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Article

Stereoelectronic Profiling of Acyclic Diamino Carbenes (ADCs)

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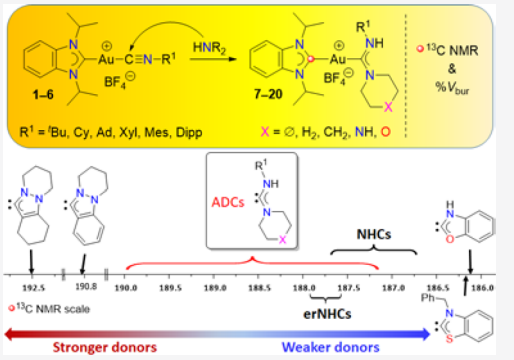
ABSTRACT: A library of 14 heterobis(carbene) complexes of the general formula $[Au(^{i}Pr_2\text{-bimy})(ADC)]BF_4$ (**7**−**20**) containing the N-heterocyclic carbene reporter $^{i}Pr_2$-bimy and various protic acyclic diaminocarbenes (ADCs) have been prepared to estimate their stereoelectronic properties by ^{13}C NMR spectroscopy and percentage buried volume ($\%V_{bur}$) determinations. Their preparation was achieved by nucleophilic attack of five secondary amines on six mixed NHC/isocyanide complexes of the type $[Au(^{i}Pr_2\text{-bimy})(CN\text{-}R)]BF_4$ (**1**−**6**). Analyses of the $^{i}Pr_2$-bimy carbene signals reveal that protic ADCs are stronger donors than classical and expanded-ring NHCs. On the other hand, they are weaker donating compared to NHCs with reduced-heteroatom stabilization. Moreover, stereoelectronic fine-tuning of these ligands is possible by a diverse range of substituents originating from the employed isocyanides and amines.



INTRODUCTION

Complexes of acyclic diamino carbenes (ADCs) were the earliest carbene complexes to be isolated.[1,2] Nevertheless, their popularity pales compared to that of N-heterocyclic carbenes (NHCs),[3,4] although they offer some advantages over classical five-membered NHCs or other acyclic carbenes. First, their enlarged N−C−N angle could impose greater steric impact on metal centers, which could lead to enhanced complex stability but also facilitate reductive elimination steps during catalysis in cross-coupling reactions.[5−7] Second, ADCs could adapt easier to structural features required in various stages of a catalytic cycle due to their inherent conformational flexibility.[8−12] In addition, the expected increased donating ability of these ligands should facilitate oxidative additions, which has been highlighted by their good performance in certain catalytic transformations.[5] Finally, and in contrast to other heteroatom stabilized acyclic carbenes, ADCs are potentially stabilized by π donations of two adjacent nitrogen atoms, which could result in a more nucleophilic ligand system.[13−15] Nevertheless, very few experimental data on the donating abilities of ADCs have been reported to date. In an early study, Herrmann and co-workers concluded from IR data (KBr) of *trans*-$[RhCl(CO)_2(L)]$ complexes that Alder's bis(diisopropylamino)-carbene is a stronger donor compared to 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) and 1,3-bis-(2,4,6-trimethylphenyl)imidazolidin-2-ylidene (SIMes).[16] Similarly, Bielawski and co-workers found using IR data (CH_2Cl_2) of *trans*-$[IrCl(CO)_2(ADC)]$ complexes that their arylmethyl-substituted ADCs are stronger donating than five-membered NHCs, but inferior to six-membered NHCs. In addition, these ADCs display conformation-dependent donicities, which further complicates matters. However, the authors also point out that carbonyl-based methodologies (e.g., TEP = Tolman electronic parameter) may not describe the electronic properties of ADCs adequately.[17] In comparison, substantially more ADCs have been evaluated for their π-accepting capability. Specifically, works by Ganter et al.[18] and Siemeling et al.[19] revealed that selenium adducts of ADCs exhibit notably more downfield ^{77}Se NMR signals compared to their NHC counterparts. This observation was attributed to the generally increased electrophilicity and better π-accepting capability of ADCs compared to NHCs. Notably, all these studies involved ADCs that purely contain carbon substituents at nitrogen, while the electronic properties of N-protic ADCs have not been systematically studied yet, although several groups including those of Hashmi, Echavarren, and Slaughter have reported excellent catalytic activities of their gold complexes.[20−22]

We have a long-standing interest in the electronic properties of molecules and their determination, since knowledge of these could help in the understanding of structure−activity relationships. In relation to this, we have introduced a unified electronic parameter that can be used to compare the (primarily) σ-donor ability of Werner-type and organometallic ligands on the same scale, i.e., Huynh Electronic Parameter (HEP), using complexes of the type *trans*-$[PdBr_2(^{i}Pr_2\text{-bimy})L]$ ($^{i}Pr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene).[23−26] The $^{13}C_{carbene}$ NMR signal of the $^{i}Pr_2$-bimy reporter ligand is sensitive to the *trans*-ligand L, and its chemical shift in parts

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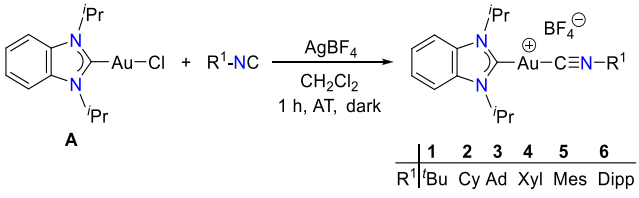
per million is abbreviated as the HEP value. In addition to such square-planar Pd^{II} complexes, linear heterobis(carbene) gold(I) complexes of the formula $[Au(^{i}Pr_2\text{-bimy})(NHC)]BF_4$ have been successfully used to gauge the donating abilities of NHCs in cases where *cis*/*trans* isomerism or increased steric bulk posed a problem in the tetracoordinated Pd^{II} complexes.[27] Recently, Yan and co-workers have also used such complexes to study halogen bonding (via σ-hole interaction) in 4-halo-1,2,3-triazolinylidenes.[28]

In this article, we are evaluating if this work on NHCs can be extended to protic ADCs using a library of $[Au(^{i}Pr_2\text{-bimy})(ADC)]BF_4$ complexes. In addition to the challenging donor strength determinations of these highly flexible ligands, $\%V_{bur}$ values were obtained to estimate their steric bulk. It is of particular interest to study how steric interferences and rotational flexibility affect the determination of electronic properties in order to properly balance the scope and limitations of our methods.

RESULTS AND DISCUSSION

Synthesis of $[Au(^{i}Pr_2\text{-bimy})(CN\text{-}R^1)]BF_4$ Complexes. Protic ADC complexes can be prepared by a template-directed approach involving nucleophilic attack of a protic amine-base on coordinated isocyanide ligands.[29−34] However, we have previously found that $[PdBr_2(^{i}Pr_2\text{-bimy})(CN\text{-}R)]$ complexes exist as inseparable mixtures of *cis* and *trans* isomers, which hampers the selective preparation of palladium-based HEP complex probes for the donor strength evaluation of ADCs.[30] To circumvent this problem, we opted for the linear gold-based analogues. Thus, it was anticipated that treatment of mixed NHC/isocyanide complexes of the type $[Au(^{i}Pr_2\text{-bimy})(CN\text{-}R)]BF_4$ with secondary amines should furnish the targeted $[Au(^{i}Pr_2\text{-bimy})(ADC)]BF_4$ complex probes. The respective precursor complexes are easily prepared by direct reaction of $[AuCl(^{i}Pr_2\text{-bimy})]$[35] (**A**) with various isocyanides in the presence of $AgBF_4$ as the chlorido scavenger. Six aliphatic and aromatic isocyanides CN-R^1 {R^1 = *tert*-butyl (^{t}Bu); cyclohexyl (Cy); adamantyl (Ad); meta-xylyl (Xyl); mesityl (Mes); 2,6-diisopropylphenyl (Dipp)} were chosen to ensure structural and electronic diversity, and the cationic complexes $[Au(^{i}Pr_2\text{-bimy})(CN\text{-}R^1)]BF_4$ (**1**−**6**) were obtained in moderate to good yields of 54−92% (Scheme 1) at ambient

Scheme 1. Preparation of $[Au(^{i}Pr_2\text{-bimy})(CN\text{-}R^1)]BF_4$-type Complexes



temperature (AT) as air- and moisture-stable white solids. The formation of these complexes is evident from NMR spectroscopy, which reveals signals due to both organometallic ligands in a 1:1 ratio. Upon halido substitution, the $^{13}C_{carbene}$ NMR signal at 178.5 ppm in complex **A** shifts downfield to 180.6−181.4 ppm in complexes **1**−**6**, indicating the presence of a stronger donor.[35] Notably, the isocyanide carbon signals were difficult to resolve, and only that for complex **1** could be detected at 144.3 ppm. The difficulty in resolving the very weak NMR signals of isocyanide carbon atoms in metal complexes is well-known and possibly a result of quadrupolar coupling to the ^{14}N nuclei. A dynamic behavior of the complexes in solution due to the potential lability of the isocyanide ligands can be excluded, since no ligand disproportionation under the formation of homoleptic complexes was observed.

