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Addition of heterocycles to electron deficient olefins and alkynes catalyzed by gold(III)

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Abstract

A gold(III)-catalyzed hydroarylation of different olefins is reported here. $AuCl_3$ works as an excellent catalyst to mediate reactions between various heterocycles and electron deficient olefins and alkynes under mild conditions. This gold(III)-based method tolerates different functional groups such as aldehyde, carboxylic acid, nitrile, and is highly efficient. We have shown that some of these reactions complete in minutes at room temperature.

Keywords: Hydroarylation; Gold; Heterocycle; Olefin; C–H Functionalization

1. Introduction

The direct addition of arenes to alkenes or alkynes to form C–C bonds via C–H functionalization provides efficient and atom-economic synthetic methods [1]. Such reactions that work under mild conditions are particularly desirable, and have attracted extensive research efforts in the past [2].

Recently, gold-mediated organic transformations in solution have emerged as important methodologies [3]. We and others have developed new methods to directly functionalize aromatic C–H groups catalyzed by gold(III). It has been known for over seven decades that gold(III) can attack arenes electrophilically to afford arylgold(III) species [4]. This interesting property of gold(III) has been studied but never really utilized in organic synthesis until 2000, when Hashmi et al. [5] reported the gold(III)-catalyze coupling of 2-methylfuran with methyl vinyl ketone to afford a new C–C bond. After Hashmi's work, Reetz and Sommer [6] and we reported the direct addition of arenes to triple bonds with slightly different catalyst systems. A combination of $AuCl_3/3AgSbF_6$ or $AuCl_3/3AgOTf$ was shown to have enhanced activity that works for many arene substrates. We also developed the cyclialkylation of electron rich arenes with tethered epoxides and the direct functionalization of arenes by primary alcohol sulfonate esters catalyzed by gold(III) [7]. Our studies suggest that gold(III) directly attacks the arenes and afford arylgold(III) species as the reaction intermediates. The similar system has also been used by Luo and Li [8] for addition of arenes to activated imines and addition of activated methylenes to olefins.

We report here the gold(III)-catalyzed addition of various heterocycles to activated olefins and alkynes. A variety of structures can be prepared with high efficiency and under mild conditions. The reactions described here can tolerate various functional groups and are practical in constructing complex molecules.

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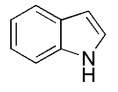
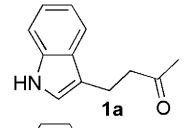
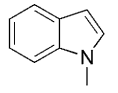
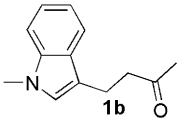
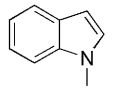
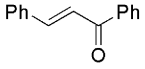
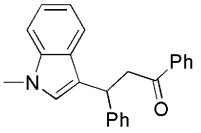
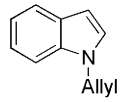
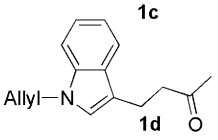
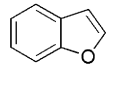
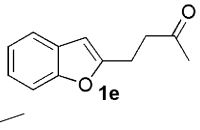
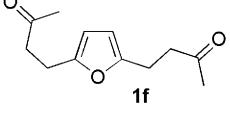
2. Results and discussion

2.1. Reactions between heterocycles and electron deficient olefins

Heterocycles, particularly those containing oxygen or nitrogen atoms in the ring, are important building blocks for natural products and pharmaceutical reagents. Thus, development of efficient methods to functionalize heterocyles is critical for synthetic chemistry [9]. Because of their electron rich nature, heterocycles should react with gold(III) readily to afford arylgold(III) species, as Hashimi et al. [5] has demonstrated with 2-methylfuran and Arcadi et al. [10] has shown with indole derivatives. We began to investigate reactions between various heterocyles and substituted olefins. We found that a variety of heterocycles can readily add to electron deficient olefins at room temperature in acetonitrile or dichloroethane (DCE) catalyzed by $AuCl_3$ Eq. (1). Good to excellent isolated yields can be obtained as summarized in Table 1.

