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Synthesis of a Coordinatively Labile Gold(III) Methyl Complex

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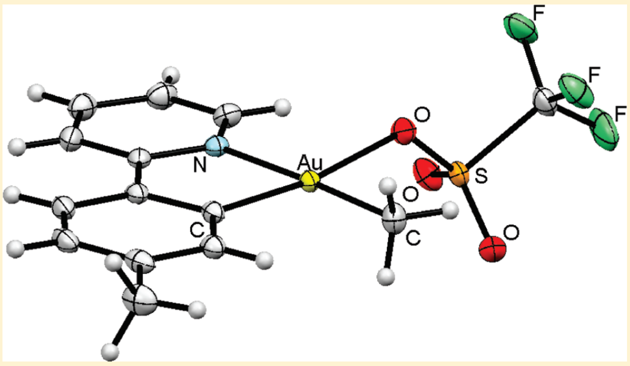
Supporting Information

ABSTRACT: Stable and isolable cyclometalated monomethyl Au(III) complexes are readily available from the precursor (tpy)Au(Me)Cl, prepared from (tpy)AuCl$_2$ and excess SnMe$_4$. Reaction of (tpy)Au(Me)Cl with suitable silver salts generates (tpy)Au(Me)(X) (X = OAc, OTf). Ligand exchange reactions with (tpy)Au(Me)(OTf) provide the cationic monomethyl Au(III) adducts [(tpy)Au(Me)(L)][OTf] (L = PPh$_3$, THT).



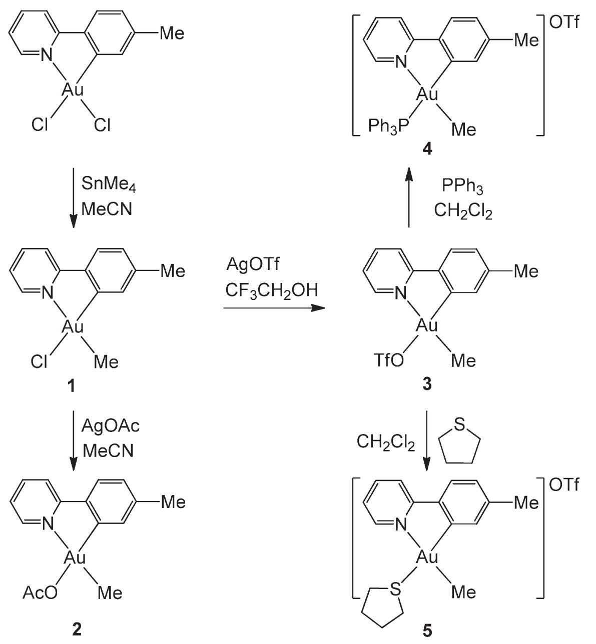
The chemistry of gold has been growing by leaps and bounds the past several years, in large part driven by the utilization of carbophilic π-acidic gold compounds as catalysts for organic transformations. While simple Au(I) or Au(III) salts are active, the ready, *in situ* generation of a large variety of coordinatively labile LAu(I)$^+$ species (L = phosphine, N-heterocyclic carbene, pyridine)[1] has allowed the design of more sophisticated Au(I) catalysts. On the other hand, there are only a handful of Au(III) catalysts that have formulations more complicated than that of AuCl$_3$ or NaAuCl$_4$, of which (2-pyridinecarboxylate)AuCl$_2$ is the most common.[2] It is also problematic that the mechanisms of the vast majority of homogeneous gold-catalyzed reactions are still speculative;[3] for example only two Au(III) catalytic intermediates have been spectroscopically identified.[2g,m] In addition to redox-neutral gold catalysis, there has been a recent burst of catalytic reactions where a Au(I)−Au(III) mechanistic pathway is the current hypothesis,[4] and Au(III) complexes resembling conjectural intermediates have been synthesized.[5] The confluence of these factors suggests that the chemistry of well-defined, coordinatively labile Au(III) compounds would be quite valuable for further advancements in gold catalysis. Such species are, however, exceedingly rare, and as far as we know only one coordinatively labile Au(III) complex has been extensively studied, namely, AuMe$_2$(OTf)(H$_2$O), which was synthesized and characterized by Kochi as early as 1977.[6] We report herein the synthesis of a new cyclometalated Au(III) methyl species, (tpy)AuMe(Cl) (tpy = 2-*p*-tolylpyridine). This is readily converted to the covalently bonded triflate species (tpy)AuMe(OTf) (OTf = OSO$_2$CF$_3$), which features a coordinatively labile OTf$^-$ ligand, as evidenced by its exchange reactions with other donor ligands.

