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Gold and Palladium Hetero-Bis-NHC Complexes: Characterizations, Correlations, and Ligand Redistributions

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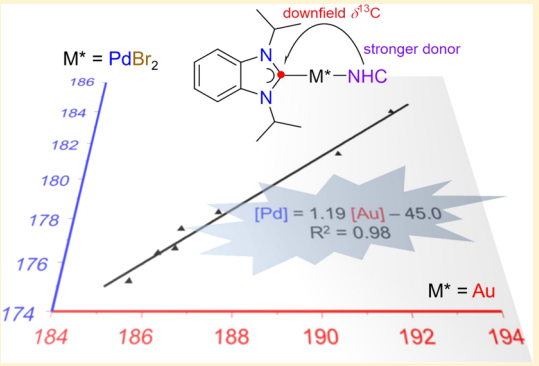
Supporting Information

ABSTRACT: A series of new Au(I) hetero-bis-NHC complexes [Au(^{i}Pr$_2$-bimy)(NHC)]X (X = BF_4, PF_6, **2**–**6**) and the hetero-tetrakis-NHC complex [Au$_2$(^{i}Pr$_2$-bimy)$_2$(μ-ditz)](BF$_4$)$_2$ (**7**) have been synthesized using the Au(I) acetato complex [Au(O_2CCH_3)(^{i}Pr$_2$-bimy)] (**C**) as a basic metal precursor (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene, ditz = 1,2,4-triazolidine-3,5-diylidene). The Au(III) hetero-bis-NHC complex *trans*-[AuCl$_2$(^{i}Pr$_2$-bimy)(Bn$_2$-bimy)]BF_4 (**12**; Bn$_2$-bimy = 1,3-dibenzylbenzimidazolin-2-ylidene) and the hetero-tetrakis-NHC complex *all-trans*-[Au$_2$Cl$_4$(^{i}Pr$_2$-bimy)$_2$(μ-ditz)](BF$_4$)$_2$ (**13**) were obtained by oxidation of their corresponding Au(I) hetero-NHC precursors. For all Au(I) hetero-NHC complexes, the ^{13}C carbene signals of the constant ^{i}Pr$_2$-bimy ligand are found to be highly correlated with those in Pd(II) analogues of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)], which could be applied to detect the σ-donating ability of the *trans*-standing NHC. In addition, an interesting ligand redistribution process was observed for some of the Au(I) hetero-bis-NHC complexes.



INTRODUCTION

N-heterocyclic carbene (NHC) complexes of Au(I) have received increased interest due to their catalytic,[1] luminescent,[2] and biological properties.[3] In addition, they have also found applications in the building of metallosupramolecular architectures.[4] A wide range of Au(I) homo-bis-NHC complexes have been previously reported,[2a,5] while Au(I) hetero-bis-NHC complexes,[6] which contain two different NHCs, have been given less attention. In addition, most compounds reported are limited to imidazolin-2-ylidene ligands,[6a,b] and an extension to other types of carbenes is highly desirable. As a contribution to the new area of gold heterocarbene chemistry, we herein report different routes to a series of Au(I) hetero-bis-NHC complexes of the type [Au(^{i}Pr$_2$-bimy)(NHC)]BF_4 (**I**; Figure 1) bearing the fixed spectator ^{i}Pr$_2$-bimy (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) and various types of additional NHC ligands. Furthermore, the Janus-type 1,2,4-triazolidine-3,5-diylidene ligand has also been included in this study, which forms a new digold hetero-tetrakis-NHC complex [Au$_2$(^{i}Pr$_2$-bimy)$_2$(μ-ditz)](BF$_4$)$_2$ (**II**; Figure 1).

It was previously found that the ^{i}Pr$_2$-bimy spectator could be employed as a highly sensitive ^{13}C NMR spectroscopic probe to determine the net donating ability of a second *trans*-standing NHC ligand in complexes of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)][7] (**III**; Figure 1). As a potential extension of this methodology to other metal–NHC systems, a comparison and correlation of the $^{13}C_{carbene}$(^{i}Pr$_2$-bimy) NMR data between Pd(II) complexes **III** and Au(I) complexes **I**/**II** is reported as well. For this purpose, three new hetero-bis-carbene complexes, *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)] (**1′**, **4′**, **8′**), were synthesized and characterized. Finally, a ligand redistribution process of Au(I) hetero-NHC complexes was observed in some cases and studied in detail.

RESULTS AND DISCUSSION

Syntheses of Au(I) Hetero-NHC Complexes. Homo-bis-NHC Au(I) complexes of the general formula [Au(NHC)$_2$]Y (Y = noncoordinating anion) can be obtained by reacting the mono-NHC precursor [AuX(NHC)] (X = halido ligand) with the respective azolium salts and a base.[2a]

Thus, this method was utilized in our initial attempts to synthesize hetero-bis-NHC complexes of the type [Au(NHC)-(NHC′)]Y bearing two different NHC ligands. Hence, the previously reported indazolin-3-ylidene complex **A**[8] was treated with the benzimidazolium salt ^{i}Pr$_2$-bimy·H$^+$BF$_4^-$ (**a**) and K_2CO_3, cleanly affording the hetero-bis-NHC complex [Au-(^{i}Pr$_2$-bimy)(Indy)]BF_4 (**1**) in a yield of 76% (Indy = 6,7,8,9-tetrahydropyridazino[1,2-*a*]indazolin-3-ylidene; Scheme 1).

On the other hand, the known mono-NHC complex **B**[9] gave product mixtures containing the desired hetero-bis-NHC complex as well as non-negligible amounts of two homo-bis-NHC complexes when treated in the same manner with triazolium (**b**) or benzimidazolium salts (**c**), as indicated by ^{1}H NMR spectroscopy (Scheme 2). It should be noted that such an observation was previously reported by Lin et al.[10]

An alternative approach to Au(I) hetero-bis-NHC complexes by in situ deprotonation of azolium salts using the basic

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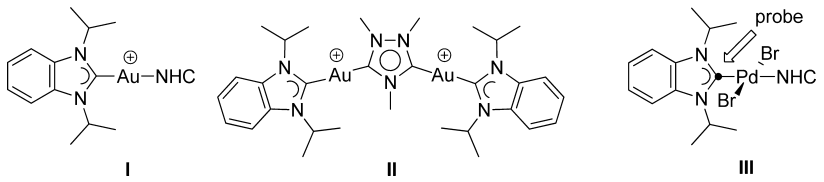
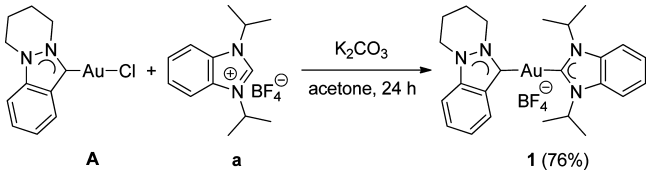
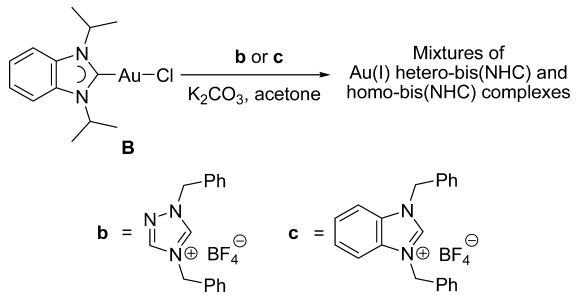


Figure 1. Au(I) and Pd(II) hetero-NHC complexes.

Scheme 1. Synthesis of Hetero-Bis-Carbene Complex [Au(^{i}Pr$_2$-bimy)(Indy)]BF$_4$ (1)



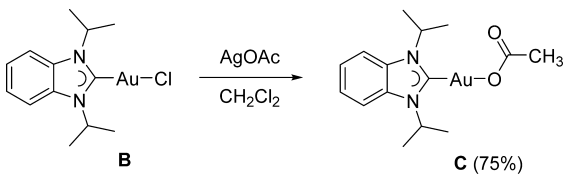
Scheme 2. Attempts To Prepare Au(I) Hetero-Bis-NHC Complexes



hydroxo complex [Au(OH)(IPr)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) was reported by Nolan and co-workers.[6b] However, preparation of the analogous complex [Au(OH)(^{i}Pr$_2$-bimy)] following the reported methods[11] was to no avail. Instead, decomposition was observed, as indicated by deposition of purple gold on the glass surface of the flask. The ^{i}Pr$_2$-bimy ligand is probably not sufficiently bulky to stabilize the highly active Au–hydroxo moiety, in contrast to the case for the IPr or SIPr (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) ligands in the reported analogues.[11]

As a suitable alternative, we opted for mixed NHC–acetato Au(I) complexes. Such complexes have been known for some time, but their potential use as basic metal precursors to hetero-bis-NHC complexes has not been studied. The chlorido complex [AuCl(^{i}Pr$_2$-bimy)] (**B**) was thus treated with 1 equiv of AgO$_2$CCH$_3$ in CH$_2$Cl$_2$ following a reported method,[12] which affords the acetato complex [Au(O$_2$CCH$_3$)(^{i}Pr$_2$-bimy)] (**C**) in a 75% yield (Scheme 3). Complex **C** is readily soluble in halogenated solvents, acetone, DMF, and DMSO but insoluble in nonpolar solvents such as diethyl ether and hexane. Even in solid form, it is not very stable under aerobic conditions, as evidenced by the observation of purple gold upon exposure to air overnight. However, when fully dried, this complex can be kept under an inert atmosphere for at least 2 weeks.

