements have recently been reported.^{12,13}

We report here the synthesis of a series of two-coordinate Au(I) chloride complexes of general composition Au(NHC)Cl. The NHC ligands used are shown in

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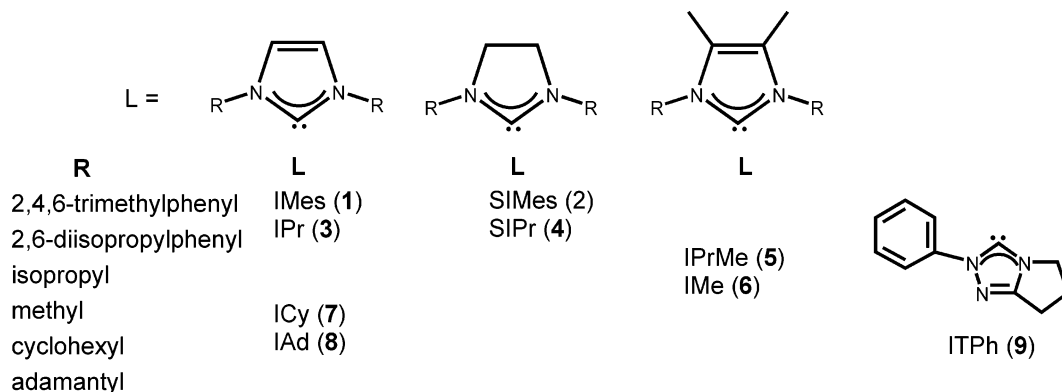


Figure 1. NHC ligands used in this study.

Figure 1 and comprise commonly used saturated and unsaturated ligands such as IMes (1), SIMes (2), IPr (3), SIPr (4), IPrMe (5), IMe (6), ICy (7), and IAd (8) as well as the triazolium ligand ITPh (9). All new Au(I)–NHC complexes were characterized by spectroscopic methods, elemental analysis, and finally by X-ray crystallography. Both X-ray crystallography and NMR spectroscopy allowed insight into the electronic characteristics of this family of complexes.¹³ C NMR data of the carbenic carbon proved to be especially useful. We present a comparison of NMR shift values of the free NHC ligands 1–9, the NHC–AuCl complexes as well as their isolobal counterparts NHC–Ni(CO)₃ and NHC–

HCl. It should be noted that structural characterization as well as catalytic uses of complex [Au(IPr)Cl] (12) have recently been reported.¹⁴

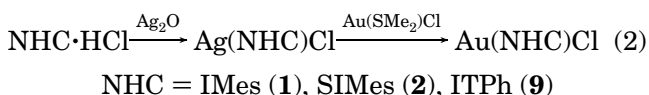
Results and Discussion

A straightforward reaction between 1 equiv of AuCl and free NHC was initially attempted as the potentially most direct route to Au(NHC)Cl complexes. This route, however, proved unsatisfactory, as it led to poor yields of Au(NHC)Cl in addition to byproducts [Au(NHC)₂]Cl and metallic gold. Similar byproducts have been observed in the attempted preparation of [Au(I^tBu)(X)] (I^tBu = 1,3-di-*tert*-butylimidazol-2-ylidene; X = BF₄, ClO₄).⁷ For that reason, an exchange reaction between a THF solution containing IPr (3), SIPr (4), IPrMe (5), IMe (6), ICy (7), IAd (8), or I^tBu and [Au(SMe₂)Cl] was investigated and produced the complexes [Au(IPr)Cl] (12), [Au(SIPr)Cl] (13), [Au(IPrMe)Cl] (14), [Au(IMe)Cl] (15), [Au(ICy)Cl] (16), and [Au(IAd)Cl] (17) and the already reported [Au(I^tBu)Cl]⁷ as white solids in high yields (eq 1). Although the synthetic approach proved



NHC = IPr (3), SIPr (4), IPrMe (5),
IMe (6), ICy (7), IAd (8)

fairly general, it was unsuccessful with IMes (1), affording a mixture of products similar to that found using the AuCl and free carbene route. We then examined an alternative approach where an equimolar amount of Au–(SMe₂)Cl is reacted with the respective *in situ* generated Ag(I)–NHC salt (NHC = IMes (1), SIMes (2), ITPh (9)), giving rise to the complexes [Au(IMes)Cl] (10), [Au–(SIMes)Cl] (11), and [Au(ITPh)Cl] (18) in moderate to high yield. The advantages of this method are that no regeneration of the free carbene is necessary. This reaction can be performed in air with no decrease in yield, and no decomposition of 10 to metallic gold is observed (eq 2) under these conditions.



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Table 1. ^{13}C NMR Data for $[\text{Au}(\text{NHC})\text{Cl}]$ Complexes

