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Au(I) Complexes Supported by Donor-Functionalized Indene Ligands: Synthesis, Characterization, and Catalytic Behavior in Aldehyde Hydrosilylation

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New Au(I) complexes featuring ligands of the type κ^1-3-R$_2$*P*-indene (κ^1-**1a**, R = ^{i}Pr; κ^1-**1b**, R = Ph) and κ^1-1-R$_2$*P*-2-Me$_2$*N*-indene (κ^1-**1c**, R = ^{i}Pr; κ^1-**1d**, R = Ph) were prepared and structurally characterized. Dicoordinate neutral complexes (κ^1-**1**)AuCl (**2**−**5**) were prepared by reacting **1** with Me$_2$SAuCl, with isolated yields ranging from 56 to 88%. Addition of a second equivalent of **1a** to **2** resulted in formation of the tricoordinate neutral species (κ^1-**1a**)$_2$AuCl (**6**; 69%). By treating **6** with AgOTf, the corresponding cationic complex [(κ^1-**1a**)$_2$Au]$^+$OTf$^-$ ([**7**]$^+$OTf$^-$; 72%) was obtained. The catalytic performance of these new Au(I) compounds in the hydrosilylation of various aldehydes was compared to that of catalyst systems derived from a combination of R$_3$P (R = Et, ^{n}Bu, ^{t}Bu, Cy, or Ph) or *N*-heterocyclic carbene ligands and Me$_2$SAuCl. While for the phosphine-substituted indene complexes, a catalyst mixture of 3 mol % **2** and 20 mol % **1a** was found to be optimal, a catalyst derived from 3 mol % Me$_2$SAuCl and 20 mol % Et$_3$P, ^{n}Bu$_3$P, or ^{t}Bu$_3$P proved to be the most effective overall, especially for reactions conducted at 24 °C. Single-crystal X-ray diffraction data are provided for **2**, **4**, **6**, and [**7**]$^+$OTf$^-$.

Introduction

While soluble platinum-group metal catalysts are employed widely in mediating a diversity of synthetically useful chemical reactions,[1] the application of Au complexes in homogeneous catalysis had, until relatively recently, received little attention. However, the numerous reports documenting Au-catalyzed substrate transformations that have emerged over the past decade serve to confirm the utility of such catalyst complexes; indeed, soluble Au complexes in some instances have provided access to reaction manifolds that cannot be reached by use of more traditional catalysts.[2] Notwithstanding this remarkable progress, and despite an early report by Hayashi and co-workers[3] that highlights the reactivity benefits of employing appropriately selected phosphine ancillary ligands in Au-mediated transformations, one consequence associated with the delayed recognition of Au catalysis is that the influence of supporting ligands on metal-centered reactivity has not been explored thoroughly.[2,4] Given the central role that fundamental ligand design studies have played in advancing the field of transition metal-mediated homogeneous catalysis,[1,5] related studies involving Au are likely to further our understanding of the factors that influence Au-centered reactivity and may ultimately enable the development of new or improved Au-catalyzed substrate transformations.

In the pursuit of new classes of metal complexes that are capable of mediating synthetically useful chemical transformations involving the activation of E−H bonds (E = main group fragment), we are exploring the reactivity behavior of coordination complexes supported by donor-substituted indene ligands, including 3-R$_2$P-indene (**1a**, R = ^{i}Pr; **1b**, R = Ph) and 1-R$_2$P-2-Me$_2$N-indene (**1c**, R = ^{i}Pr; **1d**, R = Ph).[6] In Rh-based studies, we have observed that while lithiation of **1a** followed by treatment with 0.5 equiv of [(COD)RhCl]$_2$ affords the corresponding η^5-indenylrhodium complex,[6e] under analogous condi-

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(1) For some prominent examples, see: (a) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760. (b) Knowles, W. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998. (c) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008.

(2) For selected reviews on the use of Au complexes in homogeneous catalysis, see: (a) Díaz-Requejo, M. M.; Pérez, P. J. *J. Organomet. Chem.* **2005**, *690*, 5441. (b) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6990. (c) Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387. (d) Hashmi, A. S. K. *Gold Bull.* **2004**, *37*, 51. (e) Dyker, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4237.

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tions employing **1c**, the formally zwitterionic (COD)Rh(κ^2-3-^{i}Pr$_2$*P*-2-Me$_2$*N*-indenide) is formed quantitatively.[6f] Correspondingly, we became interested in preparing Au(I) derivatives of **1a**−**d**, with an aim toward evaluating how the introduction of structural modifications to the indene framework can influence the coordination behavior of the ligand and/or the reactivity characteristics of the associated metal fragments. Furthermore, we sought to evaluate the utility of such complexes as catalysts for the addition of various E−H bonds to unsaturated organic molecules. Although several such Au-mediated addition reactions have been documented,[7] the addition of Si−H bonds is limited to a single communication in 2000 by Hosomi and coworkers, in which the hydrosilylation of various aldehydes catalyzed by a $Ph_3PAuCl/^nBu_3P$ mixture at 70 °C was described.[8a] We report herein the synthesis and characterization of neutral and cationic Au(I) coordination complexes of **1a**−**d**. Also described are our efforts to evaluate further the influence of ancillary ligands on the progress of Au-mediated Si−H addition reactions, including a head-to-head comparison of the catalytic abilities of these new Au(I) derivatives of **1a**−**d** with those of Me$_2$SAuCl/L mixtures (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene or R$_3$P, R = Et, ^{n}Bu, ^{t}Bu, Cy, or Ph) in the hydrosilylation of aldehydes at both 24 and 70 °C.

Results and Discussion

Synthesis and Characterization of New Au(I) Complexes of 1a−d. Treatment of **1a** or **1b** with 1 equiv of Me$_2$SAuCl afforded (κ^1-*P*-**1**)AuCl (**2**, R = ^{i}Pr; **3**, R = Ph) in 88 and 75% isolated yield, respectively (eq 1). The proposed structures of **2** and **3** are supported by data obtained from solution NMR studies, with the C_S symmetry of these complexes being evident in the ^{1}H and ^{13}C{^{1}H} NMR spectra. In the case of **2**, the connectivity was confirmed on the basis of data obtained from single-crystal X-ray diffraction studies. An ORTEP[9] diagram of **2** is presented in Figure 1, and relevant experimental parameters for each of the crystallographically characterized complexes reported herein are collected in Table 1. The structure of **2** is quite similar to that of the related complex ^{i}Pr$_3$PAuCl,[10] with the Au center in **2** deviating only modestly from linearity (177.20(3)°).

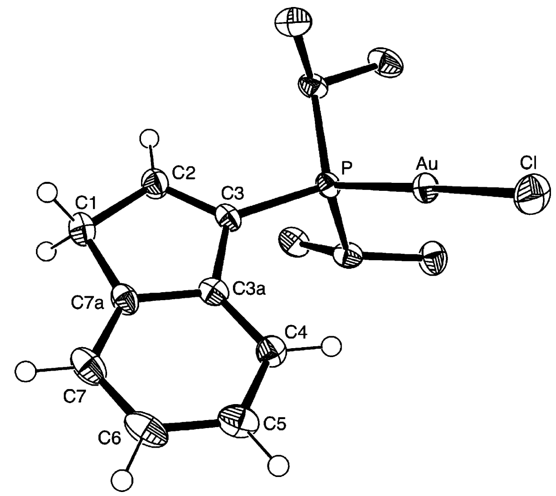


Figure 1. ORTEP diagram for **2** shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **2**: Au−P 2.2409(8); Au−Cl 2.2941(8); P−C3 1.802(3); C1−C2 1.509(4); C2−C3 1.345(4); and Cl−Au−P 177.20(3).

