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Synthetic and Structural Studies of Silver(I)- and Gold(I)-Containing N-Heterocyclic Carbene Metallacrown Ethers

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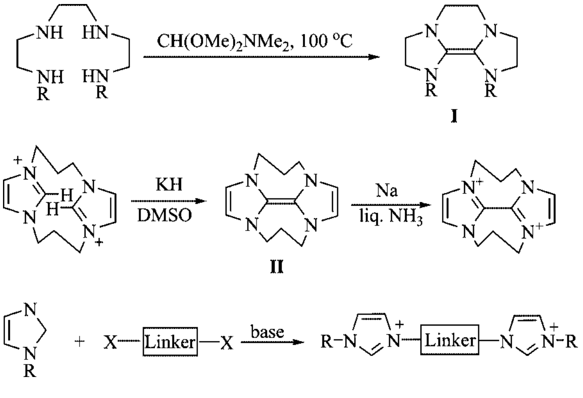
The ligands bis(imidazolium) hexafluorophosphate [RHimy-$(CH_2OCH_2)_n$-HimyR]$[PF_6]_2$ [Himy = $–C_3N_2H_3–$, imidazolium; R = 1-naphthylmethyl, n = 2 (**1a**), 3 (**2a**); R = 9-anthracenylmethyl, n = 2 (**1b**), 3 (**2b**)] with a highly flexible polyether chain were easily prepared by the reaction of substituted imidazole with the corresponding polyglycol diiodide, followed by exchange of the anions with PF_6^-. Ligands **1a**,**b** and **2a**,**b** react with Ag_2O to give monometallic Ag^I-containing N-heterocyclic carbene (NHC) metallacrown ethers **3a**,**b** and **4a**,**b** with a long and highly flexible bridging chain $(CH_2OCH_2)_n$ (n = 2, 3) between the two imidazolium units. Complexes **3a**,**b** and **4a**,**b** react with [Au(SMe$_2$)Cl] in a transmetalation reaction to give Au^I analogues **5a**,**b** and **6a**,**b**. Complexes **3a**,**b**–**6a**,**b** are novel examples of a metallacrown ether with NHCs. In contrast to the use of a high-dilution technique in the preparation of polyether chain phosphane-containing metallacrown ethers, the new *trans*-metallacrown ethers can be prepared in concentrated solution. The structures of **3a**–**6a** were confirmed by X-ray diffraction determination.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted considerable interest[1–3] since Arduengo et al. reported the first stable, crystalline N-heterocyclic carbene in 1991.[4a] A variety of N-heterocyclic carbene transition metal complexes have been synthesized and isolated and some of them have been successfully applied as homogeneous catalysts.[4–6] Nolan et al. have concluded from structural and thermochemical studies that these NHCs exhibit a similar σ-donor and low π-acceptor ability as phosphanes in metal coordination chemistry, and they have been demonstrated to have additional advantages to the widely used phosphane ligands.[7,8]

Lappert et al. have investigated a type of $(CH_2)_n$-bridged Arduengo carbene analogue, namely tetraaminoalkenes (enetetramines **I**),[9–11] in detail and have prepared the NHC Mo and Rh complexes of these enetetramines.[12–14] Later, Chen found that the bond-dissociation enthalpy of these enetetramines is only slightly larger than zero by thermochemical studies, thus indicating the existence of a very weak C=C bond in the formal dimers of singlet carbenes **II**.[15] However, a more convenient procedure to synthesize a variably bridging bis(imidazolium) salt for the preparation of NHC–metal complexes has been developed in which a dihalide and two molecules of *N*-substituted imidazole are used. The bridging spacer linking the two imidazolium units includes methylene, ethylene,[16,17] *o*,*p*-phenylenebis(methylene),[18] pyridinediyl,[19,20] an optically active 1,2-cyclohexyldiamine-derived linker,[21] and a pyridine-2,6-diylbis(methylene) linker (Scheme 1).[22–26] However, bis(imidazolium) salts with a flexible bridge have seldom been investigated. In 2003, Cavell et al. prepared an oxoether-bridged bis(imidazolium) ligand and its Ag^I-containing dimetallacrown rings of smaller size;[27] and we are interested in this type of compounds. In this paper we describe the preparation of the much longer oxoether-bridged bis(imidazolium) ligands and our studies on the structure of their NHC-containing macrocyclic metallacrown complexes.



Scheme 1.

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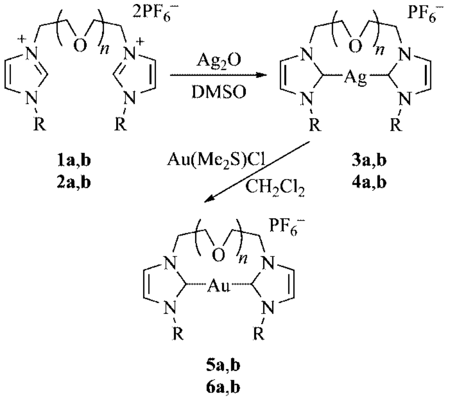
Polyether-chain phosphane-containing metallacrown ethers have been widely studied.[28–30] Because they contain both a metal atom and a polyether chain, they can act as a catalyst and a phase-transfer reagent. Due to their structural similarity with these complexes, we have strong interest in investigating NHC–metal analogues containing a polyether chain. A recent investigation showed that phosphane- and NHC-coordinated cationic Ag^I and Au^I complexes are highly efficient catalysts for many organic reactions.[31,32] For example, Herrmann has successfully used NHC–Au^I complexes as catalysts in the addition of water to 3-hexyne.[33] Here we report the synthetic and structural studies of new NHC–Ag^I (**3a**,**b** and **4a**,**b**) and NHC–Au^I (**5a**,**b** and **6ab**) cationic metallacrown ethers.[34,27]



Scheme 3. Synthesis of Ag^I- and Au^I-containing N-heterocyclic carbene metallacrown ethers.

