ORGANOMETALLICS

Janus-Type Bis(*malo*NHC) and Its Zwitterionic Gold and Silver Metal Complexes

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Supporting Information

ABSTRACT: A new Janus-type dianionic bis(*malo*NHC) (1) was synthesized and characterized by NMR spectroscopy. The utility of this extended biscarbene for the construction of homobimetallic systems has been demonstrated by its coordination to two coinage metals. The resulting zwitterionic metal complexes of the type $[(Ph_3P)M(1)M-(PPh_3)]$ (M = Au, Ag) have been fully characterized. The X-ray crystallography shows that the new ligand positions the two metal centers at a distance of 24.2 Å, the longest distance reported to date for any related NHC ligand.



INTRODUCTION

Nonchelating multitopic N-heterocyclic carbenes (NHCs) have been a subject of intense interest recently. While still an emerging field, these systems have found tremendous utility as building blocks for a variety of homo- and heterometallic complexes,¹ organic and organometallic polymers,² and supramolecular structures.³ However, despite their versatility, examples of such systems are still rare. Compounds A-G (Chart 1) are the only known neutral ditopic NHCs that display two facially opposed NHC moieties (Janus-type coordination). Due to their rigidity, carbenes A-G have been used as bridging ligands for the synthesis of a variety homobinuclear transition metal complexes (e.g., silver, rhodium, iridium, palladium, platinum, nickel, ruthenium, and iron) $^{1d-f,m,2a-c,g,4}$ or as scaffolds for the preparation of mixedvalence dimetallic species for use as catalysts in tandem reactions (e.g., Ir^{III}/Ir^I, Ir^{III}/Rh^I, and Ir^{III}/Pd^{II}).^{4d,5} Through the pioneering work of Bielawski and co-workers, it has been shown that facially opposed NHCs B and E offer a modular approach to unsaturated homopolymers, alternating polymers, and main-chain organometallic polymers (MCOPs).^{2b,c,g} These NHC-MCOPs exhibit high thermal stability and versatile electronic properties.^{2g} Triazolediylidenes A have also been used for the synthesis of polymeric silver complexes.^{1k,2e} In addition, Hahn and co-workers have recently demonstrated that supramolecular structures can be obtained from linear dinuclear metal complexes of benzobiscarbenes B and selected coligands.^{1c,3b,c,f,6} Due to the high stability of the M-C_{carbene} bond, it is quite possible that such three-dimensional architectures could lead to superior hosts for the encapsulation and catalytic transformation of various substrates with high Chart 1



selectivity and reactivity. It is now clear that the advancement of such NHC-based materials would be facilitated if a rich library

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of bridging scaffolds of various sizes and shapes is available. For example, the synthesis of new supramolecular hosts of controlled size and shapes depends on the availability of new multitopic architectures where each donor moiety functions independently of one another and where the distance between the donor moieties can be easily controlled.

While early efforts have been made to explore the chemistry of neutral multitopic nonchelating NHCs, limited progress has been made in the development of their anionic counterparts. Our group has recently introduced the first stable dianionic Janus-type bis(maloNHC) (H) (Dipp = (2,6-diisopropyl)phenvl).^{1h} This carbene is composed of two linearly opposed NHCs connected by a common *p*-phenylene fragment. In contrast to carbenes A-G, all of which are neutral ligands, carbene H contains two remote anionic functionalities (malonate moieties) within the heterocyclic backbone, which translates to a 2- overall charge of the ligand. By displacement of other anionic ligands (e.g., halides) from various transition metal precursors, this carbene leads to neutral biszwitterionic species, novel architectures that are not accessible from their neutral counterparts. Due to their unique electronic makeup, it is expected that these zwitterionic NHC-metal species would exhibit potentially valuable advantages such as enhanced catalytic activity and solubility relative to the classical cationic metal complexes of the neutral NHCs.

Herein we report the synthesis and characterization of a new bis(maloNHC), **1**. This carbene has the two linearly opposed NHCs bridged by a common *p*-terphenylene fragment. While the bis(NHC) ligand **H** can establish a separation between the two carbene centers of 11.5 Å, the new bis(NHC) **1** displays a significantly larger separation of 20.0 Å. To our knowledge, this nanosized ligand is the longest among all previously reported biscarbenes. Due to its higher conformational mobility over the planar, conjugated ligands **A**–**G**, this rod-like bis(maloNHC) is a promising candidate as building block for a large variety of homo- and heterobimetallic complexes, MCOPs, and supramolecular assemblies. Its coordination to two different coinage metals (gold and silver) is detailed herein.

