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Luminescent Di- and Tetranuclear Gold Complexes of Bis(diphenylphosphinyl)-Functionalized Dipyrido-Annulated **N-Heterocyclic Carbene**

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Supporting Information

ABSTRACT: Phosphine-functionalized N-heterocyclic carbene (NHC) ligands are known to complex group 11 metal centers to form multinuclear complexes with photoluminescence properties. This study reports a structurally rigid ortho-substituted dipyrido-annulated NHC with T-shape coordination geometry and its di- and tetranuclear gold(I) complexes. The free ligand as well as all metal complexes are found luminescent at room temperature and phosphorescent at 77 K. Although metal d¹⁰d¹⁰ interactions are evident based on their solid-state structures, their effect on the photoemission is limited, most likely due to the weak coordination of the ligand to the metal centers in solution.

INTRODUCTION

Multidentate ligands¹⁻⁸ containing both N-heterocyclic carbene (NHC) and phosphine moieties can offer combined, complementary electronic properties and coordination geometries to transition metal centers to enhance the desired physical and chemical properties.^{9–13} Since the first isolation of P-functionalized imidazolium iodide by Herrmann et al. in 1996,¹⁴ a growing number of designs of this hybrid class of ligands have been used for synthesizing multinuclear complexes of group 11 metal cations for potential photoluminescent properties. The different geometric designs of the ligand resulted in various degrees of intra- or intermolecular d¹⁰-d¹⁰ metal interactions, which have been shown to influence their photophysical properties.^{15,16}

To date, most of the phosphine-functionalized NHCs used for photoluminescent properties of multinuclear complexes have been based on the Arduengo-type imidazole scaffold, including the mono-¹⁷ and disubstituted bisphosphanyl NHC ligands¹⁸ (Chart 1A) and the more flexible NHC hybrid ligands^{3,5,7,17,19,20} with a spacer between the phosphine and carbene moieties (Chart 1B). In the former design (A), the carbene and phosphine donors align the metal cations along one axis (x-axis in Chart 1), allowing for intramolecular metalmetal interactions. Although free rotation along the N-P bond (the x-axis) is possible, coordination to metal led to $mostly^{21}$ rigid 2-D structures, where all carbene and phosphine ligands and metal centers lie within the same plane. In contrast, the latter design (Chart 1B) allows for controllable degrees of freedom in all directions depending on the spacer between the



coordination sites, permitting more diversified coordination geometries.¹⁹⁻²⁵ However, the resulting complexes usually have longer metal-metal distances, which prevent intramolecular d¹⁰-d¹⁰ interactions.^{19,20,22,25} In addition, flexibility of ligands are known to hamper the efficiency of luminescence through thermal vibrations.²⁰

Considering the above, a structurally rigid design containing carbene and phosphine that offers different coordination geometries would be highly desirable. Our group has successfully introduced thio, phosphinyl, and aryl groups into Weiss²⁷ and Kunz's²⁸⁻³² dipyrido-annulated N-heterocyclic carbene (dpa-NHC) to form pincer ligands. The steric rigidity^{33,34} and unusual weak σ -donating, π -rich, and overall strong donating nature of the backbone²⁹ as carbene are of special interest to us. Among these, the ortho-diphosphinylsubstituted derivative (dpa^{P2}-NHC, Chart 1C) has only been characterized by coordination to a rhodium center previously.³⁴

This work reports the isolation and characterization of the dpa^{P2}-NHC for the first time. Its coordination chemistry to gold(I) complexes and the photoluminescent properties of the resulting multinuclear complexes are investigated. Its rigid backbone and free rotation only along the P–C bond (y-axis) lead to previously inaccessible geometries.

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Chart 1. Phosphine-Functionalized NHC Ligands for Multinuclear Group 11 Metal Complexes and *ortho*-Substituted dpa-NHC Transition Metal Complexes



RESULTS AND DISCUSSION

The dpa^{P2}-NHC 1 is generated from deprotonation of the corresponding imidazolium salt 1(H)I. Although its in situ generation and trapping by the rhodium(I) complex have been described earlier, now free carbene 1 can be isolated in good yield (69%). The solid-state molecular structure of 1 obtained from X-ray crystallographic studies (Figure 1) shows a planar annulated dipyrido backbone with one phosphine bending slightly out of the plane ($\Phi_{PCCP} = 9.6^{\circ}$). The phenyl groups of the two phosphine moieties are on the same side of the plane due to crystal packing. The N–C–N angle of 100.2(2)° is slightly larger than Kunz's substituted carbene (99.6(2)°). The ¹³C{¹H} NMR spectrum of 1 in C₆D₆ showed a triplet at 198.3 ppm, which has been assigned to the carbene carbon C1, with a ³*I*_{CP} of 34 Hz.