Scheme 3. Synthesis of Au(I) Acetato Complex [Au(O$_2$CCH$_3$)(^{i}Pr$_2$-bimy)] (C)



The ^{1}H NMR spectrum of complex **C** shows a characteristic multiplet at 5.45 ppm due to the isopropyl C–H protons. ^{13}C NMR spectroscopy further supports the formation of **C** by a carbenoid signal at 170.2 ppm, which is shifted upfield in comparison to that in its chlorido precursor **B** (cf. 175.8 ppm). This upfield shift is attributed to the decreased σ-donating ability of the acetato compared to that of the chlorido coligand, which in turn results in a more Lewis acidic Au(I) center.[12] Furthermore, its ESI mass spectrum shows a dominant peak at m/z 601 arising from the cationic [Au(^{i}Pr$_2$-bimy)$_2$]$^+$ species. It should be noted that such Au(I) bis-NHC cations are typically observed in the ESI mass spectra of Au(I) mono-NHC complexes.[8]

The identity of complex **C** was unambiguously confirmed by X-ray diffraction. Suitable single crystals were obtained by layering a concentrated solution of **C** in CH$_2$Cl$_2$ with hexane and storing at 4 °C. Selected crystallographic data are given in Table 1, and the molecular structure depicted in Figure 2 confirms the linear coordination geometry of the Au(I) center with both ^{i}Pr$_2$-bimy and acetato ligands bound in a monodentate fashion. The Au–C bond length falls in the range typically observed for Au(I) ^{i}Pr$_2$-bimy complexes.[6c,9]

The potential use of acetato complex **C** as a basic metal precursor for the preparation of Au(I) hetero-NHC complexes was subsequently examined by treatment with a range of azolium salts (**b**–**f**) with the noncoordinating anions BF$_4^-$ and PF$_6^-$ (Scheme 4). Under the optimal conditions shown in Table 2, all desired Au(I) hetero-bis-NHC complexes **2**–**6** could be obtained in high yields.

Notably, elevated temperatures were required to facilitate the formation of complexes **5** and **6** incorporating the highly bulky IPr ligand. However, several attempts to synthesize indazolin-3-ylidene complex **1** by treating **C** with IndyH$^+$BF$_4^-$ were unsuccessful, due to the lower acidity of the indazolium salt. In addition to monodentate NHC ligands, we extended the methodology to the synthesis of digold complexes bearing the Janus-type dicarbene ligand ditz (ditz = 1,2,4- trimethyltriazolidine-3,5-diylidene), which bears two carbene donors in a single five-membered ring.[13] Very recently, Peris et al. reported one heterobimetallic Au–Ir triazolidinediylidene complex,[13b] while to the best of our knowledge, digold ditz complexes are still unknown. Indeed, the reaction of **C** with the dicationic salt ditz·(H$^+$BF$_4^-$)$_2$ (**g**) in a 2:1 ratio afforded the Au(I) heterotetrakis-NHC complex **7** in a moderate yield. Alternatively, complex **7** can be synthesized via a Ag–carbene transfer route[13a] involving the chlorido complex **B** as a precursor (Scheme 5).

All Au(I) hetero-bis-NHC complexes **1**–**6** and the heterotetrakis-NHC complex **7** are readily soluble in common

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Table 1. Selected X-ray Crystallographic Data for Complexes C, 1, 2, 6, 9, 12, and 13·3CH_2Cl_2

	C	1	2	6
formula	$C_{15}H_{21}AuN_2O_2$	$C_{24}H_{30}AuBF_4N_4$	$C_{29}H_{33}AuBF_4N_5$	$C_{40}H_{54}AuF_6N_4P$
fw	458.30	658.30	735.38	932.81
cryst size (mm)	0.54 × 0.16x 0.16	0.36 × 0.20 × 0.16	0.60 × 0.26 × 0.60	0.31 × 0.23 × 0.18
temp (K)	223(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/c$	$P2_1/n$	Pc
a (Å)	9.4713(15)	10.3775(10)	11.3640(17)	9.6056(4)
b (Å)	7.4385(12)	13.4807(13)	13.907(2)	13.1707(6)
c (Å)	10.8863(17)	17.2073(16)	18.598(3)	16.2740(8)
α (deg)	90	90	90	90
β (deg)	91.231(4)	98.989(3)	90.016(4)	95.7720(10)
γ (deg)	90	90	90	90
V (Å^3)	766.8(2)	2377.7(4)	2939.3(8)	2048.43(16)
Z	2	4	4	2
D_c (g cm^{-3})	1.985	1.839	1.662	1.512
μ (mm^{-1})	9.596	6.239	5.058	3.690
θ range (deg)	2.15−27.47	1.93−27.48	1.83−27.50	1.99−27.48
no. of unique data	1882	5436	6756	7951
max, min transmission	0.3921, 0.1722	0.4305, 0.3274	2253.4290, 0.1513	0.5564, 0.3942
final R indices ($I > 2\sigma(I)$)	R1 = 0.0345, wR2 = 0.0887	R1 = 0.0365, wR2 = 0.0731	R1 = 0.0380, wR2 = 0.0926	R1 = 0.0327, wR2 = 0.0673
R indices (all data)	R1 = 0.0376, wR2 = 0.0911	R1 = 0.0507, wR2 = 0.0776	R1 = 0.0430, wR2 = 0.0952	R1 = 0.0356, wR2 = 0.0685
goodness of fit on F^2	1.075	1.014	1.044	0.960
peak/hole (e Å^{-3})	2.249/−2.057	1.939/−0.827	3.607/−2.200	1.460/−0.655

	9	12	13
formula	$C_{42}H_{36}AuBF_4N_4$	$C_{34}H_{36}AuBCl_2F_4N_4$	$C_{31}H_{45}Au_2B_2Cl_4F_8N_7\cdot3CH_2Cl_2$
fw	880.52	855.34	1394.94
cryst size (mm)	0.50 × 0.20 × 0.12	0.24 × 0.19 × 0.11	0.20 × 0.18 × 0.16
temp (K)	100(2)	100(2)	100(2)
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Pccn$
a (Å)	8.3264(3)	10.4294(4)	20.517(2)
b (Å)	10.9307(4)	11.4264(5)	23.027(2)
c (Å)	11.1756(5)	14.3320(6)	20.4338(19)
α (deg)	68.5800(10)	89.6620(10)	90
β (deg)	86.5110(10)	84.8510(10)	90
γ (deg)	67.9390(10)	79.5560(10)	90
V (Å^3)	874.11(6)	1672.78(12)	9654.1(16)
Z	1	2	8
D_c (g cm^{-3})	1.673	1.698	1.919
μ (mm^{-1})	4.267	4.610	6.579
θ range (deg)	2.16−25.00	1.81−27.50°	1.66−27.50
no. of unique data	4009	7666	11072
max, min transmission	0.6749, 0.4824	0.6310, 0.4041	0.4191, 0.3529
final R indices ($I > 2\sigma(I)$)	R1 = 0.0179, wR2 = 0.0445	R1 = 0.0523, wR2 =0.1093	R1 = 0.0523, wR2 = 0.1093
R indices (all data)	R1 = 0.0179, wR2 = 0.0445	R1 = 0.0308, wR2 = 0.0634	R1 = 0.0878, wR2 = 0.1207
goodness of fit on F^2	1.045	1.046	1.029
peak/hole (e Å^{-3})	1.030 /−0.999	1.365/−1.078	1.990/−1.172

organic solvents, with the exception of diethyl ether and hexane.

NMR Spectroscopic Analyses of Au(I) Complexes. All complexes (**1**−**7**) were subjected to multinuclear NMR spectroscopy in $CDCl_3$. Due to their very good solubilities, resolution of the $^{13}C_{carbene}$ signals could be accomplished with less than 100 scans. The isopropyl C−H signals in the common ^{i}Pr$_2$-bimy spectator and the carbenoid resonance in all Au(I) hetero-NHC complexes described here are summarized in Table 3. The recently reported pyrazole-derived NHC complex [Au(^{i}Pr$_2$-bimy)(FPyr)]PF_6 (**8**)[6c] (Fpyr = 1,2,3,4,6,7,8,9-octahydropyridazino[1,2-*a*]indazolin-11-ylidene) was included as well for comparison.

The isopropyl C−H protons of complexes **1**−**8** exclusively give only one multiplet, indicating a free rotation of Au−$C_{carbene}$ bonds. Notably, these signals ranging from 4.36 to 5.42 ppm are at significantly higher field than those (cf. 5.34−6.44 ppm) in their previously reported Pd counterparts of the type *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(NHC)].[7a] This suggests the absence of C−H···M anagostic (or preagostic) interactions, which are typically observed for ^{i}Pr$_2$-bimy complexes of group 10 metals.[14] It was also noted that the nature of the noncoordinating counteranion has little effect on the ^{1}H and ^{13}C NMR spectra (cf. Table 3,

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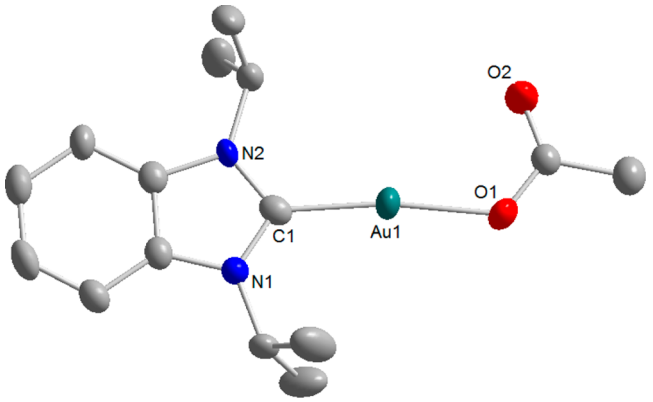
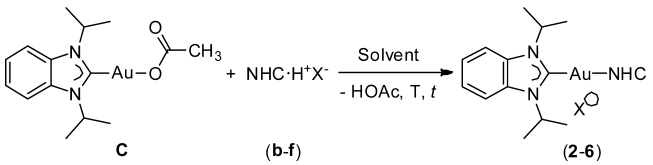


Figure 2. Molecular structure of **C** showing 50% probability ellipsoids. Hydrogen atoms and disordered atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1−C1 = 1.988(8); N1−C1−N2 = 108.5(7). Bond lengths and angles related to the acetato ligand are not given, due to the disorder in the crystal.

Scheme 4. Synthesis of Au(I) Hetero-Bis-NHC Complexes 2−6

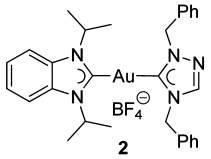
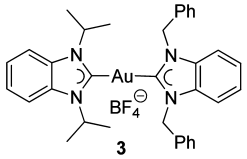
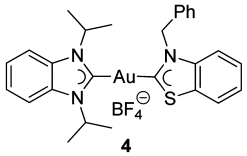
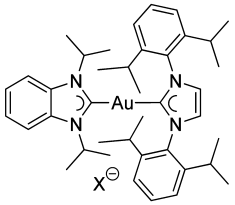


complexes **5** and **6**). However, a pronounced counteranion effect (BF_4 vs PF_6) on the NMR spectra has been observed in a study involving NH,NR-substituted Ni(II) NHC complexes.[15] In addition, the ^{1}H NMR spectrum of the heterotetrakis-NHC complex **7** shows two singlets at 4.31 and 4.13 ppm in a 2:1 integral ratio for the three *N*-methyl groups of the diylidene ligand, which indicates a 2-fold symmetry of this molecule.