The monomethyl Au(III) compound (tpy)Au(Me)Cl (**1**) was obtained in low yield (8%) from the reaction between (tpy)AuCl$_2$[7] and 6-fold excess of SnMe$_4$ in acetonitrile under reflux conditions (see Scheme 1). SnMe$_4$ is known to be one of the better methylating agents for Au(III),[8] although yields are generally poor.[9] The primary byproduct in the synthesis of **1** was metallic gold (62%). An analogous reaction between (bipy)AuCl$_2$ and excess SnMe$_4$ also proceeded in low yield and with a large amount of metallic gold as a byproduct, although in this case the dimethyl complex (bipy)AuMe$_2$ was obtained.[10] The synthesis of **1** is also in marked contrast to the high-yield synthesis of related monoaryl Au(III) compounds, such as (damp)Au(Ph)Cl from (damp)AuCl$_2$ and HgPh$_2$ (damp = C$_6$H$_4$CH$_2$NMe$_2$).[11] Compound **1** was characterized by NMR spectroscopy, elemental analysis, and mass spectrometry.[12] It is soluble in dichloromethane and toluene, and the isolated compound is air-stable at room temperature for at least several days. A CD$_2$Cl$_2$ solution of **1** exhibited a single resonance for the methyl group bound to Au at δ 1.53 and 9.2 in the ^{1}H and ^{13}C NMR spectra, respectively. Cross-peaks in a ^{1}H NOE experiment between the Au-Me protons and 6′-H, and between 6′-H and the tolyl methyl protons on the tpy ligand, provided evidence for the coordination of the Au-methyl group *trans* to the pyridyl N-atom. Compound **1** did not react with the neutral ligands triphenylphosphine, acetonitrile, acetone, diethyl ether, and water.

Treatment of **1**, however, with 1 equiv of silver acetate in either acetonitrile or dichloromethane for 8 h at room temperature

Received: April 18, 2011
Published: May 25, 2011

Scheme 1. Synthesis and Reactivity of 1 and 3



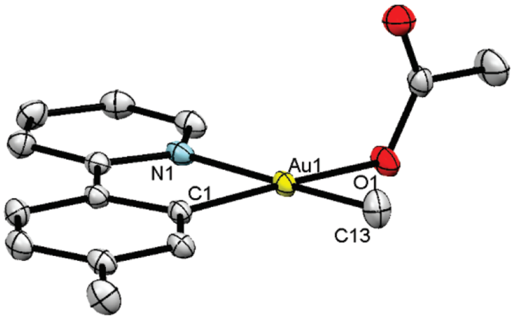


Figure 1. ORTEP view of the solid-state structure of **2**·CH_2Cl_2 with 50% probability ellipsoids. CH_2Cl_2 solvent of crystallization and hydrogen atoms are removed for clarity. Pertinent bond distances (Å) and angles (deg): Au1−C1, 2.0005(19); Au1−C13, 2.027(2); Au1−O1, 2.0861(15); Au1−N1, 2.1165(19); C1−Au1−C13, 94.21(9); C1−Au1−O1, 173.45(7); C1−Au1−N1, 81.36(7); C13−Au1−O1, 91.04(8); C13−Au1−N1, 174.69(7); O1−Au1−N1, 93.59(7).

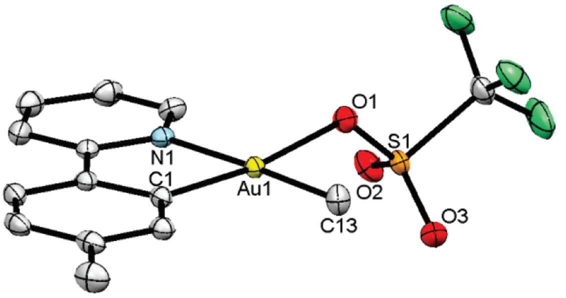


Figure 2. ORTEP view of the solid-state structure of **3** with 50% probability ellipsoids. Hydrogen atoms are removed for clarity. Pertinent bond distances (Å) and angles (deg): Au1−C1, 1.995(2); Au1−C13, 2.030(2); Au1−O1, 2.1382(17); Au1−N1, 2.1092(19); S1−O1, 1.4809(18); S1−O2, 1.4295(19); S1−O3, 1.4304(18); C1−Au1−C13, 94.34(10); C1−Au1−O1, 171.53(8); C1−Au1−N1, 82.20(8); C13−Au1−O1, 91.82(8); C13−Au1−N1, 176.47(8); O1−Au1−N1, 91.69(7); Au1−O1−S1, 129.06(11).