The two phosphines of the dipyrido-backbone can coordinate to gold(I) centers independently, shown by a reaction of the parent imidazolium salt $1(H)PF_6$ and $[AuCl(SMe_2)]$ in dichloromethane. Following complexation of $[AuCl(SMe_2)]$ with $1(H)PF_6$ in a ratio of 2:1, a bright yellow solid was isolated in 90% yield (Scheme 1). ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra of 2 in deuterated DMSO at room temperature show one set of signals, consistent to a symmetrical structure. The upfield shift of the pro-carbenic proton resonance $[1(H)PF_6, \delta_H 8.6, vs 2, \delta_H 8.3]$ and downfield shift of the phosphine resonance $[1(H)PF_6, \delta_P - 3.6, vs 2, \delta_P 27.2]$ indicate coordination of phosphines to gold. The



Figure 1. Molecular structures of **1** and **2** in the solid state. The ellipsoids are shown at 50% probability. Ellipsoids of periphery atoms and the counterion were removed for clarity. Selected bond lengths (Å) and angles (°) for 1: C1–N1 1.368(2), C1–N2 1.378(2), C4–C5 1.378(3); N1–C1–N2 100.2(2). Torsion angle $\Phi_{P1C2C3P2} = 9.6$. Selected bond lengths (Å) and angles (°) for **2**: C1–N1 1.354(5), C3–C3' 1.395(8); N1–C1–N1' 107.8(5). $\Phi_{P1C2C2'P1'} = 18.9$. CCDC for **1**, 1894301, for **2**, 1894302.

Scheme 1. Generation of the dpa^{P2}-NHC 1 from Deprotonation 1(H)I and the Coordination through Phosphine Moieties



precarbene carbon was assigned to a singlet at 146.7 ppm, very similar to that of $1(H)PF_6$, at 146.0 ppm. Meanwhile, the ESI-MS spectrum shows an ion peak at m/z = 1113.1609, as expected for the $[(AuCl)_21(H)]^+$ cation.

Single crystals of 2 obtained from dimethylformamide (DMF)/diethyl ether revealed a solid-state structure of a dinuclear gold complex with a C2 rotating axis. The two gold centers are *trans* to each other, pointing to either side of the planar ligand backbone (Figure 1), and thus show no intramolecular metal–metal interactions. In the crystal lattice, the AuCl moieties are aligned with an intermolecular Au–Cl distance of 3.550 Å and an Au–Au distance of 4.219 Å, indicating no intermolecular metal–metal interactions.

The slow addition of one equivalent of $[AuCl(SMe_2)]$ in dichloromethane (DCM) to a hexane solution of 1 afforded complex 3 as a yellow solid precipitated from the reaction mixture in 72% yield (Scheme 2). Upon recrystallization in a

Scheme 2. Synthesis of Dinuclear and Tetranuclear Gold(I) Complexes 3–5 from 1



DMF/diethyl ether mixture, single crystals of **3** were obtained. X-ray diffraction analysis showed an asymmetric dinuclear gold structure with two dpa^{P2}-NHC ligands (Figure 2). Complex **3** can be viewed as two $[Au(dpa^{P2}-NHC)Cl]$ monomers condensed together with the dissociation of one chloride



Figure 2. Molecular structures of 3 and 4 in the solid state. The ellipsoids are shown at 50% probability. Ellipsoids of periphery atoms and counterions were removed for clarity. Selected bond lengths (Å) and angles (°) for 3: Au1–Au2 2.955(2); Au1–C1 1.994(4), Au1–P1 2.937(2), Au2–P2 2.291(2), Au2–C2 2.026(4), Au2–P3 2.895(2). Selected bond lengths (Å) and angles (°) for 4: Au1–Au2 3.019(2); Au1–C1 2.053(4), Au1–P2 2.985(2), Au1–P3 2.309(2), Au2–P1 2.302(2), Au2–C2 2.045(4), Au2–P4 2.989(2); C1–Au1–P3 174.6(1), P1–Au2–C2 176.1(1). CCDC for 3, 1894303, and for 4, 1894304.