Moreover, correct isotopic envelopes for the $[Au(^{i}Pr_2\text{-bimy})(R^1NC)]^+$ cations were detected by high-resolution mass spectrometry (ESI HRMS), which confirms the proposed constitution of complexes **1**−**6**. Finally, single crystals of **2**, **3** and **5** suitable for X-ray diffraction studies were obtained by slow evaporation of their saturated solutions in a $CHCl_3$/CH_3CN solvent mixture.

Their molecular structures depicted in Figure 1 disclose Au^{I} centers that are coordinated by one NHC and one isocyanide

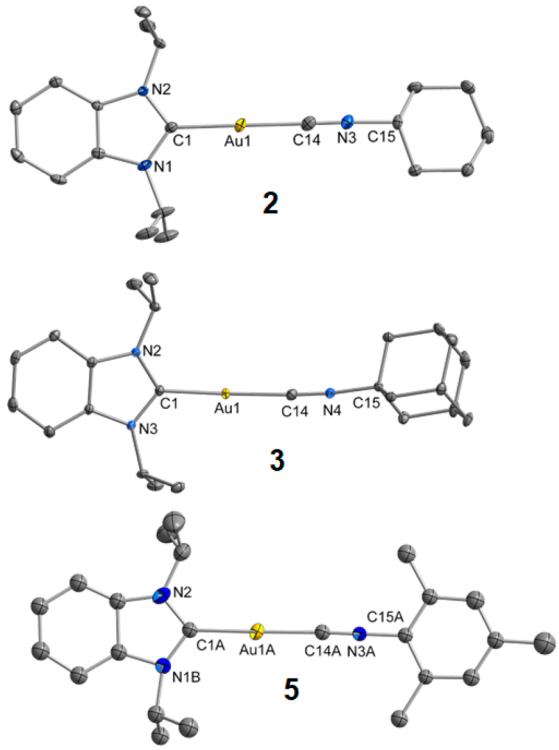


Figure 1. Molecular structures of complexes **2**, **3**·CH_3CN, and **5** showing 50% probability ellipsoids; hydrogen atoms, solvent molecules, and counteranions are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2**: Au1−C14 1.985(4), Au1−C1 2.024(4), N3−C14 1.141(5), N3−C15 1.462(5); C14−Au1−C1 177.7(2), C14−N3−C15 177.9(4), Au···Au 3.307(1). For **3**: Au1−C14 1.982(2), Au1−C1 2.019(2), N4−C14 1.144(2), N4−C15 1.458(2); C14−Au1−C1 173.6(1), C14−N4−C15 171.1(2). For **5**: Au1A−C14A 1.988(1), Au1A−C1A 2.032(1), N3A−C14A 1.129(1), N3A−C15A 1.392(1); C14A−Au1A−C1A 178.1(4), C14A−N3A−C15A 179.1(1), Au···Au 3.352(1).

in a linear geometry. The Au−C_{NHC} bond distances of 2.024(4) Å (**2**), 2.019(2) Å (**3**), and 2.032(1) Å (**5**) were found to be longer than in the parent complex **A** [1.973(7) Å], which points to a stronger trans influence of isocyanide versus chlorido ligands.[35] The Au−C_{CNR} bond distances of 1.985(4) Å (**2**), 1.982(2) Å (**3**), and 1.988(1) Å (**5**) were found to be smaller than Au−C_{NHC} bond distances but are in the typical range of gold(I) isocyanide complexes.[29] The NC bonds of 1.141(5) Å (**2**), 1.144(2) Å (**3**), and 1.129(1) Å (**5**) retain

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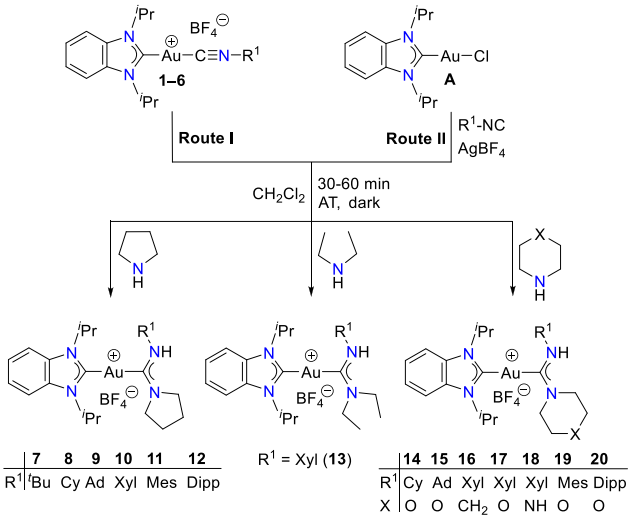
their triple-bond character indicating negligible π-back donations from the metal. Furthermore, the isocyanide ligands display a near-linear geometry with C−N−C angles ranging from 177.9(4)° to 179.1(1)° with the exception of the adamantyl isocyanide in complex **3**, which slightly deviates from linearity with an angle of 171.1(2)°. Since back donation is negligible, this deviation is supposedly due to a bulky adamantyl group, which hampers efficient packing. Last, aurophilic interactions were observed in solid-state molecular structures of complexes **2** and **5** with Au···Au distances of 3.307(1) and 3.352(1) Å, respectively, which are within the sum of the van der Waals radii (3.80 Å). Despite aurophilic interactions, no notable luminescence properties were noted for these compounds. Again, the adamantyl isocyanide complex **3** is an exception, where the bulky adamantyl group prevents such interactions, and a much larger intergold distance of 10.304 (1) Å is observed.

Synthesis of [Au(^{i}Pr$_2$-bimy)(ADC)]BF$_4$ Complexes. The isocyanide complexes **1**−**6** were subsequently exposed to a range of secondary amines HNR^2 {R^2 = pyrrolidinyl (Pyr); diethyl (Et$_2$); morpholinyl (Mor); piperidinyl (Pip); piperazinyl (Pipz)} in dichloromethane at ambient temperature, which afforded the desired [Au(^{i}Pr$_2$-bimy)(ADC)]BF$_4$ type complexes (**7**−**20**) in decent yields (57−97%, route I, Scheme 2). It turned out that prior isolation of **1**−**6** was not required.

Scheme 2. Synthetic Routes to [Au(^{i}Pr$_2$-bimy)(ADC)]BF$_4$-type Complexes (7−20)



Instead, a simplified two-step, one-pot approach can be easily adopted, which involves direct reaction of precursor **A** with isocyanides followed by the addition of the amines (route II). The sequential one-pot procedure facilitates the preparation of ADC complex libraries significantly without compromising the yield.

The formation of the targeted products **7**−**20** is supported by both LR and HR ESI mass spectrometry, which shows base peaks for the respective [Au(^{i}Pr$_2$-bimy)(ADC)]$^+$ molecular cations in the positive mode with the correct isotopic patterns. Moreover, their ^{1}H and ^{13}C NMR spectra reveal the expected presence of two different carbenes. The newly formed protic ADCs are recognizable by downfield ^{1}H NMR signals for their R^{1}NH functions. These resonate from 8.13 to 8.86 ppm for aromatic R^1 substituents and from 6.37 to 7.32 ppm for their aliphatic counterparts, respectively, which is in line with the increased deshielding effect of aryl versus alkyl groups. In the ^{13}C NMR spectra, two distinct carbene resonances are observed for each complex. The more downfield signals ranging from 198.7 to 203.8 ppm can be easily assigned to the ADC ligands,[29] while those for the ^{i}Pr$_2$-bimy reporter appear in the range of 187.2−189.8 ppm.

