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Synthesis, Characterization, and Reactivity of Cationic Gold(I) α-Diimine Complexes

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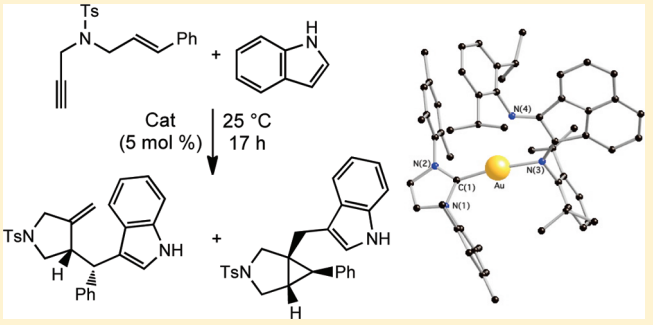
Supporting Information

ABSTRACT: A series of cationic gold(I) α-diimine complexes of the type [(NHC)Au(α-diimine)]X or [(PPh_3)Au(α-diimine)]X, where NHC = IPr, α-diimine = BIAN-dipp, X = PF_6 (**1**); X = BF_4 (**2**); X = SbF_6 (**3**); NHC = I^{t}Bu, α-diimine = BIAN-dipp, X = PF_6 (**4**); X = BF_4 (**5**); NHC = IMes, α-diimine = BIAN-dipp, X = PF_6 (**6**); PPh_3, α-diimine = BIAN-dipp, X = PF_6 (**7**); NHC = IPr, α-diimine = DAB-Mes, X = PF_6 (**8**, **10**) bearing an N-heterocyclic carbene (NHC) or a phosphine ligand, have been synthesized and characterized by NMR spectroscopy and single crystal X-ray diffraction. The stability of the new complexes and their catalytic activity for the intermolecular addition of the indole nucleophilic carbon to 1,6-enyne were also investigated.



INTRODUCTION

Gold(I), having the electronic configuration [Xe]$4f^{14}5d^{10}$ and being in the third transition series of the periodic table, is usually considered as a soft Lewis acid, binding to soft bases in the following preferential order: Si ≈ C ≈ *P* > S > Cl > *N* > O > F.[1] Cationic gold(I) species tend to disproportionate to Au(0) and Au(III) in the absence of proper stabilization by a powerful σ-donor ligand. Usually anionic nitrogen ligands such as amides (including NTf_2^-), bidentate amidinates, guanidinates, β-diketiminates, and pyrazolates are suitable for this purpose.[2] By contrast, the weakness of the dative bond between gold and a neutral nitrogen-donor renders the synthesis of cationic gold(I) complexes with such ligands more challenging. Recently, the use of NHC ligands has allowed the isolation of stable cationic complexes bearing formally neutral nitrogen donors, for example nitrile or pyridine ligands (Scheme 1).[3]

The versatility of α-diimines, such as bis-aryl/alkyl-diazabutadienes (DAB)s and bis-aryl/alkyl-acenaphthenequinonediimines (BIAN)s, which are weak σ-donors, strong π-acceptors,[4] and can be electronically active and behave as noninnocent ligands, has resulted in their use as ligands with metals and metalloids from groups 12−16,[4,5] alkaline earths, lanthanides, and transition metals such as Ti(IV), Mo(VI), Ir(III), Re(I), Ru(II), Ni(II), Pd(II), Pt(II), Cu(I), and Ag(I), including zerovalent metal atoms from groups 8−10.[5] In solution, the free BIANs exhibit a blocked cis-conformation of the α-diimine moiety, and the free DABs are mainly found in trans-conformation to minimize the steric repulsion from the *N*-alkyl/aryl substituents borne by both nitrogen atoms. Independently from their free conformation, both of these α-diimines normally act as bidentate ligands to form complexes with high activity in homogeneous catalysis for reactions such as Suzuki or Negishi coupling, epoxidation of propylene, and polymerization of alkenes.[5] In order to take advantage of their electronic versatility and their steric tunability, we decided to use α-diimines as neutral stabilizing ligands of the Au^+ center. The use of gold(I) salts in homogeneous catalysis has bewilderingly gained attention over the last 10 years and is growing very quickly.[6] The acidic character and low oxophilicity render the gold(I) cation an attractive candidate for the activation of carbon−carbon multiple bonds in functionalized organic molecules, even under air. For instance, it is now a well established catalyst for the hydration or hydroamination of alkynes, the enyne cycloisomerization, the Markovnikov hydroamination or hydroalkoxylation of allenes, the [2 + 2] or [4 + 2] cycloaddition of alkynes with alkenes, and the rearrangement of allylic acetates.[7] Herein, we also investigate a new series of cationic gold(I) complexes containing an α-diimine ligand as catalyst in the cycloisomerization of enynes.

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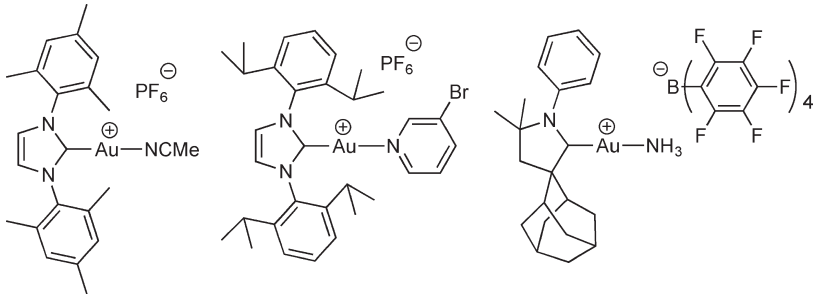
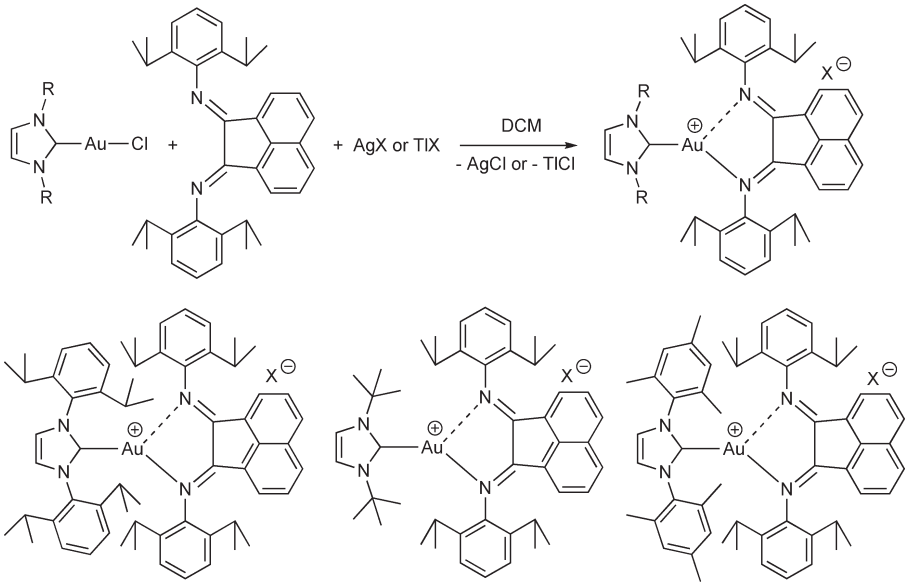
Scheme 1. Structures of Selected Cationic NHC−Au(I) Complexes with Neutral Nitrogen-Donor Ligands



Scheme 2. Synthesis of the Cationic [(NHC)Au(BIAN-dipp)]X Complexes 1−6



X = PF_6
[(IPr)Au(BIAN-dipp)]PF_6 (**1**)
X = BF_4
[(IPr)Au(BIAN-dipp)]BF_4 (**2**)
X = SbF_6
[(IPr)Au(BIAN-dipp)]SbF_6 (**3**)

X = PF_6
[(ItBu)Au(BIAN-dipp)]PF_6 (**4**)
X = BF_4
[(ItBu)Au(BIAN-dipp)]BF_4 (**5**)

X = PF_6
[(IMes)Au(BIAN-dipp)]PF_6 (**6**)