anion. Both gold(I) centers have a linear geometry, each coordinated by a carbene. Three phosphine moieties of 3 do not coordinate to the adjacent Au(I) center. The remaining one coordinates to the metal center of a second monomer. Consequently, the two metal centers are put closely together with a short Au–Au distance of 2.955(2) Å, which indicates the presence of an aurophilic interaction.^{16,35–37}

Although crystals of **3** can be obtained reproducibly in good yield, the solid-state structure cannot be maintained in solution. ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR experiments of **3** showed unassignable signals in CD₃CN, DMSO- d_6 , and CDCl₃ even at low temperatures (-40 °C), indicating complicated dynamic behavior in solution (Figure S20, Supporting Information (SI)). This is likely due to the presence of three dangling phosphine ligands as well as the lability of chloride, which may dissociate or coordinate to the gold center in solution, resulting in a mixture of monomer, dimer, or oligomers.

In attempt to cleave the dimer and isolate pure monomeric species, we added Lewis bases, such as phosphine or isonitrile, to a solution of 3. However, this did not lead to any pure product. Instead, we employed a gold precursor with weakly coordinating ligands to favor higher-ordered structures from ligand 1.

The complexation behavior of gold(I) precursors often depends on their ligands. The presence or absence of halide (X ligand), and the coordination strength of Lewis base (L ligand) have been reported to provide structurally different products. $^{\mathbf{38,39}}$ The reaction of 1 with an equimolar amount of $[Au(tht)_{2}](OTf)$ in THF led to isolation of complex 4 as an orange solid in 83% yield. The same complex 4 can also be obtained from halide abstraction of 3 by AgOTf (Scheme 2). Single crystal X-ray crystallographic studies revealed a centrosymmetric dimeric structure, in which the carbene and one phosphine of 1 coordinate to a gold center each and are capped by a second dpa^{P2}-NHC in complementary positions (4, front view; Figure 2). The gold centers bend slightly toward each other with C1-Au1-P3 and P1-Au2-C2 angles of 174.6(1)° and 176.1(1)°, respectively. The Au–Au distance of 3.019(2) Å is slightly longer than that in 3, lying in the expected range of strong d¹⁰-d¹⁰ interactions.³⁵ The distances of Au1-P2 and Au2-P4 are 2.985(2) and 2.989(2) Å, respectively, which are significantly longer than the Au1-P3 and Au2-P1 distances of 2.309(2) and 2.302(2) Å, revealing two weakly or noncoordinating outer phosphine moieties (sum of van der Waals radii, 3.46-4.22 Å).40,41 Directed by hydrogen bonding between triflate and phenyl hydrogen atoms, the two rigid dpa^{P2}-NHC backbone forms a bowl shape with phosphines orientated outward (4, side view; Figure 2).

The solution ¹H NMR of 4 in DMSO- d_6 shows two sets of signals at room temperature, assigned to the inner half and the outer half of the ligand, consistent with the solid-state structure. The ³¹P{¹H} NMR spectrum showed two virtual triplets at 29.7 and 6.8 ppm, assigned to the inner and outer phosphorus atoms. The virtual coupling indicates that the two sets of chemically different phosphorus atoms couple to each other, suggesting that, at least in solution, the outer phosphines also coordinate to the metal center. The ESI-MS spectrum shows a signal at m/z = 845.2486, corresponding to the ion peak of the dication of 4, indicating the robustness of the complex.

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Both complexes 3 and 4 are dinuclear species with each tridentate dpa^{P2}-NHC capturing only one metal center. In order to obtain complexes with higher metal content, the reaction of 1 with two or more equivalents of $[Au(tht)_2](OTf)$ was carried out. Among many attempts, the reactions of 1 or 4 with $[Au(tht)_2](OTf)$ in an 1:2 ratio lead to isolation of a pure isolable complex as an orange solid (5) in 71% yield. Recrystallization from DMF and hexane lead to single crystals of 5, which showed a symmetrical dimeric tetranuclear complex of formula $\{Au_2[dpa^{P2}-NHC](DMF)\}_2$ (5, Figure 3). Two Au(I) were captured at the carbene donors, lying in



Figure 3. Molecular structures of **5** in the solid state. The ellipsoids are shown at 50% probability. Ellipsoids of periphery atoms and counterions were removed for clarity. Selected bond lengths (Å) and angles (°) for **5**: Au1–Au2 3.1176(7), Au2'-Au1 3.0976(7), Au1–Au1' 3.318(1), Au1–C1 1.98(2), Au1–O 2.15(2); P2–Au2–P1' 157.4(2), P1–Au2'-P2' 158.4(2).⁴² CCDC for **5**, 1894305.

