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[15] Strong antiferromagnetic coupling has also been observed in a complex containing an $\{Fe^{III}(\mu\text{-}O)_2Fe^{III}\}$ rhomb.[4b]

[16] $K_2[Co(H_2\mathbf{1})_2]$ (0.021 mmol, 0.020 g) was treated with 1.1 µL (0.063 mmol) of $H_2{}^{18}O$ in DMA (5 mL)for 24 h. A small amount (less than 10%) of free ligand was also found in the FTIR spectrum, which did not hinder detection of the changes in $\tilde{\nu}_{asym}(\{Co^{III}(\mu\text{-}O)_2Co^{III}\})$.

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Ir-Catalyzed C-C Bond Formation

Iridium-Catalyzed Mizoroki–Heck-Type Reaction of Organosilicon Reagents

*Tooru Koike, Xiaoli Du, Tomoyuki Sanada, Yasuaki Danda, and Atsunori Mori**

Iridium-catalyzed C–C bond-forming reactions have recently attracted much attention.[1] However, the reaction with main group organometallic reagents containing elements such as boron, tin, and silicon has not been demonstrated so far. Although carbon–carbon bond formation with such main group reagents with an α,β-unsaturated carbonyl compound has been reported recently to undergo a Mizoroki–Heck-type or conjugate addition reaction with palladium,[2] rhodium,[3] and ruthenium[4] catalysts, the specific nature of the metal catalysts largely influences the reaction mechanism as well as the reaction course. Herein, we report that an iridium catalyst effects the Mizoroki–Heck-type addition/elimination reaction of α,β-unsaturated carbonyl compounds with several organosilicon reagents, and constitutes the first C–C bond formation with a main group reagent.[5]

The reaction of $PhSi(OMe)_3$ (**1**) with butyl acrylate (**2a**) in the presence of 5 mol% of $[\{IrCl(cod)\}_2]$ (cod = 1,5-cyclooctadiene) and tetrabutylammonium fluoride (TBAF) in toluene/H_2O (6/1) at 120 °C for 24 h afforded the addition/elimination product **3a** in 71% yield while the conjugate addition product **4a** was not obtained at all. This result sharply contrasts that of the related reaction with the rhodium catalyst $[\{RhCl(cod)\}_2]$ at 60 °C in THF/H_2O (6/1), which affords the conjugate adduct **4a** as the major product with high selectivity, **3a**/**4a** = 3/97 (Scheme 1).[6] In contrast to the combination of silicon reagent **1** and TBAF under anhydrous conditions, which is highly effective for the palladium-catalyzed cross-coupling reaction with organic halides,[7] the rhodium- or iridium-catalyzed reaction of this combination with **2a** proceeded only very slightly without the addition of water.

Table 1 summarizes the iridium-catalyzed Mizoroki–Heck-type addition/elimination reactions of several organosilicon reagents with α,β-unsaturated carbonyl compounds. Both iridium chloride and methoxide exhibited similar reactivities in the reactions with TBAF. The reaction also proceeded in THF/H_2O at lower temperature (70 °C), although a small amount of conjugate addition product was formed (70/5). Several aryl silanes bearing a substituent on the aromatic ring also effected the reaction. Although the reaction of an *ortho*-substituted aryl silane was found to be slightly slower, the Mizoroki–Heck-type product was selectively obtained over the 1,4-addition product. Alkenylsilanes, which were prepared by hydrosilylation of alkynes, could also effect the reaction to afford a diene in 67% yield.

Aryl silanediols (**7**–**9**) were also found to participate in the addition/elimination reaction. By contrast to alkoxysilanes, silanediols effected the reactions without addition of TBAF and water. However, no reaction occurred when $[\{IrCl(cod)\}_2]$ was used as the catalyst. Only $[\{Ir(OMe)(cod)\}_2]$ was found to be an effective catalyst. Worthy of note is that the reaction with silanediols can be a halogen-free process, which is in contrast to the palladium-catalyzed Mizoroki–Heck reaction with aryl halides. Reactions of other main group reagents such as those derived from boron and tin were found to proceed in a similar manner. Methyl vinyl ketone (**2b**) also underwent reaction to give **3b** in good yields.

