Table I. Reactions of Halosilanes and Organomagnesium Reagents Catalyzed by Cuprous Cyanide[a]

entry	organomagnesium reagent	halosilane	product	*T*, °C	yield,[b] %
1	$(C_8H_{17})_2Mg$	Cl_3SiCH_3	$(C_8H_{17})_3SiCH_3$	15	85 (96[c])
2	$C_8H_{17}MgBr$	Cl_3SiCH_3	$(C_8H_{17})_3SiCH_3$	0	90[c]
3	*n*-$C_{16}H_{33}MgBr$	$SiCl_4$	$(C_{16}H_{33})_4Si$	10	65
4	C_6H_5MgCl	*p*-$CH_3C_6H_4SiCl_3$	*p*-$CH_3C_6H_4Si(C_6H_5)_3$	−10	81
5	c-$C_6H_{11}MgBr$	$C_6H_5SiCl_3$	$C_6H_5Si(C_6H_{11})_2OH$	−30	83[d]

[a] General procedure: The organomagnesium reagent (from 0 to 36% excess) in tetrahydrofuran or ether–tetrahydrofuran was cooled to the indicated temperature under an inert atmosphere. The CuCN (5% based on Si) was added, followed immediately by the dropwise addition of the silyl halide at a rate which keeps the reaction temperature at or below the indicated temperature. After the reaction mixture had been allowed to warm to room temperature, it was carefully hydrolyzed with cooling, followed by ether extraction and distillation or recrystallization of the product. [b] Isolated yield, except where otherwise indicated. [c] Yield determined by gas chromatography using an internal standard. [d] Hydrolytic workup.

Table II. Yield of $(C_8H_{17})_3SiCH_3$ as a Function of Catalyst in the Reaction of $(C_8H_{17})_2Mg$ with Cl_3SiCH_3[a]

		% yield	
example	cat.	with cat.	without cat.
1	AgCN	80	16
2	$(C_4H_9)_3SnCN$	89	12
3	BrCN	94	12
4	$Hg(CN)_2$	97	12
5	$(CH_3)_3SiCN$	95	12
6	$(CH_3)_3SiNCS$	69	30
7	$Ca(SCN)_2$	73	12
8	AgSCN	79	31
9	$(C_4H_9)_4N^+SCN^-$	92	31

[a] These experiments were done by using several batches of $(C_8H_{17})_2Mg$ (molarity range, 0.45–0.78 in the THF/octene solution in which they were prepared). A reaction without catalyst was performed for each batch under conditions identical with those used with catalysts. These control reactions were allowed to proceed slightly longer than those containing catalysts. The catalyst, about 5 mol % with respect to chlorosilane, was added to a stirred solution of the organomagnesium reagent at 0 °C under argon; then the CH_3SiCl_3 was added in small portions over 2–3 min. After being stirred for 60–70 min, the reaction mixture was allowed to warm to room temperature (0.6–3.4 h). Docosane (internal standard) was added, and the amount of product present was determined by gas chromatography.

ularly important since the residual catalysts from R_2Mg preparation appear to promote formation of trialkylsilanes.[5] Yields of several representative reactions using catalytic quantities of CuCN are given in Table I. Earlier methods of preparation included 48 h at reflux in THF[7] (entry 2), high-temperature reactions[8,9] (entries 3 and 5), or the use of an organolithium reagent[3] (entry 4). That cyanide or thiocyanate are the necessary catalysts can be seen from Table II which shows the yields of methyltrioctylsilane, derived from dioctylmagnesium and methyltrichlorosilane, as a function of catalyst. It is apparent that these two pseudohalides are the important catalytic elements. Numerous other anions such as cyanate, iodide, and fluoride were inactive under these mild conditions. A few ions such as azide, nitrate, and phenylacetylide exhibited lesser degrees of catalytic activity. Other ions more closely related to cyanide such as dicyanamide and selenocyanate were good catalysts. Cuprous cyanide was generally used in preparative reactions since it is inexpensive and nonhygroscopic and generally gave good results, whether the scale was a few millimoles or several moles. It is quite possible that some of the other catalysts would be more useful in some cases.