plane with the dpa^{P2}-NHC backbone. Two more Au(I) were captured by the phosphine donors between the two antiparallel dpa^{P2}-NHC ligands. The four gold cations form a fourmembered planar gold(I) ring connecting each other by aurophilic interactions. Although the distances³⁵ of Au1–Au2 3.1176(7), and Au1–Au2' 3.0976(7) Å are slightly longer than those in complexes **3** and **4**, each outer phosphine-coordinated Au(I) displays a deviation from the linear P2–Au2–P1' arrangement ($157.4(2)^{\circ}$) toward the central carbene-coordinated gold(I) atoms, which is attributed to the attractive aurophilic interactions. This dimeric molecular 3D lattice arrangement is unique from all previously reported heteroleptic phosphine/carbene multinuclear complexes because the three donors are restricted to one plane with only rotation possible at the phosphines.

Complex **5** dissolved in DMSO- d_6 provided the sharpest signals in ¹H and ³¹P{¹H} NMR experiments in comparison to other solvents. The ¹H NMR spectrum showed a singlet at 1.12 ppm, assigned to the tBu group of the ligand backbone. The ³¹P{¹H} NMR spectrum showed one singlet at 36.3 ppm. These are consistent with the solid-state structure of **5**. In comparison, the ¹³C{¹H} NMR experiment showed a less well-resolved spectrum, suggesting dynamic behaviors in solution at room temperature, possibly due to the rotation of the phosphine groups.

The photophysical properties of the gold complexes (2-5) and the free carbene 1 were investigated in 2-methyl-THF. The absorption and emission bands of gold complexes observed at room temperature lie in the range of 320-420 and 450-600 nm, respectively, similar to those of 1 (Figures S1 and S2). It seems likely, therefore, that these electronic

transitions of the gold complexes are mostly attributed to ligand-centered (LC) transitions. Although complex 3 shows a relatively broad absorption, its excitation spectrum is similar to that of 1 and other complexes, again suggesting that LC transition is primarily involved for 3 (Figure S2). At 77 K, all these compounds provided phosphorescence. As shown in Figure S3, the PL spectra that are obtained with a 50 μ s delay after excitation show no bands around 500 nm, indicating that the PL bands observed at room temperature are likely ascribed to fluorescence. The phosphorescence bands of 3–5, however, were slightly shifted from that of 1, indicating electronic perturbation of the gold cation to the triplet state of the carbene to a limited extent (Figure S3). Lifetimes of the phosphorescence of compounds 1–5 range between 85.1 and 772.0 μ s (Figure S4).

CONCLUSION

On the basis of the newly isolated bis(diphenylphosphinyl)functionalized dipyrido-annulated NHC (1, dpa^{P2}-NHC) and its imidazolium salt precursors, di- and tetranuclear gold(I) complexes (2–5) have been synthesized and fully characterized by X-ray crystallography. The two phosphine groups fixed in proximity to the central carbene within a rigid framework allowed for the formation of multinuclear species with Au(I)–Au(I) interactions in complexes 3–5. Dynamic behaviors observed from solution of 3 and 5 by NMR spectroscopy suggest weak coordination. All the obtained gold complexes are luminescent at room temperature and phosphorescent at 77 K. However, the presence of gold(I) centers and their d¹⁰–d¹⁰ did not lead to dramatic changes of the emission. We are currently exploring the coordination chemistry of dpa^{P2}-NHC toward silver and copper ions and their photophysical properties of the resulting complexes.

EXPERIMENTAL SECTION

General Procedure. Unless otherwise noted, all the manipulations were carried out using standard Schlenk techniques under an argon atmosphere. THF and hexane were purified by passing through a glass contour solvent dispensing system under an N₂ atmosphere; other solvents used were purified and dried by standard methods. The starting material **1(H)I** was prepared according to the literature procedure.³³ ¹H (400 MHz, 600 MHz), ¹³C{¹H} (100 MHz, 150 MHz), and ³¹P{¹H} (162 MHz, 243 MHz) NMR spectra were recorded on JEOL AL-400S spectrometer and were referenced to CDCl₃ (¹H: δ = 7.26 ppm; ¹³C: δ = 77.1 ppm), C₆D₆ (¹H: δ = 7.16 ppm; ¹³C: δ = 128.0 ppm), or DMSO-*d*₆ (¹H: δ = 2.50 ppm; ¹³C: δ = 39.5 ppm) as external standards. ³¹P{¹H} NMR spectra are referenced to 85% H₃PO₄ (δ = 0.0 ppm) as external standards.