In contrast to our recent report on rhodium catalysts in which addition/elimination versus conjugate addition of esters was controlled by the addition of water, while ketones underwent conjugate addition with or without water,[3e] the iridium-catalyzed reaction predominantly proceeded through

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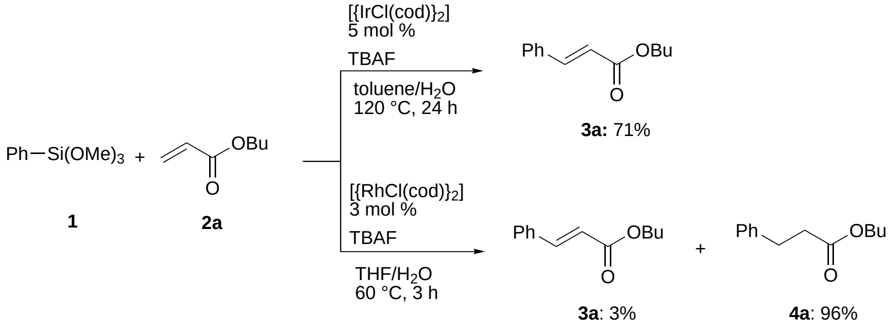


Scheme 1.

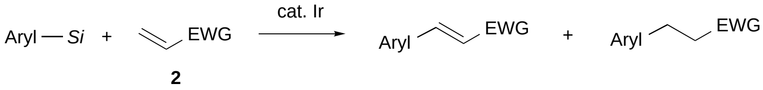
the addition/elimination reaction to form **3**, irrespective of the substrate species and the solvent system used.[8]

The iridium-catalyzed Mizoroki–Heck-type reaction proceeds as shown in Scheme 2. Similar to the rhodium case reported recently,[3c] migration of the organic group of the silicon reagent to the iridium center and insertion of **2** to the thus formed organoiridium species would afford intermediate **A**. In contrast to the rhodium-catalyzed reaction, which proceeds through a competition of β-hydride elimination and protonolysis to afford the Mizoroki–Heck-type or conjugate-addition product, the iridium-catalyzed reaction proceeds preferentially through β-hydride elimination to exclusively give **3** and the hydridoiridium **B** as a result of the lower reactivity of the carbon–iridium bond of **A** toward protonolysis.

Further transformation of **B** is also markedly different from that obtained with palladium and ruthenium catalysts, which are reported to involve redox process of metallic species to reduce the corresponding H–Pd^{II} or H–Ru^{II} species to their lower oxidation states.[2,4] Hence, an additional oxidant such as $Cu(OAc)_2$ is required in the palladium- or ruthenium-catalyzed reaction. On the other hand, the iridium-catalyzed reaction proceeds without an oxidant, and the metal species would be Ir^{I} throughout the catalytic cycle. The iridium hydride **B** might be hydrolyzed to *Ir*–OH to effect further catalytic reaction. Alternatively, **B** could react with **2** to give **A′**, which is then hydrolyzed by water or subjected to further insertion of **2**. Indeed, formation of butyl propanoate and the dimerized product **11** (EWG = COOBu) was confirmed in the reaction of butyl acrylate (**2a**).[9]