RESULTS AND DISCUSSION

To evaluate the stability of the α-diimine gold(I) complexes, IPr (*N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was initially chosen as a strong σ-donor to stabilize electronically and sterically the gold(I) center and suppress its oxidizing character. BIAN-dipp (bis(2,6-diisopropylphenyl)acenaphthenequinonediimine) was also selected as a sterically hindered diimine with a fixed cis-conformation.[8] Upon addition of $AgPF_6$, a yellow solution of (IPr)AuCl[9] and BIAN-dipp, in deuterated acetonitrile, turned dark red with the concomitant formation of AgCl. The ^{1}H NMR spectrum of the crude reaction mixture evidenced the formation of the new complex [(IPr)Au(BIAN-dipp)]PF_6 (**1**) with shifts for some protons groups. For instance, the ortho- and para-protons of the naphthalene rings of BIAN-dipp substituents, which are very sensitive to the coordination mode adopted by the ligand, were shifted downfield by 0.5 ppm whereas the septet arising from the diisopropyl groups, from both BIAN and IPr substituents, were shifted upfield by 0.15 ppm. Nevertheless, the conversion of **1** was not quantitative, and both residual free BIAN-dipp and most likely the cationic [(IPr)Au(MeCN)]PF_6 could be detected (10% approx) after 24 h while the newly formed complex did not show any sign of decomposition. As the ratio of all added reagents was precisely 1:1:1, it was plausible that a competition between acetonitrile and BIAN-dipp to bind to the gold(I) cation was taking place. An analogous reaction in deuterated THF surprisingly gave similar results. Finally, when the reaction was carried out in $CDCl_3$, a quasi-non-coordinating solvent, quantitative conversion to **1** was observed. After filtration through a plug of silica gel, **1** could be precipitated from pentane as a dark red powder which turned brown after drying. The ^{13}C NMR spectrum of **1** exhibits a signal at 164.8 ppm, typical for a carbene carbon on the cationic gold−nitrogen moiety[3] while the signal from the imine carbons shifts from 161.0 ppm to 165.0 ppm. Full assignment of the ^{13}C NMR spectrum was accomplished by a DEPT 135 experiment. A closer look at the ^{13}C spectrum also revealed a partial activation of $CDCl_3$ likely due to the presence of the silver(I) salt as evidenced

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Scheme 3. BIAN Complexes with Silver(I) and Thallium(I)

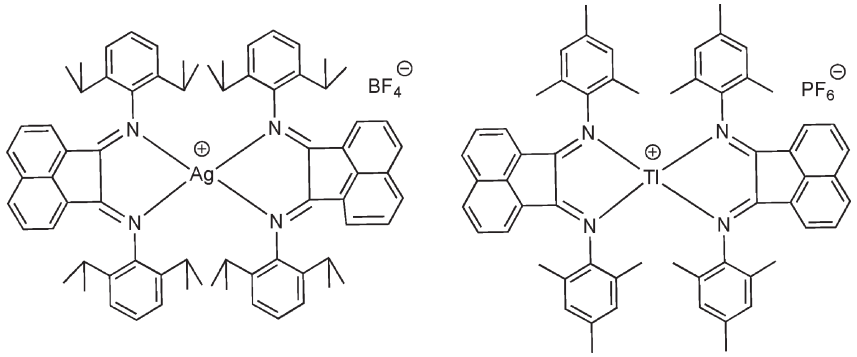

Table 1. ^{13}C and ^{31}P NMR Chemical Shifts of Selected NHC and PPh_3 Gold(I) Complexes

complexes	δ_C (ppm)	reported complexes	δ_C (ppm)	$\Delta\,\delta_C$ (ppm)
[(IPr)Au(BIAN)]PF_6 (**1**)	164.8	(IPr)AuCl[a]	175.1	−10.3 vs (**1**)
[(IPr)Au(BIAN)]BF_4 (**2**)	163.1	(IPr)Au(MeCN)PF_6[a]	166.1	−1.3 vs (**1**)
[(IPr)Au(BIAN)]SbF_6 (**3**)	166.4	(IPr)Au(Py)PF_6[a]	167.1	−2.3 vs (**1**)
[(IPr)Au(DABMes)](PF_6) (**8**)	167.6	(ItBu)AuCl[a]	168.2	−7.9 vs (**4**)
[(ItBu)Au(BIAN)]PF_6 (**4**)	160.3	(ItBu)Au(MeCN)PF_6[a]	159.7	+0.6 vs (**4**)
[(ItBu)Au(BIAN)]BF_4 (**5**)	160.7	(IMes)AuCl[a]	173.4	−9.7 vs (**6**)
[(IMes)Au(BIAN)]PF_6 (**6**)	163.7	(IMes)Au(MeCN)PF_6[a]	165.3	−1.6 vs (**6**)
complex	δ_P (ppm)	reported complexes	δ_P (ppm)	$\Delta\,\delta_P$ (ppm)
[(PPh_3)Au(BIAN)]PF_6 (**7**)	32.3	(PPh_3)AuCl	28.7	+3.6 vs (**7**)
		[(PPh_3)$_2$Au]PF_6	48.1	−15.8 vs (**7**)

[a] From the literature.

by the appearance of two new triplets (1:1:1) at 105.6 and 101.7 ppm, showing a coupling constant ($^1J(^{13}C-D)$ = 33 Hz) equal to that found for $CDCl_3$ at 77.0 ppm. The ^{31}P NMR spectrum of **1** showed the characteristic PF_6^- septet at −141.3 ppm ($^1J(^{31}P-^{19}F)$ = 712 Hz). The silver(I) cation is known to catalyze the hydrolysis of PF_6^- to PO_4^{3-} via a $PO_2F_2^-$ intermediate, and after one day in nondry $CDCl_3$, the ^{31}P NMR spectrum of **1** exhibited the characteristic broad triplet of $PO_2F_2^-$ at −15.5 ppm ($^1J(^{31}P-^{19}F)$ = 972 Hz).[10] To keep the synthesis straightforward under air conditions, $CDCl_3$ was replaced by CD_2Cl_2 and $AgPF_6$ by $TlPF_6$, which allowed the formation of **1** without any side reaction (Scheme 2).

Recently, Avilés et al. reported the coordination of [Ag(MeCN)$_4$]BF_4 with BIAN-dipp to form [(BIAN-dipp)$_2$Ag]BF_4, and Cowley et al. reported the coordination of $TlPF_6$ to BIAN-Mes (bis(2,4,6-trimethylphenyl)acenaphthenequinonediimine) with formation of (BIAN-Mes)$TlPF_6$.[11] Both silver and thallium adducts were fully characterized by NMR spectroscopy and X-ray diffraction (Scheme 3).

In order to gain insight into the species responsible for the halide abstraction from the precursor gold complex, the reactions of BIAN-dipp with $AgPF_6$ or TlCl were investigated by ^1H NMR spectroscopy. Addition of $AgPF_6$ to BIAN-dipp in CD_2Cl_2 led to a color change from yellow to bright orange accounting for a probable coordination of Ag(I), which was confirmed by ^1H NMR spectroscopy. The doublets of the ortho- and para-protons of the acenaphthene skeleton became multiplets and shifted downfield by 0.15 ppm. Interestingly, the dichloromethane seemed to interact with silver(I), and a second (1:1:1) triplet accounting for $CDHCl_2$ was found at 5.29 ppm. Even though attempts were not made to isolate the complex detected by NMR, two plausible species could be assumed to be formed in solution: [(BIAN-dipp)$_2$Ag]PF_6 and/or [(BIAN-dipp)Ag(DCM)$_X$]PF_6. Consequently, the formation of the cationic gold(I) complexes, via dehalogenation, may have occurred through a competition between gold(I) and silver(I) to coordinate the BIAN-dipp. In contrast, the addition of $TlPF_6$ to BIAN-dipp in CD_2Cl_2 did not result in any change of color of the solution, even after an excess (2.2 equiv) of thallium salt was added. In this case, the ^1H NMR spectrum revealed no noticeable shift (0.04 ppm) of the resonances for the ortho- and para-protons of the naphthalene backbone, implying that the thallium(I) center had very limited interactions with the BIAN-dipp ligand prior to halide abstraction. By following the optimized conditions for the synthesis of **1**, the analogues [(IPr)Au(BIAN-dipp)]BF_4 (**2**) and [(IPr)Au(BIAN-dipp)]SbF_6 (**3**) were also prepared starting from (IPr)AuCl, BIAN-dipp, and $AgBF_4$ or $AgSbF_6$. Both complexes exhibited ^1H and ^{13}C NMR spectra which were very similar to those of **1**. In the ^{13}C NMR spectra, the carbene carbons of **2** and **3** were, respectively, observed at 163.1 and 166.4 ppm (Table 1). In order to tune the steric environment around the gold(I) cation, the new complexes [(I^{t}Bu)Au(BIAN-dipp)]PF_6 (**4**), [(I^{t}Bu)Au(BIAN-dipp)]BF_4 (**5**), and [(IMes)Au(BIAN-dipp)]PF_6 (**6**) were synthesized, starting from the known reagents (I^{t}Bu)AuCl[12] (I^{t}Bu = *N*,*N*′-bis(*tert*-butyl)imidazol-2-ylidene) and (IMes)AuCl[9] (IMes = *N*,

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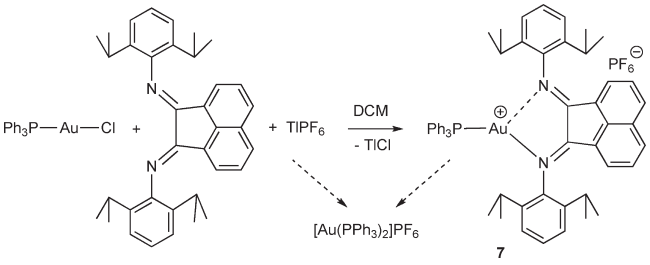
Scheme 4. Synthesis of $[(PPh_3)Au(BIAN\text{-}dipp)]PF_6$ (7)



N′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), using the same reaction conditions as described above for the formation of **1** and **2**. The ^{1}H NMR spectra of the new complexes exhibited the signals for each NHC moiety and the ortho- and para-protons borne by the naphthalene backbone (from BIAN-dipp) were slightly shifted downfield. The ^{13}C NMR spectra exhibited the characteristic signal for a carbene carbon bound to cationic gold(I) with values falling in the range between 160.3 and 163.7 ppm[3] (Table 1). After 24 h in solution, no sign of decomposition was obvious.