Synthesis of Free Carbene 1 (dpa^{P2}-NHC). The solution of 1(H)I (400.0 mg, 0.515 mmol) and KO^tBu (69.3 mg, 0.618 mmol) in THF (40 mL) was stirred at room temperature for 2 h, and then volatiles were removed under reduced pressure. Hexane (60 mL) was added, and the solution was filtered through Celite. After removal of volatiles, 1 was obtained as an orange solid. Yield: 68.7% (230.1 mg, 0.354 mmol). Suitable crystals for X-ray analysis were obtained by slow evaporation of the solution of 1 in THF/hexane. ¹H NMR (600 MHz, $C_6 D_{61} \delta$): 1.08 (s, 18H, CH₃), 6.54 (s, 2H, H₃), 6.93-7.06 (m, 12H, *m*-/*p*-CH_{Ph}), 7.42 (m, 8H, *o*-CH_{Ph}), 7.53 (s, 2H, H_b). ³¹P{¹H} NMR (243 MHz, C₆D₆, δ): -13.8. ¹³C{¹H} NMR (150 MHz, C₆D₆, δ): 30.3 (CH₃), 34.7 (C(CH₃)), 111.5 (C1/C9), 121.1 (C3/C7), 122.7 (d, ${}^{1}J_{PC} = 2$ Hz, C4/C6), 128.5 (d, ${}^{3}J_{PC} = 8$ Hz, m-C_{Ph}), 128.8 $(p-C_{\rm Ph})$, 134.7 (d, ${}^{1}J_{\rm PC} = 21$ Hz, $o-C_{\rm Ph}$), 136.9 (d, ${}^{2}J_{\rm PC} = 12$ Hz, $i-C_{\rm Ph}$), 140.3 (C10/C11), 142.0 (d, ${}^{3}J_{PC} = 14$ Hz, C2/C8), 198.3 (t, ${}^{3}J_{PC} = 33$ Hz, C_{carbene}). Element analysis calcd for $C_{43}H_{42}N_2P_2$ (648.77): C 79.61, H 6.53, N 4.32; found: C 79.37, H 6.20, N 4.84.



Synthesis of 1(H)PF₆. The solution of 1(H)I (100 mg, 0.129 mmol) and KPF₆ (47.4 mg, 0.258 mmol) in CH₂Cl₂ (20 mL) was stirred at room temperature for 24 h. After the reaction solution was concentrated to 2-3 mL under reduced pressure, hexane (10 mL) was added to precipitate the yellow solid $1(H)PF_6$ that was collected by filtration. Yield: 85.7% (87.8 mg, 0.111 mmol). ¹H NMR (400 MHz, DMSO- d_6 , δ): 1.23 (s, 18H, CH₃), 6.97 (dd, ${}^{4}J_{HH} = 2.0$ Hz, ${}^{3}J_{\rm PH}$ = 2.4 Hz, 2H, $H_{\rm a}$), 7.21–7.38 (m, 8H, o-CH_{Ph}), 7.39–7.67 (m, 12H, m-/p-CH_{Ph}), 8.64 (s, H, NCHN), 8.91 (d, ${}^{4}J_{HH} = 2.0$ Hz, 2H, $H_{\rm b}$). ³¹P{¹H} NMR (162 MHz, DMSO- d_6 , δ): -13.6 (s), -143.2 (sept, ${}^{1}J_{PF} = 720.9$ Hz, PF₆). ${}^{13}C{}^{1}H$ NMR (100 MHz, DMSO- d_{6} , δ): 29.9 (CH₃), 35.1 (C(CH₃)), 110.2 (t, ${}^{3}J_{PC}$ = 16 Hz, C5), 114.8 (C1/C9), 123.9 (C10/C11), 126.9 $(d_{1}^{2}J_{PC} = 6 \text{ Hz}, C6/C4)$, 129.0 (d, ${}^{1}J_{PC} = 6$ Hz, C7/C3), 129.9 (d, ${}^{3}J_{PC} = 8$ Hz, m-C_{Ph}), 131.2 (p-C_{Ph}), 133.1 (d, ${}^{1}J_{PC} = 25$ Hz, *i*- C_{Ph}), 133.9 (d, ${}^{2}J_{PC} = 21$ Hz, *o*- C_{Ph}), 146.0 (C2/C8). HRMS (ESI) (*m*/*z*): [M-PF₆]⁺, 649.290. Element analysis calcd for C43H43F6N2P3 (794.74): C 64.99, H 5.45, N 3.52; found: C 65.10, H 5.70, N 3.64.



