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Article

Synthesis of Gold Phosphido Complexes Derived from Bis(secondary) Phosphines. Structure of Tetrameric $[Au(MesP(CH_2)_3PMes)Au]_4$

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Treatment of 2 equiv of Au(THT)Cl (THT = tetrahydrothiophene) with the bis(secondary) phosphines HP(R)$\sim$PH(R) (linker $\sim$ = $(CH_2)_3$, R = Mes = 2,4,6-$Me_3C_6H_2$ (**1**), R = Is = 2,4,6-$(i\text{-}Pr)_3C_6H_2$ (**2**), R = Ph (**4**); $\sim$ = $(CH_2)_2$, R = Is (**3**); HP(R)$\sim$PH(R) = 1,1′-$(\eta^5\text{-}C_5H_4PHPh)_2Fe$ (**5**)), gave the dinuclear complexes $(AuCl)_2(\mu\text{-}HP(R){\sim}PH(R))$ (**6**−**10**). Dehydrohalogenation with aqueous ammonia gave the phosphido complexes $[(Au)_2(\mu\text{-}P(R){\sim}P(R))]_n$ (**11**−**15**). Ferrocenyl- and phenylphosphido derivatives **15** and **14** were insoluble; the latter was characterized by solid-state ^{31}P NMR spectroscopy. Isitylphosphido complexes **12** and **13** gave rise to broad, ill-defined NMR spectra. However, mesitylphosphido complex **11** was formed as a single product, which was characterized by multinuclear solution NMR spectroscopy, solid-state ^{31}P NMR spectroscopy, and elemental analyses. Mass spectrometry suggested that this material contained eight gold atoms ($n = 4$). A structure proposed on the basis of the ^1H NMR spectra, containing a distorted cube of phosphorus atoms, was confirmed by X-ray crystallographic structure determination. NMR spectroscopy, including measurement of the hydrodynamic radius of **11** by ^1H NMR DOSY, suggested that this structure was maintained in solution. Density functional theory (DFT) structural calculations on **11** were also in good agreement with the solid-state structure.

Introduction

The gold(I) phosphido complexes $[Au(PR_2)]_n$ adopt cyclic solid-state structures.[1] Related oligomers derived from bis(secondary) phosphines HP(R)$\sim$PH(R) might form interesting three-dimensional self-assembled structures,[2] constrained by the nature of the linker ($\sim$) and the expected linear two-coordinate geometry of the gold centers (Chart 1).[3] These include tetranuclear **A**, in which a long linker might be needed to support near-linear Au coordination, cubane **B**, in which the arrangement of the eight phosphorus atoms is analogous to the S_8 cube in the gold sulfide $[Au_{12}S_8]^{4-}$ (**C**),[4] and hexameric drum **D**, as in the alumoxane $[(t\text{-}Bu)Al(O)]_6$.[5] To investigate these possibilities, we report here synthesis and characterization of gold phosphido complexes derived from bis(secondary) phosphines.

Results and Discussion

Bis(secondary) Phosphines and Their AuCl Complexes. The solubility of the gold phosphido complexes $[Au(PR_2)]_n$ depends strongly on the substituents. For example, $[Au(PPh_2)]_n$ is insoluble,[6] but soluble $[Au(PMes_2)]_n$ (Mes = 2,4,6-$Me_3C_6H_2$) could be characterized by solution NMR spectroscopy and recrystallized to yield crystals suitable for X-ray crystallography.[1] Therefore,

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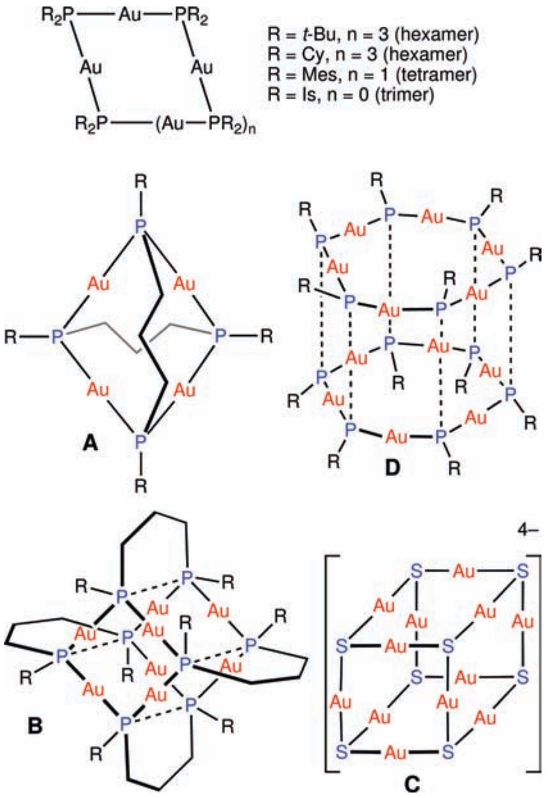
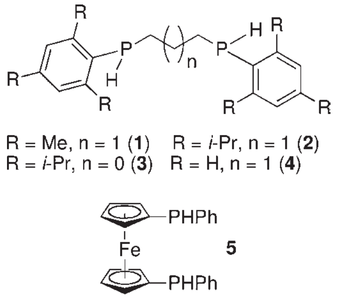
Chart 1. Structures of Gold Phosphido Complexes[1] [Au(PR$_2$)]$_n$ and Possible Structures for Analogues Derived from Bis(secondary) Phosphines[a]



[a] Ligand linker groups in these structures are shown arbitrarily as three methylenes (**A** and **B**), or removed for clarity (**D**). The dashed lines are included as a guide for the eye, to illustrate the cube (**B**) and drum (**D**) geometries.

Chart 2. Structures of the Bis(secondary) Phosphines



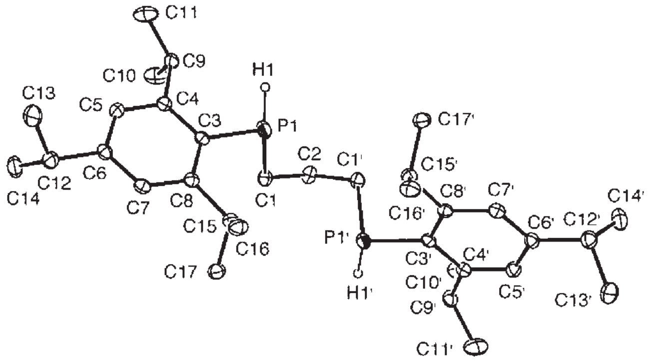


Figure 1. ORTEP diagram of *meso*-**2**. Only the P−H hydrogen atom, which was located and refined, is shown.

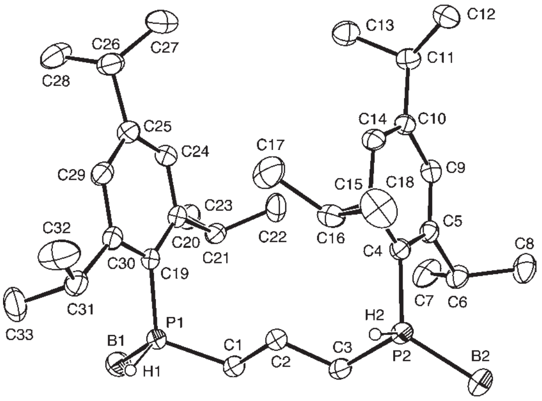
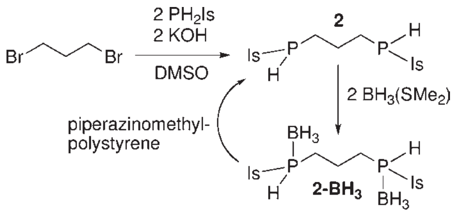


Figure 2. ORTEP diagram of *meso*-**2-BH$_3$**. Only the P−H hydrogen atoms, which were located and refined, are shown.

