substituted with aryl or alkoxy groups, disproportionation reactions at the Si–R bond predominate; thus subsequent experimentation was limited to alkylsilanes. Silanes substituted with just one hydrogen do not react to produce disilanes at observable rates (compare experiments 1 and 2 or 3 and 4). This could be due to mechanistic requirements (vide infra) or simply a lowered reactivity due to steric or electronic effects. When a mixture of Et_3SiH and Et_2SiH_2 was allowed to proceed to disilanes in the presence of **1** (experiment 6), $Et_4Si_2H_2$ and Et_5Si_2H were formed in a ratio of 7:1. Et_6Si_2, which could have been detected in amounts 100 times smaller than Et_5Si_2H, was not observed.

A number of late transition-metal catalysts were then tested with Et_2SiH_2 for disilane formation (Table II, column A).[9] The rate of disilane formation varied greatly as the catalyst was changed, although it should be noted that all reactions were performed in the same manner and no attempt was made to individually optimize conditions for each catalyst. $(PPh_3)_3RhCl$ (**2**) is the most effective catalyst found thus far. The rates observed in the presence of **1** and **2** slowed with time and did not fit integral-order kinetics with respect to silane or catalyst, although they did increase as catalyst and/or silane concentration was increased. The number of moles of disilane produced per mole of catalyst has not been optimized, although addition of excess PPh_3 to **1** or to **2** increases this value. At least 650 mol of disilane can be produced per mole of **2**.

Most of the catalysts in Table II did not convert Et_3SiH to disilane. However, Et_6Si_2 could be observed among the products (which included Et_4Si and other silanes arising from reactions with ligands on the catalyst) in reactions containing $[Pd(allyl)Cl]_2$ (**3**), $Pt(COD)Cl_2$ (**4**) (COD = 1,5-cyclooctadiene), $[Ir(COD)Cl]_2$ (**5**), and $[Rh(CO)_2Cl]_2$ (**6**).[10] With **3**, black solids were formed almost immediately in the reaction mixture; similar results have been reported by other workers.[11] No solids were observed with any other catalyst, although the possibility of colloidal heterogeneous catalysis must be considered a possibility in view of a recent report.[12]

Many of the compounds in Table II have been studied by other workers as catalysts for hydrosilation. It was suspected that Si–Si bond formation might occur at rates competitive with hydrosilation, and thus the relative rates of the two reactions were measured. Equimolar amounts of Et_2SiH_2 and 1-hexene were allowed to react in the presence of various catalysts. At low conversions where the concentrations of silane and alkene are essentially unchanged, the relative amounts of $Et_2(n\text{-hexyl})SiH$ and $HEt_2Si\text{-}SiEt_2H$ formed were used as a measure of the relative overall rates of hydrosilation and Si–Si bond formation. The data in Table II, column B, show that these vary considerably for different catalysts, and for many catalysts hydrosilation predominates. Such is the case for **2**, which is an effective catalyst for either process. However, **2** is a useful catalyst for Si–Si bond formation when an alkene is not present. For **1**, Si–Si bond formation is slightly faster.

The experiments described in Tables I and II were run in the absence of water and oxygen. When the reaction was conducted in air, disilane formed in minor amounts, and disiloxane was instead the major product. Experiments in which O_2 or water or both were added to reaction mixtures prepared under nitrogen demonstrate that either can serve as a source of the disiloxane oxygen. Reactions are more rapid in the presence of O_2.[13] When sufficient water is present, silanol also forms. For **1** and **2**, the relative rates of hydrosilation and reaction with ROH (R = H, Et) have been measured, and formation of Si–O bonds is ten to one hundred times faster than hydrosilation.[14,15] This is evidently generally true since with other catalysts, traces of water are scrubbed out of the reaction mixture by the very rapid formation of siloxane, after which the other reactions discussed here proceed.

Little is known about the mechanism of formation of Si–Si bonds in the presence of transition-metal catalysts. Although the observation that Et_2SiH_2 can and Et_3SiH cannot form disilanes in the presence of **1** and **2** seems consistent with a silylene-like intermediate $[Et_2Si{=}M]$ as suggested by Nagai et al.,[3d] the results with **3**–**6** do not support this interpretation and it is premature to make mechanistic conclusions. Investigations into the mechanism continue. These uncertainties notwithstanding, it is established that Si–Si bonds can be formed from Si–H bonds with a variety of transition-metal catalysts, often at rates competitive with hydrosilation. One can generally expect that compounds known to catalyze hydrosilation can be used for the synthesis of Si–Si bonds, within the limitations imposed by the side reactions and any mechanistic constraints.