resulted in nearly quantitative formation of (tpy)Au(Me)(OAc) (**2**). The identity of this compound was established by NMR spectroscopy, elemental analysis, and mass spectrometry. A ^1H NOE experiment showed the same two sets of cross-peaks as observed for **1**, between the Au-Me protons, 6′-H, and the tolyl methyl protons, which confirmed that **2** has a solution phase coordination stereochemistry analogous to **1**.[12] In this instance, the solid-state stereochemistry was determined by single-crystal X-ray diffraction.[13] As shown in Figure 1, **2** has the expected (slightly distorted) square-planar coordination geometry with the Au-Me group indeed located *trans* to the pyridyl N-atom. The bond distances and angles are not unusual and correspond to reported values for cyclometalated Au complexes[14] and Au(III)-Me complexes.[15] The Au1−C13 distance of 2.027(2) Å is significantly shorter than the corresponding distances in the monomethyl Au(III) complexes (Idipp)AuI_2Me (2.185(11) Å) and (Idipp)AuMeI($NC_4H_4O_2$) (2.086(3) Å), where the methyl group is *trans* to an N-heterocyclic carbene.[16] The Au1−O1 distance is intermediate between the corresponding distance for the neutral (ppy)$Au(OAc)_2$ (ppy = 2-phenylpyridine), 2.018(6) Å,[17] and the cationic [(pmpy)Au(OAc)(py)][ClO_4] (pmpy = 2-phenyl-3-methylpyridine), 2.13(3) Å.[18] The five atoms making up the central coordination geometry (Au1, C1, C13, O1, and N1) are nearly planar; the maximum deviation from the mean plane calculated from these atoms is only 0.067 Å. In the extended structure, molecules of **2** stack through partially overlapping tpy ligands, and the closest distance between the aromatic rings of adjacent molecules is 3.3 Å. The zigzag stacking pattern is governed by a crystallographic inversion symmetry element that eliminates close Au−Au contacts.

Similar to the synthesis of **2**, reaction of **1** with 1 equiv of silver triflate (AgOTf) in 2,2,2-trifluoroethanol provided (tpy)Au(Me)(OTf) (**3**). The use of 2,2,2-trifluoroethanol as solvent is key for the successful synthesis and isolation of **3**. In other solvents, such as dichloromethane or acetonitrile, this reaction did not proceed to completion, and **3** could not be isolated as a pure compound. In solution, the composition and coordination stereochemistry of **3** were unequivocally established by NMR experiments analogous to those utilized for **1** and **2**.[12] The solid-state structure[19] was again shown to be the same as the solution structure; see Figure 2. Only two other structures with covalent, unidentate Au−OTf bonding could be found in the literature: *cis*-$Me_2Au(H_2O)(OTf)$[20] and (*o*-Tol)$_3$PAu(OTf).[21] The Au-OTf structural parameters of **3** are intermediate between these two; the Au1−O1 and S−O bond distances more closely resemble the corresponding parameters of the latter, Au(I) triflate compound, while the Au1−O1−S1 bond angle is closer to that in the former example. The Au1−O1 bond distance closely matches the corresponding Au−O distance in the Au(III) nitrate (ppy)Au(CH_2COCH_3)(ONO_2).[14b] Apart from the longer Au−O bond, the coordination geometry of **3**, i.e., the bond distances, bond angles, and planarity of the central core, are very similar to the corresponding values in **2**. This similarity extends to the crystalline stacking motif exhibited by **3**, although the shortest distance between stacked aromatic rings is now 3.4 Å.

