Organogold(III) Iminophosphorane Complexes as Efficient Catalysts in the Addition of 2-Methylfuran and Electron-Rich Arenes to Methyl Vinyl Ketone

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Organogold(III) Iminophosphorane Complexes as Efficient Catalysts in the Addition of 2-Methylfuran and Electron-Rich Arenes to Methyl Vinyl Ketone

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Cycloaurated compounds containing C,N-pincer ligands have been evaluated as precatalysts in the addition reactions of 2-methylfuran and some electron-rich arenes to methyl vinyl ketone. All complexes have displayed a catalytic activity comparable to that reported for Au(I) complexes in the presence of silver salts. Compounds containing iminophosphorane ligands ($R_3P{=}NR'$) as C,N-backbones such as $[Au\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}N(C_6H_4X)\text{-}2\}Cl_2]$ (X = H, **13**; X = Me, **14**) have been found to be the more effective in both the presence and absence of silver salts. With acid-sensitive electron-rich arenes the catalytic activity of these cycloaurated complexes outperformed that of the $AuCl_3$ salt. The synthesis and characterization of new iminophosphorane coordination and organogold(III) compounds are provided along with the results for the catalytic studies.

Introduction

Due to a significant untapped potential, gold homogeneous catalysis is only now recognized as a scientific hotspot,[1] with an increasing number of publications appearing almost on a weekly basis. The significance of Au^I and Au^{III} complexes as homogeneous catalysts for several reactions (mainly nucleophilic additions to π systems, hydrogenations, and some oxidations) has been only recently addressed.[2] There is still a need, however, to fully understand reaction mechanisms in order to rationally design more efficient and selective catalysts. It should be stressed that the vast majority of homogeneous gold catalysts used to date are gold(III) halides or cationic $[Au(PPh_3)]^+$ fragments.[3] During the last three years the number of reports on gold catalysts with different ligands (and therefore with tunable electronic and steric properties) has increased,[4] but examples of coordination[5] or organometallic[6] gold(III) complexes are rather limited. There have been a number of reports on the high efficiency and selectivity of $AuCl_3$ as a catalyst on several C−C and C−heteroatom bond formations.[7] The search for gold(III) compounds as air-stable alternatives to this very hygroscopic and acidic compound thus becomes significant and truly appealing. We and others have reported on the use of organogold and coordination gold(III) compounds as catalysts in the addition of water and alcohols to alkynes[6a] and in the 1,3-dipolar cycloaddition to nitrones.[6b] We anticipated that organogold(III) compounds containing C,N-backbones may be stable and active catalysts in some C−C bond formations and/or C−H bond activations. Pincer C,N- or N,C,N-ligand frameworks are known to confer great stability on this gold high oxidation state,[8] and a large number of Au(III) compounds have been reported, many of them displaying interesting biological and medicinal properties.[9]

We have also reported on the preparation of C,N-cyclopalladated derivatives containing iminophosphorane ligands.[10] Iminophosphoranes, $R_3P{=}NR'$, are a class of compounds that can be readily prepared by different synthetic routes[11] and whose electronic and steric properties may be tuned through appropriate

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(1) Nolan, S. P. *Nature* **2007**, *445*, 496.

(2) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 78096.

(3) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395.

(4) Selected examples: (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Muñoz, M. P.; Adrio, J.; Carretero, J. C.; Echavarren, A. M. *Organometallics* **2005**, *24*, 1293. (c) Ito, H.; Takagi, K.; Miyahara, T.; Sawamura, M. *Org. Lett.* **2005**, *7*, 3001. (d) Fructos, M. R.; Belderrain, T. R.; de Frèmont, P.; Scott, N. M.; Nolan, S. P.; Díaz-Requejo, M. M.; Pérez, P. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 5284. (e) Guan, B.; Xing, D.; Cai, G.; Wan, X.; Yu, N.; Fang, Z.; Yang, L.; Shi, Z. *J. Am. Chem. Soc.* **2005**, *127*, 18004. (f) Lantos, D.; Contel, M.; Larrea, A.; Szabó, D.; Horváth, I. T. *QSAR Comb. Sci.* **2006**, *8*, 719. (g) Hashmi, A. S. K.; Blanco, M. C.; Kurpejovic, E.; Frey, W.; Bats, J. W. *Adv. Synth. Catal*. **2006**, *348*, 709. (h) Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett.* **2006**, *8*, 693. (i) Lantos, D.; Contel, M.; Sanz, S.; Bodor, A.; Horváth, I. T. *J. Organomet. Chem.* **2007**, *692*, 1799.

(5) (a) Hashmi, A. S. K.; Weyrauch, J. P.; Rudolph, M.; Kurpejovic, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 6545. (b) González-Arellano, C.; Corma, A.; Iglesias, M.; Sánchez, F. *Chem. Commun.* **2005**, 1990. (c) González-Arellano, C.; Corma, A.; Iglesia, M.; Sánchez, F. *Chem. Commun.* **2005**, 3451. (d) Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. *Org. Lett.* **2006**, *8*, 325. (e) Lo, V. K.-Y.; Liu, Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2006**, *8*, 1529.

(6) (a) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925, and references therein. (b) Adé, A.; Cerrada, E.; Contel, M.; Laguna, M.; Merino, P.; Tejero, T. *J. Organomet. Chem.* **2004**, *689*, 1788.

(7) Some significant examples: (a) Hashmi, A. S. K.; Schwarz, L.; Choi, J.-H.; Frost, T. M. *Angew. Chem.* **2000**, *112*, 2382; *Angew. Chem., Int. Ed.* **2000**, *39*, 2285. (b) Fürstner, A.; Hannen, P. *Chem. Commun.* **2004**, 2546. (c) Dorsch, D.; Burgdorf, L. T.; Gerike, R.; Beier, N.; Mederski, W. PCT Int. Appl. WO 2005123688 A2, 2005; CAN 144:69837. (d) Kusama, H.; Miyashita, Y.; Tayaka, J.; Iwasawa, N. *Org. Lett.* **2006**, *8*, 289. (e) Nguyen, R.-V.; Yao, X.; Li, C.-J. *Org. Lett.* **2006**, *8*, 2397. (f) Barluenga, J.; Diéguez, A.; Fernández, F.; Rodríguez, F. Fananás, F. J. *Angew. Chem.* **2006**, *118*, 1; *Angew. Chem., Int. Ed.* **2006**, *45*, 2091.

(8) (a) Vicente, J.; Chicote, M. T.; Bermúdez, M. D. *J. Organomet. Chem.* **1984**, *268*, 191. (b) Parish, R. V. *Met.-Based Drugs* **1999**, *6*, 271.

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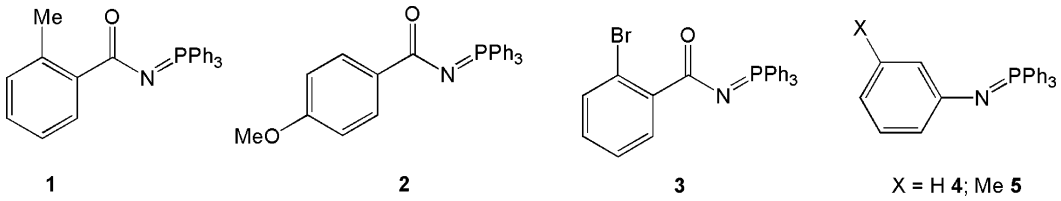
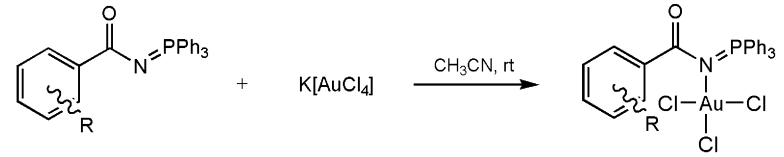
Chart 1. Stabilized (1−3) and Semistabilized (4, 5) Iminophosphorane Ligands Used in This Work



Scheme 1. Formation of Coordination Gold(III) Complexes with Stabilized Iminophosphorane Ligands 1−3



choice of R and R′. Not only does the iminophosphorane C,N-backbone confer a marked stability to the metallic center in d^8 square-planar complexes,[12] but also the PR_3 fragment can be used as a "spectroscopic marker" to follow reactions by ^{31}P NMR. This fact may become significant while studying homogeneous catalytic processes in order to ascertain the nature of the catalytically active species and/or to identify reaction intermediates.