| complex | solvent | $\delta_{\text{C}}(\text{Au}-\text{C}(1))$ | $\delta_{\text{C}}(\text{NHC})$ | ref | solvent | $\Delta\delta_{\text{C}}$ | $\delta_{\text{C}}(\text{NHC}\cdot\text{HCl})^a$ | solvent | $\Delta\delta_{\text{C}}$ |
|--|--------------------------|--|---------------------------------|-----|------------------------|---------------------------|--|-------------------|---------------------------|
| $[\text{Au}(\text{IMes})\text{Cl}]$ (10) | CDCl_3 | 173.4 | 219.7 | 17 | C_6D_6 | 46.3 | 134.76 | $\text{DMSO}-d_6$ | 38.6 |
| $[\text{Au}(\text{SIMes})\text{Cl}]$ (11) | CDCl_3 | 195.0 | 243.8 | 18 | C_6D_6 | 48.8 | 160.2 | $\text{DMSO}-d_6$ | 34.8 |
| $[\text{Au}(\text{IPr})\text{Cl}]$ (12) | CD_2Cl_2 | 175.1 | 220.6 | 18 | C_6D_6 | 45.5 | 132.22 | $\text{DMSO}-d_6$ | 42.9 |
| $[\text{Au}(\text{SIPr})\text{Cl}]$ (13) | CDCl_3 | 196.1 | 244.0 | 18 | C_6D_6 | 47.9 | 160.0 | $\text{DMSO}-d_6$ | 36.1 |
| $[\text{Au}(\text{IPrMe})\text{Cl}]$ (14) | CDCl_3 | 166.0 | 207.9 | 19 | C_6D_6 | 41.9 | | | |
| $[\text{Au}(\text{IMe})\text{Cl}]$ (15) | CD_2Cl_2 | 168.4 | 213.7 | 19 | C_6D_6 | 45.3 | | | |
| $[\text{Au}(\text{ICy})\text{Cl}]$ (16) | CD_2Cl_2 | 168.0 | 210.1 | 20 | C_6D_6 | 42.1 | 134.51 | $\text{DMSO}-d_6$ | 33.5 |
| $[\text{Au}(\text{IAd})\text{Cl}]$ (17) | CD_2Cl_2 | 166.3 | 211.4 | 17 | C_6D_6 | 45.1 | 132.11 | $\text{DMSO}-d_6$ | 34.2 |
| $[\text{Au}(\text{ITPh})\text{Cl}]$ (18) | CDCl_3 | 167.8 | | | | | 135.26 | $\text{DMSO}-d_6$ | 32.5 |
| $[\text{Au}(\text{ItBu})\text{Cl}]^b$ | CDCl_3 | 168.2 | 213.2 | 21 | C_6D_6 | 45.0 | 132.7 | $\text{DMSO}-d_6$ | 35.5 |
| $[\text{Au}(\text{Me}_2\text{-imy})\text{Cl}]^c$ | $\text{DMSO}-d_6$ | 169 | 213.7 | 22 | C_6D_6 | 44.7 | | | |
| $\text{Ni}(\text{CO})_3(\text{IMes})$ | C_6D_6 | 198.73 | 219.7 | 17 | C_6D_6 | 20.97 | 134.76 | $\text{DMSO}-d_6$ | 64.0 |
| $\text{Ni}(\text{CO})_3(\text{SIMes})$ | C_6D_6 | 220.40 | 244.0 | 18 | C_6D_6 | 23.6 | 160.2 | $\text{DMSO}-d_6$ | 60.2 |
| $\text{Ni}(\text{CO})_3(\text{IPr})$ | C_6D_6 | 198.21 | 220.6 | 18 | C_6D_6 | 22.39 | 132.22 | $\text{DMSO}-d_6$ | 66.0 |
| $\text{Ni}(\text{CO})_3(\text{SIPr})$ | C_6D_6 | 223.16 | 244.0 | 18 | C_6D_6 | 20.84 | 160.0 | $\text{DMSO}-d_6$ | 63.2 |
| $\text{Ni}(\text{CO})_3(\text{ICy})$ | C_6D_6 | 199.48 | 210.1 | 20 | C_6D_6 | 10.62 | 134.51 | $\text{DMSO}-d_6$ | 65.0 |

^a Samples of $\text{NHC}\cdot\text{HCl}$ salts were prepared and ^{13}C NMR resonances recorded. ^b Reference 7. ^c Reference 8.

The ^1H NMR spectra of complexes **10**, **12**, **16**, and **17**, containing unsaturated NHC ligands, are characterized by a single resonance at low field for the two imidazole protons (6.98–7.08 ppm), as well as signals characteristic of their corresponding side-chain R groups. For the unsaturated complexes **14** and **15**, the ^1H NMR spectra are characterized by a single resonance at low field for the two methyl groups (2.19 and 2.13 ppm, respectively) on the unsaturated imidazole backbone, in addition to their side-chain R groups. The ^{13}C NMR spectra give rise to signals attributable to the side-chain R groups in addition to characteristic low-field resonances for the carbenic carbon ranging from 166 to 173.4 ppm. Saturated complexes **10** and **11** result in ^1H NMR spectra with resonances for the imidazole ring protons occurring at 3.98 and 4.06 ppm, respectively, and the expected signals for the mesityl and isopropyl phenyl side-chain groups. The ^{13}C spectra of the saturated NHC complexes display one resonance for the carbenic carbon atom at a marginally lower field (ca. 195 ppm) compared to that observed for the unsaturated complexes. For **16**, the ^1H NMR spectrum shows resonances attributable to the phenyl sidearm substituent as well as those associated with the pyrrolidine cycle. The ^{13}C NMR spectrum shows one characteristic low-field resonance for the carbenic carbon (167.8 ppm) that is similar to that for the unsaturated NHC complexes, in addition to a low-field signal attributable to the quaternary C4 carbon on the triazolium backbone. Elemental analyses for the complexes confirm their composition.

The carbene carbons in the new gold(I) complexes resonate between 166 and 195 ppm and appear closer to the corresponding upfield imidazolium salt ($\text{NHC}\cdot\text{HCl}$) resonance (Table 1) than that of the low-field free carbene. This is in contrast with what is observed for the $\text{Ni}(\text{CO})_3\text{-NHC}$ counterparts (Table 1). In line with the isolobal principle,¹⁵ which suggests that close analogies should exist between species containing protons (H^+) or the cationic fragment $[\text{ClAu}]^+$, it is interesting to note that our $(\text{NHC})\text{AuCl}$ complexes display NMR data trends that are closely related to those of the imidazolium salt $\text{NHC}\cdot\text{HCl}$. Raubenheimer et al. have noted large chemical shift variations on oxidation of bis(carbene)gold(I) to bis(carbene)dihalogold(III) species.¹⁶