The development and isolation of cationic gold(I) complexes stabilized by bulky phosphines has undergone a very fast growth during the last 5 years. Echavarren et al. have developed a series of cationic gold(I) biphenylphosphines which are very active catalysts for the cycloisomerization of enynes.[13] In addition, various elegant cationic π-gold(I) phosphine complexes with alkynes, alkenes, and allenes have been recently isolated and characterized by single crystal X-ray diffraction.[14] In order to extend the use of the BIAN-dipp ligand to another class of cationic gold(I) complexes, a synthesis was carried out using PPh_3, instead of IPr, as stabilizing σ-donor ligand. The reaction of $(PPh_3)AuCl$ with BIAN-dipp in the presence of $TlPF_6$ in CD_2Cl_2 yielded a dark red solution and a white precipitate of TlCl. The ^{1}H NMR spectrum of the crude reaction mixture confirmed the formation of the new complex $[(PPh_3)Au(BIAN\text{-}dipp)]PF_6$ (**7**). The ortho- and para-protons of the naphthalene backbone (from the BIAN) were slightly shifted upfield and appeared as two doublets at 8.18 and 6.78 ppm, respectively. Two other sets of weak signals were also observed: the first, obviously related to BIAN-dipp, comprised three doublets at 7.96, 6.99, 6.69 ppm, and a septet at 2.98 ppm, and the second, related to PPh_3, a multiplet at 7.68 ppm. The ^{31}P NMR spectrum displayed a major peak at 32.3 ppm assignable to the coordinated PPh_3 in **7**, a smaller peak at 48.1 ppm and the signal of PF_6^- at −141.3 ppm (Table 1). After filtration through Celite and precipitation from pentane, complex **7** was obtained as a red powder with a small PPh_3-containing impurity. The supernatant pentane solution was yellow, which suggested the presence of noncoordinated BIAN-dipp. After evaporation of the pentane, the remaining solids were analyzed by NMR spectroscopy. The ^{1}H NMR spectrum showed only the signal for the free BIAN-dipp, and surprisingly the doublet at 6.99 ppm was no longer observed. In addition, the ^{31}P and ^{19}F NMR spectra did not show any signal, which ruled out the possibility of formation of $(BIAN\text{-}dipp)TlPF_6$ or $(BIAN\text{-}dipp)Au(X)PF_6$. Note that working under anhydrous conditions, or changing the stoichiometry of the synthesis, by adding an excess of BIAN-dipp and/or $TlPF_6$ could not prevent the formation of both impurities described above. In order to account for these facts, we prepared $[(PPh_3)_2Au]PF_6$ by reacting 2 equiv of PPh_3 with 1 equiv of $(CH_3)_2SAuCl$ (dimethyl sulfide gold(I) chloride) and 1 equiv of $TlPF_6$.[15] The ^{1}H and ^{31}P NMR spectra of $[(PPh_3)_2Au]PF_6$ gave, respectively, a broad multiplet centered at 7.60 ppm and a peak at 48.0 ppm, matching the signals from the second impurity found during the synthesis of **7**. The formation of $[(PPh_3)_2Au]PF_6$ was also confirmed by ESI-mass spectroscopy with an intense peak found at m/z = 721.156 accounting for $[Au(PPh_3)_2]^+$. This could also explain the release of BIAN-dipp during the reaction. In 2005, Gagosz et al. upon attempting to prepare the cationic complex $[(PPh_3)Au]PF_6$ in DCM observed only a rearrangement to $[(PPh_3)_2Au]PF_6$ and could not isolate the desired complex.[16] After a prolonged time in CD_2Cl_2, **7** also appeared to very slowly rearrange to $[(PPh_3)_2Au]PF_6$. After crystallization from a mixture of octane/DCM, **7** could be recovered pure and cocrystallized with two molecules of DCM (Scheme 4).

Attempts to extend the above method to less bulky DAB-Mes were made. Addition of $TlPF_6$ to a solution of (IPrAu)Cl and DAB-Mes in CD_2Cl_2 resulted in a color change from yellow to bright orange and formation of a white precipitate of TlCl. The ^{1}H NMR spectrum of the crude reaction mixture evidenced the formation of two new complexes, with two sets of signals related to a coordinated DAB-Mes ligand. After precipitation by addition of pentane, a bright orange powder was obtained. The ^{1}H NMR spectrum of the solid displayed only one set of signals, with integration consistent for the new complex $[(IPr)Au(DAB\text{-}Mes)](PF_6)$ (**8**). It was further characterized by ^{13}C, ^{31}P, ^{19}F NMR and by elemental analysis. The ^{13}C NMR spectrum showed a signal at 167.6 ppm characteristic for a carbene bound to an N−Au moiety.[3] The ESI-mass spectroscopy could not provide any signal clearly related to **8**. It is important to note that the formation of the side product was extremely difficult to avoid, even by changing the stoichiometry of DAB-Mes and/or $TlPF_6$.

In order to test the viability of the (BIAN-dipp)AuCl complex in the absence of a strong σ-donor stabilizing ligand, the reaction of BIAN-dipp with $(CH_3)_2SAuCl$ in CD_2Cl_2 was monitored first. After 12 h, the reaction mixture was dark orange and a gold mirror formed. The ^{1}H NMR spectrum of the crude reaction mixture showed mainly some unreacted BIAN-dipp with $(CH_3)_2SAuCl$ and $(CH_3)_2S$. A new set of signals with low intensity (10% vs free BIAN-dipp) was also observed, and it could be assigned to the formation of (BIAN-dipp)AuCl (**9**). However, attempts to crystallize it, by slow diffusion of a layer of octane, led to some yellow and white crystals which were identified as BIAN-dipp (yellow) and $(IPrNH_3)Cl$ (white) by comparison with crystallographic data from the literature (2, 6-diisopropylphenylamonium chloride).[17] As the hydrolysis of diimines is known to be catalyzed by a strong Brønsted or Lewis acid, the generation of $(IPrNH_3)Cl$ with concomitant formation of acenaphthene-1,2-dione may be facilitated by the Lewis acidity of the gold(I) center. When the reaction was carried out under anhydrous conditions, after 12 h the crude solution retained its original yellow color and no trace of gold(0) was observed. The starting materials could be recovered by crystallization. This lack of reactivity under such conditions is intriguing and points to the following: (i) the BIAN-dipp ligand was not able to displace the $(CH_3)_2S$ and had low affinity for gold(I); (ii) the hydrolysis of the BIAN-dipp might have occurred through a displacement of $(CH_3)_2S$ by H_2O followed by coordination and attack of the diimine. In a last attempt to generate (BIAN-dipp)AuCl, the reaction of AuCl and BIAN-dipp in dry CD_2Cl_2 was monitored by NMR spectroscopy. Upon addition of an excess of AuCl, the reaction mixture turned dark red with precipitation of gold(0). The spectrum of the crude reaction mixture revealed a shift of the

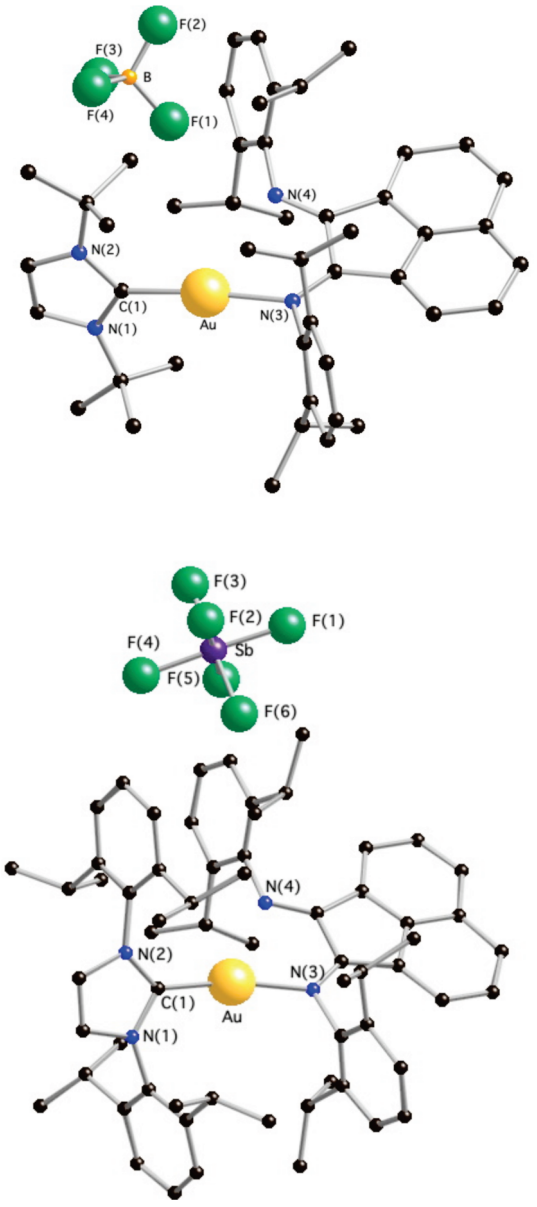


Figure 1. Ball and stick representation of [(IPr)Au(BIAN-dipp)]SbF_6 (**3**) (bottom) and [(I^{t}Bu)Au(BIAN-dipp)]BF_4 (**5**) (top). Hydrogen atoms and DCM molecules have been omitted for clarity.

