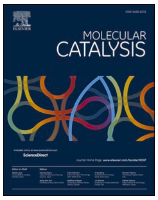
Molecular Catalysis 547 (2023) 113281

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis



$(Ph_3P)AuCl$-catalyzed homocoupling of arylboronic acids under benchtop conditions: Synthesis of biphenyls

Silvia Roscales [a,c], Francisco Sánchez-Sancho [b,c], Aurelio G. Csáky [c,*]

[a] *Facultad de Ciencias Biomédicas y de la Salud, Universidad Europea de Madrid (UEM), C. Tajo, s/n, 28670 Villaviciosa de Odón, Madrid, Spain*
[b] *Instituto de Química Médica (IQM), Agencia Estatal Consejo Superior de Investigaciones Científicas (CSIC), Calle Juan de la Cierva, 3, 28006 Madrid, Spain*
[c] *Grupo de Síntesis Orgánica y Bioevaluación, Instituto Pluridisciplinar, Universidad Complutense, Paseo de Juan XXIII, 1, 28040 Madrid, Spain*

ARTICLE INFO

Keywords:
Gold
Boronic acids
Homocoupling
Biphenyls

ABSTRACT

$(Ph_3P)AuCl$ was discovered to be a powerful catalyst in the homocoupling of arylboronic acids and potassium aryltrifluoroborates for the synthesis of symmetrical biaryls. The reactions take place under benchtop reaction conditions in 96% EtOH at temperatures between rt and 50 °C with no exclusion of air or humidity, in the presence of F-TEDA (Selectfluor™) as an oxidant. The procedure is very functional group tolerant, and affords the corresponding biaryls in high yields with large substrate scope (26 examples).

1. Introduction

Gold-catalyzed reactions show several features that render them synthetically attractive: The reaction conditions are mild, the catalysts or precatalysts are readily accessible and oxygen-tolerant, the use of ancillary ligands is minimal, and the work-up procedures are easy. In addition, Au-catalysis is orthogonal to other metal-catalyzed reactions, and present ample functional-group tolerance. As a drawback, Au(I) and Au(III) do not readily cycle between oxidation states. However, the use of a stoichiometric oxidant together with an Au(I) catalyst allows for Au (I)-Au(III) redox cycles [1].

Biaryl motifs are important structural scaffolds found in a variety of natural products, functional materials, catalysts, agrochemicals, and pharmaceutical substances [2]. Although methods for aryl–aryl bond formation have traditionally been dominated by Pd- and Cu-catalyzed coupling reactions [3], the use of Au-catalysis for the synthesis of symmetrical biaryl compounds shows great potential as an alternative strategy [4].

The synthesis of biaryls by the homocoupling of aryl halides under Au-catalysis has been performed using a periodic mesoporous organosilica supported Au-catalyst [5], Au-nanoparticles [6], and Au–Pt alloy nanocrystals in hollow silica [7]. These reactions show several improvements over other metal-catalyzed Ullmann-type couplings, such as lower temperatures and stability of the catalysts.

Besides, boronic acids and their ester and trifluoroborate derivatives are attractive materials in organic synthesis due to their high stability and low toxicity [8]. These reagents have been used as starting materials for the synthesis of biaryls by homocoupling reactions using mainly Cu and Pd catalysts [9,10,11], but also Cr [12], Rh [13], Ru [14], Ni [15], and Mn [16] catalysts. After the first reports of stoichiometric transmetalation of arylboronic acids and aryltrifluoroborates to Au(I) in the presence of a base [17], arylboronic acids have been used as substrates for the synthesis of biaryls in Au-catalyzed homocoupling reactions [4, 9]. These Au-catalyzed reactions can be hampered by the formation of catalytically-inactive gem-diaurated species [18], and the need for regeneration of a catalytically-active Au-species after the reductive elimination step [19], which requires the presence of external oxidants [1].