RESULTS AND DISCUSSION

Five steps were necessary to access the zwitterionic salt precursor 6 (Scheme 1). Initially, diethyl 4-bromophenylmalonate (2) was obtained through a copper-catalyzed α arylation of diethyl malonate with commercially available 1bromo-4-iodobenzene. Hydrolysis of 2 with NaOH in methanol led to 2-(4-bromophenyl)propanedioic acid in 70% yield. Conversion of 3 to its corresponding acyl halide 4, followed by coupling of 4 with N,N'-bis(2,6diisopropylphenyl)formamidine led to the zwitterionic salt 5 in 97% yield. Salt 5 was then utilized as the starting material in a palladium-catalyzed Suzuki coupling reaction with benzene-1,4-diboronic acid to obtain the desired zwitterionic precursor 6 in 83% yield. The ¹H and ¹³C NMR spectra of 6 are consistent with the proposed structure. In the ¹H NMR spectrum, the azolium proton apears at δ 8.18 ppm in CDCl₃, while the ¹³C shift of the NCN carbon appears at δ 147.6 ppm.

The molecular structure of **6** was unambigously determined by single-crystal X-ray diffraction (Figure 1). X-ray quality crystals were obtained by slow evaporation of a saturated toluene solution of **6** at room temperature. The asymmetric unit contains two unique half-molecules. They are closely related, seemingly differing only by a slight twisting. The benzene rings 1 (Scheme 1) are twisted by $32.06(9)^\circ$ relative to





^{*a*}Reaction conditions: (a) diethyl malonate, 5 mol % CuI, 10 mol % 2picolinic acid, Cs₂CO₃, dioxane, room temperature; (b) NaOH, methanol, 0 °C; (c) HCl; (d) PCl₅, dichloromethane, room temperature; (e) $N_{,}N'$ -bis(2,6-diisopropylphenyl)formamidine, dichloromethane, 0 °C; (f) Et₃N, 0 °C, 3 h; (g) 1,4-benzenediboronic acid, K₃PO₄, XPhosPdG₃.



Figure 1. Solid-state molecular structure of 6 with 50% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. Only one of the two unique half-molecules in the asymmetric unit is depicted. Selected bond lengths (Å) and angles (deg): C1-N1 1.316(3), C1-N2 1.312(3), N2-C2 1.457(2), N1-C4 1.467(2), C3-C4 1.417(3), C2-C3 1.424(3), C4-O2 1.224(2), C2-O1 1.225(2), N1-C1-N2 122.19(18).

each pyrimidine ring and by $37.61(10)^{\circ}$ relative to the central benzene ring 2. The central benzene ring 2 is nearly in-plane $(8.73(15)^{\circ})$ with the pyrimidine rings. The average N–C1 distance (1.314 Å) and the N1–C1–N2 angle $(122.19(18)^{\circ})$ determined are similar to those reported for the NHC·H⁺ precursor of carbene H (1.311 Å and 122.0(6)°, respectively).^{1h} The long C–N amidic bonds (N2–C2 1.457(2) Å and N1–C4 1.467(2) Å) are likely a result of the competitive delocalization of the negative charge over the C4–C3–C2 fragment and of the positive charge over the N1–C1–N2 fragment.

Once bisazolium salt **6** was characterized, subsequent efforts were focused on exploring the synthesis and characterization of the target carbene **1**. In an NMR experiment, **6** was dissolved in THF- d_8 and treated with potassium bis(trimethylsilyl)amide (KHMDS). The NMR signals of **6** dissapeared, but no signals for the carbene **1** were observed, an indication of poor solubility of **1** in THF. The same experiment was then attempted in DMSO- d_6 (Scheme 2). The reaction proceeded cleanly to afford the free carbene **1**, which was sufficiently stable to be analyzed by NMR spectroscopy. The ¹³C NMR spectrum of **1** revealed a characteristic signal at δ 242.5 ppm (DMSO- d_6),

Scheme 2. Synthetic Procedures for 1 and 7



a 94.9 ppm downfield shift relative to **6**. All attempts to grow X-ray quality crystals of **1** were not successful.

The corresponding thione 7 was formed by deprotonation of 6 with KHMDS in the presence of excess sulfur (Scheme 2). In the ¹³C NMR spectrum of thione 7, the signal for the N₂CS carbon appears at δ 176.5 ppm (DMSO- d_6), a chemical shift typically seen in this class of compounds. A single crystal of 7 suitable for X-ray crystallographic structure determination was grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of 7. X-ray crystallographic data revealed that the potassium atoms bridge the oxygen atoms of neighboring thione molecules (Figure 2 and the crystal paking



