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Gold(I) Phosphido Complexes: Synthesis, Structure, and Reactivity

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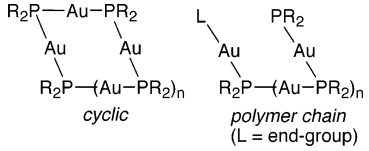
Deprotonation of the phosphine complexes $Au(PHR_2)Cl$ with aqueous ammonia gave the gold(I) phosphido complexes $[Au(PR_2)]_n$ (PR_2 = $PMes_2$ (**1**), PCy_2 (**2**), $P(t\text{-}Bu)_2$ (**3**), PIs_2 (**4**), PPhMes (**5**), PHMes* (**6**); Mes = 2,4,6-$Me_3C_6H_2$, Is = 2,4,6-$(i\text{-}Pr)_3C_6H_2$, Mes* = 2,4,6-$(t\text{-}Bu)_3C_6H_2$, Cy = cyclo-C_6H_{11}). ^{31}P NMR spectroscopy showed that these complexes exist in solution as mixtures, presumably oligomeric rings of different sizes. X-ray crystallographic structure determinations on single oligomers of **1**–**4** revealed rings of varying size (n = 4, 6, 6, and 3, respectively) and conformation. Reactions of **1**–**3** and **5** with $PPN[AuCl_2]$ gave $PPN[(AuCl)_2(\mu\text{-}PR_2)]$ (**9**–**12**, PPN = $(PPh_3)_2N^+$). Treatment of **3** with the reagents HI, I_2, ArSH, $LiP(t\text{-}Bu)_2$, and $[PH_2(t\text{-}Bu)_2]BF_4$ gave respectively $Au(PH(t\text{-}Bu)_2)(I)$ (**14**), $Au(PI(t\text{-}Bu)_2)(I)$ (**15**), $Au(PH(t\text{-}Bu)_2)(SAr)$ (**16**, Ar = $p\text{-}t\text{-}BuC_6H_4$), $Li[Au(P(t\text{-}Bu)_2)_2]$ (**17**), and $[Au(PH(t\text{-}Bu)_2)_2]BF_4$ (**19**).

Introduction

Because gold(I) thiolate complexes $[Au(SR)]_n$ have important applications in decoration of glass and ceramics and in medicine, their chemistry has been studied in detail.[1] In contrast, the isoelectronic phosphido complexes $[Au(PR_2)]_n$ have been less well investigated since their discovery in 1976.[2] Several groups have reported that $[Au(PPh_2)]_n$ is insoluble; its color depended on the base used in its preparation from $Au(PHPh_2)(Cl)$ or related precursors.[3] Parish et al. prepared several related complexes $[Au(PR_2)]_n$ (R = Et, *n*-octyl, *p*-MeC_6H_4, *p*-$(t\text{-}Bu)C_6H_4$), which could be obtained in soluble and insoluble forms, proposed to be cyclic and linear chain polymers, respectively (Chart 1).[3d]

NMR studies of these materials, although made difficult by precipitate formation, suggested that several species were present in solution.[3d] The solid-state ^{31}P NMR chemical shifts for the soluble (ca. 90 ppm) and insoluble (ca. 40 ppm) forms of $[Au(PPh_2)]_n$ were consistent with different structures. Mossbauer spectra indicated the expected linear coordination with two phosphido ligands binding a given gold center, but structural details were not available.[3d,f]

Chart 1. Proposed Structures for Gold(I) Phosphido Complexes



We report here that using bulkier R groups[4] enables the synthesis of the *soluble* gold phosphido complexes $[Au(PR_2)]_n$ (PR_2 = $PMes_2$ (**1**, Mes = 2,4,6-$Me_3C_6H_2$), PCy_2 (**2**, Cy = *cyclo*-C_6H_{11}), $P(t\text{-}Bu)_2$ (**3**), PIs_2 (**4**, Is = 2,4,6-$(i\text{-}Pr)_3C_6H_2$), PPhMes (**5**), and P(H)(Mes*) (**6**, Mes* = 2,4,6-$(t\text{-}Bu)_3C_6H_2$)). Their solubility enabled the determination of

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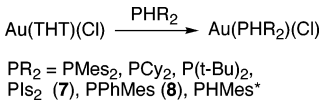
Table 1. Crystallographic Data for the Complexes [Au(PH(Ph)(Mes))(Cl)]$_2$ (**8**), [PPN][(AuCl)$_2$(μ-PCy$_2$)] (**10**), Au(PI(*t*-Bu)$_2$)(I) (**14**), Au(PH(*t*-Bu)$_2$)(I) (**15**), and [Au(PH(*t*-Bu)$_2$)]BF$_4$ (**19**)[a]

param	**8**	**10**	**14**	**15**	**19**
formula	$C_{30}H_{34}Au_2Cl_2P_2$	$C_{48}H_{52}Au_2Cl_2NP_3$	$C_8H_{18}AuI_2P$	$C_8H_{19}AuIP$	$C_{16}H_{36}AuBF_4P_2$
fw	921.35	1199.2	595.96	470.07	574.16
temp, K	223(2)	219(2)	100(2)	100(2)	218(2)
cryst size, mm^3	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.20	0.20 × 0.16 × 0.10	0.38 × 0.25 × 0.10	0.25 × 0.25 × 0.15
cryst system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a, Å	16.58(2)	9.4506(11)	8.4964(5)	23.4212(13)	23.5726(12)
b, Å	8.681(11)	18.557(2)	11.4786(9)	7.8968(4)	8.3679(4)
c, Å	22.72(3)	25.781(3)	15.7440(9)	15.4542(8)	12.7000(6)
α, deg	90	90	71.0170(10)	90	90
β, deg	105.51(2)	93.412(3)	78.5190(10)	121.4690(10)	112.2540(10)
γ, deg	90	90	78.0960(10)	90	90
V, Å^3	3152(7)	4513.2(9)	1406.21(14)	2437.9(2)	2318.5(2)
Z	4	4	4	8	4
D(calc), g/cm^3	1.942	1.721	2.815	2.561	1.645
μ(Mo Kα), mm^{-1}	9.587	6.716	14.926	14.683	6.511
R(*F*), %[b]	4.47	3.07	2.29	2.80	2.48
R(*wF*^{2}), %[b]	15.18	6.74	4.89	7.24	6.69

[a] Data acquired with a Siemens P4 CCD diffractometer using Mo Kα radiation (0.710 73 Å). [b] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$.

Scheme 1. Synthesis of Au(PHR$_2$)(Cl) Complexes



the novel cyclic structures of **1**−**4** by X-ray crystallography[5] and a survey of their reactivity.[6]

Results and Discussion

Synthesis and Structure. Vicente et al. reported that [Au(PPh$_2$)]$_n$ was conveniently prepared by treatment of Au(PHPh$_2$)(Cl) with aqueous ammonia.[3a] Related secondary and primary phosphine complex precursors and the new compounds Au(PHIs$_2$)Cl (**7**) and Au(PH(Ph)(Mes))(Cl) (**8**)[7] were prepared by a modification of the literature method, using Au(THT)(Cl)[8] (THT = tetrahydrothiophene) instead of Au(CO)(Cl) (Scheme 1).[9]

An X-ray crystallographic structure determination (Figure 1; Table 1) showed that **8** is a dimer in the solid state with Au−Au interactions, as in Au(PH(*o*-MeC$_6$H$_4$)$_2$)(Cl).[9a] With two chiral phosphines, several diastereomers of **8** are possible. The structure is complicated by an enantiomeric disorder in which the AuCl fragments occupy two different positions; each averaged site in the racemic, centrosymmetric structure is composed of ca. 80% of either *RR* or *SS* and ca. 20% of either *SS* or *RR* (Supporting Information, Figure S1). The compositional disorder is also manifest in the reduced precision obtained for the unit-cell parameters.

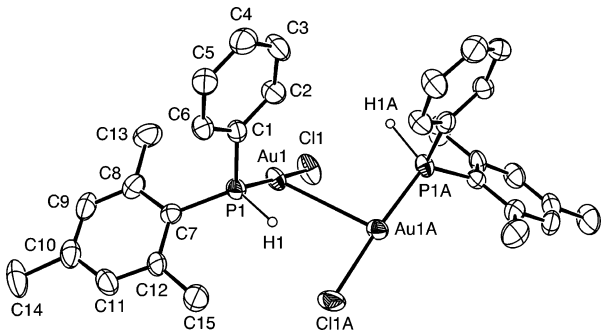
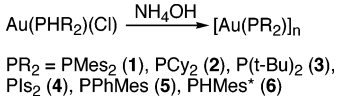


Figure 1. ORTEP diagram of [Au(PH(Ph)(Mes))Cl]$_2$ (**8**). The hydrogen atoms have been removed for clarity, except for the P−H bond. The AuCl fragments are disordered; the major (80%) component is shown. Selected bond lengths (Å) and angles (deg): for major, Au−P 2.197(3), Au−Au 3.108(4), Au−Cl 2.277(3), P−Au−Cl 176.06(10); for minor, Au−P 2.098(3), Au−Au 3.313(5), Au−Cl 2.313(12), P−Au−Cl 172.7(4).

Scheme 2. Synthesis of Au(I) Phosphido Complexes



Treatment of the precursors Au(PHR$_2$)(Cl) with aqueous ammonia in THF or CH_2Cl_2 caused precipitation of the white, toluene-soluble, air-stable phosphido complexes [Au(PR$_2$)]$_n$ (**1**−**6**) (Scheme 2).

^{31}P NMR spectra of these crude products showed the presence of several species (for **1** or **2**, 4; for **3**, 5 or 10, depending on reaction time; for **4**, only 1, for **5** or **6**, 2; Table 2).

The similarity of the chemical shifts for these species and the observation of their interconversion on cooling or heating an NMR sample of **1** in toluene suggests that they are a

(5) For related structures of Au(I) chalcogenolates and of an amide, see: (a) Schroter, I.; Strahle, J. *Chem. Ber.* **1991**, *124*, 2161−2164. (b) Bonasia, P. J.; Gindelberger, D. E.; Arnold, J. *Inorg. Chem.* **1993**, *32*, 5126−5131. (c) Wojnowski, W.; Becker, B.; Sassmanhausen, J.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1417−1421. (d) Wiseman, M. R.; Marsh, P. A.; Bishop, P. T.; Brisdon, B. J.; Mahon, M. F. *J. Am. Chem. Soc.* **2000**, *122*, 12598−12599. (e) LeBlanc, D. J.; Lock, C. J. L. *Acta Crystallogr.* **1997**, *C53*, 1765−1768. (f) Bunge, S. D.; Just, O.; Rees, W. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3082−3083.