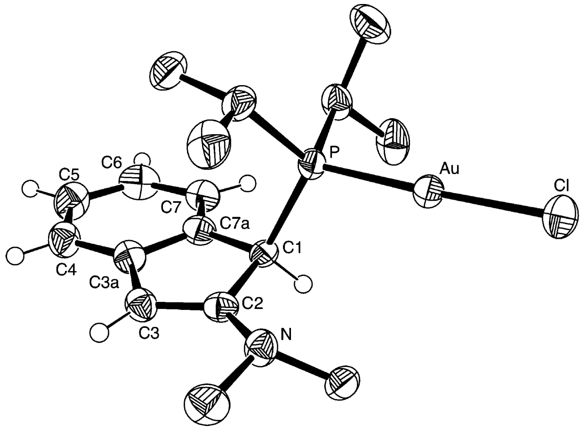
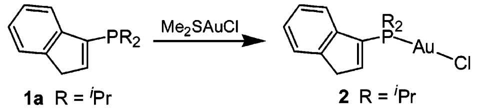


Figure 2. ORTEP diagram for **4** shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **4**: Au−P 2.247(2); Au−Cl 2.294(2); Au⋯N 3.667; P−C1 1.879(8); C1−C2 1.51(1); C2−C3 1.36(1); and Cl−Au−P 177.60(8).



(1)

1a R = ^{i}Pr
1b R = Ph

2 R = ^{i}Pr
3 R = Ph

The utility of P,N ligands in supporting catalytically active platinum-group complexes is well-established.[11] In this regard, we have demonstrated previously that such metal complexes featuring **1c** and related P,N-substituted indenes can participate

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[6] For selected examples, see: (a) Wile, B. M.; Burford, R. J.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2006**, *25*, 1028. (b) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 4981. (c) Cipot, J.; McDonald, R.; Stradiotto, M. *Chem. Commun.* **2005**, 4932. (d) Wile, B. M.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 1959. (e) Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185. (f) Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618.

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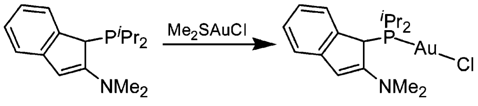
[11] For selected reviews, see: (a) Källström, K.; Munslow, I.; Andersson, P. G. *Chem.*—*Eur. J.* **2006**, *12*, 3194. (b) Guiry, P. J.; Saunders, C. P. *Adv. Synth. Catal.* **2004**, *346*, 497. (c) Chelucci, G.; Orrù, G.; Pinna, G. A. *Tetrahedron* **2003**, *59*, 9471. (d) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (e) Gavrilov, K. N.; Polosukhin, A. I. *Russ. Chem. Rev.* **2000**, *69*, 661.

Table 1. Crystallographic Data

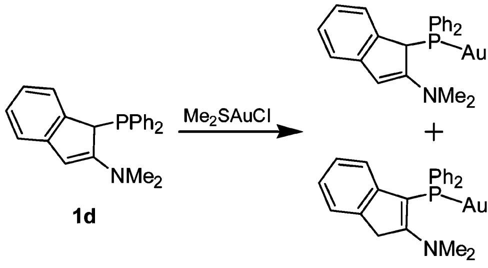
	2	**4**	**6**	[**7**]$^+$OTf$^-$
empirical formula	$C_{15}H_{21}AuClP$	$C_{17}H_{26}AuClNP$	$C_{30}H_{42}AuClP_2$	$C_{31}H_{42}AuF_3O_3P_2S$
Fw	464.70	507.77	696.99	810.61
cryst size	0.43 × 0.42 × 0.06	0.30 × 0.22 × 0.14	0.39 × 0.32 × 0.22	0.23 × 0.22 × 0.15
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$(No. 2)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)
a (Å)	15.625 (2)	9.3708 (10)	9.0257 (5)	26.567 (2)
b (Å)	7.3752 (10)	10.1136 (10)	20.3683 (11)	9.2095 (8)
c (Å)	15.269 (2)	10.3753 (11)	16.1902 (9)	13.1111 (12)
α (deg)	90	88.223 (2)	90	90
β (deg)	118.454 (2)	84.120 (2)	94.9747 (8)	90
γ (deg)	90	68.059 (2)	90	90
V (Å^3)	1546.9 (4)	907.25 (16)	2965.2 (3)	3207.9 (5)
Z	4	2	4	4
ρ_{calcd} (g cm^{-3})	1.995	1.859	1.561	1.678
μ (mm^{-1})	9.767	8.337	5.176	4.799
2θ limit (deg)	52.76	52.74	52.80	52.78
	$-19 \leq h \leq 19$	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-33 \leq h \leq 33$
	$-9 \leq k \leq 9$	$-12 \leq k \leq 12$	$-25 \leq k \leq 25$	$-11 \leq k \leq 11$
	$-19 \leq l \leq 19$	$-12 \leq l \leq 12$	$-20 \leq l \leq 20$	$-16 \leq l \leq 16$
total data collected	11475	6848	23284	24364
ind reflns	3156	3671	6071	6566
R_{int}	0.0313	0.0278	0.0219	0.0376
obsd reflns	3005	3452	5602	5666
abs correction	Gaussian integration (face-indexed)	Gaussian integration (face-indexed)	multiscan (SADABS)	multiscan (SADABS)
range of transmission	0.5918−0.1020	0.3882−0.1888	0.3955−0.2374	0.5330−0.4049
data/restraints/params	3156/0/163	3671/0/190	6071/0/307	6566/0/416
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0218	0.0444	0.0160	0.0268
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0564	0.1373	0.0405	0.0600
GOF	1.117	1.222	1.049	1.074
largest peak, hole (eÅ^{-3})	0.907, −1.549	5.825, −1.278	0.768, −0.382	2.780, −0.433

in a range of stoichiometric and/or catalytic transformations involving E−H bond activation.[6] In the pursuit of related Au(I) coordination complexes, **1c** was treated with Me_2SAuCl, affording (κ^1-*P*,N-**1c**)AuCl (**4**) in 67% isolated yield (eq 2). Data obtained from solution NMR spectroscopic studies supported the structure proposed for **4**, which was confirmed on the basis of data obtained from a single-crystal X-ray diffraction experiment. An ORTEP[9] diagram of **4** is presented in Figure 2. The nearly linear geometry at Au (177.60(8)°) as well as the Au−P (2.247(2) Å) and Au−Cl (2.294(2) Å) distances in **4** are indistinguishable from those in **2** (vide supra) and can be compared with other structurally related Au(I) complexes.[12] The Au···N separation (3.67 Å) lies outside the sum of the van der Waals radii for these elements (3.25 Å),[13] thereby confirming the κ^1-*P*,N binding mode of **1c** in **4**; similar (κ^1-*P*,N)AuCl coordination complexes of potentially bidentate P,N ligands have been reported.[12] While this monodentate coordination motif for **1c** is also observed in (κ^1-*P*,N-**1c**)Rh(COD)Cl,[6e,f] the ability of **1c** to function as a bidentate κ^2-*P*,*N* ligand has been demonstrated for both Pt and Ru.[6b,d]



1c **4** (2)

