

## Metalated-Arene-Phosphino Ligands: A Novel Approach to Open-Sided Gold Compounds

M. Rosa Axet, Marion Barbazanges, Mylène Augé, Christophe Desmarets, Jamal Moussa, Cyril Ollivier, Corinne Aubert,\* Louis Fensterbank,\* Vincent Gandon,<sup>‡</sup> Max Malacria, Lise Marie Chamoreau, and Hani Amouri\*

UPMC Université Paris 06, Institut Parisien de Chimie Moléculaire (UMR CNRS 7201), 4 Place Jussieu, C. 42, 75252 Paris Cedex 05, France. <sup>‡</sup>Univ Paris-Sud, UMR CNRS 8182, Orsay 91405, France

## Received October 22, 2010

Summary: A novel type of metalated phosphino ligands,  $[Cp^*Ru-(\eta^6-arene-PPh_2)][OTf]$  (2a-d-OTf), has been prepared in which the  $-PPh_2$  unit is attached to a metalated  $\pi$ -arene platform. This unique class of ligands 2a-d are converted to open-sided cationic gold complexes 3a-d upon treatment with [AuCl(tht)]. The structure of one of these compounds,  $[Cp^*Ru(\eta^6-C_6H_5-PPh_2-Au-Cl)][OTf]$  (3a-OTf), was ascertained by single-crystal X-ray diffraction. Preliminary studies suggest that cationic complex 3a is active in metal-catalyzed cycloisomerization reactions.

Gold complexes have received much attention due to their importance in several applications such as luminescence, supramolecular chemistry, and nanoparticles, and more recently in catalysis.<sup>1</sup> Indeed in the past decade, homogeneous gold catalysis has emerged as a powerful tool for novel organic transformations, thus providing a variety of C–C bond-forming reactions for the synthesis of complex chemical structures.<sup>2</sup> In this context, efforts have been devoted to prepare new gold complexes by tuning the electronic and/or

(2) For reviews, see: (a) Shapiro, N. D.; Toste, F. D. Synlett 2010, 5, 675. (b) Fürstner, A. Chem. Soc. Rev. 2009, 38, 3208. (c) Jiménez-Nuñez, E.; Echavarren, A. M. Chem. Rev. 2008, 108, 3326. (d) Hashmi, A. S. K. Chem. Rev. 2007, 107, 3180. For recent contributions from our laboratory, see: (e) Harrak, Y.; Simonneau, A.; Malacria, M.; Gandon, V.; Fensterbank, L. Chem. Commun. 2010, 46, 865. (f) Lemière, G.; Gandon, V.; Cariou, K.; Hours, A.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. J. Am. Chem. Soc. 2009, 131, 2993. (g) Benedetti, E.; Lemière, G.; Chapellet, L.-L.; Penoni, A.; Palmisano, G.; Malacria, M.; Goddard, J.-P.; Fensterbank, L. Org. Lett. 2010, 12, 4396.

(3) (a) Diéz-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (b) Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704.

pubs.acs.org/Organometallics

the steric properties of the donor ligand bound to the metal center, " $L \rightarrow Au$ " ( $L = PR_3$ , carbenes, cyclic aminocarbene, etc.).<sup>3,4</sup> More recently Echavarren and co-workers designed a novel family of gold complexes with bulky phosphine ligands.<sup>5</sup> The latter showed enhanced catalytic activity compared to the market available [AuCl(PPh<sub>3</sub>)] complex.

Pursuing our research in this area, we wish to report in this communication the design and synthesis of a novel family of gold complexes of the type  $L_M \rightarrow Au - Cl$  where  $L_M$  is an organometallic phosphine ligand. In this ligand, the  $-PPh_2$  moiety is now attached to a metalated  $\pi$ -arene platform (see Scheme 1). In this model complex, we sought to change the electronic and steric properties around the gold center in the hopes that this may lead to novel reactive species. To the best of our knowledge, this is the first example of such a compound to be reported in the literature.

Our group has developed the synthesis of some neutral metalated  $\pi$ -quinones. The related reactive intermediates thioquinones and selenoquinones were also stabilized and isolated for the first time as  $\pi$ -complexes of "Cp\*M" (M = Rh, Ir).<sup>6</sup> These  $\pi$ -quinonoid species were successfully used as organometallo ligands to prepare a variety of coordination assemblies and polymers with luminescent properties.<sup>7</sup> In this work we describe the synthesis of a new type of organometallo ligand where the phosphine moiety is attached to an arene complex of Cp\*Ru. However we note that metalated phosphino ligands such as rigid phosphino-ferrocenes has been widely and successfully used in homogeneous catalysis by many groups.<sup>8</sup>

<sup>\*</sup>Corresponding authors. (H.A.) Fax: (33)1-44-27-38-41. E-mail: hani.amouri@upmc.fr. (C.A.) Fax: (33)1-44-27-73-60. E-mail: corinne.aubert@upmc.fr. (L.F.) Fax: (33)1-44-27-73-60. E-mail: louis. fensterbank@upmc.fr.