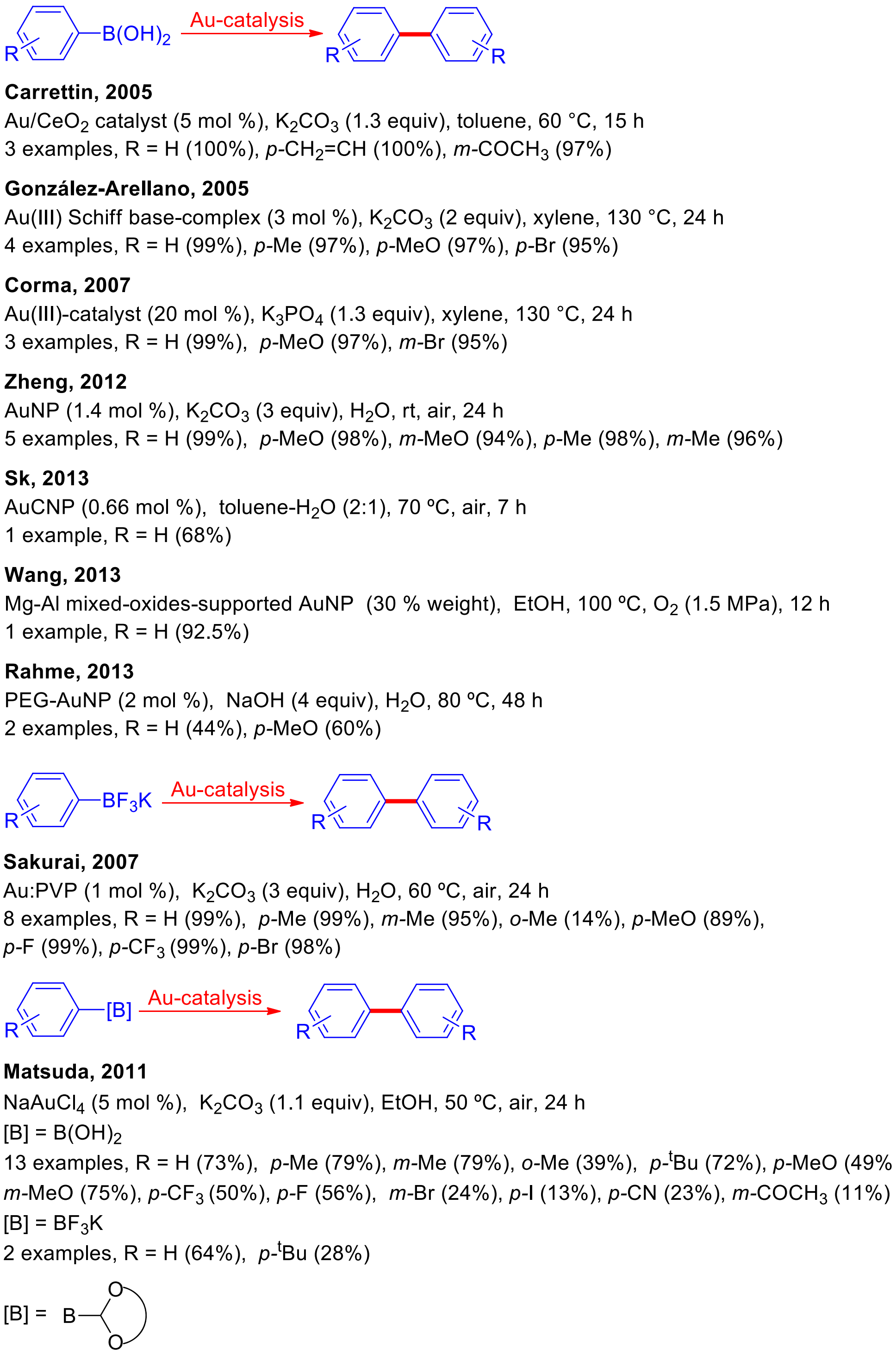
Despite these difficulties, the Au-catalyzed homocoupling of arylboronic acids has been performed (Scheme 1) using Au supported on nanocrystalline cerium(IV) oxide [20], homogeneous and heterogenized Au(III) Schiff base-complexes [21], Au(III)-complexes supported on silica-based mesoporous and laminar inorganic solids [22], nPS–PAMAM-supported Au-nanoparticles [23], an Au-C nanoparticle composite [24], Mg–Al mixed-oxides-supported Au nanoparticles [25], and PEGylated gold nanoparticles in water [26]. In addition, Au(0) nanoclusters stabilized by poly(N-vinyl-2-pyrrolidone) have been used for the homocoupling of potassium aryltrifluoroborates [27], and AuCl or $NaAuCl_4 \cdot 2H_2O$ have been applied as catalysts for the homocoupling of arylboronic acids, phenyl borates, and potassium phenyltrifluoroborate

---

* Corresponding author at: Grupo de Síntesis Orgánica y Bioevaluación, Instituto Pluridisciplinar, Universidad Complutense, Paseo de Juan XXIII, 1, 28040 Madrid, Spain.