Herein we report on the synthesis and characterization of gold(I) and -(III) coordination and organometallic complexes with the iminophosphorane ligands **1**−**5** (Chart 1).[13]

We have evaluated their catalytic activity (along with the catalytic activity of some other cycloaurated derivatives containing C,N-pincer ligands that had been previously described)[8a,14,15] in the addition reactions of electron-rich arenes to methyl vinyl ketone. Gold(III) chloride and some gold(I) complexes in the presence of silver salts have been used before as catalysts in this type of reactions.[16] We will compare our results to those previously reported to address the possibility of using organogold(III) catalysts as an alternative to $AuCl_3$.

Results and Discussion

1. Synthesis of Coordination and Cycloaurated Gold(III) Complexes. New coordination gold(III) compounds (**6**−**8**) were obtained by reaction of $Na[AuCl_4]$ with stabilized iminophosphorane ligands **1**−**3** at room temperature (Scheme 1).

The compounds are air-stable yellow solids that are almost insoluble in chlorinated solvents but soluble in highly polar solvents such as CH_3CN. It should be stressed that all attempts to prepare cycloaurated derivatives by reaction of ligands **1**−**3** with $Na[AuCl_4]$ or $AuCl_3$ in refluxing acetonitrile or THF or by heating complexes **6**−**8** have failed. Direct auration with gold(III) precursors is a method that is successful only with specific substrates.[17] To our surprise, we found that we could not prepare coordination gold(III) compounds with ligands **4** and **5** by the method described above (Scheme 1). It seems that the reactivity of semistabilized and stabilized (carbonyl-containing) iminophosphorane ligands with Au(III) salts is very different, and these reactions are currently under study in our laboratories.

We prepared cycloaurated gold(III) derivatives with semistabilized ligands by transmetalation with organomercury compounds (reactions of gold(III) salts with organolithium or organomagnesium derivatives are prevented by reduction to metallic gold).[8a] Thus treatment of **4** or **5** with PhLi in Et_2O at room temperature affords the lithiated derivatives **9**[18] and **10**, respectively, in high yields. Transmetalation of **9**[18] or **10** to $HgCl_2$ in Et_2O at room temperature affords organomercurial derivatives **11** and **12**. The reaction of **11** or **12** with $K[AuCl_4]$ in acetone at 50 °C (Scheme 2) gives the organogold(III) compounds $[Au\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}N(C_6H_4X)\text{-}2\}Cl_2]$ (X = H, **13**; X = Me, **14**).[19] Cyclometalated gold(III) complexes **13** and **14** have distinct ^{31}P NMR chemical shifts of δ 65.8 (**12**) and 65.0 (**13**) ppm that are markedly different from the ^{31}P NMR chemical shifts of the coordination gold compounds, δ 41.3 (**6**), 41.7 (**7**), and 42.1 (**8**) ppm (NMR measured in $CDCl_3$, see Experimental Section).

A more interesting and environmentally friendly (greener) synthetic method[20] is the transmetalation of the iminophospho-

(9) Some selected examples: (a) Vicente, J.; Bermúdez, M. D.; Escribano, J. *Organometallics* **1991**, *10*, 3380, and references therein. (b) Cinellu, M. A.; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2865. (c) Buckley, R.; Elsome, A.; Fricker, S.; Henderson, G.; Theobald, B.; Parish, R.; Howe, B.; Kelland, L. *J. Med. Chem.* **1996**, *39*, 5208. (d) Contel, M.; Nobel, D.; Spek, A. L.; van Koten, G. *Organometallics* **2000**, *19*, 3288. (e) Casas, J. S.; Castaño, M. V.; Cifuentes, M. C., García-Monteagudo, J. C.; Sánchez, A.: Sordo, J.; Abram, U. *J. Inorg. Biochem.* **2004**, *98*, 1009. (f) Henderson, W.; Nicholson, B. K.; Wilkins, A. L. *J. Organomet. Chem.* **2005**, *690*, 4971.

(10) Bielsa, R.; Larrea, A.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *Eur. J. Inorg. Chem.* **2005**, 1724.

(11) (a) Staudinger, H.; Meyer, J. J. *Helv. Chim. Acta* **1919**, *2*, 635. (b) Kirsanov, A. V. *Chem. Abstr.* **1951**, *45*, 1503. (c) Kirsanov, A. V. *Zh. Obshch. Khim.* **1952**, *22*, 269. (d) Kirsanov, A. V. *Chem. Abstr.* **1952**, *46*, 11135. (e) Kirsanov, A. V. *Isv. Akad. Nauk SSSR* **1950**, 426. (f) Bittner, S.; Pomerantz, M.; Assaf, Y.; Krief, P.; Xi, S.; Witczak, M. K. *J. Org. Chem* **1988**, *53*, 1.

(12) Alper, H. *J. Organomet. Chem.* ***1977****, 127, 385.*

(13) (a) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemmnicka, B. T.; Smith, C. G., *J. Org. Chem.* **1985**, *50*, 1712. (b) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353.

(14) Bonnardel, P. A.; Parish, R. V.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1996**, 3185.

(15) Constable, E. C.; Leese, T. A. *J. Organomet. Chem.* **1989**, *363*, 419.

(16) (a) Dyker, G.; Muth, E.; Hashmi, A. S. K.; Ding, L. *Adv. Synth. Catal.* **2003**, *345*, 1247. (b) Hashmi, A. S. K.; Grundl, L. *Tetrahedron* **2005**, *61*, 6231. (c) Hashmi, A. S. K.; Schwarz, L.; Rubenbauer, P.; Blanco, M. C. *Adv. Synth. Catal*. **2006**, *348*, 705. (d) Hashmi, A. S. K.; Salathe, R.; Frey, W. *Eur. J. Org. Chem.* **2007**, 1648.

