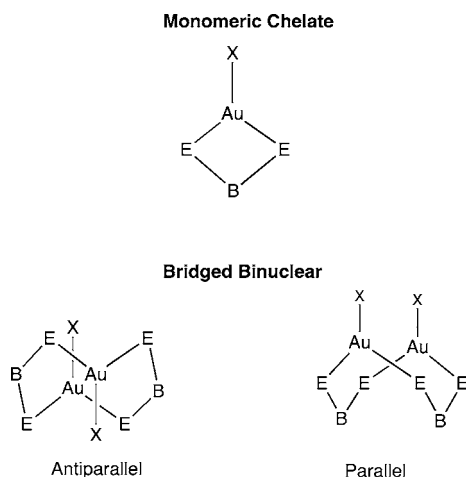


Scheme 1. Trigonal Planar Au^I Compounds

E = PPh₂, B = (CH₂)_n where n = 2, 3, 4, 5, 6; X = halide

diphosphine ligands, Ph₂P(CH₂)_nPPh₂, and that alteration of the length of the polymethylene chain would alter the P–Au–P angles in these complexes in a sensible fashion. As shown below, such chelated monomers were not obtained. Rather bridged, binuclear complexes were obtained.

RESULTS AND DISCUSSION

Synthesis and Crystal Growth. The reaction of a suspension of Au^I with the appropriate P_nP ligand (*n* = 3–6) produces colorless solids that can be crystallized from dichloromethane/diethyl ether or chloroform/diethyl ether to yield colorless crystals of the dimeric products. Infrared and ³¹P NMR spectra of these compounds are given in the Experimental Section. The ³¹P NMR spectra for all four

complexes consist of a single resonance and indicate that all phosphorus atoms in the complexes are equivalent.

Structure of Au₂(μ-P3P)₂I₂. Crystal data for all complexes considered here are given in Table 1. Selected bond distances and angles are presented in Tables 2 and 3. For comparison, structural data for the monomeric Au^I(PPh₃)₂I is included in the tables.²² A drawing of the structure of Au₂(μ-P3P)₂I₂ is shown in Figure 1. The dimeric Au₂(μ-P3P)₂I₂ molecule packs about a crystallographic center of symmetry so that one-half of the dimer resides in the asymmetric unit. The gold center is three-coordinate with bonds to two phosphorus atoms of two different bridging ligands and to the terminal iodide ligand. The Au^IP₂I unit is planar. The sum of the two P–Au–I angles and the P–Au–P angle is 359.8°, but these individual bond angles themselves differ considerably. The centrosymmetric nature of the complex positions the two polar Au^IP₂I units in an antiparallel alignment. The Au⋯Au separation is rather long, 5.0671(6) Å, and there is no significant aurophilic interaction within the molecule.

Figure 2 shows a drawing of just the 12-membered ring of atoms at the center of Au₂(μ-P3P)₂I₂. This view emphasizes the antiparallel orientation of the two Au^IP₂I planes. Figure 2 also shows a comparable view of the other three compounds reported here.

Structure of Au₂(μ-P4P)₂(μ-I)₂. A drawing of a molecule of Au₂(μ-P4P)₂(μ-I)₂ is shown in Figure 3. One half of the molecule is present in the asymmetric unit. The rest of the molecule is generated by inversion through the crystallographic center of symmetry. Within the series of four molecules considered here, Au₂(μ-P4P)₂(μ-I)₂ is the only one with four-coordinate gold ions. The gold ion is in a highly distorted tetrahedral environment with bonds to two phosphorus atoms and two bridging iodide ligands. The two Au–I distances (3.0580(3), 3.0967(4) Å) are nearly equal. These are the longest Au–I bonds seen in this series of molecules. Likewise, the two Au–P distances (2.3092(7), 2.3248(6) Å) are nearly

Table 1. Crystal Data and Structure Refinement for Au₂(μ-P_nP)₂I₂

| | Au ₂ (μ-P3P) ₂ I ₂ | Au ₂ (μ-P4P) ₂ (μ-I) ₂ | Au ₂ (μ-P5P) ₂ I ₂ ·3CHCl ₃ | Au ₂ (μ-P6P) ₂ I ₂ |
|---|---|---|--|---|
| formula | C ₅₄ H ₅₂ Au ₂ I ₂ P ₄ | C ₅₆ H ₅₆ Au ₂ I ₂ P ₄ | C ₅₈ H ₆₀ Au ₂ I ₂ P ₄ ·3(CHCl ₃) | C ₆₀ H ₆₄ Au ₂ I ₂ P ₄ |
| formula weight | 1472.58 | 1500.62 | 1885.77 | 1556.73 |
| <i>T</i> , K | 90(2) | 90(2) | 90(2) | 90(2) |
| color and habit | colorless block | colorless block | colorless block | colorless block |
| crystal system | triclinic | monoclinic | monoclinic | triclinic |
| space group | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ | <i>P</i> $\bar{1}$ |
| <i>a</i> , Å | 10.527(5) | 10.124(2) | 10.821(2) | 9.984(2) |
| <i>b</i> , Å | 10.853(5) | 18.692(2) | 20.111(4) | 11.648(2) |
| <i>c</i> , Å | 12.979(5) | 15.574(2) | 15.845(3) | 12.673(2) |
| α , deg | 91.340(5) | 90 | 90 | 101.425(5) |
| β , deg | 113.602(5) | 119.930(5) | 94.334(1) | 93.982(5) |
| γ , deg | 111.965(5) | 90 | 90 | 100.789(5) |
| <i>V</i> , Å ³ | 1233.7(9) | 2554.1(7) | 3438.4(11) | 1410.3(4) |
| <i>Z</i> | 1 | 2 | 2 | 1 |
| <i>d</i> _{calc} , g cm ⁻³ | 1.982 | 1.951 | 1.821 | 1.833 |
| μ , mm ⁻¹ | 7.356 | 7.108 | 5.639 | 6.440 |
| unique data | 5673 | 7857 | 20323 | 6463 |
| restraints | 0 | 0 | 1 | 0 |
| params. | 145 | 289 | 701 | 307 |
| R1 ^a | 0.0356 | 0.0189 | 0.0221 | 0.0140 |
| wR2 ^b | 0.0758 | 0.0396 | 0.0559 | 0.0332 |