Synthesis of Complex 2. To a solution of $1(H)PF_6$ (20.0 mg, 0.025 mmol) in CH₂Cl₂ (10 mL) was added [AuCl(SMe₂)] (14.8 mg, 0.051 mmol), and the resulting solution was stirred at room temperature for 1 h. After being concentrated to 2-3 mL under reduced pressure, hexane (15 mL) was added to precipitate the yellow solid complex 2 that was collected by filtration. Yield: 90.5% (28.5 mg, 0.023 mmol). Suitable crystals for X-ray analysis were obtained by slow diffusion of diethyl ether into the solution of 2 in dimethylformamide. ¹H NMR (400 MHz, DMSO- d_{6} , δ): 1.24 (s, 18H, CH₃), 7.14 (d, ${}^{3}J_{PH}$ = 10.4 Hz, 2H, H_a), 7.59–7.89 (m, 20H, CH_{Ph}), 8.30 (s, H, NCHN), 9.23 (s, 2H, H_b). ${}^{31}P{}^{1}H$ NMR (162 MHz, DMSO- d_6 , δ): 27.2 (s), -143.2 (sept, ${}^{1}J_{PF} = 720.9$ Hz, PF_6). ¹³C{¹H} NMR (100 MHz, DMSO- d_6 , δ): 29.9 (CH₃), 35.3 $(C(CH_3))$, 110.0 (br s, C5), 118.1 (C1/C9), 122.7 (d, ${}^{1}J_{PC} = 65$ Hz, C4/C6), 123.5 (d, ${}^{1}J_{PC} = 62$ Hz, *i*-C_{Ph}), 125.1 (d, ${}^{3}J_{PC} = 2$ Hz, C10/C11), 130.0 (d, ${}^{2}J_{PC} = 10$ Hz, C3/C7), 131.0 (d, ${}^{3}J_{PC} = 13$ Hz, m- $C_{\rm Ph}$), 134.6 (d, ${}^{4}J_{\rm PC}$ = 2 Hz, p- $C_{\rm Ph}$), 134.8 (d, ${}^{2}J_{\rm PC}$ = 10 Hz, o- $C_{\rm Ph}$), 146.7 (C2/C8), C5 can not be detected. HRMS (ESI) (m/z): [M- $PF_6]^{\scriptscriptstyle +}$, 1113.1609. Element analysis calcd for $C_{43}H_{43}Au_2Cl_2F_6N_2P_3$ (1259.58): C 41.00, H 3.44, N 2.22; found: C 40.58, H 3.24, N 2.13.



Synthesis of Complex 3. The approximately saturate solution of $[AuCl(SMe_2)]$ (74.8 mg, 0.254 mmol) in CH_2Cl_2 (6 mL) was slowly added dropwise to a solution of free carbene 1 (150.0 mg, 0.231 mmol) in hexane (80 mL), and the instantly formed yellow precipitate was collected by filtration. After recrystallization with THF at -18 °C, the desired product 3 was collected as a light-yellow solid by filtration. Yield: 72.3% (147.2 mg, 0.084 mmol). Suitable crystals for X-ray analysis were obtained by slow diffusion of diethyl ether into the solution of 3 in DMF. Due to the fluxional process in solution, the proton resonance in the ¹H NMR spectrum can not be clearly ascribed (see the Supporting Information). ¹³C{¹H} NMR

spectrum could not be obtained due to the poor solubility and harsh measurement condition, long time (more than 1 days) and low temperature (around -10 °C). ³¹P{¹H} NMR (243 MHz, CDCl₃, δ): 26.2 (s), 27.3 (s), 28.5 (s), 30.3 (s). HRMS (ESI) (m/z): [M-2Cl]²⁺, 845.2498. Element analysis calcd for C₈₆H₈₄Au₂Cl₂N₄P₄ (1762.37): C 58.61, H 4.80, N 3.18; found: C 58.37, H 4.99, N 3.18.