Solid-State Molecular Structures. Single crystals of **7**, **9**, **10**, **11**, **13**, **14**, **16**, **19**, and **20** were obtained by slow evaporation of their concentrated solutions in acetonitrile and subjected to X-ray diffraction analyses. The solid-state molecular structures of the complex cations are depicted in Figures 2 and S1, while selected bond parameters are summarized in Table 1.

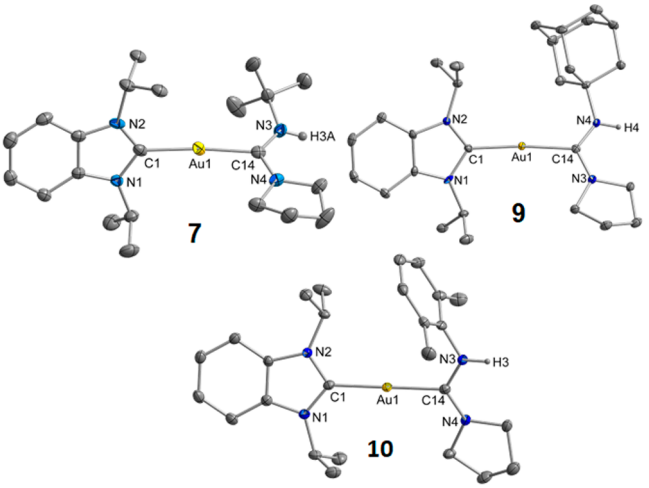


Figure 2. Molecular structures of complexes **7**, **9**, and **10** showing 50% probability ellipsoids; hydrogen atoms, solvent molecules, and counteranions are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Structurally Characterized [Au(^{i}Pr$_2$-bimy)(ADC)]BF$_4$-types Complexes

complex	Au−C$_{NHC}$ (Å)	Au−C$_{ADC}$ (Å)	C$_{NHC}$−Au−C$_{ADC}$ (deg)	N−C−N$_{ADC}$ (deg)
7	2.027(3)	2.049(3)	174.8(1)	116.6(3)
9	2.022(4)	2.043(4)	174.4(2)	116.4(3)
10	2.026(2)	2.032(2)	177.4(6)	118.1(2)
11	2.024(3)	2.030(3)	178.4(1)	117.7(2)
13	2.029(6)	2.056(7)	178.5(3)	119.6(6)
14	2.038(4)	2.055(4)	177.6(2)	118.0(4)
16	2.033(6)	2.046(6)	177.3(2)	118.2(5)
19	2.013(1)	2.039(1)	178.1(4)	119.8(1)
20	2.034(7)	2.052(7)	178.8(3)	119.9(6)

These corroborate their identities as [Au(^{i}Pr$_2$-bimy)(ADC)]BF$_4$ complexes. All complexes contain Au^I centers that are coordinated by an ADC ligand and the ^{i}Pr$_2$-bimy reporter ligand in a linear fashion with C$_{NHC}$−Au−C$_{ADC}$ angles ranging from 174 to 179°. The Au−C$_{NHC}$ bond distances are in the typical range of 1.973 to 2.038 Å, while the Au−C$_{ADC}$ bonds are slightly longer with distances ranging from 2.030 to 2.081 Å. Notably, the N−C−N angles of the ADCs range from 116 to 120°, which are larger than those of five-membered NHCs.[27] However, significantly larger angles of up to 125° were found for expanded-ring NHCs (erNHCs).[36−39]

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Carbenes with larger N−C−N angles have increased steric bulk. In addition, N-aryl substituents of such carbenes could exert an anisotropic shielding effect on the reporter ^{13}C NMR signal due to their proximity, which could negatively interfere with intended donor strength evaluation. The structures also reveal that the various ADCs adopt different dihedral angles with respect to the NHC plane. The planes through the N−C−N atoms of the ADCs can be almost coplanar or almost perpendicular to NHC. Supposedly, this would impact their π interactions with the gold(I) center and thus their electronic properties, which further complicates their evaluation.

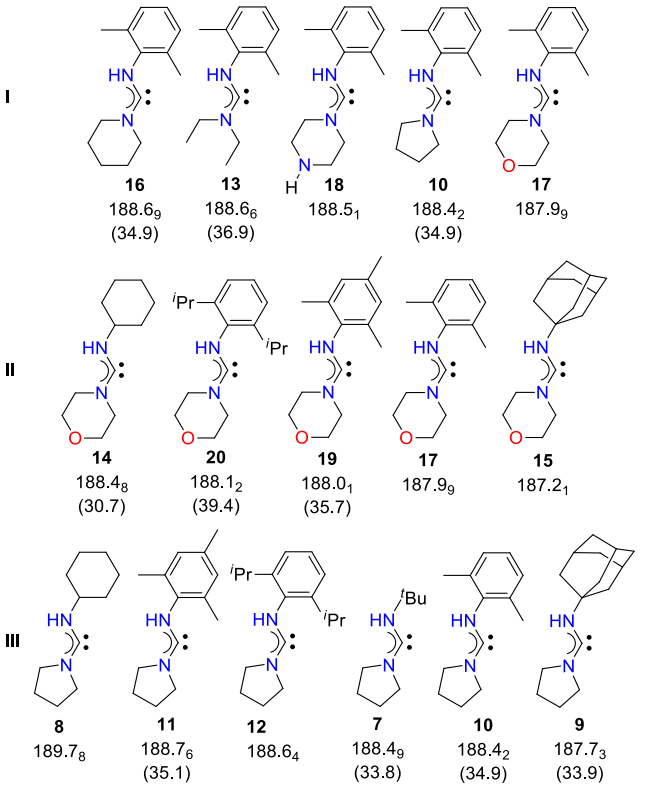
Although not depicted in Figures 2 and S1, the BF_4^- counteranions show weak interactions with the N−H moiety of the protic ADCs. Such hydrogen bonding has previously been described for protic NHC complexes in the solid state and solution (δNH > 11 ppm in CD_2Cl_2), which allowed differentiation of BF_4^- versus PF_6^- counteranions.[40] If such hydrogen bonds persist in solution, they could additionally affect the donor strengths of the ADCs. However, the significantly more upfield NH resonances measured for all ADC complexes (vide supra) could dismiss such as case. Overall, the increased steric effect, the conformational freedom and the capability to engage in hydrogen bonds, could render protic ADCs stereoelectronically flexible. As such, they are challenging, but interesting study subjects for donor strength determination.

Estimation of Steric Bulk by %V_{bur} Determination. The availability of single-crystal X-ray data allows for the experimental determination of %V_{bur} values for the ligands in order to gauge and compare their steric bulk. The calculations were carried out using the structural data for the nine [Au(^{i}Pr$_2$-bimy)(ADC)]BF_4 complexes depicted in Figure 2 with the help of the Sambvca2.0 online portal,[35] and the values obtained are listed in Chart 1. Complexes **7**, **9**, **10**, and **11** all contain pyrrolidinyl-derived ADCs, and thus the steric influence of the HNR[1] group originating from the isocyanides can be compared. The %V_{bur} values of 35.1 and 34.9 for the ADCs in complexes **11** and **10** imply that the mesityl and meta-xylyl (2,6-dimethylphenyl) substituents are sterically very similar. For the ADCs with adamantyl and *tert*-butyl groups in complexes **9** and **7**, slightly smaller but similar values of 33.9 and 33.8 were obtained. Overall, these four ADCs do not significantly differ in terms of steric bulk. More pronounced differences were observed for the morpholinyl−ADC complexes **14**, **19**, and **20** since the %V_{bur} values for their ADCs increase in the order 30.7 (**14**) < 35.7 (**19**) < 39.4 (**20**), which is consistent with increasing steric bulk going from cyclohexyl to mesityl to 2,6-diisopropylphenyl. Notably, the N−C−N angles of the protic ADCs do not reflect their %V_{bur} values, and thus, they cannot be used to compare the sterics among the ADCs.

Finally, the values for complexes **10**, **13**, and **16**, which all contain xylenyl-substituted ADCs, were determined to be 34.9, 36.9, and 34.9, respectively. Their comparison reveals that the diethyl group in complex **13** has a greater steric impact compared to the pyrrolidinyl and piperidinyl group in complexes **10** and **16**, respectively. For the latter two, identical %V_{bur} values were found, which indicates that one additional methylene group in the flexible heterocyclic substituent has very little effect on the steric properties.

