A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201901856
Angew. Chem. 10.1002/ange.201901856

Link to VoR: http://dx.doi.org/10.1002/anie.201901856
http://dx.doi.org/10.1002/ange.201901856

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Micellar Catalysis for Ruthenium(II)-Catalyzed C−H Arylation: Weak-Coordination-Enabled C−H Activation in H_2O

Santhivardhana Reddy Yetra,[a] Torben Rogge,[a] Svenja Warratz,[a] Julia Struwe,[a] Wentao Peng,[b] Philipp Vana,[b] and Lutz Ackermann*[a]

Abstract: Chemoselective C–H arylations were accomplished in terms of micellar catalysis by a versatile single-component ruthenium catalyst. The strategy provided expedient access to C–H arylated ferrocenes with wide functional group tolerance and ample scope through weak chelation assistance. The sustainability of the C–H arylation was demonstrated by an outstanding atom-economy and recycling studies. Detailed computational studies provided support for a facile C–H activation through thioketone assistance.

Transition metal-catalyzed C–H activations have surfaced as a powerful tool for molecular syntheses,[1] with transformative applications to *inter alia* material sciences[2] and pharmaceutical industries.[3] The sustainability of the C–H activation strategy could be improved when using water as a nonflammable, nontoxic, environmentally-friendly reaction medium.[4] Unfortunately, the organic compounds and catalysts of interest are usually not soluble in water, leading to limited heterogeneous catalysis not in, but rather on water.[5] In sharp contrast, specific surfactants have been identified as increasingly viable tools for realizing homogeneous metal catalysis in water.[6] Thus, pioneering studies by Lipshutz,[7] Gallou,[8] Tan,[9] and Handa,[10] among others, have indicated the major potential of designer surfactants for palladium-catalyzed coupling chemistry in terms of trace metal impurities, homogenous catalysis and improved selectivities. Despite of these indisputable advances, micellar C–H functionalization continues to be scarce,[11] while sustainable ruthenium[12] micellar C–H activation catalysis has thus far proven elusive.

Within our program on ruthenium-catalyzed C–H arylations,[13] we have now devised C–H arylations assisted by weakly-coordinating thiocarbonyls, allowing the first micellar-enabled C–H activation on substituted ferrocenes[14] – key structural motifs in organocatalysts and versatile ligands for stereoselective catalysis.[15] Salient features of our approach include (*i*) ruthenium-catalyzed C–H activation by micellar catalysis, (*ii*) a user-friendly single-component ruthenium catalyst for ferrocene C–H arylations and (*iii*) computational insights into the nature of weak thiocarbonyl coordination for C−H activation.

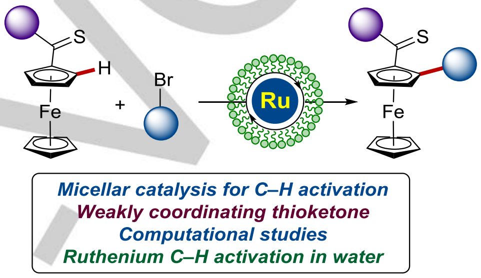

Figure 1. Micellar catalysis for ruthenium-catalyzed C–H arylation.

We commenced our studies by probing the envisioned C–H arylation of ferrocene **1a** by 4-bromo anisole (**2a**) with [$RuCl_2$(*p*-cymene)$]_2$ as the catalyst in TPGS-750M/H_2O (Table 1 and Table S–1-S–3). Notably, additive-free conditions provided unsatisfactory results (entry 1). Instead, the addition of acetic acid afforded the desired arylated ferrocene **3aa** in 62% yield (entry 2). Among various carboxylic acid additives, adamantylcarboxylic acid gave the best performance (entry 5). Moreover, single-component ruthenium catalysts were found to be more efficient in furnishing the desired arylated product **3aa**, even at reduced reaction temperatures of 50 to 70 °C (entries 6-9). Likewise, arene-free ruthenium catalysts[16] proved also effective (entries 10 and 11), while unsatisfactory results were obtained with a cationic ruthenium complex (entry 12). Variation of the surfactants did not lead to superior results (entries 13-19). Importantly, when water was used as the reaction medium we observed only trace amounts of product **3aa**, which indicates the key role of the micellar regime (entry 20). The unique catalytic performance and water tolerance of the ruthenium(II) micellar catalysis were mirrored by palladium, rhodium, cobalt and manganese complexes falling short in delivering the desired C–H arylation (entries 21-24).