E-mail address: csaky@ucm.es (A.G. Csáky).

https://doi.org/10.1016/j.mcat.2023.113281
Received 9 May 2023; Received in revised form 29 May 2023; Accepted 30 May 2023



Carrettin, 2005
Au/CeO_2 catalyst (5 mol %), K_2CO_3 (1.3 equiv), toluene, 60 °C, 15 h
3 examples, R = H (100%), *p*-CH_2=CH (100%), *m*-$COCH_3$ (97%)

González-Arellano, 2005
Au(III) Schiff base-complex (3 mol %), K_2CO_3 (2 equiv), xylene, 130 °C, 24 h
4 examples, R = H (99%), *p*-Me (97%), *p*-MeO (97%), *p*-Br (95%)

Corma, 2007
Au(III)-catalyst (20 mol %), K_3PO_4 (1.3 equiv), xylene, 130 °C, 24 h
3 examples, R = H (99%), *p*-MeO (97%), *m*-Br (95%)

Zheng, 2012
AuNP (1.4 mol %), K_2CO_3 (3 equiv), H_2O, rt, air, 24 h
5 examples, R = H (99%), *p*-MeO (98%), *m*-MeO (94%), *p*-Me (98%), *m*-Me (96%)

Sk, 2013
AuCNP (0.66 mol %), toluene-H_2O (2:1), 70 ºC, air, 7 h
1 example, R = H (68%)

Wang, 2013
Mg-Al mixed-oxides-supported AuNP (30 % weight), EtOH, 100 ºC, O_2 (1.5 MPa), 12 h
1 example, R = H (92.5%)

Rahme, 2013
PEG-AuNP (2 mol %), NaOH (4 equiv), H_2O, 80 ºC, 48 h
2 examples, R = H (44%), *p*-MeO (60%)

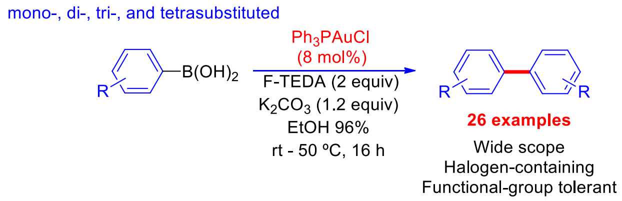
Sakurai, 2007
Au:PVP (1 mol %), K_2CO_3 (3 equiv), H_2O, 60 ºC, air, 24 h
8 examples, R = H (99%), *p*-Me (99%), *m*-Me (95%), *o*-Me (14%), *p*-MeO (89%),
p-F (99%), *p*-CF_3 (99%), *p*-Br (98%)

Matsuda, 2011
$NaAuCl_4$ (5 mol %), K_2CO_3 (1.1 equiv), EtOH, 50 ºC, air, 24 h
[B] = $B(OH)_2$
13 examples, R = H (73%), *p*-Me (79%), *m*-Me (79%), *o*-Me (39%), *p*-^{t}Bu (72%), *p*-MeO (49%
m-MeO (75%), *p*-CF_3 (50%), *p*-F (56%), *m*-Br (24%), *p*-I (13%), *p*-CN (23%), *m*-$COCH_3$ (11%)
[B] = BF_3K
2 examples, R = H (64%), *p*-^{t}Bu (28%)

Scheme 1. Previous work: Au-catalyzed homocoupling reactions of arylboronic acids and their derivatives.

[28] using air as the oxidant to regenerate the Au(III) species. These Au-catalyzed reactions have only been reported for monosubstituted aryls, and suffered from a reduced scope and little functional-group tolerance.

On the other hand, $(Ph_3P)AuCl$ is a stable commercially available user-friendly complex frequently used in Au-catalyzed organic synthesis [29]. It can also be readily prepared from elemental gold [30]. We envisioned that this popular catalyst could be advantageous over other previously reported Au-catalysts in the homocoupling of arylboronic acids for the synthesis of symmetrical biaryl compounds (Scheme 2). Given the fact that the catalytic cycle would require cycling between Au (I) and Au(III) species [1], we selected F-TEDA (Selectfluor™) as a convenient oxidant to perform this task. F-TEDA is a mild, air- and moisture-stable, non-volatile reagent used in electrophilic fluorinations. The use of F-TEDA has been reported to allow for the in situ formation of X_2Au(III)-F species [31], which exhibit high reactivity in the C–B bond activation of arylboronic acids [32].



Scheme 2. This work.

2. Results and discussion

We started our study by exploring the reaction of phenylboronic acid as a starting material to perform the optimization of the catalyst loading, and solvent (Table 1), in the presence of F-TEDA (2 equiv). All reactions were carried out at rt for 16 h. Since we wanted to develop mild benchtop conditions, all experiments were investigated with no exclusion of air or ambient humidity, using commercial-grade solvents.