Synthesis of Complex 4. Method A. The solution of complex 3 (100.0 mg, 0.057 mmol) and AgOTf (29.3 mg, 0.114 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature over 1 h in the absence of light. Then, the resulting solution was filtered through Celite, and the filtrate was concentrated to 2–3 mL under reduced pressure; hexane (15 mL) was added to precipitate complex 4, which was collected as an orange solid by filtration. Yield: 64.3% (73.0 mg, 0.0367 mmol).

Method B. The solution of free carbene 1 (50.0 mg, 0.077 mmol) and [Au(tht)₂](OTf) (40.2 mg, 0.077 mmol) in THF (10 mL) was stirred at room temperature for 2 h and then concentrated to 2-3 mL under reduced pressure; hexane (15 mL) was added to precipitate complex 4 that was collected as an orange solid by filtration. Yield: 82.6% (63.3 mg, 0.0318 mmol). Suitable crystals for X-ray analysis were obtained by slow diffusion of diethyl ether into the solution of 4 in dimethylformamide. ¹H NMR (400 MHz, DMSO- d_{6} , δ): 1.04 (s, 18H, CH₃), 1.20 (s, 18H, CH₃), 6.76 (br s, 8H, CH_{Ph}), 6.88 (s, 4H, $H_{\rm b}/H_{\rm b}'$), 7.10–7.70 (m, 32H, CH_{Ph}), 8.82 (s, 2H, $H_{\rm a}$), 8.97 (s, 2H, H_{a}^{PD}). ³¹P{¹H} NMR (162 MHz, DMSO- d_{6} , δ): 29.7 (virtual triplet), 6.8 (virtual triplet). ¹³C{¹H} NMR (100 MHz, DMSO- d_6 , δ): 29.7 (CH₃), 29.8 (CH₃), 34.7 (C(CH₃)), 34.9 (C(CH₃)), 114.8 (C1), 118.1 (C9), 119.6 (q, ${}^{1}J_{CF}$ = 345.1 Hz, CF₃), 125.5 (C4), 126.2 (C6), 126.9 (C3), 128.8 (d, ${}^{1}J_{PC}$ = 7 Hz, i'-C_{Ph}), 129.2 (m'-C_{Ph}), 129.6 (br, $p'-/m-C_{\rm Ph}$), 130.2 (C7), 130.8 ($p-C_{\rm Ph}$),131.8 (d, ${}^{1}J_{\rm PC} = 7$ Hz, $i-C_{\rm Ph}$), 132.7 (o-/o'-C_{Ph}), 135.4 (C10/C11), 142.5 (C2), 145.0 (C8), the carbene carbon could not be detected. HRMS (ESI) (m/z): [M-20₃SCF₃]²⁺, 845.2486. Element analysis calcd for C₈₈H₈₄Au₂F₆N₄O₆P₄S₂ (1989.60): C 53.12, H 4.26, N 2.82; found: C 54.24, H 4.12, N 2.87.



Synthesis of Complex 5. *Method A*. The solution of free carbene 1 (25.0 mg, 0.0385 mmol) and $[Au(tht)_2](OTf)$ (40.2 mg, 0.077 mmol) in THF (10 mL) was stirred at room temperature for 2 h and concentrated to 2–3 mL under reduced pressure; hexane (15 mL) was added to precipitate complex 5, which was collected as an orange solid by filtration. Yield: 71.3% (36.7 mg, 0.0137 mmol).

Method B. The solution of complex 4 (25.0 mg, 0.0126 mmol) and $[Au(tht)_2](OTf)$ (13.1 mg, 0.0252 mmol) in THF (15 mL) was stirred at room temperature for 3 h and concentrated to 2–3 mL under reduced pressure; hexane (15 mL) was added to precipitate complex 5, which was collected as an orange solid by filtration. Yield: 51.3% (16.1 mg, 0.006 mmol). Suitable crystals for X-ray analysis