(6) For a preliminary communication of some of these results, see: Stefanescu, D. M.; Yuen, H. F.; Glueck, D. S.; Golen, J. A.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 1046−1048. Details of the X-ray crystal structure determinations for complexes **1**−**4** are contained in the Supporting Information for this paper.

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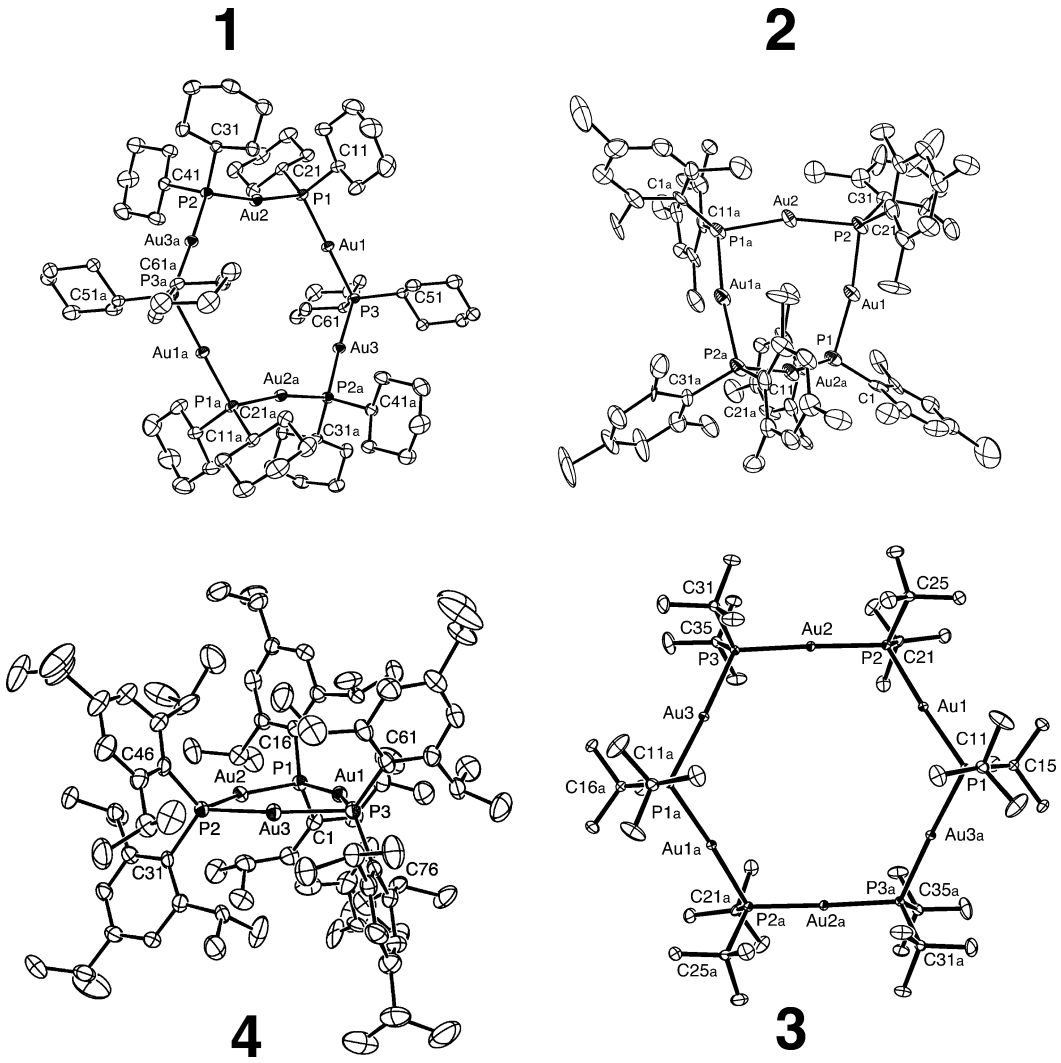


Figure 2. ORTEP diagrams of $[Au(PMes_2)]_4$ (**1**), $[Au(PCy_2)]_6 \cdot 2C_7H_8$ (**2**$\cdot 2C_7H_8$), $[Au(P(t\text{-}Bu)_2)]_6 \cdot C_7H_8$ (**3**$\cdot C_7H_8$), and $[Au(PIs_2)]_3$ (**4**). Hydrogen atoms, solvent molecules, and disorder in the isopropyl groups of **4** are not shown.

Table 2. $^{31}P\{^1H\}$ NMR Data for Phosphido Complexes **1**−**6**[a]

compd	^{31}P NMR chem shift (ppm)
$[Au(PMes_2)]_n$ (**1**)	−17.0, −18.8, −23.4, **−36.1**
$[Au(PCy_2)]_n$ (**2**)[b]	65.2, 62.4, **51.3**, 42.9
$[Au(P(t\text{-}Bu)_2)]_n$ (**3**)[c]	115.3, 114.2, **107.4**, 104.9, 89.9
$[Au(PIs_2)]_n$ (**4**)	−78.9
$[Au(P(Ph)(Mes))]_n$ (**5**)	−12.1, **−21.6**
$[Au(PHMes^*)]_n$ (**6**)	**−40.9, −42.6**

[a] Solvent = C_6D_6 for **3**−**6**, toluene-d_8 for **1**, and toluene for **2**. The chemical shift in bold font corresponds to the compound isolated (see the text). [b] This compound could not be obtained as a single isomer reproducibly; see the text for details. [c] On shorter reaction time, more peaks were observed: $^{31}P\{^1H\}$ NMR (THF): δ 115.3, 115.18, 115.12, 115.0, 114.31, 114.08, 113.68, 105.2, 104.3, 89.9.

mixture of compounds having the formula $[Au(PR_2)]_n$, consistent with the observations of Parish and co-workers.[3d] The chemical shifts of diarylphosphido complexes **1** and **5** are significantly different from that of their soluble $[Au(PPh_2)]_n$ (90 ppm), which may be due to different structures or simply to the effects of the different aryl groups.

Heating **1** in toluene caused partial conversion to a major product, which then crystallized out preferentially. Recrystallization of **2** from toluene gave a mixture of two compounds ($^{31}P\{^1H\}$ NMR (C_6D_6): δ 54.2 and 48.1) that could not be reproducibly separated, but on one occasion crystals of one of these (δ 54.2) were isolated. Recrystallization of **3** from toluene yielded a mixture of two compounds; the less soluble one was isolated after another recrystallization. Recrystallization of **5** from benzene enabled the separation of one compound, but in the case of **6**, no single product isolation was possible. Complexes **1**−**6** were further characterized by elemental analyses, multinuclear NMR, IR, and MALDI mass spectroscopy (molecular ions were observed for **1**−**4**, and mass spectral peaks were consistent with a tetrameric structure for **5**).

The crystal structures of cyclic $[Au(PMes_2)]_4$ (**1**), $[Au(PCy_2)]_6 \cdot 2C_7H_8$ (**2**$\cdot 2C_7H_8$), $[Au(P(t\text{-}Bu)_2)]_6 \cdot C_7H_8$ (**3**$\cdot C_7H_8$), and $[Au(PIs_2)]_3$ (**4**) are shown in Figure 2. In **2**$\cdot 2C_7H_8$ and **3**$\cdot C_7H_8$ toluene is included in the channels between the rings, which stack to yield an extended structure (Supporting Information, Figure S2). Increasing the size of the P substituents leads to a decreased ring size, presumably to reduce unfavorable steric interactions.

As expected, the P−Au−P angles are close to linear, and the phosphorus atoms are approximately tetrahedral (Table 3). The Au−P bond lengths are similar in all four complexes,

Table 3. Selected Bond Lengths (Å) and Angles (deg) in Au(I) Phosphido Complexes **1**, **2**·$2C_7H_8$, **3**·C_7H_8, and **4**

param	**1**	**2**·$2C_7H_8$	**3**·C_7H_8	**4**
Au−P(av)	2.315(6)	2.3155(13)	2.3309(12)	2.324(2)
P−Au−P(av)	167.0(2)	172.44(4)	176.61(4)	156.93(8)
Au−P−C(av)	114.6(7)	108.18(18)	106.93(17)	115.2(3)
Au−P−Au(av)	94.2(2)	117.51(5)	115.76(5)	83.06(7)
C−P−C(av)	105.4(9)	105.8(2)	113.5(2)	110.9(4)

and the average Au−P bond length in **3**·C_7H_8 (2.3309(12) Å) is slightly larger than that in the precursor Au(PH(*t*-Bu)$_2$)(Cl) (2.230(2) Å).[9a] Aurophilic interactions[10] are clearly present in the Au_3 triangle of **4**, with Au−Au distances ranging from 3.0661(4) to 3.0970(5) Å, and may also be important in **1**, with Au−Au distances of 3.3414 and 3.445 Å. In contrast, the shortest Au−Au separations in **2**·$2C_7H_8$ and **3**·C_7H_8 are 3.899 and 3.918 Å, respectively.

Although the ring in **2**·$2C_7H_8$ is almost planar (mean deviation from the plane is 0.1116 Å) and that in **4** is planar (mean deviation 0.0075 Å), **3**·C_7H_8 and **1** adopt puckered structures (Supporting Information, Figure S3). The structure of **1** may be described as a butterfly, with an angle between the planes of 125.24(9)°, or as a plane of gold atoms with P atoms alternating above and below the plane. In twisted **3**·C_7H_8, two intersecting planes of P atoms (P1, P2, P3, P1a and P1, P2a, P3a, P1a) are separated by an angle of 34.15(2)°.