Table 1
Hydroarylation of activated olefins with heterocycles[a]

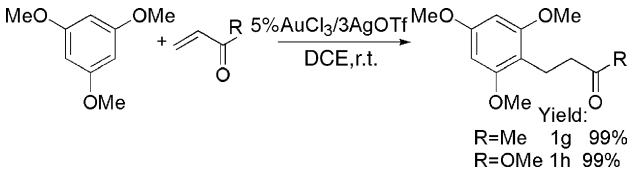
Entry	Heterocycle	Olefin	Product	Yield (%)[b]
1			 1a	95
2			 1b	97
3			 1c	92
4			 1d	87
5			 1e	57
6[c]			 1f	79

[a] All reactions were carried out with 0.5 mmol of the heterocycle at room temperature in CH_3CN (heterocycle:olefin:$AuCl_3$/1:1.5:0.05).
[b] Isolated yield.
[c] Heterocycle:olefin:$AuCl_3$/1:2.5:0.05.

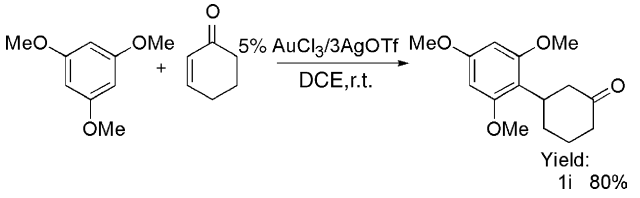
(1)

Indole and its derivatives afforded high yields of the products (entries 1–4, Table 1). Notably, indole itself can be used directly to react with methyl vinyl ketone without any protecting group and 95% isolated yield was obtained for this reaction (entry 1). Other heterocycles, furan and benzofuran (entries 5, 6) also served as good substrates under the same conditions. C–C bond formations at the 3-position for indole and 2-position for furan/benzofuran were observed, as expected. Furan can undergo double addition to two equivalents of olefins in very good yield (entry 6).

$AuCl_3$ (5 mol%) serves as a good catalyst for the reactions involving heterocycles. When 1,3,5-trimethoxybenzene was used, 3 equivalents of AgOTf is required as the co-catalyst to afford good yields of the addition product. The role of AgOTf is thought to help remove chloride from $AuCl_3$ and generate a more electrophilic cationic gold(III) species. In the presence of AgOTf, 1,3,5-trimethoxybenzene readily reacted with methyl vinyl ketone or methyl acrylate to afford almost quantitative yields of the final products at room temperature Eq. (2). When 2-cyclohexen-1-one was used as the olefin substrate, a slightly lower yield was obtained (80%), perhaps due to the steric reason Eq. (3).



(2)



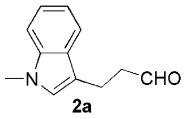
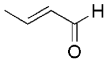
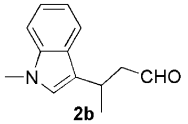
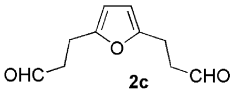
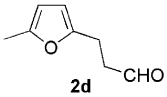
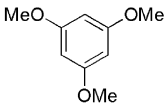
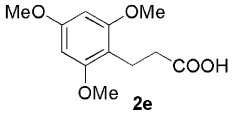
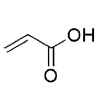
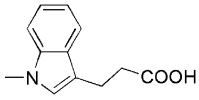
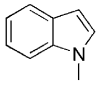
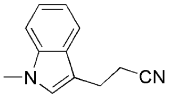
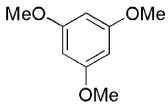
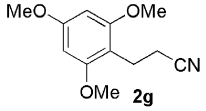
(3)

2.2. Various electron deficient olefins can be used as the substrates

We further explored the reaction with the use of different olefins. To our surprise, our catalytic system tolerates not only ketone and ester but also aldehyde, carboxylic acid, and nitrile, as shown in Table 2.

The reactions of α,β-unsaturated aldehydes with furans or a protected indole gave good yields of the

Table 2
Addition of heterocycles and electron-rich arenes to olefins with different functional groups

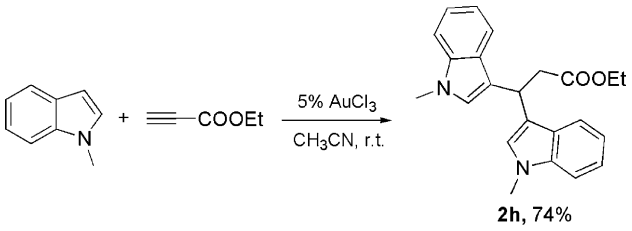
Entry	Arene	Olefin	Product	Yield (%)
1[a]			 **2a**	85
2[a]			 **2b**	80
3[a]			 **2c**	60
4[a]			 **2d**	94
5[b]			 **2e**	65
6[b,c]				64[c]
7[b]			 **2f**	52
8[b]			 **2g**	41

[a] Reactions were carried out with 5% $AuCl_3$ at room temperature in acetonitrile (heterocycle:olefin:$AuCl_3$/1:1.5:0.05).
[b] Reactions were carried out with 5% $AuCl_3$/3AgOTf at 80 °C in DCE (heterocycle:olefin/1:1.5). The isolated yields are reported except for entry 6.
[c] ^{1}H NMR yield.