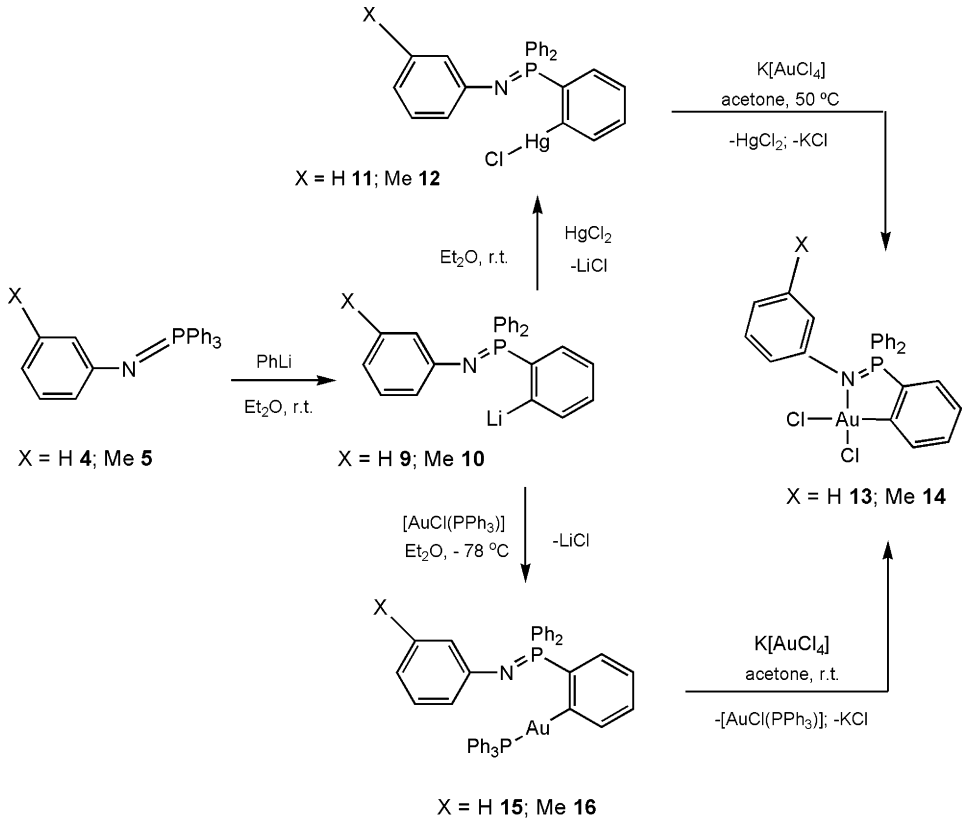
(17) Recent example: Zhu, Y.; Cameron, B. R.; Skerli, R. T. *J. Organomet. Chem.* **2003**, *677*, 57, and references therein.

(18) Stuckwish, C. G. *J. Org. Chem.* **1976**, *41*, 1173.

(19) Aguilar, D.; Contel, M.; Navarro, R.; Urriolabeitia, E. P. XXII International Conference on Organometallic Chemistry (July 2006, Zaragoza, Spain). Book of abstracts. Poster presentation included X-ray crystal structure (with selected angles and bond distances) of compound **13**.

(20) Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. *Organometallics* **2002**, *21*, 4556.

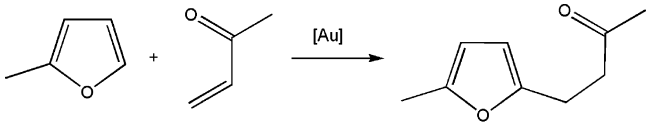
Scheme 2. Formation of Lithiated Organomercury and Organogold(I) and -(III) Complexes with Semistabilized Iminophosphorane Ligands 4 and 5



rane fragment from the Au(I) derivatives **15** and **16** to the Au(III) salt $K[AuCl_4]$ (Scheme 2) to afford the cyclometalated compounds **13** and **14** (see Experimental Section). The new gold(I) compounds **15** and **16** can be obtained as air-stable white solids by reaction of the lithiated derivatives **9**[18] and **10** with $AuCl(PPh_3)$ in Et_2O at −78 °C in high yields. While preparing this article for submission, a report on the synthesis and characterization of compounds **11** and **13** appeared.[21] The authors reported on the determination of the crystal structure of **13** by X-ray studies (we had also independently determined the structure of this compound).[19] This study showed that the Au(III) center is in a square-planar environment (to +0.05 Å), attached to two Cl ligands and to the N and an *ortho*-C atom of the $Ph_3P{=}NPh$ ligand. The five-membered metallocyclic ring generated (significantly puckered) affords a relatively rigid "bite" angle N−Au−C (84.9(2)°). As expected, the higher *trans* influence of C versus N is reflected in the longer Au−Cl(1) distance compared to Au−Cl(2).[21] While the rigid C,N-backbone affords a stable gold(III) compound, the presence of labile Cl groups will allow the preparation of new cycloaurated complexes (with different steric and electronic properties) by ligand exchange reactions. Details on the synthesis and characterization of all the new lithiated organomercury and gold complexes are provided in the Experimental Section.

2. Catalytic Studies. We were interested in testing some of these complexes as catalysts in C−C bond forming processes that are believed to proceed under C−H activation. The processes chosen were the reactions of α,β-unsaturated ketones with furans and electron-rich arenes. Dyker and Hashmi showed[16a] that $AuCl_3$ nicely catalyzes the addition of 2-methylfuran **17** to methyl vinyl ketone (MVK) **18** (Scheme 3).

Scheme 3. Gold-Catalyzed Reaction of 2-Methylfuran (17) and MVK (18)



17 **18** **19**

The amount of catalyst required is 1 mol %, and the reaction proceeds in 40 min (80−90% yield, Table 1). Some gold(I) complexes such as $[AuCl(PEt_3)]$ and [AuCl(tht)] (tht = tetrahydrothiophene) that were initially inactive in the reaction of **17** with MVK, after the addition of 1 equiv of $AgBF_4$, became active and afforded high conversions after 24 h (Table 1, entries 2 and 3). This and the fact that the addition of $AuCl_3$ (1 equiv) to a solution of 1 equiv of 2-methylfuran (**17**) modifies the signals in the ^1H NMR spectrum led to an initial working hypothesis that an electrophilic C−H activation might be the crucial step. Such a mechanism is supported by a report on the direct auration of thiophene and furan with $[Au(PPh_3)]^+$ fragments.[22] Several experiments with various electron-rich arenes were tested for the addition reactions to MVK (**18**) as a model compound. Some acids (such as $H[AuCl_4]$, HCl, or HBF_4) were also evaluated. From the different results, the authors pointed out that $AuCl_3$ in the presence of water may form a Brönsted acid with an aurate counterion that might be the active species as well. $[AuCl_4]^-$ anions catalyze the addition of nucleophiles to multiple bonds[6a] as well as some 1−3-dipolar cycloaddition reactions.[6b] However, the differences in selectivity observed with Brönsted acids and gold catalysts can be

(21) Brown, S. D. J.; Henderson, W.; Kilpin, K. J.; Nicholson, B. K. *Inorg. Chim. Acta* **2007**, *360*, 1310.

(22) Porter, K. A.; Schier, A.; Schmidbaur, H. *Organometallics* **2003**, *22*, 4922.

Table 1. Results of the Addition Reactions of Methyl Vinyl Ketone (MKV) 18 to 2-Methylfuran (17) at Room Temperature[a]

entry	catalyst (mol %)	silver salt (mol %)	time	yield (%)[c]
1	$AuCl_3$ (1)[b]	0	40 min	80−90
2	[AuCl(PEt_3)] (1)[b]	$AgBF_4$ (1)	24 h	80
3	[AuCl(tht)] (1)[b]	$AgBF_4$ (1)	24 h	90
4	**20** (1)	0	18 h	0
5	**20** (1)	AgOTf (2.2)	6 h	50
6	**20** (1)	AgOTf (2.2)	18 h	83
7	**21** (1)	0	18 h	0
8	**21** (1)	AgOTf (2.2)	6 h	65
9	**21** (1)	AgOTf (2.2)	18 h	80
10	**13** (1)	0	18 h	45
11	**13** (1)	0	6 h	35
12	**13** (2)	0	6 h	43
13	**13** (1)	AgOTf (2.2)	18 h	85
14	**13** (1)	AgOTf (2.2)	6 h	75
15	**13** (1)	AgOTf (1.1)	6 h	78
16	**14** (1)	AgOTf (2.2)	18 h	80
17	**14** (1)	AgOTf (2.2)	6 h	72
18	**14** (1)	0	6 h	38
19	**13** (1)	$AgBF_4$ (2.2)	18 h	92
20		AgOTf (2.2)	18 h	0
21		$AgBF_4$ (2.2)	18 h	0
22	**6**		18 h	0
23	**6**	AgOTf (2.2)	18 h	65[d]