Hexameric **2**·$2C_7H_8$ and **3**·C_7H_8 have the same nuclearity as [Au(S(2,4,6-(*i*-Pr)$_3$C$_6$H$_2$))]$_6$, in which the Au_6S_6 ring adopts a chair conformation.[5a,e] However, **2**·$2C_7H_8$ is almost planar and the twisted ring in **3**·C_7H_8 is closer to a boat conformation. The copper analogue of **3** is tetrameric [Cu(P(*t*-Bu)$_2$)]$_4$ with a centrosymmetric, planar Cu_4P_4 core and a Cu−P average bond length of 2.209(5) Å, smaller than in the corresponding gold complex [2.3309(12) Å].[11] The structure of cyclic tetramer **1** may be compared to that of [Au(N(SiMe$_3$)$_2$)]$_4$,[5f] which contains a planar Au_4N_4 core. The shorter Au−N bond length [2.082(3) Å] is accompanied by reduced Au−Au distances [3.0100(3) and 3.0355(3) Å].[5f] In contrast, the Au_4S_4 core in [Au(S(SiO(*t*-Bu)$_3$))]$_4$ is folded as in **1** with an angle of 157.3° with respect to the S−S diagonal,[5c] but [Au(SC(SiMe$_3$)$_3$)]$_4$ is planar and [Au(TeC(SiMe$_3$)$_3$)]$_4$ adopts a butterfly structure with a dihedral angle of 144.98(6)°.[5b]

Several planar complexes with a Au_3 triangle supported by bridging ligands are known, but these include two-atom bridges and nine-membered rings.[12] In contrast, the shorter bridges in **4** lead to unusually bent P−Au−P angles (average 156.93(8)°). We are not aware of other simple [AuX]$_n$ complexes with trinuclear structures, but recently Scheer et al. published the structure of [(CpCr)$_6$Au$_3$P$_3$], a Au(I) complex with a planar Au_3P_3 framework and bridging Cr.[13]

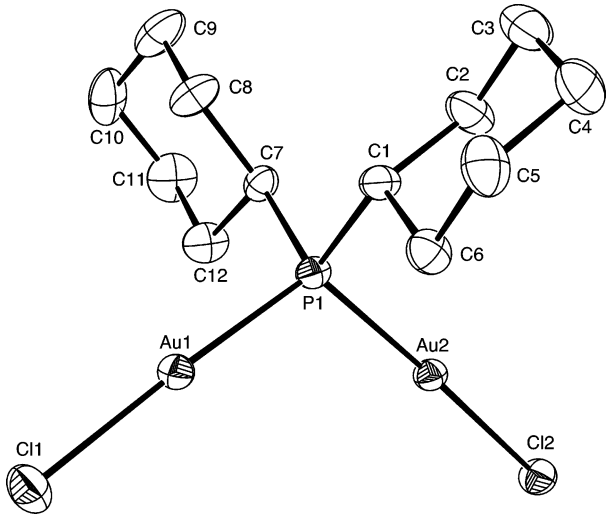
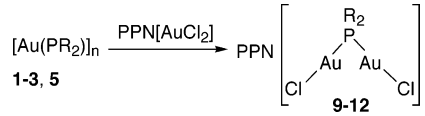


Figure 3. ORTEP diagram of [PPN][(AuCl)$_2$(μ-PCy$_2$)] (**10**). Hydrogen atoms and the PPN cation are not shown. Selected bond lengths (Å) and angles (deg): Au(1)−P(1) 2.2481(13), Au(1)−Cl(1) 2.3027(14), Au(2)−P(1) 2.2440(13), Au(2)−Cl(2) 2.3083(13), P(1)−Au(1)−Cl(1) 177.20(4), P(1)−Au(2)−Cl(2) 177.94(4), C(7)−P(1)−Au(1) 110.69(17), C(1)−P(1)−Au(1) 108.73(18), Au(2)−P(1)−Au(1) 111.82(4), C(7)−P(1)−C(1) 105.33(19), C(7)−P(1)−Au(2) 109.16(18), C(1)−P(1)−Au(2) 110.92(16).

Scheme 3. Synthesis of Phosphido-Bridged Dinuclear Complexes



Another precedent is the Au−Nb raft cluster [Au(Cp′$_2$-NbH$_2$)]$_3$ (Cp′ = η^5-C$_5$H$_4$SiMe$_3$), which also features bridging hydrides.[14] These comparisons suggest that ring size and conformation in these classes of homoleptic compounds depend strongly on the substituents and the possibility of Au−Au interactions.

Reactivity. In the only previous report on the reactivity of gold phosphido complexes, treatment of insoluble [AuPPh$_2$]$_n$ with PPN[AuX$_2$] gave the phosphido-bridged complexes PPN[(AuX)$_2$(μ-PPh$_2$)] (PPN = (PPh$_3$)$_2$N$^+$, X = Cl, Br, I).[3a] Similarly, complexes **1**−**3** and **5** reacted quickly with PPN[AuCl$_2$] to give the dinuclear complexes **9**−**12** (Scheme 3).

The crystal structures of PCy$_2$ and P(*t*-Bu)$_2$ derivatives **10** and **11** (Figure 3 and Supporting Information Figure S4; Table 1), with almost linear Cl−Au−PR$_2$ angles, tetrahedral phosphorus, and nonbonding Au−Au distances (Table 4), are very similar to that of the sole previous example of a structurally characterized gold phosphido complex, [NBu$_4$][(AuBr)$_2$(μ-PPh$_2$)] (**13**).[15]

Other reactions of di-*tert*-butylphosphido complex **3** are summarized in Scheme 4.

Treatment of **3** with I$_2$ and HI gave the air-stable gold(I) phosphine complexes Au(PI(*t*-Bu)$_2$)(I) (**14**) and Au(PH(*t*-Bu)$_2$)(I) (**15**), respectively, the results of formal addition

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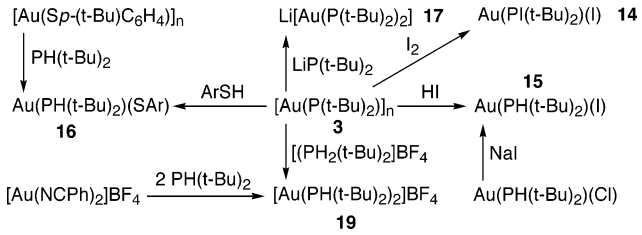
(15) Pritchard, R. G.; Dyson, D. B.; Parish, R. V.; McAuliffe, C. A.; Beagley, B. *J. Chem. Soc., Chem. Commun.* **1987**, 371−372.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Anions $[(AuX)_2(\mu\text{-}PR_2)]^-$ [a]

atom(s)	**13**[b]	**10**	**11**
X	Br	Cl	Cl
R	Ph	Cy	*t*-Bu
Au−X(av)	2.401(2)	2.3055(14)	2.3140(11)
Au−P(av)	2.243(3)	2.2460(13)	2.2568(10)
Au−Au	3.722	3.720	3.616
X−Au−P(av)	176.6(1)	177.57(4)	175.21(4)
Au−P−Au	112.1(2)	111.82(4)	106.49(4)
Au−P−C(av)	108.1(5)	109.88(18)	109.40(19)
C−P−C	102.4(8)	105.33(19)	112.58(19)

[a] Cation = PPN for **10** and **11**, NBu_4 for **13**; see: Pritchard, R. G.; Dyson, D. B.; Parish, R. V.; McAuliffe, C. A.; Beagley, B. *J. Chem. Soc., Chem. Commun.* **1987**, 371−372. [b] The two halves of **13** are symmetry-related, so only one set of bond lengths and angles is included.

Scheme 4. Reactivity of $[Au(P(t\text{-}Bu)_2)]$ (**3**)



across the Au−P bond. In contrast, MeI did not react with **3**. Compound **14** is a rare example of a dialkylhalophosphine complex; the analogous $[Au(PCl(t\text{-}Bu)_2)(Cl)]$ was synthesized previously by Schmidbaur and Aly from $P(Cl)(t\text{-}Bu)_2$ and Au(Cl)(CO).[16] Similar reactions of Fe and Os phosphido complexes with iodine to form P−I bonds were reported by Dobbie and Mason[17] and Bohle and Roper.[18] Complex **15** was also synthesized independently from $Au(PH(t\text{-}Bu)_2)(Cl)$[9a] and excess NaI.

The crystal structures of **14** and **15** (Figures 4 and 5; Table 1) showed that the I−Au−P angle is close to 180° (as expected), and the Au−P bond length is the same for both compounds (Table 5). The slightly larger Au−I bond length in **15** suggests a higher trans-influence of the $PH(t\text{-}Bu)_2$ group in comparison to $PI(t\text{-}Bu)_2$. One of the two independent molecules of **14** forms a centrosymmetric dimer with intermolecular Au−I distances of 3.729 Å (Figure 4), longer than the normal Au−I bond for the same compound (2.5551(4) Å). Long-range interactions at a Au−I distance of 3.876(1) Å in $(Me_3S)_2[AuI_4][I_3]$ have been discussed previously.[19]

Heating **3** for several days at 70 °C with $p\text{-}(t\text{-}Bu)C_6H_4SH$ gave the phosphine thiolate complex $Au(S(p\text{-}(t\text{-}Bu)C_6H_4))(PH(t\text{-}Bu)_2)$ **(16)**, which was prepared more conveniently in a fast reaction at room temperature from the known $[AuS(p\text{-}(t\text{-}Bu)C_6H_4))]_n$[20] and $HP(t\text{-}Bu)_2$. Complex **16** was stable in the solid state but decomposed in solution to form $[AuP(t\text{-}Bu)_2]_n$.

