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A Luminescent Gold Ring That Flips Like Cyclohexane**

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Coordination-directed self-assembly of metal centers and multidentate ligands has successfully created many discrete inorganic molecules with intricate supramolecular architectures.^[1] Among these compounds are metallacycles^[2] which are not only aesthetically pleasing but potentially functional as catalysts, sensors, and in molecular electronics.^[3] The modular character of the compounds allows their physical properties to be tailored readily and previous studies of metallacycles focused mainly on their photoluminescence and electrochemistry.^[2b,c, 3, 4] On the other hand, our understanding of the fluxionality of metallacycles is still relatively limited. Given the rich fluxionality of organic rings and cyclophanes,^[5] it is surprising that analogous behavior is not widely observed in their inorganic counterparts. This paucity could be a result of the rigidity of many metallacycles. Outstanding examples of metallacycle fluxionality are the PtS₅ ring inversion in [NH₄]₂[Pt(S₅)₃] and the cyclooctane-like inversion of the eight-membered ring [Pt₂Me₄(μ-Me₂PCH₂Me₂)₂] reported by Riddell et al.^[6a] and Puddephatt and co-workers,^[6b] respectively. Herein we report the synthesis of 9,10-bis(diphenylphosphino)anthracene (PANP), a ligand designed to form emissive cyclophanes with low-valent metal centers. Subsequent treatment of PANP with Au^I ions produced a fluorescent trinuclear gold ring that has structure and fluxionality reminiscent of cyclohexane.

PANP (see Scheme 1) was synthesized from the reaction of dilithioanthracene and PPh₂Cl. A similar monodentate ligand 9-diphenylphosphinoanthracene was first synthesized by Mingos and co-workers.^[7] PANP shows a singlet at δ = −21.9 in the ³¹P{¹H} NMR spectrum and its structure was confirmed by X-ray crystallography (see Supporting Information). Prolonged reflux of PANP and Me₂SAuCl (1:1) in methanol

produced a yellow solution from which a trinuclear Au^I complex [Au₃(PANP)₃][ClO₄]₃ (**1**) was isolated. Single-crystal X-ray analysis shows that the cation of **1** is a ring comprising three bridging PANP ligands and three gold atoms (Figure 1).^[8] The three anthracenyl units are nearly perpendicular to the ring, the diameter of which, taken as the

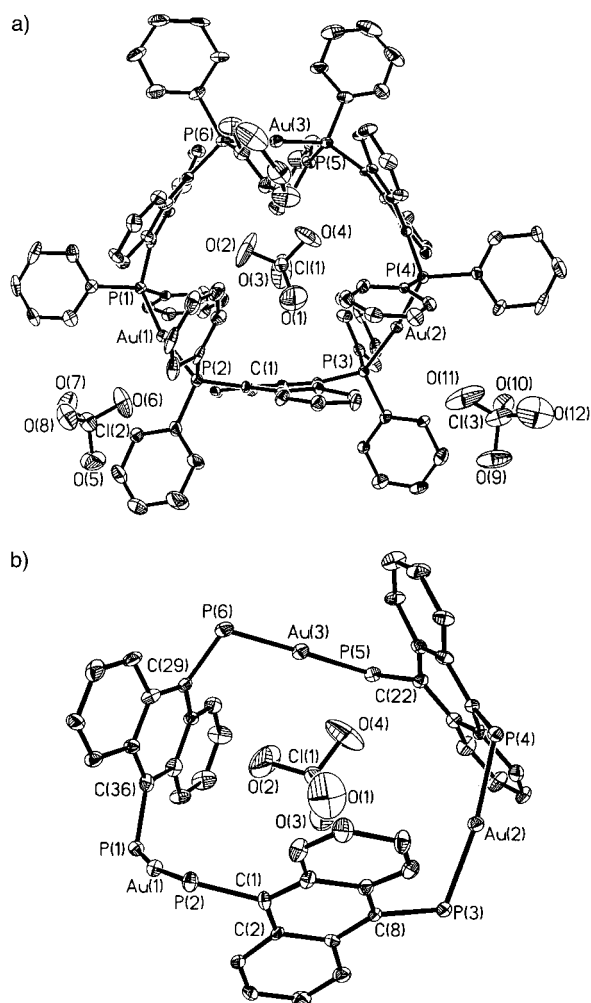


Figure 1. ORTEP drawing of **1** · 0.5 Et₂O; a) top and b) side view. H atoms, ClO₄ ions, Ph rings, and Et₂O are omitted for clarity (thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: Au(1)–P(1) 2.294(3), Au(2)–P(3) 2.312(3), Au(3)–P(5) 2.309(3), P(2)–C(1) 1.850(9), Au(1)···Au(2) 8.123(3), Au(1)···Au(3) 7.892(3), Au(2)···Au(3) 7.742(3); P(1)–Au(1)–P(2) 169.54(1), P(3)–Au(2)–P(4) 171.91(9), P(5)–Au(3)–P(6) 178.84(1), Au(1)–P(2)–C(1) 109.6(3).