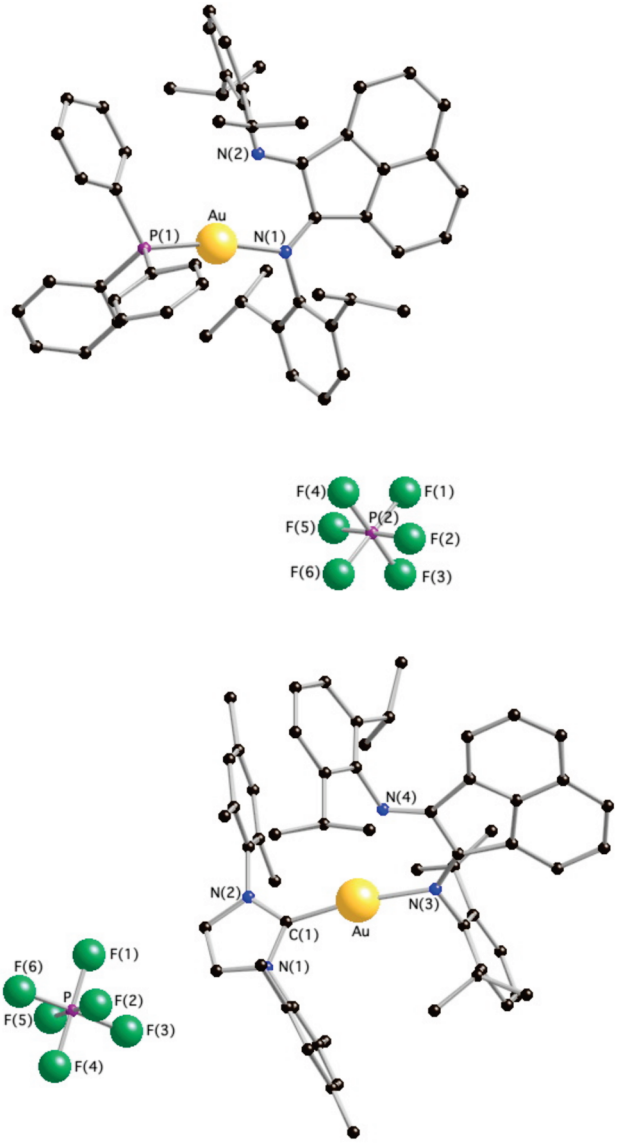


Figure 2. Ball and stick representation of [(IMes)Au(BIAN-dipp)]PF_6 (**6**) (bottom) and [(Ph_3P)Au(BIAN-dipp)]PF_6 (**7**) (top). Hydrogen atoms and DCM molecules have been omitted for clarity.

para-protons of the naphthalene backbone from 7.89 to 8.10 ppm. The other signals were split, and their separate integrations were not consistent with two species in solution. The four protons giving a sextuplet at 2.96 ppm for the free BIAN-dipp gave rise to a well-defined septet at 2.95 ppm, and an undefined sextuplet at 3.11 ppm accounting, respectively, for three and one protons. The eight methyl groups were also split into three doublets, at 1.37, 1.24, and 1.03 ppm accounting for 3, 3 + 6, and 6 + 6 protons. Such splitting for the isopropyl protons might be characteristic of an agostic interaction with the acidic gold(I) center and was not observed for the NHC and PPh_3 complexes described above. Elemental analysis confirmed the existence of (BIAN-dipp)AuCl (**9**) and thus ruled out the formation of (BIAN-dipp)Au_2Cl_2. Under the ESI-mass conditions, **9** was not detected and a major peak at m/z = 1023.610 ((BIAN-$dipp_2Na^+$) − H), a peak at m/z = 1233.62 (BIAN-$dipp_2$AuCl), and a peak at m/z = 1255.547 [((BIAN-$dipp)_2AuClNa^+$) − H] were observed. Unfortunately, we did not succeed to obtain crystals of sufficient quality for a study by X-ray diffraction, and there is a lingering doubt about the possible formation of clusters or [(BIAN-$dipp)_2Au^+$]$AuCl_2^-$ rather than **9**.

To unambiguously characterize the new gold(I) diimine complexes, X-ray quality crystals were grown from a mixture of DCM/octane for **3**, **5**, **6**, **7**, and **8**. Ball-and-stick representations are provided in Figures 1 and 2, and crystallographic data are given in Table 2. The complexes **3**, **5**, **6**, and **7** contain a two-coordinated gold atom, in the expected almost linear coordination environment.

In solution, the coordinated and free imine nitrogen atoms are likely to exchange their role rapidly on the NMR time scale, but in the solid state the gold(I) cation retains its preferred two-coordinate linear geometry. Observed Au−N distances in the range 2.09−2.11 Å are characteristic of a neutral nitrogen donor group bound to gold.[3] Au−N distances between 2.74−3.00 Å are in agreement with

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Table 2. Selected Bond Distances (Å) and N−Au−C Angles (deg) in Gold Complexes

complexes	Au−C(1)	Au−N(3)	Au···N(4)	C(1)−Au−N(3)
[(IPr)Au(BIAN)]SbF_6 (**3**)	1.983(7)	2.091(6)	3.000(7)	167.9(3)
[(ItBu)Au(BIAN)]BF_4 (**5**)	2.014(5)	2.094(4)	2.863(4)	175.59(19)
[(IMes)Au(BIAN)]PF_6 (**6**)	1.980(3)	2.088(2)	2.851(3)	170.37(12)
	Au(1)−C(1)	Au(1)−N(3)		C(1)−Au(1)−N(3)
[((IPr)Au)$_2$(DAB-Mes)]$(PF_6)_2$(**10**)	1.958(10)	2.063(9)	–	177.6(4)
	Au(2)−C(48)	Au(2)−N(4)		C(48)−Au(1)−N(4)
[((IPr)Au)$_2$(DAB-Mes)]$(PF_6)_2$(**10**)	2.007(10)	2.036(9)	–	176.6(4)
	Au−P(1)	Au−N(1)	Au···N(2)	P(1)−Au−N(1)
[(PPh_3)Au(BIAN)]PF_6 (**7**)	2.2371(15)	2.110(4)	2.742(2)	169.74(13)

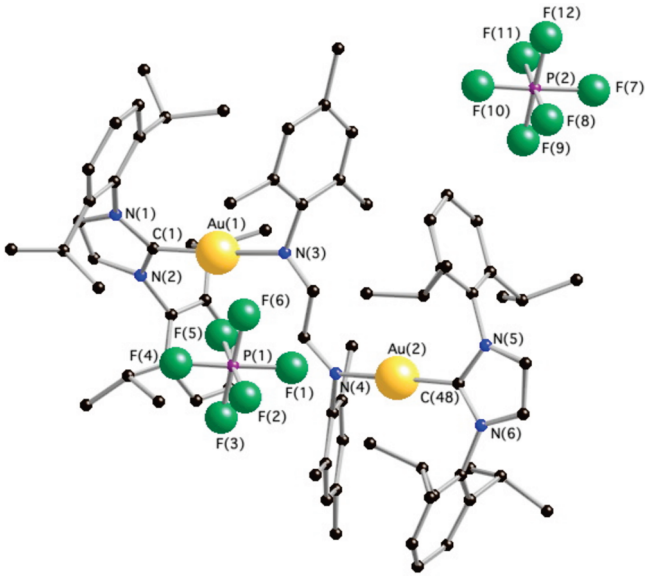

Figure 3. Ball and stick representation of [(IPr)$_2$Au(DAB-Mes)]-$(PF_6)_2$ (**10**). Hydrogen atoms and DCM molecules have been omitted for clarity.

the presence of van der Waals interactions. Since the BIAN-dipp ligand has a mirror plane of symmetry (C_{2v} symmetry) with two equivalent nitrogen positions, and tetragonal BIAN-dipp complexes with copper(I) and silver(I) are known, we would have expected a plausible structure with a tricoordinated gold atom, and two equivalent gold−nitrogen bond distances. All Au−C distances lie in the range of 1.98−2.01 Å and are in agreement with those reported for the cationic NHC−Au(I) complexes.[3] The P−Au distance is equal to 2.23 Å and is close to those reported by Echavarren et al. for cationic biphenylphosphine Au(I) complexes.[13c] The N−Au−C and N−Au−P angles are within the range between 167.9° and 176.6°. The deviation from linear coordination geometry may be due to important steric interactions brought in by the ligands, and this effect is particularly noticeable with **3** and **7**.