Results and Discussions

The carbene precursors [RHimy-$(CH_2OCH_2)_n$-imyHR]-$[I]_2$ (R = 1-naphthylmethyl, 9-anthracenylmethyl, n = 2, 3) were prepared by reaction of 1-(1-naphthylmethyl)- or 1-(9-anthracenylmethyl)imidazole with the corresponding diiodide $ICH_2(CH_2OCH_2)_nCH_2I$[35,36] in THF. The compounds [RHimy-$(CH_2OCH_2)_n$-imyHR]$[PF_6]_2$ (**1a**,**b** and **2a**,**b**) were formed by an ion-exchange reaction with NH_4PF_6 (Scheme 2). In the ^1H NMR spectra of **1a**,**b** and **2a**,**b** the imidazolium proton signals (NCHN) appear at δ = 9.18, 9.20, 8.87, and 8.90 ppm, which is consistent with the chemical shifts of known imidazolium salts.[37] The disappearance of the signals of the imidazolium protons shows the formation of the expected NHC ligands.

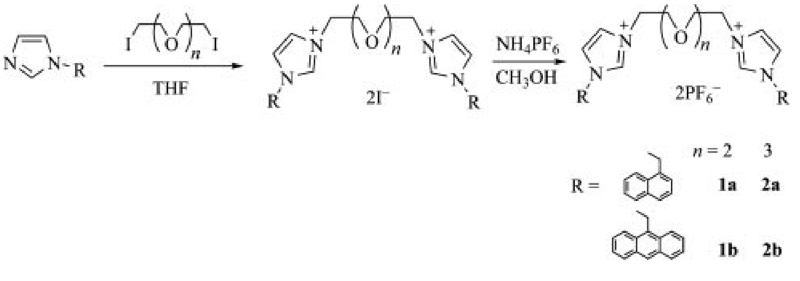
The reaction of silver(I) oxide with **1a**,**b** or **2a**,**b** in dimethyl sulfoxide in the dark afforded **3a**,**b** or **4a**,**b**, respectively, as solids. Compounds **3a**,**b** and **4a**,**b** are light-sensitive in solution, but light-stable as solids (Scheme 3). They are soluble in dimethyl sulfoxide, acetonitrile, acetone, and dichloromethane and insoluble in diethyl ether and petroleum ether. They are slightly soluble in methanol and tetrahydrofuran.

Transmetalation has proved to be a promising procedure to obtain NHC–metal complexes.[18,25,38–40] The Au analogs **5a**,**b** and **6a**,**b** were therefore formed by a transmetalation reaction between $[Au(SMe_2)Cl]$ and the Ag-containing carbenes **3a**,**b** and **4a**,**b**, respectively (Scheme 3). The Au complexes are stable to air and moisture and their solubilities are similar to **3a**,**b** and **4a**,**b**. Compounds **3a**,**b**–**6a**,**b** were characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy, and some of them were subjected to a single-crystal X-ray structural analysis.

In the ^{13}C NMR spectra, the chemical shifts of the carbene carbon atoms of the Au–NHC complexes appear at $\delta \approx 183$ ppm and those of the Ag complex **4a** at δ = 208 ppm. However, the resonances for the carbene carbon atoms of the Ag complexes **3a**, **3b**, and **4b** were not observed. This has precedent in the literature and is thought to be due to the fluxional behavior of the NHC complexes in solution.[27,41]

In contrast to high-dilution syntheses of polyether-chain diphosphane metallacrown ethers, it is worthy to note that a high yield of NHC metallacrown ethers **3a**,**b**–**6a**,**b** can be obtained in concentrated solutions. This phenomenon might be due to the different reactivity of the Ag sources. The reaction of a diphosphane with Ag^+ in dilute solution gives a metallacrown ether, but in concentrated solution it might give a polymer; this is controlled by entropy effects. In the reactions of bis(imidazolium) ligands with Ag_2O, however, NHC metallacrown ethers can be formed both in concentrated or in dilute solution; a template effect of Ag_2O could be responsible for this reaction.

Crystals of **3a** and **4a** suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a solution of the complex in CH_3CN and chlorobenzene (3:1). Details of the solid-state structure determination are given in the Experimental Section, and selected bond lengths and angles are listed in Table 1. The X-ray structural analysis of **3a** shows that the central metal atoms have a linear, two-coordinate structure and the bis(carbene) is a didentate chelate ligand



Scheme 2. Synthesis of bis(imidazolium hexafluorophosphate)s.