Scheme 1. Synthesis of Bis(secondary) Isitylphosphine **2**



we sought bis(secondary) phosphines with bulky, solubilizing substituents (Chart 2). The diphosphine MesPH(CH$_2$)$_3$PHMes (**1**) is known.[7] The analogous IsPH(CH$_2$)$_3$PHIs (**2**, Is = isityl = 2,4,6-(i-Pr)$_3$C$_6$H$_2$) was prepared by a similar method (Scheme 1), and we recently reported synthesis of ethano-bridged IsPH(CH$_2$)$_2$PHIs (**3**).[8] The phenylphosphino derivative PhPH(CH$_2$)$_3$PHPh (**4**) was used to test the structure-solubility hypothesis; both it and ferrocenylphosphine **5** were commercially available. The new bis(phosphine) **2** was protected as borane adduct **2-BH$_3$** to simplify purification, then regenerated using a polymer-supported amine to yield a mixture of *rac* and *meso* diastereomers (see Scheme 1 and the Experimental Section).[9]

The crystal structures of the bis(phosphine) *meso*-**2** and bis(phosphine)-borane *meso*-**2-BH$_3$** are shown in Figures 1 and 2. See Table 1 for crystallographic data, Table 2 for selected bond lengths and angles, and the Supporting Information for additional details.

As expected, borane complexation resulted in a larger CPC angle and shorter P−C bonds (Table 2);[10] the difficulty in finding H atoms by X-ray crystallography makes the bond lengths and angles involving the P−H group less reliable. Presumably because of the disparity in size between the large isityl and the small hydrogen substituents, the P angles in **2-BH$_3$** ranged from 102.9(11)

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Table 1. Crystallographic Data for Phosphine **2**, Phosphine-Borane **2-BH$_3$**, and Gold Complex **11**·2toluene

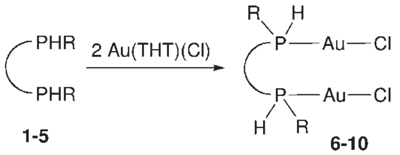
	2	**2-BH$_3$**	**11**·2toluene
formula	$C_{33}H_{54}P_2$	$C_{33}H_{60}B_2P_2$	$C_{98}H_{128}Au_8P_8$
formula wt	512.70	540.37	3129.50
space group	$C2/c$	$P2(1)/n$	$P\overline{1}$
a, Å	35.954(4)	9.2040(12)	15.693(7)
b, Å	8.3397(9)	33.389(4)	16.377(7)
c, Å	10.7464(11)	12.1610(16)	21.381(9)
α, deg	90	90	84.064(5)
β, deg	100.6680(10)	109.068(2)	78.114(5)
γ, deg	90	90	70.485(5)
V, Å^3	3166.5(6)	3532.2(8)	5065(4)
Z	4	4	2
D(calcd), g/cm^3	1.075	1.016	2.052
μ(MoKα), mm^{-1}	0.156	0.142	11.708
temp, K	153(2)	208(2)	150(2)
$R(F)$, %^{a}	4.50	5.88	5.08
$R_w(F^2)$, %^{a}	11.75	13.53	11.08

[a] Quantity minimized: $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$. A Bruker CCD diffractometer was used in all cases.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Phosphine **2** and Phosphine-Borane **2-BH$_3$**

	2	**2-BH$_3$**
P−C(Is)	1.8433(18)	1.824(3), 1.824(3)
P−C(CH_2)	1.8498(19)	1.817(3), 1.805(3)
P−H	1.35(5)	1.37(3), 1.42(3)
C−P−C	101.53(8)	112.16(12), 106.41(13)
C(Is)−P−H	109.8(19)	102.9(12), 102.9(11)
C(CH_2)−P−H	107(2)	100.1(13), 101.6(11)
C−P−B		112.23(17), 113.82(16) (CH_2) 118.74(16), 122.57(16) (Is)
B−P−H		108.4(12), 107.0(11)

Scheme 2. Synthesis of AuCl Complexes **6−10**^{a}

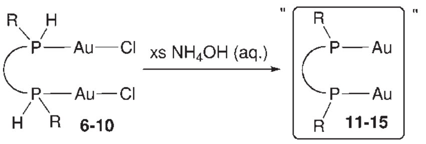


[a] The diphosphines RHP∼PHR were MesHP(CH_2)$_3$PHMes (**1** and **6**), IsHP(CH_2)$_3$PHIs (**2** and **7**), IsHP(CH_2)$_2$PHIs (**3** and **8**), PhHP(CH_2)$_3$PHPh (**4** and **9**), and PhHPC$_5$H$_4$FeC$_5$H$_4$PHPh (**5** and **10**).

to 122.57(16)°, with an average of 109.1°, as expected, close to the tetrahedral angle.

Treatment of the bis(phosphines) **1−5** with 2 equiv of Au(THT)(Cl) (THT = tetrahydrothiophene) gave the dinuclear complexes $(AuCl)_2(\mu\text{-}HP(R){\sim}PH(R))$ **6−10** in high yield as mixtures of diastereomers (Scheme 2), whose ratio (typically about 1:1) could be determined by ^{31}P NMR spectroscopy. As in related gold complexes of secondary phosphines,[1,11] the PH groups gave rise to ^1H NMR signals in CD_2Cl_2 around 6−7 ppm with large $^1J_{PH}$ couplings of about 400 Hz, and IR absorptions near 2400 cm^{-1} (see the Experimental Section for details). Although *cis* AuCl groups are arbitrarily shown in Scheme 2, we did not investigate the conformations of these complexes.

Scheme 3. Synthesis of Phosphido Complexes **11−15**^{a}



[a] See Chart 2 for the structures of the diphosphine ligands in complexes **6−10**. The bis(phosphido) ligands RP∼PR were MesP(CH_2)$_3$PMes (**11**), IsP(CH_2)$_3$PIs (**12**), IsP(CH_2)$_2$PIs (**13**), PhP(CH_2)$_3$PPh (**14**), and PhPC$_5$H$_4$FeC$_5$H$_4$PPh (**15**)

Preparation of Phosphido Complexes 11−15. Dehydrohalogenation of **6−10** with aqueous ammonia in CH_2Cl_2 gave phosphido complexes **11−15** (Scheme 3). Two of these, derived from 1,3-bis(phenylphosphino)propane (**14**) and the ferrocene-based diphosphine (**15**), were isolated as insoluble yellow or orange solids, which were identified by elemental analyses and IR spectra. Complex **14** was also characterized by solid-state NMR spectroscopy (see the Experimental Section).

As desired, isitylphosphido complexes **12−13** were soluble in a variety of solvents. However, both showed broad, overlapping peaks in their ^1H and ^{31}P NMR spectra, and the ^{31}P NMR signals were low in intensity at room temperature. Recording the ^1H NMR spectrum of **12** at low temperature did not yield an improved spectrum. Although elemental analyses suggested that the expected phosphido complexes had formed, recrystallization did not afford pure material, and the NMR spectra could not be interpreted readily. Hence, complete characterization of these complexes was not pursued.