There is an inclusion of disordered molecules of DCM in the crystal lattice, but they do not interact with the gold(I) cation to form a halonium adduct.[18] Moreover, there is no trace of residual thallium(I) even though the chemistry of gold(I)−thallium(I) clusters is rich.[19] Note that a monodentate coordination mode for the BIAN-dipp is extremely rare. The attempt to resolve the crystal structure of [(IPr)Au(DAB-Mes)](PF_6) (**8**) revealed the unexpected formation of the dinuclear complex [((IPr)Au)$_2$(DAB-Mes)]$(PF_6)_2$ (**10**). In this complex, the DAB-Mes adopts a trans-configuration probably mandatory to anchor two bulky (IPr)Au$^+$ fragments (Figure 3). The C−Au bond distances are equal to 1.96 and 2.00 Å. The N−Au bond distances are equal to 2.04 and 2.07 Å. Both gold(I) cations are two-coordinate with an almost linear coordination geometry; the N−Au−C angles are equal to 177.6 and 176.6° (Table 2). There are two molecules of DCM cocrystallized, not interacting with the gold(I) centers.

Additional attempts to crystallize **8** yielded the formation of a yellow solution containing some orange crystals having the cell parameters of **10**. These crystals were dried under vacuum and then dissolved in CD_2Cl_2. Their ^{1}H NMR spectrum confirmed the clean formation of **10** with a new set of signals different from those of **8** having an integration fitting a ratio DAB-Mes/IPr equal to 2:1. The yellow octane solution was taken to dryness, and the residue was analyzed by ^{1}H NMR spectroscopy, revealing the presence of free-DAB-Mes. It is very important to note that **10** was in fact already detected as a side product during the formation of **8** in the crude mixture. It is not clear whether the complete rearrangement from **8** to **10** is seen as triggered by changing slowly the polarity of the solution from DCM to octane, but **8** and **10** can be kinetic and thermodynamic products, respectively, upon addition of DAB-Mes to the (IPr)Au$^+$ fragment.

Reactivity Studies. The new BIAN-dipp gold(I) complexes having their synthesis rationalized, **1**, **2**, **3**, **4**, **6**, and **7**, were tested to mediate the addition of a nucleophilic carbon to an 1,6-enyne. Recently, Echavarren et al. have published a series of elegant results, supported with detailed mechanistic studies, on the addition of indole to *N*-cinnamyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**11**). They used some bulky cationic phophine, phosphite, and NHC gold(I) complexes such as [(dtBubP)Au(MeCN)]SbF_6 (**12**) (dtBubP = ditertbutylbiphenylphosphine), [(IPrAu)Au(Bzn)]SbF_6 (**13**) (Bzn = benzonitrile), [(IMesAu)Au(Tmb)]SbF_6 (**14**) (Tmb =2,4,6-trimethoxybenzonitrile), or [(I^{t}BuAu)Au(Tmb)]SbF_6 (**15**) to perform the catalysis.[13] For the sake of comparison, similar reaction conditions were used: 5 mol % of [Au(I)] and 0.25 M of (**11**) in DCM, at room temperature. The reaction time was set at 17 h because the NHC-Au(I) systems are known to catalyze the reaction slowly. The addition of indole with the BIAN-dipp complexes generated the formation of 3-((*S*)-((*S*)-4-methylene-1-tosylpyrrolidin-3-yl)(phenyl)methyl)-1*H*-indole (**16**) and

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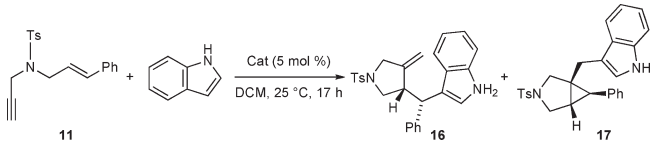
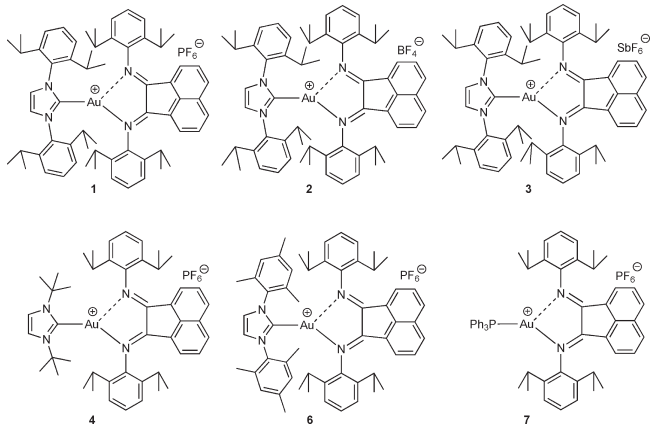
Table 3. Indole Addition to 1,6-Enynes Catalyzed by Various Au(I) Complexes



entry	catalyst	isolated yield (%)	ratio **16**/**17**[a]	catalyst	isolated yield (%)	ratio **16**/**17**[a]
1	$TlPF_6$	NR	–	AuCl[d]	NR	–
2	**1**	92	50:50	**13**[d]	57	25:75
3	**2**	93	48:52	–	–	–
4	**3**	95	47:53	–	–	–
5	**4**	65	71:29	**14**[d]	62[b]	40:60
6	**6**	30	85:14	**15**[d]	68	39:61
7	**7**	39	>98:2	**12**[d]	74[c]	80:20

[a] Ratio determined by NMR. [b] Reaction time: 19 h. [c] Reaction time 1 h. [d] Results from Echavarren et al.[13]



3-(((1*R*,5*S*,6*R*)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)-methyl)-1*H*-indole (**17**) together with different ratios.[13,20] The reaction likely proceeded in three steps: coordination and activation by Au(I) of the alkyne function; rearrangement involving the alkene function to a distorted anticyclopropyl gold(I) carbene via an 5-exodig process; attack of the indole to the carbene gold(I) or the cyclopropyl ring leading, respectively, to **16** and **17**.

A first glance at Table 3 shows that all the BIAN-dipp complexes are active, whereas $TlPF_6$ is inert. The best yields are obtained with **1**, **2**, and **3** bearing an IPr moiety, and the reaction is almost quantitative. The yields decrease by 30% when using IMes and are further lowered by 25% with PPh_3 and I^{t}Bu. Surprisingly, the trend of the reaction yield versus the σ-donor ligand for **3**, **4**, **6**, and **7** is roughly reversed compared to the one described by for **12**, **13**, **14**, and **15**. The (IPr)Au(BIAN)$^+$ moiety gives the same amount of **16** and **17** (around 50:50) regardless of the noncoordinating anions employed. The formation of **16** is favored by 25% with **4** and **6** and is almost quantitative with the phosphine complex **7**. The preferred formation of **16** over **17** seems to be governed by the nature of the σ-donor ligand (NHC or phosphine) and more specifically its steric bulk.[13,20,21] Thus, the BIAN-dipp is likely to remain uncoordinated during the catalytic cycle to allow substrate approach. A more sterically demanding NHC such as IPr will facilitate the release of the BIAN-dipp and therefore enhance the catalytic activity. The selectivity for the formation of **16** over **17** is also apparently correlated to the steric hindrance of the σ-donor ligand. For gold, steric parameters have been ranked as follows from the more to the less crowed IPr > I*t*Bu > IMes > PPh_3.[21] Increasing the ligand steric bulk leads to a decrease of the selectivity of the reaction. This illustrates perfectly the difficulty to associate in catalysis selectivity and activity.

CONCLUSIONS

We have emphasized the ability of α-diimines to form stable adducts with the gold(I) cation. The use of BIAN-dipp allows for the formation of a series of PPh_3 and NHC cationic complexes characterized by NMR and X-ray diffraction. The gold atom is two-coordinate with an almost linear environment, and an unusual monochelating mode for the BIAN-dipp ligand was evidenced. The replacement of BIAN-dipp by DAB-Mes leads to the formation of a monogold adduct which rearranges into a bis-gold adduct during the formation of crystals in a nonpolar solvent. All the BIAN-dipp complexes were active to catalyze the addition of indole to 1,6-enyne. In this regard, the phosphine-based complex is less active than anticipated. More importantly, the BIAN-dipp ligand appears to play a role determining the

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regioselectivity of the reaction. Studies aimed at exploring the stability/reactivity of complexes with bulkier α-diimines are currently ongoing in our laboratory.