In the $\text{Au}(\text{NHC})\text{Cl}$ system, a variation in donicity as a function of NHC substitution should directly affect the chemical shift of the carbene carbon, due to the change of Lewis acidity at the metal. Such a difference should be able to be quantified by subtraction of the experimental chemical shift value for the complexes' NHC carbenic carbon from that determined for the corresponding free NHC or imidazolium salt resonances, shown in Table 1. Overall, the experimental values indicate that no significant electronic variations among the NHC ligand class occur upon coordination to gold. The saturated SIMes and SIPr gold(I) complexes exhibit the largest upfield shift from the free carbene of δ 48.8 and 47.9 ppm, respectively. Within the unsaturated NHC class, the alkyl-substituted NHCs are expected to be better donors than their aryl counterparts; however, it appears that the aryl-substituted NHC ligands are slightly more donating when bound to gold! Analysis of the $\text{Au}-\text{C}(\text{NHC})$ bond lengths as determined from the structural studies (see below) also suggests that there are no major electronic differences between the various NHC ligands examined on coordination to the gold center.

To unambiguously characterize these complexes and to gain possible insight into fine structural differences between different NHCs and the gold(I) center, X-ray-quality crystals were grown of $[\text{Au}(\text{IMes})\text{Cl}]$ (**10**), $[\text{Au}(\text{SIMes})\text{Cl}]$ (**11**), $[\text{Au}(\text{IPr})\text{Cl}]$ (**12**), $[\text{Au}(\text{SIPr})\text{Cl}]$ (**13**), $[\text{Au}(\text{IPrMe})\text{Cl}]$ (**14**), $[\text{Au}(\text{IMe})\text{Cl}]$ (**15**), $[\text{Au}(\text{ICy})\text{Cl}]$ (**16**), $[\text{Au}(\text{IAd})\text{Cl}]$ (**17**), and $[\text{Au}(\text{ITPh})\text{Cl}]$ (**18**). Ball and stick representations are shown in Figure 2 (**10–13**), Figure 3 (**14–17**), and Figure 4 (**18**). A comparison of selected bond distances and angles is presented in Table 2.

All complexes have a two-coordinate gold(I) atom, in an essentially linear environment with $\text{C}-\text{Au}-\text{Cl}$ bond angles close to 180° . In **10**, **13**, and **14**, half of the molecule comprises the asymmetric unit of the structure, with a crystallographic 2-fold axis along the $\text{C}-\text{Au}-\text{Cl}$ array (which have to be linear) which bisects the NHC ligand. For **16** and **18**, two independent molecules comprise the asymmetric unit; in all other cases, a single molecule comprises the asymmetric unit. For all the compounds (except **12**), the $\text{Au}-\text{C}(\text{NHC})$ distances lie in the range 1.979–1.998 Å. While the

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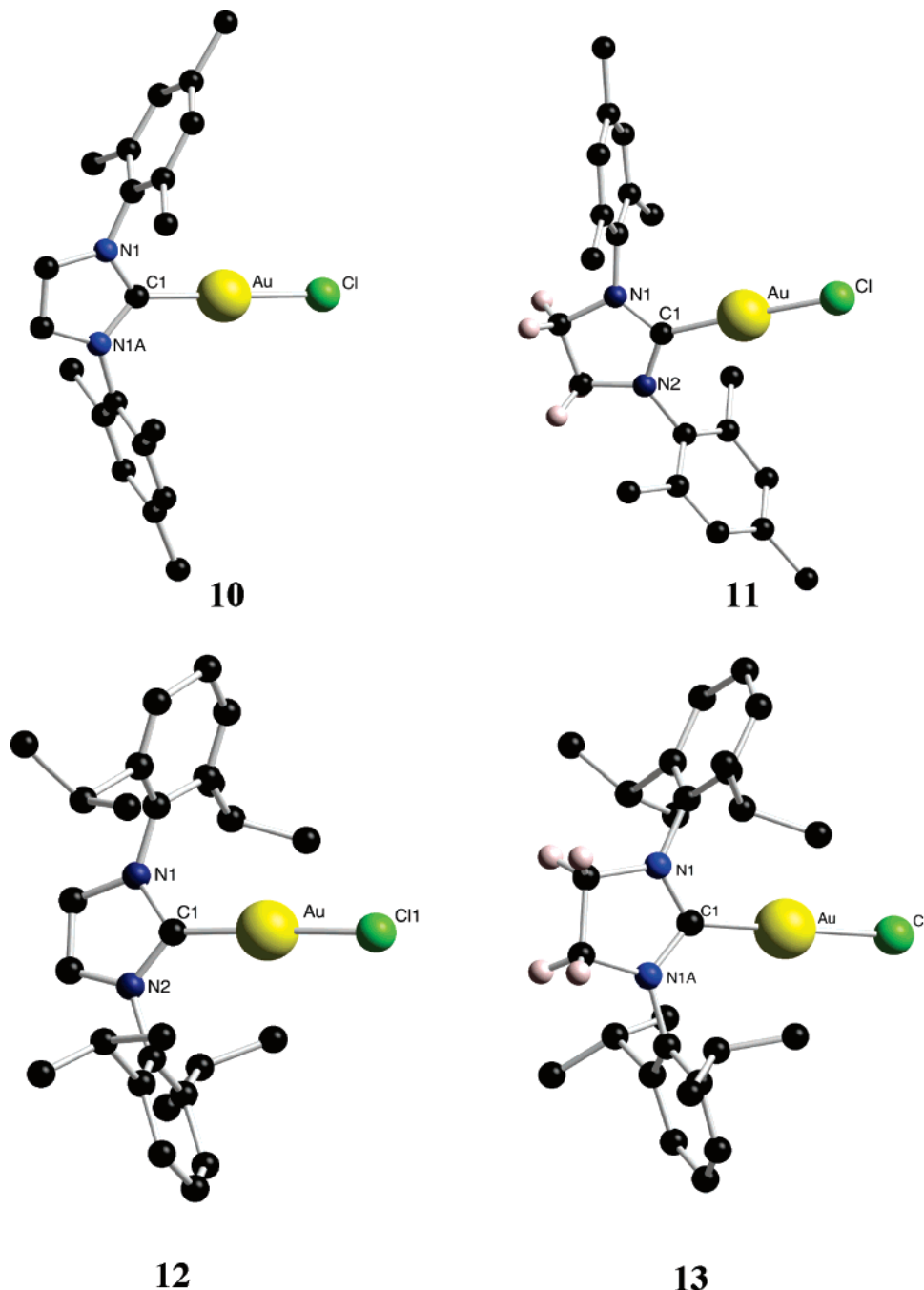