Structure of 11. Similarly, mesitylphosphido complex **11** was soluble in chloroform and methylene chloride, and sparingly soluble in toluene. In contrast to **12** and **13**, however, it could be recrystallized to give pure white solid which analyzed, as expected, for $[Au(MesP(CH_2)_3P\text{-}Mes)Au]_n$. This material did not melt up to 222 °C, when it changed from white to pink to purple, becoming black at 231 °C. Complex **11** gave rise to simple, well-behaved NMR spectra characteristic of a single species both at room temperature and at low temperature in CD_2Cl_2. For example, a sharp ^{31}P NMR singlet was observed at −7.2 ppm in CD_2Cl_2 and −6.4 ppm in toluene-d$_8$ (21 °C). The solid-state ^{31}P NMR spectra of different samples of **11** showed a broad envelope of peaks (fwhm ∼ 1000 Hz); approximate fits gave isotropic chemical shift values of −0.7, −1.0, and −2.5 ppm, suggesting that the solution structure is maintained in the solid state. For solid-state ^{31}P NMR spectra and additional discussion, see the Supporting Information. The matrix-assisted laser desorption/ionization (MALDI) mass spectrum of **11** showed a peak at m/z 2946, consistent with a tetramer of Au_8P_8 stoichiometry ($n = 4$; calculated m/z = 2944).

The simplest structure for a tetramer is cubane **B** (Charts 1 and 3), with idealized D_{4h} symmetry. In this complex, a mirror plane which includes two P(CH_2)$_3$P linkers and cuts diagonally through the cube of P atoms (Chart 3) would make the hydrogens in a given CH_2 group, which appear on either side of the plane, equivalent. This discussion assumes that the chelate, as commonly observed, is conformationally flexible and can access the highly

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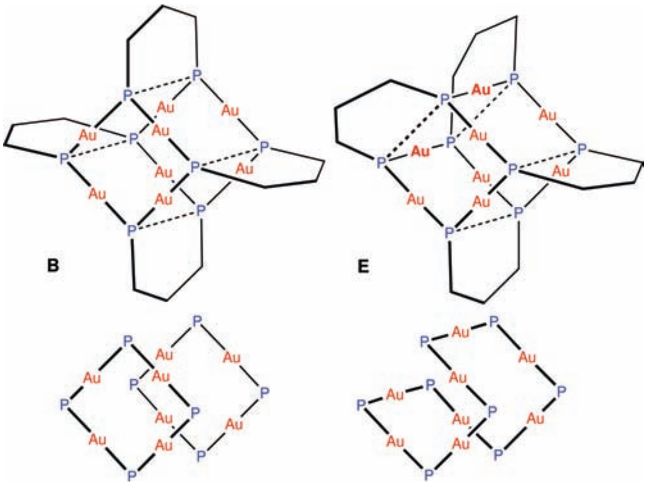
Chart 3. Possible Structures for Tetrameric **11**: Cubane **B** and Distorted Cube **E**[a]



[a] Mesityl groups are removed for clarity (top). The dashed lines are included as a guide for the eye, to illustrate the cube structure of both **B** and **E**. The bottom structures show only the Au_8P_8 cores. Cubane **B** contains two Au_4P_4 planes, while **E** contains a 16-membered alternating Au_8P_8 ring.

symmetric structure containing this symmetry plane.[12] Hence, two ^1H NMR signals in a 2:1 ratio are expected for the P-$CH_2CH_2CH_2$ and the P-$CH_2CH_2CH_2$ hydrogens.

An alternative tetrameric structure (**E**, Chart 3, with idealized D_{2d} symmetry), is formally derived from cubane **B** by rotating a Au_2P_4(linker)$_2$ plane by 90°. It retains the P_8 cube and two linkers in the same positions, but two gold atoms, shown in bold, have moved, and so have the other two linkers. This change destroys the mirror plane present in **B** and predicts a 2:2:1:1 ratio of ^1H NMR signals in the methylene linkers: 2(P$-$CH_aH$_b$):2(P-CH$_a$$H_b$):1(P-CH$_2CH_cH_dCH_2$):1(P-CH$_2CH_c$$H_dCH_2$).

The ^1H NMR spectrum of **11** in toluene-d_8 showed four CH_2 signals in a 2:2:1:1 ratio. In C_6D_6, some of these peaks overlapped, resulting in a 2:2:2 ratio, and in $CDCl_3$, only two broad signals (2:1 ratio) were observed. Two-dimensional NMR experiments (see the Supporting Information) correlated the CH_2 ^1H NMR signals to each other (COSY) and to the CH_2 carbons (gHMQC), consistent with these assignments. While the spectra in $CDCl_3$ are consistent with cube **B**, those in toluene and benzene are not. Since the ^{31}P NMR chemical shifts of **11** are very similar in all three solvents and in the solid state, and the remaining ^1H NMR signals also show little change, these observations can be explained most simply if **11** adopts the same structure (distorted cube **E**) in the different solvents, and the CH_2 ^1H NMR signals overlap in $CDCl_3$, as described above.

This proposed structure was confirmed by X-ray crystallography. Crystals of **11** grown from either toluene or chloroform adopted structure **E** (see Figures 3−5 for ORTEP diagrams; Table 3), with a cube of eight phosphorus atoms. As in Chart 3, the structure is related to cube **B**, which contains two Au_4P_4 planes, by the formal motion of two Au atoms (Au4 and Au8) to yield a 3:3:2 array of Au atoms (Au1, Au2, Au3; Au5, Au6, Au7; Au4, Au8).

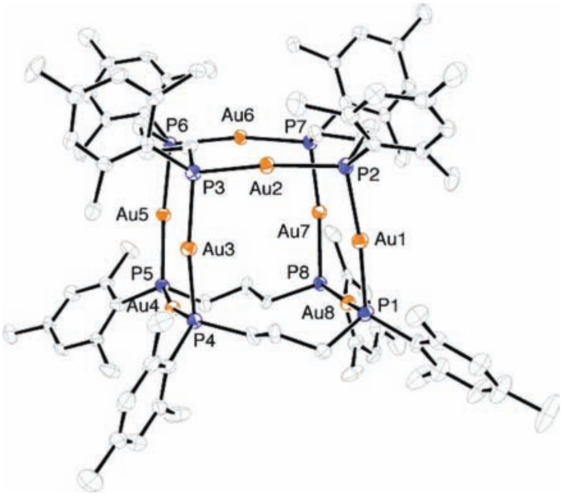


Figure 3. ORTEP diagram of $[Au(PMes(CH_2)_3PMes)Au]_4\cdot 2$toluene (**11**·2toluene). The toluene molecules are not shown.

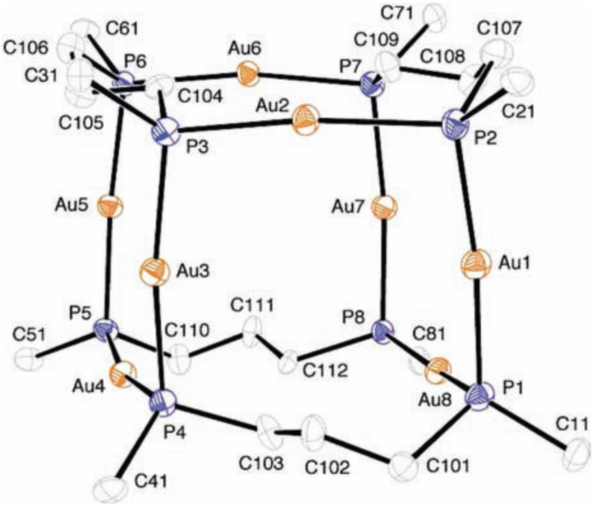


Figure 4. ORTEP diagram of **11**·2toluene with solvent molecules omitted and only the P-bound mesityl carbons shown.

