ORGANOMETALLICS

Effective Transmetalation from Gold to Iron or Ruthenium

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Supporting Information

ABSTRACT: The transmetalation of aryl, alkynyl, and alkyl groups from organogold compounds to iron complexes offers an efficient synthesis of organoiron complexes under very mild conditions. This method could be extended to ruthenium complexes.



In the past decade gold has emerged as a powerful tool to achieve many organic transformations through carbon-carbon or carbon-heteroatom bond formation.¹ The cycloisomerizations of enynes² and the hydrofunctionalizations of alkenes, allenes, and alkynes with nucleophilic heteroatoms are representative examples.³ These catalysis reactions proceed under very mild conditions and are based on the high carbophilic character of gold(I/III) complexes. However, the catalytic cycle for most of these reactions does not involve changes in the oxidation state of the catalyst.⁴ Gold catalysts do not undergo oxidative addition reactions easily.⁵ To circumvent this problem, transmetalation of isolated or in situ generated organogold species to other transition metals with pronounced redox ability allows broadening the scope of gold catalysis. Different groups have addressed the palladium-catalyzed cross-coupling reaction of organogold compounds.⁶ While transmetalation between gold and palladium has since been studied more extensively,7 publications reporting transmetalation between gold and other metals remain sporadic. Blum and co-workers recently reported the nickel-catalyzed crosscoupling reactions of stoichiometric organogold compounds9 and studied the transmetalation between organogold and rhodium complexes.¹⁰ Due to the recent success of iron-catalyzed crosscoupling in organic synthesis,¹¹ we turned our attention to the transmetalation between gold and iron. Iron is a very cheap and nontoxic metal, which has proven to be a powerful catalyst in many reaction types, including cross-coupling. Reports of a transmetalation step between gold and iron complexes are scarce; van Koten and coworkers published the transmetalation of an (*o*-amine)aryl moiety,⁸ and Low et al. reported the transmetalation of an alkynyl group.^{8j}

In the search for a stable iron complex as a potential transmetalation partner, our interest focused on the coordinatively saturated piano-stool iron complex. Oshima et al. reported the synthesis of aryliron compounds using the dicarbonylcyclopentadienyliodoiron complex $CpFe(CO)_2I$ (2a) from different organometallic reagents.¹² Their method is efficient but requires the use of a palladium catalyst and/or different additives. Herein we report transmetalation between organogold and iron complexes, showing that this type of reaction might be incorporated in catalytic cycles in the future.

We started using the simplest reaction conditions, by mixing the arylgold 1a with iron complex 2a in chloroform at room

temperature and monitoring the reaction by NMR. We were delighted to detect that within a few minutes the transfer of the aryl group from gold to iron was complete, leading to the organoiron complex 3a. The reaction progress was even detectable by a color change; the initially dark brown solution had turned bright yellow. The complex was purified by column chromatography and isolated in 84% yield. Ph₃PAuI could also be isolated in 87% yield. Then we explored the scope of the reaction using other organogold compounds. Electron-rich aromatic moieties, such as *p-tert*-butylphenyl, could be transmetalated in excellent yield (Table 1, entry 4). The presence of a coordinating methoxy substituent on the aromatic ring did not affect the reaction (Table 1, entry 5), and even the sterically hindered *m*-methoxyphenyl moiety (Table 1, entry 6) could be transmetalated completely; the corresponding organoiron species 3d was isolated in 82% yield. Organogold complexes bearing electron-deficient aryl groups were also investigated. Both the weakly electron withdrawing fluoro substituent (Table 1, entry 9) and strongly electron withdrawing nitro group in para position (Table 1, entry 11) were transferred easily. With the nitro group in the meta position (Table 1, entry 15), complete ligand exchange was achieved within 1 h and product 3h could be isolated in good yield. The transmetalation between the sterically hindered Hammond furanone gold complex 1i,¹³ a stable intermediate of a gold-catalyzed cycloisomerization, and iron complex 2a (Table 1, entry 18) was slower than for arylgold species, but clean conversion at room temperature delivered 3i in good yield. Focusing on the influence of the hybridization, the transmetalation of an sp-hybridized phenylacetylene moiety (Table 1, entry 19) afforded the organoiron species 3j in excellent yield. In contrast to the furanone 1i, the transfer of a simpler sp²-hybridized vinyl group (Table 1, entry 20) did not deliver the expected compound 3k. Monitoring the reaction by ¹H and ³¹P NMR showed consumption of the vinylgold compound 1k, but instead of the expected formation of Ph_3PAuI at 39 ppm in ³¹P NMR, one major peak was observed at 61 ppm. ¹H NMR and COSY showed the presence of two different vinyl species, which were not consistent with NMR data reported for the desired product 3k. These species