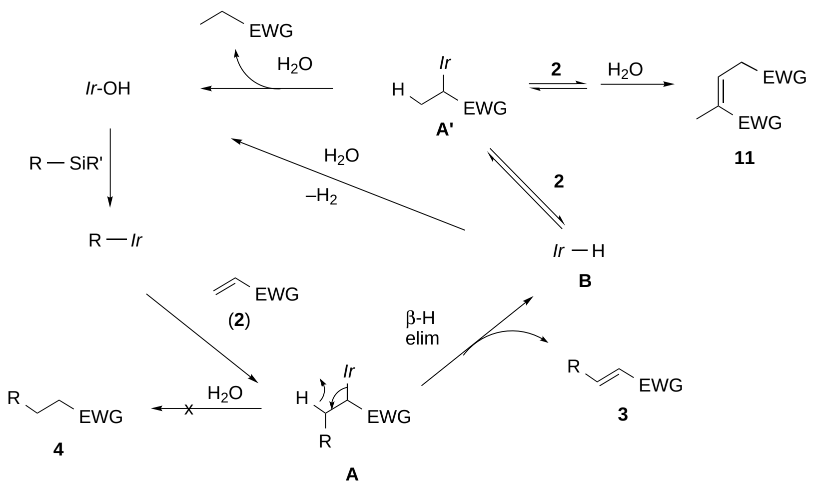
As shown in the last entry of Table 1, only the conjugate-addition product was obtained from the iridium-catalyzed reaction of methyl vinyl ketone (**2b**) with $PhSi(OMe)_3$ (**1**) and TBAF. Nevertheless, the reaction is also considered to proceed by a pathway different from the rhodium-catalyzed reaction, which proceeds through the protonolysis of intermediate **A**. The iridium-catalyzed formation of the conjugate adduct could take place by the reduction of the Mizoroki–Heck-type product **3b** with the formed hydridoiridium **B**.

Table 1: Iridium-catalyzed Mizoroki–Heck-type reaction of organosilicon and the related reagents.[a]



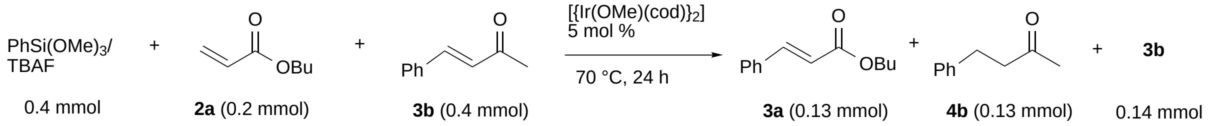
Silicon reagent	**2**, EWG	Catalyst (mol %)[b]	Solvent(s)[c]	*T* [°C]	Yield [%]	
					MH	1,4-
$PhSi(OMe)_3$ (**1**)/TBAF	COOBu (**2a**)	$[\{IrCl(cod)\}_2]$ (5)	toluene/H_2O (6/1)	120	71	0
		$[\{Ir(OMe)(cod)\}_2]$ (5)		120	70	5
		$[\{IrCl(cod)\}_2]$ (5)	THF/H_2O (6/1)	70	62	3
$(4\text{-}MeOC_6H_4)Si(OEt)_3$(**5**)/TBAF				70	70	0
$(2\text{-}MeC_6H_4)Si(OEt)_3$/TBAF (**6**)		$[\{IrCl(cod)\}_2]$ (7.5)		70	61	0
$PhEtSi(OH)_2$ (**7**)		$[\{Ir(OMe)(cod)\}_2]$ (3)	toluene	120	64	0
		$[\{IrCl(cod)\}_2]$ (3)		120	0	0
$(4\text{-}MeC_6H_4)EtSi(OH)_2$ (**8**)		$[\{Ir(OMe)(cod)\}_2]$ (5)	toluene/H_2O (6/1)	120	63	0
$(4\text{-}MeOC_6H_4)EtSi(OH)_2$ (**9**)				120	62	0
$(4\text{-}MeC_6H_4)SnBu_3$/TBAF				70	79	2
$PhB(OH)_2$		$[\{Ir(OMe)(cod)\}_2]$ (3)	DME/H_2O (2/1)	80	72	0
(*E*)-PhCH=CHSiMe$(OEt)_2$/TBAF (**10a**)	COOEt(**2a′**)	$[\{IrCl(cod\}_2]$ (5)	THF/H_2O (6/1)	70	41	0
(*E*)-PhCH=CHSi$(OEt)_3$/TBAF (**10b**)				70[d]	67	0
7	COMe (**2b**)	$[\{Ir(OMe)(cod)\}_2]$ (3)	toluene	120	50	4
			toluene/H_2O (6/1)	120	41	8
8				120	52	0
1/TBAF		$[\{IrCl(cod)\}_2]$ (5)		120	0	52

[a] Unless noted, the reaction was carried out with 0.3 mmol of silicon reagent, 0.9 mmol of **2** (and 0.3 mmol of TBAF), with stirring for 24 h. The product was obtained as an unseparable mixture of Mizoroki–Heck-type (MH-type) and 1,4-addition products, whose ratio was determined by ^1H NMR analysis. [b] The catalyst loading is shown based on the amount of silicon reagent used. [c] The solvent ratio is shown in parenthesis. [d] The reaction was carried out for 8 h. DME = 1,2-dimethoxyethane.



