JOC Article

Catalytic Cross-Coupling Reaction of Esters with Organoboron Compounds and Decarbonylative Reduction of Esters with $HCOONH_4$: A New Route to Acyl Transition Metal Complexes through the Cleavage of Acyl−Oxygen Bonds in Esters

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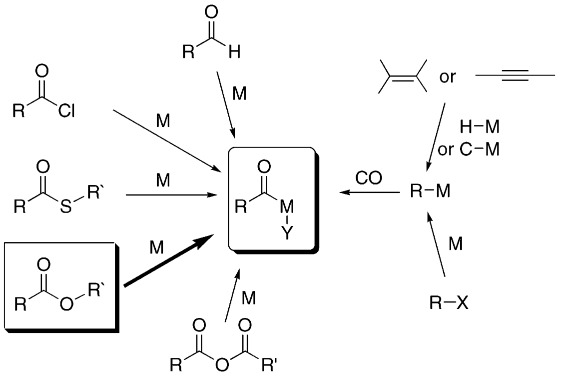
The $Ru_3(CO)_{12}$-catalyed cross-coupling reaction of esters with organoboron compounds leading to ketones is described. A wide variety of functional groups can be tolerated under the reaction conditions. Aromatic boronates function as a coupling partner to give aryl ketones. Acyl−alkyl coupling to dialkyl ketones is also achieved by the use of 9-alkyl-9-BBN in place of boronates. The $Ru_3(CO)_{12}$-catalyzed decarbonylative reduction of esters with ammonium formate ($HCOONH_4$) leading to hydrocarbons is also described. No expected aldehydes are produced, and controlled experiments indicate that aldehydes are not intermediate for the transformation. A hydrosilane can also be used as a reducing reagent in place of $HCOONH_4$. A wide variety of functional groups are compatible for both reactions. The key step for both catalytic reactions is the directing group-promoted cleavage of an acyl carbon−oxygen bond in esters, leading to the generation of acyl transition metal alkoxo complexes.

Introduction

Acyl transition metal complexes are ubiquitous in organometallic chemistry, and serve as important metallic species for a variety of transition metal-catalyzed reactions.[1] A variety of methods are available for generating acyl transition metal complexes (Scheme 1). The insertion of CO into a carbon−metal bond in alkyl, aryl, or vinyl transition metal complexes, which are formed via the hydrometalation or carbometalation of alkenes (or alkynes), the oxidative addition of halides (or pseudo halides), and so on, all generate acyl transition metal complexes. The oxidative addition of various carbonyl compounds, such as aldehydes, acid halides, acid anhydrides, and thioesters, is another candidate to generate acyl complexes. Many catalytic and stoichiometric studies have been conducted,[2] but fewer studies have been conducted on the oxidative addition of acyl carbon−oxygen bonds in esters to transition metal complexes.[3] The example of the oxidative addition of acyl−O bonds in esters is very rare because the alkoxy group is not a good leaving group. Yamamoto reported that phenyl acetate adds oxidatively to $Ni(cod)_2$/bipyridine to give a methylnickel phenoxide complex, which is formed by decarbonylation of the intermediate acetylnickel complex.[4] Other complexes, such as $Ni(cod)_2/PPh_3$,[4] $Mo(N_2)_2(dppe)_2$,[5] $HRh(PPh_3)_4$,[6] $Ru(CO)_2(PPh_3)_3$,[7] and $Cp^*RhCl(mdmpp\text{-}\kappa P,\kappa O)$,[8] have also been found to cleave acyl−O bonds of esters, with the ester carbonyl group being ultimately converted to a metal-coordinated CO ligand.

SCHEME 1. Generation of Acyl Transition Metal Complexes



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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice Hall: Upper Saddle River, NJ, 1996. Tsuji, J. *Transition Metal Reagents and Catalysts*; Wiley: Chichester, U.K., 2000.

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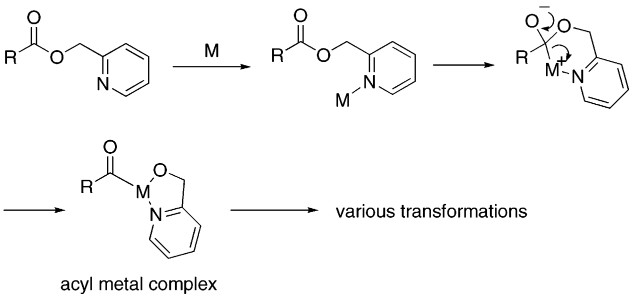
10.1021/jo0492719 CCC: $27.50

Grotjahn isolated an acyl rhodium complex from the reaction of an aryl acetate containing a phosphine moiety with a Rh(I) complex.[9] Yamamoto also isolated (aryloxo)(trifluoroacetyl)palladium complexes, produced by the oxidative addition of aryl trifluoroacetates to Pd(0) under mild conditions.[10] To the best of our knowledge, only two catalytic reactions, which involve the cleavage of acyl−O bonds in esters, are known. Yamamoto reported on the Pd-catalyzed coupling reaction of aryl trifluoroacetates with arylboronic acids under relatively mild reaction conditions, leading to aryl trifluoromethyl ketones.[11] Goo*β*en found that the Mizoroki−Heck-type reaction of esters proceeds when *p*-nitrophenyl or pentafluorophenyl esters are employed.[12] All esters that are used for the catalytic cleavage of acyl−O bonds in esters are electronically activated by the presence of an electron-withdrawing group at the carboxylic or alcoholic moiety.