In contrast to the preparation of **4**, during which products derived from the isomerization of the ancillary ligand **1c** were not detected by use of NMR spectroscopic methods, treatment of **1d** with Me_2SAuCl generated cleanly (^1H and ^{31}P NMR) an inseparable 2:3 isomeric mixture of (κ^1-*P*,N-**1d**)AuCl (**5a**) and (κ^1-3-R_2*P*-2-Me_2N-indene)AuCl (**5b**), which was isolated as an analytically pure solid in 56% yield and characterized by use of 1-D and 2-D NMR techniques (eq 3). Whereas in solution the 1-R_2P-indenes (R = ^{i}Pr,[6e] Ph[14]) are converted readily into **1a** and **1b** either with heating or upon treatment with NEt_3, we have shown previously that both **1c** and **1d** evolve slowly to an equilibrium mixture of **1c**,**d** and the corresponding 3-R_2P-2-Me_2N-indene isomer, with the resultant isomeric mixture being retained under the conditions that resulted in the quantitative isomerization of the aforementioned 1-R_2P-indenes.[6e] Consistent with these observations, and in keeping with (κ^1-*P*,N-**1c**)Rh(COD)Cl, which also resists rearranging to (κ^1-3-R_2*P*-2-Me_2N-indene)Rh(COD)Cl,[6e,f] neither **5a** nor **5b** could be converted to its isomer, either with heating (50 °C, 6 days) or upon exposure to NEt_3, ^{i}PrOH, or H_2O in THF solution. Notably, under similar conditions, Ru and Pt (κ^2-*P*,N-**1c**)ML$_n$ species have been observed to isomerize cleanly to the corresponding κ^2-3-R_2*P*-2-Me_2*N*-indene complexes.[6b,d]



1d **5a** **5b** (3)

In the pursuit of an L_2AuCl species, complex **2** was treated with 1 equiv of **1a**, thereby allowing for the isolation of (κ^1-*P*-**1a**)$_2$AuCl (**6**) as an analytically pure light brown crystalline solid in 69% yield (Scheme 1). An ORTEP[9] diagram of **6** is

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[12] For selected examples, see: (a) Kreiter, R.; Firet, J. J.; Ruts, M. J. J.; Lutz, M.; Spek, A. L.; Gebbink, R. J. M. K.; van Koten, G. *J. Organomet. Chem.* **2006**, *691*, 422. (b) Bowen, R. J.; Fernandes, M. A.; Gitari, P. W.; Layh, M.; Moutloali, R. M. *Eur. J. Inorg. Chem.* **2005**, 1955. (c) Papathanasiou, P.; Salem, G.; Waring, P.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3435. (d) Assmann, B.; Angermaier, K.; Paul, M.; Riede, J.; Schmidbaur, H. *Chem. Ber.* **1995**, *128*, 891.

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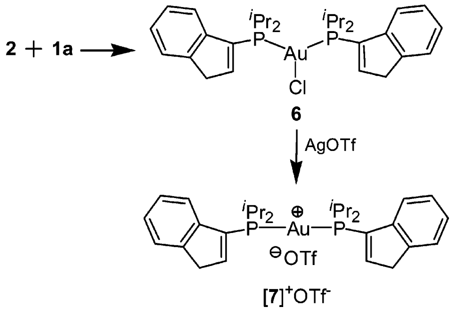
Scheme 1



presented in Figure 3, which highlights a distorted trigonal planar coordination geometry at Au ($\Sigma_{\text{angles at Au}} \approx 360°$) that is also evident in some other crystallographically characterized $(R_3P)_2$AuCl complexes.[4q,15] Notably, the Au−P (2.3181(5) and 2.3050(5) Å) and Au−Cl (2.6577(6) Å) distances in **6** are lengthened significantly relative to those found in both **2** and **4**. In contrast to the dissimilar Au−P distances in **6** that may arise due to crystal packing effects, both ^{1}H and ^{13}C NMR data for this complex are consistent with an effective C_{2V} symmetric solution structure for **6**.

The preparation of (κ^1-*P*,N-**1c**)$_2$AuCl complexes proved to be less straightforward. Following the addition of 1 equiv of **1c** to **4** in THF, the ^{31}P{^{1}H} NMR spectrum of the reaction mixture revealed multiple broad resonances centered around 62 and −5 ppm. Upon cooling from 300 to 170 K, several decoalescence events were noted, eventually resulting in a complicated spectrum that could not be unambiguously assigned. In addition to the spectral complexities arising from the anticipated presence of isomeric *meso*- and *rac*-(κ^1-*P*,N-**1c**)$_2$AuCl and/or [(κ^1-*P*,N-**1c**)$_2$Au]$^+$Cl$^-$ products in this reaction, it is possible that oligomeric Au complexes, in which **1c** serves to bridge metal centers, are also formed.[4q,10,16,17] All efforts to isolate pure materials from such reactions were unsuccessful.

In exploring the synthetic viability of [(κ^1-*P*-**1a**)$_2$Au]$^+$X$^-$ species, complex **6** was treated with 1 equiv of AgOTf (Scheme 1). Subsequent examination of the reaction mixture by use of ^{31}P{^{1}H} NMR methods revealed the consumption of **6**, along with the clean formation of a single phosphorus-containing product ([(κ^1-*P*-**1a**)$_2$Au]$^+$OTf$^-$, [**7**]$^+$OTf$^-$), giving rise to a sharp singlet at 53 ppm (300 K). Complex [**7**]$^+$OTf$^-$ was isolated in 72% yield and characterized by the use of NMR spectroscopic and X-ray crystallographic methods. An ORTEP[9] diagram of [**7**]$^+$OTf$^-$ is presented in Figure 4. The linear Au coordination environment in [**7**]$^+$OTf$^-$ (179.26(4)°) is found commonly in [L$_2$Au]$^+$X$^-$ complexes.[12d,17d,18] No close Au···OTf or Au···Au contacts were found in the crystal structure of [**7**]$^+$OTf$^-$, and the Au−P distances in this complex (2.310(1) and 2.315(1) Å) differ only modestly from those found in **6**. The solution characterization of [**7**]$^+$OTf$^-$ is consistent with the solid-state structure of this complex. Interestingly, virtual coupling to phosphorus is observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of [**7**]$^+$OTf$^-$.[19] For example, whereas the ^{1}H NMR signal for each of the diastereotopic methyl groups within the ^{i}Pr$_2$P fragments of **1a**, **2**, and **6** appears as a doublet of doublets, similar signals in [**7**]$^+$OTf$^-$ appear as a virtual doublet of triplets—a result of coupling to both P atoms that presumably is enabled by the linearity of the P−Au−P unit in [**7**]$^+$OTf$^-$.

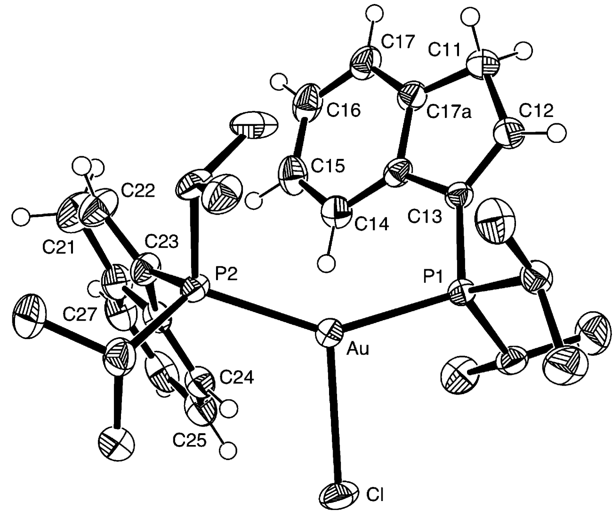


Figure 3. ORTEP diagram for **6** shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **6**: Au−P1 2.3181(5); Au−P2 2.3050(5); Au−Cl 2.6577(6); P1−C13 1.814(2); P2−C23 1.816(2); C11−C12 1.500(3); C12−C13 1.344(3); C21−C22 1.504(3); C22−C23 1.341(3); Cl−Au−P1 102.23(2); Cl−Au−P2 112.34(2); and Pl−Au−P2 145.26(2).