Acknowledgment. The capable technical assistance of S. Gravelle and J. Chamberlain is gratefully acknowledged. J. Schroepfer, 3M Analytical and Properties Research Laboratory, provided valuable GC/MS data.

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[9] For all experiments reported in Table II, experiments were performed in a manner similar to that described for 1 (footnote 8) using amounts of catalyst, silane, and hexene as indicated, with hexadecane as internal standard. Products were analyzed by gas chromatography. In experiments where it was desired to vary concentrations to obtain kinetics data, 1 or 2 and silane were separately dissolved in tetrahydrofuran and mixed at $t = 0$. Relative rates were the same with or without solvent.

[10] For catalysts which are very inefficient (e.g., H_2PtCl_6), the limits of detection preclude observation of Et_6Si_2 at rates that are less than one-tenth that of disilane formation from Et_2SiH_2.

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[14] In the glovebox, 1 mmol each of Et_3SiH, 1-hexene, and ROH (R = Et or H) were placed in a vial. For R = H, 0.5 mL of tetrahydrofuran was added to create a homogeneous solution. Catalyst 1 or 2 (0.01 mmol) was then added, and the reaction was monitored by gas chromatography. The ratio area $[Et_3SiOR]$/area $[Et_3Si(n\text{-hexyl})]$, corrected for GC response factors, was used as a measure of the overall rates of reaction. The ratios are as follows: for 1, R = Et, 10, R = H, >100; for 2, R = Et, 25, R = H, 110.

[15] For a discussion of mechanistic considerations and the rates of silane reaction with various alcohols, see: Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265 and references therein.

Palladium Chloride Catalyzed Olefin–Formate Ester Carbonylation Reactions. A Simple, Exceptionally Mild, and Regioselective Route to Branched Chain Carboxylic Esters

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Summary: Olefins react with formate esters, carbon monoxide, oxygen, hydrochloric acid, copper chloride, and palladium chloride as the catalyst, at room temperature and atmospheric pressure, to give mainly branched chain carboxylic esters in fair to good yields.

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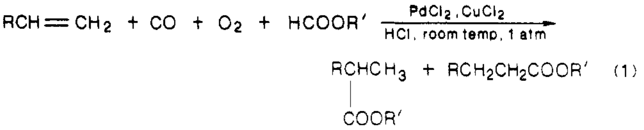
Table I. Reaction of Olefins with Formate Esters/CO/O_2/$PdCl_2$/$CuCl_2$/HCl

olefin	HCOOR′, R′ =	solv[a]	HCl,[b] ml	reaction time, h	yield of ester, %	ratio of esters,[c] branched/linear
1-decene	*n*-C_4H_9	D	0.5	23	66	7.0
		D	0.5	23	52	7.0
		D[d]	0.3	25	41	4.0
		D[e]	0.3	24	58	6.5
		D[f]	0.3	25	21	5.4
		D[g]	0.3	24	38	6.0
		B	0.3	22	63	6.0
	sec-C_4H_9	D	0.3	67	84	5.3
	CH_3	D	0.3	72	58	5.2
1-octene	*n*-C_4H_9	D	0.3	95	62	5.0
	CH_3	D	0.5	46	60	5.1
p-methylstyrene	*n*-C_4H_9	D	0.5	24	28[h]	12.6
	CH_3	D	0.5	95	29[h]	9.5
cis-2-nonene	*n*-C_4H_9	D	0.5	42	42	7.5
trans-2-nonene	*n*-C_4H_9	D	0.5	46	34	14.0
cis-2-decene	*n*-C_4H_9	D	0.5	46	44	6.7
		D	0.3	46	45	6.6
		B	0.3	48	24	≥100
	CH_3	D	0.5	68	60	9.5
trans-2-decene	*n*-C_4H_9	D	0.5	54	21	22.0
		B	0.3	48	10	≥100
	CH_3	D	0.5	72	24	7.0
cyclooctene	*n*-C_4H_9	D	0.5	46	63	
cyclododecene	*n*-C_4H_9	D	0.5	52	35	

[a] D = dioxane; B = *n*-butyl formate. [b] Reaction conditions using 0.3 mL of HCl/$PdCl_2$ (0.3 mmol), HCOOR′ (4 mL), dioxane (10 mL), $CuCl_2$ (1.5 mmol), and olefin (5.4 mmol). For 0.5 mL of HCl/$PdCl_2$ (0.15 mmol), $CuCl_2$ (0.3 mmol), HCOOR′ (4 mL), dioxane (10 mL), and olefin (5.4 mmol). [c] Ester ratios were determined by gas chromatography and by NMR spectroscopy. [d] Using 1:1 $HCOOC_4H_9$/1-decene. [e] $Cu(OAc)_2$ instead of $CuCl_2$. [f] Copper triflate instead of $CuCl_2$. [g] $Pd(OAc)_2$/$Cu(OAc)_2$ instead of $PdCl_2$/$CuCl_2$. [h] The main product (50–53%) is the ether *p*-$CH_3C_6H_4CH(CH_3)OR$ (R = C_4H_9 or CH_3).