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[a] Dr. S. R. Yetra, T. Rogge, Dr. S. Warratz, J. Struwe
Prof. Dr. L. Ackermann
Institut für Organische und Biomolekulare Chemie
Georg-August-Universität Göttingen
Tammannstrasse 2, 37077 Göttingen, Germany
E-mail: Lutz.Ackermann@chemie.uni-goettingen.de
Homepage:http://www.ackermann.chemie.uni-goettingen.de/
[b] W. Peng, Prof. Dr. P. Vana
Institut für Physikalische Chemie
Georg-August-Universität Göttingen
Tammannstrasse 6, 37077 Göttingen, Germany

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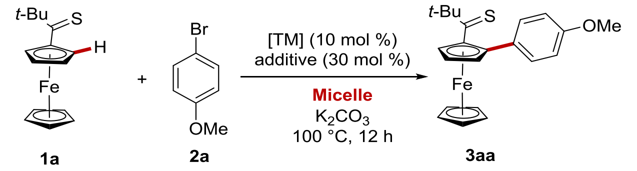
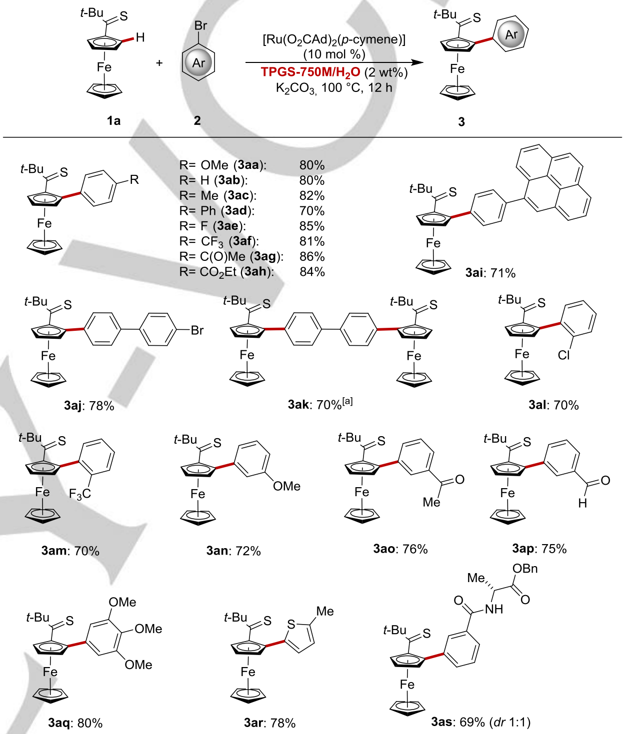
Table 1. Thiocarbonyl-assisted C−H arylation.[a]



Entry	[TM]	Additive	Micelle	Yield (%)
1	$[RuCl_2(p\text{-cymene})]_2$	---	TPGS-750M/H_2O	-
2	$[RuCl_2(p\text{-cymene})]_2$	AcOH	TPGS-750M/H_2O	62
3	$[RuCl_2(p\text{-cymene})]_2$	CF_3CO_2H	TPGS-750M/H_2O	64
4	$[RuCl_2(p\text{-cymene})]_2$	$MesCO_2H$	TPGS-750M/H_2O	65
5	$[RuCl_2(p\text{-cymene})]_2$	$AdCO_2H$	TPGS-750M/H_2O	76
6	$[Ru(O_2CMes)_2(p\text{-cymene})]$	---	TPGS-750M/H_2O	69
7	***$[Ru(O_2CAd)_2(p\text{-cymene})]$***	***---***	TPGS-750M/H_2O	***80***
8	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	TPGS-750M/H_2O	51[b]
9	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	TPGS-750M/H_2O	69[c]
10	***$[Ru(OAc)_2(PPh_3)_2]$***	***---***	TPGS-750M/H_2O	***70***
11	$[Ru(O_2CAd)_2(PPh_3)_2]$	---	TPGS-750M/H_2O	67
12	$[Ru(NCCH_3)_6][SbF_6]_2$	$AdCO_2H$	TPGS-750M/H_2O	10
13	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	SPGS-550M/H_2O	65
14	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	PTS/H_2O	27
15	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	Triton X-100/H_2O	66
16	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	SDS/H_2O	70
17	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	Tween 20/H_2O	55
18	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	Brij 35/H_2O	71
19	$[Ru(O_2CAd)_2(p\text{-cymene})]$	---	Brij 93/H_2O	73
20	$[Ru(O_2CAd)_2(p\text{-cymene})]$	-	H_2O	<5
21	$Pd(OAc)_2$	-	TPGS-750M/H_2O	-
22	$[Cp^*RhCl_2]_2$	-	TPGS-750M/H_2O	-
23	$Cp^*Co(CO)I_2$	-	TPGS-750M/H_2O	-
24	$MnBr(CO)_5$	-	TPGS-750M/H_2O	-