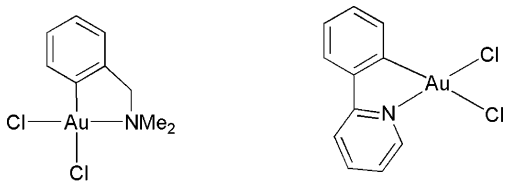
[a] Reaction conditions: the reactions were performed at 25 °C in a Kontex tube using 2 mmol of **17**, 2 mmol of **18**, 0.02 mmol of gold complex, and 0.044 mmol (or 0.022 mmol) of silver salt in 5 mL of CH_3CN as solvent. [b]Reference 16. [c]Yields were obtained on isolated product. Details on procedures and workup of the reaction mixture are given in the Supporting Information. [d]Abundant decomposition to metallic gold observed.

explained either by specific acid catalysis or by direct participation of the metal. They concluded that although these experiments do not rule out a C−H activation of the aromatic system by the gold catalyst, the interpretation of the results with acidic metal catalysts has to be considered in a careful way. More recently Hashmi et al. have reported on similar hydroarylation reactions (carbonyl compounds with furans, electron-rich arenes, and even pyrroles) catalyzed by gold(III) salts.[16b−d] Shi and He reported analogous reactions of electron-rich arenes with acceptor-susbtituted alkenes and alkynes (catalyzed by *in situ* generated "$Au(Otf)_3$" species).[23] In all these reactions it is not clear whether the gold activates the double or triple C−C bonds or if there is a C−H activation of the electron-rich arenes. More recent work of Shi and He (unusual regioselectivity in the gold-catalyzed reaction of epoxides and arenes[24a] and a report on the gold-catalyzed alkylation of primary sulfonate esters with arenes[24b]) has pointed out a contribution of arylgold species and thus electrophilic C−H activation. Ascertaining the nature of the gold species involved in these reactions has become, therefore, a matter of increasing interest. We anticipated that gold(III) complexes with C,N-backbones may be stable catalysts in the above-described reactions while allowing the identification of some gold intermediates by NMR spectroscopy.

We tested two organogold(III) complexes with C,N-pincer ligands (**20**, **21**; Chart 2) whose synthesis had been previously addressed[8a,14,15] in the reaction of **17** and **18** (Table 1). We observed that although the compounds were completely inactive, the addition of 2 equiv of a silver salt (AgOTf, OTf = $OSO_2CF_3^-$) generates a catalytically active species, as product **19** was obtained in yields of 83% (**20**) and 80% (**21**) after 18 h (entries 6 and 9).

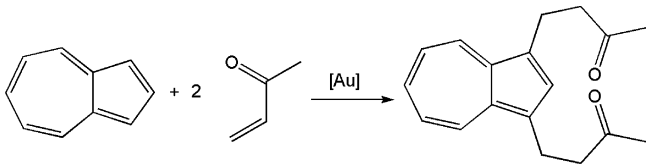
(23) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669.
(24) (a) Shi, Z.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 5964. (b) Shi, Z.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 13596.

Chart 2. Previously Reported Organometallic Gold(III) Compounds with C,N-Pincer Ligands Used as Catalysts in the Gold-Catalyzed Addition Reaction of 2-Methylfuran (17) and MKV (18)



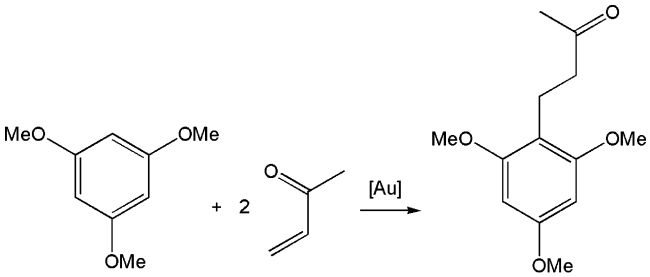
20 (references 8a,14) **21** (reference 15)

Scheme 4. Gold-Catalyzed Reaction of Azulene (22) and MVK (18)



22 **18** **23**

Scheme 5. Gold-Catalyzed Reaction of 1,3,5-Trimethoxybenzene (24) and MVK (18) to Afford the Monoaddition Product 25



24 **18** **25**

These results encouraged us to test the new cycloaurated compounds containing iminophosphorane ligands (Table 1). Compounds [Au{κ^2-C,N-$C_6H_4(PPh_2{=}N(C_6H_4X))$-2}$Cl_2$] (X = H, **13**; X = Me-3, **14**) were active in the presence of 2.2 equiv of AgOTf or $AgBF_4$ in the reaction between 2-methylfuran and MVK (eq 3, entries 13, 14, 16, 17, 19). We demonstrated that both $AgBF_4$ and AgOTf are completely inactive in these addition reactions (entries 20 and 21) and that high yields (75 to 85%) could be obtained with 1 mol % of gold catalyst after 18 (entries 13 and 16) or even 6 h (entries 14 and 17). The reaction affords similar yields when performed in the presence of a substoichiometric amount of silver salt (entry 15). Even in the absence of silver salts both compounds displayed catalytic activity, although the yields of product were lower (entries 10−12 and 18). We evaluated a coordination gold(III) compound (derivative **6**). In the absence of silver salts the derivative was totally inactive (entry 22). By addition of 2 equiv of AgOtf we got a conversion of 65% (entry 23). We observed, however, that the compound decomposes to metallic gold during the catalytic process (as opposed to the reactions with cycloaurated compounds). The C,N-backbone is thus conferring stability to the Au(III) center, as it will be described later on.

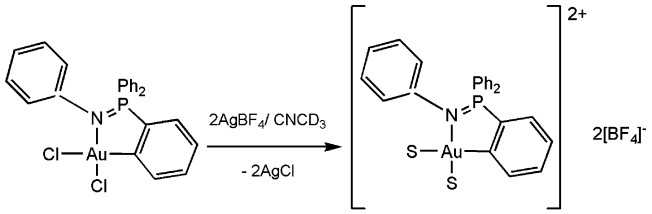
Other addition reactions of electron-rich arenes and MVK were also evaluated (Schemes 4 and 5). We chose acid-sensitive azulene (**22**) and 1,3,5-trimethoxybenzene (**24**), which had given the double addition product (**23**) and the monoaddition product (**25**) with $AuCl_3$ as catalyst with tremendous selectivity.

Table 2. Results of the Addition Reactions of Methyl Vinyl Ketone (MKV) 18 to Electronrich Arenes Ar−H (22 and 24) at Room Temperature[a]

entry	arene	catalyst (mol %)	silver salt (mol %)	time	yield (%)[c]
1	**22**	$AuCl_3$ (1)[b]	0	2 min−3 d	50−55
2	**22**	**13** (1.5)	AgOTf (3.3)	24 h	88
2	**24**	$AuCl_3$ (1)[b]	0	24 h	99
3	**24**	**13** (1.5)	AgOTf (3.3)	24 h	73
4	**22**	**14** (1.5)	AgOTf (3.3)	24 h	80
5	**24**	**14** (1.5)	AgOTf (3.3)	24 h	71

[a] Reaction conditions: the reactions were performed at 25 °C in a Kontex tube using 2 mmol of **17**, 2 mmol of **18**, 0.03 mmol of gold complex, and 0.066 mmol of silver salt in 5 mL of CH_3CN as solvent. [b]Reference 16. [c]Yields were obtained on isolated product. Details on procedures and workup of the reaction mixture are given in the Supporting Information.

Scheme 6. Formation of New Cationic Solvated Cycloaurated Species 26 (NMR Experiment Conditions)



13 **26**

Cycloaurated compounds **13** and **14** were efficient catalysts in the presence of silver salts (Table 2). It is remarkable that with $AuCl_3$ compound **23** could be obtained in only a 55% yield after 3 days (Table 2, entry 1), whereas for **13** or **14** yields of 90% can be obtained after 24 h (entries 2 and 4). In this case the more acidic character of $AuCl_3$ versus the less acidic character of **13** or **14** (even less so by removal of the Cl ligands) may be responsible for a lower yield. This is an indication that electronic and/or steric modifications of the coordination environment around the gold(III) center may result in an improved catalytic performance. The organogold(III) compounds are a better alternative to $AuCl_3$ for acidic-sensitive substrates.