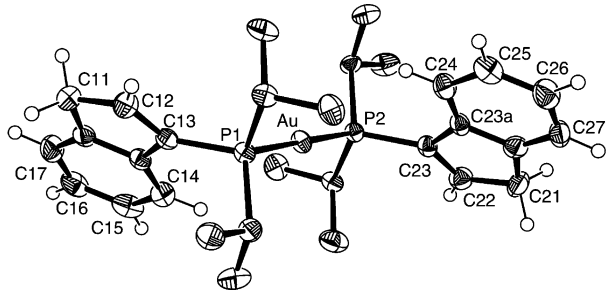


Figure 4. ORTEP diagram for [**7**]$^+$OTf$^-$ shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms and the triflate counterion have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for [**7**]$^+$OTf$^-$: Au−P1 2.310(1); Au−P2 2.315(1); P1−C13 1.800(4); P2−C23 1.804(4); C11−C12 1.507(7); C12−C13 1.326(7); C21−C22 1.483(7); C22−C23 1.333(7); and Pl−Au−P2 179.26(4).

Au-Catalyzed Hydrosilylation of Aldehydes. The addition of Si−H bonds to carbonyl compounds provides a direct and

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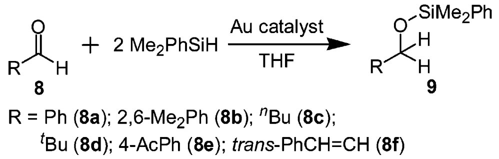
Scheme 2



atom-economical route to synthetically useful O-protected silyl alcohols.[20] While a diversity of carbonyl hydrosilylation catalysts have been identified,[20] Cu complexes supported by phosphine or *N*-heterocyclic carbene (NHC) ligands have proven particularly effective, and the development of such catalysts continues to attract attention.[21] In contrast, only a single report for each of Ag[22] and Au[8a] documents the catalytic abilities of the heavier group 11 elements in hydrosilylation chemistry. With regard to the study of ligand effects in Au-catalyzed hydrosilylations, Hosomi and co-workers noted that while catalysts comprised of 3 mol % Ph_3PAuCl and *X* mol % Ph_3P ($X = 0$ or 20) were ineffective in mediating the addition of Me_2PhSiH to benzaldehyde at 70 °C, a catalyst mixture comprised of 3 mol % Ph_3PAuCl and 20 mol % $^nBu_3P$ proved capable of mediating the hydrosilylation of various aldehyde substrates under similar conditions.[8a,23] Building upon these preliminary observations, we sought to evaluate the catalytic abilities of the Au(I) derivatives of **1a**−**d** reported herein, as well as those of Me_2SAuCl/L mixtures (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene or R_3P, R = Et, ^nBu, ^tBu, Cy, or Ph), in the hydrosilylation of aldehydes at both 70 and 24 °C (Scheme 2).

Our preliminary hydrosilylation survey was conducted using benzaldehyde (**8a**) and Me_2PhSiH, under conditions similar to those employed by Hosomi and co-workers (70 °C, THF, 3 mol % Au);[8a] the results of these experiments are summarized in Table 2. Reactions employing 3 mol % **2** proceeded to a limited extent, affording **9a** in 50% yield after 24 h (entry 2-1). Given the possibility that loss of HCl may play a role in the formation of the active Au(I) catalyst, the catalytic abilities of a 3 mol % **2**/6 mol % Et_3N mixture were examined under similar conditions, with disappointing results (entry 2-2). In light of the observation by Hosomi and co-workers that the addition of 20 mol % $^nBu_3P$ to 3 mol % Ph_3PAuCl was required to generate an active hydrosilylation catalyst,[8a] the use of 3 mol % **2** in combination with added 3-$^iPr_2P$-indene (**1a**) was explored. While no reactivity benefits were derived from the use of a 3 mol % **2**/3 mol % **1a** mixture (entry 2-3), nearly quantitative conversion of **8a** to **9a** was achieved in 12 h by use of a catalyst mixture comprised of 3 mol % **2**/20 mol % **1a** (entry 2-4). By comparison, analogous Au catalysts based on 3-Ph_2P-indene performed poorly (entries 2-5 and 2-6). Encouraged by the performance of Au(I) species supported by **1a**, and in light of the established reactivity benefits associated with the use of bidentate P,N ligands in platinum-group metal catalysis,[11] the catalytic abilities of **4** and **5a**/**5b** were evaluated. Although the 1-R_2P-2-Me_2N-indene ligands in **4** and **5a**/**5b** are bound exclusively through phosphorus, we envisioned that the pendent nitrogen fragment may help to temporarily stabilize coordinatively unsaturated reactive Au intermediates with respect to bimolecular decomposition, thereby precluding the need for excess phosphine. However, both **4** and **5a**/**5b** performed poorly as catalysts, even in the presence of excess **1c** or **1d** (entries 2-7 to 2-10).

Table 2. Au(I)-Catalyzed Addition of Me_2PhSiH to Benzaldehyde (8a) at 70 °C[a]

entry	mol % catalyst	time (h)	yield **9a** (%)[b]	yield other (%)[b]
2-1	3% **2**[c]	24	50	2
2-2	3% **2** + 6% Et_3N[c]	24	1	<1
2-3	3% **2** + 3% **1a**[c]	24	42	<1
2-4	3% **2** + 20% **1a**[c]	12	99	1
2-5	3% **3**[d]	24	47	1
2-6	3% 3 + 20% **1b**	24	4	<1
2-7	3% 4	24	<1	<1
2-8	3% 4 + 20% **1c**	24	7	4
2-9	3% 5a/5b	24	5	<1
2-10	3% 5a/5b + 20% **1d**	24	31	1
2-11	3% **6**[c]	24	42	<1
2-12	3% 6 + 20% **1a**	12	99	1
2-13	3% $[7]^+OTf^-$	24	<1	<1
2-14	3% $[7]^+OTf^-$ + 20% **1a**	24	52	1
2-15	3% Me_2SAuCl	3	27	<1
2-16	3% Me_2SAuCl + 20% Ph_3P[c]	3	2	<1
2-17	3% Me_2SAuCl + 20% $^nBu_3P$[c]	3	98	2
2-18	3% Me_2SAuCl + 20% Et_3P[c,d]	3	97	<1
2-19	3% Me_2SAuCl + 20% $^tBu_3P$	3	98	1
2-20	3% Me_2SAuCl + 20% Cy_3P	3	53	2
2-21	3% Me_2SAuCl + 20% NHC[e]	3	31	1
2-22	3% Ph_3PAuCl + 20% $^nBu_3P$	3	99	<1

[a] Reactions conducted in THF at 70 °C with 2 equiv of Me_2PhSiH relative to benzaldehyde. [b] Yields quoted with respect to benzaldehyde consumed at the time quoted based on GC-MS and GC-FID data (average of two runs). [c] A precipitate of metallic gold was observed at the conclusion of the reaction. [d] Under these conditions, Ph_2SiH_2 (86%, <3% double hydrosilylation product), Et_3SiH (34%), and $(EtO)_3SiH$ (7%) all proved inferior to Me_2PhSiH. [e] NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene.

As anticipated, the results of catalytic experiments conducted using 3 mol % (κ^1-*P*-**1a**)$_2$AuCl (**6**) (entry 2-11) or 3 mol % **6**/20 mol % **1a** (entry 2-12) were indistinguishable from those obtained when employing 3 mol % **2**/3 mol % **1a** (entry 2-3) or 3 mol % **2**/20 mol % **1a** (entry 2-4), respectively. In an effort to identify more active Au hydrosilylation catalysts, (κ^1-*P*-**1a**)$_2$Au$^+$ complexes were viewed as interesting targets. Given the recently established activity of AgOTf in aldehyde hydrosilylation,[22] we opted to study the catalytic behavior of preformed $[7]^+OTf^-$, rather than (κ^1-*P*-**1a**)$_2$AuCl/AgOTf mixtures. Unfortunately, $[7]^+OTf^-$ proved vastly inferior to **6** under similar conditions (entries 2-13 and 2-14).