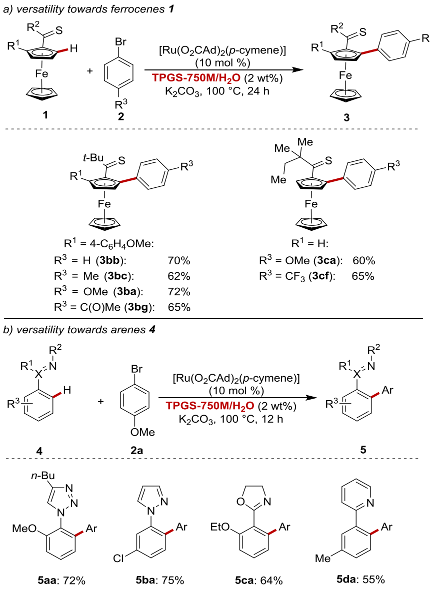
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), additive (30 mol %), [TM] (10 mol %), micelle/H_2O (1.0 mL), 100 °C, 12 h, under N_2. Yields of isolated product, TM: transition metal. [b] With NaCl (3M) at 50 °C. [c] 70 °C.[17]

With these optimized reaction conditions in hand, we then examined the substrate scope of the ruthenium-catalyzed C–H arylation with micelle TPGS-750M/H_2O (Scheme 1). First, we evaluated various aryl bromides **2**. Electron-donating and electron-withdrawing substitutents were well tolerated, leading to arylated ferrocenes with high efficacy (**3aa**-**3ai**). With dibromoarenes selective mono C–Br cleavage was observed, while both C–Br bonds could be functionalized when an excess of ferrocene **1a** was employed (**3aj, 3ak**). The outstanding chemoselectivity of the versatile ruthenium(II) catalyst was reflected by fully tolerating valuable functional groups, such as chloro, bromo, ester, ketone and aldehyde substituents. Further, heteroaryl (**3ar**), and peptide-substituted (**3as**) ferrocenes were obtained in a chemoselective manner.



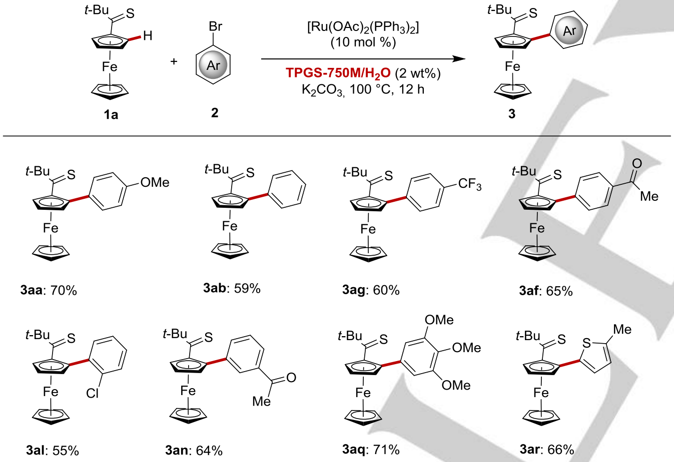
Scheme 1. C–H arylations with aryl bromides **2**. [a] **1a** (2.0 equiv), **2j** (1.0 equiv), 24 h.

The versatile ruthenium-catalyzed C–H arylation was not limited to mono-substituted ferrocenes. Indeed the ferrocenes **1b-c** were likewise identified as viable substrates to obtain the arylated products **3** (Scheme 2a). Moreover, differently substituted arenes **4** were found to be arylated within the ruthenium-catalyzed C–H activation manifold (Scheme 2b).