EXPERIMENTAL SECTION

General Considerations. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75.5 MHz), a BrukerAVANCE 400 spectrometer (^{1}H, 400 MHz; ^{13}C{^{1}H}, 100.6 MHz; ^{19}F{^{1}H}, 283.0 MHz; ^{31}P{^{1}H}, 121.9 MHz), and referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance, or BF_4 and PF_6 anions signals (^{31}P{^{1}H}, ^{19}F{^{1}H}). Elemental analyses were performed by the "Service de Microanalyses", Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas.

X-ray Data Collection, Structure Solution, and Refinement for All Compounds. Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer 88 (graphite-monochromated Mo−Kα radiation, $\lambda = 0.71073$ Å). Crystallographic and experimental details for the structures are provided in the Supporting Information. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms.[22] The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined, riding on the corresponding parent atoms. The crystal lattice contains some highly disordered DCM molecules; the diisopropyl substituents of the BIAN-dipp or NHC ligands are slightly disordered.

General Procedure: Synthesis of the Gold Complexes. All reactions using (NHC)AuCl and (PPh_3)AuCl as starting materials were carried out in air with nondried solvents, unless stated otherwise. CD_2Cl_2 and CD_3CN were distilled from CaH_2, degassed, and stored over 4 Å molecular sieves. THF(d_8) was bought dry and used directly from a sealed bottle. All other reagents were used as received from commercial suppliers. Yields of the new complexes are based on the precursor gold complexes. The reactions involving silver salts were made under normal light conditions. However, these salts were stored away from light under argon prior to use.

*Synthesis of [(IPr)Au(BIAN)]PF_6 (**1**).* In a flask, (IPr)AuCl (200 mg, 1 equiv, 0.32 mmol) was dissolved in 5 mL of dichloromethane with BIAN (163 mg, 1.01 equiv, 0.33 mmol). Then $TlPF_6$ was added (124 mg, 1.1 equiv, 0.35 mmol), and the solution was stirred at room temperature for 24 h. The color of the reaction mixture went from yellow to dark red with the formation of a white precipitate of TlCl. The solution was filtered through a plug of silica gel (3 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added that led to the appearance of a brownish precipitate. This precipitate was filtered, washed with 5 mL of cold pentane, and dried to afford the desired complex. Yield: 361 mg (91%). ^{1}H NMR (CD_2Cl_2): δ 7.99 (d, J = 7.8 Hz, 2H, C*H*-aromatic), 7.48 (m, 2H, C*H*-aromatic), 7.37 (broad m, 4H, C*H*-aromatic), 7.29 (m, 4H, C*H*-aromatic), 7.20 (m, 4H, C*H*-aromatic), 7.11 (s, 2H, C*H*-imidazole), 6.11 (d, J = 7.5 Hz, 2H, C*H*-aromatic), 2.69 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.54 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.07 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.94 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.86 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.68 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 165.0 (s, NC-imine), 164.8 (s, *C*-carbene), 145.3 (s, *C*-aromatic), 144.3 (s, *C*-aromatic), 141.2 (s, *C*-aromatic), 136.5 (s, *C*-aromatic), 134.4 (s, *C*-aromatic), 131.5 (s, *C*-aromatic), 131.4 (s, *C*-aromatic), 130.8 (s, *C*-aromatic), 128.5 (s, *C*-aromatic), 128.3 (s, *C*-aromatic), 127.2 (s, *C*-aromatic), 125.9 (s, *C*-aromatic), 125.7 (s, *C*-aromatic), 124.9 (s, *C*-aromatic), 124.5 (s, *C*-imidazole), 28.8 (s, *C*H (CH_3)$_2$), 28.7 (s, *C*H (CH_3)$_2$), 24.1 (s, CH (CH_3)$_2$), 23.4 (s, CH (CH_3)$_2$), 23.1 (s, CH (CH_3)$_2$), 23.0 (s, CH (CH_3)$_2$); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −141.3 (septet, ^1J(^{31}P−^{19}F) = 712.1 Hz, PF_6^-); ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −74.0 (septet, ^1J(^{31}P−^{19}F) = 712.1 Hz, PF_6^-). Anal. Calcd for $C_{63}H_{76}N_4AuPF_6$ (1231.24): C, 61.52; H, 6.20; N, 4.54. Found: C, 61.17; H, 6.27; N, 4.28.

*Synthesis of [(IPr)Au(BIAN)]BF_4 (**2**).* In a flask, (IPr)AuCl (200 mg, 1 equiv, 0.32 mmol) was dissolved in 5 mL of dichloromethane with BIAN (163 mg, 1.01 equiv, 0.33 mmol). Then $AgBF_4$ was added (64 mg, 1.02 equiv, 0.33 mmol), and the solution was stirred at room temperature for 24 h. The color of the reaction mixture color went from yellow to dark red with the formation of a white precipitate of AgCl. The solution was filtered through a plug of silica gel (3 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added that led to the appearance of a clear orange precipitate. This precipitate was filtered, washed with 5 mL of cold pentane, and dried to afford the desired complex. Yield: 328 mg (87%). ^{1}H NMR (CD_2Cl_2): δ 7.99 (d, J = 8.4 Hz, 2H, C*H*-aromatic), 7.48 (m, 2H, C*H*-aromatic), 7.36 (broad m, 4H, C*H*-aromatic), 7.28 (m, 4H, C*H*-aromatic), 7.21 (m, 4H, C*H*-aromatic), 7.11 (s, 2H, C*H*-imidazole), 6.11 (d, J = 7.5 Hz, 2H, C*H*-aromatic), 2.69 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.54 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.07 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.94 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.86 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.68 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.9 (s, NC-imine), 163.1 (s, *C*-carbene), 145.4 (s, *C*-aromatic), 145.3 (s, *C*-aromatic),141.2 (s, *C*-aromatic), 136.5 (s, *C*-aromatic), 134.4 (s, *C*-aromatic), 131.5 (s, *C*-aromatic), 131.4 (s, *C*-aromatic), 130.8 (s, *C*-aromatic), 128.5 (s, *C*-aromatic), 128.3 (s, *C*-aromatic), 127.2 (s, *C*-aromatic), 125.9 (s, *C*-aromatic), 125.7 (s, *C*-aromatic), 124.9 (s, *C*-aromatic), 124.5 (s, *C*H-imidazole), 28.8 (s, *C*H (CH_3)$_2$), 28.7 (s, *C*H (CH_3)$_2$), 24.1 (s, CH (CH_3)$_2$), 23.4 (s, CH (CH_3)$_2$), 23.1 (s, CH (CH_3)$_2$), 22.9 (s, CH (CH_3)$_2$); ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −153.7 (s, BF_4^-). Anal. Calcd for $C_{63}H_{76}N_4AuBF_4$ (1173.08): C, 64.51; H, 6.54; N, 4.83. Found: C, 64.62; H, 6.46; N, 4.53.

*Synthesis of [(IPr)Au(BIAN)]SbF_6 (**3**).* In a flask, (IPr)AuCl (200 mg, 1 equiv, 0.32 mmol) was dissolved in 5 mL of dichloromethane with BIAN (163 mg, 1.01 equiv, 0.33 mmol). Then $AgSbF_6$ was added (121 mg, 1.1 equiv, 0.35 mmol), and the solution was stirred at room temperature for 24 h. The color of the reaction mixture went from yellow to dark red with the formation of a white precipitate of AgCl. The solution was filtered through a plug of silica gel (2 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added that led to the appearance of a bright orange precipitate. This precipitate was filtered, washed with 5 mL of cold pentane, and dried to afford the desired complex. Yield: 364 mg (86%). ^{1}H NMR (CD_2Cl_2): δ 7.99 (d, J = 7.8 Hz, 2H, C*H*-aromatic), 7.46 (m, 2H, C*H*-aromatic), 7.36 (broad m, 4H, C*H*-aromatic), 7.29 (m, 4H, C*H*-aromatic), 7.21 (m, 4H, C*H*-aromatic), 7.11 (s, 2H, C*H*-imidazole), 6.11 (d, J = 7.5 Hz, 2H, C*H*-aromatic), 2.69 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.55 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.07 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.94 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.86 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.68 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) = 166.4 (s, *C*-carbene), 164.8 (s, NC-imine), 145.6 (s, *C*-aromatic), 145.3 (s, *C*-aromatic), 139.4 (s, *C*-aromatic), 136.5 (s, *C*-aromatic), 134.4 (s, *C*-aromatic), 131.5 (s, *C*-aromatic), 131.4 (s, *C*-aromatic), 130.8 (s, *C*-aromatic), 128.5 (s, *C*-aromatic), 128.3 (s, *C*-aromatic), 127.2 (s, *C*-aromatic), 125.9 (s, *C*-aromatic), 125.7 (s, *C*-aromatic), 124.9 (s, *C*-aromatic), 124.5 (s, *C*H-imidazole), 28.8 (s, *C*H (CH_3)$_2$), 28.7 (s, *C*H (CH_3)$_2$), 24.1 (s, CH (CH_3)$_2$), 23.4 (s, CH (CH_3)$_2$), 23.1 (s, CH (CH_3)$_2$), 23.0 (s, CH (CH_3)$_2$). Anal. Calcd for $C_{63}H_{76}N_4AuSbF_6$ (1322.02): C, 57.22; H, 5.72; N, 4.24. Found: C, 57.10; H, 5.80; N, 4.07.