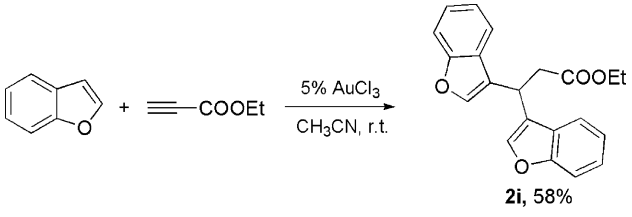
addition products at room temperature (entries 1–4, Table 2). Two equivalents of the olefin were attached to furan to afford the di-substituted furan (entry 3), as also observed in reactions described in Table 1. In entry 5, acrylic acid was used to react with 1,3,5-trimethoxybenzene with 5 mol% of $AuCl_3$/3AgOTf to afford a good yield of the addition product. In fact, a reaction between *N*-methylindole and acrylic acid was also tested. A product yield of 64% was observed based on ^{1}H NMR with an internal standard. The product was not isolated due to difficulties in its separation by column chromatography (entry 6). These results show a significant advantage of this method: substrates bearing aldehydes and acids do not need to be protected. We further examined the reactivity of acrylonitrile with *N*-methylindole and 1,3,5-trimethoxybenzene (entries 7 and 8). Reasonable yields of the products (52% and 41%, respectively) were obtained from these reactions. The reactions between arenes and acrylic acid or acrylonitrile were performed at 80 °C to give the best yields. We want to point out that most of the reactions described in Tables 1 and 2 can be run in the absence of solvents. Similar or better yields were typically obtained under the solvent-free conditions.

2.3. Reaction with ethyl propiolate

When ethyl propiolate was used to react with indole and 2,3-benzofuran (1:1.2/arene:alkyne) in acetonitrile, we were surprised to find that the only products we observed and isolated were the double addition products, as shown in Eqs. 4 and 5. Two equivalents of the heterocycles were added to one molecule of ethyl propiolate in this reaction. These results may indicate that the first addition of the arene to ethyl propiolate gives an activated alkene, which reacts faster with the second equivalent of arene to afford the final product. Similar double addition result has been reported by Fujiwara and coworkers [11] using acetic acid. However, when 1,3,5-trimethoxybenzene was used, no double addition product was obtained under the same condition. In addition, ethyl propiolate did not react with indole in the presence of 20 mol% of HCl without $AuCl_3$ under the same conditions. It appears that the α,β unsaturated ketone intermediates with a heterocycle at the β position are quite reactive and can react further with the heterocycle in this system.



(4)



(5)

The reaction rate between indole and methyl vinyl ketone at room temperature was monitored by ^{1}H NMR in $CDCl_3$. To a mixture of these two substrates in a NMR tube was added 3% $AuCl_3$/3AgOTf and the ^{1}H NMR spectrum was taken immediately after the addition. Only the product peak could be identified from the spectrum. The reaction completed in less than 5

min at room temperature. Another arene substrate, 1,3,5-trimethoxybenzene, was examined with $AuCl_3$/3AgOTf in the same manner, and the similar result was detected by ^1H NMR.

3. Summary

In this paper, we presented a highly efficient method to functionalize heterocycles with electron deficient alkenes and alkynes. Indole, furan and benzofuran all serve as good substrates for the gold(III)-catalyzed hydroarylation of the activated alkenes/alkynes at ambient temperatures. Functional groups such as aldehyde, carboxylic acid and nitrile can be tolerated. The reactions also proceed remarkably fast and complete in minutes at room temperature. The method described here can be broadly utilized to construct heterocycle-based structures.

4. Experimental

All reagents were obtained commercially and used without further purification unless otherwise noted. All reactions were performed under air atmosphere in acetonitrile or dichloroethane. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35–75 μm). Thin layer chromatography was performed on EM Science silica gel 60 F254 plates (250 μm). Proton nuclear magnetic resonance (NMR) spectra were referenced internally according to residual protio solvent signals. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

*4.1. 4-(1H-Indol-3-yl)-butan-2-one (**1a**)*

^1H NMR ($CDCl_3$/TMS): δ 8.11 (b, 1H), 7.55 (m, 1H), 7.25 (m, 1H), 7.15 (m, 1H), 7.07 (m, 1H), 6.86 (m, 1H), 3.03 (t, J = 7.6 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS): δ 209.1, 136.1, 127.0, 121.8, 121.5, 119.1, 118.5, 114.7, 111.1, 43.9, 29.9, 19.2.