Having examined the utility of indenylphosphine ligands in the Au-mediated hydrosilylation of benzaldehyde, we turned our attention to the use of more conventional, commercially available phosphines in this chemistry. Expanding on the preliminary report by Hosomi and co-workers,[8a] in which the divergent performance of catalysts derived 3 mol % Ph_3PAuCl and 20 mol % R_3P (R = Ph or ^nBu) at 70 °C is described, we sought to evaluate more thoroughly the influence of phosphine substitution, as well as NHC ligation, on Au-catalyzed hydrosilylation under similar conditions. For convenience, Me_2SAuCl was employed in place of Ph_3PAuCl as a source of AuCl. While both Me_2SAuCl alone (entry 2-15) and 3 mol % Me_2SAuCl/20 mol % Ph_3P (entry 2-16) exhibited poor catalytic properties, mixtures of 3 mol % Me_2SAuCl/20 mol % R_3P (R = ^nBu, entry 2-17; R = Et, entry 2-18; or R = ^tBu, entry 2-19) were found

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(23) It has been shown previously that 20 mol % R_3P (R = $^nBu^{8a}$ or Et^{22}) alone is incapable of catalyzing the addition of Me_2PhSiH to benzaldehyde under these conditions.

Table 3. Au(I) Catalyzed Addition of Me_2PhSiH to Aldehydes (8) at 24 °C[a]

entry	mol % catalyst	aldehyde	yield **9** (%)[b]	yield other (%)[b]
3-1	3% **2** + 20% **1a**	**8a**	3	1
3-2	3% Me_2SAuCl + 20% Et_3P	**8a**	99	<1
3-3	3% Me_2SAuCl + 20% ^{n}Bu$_3$P	**8a**	98	1
3-4	3% Me_2SAuCl + 20% ^{t}Bu$_3$P	**8a**	99	1
3-5	3% Me_2SAuCl + 20% Et_3P	**8b**	88	1
3-6	3% Me_2SAuCl + 20% ^{n}Bu$_3$P	**8b**	98	2
3-7	3% Me_2SAuCl + 20% ^{t}Bu$_3$P	**8b**	97	2
3-8	3% Me_2SAuCl + 20% Et_3P	**8c**	74	4
3-9	3% Me_2SAuCl + 20% ^{n}Bu$_3$P	**8c**	85	7
3-10	3% Me_2SAuCl + 20% ^{t}Bu$_3$P	**8c**	85	5
3-11	3% Me_2SAuCl + 20% Et_3P	**8d**	45	<1
3-12	3% Me_2SAuCl + 20% ^{n}Bu$_3$P	**8d**	79	3
3-13	3% Me_2SAuCl + 20% ^{t}Bu$_3$P	**8d**	78	2
3-14	3% Me_2SAuCl + 20% Et_3P	**8e**	>99	<1
3-15	3% Me_2SAuCl + 20% ^{n}Bu$_3$P	**8e**	98	2
3-16	3% Me_2SAuCl + 20% ^{t}Bu$_3$P	**8e**	98	2
3-17	3% Me_2SAuCl + 20% Et_3P	**8f**	97	<1
3-18	3% Me_2SAuCl + 20% ^{n}Bu$_3$P	**8f**	97	2
3-19	3% Me_2SAuCl + 20% ^{t}Bu$_3$P	**8f**	90	3

[a] Reactions conducted in THF at 24 °C with 2 equiv. Me_2PhSiH relative to aldehyde. [b] Yields quoted with respect to aldehyde consumed at 24 h based on GC-MS and GC-FID data (average of two runs).

to be as effective as the 3 mol % Ph_3PAuCl/20 mol % ^{n}Bu$_3$P catalyst system reported by Hosomi (entry 2-22) under similar conditions,[8a] providing **9a** in high yield after 3 h. Conversely, catalysts comprised of 3 mol % Me_2SAuCl/20 mol % L, where L = Cy_3P (entry 2-20) or 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (entry 2-21), proved inferior under such experimental conditions. These preliminary findings appear to suggest that Au-catalyzed benzaldehyde hydrosilylation is enabled by a strongly donating trialkylphosphine, although the poor performance of the catalyst system employing Cy_3P (~170°) versus those based on Et_3P (~130°) or ^{t}Bu$_3$P (~180°) suggests that there is no simple correlation between catalytic performance and phosphine cone angle.[24] Moreover, the lackluster conversion achieved by use of the NHC ligand in this chemistry is also surprising, given the utility of such ligands in carbonyl hydrosilylation catalysis involving either Cu[25] or Ag.[22] Notably, the benzaldehyde trimer was not detected as a side product in these Au-mediated reactions, in contrast to our observations made when employing related Ag-based hydrosilylation catalysts.[22]

Whereas the ability of 3 mol % Ph_3PAuCl/20 mol % ^{n}Bu$_3$P to mediate the hydrosilylation of various aldehydes at 70 °C has been demonstrated,[8a] studies examining the utility of Au-based hydrosilylation catalysts at ambient temperatures have not been reported. In an effort to evaluate further the scope of Au-mediated aldehyde hydrosilylation, the previously surveyed catalyst systems that afforded >95% benzaldehyde conversion at 70 °C (i.e., 3% **2** + 20% **1a**; 3% Me_2SAuCl + 20% R_3P, R = Et, ^{n}Bu, or ^{t}Bu) were examined for catalytic activity at 24 °C (Table 3). Although negligible conversion was achieved with 3% **2**/20% **1a** (entry 3-1), the trialkylphosphine-based Au catalysts provided **9a** in nearly quantitative yield (entries 3-2 to 3-4). In light of these results, the hydrosilylation of some alternative aldehyde substrates at 24 °C was studied. Although the high yield reduction of 2,6-dimethylbenzaldehyde (**8b**) was achieved when employing 3 mol % Me_2SAuCl/20 mol % R_3P (R = Et, entry 3-5; R = ^{n}Bu, entry 3-6; or R = ^{t}Bu, entry 3-7), the conversions achieved with Et_3P were less than those obtained by use of either ^{n}Bu$_3$P or ^{t}Bu$_3$P. A similar ligand dependence on conversion was also noted for the hydrosilylation of the aliphatic aldehydes **8c** and **8d** (entries 3-8 to 3-10 and entries 3-11 to 3-13, respectively). While for substrates **8c** and **8d**, the lower yields relative to those achieved in the reduction of **8a** or **8b** were also accompanied by a loss in selectivity; the aldehyde trimer was still not a significant contributor to the product distribution. As well, the chemoselective hydrosilylation of 4-acetylbenzaldehyde (**8e**) and *trans*-cinnamaldehyde (**8f**) was achieved in high yield at 24 °C (entries 3-14 to 3-16 and entries 3-17 to 3-19, respectively).[26]

Conclusion

In summary, a series of new Au(I) complexes featuring κ^1-3-R$_2$*P*-indene (R = ^{i}Pr, **1a**; R = Ph, **1b**) and κ^1-1-R$_2$*P*-2-Me$_2$N-indene (R = ^{i}Pr, **1a**; R = Ph, **1b**) ligands have been prepared and structurally characterized. In studies exploring the utility of these Au(I) species as catalysts for the hydrosilylation of benzaldehyde at 70 °C, complexes supported by the P,N ligands **1c** or **1d** proved to be inferior to those featuring the indenylphosphines **1a** or **1b**. While nearly quantitative conversion was achieved by use of 3% (κ^1-**1a**)AuCl/20% **1a** at 70 °C, this catalyst mixture performed poorly at 24 °C. In contrast, among the other 3% Me_2AuCl/20% L catalyst mixtures examined (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene or R_3P, R = Et, ^{n}Bu, ^{t}Bu, Cy, or Ph), those employing Et_3P, ^{n}Bu$_3$P, or ^{t}Bu$_3$P proved to be both active and selective for the hydrosilylation of various aldehydes at 70 °C (3 h) or 24 °C (24 h). Notably, this represents the first application of Au complexes as carbonyl hydrosilylation catalysts at ambient temperatures and underscores the important influence of ancillary ligand structure on such Au-mediated transformations. Although the specific role that excess phosphine plays in generating an active Au hydrosilylation catalyst in this context is not clear,[23] it is plausible that the shift of an equilibrium in the direction of what might be more catalytically competent, higher coordination number Au species may occur. As well, we are currently unable to comment as to whether the active Au catalysts in these systems are homogeneous or heterogeneous in nature, and as such, catalysis by colloidal species resulting from the reduction of Au(I) precursors cannot be ruled out on the basis of our findings. However, the known instability of monomeric L_nAuH species,[27] in contrast to L_nAuSiR_3 complexes,[28] suggests that the latter may represent more viable intermediates in a homogeneous catalytic cycle. Further studies directed toward identifying the nature of the active catalyst involved in these transformations, as well as developing a more thorough understanding of ancillary ligand effects in Au-mediated E−H activation catalysis, are underway and will be reported on in due course.