As expected, the ^{13}C NMR spectra of **1−8** all display two carbenoid resonances in the downfield regions, which fall in a wide range from 182.4 to 214.8 ppm. Baker and co-workers have reported a correlation of the $^{13}C_{carbene}$ signal in neutral [AuX(NHC)] complexes with the donating ability of the anionic ligand X.[12] Interestingly, it was found that the constant ^{i}Pr$_2$-bimy ligand in complexes **1−8** could be employed as a ^{13}C NMR spectroscopic probe to determine the donor strength of the *trans*-standing second NHC, whereby stronger donating ligands would lead to a more downfield shift (Figure 3). Among the NHCs investigated herein, the weakest triazolidinediylidene (ditz)[13a,c] ligand in complex **7** leads to the most upfield ^{i}Pr$_2$-bimy carbenoid signal, while the strongest pyrazole-derived ligand (FPyr) in complex **8** gives rise to the most downfield ^{i}Pr$_2$-bimy carbene signal. Remarkably, these ^{13}C NMR values nicely correlate with those found in their Pd(II) counterparts (vide infra).

Ligand Redistribution of Au(I) Hetero-NHC Complexes. During the synthesis of complexes **2−4** and **7** it was observed that prolonging the reaction time beyond the tabulated value (Table 2) generally favored ligand redistribution processes, which are irreversible and led to the generation of homo-bis-NHC complexes as side products. This process

Table 2. Optimal Conditions for Synthesis of Complexes 2−6

Entry	Complex	Solvent	T (°C)[a]	*t* (h)	Yield%
1	 **2**	CH_2Cl_2	A.T.	5	80
2	 **3**	CH_2Cl_2	A.T.	24	82
3	 **4**	CH_2Cl_2	A.T.	16	76
4	 **5**: X = BF_4 **6**: X = PF_6	acetone	80	48	88
5		acetone	80	48	86

[a]A.T. = ambient temperature.

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Scheme 5. Synthesis of Au(I) Hetero-Tetrakis-NHC Complex 7

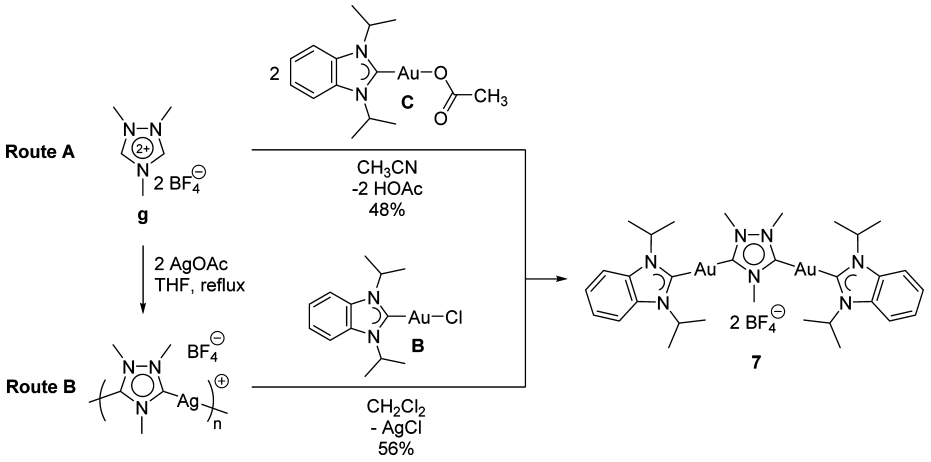

Table 3. Selected NMR Spectroscopic Data for Complexes 1−8 of the Type [Au(^{i}Pr$_2$-bimy)(NHC)]X (X = BF_4/PF_6)

complex[a]	δ_{H1}[b] (ppm)	δ_{C1}[c] (ppm)	δ_{C2}[c] (ppm)
[Au(^{i}Pr$_2$-bimy)(Indy)]BF_4 (**1**)	5.42	190.8	182.4
[Au(^{i}Pr$_2$-bimy)(Bn_2-tazy)]BF_4 (**2**)	5.08	186.6	186.7
[Au(^{i}Pr$_2$-bimy)(Bn_2-bimy)]BF_4 (**3**)	5.18	187.6	191.5
[Au(^{i}Pr$_2$-bimy)(Bn-btzy)]BF_4 (**4**)	5.25	186.2	214.8
[Au(^{i}Pr$_2$-bimy)(IPr)]BF_4 (**5**)	4.36	186.7	187.3
[Au(^{i}Pr$_2$-bimy)(IPr)]PF_6 (**6**)	4.36	186.7	187.3
[Au_2(^{i}Pr$_2$-bimy)$_2$(μ-ditz)]$(BF_4)_2$ (**7**)	5.31	185.6	189.4
[Au(^{i}Pr$_2$-bimy)(FPyr)]PF_6 (**8**)[6c]	5.33	192.5	179.6

[a]Abbreviations: ^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; Indy = 6,7,8,9-tetrahydropyridazino[1,2-*a*]indazolin-3-ylidene; Bn_2-tazy = 1,4-dibenzyl-1,2,4-triazolin-5-ylidene; Bn_2-bimy = 1,3-dibenzyl-benzimidazolin-2-ylidene; Bn-btzy = 3-benzylbenzothiazolin-2-ylidene; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; ditz = 1,2,4-triazolidine-3,5-diylidene; Fpyr = 1,2,3,4,6,7,8,9-octahydropyridazino[1,2-*a*]indazolin-11-ylidene. [b]δ_{H1} refers to the isopropyl C−H signals in the constant ^{i}Pr$_2$-bimy ligands. [c]δ_{C1} refers to the carbenoid signal of the spectator ligand ^{i}Pr$_2$-bimy, and δ_{C2} refers to the carbenoid signal of the NHC *trans* to the ^{i}Pr$_2$-bimy ligand. ^{13}C NMR spectra were measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm relative to TMS.

can be monitored by ^{1}H NMR spectroscopy and is demonstrated for complex **3** as a representative in Figure 4.

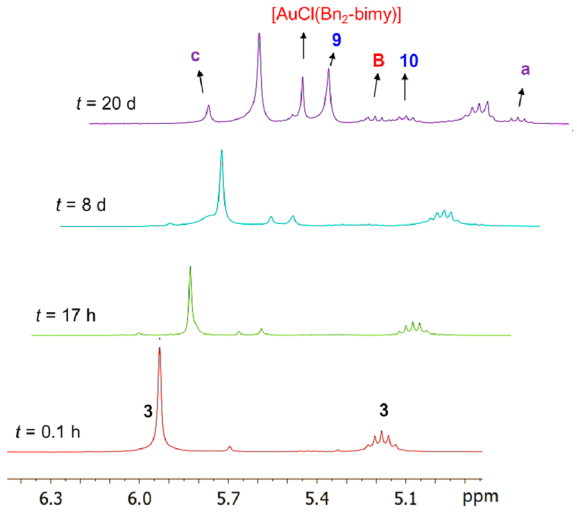

Figure 4. Time-dependent ^{1}H NMR spectra showing the ligand redistribution of complex **3** in $CDCl_3$.

While initially only signals due to the hetero-bis-NHC complex **3** are present, new signals due to the homoleptic bis-carbene complexes **9** and **10** (Scheme 6) start evolving with time. In addition, signals due to the azolium salts ^{i}Pr$_2$-bimy·H$^+$$BF_4^-$ (**a**) and Bn_2-bimy·H$^+$$BF_4^-$ (**c**) are also observed with time, supposedly due to hydrolysis of free carbenes, which

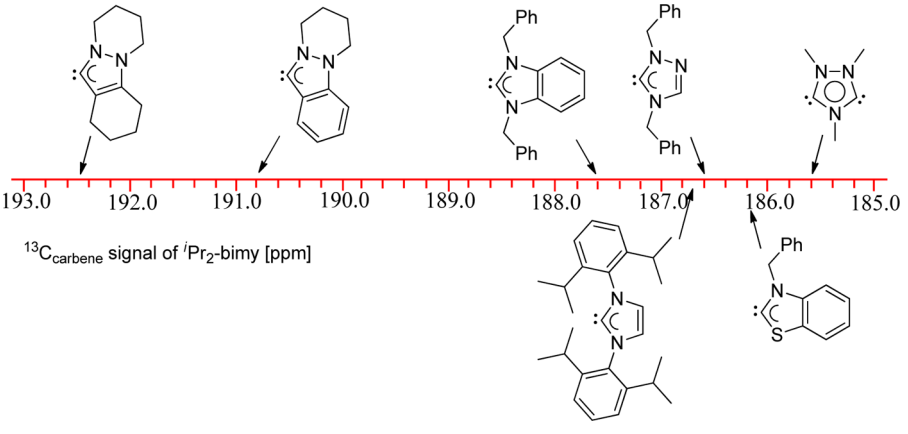

Figure 3. Donor abilities of NHCs on the ^{13}C NMR scale.