First, the effect of the base was investigated. It is known that the base may have the role to activate the arylboronic acid for transmetalation, as well as neutralizing the XB(OH)$_2$ by-product produced in the reaction, thus preventing the deterioration of the catalyst [20]. Using CH_2Cl_2 as the solvent and 5 mol% of the catalyst, we found that no homocoupling took place in the absence of a base (entry 1). In the presence of a base (1.2 equiv), low yields of the homocoupling product **1** were observed with $KHCO_3$ or K_3PO_4 (entries 2, 3). The use of K_2CO_3 instead rendered **1** in 84% yield (entry 4). Lowering the amount of K_2CO_3 (0.6 equiv) had a negative effect on the yield (entry 5). Next, we investigated other solvents, looking for greener alternatives to CH_2Cl_2. No yield improvement was found when using toluene, 2-Me-THF, acetonitrile, or acetone (entries 6–9). The use of EtOH provoked a significant increase in the yield (entry 10), which was further improved when using commercial 96% EtOH (entry 11). This suggested the participation of water in the arylboronic acid hydrolysis step or the solubilization of the base and F-TEDA. However, increasing the amount of water in the solvent had a negative effect on yield (entry 12). Finally, the catalyst loading was optimized (entries 13, 14). The use of 10 mol% of the catalyst (entry 14) was found to be optimum in terms of economy, since a further increase to 10 mol% did not improve the yield. Thus, the optimal condition for this homocoupling reaction was established by using 8 mol% of Ph$_3$PAuCl in 96% EtOH at rt (entry 13).

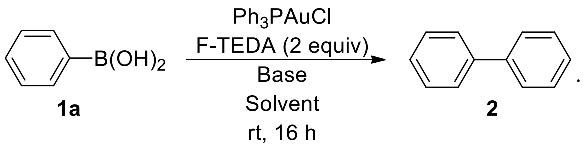
Using these optimized reaction conditions, we explored the scope and limitations of the procedure with regard to the arylboronic acids (Scheme 3). We found that the reaction took place smoothly at rt in the case of monosubstituted alkyl- or halogen-containing arylboronic acids (**3**–**8**), even tolerating *o*-substitution (**6**–**8**). On the other hand, functional group-containing substrates required heating at 50 °C (**9**–**15**), regardless of the electron-donor or electron-acceptor characteristics of the substituent. Lower yields were observed in the case of arylboronic acids functionalized at their *o*-positions with polar groups such as OMe (**9**) or CHO (**10**) in comparison to their halogen counterparts (**6–8**). Excellent yields were obtained for compounds containing aldehyde, cyano, and nitro groups at their *m*- or *p*-positions (**11**–**14**). However, lower yields were obtained in the case of *p*-CO$_2$Me (**15**). For disubstituted arylboronic acids (**16**–**25**), we observed that the reaction was highly sensitive to steric hindrance, since we were not able to obtain compounds **16** or **17** even upon heating, although the presence of a single *o*-substituent was well tolerated (**18**–**24**). Similar observations were made when dealing with tri- (**26, 27**) or tetrasubstituted (**28**) arylboronic acids. Again, the coupling of arylboronic acids containing two (**20**–**25**) or three halogens (**26, 27**) was performed at rt, but the synthesis of **28** required heating at 50 °C. In general, the ability to couple halogen-containing substrates was remarkable. The coupling of Br- and Cl-containing materials supplies a practical handle for additional functionalization by hydrogenation or cross-coupling reactions. The reaction was also extended to **29**, as an example of the coupling of heteroarylboronic acids.

Finally, we checked the possibility of replacing arylboronic acids with potassium aryltrifluoroborates (Scheme 4). We observed that the reaction did not proceed either in the absence of a base, or when using K_2CO_3. This result was rather disappointing, as *ate* species should be more prone to transmetalation than boronic acids. However, in the presence of LiOH, the synthesis of **18, 20, 27**, and **29** took place readily at rt, but yields were lower than when using the corresponding arylboronic acids as starting materials. Presumably, the role of the base is to convert the aryltrifluoroborate into the corresponding arylboronic acid prior to transmetalation [33]. An essay performed in EtOH—H$_2$O (8:2) to increase the solubility of the potassium aryltrifluoroborate in the reaction medium gave **18** in 58% yield.

These reactions can be understood by a catalytic cycle that begins with transmetalation of the aryl moiety from B to Au^{I} (**I**), followed by oxidation to Au^{III} (**II**), second transmetalation (**III**), and reductive coupling (Scheme 5).