Experimental Procedures

General Considerations. Except where noted, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) and Al_2O_3 (Fisher, neutral, Brockman Activity I, 60−325 mesh) were oven-dried (130 °C) for 5 days and then evacuated

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(26) The identities of **9e** and **9f** were confirmed on the basis of ^{1}H and ^{13}C NMR data.

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for 24 h prior to use. Non-deuterated solvents tetrahydrofuran, dichloromethane, toluene, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Tetrahydrofuran and dichloromethane were purified over two alumina-packed columns, while toluene, benzene, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. The solvents used within the glovebox were stored over activated 4 Å molecular sieves. All liquid reagents, including the deuterated solvents C_6D_6 (Aldrich), CD_2Cl_2 (Cambridge Isotope Laboratories), $CDCl_3$ (CIL), and all silanes (Aldrich) were degassed using three repeated freeze−pump−thaw cycles and stored over 4 Å molecular sieves for a minimum of 24 h prior to use, unless otherwise noted. Compounds **1a**,[6e] **1b**,[14] **1c**,[6f] **1d**,[6e] 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene,[29] and Me_2SAuCl[30] were prepared employing reported methods. Benzaldehyde (ACP) was washed with 10% aqueous sodium bicarbonate until no further CO_2 was evolved, followed by saturated aqueous sodium sulfite, then dried over magnesium sulfate and distilled under reduced pressure. With the exception of the phosphines, which were obtained from either Alfa (Et_3P) or Strem (all others), all other chemicals were obtained from Aldrich in high purity. AgOTf (Aldrich) was dried in vacuo for a minimum of 48 h prior to use. All ^{1}H, ^{13}C, and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H and ^{13}C) or 85% H_3PO_4 in D_2O (for ^{31}P). In some cases, slightly fewer than expected independent ^{1}H or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^{1}H and ^{13}C NMR chemical shift assignments were based on data obtained from ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, and DEPT NMR experiments. GC-MS and GC-FID were performed on a Perkin-Elmer AutoSystem XL gas chromatograph equipped with a TurboMass mass spectrometer. GC-MS analyses were performed using a Supelco 30 m × 0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm, temperature programmed: 60 °C, 1 min; 20 °C/min to 200 °C, 7 min; and 45 °C/min to 280 °C, 7 min. GC-FID analyses were done in a similar way except on a Supelco DB200 column. Melting points were obtained on an electrothermal apparatus using samples sealed in capillaries under dinitrogen. Elemental analyses for all compounds were performed by Canadian Microanalytical Service Ltd., with the exception of **4**, which was performed by Desert Analytics.

Preparation of 2. To a magnetically stirred solution of **1a** (0.077 g, 0.33 mmol) in CH_2Cl_2 (3 mL) was added a suspension of Me_2SAuCl (0.097 g, 0.33 mmol) in CH_2Cl_2 (2 mL). After 0.25 h at 24 °C, stirring was arrested, and residual solvent along with other volatiles was removed in vacuo. The residue was washed with pentane (2 × 3 mL) and recrystallized from CH_2Cl_2/EtOH to yield **2** as a white solid (0.014 g, 0.29 mmol, 88%). Crystals suitable for X-ray diffraction were grown from a diffusion of pentane into a CH_2Cl_2 solution at room temperature. Melting point 160−163 °C. Anal. (%) Calcd for $C_{15}H_{21}AuClP$: C, 38.77; H, 4.55. Found: C, 38.79; H, 4.66. ^{1}H NMR (C_6D_6): δ 7.64 (d,$^{3}J_{HH}$ = 7.4 Hz, 1H, C7-H), 7.10 (t,$^{3}J_{HH}$ = 8.8 Hz, 1H, C5-H), 7.06 (t,$^{3}J_{HH}$ = 8.8 Hz, 1H, C6-H), 6.63 (d,$^{2}J_{PH}$ = 10.2 Hz, 1H, C2-H), 2.90 (s, 2H, CH_2), 1.91 (m, 2H, $P(C\mathit{H}CH_3CH_3)_2$), 0.86 (dd, 6H,$^{3}J_{PH}$ = 19.1 Hz,$^{3}J_{HH}$ = 6.9 Hz, $P(CHC\mathit{H}_3CH_3)_2$), 0.64 (dd, 6H,$^{3}J_{PH}$ = 17.4 Hz,$^{3}J_{HH}$ = 7.1 Hz, $P(CHCH_3C\mathit{H}_3)_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 151.4 (d,$^{2}J_{PC}$ = 11 Hz, C2), 144.0 (d, J_{PC} = 7 Hz, C7a or C3a), 142.9 (d, J_{PC} = 9 Hz, C3a or C7a), 131.0 (d,$^{1}J_{PC}$ = 50 Hz, C3), 126.6 (C5), 125.7 (C6), 124.1 (C4), 121.5 (C7), 39.5 (d,$^{3}J_{PC}$ = 12 Hz, CH_2), 24.6 (d,$^{1}J_{PC}$ = 36 Hz, $P(\mathit{C}HCH_3CH_3)_2$), 19.6 (d,$^{2}J_{PC}$ = 5 Hz, $P(CH\mathit{C}H_3CH_3)_2$), 18.4 ($P(CHCH_3\mathit{C}H_3)_2$); ^{31}P{^{1}H} NMR (C_6D_6): δ 44.4.

Preparation of 3. To a magnetically stirred solution of **1b** (0.31 g, 1.1 mmol) in CH_2Cl_2 (8 mL) was added a suspension of Me_2SAuCl (0.31 g, 1.1 mmol) in CH_2Cl_2 (4 mL). The reactant mixture was noted to clear almost immediately, and after 0.25 h at 24 °C, stirring was arrested, and residual solvent along with other volatiles was removed in vacuo. The residue was washed with pentane (2 × 3 mL), and solvent and other volatile materials were removed in vacuo to yield **3** as a white solid (0.42 g, 0.79 mmol, 75%). Melting point 155−157 °C. Anal. (%) Calcd for $C_{21}H_{17}AuClP$: C, 47.34; H, 3.22. Found: C, 47.44; H, 3.54. ^{1}H NMR (C_6D_6): δ 7.34 (m, 1H, C7-H), 7.28−7.19 (m, 4H, ortho Ph-H), 7.16 (m, 1H, C4-H), 7.02−6.96 (m, 2H, para Ph-H), 6.93 (m, 1H, C5-H), 6.88−6.81 (m, 4H, meta Ph-H), 6.76 (m, 1H, C6-H), 5.96 (d, 1H,$^{3}J_{PH}$ = 8.0 Hz, C2-H), 2.93 (s, 2H, CH_2); ^{13}C{^{1}H} NMR (C_6D_6): δ 148.2 (d,$^{2}J_{PC}$ = 7 Hz, C2), 143.7 (d,$^{3}J_{PC}$ = 9 Hz, C7a), 142.2 (d,$^{2}J_{PC}$ = 15 Hz, C3a), 133.9 (d,$^{2}J_{PC}$ = 14 Hz, ortho Ph-C), 133.8 (d,$^{1}J_{PC}$ = 61 Hz, ipso Ph-C), 133.2 (d,$^{1}J_{PC}$ = 15 Hz, C3), 131.6 (para Ph-C), 129.0 (d,$^{3}J_{PC}$ = 12 Hz, meta Ph-C), 126.9 (C6), 126.0 (C5), 124.0 (C4), 121.5 (C7), 39.9 (d,$^{3}J_{PC}$ = 12 Hz, CH_2); ^{31}P{^{1}H} NMR (C_6D_6): δ 15.2.