Figure 2. Ball and stick representations of aryl-substituted NHC–AuCl complexes: [Au(IMes)Cl] (**10**), [Au(SIMes)Cl] (**11**), [Au(IPr)Cl] (**12**), and [Au(SIPr)Cl] (**13**). Most hydrogen atoms have been omitted for clarity.

saturated NHC complex **11** shows a slightly shorter bond distance than its corresponding unsaturated analogue **10** (1.983(4) Å for **11** versus 1.998(5) Å for **10**), the saturated NHC complex **13** was found to have an Au–C(NHC) bond length greater than for its corresponding unsaturated analogue **12** (1.979(3) Å for **13** versus 1.942(3) Å for **12**). These differences are very small and lie within experimental error in the range for other Au–C(NHC) bond lengths. For compounds **10**–**18**, the Au–C(NHC) distance suggests a single-bond character, in good accordance with their strong σ -donor characteristics.^{3c,23} They are comparable to those re-

ported for other Au(I)(carbene) complexes^{6a,7,8,24} and, as also found in solution studies (see above), the electronic difference governing the NHC ligand class is relatively small. The Au–Cl distances in **10**–**18** lie in the range 2.2756(12)–2.306(3) Å and are marginally longer than

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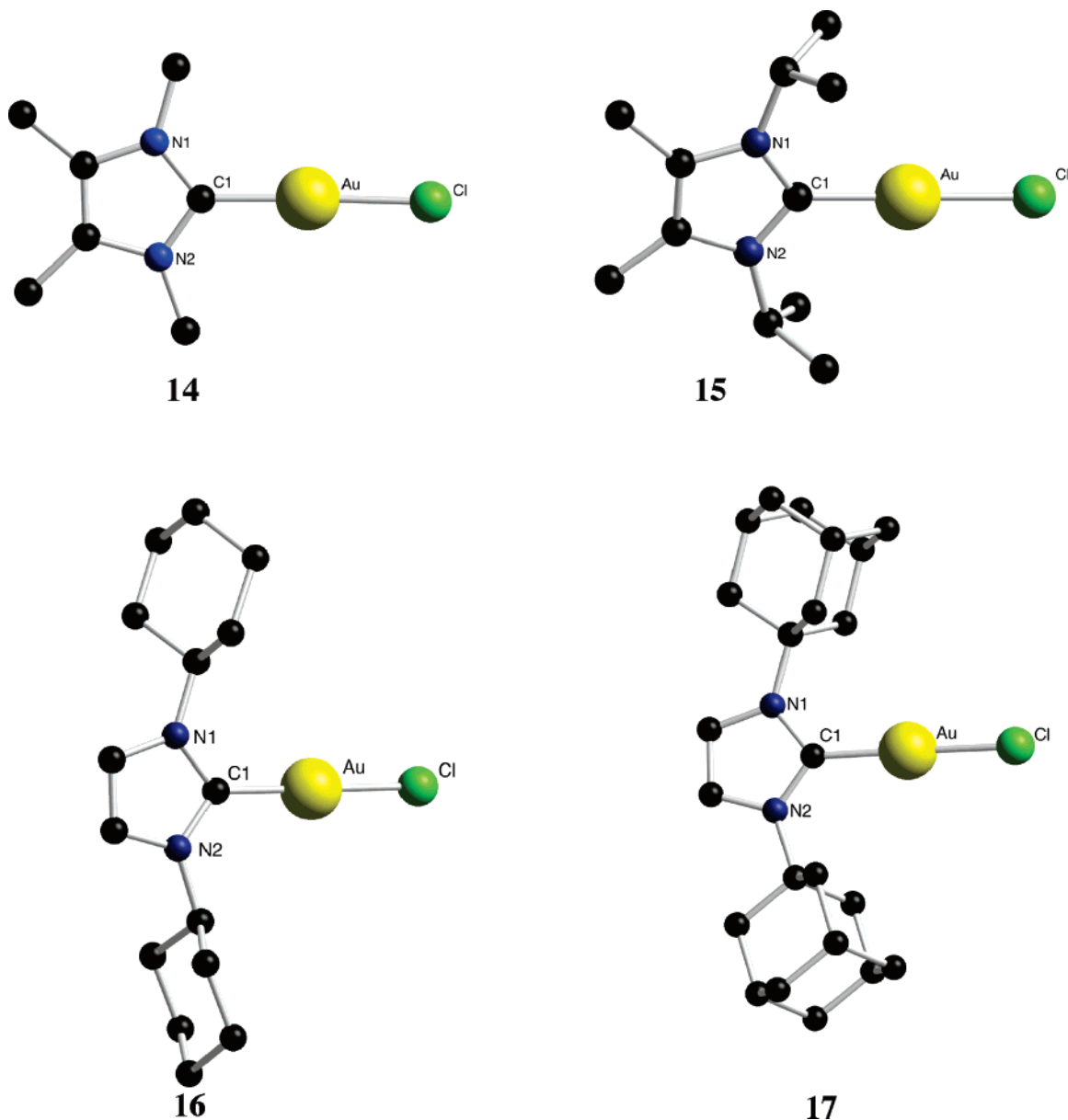