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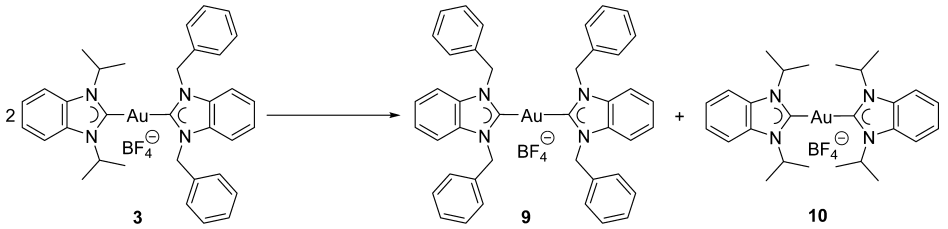
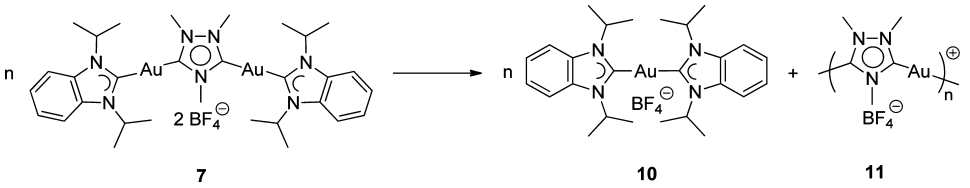
Scheme 6. Ligand Redistribution of Hetero-Bis-NHC Complex 3



Scheme 7. Ligand Redistribution of the Hetero-Tetrakis-NHC Complex 7



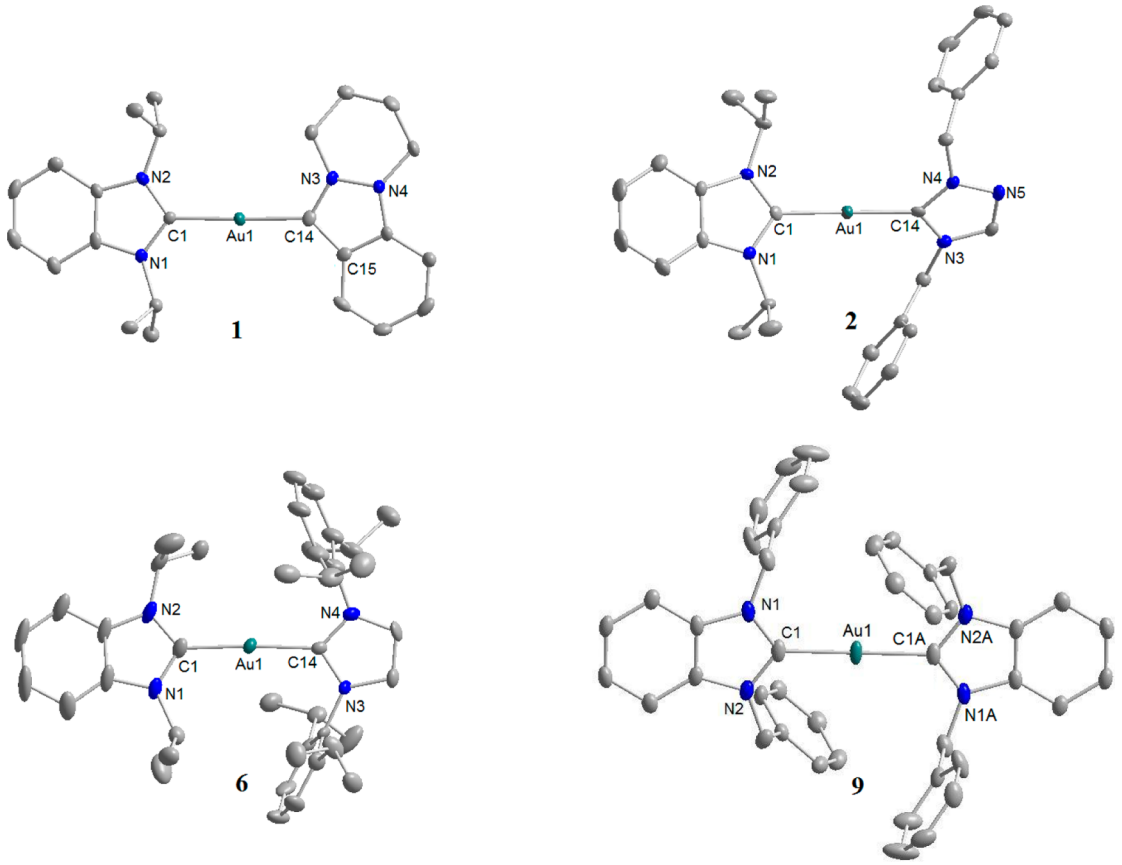


Figure 5. Molecular structures of **1**, **2**, **6**, and **9** showing 50% probability ellipsoids. Hydrogen atoms and counteranions are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. Complex **1**: Au1−C14 = 2.025(5), Au1−C1 = 2.035(5); C14−Au1−C1 = 178.51(19), N2−C1−N1 = 107.2(4), N3−C14−C15 = 104.8(4). Complex **2**: Au1−C14 = 1.995(4), Au1−C1 = 2.021(4); C14−Au1−C1 = 176.93(15), N2−C1−N1 = 107.2(3), N4−C14−N3 = 101.8(3). Complex **6**: Au1−C14 1.996(5), Au1−C1 2.015(5); C14−Au1−C1 176.1(2), N2−C1−N1 107.8(5), N4−C14−N3 103.9(4). Complex **9**: Au1−C1 = 2.022(2); C1−Au1−C1A = 180.00(13), N1−C1−N2 = 106.59(17).

may point to a dissociative pathway. Interestingly, signals of the mono-carbene complexes [AuCl(Bn_2-bimy)] and [AuCl($^iPr_2$-bimy)] (**B**) are also present. The last two are formed by capture of chlorido ligands present in the chlorinated solvent.

Notably, the rearrangement for the dinuclear complex **7** bearing a triazolidine-3,5-diylidene bridge is markedly faster than that for mononuclear hetero-bis-NHC analogues. Within 1 h, a white precipitate formed from its $CDCl_3$ solution that was insoluble in common organic solvents, thus hampering further characterization. This supposedly polymeric/oligomeric complex **11** (Scheme 7) further decomposes to purple gold upon prolonged standing.

Similar ligand redistribution processes in solution have been observed for complexes of the type [Au(X)(NHC)] (X = anionic ligand) and [Au(NHC)(PPh_3)]CF_3SO_3.[6a,16] However, to the best of our knowledge, these are the first reports on the

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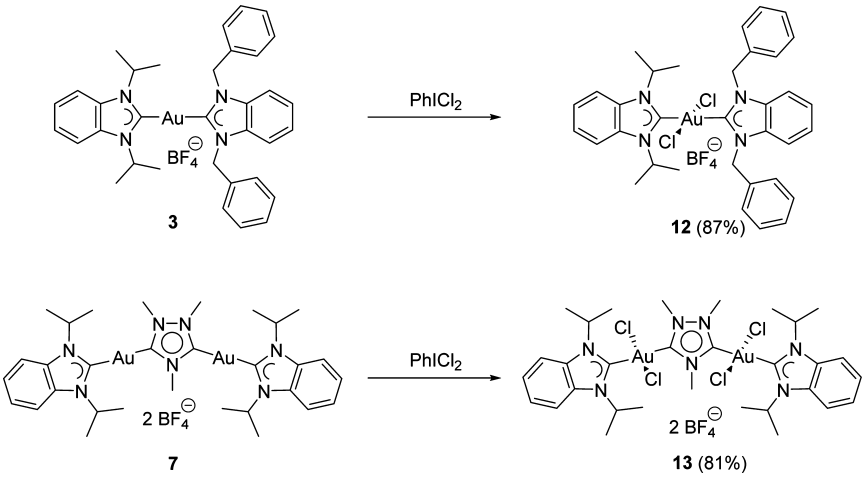
Scheme 8. Synthesis of Au(III) Hetero-NHC Complexes 12 and 13



ligand redistribution of Au(I) hetero-bis- or hetero-tetrakis-NHC complexes. The process is likely to be triggered by the presence of two or more different carbene ligands with different donating abilities and *trans* influences, resulting in Au−$C_{carbene}$ bonds of different strengths. The thermodynamically stable rearrangement products, on the other hand, are homoleptic complexes with only one type of Au−$C_{carbene}$ bond of the same strength, rendering them more stable than their kinetically controlled heteroleptic counterparts. The presence of azolium salts as hydrolysis products of free NHCs may point to a dissociative rearrangement pathway involving de- and recoordination of carbene ligands (Figure 4). However, the nature of this redistribution process remains to be explored in the future.

Finally, it should be noted that the redistribution process is slow in comparison to the time required for the acquisition of ^{13}C NMR spectra and thus poses no problem in the detection of the respective $^{13}C_{carbene}$ signals for all Au(I) hetero-carbene complexes described here.

Interestingly, for complexes **1**, **5**, **6**, and **8**, such ligand redistributions were not observed. The nonclassical indazole-derived carbene (Indy) in **1** and pyrazole-derived carbene (FPyr) in **8** are known to be the strongest carbene donors studied here (Figure 3).[7a] The increased electron density in these two complexes may result in stronger Au−carbene bonds due to enhanced π back-donation, which are non-negligible in d^{10} complexes, hindering further ligand redistribution.

For complexes **5** and **6**, electronic factors certainly do not play a major role, since these complexes contain the very bulky IPr ligand. Apparently, the formation of the cationic $[Au(IPr)_2]^+$ species is disfavored due to steric factors, and the hetero-bis-NHC complexes remain stable.

X-ray Diffraction Study of Au(I) Complexes. Single crystals of the hetero-bis-NHC complexes **1**, **2**, and **6** suitable for X-ray diffraction analyses were obtained by slow evaporation of concentrated CH_2Cl_2/hexane solutions. On the other hand, attempted crystallization of the hetero-bis-NHC complex $[Au(^iPr_2\text{-bimy})(Bn_2\text{-bimy})]BF_4$ (**3**) from a concentrated CH_2Cl_2/hexane solution afforded crystals of the homoleptic bis-NHC complex $[Au(Bn_2\text{-bimy})_2]BF_4$ (**9**; Bn_2-bimy = 1,3-dibenzylbenzimidazolin-2-ylidene) due to the aforementioned redistribution processes (vide supra).

In the molecular structures of **1**, **2**, and **6** depicted in Figure 5, the $^iPr_2$-bimy and the second carbene ligand adopt a linear arrangement about the gold(I) center with C−Au−C bond angles close to 180°. The two carbene planes are twisted by angles of 8.43° (**1**), 43.97° (**2**), and 10.74° (**6**), respectively. The Au−C($^iPr_2$-bimy) bond lengths of 2.015(5)−2.035(5) Å are comparable to those in Au(I) homo-bis-$^iPr_2$-bimy complexes.[9] The *N*-dipp substituents of the IPr ligand in **6** are oriented perpendicularly to the imidazole-based carbene ring, which is typically observed in Au−IPr complexes.[6b] On the other hand, the molecular structure of **9** reveals an Au(I) center coordinated by two Bn_2-bimy ligands in a linear arrangement. The two carbene ligands are related to each other by a crystallographic inversion center and are thus coplanar, with their benzyl substituents pointing to opposite directions to reduce the steric hindrance. It should finally be noted that no aurophilic[17] interactions were observed in any of the molecular structures, probably due to the steric bulk of the NHC ligands.

Syntheses and Characterization of Au(III) Hetero-NHC Complexes. As discussed above, complexes **3** and **7** readily undergo ligand redistribution in solution upon standing, which hampers their crystallization. To provide a more conclusive evidence for their formation, they were subjected to oxidative addition using a slight excess of $PhICl_2$ in an attempt to form their Au(III) derivatives (Scheme 8).