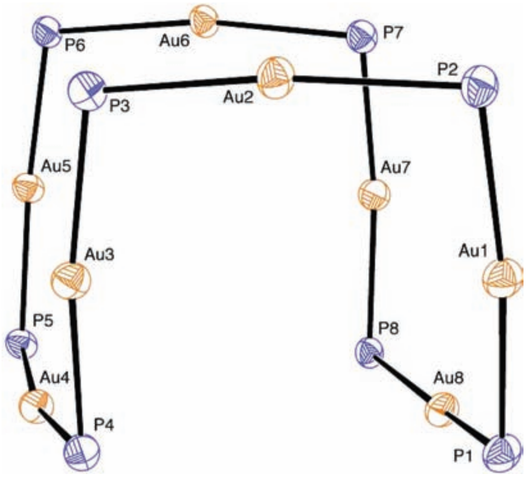


Figure 5. ORTEP diagram showing only the 16-membered ring of the Au_8P_8 core in **11**·2toluene.

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[12] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry. Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; pp 498−502.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in Gold Cluster **11**·2toluene

Au−P	Au−Au	P−Au−P	Au−P−Au
Au(1)−P(2) 2.329(3) Au(1)−P(1) 2.333(3)	Au1−Au2 3.574	P(2)−Au(1)−P(1) 172.53(11)	Au(1)−P(1)−Au(8) 103.22(12)
Au(2)−P(3) 2.329(3) Au(2)−P(2) 2.336(3)	Au2−Au3 3.592	P(3)−Au(2)−P(2) 167.96(12)	Au(1)−P(2)−Au(2) 100.02(12)
Au(3)−P(3) 2.315(3) Au(3)−P(4) 2.318(3)	Au3−Au4 3.530	P(3)−Au(3)−P(4) 168.39(11)	Au(3)−P(3)−Au(2) 101.32(13)
Au(4)−P(4) 2.326(3) Au(4)−P(5) 2.330(3)	Au4−Au5 3.633	P(4)−Au(4)−P(5) 167.85(11)	Au(3)−P(4)−Au(4) 98.97(11)
Au(5)−P(6) 2.321(3) Au(5)−P(5) 2.327(3)	Au5−Au6 3.614	P(6)−Au(5)−P(5) 173.32(11)	Au(5)−P(5)−Au(4) 102.52(12)
Au(6)−P(6) 2.324(3) Au(6)−P(7) 2.328(3)	Au6−Au7 3.507	P(6)−Au(6)−P(7) 168.06(10)	Au(5)−P(6)−Au(6) 102.14(12)
Au(7)−P(7) 2.304(3) Au(7)−P(8) 2.319(3)	Au7−Au8 3.486	P(7)−Au(7)−P(8) 171.04(11)	Au(7)−P(7)−Au(6) 98.40(12)
Au(8)−P(8) 2.330(3) Au(8)−P(1) 2.335(3)	Au1−Au8 3.659	P(8)−Au(8)−P(1) 167.51(12)	Au(7)−P(8)−Au(8) 97.15(12)

The expected approximately linear coordination at gold was observed (average P−Au−P angle = 169.58(12)°). The Au−P distances, which ranged from 2.304(3) to 2.336(3) Å, were similar to those observed in the previously characterized cyclic gold phosphido complexes.[1] So were the Au−P−Au angles, which ranged from 97.15(12) to 103.22(12)°; coordination at phosphorus was approximately tetrahedral. The Au−Au distances (range = 3.486−3.659 Å) were at the high end of the range (2.8−3.5 Å) usually cited for aurophilic interactions.[13] Hence it is likely that these distances are not indicative of significant Au−Au bonding, and instead are a consequence of the distorted-cube structure.

As noted above, the solution ^{1}H NMR spectrum of **11** was consistent with this solid-state structure. DOSY-NMR studies[14] using $Si(SiMe_3)_4$ and other internal standards[15] were also consistent with the tetrameric solution structure. They gave a hydrodynamic radius r_H of 9(1) Å. For comparison, we calculated the solid-state radius of **11**, assuming it is spherical, from its crystallographic unit cell volume to be $r_{X\text{-ray}} = 8.5$ Å, consistent with the DOSY result. For more information on DOSY experiments, including attempts to measure the solution molecular weight (MW) of **11** by the established correlation of MW with diffusion coefficient,[16] see the Supporting Information.

We also investigated possible structures **B** and **E** for **11** computationally by density functional theory (DFT) methods. The computed structures of models with $Au_8(PR)_8$ cores (R = Ph or H) were in good agreement with the crystal structure. For example, Figure 6 shows an overlay of the crystal structure (R = Mes) and the optimized DFT structure (R = Ph).

Interestingly, cube **B** was calculated to have a lower free energy than distorted cube **E** by 10 (R = Ph) or 12 (R = H) kcal/mol; apparently the intrinsic core structure is mainly responsible for the energy difference, and the P-substituents have a smaller effect. If this energy difference is reliable, it is possible that **E** is the kinetic product of self-assembly of putative “monomer” $(Au)MesP(CH_2)_3PMes(Au)$. An attempt to investigate possible rearrangement of **E** to **B** was inconclusive; no reaction occurred when **11** was heated in toluene.

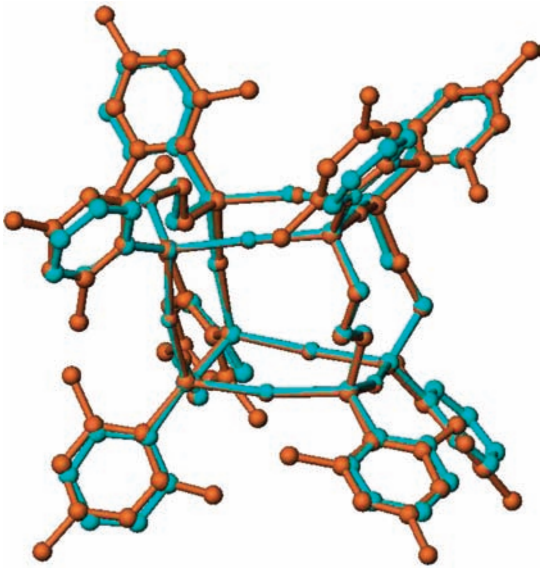

Figure 6. Superposition of the $Au_8(PPh)_8$ core (Blue, DFT) and the $Au_8(PMes)_8$ core of **11** (Bronze, X-ray).

Conclusion

As desired, the bulky, solubilizing bis(secondary) phosphine **1** formally yielded a dinuclear bis(phosphido)gold fragment, which self-assembled into the unusual structure **E**, instead of the higher-symmetry cubane **B**. Rational control of such chemistry remains elusive; we could not predict these structural details, and apparently small changes in the diphosphine (**2** and **3**) led to poorly behaved materials which could not be characterized. However, we have shown that spectroscopic techniques, especially NMR, complement X-ray crystallography in determining the nuclearity and structure of such oligomers.

Experimental Section

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, tetrahydrofuran (THF), toluene, and CH_2Cl_2 were dried using columns of activated alumina.[17] NMR spectra were recorded using

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Varian 300 or 500 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported versus Me$_4$Si and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported versus H_3PO_4 (85%) used as an external reference. Coupling constants are reported in hertz (Hz) as absolute values. Unless indicated, peaks in NMR spectra are singlets. ^{1}H DOSY NMR spectra were collected using the Bipolar Pulse Pair Stimulated Echo with Convection Compensation pulse sequence (Dbppste_cc), a proprietary pulse sequence from Varian. For ^{1}H PGSE diffusion measurements, 15−16 points were collected over the entire gradient range with 8−16 scans per point depending on the experiment.