Table 1. Selected bond lengths [Å] and angles [°] for **3a**–**6a**.

3a		**4a**		**5a**		**6a**	
Ag(1)–C(2)	2.101(3)	Ag(1)–C(12)	2.066(7)	Au(1)–C(21)	2.005(17)	Au(1)–C(25)	2.0283(12)
Ag(1)–C(1)	2.104(3)	Ag(1)–C(1)	2.078(7)	Au(1)–C(1)	2.038(14)	Au(1)–C(14)	2.0370(12)
N(1)–C(1)	1.360(4)	N(1)–C(1)	1.350(9)	N(1)–C(1)	1.313(18)	N(1)–C(14)	1.3336(8)
N(2)–C(1)	1.351(4)	N(1)–C(2)	1.368(10)	N(1)–C(2)	1.438(18)	N(2)–C(14)	1.3571(8)
C(2)–Ag(1)–C(1)	170.63(12)	C(12)–Ag(1)–C(1)	178.3(3)	C(21)–Au(1)–C(1)	177.1(7)	C(25)–Au(1)–C(14)	176.813(17)
N(1)–C(1)–Ag(1)	122.5(2)	N(1)–C(1)–Ag(1)	129.0(5)	N(1)–C(1)–Au(1)	126.9(13)	N(1)–C(14)–Au(1)	125.83(5)
N(2)–C(1)–Ag(1)	133.2(3)	N(2)–C(1)–Ag(1)	126.3(5)	N(2)–C(1)–Au(1)	126.4(12)	N(2)–C(14)–Au(1)	127.01(3)
N(3)–C(2)–Ag(1)	127.3(2)	N(3)–C(12)–Ag(1)	129.3(5)	N(3)–C(21)–Au(1)	129.8(10)	N(3)–C(25)–Au(1)	127.15(3)

with a long flexible linkage (Figure 1). As shown in Figure 1, the cation has a typical linear conformation with a C(2)–Ag(1)–C(1) angle of 170.63(12)°. The Ag(1)–C(1) and Ag(1)–C(2) bond lengths are 2.104(3) Å and 2.101(3) Å, respectively, slightly longer than those found by Lin (2.073 and 2.052 Å) and Danopoulos (2.06–2.1 Å).[38,46] The dihedral angle of the two imidazolium rings is 118.4°.

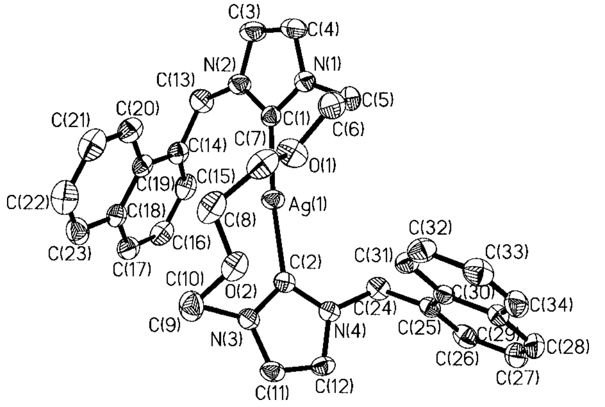


Figure 1. Molecular structure and atom numbering of the cation in **3a**. Hydrogen atoms, anions, and solvent molecules have been omitted for clarity. Thermal ellipsoids at 35% probability. Selected bond lengths [Å] and angles [°]: Ag(1)–C(1) 2.104(3), Ag(1)–C(2) 2.101(3); C(2)–Ag(1)–C(1) 170.63(12).

The C(12)–Ag(1)–C(1) bond angle in complex **4a** is 178.3(3)° and the Ag(1)–C(12) and Ag(1)–C(1) bond lengths are 2.066(7) and 2.078(7) Å, respectively, somewhat shorter than those in complex **3a**. The average Ag–C(carbene) bond length and the C–Ag–C angle are quite normal when compared to the corresponding values reported for other [Ag(carbene)$_2$] complexes.[17,22,23,42–47] The Ag–C(carbene) bond lengths of the bis(carbene)silver complexes **3a** and **4a** are shorter than those of the mono(carbene)silver complexes owing to the variation of the coordination environment of the silver atoms.[35] The dihedral angle of the two imidazolium rings is 48.8° (Figure 2). When the complex has a longer ether chain linkage, the coordination geometry at the silver atom tends to be linear [178.3(3)° in **4a** vs. 170.63(12)° in **3a**] due to the flexibility of the long oxoether bridge. The dihedral angles of the two imidazolium rings are remarkably different in **3a** (118.4°) and **4a** (48.8°), due to the size of the *trans*-metallacrown ether ring. The dihedral angle of the large metallacrown ether ring in **4a** is significantly smaller than that in **3a**.