Figure 2. Solid-state molecular structure of 7 with 50% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–S1 1.665(2), C1–N1 1.369(3), C1–N2 1.369(3), N2–C2 1.435(3), N1–C4 1.424(3), C3–C4 1.403(3), C2–C3 1.404(3), C4–O2 1.240(3), C2–O1 1.240(3), N1–C1–N2 115.68(18).

diagram in the Supporting Information), resulting in relatively strong K–O bonds (2.6–2.7 Å). Additionally, the benzene rings 1 are significantly more twisted (54.90(7)° relative to each pyrimidine ring) in this structure than in its zwitterion counterpart **6**. This likely occurs in order to bring the π system of these rings into a bonding arrangement with the potassium ions (K1–C6 = 3.215(2) Å). Rings 1 and 2 are inclined at 30.48(11)° to one another, similar to **6**, but in the case of 7 it is an additive twisting that brings ring 2 into a nearly perpendicular orientation (85.07(8)°) relative to the pyrimidine rings.

To investigate the nucleophilic behavior of 1, homobimetallic complexes of gold and silver were targeted. The *in situ* generated carbene 1 was treated with the phosphine-stabilized precursors (Ph_3PAuCl or $Ph_3PAgOTf$) to yield the corresponding complexes 8 and 9 in 71% and 72% yield, respectively (Scheme 3). The complexes are air stable since they can be purified by column chromatography on silica gel. The identity of these complexes was confirmed by ¹H and ¹³C NMR spectroscopy, as well as elemental analysis. The gold complex 8





^{*a*}Reaction conditions: (a) KHMDS, THF, room temperature; (b) for 8: PPh₃AuCl, THF, room temperature; for 9: PPh₃AgOTf, THF, room temperature.

exhibits its carbene carbon resonance as a doublet at δ 202.1 ppm (J_{P-C} = 119.8 Hz), comparable to that displayed by the corresponding gold complex of H (δ 199.8 ppm, J_{P-C} = 120.1 Hz).^{1h} The carbene signal of 9 in the ¹³C spectrum was not detected, a result of much lower solubility of 9 and the expected multiplicity of the resonance arising from coupling with not only the phosphorus atom of PPh₃ but also the two isotopes of silver (¹⁰⁷Ag and ¹⁰⁹Ag).

Single crystals of 8 and 9 suitable for X-ray crystallographic structure determinations were grown by slow evaporation of saturated solutions of 8 and 9 in a mixture of dichloromethane/ toluene. Both structures are isostructural (Figures 3 and 4), and



Figure 3. Solid-state molecular structure of **8** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1-C1 2.057(5), Au1-P1 2.2872(13), C1-N1 1.337(6), C1-N2 1.339(6), N2-C2 1.453(6), N1-C4 1.450(6), C3-C4 1.408(7), C2-C3 1.404(7), C4-O2 1.232(6), C2-O1 1.220(7), P1-Au1-C1 171.21(13), N1-C1-N2 116.6(4).



Figure 4. Solid-state molecular structure of 9 with 50% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1-C1 2.124(4), Ag1-P1 2.3577(11), C1-N1 1.335(5), C1-N2 1.336(5), N2-C2 1.440(5), N1-C4 1.446(5), C3-C4 1.415(6), C2-C3 1.417(6), C4-O2 1.231(5), C2-O1 1.229(6), P1-Ag1-C1 170.03(11), N1-C1-N2 117.2(4).

they crystallize in the same monoclinic space group C2/c. The packing diagrams show large voids that are occupied by toluene molecules. In both cases, only half of each molecule is unique. The metal centers are coordinated in a linear fashion by the carbene moieties and PPh₃ (C1-Au1-P1 = 171.21(13)° and C1-Ag1-P1 = 170.03(11)°). As expected, the N1-C1-N2 angles of 8 and 9 (116.6(4)° and 117.2(4)°, respectively) are smaller than the corresponding angle of the zwitterionic salt 6

(122.19(18)°). The Au–C1 and Ag–C1 bond distances are 2.057(5) and 2.124(4) Å, respectively, and they are comparable to those reported for the corresponding metal complexes of H (Au: 2.027(7); Ag: 2.110(6) Å).^{1h} The arrangement of the central ring structure in 8 and 9 closely resembles that of 6. The benzene rings 1 are twisted by $35.28(14)^\circ$ relative to each pyrimidine ring in 8 and $35.21(12)^\circ$ in 9. Ring 2 is inclined at 7.67(4)° and 7.59(3)° relative to the pyrimidine rings in 8 and 9, respectively. Furthermore, the new ligand places the two metal centers at a distance of 24.2 Å, about 8.5 Å longer than its analogue, carbene H. The longest Janus-type carbene reported previously in the literature, carbene G, displays an intramolecular distance between the two carbene centers of 18.4 Å and a gold–gold distance of 22.4 Å.¹ⁱ