 <sup>(1) (</sup>a) Gold Chemistry: Applications and Future Directions in the Life Sciences; Mohr, F., Ed.; Wiley-VCH: Weinheim, 2009. (b) Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications; Laguna, A., Ed.; Wiley-VCH: Weinheim, 2008. (c) Yu, S.-Y.; Sun, Q.-F.; Lee, T. K.-M.; Cheng, E. C.-C.; Li, Y.-Z.; Yam, V. W. W. Angew. Chem., Int. Ed. **2008**, 47, 4551. (d) De Quadras, L.; Shelton, A. H.; Kuhn, H.; Hampel, F.; Schanze, K. S.; Gladysz, J. A. Organometallics **2008**, 27, 4979. (e) Liau, R.-Y.; Schier, A.; Schmidbaur, H. Organometallics **2003**, 22, 3199. (f) Stefanescu, D. M.; Yuen, H. F.; Glueck, D. S.; Golen, J. A.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L. Inorg. Chem. **2003**, 42, 8891. (g) Landgraf, G. In Gold. Progress in Chemistry, Biochemistry and Technology; Schmidbaur, H., Ed.; John Wiley and Sons: Chichester, U.K., 1999; pp 143–171. (h) Puddephatt, R. J. Coord. Chem. Rev. **2001**, 216–217, 313.

<sup>(4) (</sup>a) Bartolomé, C.; Carrasco-Rolando, M.; Coco, Ś.; Cordovilla, C.; Espinet, P.; Martin-Alvarez, J. M. *Dalton Trans.* **2007**, 5339. (b) Bartolomé, C.; Carrasco-Rando, M.; Coco, S.; Cordovilla, C.; Martín-Alvarez, J. M.; Espinet, P. *Inorg. Chem.* **2008**, *47*, 1616. (c) Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadieu, B.; Bertrand, G. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 13569. (d) Zeng, X.; Soleilhavoup, M.; Bertrand, G. *Org. Lett.* **2009**, *11*, 3166.

<sup>(5) (</sup>a) Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178. (b) Perez-Galan, P.; Delpont, N.; Herrero-Gomez, E.; Maseras, F.; Echavarren, A. M. *Chem.—Eur. J.* **2010**, *16*, 5324.

<sup>(6) (</sup>a) Le Bras, J.; Amouri, H.; Vaissermann, J. Organometallics **1998**, *17*, 1116. (b) Moussa, J.; Guyard-Duhayon, C.; Herson, P.; Amouri, H.; Rager, M. N.; Jutand, A. Organometallics **2004**, *23*, 6231. (c) Moussa, J.; Lev, D. A.; Boubekeur, K.; Rager, M. N.; Amouri, H. Angew. Chem., Int. Ed. **2006**, *45*, 3854. (d) Moussa, J.; Rager, M. N.; Boubekeur, K.; Amouri, H. Eur. J. Inorg. Chem. **2007**, 2648. (e) Amouri, H.; Moussa, J.; Renfrew, A. K.; Dyson, P. J.; Rager, M. N.; Chamoreau, L.-M. Angew. Chem., Int. Ed. **2010**, *49*, 7530.

<sup>(7) (</sup>a) Moussa, J.; Wong, K. M.-C.; Chamoreau, L.-M.; Amouri, H.; Yam, V. W.-W. *Dalton Trans.* **2007**, 3526. (b) Moussa, J.; Guyard-Duhayon, C.; Boubekeur, K.; Amouri, H.; Yip, S. K.; Yam, V. W. W. *Cryst. Growth Des.* **2007**, 7, 962. (c) Moussa, J.; Amouri, H. *Angew. Chem., Int. Ed.* **2008**, 47, 1372. (d) Moussa, J.; Rager, M. N.; Chamoreau, L.-M.; Ricard, L.; Amouri, H. *Organometallics* **2009**, *28*, 397. (e) Damas, A.; Moussa, J.; Rager, M. N.; Amouri, H. *Chirality* **2010**, *22*, 889.