Figure 3. Ball and stick representations of alkyl-substituted NHC ligand complexes: [Au(IPrMe)Cl] (**14**), [Au(IME)Cl] (**15**), [Au(ICy)Cl] (**16**), and [Au(IAd)Cl] (**17**). Hydrogen atoms have been omitted for clarity.

that found for $[\text{AuCl}_2]^-$ (2.257 \AA),²⁵ a consequence of the trans influence of the carbene.^{6c,9,24d,e,g}

As seen for other crystallographically characterized complexes containing NHC ligands with aryl substituents, the R groups are rotated near perpendicular with respect to the imidazole backbone plane, resulting in a favorable arrangement around the metal center. In addition, the saturated imidazole backbones in SIMes and SIPr compounds, due to the presence of two sp^3 carbons in the heterocyclic ring, show torsion angles of

$8.2(4)^\circ$ (for **11**) and $5.8(2)^\circ$ (for **13**). These torsion values are significantly smaller than for free SIMes (13.4°), suggesting that some restriction in rotation is present on coordination with the gold center. For the unsaturated NHC complexes **14** and **15** the methyl substituents are positioned in the same plane as the imidazole backbone. The disposition of the isopropyl substituents in **14** is such that the two methyl substituents straddle the ring plane to either side and are directed toward the gold atom, with associated hydrogen atoms contacting it at 2.713 \AA ($\text{Au}\cdots\text{H5A}$ of C5) and 2.948 \AA ($\text{Au}\cdots\text{H6C}$ of C6). Closer $\text{Au}\cdots\text{H}-\text{C}$ contacts can be found in complexes **17** and **18**, with the former having two α -carbon atoms from both side-chain adamantyl groups approaching the metal center ($\text{Au}\cdots\text{H23A}$, 2.652 \AA ; $\text{Au}\cdots\text{H24A}$, 2.694 \AA ; $\text{Au}\cdots\text{H11A}$, 2.675 \AA ; $\text{Au}\cdots\text{H12A}$, 2.708 \AA). This $\text{Au}\cdots\text{H}-\text{C}$ interaction has been reported by others for intermolecular association.²⁶ For the triazolium NHC complex **18**, the plane of the phenyl sidearm substituent is rotated $32.8(2)^\circ$ with respect to

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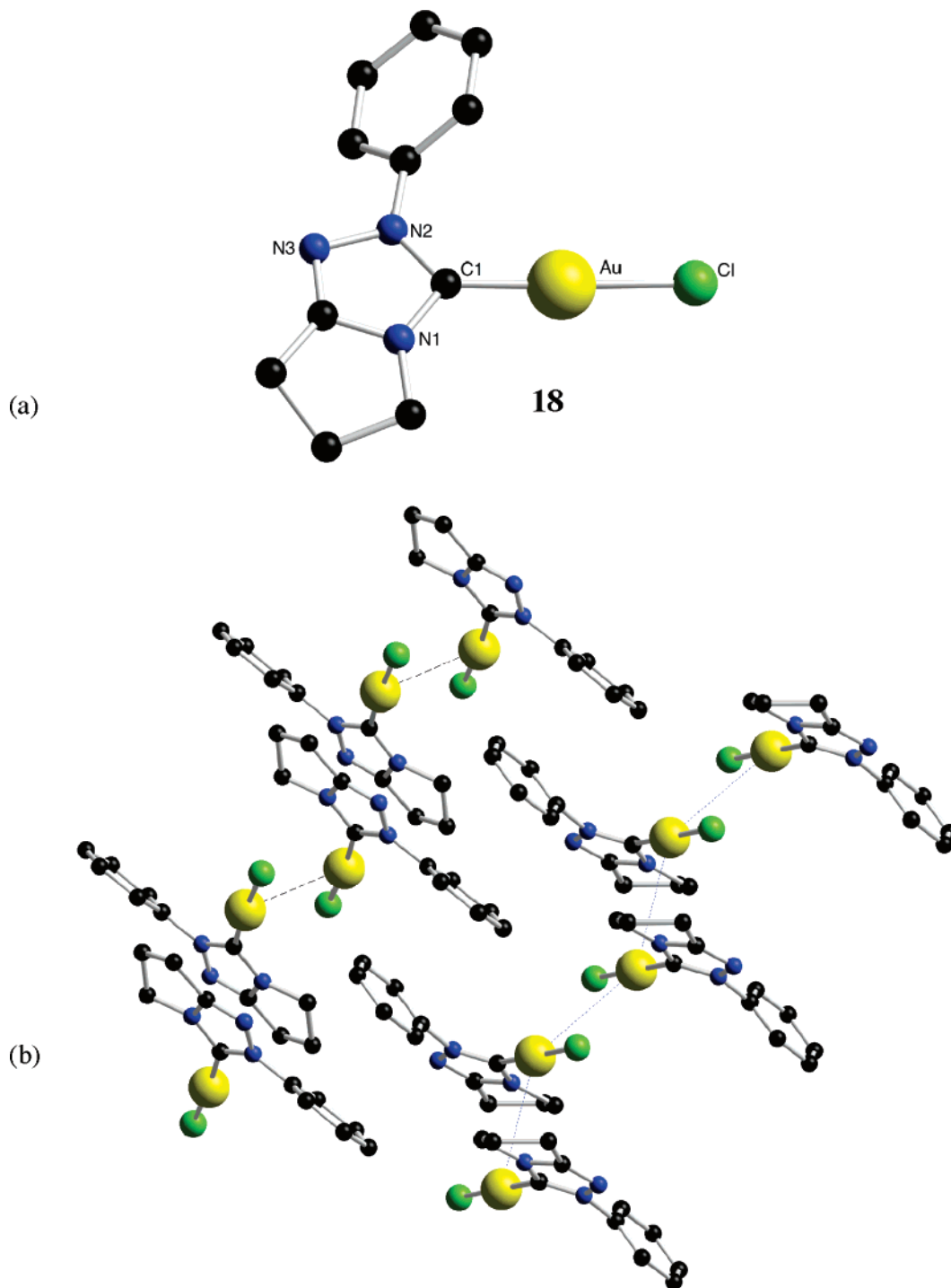