Indeed, these reactions gave the respective hetero-bis-NHC and hetero-tetrakis-NHC complexes *trans*-$[AuCl_2(^iPr_2\text{-bimy})(Bn_2\text{-bimy})]BF_4$ (**12**) and *all-trans*-$[Au_2Cl_4(^iPr_2\text{-bimy})_2(\mu\text{-ditz})](BF_4)_2$ (**13**) in good yields (Scheme 8). They are soluble in CH_2Cl_2 and DMSO but less soluble in $CHCl_3$ and insoluble in nonpolar solvents such as diethyl ether and hexane. In their ESI mass spectra, base peaks were found at *m*/*z* 769 and 526 arising from the cationic and dicationic species $[\mathbf{12} - BF_4]^+$ and $[\mathbf{13} - 2BF_4]^{2+}$, respectively. Their ^1H NMR spectra recorded in CD_2Cl_2 show the isopropyl C−H protons of the $^iPr_2$-bimy ligand as a multiplet at 4.49 (**12**) and 5.38 ppm (**13**), suggesting rotational freedom of the Au−C($^iPr_2$-bimy) bonds despite the coordination of the additional two chlorido coligands. Notably, all $^{13}C_{carbene}$ NMR signals of complexes **12** and **13** found at 153.4−168.6 ppm show significant upfield shifts ($\Delta\delta_C$ = 20.7−32.1 ppm) in comparison to those in their respective Au(I) precursor complexes **3** and **7**.

The formation of complexes **12** and **13** was unambiguously confirmed by X-ray diffraction studies of single crystals obtained by slow evaporation of concentrated solutions of **12** and **13** in CH_2Cl_2/hexane. The molecular structures are

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depicted in Figure 6. In complex **12**, the Au(III) center adopts a square-planar coordination geometry with the two different

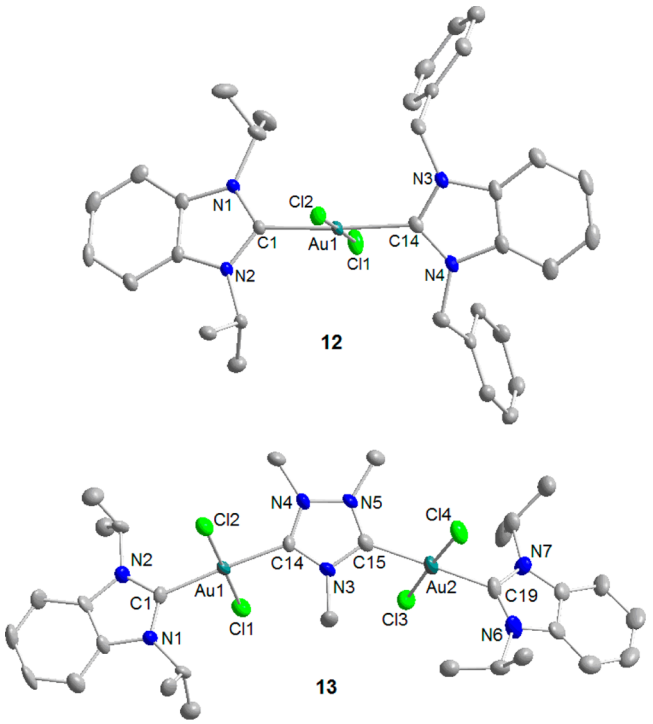


Figure 6. Molecular structures of **12** and **13** showing 50% probability ellipsoids. Hydrogen atoms and counteranions are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. Complex **12**: Au1−C1 = 2.042(3), Au1−C14 = 2.046(3), Au1−Cl1 = 2.2745(8), Au1−Cl2 = 2.2790(8); C1−Au1−C14 = 175.78(12), C1−Au1−Cl1 = 87.17(9), C14−Au1−Cl1 = 90.41(9), C1−Au1−Cl2 = 92.36(9), C14−Au1−Cl2, = 90.11(9), Cl1−Au1−Cl2 = 178.97(3). Complex **13**: Au1−C1 = 2.031(8), Au1−C14 = 2.056(7), Au1−Cl2 = 2.277(2), Au1−Cl1 = 2.280(2), Au2−C19 = 2.030(9), Au2−C15 = 2.061(8), Au2−Cl4 = 2.281(2), Au2−Cl3 = 2.283(2); C1−Au1−C14 = 177.2(3), C1−Au1−Cl2 = 89.9(2), C14−Au1−Cl2 = 91.2(2), C1−Au1−Cl1 = 89.5(2), C14−Au1−Cl1 = 89.4(2), Cl2−Au1−Cl1 = 177.62(8), C19−Au2−C15 = 175.8(3), C19−Au2−Cl4 = 89.7(3), C15−Au2−Cl4 = 94.1(2), C19−Au2−Cl3 = 87.6(2), C15−Au2−Cl3 = 88.6(2), Cl4−Au2−Cl3 = 177.27(8).

benzimidazolin-2-ylidene ligands and two chlorido ligands in a *trans* arrangement. The C1−Au−C14 and Cl1−Au−Cl2 bonds are almost linear with angles of 175.78(12) and 178.97(3)°, respectively. The Au−$C_{carbene}$ bond lengths of 2.042(3) and 2.046(3) Å are in good agreement with those found in other chlorido Au^{III}−NHC complexes.[18]

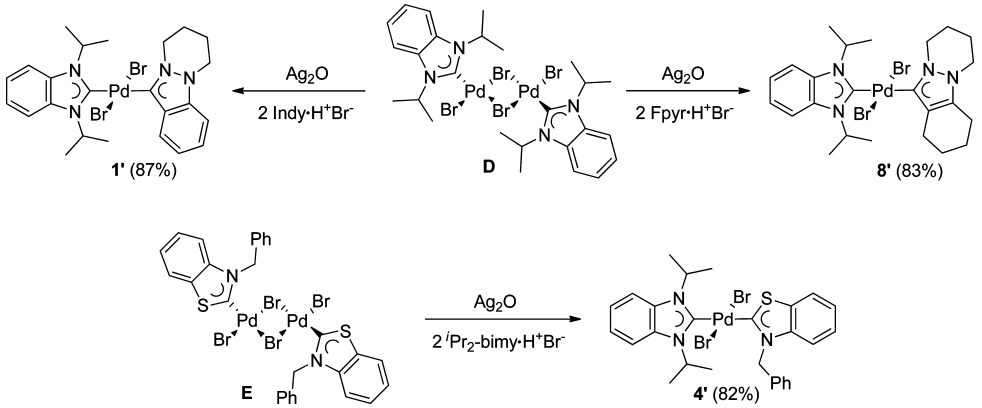
Notably, and unlike the case for their Au(I) precursors **3** and **7**, Au(III) complexes **12** and **13** are much more stable, and no ligand redistributions in CH_2Cl_2 solutions were observed even on standing for a couple of days. The increased Lewis acidity of Au(III) versus Au(I) would probably lead to stronger Au^{III}−NHC bonds, stabilizing the Au(III) hetero-NHC complexes and thus hampering the ligand redistribution process.

Palladium Hetero-NHC Complexes. Previously, we evaluated the donating abilities of various types of NHCs by comparing the $^{13}C_{carbene}$(^{i}Pr$_2$-bimy) chemical shifts in hetero-bis-NHC complexes of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)].[7,13a] With the aim of a more detailed comparison with all analogous Au(I) hetero-NHC complexes described above, the three new Pd(II) hetero-bis-NHC complexes *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(FPyr)] (**1′**), *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Bn-btzy)] (**4′**), and *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Indy)] (**8′**) were synthesized, following a straightforward Ag−carbene transfer protocol (Scheme 9).[7] Complexes **1′** and **8′** could be afforded by a one-pot bridge-cleavage reaction involving the dimeric complex [PdBr$_2$(^{i}Pr$_2$-bimy)]$_2$ (**D**), Ag_2O, and the corresponding azolium salts. However, in the case of the 3-benzylbenzothiazolin-2-ylidene complex *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Bn-btzy)] (**4′**), this transmetalation approach was unsuccessful and instead led to ring opening of the benzothiazolium salt. Thus, the "inverse" bridge-cleavage reaction of the previously reported dimeric complex [PdBr$_2$(Bn-btzy)]$_2$ (**E**)[19] using the benzimidazolium salt ^{i}Pr$_2$-bimy·H$^+$Br$^-$ was attempted, which gave the desired complex **4′** in a good yield.

Complexes **1′**, **4′**, and **8′** were isolated in good yields as yellow solids, which are soluble in most organic solvents with the exception of nonpolar solvents such as diethyl ether and hexane. In all three cases, their formation was supported by ESI mass spectra, where a base peak corresponding to the [M − Br]$^+$ fragment was observed. In contrast to the aforementioned Au(I) analogues **1**, **4**, and **8**, the ^{1}H NMR spectra of **1′**, **4′**, and **8′** all display two multiplets due to the two inequivalent ^{i}Pr$_2$-bimy isopropyl C−H protons, suggesting a hindered rotation of Pd−$C_{carbene}$ bonds.

In their ^{13}C NMR spectra, two carbene signals are observed, as expected. The ^{i}Pr$_2$-bimy carbenoid ^{13}C signals are found at 181.4 (**1′**), 176.4 (**4′**), and 184.0 ppm (**8′**), respectively. In comparison to the donor strengths of other carbene ligands

Scheme 9. Synthesis of Pd(II) Hetero-Bis-NHC Complexes 1′, 4′, and 8′



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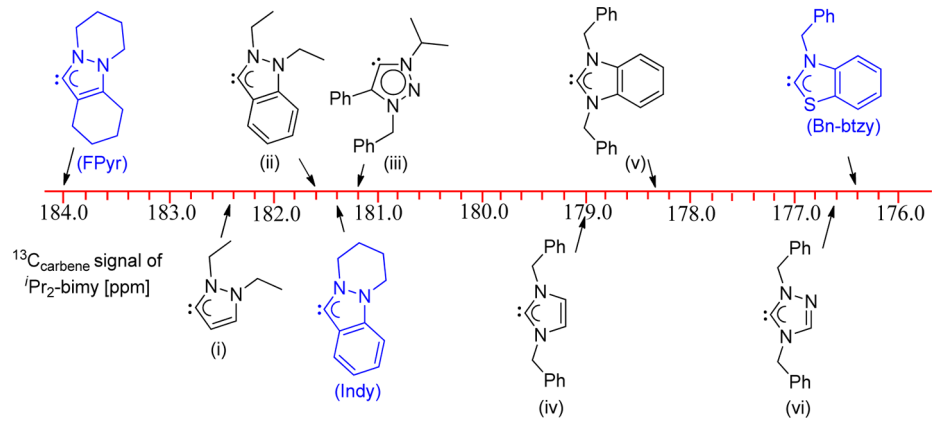
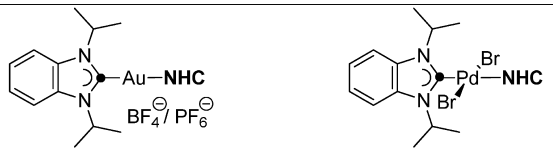


Figure 7. Donor abilities of NHCs on the ^{13}C NMR scale.