CONCLUSIONS

In summary, this paper describes the synthesis and characterization of a new dianionic bis(maloNHC), 1. The corresponding thione was generated by the reaction of 1 with an excess of sulfur. The utility of this carbene as a bridging ligand in organometallic chemistry has been demonstrated by its incorporation in two new dinuclear gold and silver complexes (8 and 9). These zwitterionic complexes have been fully characterized by spectroscopic techniques and X-ray crystallography. They exhibit a remarkably long metal-to-metal throughspace distance of 24.2 Å, to our knowledge the longest distance reported so far for a Janus-type bis(NHC) ligand. With its unique topological properties, this system has the potential to serve as building blocks for the preparation of novel metalorganic frameworks such as supramolecular cages and organometallic polymers, systems not accessible with the current arsenal of neutral Janus-type bis(NHC)s. Further studies aimed at the construction of such supramolecular systems are under way in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reactions, unless otherwise noted, were performed using standard Schlenk techniques under an atmosphere of argon or in a nitrogen-filled gloxebox. Glassware was dried at 180 °C in an oven for at least 12 h prior to use. Reagents were purchased from commercial sources and used as supplied. THF was distilled from sodium/benzophenone. Dry dichloromethane (DCM) was purchased from Aldrich and used as received. N,N'-Bis(2,6-diisopropylphenyl)formamidine was prepared following known methods.⁷ Column chromatography was performed using the solvent systems indicated on silica gel (63–200 μ m) or basic alumina (Act.1 50–200 μ m). ¹H, ¹³C, and ³¹P NMR spectra were recorded using a Bruker DPX 300 MHz spectrometer. Chemical shifts are reported in ppm and are referenced to internal SiMe₄ (¹H and ¹³C) or external H₃PO₄ (³¹P). Solid-state infrared spectra of 5-9 were recorded on a PerkinElmer Frontier FT-IR/NIR spectrometer. Elemental analyses were performed at Atlantic Microlab (Norcross, GA, USA). Single-crystal X-ray diffraction measurements were performed using a Bruker D8 Venture diffractometer with an Incoatec microfocus source and a Photon 100 CMOS detector. Diffraction data for compounds 6-9 were collected under nitrogen at 100 K using Mo K α (λ = 0.71073 Å) radiation. The purity of all new compounds was determined by elemental analysis, except for compounds 1 and 3, for which the purity was inferred by ¹H and ¹³C NMR spectroscopy.

Synthesis of 2. In the drybox, a 250 mL oven-dried pressure flask was charged with 1-bromo-4-iodobenzene (9.00 g, 31.8 mmol), copper iodide (0.303 g, 1.59 mmol), 2-picolinic acid (0.439 g, 3.56 mmol), and cesium carbonate (31.24 g, 95.86 mmol). Anhydrous 1,4-dioxane (31.9 mL) was added to the reaction flask, followed by distilled diethyl malonate (4.85 mL, 31.8 mmol). The reaction was heated to 94 °C for

65 h. The reaction mixture was allowed to cool, and 25 mL of a saturated aqueous solution of ammonium chloride was added. The reaction mixture was extracted with ethyl acetate. The organic layer was washed with deionized water, dried over sodium sulfate, and filtered. The solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica, 4:7 hexanes/DCM) to afford **2** as a colorless oil in 70% yield (7.0 g). The NMR spectra are in accord with the previously published data.⁸ ¹H NMR (CDCl₃, 300 MHz): δ 7.50 (d, ³*J* = 8.4 Hz, 2H, Ar-CH), 7.29 (d, ³*J* = 8.4 Hz, 2H, Ar-CH), 4.56 (s, 1H, CH(CO₂Et)₂), 4.22 (m, 4H, CH₂CH₃), 1.26 (t, ³*J* = 7.1 Hz, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 167.7 (C-O), 131.8, 131.7, 131.0, 122.5, 61.9, 57.3, 14.0. Anal. Calcd for C₁₃H₁₅O₄Br: C, 49.54; H, 4.80. Found: C, 49.64; H, 4.88.