Since all nine complexes contain the ^{i}Pr$_2$-bimy reporter ligand, it would be interesting to study to what extent different coligands would affect the sterics of one given ligand. Indeed,

Chart 1. Three Series of Protic ADC Ligands and the ^{i}Pr$_2$-bimy Carbene Signals (in ppm with the Second Decimal Place in Subscript) of Their [Au(^{i}Pr$_2$-bimy)(ADC)]BF_4 Complexes [%V_{bur} Values Where Applicable Are Listed in Brackets]



the %V_{bur} values determined for the same NHC ligand range from 27.1 to 33.1 (see Supporting Information). The fact that different values are obtained is not surprising, although the range observed here is rather large. Notably, the smallest value for the NHC was obtained using complex **14**, which also contains the supposedly smallest ADC. Similarly, the largest value for the NHC was obtained for complex **20** bearing the largest ADC. This observation is not intuitive and may hint at some limitations of the methodology.

Donor Strength Evaluation. Previously, we established an excellent correlation of ^{i}Pr$_2$-bimy carbene chemical shifts observed in [Au(^{i}Pr$_2$-bimy)(NHC)]BF_4 complexes to the palladium-based HEP values for various NHCs. Thus, it is of interest to see if the ^{i}Pr$_2$-bimy ligand in the [Au(^{i}Pr$_2$-bimy)(ADC)]BF_4 complexes **7**−**20** could also be employed to determine the donor strengths of the respective ADC ligands in analogy to HEP. Comparison of the ^{i}Pr$_2$-bimy carbene signals ranging from 187.2 to 189.8 ppm with those reported for [Au(^{i}Pr$_2$-bimy)(NHC)]BF_4 complexes reveals that ADCs induce more downfield shifts and could be stronger donating than most classical five-membered NHCs, which is widely accepted. Our analysis also shows that most ADCs are stronger donors compared to benzothiazolin-2-ylidenes,[27,41] benzoxazolin-2-ylidenes,[42] and saturated, expanded-ring NHCs (erNHCs).[36] However, they are significantly weaker than nonclassical indazolin-3-ylidenes and pyrazolin-3-ylidenes, which have a reduced heteroatom stabilization (Figure 3).[27]

From the 187.2 to 189.8 ppm range of the ^{i}Pr$_2$-bimy reporter signals, it seems possible to fine-tune the electronic properties

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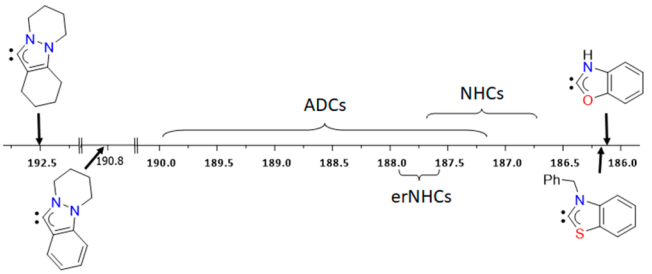

Figure 3. Comparison of the $^{13}C_{NCN}$ NMR signals of the $^{i}Pr_2$-bimy reporter for various [Au($^{i}Pr_2$-bimy)(carbene)]BF_4 complexes.

of the protic ADCs by choice of the N-substituents originating from either the isocyanide (HNR^1) or the amine (NR^2). To study these substituent effects separately, either R^1 or R^2 has to be fixed. For example, five of the 14 ADC complexes contain the meta-xylyl R^1 substituent, but vary in the R^2 substituents. Five complexes contain morpholinyl and six contain pyrrolidinyl-derived ADCs with varying R^1 substituents. Altogether, these give rise to three series, I–III, of ADCs that are summarized in Chart 1 along with the respective carbene signals of the $^{i}Pr_2$-bimy reporter ligand. ^{13}C NMR chemical shifts are routinely rounded to the first decimal place (d.p.). For the HEP and related carbene signals, a standard deviation of σ = 0.01 ppm has been estimated from the full-width-at-half-maximum (fwhm ~0.02 ppm). Thus, changes in the second d.p. are significant and worth reporting. As a compromise, we opted to report the second d.p. of the carbene signal in the subscript for the comparison between electronically similar ligands.

The chemical shifts of the first series reveal that the piperidinyl group has a very similar electronic impact to that of the diethylamino group. Formal removal of a methylene unit in the six-membered heterocycle leads to pyrrolidinyl-substituted ADC with reduced donor ability. Substitution of the same methylene unit with electronegative heteroatoms also leads to a reduction of donating ability, whereby the impact of an oxygen atom is greater than that of a NH group in line with their electronegativities. Overall, the donor strengths of meta-xylyl-derived ADCs decrease rationally in the order Pip > NEt_2 > Pipz > Pyr > Mor. The ADCs in series II all contain the morpholinyl group, which in principle allows for comparison of the R^1 substituents. The carbene chemical shifts suggest decreasing donor abilities in the order Cy > Dipp > Mes > Xyl > Ad. This order is reasonable, but purely based on inductive effects, the relative position of the very bulky adamantyl substituent seems surprising. On the other hand, it is possible for the three aryl substituents to alter their positive mesomeric (+M) contributions to the carbene donor by rotation around the N–C bond. The change of the dihedral angle of the aryl ring with respect to the NCN plane affects the degree of π overlap.[43] A similar observation was made with ADCs of series III containing the fixed pyrrolidinyl group. Again, ADCs with very bulky *tert*-butyl and adamantyl substituents seem out of place considering their positive inductive (+I) effects. In these cases, steric bulk could likely prevent the most efficient ligand–metal interaction leading to a smaller impact on the reporter ligand. In addition, the Dipp and Mes substituents have swapped their relative positions, which is not very surprising since their electronic contributions are very similar. All in all, the results obtained here are reasonable and can be explained with chemical intuition. The choice of the $^{i}Pr_2$-bimy carbene resonances as reporter signals can be justified as follows: (i) the signals appear in a unique range with very little interferences from other signals; (ii) the carbene atom is close to the trans-ligand of interest and is expected to be more sensitive to changes. A comparison of chemical shift changes between our reporter signal versus those of the aromatic carbon atoms of the benzimidazolin-2-ylidene agrees well with this notion. While the $^{i}Pr_2$-bimy carbene resonances are sensitive to the trans ligand and their substituents, the aromatic signals remain almost constant (Figures S2 and S3 in the Supporting Information). Overall, complex **8** bears the strongest donating ADC of this work, which contains cyclohexyl and pyrrolidinyl groups. Complex **15** contains the seemingly weakest ADC with adamantyl and morpholinyl

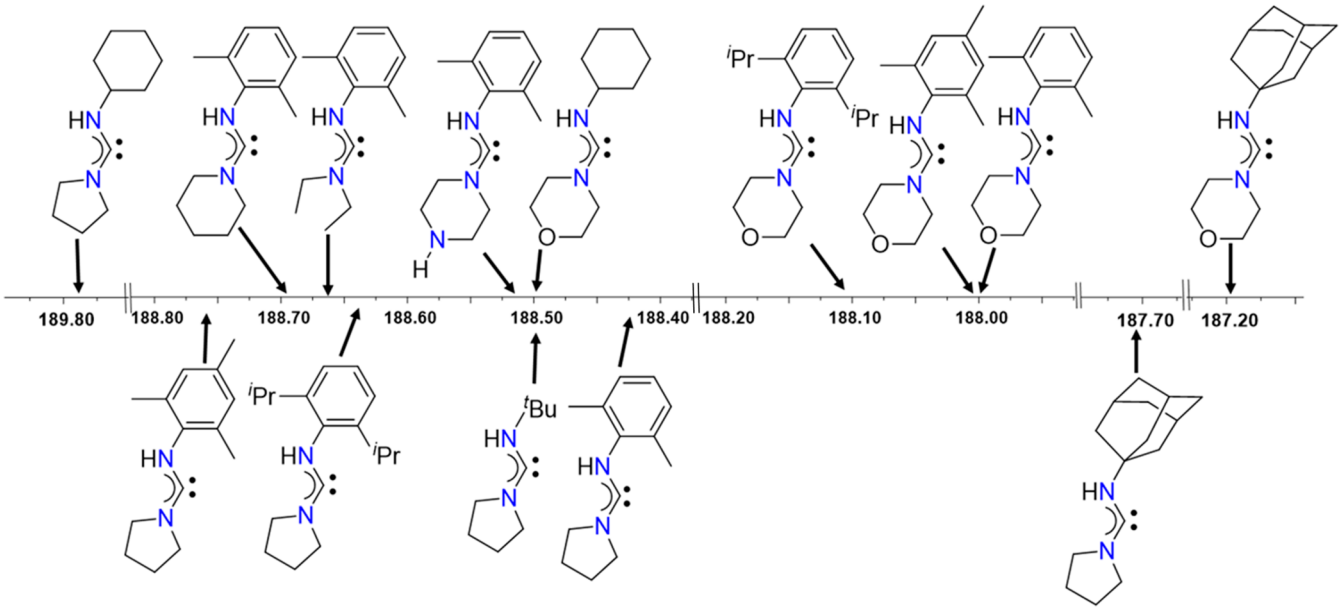

Figure 4. Comparison of donor abilities of ADCs on the ^{13}C NMR scale.