Preparation of 4. To a magnetically stirred solution of Me_2SAuCl (1.1 g, 3.5 mmol) in CH_2Cl_2 (10 mL) was added a solution of **1c** (1.0 g, 3.5 mmol) in CH_2Cl_2 (10 mL). After 0.25 h at 24 °C, stirring was arrested, and residual solvent along with other volatiles was removed in vacuo. The solid material was recrystallized from CH_2Cl_2 to yield **4** as a light gray powder (1.2 g, 2.3 mmol, 67%). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at 24 °C. Melting point 194−195 °C. Anal. (%) Calcd for $C_{17}H_{26}AuClNP$: C, 40.21; H, 5.16; N, 2.76. Found: C, 40.17; H, 5.23; N, 2.39. ^{1}H NMR ($CDCl_3$): δ 7.29 (d,$^{3}J_{HH}$ = 7.5 Hz, 1H, C7-H), 7.23 (t,$^{3}J_{HH}$ = 7.5 Hz, 1H, C6-H), 7.14 (d,$^{3}J_{HH}$ = 7.5 Hz, 1H, C4-H), 6.96 (t,$^{3}J_{HH}$ = 7.5 Hz, 1H, C5-H), 5.72 (s, 1H, C3-H), 4.30 (d,$^{2}J_{PH}$ = 10.0 Hz, 1H, C1-H), 2.90 (s, 6H, $N(CH_3)_2$), 2.59 (m, 1H, $P(C\mathit{H}CH_3aCH_3b)$), 1.88 (m, 1H, $P(C\mathit{H}CH_3cCH_3d)$), 1.54 (dd, 3H,$^{3}J_{PH}$ = 18.0 Hz,$^{3}J_{HH}$ = 6.5 Hz, $P(CHC\mathit{H}_3aCH_3b)$), 1.30 (dd, 3H,$^{3}J_{PH}$ = 18.5 Hz,$^{3}J_{HH}$ = 6.0 Hz, $P(CHCH_3aC\mathit{H}_3b)$), 0.98 (dd, 3H,$^{3}J_{PH}$ = 19.5 Hz,$^{3}J_{HH}$ = 7.5 Hz, $P(CHC\mathit{H}_3cCH_3d)$), 0.72 (dd, 3H,$^{3}J_{PH}$ = 15.0 Hz,$^{3}J_{HH}$ = 7.0 Hz, $P(CHCH_3cC\mathit{H}_3d)$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.8 (d,$^{2}J_{PC}$ = 3 Hz, C2), 145.6 (d,$^{2}J_{PC}$ = 2 Hz, C7a), 135.5 (d,$^{3}J_{PC}$ = 7 Hz, C3a), 128.4 (C6), 123.5 (C7), 122.0 (C5), 119.4 (C4), 106.6 (C3), 44.5 (d,$^{1}J_{PC}$ = 21 Hz, C1), 43.8 ($N(CH_3)_2$), 23.4 (d,$^{1}J_{PC}$ = 20 Hz, $P(\mathit{C}HCH_3cCH_3d)$), 22.9 (d,$^{1}J_{PC}$ = 20 Hz, $P(\mathit{C}HCH_3aCH_3b)$), 22.8 (d,$^{2}J_{PC}$ = 5 Hz, $P(CH\mathit{C}H_3cCH_3d)$), 20.7 (d,$^{2}J_{PC}$ = 5 Hz, $P(CHCH_3a\mathit{C}H_3b)$), 20.0 (d,$^{2}J_{PC}$ = 3 Hz, $P(CH\mathit{C}H_3aCH_3b)$), 18.3 (d,$^{2}J_{PC}$ = 2 Hz, $P(CHCH_3c\mathit{C}H_3d)$); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.3.

Preparation of 5a/5b. To a magnetically stirred suspension of Me_2SAuCl (0.11 g, 0.36 mmol) in toluene (2 mL) was added a solution of **1d** (0.12 g, 0.35 mmol) in toluene (3 mL). After 2 h at 24 °C, stirring was arrested, and residual solvent along with other volatiles was removed in vacuo. The residue was dissolved in minimal THF (2−3 mL) and filtered through Celite to remove the black solid material that had formed in the reaction. THF and other volatiles were removed in vacuo, and the resulting solid was washed with pentane (2 × 3 mL). Solvent and other volatiles were removed in vacuo, yielding **5a**/**5b** as a yellow/brown solid (0.11 g, 0.20 mmol, 56%). Anal. (%) Calcd for $C_{23}H_{22}AuClNP$: C, 47.97; H, 3.85; N, 2.43. Found: C, 47.72; H, 3.76; N, 2.39. ^{1}H NMR (CD_2Cl_2): δ 7.81−7.44 (m, 20H, **5a** and **5b**, Ph-H), 7.30 (d,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5b**, C4-H or C7-H), 7.18 (t,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5a**, C5-H or C6-H), 7.04 (d,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5a**, C7-H), 6.89 (t,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5b**, C5-H or C6-H), 6.78 (t,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5b**, C5 or C6), 6.72 (t,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5a**, C5 or C6), 6.51 (d,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5a**, C4-H), 6.21 (d,$^{3}J_{HH}$ = 7.5 Hz, 1H, **5b**, C4-H or C7-H), 5.60 (s, 1H, **5a**, C3-H), 4.85 (d,$^{2}J_{PH}$ = 11.5 Hz, 1H, **5a**, C1-H), 3.79 (s, 2H, **5b**, CH_2), 3.08 (s, 6H, **5b**, $N(CH_3)_2$), 2.62 (s, 6H, **5a**, $N(CH_3)_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 173.2 (**5b**, C2), 157.0 (**5a**, C2), 146.5 (**5a**, C3a or C7a), 135.4 (d, J_{PC} = 14 Hz, aryl C-H),

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134.8 (quaternary-C), 133.8 (d, $J_{PC} = 13$ Hz, aryl C-H), 133.3 (d, $J_{PC} = 14$ Hz, aryl C-H), 132.5 (aryl C-H), 131.3 (aryl C-H), 129.0 (d, $J_{PC} = 12$ Hz, aryl C-H), 128.6 (d, $J_{PC} = 21$ Hz, aryl C-H), 128.5 ($J_{PC} = 22$ Hz, aryl C-H), 128.3 (**5a**, C5 or C6), 126.0 (**5b**, C5 or C6), 124.0 (d,$^4J_{PC} = 4$ Hz, **5a**, C4), 122.7 (**5b**, C4 or C7), 121.4 (2 overlapping s, **5a**, C5 or C6, and **5b**, C5 or C6), 119.1 (**5b**, C4 or C7), 118.8 (**5a**, C7), 106.0 (**5a**, C3), 47.5 (d,$^1J_{PC} = 25$ Hz, **5a**, C1), 45.2 (**5b**, $N(CH_3)_2$), 42.1 (**5a**, $N(CH_3)_2$), 40.7 (d,$^3J_{PC} = 9$ Hz, **5b**, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.9 (**5a**), 14.8 (**5b**).