Table 1

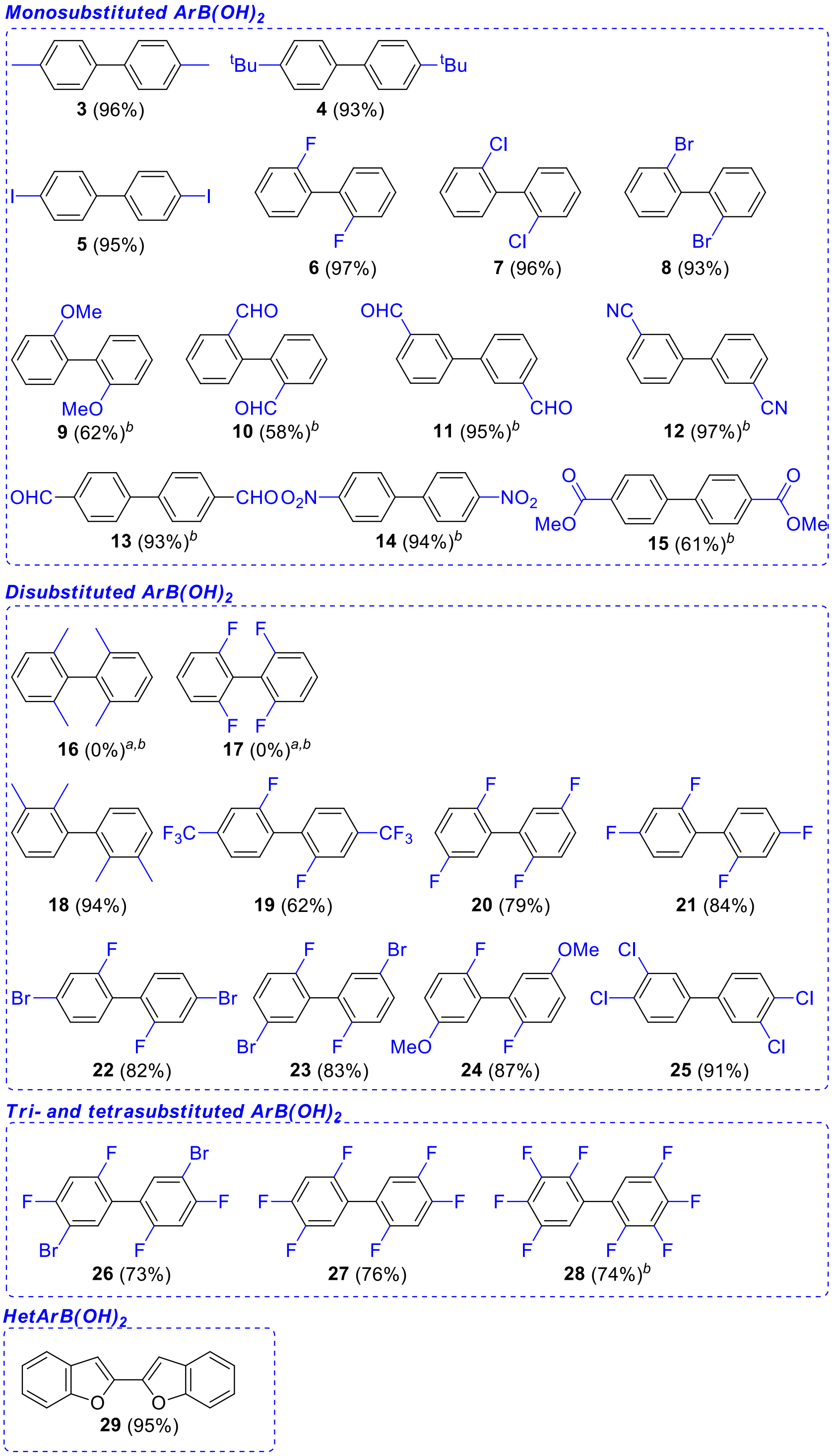
Optimization of conditions for the homocoupling of PhB(OH)$_2$ with Ph$_3$PAuCl.[a]



entry	Ph$_3$PAuCl (mol%)	Solvent	Base	**2** (mol%)
1	5	CH_2Cl_2	—	0
2	5	CH_2Cl_2	$KHCO_3$	44
3	5	CH_2Cl_2	K_3PO_4	62
4	5	CH_2Cl_2	K_2CO_3	84
5[b]	5	CH_2Cl_2	K_2CO_3	32
6	5	Toluene	K_2CO_3	78
7	5	2-Me-THF	K_2CO_3	63
8	5	Acetonitrile	K_2CO_3	51
9	5	Acetone	K_2CO_3	48
10	5	EtOH	K_2CO_3	89
11	5	EtOH 96%	K_2CO_3	91
12	5	EtOH:H$_2$O, 10:1	K_2CO_3	78
13	8	EtOH 96%	K_2CO_3	93
14	10	EtOH 96%	K_2CO_3	97