Table 4. Selected NMR Data of Au(I) Hetero-NHC Complexes 1−8 and Pd(II) Analogues 1′−8′



Entry	Comp.	$^{13}C_{carbene}$ (Au)[a] [ppm]	Comp.	$^{13}C_{carbene}$ (Pd)[a] [ppm]	NHC
1	**8**[b]	192.5	**8'**	184.0	FPyr
2	**1**	190.8	**1'**	181.4	Indy
3	**3**	187.6	**3'**[b]	178.3	Bn_2-bimy
4	**5**	186.7	**5'/6'**[b]	177.5	IPr
5	**6**	186.7			
6	**2**	186.6	**2'**[b]	176.6	Bn_2-tazy
7	**4**	186.2	**4'**	176.4	Bn-btzy
8	**7**	185.6	**7'**[b]	175.2	ditz

[a]Measured in $CDCl_3$ and internally referenced to the solvent residual signal at 77.7 ppm relative to TMS. [b]Values are from a previous study.[6c,7a,13a]

previously determined on the Pd(II) ^{13}C NMR spectroscopic scale[7] (Figure 7), pyrazole-derived FPyr in **1′** and indazole-derived Indy in **8′** prove to be stronger donors than the classical NHC ligands **iv** and **v** (Figure 7). The donor ability of the alicyclic FPyr ligand is even stronger than that of 1,2-diethylpyrazolin-3-ylidene (**i**), which could be rationalized by the greater +I effect of two alicyclic moieties in FPyr versus only two ethyl substituents in **i** (Figure 7). In addition, the donating ability of the alicyclic indazolin-3-ylidene (Indy) falls in the range between those of its diethyl analogue **ii** and 1,2,3-triazolin-5-ylidene **iii** (Figure 7). Finally, the benzothiazole-derived ligand Bn-btzy in **4′** turns out to a be relatively weaker donor comparable to the 1,2,4-triazolin-5-ylidene **vi**.

Au(I)/Pd(II) Correlation of $^{13}C_{carbene}(^{i}Pr_2$-bimy) Signals. The $^{i}Pr_2$-bimy carbenoid NMR signals in both [Au($^{i}Pr_2$-bimy)(NHC)]BF_4/PF_6 and *trans*-[$PdBr_2$($^{i}Pr_2$-bimy)(NHC)] hetero-NHC complexes were found to be good indicators of the donor strengths of the *trans*-standing NHC ligands, whereby stronger donating ligands would lead to a greater downfield shift. A direct comparison between the $^{i}Pr_2$-bimy carbenoid signals in Au(I) complexes **1**−**8** and their Pd(II) analogues **1′**−**8′** is summarized in Table 4. Notably, the $^{13}C_{carbene}$ signals of $^{i}Pr_2$-bimy in the Au(I) systems are generally more downfield ($\Delta\delta_C \approx 10$ ppm) in comparison to those in their corresponding Pd(II) analogues (Table 4), which again reflects a more Lewis acidic metal center in the latter. In addition, the $^{13}C_{carbene}$ ($^{i}Pr_2$-bimy) values in Au(I) complexes fall in a narrower region in comparison to those in Pd(II) analogues, which may suggest a reduced resolution of the Au(I) system with respect to a donor strength evaluation of *trans*-standing NHC ligands.

Donating capacities of NHC ligands are also known to be evaluated by Tolman's electronic parameter (TEP), and the correlation of TEP values between different metal systems (Ni(0), Ir(I), Rh(I)) has been established.[20] To examine how our $^{13}C_{carbene}(^{i}Pr_2$-bimy) based electronic parameter correlates between Pd(II) and Au(I) systems described in this work, the data sets in Table 4 were subjected to linear regression, and the resulting graphical presentation is shown in Figure 8. Notably, the regression coefficient $R^2 = 0.98$ was obtained, which clearly indicates a very good linear correlation between the $^{13}C_{carbene}(^{i}Pr_2$-bimy) values of these two metal systems. This further supports that $^{i}Pr_2$-bimy carbenoid signals in [Au($^{i}Pr_2$-bimy)(NHC)]BF_4/PF_6 and *trans*-[$PdBr_2$($^{i}Pr_2$-bimy)(NHC)] could both reliably be employed as an electronic parameter for NHC ligands. Interconversion between the Au(I) and Pd(II) systems can be easily achieved by applying eq 1, where [Pd] and [Au] are the $^{13}C_{carbene}(^{i}Pr_2$-bimy) chemical shift values in ppm.

$$[Pd] = 1.19[Au] - 45.0 \quad (1)$$

The introduction of Au(I) as an alternative metal center increases the versatility of future complex probe syntheses, which broadens the scope of our ^{13}C NMR based electronic

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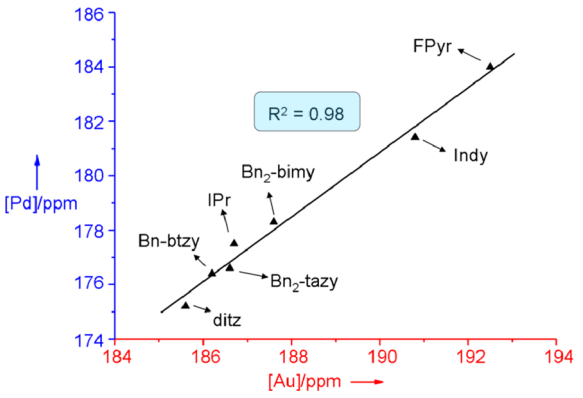

Figure 8. Correlation of the $^{13}C_{carbene}$($^{i}Pr_2$-bimy) NMR values of [Au($^{i}Pr_2$-bimy)(NHC)]BF_4/PF_6 and *trans*-[$PdBr_2$($^{i}Pr_2$-bimy)(NHC)] complexes.

parameter. Finally, it should be noted that the solubility of Au(I) hetero-NHC complexes in $CDCl_3$ is significantly better than that of their Pd(II) congeners. This advantage will allow a much faster detection of the $^{i}Pr_2$-bimy ^{13}C NMR signals, which can generally be accomplished in less than 100 scans.

CONCLUSION

We have reported the synthesis of the Au(I) acetato benzimidazolin-2-ylidene complex [Au(O_2CCH_3)($^{i}Pr_2$-bimy)] (**C**), which represents a new versatile precursor to a wide range of Au(I) hetero-bis-NHC complexes (**2**–**6**) as well as one hetero-tetrakis-NHC complex (**7**). The constant 1,3-diisopropylbenzimidazolin-2-ylidene ligand ($^{i}Pr_2$-bimy) in complexes of the type [Au($^{i}Pr_2$-bimy)(NHC)]BF_4/PF_6 (**1**–**8**) was found to be a useful spectroscopic probe to determine the donating abilities of *trans*-standing NHC ligands. Some of the Au(I) hetero-NHC complexes were found to undergo ligand redistributions, which depend on the donor strength and bulkiness of the incorporated NHC ligands. A very good linear correlation was found between the $^{13}C_{carbene}$($^{i}Pr_2$-bimy) NMR signals of the Au(I) complexes and their respective Pd(II) analogues *trans*-[$PdBr_2$($^{i}Pr_2$-bimy)(NHC)]. This allows the determination of our ^{13}C NMR based electronic parameter for a wider range of NHC ligands. Research in our laboratories is underway to broaden the scope of this new electronic parameter as well as to study its limitations.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all manipulations were carried out without taking precautions to exclude air and moisture. All chemicals and solvents were used as received without further purification if not mentioned otherwise. Complexes **A**,[8] **B**,[9] **D**,[14a] and **8**[6c] and the salt **g**[13a] were synthesized as previously reported. Complex **E** was synthesized via a modified procedure.[19] ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker ACF 300 and Bruker AMX 500 spectrometers, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to [$Si(CH_3)_4$] (^{1}H, ^{13}C) or externally to CF_3CO_2H (^{19}F). ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were done on an Elementar Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore.

General Procedure for Synthesis of Mono-NHC·H$^+$X$^-$ (X = BF_4, PF_6). All carbene precursor salts (**a**–**f**) were obtained by anion exchange of the corresponding NHC·H$^+$Br$^-$/Cl$^-$ with excess $NaBF_4$ in CH_3CN or KPF_6 in H_2O. NHC·H$^+$Br$^-$/Cl$^-$ were synthesized according to reported methods.[7a,14]

[Au($^{i}Pr_2$-bimy)(Indy)]BF_4 (1). K_2CO_3 (29 mg, 0.2 mmol) was added to a solution of the chlorido complex **A** (42 mg, 0.1 mmol) and 1,3-diisopropylbenzimidazolium tetrafluoroborate (**a**; 30 mg, 0.1 mmol) in acetone (30 mL). The reaction mixture was stirred for 24 h at ambient temperature, and the solvent of the reaction mixture was then removed under vacuum. The residue was suspended in CH_2Cl_2 (15 mL) and subsequently filtered over Celite. The solvent of the filtrate was then removed under vacuum. The residue was washed with ethyl acetate (3 × 10 mL) and dried under vacuum, affording the product as an off-white powder (52 mg, 0.08 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, 1 H, Ar-H), 7.70 (dd, 2 H, Ar-H), 7.68 (d, 1 H, Ar-H), 7.57 (d, 1 H, Ar-H), 7.43 (dd, 2 H, Ar-H), 7.36 (t, 1 H, Ar-H), 5.42 (m, 2 H, $CH(CH_3)_2$, ^{3}J(H,H) = 6.90 Hz), 4.85 (br t, 2 H, NCH_2), 4.37 (br t, 2 H, NCH_2), 2.37 (br m, 4 H, CH_2), 1.87 (d, 12 H, $CH(CH_3)_2$, ^{3}J(H,H) = 6.90 Hz). $^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): δ 190.8 (s, NCN), 182.4 (s, NCC), 141.7, 133.3, 132.9, 131.1, 127.3, 125.1, 124.1, 113.6, 110.6 (s, Ar-C), 54.3 (s, $CH(CH_3)_2$), 54.0, 48.0 (s, NCH_2), 23.3 (s, $CH(CH_3)_2$), 22.4, 21.3 (s, NCH_2). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ −77.88 (s, $^{10}BF_4$), −77.94 (s, $^{11}BF_4$). MS (ESI): *m*/*z* 571 [M − BF_4]$^+$. Anal. Calcd for $C_{24}H_{30}N_4AuBF_4$: C, 43.79; H, 4.59; N, 8.51. Found: C, 43.88; H, 4.42; N, 8.47%.