Although the mechanism was not studied, several possibilities can be considered. Since many of the catalysts used in this work are known reagents[10] for the synthesis of silyl cyanides or silyl isothiocyanates, the intermediacy of such species is suggested. These silyl pseudohalides are known to react with Grignard reagents by displacement of the pseudohalide.[11] The possibility that a pentacoordinate species such as $R_3SiCl(CN)^-$ is the active intermediate is suggested by the findings of Corriu and coworkers who have shown that several types of pentacoordinated silicon anions have greatly enhanced tendencies to undergo nucleophilic substitution.[12] Finally, the possibility exists that complex anions such as R_2MgCN^-,[13] R_2MgSCN^-,[14] or $RMg(X)CN^-$ have enhanced nucleophilic properties. Regardless of mechanistic detail, the use of CN^- or NCS^- catalysts greatly increases the utility of organomagnesium reagents for the preparation of tetraorganosilanes.

Acknowledgment. We thank Professors Peter Beak and Robert Grubbs for helpful discussions.

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(5) The first step in the preparation of R_2Mg is the hydrogenation of Mg using either Ti or Cr catalysts. The second step is the Zr-catalyzed addition of MgH_2 across the double bond of a terminal olefin. It has been shown that Ti and Ni complexes can catalyze the formation of trialkylsilanes from reducing Grignards and halosilanes.[6] Thus the formation of considerable $(C_8H_{17})_2(CH_3)SiH$ using unpurified $(C_8H_{17})_2Mg$, and very little of it using $C_8H_{17}MgBr$ or $C_8H_{17}MgCl$ suggests that one or more of the catalysts used in the R_2Mg preparation is responsible for the reduction to trialkylsilane.

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(9) Cusa, N. W.; Kipping, F. S. *J. Chem. Soc.* **1932**, 2205–2209.

(10) Pike, R. M.; Mangano, M. F. *J. Organomet. Chem. Libr.* **1981**, *12*, 53–96.

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(14) Klopsch, A.; Dehnicke, K. *Chem. Ber.* **1975**, *108*, 420–432.

A Search for α-Hydrogen Migration in Iron-Alkyl Negative Ion Complexes in the Gas Phase

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Summary: The (adduct − H_2) product negative ion formed in the reaction of $(OC)_2Fe^{\bullet-}$ with $(CH_3)_2O$ was shown to be the carbene complex $(OC)_2Fe{=}CHOCH_3^{\bullet-}$, the product of C–H bond activation followed by α-hydrogen mi-

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gration and reductive elimination of H_2. The reactions of $(OC)_2Fe^{\bullet-}$ with CH_4 and $(CH_3)_4C$ yielded only the C–H bond activation adduct negative ions.

In our reported results of the gas-phase reactions of $(OC)_3Mn^-$ with alkanes and CH_3OH, formation of the product negative ions $(OC)_3Mn(olefin)^-$ and $(OC)_3Mn(H_2CO)^-$, respectively, was rationalized as initial C–H bond oxidative insertion by the metal center followed by a fast intramolecular migration of a hydrogen from C_β or O to Mn and reductive elimination of H_2.[1,2] No product negative ions resulting from competitive migration of a hydrogen from C_α to the metal (α-hydrogen migration) in the C–H bond activation intermediate were observed. To search for α-hydrogen migrations in gas-phase metal–alkyl negative ion complexes, we have employed the strategy of condensed-phase investigators using substrates devoid of C_β–H bonds.[3] In the present study, we examine the reactions of the 13-electron complex $(OC)_2Fe^{\bullet-}$[4] with CH_4, $(CH_3)_4C$, and $(CH_3)_2O$.

The experiments were carried out in a previously described flowing afterglow (FA) apparatus.[5] A mixture of $(OC)_{2-4}Fe^{\bullet-}$ (*m/z* 112, 140, 168) was generated by dissociative attachment of energetic electrons with $Fe(CO)_5$ in a fast flow of helium buffer gas (P_{He} = 0.9 Torr, $\bar{v}$ = 57 m s^{-1}, 298 K).[6] Both $(OC)_4Fe^{\bullet-}$ and $(OC)_3Fe^{\bullet-}$ failed to react with the three neutral substrates ($k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}).