Jones et al. reported that treatment of $[Cu(P(t\text{-}Bu)_2)]_4$ with $LiP(t\text{-}Bu)_2$ gave the anionic complex $Li[Cu(P(t\text{-}Bu)_2)_2]$.[11] A similar reaction with **3** gave $Li[Au(P(t\text{-}Bu)_2)_2]$ **(17)** as a white solid, characterized by ^1H and ^{31}P NMR spectroscopy. However, this compound decomposed readily in solution and could not be obtained in pure form. Similarly, the reaction of **3** with BuLi gave a single product (^{31}P NMR (THF): δ 62.8), presumably the anion $Li[Au(P(t\text{-}Bu)_2)(n\text{-}Bu)]$ **(18)** in analogy to the chemistry of $[Cu(P(t\text{-}Bu)_2)]_4$, but it decomposed on attempted isolation.[21]

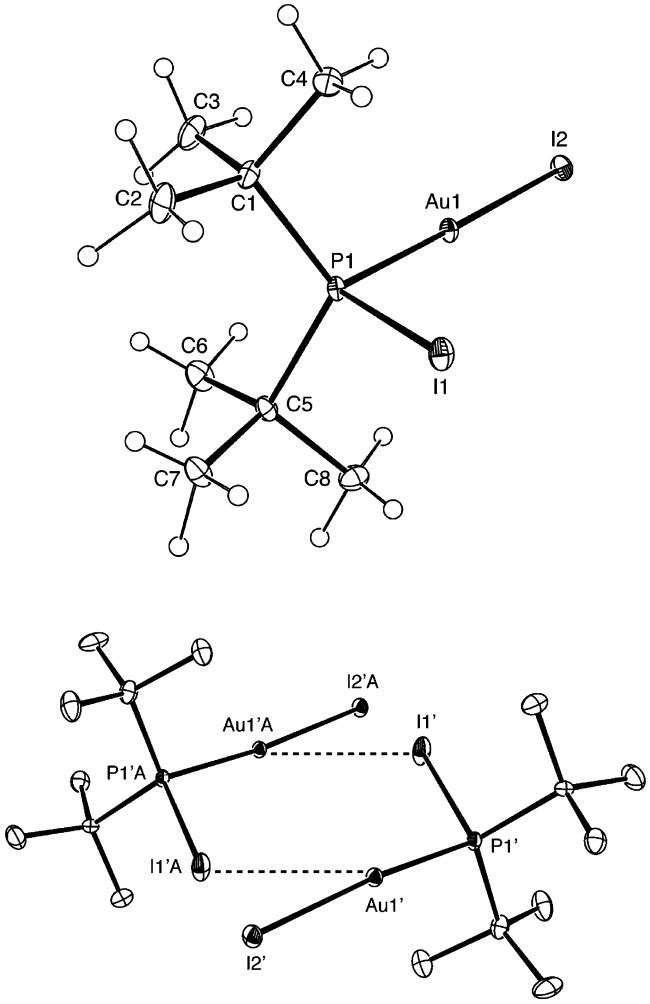


Figure 4. ORTEP diagrams of $Au(PI(t\text{-}Bu)_2)(I)$ (**14**). One of the two independent molecules is shown, along with the centrosymmetric dimeric unit (hydrogens omitted) formed by the other molecule. Selected average bond lengths (Å) and angles (deg): Au(1)−P(1) 2.2532(12), Au(1)−I(2) 2.5521(4), I(1)−P(1) 2.4407(12), P(1)−Au(1)−I(2) 176.74(3), C(5)−P(1)−C(1) 115.5(2), C(5)−P(1)−Au(1) 111.19(15), C(1)−P(1)−Au(1) 111.85(17), C(5)−P(1)−I(1) 103.11(15), C(1)−P(1)−I(1) 105.24(15).

Treatment of **3** with the phosphonium salt $[PH_2(t\text{-}Bu)_2]BF_4$ gave the linear two-coordinate phosphine complex $[Au(PH(t\text{-}Bu)_2)_2]BF_4$ (**19**).[22] The limited solubility of **3** and of the salt made this reaction inconvenient; it was very slow in CH_2Cl_2 at room temperature. Although reaction was faster in bromobenzene at 85 °C over 2 d, an unidentified byproduct was also formed in these reactions. Therefore, **19** was

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(22) This phosphonium salt was reported previously with a different anion (SO_3F^-). See: Krech, F.; Zschunke, A. *Z. Anorg. Allg. Chem.* **1978**, *440*, 45−51.

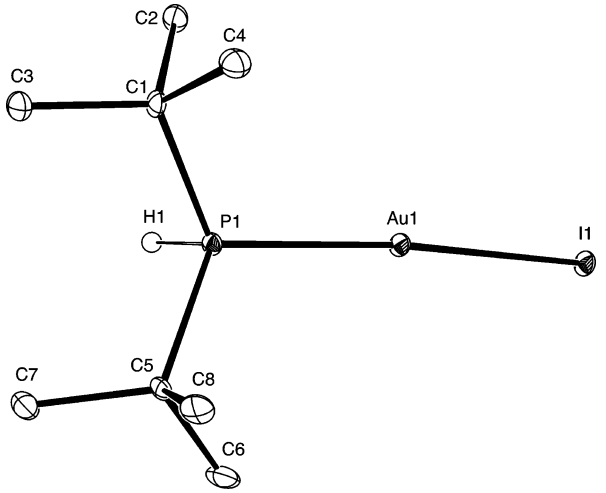

Figure 5. ORTEP diagram of Au(PH(*t*-Bu)$_2$)(I) (**15**). Hydrogen atoms, except for the P−H, are not shown. Selected bond lengths (Å) and angles (deg): Au(1)−P(1) 2.2581(12), Au(1)−I(1) 2.5731(4), P(1)−H(1) 1.31-(5), P(1)−Au(1)−I(1) 168.75(3), C(5)−P(1)−C(1) 117.2(2), C(5)−P(1)−Au(1) 112.25(15), C(1)−P(1)−Au(1) 115.03(15), C(5)−P(1)−H(1) 100(2), C(1)−P(1)−H(1) 99(2).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Au(PI(*t*-Bu)$_2$)(I) (**14**, Averages) and Au(PH(*t*-Bu)$_2$)(I) (**15**)

complex	Au−I (Å)	Au−P (Å)	I−Au−P (deg)
Au(PI(*t*-Bu)$_2$)(I) (**14**)	2.5521(4)	2.2532(12)	176.74(3)
Au(PH(*t*-Bu)$_2$)(I) (**15**)	2.5731(4)	2.2581(12)	168.75(3)

prepared more readily by addition of di-*tert*-butylphosphine to [Au(NCPh)$_2$]BF$_4$.[23] The ^{1}H and ^{31}P NMR spectra of this compound in CD_2Cl_2 (Figure S5, Supporting Information) showed the expected [AMX$_{18}$]$_2$ spin system.[24] In the ^{1}H NMR spectrum, the *tert*-butyl protons gave rise to a multiplet at 1.5 ppm, and the P−H part of the spectrum was a multiplet centered at 5.2 ppm. Analysis of the spectra[25] and simulation using gNMR[26] yielded the coupling constants $^1J_{PH} = 363$, $^2J_{PP} = 278$, $^3J_{PH'} = 2$, $^3J_{P-H(t-Bu)} = 18$, and $J_{HH'} = 0$ Hz. The trans J_{PP} value is similar in magnitude to that observed in two other examples of linear Au(I) complexes containing mutually trans phosphines.[27] The Au−P bond length (Figure 6; Table 1) was 2.3119(8) Å, smaller than in the corresponding oligomer, [AuP(*t*-Bu)$_2$]$_n$ (**3**) (2.3309(12) Å) but larger than in the phosphido-bridged complex, [PPN][(AuCl)$_2$(μ-P(*t*-Bu)$_2$] (**11**) (2.2568(10) Å).

The chalcogenolate complexes [Au(ER)]$_n$ (E = Te, Se, S) can be readily cleaved by tertiary phosphines to give compounds such as Au(PPh$_3$)(ER).[5b,20] Similarly, polymeric [Cu(PPh$_2$)]$_n$ reacts with PHPh$_2$ to give [Cu(PPh$_2$)(PHPh$_2$)]$_n$[28] and with chelating dinitrogen ligands, like bipy, to give

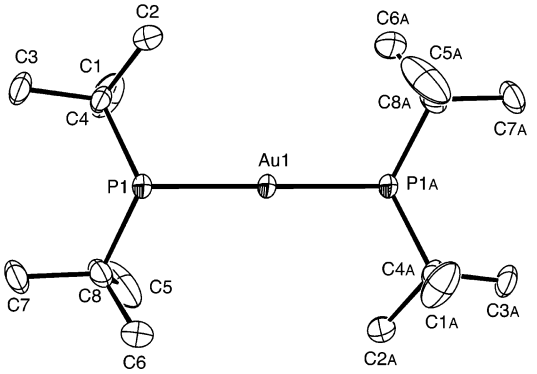

Figure 6. ORTEP diagram of [Au(PH(*t*-Bu)$_2$)]BF$_4$ (**19**). Hydrogen atoms and the distorted anion are not shown. Selected bond lengths (Å) and angles (deg): Au(1)−P(1) 2.3119(8), Au(1)−P(1A) 2.3119(8), P(1A)1−Au(1)−P(1) 180.0, C(4)−P(1)−C(8) 119.3(2), C(4)−P(1)−Au(1) 110.89(11), C(8)−P(1)−Au(1) 111.30(13).

[Cu(bipy)(PPh$_2$)]$_n$,[29] while treatment of CuCl or AgCl with silylphosphines PR$_2$SiMe$_3$ in the presence of tertiary phosphines PR′$_3$ yields the phosphine phosphido complexes [M(PR$_2$)(PR′$_3$)$_x$]$_n$.[30]

However, Puddephatt and Thompson's original synthesis of [AuPPh$_2$]$_n$ from HPPh$_2$ and [AuMe(PMe$_2$Ph)] with dissociation of the tertiary phosphine suggests that gold phosphido complexes might not readily undergo such reactions with donor ligands.[2] Treatment of [Au(P(*t*-Bu)$_2$)]$_n$ (**3**) with the multidentate phosphines triphos [MeC(CH$_2$PPh$_2$)$_3$] and tetraphos [P(CH$_2$CH$_2$PPh$_2$)$_3$] or addition of bipy to [AuPMes$_2$]$_n$ (**1**) did not result in reaction even on heating. Similarly, [Au(P(*t*-Bu)$_2$)]$_n$ (**3**) did not react at room temperature with PPh$_3$, PEt$_3$, or PH(*t*-Bu)$_2$. However, on heating of samples to 60−90 °C, mixtures of unidentified products, presumably [Au(PR$_3$)$_x$(P(*t*-Bu)$_2$)$_y$]$_n$ in analogy to the known copper and silver chemistry, were formed. Surprisingly, peaks in the ^{31}P NMR spectra of these mixtures showed no P−P coupling. However, Stelzer et al. reported that reaction of [CuPPh$_2$]$_n$ with PMe$_3$ gave [Cu$_4$(PPh$_2$)$_4$(PMe$_3$)$_4$], whose ^{31}P NMR spectrum showed broad resonances and no P−P coupling.[31] In contrast, Caulton et al. reported a large J_{PP} as evidence for monomeric Cu(PPh$_2$)(PPh$_3$).[28] For similar Ag phosphido phosphine complexes, no ^{31}P NMR data were reported.[30]

The reaction of **3** with the secondary phosphine might initially make the phosphine−phosphide complex [Au(P(*t*-Bu)$_2$)(PH(*t*-Bu)$_2$)], which could react further to form a mixture of compounds. However, attempts to synthesize this complex independently by deprotonation (KO(*t*-Bu)) of the bis(phosphine) cation [Au(PH(*t*-Bu)$_2$)]BF$_4$ (**19**) or by protonation (HBF$_4$) of the anion Li[Au(P(*t*-Bu)$_2$)$_2$] (**17**) gave mixtures of unknown compounds.