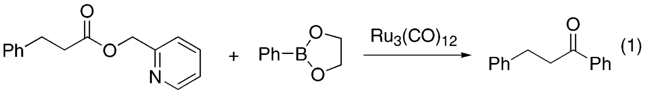
The reactivity of acyl transition metal complexes could be changed or controlled by the nature of the Y group on the metal (Scheme 1). However, little is known concerning the reactivity of acyl alkoxo complexes ($Y = OR'$) because no appropriate method for their generation has been reported, as described above. The cleavage of an acyl−O bond in esters represents a good candidate for use in generating acyl alkoxo complexes. Our strategy for generating acyl transition metal complexes directly from esters is based on the accepted dogma that heteroatom-directing groups promote the cleavage of unreactive bonds. We have previously reported on catalytic reactions which involve the facile cleavage of C−H,[13] C−C,[14] C−F,[15] and C−O bonds[16] by taking advantage of the coordination of the directing group on the transition metals. The coordination of a carbonyl oxygen or sp^2-nitorogen to transition metals is a key step in these catalytic reactions. We subsequently chose 2-pyridylmethyl esters as the substrate for generating acyl alkoxo complexes. The coordination of the pyridine nitrogen in the ester would be expected to facilitate the cleavage of acyl−O bonds in esters, as shown in Scheme 2. Most importantly, various combinations of catalysts and directing groups would be available, suggesting the possibility of generating a wide variety of acyl alkoxo transition metal complexes. Our purpose is to provide new *catalytic* reactions based on a new method for the generation of acyl alkoxo transition metal complexes. We wish to report herein on some new transformations of $Ru_3(CO)_{12}$-catalyzed reaction of esters involving the cleavage of acyl−O bonds: (i) cross-coupling reactions with organoboron compounds and (ii) decarbonylative reductions with $HCOONH_4$.

SCHEME 2. Our Strategy to Generate of Acyl Complexes



Results and Discussion

Cross-Coupling Reaction with Organoboron Compounds. The cleavage of acyl−O bonds in esters could lead to acyl alkoxo transition metal species, as shown in Scheme 2. It is well-known that alkoxo or hydroxo transition metal species are much more reactive with respect to the transmetalation of organoboron reagents.[17,18] We then focused our initial efforts on cross-coupling reactions of esters with organoboron compounds. 3-Phenylpropionic acid 2-pyridinylmethyl ester (**1**) and $PhB(OCH_2CH_2O)$ (**2a**) were selected as the first substrate and reagent for screening a broad spectrum of transition metal complexes. Among the various transition metal complexes examined, only $Ru_3(CO)_{12}$ showed a catalytic activity for eq 1. The reaction of **1** (1 mmol) and phenylboronate **2a** (1.5 mmol) in the presence of $Ru_3(CO)_{12}$ (0.03 mmol) in toluene (3 mL) at 160 °C for 20 h in a 9-mL sealed tube gave 1,3-diphenylpropan-1-one (**3a**) and its branched isomer in 71% GC yield in a ratio of 94:6. In addition, benzophenone, which was formed by the reaction of **2a** with $Ru_3(CO)_{12}$, was produced in <5% yield. The corresponding benzyl ester failed to react, indicating that the presence of nitrogen in the substrate is essential for the reaction to proceed. Of the solvents examined, toluene was the best (chlorobenzene 63%, dioxane 58%, DMF 48%, CH_3CN 34%). The use of a CO atmosphere had no effect on the efficiency of the reaction (67%, n:i = 97:3). Some phenyl donors, such as $PhB(OH)_2$ (11%), $PhB(OCH_2CH_2CH_2O)$ (68%), $PhB(OCH_2CMe_2CH_2O)$ (67%), and $NaBPh_4$ (11%), were screened, and we rapidly discovered that **2a** was a superior phenyl donor, resulting in the highest yield of **3a**. Lowering the reaction temperature (120 °C) slightly improved both the yield to 83% isolated yield (86% GC yield) and the ratio (n:i = 99:1), as shown in entry 1 of Table 1.



1 **2a** **3a** (1)

As expected from the results of the Suzuki−Miyaura coupling reaction,[17] various functional groups, such as ethers, halides, ketones, and esters, were compatible with the cross-coupling reaction (Table 1). The presence of a

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[10] Nagayama, K.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 799.

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[12] Goo*β*en, L. J.; Paetzold, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1237.

[13] Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. Asaumi, T.; Chatani, N.; Matsuo, T.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **2003**, *68*, 7538 and references therein.