^aFor data with *I* > 2 σ *I*, R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^bFor all data. wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Experimental and Computed Bond Distances (Å) for Au₂(μ-PnP)₂I₂ and AuI(PPh₂R)I

| bond lengths, Å | Au ₂ (μ-P3P) ₂ I ₂ | Au ₂ (μ-P4P) ₂ I ₂ | Au ₂ (μ-PSP) ₂ I ₂ ·3CHCl ₃ | Au ₂ (μ-P6P) ₂ I ₂ | AuI(PPh ₂ R)I |
|-----------------|---|---|---|---|--|
| Au1–I1 | 2.9310(14) ^a {3.051} ^b [3.115] ^c | 3.0580(3) | 3.0006(6) {3.007} [3.079] | 2.8052(4) {2.973} ^v [2.953] | 2.754(1) Ph ^d {2.970} Me [2.906] Me |
| Au2–I2 | | 3.0967(4) | 3.0831(7) {3.016} [3.098] | | |
| Au1–P1 | 2.3048(18) {2.372} [2.383] | 2.3092(7) | 2.3089(9) {2.378} [2.354] | 2.3347(6) {2.402} [2.385] | 2.333(2) Ph ^d {2.409} Me [2.662] Me |
| Au1–P2 | 2.3217(17) {2.393} [2.390] | 2.3248(6) | 2.3017(9) {2.378} [2.365] | 2.2997(6) {2.375} [2.384] | |
| Au2–P3 | | | 2.3093(8) {2.379} [2.386] | | |
| Au2–P4 | | | 2.3115(8) {2.379} [2.341] | | |
| Au...Au | 5.0671(6) {5.151} [5.247] | 4.1952(2) | 8.0206(3) {8.089} [8.242] | 5.3095(2) {5.595} [7.011] | |

^aExperimental. ^b{ } Computed for the Ground State. ^c[] Computed for the First Excited Triplet. ^dData from Bowmaker, G. A.; Dyason, J. C.; Healy, P. C.; Engelhardt, M.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1089.

Table 3. Selected Experimental and Computed Bond Angles (deg) for Au₂(μ-PnP)₂I₂ and AuI(PPh₂R)₂I

| bond angles (deg) | Au ₂ (μ-P3P) ₂ I ₂ | Au ₂ (μ-P4P) ₂ (μ-I) ₂ | Au ₂ (μ-PSP) ₂ I ₂ ·3CHCl ₃ | Au ₂ (μ-P6P) ₂ I ₂ | AuI(PPh ₂ R) ₂ I |
|-------------------|--|---|---|---|---|
| P1–Au1–P2 | 152.88(5) ^a {155.0} ^b [163.3] ^c | 143.31(2) | 164.63(3) {164.0} [175.3] | 133.042(19) {136.1} [158.3] | 132.13(7) Ph ^d {147.3} Me [179.8] Me |
| P3–Au2–P4 | | | 172.32(3) {164.9} [170.6] | | |
| P1–Au1–I1 | 109.14(4) {108.9} [103.3] | 96.218(15) | 94.19(2) {96.7} [90.2] | 102.311(19) {115.7} [106.8] | 113.93(5) Ph ^d {107.1} Me [90.0] Me |
| P1–Au1–I1A | | 105.098(15) | | | |
| P2–Au1–I1 | 97.77(4) {96.0} [93.4] | 115.841(16) | 101.01(2) {98.2} [88.7] | 123.086(15) {102.1} [94.5] | {105.4} Me [90.5] Me |
| P2–Au1–I1A | | 92.369(19) | | | |
| P3–Au2–I2 | | | 93.45(2) {98.5} [95.3] | | |
| P4–Au2–I2 | | | 93.36(2) {97.2} [94.0] | | |
| I1–Au1–I1A | | 94.061(10) | | | |

^aExperimental. ^b{ } Computed for the Ground State. ^c[] Computed for the First Excited Triplet. ^dData from Bowmaker, G. A.; Dyason, J. C.; Healy, P. C.; Engelhardt, M.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1089.

equivalent and are similar to those of the other molecules reported here. As best seen in Figure 2, the iodide ligands lie well outside of the planes of the two P–Au–P units.

Structure of Au₂(μ-P5P)₂I₂. The structure of Au₂(μ-PSP)₂I₂ is shown in Figure 4. This is the only non-centrosymmetric molecule in the series reported here. It has no crystallographically imposed symmetry, and there are some significant differences in the bond lengths and angles involving the two gold centers. Each gold ion has planar, three-coordinate

geometry. For Au1, the sum of the two P–Au–I angles and the P–Au–P angle is 359.83°, while for Au2 that sum is 359.13°. Notice that the P–Au–P angles (164.63(3), 172.32(3)°) are quite wide. Remarkably, the two polar Au^IP₂I units are aligned in parallel fashion as can be seen in Figures 2 and 4.