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substituents. A comparison of all protic ADCs on the ^{13}C NMR scale is depicted in Figure 4.

The aim of stereoelectronic parameters is to reveal structure−activity relationships in order to improve performances of compounds by rational design. In this aspect, it is worth mentioning that Hashmi and co-workers[22] have reported the catalytic activities of gold complexes containing protic ADCs in the addition of water to phenylacetylene under similar reaction conditions. Four ADCs reported here were also found to catalyze the reaction with different outcomes, which allows for a preliminary correlation of stereoelectronic properties versus catalytic activities (see Table S5 in the Supporting Information). The simple comparison reveals that the catalytic efficiency of the complexes increases with decreasing donor ability of the ADCs, while $\%V_{bur}$ values appear to be less important. This seems to suggest that stronger donating ADCs are less efficient ligands since the reduced electrophilicity of the cationic alkyne-bound intermediate would slow down the nucleophilic attack of water.

CONCLUSIONS

The stereoelectronic properties of protic acyclic diaminocarbenes (ADCs) were probed with a library of [Au(^{i}Pr$_2$-bimy)(ADC)]BF_4 complexes (**7**−**20**), which were prepared by nucleophilic attack of five cyclic and acyclic secondary amines on six mixed NHC/isocyanide complexes of the type [Au(^{i}Pr$_2$-bimy)(CN-R)]BF_4 (**1**−**6**). The donor abilities of the ADCs were estimated using the ^{13}C NMR carbene signal of the ^{i}Pr$_2$-bimy reporter ligand, while the steric bulk was probed using $\%V_{bur}$ determinations using solid-state molecular structures of nine representative ADC complexes. Overall, it was found that ADCs are stronger donors compared to classical five-membered NHCs and expanded-ring NHCs. However, they are weaker than NHC with reduced heteroatom stabilization. Moreover, their stereoelectronic profiles can be fine-tuned by the choice of substituents that originate from the isocyanide or amines. Notably, ADCs possess a certain degree of flexibility with regard to their sterics and electronics, which can be altered by different orientations of the substituents. This increased flexibility compared to typical NHCs could result in different reactivities, which warrants further studies of ADCs and their applications.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk techniques. ^{i}Pr$_2$-bimy·HBF_4 was prepared according to a literature procedure.[27] ^1H, ^{13}C, and $^{19}F\{^1H\}$ NMR spectra were recorded on Bruker 400 MHz or Bruker 500 MHz NMR spectrometers. ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), broad (br), doublet of doublets (dd), multiplet (m), and septet (sept). HRMS (ESI) mass spectra were measured using a microTOF-QII10269 spectrometer. Elemental analyses were done on an Elementar Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs,[44] and refinement parameters are summarized in Tables S2−S4.

*General Procedure for the Synthesis of [Au(^{i}Pr$_2$-bimy)(R^{1}NC)]BF_4 (**1**−**6**).* To a solution of [AuCl(^{i}Pr$_2$-bimy)] (0.23 mmol, 1 equiv) in CH_2Cl_2 (*ca.* 20 mL), the respective isocyanide (0.276 mmol, 1.2 equiv) and $AgBF_4$ (0.276 mmol, 1.2 equiv) were added and stirred for 1 h at room temperature in the absence of light.

The reaction mixture was filtered through a thin Celite pad, and the solvent was concentrated under reduced pressure to 5 mL. Et_2O (*ca.* 30 mL) was added to precipitate the product as a white powder. The white powder was further washed with EtOAc (3 × 10 mL) to get the pure product as white powder.

*[Au(CN-^{t}Bu)(^{i}Pr$_2$-bimy)]BF_4 (**1**).* Yield: 0.075 g, 57%. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.70 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.41 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 5.27 (sept, 2H, $^3J_{HH}$ = 7 Hz ($CH(CH_3)_2$), 1.75 (d, 12H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$), 1.64 (s, 9H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 181.0_0 (C_{Probe}), 144.3 (CN), 132.9, 125.6, 114.0, (Ar−C), 60.7 $(CH_3)_3C$), 55.1 ($CH(CH_3)_2$), 30.1 $(CH_3)_3C$), 23.0 (CH_3). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −152.99 (s, $^{10}BF_4$), −153.05 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{27}AuN_3$ [M − BF_4]$^+$: 482.1865. Found: 482.1868.

*[Au(CN-Cy)(^{i}Pr$_2$-bimy)]BF_4 (**2**).* Yield: 0.081 g, 59%. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.69 (br, 2H, Ar−H), 7.42 (br, 2H, Ar−H), 5.25 (sept, 2H, $^3J_{HH}$ = 7 Hz ($CH(CH_3)_2$), 4.16 (br, 1H, C_6H_{11}), 2.07 (br, 2H, C_6H_{11}), 1.83 (br, 3H, C_6H_{11}), 1.75 (m, 15H, ($CH(CH_3)_2$ and C_6H_{11}), 1.47 (br, 5H, C_6H_{11}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 180.9_2 (C_{Probe}), 132.9, 125.6, 114.0, (Ar−C), 55.9 (C_6H_{11}), 55.0 ($CH(CH_3)_2$), 31.9 (C_6H_{11}), 25.0 (C_6H_{11}), 23.3 (C_6H_{11}), 23.0 (CH_3). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −153.46 (s, $^{10}BF_4$), −153.51 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{29}AuN_3$ [M − BF_4]$^+$: 508.2022. Found: 508.2019. Anal. Calcd for $C_{20}H_{29}AuN_3BF_4$: C, 40.36; H, 4.91; N, 7.06. Found: C, 40.30; H, 4.88; N, 7.13.

*[Au(CN-Ad)(^{i}Pr$_2$-bimy)]BF_4 (**3**).* Yield: 0.108 g, 72%. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.71 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.44 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 5.31 (sept, 2H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$), 2.24 (s, 6H, CH_2), 2.19 (s, 3H, CH), 1.77 (d, 12H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$), 1.71 (s, 6H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 181.3_8 (C_{Probe}), 133.0, 125.6, 114.1, (Ar−C), 66.5 (C1-Ad), 60.1 (CH), 55.1 (CH), 42.7 (CH_2), 35.7 (CH_2), 29.2 (CH_2), 23.0 (CH_3). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −152.94 (s, $^{10}BF_4$), −152.96 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{29}AuN_3$ [M − BF_4]$^+$: 560.2335. Found: 560.2340. Anal. Calcd for $C_{24}H_{33}AuN_3BF_4$: C, 44.53; H, 5.14; N, 6.49. Found: C, 44.13; H, 5.16; N, 6.71.

*[Au(CN-Xyl)(^{i}Pr$_2$-bimy)]BF_4 (**4**).* Yield: 0.117 g, 82%. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.75 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.46 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.36 (t, 1H, $^3J_{HH}$ = 8 Hz, Ar−H), 7.20 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar−H), 5.39 (m, 2H, ($CH(CH_3)_2$), 2.55 (s, 6H, CH_3), 1.82 (d, 12H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 181.1_3 (C_{Probe}), 137.6, 133.1, 132.3, 129.2, 125.7, 114.3, (Ar−C), 55.5 ($CH(CH_3)_2$), 23.1 (CH_3), 19.5 (CH_3). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −152.73 (s, $^{10}BF_4$), −152.78 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{27}N_3Au$ [M − BF_4]$^+$: 530.1870. Found: 530.1865.