Solid-state ^{31}P NMR spectra of [AuP(Mes)(CH$_2$)$_3$(Mes)PAu]$_4$ (**11**) were acquired on Chemagnetics CMX Infinity 200 (4.70 T) or Bruker Avance 300 (7.05 T) NMR spectrometers. Approximately 50 mg of sample was packed into 4 mm NMR rotors. Spectra of magic angle spinning (MAS) and stationary samples were referenced to 85% phosphoric acid ($\delta_{\text{iso}} = 0$) by setting the isotropic peak of ammonium dihydrogen phosphate to 0.8 ppm.[18] All spectra were acquired using the cross-polarization (CP) technique, with ^{1}H 90° pulse lengths of 2.5 or 4.0 μs for spectra acquired at 4.70 and 7.05 T, respectively. Contact times of 1.0 to 2.0 ms and recycle delays of 1.0 to 5.0 s were used, and ^{1}H decoupling was accomplished using the two-pulse phase modulation scheme of Griffin and co-workers.[19] A line broadening factor of 100 Hz was applied to all spectra prior to Fourier transformation.

IR spectra were recorded on KBr disks and are reported in cm^{-1}. Elemental analyses were provided by Quantitative Technologies Inc. Mass spectra were recorded at the University of Illinois Urbana−Champaign. Reagents were from commercial suppliers, except for MesPH(CH$_2$)$_3$PHMes,[7] PH$_2$Is,[20] IsHP(CH$_2$)$_2$PHIs,[8] and Au(THT)(Cl),[21] which were prepared by literature methods.

(BH$_3$)(Is)HP(CH$_2$)$_3$PH(Is)(BH$_3$) (2-BH$_3$). To a mixture of PH$_2$Is (79% purity by ^{1}H NMR spectroscopy, containing 21% 1,3,5-triisopropylbenzene, 1.18 g, 4.23 mmol, 2 equiv) and anhydrous K_2CO_3 (691 mg, 5 mmol, 2.4 equiv) in DMSO (ca. 70 mL) was added freshly crushed KOH (300 mg, 5.35 mmol, 2.5 equiv). As the KOH dissolved the solution turned yellow. The solution was stirred overnight, and then 1,3-dibromopropane (216 μL, 2.12 mmol, 1 equiv) was injected dropwise via microliter syringe over 10 min. The solution turned colorless upon complete addition of 1,3-dibromopropane, but no precipitate was observed. The reaction was complete after 54 h as judged by disappearance of starting PH$_2$Is (monitored by ^{31}P NMR spectroscopy) and the formation of a white precipitate.[22] The reaction mixture was cooled to 0 °C and quenched with 20 mL of degassed H_2O. The aqueous layer was extracted with 3 × 30 mL portions of petroleum ether and dried over MgSO$_4$. The solution was cooled to 0 °C and BH$_3$(SMe$_2$) (4.5 mL, 2.0 M in THF, 9.0 mmol, 2.1 equiv) was added via cannula. The mixture was stirred for 12 h, and a white precipitate formed. The solvent was removed under reduced pressure and the white solid was recrystallized from THF/petroleum ether to give 300 mg (26% yield) of white solid, which contained crystals suitable for X-ray analysis.

Anal. Calcd for $C_{33}H_{60}B_2P_2$: C, 73.34; H, 11.19. Found: C, 72.07; H, 10.82. These unsatisfactory results may be due to oxidation of the air-sensitive diphosphine after loss of the labile borane, which was also observed by mass spectrometry: HRMS (ES+) calcd for $C_{33}H_{55}O_2P_2$ (MO$_2$H)$^+$: *m*/*z* 545.3677. Found: *m*/*z* 545.3692. ^{31}P{^{1}H} NMR (CDCl$_3$): δ −26.4 (broad). ^{1}H NMR (CDCl$_3$): δ 7.05 (d, J = 4, 4H, Is), 4.36 (d sextets, J_{PH} = 370, J_{HH} = 7, 2H, P−H), 3.28 (broad, 4H, *i*-Pr-CH), 2.88 (sep, J = 7, 2H, *i*-Pr-CH), 2.14−1.92 (m, 5H, CH$_2$), 1.72−1.61 (m, 1H, CH$_2$), 1.26 (m, 24H, *i*-Pr-CH$_3$), 1.20 (d, J = 7, 12H, *i*-Pr-CH$_3$). The BH$_3$ signals were not observed. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 152.4 (apparent d, J = 2, quat, Ar), 122.5 (d, J = 8, CH, Ar), 118.5 (d, J = 53, quat, P−C), 34.3 (CH, *i*-Pr), 32.3 (d, J = 7, CH, *i*-Pr), 25.4 (dd, J = 32, 11, CH$_2$), 24.6 (CH$_3$, *i*-Pr), 24.3 (br, CH$_2$), 23.7 (d, J = 2, CH$_3$, *i*-Pr), 23.5 (t, J = 4, CH$_2$). The fourth expected ^{13}C aryl signal may overlap the 152.4 peak, which might also be assigned as two different singlets. Similar observations were made in the spectrum of the related compound (BH$_3$)(Is)HP(CH$_2$)$_2$PH(Is)(BH$_3$).[8]

IsHP(CH$_2$)$_3$PHIs (2). Crude bis(phosphine)(borane) **2-BH$_3$** (ca. 1.1 g, 2 mmol) was deprotected with piperazinomethyl polystyrene (3.0 g, 2.7 mmol/g, 4 equiv)[9] in toluene at 50 °C for 24 h. The mixture was filtered, and the resin was washed with toluene. The combined solutions were pumped down to give a white solid, which was washed with three 10 mL portions of DMSO to give 520 mg (51% yield, based on PH$_2$Is) of pure **2**.

Anal. Calcd for $C_{33}H_{54}P_2$: C, 77.30; H, 10.62. Found: C, 76.19; H, 10.47. These unsatisfactory results may be due to oxidation of the air-sensitive diphosphine. HRMS (ES+) calcd for $C_{33}H_{55}P_2$ (MH$^+$): *m*/*z* 513.3779. Found: *m*/*z* 513.3782. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −95.1, −95.2 (mixture of diastereomers, ∼1:1 ratio). ^{1}H NMR (C$_6$D$_6$): δ 7.10 (d, J = 2, 4H, Is), 4.36 (dm, J = 211, 2H, P−H), 3.81−3.73 (m, 4H, *i*-Pr-CH), 2.74 (sep, J = 7, 2H, *i*-Pr-CH), 1.90−1.84 (m, 2H, CH$_2$), 1.72−1.60 (m, 4H, CH$_2$), 1.29 (d, J = 7, 12H, *i*-Pr-CH$_3$), 1.24−1.17 (m, 24H, *i*-Pr-CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 153.2 (d, J = 7, quat, Is), 149.8 (quat, Is), 128.7 (d, J = 16, quat, P−C), 121.6 (d, J = 3, CH, Is), 34.7 (*i*-Pr-CH), 33.0 (d, J = 14, *i*-Pr-CH), 27.9−27.6 (m, CH$_2$), 25.9−25.7 (m, CH$_2$), 25.0 (apparent d, J = 3, *i*-Pr-CH$_3$), 24.5 (apparent d, J = 2, *i*-Pr-CH$_3$), 24.1 (apparent d, J = 5, *i*-Pr-CH$_3$).