Figure 4. (a) Ball and stick representation of the triazole–NHC ligand complex $[\text{Au}(\text{ITPh})\text{Cl}]$ (**18**). Hydrogen atoms have been omitted for clarity. (b) Stacking of $[\text{Au}(\text{ITPh})\text{Cl}]$, showing head-to-tail ring–ring interactions as well as intermittent $\text{Au}\cdots\text{Au}$ contacts among the molecules.

the triazolium backbone plane. As a result, one *ortho* carbon atom approaches the gold atom with a distance ($\text{Au}\cdots\text{H7}$, 2.892 Å; $\text{Au}\cdots\text{H22}$, 2.946 Å) that is within the range for reported $\text{Au}\cdots\text{H}$ interactions. This rotation may also be a result of π – π stacking from the phenyl ring of neighboring molecules that are aligned in a head-to-tail fashion, as illustrated in Figure 4b, with the closest π – π contact of 3.307 Å indicating such an

interaction. Furthermore, the packing diagram shows that there are also sets of two molecules that have a $\text{Au1}\cdots\text{Au1'}$ interaction of 3.580(3) Å. Adjacent to this is a one-directional linear chain that is linked through intermolecular gold–gold contacts (3.851, 4.059 Å). Although these contacts are longer than the sum of van der Waals radii for two gold atoms of 3.6 Å, they are sufficiently strong to influence the packing of the molecules in the solid state. For the other complexes (**10**–**17**) no case of $\text{Au}\cdots\text{Au}$ interactions or other notable packing features are observed.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Au(NHC)Cl] Complexes

| complex | Au–C(1) | Au–Cl | C(1)–Au(1)–Cl |
|---|-----------------------|------------------------|---------------------|
| [Au(IMes)Cl] (10) | 1.998(5) | 2.2756(12) | 180(–) |
| [Au(SIMes)Cl] (11) | 1.983(4) | 2.2766(10) | 177.68(11) |
| [Au(IPr)Cl] (12) ^b | 1.942(3) | 2.2698(11) | 177.0(4) |
| [Au(SIPr)Cl] (13) | 1.979(3) | 2.2761(10) | 180(–) |
| [Au(IPrMe)Cl] (14) | 1.996(9) | 2.279(2) | 180(–) |
| [Au(IMe)Cl] (15) | 1.987(8) | 2.288(2) | 178.9(3) |
| [Au(ICy)Cl] (16) ^a | 1.990(13), | 2.306(3), | 178.2(4), |
| | 1.996(12) | 2.281(3) | 177.2(3) |
| [Au(IAd)Cl] (17) | 1.989(2) | 2.2761(6) | 178.07(7) |
| [Au(ITPh)Cl] (18) ^a | 1.979(5), | 2.2880(13), | 175.59(15), |
| | 1.972(5) | 2.2835(13) | 178.74(16) |
| [Au(ItBu)Cl] ^c | 2.018(3) ^c | 2.2742(7) ^c | 180(–) ^c |
| [Au(Me ₂ -imy)Cl] ^d | 1.979(11) | 2.288(3) | 178.8(2) |
| [Au(R ₂ -imy)Cl] ^e | 1.965(5) | 2.3061(11) | 177.41(15) |

^a Contains two molecules in the asymmetric unit. ^b Reference 14. ^c Reference 7. ^d Reference 8. ^e Reference 9; R = R₂-imy = 1-(diphenylmethyl)-3-methylimidazol-2-ylidene.

Conclusion

The developing Au-mediated catalysis will benefit from a detailed understanding of ligand electronic effects. In the present contribution we have developed simple synthetic protocols leading to a series of well-defined [Au(NHC)Cl] complexes. Although competing disproportionation and decomposition processes were observed in reactions involving AuCl and free NHC, [Au(NHC)Cl] complexes were isolated in good yields by transfer of free NHC or by use of an *in situ* generated silver(I) NHC salt with [Au(SMe₂)Cl]. NMR and structural analyses of all reported [Au(NHC)Cl] complexes allow us to state that no significant difference in donor ability between the saturated and unsaturated NHC ligands was observed in the present Au(I) system. Since the chloride ligand can be readily substituted or abstracted, the [Au(NHC)Cl] series will serve as very useful starting materials for the development of new NHC–Au(I) compounds that can be utilized for a variety of medicinal and catalytic applications. With the data on hand, it would appear that electronic control/variation through NHC modification may be difficult. Reactivity/selectivity in catalytic applications may very well be controlled as a function of ligand sterics in [Au(NHC)] systems. This hypothesis is presently being tested in our laboratories.