<sup>(8) (</sup>a) Ferrocenes: Homogeneous Catalysis/Organic Synthesis/Materials Science; Togni, A., Hayashi, T., Eds.; Wiley-VCH: Weinheim, 1995. (b) Arrayas, R. G.; Adrio, J.; Carretero, J. C. Angew. Chem., Int. Ed. 2006, 45, 7674, and references therein.

Scheme 1. Preparation of a Family of Gold Complexes, [Cp\*Ru( $\eta^6$ -arene-PPh<sub>2</sub>-Au-Cl)][OTf] (3a-d-OTf)



The synthesis of the organometallic phosphine ligand **2a** was performed in two steps (see Scheme 1). The first step involves the preparation of the halogen arene metal compound [Cp\*Ru- $(\eta^6$ -C<sub>6</sub>H<sub>5</sub>Cl][OTf] (**1a-OTf**) from chlorobenzene and the solvated ruthenium complex [Cp\*Ru(CH<sub>3</sub>CN)<sub>3</sub>][OTf].<sup>9</sup> Compound **1a-OTf** was obtained as a white microcrystalline complex in 83% yield.

In a second step, we treated **1a-OTf** with 1 equiv of KPPh<sub>2</sub> in THF for 1 h. Reaction workup and analysis by <sup>1</sup>H NMR spectroscopy allowed us to identify the formation of the new compound as  $[Cp^*Ru(\eta^6-C_6H_5-PPh_2)][OTf]$  (**2a-OTf**). Compound 2a-OTf was obtained in 81% yield as a white, microcrystalline, analytically pure material. The <sup>1</sup>H NMR spectrum of **2a-OTf** recorded in  $CD_2Cl_2$  showed a singlet at  $\delta$  1.99 ppm attributed to the Cp\*Ru methyl protons, while three multiplets are visible at  $\delta$  5.45, 5.82, and 5.94 ppm, attributed to the protons of the  $\eta^6$ -C<sub>6</sub>H<sub>5</sub> ring. We also note the presence of a set of multiplets at  $\delta$  7.46 ppm attributed to the phenyl protons of the  $-PPh_2$  moiety. Furthermore, the <sup>31</sup>P NMR spectrum recorded in  $CD_2Cl_2$  showed a singlet at  $\delta$  -13.3 ppm, which is in agreement with the proposed formula of 2a-OTf. In a similar way the related phosphino ligands 2b-d with different substituents at the metalated arene ring were prepared and fully characterized, suggesting that our method is versatile and allows the preparation of a wide range of metalated phosphino ligands (see Supporting Information). It is noteworthy that phosphinobenzene chromium complexes were reported following a completely different approach.<sup>10</sup>

To attain the target gold compound **3a-OTf**, we treated the organometallic phosphine ligand **2a** with 1 equiv of [AuCl(tht)] in dichloromethane. The reaction proceeded smoothly and was left for 1 h. Reaction workup provided an off-white compound in 85% yield. Elemental analysis and spectroscopic data suggested the formation of [Cp\*Ru-( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>-PPh<sub>2</sub>-Au-Cl)][OTf] (**3a-OTf**). As expected, the <sup>1</sup>H NMR recorded in CD<sub>2</sub>Cl<sub>2</sub> exhibited a singlet at  $\delta$  2.02 ppm, assigned to the Cp\*Ru methyl protons, and a set of three multiplets in the range  $\delta$  6.03–6.20 ppm, attributed to the protons of the  $\eta^6$ -C<sub>6</sub>H<sub>5</sub>- moiety, which are now downfield relative to the organometallic phosphine ligand **2a**.



**Figure 1.** Molecular structure of **3a**, showing (i) the orientations of the free and metalated phenyl groups and (ii) the coordination of the Cp\*Ru to the phenyl ring. Selected bond distances (Å) and angles (deg): P1---Au1: 2.218(1); P1---C1: 1.817(3); P1---C1: 1.819(3): P1---C23: 1.815(4); Au1---C11: 2.270(1); Ru1---C1: 2.217(3); Ru1---C2: 2.205(3); Ru1---C3: 2.209(3); Ru1---C4: 2.212(3); Ru1---C5: 2.197(3); Ru1---C6: 2.200(3); P1-Au1-C11: 176.34(4). Thermal ellipsoids are drawn at 50% probability. Color code for atoms: Ru: pink; Au: blue; C: gray; Cl: green; P: orange.

Furthermore, another set of multiplets are visible at  $\delta$  7.60–7.67 ppm, which we attribute to the phenyl protons of the –PPh<sub>2</sub> moiety. The <sup>31</sup>P NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> was the most informative and showed a singlet at  $\delta$  35.6 ppm, downfield relative to starting material. This downfield shift confirms the coordination of the gold center by the organometallic phosphine ligand. To ascertain the structure of this novel binuclear Ru–Au compound, a single-crystal X-ray structure determination was carried out.