*4.2. 4-(1-Methyl-1H-indol-3-yl)-butan-2-one (**1b**)*

^1H NMR ($CDCl_3$/TMS): δ 7.57 (m, 1H), 7.27 (m, 2H), 7.11 (m, 1H), 6.81 (s, 1H), 3.72 (s, 3H), 3.05 (t, J = 7.4 Hz, 2H), 2.82 (t, J = 7.4 Hz, 2H), 2.14 (s, 3H).

*4.3. 3-(1-Methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (**1c**)*

^1H NMR ($CDCl_3$/TMS): δ 7.93 (m, 2H), 7.53 (m, 1H), 7.44 (m, 3H), 7.36 (m, 2H), 7.25 (m, 3H), 7.13 (m, 2H), 7.01 (m, 1H), 6.8 (s, 1H), 5.06 (t, J = 7.0 Hz, 1H), 3.77 (tt, J = 7.0 Hz, 5.2 Hz, 2H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS): δ 198.2, 144.4, 137.3, 137.1, 133.0, 128.6, 128.4, 128.1, 127.8, 126.9, 126.2, 121.7, 119.6, 118.8, 117.8, 109.2, 45.3, 38.05, 32.7.

*4.4. 4-(1-Allyl-1H-indol-3-yl)-butan-2-one (**1d**)*

^1H NMR ($CDCl_3$/TMS): δ 7.57 (m, 1H), 7.27 (m, 1H), 7.20 (m, 1H), 7.10 (m, 1H), 6.86 (s, 1H), 5.95 (m, 1H), 5.16 (d, J = 11.4 Hz, 1H), 5.04 (d, J = 11.4 Hz, 1H), 4.63 (d, J = 4 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR: δ 208.7, 136.3, 133.5, 127.7, 125.2, 121.5, 118.8, 118.7, 117.1, 114.0, 109.5, 48.5, 44.1, 30.0, 19.2.

*4.5. 4-Benzofuran-2-yl-butan-2-one (**1e**)*

^1H NMR ($CDCl_3$/TMS): δ 7.46 (m, 1H), 7.40 (m, 1H), 7.21 (m, 2H), 6.39 (s, 1H), 3.06 (t, J = 7.1 Hz, 2H), 2.89 (t, J = 7.1 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS): δ 206.7, 157.6, 154.6, 128.7, 123.3, 122.5, 120.3, 110.6, 102.3, 41.2, 29.9, 22.5.

*4.6. 4-[5-(3-Oxo-butyl)-furan-2-yl]-butan-2-one (**1f**)*

^1H NMR ($CDCl_3$/TMS): δ 5.86 (s, 2H), 2.85 (t, J = 7.8 Hz, 4H), 2.77 (t, J = 7.8 Hz, 4H), 2.17 (s, 6H); ^{13}C NMR ($CDCl_3$/TMS): δ 185.2, 152.3, 105.7, 41.7, 29.9, 22.2.

*4.7. 4-(2,4,6-Trimethoxy-phenyl)-butan-2-one (**1g**)*

^1H NMR ($CDCl_3$/TMS): δ 6.11 (s, 2H), 3.79 (s, 6H), 3.77 (s, 3H), 2.83 (t, J = 7.5 Hz, 2H), 2.55 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS): δ 209.7, 159.4, 158.6, 109.3, 90.3, 55.5, 55.2, 43.5, 29.5, 17.4; MS m+ (%): 238.

*4.8. 3-(2,4,6-Trimethoxy-phenyl)-propionic acid methyl ester (**1h**)*

^1H NMR ($CDCl_3$/TMS): δ 6.11 (s, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 3.67 (s, 3H), 2.90 (t, J = 7.9 Hz, 2H), 2.45 (t, J = 7.9 Hz, 2H), ^{13}C NMR ($CDCl_3$/TMS): δ 174.2, 159.5, 158.6, 109.0, 90.2, 55.4, 55.1, 51.3, 33.6, 18.3; MS m+ (%): 254.