Synthesis of 3. Diethyl 4-bromophenylmalonate (2.16 g, 6.85 mmol) was dissolved in methanol (11.6 mL), and the solution was cooled to 0 $^\circ$ C. An ice cold solution of sodium hydroxide (0.81 g, 20.3 mmol) in deionized water (11.6 mL) was added dropwise to the stirring solution of diethyl 4-bromophenylmalonate. The reaction mixture was stirred for 2 h at room temperature. The solvent was removed, and the remaining aqueous layer was washed with diethyl ether and acidified to pH 1 by dropwise addition of concentrated HCl at 0 °C. The product was extracted with ethyl acetate. The organic layer was washed with acidified brine and dried over sodium sulfate. The solvent was removed in vacuo. The resulting white solid was purified by trituration with dichloromethane (5 times) and pentane (2 times) to afford the title compound 3 as a white solid (1.25 g, 70% vield). The product contains trace amounts of 4-bromophenylacetic acid, and it decarboxylates slowly in solution. ¹H NMR (DMSO-d₆, 300 MHz): δ 13.04 (s, COOH) 7.56 (d, ³J = 8.4 Hz, 2H, Ar-CH), 7.35 (d, ${}^{3}J = 8.4$ Hz, 2H, Ar-CH), 4.71 (s, 1H, CH(CO₂H)₂).

Synthesis of 5. A mixture of the carboxylic acid 3 (0.050 g, 0.19 mmol) and PCl₅ (0.082 g, 0.39 mmol) in anhydrous DCM (1 mL) was stirred at room temperature for 2 h under argon. The reaction mixture was then concentrated to dryness under reduced pressure. To the resulting crude acyl halide 4 were added N,N'-bis(2,6diisopropylphenyl)formamidine (0.104 g, 0.285 mmol) and 2 mL of anhydrous DCM at 0 °C. The reaction mixture was allowed to stir at 0 $^\circ \mathrm{C}$ for 30 min. Et_3N (0.054 mL, 0.39 mmol) was added gradually over the course of 10 min. The mixture was stirred for 3 h at 0 °C, and the volatiles were removed in vacuo. The resulting deep yellow solid was triturated with water, filtered, and purified by column chromatography (silica, DCM) to afford the title compound 5 as a bright yellow solid (0.11 g, 97% yield); mp >250 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.18 (s, 1H, NCHN), 7.93 (d, ${}^{3}J$ = 8.6 Hz, 2H, Ar-CH), 7.48 (d, ${}^{3}J$ = 7.3 Hz, 2H, Ar-CH), 7.44 (t, ${}^{3}J$ = 8.6 Hz, 2H, Ar-CH), 7.29 (d, ${}^{3}J$ = 7.8 Hz, 4H, Ar-CH), 2.85 (sept, ${}^{3}J$ = 6.6 Hz, 4H, CH(CH₃)₂), 1.31 (d, ${}^{3}J$ = 6.7 Hz, 12H, CH₃), 1.22 (d, ${}^{3}J$ = 6.8 Hz, 12H, CH₃). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 75.5 MHz): δ 158.5 (C-O), 147.9 (NCHN), 145.8, 133.2, 132.0, 131.9, 131.2, 130.5, 124.6, 119.5, 97.7 (C-CO), 29.4 $(CH(CH_3)_2)$, 24.3 (CH_3) . ¹³C{¹H} NMR (THF- d_8 , 75.5 MHz): δ 159.7 (C-O), 152.4 (NCHN), 147.6, 136.3, 134.5, 133.3, 131.7, 130.9, 125.5, 119.3, 97.0 (C-CO), 30.7 (CH(CH₃)₂), 24.9 (CH₃), 24.8 (CH₃). FT-IR (solid ATR): 3051, 2965, 2925, 2870, 1663 (CO), 1598, 1486, 1460, 1322, 1262, 1056, 1005, 932, 807, 763 cm⁻¹. Anal. Calcd for C₃₄H₃₉O₂N₂Br: C, 69.50; H, 6.69; N, 4.77. Found: C, 69.29; H, 6.65; N, 4.75.