Because treatment of the phosphido complexes with donor ligands did not readily yield monomeric two-coordinate

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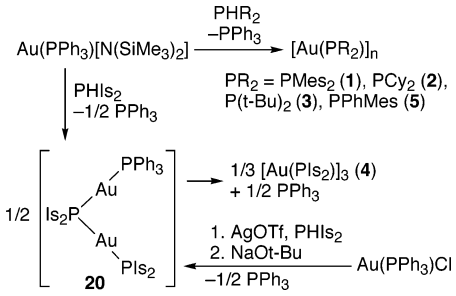
(31) Brauer, D. J.; Hessler, G.; Knueppel, P. C.; Stelzer, O. *Inorg. Chem.* **1990**, *29*, 2370−2375.

Scheme 5. Reactions of $Au(PPh_3)[N(SiMe_3)_2]$ with Secondary Phosphines



products $Au(L)(PR_2)$, we attempted to prepare such terminal phosphido complexes by a different route. Arnold et al. reported that reaction of $Au(PPh_3)[N(SiMe_3)_2]$ with bulky thiols and selenols gave $HN(SiMe_3)_2$ and $Au(PPh_3)(ER)$.[5b] Scheme 5 shows that similar reactions with secondary phosphines quickly gave PPh_3 and $[Au(PR_2)]_n$ (**1**−**3** and **5**) as a mixture of the presumed isomers; we assume that $HN(SiMe_3)_2$ is also formed. The bulkier $PHIs_2$ gave instead, initially, PPh_3 and a yellow complex formulated as PPh_3-$Au(\mu\text{-}PIs_2)Au(PIs_2)$ (**20**) on the basis of its ^{31}P NMR spectrum (toluene; δ 44.0 (d, $J = 267$, PPh_3), −15.4 (dd, $J = 267$, 148, μ-PIs_2), −54.3 (d, $J = 148$, PIs_2); this intermediate decomposed over 2 d to yield PPh_3 and $[Au(PIs_2)]_3$ (**4**). Yellow **20** was generated independently, along with PPh_3, by treatment of $Au(PPh_3)Cl$ with AgOTf and $PHIs_2$, followed by addition of NaO*t*-Bu.

These observations suggest that the phosphido group has a strong tendency to bridge in these Au(I) complexes and are also consistent with its expected large trans influence;[32] this ligand thus behaves differently from the isoelectronic chalcogenolates.

Conclusions

X-ray crystallographic studies of Au(I) phosphido complexes have for the first time established the structures of this class of compounds as cyclic oligomers. ^{31}P NMR spectroscopy showed that several species, presumably rings of different sizes, exist in solution and that they can interconvert in some cases. A brief reactivity survey showed that the reagents HI, I_2, ArSH, $[PH_2(t\text{-}Bu)_2]BF_4$, and PPN-$[AuCl_2]$ led to the products of addition across the Au−P bond. The anions $LiP(t\text{-}Bu)_2$ and *n*-BuLi also appeared to cleave the oligomeric structure of **3**, although the products could not be obtained in pure form.

Although similar oligomeric Cu and Ag phosphides or Au chalcogenolates are cleaved readily by donor ligands such as phosphines or bipy, it is more difficult to break up the oligomeric structure of the gold phosphido oligomers or to prepare terminal phosphido complexes $Au(L)PR_2$ directly. This is consistent with a particularly strong Au−P bond and a preference for μ_2-bridging coordination, as observed for platinum phosphido complexes; for example, Chatt and Davidson observed that Pt−PR_2 bridges resisted cleavage even in boiling $P(n\text{-}Pr)_3$.[33]

Experimental Section

General Details. Manipulations and reactions of secondary phosphines were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. NMR spectra were recorded (at 21 °C unless otherwise noted) with Varian 300 or 500 MHz spectrometers. ^1H or ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in Hz, as absolute values unless noted otherwise. Unless indicated, peaks in NMR spectra are singlets. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer 1600 series FTIR machine and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. MALDI-TOF mass spectroscopy was performed at the University of Illinois using an Applied Biosystems Voyager-DE STR. The spectra were obtained in linear mode, with accuracy of 0.05−0.1%. Thus, an error of 1 or 2 amu at 2000 amu is expected. In the assignment of the mass spectra of **1**−**6**, the observed peaks match the calculated ones within this experimental error; in addition, protonating complexes **1**−**6** to make cations could also cause small changes in their observed mass spectra.

Unless otherwise noted, reagents were from commercial suppliers. The complexes $Au(PHR_2)(Cl)$ (R = Mes, Cy, *t*-Bu) and $Au(PH_2Mes^*)(Cl)$ were prepared by a modification of the literature method: Au(THT)(Cl)[8] was used instead of Au(CO)Cl.[9] $PHIs_2$,[34] PH(Ph)(Mes),[35] $PHMes_2$,[36] PH_2Mes^*,[37] $[AuSC_6H_4(p\text{-}(t\text{-}Bu))]_n$,[20] $[Au(NCPh)_2]BF_4$,[23] $Au(PPh_3)[N(SiMe_3)_2]$,[38] and PPN$[AuCl_2]$[3a] were prepared by literature procedures.

$[Au(PMes_2)]_n$ (1). About 5 mL of aqueous ammonia (29.6%, 78 mmol) was added to a solution of $[Au(PHMes_2)(Cl)]$ (340 mg, 0.68 mmol) in 10 mL of THF; a white precipitate formed. After the mixture was stirred for 30 min, the solvent was pumped off, and the resulting white solid was washed with 30 mL of water to give 220 mg of **1**, 69%.

$^{31}P\{^1H\}$ NMR (toluene-d_8): δ −17.0 (major), −18.8 (minor), −23.4 (minor), −36.1 (minor). This material was dissolved in toluene by heating to 70 °C. Slow evaporation of toluene at room temperature yielded a single product, shown to be a cyclic tetramer by X-ray crystallography. Typical yield of this pure compound from the mixture was about 42%.

Anal. Calcd for $C_{72}H_{88}Au_4P_4$: C, 46.36, H, 4.76. Found: C, 46.20; H, 4.58. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −36.1. ^1H NMR (C_6D_6): δ 6.70 (16H), 2.65 (48H), 2.07 (24H). IR: 3015, 2954, 2915, 1715, 1592, 1546, 1454, 1392, 1292, 1246, 1015, 838, 700, 615, 554, 423. MALDI TOF-MS (cyano-4-hydroxycinnamic acid): *m*/*z* 2800 ($(AuPMes_2)_6$), 2530 ($Au_6(PMes_2)_5$), 2333 ($(AuPMes_2)_5$), 2202, 2153, 2108, 2064 ($Au_5(PMes_2)_4$), 1884, 1867 ($(AuPMes_2)_4$), 1783, 1717, 1641, 1597 ($Au_4(PMes_2)_3$), 1417, 1317, 1237, 1175, 951.

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[Au(PCy$_2$)]$_n$ (2). Aqueous ammonia (5 mL, 29.6%, 78 mmol) was added to a solution of [Au(PHCy$_2$)(Cl)] (815 mg, 1.9 mmol) in 5 mL of THF, forming a white precipitate. The mixture was stirred for 15 min, and the white solid was filtered off to give **2** (720 mg, 96%) as a mixture. ^{31}P{^{1}H} NMR (toluene): δ 65.2, 62.4, 51.3, 42.9 (ratios varied depending on the experiment). Recrystallization from toluene/acetonitrile (or simply heating in toluene) gave a mixture of two species in ca. 1:1 ratio. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 54.2, 48.2. ^{1}H NMR (C$_6$D$_6$): δ 2.61−2.54 (m, 2H), 2.33−2.25 (m, 4H), 1.89−1.66 (m, 10H), 1.35−1.21 (m, 6H). [This material was a toluene solvate, but recrystallization from CH$_2$Cl$_2$ gave a solvent-free sample for elemental analysis: Anal. Calcd for C$_{12}$H$_{22}$PAu: C, 36.56; H, 5.62. Found: C, 36.77; H, 5.42.] These compounds could not be separated reproducibly, but on one occasion, slow evaporation from toluene gave crystals shown to be a single compound by X-ray crystallography and NMR.