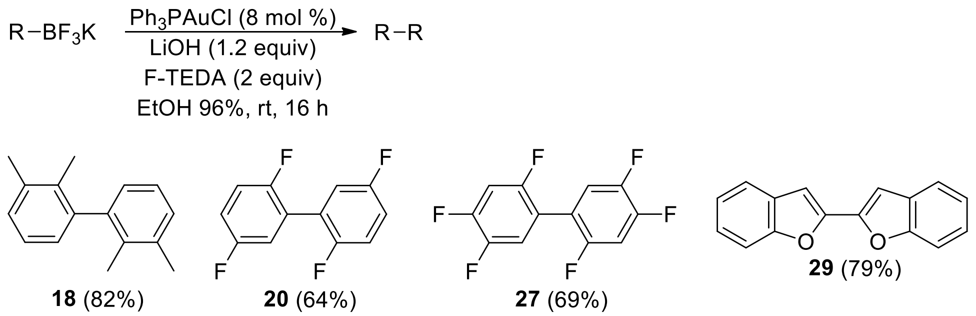
[a] Conditions: **1a** (0.123 mmol), F-TEDA (2 equiv), Base (1.2 equiv), Solvent (1.0 mL), rt, 16 h.

[b] Reaction with 0.6 equiv of K_2CO_3.



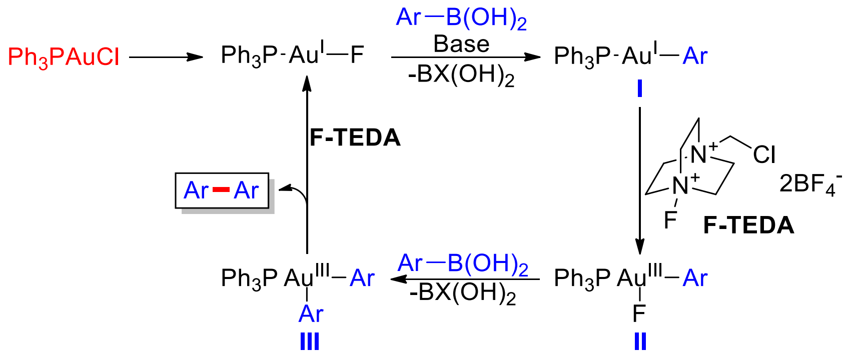
Scheme 3. Ph_3PAuCl-catalyzed synthesis of biaryls.[a]

[a] Conditions: Ph_3PAuCl (8 mol%), arylboronic acid (0.123 mmol), F-TEDA (2 equiv), K_2CO_3 (1.2 equiv), EtOH 96% (1.0 mL), rt, 16 h (isolated yields). [b] Reaction at 50 °C.



Scheme 4. Ph_3PAuCl-catalyzed coupling of potassium aryltrifluoroborates.[a]

[a]Conditions: Ph_3PAuCl (8 mol%), potassium aryltrifluoroborate (0.123 mmol), F-TEDA (2 equiv), LiOH (1.2 equiv), EtOH 96% (1.0 mL), rt, 16 h (isolated yields).



Scheme 5. Mechanistic proposal.

3. Conclusion

In summary, we have demonstrated a new use of $(Ph_3P)AuCl$ in application-driven catalysis. $(Ph_3P)AuCl$ is more efficient than previously reported Au-catalysts for the homocoupling of arylboronic acids. The reaction does not require any extra ligands for Au, and proceeds efficiently under benchtop conditions (no exclusion of air or humidity, 96% EtOH, rt-50 °C) using F-TEDA as the oxidant and K_2CO_3 to ensure transmetalation. A range of mono-, di-, tri-, and tetrasubstituted arylboronic acids (26 examples) could undergo the homocoupling reaction to afford the corresponding biphenyls in good to excellent yields, with high functional-group tolerance, including halogen-containing substrates. The scope of this procedure is wider than using previously reported Au-catalysts. The reaction was also extended to the coupling of potassium aryltrifluoroborates (4 examples).

Funding

This work was supported by the Ministry of Science and Education, Spain, grant no. PID2021–124419NB-I00.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.113281.

References

[1] (a) R.T. Mertens, S.G. Awuah, ACS Symposium Series 1317 (2019) 19–55;
(b) X. Ye, P. Zhao, S. Zhang, Y. Zhang, Q. Wang, C. Shan, L. Wojtas, H. Guo, H. Chen, X. Shi, Angew. Chem. Int. Ed. 58 (2019) 17226–17230;
(c) L. Rocchigiani, M. Bochmann, Chem. Rev. 121 (2021) 8364–8451.