Structure of Au₂(μ-P6P)₂I₂. Figure 5 shows a drawing of the Au₂(μ-P6P)₂I₂ molecule. The molecule resides at a crystallographic center of symmetry with one-half of the molecule in the asymmetric unit. The structure of Au₂(μ-

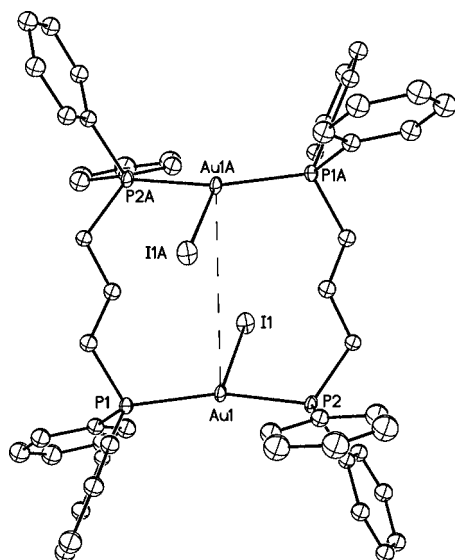


Figure 1. Drawing of the structure of $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity.

$\text{P6P})_2\text{I}_2$ is similar to that of $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$ with the two planar AuP_2I units arranged in antiparallel fashion as is apparent in the perspective used in Figure 2. The sum of the two P–Au–I angles and the P–Au–P angle is 358.44° .

Luminescence. Each of the compounds is luminescent at room temperature. Figure 6 shows the emission and excitation spectra for the planar, three-coordinate complexes, $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$, $\text{Au}_2(\mu\text{-P5P})_2\text{I}_2$, and $\text{Au}_2(\mu\text{-P6P})_2\text{I}_2$. The excitation profiles for these three complexes are similar, but the emission maxima differ. The absorption maxima increase as the length of the methylene chain (and hence n) increases, but there is no apparent correlation of the emission energies with the P–Au–P angles in the ground state of these molecules. Four-coordinate $\text{Au}_2(\mu\text{-P4P})_2(\mu\text{-I})_2$ is also luminescent with an excitation maximum at 353 nm and emission maximum at 440 nm.

Optimized Geometric Structures from Computational Studies. To better understand the connection between the structure of these complexes and their corresponding luminescence properties, electronic structure calculations of these complexes were performed. To obtain input structures for these compounds, geometry optimizations (GOs) were performed using the widely employed B3LYP hybrid density functional on the compounds $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$ ($n3$), $\text{Au}_2(\mu\text{-P5P})_2\text{I}_2$ ($n5$), and $\text{Au}_2(\mu\text{-P6P})_2\text{I}_2$ ($n6$). To determine the influence of the tether on the AuP_2I unit, we also performed a GO at the B3LYP level on the unconstrained compound $\text{Au}(\text{PPh}_2\text{Me})_2\text{I}$. These calculations utilized a large def2-TZVPP basis set²³ for all atoms except gold, which was treated with a VTZ-PP basis set on the valence electrons²⁴ and the Stuttgart/Bonn pseudopotential (ECO60MDF) on all core electrons.²⁵ The resulting singlet state GO structures of $n3$ and $n6$ are in good agreement with the experimental data (Tables 2 and 3). We note that there is a small but consistent overestimation of the Au–ligand bond lengths in the B3LYP structures vs the experimentally determined bond lengths; however, this is a well-known artifact of the B3LYP functional.²⁶

For $n5$ the computations produced the unusual parallel alignment of the two AuP_2I units seen in Figures 2 and 4, but the large differences in the two gold(I) centers observed