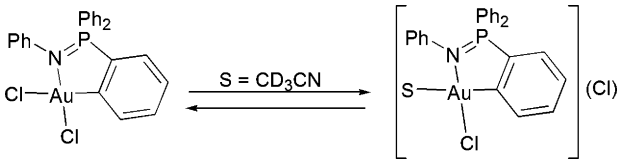
As previously reported by Dyker and Hashmi,[16a] we found tremendous selectivity in the reaction of **24** with MVK, and the monoaddition product **25** was the only product obtained. However, the yield obtained after 24 h (73%, entry 4) was lower than that obtained with $AuCl_3$ (99%, entry 3).

In order to prove that the only effect that the addition of silver salts had on these C,N-organometallic complexes was the formation of new cationic species by removal of the chloride ligands, some NMR experiments were carried out (Scheme 6).

New cationic solvated species **26** were spectroscopically identified (although they could not be isolated; see Experimental Section). The cationic character of these species can be inferred from the downfield shift of the ^{31}P signal (from 65.6 ppm in **13** to 66.9 ppm in **26**). Species **26** is stable in CD_3CN solution at 5 °C during at least 30 h and more than 15 h at room temperature. These observations indicate that, in the absence of other substrates, the catalytically active species is stable under reaction conditions (room temperature, polar solvent).

We tested the addition of 2-methylfuran (**17**) to these cationic species (molar ratio 1:1) at low and room temperatures (NMR experiments). We could not observe, however, a considerable change in the δ of the signals assigned to 2-methylfuran in the ^1H NMR spectrum or to those assigned to the solvated species. Similar results were obtained while adding MVK (molar ratio 1:1) to a solution of **26** in CD_3CN, since no changes could be observed in the shape and positions of the NMR signals (^1H and ^{31}P NMR spectra) of the organogold solvate and/or those assigned to the organic substrates.

Scheme 7. Equilibrium of Neutral and Cationic Cycloaurated Species in a Polar Solvent



The addition of MVK (**18**) and **17** to a CD_3CN solution of **26** (molar ratio 15:15:1) gives product **18** over time (peaks that can be assigned to product **18** appeared almost immediately after mixing the reagents in the NMR tube; see Supporting Information) without apparent change in the ^{31}P and ^1H NMR chemical shifts for **26**. This fact suggests that the limiting step of the catalytic cycle is the coordination of the substrates to the metallic center and that any other further steps should be very fast. While the catalysis is taking place, a little decomposition to metallic gold is observed for longer reaction periods (18−24 h), but most of the original catalyst is still present at the end of the reaction, as demonstrated by ^{31}P NMR experiments (see Figure 1c in Supporting Information). Thus, the gold(III) cationic solvated species behaves as an active and stable catalyst. Although we have not been able to identify a reaction intermediate to demonstrate that the reaction takes place by electrophilic C−H activation, in the case of our cycloaurated catalytic systems there is little room for thinking in acid catalysis mechanisms (via formation of $[AuCl_n(OH)_x]^-$ anions $\{n + x = 4\}$ and H^+ as counterion). The cycloaurated complexes described here are much less acidic than $AuCl_3$. Although the C−H activation of ketones by organogold(III) complexes containing C,N-pincer ligands has been documented,[25] we have not seen the formation of ketonylgold(III) complexes in the reaction of **26** with MVK (the reactivity of **26** and related species with akynes and alkenes is currently being investigated in our laboratories). An interpretation of Hashmi and Dyker's and our own results may be that both Au(III) and Au(I) cationic species are able to catalyze these additions by electrophilic C−H activation of the furan or arenes. In the case of $AuCl_3$ electrophilic C−H activation as well as specific acid catalysis may be responsible for the high catalytic activity observed. Moreover, with acidic-sensitive substrates the catalytic activity with $AuCl_3$ is moderate, whereas the cycloaurated gold(III) derivatives display a higher catalytic performance.

As pointed out before, neutral complexes **13** and **14** are able to catalyze this reaction in the absence of silver salts, but they afford lower yields. The formation of a cationic species, by "*in situ*" dissociation of a chloride ligand, can be easily inferred taking into account the high polarity of the solvent (MeCN), the zwitterionic nature of the cycloaurated ligand, and the high *trans* effect of the arylic carbon atom. This transient cationic species, in equilibrium with its neutral form (Scheme 7), could be responsible for the catalytic activity observed.

The differences in catalytic performance, in the absence of silver salts, between cycloaurated complex **20** or **21** and the orthometalated derivatives **13** and **14** is quite surprising. Subtle differences in the charge distribution over the cycloaurated ring containing the PPh_3 fragment (in the case of the iminophosphorane ligands) may be related to the different behavior observed. While cycloaurated compounds generate stable cat-

(25) Vicente, J.; Bermúdez, M. D.; Carrillo, M.-P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1992**, 1975.

ionic complexes that may be the active catalytic species, coordination compounds also generate cationic species (by removal of Cl^- anions with silver salts) that display moderate catalytic performance. The main difference between the organogold and coordination gold(III) complexes is that the latter decompose to metallic gold under reaction conditions. The C,N-backbone is thus an important tool to stabilize the gold(III) centers and to generate stable and active catalytic species.

Conclusion

In conclusion, we have prepared new cycloaurated gold(III) compounds with iminophosphorane ligands that are efficient catalysts in the addition of 2-methylfuran and electron-rich arenes to methyl vinyl ketone in the presence of silver salts. From NMR experiments it can be concluded that cyclometalated gold(III) cationic derivatives might be the catalytically active species in these addition reactions by, more plausibly, electrophilic gold C−H activation of 2-methylfuran or the electron-rich arenes as a first step. These promising preliminary results may be the basis for future studies on organogold(III) derivatives as a replacement for $AuCl_3$ in some catalytic reactions by tuning the electronic and steric properties on the iminophosphorane ligand or by ligand exchange reactions of the labile Cl on these molecules.

Experimental Section

Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyzer. Infrared spectra (4000−200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ or CD_3CN or solutions at 25 °C (other temperatures were specified) on Bruker ARX-300, AvanceII-300, Avance-400, and Avance-500 spectrometers (δ, ppm; J, Hz); ^1H and $^{13}C\{^1H\}$ NMR were referenced using the solvent signal as internal standard, while $^{31}P\{^1H\}$ NMR was externally referenced to H_3PO_4 (85%). The mass spectra (MALDI+) were recorded from CH_2Cl_2 solutions on a MALDI-TOF Microflex (Bruker) spectrometer (DCTB as matrix). Compound **9** was prepared as previously reported.[18] Complexes **11** and **13** have been recently reported,[21] and experimental details will not be included here.