Bis(phosphine) **2** could also be prepared directly without BH$_3$ protection, as follows: to a solution of PH$_2$Is (1.17 g, 73% purity by ^{1}H NMR spectroscopy, containing 27% 1,3,5-triisopropylbenzene, 4 mmol, 2 equiv) and anhydrous K_2CO_3 (553 mg, 4.0 mmol, 2 equiv) in DMSO (ca. 20 mL) was added freshly crushed KOH (225 mg, 4 mmol, 2 equiv). As the KOH dissolved the solution turned yellow. The solution was stirred for 30 min, and 1,3-dibromopropane (204 μL, 2 mmol, 1 equiv) was injected dropwise via microliter syringe over 10 min. The solution turned colorless upon complete addition of 1,3-dibromopropane but no precipitate was observed. The solution was stirred overnight resulting in the formation of milky white solution. To this was added 10 mL of degassed H_2O and then 30 mL of petroleum ether. Addition of the petroleum ether dissolved the white precipitate. The organic layer was removed and the aqueous layer was extracted with three 20 mL portions of petroleum ether. The combined extracts were dried over MgSO$_4$, filtered and pumped down to leave an oily white solid containing residual PH$_2$Is and 1,3,5-triisopropylbenzene, according to ^{31}P and ^{1}H NMR spectroscopy. The white solid was washed with four 5 mL portions of DMSO and then recrystallized from a minimal amount of petroleum ether at −29 °C to yield 463 mg of white crystals suitable for X-ray analysis. A second crop gave an additional 81 mg of spectroscopically pure white crystalline solid (53% overall yield).

(MesHP(CH$_2$)$_3$PHMes)(AuCl)$_2$ (6). A solution of MesPH(CH$_2$)$_3$PHMes (**1**; 305 mg, 0.886 mmol) in 10 mL of CH$_2$Cl$_2$ was

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(22) This reaction was significantly slower than the synthesis of the mesitylphosphino analogue MesHP(CH$_2$)$_3$PHMes (ref 7), presumably for steric reasons. Reactions with added K_2CO_3, as reported here (see Tsvetkov, E. N.; Bondarenko, N. A.; Malakhova, I. G.; Kabachnik, M. I. *Synthesis* **1986**, 198–208), were no faster than those in its absence.

added to a solution of Au(THT)(Cl) (562 mg, 1.75 mmol) in 20 mL of methylene chloride. The resulting solution was stirred for 30 min; then the solvent was removed under vacuum, yielding a white solid, which was recrystallized from CH_2Cl_2/ether at −21 °C to give a pure white solid (663 mg, 94%).

Anal. Calcd. for $C_{21}H_{30}Au_2Cl_2P_2$: C, 31.17; H, 3.74. Found: C, 30.89; H, 3.62. MS *m*/*z* calcd. for $C_{21}H_{30}Au_2Cl_2P_2$: 808.05; *m*/*z* calcd. for $C_{21}H_{30}Au_2ClP_2$ $(M - Cl)^+$ = 773.08. FAB-MS (NBA) *m*/*z* = 773.1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −38.3, −38.5, 1.1:1 ratio of diastereomers. ^1H NMR (CD_2Cl_2): δ 7.02 (8H, Ar), 6.28 (overlapping br dt, J_{PH} = 394, 7, 4H, PH), 2.59 (24H, CH_3), 2.35 (12H, CH_3), 2.28−2.17 (m, 8H, CH_2), 1.92−1.82 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 142.7 (Ar), 141.6 (d, *J* = 9, Ar), 130.8 (d, *J* = 9, Ar), 119.0 (d, *J* = 15, Ar, a), 118.5 (d, *J* = 15, Ar, b), 110.0 (Ar), 25.1 (d, *J* = 11, CH_2), 24.5−24.2 (m, CH_2), 23.4 (d, *J* = 11, CH_3), 21.2 (CH_3). IR: 2932, 2845, 2409 (PH), 1600, 1556, 1441, 1376, 1289, 1246, 1186, 1066, 1022, 946, 853, 695, 673, 619, 548, 537.

(IsHP(CH_2)$_3$PHIs)(AuCl)$_2$ (7). Under N_2, a solution of IsPH(CH_2)$_3$PHIs (**2**; 104 mg, 0.203 mmol) in 12 mL of CH_2Cl_2 was added to a solution of Au(THT)(Cl) (133 mg, 0.415 mmol) in 12 mL of CH_2Cl_2. The resulting solution was stirred for 30 min; then the solvent was removed under vacuum, yielding a white solid (225 mg, 91%). Recrystallization from methylene chloride gave a solvate, as observed by ^1H NMR ($CDCl_3$). Quantifying the amount of CH_2Cl_2 by NMR spectroscopy was not possible because the samples appeared to lose CH_2Cl_2 on standing. Elemental analyses of different samples were consistent with the presence of one or fewer equiv of CH_2Cl_2: Anal. Calcd. for $C_{33}H_{54}Au_2Cl_2P_2\cdot 0.5CH_2Cl_2$: C, 39.45; H, 5.43. Found: C, 39.15; H, 5.64. Anal. Calcd. for $C_{33}H_{54}Au_2Cl_2P_2\cdot 0.75CH_2Cl_2$: C, 38.93; H, 5.37. Found: C, 38.96; H, 5.38. Anal. Calcd. for $C_{33}H_{54}Au_2Cl_2P_2\cdot 1CH_2Cl_2$: C, 38.43; H, 5.31. Found: C, 38.20; H, 5.32. HRMS *m*/*z* calcd. for $C_{33}H_{54}Au_2ClP_2$ $(M - Cl)^+$: 941.2721. Found: 941.2707. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −42.8, −43.0, 1:1 ratio of diastereomers. ^1H NMR (CD_2Cl_2): δ 7.16 (d, *J* = 4, 4H, Ar), 7.14 (d, *J* = 4, 4H, Ar), 6.42 (br dm, J_{PH} = 390, 4H, PH), 3.52 (br, 4H, CH_2), 2.96−2.90 (m, 4H, CH), 2.32−2.20 (br m, 8H, CH), 2.05−1.99 (m, 4H, CH_2), 1.36 (d, *J* = 6, 12H, CH_3), 1.34 (d, *J* = 6, 12H, CH_3), 1.29 (overlapping d, *J* = 7, 12H, CH_3), 1.28 (overlapping d, *J* = 7, 12H, CH_3), 1.272 (overlapping d, *J* = 7, 12H, CH_3), 1.269 (overlapping d, *J* = 7, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 153.7 (Ar), 152.5 (Ar), 123.2 (d, *J* = 9, Ar), 117.1 (d, *J* = 31, Ar), 116.6 (d, *J* = 31, Ar), 34.6 (CH, *i*-Pr), 33.4 (br, CH, *i*-Pr), 26.7−26.3 (m, CH_2), 25.3 (d, *J* = 13, CH_2), 24.59 (overlapping, CH_3, *i*-Pr), 24.58 (overlapping, CH_3, *i*-Pr), 24.23 (CH_3, *i*-Pr), 24.21 (CH_3, *i*-Pr), 23.66 (overlapping, CH_3, *i*-Pr), 23.63 (overlapping, CH_3, *i*-Pr). IR: 2960, 2924, 1652, 1601, 1558, 1540, 1495, 1456, 1419, 1385, 1363. A PH stretching vibration could not be confidently assigned.

(IsHP(CH_2)$_2$PHIs)(AuCl)$_2$ (8). Under N_2, a solution of IsPH(CH_2)$_2$PHIs (**3**; 189 mg, 0.379 mmol) in 12 mL of CH_2Cl_2 was added to a solution of Au(THT)(Cl) (244 mg, 0.761 mmol) in 12 mL of CH_2Cl_2. The resulting solution was stirred for 30 min, during which it changed from clear to a light yellow color, and finally to pink. The mixture was filtered through Celite, yielding a light yellow solution. The solvent was removed under vacuum to give a white solid containing visible black impurities. Recrystallization from CH_2Cl_2/ether at −21 °C gave an off-white solid (239 mg, 65%).