There are relatively few reports of metal-catalyzed reactions of formate esters. Examples include the isomerization of such esters to acids using chloro(1,5-cyclooctadiene)iridium(I) or -rhodium(III) chloride as the catalyst,[1,2] the rhodium(I)-catalyzed reaction of halides with formate esters and carbon monoxide to give carboxylic esters,[3] and the homogeneous decarbonylation of formate esters catalyzed by Vaska's complex $[(Ph_3P)_2Ir(CO)Cl]$.[4] In addition, methyl formate has attracted considerable interest as a possible C_1 intermediate.[5] We now describe a simple, exceptionally mild, palladium-catalyzed oxidative carbonylation reaction of formate esters and olefins.

Treatment of 1-decene with *n*-butyl formate, carbon monoxide, oxygen, cupric chloride, and hydrochloric acid in dioxane, using palladium chloride as the catalyst, for 24 h at room temperature and 1-atm pressure, afforded esters in 52% yield (eq 1). The ratio of branched to linear ester was 6.3. The proportion of olefin/$CuCl_2$/$PdCl_2$ was 18/5/1, and an approximately 1:1 carbon monoxide–oxygen ratio was used in the reaction. Higher yields as well as branched/linear ester ratios are realized by using excess rather than equimolar amounts of butyl formate. Principal byproducts of the reaction are isomeric olefins, together with unreacted 1-decene. Only traces of 1-decene are converted to product in the absence of any one of the following: acid, oxygen, or cupric chloride. Only minute amounts of carboxylic ester are formed by the use of excess (i.e., 5–10 times) cupric chloride, but no oxygen. In other words, oxygen is essential for this reaction. Carbon monoxide must be bubbled through the reaction mixture, otherwise no reaction takes place. Indeed, when the 1-decene- butyl formate reaction was repeated by using labeled carbon monoxide (^{13}CO), the carbonyl is derived to an extent greater than 99% from labeled CO.



$$RCH{=}CH_2 + CO + O_2 + HCOOR' \xrightarrow[\text{HCl, room temp, 1 atm}]{PdCl_2,\,CuCl_2} \underset{\displaystyle COOR'}{RCHCH_3} + RCH_2CH_2COOR' \qquad (1)$$

Palladium acetate can be used instead of palladium chloride, and both cupric acetate and triflate can be employed, but the yields of carboxylic esters are inferior when compared with results obtained by using cupric chloride (see Table I). Nitric acid and 48% aqueous tetrafluorobonic acid can be substituted for hydrochloric acid, but glacial acetic acid is inert.

The results for the reaction of a series of olefins with formates are given in Table I. The reaction is applicable to a variety of terminal and cyclic olefins using methyl, *n*-butyl, or *sec*-butyl formate, with a longer reaction time usually required for the methyl and *sec*-butyl formates. Note that some straight-chain ester (e.g., *n*-butyl undecanoate) was formed when *cis*- or *trans*-2-decene or *cis*- or *trans*-2-nonene was used as the reactant. Higher regioselectivity for the 2-ester was observed when *trans*-2-decene or -2-nonene was used as the substrate in reaction with butyl formate in dioxane than when the cis isomers of either of these olefins was employed as the reactant. The reverse behavior was found if methyl formate was used instead of the butyl analogue. Interestingly, when the reaction of *cis*- or *trans*-2-decene is run in neat *n*-butyl formate (rather than in dioxane), then the regioselectivity for the branched chain carboxylic ester is enhanced, although the yield is reduced. Such a significant change in regioselectivity was not observed for the terminal olefin 1-decene.

The nature of the catalytically active species needs to be established. However, it is instructive to note that solid is precipitated by pretreatment of *n*-butyl formate with

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$PdCl_2$, $CuCl_2$, HCl, CO, and O_2 (i.e., in the absence of the olefin). If the mixture is filtered and the filtrate is treated with 1-decene for 48 h (CO/O_2), then carboxylic esters are formed in 42% yield, with the branched/linear ratio being 6.0. Furthermore, exposure of the filtered solid to fresh *n*-butyl formate, 1-decene, CO, O_2, and HCl (but no $PdCl_2$ or $CuCl_2$) for 24 h afforded the esters in 43% yield (branched/linear ratio of 6.9). These observations show that the thus far uncharacterized solid material, as well as the filtrate, are active catalysts for converting olefins and formate esters to carboxylic esters.