[Au(O_2CCH_3)($^{i}Pr_2$-bimy)] (C). CH_2Cl_2 (10 mL) was added to a mixture of complex **B** (43.5 mg, 0.1 mmol) and silver acetate (20 mg, 0.12 mmol). The reaction mixture was stirred for 1 h while it was shielded from light and subsequently filtered through Celite. Removal of the solvent from the filtrate under vacuum yielded the product as a white powder (34.3 mg, 0.075 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64–7.61 (m, 2 H, Ar-H), 7.36–7.33 (m, 2 H, Ar-H), 5.45 (m, 2 H, $CH(CH_3)_2$, ^{3}J(H,H) = 6.9 Hz), 2.09 (s, CH_3COO), 1.75 (d, 12 H, $CH(CH_3)_2$, ^{3}J(H,H) = 6.9 Hz). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 178.0 (s, CH_3COO), 170.2 (s, NCN), 133.1, 125.5, 124.4, 113.5 (s, Ar-C), 54.8 (s, $CH(CH_3)_2$), 24.3 (s, CH_3COO), 22.3 (s, $CH(CH_3)_2$). MS (ESI): *m*/*z* 601 [M − CH_3COO + L]$^+$. Anal. Calcd for $C_{15}H_{21}AuN_2O_2$: C, 39.31; H, 4.62; N, 6.11. Found: C, 39.14; H, 4.35; N, 6.06.

General Procedure for [Au($^{i}Pr_2$-bimy)(NHC)]X (X = BF_4/PF_6, 2–7). Complex **C** (46 mg, 0.1 mmol) and the chosen azolium salt NHC·H$^+$X$^-$ (**b**–**f**; 0.1 mmol) were mixed in the chosen solvent (10 mL), and the reaction mixture was stirred at the temperature and time indicated in Table 2. The reaction mixture was filtered via Celite, and the filtrate was concentrated under vacuum. Hexane was added, and the resulting white precipitate was collected and dried under vacuum, affording the product as a white solid.

[Au($^{i}Pr_2$-bimy)(Bn_2-tazy)]BF_4 (2). The general procedure afforded **2** as a white solid (59 mg, 0.08 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1 H, NC*H*N), 7.69–7.65 (m, 2 H, Ar-H), 7.43–7.40 (m, 2 H, Ar-H), 7.33 (br, m, 10 H, Ar-H), 5.57 (s, 4 H, CH_2Ph), 5.08 (m, 2 H, $CH(CH_3)_2$, ^{3}J(H,H) = 6.9 Hz), 1.65 (d, 12 H, $CH(CH_3)_2$, ^{3}J(H,H) = 6.9 Hz). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 186.6 (s, NCN-$^{i}Pr_2$-bimy), 186.6 (s, NCN-Bn_2-bimy), 145.0, 135.7, 135.5, 133.1, 129.75, 129.66, 129.3, 128.4, 128.2, 125.3, 113.9 (s, Ar-C), 57.7 (s, CH_2Ph), 53.0 (s, $CH(CH_3)_2$), 22.9 (s, $CH(CH_3)_2$). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −76.33 (s, $^{10}BF_4$), −76.39 (s, $^{11}BF_4$). MS (ESI): *m*/*z* 648 [M − BF_4]$^+$. Anal. Calcd for $C_{29}H_{33}AuBF_4N_5$: C, 47.36; H, 4.52; N, 9.52. Found: C, 47.44; H, 4.74; N, 9.20.

[Au($^{i}Pr_2$-bimy)(Bn_2-bimy)]BF_4 (3). The general procedure afforded **3** as a white solid (64 mg, 0.082 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66–7.63 (m, 2 H, Ar-H), 7.55–7.52 (m, 2 H, Ar-H), 7.41–7.31 (m, 14 H, Ar-H), 5.89 (s, 4 H, CH_2Ph), 5.14 (m, 2 H, ^{3}J(H,H) = 6.9 Hz, $CH(CH_3)_2$), 1.64 (d, 12 H, ^{3}J(H,H) = 6.9 Hz, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$): δ 191.5 (s, NCN-Bn_2-bimy), 187.6 (s, NCN-$^{i}Pr_2$-bimy), 135.8, 134.2, 133.0, 129.7, 129.0, 127.2, 126.0, 125.2, 113.7, 112.9 (s, Ar-C), 54.4, 52.6 (s, CH_2Ph and $CH(CH_3)_2$), 22.9 (s, $CH(CH_3)_2$). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −76.87 (s, $^{10}BF_4$), −76.92 (s, $^{11}BF_4$). MS (ESI): *m*/*z* 697 [M − BF_4]$^+$. Anal. Calcd for $C_{34}H_{36}AuBF_4N_4$: C, 52.06; H, 4.63; N, 7.14. Found: C, 52.31; H, 4.42; N, 7.03.

[Au(Bn-btay)($^{i}Pr_2$-bimy)]PF_6 (4). The general procedure afforded **4** as a white solid (58 mg, 0.076 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69–7.30 (m, 13 H, Ar-H), 6.21 (s, 2 H, CH_2Ph), 5.25 (s,

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2 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 1.74 (d, 12 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 214.8 (s, NCS), 186.2 (s, NCN), 143.7, 134.5, 133.2, 131.3, 130.4, 129.9, 129.4, 127.7, 127.1, 125.3, 123.7, 116.9, 113.9, 113.8 (s, Ar-C), 59.4 (s, CH_2Ph), 54.7 (s, $CH(CH_3)_2$), 23.0 (s, $CH(CH_3)_2$). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −75.92 (s, $^{10}BF_4$), −75.97 (s, $^{11}BF_4$). MS (ESI): *m/z* 624 $[M - PF_6]^+$. Anal. Calcd for $C_{27}H_{29}AuBF_4N_3S$: C, 45.59; H, 4.11; N, 5.91. Found: C, 45.61; H, 4.31; N, 6.04.

*[Au(IPr)(^{i}Pr$_2$-bimy)]BF$_4$ (**5**).* The general procedure afforded the product as a white solid (77 mg, 0.088 mmol, 88%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.64−7.27 (m, 12 H, Ar-H), 4.36 (m, 2 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 2.56 (m, 4 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 1.27−1.24 (d, 36 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 187.3 (s, NCN−IPr), 186.7 (s, NCN-^{i}Pr$_2$-bimy), 146.6, 134.5, 133.0, 131.6, 125.4, 125.2, 125.0, 113.5 (s, Ar-C), 53.9 (s, $CH(CH_3)_2$-^{i}Pr$_2$-bimy), 29.5 (s, $CH(CH_3)_2$-IPr), 25.2, 24.8, 22.6 (s, $CH(CH_3)_2$). ^{19}F NMR (282.37 Hz, $CDCl_3$): δ −77.90 (s, $^{10}BF_4$), −77.94 (s, $^{11}BF_4$). MS (ESI): *m/z* 788 $[M - BF_4]^+$. Anal. Calcd for $C_{40}H_{54}AuBF_4N_4$: C, 54.93; H, 6.22; N, 6.41. Found: C, 54.90; H, 6.13; N, 6.25.

*[Au(IPr)(^{i}Pr$_2$-bimy)]PF$_6$ (**6**).* The general procedure afforded the product as a white solid (80 mg, 0.086 mmol, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.64−7.27 (m, 12 H, Ar-H), 4.36 (m, 2 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 2.57 (m, 4 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 1.27 (d, 24 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 1.26 (d, 12 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 187.3 (s, NCN−IPr), 186.7(s, NCN-^{i}Pr$_2$-bimy), 146.5, 134.5, 133.0, 131.6, 125.3, 125.1, 125.0, 113.5 (s, Ar-C), 53.9 (s, $CH(CH_3)_2$-^{i}Pr$_2$-bimy), 29.4 (s, $CH(CH_3)_2$-IPr), 25.1, 24.8, 22.6 (s, $CH(CH_3)_2$). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ −143.7 (sept, ^2J(P,F) = 712.4 Hz). ^{19}F NMR (282.37 Hz, $CDCl_3$): δ 2.395 (d, ^2J(P,F) = 712.4 Hz). MS (ESI): *m/z* 788 $[M - PF_6]^+$. Anal. Calcd for $C_{40}H_{54}AuF_6N_4P$: C, 51.50; H, 5.83; N, 6.01. Found: C, 51.74; H, 5.57; N, 5.55.

*[Au(^{i}Pr$_2$-bimy)]$_2$(μ-ditz)(BF$_4$)$_2$ (**7**).* The general procedure followed by flash column chromatography (ethyl acetate) afforded **7** as a white solid (52 mg, 0.048 mmol, 48%). Complex **7** could be alternatively synthesized via Ag−carbene transfer method in a yield of 56%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.68−7.66 (m, 4 H, Ar-H), 7.39−7.37 (m, 4 H, Ar-H), 5.31 (m, 4 H, $CH(CH_3)_2$, ^3J(H,H) = 7.0 Hz), 4.31 (s, 6 H, NCH_3), 4.13 (s, 3 H, NCH_3), 1.75 (d, 24 H, ^3J(H,H) = 7.0 Hz). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 189.4 (s, NCHN, ditz), 185.6 (s, NCHN, ^{i}Pr$_2$-bimy), 133.0, 125.1, 113.7 (s, Ar-C), 54.5 (s, $CH(CH_3)_2$), 40.5 (s, NCH_3), 38.6 (s, NCH_3), 22.9 (s, $CH(CH_3)_2$). ^{19}F NMR (282.37 Hz, $CDCl_3$): δ −77.30 (s, $^{10}BF_4$), −77.35 (s, $^{11}BF_4$). MS (ESI): *m/z* 455 $[M - 2BF_4]^{2+}$, 996 $[M - BF_4]^+$. Elemental analyses were not available due to fast decomposition.