1. Synthesis of the New Compounds. 1a. Synthesis and Characterization of the Gold(III) Coordination Compounds (6−8) with Stabilized Iminophosphorane Ligands (1−3). [$AuCl_3${N(=PPh$_3$)C(O)C$_6$H$_4$Me-2}], 6. To a solution of **1** (0.100 g, 0.25 mmol) in CH_3CN (20 mL) was added $Na[AuCl_4]$ (0.101 g, 0.25 mmol). The resulting yellow reaction mixture was stirred at room temperature during 24 h. The solvent was removed under vacuum, and the oily residue obtained was dissolved in CH_2Cl_2 (10 mL) and filtered through a Celite pad. The clear yellow solution was evaporated to dryness and the residue treated with a mixture of Et_2O and *n*-hexane (3:1) to give **6** as a yellow solid, which was filtered and dried under vacuum. Yield: 0.146 g, 0.21 mmol, 83.6%. Complex **6** was crystallized from a CH_2Cl_2/*n*-hexane mixture, giving microcrystals of **6**·$1.5CH_2Cl_2$, which were subsequently used for analytic purposes. Anal. Calcd for $[C_{26}H_{22}AuCl_3NOP]\cdot 1.5CH_2Cl_2$ (826.16): C, 39.98; H, 3.05; N, 1.69. Found: C, 40.32; H, 3.02; N, 1.92. MS (FAB+): 592 (5%) $[M - Cl_3]^+$. IR: ν 1644 (ν_{CO}), 1298 (ν_{PN}) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.4. ^1H NMR ($CDCl_3$): δ 2.43 (s, 3H, Me),7.16 (d, 1H, H_3, $^3J_{H3-4}$ = 7.7 Hz), 7.26 (td, 2H, $H_{4,5}$,$^3J_{H4-3,5}$ = 7.5 Hz, $^4J_{H4-H6}$ = 1.5 Hz), 7.57−7.61 (m, 6H, H_m-PPh_3), 7.68−7.72 (m, 3H H_p-PPh_3), 7.92−7.97 (m, 6H, H_o-PPh_3), 7.99 (dd, 1H, H_6, $^3J_{H6-5}$ = 7.4 Hz, $^4J_{H6-H4}$ = 1.4 Hz).

[$AuCl_3${N(=PPh$_3$)C(O)C$_6$H$_4$OMe-4}], 7. Complex **7** was prepared following the same method as that reported for **6**. **2** (0.200 g, 0.48 mmol) reacted with $Na[AuCl_4]$ (0.193 g, 0.48 mmol) in CH_3CN (20 mL) to give **7** as a yellow solid. Yield: 0.221 g, 0.31 mmol, 63.6%. Complex **7** was crystallized from a CH_2Cl_2/Et_2O mixture, giving crystals of **7**·$0.8CH_2Cl_2$, which were subsequently used for analytic purposes. Anal. Calcd for $[C_{26}H_{22}AuCl_3NO_2P]\cdot 0.8CH_2Cl_2$ (782.71): C, 41.12; H, 3.04; N, 1.79. Found: C, 40.93; H, 3.15; N, 2.01. MS (FAB+): 608 (15%) $[M - Cl_3]^+$. IR: ν 1625 (ν_{CO}), 1269 (ν_{PN}) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.7. ^1H NMR 300 MHz ($CDCl_3$): δ 3.86 (s, 3H, OMe),7.98 (d, 2H, $H_{3,5}$, $^3J_{H3-2}$ = Hz), 7.62−7.67 (m, 6H, H_m-PPh_3), 7.73−7.80 (m, 3H H_p-PPh_3), 7.93−8.00 (m, 6H, H_o-PPh_3), 8.21 (d, 2H, $H_{2,6}$, $^3J_{H2-3}$ = Hz).

[$AuCl_3${N(=PPh$_3$)C(O)C$_6$H$_4$Br-2}], 8. Complex **8** was prepared following the same method as that reported for **6**. **3** (0.200 g, 0.43 mmol) was reacted with $Na[AuCl_4]$ (0.173 g, 0.43 mmol) in CH_3CN (20 mL) to give **8** as a yellow solid. Yield: 0.195 g, 0.25 mmol, 59.0%. Complex **8** was crystallized from a CH_2Cl_2/Et_2O mixture, giving crystals of **8**·CH_2Cl_2, which were subsequently used for analytic purposes. Anal. Calcd for $[C_{25}H_{19}AuBrCl_3NO_2P]\cdot CH_2Cl_2$ (848.56): C, 36.80; H, 2.50; N, 1.65. Found: C, 36.50; H, 2.90; N, 2.01. MS (FAB+): 657 (10%) $[M - Cl_3]^+$. IR: ν 1641 (ν_{CO}), 1306 (ν_{PN}) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.2. ^1H NMR 300 MHz ($CDCl_3$): δ 7.08 (td, 1H, H_4, $^3J_{H4-5,3}$ = 7.6 Hz, $^4J_{H4-6}$ = 1.8 Hz), 7.20 (td, 1H, H_5, $^3J_{H5-4,6}$ = 7.5 Hz, $^4J_{H5-3}$ = 1.1 Hz), 7.39−7.44 (m, 6H, H_m-PPh_3), 7.48−7.52 (m, 4H, H_3 + H_p-PPh_3), 7.75−7.81 (m, 7H, H_6 + H_o-PPh_3).

1b. Synthesis and Characterization of the New Organomercury (12), Organogold(III) (14), and Organogold(I) (15, 16) Derivatives with the Semistabilized Iminophosphorane Ligands (4, 5). [Hg{C$_6$H$_4$(PPh$_2$=N(C$_6$H$_4$Me))-2}Cl], 12. To a solution of $[Li\{C_6H_4(PPh_2{=}N(C_6H_4Me))\text{-}2\}]_n$ (**10**) (generated *in situ* by mixing 2.72 mmol, 1.0 g, of **5** and 2.1 mL, 3.8 mmol, of PhLi 1.8 M) in dry Et_2O at room temperature under N_2 was added $HgCl_2$ (0.492 g, 1.81 mmol). The reaction mixture was stirred for 5 h. The Et_2O was completely removed, and the white residue was extracted with CH_2Cl_2. The resulting colorless solution was filtered through Celite and the solvent subsequently removed under vacuum to yield an oily product that gave **12** as a white solid compound after treatment with 15 mL of *n*-hexane. Yield: 0.790 g, 1.31 mmol, 72.3%. $C_{24}H_{19}NPHgCl$ (MW = 602.50 g/mol). MS(MALDI+) [*m*/*z*, (%)]: 603 $[M]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.6. ^1H NMR ($CDCl_3$): δ 1.74 (s, 3H, Me), 6.31−6.32 (m, 2H), 6.53 (s, 1H), 6.64 (t, 1H, $J_{H5-H4,6}$ = 7.7 Hz), 7.19 (tdd, 1H, $^4J_{H4'-P}$ = 4.0 Hz, $^4J_{H4'-H6'}$ = 1.3 Hz, $^3J_{H4'-H3',5'}$ = 7.6 Hz), 7.27−7.31 (m, 4H, H_m-PPh_2), 7.38−7.49 (m, 4H, $H_{5'}$ + $H_{3'}$ + H_p-PPh_2), 7.67−7.71 (m, 4H, H_p-PPh_2), 7.77 (dd, 1H, $H_{6'}$, $^4J_{H6'-H4'}$ = 1.5 Hz, $^3J_{H6'-H5'}$ = 7.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.07 (Me), 117.94 (s, C_4, NPh), 119.47 (d, C_6, NPh, $^3J_{PC}$ = 14.1), 125.65 (d, C_2, NPh, $^3J_{PC}$ = 19.9), 125.90 (d, $C_{4'}$, C_6H_4, $^3J_{PC}$ = 14.9), 127.61 (s, C_5, NPh), 128.41 (d, C_m, PPh_2, $^3J_{PC}$ = 11.4), 130.19 (d, $C_{5'}$, C_6H_4, $^4J_{PC}$ = 3.4), 131.23 (d, C_p, PPh_2, $^4J_{PC}$ = 2.7), 131.47 (d, C_{ipso}, PPh_2, $^1J_{PC}$ = 84.2), 132.73 (d, $C_{3'}$, C_6H_4, $^2J_{PC}$ = 19.2), 133.00 (d, C_o, PPh_2, $^2J_{PC}$ = 9.4), 137.58 (d, C_3, NPh, $^4J_{PC}$ = 2.2), 138.79 (d, $C_{2'}$, C_6H_4, $^1J_{PC}$ = 131.2), 139.56 (d, $C_{6'}$, C_6H_4, $^3J_{PC}$ = 15.7), 150.46 (d, C_1, NPh, $^2J_{PC}$ = 3.0), 174.23 (d, $C_{1'}$, C_6H_4, $^2J_{PC}$ = 18.3).