As with **1**, no reactions were observed between **2** and the neutral ligands triphenylphosphine, acetonitrile, acetone, and diethyl ether in CD_2Cl_2. In contrast, similar experiments with **3** containing the more labile OTf^- ligand resulted in ligand exchange reactions and the formation of cationic, monomethyl

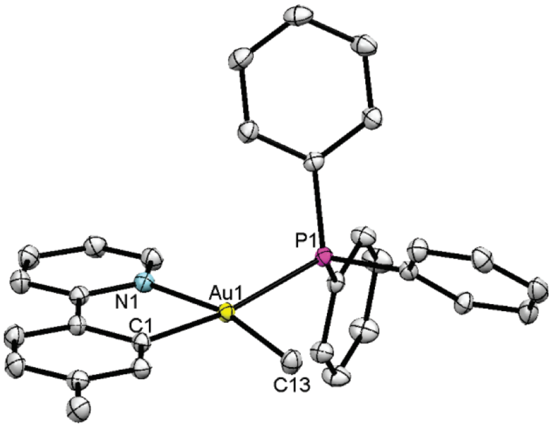


Figure 3. ORTEP view of the solid-state structure of **4** with 50% probability ellipsoids. The triflate anion and hydrogen atoms are removed for clarity. Pertinent bond distances (Å) and angles (deg): Au1−C1, 2.0513(19); Au1−C13, 2.053(2); Au1−P1, 2.4026(5); Au1−N1, 2.1457(17); C1−Au1−C13, 90.06(8); C1−Au1−P1, 169.36(5); C1−Au1−N1, 80.68(7); C13−Au1−P1, 91.57(6); C13−Au1−N1, 166.90(8); P1−Au1−N1, 99.25(5).

Au(III) complexes (see Scheme 1). Reaction of **3** with PPh_3 resulted in displacement of OTf^- and formation of the cationic complex $[(tpy)Au(Me)(PPh_3)][OTf]$, **4**. Coupling between P and the Au-Me protons (δ 1.47, $^3J_{PH} = 7.7$ Hz) was observed in the ^1H NMR spectrum of **4**, confirming the coordination of the PPh_3 ligand to Au in solution. All other analytical and spectroscopic data for **4** are consistent with the proposed formulation,[12] which was also confirmed by determination of the solid-state structure[22] of **4**, as shown in Figure 3. In contrast to **2** and **3**, the coordination sphere of **4** is severely distorted from a square-planar geometry. While the constituent atoms of the calculated mean square plane formed by Au1, N1, C1, and C13 show a distance from this plane comparable to that in **2**, the P1 atom is located nearly 0.7 Å away. This distortion is likely due to packing forces, as there is a significant number of nonbonding contacts between the phenyl groups of any one PPh_3 ligand and both triflate anions and neighboring phenyl groups. Apart from this distortion, there are no other anomalies in the structure; all bond distances and angles, including the Au−P bond distance for P *trans* to a sp^2 C-atom,[23] are within established ranges. The cyclometalate moiety in **4** is slightly more distant from the Au center than in **2** and **3**, perhaps because of the steric requirements of the PPh_3 ligand. The supramolecular stacking of **4** is analogous to that of **2** and **3**, and the closest distance between the tpy planes of neighboring molecules is 3.4 Å.

In order to establish some generality of the ligand exchange reactions with **3**, the reaction between **3** and 1 equiv of tetrahydrothiophene (THT) was monitored via ^1H NMR spectroscopy in CD_2Cl_2. All spectroscopic data confirmed the formation of the expected product $[(tpy)Au(Me)(THT)][OTf]$, **5**. The ^1H NMR spectrum consisted of two broadened peaks for the α- and β-protons of THT at δ 3.38 and 2.23, respectively, in addition to the two methyl signals for the Au-Me and tpy ligand. Curiously, with the addition of another 1.3 equiv of THT, the THT peaks grew in intensity and shift to δ 3.06 and 2.06, respectively.[12] The growth and shift of these signals suggest that the exchange of bound and free THT is fast on the NMR time scale.

In conclusion, we have successfully synthesized stable and isolable examples of neutral and cationic monomethyl complexes of Au(III). In particular, **3** and its congeners may well prove to be important mechanistic probes of catalytic reactions involving Au(III) intermediates, which will hopefully lead to new insights into these transformations. For instance, while reactions catalyzed by gold are generally proposed to involve π-bound alkynes, alkenes, or arenes as intermediates, no well-characterized Au(III) π-complexes of these ligands are known.[24] Furthermore, the availability of a coordination site *cis* to a methyl group may allow validation of the potential of Au complexes as C−H activation and functionalization catalysts for light alkanes. Improvements in the yield of **1** and the scope of the ligand exchange reactions for **3** are the subjects of current studies within the Oslo Gold Team, and the results of these studies will be presented in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and full characterization data (EA, MS, and ^1H, ^{13}C, ^{19}F, ^{31}P, COSY, and NOESY NMR spectra) for **1**−**5** and crystallographic experimental details and structural data for $\mathbf{2 \cdot CH_2Cl_2}$, **3**, and **4**. This information is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank the GASSMAKS program of the Norwegian Research Council (grant no. 185513/I30) for generous financial support, Drs. Ole Swang and Manik Kumer Ghosh (SINTEF) for helpful discussions, Osamu Sekiguchi (U. Oslo) for assistance with the MS experiments, and Aud Mjærum Bouzga (SINTEF) and Dirk Petersen (U. Oslo) for assistance with the NMR spectroscopy experiments.