*4.9. 3-(2,4,6-Trimethoxy-phenyl)-cyclohexanone (**1i**)*

^1H NMR ($CDCl_3$/TMS): δ 6.12 (s, 2H), 3.78 (s, 3H), 3.76 (s, 6H), 3.62 (m, 1H), 3.10 (t, J = 12.3 Hz, 1H), 2.36 (m, 2H), 2.26 (m, 2H), 2.03 (m, 1H), 1.70 (m, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ 212.4, 159.4, 158.8, 112.2, 90.7, 55.3, 55.0, 45.3, 41.2, 33.8, 28.8, 25.4, MS m+ (%): 265.0 ($M + 1^+$).

*4.10. 3-(1-Methyl-1H-indol-3-yl)-propionaldehyde (**2a**)*

^{1}H NMR ($CDCl_3$/TMS): δ 9.79, (s, 1H), 7.54 (m, 1H), 7.26 (m, 2H), 7.07 (m, 1H), 6.81 (s, 1H), 3.69 (s, 3H), 3.07 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ 202.6, 136.9, 127.3, 126.3, 121.6, 118.7, 118.6, 112.9, 109.2, 44.1, 32.5, 17.6.

*4.11. 3-[5-(3-Oxo-propyl)-furan-2-yl]-propionaldehyde (**2c**)*

^{1}H NMR ($CDCl_3$/TMS): δ 9.81 (s, 2H), 5.89 (s, 2H), 2.98 (t, J = 7.2 Hz, 4H), 2.79 (t, J = 7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$/TMS): δ 201.2, 152.5, 106.0, 41.8, 20.7.

*4.12. 3-(5-Methyl-furan-2-yl)-propionaldehyde (**2d**)*

^{1}H NMR ($CDCl_3$/TMS): δ 9.75 (s, 1H), 5.87 (d, J = 19 Hz, 2H), 2.92 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 2H), 2.22 (s, 3H).

*4.13. 3-(2,4,6-Trimethoxy-phenyl)-propionic acid (**2e**)*

^{1}H NMR ($CDCl_3$/TMS): δ 6.12 (s, 2H), 3.80 (s, 3H), 3.79 (s, 6H), 2.92 (t, J = 6.5 Hz, 2H), 2.51 (t, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ 180.4, 159.6, 158.7, 108.8, 90.3, 55.5, 55.2, 33.7, 18.1.

*4.14. 3-(1-Methyl-1H-indol-3-yl)-propionitrile (**2f**)*

^{1}H NMR ($CDCl_3$/TMS): δ 7.54 (m, 1H), 7.33 (m, 1H), 7.25 (m, 1H), 7.14 (m, 1H), 7.00 (s, 1H), 3.76 (s, 3H), 3.12 (t, J = 6.0 Hz, 2H), 2.68 (t, J = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ 136.9, 126.9, 126.8, 121.9, 119.8, 119.1, 118.2, 111.0, 109.5, 32.7, 21.5, 18.9; MS m+ (%): 184.

*4.15. 3-(2,4,6-Trimethoxy-phenyl)-propionitrile (**2g**)*

^{1}H NMR ($CDCl_3$/TMS): δ 6.13 (s, 2H), 3.82 (s, 6H), 3.63 (s, 3H), 2.95 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ 160.3, 158.8, 120.2, 107.0, 90.3, 55.6, 55.3, 18.9, 16.8; MS m+ (%): 221.

*4.16. 3,3-Bis-(1-methyl-1H-indol-3-yl)-propionic acid ethyl ester (**2h**)*

^{1}H NMR ($CDCl_3$/TMS): δ 7.60-7.59 (m, 2H), 7.25–7.23 (m, 2H), 7.19–7.16 (m, 2H), 7.04–7.01 (m, 2H), 6.85 (s, 2H), 5.10 (t, J = 7.5 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 3.66 (s, 6H), 3.16 (d, J = 7.5 Hz), 1.08 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS): δ 172.4, 137.2, 126.9, 126.3, 121.4, 119.6, 118.6, 117.3, 109.1, 66.3, 41.5, 32.6, 30.6, 14.1.

*4.17. 3,3-Bis-benzofuran-3-yl-propionic acid ethyl ester (**2i**)*

^{1}H NMR ($CDCl_3$/TMS): δ 7.61–7.42 (m, 2H), 7.43–7.42 (m, 2H), 7.28–7.25 (m, 2H), 7.21–7.20 (m, 2H), 7.19 (s, 2H), 4.95 (t, J = 7.5 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 3.23 (d, J = 7.5 Hz, 2H) 1.19 (q, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS): δ 170.7, 155.9, 154.8, 128.3, 124.0, 122.8, 120.8, 111.1, 103.7, 60.9, 37.0, 36.1, 14.1.

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