*Synthesis of [(I^{t}Bu)Au(BIAN)]PF_6 (**4**).* A protocol similar to that used for **1** gave **4** (from 100 mg, 0.24 mmol of (I^{t}Bu)AuCl)) as a clear brown solid. Yield: 235 mg (94%). ^{1}H NMR (CD_2Cl_2): δ 8.10 (d, J = 8.4 Hz, 2H, C*H*-aromatic), 7.51−7.45 (broad m, 3H, C*H*-aromatic), 7.43 (m, 1H, C*H*-aromatic), 7.39 (m, 2H, C*H*-aromatic), 7.36 (m, 2H,

C*H*-aromatic), 7.19 (s, 2H, C*H*-imidazole), 6.50 (d, J = 7.2 Hz, 2H, C*H*-aromatic), 3.12 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.74 (s, 18H, C(CH_3)$_3$), 1.22 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.86 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 165.3 (s, NC-imine), 160.3 (s, *C*-carbene), 144.2 (s, *C*-aromatic), 141.5 (s, *C*-aromatic), 137.1 (s, *C*-aromatic), 131.7 (s, *C*-aromatic), 128.7 (s, *C*-aromatic), 128.0 (s, *C*-aromatic), 127.5 (s, *C*-aromatic), 126.0 (s, *C*-aromatic), 124.9 (s, *C*-aromatic), 117.7 (s, *C*H-imidazole), 58.9 (s, *C*(CH_3)$_3$), 31.3 (s, C-(CH_3)$_3$), 28.8 (s, *C*H (CH_3)$_2$), 23.8 (s, CH (CH_3)$_2$), 23.5 (s, CH (CH_3)$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −141.3 (septet, $^1J(^{31}P-^{19}F)$ = 712.1 Hz, PF_6^-); $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −73.9 (septet, J^1-($^{31}P-^{19}F$) = 712.1 Hz, PF_6^-). Anal. Calcd for $C_{47}H_{60}N_4AuPF_6$ (1022.94): C, 55.18; H, 5.91; N, 5.48. Found: C, 55.17; H, 6.56; N, 5.54.

*Synthesis of [(I^{t}Bu)Au(BIAN)]BF$_4$ (**5**).* A protocol similar to that used for **2** gave **5** (from 100 mg, 0.24 mmol of (I^{t}Bu)AuCl)) as an orange solid. Yield: 0.210 g (89%). ^1H NMR (CD_2Cl_2): δ 8.12 (d, J = 8.1 Hz, 2H, C*H*-aromatic), 7.52−7.45 (broad m, 3H, C*H*-aromatic), 7.43 (m, 1H, C*H*-aromatic), 7.40 (m, 2H, C*H*-aromatic), 7.37 (m, 2H, C*H*-aromatic), 7.24 (s, 2H, C*H*-imidazole), 6.51 (d, J = 7.5 Hz, 2H, C*H*-aromatic), 3.13 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.75 (s, 18H, C(CH_3)$_3$), 1.22 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.87 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 165.7 (s, NC-imine), 160.7 (s, *C*-carbene), 144.6 (s, *C*-aromatic), 142.0 (s, *C*-aromatic), 137.5 (s, *C*-aromatic), 132.2 (s, *C*-aromatic), 131.4 (s, *C*-aromatic), 129.1 (s, *C*-aromatic), 128.4 (s, *C*-aromatic), 127.9 (s, *C*-aromatic), 126.4 (s, *C*-aromatic), 125.3 (s, *C*-aromatic), 118.2 (s, *C*H-imidazole), 59.2 (s, *C*(CH_3)$_3$), 31.7 (s, C(*C*H$_3$)$_3$), 29.2 (s, *C*H (CH_3)$_2$), 24.2 (s, CH (CH_3)$_2$), 23.9 (s, CH (CH_3)$_2$); $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −153.7 (s, BF_4^-). Anal. Calcd for $C_{47}H_{60}N_4AuBF_4$ (964.97): C, 58.50; H, 6.21; N, 5.80. Found: C, 58.81; H, 6.29; N, 5.87.

*Synthesis of [(IMes)Au(BIAN)]PF$_6$ (**6**).* A protocol similar to that used for **1** and **4** gave **6** (from 150 mg, 0.28 mmol of (IMes)AuCl)) as a clear orange solid. Yield: 0.270 g (85%). ^1H NMR (CD_2Cl_2): δ 8.06 (d, J = 8.1 Hz, 2H, C*H*-aromatic), 7.46−7.40 (broad m, 4H, C*H*-aromatic), 7.31 (m, 4H, C*H*-aromatic), 7.10 (s, 2H, C*H*-imidazole), 6.81 (S, 4H, C*H*-aromatic), 6.56 (d, J = 7.2 Hz, 2H, C*H*-aromatic), 2.74 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.28 (s, 6H, C*H*$_3$), 1.89 (s, 12H, C*H*$_3$); 0.94 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.81 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 165.5 (s, *C*-carbene), 163.7 (s, NC-imine), 144.3 (s, *C*-aromatic), 141.6 (s, *C*-aromatic), 139.9 (s, *C*-aromatic), 136.3 (s, *C*-aromatic), 134.4 (s, *C*-aromatic), 131.5 (s, *C*-aromatic), 131.0 (s, *C*-aromatic), 129.6 (s, *C*-aromatic), 129.0 (s, *C*-aromatic), 128.7 (s, *C*-aromatic), 127.9 (s, *C*-aromatic), 127.2 (s, *C*-aromatic), 125.4 (s, *C*-aromatic), 124.5 (s, *C*H-imidazole), 123.9 (s, *C*-aromatic), 28.9 (s, CH (CH_3)$_2$), 22.9 (s, CH (CH_3)$_2$), 22.5 (s, CH (CH_3)$_2$), 20.8 (s, C*H*$_3$), 17.2 (s, C*H*$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −141.3 (septet, $^1J(^{31}P-^{19}F)$ = 712.0 Hz, PF_6^-); $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −74.0 (septet, $^1J(^{31}P-^{19}F)$ = 712.0 Hz, PF_6^-). Anal. Calcd for $C_{57}H_{64}N_4AuPF_6$ (1147.08): C, 59.68; H, 5.62; N, 4.88. Found: C, 59.27; H, 5.42; N, 4.66.

*Synthesis of [(PPh$_3$)Au(BIAN)]PF$_6$ (**7**).* In a flask, (PPh_3)AuCl (200 mg, 1 equiv, 0.40 mmol) was dissolved in 5 mL of dichloromethane with BIAN (202 mg, 1.01 equiv, 0.41 mmol). Then $TlPF_6$ was added (157 mg, 1.1 equiv, 0.45 mmol), and the solution was stirred at room temperature for 16 h. The color of the reaction mixture went from yellow to dark red with the formation of a white precipitate of TlCl. The solution was filtered through a plug of silica gel (3 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added that led to the appearance of a dark red precipitate. This precipitate was filtered and washed with 5 mL of cold pentane. ^1H and ^{31}P NMR spectra exhibited the desired complex slightly contaminated (less than 5%) by [Au(PPh_3)$_2$]PF_6 as a side product from the synthesis. This impurity was discarded by slow crystallization from a mixture of octane and DCM. Yield: 349 mg (79%). ^1H NMR (CD_2Cl_2): δ 8.18 (d, J = 8.4 Hz, 2H, C*H*-aromatic), 7.59−7.46 (broad m, 8H, C*H*-aromatic), 7.44 (m, 4H, C*H*-aromatic), 7.33−7.26 (broad m, 11H, C*H*-aromatic), 6.78 (d, J = 7.2 Hz, 2H, C*H*-aromatic), 3.08 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.11 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 0.99 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) = 165.2 (d, $^3J(^{31}P-^{13}C)$ = 3.8 Hz, NC-imine), 144.0 (s, *C*-aromatic), 144.0 (s, *C*-aromatic), 143.1 (s, *C*-aromatic), 137.5 (s, *C*-aromatic), 134.6 (d, $^2J(^{31}P-^{13}C)$ = 12.0 Hz, *C*-aromatic), 134.5 (d, $^2J(^{31}P-^{13}C)$ = 11.9 Hz, *C*-aromatic), 134.1 (d, $^1J(^{31}P-^{13}C)$ = 22.3 Hz, *C*-aromatic), 133.3 (m, *C*-aromatic), 133.2 (m, *C*-aromatic), 132.8 (d, $^3J(^{31}P-^{13}C)$ = 5.5 Hz, *C*-aromatic), 132.7 (d, $^3J(^{31}P-^{13}C)$ = 4.4 Hz, *C*-aromatic), 131.8 (s, *C*-aromatic), 130.4 (d, $^2J(^{31}P-^{13}C)$ = 9.4 Hz, *C*-aromatic), 130.3 (d, $^2J(^{31}P-^{13}C)$ = 9.8 Hz, *C*-aromatic), 129.8 (d, $^1J(^{31}P-^{13}C)$ = 19.5 Hz, *C*-aromatic), 129.6 (d, $^1J(^{31}P-^{13}C)$ = 19.5 Hz, *C*-aromatic), 128.5 (s, *C*-aromatic), 128.3 (s, *C*-aromatic), 127.6 (s, *C*-aromatic), 127.4 (d, $^3J(^{31}P-^{13}C)$ = 3.7 Hz, *C*-aromatic), 126.2 (s, *C*-aromatic), 125.3 (s, *C*-aromatic), 29.7 (s, *C*H (CH_3)$_2$), 23.5 (s, CH (CH_3)$_2$), 23.4 (s, CH (CH_3)$_2$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.3 (s, *P*Ph$_3$), −141.3 (septet, $^1J(^{31}P-^{19}F)$ = 712.4 Hz, PF_6^-); $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −73.5 (septet, $^1J(^{31}P-^{19}F)$ = 712.4 Hz, PF_6^-). Anal. Calcd with crystals for $C_{56}H_{59}N_2AuP_2F_6Cl_4$ (1272.81): C, 52.76; H, 4.62; N, 2.19. Found: C, 52.60; H, 4.81; N, 2.06.