When CH_4 was added to the helium flow containing $(OC)_2Fe^{\bullet-}$ (*m/z* 112), a very slow reaction ($k_{app} = 2.3 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1})[7] was observed with formation of the ion signal of the adduct at *m/z* 128 (eq 1).[8] Since the amount of the *m/z* 128 adduct negative ion was too small to allow for its characterization by further ion–molecule reactions, the reaction of $(OC)_2Fe^{\bullet-}$ with $(CH_3)_4C$ was carried out (eq 2).[10] The larger rate constant ($k_{app} = 6.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1})[7] generated sufficient ion signal for structure determination of the adduct negative ion at *m/z* 184. When D_2 was added via a gas inlet located 40 cm downstream of the $(CH_3)_4C$ inlet, we observed conversion of the *m/z* 184 adduct into a new adduct ion at *m/z* 185, *the product of a single H/D exchange (eq 3)*.[11]

$$\underset{m/z\ 112}{(OC)_2Fe^{\bullet-}} + CH_4 \xrightarrow{He} \underset{m/z\ 128}{(OC)_2Fe(CH_4)^{\bullet-}} \qquad (1)$$

$$\underset{m/z\ 112}{(OC)_2Fe^{\bullet-}} + (CH_3)_4C \xrightarrow{He} \underset{m/z\ 184}{(OC)_2Fe(H)(CH_2C(CH_3)_3)^{\bullet-}} \qquad (2)$$

$$\underset{m/z\ 184}{(OC)_2Fe(H)(CH_2C(CH_3)_3)^{\bullet-}} + D_2 \rightarrow \underset{m/z\ 185}{(OC)_2Fe(D)(CH_2C(CH_3)_3)^{\bullet-}} + HD \qquad (3)$$

This latter result established the presence of *one unique hydrogen* in the *m/z* 184 adduct and is consistent with the adduct structure being that of the product of C–H bond oxidative insertion. Further, this result rules out a significant equilibrium between the 15-electron hydrido–neopentyl and the 17-electron dihydrido–neopentylidene complexes, the product of α-hydrogen migration, since up to three H/D exchanges could occur in the latter structure. We suggest that the structure of the adduct in the CH_4 reaction (eq 1) is the analogous $(OC)_2Fe(H)(CH_3)^{\bullet-}$ complex.

The presence of C–H bond activation *without* α-hydrogen migration in the above two examples suggested to us that an electronegative substituent on the carbene carbon might stabilize the $(OC)_2Fe(H)_2({=}CHX)^{\bullet-}$ complex and allow the α-hydrogen migration step to occur. The reaction of $(OC)_2Fe^{\bullet-}$ with $(CH_3)_2O$ yielded two product ions, the adduct at *m/z* 158 and the (adduct – H_2) at *m/z* 156, with $k_{total} = 7.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (eq 4).

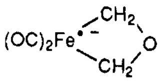
$$\underset{m/z\ 112}{(OC)_2Fe^{\bullet-}} + (CH_3)_2O \xrightarrow[0.38]{He} \underset{m/z\ 158}{(OC)_2Fe(C_2H_6O)^{\bullet-}} \qquad (4a)$$

$$(OC)_2Fe^{\bullet-} + (CH_3)_2O \xrightarrow[0.62]{} \underset{m/z\ 156}{(OC)_2Fe(C_2H_4O)^{\bullet-}} + H_2 \qquad (4b)$$

Assuming that the first step in reaction 4 is C–H bond oxidative insertion,[12] the structures considered most likely for the *m/z* 156 product negative ions are the carbene complex **1** formed by α-hydrogen migration followed by

$(OC)_2Fe(=CHOCH_3)^{\bullet-}$

1



2

reductive elimination of H_2[14] and the 3-oxametallacyclobutane **2**[16] produced by oxidative insertion into a C_γ–H

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[1] McDonald, R. N.; Jones, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 8097.

[2] McDonald, R. N.; Jones, M. T. *Organometallics* **1987**, *6*, 1991.

[3] For example, see: (a) Schrock, R. R. *Acc. Chem Res.* **1979**, *12*, 98. (b) Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481. (c) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

[4] $(OC)_3Mn^-$ does not react with CH_4 or $(CH_3)_4C$ within the time constraints of the FA experiments ($k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}): Jones, M. T. Ph.D. Thesis, Kansas State University, 1987.

[5] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* **1980**, *102*, 6491.

[6] McDonald, R. N.; Chowdhury, A. K.; Jones, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 3105.

[7] It is assumed that observation of adduct negative ions in these gas-phase reactions requires collisional stabilization of the adduct with the helium buffer gas to remove excess vibrational energy. The apparent bimolecular rate constants, k_{app}, are given for these formally termolecular processes.