Synthesis of 6. Zwitterion 5 (0.50 g, 0.85 mmol), 1,4benzenediboronic acid (0.071 g, 0.43 mmol), K_3PO_4 (0.181 g, 0.853 mmol), and XPhosPdG₃ (0.067 g, 0.078 mmol) were added to a pressure tube under inert conditions. Anhydrous 1,4-dioxane (8 mL) was added to the reaction flask under argon. Degassed water (1.6 mL) was added, and the reaction was allowed to stir for 15 h at 60 °C. The volatiles were removed *in vacuo*, and the resulting yellow solid was purified by column chromatography (silica, gradient of 1:3 hexanes/EtOAc, then 4:3 hexanes/EtOAc) to yield the title compound **6** in 83% yield (0.38 g); mp >250 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.18 (s, 2H, NCHN), 8.14 (d, ³J = 8.6 Hz, 4H, Ar-CH), 7.66 (s, 4H, Ar-CH), 7.61 (d, ³J = 8.6 Hz, 4H, Ar-CH), 7.47 (t, ³J = 7.7 Hz, 4H, Ar-CH), 7.30 (d, ³J = 7.7 Hz, 8H, Ar-CH), 2.90 (sept, ³J = 6.71 Hz, 8H, CH(CH₃)₂), 1.33 (d, ³J = 6.7 Hz, 24H, CH₃), 1.23 (d, ³J = 6.8 Hz, 24H, CH₃). ¹H NMR (DMSO- d_6 , 300 MHz): δ 9,90 (s, 2H, NCHN), 7.87 (d, ³*J* = 7.94 Hz, 4H, Ar-CH), 7.75 (s, 4H, Ar-CH), 7.65 (d, ³*J* = 8.1 Hz, 4H, Ar-CH), 7.51 (t, ³*J* = 7.5 Hz, 4H, Ar-CH), 7.38 (d, ³*J* = 7.6 Hz, 8H, Ar-CH), 2.76 (sept, ³*J* = 6.5 Hz, 8H, CH(CH₃)₂), 1.21 (d, ³*J* = 3.2 Hz, 48H, CH₃). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 158.7 (C-O), 147.6 (NCHN), 145.9, 140.3, 138.4, 133.2, 132.2, 131.1, 130.6, 127.5, 126.2, 124.6, 98.5 (C-CO), 29.4 (CH(CH₃)₂), 24.4 (CH₃). FT-IR (solid ATR): 2960, 2922, 2868, 1667 (CO), 1599, 1466, 1325, 1057, 1033, 1006, 821, 812, 805, 784, 764, 670 cm⁻¹. Anal. Calcd for C₇₄H₈₂O₄N₄: C, 81.43; H, 7.57; N, 5.13. Found: C, 81.15; H, 7.63; N, 5.04.

Synthesis of 1. A solution of KHDMS (0.021 g, 0.11 mmol) in anhydrous THF (2 mL) was slowly added to a stirring suspension of 6 (0.026 g, 0.024 mmol) in anhydrous THF (3 mL). The carbene precipitated out of solution. The reaction mixture was allowed to stir for 45 min. The solvent was decanted, and the remaining solid was washed with THF. The product was dried in vacuo to yield 0.021 g of 1 (76% yield). NMR experiment: In the drybox, precursor 6 (0.026 g, 0.024 mmol) was dissolved in about 1 mL of DMSO-d₆, and KHDMS (0.014 g, 0.070 mmol) was added directly to this NMR tube. The ¹³C and ¹H NMR spectra were recorded, and they supported the formation of the carbene. ¹H NMR (DMSO- d_{6} , 300 MHz): δ 8.06 (d, ³*J* = 8.1 Hz, 4H, Ar-CH), 7.68 (s, 4H, Ar-CH), 7.48 (d, ³*J* = 8.1 Hz, 4H, Ar-CH), 7.24 (t, ${}^{3}J$ = 6.5 Hz, 4H, Ar-CH), 7.15 (d, ${}^{3}J$ = 7.0 Hz, 8H, Ar-CH), 3.04 (sept. ${}^{3}J$ = 6.5 Hz, 8H, CH(CH₃)₂), 1.15 (d, ${}^{3}J$ = 6.5 Hz, 24H, CH₃), 1.09 (d, ${}^{3}J$ = 6.5 Hz, 24H, CH₃). ${}^{13}C{}^{1}H$ NMR (DMSO-d₆, 75.5 MHz): δ 242.5 (NCN), 160.8 (C-O), 144.9, 141.6, 138.9, 138.2, 133.6, 130.3, 126.5, 126.4, 124.0, 122.5, 92.9 (C-CO), 27.8 (CH(CH₃)₂), 23.8 (CH₃), 23.3 (CH₃).

Synthesis of 7. A solution of KHDMS (0.033 g, 0.17 mmol) in anhydrous THF (1 mL) was slowly added to a stirring suspension of 6 (0.050 g, 0.046 mmol) in anhydrous THF (4 mL). To the in situ generated carbene was added excess sulfur (0.027 g, 0.84 mmol). The reaction mixture was allowed to stir for 12 h at room temperature. The solvent was removed in vacuo, and the crude product was dissolved in acetonitrile and filtered through Celite to remove the excess sulfur. The pale orange residue was purified by trituration with ether, hexanes, and hot toluene. Thione 7 was obtained as an off-white solid in 69% yield (0.039 g). ¹H NMR (DMSO- d_{6} , 300 MHz): δ 7.97 (d, ³J = 8.2 Hz, 4H, Ar-CH), 7.68 (s, 4H, Ar-CH), 7.49 (d, ${}^{3}J$ = 8.2 Hz, 4H, Ar-CH), 7.23 (t, ${}^{3}J$ = 7.3 Hz, 4H, Ar-CH), 7.14 (d, ${}^{3}J$ = 7.3 Hz, 8H, Ar-CH), 2.90 (sept, ${}^{3}J$ = 6.5 Hz, 8H, CH(CH₃)₂), 1.20 (d, ${}^{3}J$ = 6.5 Hz, 24H, CH_3), 1.15 (d, ${}^{3}J$ = 6.5 Hz, 24H, CH_3). ${}^{13}C{}^{1}H$ NMR (DMSOd₆, 75.5 MHz): δ 176.5 (NCN), 161.3 (C-O), 145.1, 138.9, 137.9, 137.7, 133.9, 130.1, 127.2, 126.5, 124.2, 122.9, 90.4 (C-CO), 28.6 (CH(CH₃)₂), 24.3 (CH₃), 23.1 (CH₃). FT-IR (solid ATR): 3393, 2963, 2869, 1699, 1579 (CO), 1395, 1302, 1120, 1055, 937, 804, 747, 670 cm $^{-1}$ Anal. Calcd for $C_{74}H_{80}O_4N_4S_2K_2\cdot 1.5CH_2Cl_2:$ C, 66.72; H, 6.15; N, 4.12. Found: C, 66.74; H, 6.43; N, 4.17.