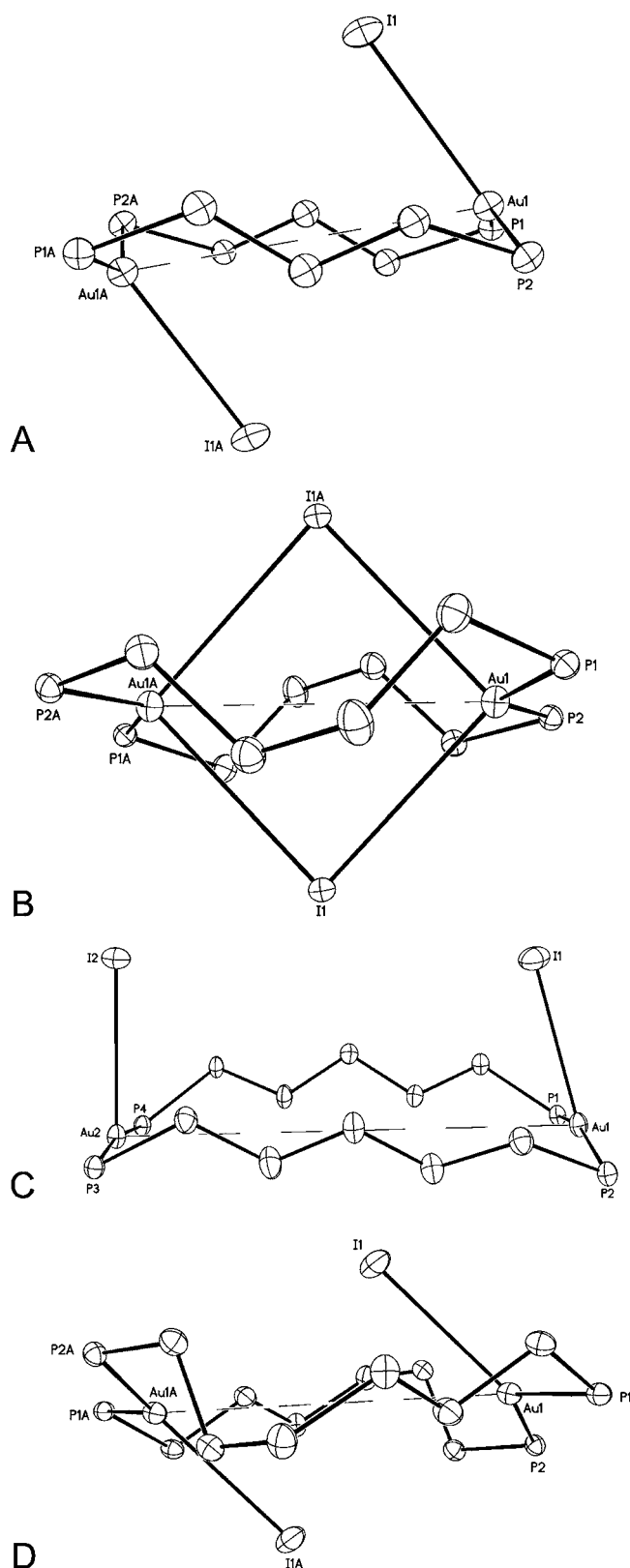


Figure 2. Comparison of the ring conformations of $\text{Au}_2(\mu\text{-PnP})_2\text{I}_2$; (A) $n = 3$, (B) $n = 4$, (C) $n = 5$, (d) $n = 6$. For reference, the dashed lines connect the gold centers.

experimentally could not be reproduced; we find that both gold(I) centers in the GO structure of $n5$ are similar to one another. Although some asymmetry is observed between the

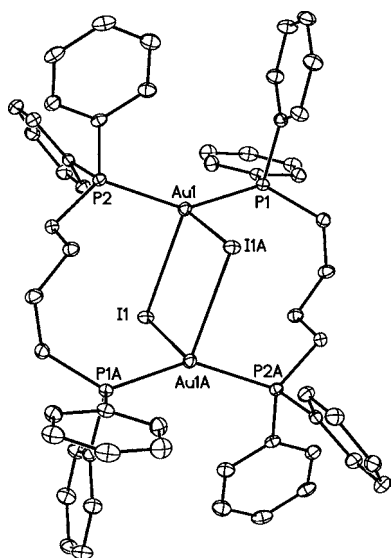


Figure 3. Drawing of the structure of $\text{Au}_2(\mu\text{-P4P})_2(\mu\text{-I})_2$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity.

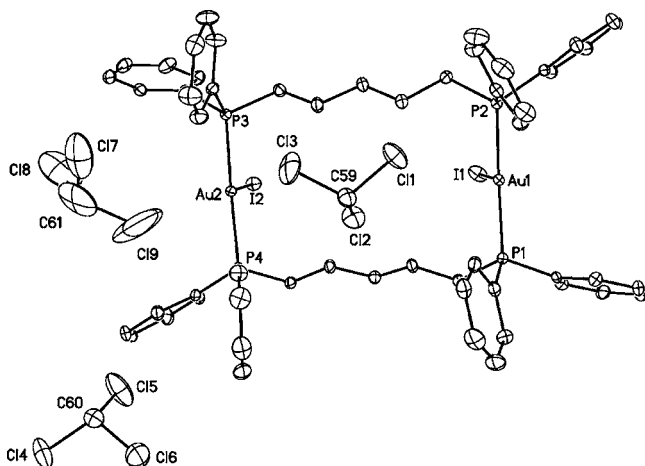


Figure 4. Drawing of the structure of $\text{Au}_2(\mu\text{-P5P})_2\text{I}_2 \cdot 3\text{CHCl}_3$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity.

two gold(I) centers, the difference between the two gold(I) geometries is minor (Tables 2 and 3). The two Au-centers in the GO structure of $n5$ are most consistent with the less open P–Au–P bond angle of $\text{Au}_2(\mu\text{-P5P})_2\text{I}_2$ (labeled Au2) derived crystallographically. Even at the MP2 level of theory the asymmetry observed for the two gold(I)-centers in $\text{Au}_2(\mu\text{-P5P})_2\text{I}_2$ cannot be reproduced; we observe that the two P–Au–P bond angles remain at $\sim 165^\circ$.

There are two key metric parameters of note in the discussion below: the P–Au–P bond angles and the Au–I bond lengths (Tables 2 and 3). The calculated P–Au–P bond angles increase from 136.1° ($n6$) to 155.0° ($n3$) to 164.1° ($n5$), as is observed crystallographically. Compound $n6$ possesses metric parameters that are the closest to $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$, but it still demonstrates significant distortions from the untethered compound. Thus, all of the tethered complexes demonstrate significant asymmetry from the unconstrained compound $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$. These differences in metric parameters between the complexes are likely a result of the polymethylene

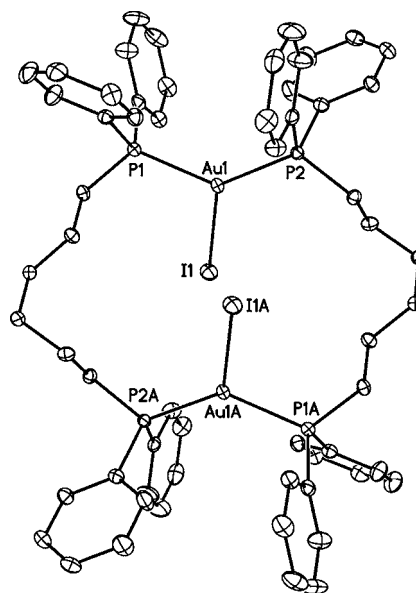


Figure 5. Drawing of the structure of $\text{Au}_2(\mu\text{-P6P})_2\text{I}_2$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity.