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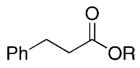
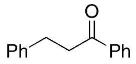
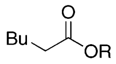
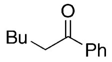
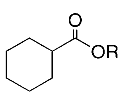
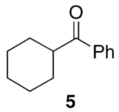
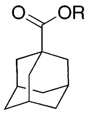
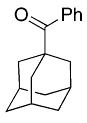
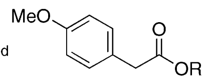
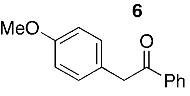
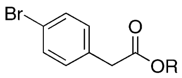
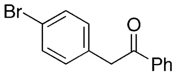
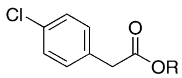
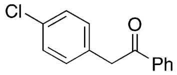
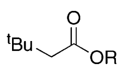
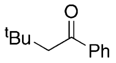
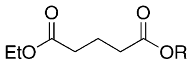
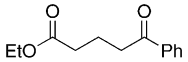
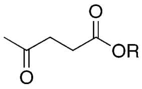
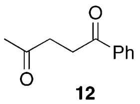
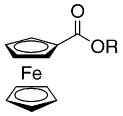
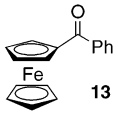
[16] Kakiuchi, F.; Usui, M.; Ueno, S.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **2004**, *126*, 2706.

[17] For reviews on the Suzuki−Miyaura coupling, see: Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. Miyaura, N. *J. Organomet. Chem.* **2002**, *653*, 54. Kohta, S.; Lahirir, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633.

[18] Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169.

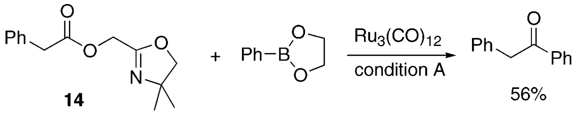
TABLE 1. $Ru_3(CO)_{12}$-Catalyzed Coupling Reaction of Esters with Phenylboronic Ester 2a[a]

enrty	ester	product	isolated yield
1[d]	 **1**	 **3a**	83% (n:i = 99:1)
2[b]		 **4**	72% (n:i = 96:4)
3[b]		 **5**	76%
4[c]		 **6**	52%
5[d]		 **7**	73%
6[d]		 **8**	64%
7[d]		 **9**	63%
8[b]		 **10**	79%
9[d]		 **11**	72% (n:i = 97:3)
10[b]		 **12**	41%
11		 **13**	53%

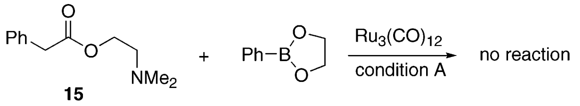
[a] R = 2-pyridinylmethyl. [b] Reaction conditions A: ester (1 mmol), **2** (1.5 mmol) and $Ru_3(CO)_{12}$ (0.03 mmol) in toluene (3 mL) at 140 °C for 20 h. [c] Reaction conditions B: for 40 h, otherwise the same reaction conditions as reaction condition A. [d] Reaction conditions C: ester (1 mmol), **2** (1.5 mmol), and $Ru_3(CO)_{12}$ (0.03 mmol) in toluene (1 mL) at 120 °C for 40 h.

bulky substituent led to a slight decrease in product yield (entry 4). The result in entry 9 again shows that the presence of a pyridine ring appears to be essential for the reaction to proceed. The reaction was also applicable to the ferrocene ring.

A pyridine ring is not only a directing group, but an oxazoline ring also can be used as the directing group (eq 2). However, an sp^3 nitrogen, as in **15**, does not serve as a directing group (eq 3).

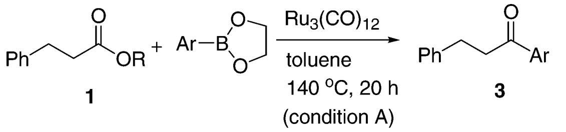


(2)



(3)

It was found that the electronic nature of aryl boronates has a significant effect on the efficiency of the reaction and the ratio of normal to branched isomers (eq 4). To compare the reactivity of aryl boronates, the

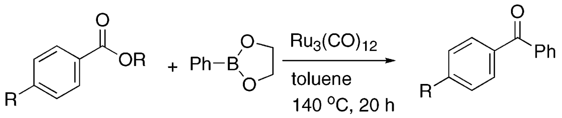


(4)

Ar = 4-$Me_2NC_6H_4$ (**2b**)	85% (n:i = >99:1)
Ar = 4-$MeOC_6H_4$ (**2c**)	86% (n:i = >99:1)
Ar = C_6H_5 (**2a**)	79% (n:i = 96:4)
Ar = 4-ClC_6H_4 (**2d**)	90% (n:i = >99:1)
Ar = 4-$CF_3C_6H_4$ (**2e**)	88% (n:i = 97:3)
Ar = 4-$MeO_2CC_6H_4$ (**2f**)	63% (n:i = 80:20)
Ar = 4-CNC_6H_4 (**2g**)	48% (n:i = 82:18)

reactions were carried out under the same reaction conditions (condition A, see the footnote in Table 1) in all cases. The reaction of **1** with **2b** gave the corresponding ketone **3b** in high yield with complete normal selectivity. The substitution of a methoxy group, as in **2c**, also resulted in a high yield and a high ratio. On the other hand, an aryl boronate containing an electron-withdrawing group, as in **2f** and **2g**, gave the corresponding products in relatively low yields with low n:i ratios.

We next examined the electronic effects of a substituent on benzoates (eq 5). Curiously, the substitution of an electron-donating group on the phenyl ring resulted in no reaction, in sharp contrast to an electron-withdrawing group, such as CF_3, which gave the corresponding diaryl ketones **16** in good yields.