[2] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483;
(b) P. Lloyd-Williams, E. Giralt, Chem. Soc. Rev. 30 (2001) 145–157;
(c) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359–1469;
(d) Y. Chen, S. Yekta, A.K. Yudin, Chem. Rev. 103 (2003) 3155–3212;
(e) D.A. Horton, G.T. Bourne, M.L. Smythe, Chem. Rev. 103 (2003) 893–930;
(f) H. Meier, Angew. Chem. Int. Ed. 44 (2005) 2482–2506;
(g) M.C. Kozlowski, B.J. Morgan, E.C. Linton, Chem. Soc. Rev. 38 (2009) 3193–3207.

[3] (a) Cross-Coupling Reactions: A Practical Guide, In Topics in Current Chemisty, Vol. 219; Miyaura, N., Ed.; Springer: Berlin, 2002; (b) Handbook of Organopalladium Chemistry for Organic Synthesis; Negishi, E., Ed.; Wiley: New York, 2002; (c) Metal-Catalyzed Cross-Coupling Reactions, 2nd ed; de Meijere, A.; Diederich, F., Ed.; Wiley-VCH: Weinheim, 2004; (d) J.P. Corbet, G. Mignani, Chem. Rev. 106 (2006) 2651–2710; (e) G.P. McGlacken, L.M. Bateman, Chem. Soc. Rev. 2009, 38, 2447–2464.

[4] (a) S.N.S. Vasconcelos, J.S. Reis, I.M. de Oliveira, M.N. Balfour, H.A. Stefani, Tetrahedron 75 (2019) 1865–1959;
(b) S. Kramer, Synthesis 52 (2020) 2017–2030;
(c) C. Fricke, W.B. Reid, F. Schoenebeck, Eur. J. Org. Chem. (2020) 7119–7130.

[5] B. Karimi, F.K. Esfahani, Chem. Commun. 47 (2011) 10452–10454.

[6] (a) K. Layek, H. Maheswaran, L. Kantam, Catal. Sci. Technol. 3 (2013) 1147–1150;
(b) W. Yao, W.-J. Gong, H.-X. Li, F.-L. Li, J. Gaoa, J.-P. Lang, Dalton Trans 43 (2014) 15752–15759.

[7] X. Wu, L. Tan, D. Chen, X. Meng, F. Tang, Chem. Commun. 50 (2014) 539–541.

[8] M.A. Soriano-Ursúa, E.D. Farfán-García, Y. López-Cabrera, E. Querejeta, J. G. Trujillo-Ferrara, NeuroToxicology 40 (2014) 8–15.

[9] R.N. Dhital, H. Sakurai, Asian J. Org. Chem. 3 (2014) 668–684, and references cited therein.

[10] (a) P. Puthiaraj, P. Suresha, K. Pitchumani, Green Chem 16 (2014) 2865–2875;
(b) Y.-N. Cao, X.-C. Tian, X.-X. Chen, Y.-X. Yao, F. Gao, X.-L. Zhou, Synlett 28 (2016) 601–606;

(c) K. Zheng, L.R. Qiao, R. Mo, X. Deng, B. Sun, W. Wang, Z. Xiao, C. Qin, Arab. J. Chem. 15 (2022), 104170;
(d) A. Salame, J. Rio, I. Ciofini, L. Perrin, L. Grimaud, P.–A. Payard, Molecules 27 (2022) 7517;
(e) J. Lakshmidevi, B.R. Naidu, K. Venkateswarlu, M.M. Hanafiah, S. K. Lakkaboyana, Green Chem. Lett. Rev. 15 (2022) 529–536;
(f) H. Xia, G. Wang, D. Zhao, C. Zhu, Adv. Synth. Catal. 364 (2022) 922–929.

[11] (a) E.R. Darzi, B.M. White, L.K. Loventhal, L.N. Zakharov, R. Jasti, J. Am. Chem. Soc. 139 (2017) 3106–3114;
(b) S. Dwivedi, S. Bardhan, P. Ghosh, S. Das, RSC Adv. 4 (2014) 41045–41050;
(c) B. Kar, S. Bardhan, P. Ghosh, B. Ganguly, K. Kundu, S. Sarkar, B.K. Paul, S. Das, ChemistrySelect 2 (2017) 1079–1088;
(d) V. Sable, K. Maindan, A.R. Kapdi, P.S. Shejwalkar, K. Hara, ACS Omega 2 (2017) 204–217;
(e) X. Xu, S. Gao, W. Chen, Z. Gao, J. Luo, ChemistrySelect 3 (2018) 8863–8866;
(f) Y.P. Budiman, A. Jayaraman, A. Friedrich, F. Kerner, U. Radius, T.B. Marder, J. Am. Chem. Soc. 142 (2020) 6036–6050;
(g) M.B. Minus, S.R. Moor, F.F. Pary, L.P.T. Nirmani, M. Chwatko, B. Okeke, J. E. Singleton, T.L. Nelson, N.A. Lynd, E.V. Anslyn, Org. Lett. 23 (2021) 2873–2877;
(h) N. Pourmorteza, M. Jafarpour, F. Feizpour, A. Rezaeifard, RSC Adv. 12 (2022) 4931–4938;
(i) R.M. Appa, J. Lakshmidevi, B.R. Naidu, K. Venkateswarlu, Mol. Cat. 501 (2021), 111366;
(j) S.S. Prasad, B.R. Naidu, M.M. Hanafiah, J. Lakshmidevi, R.K. Marella, S. K. Lakkaboyana, K. Venkateswarlu, Molecules 26 (2021) 5390.