 Received:
 April 28, 2011

 Published:
 June 13, 2011

Table 1. Transmetalation between Organogold Compounds and Iron Complexes^c

				R-Au-PF	^{2h} 3 + OC-F	e x	CHCl ₃	→ OC-Fe OC R				
				1a-I	2 2 2	2a X= I 2b X= B 2c X= C	r I	3a-I				
Entry	1	2	time	3	Yield of 3		Entry	1	2	time	3	Yield of 3
1		2a	15 min	OC-Fe	84%		13	Au-PPh3	2a	30 min	OC-Fe OC	87%
2	 1a	2b	1 h		86%		14	F ₃ C	2h	1 h	CF3	94%
3		2c	5 h ^a	3a	61%			Ig	20		3g	5170
				Ç, Fe ∧			15	Au-PPh3	2a	45 min	OC-Fe OC	80%
4	Au-PPh ₃	2a	15 min		98%		16	O ₂ N	2b	2 h	NO ₂	79%
	1b			3b			17	In	2c	4 h ^a	3h	71%
5	MeO-Au-PPh3	2a	15 min	OC-Fe OC OMe	90%		18	o Au-PPh3	2a	12 h	OC-Fe OC O	75%
	1c			3c							3i	
6	ОМе	2a	30 min	OMe OC-Fe	82%		19	Au-PPh3	2.9	1 h	OC-Fe OC	93%
7	Au-PPh3	2b	1 h	oc	83%		.,	1j	24		31	
8	1d	2c	3 h ^a	3d	82%							
9		2a	15 min	P	86%		20	/ ^{−Au−PPh} 3	2a	2 h	oc-Fe oc	Formation of
	F			OC-Fé OC				1k			3k	3k not observed
10	1e	2b	1 h	3e	82%		21	—Au—PPh3	2a	2 h		93% ^b
11		2a	15 min		88%			11		10.1.9	31	ND
10	~2"		1 %	NO2	019/		22	Au-IPr	2a	12 h"	OC-Fe OC	N.R.
12	11	20		3f	9170		23	4a ^c	2 b	12 h ^a	3a	N.R.

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^{*a*} Reaction was carried out at 60 °C. ^{*b*} Yield determined by NMR. ^{*c*} IPr = [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene].

could not be isolated for characterization. An sp³-hybridized methyl group could almost be fully transferred to the iron complex (93% conversion based on ¹H and ³¹P NMR integration), but the product decomposed upon purification. In order to examine the reactivity toward transmetalation of other iron complexes, we tested the transmetalation between representative organogold compounds and the corresponding bromo and chloro iron complexes (**2b**,**c**). The bromo complex **2b** showed reactivity comparable with that of the iodo complex **2a**. Though the transmetalation proceeded slightly more slowly, the yield was not affected (Table 1, entries 2, 7, 10, 12, 14, and 16). The conversion of the chloro complex **2c** was found to be slow at room temperature, but upon heating at 60 °C, the organoiron complexes could be

isolated in modest to good yield (Table 1, entries 3, 8, and 17). To get a more reliable insight into the transmetalation kinetics, we monitored the reaction by ³¹P NMR, combining the organogold compounds 1f,h and the three different iron complexes 2a-c. Transmetalation between the *p*-nitrophenylgold complex 1f (Figure 1) and the iodo iron complex 2b was achieved within 5 min, while with the bromo iron complex 2b, completion was observed after 15 min. For the chloro complex 2c, after almost 2 h, the conversion reached 67% and did not evolve. As expected for the *m*-nitrophenyl group (Figure 2), the reaction was slower than for 1f with the iron complexes 2a,b and for 2c the transmetalation reached only 28% conversion after prolonged reaction times.



Figure 1. NMR-monitored kinetics for the formation of 3f (with respect to Ph_3PAuX formation) from complexes 2a-c.



Figure 2. NMR-monitored kinetics for the formation of 3h (with respect to Ph₃PAuX formation) from complexes 2a-c.