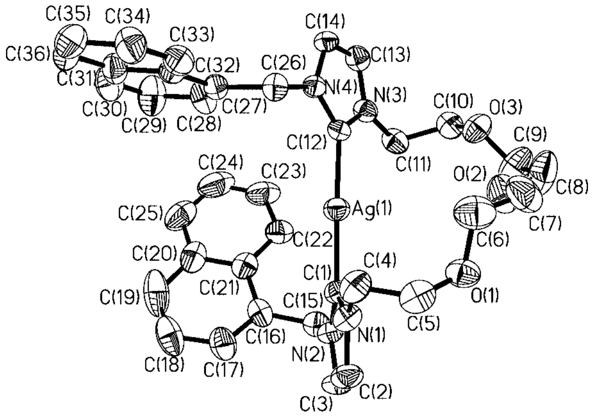


Figure 2. Molecular structure of the cation of **4a**. Hydrogen atoms, anions, and solvent molecules have been omitted for clarity. Thermal ellipsoids at 35% probability. Selected bond lengths [Å] and angles [°]: Ag(1)–C(12) 2.066(7), Ag(1)–C(1) 2.078(7); C(12)–Ag(1)–C(1) 178.3(3).

Gray reported the structures of the metallacrown ethers *trans*-[Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$-*P,P′*}] (n = 3–5) in 2001.[48] When n = 3, the three ether O atoms form an isosceles triangle with three O–O distances of 3.047, 3.040, and 5.527 Å. In **4a**, the three ether O atoms also form a similar isosceles triangle with O(1)–O(2), O(2)–O(3), and O(1)–O(3) distances of 2.866, 2.831, and 5.475 Å, respectively. The O–O distance is slightly shorter than in the *trans*-metallacrown ether and longer than in the *cis*-metallacrown ether, containing phosphane.[23,30c] The three O atoms and the silver atom lie almost in the same plane, the distance between the silver atom and the least-squares plane of the oxygen atoms being 0.116(40) Å.

The Au(1)–C(1) and Au(1)–C(21) bond lengths in complex **5a** (Figure 3) are 2.038(14) and 2.005(17) Å, respectively, and the C(21)–Au(1)–C(1) bond angle is 177.1(7)° (Table 1). The average Au–C(carbene) bond length is in the expected range reported for other related two-coordinate gold–carbene complexes.[49] The dihedral angle of the two imidazolium rings is 92.5°.

The Au(1)–C(14) [2.0370(12) Å] and Au(1)–C(25) [2.0283(12) Å] bond lengths and the C(25)–Au(1)–C(14) bond angle [176.813(17)°] in **6a** (Figure 4) are similar to those in **5a**. The dihedral angle of the two imidazolium rings (39.3°) is smaller than that in **5a** (92.5°); 1.5 equiv. of water are found in the crystal of **6a** with an occupancy factor for the oxygen atoms of 50%. The three oxygen atoms

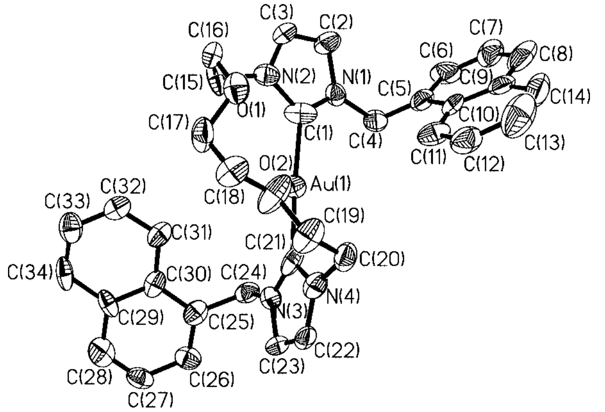


Figure 3. Molecular structure of the cation of **5a**. Hydrogen atoms, anions, and solvent molecules have been omitted for clarity. Thermal ellipsoids at 35% probability. Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 2.038(14), Au(1)–C(21) 2.005(17); C(21)–Au(1)–C(1) 177.1(7).

in the ether chain also form an isosceles triangle, with three O–O distances of 2.845, 2.877, and 5.517 Å, respectively. The O(1)–O(3) distance is slightly longer than in **4a** and shorter than in the *trans*-metallacrown ether, containing phosphane. The gold atom and the three O atoms lie almost in the same plane, the distance between the gold atom and the least-squares plane of the ether oxygen atoms being 0.147(2) Å. The geometric configurations of **5a** and **6a** are very similar to the corresponding Ag analogues **3a** and **4a**.

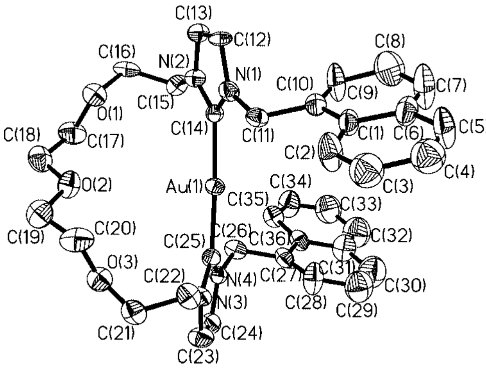


Figure 4. Molecular structure and atom numbering of **6a**. Hydrogen atoms, anions, and H_2O molecules have been omitted for clarity. Thermal ellipsoids at 35% probability. Selected bond lengths [Å] and angles [°]: Au(1)–C(14) 2.0370(12), Au(1)–C(25) 2.0283(12); C(25)–Au(1)–C(14) 176.813(17).