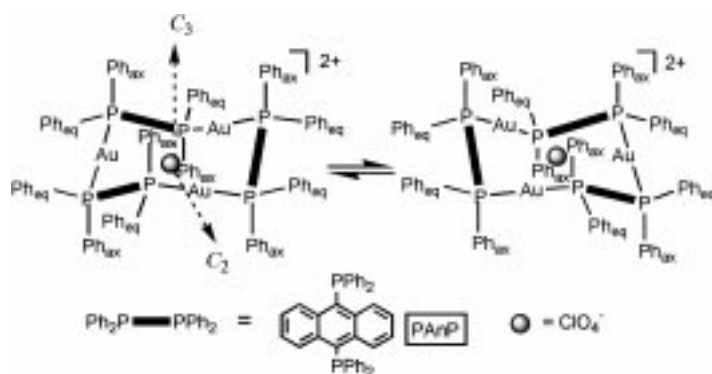
distance between P(1) and P(4), is 10.04 Å. One of the three ClO₄[−] ions is in the center of the ring and three of its oxygen atoms (O(1), O(2), and O(4)) are directed towards, and are almost equidistant from, the central rings of the three PANP anthracene units (3.083(3)–3.170(3) Å). Notably, the anthracenyl rings curve slightly from the center of the cavity, with a dihedral angle of 15.3° between the two lateral benzene rings. Similar ring distortion has been observed in 9,10-bis(trimethylsilyl)anthracene,^[9] and possibly occurs in **1** to alleviate steric congestion between the peripheral protons of anthracenyl and Ph rings. The coordination geometry of the Au atoms is close to linear (169.54(1)–178.84(1)°) and the

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average Au–P bond of 2.309 Å compares favorably with those observed in other Au^I–phosphane compounds.^[10] The long intra-annular Au...Au separations (7.742(3)–8.123(3) Å) preclude any aurophilic interaction between the gold atoms.^[10] The side view of the structure shows that the ring is puckered, displaying a chair conformation similar to that of cyclohexane (Figure 1b). While internal C–C–C angle of cyclohexane is 111.4°,^[11] the internal C(anthracenyl)–P–Au angles (108.4(3)–110.6(3)°) of the gold ring are very close to the ideal tetrahedral. Gold(II) metallacycles are known^[12] but **1** is the only one that shows a chair conformation. A similar conformation was reported by Che and co-workers for a luminescent Pt^{II} metallacycle.^[13] Like cyclohexane, which has axial and equatorial H atoms,^[5] **1** has two geometrically different sets of phenyl rings: six axial phenyl rings (Ph_{ax}) lying up and down along the central axis of the ring and six equatorial phenyl rings (Ph_{eq}) alternating about a plane at right angles to the central axis (Scheme 1). The Ph_{ax} and Ph_{eq} rings are diastereotopic.



Scheme 1.

Whereas the crystal structure of **1** slightly deviates from the maximum *D*₃ point group symmetry, the solution ³¹P{¹H} NMR spectrum shows a sharp singlet at δ = 34.9 (Figure 2b) which displays no significant change in line shape throughout temperature range of 302–213 K. This indicates that the gold ring reverts to *D*₃ symmetry in solution and its six P atoms, related by *C*₃- and *C*₂-rotations (Scheme 1), are equivalent. The gold ring is stable in solution and no NMR signals arising from free ligand or other species are observed even after

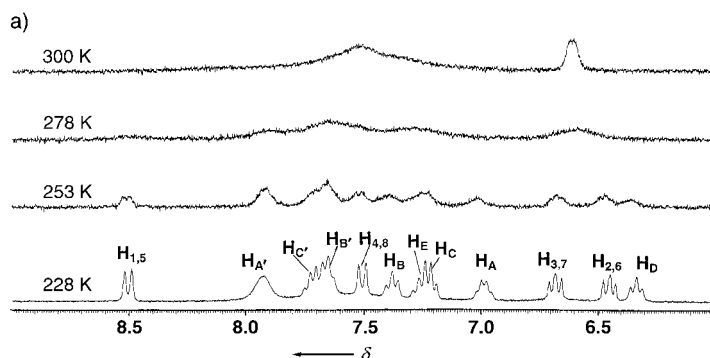


Figure 2. a) Variable temperature ¹H NMR spectra of **1** (300 MHz, CD₂Cl₂) and labeling scheme for the protons in the PAnP ligand in **1**; b) variable temperature ³¹P{¹H} NMR spectra of **1** (300 MHz, CD₂Cl₂).