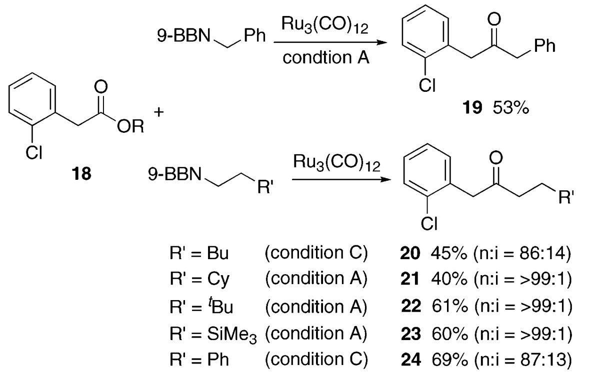


(5)

R = CF_3 **16** 56%
R = OMe **17** trace

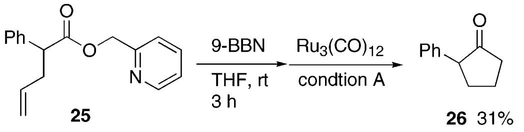
Next, our attention was directed to the coupling with alkyl boronates. However, no reaction took place when butylboronate, $BuB(OCH_2CH_2O)$, was used as a coupling reagent under various reaction conditions. Finally, we found that a benzyl group can be coupled with esters **18** to give **19** when 9-benzyl-9-BBN is used as a coupling reagent (Scheme 3). Encouraged by this result, attention was directed toward the coupling of esters with 9-alkyl-9-BBN, which are easily prepared by the hydroboration of alkenes with 9-BBN. In recent years, a great deal of progress has been made in the development of cross-

SCHEME 3. Coupling with 9-Alkyl-9-BBN



coupling reactions of activated carboxylic acid derivatives, such as acid chlorides,[19] anhydrides,[20] thioesters,[21] and others[22] with organoboron reagents leading to ketones. While most of the reactions reported thus far have been directed to the preparation of diaryl ketones via aryloyl–aryl coupling, using aromatic acid derivatives and aromatic boron compounds, only one example of aliphatic acyl–alkyl coupling exists, to the best of our knowledge.[19e,23] While the results shown in Scheme 3 did not reach a satisfactory synthetic level at the present time, these are rare examples of a dialkyl ketone synthesis via acyl–alkyl coupling with alkyl organoboron compounds.

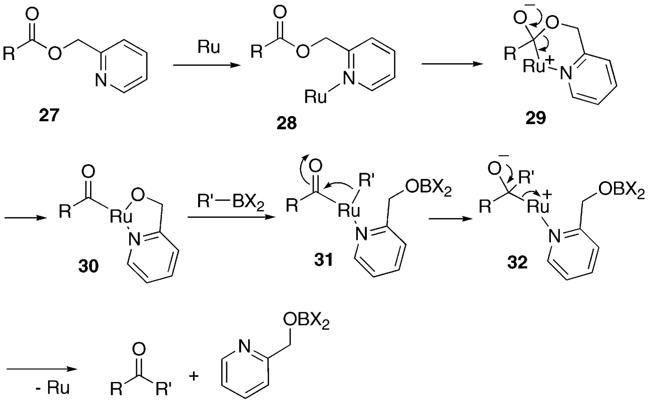
An intramolecular coupling with **25** resulted in cyclization to give 2-phenylcyclopentanone **26** (eq 6).



(6)

The proposed mechanism is shown in Scheme 4. Although our efforts, which were directed toward the isolation of the acyl alkoxo complex **30**, were in vain, we propose the intermediacy of the acyl ruthenium species **30**. The coordination of the nitrogen in **27** to Ru gives

SCHEME 4. A Proposed Reaction Mechanism



28. The ruthenium in **28** attacks the ester-carbonyl group to give the tetrahedral intermediate **29**. C–O bond cleavage takes place to afford an acyl alkoxo ruthenium complex **30**.[24] The transmetalation of species **30** with a boron compound followed by reductive elimination gives a ketone and a regenerated ruthenium. A branched isomer is formed from **30** or **31** via the decarbonylation/β-hydride elimination/reinsertion/CO insertion leading to a branched acyl ruthenium complex, which reacts with a boron compound to give a branched isomer. While the presence of inorganic bases is essential in reactions with organoboron compounds,[17,18] the present reaction does not require the bases because of the direct generation of alkoxo complexes from the cleavage of an acyl–O bond in esters.

The ratio of normal and branched isomers parallels the nucleophilicity of aryl boronates, as shown in eq 4. When an electron-rich aryl boronate, such as **2b** and **2c**, was used, no branched isomers were produced. On the other hand, the use of electron-poor aryl boronates, such as **2f** and **2g**, decreased the n:i ratio to 8:2. These results can be rationalized by assuming that the more nucleophilic R′ group on the ruthenium in **31** readily attacks the carbon of the ruthenium-bound acyl ligand to give **32**, the C–Ru bond of which is then cleaved, forming the final product (Scheme 4).[25] This mechanism is unusual for a concerted reductive elimination, but is similar to that proposed for the reductive elimination of C–O from palladium complexes proposed by Buchwald[26] and Hartwig.[27] The results obtained from eq 5 also support the above proposal. When R is 4-$CF_3C_6H_4$, the nucleophilic attack of R′ on the acyl carbon in **31** would be facilitated because of its electron-withdrawing nature. On