Experimental Section

General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon or in an MBraun glovebox containing dry argon and less than 1 ppm of oxygen. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Aldrich and degassed prior to use by purging with dry argon and kept over molecular sieves. Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were collected on a 400 MHz Varian Gemini spectrometer. Elemental analyses were performed by Robertson Microlit Labs. Carbene ligands **1–9** were synthesized by following literature procedures.^{18,19} AuCl and SMe₂ were obtained from Strem and Acros, respectively, and [Au(SMe₂)Cl] was prepared according to the reported procedure.²⁷

Synthesis of [Au(IMes)Cl] (10**).** A mixture of silver(I) oxide (50 mg, 0.21 mmol) and 1,3-dimesitylimidazolium chlo-

ride (122 mg, 0.36 mmol) in dichloromethane (50 mL) was stirred for 4 h. The mixture was filtered, and (dimethyl sulfide)gold(I) chloride (100 mg, 0.34 mmol) was added. The resulting mixture was stirred for 3 h and filtered, and activated carbon was added to the filtrate. The mixture was filtered through Celite, the solvent was removed in vacuo, and then dichloromethane (3 mL) was added. Pentane (10 mL) was added to the solution, resulting in an immediate precipitation of a bright white solid. The solid was further washed with pentane (3 × 5 mL) and dried under vacuum. Yield: 116 mg (63%). ¹H NMR (CDCl₃): δ 7.09 (s, 2H, CH imidazole), 6.99 (s, 4H, CH aromatic), 2.35 (s, 6H, CH₃), 2.10 (s, 12H, CH₃). ¹³C NMR (CDCl₃): δ 173.42 (s, C carbene), 139.82 (s, CH aromatic), 134.72 (s, CH aromatic), 134.65 (s, CH aromatic), 129.52 (s, CH aromatic), 122.17 (s, CH imidazole), 21.14 (s, CH₃), 17.76 (s, CH₃) ppm. Anal. Calcd for C₂₁H₂₄N₂AuCl (537.62): C, 46.91; H, 4.46; N, 5.21. Found: C, 47.13; H, 4.32; N, 5.13.

Synthesis of [Au(SIMes)Cl] (11**).** A preparation method similar to that used for compound **10** gave a white solid of **11**. Yield: 72 mg (51%). ¹H NMR (CDCl₃): δ 6.94 (s, 4H, CH aromatic), 3.98 (s, 4H, CH₂ imidazole), 2.31 (s, 12H, CH₃), 2.29 (s, 6H, CH₃). ¹³C NMR (CDCl₃): δ 195.03 (s, C carbene), 138.97 (s, CH aromatic), 135.53 (s, CH aromatic), 134.60 (s, CH aromatic), 129.81 (s, CH aromatic), 50.67 (s, CH₂ imidazole), 21.08 (s, CH₃), 17.97 (s, CH₃) ppm. Anal. Calcd for C₂₁H₂₆N₂AuCl (539.62): C, 46.74; H, 4.81; N, 5.19. Found: C, 46.71; H, 5.01; N, 5.12.

Synthesis of [Au(IPr)Cl] (12**).** In a glovebox a 100 mL Schlenk flask was charged with IPr (686 mg, 1.76 mmol) and 50 mL of THF, and then (dimethyl sulfide)gold(I) chloride (500 mg, 1.70 mmol) 50 mg (0.17 mmol) was added. The resulting solution was kept in the dark and stirred at room temperature for 12 h. The remaining steps were then carried out in air. The resulting solution was filtered through Celite, and activated carbon was added to the filtrate, which was stirred for 4 h. The colorless solution was filtered through Celite, the solvent was reduced to dryness under vacuum, and 10 mL of dichloromethane was added. Pentane (20 mL) was added to the solution, resulting in the immediate precipitation of a white solid. The solid was further washed with pentane (3 × 10 mL) and dried under vacuum, to afford a bright white powder. Yield: 820 mg (75%). ¹H NMR (CD₂Cl₂): δ 7.57 (t, *J* = 7.8 Hz, 2H, CH aromatic), 7.35 (d, *J* = 7.8 Hz, 4H, CH aromatic), 7.24 (s, 2H, CH imidazole), 2.57 (septet, *J* = 6.8 Hz, 4H, CH(CH₃)₂), 1.34 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.23 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C NMR (CD₂Cl₂): δ 175.09 (s, C carbene), 145.78 (s, CH aromatic), 134.05 (s, CH aromatic), 130.68 (s, CH aromatic), 124.28 (s, CH aromatic), 123.32 (s, CH imidazole), 28.79 (s, CH(CH₃)₂), 24.17 (s, CH(CH₃)₂), 23.74 (s, CH(CH₃)₂) ppm. Anal. Calcd for C₂₇H₃₆N₂AuCl (621.69): C, 52.11; H, 5.79; N, 4.50. Found: C, 51.70; H, 5.61; N, 4.38.

Synthesis of [Au(SIPr)Cl] (13**).** In a glovebox a 100 mL Schlenk flask was charged with 63 mg (0.16 mmol) of SIPr and 15 mL of THF, and then 50 mg (0.17 mmol) of (dimethyl sulfide)gold(I) chloride was added. The resulting solution was kept in the dark and stirred at room temperature for 12 h. The remaining synthetic steps were then carried out in air. The resulting solution was filtered through Celite, and activated carbon was added to the filtrate, which was stirred for 4 h. The colorless solution was filtered through Celite, the solvent was reduced to dryness under vacuum, and 5 mL of dichloromethane was added. Pentane (10 mL) was added to the solution, resulting in the immediate precipitation of a bright white solid. The solid was further washed with pentane (3 × 5 mL) and dried under vacuum. Yield: 80 mg (81%). ¹H NMR (CDCl₃): δ 7.43 (t, *J* = 7.8 Hz, 2H, CH aromatic), 7.25 (d, *J* = 7.8 Hz, 4H, CH aromatic), 4.06 (s, 4H, CH₂ imidazole), 3.07 (septet, *J* = 6.8 Hz, 4H, CH(CH₃)₂), 1.43 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.36 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C NMR

(CDCl₃): δ 196.07 (s, C carbene), 146.55 (s, CH aromatic), 134.06 (s, CH aromatic), 130.06 (s, CH aromatic), 124.65 (s, CH aromatic), 53.47 (s, CH₂ imidazole), 28.97 (s, CH(CH₃)₂), 25.14 (s, CH(CH₃)₂), 24.13 (s, CH(CH₃)₂) ppm. Anal. Calcd for C₂₇H₃₈N₂AuCl (623.69): C, 51.99; H, 6.09; N, 4.49. Found: C, 52.02; H, 6.22; N, 4.27.