[AuCl$_2$(Bn$_2$-bimy)(^{i}Pr$_2$-bimy)]BF$_4$ (12). Complex **3** (78 mg, 0.1 mmol) and $PhICl_2$ (30 mg, 0.11 mmol) were mixed, and CH_2Cl_2 (10 mL) was added. The reaction mixture was stirred at ambient temperature overnight while it was shielded from light. All volatiles were removed under vacuum, and the residue was washed with diethyl ether (3 × 5 mL), yielding an off-white solid (75 mg, 0.87 mmol, 87%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.72−7.71 (m, 4 H, Ar-H), 7.61−7.60 (m, 2 H, Ar-H), 7.48−7.46 (m, 8 H, Ar-H), 7.32−7.29 (m, 4 H, Ar-H), 6.03 (s, 4 H, CH_2Ph), 4.49 (m, 2 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz), 1.53 (d, 12 H, $CH(CH_3)_2$, ^3J(H,H) = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 165.3 (s, NCN, Bn$_2$-bimy), 158.7 (s, NCN, ^{i}Pr$_2$-bimy), 134.5, 134.0, 133.0, 129.8, 129.3, 127.0, 126.7, 125.6 (s, Ar-C), 55.4 (s, CH_2Ph), 51.3 (s, $CH(CH_3)_2$), 21.1 (s, $CH(CH_3)_2$). ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ −77.52 (s, $^{10}BF_4$), −77.57 (s, $^{11}BF_4$). MS (ESI): *m/z* 769 $[M - BF_4]^+$. Anal. Calcd for $C_{34}H_{36}AuBF_4N_4$: C, 47.74; H, 4.24; N, 6.55. Found: C, 47.66; H, 4.19; N, 6.68.

[AuCl$_2$(^{i}Pr$_2$-bimy)]$_2$(μ-ditz)(BF$_4$)$_2$ (13). This complex was synthesized in analogy to the procedure for complex **12**, with the exception of decreasing the reaction temperature to 0 °C. Fractional crystallization afforded **13** as an off-white solid in a yield of 81%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.86−7.85 (Ar-H, m, 4H), 7.54−7.52 (Ar-H, m, 4 H), 5.38 ($CH(CH_3)_2$, m, 4 H, ^3J(H,H) = 6.5 Hz), 4.60 (s, 6 H, NCH_3), 4.59 (s, 3 H, NCH_3), 1.87 ($CH(CH_3)_2$, d, 12 H, ^3J(H,H) = 6.5 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 168.6 (s, NCHN, ditz), 153.4 (s, NCHN, ^{i}Pr$_2$-bimy), 133.4, 125.8, 114.9 (s, Ar-C), 56.4 (s, $CH(CH_3)_2$), 41.6 (s, NCH_3), 39.8 (s, NCH_3), 21.3 (s, $CH(CH_3)_2$). ^{19}F NMR (300 MHz, CD_2Cl_2): δ −76.75 (s, $^{10}BF_4$), −76.80 (s, $^{11}BF_4$). MS (ESI): *m/z* 1138 $[M - BF_4]^+$, 526 $[M - 2BF_4]^{2+}$. Anal. Calcd for $C_{31}H_{45}Au_2B_2Cl_4F_8N_7$: C, 30.39; H, 3.70; N, 8.00. Found: C, 30.18; H, 3.87; N, 7.82.

[PdBr$_2$(Indy)(^{i}Pr$_2$-bimy)] (1′). Dimeric complex **D** (105 mg, 0.11 mmol) and Indy·H$^+$Br$^-$ (57 mg, 0.23 mmol) were suspended in CH_2Cl_2 (25 mL). Ag_2O (36 mg, 0.16 mmol) was added to the mixture, and the resulting suspension was stirred for 12 h while it was shielded from light. The reaction mixture was then filtered over Celite, and the solvent of the filtrate was removed under vacuum, yielding the crude product. The crude product was redissolved in a minimal volume of $CHCl_3$, and the solution was filtered over Celite. A large excess of diethyl ether was added to the filtrate to precipitate the product. The precipitate was collected and dried under vacuum, yielding the product as a pale orange powder (125 mg, 0.20 mmol, 87%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, 1 H, Ar-H), 7.54−7.64 (m, 3 H, Ar-H), 7.36 (t, 1 H, Ar-H), 7.27 (d, 1 H, Ar-H), 7.23 (dd, 2 H, Ar-H), 6.47 (br m, 1 H, NC*H*), 6.23 (br m, 1 H, NC*H*), 5.08 (br t, 2 H, NCH_2), 4.01 (br t, 2 H, NCH_2), 2.25 (br m, 4 H, CH_2), 1.93 (br d, 6 H, CH_3), 1.87 (br d, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 181.4 (s, $C_{carbene}$ (^{i}Pr$_2$-bimy)), 179.6 (s, $C_{carbene}$ (Indy)), 142.9, 134.5, 134.3, 131.9, 131.6, 130.5, 123.3, 122.5, 113.2, 109.6 (s, Ar-C), 54.3 (s, NCH), 53.1, 48.4 (s, NCH_2), 23.3, 22.1 (s, CH_2), 21.9 (s, CH_3). MS (ESI): *m/z* 561 $[M - Br]^+$. Anal. Calcd for $C_{24}H_{30}N_4PdBr_2$: C, 44.99; H, 4.72; N, 8.74. Found: C, 45.00; H, 4.93; N, 8.57.

[PdBr$_2$(Bn-btay)(^{i}Pr$_2$-bimy)] (4′). The precursor salt ^{i}Pr$_2$-bimy·H$^+$Br$^-$ (16 mg, 0.06 mmol) and Ag_2O (7 mg, 0.03 mmol) were suspended in CH_2Cl_2 (5 mL) and stirred for 3 h. The resulting mixture was filtered into a CH_2Cl_2 solution of dimeric complex **E** (28 mg, 0.03 mmol) and stirred for 1 h. The suspension was filtered over Celite, and the solvent of the filtrate was removed under vacuum. The product was obtained as a yellow solid after recrystallization from CH_2Cl_2/toluene (32 mg, 0.05 mmol, 82%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.85−7.83 (m, 1 H, Ar-H), 7.65−7.59 (m, 5 H, Ar-H), 7.43−7.34 (m, 5 H, Ar-H), 7.21−7.18 (m, 2 H, Ar-H), 6.54 (s, 2 H, NCH_2), 6.05 (m, 2 H, $CH(CH_3)_2$, ^3J(H, H) = 7.1 Hz), 1.71 (d, 12 H, $CH(CH_3)_2$, ^3J(H, H) = 7.1 Hz). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ 217.7 (s, NCS), 176.4 (s, NCN-^{i}Pr$_2$-bimy), 144.3, 137.2, 135.0, 134.3, 129.7, 128.9, 128.1, 127.3, 125.6, 122.8, 122.7, 115.3, 113.3 (s, Ar-C), 59.1 (s, NCH), 54.6 (s, NCH_2), 21.6 (s, CH_3). MS (ESI): *m/z* 614 $[M - Br]^+$. Anal. Calcd for $C_{27}H_{29}Br_2N_3PdS$: C, 46.74; H, 4.21; N, 6.06. Found: C, 46.39; H, 4.55; N, 5.66.

[PdBr$_2$(FPyr)(^{i}Pr$_2$-bimy)] (8′). Dimeric complex **D** (99 mg, 0.11 mmol) and FPyr·H$^+$Br$^-$ (54 mg, 0.21 mmol) were suspended in CH_2Cl_2 (20 mL). Ag_2O (29 mg, 0.13 mmol) was added to the mixture, and the resulting suspension was stirred for 12 h while it was shielded from light. The reaction mixture was then filtered over Celite, and the solvent of the filtrate was removed under vacuum, yielding the crude product. Recrystallization of the crude product from a solution in CH_2Cl_2 layered with toluene produced a yellow crystalline product (113 mg, 0.18 mmol, 83%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, 2 H, Ar-H), 7.16 (dd, 2 H, Ar-H), 6.31 (m, 1 H, NC*H*, ^3J(H,H) = 6.95 Hz), 6.13 (m, 1 H, NC*H*, ^3J(H,H) = 6.95 Hz), 4.75 (t, 2 H, NCH_2, ^3J(H,H) = 5.70 Hz), 3.84 (t, 2 H, NCH_2, ^3J(H,H) = 5.65 Hz), 2.93 (t, 2 H, CH_2, ^3J(H,H) = 5.65 Hz), 2.43 (t, 2 H, CH_2, ^3J(H,H) = 6.30 Hz), 2.14 (m, 2 H, CH_2), 2.08 (m, 2 H, CH_2), 1.84 (d, 6 H, CH_3, ^3J(H,H) = 6.95 Hz), 1.81 (d, 6 H, CH_3, ^3J(H,H) = 6.95 Hz) (signals due to another two CH_2 groups of the FPyr ligand were overlapped with the signals due to the CH_3 groups of the ^{i}Pr$_2$-bimy ligand, in the 1.75−1.85 ppm region). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 184.0 (s, $C_{carbene}$ (^{i}Pr$_2$-bimy)), 171.4 (s, $C_{carbene}$ (FPyr)), 142.5 (s, $NCCH_2$), 134.6 (s, Ar-C), 134.3 (s, Ar-C), 125.2 (s, $NC_{carbene}CCH_2$), 122.3 (s, Ar-C), 113.0 (s, Ar-C), 54.1 (s, NCH), 53.9 (s, NCH), 51.2 (s, NCH_2), 46.0 (s, NCH_2), 23.6, 23.1, 22.8, 22.7, 22.03, 21.99, 21.7, 21.4 (s, CH_2 and CH_3). MS (ESI): *m/z* 565 $[M - Br]^+$. Anal. Calcd for

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$C_{24}H_{34}N_4PdBr_2 \cdot 0.2C_7H_8$: C, 46.00; H, 5.41; N, 8.45. Found: C, 45.77; H, 5.08; N, 8.50.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs.[21] Data were processed and corrected for Lorentz and polarization effects with SAINT[22] and for absorption effects with SADABS.[23] Structural solution and refinement were carried out with the SHELXTL suite of programs.[24] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were placed at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for **C**, **1**, **2**, **6**, **9**, **12**, and **13**·3CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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