Anal. Calcd. for $C_{32}H_{52}Au_2Cl_2P_2$: C, 39.89; H, 5.44. Found: C, 39.53; H, 5.27. HRMS *m*/*z* calcd. for $C_{32}H_{52}Au_2ClP_2$ $(M-Cl)^+$: 927.2564. Found: 927.2527. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −39.1. ^1H NMR (CD_2Cl_2): δ 7.13 (4H, Ar), 6.54 (br dm, J_{PH} = 392, 2H, PH), 3.48 (br, 4H, CH), 2.91 (sept, *J* = 7, 2H, CH), 2.43 (m, 2H, CH_2), 2.25−2.21 (m, 2H, CH_2), 1.35 (d, *J* = 7, 12H, CH_3), 1.26−1.24 (overlapping d, *J* = 7, 12H, CH_3), 1.12 (d, *J* = 6, 12H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.4 (br, Ar), 153.3 (Ar), 123.0 (Ar), 117.0 (3-line pattern, apparent *J* = 31, Ar), 34.5 (CH, *i*-Pr), 33.3 (br, CH, *i*-Pr), 24.8 (CH_3, *i*-Pr), 24.5−24.2 (m, CH_2), 24.2 (overlapping previous peak, CH_3, *i*-Pr), 23.6 (CH_3, *i*-Pr). IR: 2960, 2925, 2868, 2416 (PH), 1676, 1600, 1560, 1460, 1423, 1385, 1364, 1318, 1262, 1194.

(PhHP(CH_2)$_3$PHPh)(AuCl)$_2$ (9). Under N_2, to a solution of Au(THT)(Cl) (494 mg, 1.54 mmol) in 12 mL of CH_2Cl_2 was added a solution of PhHP(CH_2)$_3$PHPh (**4**; 201 mg, 0.773 mmol) in 12 mL of CH_2Cl_2. The resulting mixture was stirred for 15 min and then filtered through Celite to remove a brown impurity. The solvent was removed under vacuum to give a white solid, which was recrystallized three times from methylene chloride/ether to remove THT, finally yielding a white solid (545 mg, 97%).

Anal. Calcd for $C_{15}H_{18}Au_2Cl_2P_2\cdot 0.1Et_2O$: C, 25.25; H, 2.61. Found: C, 25.43; H, 2.52. The presence of ether was confirmed quantitatively by integration of the ^1H NMR spectrum (CD_2Cl_2). MS *m*/*z* calcd. for $C_{15}H_{18}Au_2Cl_2P_2$: 723.96; *m*/*z* calcd. for $C_{15}H_{18}Au_2ClP_2$ $(M - Cl)^+$ = 688.99. Found: FAB-MS (NBA) *m*/*z* = 688.9. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −8.9, −9.2; 1.1:1 ratio of diastereomers. ^1H NMR (CD_2Cl_2): δ 7.72−7.64 (m, 4H, Ar), 7.58−7.54 (m, 2H, Ar), 7.49−7.45 (m, 4H, Ar), 6.19 (br dt, J_{PH} = 400, 6, 1H, PH, a), 6.16 (br dt, J_{PH} = 400, 6, 1H, PH, b), 2.44−2.37 (br m, 4H, CH_2), 1.93−1.89 (br m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.4 (d, *J* = 5, Ar, a), 134.3 (d, *J* = 5, Ar, b), 132.7 (Ar), 129.9−129.8 (m, Ar), 124.6 (br d, *J* = 63, Ar), 26.0−25.6 (m, CH_2), 23.0 (d, *J* = 33, CH_2). IR: 3041, 2910, 2355 (PH), 1812, 1572, 1480, 1436, 1398, 1305, 1246, 1186, 1110, 989, 864, 739, 690.

(1,1′-C_5H_4PHPh)$_2$Fe)(AuCl)$_2$ (10). Under nitrogen, to a solution of Au(THT)Cl (203 mg, 0.633 mmol) in 12 mL of CH_2Cl_2 was added a solution of 1,1′-(PHPh)$_2C_5H_4FeC_5H_4$ (**5**; 129 mg, 0.321 mmol) in 12 mL of CH_2Cl_2. The resulting dark orange solution was stirred for 35 min. The solvent was removed under vacuum to yield a dark orange solid, which was recrystallized from CH_2Cl_2/ether at −60 °C to yield a yellow solid (222 mg, 81%).

Anal. Calcd. for $C_{22}H_{20}Au_2Cl_2P_2Fe$: C, 30.48; H, 2.33. Found: C, 30.21; H, 2.26. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −10.3, −11.0; 1.2:1 ratio of diastereomers. ^1H NMR ($CDCl_3$): δ 7.74−7.66 (m, 7H, Ar), 7.57−7.48 (br m, 13H, Ar), 7.12 (d, J_{PH} = 406, 4H, PH, overlapping Ar signals), 4.83 (4H, Cp), 4.80 (2H, Cp), 4.78 (2H, Cp), 4.75−4.74 (br m, 4H, Cp), 4.66 (2H, Cp), 4.54 (2H, Cp). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.8 (d, *J* = 14, Ar), 133.5 (d, *J* = 14, Ar), 132.5 (d, *J* = 16, Ar), 129.7 (d, *J* = 3, Ar), 129.6 (d, *J* = 3, Ar), 77.7 (d, *J* = 20, Cp), 76.6 (d, *J* = 11, Cp), 76.1 (d, *J* = 18, Cp), 75.6 (m, Cp), 75.0−74.4 (m, Cp). IR: 3052, 2932, 2845, 2355 (PH), 1654, 1474, 1431, 1387, 1305, 1262, 1175, 1104, 1028, 902, 886, 831, 739, 695, 635.

[Au(MesP)(CH_2)$_3$(PMes)Au]$_4$ (11). A solution of MesHP(AuCl)(CH_2)$_3$PHMes(AuCl) (**6**, 115 mg, 0.142 mmol) in 10 mL of CH_2Cl_2 was treated with 15 mL of aqueous NH_4OH (0.3 M, 3.8 mmol, 27 equiv) and then stirred for 30 min, which led to the formation of an orange oil in a clear solution. A pipet was used to collect the oil, which was refrigerated overnight at −21 °C to yield a white precipitate. The remaining orange oil was removed using a pipet. The white precipitate was treated with 5 mL of CH_2Cl_2 to extract any residual orange oil, and the mixture was cooled in the refrigerator for another hour. The CH_2Cl_2 was then removed using a pipet, and the precipitate was dried under vacuum to yield a white solid. The combined orange oils were recooled as above, and this process was repeated once more to yield the product (70 mg, 67%).

In a larger-scale procedure with a slightly modified workup, to a solution of **6** (324 mg, 0.4 mmol) in 15 mL of CH_2Cl_2 was added slowly, with gentle stirring, 15 mL of aqueous NH_4OH (0.5 M, 10 mmol, 25 equiv). The mixture was stirred slowly for 4.5 h during which time a white precipitate developed at the interface of the aqueous and CH_2Cl_2 layers. The CH_2Cl_2 layer became yellow-orange and was extracted and concentrated under reduced pressure then cooled over 8 days at −28 °C to give 240 mg of light orange solid. The solid was washed four times with 3−4 mL of cold CH_2Cl_2 until the washes were colorless. This afforded 106 mg of white solid. Collecting and pumping down the washes gave additional orange solid. Repeating the washing a second time gave an additional 37 mg of white solid for a total of 143 mg (49% yield).