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(19) For recent papers on cross-coupling reactions of acid chlorides with organoboron compounds, see: (a) Cho, C. S.; Itotani, K.; Uemura, S. *J. Organomet. Chem.* **1993**, *443*, 253. (b) Bumagin, N. A.; Bykov, V. V. *Tetrahedron* **1997**, *53*, 14437. (c) Bumagin, N. A.; Korolev, D. N. *Tetrahedron Lett.* **1999**, *40*, 3057. (d) Haddach, M.; McCarthy, J. R. *Tetrahedron Lett.* **1999**, *49*, 3109. (e) Kabalka, G. W.; Malladi, R. R.; Tejedor, D.; Kelley, S. *Tetrahedron Lett.* **2000**, *41*, 999. (f) Chen, H.; Deng, M.-Z. *Org. Lett.* **2000**, *2*, 1649. (g) Wang, J.-X.; Wei, B.; Hu, Y.; Liu, Z.; Yang, Y. *Synth. Commun.* **2001**, *31*, 3885. (h) Urawa, Y.; Ogura, K. *Tetrahedron Lett.* **2003**, *44*, 271. (i) Urakawa, Y.; Nishiura, K.; Souda, S.; Ogura, K. *Synthesis* **2003**, 2882.

(20) For recent papers on cross-coupling reactions of acid anhydrides with organoboron compounds, see: (a) Gooβen, L. J.; Ghosh, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 3458. (b) Frost, C. G.; Wadsworth, K. J. *Chem. Commun.* **2001**, 2316. (c) Kakino, R.; Narahashi, H.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **2001**, 1242. (d) Kakino, R.; Yasumi, S.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 137. (e) Oguma, K.; Miura, M.; Satoh, T.; Nomura, M. *J. Organomet. Chem.* **2002**, *648*, 297. (f) Kakino, R.; Narahashi, H.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1333. (g) Gooβen, L. J.; Winkle, L.; Döhring, A.; Ghosh, K.; Paetgold, J. *Synlett* **2002**, 1237. (h) Yamamoto, A.; Kakino, R.; Shimizu, I. *Helv. Chim. Acta* **2001**, *84*, 2996. (i) Gooβen, L. J.; Ghosh, K. *Eur. J. Org. Chem.* **2002**, 3254.

(21) For recent papers on cross-coupling reactions of thioesters with organoboron compounds, see: (a) Zeysing, B.; Gosch, C.; Terfort, A. *Org. Lett.* **2000**, *2*, 1843. (b) Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2000**, *2*, 3229. (c) Liebeskind, L. S.; Srogl, J. *J. Am. Chem. Soc.* **2000**, *122*, 11260. (d) Yu, Y.; Liebeskind, L. S. *J. Org. Chem.* **2004**, *69*, 3554.

(22) Gooβen, L. J.; Ghosh, K. J. *Chem. Commun.* **2001**, 2084.

(23) Gooβen described that alkylboronic acids were not converted under any of the given conditions. See ref 20b. A cross-coupling reaction of cyclopropylboronic acids with acid chlorides was achieved by the use of palladium complexes and base. See ref 20a. While we were preparing the paper, Liebeskind reported the coupling reaction of aliphatic thioesters with alkyl-(9-BBN) in the presence of a stoichiometric amount of copper(I) thiophene-2-carboxylate and palladium catalyst. See ref 21d.

(24) Ko, S.; Lee, C.; Choi, M.-G.; Na, Y.; Chang, S. *J. Org. Chem.* **2003**, *68*, 1607.

(25) The positive ρ values were observed in the Pd-catalyzed cross-coupling reaction of in situ generated acid anhydrides with arylboronic acids, indicating that arylboronic acids bearing an electron-withdrawing group react faster than those having a more electron-donating group. See ref 20f.

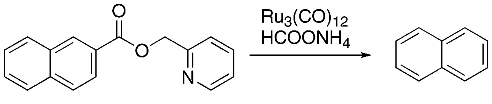
(26) Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504.

(27) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852.

the other hand, when R is 4-$MeOC_6H_4$, the nucleophilic attack of R′ would be retarded because of the electron-donating nature of the methoxy group.

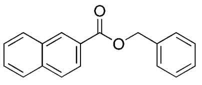
The present reaction represents a new method for the direct synthesis of unsymmetrical ketones from esters. Although various carboxylic acid derivatives, such as acid chlorides, anhydrides, thioesters, and related groups, were utilized as the substrates for the coupling reaction,[19−22] catalytic coupling reactions of esters are rare.[11] Although some issues remain to be solved, such as the effect of higher reaction temperatures and the formation of branched isomers, the present work provides a rare example of a dialkyl ketone synthesis via an aliphatic acyl−alkyl coupling with use of alkyl boron compounds.[19e,28] A wide variety of functional groups can be tolerated in the reaction even under relatively severe reaction conditions

Decarbonylative Reduction with $HCOONH_4$. In the course of screening various combinations of catalysts and nucleophiles in coupling reactions of esters, we found a clean but an unexpected reaction, as shown in eq 7.[29] We expected that the reaction of the 2-pyridylmethyl ester with a hydride donor would give naphthalenecarbaldehyde, analogous to the Rosenmund-type reduction.[30,31] However, the reaction of naphthalene-2-carboxylic acid pyridin-2-ylmethyl ester (**33**) with ammonium formate, $HCOONH_4$, in the presence of $Ru_3(CO)_{12}$ as the catalyst, instead, resulted in decarbonylative reduction to give naphthalene (**34**) in good yield and the expected product, naphthalenecarbaldehyde, was not formed.