Synthesis of 8. A solution of KHDMS (0.081 g, 0.41 mmol) in anhydrous THF (1 mL) was slowly added to a stirring suspension of 6 (0.074 g, 0.068 mmol) in anhydrous THF (5 mL). AuCl(SMe₂) (0.086 g, 0.29 mmol), PPh₃ (0.079 g, 0.30 mmol), and anhydrous THF (2 mL) were stirred in a separate vial to ensure the precoordination of PPh₃ to the gold center. After 30 min, the latter solution was added dropwise to the carbene suspension. The reaction mixture was allowed to stir for 12 h. THF was removed in vacuo. The resulting solid was dissolved in DCM and filtered. Hexane was then added to precipitate the product. The crude product was purified by column chromatography (silica, 1:30 MeOH/DCM) to afford the gold complex 8 as a yellow solid (0.097 g, 71% yield). ¹H NMR (CDCl₃, 300 MHz): δ 8.24 (d, 4H, J = 8.5 Hz, Ar-CH), 7.63 (s, 4H, Ar-CH), 7.55 (d, 4H, J = 8.6 Hz, Ar-CH), 7.46 (td, 6H, ${}^{3}J_{CC} = 7.4$ Hz, $J_{CP} = 1.8$ Hz, Ar-CH), 7.28–7.42 (m, 16H, CH_{PPh3} and Ar-CH), 7.21 (d, ${}^{3}J =$ 7.7 Hz, 8H, Ar-CH), 6.86 (dd, 12H, ${}^{3}J_{CC} =$ 6.8 Hz, $J_{CP} =$ 12.9 Hz, CH_{PPh3}), 3.04 (sept. ${}^{3}J =$ 6.7 Hz, 8H, CH(CH₃)₂), 1.27 (d, ${}^{3}J =$ 6.8 Hz, 24H, CH₃), 1.09 (d, ${}^{3}J =$ 6.8 Hz, 24H, CH₃). ${}^{13}C{}^{14}$ NMR (CD₂Cl₂) 75.5 MHz): δ 202.1 (d, J = 119.8 Hz, NCN), 161.3 (d, J_{CP} = 3.7 Hz), 147.1, 140.4, 138.7, 137.4, 135.9, 134.4 (d, $J_{CP} = 13.9$ Hz), 132.4 (d, $J_{\rm CP}$ = 11.1 Hz), 131.4, 129.6 (d, $J_{\rm CP}$ = 11.6 Hz), 129.0, 128.3, 127.6,

125.9, 124.4, 97.1 (C-CO), 29.4 $(CH(CH_3)_2)$, 24.6 (CH_3) , 24.3 (CH_3) . ³¹P NMR (CDCl₃, 121.49 MHz): δ 39.2. FT-IR (solid ATR): 3448, 3052, 3027, 2959, 2922, 2867, 2162, 1615 (CO), 1481, 1436, 1383, 1328, 1274, 1101, 826, 789, 745, 711, 692 cm⁻¹. Anal. Calcd for C₁₁₀H₁₁₀O₄N₄Au₂P₂: C, 65.80; H, 5.52; N, 2.79. Found: C, 65.78; H, 5.71; N, 2.79.