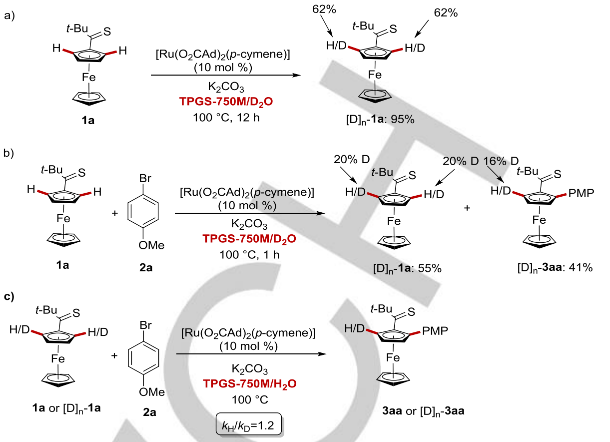
Scheme 2. a) C–H arylations of ferrocenes **1**. b) Micellar C–H arylations of arenes.

Next, we probed the versatility of the arene ligand-free-catalyst [Ru(OAc)$_2$(PPh$_3$)$_2$] in micellar catalysis. Various aryl bromides **2** as well as heteroaryl electrophiles were well accepted here likewise (Scheme 3).



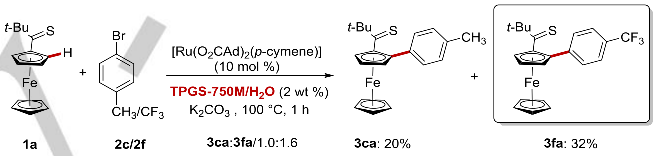
Scheme 3. C–H arylation with arene-free ruthenium catalyst.

Given the versatility of the ruthenium-catalyzed C–H arylation, we became intrigued to delineate its mode of action. To this end, C–H arylations in the presence of isotopically labeled cosolvents led to H/D scrambling in proximity to the thiocarbonyl group (Scheme 4). Furthermore, we observed a negligible kinetic isotopic effect (KIE) of $k_H/k_D = 1.2$. These findings are indicative of a fast organometallic C–H ruthenation.



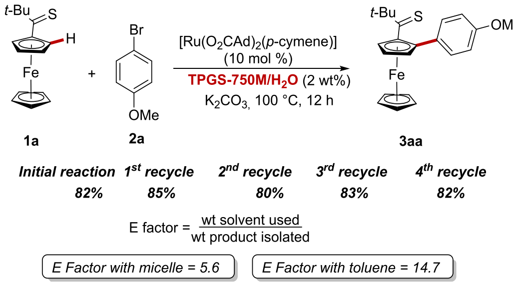
Scheme 4. Key mechanistic studies.

Next, intermolecular competition experiments with differently substituted aryl bromides **2** revealed the more electron-deficient aryl bromide **2f** to react preferentially (Scheme 5).



Scheme 5. Intermolecular competition experiment.

We were further pleased that the designer surfactant could be recycled up to four times without affecting the catalytic performance. Based on the organic solvent employed during the workup procedures, the parent reaction resulted in a very low E factor value of 5.6, thus indicating the sustainability of the present reaction (Scheme 6).



Scheme 6. Measure of sustainability by E factor and recycling study.

Furthermore, nano micelles of TPGS-750M played a crucial role in the catalysis. A dynamic light scattering (DLS) experiment revealed the existence of micelles with an average diameter of 52 nm (Figure 2). After full conversion, the particle size of the surfactant solution significantly increased to 130 nm, indicating the accommodation of the organic compounds and catalyst in the micelles.

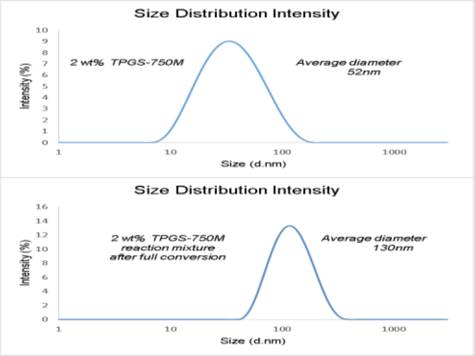


Figure 2. DLS studies of the micelles.