<sup>(9) (</sup>a) Dembek, A. A.; Fagan, P. J. *Organometallics* 1995, *14*, 3741.
(b) O'Connor, J. M.; Friese, S. J.; Rodgers, B. L.; Rheingold, A. L.; Zakharov, L. *J. Am. Chem. Soc.* 2005, *127*, 9346.

<sup>(10) (</sup>a) Yamamoto, Y.; Danjo, H.; Yamaguchi, K.; Imamoto, T. J. Organomet. Chem. 2008, 693, 3546. (b) Gibson, S. E.; Ibrahim, H. Chem. Commun. 2002, 2465. (c) Bolm, C.; Muniz, K. Chem. Soc. Rev. 1999, 28, 51.



**Figure 2.** Comparative structural study between [AuCl(PPh<sub>3</sub>)] and complex **3a**. Full space-filling projection shows that the two sides around the gold center are no longer equivalent.

Crystals of **3a-OTf** were grown by vapor diffusion of diethyl ether into a  $CH_2Cl_2$  solution.<sup>11</sup> The structure indeed confirmed the formation of the binuclear triflate salt **3a-OTf** and revealed the presence of the "-PPh<sub>2</sub>-Au-Cl" unit, which is attached to the metalated arene platform "Cp\*Ru(C<sub>6</sub>H<sub>5</sub>-)" (Figure 1). Due to the orientation of the phenyl groups, the Au-Cl leans toward the "Cp\*Ru" moiety, perhaps to minimize any steric hindrance (Figure 1). We also note that the Cp\*Ru moiety is symmetrically coordinated to the  $\eta^6$ -phenyl group. The other three cationic gold complexes, **3b-d**, were prepared in a similar way starting from the metalated phosphino ligands **2b-d**. All these compounds were fully characterized by spectroscopic methods and elemental analysis (see Supporting Information).

For comparison purposes and in order to establish a structure– reactivity relationship, we compared the solid-state structure of our compound 3a to the well-known complex [AuCl-(PPh<sub>3</sub>)] (Figure 2).<sup>12</sup> At first glance and in contrast to that of [AuCl(PPh<sub>3</sub>)], the two sides of the cationic gold complex 3a are no longer equivalent at least in the solid state. Indeed one face of this complex is closer to the Cp\*Ru, which would hinder the approach of the substrate, while the other side is open; thus one may expect a different reactivity compared to the parent compound [AuCl(PPh<sub>3</sub>)].

On the other hand, when compound **3a-OTf** was treated with AgOTf in CD<sub>3</sub>CN, a white precipitate was obtained due to the formation of AgCl. Analysis by <sup>1</sup>H and <sup>31</sup>P NMR suggested formation of the presumably solvated species [Cp\*Ru( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>-PPh<sub>2</sub>-Au-solvent)]<sup>2+</sup>, thus precluding any decomposition reaction.

The catalytic activity of the novel binuclear compound **3a-OTf** was then tested in an alkoxycyclization process and compared to its homologue [AuCl(PPh<sub>3</sub>)]. When  $\beta$ -hydroxy-allenynes **4** and **5** were submitted to 2 mol% of **3a-OTf**/AgSbF<sub>6</sub> in dichloromethane at room temperature, the allenic moiety was activated selectively and dihydropyrans **6** and **7** were formed in 75% and 72% yield, respectively (Scheme 2).<sup>13</sup> This catalytic system provided fast and efficient transformations, whereas under the same conditions, only 16% (for **6**) and 9%

Scheme 2. Cyclization of  $\beta$ -Hydroxy-Allenynes

ŀ

	catalyst (2 mol%) AgSbF <sub>6</sub> (2 mol%)	R
$\times$	CH <sub>2</sub> Cl <sub>2</sub> , rt, 15 min	× <sup>6</sup>
R	Catalyst	Yield
<b>4</b> , R = OMe	3a-OTf	<b>6</b> , R = OMe, 75%
<b>4</b> , R = OMe	PPh <sub>3</sub> AuCl	6, R = OMe, 16% (conversion)
5, R = OTBDPS	3a-OTf	7, R = OTBDPS, 72%
5, R = OTBDPS	PPh <sub>3</sub> AuCl	7, R = OTBDPS, 9% (conversion)