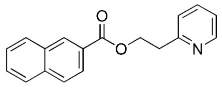


33 **34** (7)

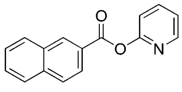
The reaction of **33** (0.2 mmol) with $HCOONH_4$ (0.6 mmol) in the presence of $Ru_3(CO)_{12}$ (0.01 mmol) in toluene (0.6 mL) at 160 °C for 40 h gave naphthalene (**34**) in 55% GC yield, along with 17% of unreacted **33** (eq 7). The ^1H NMR spectrum indicated that 2-pyridylmethanol is formed in a yield comparable to that of **34**. The use of dioxane as the solvent improved the yield to 95%. Of the solvents examined, dioxane was the solvent of choice, although the type of solvent had no significant effect on the yield of **34** (anisole 68%, *p*-xylene 51%, PrCN 71%, CH_3CONMe_2 84%). When the reaction was carried out even at 1 atm of CO, no reaction took place. Lowering the reaction temperature decreased the yields (68% yield at 140 °C, 14% at 120 °C). The corresponding benzyl ester **35** did not react with $HCOONH_4$, indicating that the presence of a nitrogen in the substrate is essential for the reaction to proceed. It was also found that the tether of the alcohol moiety is important. Thus, the use of 2-pyridinylethyl **36** or 2-pyridinyl ester **37** did not give **34**. Other directing groups such as sp^3 nitrogen, as in **15**, did not function as a directing group in the reaction with $HCOONH_4$.



35

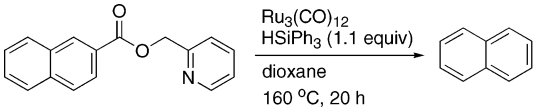


36



37

The use of other hydrogenation reagents, such as HCOONa (26%) and *i*-PrOH (0%), was not effective; however, $HSiPh_3$ was also found to function as the hydrogenation reagent to afford naphthalene (eq 8). This reaction also gave no aldehyde.



33 **34** 67% (8)

This method was quite compatible with various functional groups, such as methoxy, chloro, fluoro, acetal, sulfonate, ester, imido, protected amine, and even a free amine, as shown in Table 2. Electron-donating or -withdrawing groups on a benzene ring had no appreciable affect on the reaction. However, the reaction of a 4-nitro ester, such as **38f**, resulted in the reduction of the nitro group to give 2-pyridylmethyl 4-aminobenzoate in 27% yield with no nitrobenzene **39f** detected. An ester group (COOMe) at the 4-position of the phenyl ring, as in **38k**, was tolerated. On the other hand, the use of a cyano-substituted ester, such as **37h**, resulted in a low yield of benzonitrile **39h** because **39h** also was reduced by $HCOONH_4$ under the reaction conditions employed. In fact, the reaction of 2-naphthalenecarbonitrile under identical reaction conditions gives 2-methylnaphthalene in 27% yield and unidentified products. A keto functionality also did not survive under the reaction conditions, as in **38r**. Steric bulkiness around the carbonyl group, as in **38b**, led to a low conversion. The reaction is not limited to a benzene ring system, but it is applicable to a pyridine ring as well. The reaction of **38t** gave indole (**39t**) in 23% yield, but changing solvent to toluene increased the product yield to 70%. The reaction of ferrocenecarboxylic ester **38v** gave ferrocene (**39s**) in 56% yield.

It was found that aliphatic esters **40a**, **40b**, and **40c** give ethylbenzenes in good yields. A steric bulkiness around a carbonyl group retarded the reaction. Thus, the reaction of **40e** resulted in no reaction. Adamantanecarboxylate **40f** also did not give the expected adamantane, although it works well as the substrate in cross-coupling reactions with the phenyl boron compound **2a**, as shown in Table 1.

The reaction was not limited to esters, in which a 2-pyridylmethyl group is attached as the directing group at the alcohol moiety in the substrates (Table 4). The results, as listed in Tables 1−4, show the apparent potential utility of this transformation in terms of its application to organic synthesis.

The proposed reaction mechanism is essentially the same as that for the cross-coupling reaction shown in Scheme 3, except for accompanying decarbonylation