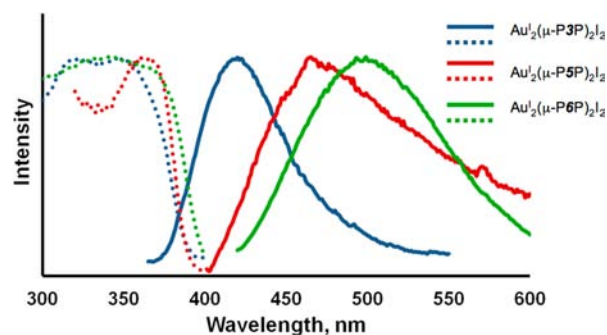


Figure 6. Emission spectra for crystals of the planar, three-coordinate complexes $\text{Au}_2(\mu\text{-P}n\text{P})_2\text{I}_2$ ($n = 3, 5, 6$) at room temperature.

tether, which is undoubtedly influencing the geometry about the gold(I) center.

Unlike the P–Au–P bond angles, the Au–I bond lengths display a systematic trend across the $n3$ – $n6$ series. As the polymethylene tether increases there is a systematic decrease in the Au–I bond length; the bond-length decreases from 3.051 \AA ($n3$) to 2.973 \AA ($n6$). At 2.970 \AA , the unconstrained compound $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$ demonstrates the shortest Au–I bond length of the compounds examined computationally. The elongation of the Au–I bond length as the polymethylene tether is shortened can be readily rationalized. There are significant steric interactions between the I atom and the methylene H atoms. As the tether is elongated the phenyl groups are more capable of “splaying open” allowing the methylene groups to open up away from the Au–Au central axis. Thus, the Au–I bond length can contract.

In addition to the ground state singlet structure (S_0), we also performed GOs of the first triplet excited state (T_1) of $n3$, $n5$, $n6$, and $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$. Selected metric parameters are shown in Tables 2 and 3. The untethered complex $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$ displays an excited state geometry with all of the hallmarks of those reported for other three coordinate gold(I) complexes in their first excited triplet state.^{16,17} The overall structure is best described as T-shaped; the P–Au–I bond angle compresses to

$\sim 90^\circ$ and the P–Au–P opens to 179.8° . The Au–P bond length increases by ~ 0.3 Å to 2.66 Å, while the Au–I bond length undergoes a contraction to 2.91 Å. In contrast, the T1 surface for n3, n5, and n6 are not T-shaped. Furthermore, the same nonsystematic changes in the P–Au–P bond angle observed on the S0 surface are reflected on the T1 surface. The P–Au–P bond angles become progressively more open from n6 (158.3°) to n3 (163.3°) to n5 ($170.6/175.3^\circ$). Thus, the polymethylene tether is imposing significant geometric constraints on the T1 surface as well as the S0 surface.

Calculated Excitation and Emission Energies. Using the GO structures from above we calculated the energies of the $S1 \leftarrow S0$ and $T1 \rightarrow S0$ transition energies. To achieve a high degree of accuracy for these excitation and emission energies we employed Neese's spectroscopically oriented configuration interaction (SORCI) methodology.²⁷ Unlike time-dependent density functional theory (TD-DFT) methods, the SORCI method is a true multiconfigurational, ab initio computational technique, and thus yields far more accurate excited state energies.²⁸ For these SORCI calculations, a modest CAS(4,4) reference space was utilized, which proved adequate to reproduce the experimentally observed excitation and emission energies (Table 4). The $S1 \leftarrow S0$ excitation energies for n3, n5,

Table 4. Computed and Experimental Excitation and Emission Maxima for Trigonal Planar Gold(I) Complexes

| compd | | n3 | n5 | n6 | Au ^I IP ₂ |
|------------------------------------|--------------|--------|-----|-----|---------------------------------|
| $S1 \leftarrow S0$ (nm) excitation | computed | 387 | 388 | 391 | 390 |
| | experimental | 370 sh | 370 | 380 | |
| $T1 \rightarrow S0$ (nm) emission | computed | 425 | 486 | 505 | 529 |
| | experimental | 420 | 465 | 499 | |

n6, and Au^I(PPh₂Me)₂I are all similar to one another, and similar to those experimentally observed. In all cases we see the lowest energy excitation corresponds to a wavelength of ~ 390 nm. Thus, the calculations strongly suggest that the nature of the initial excitation process is best described as an excitation from the first to second singlet surfaces. In all of these cases the excitation process is best described as a metal-to-ligand charge-transfer (MLCT) process originating from a state composed of mostly Au(*Sd_{xy}*)/I(*Sp_x*) antibonding character to a state that is composed of exclusively phosphine ligand character (Figure 7a).

The lowest energy $T1 \rightarrow S0$ emission process corresponds to roughly the inverse of the excitation process; it corresponds to a decay from a state corresponding to phosphine-ligand character to a state composed of Au(*Sd_{xy}*)/I(*Sp_x*) antibonding

character (Figure 7b). Despite the fact that the lowest energy emissions are all $T1 \rightarrow S0$ processes originating from similar states, we calculate different emission energies for all four compounds investigated. There is a systematic red-shift in emission energies as the polymethylene tether is elongated. Compound n3 has a calculated emission energy of 425 nm, n5 has an emission energy of 476 nm, while n6 has its emission maximum at 505 nm. Untethered Au^I(PPh₂Me)₂I displayed the most red-shifted emission energy of all of the compounds investigated (529 nm).