*Synthesis of [(IPr)Au(DAB-Mes)](PF$_6$) (**8**).* In a flask, (IPr)AuCl (200 mg, 1 equiv, 0.32 mmol) was dissolved in 2 mL of dichloromethane with DAB-Mes (495 mg, 5 equiv, 1.60 mmol). Then $TlPF_6$ was added (123 mg, 1.1 equiv, 0.35 mmol), and the solution was stirred at room temperature for 16 h. The color of the reaction mixture went from yellow to bright orange with the appearance of an intense orange precipitate of TlCl. The solution was filtered over a plug of silica gel (3 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added that led to the appearance of an orange precipitate. This precipitate was filtered and washed with 5 mL of cold pentane. Yield: 274 mg (84%). ^1H NMR (CD_2Cl_2): δ 8.09 (s, 2H, NC*H*), 7.40 (t, J = 7.8 Hz, 2H, C*H*-aromatic), 7.38 (s, 2H, C*H*-imidazole), 7.18 (d, J = 7.8 Hz, 4H, C*H*-aromatic), 6.90 (s, 4H, C*H*-aromatic), 2.38 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.33 (s, 6H, C*H*$_3$), 1.83 (s, 12H, C*H*$_3$), 1.18 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$), 1.34 (d, J = 6.9 Hz, 12H, CH (CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 167.6 (s, *C*-carbene), 165.2 (s, NC-imine), 145.5 (s, *C*-aromatic), 144.7 (s, *C*-aromatic), 137.8 (s, *C*-aromatic), 133.0 (s, *C*-aromatic), 131.3 (s, *C*-aromatic), 129.4 (s, *C*-aromatic), 127.2 (s, *C*-aromatic), 124.8 (s, *C*-aromatic), 124.2 (s, *C*-aromatic), 28.7 (s, *C*H (CH_3)$_2$), 24.0 (s, CH (CH_3)$_2$), 23.7 (s, CH (CH_3)$_2$), 20.6 (s, C*H*$_3$), 17.7 (s, C*H*$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −141.3 (septet, $^1J(^{31}P-^{19}F)$ = 712.5 Hz, PF_6^-); $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −74.1 (septet, $^1J(^{31}P-^{19}F)$ = 712.5 Hz, PF_6^-). Anal. Calcd for $C_{47}H_{60}N_4AuPF_6$ (1022.94): C, 55.18; H, 5.87; N, 5.47. Found: C, 55.10; H, 6.11; N, 5.27.

*Synthesis of (BIAN-dipp)AuCl (**9**).* In a flask, BIAN-dipp (60 mg, 1 equiv, 0.12 mmol) was dissolved in 2 mL of dichloromethane, and AuCl was added (84 mg, 3 equiv, 0.36 mmol). The solution was stirred at room temperature for 16 h. The color of the reaction mixture went from yellow to dark red with the appearance of a metallic gold(0) precipitate. The solution was filtered over a plug of silica gel (2 g). After reduction of the volume of DCM to 0.5 mL, 5 mL of pentane was added that led to the appearance of a brick red precipitate. This precipitate was filtered, washed with 5 mL of cold pentane. Yield: 56 mg (64%). ^1H NMR (CD_2Cl_2): δ 8.09 (broad d, J = 8.1 Hz, 2H, C*H*-aromatic), 7.51 (t, J = 7.8 Hz, 2H, C*H*-aromatic), 7.41−7.35 (broad m, 6H, C*H*-aromatic), 6.83 (d, J = 6.9 Hz, 1.35H, C*H*-aromatic), 6.67 (d, J = 6.9 Hz, 0.64H, C*H*-aromatic), 3.10 (broad m, 1H, C*H*(CH_3)$_2$), 2.95 (septet, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.37 (d, J = 6.9 Hz, 3H, CH (CH_3)$_2$), 1.24 (d, J = 6.6 Hz, 9H, CH (CH_3)$_2$), 1.03 (m, 12H, CH (CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.3 (s, NC-imine), 144.7 (s, *C*-aromatic), 142.1 (s, *C*-aromatic), 141.6 (s, *C*-aromatic), 136.9 (s, *C*-aromatic), 131.2 (s, *C*-aromatic), 130.6 (s, *C*-aromatic), 129.0 (s, *C*-aromatic), 128.4 (s, *C*-aromatic), 128.1 (s, *C*-aromatic), 127.4 (s, *C*-aromatic), 125.7 (s, *C*-aromatic), 124.6 (s, *C*-aromatic), 124.4 (s, *C*-aromatic), 123.9 (s, *C*-aromatic), 29.0 (s, *C*H (CH_3)$_2$), 28.9 (s, *C*H

(CH_3)$_2$), 23.4 (s, CH (CH_3)$_2$), 22.9 (s, CH (CH_3)$_2$), 22.6 (s, CH (CH_3)$_2$). Anal. Calcd for $C_{36}H_{40}N_2AuCl$ (733.14): C, 59.42; H, 4.45; N, 3.81. Found: C, 59.65; H, 5.68; N, 3.67.

*Synthesis of [((IPr)Au)$_2$(DABMes)](PF$_6$)$_2$ (**10**).* In a vial, 100 mg of **8** was placed and dissolved in 0.5 mL of DCM. Then a thin layer of *n*-octane was added, triggering the formation of dark orange crystals in a pale yellow solution after 24 h. X-ray diffraction of two different sets of crystals revealed the unexpected formation of **10**. This transformation from **8** to **10** appeared quantitative and was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 7.97 (s, 2H, NC*H*), 7.43 (t, J = 7.8 Hz, 4H, C*H*-aromatic), 7.32 (s, 4H, C*H*-imidazole), 7.13 (d, J = 7.8 Hz, 8H, C*H*-aromatic), 6.88 (s, 4H, C*H*-aromatic), 2.41 (s, 6H, CH_3), 2.28 (septet, J = 6.9 Hz, 8H, C*H*(CH_3)$_2$), 1.46 (s, 12H, CH_3), 1.12 (d, J = 6.9 Hz, 24H, CH (CH_3)$_2$), 0.91 (d, J = 6.9 Hz, 24H, CH (CH_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −141.3 (septet, ^1J(^{31}P−^{19}F) = 712.1 Hz, PF_6^-); ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −74.0 (septet, ^1J(^{31}P−^{19}F) = 712.1 Hz, PF_6^-).

Cycloisomerization General Procedure. A Schlenk flask, under nitrogen, was charged with the catalyst (0.025 mmol, 0.05 equiv) and dry dichloromethane (1 mL), and then enyne **11** (162 mg, 0.5 mmol, 1 equiv) and indole (60 mg, 0.55 mmol, 1.1 equiv) in solution in dichloromethane (1 mL) were added. The mixture was stirred for 17 h at room temperature. Reaction progress was monitored by TLC (pentane/ether 8:2). The reaction mixture was directly purified by column chromatography on silica gel (dichloromethane) to afford the products as an inseparable mixture. NMR data were found in good agreement with the literature.[13] They are reported in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and/or characterizations of **10**, **11**, **16**, and **17**. Crystallographic information files (CIF) of the complexes **3**, **5**, **6**, **7**, and **10**. (CIF files have also been deposited with the CCDC, 12 Union Rd., Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 802668−802672.) This material is available free of charge via the Internet at http://pubs.acs.org.

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