*[Au(CN-Mes)(^{i}Pr$_2$-bimy)]BF_4 (**5**).* Yield: 0.134 g, 92%. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.75 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.45 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.99 (s, 2H, Ar−H), 5.38 (br, 2H, ($CH(CH_3)_2$), 2.50 (s, 6H, CH_3), 2.34 (s, 3H, CH_3), 1.82 (d, 12H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 181.3_3 (C_{Probe}), 143.1, 137.3, 133.1, 129.9, 125.6, 114.3, (Ar−C), 55.1 ($CH(CH_3)_2$), 23.1 (CH_3), 22.1 (CH_3), 19.4 (CH_3). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −152.98 (s, $^{10}BF_4$), −153.03 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{29}AuN_3$ [M − BF_4]$^+$: 544.2022. Found: 544.2024. Anal. Calcd for $C_{23}H_{29}AuN_3BF_4$: C, 43.76; H, 4.63; N, 6.66. Found: C, 43.21; H, 4.60; N, 6.66.

*[Au(CN-DIPP)(^{i}Pr$_2$-bimy)]BF_4 (**6**).* Yield: 0.083 g, 54%. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.76 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.52 (t, 1H, $^3J_{HH}$ = 8 Hz, Ar−H), 7.46 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.28 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar−H), 5.34 (sept, 2H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$), 3.33 (sept, 2H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$), 1.82 (d, 12H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$), 1.34 (d, 12H, $^3J_{HH}$ = 7 Hz, ($CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 180.5_7 (C_{Probe}), 147.6, 133.1, 133.0, 125.8, 124.8, 121.8, 114.2, (Ar−C), 55.2 ($CH(CH_3)_2$), 30.6 ($CH(CH_3)_2$), 23.3 (CH_3), 23.2 (CH_3). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −153.30 (s, $^{10}BF_4$), −153.35 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{26}H_{35}N_3Au$ [M − BF_4]$^+$ 586.2491. Found: 586.2483.

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General Procedure for the Synthesis of [Au(^{i}Pr$_2$-bimy)-(ADC)]BF$_4$ (7−20): Route I. To a solution of [Au(CN-R^1)(^{i}Pr$_2$-bimy)]BF$_4$ (0.203 mmol, 1 equiv) in CH_2Cl_2 (*ca.* 20 mL), cyclic secondary amine (0.607 mmol, 3 equiv) was added and stirred for 1 h at room temperature in the absence of light. The reaction mixture was filtered through a thin Celite pad, and the solvent was concentrated under reduced pressure to 5 mL. Et_2O (*ca.* 30 mL) was added to precipitate the product as white powder. The white powder was further washed with EtOAc (3 × 10 mL) to get the pure product.

Route II. To a solution of [AuCl(^{i}Pr$_2$-bimy)] (0.23 mmol, 1 equiv) in CH_2Cl_2 (*ca.* 10 mL), adamantyl isocyanide (0.276 mmol, 1.2 equiv) and $AgBF_4$ (0.276 mmol, 1.2 equiv) were added and stirred for 30 min at room temperature in the absence of light. After 30 min, the reaction mixture was treated with activated charcoal and filtered through a pad of Celite. Subsequently, a solution of cyclic secondary amine (0.345 mmol, 1.5 equiv) in CH_2Cl_2 (*ca.* 10 mL) was added to the solution. After 30 min, the solution was treated with activated charcoal and filtered. Solvent volume has been reduced under reduced pressure to 5 mL. Et_2O (*ca.* 30 mL) was added to precipitate the product as white powder.

*[Au(^{i}Pr$_2$-bimy)(^{t}Bu-Pyr)]BF$_4$ (**7**).* Yield: route I, 0.083 g, 64%; route II, 0.099 g, 67%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.69 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.43 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.58 (s, 1H, NH), 5.38 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 3.96 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.42 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 2.09 (quint, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 1.95 (quint, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 1.78 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.64 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 202.0$_6$ (C$_{ADC}$), 188.5$_0$ (C$_{Probe}$), 133.3, 125.1, 113.9 (Ar−C), 56.9 (CH-(CH$_3$)$_2$), 54.7, 54.5 (C$_4$H$_8$N), 46.2 (C(CH$_3$)$_3$), 32.5 (C(CH$_3$)$_3$), 25.6, 25.5 (C$_5$H$_{10}$N), 22.7 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.33 (s, $^{10}BF_4$), −152.38 (s, $^{11}BF_4$). HRMS (ESI) *m/z* calcd. for $C_{22}H_{36}AuN_4$ [M − BF_4]$^+$: 553.2599. Found: 553.2600. Anal. Calcd for $C_{22}H_{36}AuBF_4N_4$: C, 41.27; H, 5.67; N, 8.75. Found: C, 41.08; H, 5.74; N, 8.77.

*[Au(^{i}Pr$_2$-bimy)(Cy-Pyr)]BF$_4$ (**8**).* Yield: route I, 0.077 g, 0.116 mmol, 57%; route II, 0.094 g, 61%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.68 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.43 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.90 (d, 1H, $^3J_{HH}$ = 8 Hz, NH), 5.33 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 3.86 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.44 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 2.08 (pent, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 2.02−2.00 (m, 2H, C$_6$H$_{11}$), 1.93 (pent, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 1.81 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.70−1.65 (m, 2H, C$_6$H$_{11}$), 1.63−1.57 (m, 4H, C$_6$H$_{11}$), 1.26−1.17 (m, 3H, C$_6$H$_{11}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 198.6$_8$ (C$_{ADC}$), 189.7$_8$ (C$_{Probe}$), 133.3, 125.2, 113.7 (Ar−C), 61.0 (Cy), 55.7 (*C*H(CH$_3$)$_2$), 54.3, 47.1 (C$_4$H$_8$N), 34.7, 26.3 (Cy), 26.0, 25.7 (C$_4$H$_8$N), 25.5 (Cy), 23.1 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −151.80 (s, $^{10}BF_4$), −151.85 (s, $^{11}BF_4$). HRMS (ESI) *m/z* calcd. for $C_{24}H_{38}AuN_4$ [M − BF_4]$^+$: 579.2757. Found: 579.2761. Anal. Calcd for $C_{24}H_{38}AuBF_4N_4$: C, 43.26; H, 5.75; N, 8.41. Found: C, 43.07; H, 5.68; N, 8.64.

*Au(^{i}Pr$_2$-bimy)(Ad-Pyr)]BF$_4$ (**9**).* Yield: route I, 0.137 g, 0.191 mmol, 94%; route II, 0.154 g, 93%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.70 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.42 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.37 (s, 1H, NH), 5.39 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 3.96 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.40 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 2.30 (s, 6H, adamantyl), 2.13 (s, 6H, adamantyl), 1.96 (pent, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 1.77 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.66 (br, 2H, C$_4$H$_8$N; 5H, adamantyl). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 199.1$_4$ (C$_{ADC}$), 187.7$_3$ (C$_{Probe}$), 133.1, 125.0, 113.8 (Ar−C), 56.9 (*C*H(CH$_3$)$_2$), 54.1 (C$_4$H$_8$N), 45.9, 45.4, 36.5 (adamantyl), 30.3 (C$_4$H$_8$N), 25.4, 25.3 (adamantyl), 22.6 (CH$_3$).^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.62 (s, $^{10}BF_4$), −153.67 (s, $^{11}BF_4$). HR-MS (ESI) *m/z* calcd. for $C_{28}H_{42}AuN_4$ [M − BF_4]$^+$ 631.3070. Found: 631.3078. Anal. Calcd for $C_{28}H_{42}AuBF_4N_4$: C, 46.81; H, 5.89; N, 7.80. Found: C, 45.71; H, 5.59; N, 7.97.

*[Au(^{i}Pr$_2$-bimy)(Xyl-Pyr)]BF$_4$ (**10**).* Yield: route I, 0.119 g, 0.173 mmol, 85%; route II, 0.1427 g, 90%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.13 (s, 1H, NH), 7.56 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.34 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.13 (t, 1H, $^3J_{HH}$ = 7 Hz, Ar−H), 7.08 (d, 2H, $^3J_{HH}$ = 7 Hz, Ar−H), 4.71 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 3.98 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.72−3.68 (m, 2H, C$_4$H$_8$N), 2.31 (s, 6H, 2,6-(CH$_3$)$_2$C$_6$H$_3$), 2.22−2.18 (m, 2H, C$_4$H$_8$N), 2.04 (quint, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 1.54 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 202.0$_1$ (C$_{ADC}$), 188.4$_2$ (C$_{Probe}$), 139.0, 137.6, 132.9, 128.6, 128.5, 124.7, 113.5 (Ar−C), 55.5 (*C*H(CH$_3$)$_2$), 53.9, 46.9, 25.8, 25.3 (C$_4$H$_8$N), 22.5 (CH$_3$), 19.3 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.72 (s, $^{10}BF_4$), −152.77 (s, $^{11}BF_4$). HRMS (ESI) *m/z* calcd. for $C_{26}H_{36}AuN_4$ [M − BF_4]$^+$: 601.2608. Found: 601.2600. Anal. Calcd for $C_{26}H_{36}AuBF_4N_4$: C, 45.37; H, 5.27; N, 8.14. Found: C, 45.50; H, 5.44; N, 8.25.