several days. Surprisingly, the ¹H NMR spectrum of **1** is highly temperature dependent; the 300 K spectrum shows very broad signals (Figure 2a) which are better resolved as the temperature decreases. These seemingly contradictory ³¹P{¹H} and ¹H NMR results suggest that **1** exchanges between two conformations in which all the P atoms (but not the protons) have identical chemical environments. Given the structural resemblance between the gold ring and cyclohexane, we propose that the fluxional process is a ring inversion arising from the rotations of skeletal Au–P and P–C(anthracenyl) bonds (Scheme 1).

The proposed fluxional process was supported by low temperature NMR spectroscopy studies. The broad resonance signals in the ¹H NMR spectrum resolve into twelve multiplets as the fluxional process is slowed down at 228 K. Based on the ¹H–¹H COSY spectrum of **1** recorded at the same temperature (Figure 3), the multiplets can be assigned to the protons

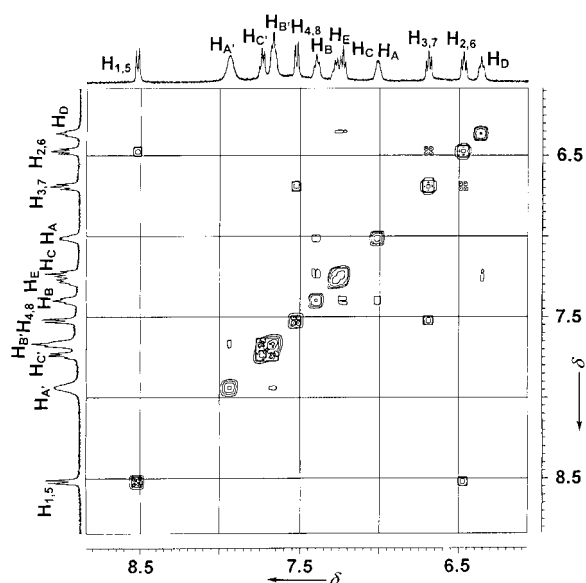
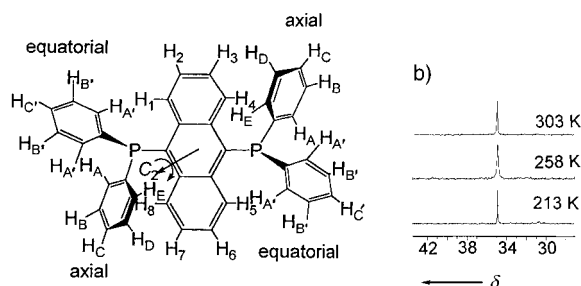


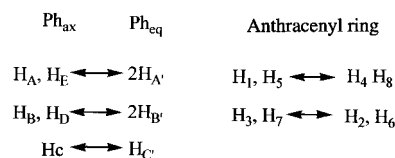
Figure 3. ¹H–¹H COSY spectrum of **1** recorded at 228 K (500 MHz, CD₂Cl₂).

in PAnP. (In the following discussion, the assignment is only made to one PAnP unit since the three ligands in **1** are equivalent). The diastereotopic Ph_{ax} and Ph_{eq} are expected to display different NMR signals. Indeed, COSY spectrum



shows that 8 of the 12 multiplets are attributable to the Ph_{ax} (in total 10 H, $\delta = 6.99$ (2 H, H_{A}), 7.38 (2 H, H_{B}), 7.21 (2 H, H_{C}), 6.34 (2 H, H_{D}), 7.24 (2 H, H_{E})), and Ph_{eq} (in total 10 H, $\delta = 7.92$ (4 H, H_{A}), 7.68 (4 H, H_{B}), 7.73 (2 H, H_{C})) rings.^[14] The observation of five distinct signals for Ph_{ax} protons implies a slow rotation of the ring around the P–C bond, probably hindered by the anthracenyl ring (the X-ray structure of **1** shows that the Ph_{ax} and anthracenyl rings are close to each other). On the other hand, the resonance signals arising from the $o\text{-H}_{\text{A'}}$ and $m\text{-H}_{\text{B'}}$ atoms of the Ph_{eq} ring remain broad and unresolved even at 228 K, indicating that the rotation of the ring, which is directed outward, is still fast on the NMR timescale. Because of the orientation of the diastereotopic Ph rings, the PAnP ligands show a local C_2 symmetry and the remaining four multiplets can be assigned to the four pairs of equivalent protons in the anthracenyl ring (in total 8 H, $\delta = 8.51$ (2 H, $\text{H}_{1,5}$), 7.51 (2 H, $\text{H}_{4,8}$), 6.70 (2 H, $\text{H}_{3,7}$), and 6.45 (2 H, $\text{H}_{2,6}$)).^[14]