■ REFERENCES

(1) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410.

(2) (2-Pyridinecarboxylate)$AuCl_2$: (a) Hashmi, A. S. K.; Weyrauch, J. P.; Rudolph, M.; Kurpejović, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 6545. (b) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006**, *128*, 14274. (c) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 9244. (d) Davies, P. W.; Albrecht, S. J.-C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8372. (e) Shapiro, N. D.; Shi, Y.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 11654. (f) Gung, B. W.; Craft, D. T.; Bailey, L. N.; Kirschbaum, K. *Chem.—Eur. J.* **2010**, *16*, 639. (Iminophosphorane)$AuCl_2$:(g) Aguilar, D.; Contel, M.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2007**, *26*, 4604. (h) Aguilar, D.; Contel, M.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2009**, *694*, 486. $[(Salen)Au]^{2+}$ or $[(ONN\text{-}ligated)AuCl]^+$:(i) González-Arellano, C.; Corma, A.; Iglesias, M.; Sánchez, F. *Chem. Commun.* **2005**, 1990. (j) Lo, V. K.-L.; Liu, Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2006**, *8*, 1529. (k) Debono, N.; Iglesias, M.; Sánchez, F. *Adv. Synth. Catal.* **2007**, *349*, 2470. (l) Corma, A.; González-Arellano, C.; Iglesias, M.; Navarro, M. T.; Sánchez, F. *Chem. Commun.* **2008**, 6218. $[(aryl)_xAuCl_{4-x}]^-$:(m) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz., S. *J. Am. Chem. Soc.* **2003**, *125*, 11925. (n) Adé, A.; Cerrada, E.; Contel, M.; Laguna, M.; Merino, P.; Tejero, T. *J. Organomet. Chem.* **2004**, *689*, 1788. Others:(o) Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. *Org. Lett.* **2006**, *8*, 325. (p) Lo, V. K.-Y.; Kung, K. K.-Y.; Wong, M.-K.; Che, C.-M. *J. Organomet. Chem.* **2009**, *694*, 583. (q) Corma, A.;

Domínguez, I.; Doménech, A.; Fornés, V.; Gómez-García, C. J.; Ródenas, T.; Sabater, M. J. *J. Catal.* **2009**, *265*, 238. (r) Oña-Burgos, P.; Fernández, I.; Roces, L.; Torre Fernández, L.; García-Granda, S.; López Ortiz, F. *Organometallics* **2009**, *28*, 1739. (s) Pažický, M.; Loos, A.; Ferreira, M. J.; Serra, D.; Vinokurov, N.; Rominger, F.; Jäkel, C.; Hashmi, A. S. K.; Limbach, M. *Organometallics* **2010**, *29*, 4448.

(3) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232.

(4) (a) Peng, Y.; Cui, L.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2009**, *131*, 5062. (b) Zhang, G.; Peng, Y.; Cui, L; Zhang, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3112. (c) Iglesias, A.; Muñiz, K. *Chem.—Eur. J.* **2009**, *15*, 10563. (d) Zhang, G.; Cui, L.; Wang, Y.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 1474. (e) Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Org. Lett.* **2010**, *12*, 4724. (f) Brenzovich, W. E., Jr.; Brazeau, J.-F.; Toste, F. D. *Org. Lett.* **2010**, *12*, 4728. (g) Melhado, A. D.; Brenzovich, W. E., Jr.; Lackner, A. D.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 8885. (h) Hopkinson, M. N.; Tessier, A.; Salisbury, A.; Giuffredi, G. T.; Combettes, L. E.; Gee, A. D.; Gouverneur, V. *Chem.—Eur. J.* **2010**, *16*, 4739. (i) Brenzovich, W. E., Jr.; Benitez, D.; Lackner, A. D.; Shunatona, H. P.; Tkatchouk, E.; Goddard, W. A., III; Toste, F. D. *Angew. Chem., Int. Ed.* **2010**, *49*, 5519. (j) de Haro, T.; Nevado, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 906. (k) Zhang, G.; Luo, Y.; Wang, Y.; Zhang, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4450.