The following general procedure was used; carbon monoxide was bubbled through a dioxane (10 mL)-formate ester (4 mL) solution for 15 min. Palladium chloride (0.3 mmol) was then added, followed by 0.3 mL of concentrated hydrochloric acid. Once most of the palladium chloride had dissolved, cupric chloride (1.5 mmol) was added, oxygen bubbling was begun together with carbon monoxide, and the olefin (5.4 mmol) was added. After being stirred at room temperature and 1 atm, the mixture was filtered, the filtrate was treated with an equal volume of water (~15 mL), and the products were extracted with ether and distilled.

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Polysilane-Metal Interactions. Migration, with Rearrangement, of the Disilylmethyl Group from Iron to the Cyclopentadienyl Group in $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}CH_2SiMe_2SiMe_3$[1]

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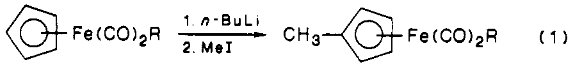
Summary: Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}R$ (R = CH_2SiMe_3, $CH_2SiMe_2SiMe_3$) with lithium diisopropylamide at -80 °C leads to cyclopentadienyl ring metalation. Reaction of the metalated product with CH_3I gives $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2\text{-}R$. If the reaction is performed at 0 °C, the same product is obtained for R = CH_2SiMe_3; however, with R = $CH_2SiMe_2SiMe_3$ a new product is obtained involving migration, with rearrangement, of the disilylmethyl group $(\eta^5\text{-}Me_3SiCH_2SiMe_2C_5H_4)Fe(CO)_2\text{-}CH_3$.

There is current interest in deprotonation reactions of transition-metal cyclopentadienyl carbonyls that lead to ring metalations with or without[2-6] migrations of σ-bonded groups from the transition metal, and we recently reported migrations of polysilyl groups from Fe to the cyclopentadienyl group of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SiMe_2)_n\mathit{SiMe_3}$ upon treatment with *n*-butyllithium.[7]

We found that deprotonation of the related iron disilylmethyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}CH_2SiMe_2SiMe_3$ (**1**) at -78 °C resulted only in ring metalation with no migration, and the same result was observed with $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_3$ (**2**) (eq 1).

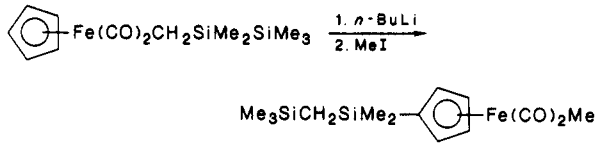


1 (2) 3 (4)

R = $CH_2SiMe_2SiMe_3$ (1, 3), CH_2SiMe_3 (2, 4)

This result was in keeping with previous studies which showed that simple alkyl groups σ-bonded to metals were not prone to migration,[2] in contrast to silyl,[2,3,7] germyl,[8,9] stannyl,[9] plumbyl,[9] and acyl groups.[4,6]

Our continuing studies have indicated that changes in temperature have a profound effect upon the outcome of the reaction of the disilylmethyl complex with *n*-butyllithium. When we performed the reaction at room temperature instead of -78 °C, different results were observed; a high yield of a product (**5**) was obtained in which the original $Me_5Si_2CH_2$ group had migrated *and* rearranged (eq 2).



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We found that the yields were higher when the reaction was carried out at 0 °C, using lithium diisoproplyamide (LDA) as the base. In a typical reaction, 0.54 g (1.75 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_2SiMe_3$ dissolved in oxygen-free THF at 0 °C was treated with 4.0 mL (2.2 mmol) of freshly prepared LDA in THF. The solution immediately changed color from orange to deep red, and after 20 min the CO stretching frequencies of the starting material (2002, 1945 cm^{-1}) had been replaced by bands typical of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ (ν(CO) 1881, 1865, 1811, 1751 cm^{-1}[11,12]). An excess of methyl iodide (2.0 g, 14.1 mmol) was added, and the solution was stirred for 20 min after which time all anion CO bands had been replaced by two bands at 2001 and 1944 cm^{-1}. The solvent was removed in vacuo and the residue dissolved in a minimum of hexane and chromatographed (1 × 10 cm alumina column). A single yellow band was eluted with hexane to produce 0.39 g (70%) of $(\eta^5\text{-}Me_3SiCH_2SiMe_2C_5H_4)Fe(CO)_2CH_3$ (**5**).[10] Pertinent spectral data for this and other complexes are recorded in Table I.

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