Perspective views of the cation of complexes **3a**–**6a** are depicted in Figures 1–4. Both **3a** and **5a** are chiral and possess analogous *trans* configurations, with two naphthyl rings of the NHC–M–NHC units in *trans* positions. Owing to their longer flexible polyether chains, **4a** and **6a** adopt *cis* configurations, with two naphthyl rings of the NHC–M–NHC units in *cis* positions.

Conclusion

Polyether chain containing bis(carbene)Ag^I and -Au^I complexes can be easily prepared in good yields. The X-ray diffraction analysis shows that the interaction of this kind of bis(NHC) ligand with silver(I) or gold(I) tends to form *trans*-macrocyclic structures, which provide a good method for the preparation of this kind of metallacrown ethers under non-high-dilution conditions.

Experimental Section

General: All manipulations were performed using standard Schlenk techniques, and solvents were purified by standard procedures. All the reagents for syntheses and analyses were of analytical grade and were used without further purification. 1-(1-Naphthylmethyl)-imidazole, 1-(9-anthracenylmethyl)imidazole,[35] and 1,2-bis(2-iodoethoxy)ethane[36] were synthesized according to literature procedures. Melting points were determined with a Boetius Block apparatus. ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury Vx 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts are reported in ppm relative to the internal standard TMS for both ^1H and ^{13}C NMR spectroscopy. Elemental analyses were measured with a Perkin–Elmer 2400C Elemental Analyzer.

Preparation of 1a: A solution of 1,2-bis(2-iodoethoxy)ethane (4.5 g, 12.5 mmol) and 1-(1-naphthylmethyl)imidazole (5 g, 24.1 mmol) in THF (60 mL) was stirred and refluxed for 3 d; a viscous, dense oil was formed gradually under the solvent. After removal of the upper organic phase, the analytically pure bis(imidazolium iodide) was obtained from the dense oil by recrystallization from methanol and diethyl ether. Yield: 9.04 g (92%). NH_4PF_6 (3.75 g, 23 mmol) was added to a methanol solution of the obtained iodide salt whilst stirring and a white precipitate formed immediately. The white powder was collected by filtration, washed with small portions of cold methanol, and dried in vacuo. Yield: 9.17 g (97%). $C_{34}H_{36}F_{12}N_4O_2P_2$ (822.6): calcd. C 49.64, H 4.38, N 6.81; found C 49.60, H 4.40, N 6.90. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 9.18 (s, 2 H), 8.10 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H), 8.01 (d, $^3J_{H,H}$ = 6.4 Hz, 4 H), 7.80 (t, $^3J_{H,H}$ = 1.6 Hz, 2 H), 7.71 (t, $^3J_{H,H}$ = 1.6 Hz, 2 H), 7.61 (m, 6 H), 7.50 (d, $^3J_{H,H}$ = 6.7 Hz, 2 H), 5.94 (s, 4 H), 4.29 (t, $^3J_{H,H}$ = 4.0 Hz, 4 H), 3.66 (t, $^3J_{H,H}$ = 4.0 Hz, 4 H), 3.385 (s, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 136.6, 133.4, 130.3, 130.0, 129.6, 128.9, 127.5, 127.1, 126.4, 125.6 (Ar-*C*), 122.9, 122.7, 122.6 (im-*C*), 69.2, 67.9 (O*C*H$_2$), 49.8 (Ar*C*H$_2$N), 48.9 (N*C*H$_2$) ppm.

Preparation of 1b: The same procedure as that for **1a** was applied with diiodotriethyleneglycol (5 g, 13.5 mmol), 1-(9-anthracenylmethyl)imidazole (6.97 g, 27 mmol), and NH_4PF_6 (4.5 g, 27 mmol) to give 11.8 g of **1b** as a yellow powder. Yield: 95%. $C_{42}H_{40}F_{12}N_4O_2P_2$ (922.72): calcd. C 54.67, H 4.37, N 6.07; found C 54.60, H 4.40, N 6.15. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.87 (s, 2 H), 8.83 (s, 2 H), 8.49 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H), 8.23 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H), 7.72 (m, 12 H), 6.52 (s, 4 H), 4.22 (t, $^3J_{H,H}$ = 4.2 Hz, 4 H), 3.56 (t, $^3J_{H,H}$ = 3.5 Hz, 4 H), 3.25 (s, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 135.8, 131.0, 130.5, 130.1, 129.3, 127.7, 125.5, 123.4 (Ar-*C*), 123.2, 122.8, 122.3 (im-*C*), 69.0, 67.9 (O*C*H$_2$), 48.6 (Ar*C*H$_2$N), 44.8 (N*C*H$_2$) ppm.