[Au{κ^2-C,N-C$_6$H$_4$(PPh$_2$=N(C$_6$H$_4$Me))-2}Cl$_2$], 14. To a solution of **12** (0.200 g, 0.33 mmol) in 20 mL of acetone was added $K[AuCl_4]$ (0.125 g, 0.33 mmol). The resulting yellow solution was stirred at 40 °C during 1 h. The acetone was completely removed and the orange residue extracted with CH_2Cl_2 to afford an oily compound that gave **14** as a yellow solid after treatment with *n*-hexane/Et_2O (1:2). Yield: 0.125 g, 0.20 mmol, 60%. Anal. Calcd for $C_{25}H_{21}AuCl_2NP$ (634.05): C, 47.36; H, 3.34; N, 2.21. Found: C, 46.90; H, 3.05; N, 2.13. MS(MALDI+) [*m*/*z*, (%)]: 634.33 $[M]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.0. ^1H NMR ($CDCl_3$): δ 2.13 (s, 3H,

Me), 6.77 (s, 1H, H_2, NAr), 6.82−6.85 (m, 2H, H_4+H_6, NAr), 6.96 (t, 1H, H_5, NAr, $^3J_{HH} = 7.7$), 7.13 (dd, 1H, $H_{3'}$, C_6H_4, $^4J_{HH} = 1.5$, $^3J_{HH} = 7.5$), 7.36 (td, 1H, $H_{4'}$, C_6H_4, $^4J_{HH} = 0.6$, $^3J_{HH} = 7.4$), 7.50 (td, 1H, $H_{5'}$, C_6H_4), 7.59 (t, 4H, H_m, PPh_2), 7.70−7.77 (m, 6H, H_p+H_o, PPh_2), 8.38 (dd, 1H, $H_{6'}$, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.16 (Me), 124.56 (d, C_i, PPh_2, $^1J_{PC} = 93.9$), 126.61 (d, C_6, NAr, $^3J_{PC} = 5.7$), 127.14 (d, C_4, NAr, $^5J_{PC} = 2.2$), 128.03 (d, C_5, NAr, $^4J_{PC} = 1.7$), 128.39 (d, $C_{4'}$, C_6H_4, $^3J_{PC} = 13.1$), 129.53 (d, C_m, PPh_2, $^3J_{PC} = 12.7$), 129.74 (d, $C_{3'}$, C_6H_4, $^2J_{PC} = 18.3$), 130.63 (d, C_2,NAr, $^4J_{PC} = 5.9$), 133.44 (d, C_o, PPh_2, $^2J_{PC} = 10.7$), 133.56 ($C_{6'}$, C_6H_4, $^3J_{PC} = 14.4$), 133.79 (d, $C_{5'}$, C_6H_4, $^4J_{PC} = 2.9$), 134.47 (d, C_p, PPh_2, $^4J_{PC} = 2.9$), 134.81 (d, $C_{2'}$, C_6H_4, $^1J_{PC} = 126.9$), 138.08 (d, C_3, NAr, $^2J_{PC} = 1.6$), 142.32 (d, C_1, NAr, $^2J_{PC} = 2.5$), 149.19 (d, C_1, C_6H_4, $^2J_{PC} = 15.6$).

[Au{C_6H_4(PPh_2=N(C_6H_5))-2}(PPh_3)], 15. The lithium derivative **9**[19] was generated by reaction of **4** (0.600 g, 1.70 mmol) with 1.8 M PhLi (1.3 mL, 2.38 mmol) in 10 mL of dry Et_2O during 30 min at room temperature. This solution was subsequently cooled at −78 °C, and [AuCl(PPh_3)] was added (0.646 g, 1.31 mmol). The reaction mixture was stirred at −78 °C during 1 h and a further 2 h at room temperature. After complete removal of the Et_2O, the residue was extracted with CH_2Cl_2. The solvent was completely removed under vacuum to afford a crude material that can be crystallized from a CH_2Cl_2/*n*-hexane mixture (15 mL) to yield **15** as a microcrystalline white solid. The amount of crystallization solvent was inferred from the ^1H NMR spectrum (by integration). Yield: 0.763 g, 0.94 mmol, 71.0%. Anal. Calcd for [$C_{42}H_{34}AuNP_2$]·0.75CH_2Cl_2 (875.34): C, 58.65; H, 4.09; N, 1.60. Found: C, 59.20; H, 4.61; N, 1.92. MS(MALDI+) [*m*/*z*, (%)]: 812 $[M]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.8 ($NPPh_2$), 42.2 (Au−PPh_3). ^1H NMR ($CDCl_3$): δ 6.57 (t, 1H, H_p, NPh, $^3J_{HH} = 7.2$), 6.91 (d, 2H, H_o, NPh, $^3J_{HH} = 8.1$), 6.97 (t, 2H, H_m, NPh), 7.13 (tdd, 1H, H_4, C_6H_4, $^4J_{PH} = 3.7$, $^4J_{HH} = 1.2$, $^3J_{HH} = 7.5$), 7.21−7.26 (m, 4H, H_m, PPh_2), 7.33−7.38 (m, 9H, H_m + H_p, $AuPPh_3$), 7.40−7.54 (m, 10H, H_3 + H_5 + H_p(PPh_2) + H_o($AuPPh_3$)), 7.75−7.80 (m, 4H, H_o, PPh_2), 7.83 (d, 1H, H_6, C_6H_4, $^3J_{HH} = 7.8$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 116.04 (C_p, NPh), 123.50 (d, C_o, NPh, $^3J_{PC} = 18.1$), 124.80 (d, C_4, C_6H_4, $^3J_{PC} = 13.1$), 127.97 (d, C_m, PPh_2, $^3J_{PC} = 11.7$), 128.32 (d, C_m, NPh, $^4J_{PC} = 1.6$), 128.72 (d, C_m, PPh_3, $^3J_{PC} = 10.8$), 130.59 (d, C_p, PPh_2, $^4J_{PC} = 2.6$), 130.77 (d, C_p, PPh_3, $^4J_{PC} = 2.2$), 130.97 (d, C_i, PPh_2, $^1J_{PC} = 57.4$), 133.02 (d, C_o, PPh_2, $^2J_{PC} = 8.8$), 133.69 (d, C_i, PPh_3, $^1J_{PC} = 99.8$), 134.47 (d, C_o, PPh_3, $^2J_{PC} = 13.9$), 140.66 (d, C_6, C_6H_4, $^3J_{PC} = 19.0$), 152.73 (d, C_i, NPh, $^2J_{PC} = 2.7$), 179.31 (d, C_1, C_6H_4, $^2J_{PC} = 21.7$). Signals due to C_2, C_3, and C_5 were not observed.