Origin of the Differential Emission Energies. Of the different structural parameters, the two parameters that vary the most from the S0 to the T1 structures are the Au–I bond length and the P–Au–P bond angle. The potential energy surfaces (PESs) of Au^I(PPh₂Me)₂I were, therefore, constructed for the lowest energy singlet and triplet surfaces to examine the influence of the P–Au–P bond angle distortion and the Au–I bond length. Geometries for the PESs were constructed at the B3LYP level of theory using Au^I(PPh₂Me)₂I. To deconvolve the influence of the P–Au–P bond angle on the Au–I bond length and the Au–I bond length on the P–Au–P bond angle constrained GOs were performed. The PESs examining the P–Au–P bond distortion (from 105 to 180° in 2.5° increments) utilized a constrained Au–I bond length of 3.000 Å, while the PESs examining the Au–I bond length (from 2.800 to 3.150 Å in 0.025 Å increments) utilized a P–Au–P bond angle of 160°. Final single-point energies for each GO structure along the S0 and T1 surfaces were calculated using the B2PLYP double-hybrid functional.²⁹ This functional is similar to the B3LYP hybrid-functional, except it also mixes in a second-order Møller–Plesset perturbation theory (MP2) correction (along with the Hartree–Fock (HF) correction) to the DFT derived energies yielding highly accurate energies.^{29,30}

The PES for the S0 state results in a rather shallow energy profile as the P–Au–P (Figure 8a). There is a minimum on the PES for Au^I(PPh₂Me)₂I (Au–I bond length 3.000 Å) at 138.3° , which increase to 9.9 kJ mol⁻¹ at 180° . There is another maximum observed at 105° , which at 9.4 kJ mol⁻¹ is not as positive in energy as the point at 180° . This can be contrasted with the T1 surface, where the range of 132 – 136° represents a maximum on the T1 surface. In contrast there is a minimum of the T1 surface at 175.3° , which is 19.3 kJ mol⁻¹ lower in energy than the maximum at 132.2° . This is consistent with the nature of the electronic structures of the two states. Along the T1 surface the highest occupied molecular orbital (HOMO) is made of a P(σ)-Au(6s) antibonding interaction. As the bond distorts from 180° to 132.2° more Au(6s) character becomes mixed into the HOMO, and the Au–P bonds become more

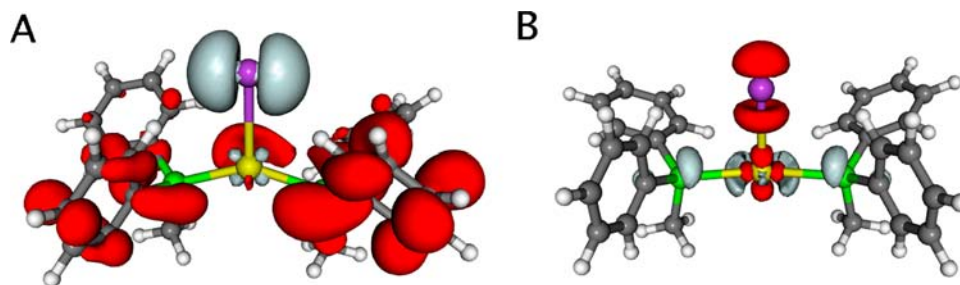


Figure 7. Isosurface transition difference plots derived from the SORCI calculations (TZVPP/VTZ-PP-ECP) for the (A) $S1 \leftarrow S0$ and (B) $T1 \rightarrow S0$ transitions for Au^IIP₂. The red areas correspond to the regions of the molecule that are gaining electron density while the ice-blue areas correspond to regions of the molecule that are losing electron density.