Preparation of 2a: The same procedure as that for **1a** was applied with diiodotetraethyleneglycol (6.28 g, 0.015 mol), 1-(1-naphthylmethyl)imidazole (6.25 g, 0.030 mol), and NH_4PF_6 (4.5 g, 27 mmol) to give 11.2 g of **2b** as a white powder. Yield: 96%. $C_{36}H_{40}F_{12}N_4O_3P_2$ (866.66): calcd. C 49.89, H 4.65, N 6.46; found C 49.82, H 4.58, N 6.52. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 9.20 (s, 2 H), 8.11 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 8.01 (d, $^3J_{H,H}$ =

7.2 Hz, 4 H), 7.80 (s, 2 H), 7.75 (s, 10 H), 7.50–7.61 (m, 8 H), 5.95 (s, 4 H), 4.33 (t, $^3J_{H,H}$ = 4.6 Hz, 4 H), 3.72 (t, $^3J_{H,H}$ = 4.6 Hz, 4 H), 3.44 (t, $^3J_{H,H}$ = 4.4 Hz, 4 H), 3.34 (t, $^3J_{H,H}$ = 4.4 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 133.3, 130.3, 129.9, 129.6, 128.8, 127.4, 127.1, 126.3, 125.5, 122.9 (Ar-*C*), 122.7, 122.5 (im-*C*), 69.3, 67.9 (O*C*H$_2$), 49.8 (Ar*C*H$_2$N), 48.8 (N*C*H$_2$) ppm.

Preparation of 2b: The same procedure as that for **1a** was applied with diiodotetraethyleneglycol (5 g, 12.1 mmol), 1-(9-anthracenylmethyl)imidazole (6.45 g, 25 mmol), and NH$_4$PF$_6$ (4.2 g, 25 mmol) to give 11.0 g of **2b** as a yellow powder. Yield: 94%. $C_{44}H_{44}F_{12}N_4O_3P_2$ (966.77): calcd. C 54.66, H 4.59, N 5.80; found C 54.71, H 4.49, N 5.86. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.90 (s, 2 H), 8.84 (s, 2 H), 8.50 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H), 8.24 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H), 7.72 (m, 12 H), 6.52 (s, 4 H), 4.26 (t, $^3J_{H,H}$ = 3.9 Hz, 4 H), 3.66 (t, $^3J_{H,H}$ = 3.9 Hz, 4 H), 3.26 (s, $^3J_{H,H}$ = 4.2 Hz, 4 H), 3.23 (t, $^3J_{H,H}$ = 4.2 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 135.8, 131.0, 130.5, 130.1, 129.3, 127.7, 125.5, 123.4 (Ar-*C*), 123.2, 122.8, 122.3 (imi-*C*), 69.3, 68.0 (O*C*H$_2$), 48.6, 44.8 (N*C*H$_2$) ppm.

Preparation of Complex 3a: Ag$_2$O (364 mg, 1.57 mmol) was added, under argon, to a solution of **1a** (645 mg, 0.785 mmol) in DMSO (30 mL) and the mixture was heated at 90 °C for 8 h. The resulting suspension was filtered through Celite, and water (60 mL) was added to give a white powder. The precipitate was filtered, washed with diethyl ether, and a pure product was obtained by recystallization from CH$_2$Cl$_2$ and diethyl ether. Yield: 430 mg (70%). Colorless crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into a solution in acetonitrile/chlorobenzene (3:1). $C_{34}H_{34}AgF_6N_4O_2P$ (783.49): calcd. C 52.11, H 4.34, N 7.15; found C 52.21, H 4.29, N 7.20. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.02 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.95 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.87 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.51 (m, 8 H), 7.38 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H), 7.24 (d, $^3J_{H,H}$ = 6.7 Hz, 2 H), 5.70 (s, 4 H), 3.99 (s, 4 H), 3.56 (s, 4 H), 3.31 (s, 4 H) ppm.^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 133.3, 132.5, 130.4, 128.6, 126.6, 126.5, 126.0, 125.3, 123.1 (Ar-*C*), 122.4, 121.5 (im-*C*), 69.3 (O*C*H$_2$), 51.8 (Ar*C*H$_2$N), 50.8 (N*C*H$_2$) ppm.

Preparation of Complex 3b: Complex **3b** was prepared in a manner analogous to that for **3a**, starting from **1b** (1.0 g, 1.08 mmol) and Ag$_2$O (501 mg, 2.16 mmol), as a yellow powder (572 mg, 60%). $C_{42}H_{38}AgF_6N_4O_2P$ (883.61): calcd. C 57.09, H 4.33, N 6.34; found C 57.14, H 4.22, N 6.31. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.75 (s, 2 H), 8.33 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H), 8.15 (d, $^3J_{H,H}$ = 9.1 Hz, 4 H) 7.51 (m, 8 H), 7.37 (s, 4 H), 6.06 (s, 4 H), 3.74 (t, $^3J_{H,H}$ = 3.7 Hz, 4 H), 3.42 (t, $^3J_{H,H}$ = 3.7 Hz, 4 H), 3.13 (s, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 131.0, 130.3, 129.1, 128.9, 127.1, 126.4, 125.2, 123.8 (Ar-*C*), 121.8, 121.1 (im-*C*), 69.1, 68.8 (O*C*H$_2$), 50.8 (Ar*C*H$_2$N), 46.1 (N*C*H$_2$) ppm.