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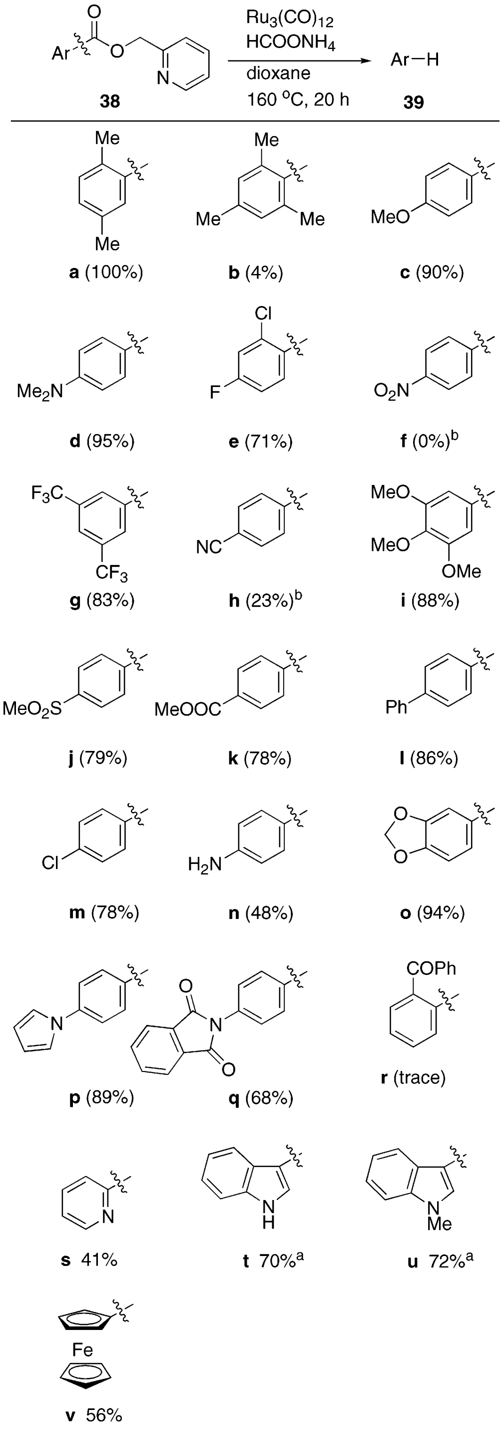
(28) Carbonylative cross-coupling with 9-alkyl-9-BBN was reported. Wakita, Y.; Yasunaga, T.; Akita, M.; Kojima, M. *J. Organomet. Chem.* **1986**, *301*, C17. Ishiyama, T.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1991**, *32*, 6923.

(29) A preliminary report has been communicated. Chatani, N.; Tatamidani, H.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 4849.

(30) For a review on the Rosenmund reduction, see: Mosettig, E.; Mozingo, R. *Org. React.* **1948**, *4*, 362. For a recent paper, see: Grushin, V. V.; Alper, H. *J. Org. Chem.* **1991**, *56*, 5159.

(31) Nagayama, K.; Kawataka, F.; Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 799.

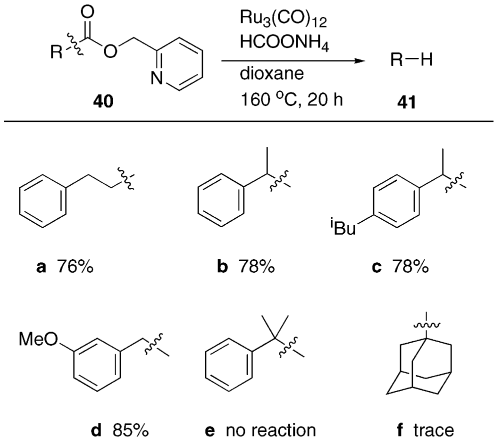
TABLE 2. Reductive Decarbonylation of Aromatic Esters Leading to Arenes[a,c]



[a] Toluene was used as the solvent in place of dioxane. [b] See text. [c] Reaction conditions: ester (0.2 mmol), HCOONH$_4$ (0.6 mmol), and dioxane (0.6 mL) at 160 °C for 20 h.

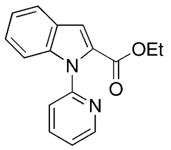
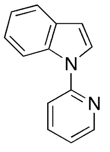
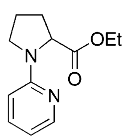
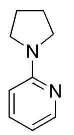
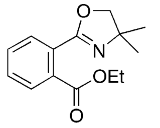
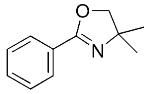
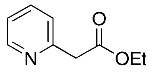
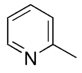
(Scheme 5). Decarbonylation took place in the reaction with HCOONH$_4$, but not in the cross-coupling reaction with organoboron compounds. In contrast to organoboron compounds, HCOO$^-$ (or H$^-$) does not allow ligand exchange (transmetalation) to proceed efficiently with respect to **30**. The low reactivity of HCOONH$_4$ toward **30** is responsible for the facile decarbonylation.

TABLE 3. The Ru$_3$(CO)$_{12}$-Catalyzed Reaction of Esters with HCOONH$_4$[a]



[a] Reaction conditions: ester (0.2 mmol), HCOONH$_4$ (0.6 mmol), and dioxane (0.6 mL) at 160 °C for 20 h.