Synthesis of 9. A solution of KHDMS (0.100 g, 0.501 mmol) in anhydrous THF (2 mL) was slowly added to a stirring suspension of 6 (0.100 g, 0.092 mmol) in anhydrous THF (8 mL). In a separate vial, PPh₃ (0.099 g, 0.38 mmol) and AgOTf (0.098 g, 0.38 mmol) were stirred in anhydrous THF (2 mL). After 30 min, the latter solution was added dropwise to the carbene suspension. The reaction mixture was allowed to stir for 12 h, and the volatiles were removed in vacuo. The product was dissolved in DCM and precipitated with diethyl ether. The solid was then triturated with hexane in order to remove the excess PPh₃. The crude product was purified by column chromatography (silica, 1:30 MeOH/DCM) to afford the yellow silver complex 9 in 72% yield (0.12 g). ¹H NMR (CDCl₃, 300 MHz): δ 8.25 (d, 4H, J = 8.5 Hz, Ar-CH), 7.64 (s, 4H, Ar-CH), 7.56 (d, 4H, J = 8.4 Hz, Ar-CH), 7.46 (td, 6H, ${}^{3}J_{CC}$ = 7.6 Hz, J_{CP} = 1.8 Hz, Ar-CH), 7.30–7.40 (m, 16H, CH_{PPh3} and Ar-CH), 7.22 (d, ³J = 7.7 Hz, 8H, Ar-CH), 6.86 (dd, 12H, ${}^{3}J_{CC} = 7.3$ Hz, $J_{CP} = 12.5$ Hz, CH_{PPh3}), 3.11 (sept, ${}^{3}J = 6.7$ Hz, 8H, $CH(CH_3)_2$, 1.29 (d, ${}^{3}J$ = 6.8 Hz, 24H, CH₃), 1.08 (d, ${}^{3}J$ = 6.8 Hz, 24H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ C2 not detected, 161.4 (d, J = 6.26 Hz), 146.9, 140.7 (d, J = 2.3 Hz), 140.4, 137.2, 136.2, 134.1 (d, J = 15.9 Hz), 132.1, 131.5, 129.7 (d, J = 10.8 Hz), 129.2, 128.6, 127.6, 125.9, 124.6, 97.0 (C-CO), 29.3 (CH(CH₃)₂), 24.7 (CH₃), 24.6 (CH₃). ³¹P NMR (CDCl₃, 121.49 MHz): δ 18.3 (d + d, $J({}^{31}P-{}^{109}Ag) = 538.8 \text{ Hz}$, $J({}^{31}P-{}^{107}Ag) = 466.8 \text{ Hz}$). FT-IR (solid ATR): 3055, 3030, 2959, 2922, 2867, 1610 (CO), 1480, 1436, 1382, 1327, 1275, 1098, 843, 824, 787, 743, 692 cm⁻¹. Anal. Calcd for C₁₁₀H₁₁₀O₄N₄Ag₂P₂: C, 72.21; H, 6.06; N, 3.06. Found: C, 72.09; H, 6.22; N, 2.94.

X-ray Crystallography. Single-crystal X-ray diffraction data were collected using a Bruker D8 Venture diffractometer with Mo K α (λ = 0.71073 Å) radiation from an Incoatec microfocus source and a Photon 100 CMOS detector. Data processing and scaling corrections were performed using the Apex3 software suite (SAINT, SADABS routines).⁹ Evaluation of the systematic absences led to unambiguous space group determinations, and the structures were subsequently solved by intrinsic phasic (SHELXT) and then refined by full-matrix least-squares on F^2 (SHELXL) using the SHELXTL software suite.¹⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were placed geometrically using appropriate riding models. During the structure refinements, the formula units of compounds 6-9 were found to contain several solvent molecules. In the case of compound 6, three toluene molecules were modeled directly from the difference map, and additional toluene molecules were found to be highly disordered in remaining structural voids. The latter disordered solvent molecules were modeled using the SQUEEZE algorithm of PLATON (286 total electrons present in 965 Å³ of voids, corresponding to 1.4 C_7H_8 per formula unit).¹¹ In 7, one acetonitrile solvent molecule per formula unit was found to be coordinated to the potassium ion (half-occupancy based on evaluation of the ADPs), and an additional two acetonitrile molecules were disordered over several arrangements in the structural voids and modeled using SQUEEZE (80 total electrons present in 610 Å³ of voids). Compounds 8 and 9 both contained one toluene molecule per formula unit, and these were modeled from the difference map. Data from the structure refinements are included in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00206.

NMR spectra of compounds 2, 3, 5–9 and crystallographic information on 6–9 (PDF) X-ray crystallographic data for compounds 6–9 (CIF) Optimized Cartesian coordinates (XYZ)

- (XYZ)
- (XYZ)
- (XYZ)

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Notes

The authors declare no competing financial interest.

Crystallographic details were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The reference numbers are 1534519 ($6 \cdot x C_7 H_8$), 1534520 ($7 \cdot 3 C_2 H_3 N$), 1534521 ($8 \cdot C_7 H_8$), and 1534522 ($9 \cdot C_7 H_8$).

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