^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 54.2. IR: 3144, 2911, 2844, 1628, 1444, 1400, 1339, 1261, 1172, 1100, 994, 883, 840, 728, 700. MALDI TOF-MS (cyano-4-hydroxycinnamic acid): *m*/*z* 2805, 2761 ((AuP-Cy$_2$)$_7$), 2608, 2564, 2384, 2366 ((AuPCy$_2$)$_6$), 2284, 2212, 2171 (Au$_5$-(PCy$_2$)$_6$), 2085, 2016, 1972 ((AuPCy$_2$)$_5$), 1818, 1776 (Au$_4$(PCy$_2$)$_5$), 1623, 1578 ((AuPCy$_2$)$_4$), 1398, 1382 (Au$_3$(PCy$_2$)$_4$), 1200, 1093, 1004, 988. In addition to the molecular ion peaks, MALDI mass spectra for this compound and for **1**−**4** also showed signals at higher *m*/*z* ratios. These peaks may be due to higher mass oligomers of the Au complexes and/or to formation of multimers, which is commonly observed in MALDI-MS.[39]

[Au(P(*t*-Bu)$_2$)]$_n$ (3). Under N$_2$, aqueous ammonia (5 mL, 29.6%, 78 mmol) was added to a solution of [Au(PH(*t*-Bu)$_2$)(Cl)] (450 mg, 1.19 mmol) in 5 mL of THF; a white precipitate formed. The mixture was stirred for 2 h and then filtered in air. The white solid was washed with 30 mL of water and 20 mL of acetone. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 115.3, 114.2, 107.4 (major), 104.9 (major), 89.9. [When the mixture was stirred for only 15 min, different speciation was observed by ^{31}P{^{1}H} NMR (THF): δ 115.3, 115.18, 115.12, 115.0, 114.31, 114.08, 113.68, 105.2, 104.3, 89.9, with major peaks the ones around 114−115 ppm.] The solid was dissolved in toluene at ca. 50 °C and then cooled to room temperature. Acetonitrile (10 mL) was added, and overnight cooling to 0 °C gave 350 mg (86%) of **3** as a mixture of two species with ^{31}P NMR shifts of 107.4 and 104.9 (ca. 2:1). IR: 2978, 2933, 2889, 2856, 1461, 1383, 1357, 1172, 1011, 933, 811, 728, 694, 603, 581, 475 cm^{-1}. MALDI TOF-MS (cyano-4-hydroxycinnamic acid): *m*/*z* 2515, 2172, 2078, 2055 ((AuP(*t*-Bu)$_2$)$_6$), 1999, 1911 (Au$_6$(P(*t*-Bu)$_2$)$_5$), 1855 (Au$_5$(P(*t*-Bu)$_2$)$_6$), 1830, 1796, 1713 ((AuP(*t*-Bu)$_2$)$_5$), 1664, 1652, 1595, 1568 (Au$_5$-(P(*t*-Bu)$_2$)$_4$), 1540, 1491, 1488, 1370 ((AuP(*t*-Bu)$_2$)$_4$), 1279, 1226 (Au$_4$(P(*t*-Bu)$_2$)$_3$), 1162, 1147, 1105, 1046, 1030, 958, 927, 898, 894, 867.

The mixture of two compounds was dissolved in toluene at 55 °C and then the solution slowly cooled to room temperature, affording small off-white crystals, which were collected by filtration and shown to be a single product which contained cocrystallized toluene by X-ray crystallography and NMR. Anal. Calcd for (C$_8$H$_{18}$-PAu)$_6$·toluene: C, 30.80; H, 5.45. Found: C, 30.99; H, 5.37. ^{31}P-{^{1}H} NMR (C$_6$D$_6$): δ 107.3. ^{1}H NMR (C$_6$D$_6$): δ 1.57. The ^{31}P NMR spectrum of the filtrate showed the presence of **3** and the other compound, in ca. 1:2 ratio. Typical yield of pure **3** from the mixture was 60%.

[Au(PIs$_2$)]$_3$ (4). To a solution of [Au(THT)(Cl)] (552 mg, 1.72 mmol) in 10 mL of dry, degassed CH$_2$Cl$_2$ was added a solution of PHIs$_2$ (765 mg, 1.74 mmol) in 4 mL of dry, degassed CH$_2$Cl$_2$. The resulting pale pink solution was stirred under nitrogen for 20 min and then evaporated to dryness in vacuo. The crude product **[Au(PHIs$_2$)(Cl)]** (**7**) was washed with 25 mL of hexane twice to give 696 mg of white solid. The hexane solution was evaporated to dryness giving a sticky yellow solid, which was washed with 5 mL of hexane to yield 125 mg more product (total yield 821 mg (71%)).

A sample for elemental analysis was obtained as follows. After the reaction mixture was stirred for 20 min, the white-pink product was precipitated with methanol at −60 °C. It was redissolved in CH$_2$Cl$_2$ and filtered to remove some pink undissolved solid. The solvent was pumped off from the clear filtrate to give an off-white solid.

Anal. Calcd for C$_{30}$H$_{47}$ClPAu: C, 53.69; H, 7.06. Found: C, 53.50; H, 7.10. ^{31}P NMR (C$_6$D$_6$): δ −56.4 (J_{P-H} = 400). ^{1}H NMR (C$_6$D$_6$): δ 7.0 (d, J = 4, 4H, Ar), 6.95 (d, P−H, J_{P-H} = 400), 3.67 (m, 4H, *o*-CH), 2.64 (septet, J = 7, 2H, *p*-CH), 1.09 (d, J = 7, 12H, Me), 1.04 (d, J = 7, 12H, Me), 0.96 (d, J = 7, 12H, Me). IR: 2950, 2925, 2866, 2410 (w, P−H), 1601, 1551, 1460, 1419, 1381, 1361, 1316, 1258, 1238, 1190, 1166, 1135, 1101, 1060, 1043, 940, 906, 879, 848, 810, 749, 701, 650, 574, 523, 492, 427.

Aqueous ammonia (3 mL, 29.6%, 47 mmol) was added under N$_2$ to a solution of [Au(PHIs$_2$)(Cl)] (335 mg, 0.5 mmol) in 5 mL of THF. The solution turned yellow. After the mixture was stirred for 30 min, the solution became turbid. The solvent was evaporated, giving a white solid that was washed with 20 mL of water to give 243 mg (77%) of [Au(PIs$_2$)]$_3$ (**4**). Crystals suitable for X-ray crystallography were obtained by slow evaporation of hexane at 0 °C. Recrystallization from benzene/methanol at 0 °C gave a sample for elemental analysis.

Anal. Calcd for C$_{30}$H$_{46}$AuP: C, 56.78; H, 7.31. Found: C, 56.75; H, 7.59. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −78.9. ^{1}H NMR (C$_6$D$_6$): δ 7.17 (6H), 7.01 (6H), 5.56−5.52 (m, 6H), 3.82−3.78 (m, CH, 6H), 2.80−2.70 (m, CH, 6H), 1.56 (d, J = 7, 18H), 1.37 (d, J = 7, 18H), 1.21−1.18 (m, 36 H), 1.09 (d, J = 7, 18H), 0.70 (d, J = 7, 18H). IR: 2959, 2867, 1601, 1556, 1460, 1417, 1383, 1361, 1306, 1100, 878. MALDI TOF-MS (cyano-4-hydroxycinnamic acid): 2976, 2774, 2687, 2571, 2539 ((AuPIs$_2$)$_4$), 2336, 2287, 2217, 2145 (Au$_2$(PIs$_2$)$_4$), 2101 (Au$_4$(PIs$_2$)$_3$), 2090, 1904 ((AuPIs$_2$)$_3$), 1890, 1724, 1708, 1694, 1505, 1456, 1315, 1270 ((AuPIs$_2$)$_2$), 1088, 1074 (Au(PIs$_2$)$_2$).

[Au(P(Ph)(Mes))]$_n$ (5). Under N$_2$, a solution of 0.457 g (2 mmol) of PH(Ph)(Mes) in 2 mL of CH$_2$Cl$_2$ was added to 0.640 g (2 mmol) of solid Au(THT)Cl to give a turbid solution which became clear after addition of 5 mL of CH$_2$Cl$_2$. The solution was stirred for 15 min, and then 10 mL of pentane was added and a white precipitate formed. Two recrystallizations from THF/pentane gave pure **Au(PH(Ph)(Mes))Cl** (**8**) (350 mg, 38%). X-ray-quality crystals were obtained by slow evaporation of methylene chloride at room temperature.

Anal. Calcd for C$_{15}$H$_{17}$AuClP: C, 39.11; H, 3.72. Found: C, 39.01; H 3.50. ^{31}P NMR (CD$_2$Cl$_2$): δ −31.8 (d, J = 403). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.68−7.64 (m, 2H, Ar), 7.57−7.55 (m, 1H, Ar), 7.49−7.46 (m, 2H, Ar), 7.30 (d, 1H, J_{PH} = 403), 7.05 (m, 2H, Ar), 2.51 (6H, *o*-Me), 2.37 (3H, *p*-Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 142.8 (d, J = 2.5), 142.0 (d, J = 9), 134.3 (d, J = 14), 132.25 (d, J = 9), 130.6 (d, J = 2.5), 129.5 (d, J = 13), 124.9 (d, J = 63), 120.0 (d, J = 66), 23.2 (d, J = 11, *o*-Me), 21.2 (d, J = 1, *p*-Me).

Aqueous ammonia (10 mL, 29.6%, 86 mmol) was added to a solution of Au(PH(Ph)(Mes))Cl (1.4 g, 3 mmol) in 15 mL of THF, and the mixture was stirred for 30 min. The resulting white-yellow precipitate was filtered off and washed with 50 mL of H$_2$O.

(39) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299−2301.

Recrystallization from THF gave a white solid (1.1 g, 85%) which was a mixture of two isomers.

Anal. Calcd for $AuPC_{15}H_{16}$: C, 42.47; H, 3.80. Found: C, 42.10; H, 3.78. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −12.1 (minor), −21.6 (major). ^1H NMR (C_6D_6): δ 7.80−7.49 (m, 2H), 6.92−6.86 (m, 2H), 6.82−6.70 (m, 3H), 2.90−2.83 (m, 6H, *o*-Me), 2.08−2.03 (m, 3H, *p*-Me). IR: 3056, 3011, 2956, 1600, 1583, 1456, 1428, 1400, 1372, 1289, 1067, 1022, 844, 739, 689, 622, 556, 483, 456. MALDI TOF-MS (cyano-4-hydroxycinnamic acid): *m*/*z* 3167 ($Au_8(PPhMes)_7$), 2922, 2743 ($Au_7(PPhMes)_6$), 2499, 2363, 2318 ($Au_6(PPhMes)_5$), 2122 ($AuPPhMes)_5$, 2074, 1982, 1938, 1910, 1894 ($Au_5(PPhMes)_4$), 1834, 1742, 1714, 1697 ($AuPPhMes)_4$, 1666 ($Au_5(PPhMes)_3$), 1590, 1514, 1470 $Au_4(PPhMes)_3$, 1381, 1274 ($AuPPhMes)_3$, 1090, 1077.

Recrystallization from benzene gave a single compound ($^{31}P\{^1H\}$ NMR (C_6D_6): δ −21.6; 43% recovery). ^1H NMR (C_6D_6): δ 7.52 (2H), 7.42 (1H), 6.90 (2H), 6.79 (2H), 2.92 (6H, *o*-Me), 2.08 (3H, *p*-Me). The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6) of the filtrate showed two peaks at −12.1 and −21.6 ppm, in a ratio of ∼ 1:1.