It is well known that the axial and equatorial protons interchange their positions in the ring inversion of cyclohexane.^[5] Likewise, one would expect to see exchange of the Ph_{ax} and Ph_{eq} rings ($\text{Ph}_{\text{ax}} \leftrightarrow \text{Ph}_{\text{eq}}$) in the gold ring inversion. In addition, the flipping of Ph rings would also lead to a swapping of the anthracenyl proton positions (Scheme 2).



Scheme 2. Exchanges of position expected on ring inversion.

Cross-peaks corresponding to these exchanging pairs are clearly observed in the ^1H 2D-EXSY spectrum recorded at 228 K (Figure 4), confirming that the gold ring undergoes cyclohexane-like ring inversion in solution. The spectrum also

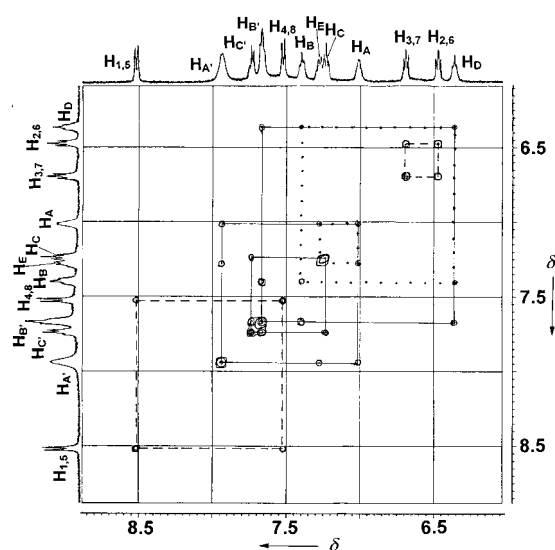


Figure 4. ^1H 2D-EXSY spectrum of **1** (500 MHz, CD_2Cl_2). Cross-peaks for the flipping of $\text{Ph}_{\text{eq}} \leftrightarrow \text{Ph}_{\text{ax}}$ (—), exchange of $\text{H}_{1,5} \leftrightarrow \text{H}_{4,8}$ and $\text{H}_{3,7} \leftrightarrow \text{H}_{2,6}$ in the anthracenyl ring (---) and rotation of the Ph_{ax} ring (·····).

shows exchange cross-peaks for $\text{H}_{\text{A}} \leftrightarrow \text{H}_{\text{E}}$ and $\text{H}_{\text{B}} \leftrightarrow \text{H}_{\text{D}}$, supporting the idea that the Ph_{ax} ring is rotating, albeit slowly at 228 K. Since the signals of the exchanging pair $\text{H}_{3,7} \leftrightarrow \text{H}_{2,6}$ are well removed from the other signals, their coalescence temperature (278 K) is used to calculate the rate constant (k_{278}) and free enthalpy of activation ($\Delta G_{278}^\ddagger$) of the ring inversion which are 155 s^{-1} and 56 kJ mol^{-1} , respectively.^[15] The 2D-EXSY results clearly show that ring inversion is the *only* fluxional process displayed by **1**. Notably, all of the P atoms at the “corners” would remain equivalent throughout the process, which is consistent with the observation of a sharp singlet in the variable temperature ^{31}P NMR spectra (Figure 2b). Since the gold ring is chiral, the ring inversion can be regarded as enantiomerization. Although the hexanuclear cyclo- $[\{\text{ReH}(\text{CO})_4\}_6]$ complex is known as an inorganic structural analogue of cyclohexane,^[16] **1** shows both *structure* and *fluxionality* akin to that of the organic ring.

UV/Vis absorption spectra of PAnP and **1** show intense vibronic bands at 396 nm ($\epsilon_{\text{max}} 9285 \text{ M cm}^{-1}$) and 424 nm ($\epsilon_{\text{max}} 32857 \text{ M cm}^{-1}$) attributable to $^1\pi \rightarrow \pi^*$ transitions in the anthracenyl ring (see the Supporting Information). Excitation of an aerated or degassed CH_3CN solution of **1** at 400 nm gives an emission maximum at 475 nm with a quantum yield of 0.05 (Figure 5). On the contrary, PAnP is nonemissive.