*[Au(^{i}Pr$_2$-bimy)(Mes-Pyr)]BF$_4$ (**11**).* Yield: route I, 0.131 g, 0.186 mmol, 92%; route II, 0.157 g, 97%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.98 (s, 1H, NH), 7.57 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.33 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.86 (s, 2H, Ar−H), 4.74 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 3.97 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.64 (br, 2H, C$_4$H$_8$N), 2.24 (s, 9H, 2,4,6-(CH$_3$)$_3$C$_6$H$_2$), 2.15 (br, 2H, C$_4$H$_8$N), 2.03 (br, 2H, C$_4$H$_8$N), 1.53 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 202.1$_8$ (C$_{ADC}$), 188.7$_6$ (C$_{Probe}$), 137.9, 137.3, 136.6, 133.0, 129.4, 124.9, 113.6 (Ar−C), 55.5 (*C*H(CH$_3$)$_2$), 54.0, 46.9 (C$_4$H$_8$N), 25.6, 24.4 (C$_4$H$_8$N), 22.6 (CH$_3$), 21.7 (CH$_3$), 19.3 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.80 (s, $^{10}BF_4$), −152.85 (s, $^{11}BF_4$). HRMS (ESI) *m/z* calcd. for $C_{27}H_{38}AuN_4$ [M − BF_4]$^+$: 615.2757. Found: 615.2757. Anal. Calcd for $C_{27}H_{38}AuBF_4N_4$: C, 46.17; H, 5.45; N, 7.98. Found: C, 46.39; H, 5.51; N, 8.15.

*[Au(^{i}Pr$_2$-bimy)(Dipp-Pyr)]BF$_4$ (**12**).* Yield: route I, 0.142 g, 94%; route II, 0.156 g, 91%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.19 (s, 1H, NH), 7.57 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.35−7.32 (m, 3H, Ar−H), 7.18 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar−H), 4.59 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 3.99 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.69 (t, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 3.24 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 2.18 (pent, 2H, $^3J_{HH}$ = 7 Hz, C$_4$H$_8$N), 2.08−2.02 (m, 2H, C$_4$H$_8$N), 1.51 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.25 (d, 6H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.21 (d, 6H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 202.3$_9$ (C$_{ADC}$), 188.6$_4$ (C$_{Probe}$), 148.1, 136.3, 133.0, 129.4, 124.9, 124.1, 113.9 (Ar−C), 55.7 (*C*H(CH$_3$)$_2$), 54.3, 47.2 (C$_4$H$_8$N), 28.8 (*C*H(CH$_3$)$_2$), 26.6, 25.5 (C$_4$H$_8$N), 24.3 (CH$_3$), 22.6 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.56 (s, $^{10}BF_4$), −152.61 (s, $^{11}BF_4$). HR-MS (ESI) *m/z* calcd. for $C_{30}H_{44}AuN_4$ [M − BF_4]$^+$ 657.3244. Found: 657.3226. Anal. Calcd for $C_{30}H_{44}AuBF_4N_4$: C, 48.40; H, 5.96; N, 7.53. Found: C, 48.14; H, 6.16; N, 7.70.

*[Au(ADC)(^{i}Pr$_2$-bimy)]BF$_4$ (**13**).* Yield: route I, 0.060 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (br s, 1 H, NH), 7.57 (br s, 2 H, Ar−H), 7.34 (br s, 2 H, Ar−H), 7.14−7.07 (m, 3 H, Ar−H), 4.69 (m, 2 H, ^3J(H,H) = 6.95 Hz, NCH), 3.95 (br m, 2 H, NCH$_2$), 3.68 (br m, 2 H, NCH$_2$), 2.29 (s, 6 H, CH$_3$), 1.53 (d, 12 H, ^3J(H,H) = 6.95 Hz, NCH(C*H*$_3$)$_2$), 1.39 (br m, 6 H, NCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 203.4$_6$ (C$_{ADC}$), 188.6$_6$ (C$_{Probe}$), 139.0, 137.9, 133.0, 128.8, 128.7, 124.9, 113.8 (Ar−C), 54.2 (NCH), 53.0, 42.8 (NCH$_2$), 22.5 (NCH(CH$_3$)$_2$), 19.4 (CH$_3$), 16.0, 13.0 (NCH$_2$CH$_3$). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ −77.16 (s, $^{10}BF_4$), −77.21 (s, $^{11}BF_4$). MS (ESI): *m/z* 603 [M − BF_4]$^+$. Anal. Calc. for $C_{26}H_{38}N_4AuBF_4$: C, 45.23; H, 5.55; N, 8.12. Found: C, 45.23; H, 5.29; N, 7.96%.

*[Au(^{i}Pr$_2$-bimy)(Cy-Mor)]BF$_4$ (**14**).* Yield: route I, 0.093 g, 67%; route II, 0.102 g, 65%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.68 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.41 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.32 (d, 1H, $^3J_{HH}$ = 8 Hz, NH), 5.28 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.05−4.03 (m, 2H, OC$_4$H$_8$N), 4.01−3.95 (m, 1H, C$_6$H$_{11}$), 3.78−3.75 (m, 4H, OC$_4$H$_8$N), 3.60−3.59 (m, 2H, OC$_4$H$_8$N), 1.98 (d, 2H, $^3J_{HH}$ = 13 Hz, C$_6$H$_{11}$), 1.77 (d, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$ and C$_6$H$_{11}$), 1.16−1.15 (m, 3H, C$_6$H$_{11}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 200.3$_0$ (C$_{ADC}$), 188.4$_8$ (C$_{Probe}$), 133.1, 125.2, 113.7 (Ar−C), 67.5, 66.6 (OC$_4$H$_8$N), 60.9 (C$_6$H$_{11}$), 56.0 (*C*H(CH$_3$)$_2$), 54.2, 45.6 (OC$_4$H$_8$N), 34.1, 26.0, 25.3 (C$_6$H$_{11}$), 22.9 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −151.21 (s, $^{10}BF_4$), −151.26 (s, $^{11}BF_4$). HRMS (ESI) *m/z* calcd. for $C_{24}H_{38}AuN_4O$ [M − BF_4]$^+$: 595.2706. Found: 595.2714. Anal. Calcd for

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$C_{24}H_{38}AuBF_4N_4O$: C, 42.24; H, 5.61; N, 8.21. Found: C, 42.12; H, 6.03; N, 8.48.

*[Au(^{i}Pr$_2$-bimy)(Ad-Mor)]BF$_4$ (**15**).* Yield: route I, 0.091 g, 61%; route II: 0.112 g, 66%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.69 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.41 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.97 (s, 1H, NH), 5.32 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.17 (br, 2H, OC$_4$H$_8$N), 3.78 (br, 4H, OC$_4$H$_8$N), 3.61 (br, 2H, OC$_4$H$_8$N), 2.32 (br, 5H, adamantyl), 2.09 (s, 3H, adamantyl), 1.74 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.61−1.59 (m, 7H, adamantyl). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 201.5$_7$ (C_{ADC}), 187.2$_1$ (C_{Probe}), 133.1, 125.1, 113.9 (Ar−C), 67.4 (OC$_4$H$_8$N), 66.6 (OC$_4$H$_8$N), 58.4 (C*H*(CH$_3$)$_2$), 55.3 (OC$_4$H$_8$N), 54.6 (OC$_4$H$_8$N), 45.1, 36.5, 30.3 (adamantyl), 22.5 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −151.23 (s, $^{10}BF_4$), − 151.29 (s, $^{11}BF_4$). HR-MS (ESI) *m*/*z* calcd. for $C_{28}H_{42}AuN_4O$ [M − BF_4]$^+$ 647.3019. Found: 647.3028. Anal. Calcd for $C_{28}H_{42}AuBF_4N_4O$: C, 45.79; H, 5.76; N, 7.63. Found: C, 45.31; H, 6.11; N, 7.59.