[Au(PHMes*)]$_n$ (6). Under N_2, aqueous ammonia (3 mL, 29.6%, 47 mmol) was added to a solution of $Au(PH_2Mes^*)Cl$ (330 mg, 0.65 mmol) in 5 mL of THF; a white precipitate formed. The mixture was stirred for 15 min, and then the solvent was evaporated. The white-yellowish solid was washed with 30 mL of water. The yield was 164 mg, 53%. The compound was recrystallized from toluene and ethanol.

^1H NMR (toluene-d_8): δ 7.64−7.48 (m, 2H, Ar), 6.04 (broad, 1H, J_{P-H} = 230), 1.92−1.78 (m, 18H, *o*-*t*-Bu), 1.33−1.24 (m, 9H, *p*-*t*-Bu). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ −40.9, −42.6 (ratio ca. 1:1). IR: 2944, 2867, 2456 (P−H), 2378 (P−H), 1756, 1594, 1539, 1467, 1394, 1356, 1278, 1233, 1205, 1183, 1122, 1072, 1028, 922, 900, 872, 856, 744, 644. MALDI TOF-MS (cyano-4-hydroxycinnamic acid): *m*/*z* 3075, 2798, 2601, 2569 ($Au_6(PHMes^*)_5$), 2357, 2325, 2175 ($Au_4(PHMes^*)_5$), 2084, 2079, 1947, 1854, 1717, 1701 ($Au_3(PHMes^*)_4$), 1624, 1609, 1473, 1456, 1379, 1226 ($Au_2(PHMes^*)_3$), 1152, 1136, 997, 987, 982, 906, 778, 752 ($Au(PHMes^*)_2$), 725, 664, 610. Anal. Calcd for $C_{18}H_{30}AuP$: C, 45.58; H, 6.37. Found: C, 45.69; H, 6.34.

At lower temperatures the ^1H and ^{31}P NMR peaks due to **6** in toluene-d_8 became broader. At temperatures above 25 °C, the ^{31}P NMR spectrum showed, instead of two broad peaks, multiple sharp peaks in the same region, suggesting that additional species were formed on heating. These changes were reversible.

[PPN][(AuCl)$_2$(μ-PMes$_2$)] (9). To a slurry of 70 mg (0.15 mmol) of $[AuPMes_2]_n$ in 20 mL of CH_2Cl_2 was added 120 mg (0.15 mmol) of $[PPN][AuCl_2]$. After being stirred for 1 h, the solution darkened from yellow to violet and became cloudy. The reaction mixture was filtered to give a clear yellow solution, which was reduced in volume to ca. 10 mL and then treated with ether to precipitate the product as a white solid, which was recrystallized from CH_2Cl_2/ether for elemental analysis. Integration of the ^1H NMR spectrum of this sample showed that it contained both solvents. Yield = 102 mg, 53%.

Anal. Calcd for $C_{54}H_{52}Au_2Cl_2NP_3(CH_2Cl_2)_{0.5}[Et_2O]_{0.33}$: C, 50.05; H, 4.24; N, 1.05. Found: C, 49.94; H, 4.05; N, 1.15. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.3 (PPN), −53.6 ($PMes_2$). ^1H NMR ($CDCl_3$): δ 7.71−7.68 (m, 6H, Ph), 7.55−7.50 (m, 24H, Ph), 6.75 (d, J = 3, 4H, Mes), 2.60 (12H, *o*-CH_3), 2.23 (6H, *p*-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.9 (d, J = 9), 137.0, 134.15, 132.5−132.3 (m), 130.4 (d, J = 8), 130.0−129.8 (m), 127.9, 126.5, 25.8 (d, J = 11, *o*-CH_3), 21.0 (*p*-CH_3).

[PPN][(AuCl)$_2$(μ-PCy$_2$)] (10). To a slurry of 152 mg (0.386 mmol) of $[AuPCy_2]_n$ in 35 mL of CH_2Cl_2 was added 311 mg (0.386 mmol) of $[PPN][AuCl_2]$. After being stirred for 3 h, the reaction mixture was almost clear. It was filtered, and the solvent was evaporated from the filtrate yielding a white-yellowish powder, which was recrystallized twice from CH_2Cl_2 and ether to give a material containing both these solvents as shown by NMR integration and elemental analysis. Yield = 170 mg, 37%. Crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a CH_2Cl_2 solution.

Anal. Calcd for $C_{48}H_{52}Au_2Cl_2NP_3(CH_2Cl_2)_{0.17}[Et_2O]_{0.06}$: C, 47.68; H, 4.38; N, 1.15. Found: C, 47.38; H, 4.14; N, 1.20. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.8 (PCy_2), 22.2 (PPN). ^1H NMR (CD_2Cl_2): δ 7.76−7.72 (m, 6H, Ph), 7.60−7.52 (m, 24H, Ph), 2.12−1.99 (m, 6H, Cy), 1.80−1.78 (m, 4H, Cy), 1.67 (m, 2H, Cy), 1.47−1.27 (m, 10H, Cy). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.0, 132.5−132.3 (m), 129.9−129.6 (m), 128.0, 126.6, 35.5 (d, J = 29), 34.3 (d, J = 2), 27.2 (d, J = 13), 26.6.

[PPN][(AuCl)$_2$(μ-P(*t*-Bu)$_2$)] (11). To a slurry of 100 mg (0.3 mmol) of $[AuP(t\text{-}Bu)_2]_n$ in 20 mL of CH_2Cl_2 was added 311 mg (0.386 mmol) of $[PPN][AuCl_2]$. After being stirred for 3 h, the reaction mixture was clear and pale red. The reaction mixture was filtered to give a clear solution, from which the solvent was evaporated to yield a white solid, which was recrystallized twice from CH_2Cl_2/ether. Yield = 238 mg, 69%. Crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a CH_2Cl_2 solution.

Anal. Calcd for $C_{44}H_{48}Au_2Cl_2P_3N$: C, 46.01; H, 4.21; N, 1.22. Found: C, 45.89; H, 4.08; N, 1.14. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 82.5 ($P(t\text{-}Bu)_2$), 22.2 (PPN). ^1H NMR ($CDCl_3$): δ 7.74−7.69 (m, 6H, Ph), 7.54−7.47 (m, 24H, Ph), 1.42 (d, 18H, J = 15, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.2, 132.5−132.3 (m), 130.0−129.8 (m), 127.9, 126.5, 37.9 (d, J = 22, *C*Me_3), 34.2 (d, J = 8, Me).

[PPN][(AuCl)$_2$(μ-P(Ph)(Mes))] (12). To a slurry of 127 mg (0.3 mmol) of $[AuPPhMes]_n$ in 20 mL of CH_2Cl_2 was added 242 mg (0.3 mmol) of $[PPN][AuCl_2]$, and this mixture was stirred for 30 min. The reaction mixture cleared almost immediately and turned colorless. Upon the addition of ether a white precipitate formed. Recrystallization from CH_2Cl_2/ether gave an ether solvate as quantified by ^1H NMR integration. Yield = 128 mg, 35%.

Anal. Calcd for $C_{51}H_{46}Au_2Cl_2NP_3[Et_2O]_{0.5}$: C, 50.21; H, 4.05; N, 1.10. Found: C, 50.42; H, 3.64; N, 1.12. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.6 (PPN), −25.6 (P(Ph)(Mes)). ^1H NMR ($CDCl_3$): δ 7.68−7.65 (m, 6H, Ph), 7.52−7.46 (m, 26H, Ph), 7.08−7.06 (m, 3H, Ph), 6.82 (d, J = 3.5, 2H, Mes), 2.78 (6H, *o*-Me), 2.24 (3H, *p*-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.6 (d, J = 9), 139.7, 139.3, 138.4, 135.8, 134.4−134.3 (m), 134.1, 133.4 (d, J = 14), 130.6 (d, J = 8), 129.9−129.8 (m), 127.9 (d, J = 11), 127.6, 126.7 (d, J = 2), 27.2 (d, J = 11, *o*-Me), 21.1 (*p*-Me).

Au(PI(*t*-Bu)$_2$)(I) (14). To a slurry of 85 mg (0.25 mmol) of $[AuP(t\text{-}Bu)_2]_n$ in 40 mL of toluene was added 67 mg (0.26 mmol) of I_2 in 5 mL of toluene. After 15 min of stirring, the white slurry turned into a reddish solution. After another 1 h of stirring, the solvent was evaporated, yielding a yellow solid. The solid was washed carefully with 5 mL of ethanol, since the product is slightly soluble in this solvent. Yield = 90 mg, 60%, of analytically pure light yellow solid. White crystals suitable for X-ray crystallography were obtained by slow evaporation of hexane from a solution of $Au(PI(t\text{-}Bu_2))(I)$.

Anal. Calcd for $C_8H_{18}AuPI_2$: C, 16.12; H, 3.04. Found: C, 16.43; H, 2.99. ^1H NMR (C_6D_6): δ 0.90 (d, J = 18). ^{31}P NMR (C_6D_6): δ 116.3 (m, J_{PH} = 18). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 39.5 (d, J = 3), 28.9 (d, J = 8).

Au(PH(*t*-Bu)$_2$)(I) (15). To a slurry of 103 mg (0.3 mmol) of $[AuP(t\text{-}Bu)_2]_n$ in 40 mL of toluene was added 60 μL of a 55−58% aqueous HI solution (58 mg, 0.45 mmol), which was then stirred

for 15 h under nitrogen atmosphere. Then the solvent was evaporated yielding a white-yellow solid. Yield = 88 mg, 62%. The compound was recrystallized from THF/hexane to give white crystals. White crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a THF solution of Au(PH(*t*-Bu)$_2$)(I). ^{31}P{^{1}H} NMR (C_6D_6): δ 59.9.

This compound was also synthesized independently from Au(PH(*t*-Bu)$_2$)(Cl) and NaI and further characterized. To a solution of 150 mg (0.44 mmol) of Au(PH(*t*-Bu)$_2$)(Cl) in 5 mL of THF was added an excess of NaI (130 mg, 0.87 mmol) in 5 mL of THF. After NaI addition, the solution became turbid and the mixture was stirred for 2 h. The turbid solution was filtered through Celite, giving a clear filtrate to which 20 mL of hexane were added; a white precipitate formed. Yield = 148 mg, 72%. For elemental analysis, the sample was dissolved in toluene and then filtered. The solvent was evaporated from the filtrate under vacuum to give a white solid.