(5) Mankad, N. P.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 12859.

(6) Komiya, S.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 2138.

(7) Shaw, A. P.; Tilset, M.; Heyn, R. H.; Jakobsen, S. *J. Coord. Chem.* **2011**, *64*, 38.

(8) Paul, M.; Schmidbaur, H. *Z. Naturforsch.* **1994**, *49b*, 647.

(9) Schuster, O.; Schmidbaur, H. *Z. Naturforsch.* **2006**, *61b*, 1.

(10) Venupogal, A.; Heyn, R. H., unpublished results.

(11) Vicente, J.; Chicote, M. T.; Bermúdez, M. D.; Sanchez-Santano, M. J.; Jones, P. G. *J. Organomet. Chem.* **1988**, *354*, 381.

(12) See Supporting Information.

(13) Crystal data for **2**·CH_2Cl_2: $C_{15}H_{16}AuNO_2\cdot CH_2Cl_2$, M = 524.18, triclinic, a = 7.2103(2) Å, b = 10.7553(3) Å, c = 12.4878(5) Å, α = 108.622(1)°, β = 102.576(1)°, γ = 101.895(1)°, V = 855.00(5) Å^3, d_{calc} = 2.036 g cm^{-3}, T = 123(2) K, space group $P\bar{1}$, Z = 2, R1 = 0.0167, wR2 = 0.0437, CCDC number 790402.

(14) (a) Cocco, F.; Cinellu, M. A.; Minghetti, G.; Zucca, A.; Stoccoro, S.; Maiore, L.; Manassero, M. *Organometallics* **2010**, *29*, 1064. (b) Fan, D.; Meléndez, E.; Ranford, J. D.; Loo, P. F.; Vittal, J. J. *J. Organomet. Chem.* **2004**, *689*, 2969.

(15) Venugopal, A.; Kumer Ghosh, M.; Jürgens, H.; Törnroos, K. W.; Swang, O.; Tilset, M.; Heyn, R. H. *Organometallics* **2010**, *29*, 2248, and references therein.

(16) Scott, V. J.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2010**, *29*, 4090.

(17) Fan, D.; Yang, C.-T.; Ranford, J. D.; Lee, P. F.; Vittal, J. J. *Dalton Trans* **2003**, 2680.

(18) Parish, R. V.; Wright, J. P.; Pritchard, R. G. *J. Organomet. Chem.* **2000**, *596*, 165.

(19) Crystal data for **3**: $C_{14}H_{13}AuF_3NO_3S$, M = 529.28, monoclinic, a = 6.8255(3) Å, b = 15.5573(6) Å, c = 14.4009(5) Å, β = 93.975(1)°, V = 1525.5(1) Å^3, d_{calc} = 2.305 g cm^{-3}, T = 103(2) K, space group $P2_1/c$, Z = 4, R1 = 0.0174, wR2 = 0.0441, CCDC number 790403.

(20) See ref 6. Au—O, 2.201(6) Å, S—O, 1.456(6), 1.439(4), and 1.439(4) Å, Au—O—S, 128.7(4)°.

(21) Preisenberger, M.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1645. Au—O, 2.110(3) Å, S—O, 1.470(3), 1.432(4), and 1.426(3) Å, Au—O—S, 120.4(2)°.

(22) Crystal data for **4**: $[C_{31}H_{28}AuNP]^+$, $[CF_3O_3S]^-$, M = 791.55, triclinic, a = 9.0011(3) Å, b = 9.7120(3) Å, c = 16.8412(5) Å, α = 81.2501(4)°, β = 86.7247(4)°, γ = 83.6293(3)°, V = 1444.90(8) Å^3, d_{calc} = 1.819 g cm^{-3}, T = 123(2) K, space group $P\bar{1}$, Z = 2, R1 = 0.0170, wR2 = 0.0430, CCDC number 790404.

(23) Contel, M.; Edwards, A. J.; Garrido, J.; Hursthouse, M. B.; Laguna, M.; Terroba, R. *J. Organomet. Chem.* **2000**, *607*, 129.

(24) Schmidbaur, H.; Schier, A. *Organometallics* **2010**, *29*, 2.