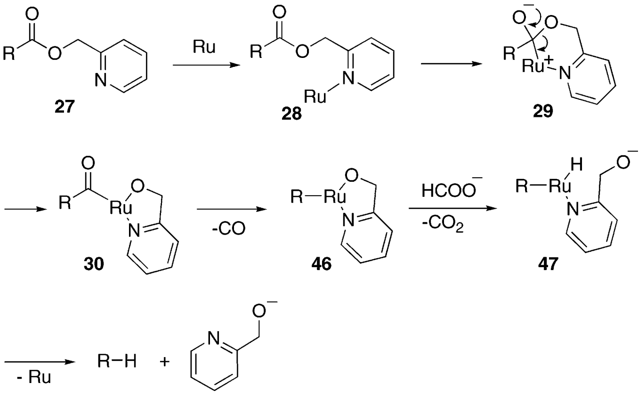
TABLE 4. The Ru$_3$(CO)$_{12}$-Catalyzed Reaction of Esters with HCOONH$_4$[a]

substrate	product	yield
	 **42**	81%
	 **43**	100%
	 **44**	97%
	 **45**	81%

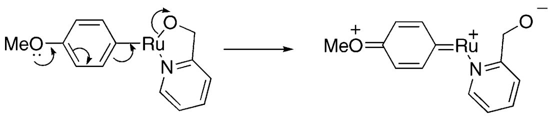
[a] Reaction conditions: ester (0.2 mmol), HCOONH$_4$ (0.6 mmol), and toluene (0.6 mL) at 160 °C for 20 h.

A considerable difference in the electronic effects of the substituent on aromatic esters was observed for the two reactions. As shown in eq 4, the electronic nature of the substituents had a significant effect on the reactivity in the cross-coupling reaction. Thus, an electron-donating group, such as a methoxy group, inhibited the coupling reaction with phenyl boronate, in sharp contrast to a CF$_3$ group, which gave the corresponding ketone in a good yield. On the other hand, the decarbonylative reduction reaction was not significantly affected by the electronic nature of a substituent on the benzene ring, but the substitution of an electron-donating group on the benzene ring makes the reaction slightly more efficient than

SCHEME 5. A Proposed Reaction Mechanism



SCHEME 6



substitution of an electron-withdrawing group, such as an ethoxycarbonyl group. Similarly, a difference in the steric effects was also observed in the two reactions. Thus, adamandanecarboxylate served as a good substrate in the cross-coupling reaction (entry 4 in Table 1), but no reaction took place in the reactions with $HCOONH_4$ (Table 3). Ligand substitution (**46** → **47**) by formate anion, which is a weak nucleophile, is accelerated by the resonance effect of the electron-donating group, such as a methoxy group (Scheme 6), and/or the reductive elimination from **47** is promoted by the electron-donating nature of the methoxy group. On the other hand, ligand substitution does not take place from **30** because the acyl ligand is a strong electron-withdrawing group. In addition, decarbonylation from **30** (R = adamantly) is suppressed by its bulkiness in the case of **40g** and ligand exchange after decarbonylation cannot proceed. This proposal is supported by the fact that this reaction did not proceed even at 1 atm of CO under which decarbonylation was suppressed. On the other hand, it is known that alkoxo metal complexes easily undergo transmetalation with organoboron compounds because of the oxophilicity of the boron atom, and so **30** undergoes the transmetalation with organoboron compounds prior to decarbonylation.

It was anticipated that aldehydes, which are formed via the reduction of esters by $HCOONH_4$, would be produced initially and then undergo decarbonylation to give hydrocarbons under the reaction conditions used here. To examine this possibility, some selected controlled experiments were performed. The reaction of 2-naphthalenecarbaldehyde (**33**) under reaction conditions identical with those in eq 7 gave naphthalene in 23% GC yield, along with a 7% GC yield of 2-naphthalenemethanol (determined as a silyl ether) and a 61% yield of 2-methylnaphthalene. Treatment of a mixture of **33** and 2-pyridylmethyl 3,4,5-trimethoxybenzoate (**37i**) with $HCOONH_4$ under identical conditions gave a 91% recovered yield of **37i** and 2-naphthalenemethanol (45% GC yield). The expected 1,2,3-trimethoxybenzene (**38i**) was obtained in trace amounts, and naphthalene and 2-methylnaphthalene were not detected by GC. These results show that the present decarbonylative reduction does not involve an aldehyde intermediate and that the formation of aldehyde inhibits the reaction.

The present reaction represents a new type of decarbonylative reduction in which esters can be directly converted to hydrocarbons, similar to the decarbonylation of aldehydes, a reaction that is frequently employed in organic synthesis.[32] In addition, a wide variety of functional groups can be tolerated in the reaction.

Summary

A new approach for generating acyl alkoxo transition metal complexes starting from esters by taking advantage of the coordination of sp^2 nitrogen to ruthenium is described. Two catalytic reactions were explored on the basis of the methodology:[33] a cross-coupling reaction with organoboron compounds and a decarbonylative reduction with $HCOONH_4$ (or a hydrosilane). Further investigations of the catalytic conversion of esters into carbonyl compounds with pronucleophiles, in which the pyridinemethoxy group functions as a base, are currently underway. Various types of acyl transition metal alkoxo complexes would be generated from esters by various combinations of catalysts and directing groups, suggesting a wide spectrum of catalytic reactions could be explored.

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Supporting Information Available: Experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0492719

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[32] For reviews on the decarbonylation of aldehydes, see: Baird, M. C. *The Chemistry of Acid Derivatives*; Patai, S., Ed.; Wiley: New York, 1979; pp 825−857. Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*: *Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York and London, 1991. Tsuji, J. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: New York, 2002; pp 2643−2653.

[33] Na, Y.; Park, S.; Han, S. B.; Han, H.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2004**, *126*, 250.