Scheme 2. EWG = electron-withdrawing group. *Ir* = iridium catalyst.

When the iridium-catalyzed reaction of butyl acrylate (**2a**) with **1**/TBAF was carried out in the presence of **3b**, which was the Mizoroki–Heck product of **2b**, reduction of **3b** took place to afford **4b** together with **3a** [Eq. (1)]. This observation suggests that the resulting formation of the conjugate-addition product would be the sequential Mizoroki–Heck-type addition/elimination followed by conjugate reduction. The similar reaction with [{Rh(OH)(cod)}$_2$] instead of the analogous iridium catalyst resulted in a trace amount of **4b** and the recovery of **3b**.[10] Hence, **3b** can serve as a hydride acceptor to avoid the use of excess amounts of acrylate **2a**.



(1)

In summary, an iridium-catalyzed Mizoroki–Heck-type reaction, which is a new class of iridium-catalyzed C–C bond-forming reaction, with organosilicon reagents was described. In contrast to related rhodium-catalyzed reactions, the preference for a Mizoroki–Heck-type reaction pathway is independent of the substrate and solvent system. This difference could be caused by the formation of a stable iridium–carbon bond at the position α to the carbonyl group in the intermediate.

Experimental Section

3a: A 1 M solution of TBAF (0.2 mL) in THF was added to a mixture of phenyltrimethoxysilane (0.037 mL, 0.2 mmol), butyl acrylate (0.086 mL, 0.6 mmol), and [{IrCl(cod)}$_2$] (6.7 mg, 0.01 mmol) in THF (2 mL) and H_2O (0.33 mL) under an argon atmosphere. The resulting solution was allowed to warm to 70 °C and the reaction was continued for 24 h. After cooling the solution to room temperature it was passed through a short celite pad and the filtrate was concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel to afford 31 mg of the product as a mixture of **3a** and **4a**, whose ratio was estimated to be 70/5 by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.48$ (d, $J = 16$ Hz, 1H; PhC*H*=CHCOO-), 7.77 (d, $J = 16$ Hz, 1H; PhCH=C*H*COO-) for **3a** (major product), 2.64 (t, $J = 7.8$ Hz, 2H; PhCH_2CH$_2$COO-), 2.96 ppm (t, $J = 7.8$ Hz, 2H; PhCH$_2$CH_2COO-) for **4a** (minor product).

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[9] H. Nakagawa, S. Sakaguchi, Y. Ishii, 81st Annual Meeting of the Chemical Society of Japan, 1G549 (**2002**). In our present study, the reaction of (4-MeC_6H_4)$EtSi(OH)_2$ (0.3 mmol) with butyl acrylate **2a** (0.9 mmol) in toluene/H_2O at 120 °C in the presence of [{Ir(OMe)(cod)}$_2$] (3 mol %) afforded the Mizoroki–Heck-type product(46 %), in which 36 % of **2a** was converted into **9**.

[10] The rhodium-catalyzed reaction under similar conditions (3 mol % of [{Rh(OH)(cod)}$_2$], 4-$MeC_6H_4SiEt(OH)_2$ (0.6 mmol), **2a** (0.3 mmol), and **3b** (0.6 mmol) in THF (3 mL) at 70 °C for 24 h) afforded 27 % of the Mizoroki–Heck-type product **3a** and 3 % of **4b** with 75 % recovery of **3b**.