Synthesis of [Au(IPrMe)Cl] (14). A preparation method similar to that used for compound **13** gave **14** as a white solid. Yield: 63 mg (58%). ¹H NMR (CDCl₃): δ 4.97 (m, 2H, NCH isopropyl), 2.19 (s, 6H, CH₃ imidazole), 1.61 (d, J = 7.32 Hz, 12H, CH(CH₃)₂); ¹³C NMR (CDCl₃): δ 165.99 (s, C carbene), 124.44 (s, C=C imidazole), 53.73 (s, CH(CH₃)₂), 22.81 (s, CH(CH₃)₂), 9.92 (s, CH₃ imidazole) ppm. Anal. Calcd for C₁₁H₂₀N₂AuCl (413.48): C, 31.95; H, 4.83; N, 6.77. Found: C, 31.80; H, 4.71; N, 6.57.

Synthesis of [Au(IME)Cl] (15). A preparation method similar to that used for compound **13** gave **15** as a bright white solid. Yield: 180 mg (58%). ¹H NMR (CD₂Cl₂): δ 3.68 (s, 6H, NCH₃), 2.13 (s, 6H, CH₃). ¹³C NMR (CD₂Cl₂): δ 168.41 (s, C carbene), 125.14 (s, CH imidazole), 35.43 (s, CH₃), 8.94 (s, CH₃) ppm. Anal. Calcd for C₇H₁₂N₂AuCl (357.44): C, 23.52; H, 3.33; N, 7.82. Found: C, 23.73; H, 3.00; N, 7.77.

Synthesis of [Au(ICy)Cl] (16). A preparation method similar to that used for compound **13** gave **16** as a bright white solid. Yield: 87 mg (67%). ¹H NMR (CD₂Cl₂): δ 6.98 (s, 2H, CH imidazole), 4.55 (tt, J_1 = 3.9 Hz, J_2 = 11.7 Hz, 2H, NCH cyclohexyl), 2.07 (m, 4H, CH₂), 1.86 (m, 4H, CH₂), 1.74 (m, 2H, CH₂), 1.65–1.41 (m, 8H, CH₂), 1.27–1.15 (m, 2H, CH). ¹³C NMR (CD₂Cl₂): δ 167.99 (s, C carbene), 117.35 (s, CH imidazole), 60.94 (s, NCH cyclohexyl), 34.00 (s, CH₂), 25.30 (s, CH₂), 25.03 (s, CH₂) ppm. Anal. Calcd for C₁₅H₂₄N₂AuCl (464.57): C, 38.78; H, 5.16; N, 6.02. Found: C, 38.90; H, 5.12; N, 5.85.

Synthesis of [Au(IAd)Cl] (17). A preparation method similar to that used for compound **13** gave **17** as a white solid. Yield: 103 mg (78%). ¹H NMR (CD₂Cl₂): δ 7.08 (s, 2H, CH imidazole), 2.57 (m, 14H, CH₂), 2.28 (s, 6H, CH₂), 1.77 (m, 10H, CH₂). ¹³C NMR (CD₂Cl₂): δ 166.32 (s, C carbene), 115.52 (s, CH imidazole), 59.21 (s, NCH adamantyl), 44.10 (s, CH₂), 35.79 (s, CH₂), 30.09 (s, CH₂) ppm. Anal. Calcd for C₂₃H₃₂N₂AuCl (568.65): C, 48.58; H, 5.63; N, 4.92. Found: C, 48.53; H, 5.64; N, 4.66.

Synthesis of [Au(ITPh)Cl] (18). A mixture of silver(I) oxide (37 mg, 0.16 mmol) and 2-phenyl-6,7-dihydro-5H-pyrrolo-[2,1-c][1,2,3]triazol-2-ium chloride (61 mg, 0.28 mmol) in dichloromethane (10 mL) was stirred for 4 h at room temperature. The mixture was filtered, and (dimethyl sulfide)gold(I) chloride (100 mg, 0.34 mmol) was added. The resulting mixture was stirred for 3 h and filtered, and activated carbon was added to the filtrate. The mixture was filtered over Celite, the solvent was removed in vacuo, and then dichloromethane (3 mL) was added. Pentane (10 mL) was added to the solution, resulting in an immediate precipitation of a bright white solid. The solid was further washed with pentane (3 \times 5 mL) and dried under vacuum. Yield: 72 mg (63%). ¹H NMR (CDCl₃): δ 7.96 (m, 2H, CH aromatic), 7.48 (m, 3H, CH aromatic), 4.26 (t, J = 7.32 Hz, 2H, CH₂ pyrrolidine), 3.15 (t, J = 7.81 Hz, 2H, CH₂ pyrrolidine), 2.77 (m, 2H, CH₂ pyrrolidine). ¹³C NMR (CDCl₃): δ 167.82 (s, C carbene), 160.47 (s, NC=N), 139.27 (s, NC aromatic), 129.41 (s, CH aromatic), 129.40 (s, CH aromatic), 123.41 (s, CH aromatic), 46.35 (s, CCHN pyrrolidine), 25.78 (s, CH₂ pyrrolidine), 21.88 (s, CH₂ pyrrolidine) ppm. Anal. Calcd for C₁₁H₁₁N₂AuCl (417.48): C, 31.64; H, 2.63; N, 10.06. Found: C, 31.74; H, 2.30; N, 9.72.

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Supporting Information Available: Crystallographic information format (CIF) files of complexes **9–16**. This material is available free of charge via the Internet at <http://pubs.acs.org>. These files have also been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 263603–263610.

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