*[Au(^{i}Pr$_2$-bimy)(Xyl-Pip)]BF$_4$ (**16**).* Yield: route I, 0.135 g, 95%; route II, 0.157 g, 97%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.46 (s, 1H, NH), 7.56 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.35 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.12 (t, 1H, $^3J_{HH}$ = 8 Hz, Ar−H), 7.07 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar−H), 4.71 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.13 (br, 2H, C$_5$H$_{10}$N), 3.83 (br, 2H, C$_5$H$_{10}$N), 2.31 (s, 6H, 2,6-(CH$_3$)$_2$C$_6$H$_3$), 1.83 (br, 6H, C$_5$H$_{10}$N), 1.55 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 202.3$_2$ (C_{ADC}), 188.6$_9$ (C_{Probe}), 138.7, 137.7, 133.1, 128.8, 128.7, 124.9, 113.7 (Ar−C), 55.8 (C*H*(CH$_3$)$_2$), 54.1, 46.8 (C$_5$H$_{10}$N), 28.0 (C*H*(CH$_3$)$_2$), 26.6, 25.0 (C$_5$H$_{10}$N), 22.6 (CH$_3$), 19.3 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.52 (s, $^{10}BF_4$), −152.57 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{38}AuN_4$ [M − BF_4]$^+$ 615.2757. Found: 615.2750. Anal. Calcd for $C_{27}H_{38}AuN_4BF_4$: C, 46.17; H, 5.45; N, 7.98. Found: C, 45.89; H, 5.58; N, 8.07.

*[Au(^{i}Pr$_2$-bimy)(Xyl-Mor)]BF$_4$ (**17**).* Yield: route I, 0.15 g, 90%), route II: 0.136 g, 84%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.73 (s, 1H, NH), 7.57 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.35 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.13 (t, 1H, $^3J_{HH}$ = 7 Hz, Ar−H), 7.08 (d, 2H, $^3J_{HH}$ = 7 Hz, Ar−H), 4.69 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.16−4.15 (m, 2H, C$_4$H$_8$NO), 3.94−3.88 (m, 6H, C$_4$H$_8$NO), 2.31 (s, 6H, 2,6-(CH$_3$)$_2$C$_6$H$_3$), 1.55 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 203.6$_0$ (C_{ADC}), 188.0$_0$ (C_{Probe}), 138.3, 137.7, 133.0, 128.9, 128.8, 125.4, 124.9, 113.7 (Ar−C), 68.0, 67.1 (C$_4$H$_8$NO), 56.1 (C*H*(CH$_3$)$_2$), 54.1, 46.4 (C$_4$H$_8$NO), 22.6 (CH$_3$), 19.2 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −151.98 (s, $^{10}BF_4$), −152.03 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{26}H_{36}AuN_4O$ [M − BF_4]$^+$: 617.2555. Found: 617.2549. Anal. Calcd for $C_{26}H_{36}AuBF_4N_4O$: C, 44.34; H, 5.15; N, 7.95. Found: C, 44.55; H, 5.5; N, 8.32.

*[Au(^{i}Pr$_2$-bimy)(Xyl-Pipz)]BF$_4$ (**18**).* Yield: route I, 0.112 g, 78%; route II, 0.124 g, 76%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.86 (s, 1H, NH), 7.56 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.33 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 7.11 (t, 1H, $^3J_{HH}$ = 8 Hz, Ar−H), 7.06 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar−H), 4.69 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.13 (br, 2H, NC$_4$H$_8$NH), 3.88 (br, 2H, NC$_4$H$_8$NH), 3.05 (br, 2H, NC$_4$H$_8$NH), 3.01 (br, 2H, NC$_4$H$_8$NH), 2.28 (s, 6H, 2,6-(CH$_3$)$_2$C$_6$H$_3$), 2.02 (s, 1H, NC$_4$H$_8$NH), 1.52 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 202.7$_1$ (C_{ADC}), 188.5$_1$ (C_{Probe}), 138.7, 137.8, 133.0, 128.8, 128.7, 124.9, 113.7 (Ar−C), 61.0, 57.4 (NC$_4$H$_8$NH), 54.1 (C*H*(CH$_3$)$_2$), 47.7, 46.6 (NC$_4$H$_8$NH), 25.6 (CH$_3$), 19.4 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.33 (s, $^{10}BF_4$), −152.39 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{26}H_{37}AuN_5$ [M − BF_4]$^+$ 616.275714. Found: 616.2721. Anal. Calcd for $C_{27}H_{38}AuN_4BF_4$: C, 44.40; H, 5.30; N, 9.96. Found: C, 44.57; H, 5.24; N, 9.88.

*[Au(^{i}Pr$_2$-bimy)(Mes-Mor)]BF$_4$ (**19**).* Yield: route I, 0.108 g, 74%; route II, 0.124 g, 75%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.65 (s, 1H, NH), 7.57 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.36 (dd, 2H, $^3J_{HH}$ = 6 Hz, 3 Hz, Ar−H), 6.88 (s, 2H, Ar−H), 4.73 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.16−4.14 (m, 2H, C$_4$H$_8$NO), 3.92−3.87 (m, 6H, C$_4$H$_8$NO), 2.26 (s, 9H, 2,4,6-(CH$_3$)$_3$C$_6$H$_2$), 1.55 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 203.6$_1$ (C_{ADC}), 188.0$_1$ (C_{Probe}), 138.2, 137.2, 135.7, 132.9, 129.5, 124.9, 113.7 (Ar−C), 67.9, 67.0 (C$_4$H$_8$NO), 56.0 (C*H*(CH$_3$)$_2$), 54.1, 46.2 (C$_4$H$_8$NO), 22.4 (CH$_3$), 21.7 (CH$_3$), 19.1 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −151.95 (s, $^{10}BF_4$), −152.00 (s, $^{11}BF_4$). HR-MS (ESI) *m*/*z* calcd. for $C_{27}H_{38}AuN_4O$ [M − BF_4]$^+$ 631.2712. Found: 631.2706. Anal. Calcd for $C_{27}H_{38}AuN_4BF_4O$: C, 46.14; H, 5.33; N, 7.80. Found: C, 45.11; H, 5.45; N, 8.05.

*[Au(^{i}Pr$_2$-bimy)(Dipp-Mor)]BF$_4$ (**20**).* Yield: route I, 0.137 g, 89%, route II: 0.164 g, 94%. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.80 (s, 1H, NH), 7.59 (dd, 2H, $^3J_{HH}$ = 7 Hz, 3 Hz, Ar−H), 7.34 (m, 3H, Ar−H), 7.18 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar−H), 4.57 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 4.18−4.16 (m, 2H, C$_4$H$_8$NO), 3.94−3.93 (m, 2H, C$_4$H$_8$NO), 3.90−3.85 (m, 4H, C$_4$H$_8$NO), 3.22 (sept, 2H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.50 (d, 12H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.26 (d, 6H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$), 1.21 (d, 6H, $^3J_{HH}$ = 7 Hz, (C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 °C): δ 203.7$_8$ (C_{ADC}), 188.1$_2$ (C_{Probe}), 148.1, 135.7, 133.0, 129.7, 125.0, 124.3, 114.1 (Ar−C), 68.1, 67.4 (C$_4$H$_8$NO), 56.2 (C*H*(CH$_3$)$_2$), 54.5, 46.7 (C$_4$H$_8$NO), 28.9 (C*H*(CH$_3$)$_2$), 24.3 (CH$_3$), 22.5 (CH$_3$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −152.030 (s, $^{10}BF_4$), −152.08 (s, $^{11}BF_4$). HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{44}AuN_4O$ [M − BF_4]$^+$ 673.3176. Found: 673.3176. Anal. Calcd for $C_{30}H_{44}AuBF_4N_4O$: C, 47.38; H, 5.83; N, 7.37. Found: C, 47.37; H, 5.55; N, 8.03.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00886.

Selected crystallographic data, NMR spectra, and HRMS spectra (PDF)

Accession Codes

CCDC 1970601−1970603, 1970620−1970624, and 1976794−1976797 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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■ DEDICATION

Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 65th birthday

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