(for 7) conversions were observed after 15 min when using [AuCl(PPh<sub>3</sub>)]/AgSbF<sub>6</sub>. We feel that these interesting results highlight a different behavior between our catalyst system and the well-known [AuCl(PPh3)] catalyst. This difference in reactivity could find its origin from electronic and steric factors as well. In fact the  $\pi$ -acid property of our catalyst precursor was measured by converting 2a-OTf to the related selenide complex  $[Cp*Ru(\eta^6-C_6H_5-PPh_2=Se)][OTf]$  (8-OTf); subsequent measurement of the  ${}^{1}J_{P-Se}$  coupling constant provides a value of 775 Hz, which is higher than that obtained for PPh<sub>3</sub>=Se (9) with  ${}^{1}J_{P-Se} = 724$  Hz. These data suggest that coordination to Cp\*Ru decreases the electron density on the phosphine ligand.<sup>14</sup> Furthermore the steric hindrance around the cationic gold complex 3a is also increased due to the metalated phosphino ligand 2a by comparison to the [AuCl(PPh<sub>3</sub>)] catalyst. All in all, these metalated phosphino ligands provide an interesting type of gold complexes with different electronic and steric properties from known gold compounds. Therefore we intend in the future to fully investigate the catalytic activity of this novel type of gold complexes anchored to metalated arene platforms.

In conclusion, we have reported a novel approach to prepare metalated phosphino ligands 2a-d, which can be easily converted to a unique type of cationic gold complexes, 3a-d, where the  $-PPh_2-Au-Cl$  unit is now attached to a metalated  $\pi$ -arene platform, [Cp\*Ru( $\eta^6$ -arene)][OTf]. Preliminary studies suggest that 3a-OTf is active in metalcatalyzed cyclization reactions and especially toward  $\beta$ hydroxy-allenynes 4 and 5, where our catalyst is more efficient than the well-known [AuCl(PPh<sub>3</sub>)] complex. Further studies are underway to tackle the electronic and steric properties of such metalated phosphino ligands and the influence of the functionalized group at the  $\pi$ -arene on the selectivity and catalytic activity of the gold complexes. These results will be reported in future reports. We also intend to prepare novel compounds with planar chirality.<sup>15</sup>

Acknowledgment. This work was supported by the CNRS, IUF, and Agence Nationale de la Recherche (grant SACCAOR, ANR-09-BLAN0108), which we gratefully acknowledge.

Supporting Information Available: Experimental procedures, spectroscopic data of all metal complexes and organic products, as well as a CIF file including X-ray crystallographic data for **3a-OTf**. This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(11)</sup> Crystal data of **3a** (CCDC-780252):  $C_{28}H_{30}AuClPRu$ , CF<sub>3</sub>O<sub>3</sub>S, CH<sub>2</sub>Cl<sub>2</sub>, M = 964.97 g/mol, monoclinic system, space group  $P2_1/c$ , a = 9.3654(10) Å, b = 15.6752(19) Å, c = 22.506(3) Å,  $\beta = 90.619(11)^\circ$ , V = 3303.8(7), Å<sup>3</sup>, Z = 4,  $\rho = 1.940$  g·cm<sup>-3</sup>,  $\mu = 5.295$  mm<sup>-1</sup>, T = 200(2) K,  $\lambda = 0.71073$  Å (Mo K $\alpha$ ), 31 622 reflections measured, 10 209 unique,  $R_{int} = 0.0430$ ,  $R_1[I > 2\sigma(I)] = 0.0322$ ,  $wR_2(all data) = 0.0722$ .  $\Delta \rho_{min/max} = -1.16/0.79$  e<sup>-</sup>/Å<sup>3</sup>.

<sup>(12)</sup> Baenziger, N. C.; Bennett, W. E.; Soborofe, D. M. Acta Crystallogr. 1976, B32, 962.

<sup>(13)</sup> Zriba, R.; Gandon, V.; Aubert, C.; Fensterbank, L.; Malacria, M. *Chem.—Eur. J.* **2008**, *14*, 1482.

<sup>(14)</sup> We would like to thank the reviewer for pointing this out. (a) Allen, D. W.; Taylor, B. F. J. Chem. Soc., Dalton Trans. **1982**, 51. (b) Allen, D. W.; March, L. A. I.; Nowell, W. J. Chem. Soc., Dalton Trans. **1984**, 483. (c) Muller, A.; Otto, S.; Roodt, A. Dalton Trans. **2008**, 650.

<sup>(15) (</sup>a) Gladysz, J. A.; Boone, B. J. Angew. Chem., Int. Ed. **1997**, 36, 550. (b) Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials; Amouri, H., Gruselle, M., Eds.; Wiley: Chichester, UK, 2008.