Preparation of Complex 4a: Complex **4a** was prepared in a manner analogous to that for **3a**, from **2a** (900 mg, 1.04 mmol) and Ag$_2$O (482 mg, 2.08 mmol), as a white powder (570 mg, 60%). $C_{36}H_{38}AgF_6N_4O_3P$ (827.54): calcd. C 52.24, H 4.59, N 6.77; found C 52.34, H 4.52, N 6.71. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 8.04 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.95 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H), 7.89 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H) 7.38 (m, 10 H), 7.24 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H) 5.80 (s, 4 H), 4.12 (t, $^3J_{H,H}$ = 5.0 Hz, 4 H), 3.71 (t, $^3J_{H,H}$ = 5.0 Hz, 4 H), 3.41 (m, 8 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 208.1 (N*C*N), 135.8, 134.3, 132.7, 130.9, 130.7, 128.7, 128.3, 128.1, 127.3, 124.8 (Ar-*C*), 124.2, 123.7 (im-*C*), 72.4, 72.3, 71.9 (O*C*H$_2$), 54.5 (Ar*C*H$_2$N), 50.8 (N*C*H$_2$) ppm.

Preparation of Complex 4b: Complex **4b** was prepared in a manner analogous to that for **3a**, from **2b** (1.0 g, 1.04 mmol) and Ag$_2$O (482 mg, 2.08 mmol), as a yellow powder (598 mg, 62%). $C_{44}H_{42}AgF_6N_4O_3P$ (927.66): calcd. C 56.97, H 4.56, N 6.04; found C 57.04, H 4.42, N 6.11. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.75 (s, 2 H), 8.31 (d, $^3J_{H,H}$ = 9.4 Hz, 4 H), 8.15 (d, $^3J_{H,H}$ = 9.6 Hz, 4 H) 7.52 (m, 8 H), 7.39 (s, 4 H), 6.13 (s, 4 H), 3.69 (t, $^3J_{H,H}$ = 5.3 Hz, 4 H), 3.47 (t, $^3J_{H,H}$ = 5.3 Hz, 4 H), 3.15 (t, $^3J_{H,H}$ = 3.5 Hz, 4 H), 3.05 (t, $^3J_{H,H}$ = 3.5 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 131.0, 130.3, 129.1, 129.0, 127.1, 126.4, 125.3, 123.7 (Ar-*C*), 122.1, 121.3 (im-*C*), 69.9, 69.6, 69.4 (O*C*H$_2$), 51.4 (Ar*C*H$_2$N), 46.2 (N*C*H$_2$) ppm.

Preparation of Complex 5a: [Au(SMe$_2$)Cl] (37.6 mg, 0.128 mmol) was added to a solution of **3a** (100 mg, 0.128 mmol) in CH$_2$Cl$_2$ (30 mL) and the resulting solution was stirred for 2 h. During this time a white precipitate formed. This precipitate was removed by filtration through Celite, and the remaining clear colorless solution was reduced to 5 mL under vacuum. The precipitate that formed after the addition of diethyl ether (20 mL) to the clear solution was collected by filtration and dried to give the gold complex (105 mg, 95%). Recrystallization from CH$_3$CN/diethyl ether yielded a colorless, crystalline product. $C_{34}H_{34}AuF_6N_4O_2P$ (872.59): calcd. C 46.79, H 3.90, N 64.22; found C 46.85, H 3.81, N 64.16. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.16 (d, $^3J_{H,H}$ = 8.33 Hz, 2 H), 7.94 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.89 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H) 7.40 (m, 10 H), 7.24 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H), 5.79 (s, 4 H), 4.21 (t, $^3J_{H,H}$ = 4.2 Hz, 4 H), 3.71 (t, $^3J_{H,H}$ = 4.2 Hz, 4 H), 3.56 (t, $^3J_{H,H}$ = 4.7 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 183.4 (N*C*N), 133.2, 132.2, 130.2, 128.6, 126.1, 126.0, 125.2, 123.0 (Ar-*C*), 122.7, 122.4 (im-*C*), 69.3 (O*C*H$_2$), 51.3 (Ar*C*H$_2$N), 50.0 (N*C*H$_2$) ppm.

Preparation of Complex 5b: The same procedure as that for **5a** was applied to give 0.105 g of **5b** as a white powder from **3b** (100 mg, 0.113 mmol). Yield: 96%. $C_{42}H_{38}AuF_6N_4O_2P$ (972.71): calcd. C 51.86, H 3.94, N 5.76; found C 51.78, H 4.10, N 5.82. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.77 (s, 2 H), 8.44 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H), 8.15 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H), 7.38–7.59 (m, 8 H), 7.16 (s, 4 H), 6.26 (s, 4 H), 4.13 (t, $^3J_{H,H}$ = 4.0 Hz, 4 H), 3.78 (t, $^3J_{H,H}$ = 4.0 Hz, 4 H), 3.21 (s, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 183.3 (N*C*N), 131.0, 130.5, 130.4, 129.2, 127.1, 125.9, 125.8 (Ar-*C*), 123.8, 122.1, 121.8 (im-*C*), 69.3, 68.8 (O*C*H$_2$), 50.2 (Ar*C*H$_2$N), 46.1 (N*C*H$_2$) ppm.