Table 1. Crystallographic Data for Compounds 1-5

	1	2	3	4	5
CCDC No.	1894301	1894302	1894303	1894304	1894305
formula	$C_{43}H_{42}N_2P_2 \\$	$\begin{array}{c} C_{43}H_{43}Au_{2}Cl_{2}F_{6}N_{2}O_{6}P_{3}\cdot\\ 4(CH_{3})_{2}NCHO\end{array}$	$\begin{array}{c} C_{86}H_{84}Au_{2}Cl_{2}N_{4}P_{4}\cdot\\ 2(CH_{3})_{2}NCHO \end{array}$	$\begin{array}{c} C_{88}H_{84}Au_{2}F_{6}N_{4}O_{6}P_{4}S_{2}\cdot(CH_{3})_{2}NCHO\cdot\\ CH_{3}CH_{2}OCH_{2}CH_{3} \end{array}$	$\begin{array}{c} C_{90}H_{84}Au_{4}F_{12}N_{4}O_{12}P_{4}S_{4}\!\cdot\!\\ 4(CH_{3})_{2}NCHO \end{array}$
formula weight	648.72	1551.92	1908.47	2209.83	2964.90
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	Pbca	C2/c	$P2_1/n$	P2 ₁ /c	P-1
temperature (K)	123	173	123	123	123
a (Å)	14.093(2)	22.392(5)	14.259(11)	15.779(12)	15.762(2)
b (Å)	16.545(2)	16.519(4)	31.08 (2)	25.547(19)	15.767(2)
c (Å)	30.850(5)	16.628(4)	20.805(16)	24.151(19)	23.977(4)
α (°)	90	90	90	90	82.204(2)
β (°)	90	98.342(3)	99.714(13)	97.082 (15)	78.435(2)
γ (°)	90	90	90	90	85.067(2)
V (Å ³)	7193.3(18)	6086(2)	9088(12)	9662(13)	5773.2(15)
Ζ	8	4	4	4	2
$d_{\rm calcd}~({\rm g~cm^{-3}})$	1.198	1.694	1.395	1.519	1.620
$\mu \ (\mathrm{mm}^{-1})$	0.153	5.049	3.402	3.213	5.270
F ₀₀₀	2752	3064	3840	4456	2744
no. reflns	32784	15774	54785	58187	30206
no. unique reflns	6331	6215	22722	24011	22790
$R_{\rm int}$	0.0829	0.0274	0.0311	0.0240	0.0287
$R_1 \left[I > 2\sigma(I) \right]$	0.0429	0.0351	0.0384	0.0341	0.0612
wR ₂ (all data)	0.1005	0.1005	0.0930	0.0921	0.1975
GOF	0.957	1.087	1.019	1.016	1.033

were obtained by slow diffusion of diethyl ether into the solution of **5** in dimethylformamide. ¹H NMR (400 MHz, DMSO- d_{60} , δ): 1.12 (s, 36H, CH₃), 6.65 (s, 4H, H_b), 6.91–8.21(m, 40H, CH_{Ph}), 9.06 (d, ³J_{PH} = 22.0 Hz, 4H, H_a). ³¹P{¹H} NMR (162 MHz, DMSO- d_{60} , δ): 36.3 (s). ¹³C{¹H} NMR (100 MHz, DMSO- d_{60} , δ): 29.7 (CH₃), 34.7(C(CH₃)), 118.2 (C1/C9), 119.1 (C4/C6), 122.4 (C10/C11), 125.9 (C3/C7), 129.5 (*i*-C_{Ph}), 130.2 (*m*-C_{Ph}), 132.0 (*p*-C_{Ph}), 133.2 (*o*-C_{Ph}), 143.4 (C2/C8), the carbene carbon and carbons of triflates could not be detected. HRMS (ESI) (*m*/*z*): [M-4O₃SCF₃]⁴⁺, 521.1086. Element analysis calcd for C₉₀H₈₄Au₄F₁₂N₄O₁₂P₄S₄ (2681.66): C 40.31, H 3.16, N 2.09; found: C 39.87, H 3.32, N 1.77.



X-ray Diffraction Studies. Crystals suitable for the X-ray structural determination were mounted on a Bruker SMART APEXII CCD diffractometer and irradiated with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) for data collection. The data were processed using the APEX3 program suite and be seen in Table 1. All structures were solved using an intrinsic phasing method with the SHELXT program (ver. 2014/4–2014/5).⁴³ Refinement on F2 was carried out using full-matrix least-squares with the SHELXL⁴⁴ and expanded using Fourier techniques. All non-hydrogen atoms, except those of disordered solvents, were refined using anisotropic thermal parameters. Hydrogen atoms were assigned to idealized geometric positions and included in structure factor calculations. The SHELX was interfaced with SHELXLE GUI for most of refinement steps.⁴⁵ The pictures of molecules were prepared using Pov-Ray 3.6.⁴⁶ Crystallographic data (CCDC 1894301–1894305) can be obtained

from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00514.

NMR spectra, crystallographic data (PDF)

Accession Codes

CCDC 1894301–1894305 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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