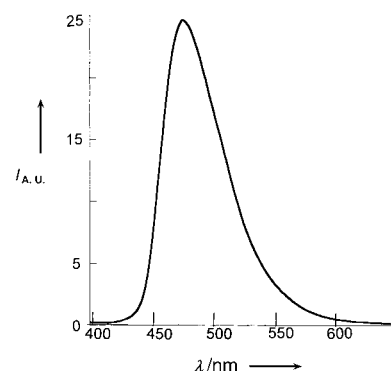


Figure 5. Emission spectrum of **1** in CH_3CN at 297 K. Excitation wavelength 400 nm. Excitation and emission slit widths 5 nm.

Probably the emitting state of PAnP is quenched by a rapid intramolecular electron transfer from the PPh_2 groups. Similar quenching has been observed in anthracenes containing electron-rich substituents.^[17] On the other hand, **1** is fluorescent because the lone-pairs of the PPh_2 groups, being donated to the Au^{I} ions, are not available for quenching. Unlike the highly vibronic fluorescence of anthracene and 9,10-disubstituted anthracenes,^[18] the emission of **1** shows no structure and is red shifted by $\sim 4000 \text{ cm}^{-1}$. As the absorption spectra of **1** and the free ligand are similar, the unique emission of **1** could not arise from a ground state interaction between anthracenyl rings; in fact, the red shift and the absence of vibronic structure suggest that the emission is excimeric in nature.^[19]

In conclusion a luminescent gold ring was shown to be an inorganic analogue of cyclohexane in terms of structure and solution dynamics. We are currently investigating the effect of the anion on the ring inversion of **1** and coordination chemistry of PAnP with other metals.

Experimental Section

All syntheses were carried out using standard Schlenk techniques. Solvents used for spectroscopic measurements were purified according to the literature methods.

Synthesis of 9,10-bis(diphenylphosphino)anthracene (PAnP): *n*BuLi (12 mmol) was added to a suspension of 9,10-dibromoanthracene (2.0 g, 6 mmol) in Et₂O (100 mL). The solution was stirred for 10 min before addition of PPh₂Cl (3.2 mL, 12 mmol). The suspension was stirred for 12 h, collected by filtration, and the yellow solid thus obtained washed with diethyl ether. Crystals were obtained from CH₂Cl₂/Et₂O by slow diffusion, yield 75%; elemental analysis calcd (%) for C₃₈H₂₈P₂: C 83.5, H 5.0; found: C 83.4, H 5.1, ¹H NMR (CD₂Cl₂, 300 MHz): δ = 7.23 (m, 4H, H_{2,3,6,7}, An), 7.25–7.43 (m, 20H, Ph), 8.85 (m, 4H, H_{1,4,5,8}, An). ³¹P{¹H} NMR (CDCl₃, 300 MHz): δ = –21.9; m.p. 260 °C (decomp).

1: A methanol suspension (50 mL) of PAnP (1.0 g, 1.8 mmol) and Me₃SAuCl (0.53 g, 1.8 mmol) was heated at reflux for 4 days, insoluble material was then removed by filtration. Excess LiClO₄ was added to the yellow filtrate and the resulting yellow solid was crystallized from CH₃CN/Et₂O at –20 °C, yield 40%, elemental analysis calcd (%) for C₁₁₄H₈₄Au₃Cl₃O₁₂P₆: C 54.1, H 3.4, P 7.4; found: C 54.3, H 3.5, P 7.3; m.p. 124 °C (decomp); for NMR data, see text.

Physical measurements: The UV/Vis absorption and emission spectra of the complexes were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer and a Perkin-Elmer LS-50D fluorescence spectrophotometer, respectively. Anthracene was used as a standard in measuring the quantum yield of emission. ¹H and ³¹P{¹H} NMR spectra were recorded at 25 °C on either a Bruker ACF 300 spectrometer or a Bruker AMX500 spectrometer. All chemical shifts are quoted relative to SiMe₄ (¹H) or H₃PO₄ (³¹P). Variable temperature spectra were obtained by using a Bruker variable temperature unit B-VT2000 to control the probe temperature. The sample temperature is considered to be accurate to ±1 °C. ¹H 2D-EXSY and COSY spectra were obtained using standard NOESYPH.AU (mixing time of 0.5 s) and COSY-AU programs, respectively. Elemental analyses of the complexes were carried out in the microanalysis laboratory in the department of chemistry, the National University of Singapore.

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