Next we investigated the influence of organogold ligand hindrance. A drastic influence on the reactivity was observed with the organogold species 4a, bearing the very bulky N-heterocyclic carbene ligand IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and transfer of the *p*-tolyl group to the iron complex to form 3a was not observed, although the reaction mixture was heated to $60 \,^\circ C$ (Table 1, entry 22). Using the bromo iron complex 2b led to the same result (Table 1, entry 23).

Even though Ph₃PAuX (X = I, Br, Cl) could be isolated in very good yield, our next focus was to achieve the transmetalation using a catalytic amount of the gold complex. Phenylacetylene seemed to be the proper choice, as it can easily form the corresponding organogold complex 1j in the presence of a base, without silver salt activation. Using Et₃N as a base, 10 mol % of Ph₃PAuCl with iron complexes 2a-c at 60 °C led to stoichiometric formation of organoiron 3j in modest to good yield depending on the iron precursor (Table 2, entry 2). Changing the gold catalyst to the conformationally more flexible noncyclic amino carbene (NAC)¹⁴ ligand 6 gave an excellent yield, except for the chloro iron complex 2c (Table 2, entry 3). The catalyst loading could be even reduced to 3 mol % without affecting the yield of the reaction (Table 2, entry 4). The control experiment showed that, in the absence of the gold catalyst, the amount of 3j formed was very low; in the case of 2c it failed completely (Table 2, entry 1).¹⁵

To further emphasize the synthetic advantages of this methodology, we decided to test a subsequent coupling reaction of 3jwith 3-bromo-2-methylpropene (7), which had been found by Oshima and co-workers to be a good coupling partner.^{8b,d} The conversion was conducted as a one-pot reaction with sequential addition: first the gold-catalyzed formation of 3j, followed by a coupling reaction with 7 under UV irradiation. The formation of the sp-sp³ coupling product 8 could be achieved in 34-46%yield (Scheme 1).

Table 2. Yield of Gold-Catalyzed Formation of Organoiron 3j^a



Entry		OC-Fe_I	OC-Fe. Br	OC-Fe OC
	Catalyst	2a	2b	2c
1	None	9%	5%	N.R.
2	10 mol% of 5	72%	83%	44%
3	10 mol% of 6	98%	94%	16%
4	3 mol% of 6		95%	

^{*a*} The structures of **5** and **6** are as follows:



Encouraged by the results for the transmetalation from gold to iron, we decided to explore another group 8 metal, ruthenium. Piano-stool ruthenium cymene complexes appeared to be the proper choice; they behave quite similarly to the corresponding iron compounds. Complexes **9a**,**b** were both synthesized from the corresponding dimer. In order to avoid ligand exchange between chlorinated solvent and complex **9b**, the reaction was carried out in THF at 40 °C. Two representative organogold compounds were tested. The activated *p*-methylphenyl group was transferred to ruthenium complexes **9a**,**b**, leading to the formation of organoruthenium species **10aa**,**ab** in good yields. Transmetalation of a deactivated *m*-nitrophenyl group could be achieved even more efficiently for both chloro and bromo complexes **9a**,**b** (Scheme 2).

We have presented in this publication a very efficient and mild method for the synthesis of organoiron and -ruthenium complexes by transmetalation with organogold complexes. This method also allows the use of a catalytic amount of gold catalyst for the formation of iron phenylacetylene complexes. The transmetalation from gold to iron and ruthenium might in the future serve as the basis for combining the very successful ironcatalyzed coupling methods with gold catalysis. This would extend the possibilities, which are currently limited to gold/ palladium and gold/nickel systems. On the other hand, this efficient transmetalation differs from previous work on the transmetalation from organozinc and organomagnesium compounds or boronic acids, which requires a palladium catalyst.^{12a} We assume that, different from the case for zinc, magnesium, or boron, the high affinity of the soft gold(I) for iodine and bromine creates an additional driving force for the transmetalation, an effect which

Scheme 1. One-Pot sp-sp³ Cross-Coupling Reaction



Scheme 2. Transmetalation between Arylgold Compounds and Ruthenium Complexes



was also visible in our previous investigation of the gold/palladium systems.^{6a,7c} Investigations addressing this point are in progress.

ASSOCIATED CONTENT

Supporting Information. Text and figures giving characterization data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENT

This work was supported by Umicore AG & Co. KG and by the Deutsche Forschungsgemeinschaft (SFB 623).

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