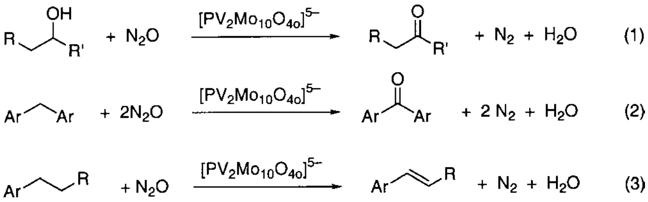
Polyoxometalate Catalysts

Activation of Nitrous Oxide and Selective Oxidation of Alcohols and Alkylarenes Catalyzed by the $[PV_2Mo_{10}O_{40}]^{5-}$ Polyoxometalate Ion**

*Revital Ben-Daniel and Ronny Neumann**

Nitrous oxide is a potentially interesting oxidant for selective oxidation of organic substrates since it contains 36 wt % oxygen, and the by-product of an oxidation reaction would be environmentally benign molecular nitrogen. These advantages are difficult to realize since N_2O is generally considered to be both inert[1] and a poor ligand.[2] Thus, very few catalysts have been reported for the activation of N_2O and its use as a selective oxidant in hydrocarbon oxidation. In the area of heterogeneous catalysis, various metal oxides have been investigated.[3] The most effective catalysts appear to be iron-containing acidic zeolites[4] which at elevated temperatures are thought to yield surface-activated iron–oxo species (α-oxygen).[5] These species are capable of oxygen transfer to rather inert hydrocarbons, such as benzene and methane, to yield phenol and methanol, respectively.[6] In homogeneous media, noncatalytic oxygen transfer from nitrous oxide to alkyl, alkyne, and imido ligands of transition-metal complexes has been observed.[7] Molybdenum(III) complexes have cleaved nitrogen–nitrogen bonds[8] and N_2O has been decomposed at subambient temperatures to N_2 and O_2 using a ruthenium complex.[9] More relevant to the work reported herein is the reported oxygen transfer from nitrous oxide to form metal–oxo species.[10] In one particular case,[11] a ruthenium porphyrin has been used to prepare a high-valent ruthenium–dioxo species capable of oxygen-transfer to nucleophiles such as alkenes and sulfides. Under more extreme conditions (140 °C, 10 atm N_2O), the ruthenium porphyrin has recently been shown to catalyze oxygen transfer to trisubstituted alkenes,[12] and the oxidation of alcohols to ketones.[13]

With regard to the ongoing interest in the catalytic activity of polyoxometalates in oxidation reactions,[14] especially with benign oxidants such as O_2 and H_2O_2, we have very recently found that a manganese-substituted "sandwich"-type polyoxometalate can also activate N_2O and lead to the highly selective epoxidation of alkenes.[15] In this paper we will describe a different set of N_2O-activation reactions involving the vanadium-containing Keggin-type polyoxomolybdate, $[\{nBu_4N\}_5\{PV_2Mo_{10}O_{40}\}]$. In this case, selective oxidation by C–H bond activation was possible leading to the oxidation of a) primary and secondary alcohols to aldehydes and ketones, respectively (Equation (1)) and b) alkyl aromatics to ketones (Equation (2)), or alternatively leading to their oxydehydrogenation (Equation (3)).



For the oxidation of alcohols (Table 1) it was shown that secondary and primary alcohols were oxidized selectively (greater than 99.9 %) to ketones and aldehydes, respectively,

Table 1: Oxydehydrogenation of alcohols with N_2O catalyzed by $[\{nBu_4N\}_5\{PV_2Mo_{10}O_{40}\}]$.[a]

Substrate	Product	Conversion [mol %]
1-octanol	1-octanal	42.5
2-octanol	2-octanone	48.1
cyclohexanol	cyclohexanone	68.2
cyclooctanol	cyclooctanone	89
cis-2-hexen-1-ol	2-hexenal[b]	50.5
trans-2-hexen-1-ol	2-hexenal[b]	50.3
1-octene-3-ol	1-octen-3-one	56.8
benzyl alcohol	benzaldehyde	> 99

[a] Reaction conditions: alcohol (1 mmol), $[\{nBu_4N\}_5\{PV_2Mo_{10}O_{40}\}]$ (0.02 mmol), N_2O (1 atm), benzonitrile (1 mL), 150 °C, 15 h. Selectivity to the aldehyde or ketone was > 99.9 %. [b] The configuration of the unsaturated aldehyde was not definitively determined. However, since the catalytic system is inert to alkenes it is likely, but not certain, that the configuration was retained.

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