[12] J.R. Falck, S. Mohapatra, M. Bondlela, S.K. Venkataraman, Tetrahedron Lett 43 (2002) 8149–8151.

[13] T. Vogler, A. Studer, Adv. Synth. Catal. 350 (2008) 1963–1967, 350.

[14] D. Tyagi, C. Binnani, R.K. Rai, A.D. Dwivedi, K. Gupta, P.-Z. Li, Y. Zhao, S.K. Singh, Inorg. Chem. 55 (2016) 6332–6343.

[15] G.-Y. Liu, Q.-L. Du, J.-J. Xie, K.-L. Zhang, X.-C. Tao, Cuihua Xuebao 27 (2006) 1051–1052.

[16] A.S. Demir, O. Reis, M. Emrullahoglu, J. Org. Chem. 68 (2003) 10130.

[17] (a) D.V. Partyka, M. Zeller, A.D. Hunter, T.G. Gray, Angew. Chem. Int. Ed. 45 (2006) 8188–8191;
(b) S. Gaillard, A.M.Z. Slawin, S.P. Nolan, Chem. Commun. 46 (2010) 2742–2744.

[18] A. Gomez-Suarez, S.P. Nolan, Angew. Chem. Int. Ed. 51 (2012) 8156–8159.

[19] (a) N.P. Mankad, F.D. Toste, J. Am. Chem. Soc. 132 (2010) 12859–12861;
(b) D.V. Partyka, M. Zeller, A.D. Hunter, T.G. Gray, Inorg. Chem. 51 (2012) 8394–8401.

[20] S. Carretin, J. Guzman, A. Corma, Angew. Chem. Int. Ed. 44 (2005) 2242–2245.

[21] C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, Chem. Commun. (2005) 1990–1992.

[22] A. Corma, C. González-Arellano, M. Iglesias, S. Pérez-Ferreras, F. Sánchez, Synlett 11 (2007) 1771–1774.

[23] J. Zheng, S. Lin, X. Zhu, B. Jiang, Z. Yang, Z. Pan, Chem. Commun. 48 (2012) 6235–6237.

[24] M.P. Sk, C.K. Jana, A. Chattopadhyay, Chem. Commun. 49 (2013) 8235–8237.

[25] L. Wang, H. Wang, W. Zhang, J. Zhang, J.P. Lewis, X. Meng, F.-S. Xiao, J. Catal. 298 (2013) 186–197.

[26] K. Rahme, M.T. Nolan, T. Doody, G.P. McGlacken, M.A. Morris, C. O'Driscoll, J. D. Holmes, RSC Adv. 3 (2013) 21016–21024.

[27] H. Sakurai, H. Tsunoyama, T. Tsukuda, J. Organomet. Chem. 692 (2007) 368–374.

[28] T. Matsuda, T. Asai, S. Shiose, K. Kato, Tetrahedron Lett 52 (2011) 4779–4781.

[29] (a) D.J. Gorin, B.D. Sherry, F.D. Toste, In Encyclopedia of Reagents for Organic Synthesis, (2008); (b) A.C.J. Heinrich, Synlett 26 (2015) 1135–1136.

[30] M.-C. Brandys, M.C. Jennings, R.J. Puddephatt, R.J. Dalton Trans. (2000) 4601.

[31] G. Zhang, L. Cui, Y. Wang, L. Zhang, J. Am. Chem. Soc. 132 (2010) 1474–1475.

[32] For the use of $PhI(OAc)_2$ as an oxidant, see M. Hofer, A. Genoux, R. Kumar, C. Nevado, Angew. Chem. Int. Ed. 56 (2017) 1021–1025.

[33] A.K.L. Yuena, C.A. Hutton, Tetrahedron Lett 46 (2005) 7899–7903.