To gain further insights into the nature of the thioketone weak coordination, we explored the key C–H activation step by means of density functional theory (DFT) studies. Calculations at the PW6B95-D3(BJ)/def2-TZVP+COSMO//TPPS-D3(BJ)/def2-TZVP level of theory revealed the C–H activation to proceed via the formation of agostic intermediate **B** with an energy barrier of 10.9 kcal mol^{-1} (Figure 3 and Figure S2).[17] A comparison with ketone directing group showed the ketone to be energetically less favorable by 13.0 kcal mol^{-1}. Distortion-Interaction analysis of **TS1** resulted in similar distortion energies for both motifs with values of 29.1 kcal mol^{-1} for the ketone and 28.1 kcal mol^{-1} for the thioketone (Table S2). The interaction energies illustrated a significant difference with -15.2 kcal mol^{-1} and -26.9 kcal mol^{-1} for oxygen and sulfur, respectively, highlighting the considerably stronger interactions between the thioketone and the ruthenium complex.

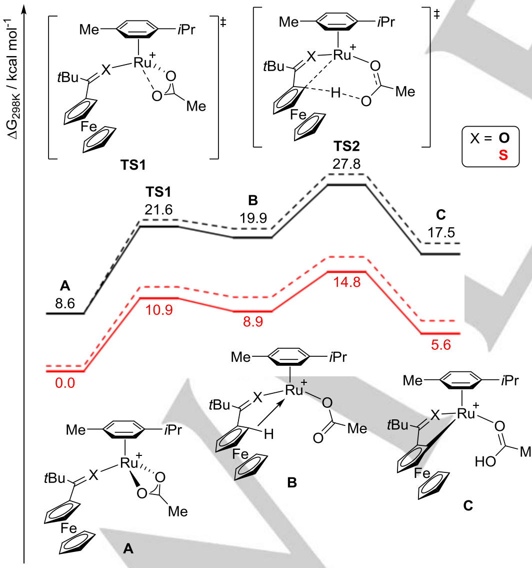


Figure 3. Calculated Gibbs free energy profile for the C–H activation step with ketone and thioketone directing groups at the PW6B95-D3(BJ)/def2-TZVP+COSMO//TPPS-D3(BJ)/def2-TZVP level of theory. Dashed lines correspond to energies without D3(BJ) correction.

In summary, we have developed an unprecedented ruthenium(II)-catalyzed C–H arylation by a micellar regime. Thus, the single-component complex [Ru(O$_2$CAd)$_2$(p-cymene)] and the arene-ligand-free [Ru(OAc)$_2$(PPh$_3$)$_2$] set the stage for homogeneous C–H arylations in H$_2$O. The first micellar-enabled ruthenium-catalyzed C–H activation features full tolerance of sensitive functional groups and H$_2$O by an organometallic C–H activation manifold as well as a strategy for effective micelle recovery and reuse. The facile C–H activation by weak thioketone assistance was rationalized by experimental and computational studies.

Acknowledgements

Generous support by the DFG (Gottfried-Wilhelm-Leibniz-Preis to LA and SPP1807) is gratefully acknowledged.

Keywords: C–H activation • micellar catalysis • thioketone • ruthenium • arylation

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[17] For detailed information, see the Supporting Information.

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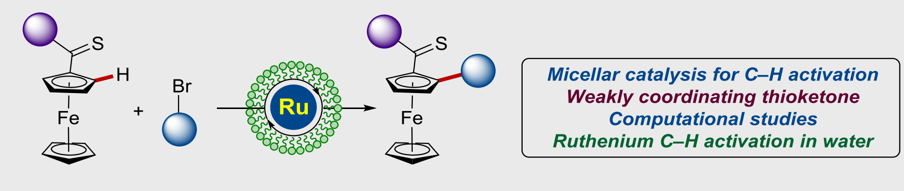

*Santhivardhana Reddy Yetra, Torben Rogge, Svenja Warratz, Julia Struwe, Wentao Peng, Philipp Vana, and Lutz Ackermann**

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Micellar Catalysis for Ruthenium(II)-Catalyzed C−H Arylation: Weak-Coordination-Enabled C−H Activation in H_2O

Micelle: Weak-coordination enabled versatile ruthenium-catalyzed C−H arylations by micellar catalysis in H_2O.