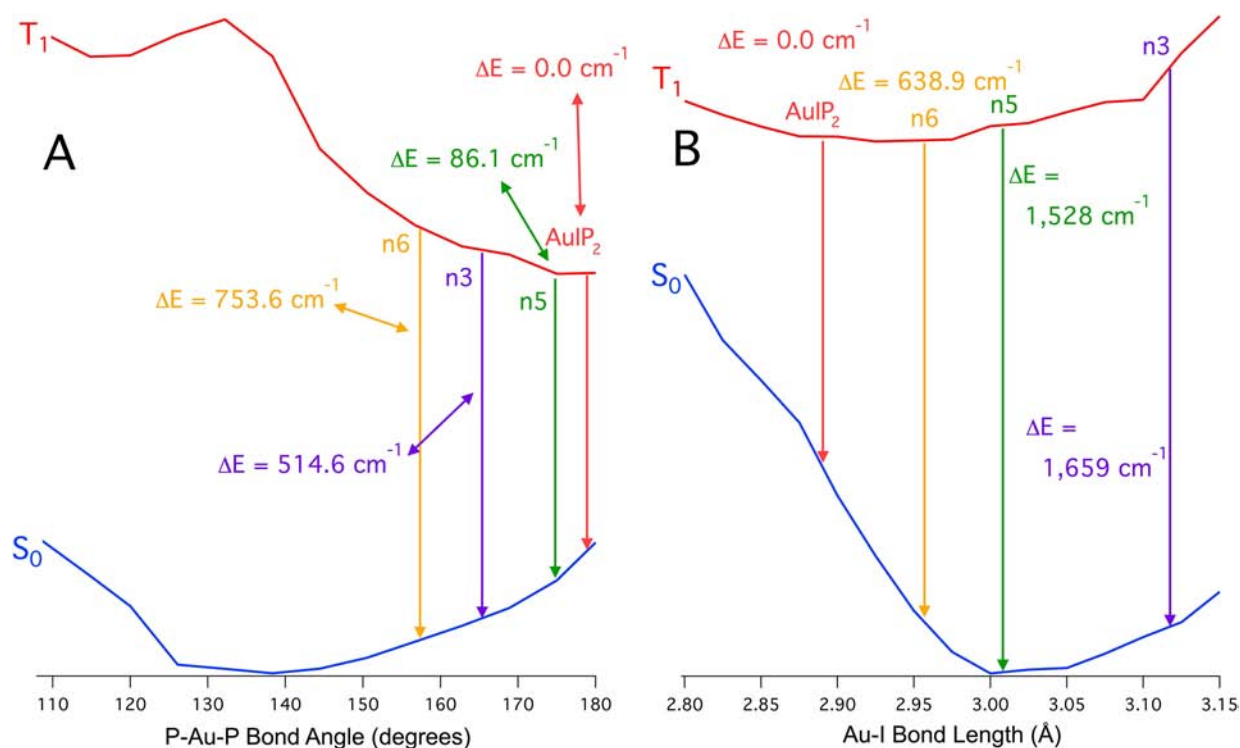


Figure 8. (A) B2PLYP (TZVPP/VTZ-PP-ECP) PES constructed for the P–Au–P bond angle distortion maintaining a constant Au–I bond length. The vertical lines represent the transitions from the T₁ to S₀ surfaces based on the predicted excited state P–Au–P bond angles from the B3LYP geometry optimized structures. Energies are relative to the Au^IP₂I T₁ → S₀ transition. (B) B2PLYP (TZVPP/VTZ-PP-ECP) PES constructed for Au–I bond length distortion with a fixed P–Au–P bond angle.

covalent. Thus, the antibonding HOMO of the T₁ state increases in energy as the P–Au–P bond angle contracts, and the overall energy of the compound increases. In contrast, the P(σ)–Au(6s) covalency is not strongly affected along the S₀ surface as the bond distorts, hence the rather small influence on the energy of the S₀ state as the P–Au–P bond angle is distorted.

This can be contrasted with the changes in the energy of the S₀ and T₁ surfaces as the Au–I bond length is altered (Figure 8b). For the S₀ state there is a large change in energy as the Au–I bond length changes. There is a minimum along the S₀ PES for Au^I(PPh₂Me)₂I at 2.982 Å (P–Au–P bond angle 160°). Contraction of the Au–I bond length to 2.800 Å leads to a 37.6 kJ mol⁻¹ increase in energy, while elongation to 3.150 Å leads to only a 7.7 kJ mol⁻¹ increase in energy. In contrast with the S₀ surface, the T₁ surface shows little influence in the change of energy as the Au–I bond length is altered. A contraction of the Au–I bond length from the equilibrium bond length of 2.911 Å on the T₁ surface to 2.800 Å shows an increase in energy of only 3.8 kJ mol⁻¹, while elongation of the bond to 3.150 Å leads to an increase of 11.81 kJ mol⁻¹. Once again, we can relate this to the electronic structure of the S₀ vs T₁ states. The HOMO of the S₀ state is composed of a Au(Sd_{x₂-y₂)₂)/I(5p_z) antibonding interaction. As one compresses the Au–I bond, the Au–I bond covalency increases and the energy of the HOMO increases. Hence, the energy of the state increases. In contrast, contraction of the Au–I bond length leaves the T₁ surface virtually unaltered; as we have relieved antibonding character in the Au–I bond, contraction of the Au–I bond is not as energetically unfavorable on the T₁ PES.}

Using the constructed PESs we can determine the emission energies of Au^I(PPh₂Me)₂I as a function of P–Au–P bond

angle and Au–I bond length. Along the P–Au–P PES we predict a small change in the T₁ → S₀ energy as the bond P–Au–P bond angle is closed, with a ΔE = 753.6 cm⁻¹ going from the least energetic emission energy (Au^I(PPh₂Me)₂I) to the largest emission energy (n6). For the Au–I bond length PES we see a more dramatic change in emission energy as a function of Au–I bond length with a ΔE = 1,659 cm⁻¹ going from Au^I(PPh₂Me)₂I to n3.

Combining the energies of the two PESs allows us to understand the origins in the emission energies. Although the observed ΔE from the PESs are underestimated by at least one-half, the trend obtained in the SORCI calculations and the experimental data is observed. From the PES results we derive a systematic change in emission energies as the polymethylene tether length is increased. Compound n3 would be predicted to have the highest emission energy while Au^I(PPh₂Me)₂I will have the lowest emission energy. This compares well with both the SORCI calculations for all four compounds and the experimental data for n3, n5, and n6. Thus, it is reasonable to propose that the differences in emission energy observed experimentally are largely a result of changes in the Au–I bond length with minor contributions from the P–Au–P bond angle distortions.

CONCLUSIONS

The results reported here show that the diphosphine ligands prefer to form bridged, binuclear complexes rather than chelated monomers. The dimers with an odd number of methylene groups in the P*n*P ligand have these methylene groups arranged in a regular zigzag fashion. However, when an even number of methylene groups is present, these groups assume a less regular, kinked arrangement. These features are

seen in the related, bridged, binuclear complexes that have been observed for a number of planar, four-coordinate metal complexes formed from *Pn*P-type ligands.^{31–34} As the computational and experimental studies show, the tether between the phosphorus atoms imposes interesting constraints on bond distances and angles within the gold coordination sphere.

Unlike the situation with $\text{Au}_2(\mu\text{-dpe})_2\text{Br}_2$ and $\text{Au}_2(\mu\text{-dpe})_2\text{I}_2$, where the crystallization of a variety of different solvates produced significant changes in the aurophilic interactions and luminescence because of the flexibility within the molecule,^{15,16} we did not encounter such variations in the complexes reported here. Only $\text{Au}_2(\mu\text{-PSP})_2\text{I}_2 \cdot 3\text{CHCl}_3$ crystallized as a solvate. The others did not need incorporation of solvent molecules to crystallize. In none of the compounds reported here did the gold centers approach one another close enough to allow aurophilic interactions.