MALDI-MS: m/z calcd for $C_{84}H_{112}Au_8P_8$ (M^+): m/z 2944.4. Found: m/z 2946.2. Anal. Calcd. for the "monomeric" $C_{21}H_{28}Au_2P_2\cdot 0.1CH_2Cl_2$: C, 34.03; H, 3.82. Found: C, 33.70; H, 3.52. The presence of methylene chloride was confirmed quantitatively by integration of the ^{1}H NMR spectrum ($CDCl_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.2. ^{1}H NMR ($CDCl_3$): δ 6.86 (4H, Ar), 2.97 (12H, CH_3), 2.75 (broad, 4H, CH_2), 2.50 (broad, 2H, CH_2), 2.24 (6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.0 (Ar), 138.1 (Ar), 133.5 (Ar), 130.4 (Ar), 31.9 (CH_2), 31.5 (CH_2), 27.3 (CH_3), 21.1 (CH_3). IR: 2913, 1602, 1551, 1448, 1372, 1242, 1024, 946, 847, 817, 617, 552. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ −6.4. ^{1}H NMR (toluene-d_8): δ 6.77 (4H, Ar), 3.12−3.04 (broad m, 1H, CH_2), 3.05 (12H, CH_3), 2.99−2.92 (broad m, 1H, CH_2), 2.88−2.82 (m, 2H, CH_2), 2.59−2.54 (m, 2H, CH_2), 2.09 (6H, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −7.0. ^{1}H NMR (C_6D_6): δ 6.79 (4H, Ar), 3.22−3.12 (broad m, 2H, CH_2), 3.08 (12H, CH_3), 2.93−2.87 (m, 2H, CH_2), 2.65−2.58 (m, 2H, CH_2), 2.07 (6H, CH_3). $^{31}P\{^1H\}$ NMR (Solid State): see the Supporting Information for spectra.

[Au(IsP)(CH$_2$)$_3$(PIs)Au]$_n$ (12). A solution of IsPH(AuCl)-$(CH_2)_3$PH(AuCl)Is (**7**, 48 mg, 0.049 mmol) in 12 mL of CH_2Cl_2 was treated with 25 mL of aqueous NH_4OH (0.3 M, 3.8 mmol, 78 equiv) and then stirred for 35 min to give two layers, a white emulsion on the bottom and a clear solution on the top. The two layers were separated using a pipet. Once the emulsion settled, it formed a clear solution over an oily emulsion. This clear solution was separated by pipet, and the solvent was removed under vacuum, yielding a yellowish-white solid (20 mg, 45%). Attempts at purifying this material by recrystallization were unsuccessful.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.3. ^{1}H NMR (CD_2Cl_2): δ 7.05−6.97 (br, 4H, Ar), 5.02−4.50 (br, 2H, CH), 2.84 (br, 2H, CH_2), 2.35−2.17 (br, 4H, CH), 1.54 (br, overlapping, 4H, CH_2), 1.42−1.10 (br m, 36H, CH_3).

[Au(IsP)(CH$_2$)$_2$(PIs)Au]$_n$ (13). A solution of IsPH(AuCl)-$(CH_2)_2$PH(AuCl)Is (**8**, 112.0 mg, 0.116 mmol) in 25 mL of 1:1 $CH_2Cl_2/CHCl_3$ was treated with 30 mL of aqueous NH_4OH (0.3 M, 3.8 mmol, 33 equiv) and then stirred for 30 min to give two layers, a yellow solution below an emulsion. The yellow solution was pipetted into a separate flask, and the solvent was removed under vacuum, yielding a yellow solid (49 mg, 48%). Attempts at purifying this material by recrystallization were unsuccessful.

The mass spectrum was consistent with fragmentation. MS: m/z calcd. for $C_{31}H_{47}Au_2P_2$ $(M - CH_3)^+$: 875.2562. Found: 875.1; m/z calcd. for $C_{28}H_{38}Au_2P_2$ $(M - 4CH_3)^+$: 834.2093; Found: 834.1. Anal. Calcd. for $C_{33}H_{50}Au_2P_2$: C, 43.15; H, 5.66. Found: C, 42.56; H, 5.74. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 2.5. ^{1}H NMR ($CDCl_3$, 21 °C): δ 7.02 (br m, 4H, Ar), 4.87−4.70 (br, 2H, CH), 2.82 (br, 4H, CH), 1.63 (br, 2H, CH_2), 1.27−1.18 (br m, 38H, overlapping CH_2 and CH_3). ^{1}H NMR (CD_2Cl_2, −75 °C): δ 7.06 (br m, Ar), 4.66−4.39 (br, CH), 2.79 (br, CH), 1.35 (br, CH_2), 1.18−1.14 (br m, overlapping CH_2 and CH_3). IR: 2956, 2867, 1684, 1600, 1554, 1459, 1418, 1382, 1361, 1309, 1161, 1102, 939, 878, 807, 652.

[Au(PhP(CH$_2$)$_3$(PPh)Au]$_n$ (14). A solution of PhPH(AuCl)-$(CH_2)_3$PH(AuCl)Ph (**9**, 130 mg, 0.179 mmol) in 10 mL of CH_2Cl_2 was treated with 15 mL of aqueous NH_4OH (0.3 M, 3.8 mmol, 21 equiv) and then stirred for 20 min, which led to the formation of a light yellow precipitate in a clear solution. After suction filtration on a frit, the precipitate was washed with 10 mL of H_2O and dried on the frit. The solid was scraped into a vial and washed with 5 mL of THF, then dried under vacuum to give a light yellow insoluble solid (117 mg, 87%).

Anal. Calcd. for $C_{15}H_{18}Au_2P_2$: C, 27.62; H, 2.47. Found: C, 27.54; H, 2.60. IR: 3134, 2922, 1806, 1657, 1582, 1476, 1432, 1402, 1301, 1097, 1025, 813, 740, 693. $^{31}P\{^1H\}$ NMR (solid-state): δ 28 (fwhm = 3000 Hz); see the Supporting Information.

[Au(PPh)(C$_5$H$_4$FeC$_5$H$_4$)(PPh)Au]$_n$ (15). A solution of $(AuCl)_2$-$(C_5H_4FeC_5H_4)(PHPh)_2$ (**10**, 87 mg, 0.10 mmol) in 20 mL of CH_2Cl_2 was treated with 25 mL of aqueous NH_4OH (0.5 M, 51.4 mmol, 514 equiv) and then stirred for 30 min; an orange emulsion in a clear solution formed. The solution was removed using a pipet, and the remaining emulsion was washed with THF; the wash solution was removed using a pipet. The resulting wet orange solid was dried under vacuum to yield the product (63 mg, 80%). This material was insoluble in common solvents, precluding characterization by solution NMR.

Anal. Calcd. for $C_{22}H_{18}Au_2FeP_2$: C, 33.27; H, 2.28. Found: C, 32.93; H, 2.40. IR: 3064, 1582, 1476, 1432, 1166, 1025, 820, 742, 694, 628.

DFT Computations. Gas phase structures were optimized using the hybrid B3LYP functional[23] and the triple-ζ LACV3P**++ basis set,[24] which uses extended core potentials on heavy atoms and a 6-311G**++ basis for other atoms, as implemented in the Jaguar suite of programs (*Jaguar, versions 7.0−7.5*, Schrödinger, LLC, New York, NY: 2007−2009). All computed structures were confirmed as energy minima by calculating the vibrational frequencies by second derivative analytic methods, and confirming the absence of imaginary frequencies. Thermodynamic quantities were calculated assuming an ideal gas, and are zero point energy corrected.

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Supporting Information Available: X-ray crystallographic details (including CIF), NMR spectra, and details of the NMR experiments and the computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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