[Au{C_6H_4(PPh_2=N(C_6H_4Me))-2}(PPh_3)], 16. 16 was obtained following the same experimental procedure as that described for **15** above. **5** (0.338 g, 0.91 mmol) was reacted with LiPh (0.71 mL, 1.8 M, 1.29 mmol) for 30 min at 25 °C in Et_2O (15 mL) to afford **10**, which was subsequently reacted *in situ*. The suspension of **10** (0.91 mmol) in Et_2O was reacted with $ClAuPPh_3$ (0.35 g, 0.71 mmol) at −78 °C for 1 h. The stirring was maintained during 2 h while the temperature rose slowly to 25 °C. The solvent was removed under vacuum, and the yellow residue obtained was extracted with two portions of CH_2Cl_2 (2 × 10 mL). The mixture was filtered through Celite, and the resulting clear solution evaporated to dryness. Crystallization of the residue from CH_2Cl_2/Et_2O gave **16**·0.5CH_2Cl_2 as yellow crystals. Yield: 0.35 g (60.6%). Anal. Calcd for [$C_{43}H_{36}AuNP_2$]·0.5CH_2Cl_2 (825.7): C, 59.51; H, 4.18; N, 1.61. Found: C, 59.42; H, 4.90; N, 1.88. MS (MALDI +) [*m*/*z*]: 826 $[M]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.0 (d, $NPPh_2$, $^4J_{PP} = 8.3$), 42.1 (d, $AuPPh_3$). ^1H NMR ($CDCl_3$): δ 1.94 (s, 3H, Me), 6.30 (d, 1H, H_4, NPh, $^3J_{HH} = 7.4$), 6.41 (d, 1H, H_6, NPh, $^3J_{HH} = 7.9$), 6.51 (s, 1H, H_2, NPh), 6.69 (t, 1H, H_5, NPh, $^3J_{HH} = 7.7$), 7.03 (tdd, 1H, $H_{4'}$, C_6H_4, $^4J_{PH} = 3.6$, $^4J_{HH} = 1.6$, ^3J= 7.4), 7.13 (m, 4H, H_m, PPh_2), 7.19 (m, 6H, H_m, PPh_3), 7.21−7.30 (m, 10H, $H_{5'}$ (C_6H_4) + H_p + H_o (PPh_3)), 7.35 (m, 2H, H_p, PPh_2), 7.44 (m, 1H, $H_{3'}$, C_6H_4), 7.68 (m, 4H, H_o, PPh_2), 7.73 (m, 1H, $H_{6'}$, C_6H_4,). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.45 (Me), 116.97 (C_4, NPh), 119.89 (d, C_6, NPh, $^3J_{PC} = 16.0$), 124.74 (d, $C_{4'}$, C_6H_4, $^3J_{PC} = 12.8$), 124.80 (d, C_2, NPh, $^3J_{PC} = 20.4$), 127.89 (d, C_m, PPh_2, $^3J_{PC} = 11.5$), 128.65 (overlapped C_5, NPh + C_m, PPh_3), 129.31 (dd, $C_{5'}$, C_6H_4, $^4J_{PC} = 3.6$, $^4J_{PC} = 4.9$), 130.51 (d, C_p, PPh_2, $^4J_{PC} = 2.6$), 130.72 (d, C_p, PPh_3, $^4J_{PC} = 2.2$), 130.89 (d, C_{ipso}, PPh_2, $^1J_{PC} = 50.0$), 132.96 (d, C_o, PPh_2, $^2J_{PC} = 8.8$), 133.63 (d, C_{ipso}, PPh_3, $^1J_{PC} = 99.9$), 133.81 (dd, $C_{3'}$, C_6H_4, $^2J_{PPh2C} = 17.0$, $^4J_{PPh3C} = 6.2$), 134.39 (d, C_o, PPh_3, $^2J_{PC} = 13.9$), 136.60 (d, C_3, NPh, $^4J_{PC} = 2.4$), 137.94 (d, $C_{2'}$, C_6H_4, $^1J_{PC} = 105.5$), 140.54 (d, $C_{6'}$, C_6H_4, $^3J_{PC} = 18.9$), 152.45 (d, C_1, NPh, $^2J_{PC} = 2.9$), 178.80 (d, $C_{1'}$, C_6H_4, $^2J_{PPh3C} = 114.6$, $^2J_{PPh2C} = 21.7$).

1c. Greener Transmetalation Reactions with Organogold(I) Derivatives 15 and 16 to Afford the Cycloaurated Gold(III) Compounds 13 and 14. 15 (0.100 g, 0.123 mmol) was dissolved in Me_2CO (20 mL) at room temperature. This solution was reacted with K[$AuCl_4$] (0.036 g, 0.095 mmol) and stirred during 20 min at the same temperature. The solvent was subsequently evaporated to a small volume (∼1 mL), and Et_2O (15 mL) added to give a yellow solid, which was identified as a (1:1) mixture of **13** and $ClAuPPh_3$ This yellow solid was subjected to low-temperature (0 °C) flash chromatography (jacketed column, silica, CH_2Cl_2 as eluent). The first colorless band is the gold(I) complex, followed by a deep yellow band containing complex **13** exclusively. Evaporation of the solvent to dryness from the yellow fraction and Et_2O addition gave **13** as a yellow solid. Yield: 40%. Complex **14** can be obtained from **16** by aryl transmetalation following a synthetic procedure strictly analogous to that described for **13**. Thus, **16** (0.100 g, 0.12 mmol) was reacted with K[$AuCl_4$] (0.035 g, 0.090 mmol) in acetone at 25 °C to give analytically pure **14** after column purification. Yield: 50%. *Note*: the moderate yields are due to the small amounts of mixture (0.12 mmol) subjected to flash chromatography.

1d. Synthesis of [Au{κ^2-C,N-C_6H_4(PPh_2=N(C_6H_4Me))-2}(CD_3CN)$_2$](BF_4)$_2$ 26 and *in Situ* NMR Characterization. To a solution of **13** (0.012 g, 0.02 mmol) in CD_3CN (0.5 mL) under Ar was added 0.04 mmol (0.011 g) of $AgBF_4$. The resulting suspension was stirred for 20 min with exclusion of light at 25 °C, then filtered, and the resulting reddish solution was transferred to an NMR tube. The NMR spectra of the sample were immediately measured. See drawing of the molecule that includes the numbers for H atoms in the Supporting Information. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 66.9 [**13**: $^{31}P\{^1H\}$ NMR (CD_3CN) δ 65.5]. ^1H NMR (CD_3CN): δ 7.13−7.31 (m, 6H, 5H (NPh) + H_3 (C_6H_4)), 7.51 (dd, 1H, H_4, C_6H_4, $^3J_{HH} = 7.4$, $^4J_{PH} = 4.5$), 7.59 (m, 1H, H_5, C_6H_4), 7.65−7.70 (m, 4H, H_m, PPh_2), 7.83−7.88 (m, 6H, H_p+H_o, PPh_2), 8.16 (dd, 1H, H_6, C_6H_4, $^4J_{PH} = 2.4$, $^3J_{HH} = 8.5$).

2. Catalytic Studies. All catalytic reactions were performed at 25 °C in a Kontex tube using distilled and degassed solvents and under an argon atmosphere. Procedure for the addition of MVK (**18**) to 2-methylfuran (**17**): 2 mmol of **17**, 2 mmol of **18**, 0.02 mmol of the corresponding gold complex, and 0.044 mmol (or 0.022 mmol) of silver salt (when necessary) were mixed in 5 mL of CH_3CN, and this mixture was stirred for a period of 6 or 18 h (Table 1). After the reaction time was completed, the resulting mixture was filtered through a short silica gel column using 20 mL of a Et_2O/*n*-hexane (3:1) mixture as eluent. The yellow solution was evaporated to dryness under vacuum, affording pure **19**. Procedure for the addition of MVK (**18**) to electron−rich arenes (**22** or **24**): 2 mmol of **22** (**24**), 2 mmol of **18**, 0.03 mmol of the corresponding gold complex (0.02 mmol in the case of $AuCl_3$), and 0.066 mmol of silver salt (when necessary) were mixed in 5 mL of CH_3CN, and this mixture was stirred for 24 h (Table 2). After the reaction time, the resulting mixture was filtered through a short silica gel column using 20 mL of a Et_2O/*n*-hexane (3:1)

mixture as eluent. The yellow solution was evaporated to dryness under vacuum, affording pure **23** (**25**).

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Supporting Information Available: Detailed NMR spectra of **13** and **26** in CD_3CN as well as spectra of catalytic reactions followed by NMR. Drawings of the new compounds including numbers for H atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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