Preparation of 6. To a magnetically stirred solution of **2** (0.12 g, 0.26 mmol) in THF (2 mL) was added a solution of **1a** (0.062 g, 0.27 mmol) in THF (1.5 mL). After stirring 0.1 h at 24 °C, the yellow solution was filtered through Celite, pentane (10 mL) was added, and the solution was placed in a −35 °C freezer. After several days, the supernatant was decanted, and the resulting crystals were washed with pentane (2 × 3 mL), then solvent and other volatiles were removed in vacuo to yield light brown crystals, **6** (0.13 g, 0.18 mmol, 69%). Crystals suitable for X-ray diffraction were grown from a concentrated sample of **6** in THF at −35 °C. Melting point 160−161 °C. Anal. (%) Calcd for $C_{30}H_{42}AuClP_2$: C, 51.69; H, 6.07; N, 0. Found: C, 51.73; H, 6.11; N, <0.3. ^1H NMR (C_6D_6): δ 7.93 (d,$^3J_{HH} = 7.5$ Hz, 2H, C4-H or C7-H), 7.19 (d,$^3J_{HH} = 7.5$ Hz, 2H, C4-H or C7-H), 7.15 (t,$^3J_{HH} = 7.5$ Hz, 2H, C5-H or C6-H), 7.08 (t,$^3J_{HH} = 7.0$ Hz, 2H, C5-H or C6-H), 6.97 (d,$^3J_{PH} = 7.0$ Hz, 2H, C2-H), 3.01 (s, 4H, CH_2), 2.42 (m, 4H, $\mathrm{P(C}H\mathrm{CH_3CH_3)_2}$), 1.24 (dd,$^3J_{PH} = 17.5$ Hz,$^3J_{HH} = 10.0$ Hz, 12H, $\mathrm{P(CHC}H_3\mathrm{CH_3)_2}$), 0.96 (dd,$^3J_{PH} = 15.5$ Hz,$^3J_{HH} = 6.5$ Hz, 12H, $\mathrm{P(CHCH_3C}H_3\mathrm{)_2}$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.9 (C2), 145.1 (d, $J_{PC} = 11$ Hz, C3a or C7a), 144.1 (d, $J_{PC} = 6$ Hz, C3a or C7a), 134.4 (d, $J_{PC} = 26$ Hz, C3), 126.3 (aryl CH), 125.3 (aryl CH), 123.8 (aryl CH), 122.1 (aryl CH), 39.6 (d,$^3J_{PC} = 9$ Hz, CH_2), 24.4 (d,$^1J_{PC} = 21$ Hz, $\mathrm{P(}C\mathrm{HCH_3CH_3)_2}$), 19.8 (d,$^2J_{PC} = 8$ Hz, $\mathrm{P(CHCH_3}C\mathrm{H_3)_2}$), 18.8 ($\mathrm{P(CH}C\mathrm{H_3CH_3)_2}$); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.2 ($\Delta\nu_{1/2} = \sim 950$ Hz).

Preparation of [7]$^+$OTf$^-$. To a magnetically stirred solution of **6** (0.065 g, 0.093 mmol) in THF (3 mL) was added a solution of AgOTf (0.024 g, 0.094 mmol) in THF. After 0.75 h at 24 °C, stirring was arrested, and the light yellow solution was filtered through Celite. The solution was placed in a −35 °C freezer, and after 2 weeks, light yellow crystals formed, which proved to be suitable for X-ray crystallographic studies. Crystals were isolated and washed with pentane (2 × 3 mL), and residual solvent and other volatiles were removed in vacuo to yield [**7**]$^+$OTf$^-$ (0.054 g, 0.067 mmol, 72%). Melting point 142 °C. Anal. (%) Calcd for $C_{31}H_{42}AuF_3O_3P_2S$: C, 45.93; H, 5.52; N, 0. Found: C, 45.81; H, 5. 34; N, <0.3. ^1H NMR (CD_2Cl_2): δ 7.85 (d,$^3J_{HH} = 7.5$ Hz, 2H, C4-H or C7-H), 7.62 (d,$^3J_{HH} = 7.5$ Hz, 2H, C4-H or C7-H), 7.35 (m, 2H, C5-H or C6-H), 7.31 (t,$^3J_{HH} = 7.0$ Hz, 2H, C5-H or C6-H), 7.26 (m, 2H, C2-H), 3.76 (s, 4H, CH_2), 2.96 (virtual t of septets, $^{2/\,4}J_{PH} = 2.5$ Hz,$^3J_{HH} = 7.0$ Hz, 4H, $\mathrm{P(C}H\mathrm{CH_3CH_3)_2}$), 1.43 (virtual d of t, $^3J_{HH} = 7.0$ Hz, $^{3/5}J_{PH} = 10.0$ Hz, 12H, $\mathrm{P(CHC}H_3\mathrm{CH_3)_2}$), 1.28 (virtual d of t, $^3J_{HH} = 7.0$ Hz, $^{3/5}J_{PH} = 8.5$ Hz, 12H, $\mathrm{P(CHCH_3C}H_3\mathrm{)_2}$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 150.8 (C2), 144.1 (C3a or C7a), 143.4 (C3a or C7a), 129.9 (m, C3), 126.7 (C5 or C6), 126.5 (C5 or C6), 124.7 (C4 or C7), 121.1 (C4 or C7), 41.0 (virtual t, $^{3/5}J_{PC} = 6$ Hz, CH_2), 25.2 (virtual t, $^{1/3}J_{PC} = 16$ Hz, $\mathrm{P(}C\mathrm{HCH_3CH_3)_2}$), 20.0 ($\mathrm{P(CH}C\mathrm{H_3CH_3)_2}$), 19.1 ($\mathrm{P(CHCH_3}C\mathrm{H_3)_2}$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 53.0.

Crystallographic Solution and Refinement Details. Crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and multiscan absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by use of direct methods in the case of **2** and **6**, or Patterson search/structure expansion in the case of **4** and [**7**]$^+$OTf$^-$, and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. For [**7**]$^+$OTf$^-$, the final refined value of the absolute structure parameter (0.183(6)) supported that the correct absolute structure had been correctly chosen.[31] Further details are provided in the Supporting Information.

General Protocol for the Hydrosilylation of Aldehydes. The protocol used for the hydrosilylation of benzaldehyde with dimethylphenylsilane, employing 3 mol % Me_2SAuCl and 20 mol % Et_3P in THF, is provided as a representative procedure. To a suspension of Me_2SAuCl in THF (0.022 g, 0.072 mmol in 1.6 mL of THF) was added Et_3P (0.071 mL, 0.057 g, 0.48 mmol). The clear, colorless solution was allowed to equilibrate for 5 min under the influence of magnetic stirring, at which point benzaldehyde (0.25 mL, 2.4 mmol) was added by use of an Eppendorf pipet. The resultant solution was stirred for an additional 5 min to ensure equilibration of the benzaldehyde with the catalyst, after which dimethylphenylsilane (0.73 mL, 0.65 g, 4.8 mmol) was added. Subsequently, 0.7 mL aliquots were placed in 13 × 100 mm borosilicate tubes and sealed with a PTFE valve. Reactor cells were immediately transferred to a temperature-controlled mineral oil bath. Magnetic stirring of the solutions was initiated, and the headspace vapor pressure was reduced to approximately 0.5 mmHg. Occasionally, color changes and/or formation of metal precipitate were noted during the course of the reaction, as indicated in the footnote of Table 2 (see text). At the desired sampling time, the reactor cells were opened and filtered through a short Al_2O_3 column (5 cm long × 0.5 cm diameter) from which clear, colorless solutions eluted. Benzene was passed through the column to increase the total eluted volume to between 1.0 and 1.5 mL. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, and quantitative data were obtained from GC-FID analysis. Tabulated data represent the average of two runs.

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Supporting Information Available: Single-crystal X-ray diffraction data in CIF format for **2**, **4**, **6**, and [**7**]$^+$OTf$^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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