Preparation of Complex 6a: The same procedure as that for **5a** was applied to give 0.116 g of **6a** as a white powder from **4a** (109 mg, 0.132 mmol). Yield: 96%. $C_{36}H_{38}AuF_6N_4O_3P$ (916.64): calcd. C 47.17, H 4.18, N 6.11; found C 47.24, H 4.10, N 6.03. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.03 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.92 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.87 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.38–7.55 (m, 10 H), 7.09 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H), 5.79 (s, 4 H), 4.16 (t, $^3J_{H,H}$ = 5.0 Hz, 4 H), 3.74 (t, $^3J_{H,H}$ = 5.0 Hz, 4 H), 3.39 (s, 8 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 183.8 (N*C*N), 133.2, 132.3, 130.1, 128.6, 126.6, 126.1, 125.7, 125.3, 122.8 (Ar-*C*), 122.6, 122.2 (im-*C*), 70.1, 69.6, 69.3 (O*C*H$_2$), 51.4 (Ar*C*H$_2$N), 50.5 (N*C*H$_2$) ppm.

Preparation of Complex 6b: The same procedure as that for **5a** was applied to give 0.105 g of **6b** as a white powder from **4b** (100 mg, 0.108 mmol). Yield: 96%. $C_{44}H_{42}AuF_6N_4O_3P$ (1016.8): calcd. C 51.98, H 4.16, N 5.51; found C 51.88, H 4.10, N 5.72. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.77 (s, 2 H), 8.48 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H), 8.17 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H) 7.50–7.60 (m, 8 H), 7.44 (d, $^3J_{H,H}$ = 1.7 Hz, 2 H), 7.12 (d, $^3J_{H,H}$ = 1.7 Hz, 2 H), 6.33 (s, 4 H), 4.06 (t, $^3J_{H,H}$ = 5.2 Hz, 4 H), 3.72 (t, $^3J_{H,H}$ = 5.2 Hz, 4 H),

Table 2. Crystal data and structure refinement for **3a**–**6a**.

	3a	**4a**	**5a**	**6a**
Empirical formula	$C_{34}H_{34}AgF_6N_4O_2P$	$C_{36}H_{38}AgF_6N_4O_3P$	$C_{34}H_{34}AuF_6N_4O_2P$	$C_{36}H_{41}AuF_6N_4O_{4.50}P$
Formula mass	783.49	827.54	872.59	943.66
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$Fddd$
a [Å]	8.110(4)	29.378(9)	25.620(7)	50.51(3)
b [Å]	11.433(5)	11.289(3)	11.505(3)	42.95(3)
c [Å]	18.481(8)	26.110(8)	25.608(7)	15.093(9)
α [°]	85.505(8)	90	90	90
β [°]	83.406(7)	123.276(6)	116.947(5)	90
γ [°]	77.435(7)	90	90	90
V [Å]^3	1659.0(13)	7240(4)	6729(3)	32743(36)
Z	2	8	8	32
$D_{\text{calcd.}}$ [Mg m^{-3}]	1.568	1.518	1.723	1.531
Absorption coefficient [mm^{-1}]	0.728	0.673	4.491	3.702
$F(000)$	796	3376	3440	15008
Crystal size [mm]	0.22 × 0.12 × 0.10	0.26 × 0.18 × 0.14	0.20 × 0.18 × 0.14	0.20 × 0.16 × 0.10
$\theta_{\min}$, $\theta_{\max}$ [°]	1.11, 26.47	1.99, 25.00	0.89, 26.44	2.00, 25.01
T [K]	293(2)	293(2)	293(2) K	293(2) K
No. of data collected	9654	18182	13795	40415
No. of unique data	6734	6370	216	108
No. of refined parameters	488	519	970	488
Goodness-of-fit on F^{2}[a]	1.022	1.175	1.001	1.151
Final R indices[b] [$I > 2\sigma(I)$]				
$R1$	0.0391	0.0746	0.0655	0.0844
$wR2$	0.0725	0.1633	0.1360	0.2283
R indices (all data)				
$R1$	0.0615	0.1067	0.1245	0.1196
$wR2$	0.0839	0.1772	0.1600	0.2528

[a] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined. [b] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

3.35 (s, 4 H), 3.29 (t, $^3J_{H,H}$ = 4.5 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 182.8 (N*C*N), 131.0, 130.5, 129.2, 129.2, 127.1, 125.9, 125.3, 123.8 (Ar-*C*), 122.0, 121.5 (im-*C*), 70.2, 69.6, 69.5, 69.4 (O*C*H$_2$), 50.8 (Ar*C*H$_2$N), 46.2 (N*C*H$_2$) ppm.

X-ray Crystallography: Suitable crystals of **3a**–**6a** were mounted on a glass fiber in a random orientation. The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package.[50] Data collection was performed at room temperature with a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo-K_α radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[51] All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and included in structure-factor calculations. More details of the data collection and structure refinement are contained in Table 2. The PF_6^- anions in complexes **3a**–**5a** are disordered in their F atoms; these groups were refined as two groups sharing the same P atom. The P–F distances were restrained to within 0.01 Å of each other. Additionally, the vibration of the disordered atoms was restrained to be approximately isotropic. In complex **6a**, the H_2O molecule is disordered over two positions. CCDC-257901, -257902, -257904, and -257903 (**3a**–**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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