The four complexes reported here are luminescent as solids at room temperature. For the three trigonal planar complexes, the emission energy is more strongly correlated with changes in the Au–I bond length rather than changes in the P–Au–P angle. This observation was rationalized in terms of bonding interactions involved in these gold complexes; contraction of the Au–I bond results in a significant destabilization of the S0 surface because of an increase in the energy of the antibonding $\text{Au}(\text{Sd}_{x_2-y_2})/1(\text{Sp}_z)$ orbital. Such a large destabilization of the filled $\text{Au}(\text{Sd}_{x_2-y_2})/1(\text{Sp}_z)$ antibonding orbital is not produced upon P–Au–P bond angle distortions.

EXPERIMENTAL SECTION

Materials. A previously reported procedure was used for the preparation of (tth)AuCl (tth = tetrahydrothiophene).³⁵ The phosphine ligands were purchased from Alfa Inorganics.

$\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$. A 100 mg (0.309 mmol) portion of AuI was suspended in 30 mL of dichloromethane. 1,3-Bis(diphenylphosphino)propane (250 mg, 0.606 mmol) was added to this suspension. After stirring for 2 h, all the solids dissolved. The solution was filtered, and then the solvent was removed in a vacuum. The white solid was collected and washed with diethyl ether: yield, 160 mg (70.3%). Colorless prisms suitable for the X-ray structure determination and emission spectroscopy were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the product.

Infrared spectrum: 3050w, 2923w, 1481m, 1434s, 1305w, 1097s, 1028w, 995w, 949m, 841w, 741m, 688s, 528m, 510s, 478s, 456m.

³¹P NMR spectrum: singlet at 35.1 ppm.

$\text{Au}_2(\mu\text{-P4P})_2(\mu\text{-I})_2$. This complex was prepared using the method outlined for $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$ from 100 mg (0.309 mmol) of AuI and 260 mg (0.610 mmol) of 1,4-bis(diphenylphosphino)butane: yield, 190 mg (81.8%). Colorless blocks suitable for the X-ray structure determination and emission spectroscopy were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the product.

Infrared spectrum: 3049w, 2922w, 1479m, 1435s, 1401w, 1099s, 1028w, 996w, 893w, 742m, 693s, 517m, 481m, 454m.

³¹P NMR spectrum: singlet at 35.6 ppm.

$\text{Au}_2(\mu\text{-P5P})_2\text{I}_2 \cdot 3(\text{CHCl}_3)$. This complex was prepared using the method outlined for $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$ from 265 mg (0.602 mmol) of 1,5-bis(diphenylphosphino)pentane: yield, 200 mg (84.6%). Colorless blocks suitable for the X-ray structure determination and emission spectroscopy were obtained by slow diffusion of diethyl ether into a chloroform solution of the product.

Infrared spectrum: 3049w, 2919w, 1480m, 1428s, 1406w, 1102s, 1013w, 993w, 947m, 840w, 741m, 685s, 527m, 503s, 476s, 451m.

³¹P NMR spectrum: singlet at 35.7 ppm.

$\text{Au}_2(\mu\text{-P6P})_2\text{I}_2$. This complex was prepared using the method outlined for $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$ from 275 mg (0.605 mmol) of 1,5-

bis(diphenylphosphino)hexane: yield, 200 mg (83.2%). Colorless blocks suitable for X-ray structure determination and emission spectroscopy were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the product.

Infrared spectrum: 3044w, 2913w, 1585w, 1478m, 1428s, 1401w, 1102s, 1024w, 976w, 947m, 854w, 773w, 739m, 687s, 528m, 504s, 473s, 447m.

³¹P NMR spectrum: singlet at 35.6 ppm.

X-ray Crystallography and Data Collection. The crystals were removed from the glass tubes in which they were grown together with a small amount of mother liquor and immediately coated with a hydrocarbon oil on a microscope slide. A suitable crystal of each compound was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker SMART 1000 CCD with graphite monochromated Mo K α radiation at 90(2) K.

The structures were solved by direct methods and refined using all data (based on F^2) using the software SHELXTL 5.1. A semiempirical method utilizing equivalents was employed to correct for absorptions. Hydrogen atoms were added geometrically and refined with a riding model.³⁶

Physical Measurements. Infrared spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LSS0B luminescence spectrophotometer.

Computational Details. GOs on ground and triplet excited states were performed using Turbomole v. 6.3³⁷ with the crystallographic data as input structures. In addition, the singlet and triplet structures of $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$ were initially calculated within Turbomole. Absorption and emission spectra were simulated using ORCA v. 2.9.0.³⁸ The PES was constructed for the molecule $\text{Au}^1(\text{PPh}_2\text{Me})_2\text{I}$ using ORCA v. 2.8.20. All calculations utilized an all electron doubly polarized basis set of triple- ζ quality on all atoms except gold, which utilized a Stuttgart/Bonn pseudopotential and corresponding 19-valence electron triple-basis set. GOs were performed at the B3LYP level of theory,³⁹ which in ORCA made use of the RIJCXX approximation.⁴⁰ Single point energies were calculated using the B2PLYP double-hybrid functional of Grimme and co-workers.⁴¹ Absorption and emission spectra were simulated using the spectroscopically oriented configuration interaction (SORCI) approach,⁴² using a CAS(4,4) reference space, a selection threshold of $1 \times 10^{-6} E_h$, a prediagonalization threshold of 10^{-4} , and a natural orbital threshold of 10^{-5} .

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files in CIF format for $\text{Au}_2(\mu\text{-P3P})_2\text{I}_2$, $\text{Au}_2(\mu\text{-P4P})_2(\mu\text{-I})_2$, $\text{Au}_2(\mu\text{-P5P})_2\text{I}_2 \cdot 3(\text{CHCl}_3)$, and $\text{Au}_2(\mu\text{-P6P})_2\text{I}_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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