Anal. Calcd for $C_8H_{19}AuPI$: C, 20.44; H, 4.07. Found: C, 20.71, H, 4.10. ^{1}H NMR (C_6D_6): δ 3.94 (d, J = 361, 1H, P−H), 0.80 (d, J = 17, 18H, *t*-Bu). ^{31}P NMR (C_6D_6): δ 59.8 (dm, J_{PH} = 361, J_{P-t-Bu} = 17). ^{13}C{^{1}H} NMR (C_6D_6): δ 33.7 (d, J = 26), 29.9 (d, J = 6). IR: 2944, 2856, 2322 (P−H), 1633, 1467, 1389, 1362, 1179, 1029, 901, 826, 622, 594, 472.

Au(S(*p*-(*t*-Bu)C$_6$H$_4$)(PH(*t*-Bu)$_2$) (16). To a solution of 150 mg (0.414 mmol) of [Au(S(*p*-(*t*-Bu))C$_6$H$_4$)]$_n$ in 2 mL of toluene was added 60 mg (0.414 mmol) of HP(*t*-Bu)$_2$ in 3 mL of toluene. On phosphine addition, the solution turned from yellow to colorless. A small amount of solid was removed by filtration through Celite and the solvent was evaporated, yielding a white solid, which was washed with 10 mL of hexane and dried. Yield = 109 mg, 52%.

Anal. Calcd for $C_{18}H_{32}AuPS$: C, 42.52; H, 6.34. Found: C, 42.62; H, 6.56. ^{1}H NMR (C_6D_6): δ 8.00 (d, J = 8, 2H), 7.2 (d, J = 8, 2H), 3.84 (d, J = 351, 1H), 1.24 (9H), 0.85 (d, J = 16, 18H). ^{31}P{^{1}H} NMR (C_6D_6): δ 59.7. IR: 3065, 2953, 2863, 2340 (P−H), 1591, 1490, 1466, 1394, 1366, 1267, 1183, 1119, 1080, 1026, 817.

The same compound was also synthesized from 68 mg (0.2 mmol) of [AuP(*t*-Bu)$_2$]$_n$ and 34 mg (0.2 mmol) of *p*-(*t*-Bu)C$_6$H$_4$-SH in 35 mL of toluene. The mixture was stirred under N_2 for 48 h at room temperature and then heated for 24 h at 70 °C. The solution was initially turbid, but turned clear at the end of the reaction. The solvent was pumped off, yielding a white solid. The solid was dissolved in toluene giving a turbid solution, which was filtered through Celite. Addition of ethanol to the filtrate precipitated some impurities, which were filtered off. Evaporation of the filtrate gave a white solid. ^{31}P NMR (C_6D_6): δ 59.9 (J_{P-H} = 357).

Li[Au(P(*t*-Bu)$_2$)$_2$] (17). To a solution of 29 mg (0.2 mmol) of HP(*t*-Bu)$_2$ in 1 mL of THF was added 125 μL of *n*-BuLi (1.6 M hexane solution, 0.2 mmol). The mixture turned instantly from colorless to yellow. To the solution, 68 mg (0.2 mmol) of [AuP-(*t*-Bu)$_2$]$_n$ was added. The yellow slurry formed was filtered through Celite, yielding a clear yellow filtrate. The solvent was pumped off, leaving a yellow sticky solid behind. This solid was washed with hexane, yielding a white solid. Yield = 30 mg, 30%. The compound decomposes readily in THF at 25 °C, and it could not be obtained in analytically pure form. An attempt to stabilize the anion by cation exchange with PPNCl caused rapid decomposition. ^{1}H NMR (THF-d_8): δ 1.35 (m). ^{31}P{^{1}H} NMR (THF-d_8): δ 80.6.

Addition of BuLi to [Au(P(*t*-Bu)$_2$)]$_n$. To a solution of [Au(P(*t*-Bu)$_2$)]$_n$ (29 mg, 0.085 mmol) in 2 mL of THF was added BuLi (125 μL of 1.6 M solution in hexanes (0.2 mmol)) in 2 mL of THF. After the mixture was stirred for 15 min, the ^{31}P NMR spectrum (THF) of the yellow slurry showed a peak at 62.8 ppm. Filtration through Celite gave a yellow solution, but attempts to crystallize and isolate this material were unsuccessful.

[PH$_2$(*t*-Bu)$_2$]BF$_4$. To a solution of PH(*t*-Bu)$_2$ (400 mg, 2.74 mmol) in 5 mL of ether was added HBF$_4$·Me$_2$O (ca. 500 mg, 3.7 mmol). A white solid formed immediately, and the mixture became hot and bubbled. After addition of 5 mL of ether, the white slurry was stirred and then allowed to settle. The ether was decanted to yield a sticky white solid, which was washed with about 10 mL more ether and then dried under vacuum to give 604 mg of white powder (94%).

Anal. Calcd for $C_8H_{20}BF_4P$: C, 41.06; H, 8.61. Found: C, 40.72; H, 8.62. ^{31}P{^{1}H} NMR (CD_3CN): δ 24.4. ^{1}H NMR (CD_3CN): δ 5.91 (d, J = 470, 2H), 1.51 (d, J = 18, 18H). ^{13}C{^{1}H} NMR (CD_3-CN): δ 32.3 (d, J = 35, *C*Me$_3$), 27.7 (d, J = 2, C*Me*$_3$).

Formation of [Au(PH(*t*-Bu)$_2$)$_2$]BF$_4$ (19) from [Au(P(*t*-Bu)$_2$)]$_n$ and [PH$_2$(*t*-Bu)$_2$]BF$_4$. A white slurry of [Au(P(*t*-Bu)$_2$)]$_n$ (10 mg, 0.044 mmol) and [PH$_2$(*t*-Bu)$_2$]BF$_4$ (15 mg, 0.044 mmol) in 1 mL of CH_2Cl_2 was prepared in an NMR tube, which was suspended in an ultrasonic cleaning bath for 1 h and then allowed to stand. Monitoring by ^{31}P NMR showed slow formation of [Au(PH(*t*-Bu)$_2$)$_2$]BF$_4$ over several days. Another NMR tube reaction was carried out on the same scale in bromobenzene. After the sample was heated for 5 h at 85 °C, ^{31}P NMR monitoring showed starting materials, some of the desired product, and an unknown impurity (multiplet patterns, δ 109.2, 66.6). On further heating, most of the white solid dissolved; the major species present were cation **19** and the impurity (which was also observed in the CH_2Cl_2 experiment above after 6 d).

[Au(PH(*t*-Bu)$_2$)$_2$]BF$_4$ (19). A sample of [Au(NCPh)$_2$]BF$_4$ (48 mg, 0.1 mmol) was dissolved in 2 mL of acetonitrile. The turbid solution was filtered through Celite. To the colorless filtrate was added 29 mg (0.2 mmol) of HP(*t*-Bu)$_2$ in 2 mL of acetonitrile, and the mixture was stirred for 15 min. The solvent was pumped off yielding a white-yellow solid, which was recrystallized from CH_2-Cl_2/hexane to give 36 mg (63%) of analytically pure white solid. White crystals suitable for X-ray crystallography were obtained by slow evaporation of CH_2Cl_2 at −30 °C. NMR spectra were done on a sample recrystallized from THF/hexane.

Anal. Calcd for $C_{16}H_{38}AuP_2BF_4$: C, 33.35; H, 6.65. Found: C, 33.62; H, 6.83. ^{1}H NMR (CD_2Cl_2): δ 5.46−4.72 (m, 2H), 1.48−1.44 (m, 36H). ^{1}H{^{31}P} NMR (CD_2Cl_2): δ 5.12 (m, 2H), 1.47 (36H). ^{31}P NMR (CD_2Cl_2): δ 65.5 (m, J_{PP} = 278, J_{PH} = 363, $J_{PH'}$ = 2, $J_{PH(t-Bu)}$ = 18, $J_{HH'}$ = 0). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 35.0 (t, J = 13), 30.8 (t, J = 3). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −153.1. IR: 2948, 2894, 2863, 2334 (P−H), 1625, 1467, 1394, 1366, 1301, 1181, 1083, 1037, 943, 902, 818, 792, 699.

Reaction of Au(PPh$_3$)[N(SiMe$_3$)$_2$] with Secondary Phosphines. Method 1. To a clear solution of Au(PPh$_3$)[N(SiMe$_3$)$_2$] (18 mg, 0.029 mmol) in 1 mL of toluene in an NMR tube was added dimesitylphosphine (8 mg, 0.03 mmol). The ^{31}P NMR spectrum of the solution after 5 min showed the formation of PPh$_3$ and of [Au-(PMes$_2$)]$_n$. Reactions with PHCy$_2$, PH(*t*-Bu)$_2$, and PH(Ph)(Mes) were carried out similarly.

Method 2. To a clear solution of Au(PPh$_3$)[N(SiMe$_3$)$_2$] (15 mg, 0.024 mmol) in 1 mL of toluene in an NMR tube was added diisitylphosphine (11 mg, 0.025 mmol). The solution immediately became yellow. ^{31}P NMR after 15 min showed the formation of PPh$_3$ and of a new complex (**20**): δ 44.0 (d, J = 267, PPh$_3$), −15.4 (dd, J = 267, 148, μ-PIs$_2$), −54.3 (d, J = 148, PIs$_2$). When the sample was left standing at room temperature over 2 d, the yellow color slowly bleached and this species disappeared; [Au(PIs$_2$)]$_3$ and PPh$_3$ were observed. Intermediate **20** was generated independently, along with PPh$_3$, as follows. A solution of Au(PPh$_3$)Cl (10 mg,

0.02 mmol) in 1 mL of THF was treated with AgOTf (5 mg, 0.02 mmol) to give a slurry that was filtered through Celite onto solid $PHIs_2$ (9 mg, 0.02 mmol). The resulting clear solution was filtered and allowed to stand for 1 day before addition of NaO*t*-Bu (2 mg, 0.02 mmol), which caused immediate color change to yellow. The ^{31}P NMR spectrum showed that **20**, PPh_3, and some $PHIs_2$ were present.

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Supporting Information Available: Figures S1−S5 (PDF) and details of the X-ray crystallographic studies (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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