[8] The reactions of Fe^+, Co^+, and Ni^+ with methane forming MH^+, MCH_3^+, and MCH_2^+ are *endothermic* processes.[9a] Formation of $CoCH_2^+$ from Co^+ and CH_4 was shown to be 1.1 eV endothermic.[9b] Similarly, other atomic metal cations, e.g. Ti^+ [9c] and Rh^+,[9d] do not react with CH_4. However, NiD^+, but not FeD^+ and CoD^+, reacted with CH_4 to yield NiH^+ and $NiCH_3^+$.[9e]

[9] (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (b) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (c) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (d) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944). (e) Carlin, T. J.; Sallans, L.; Cassady, D. B.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320.

[10] The use of the larger $(CH_3)_4C$ molecule compared to CH_4 should significantly increases the density of states in the excited C–H bond activation adduct with neopentane, thus allowing for an increase in the efficiency of collisional stabilization of this adduct and/or the α-hydrogen migration process.

[11] $(OC)_{2,3}FeD_2^{\bullet-}$ ions are also formed in this reaction, but neither of these ions reacted with $(CH_3)_4C$.

[12] C–O bond oxidative insertion was not considered likely since this insertion mode was not observed in the reactions of $(OC)_2Fe^{\bullet-}$[13] or $(OC)_3Mn^-$ with CH_3OH.[2]

[13] McDonald, R. N.; Chowdhury, A. K., unpublished results.

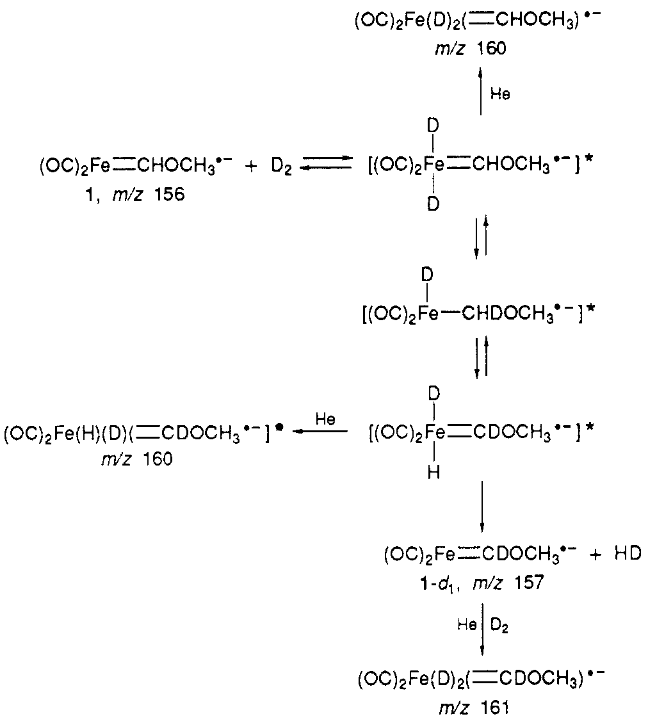
[14] The reaction of $(CH_3)_2O$ with Fe^+ giving $Fe(CH_2O)^+$ and CH_4 was considered to proceed by initial insertion into the C–O bond followed by a β-hydride shift and reductive elimination of CH_4.[15a] Although Ti^+ + $(CH_3)_2O$ did not yield a product ion, the reaction of $(CH_3)_2O$ with $TiCl^+$ formed $TiClOCH_3^+$ by apparent C–O insertion.[15b] Both Ti^+ and $TiCl^+$ reacted with ethylene oxide, 2,5-dihydrofuran, and tetrahydrofuran by exclusive O-atom extraction.[15b]

[15] (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 163.

[16] For examples of 2-oxa- and 2-azametallacyclobutanes, see: Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704.

Organometallics **1989**, *8*, 1124-1125

Scheme I



bond followed by expulsion of H_2. The 17-electron hydrido–carbyne structure $(OC)_2Fe(H)(\equiv COCH_3)^{\bullet -}$ (3) was considered to be less probable than 1.

To determine the structure of the m/z 156 ions, the reaction of D_2 with the mixture of m/z 156 and 158 ions from reaction 4 was carried out. Only the m/z 156 ions react yielding two primary negative ion products at m/z 157 (H/D exchange; 23%) and 160 (addition; 77%) and a secondary ion product at m/z 161 (H/D exchange + addition). These results are consistent with 1 being the structure of the (adduct − H_2) ions at m/z 156. If the hydrido–carbyne complex 3 were the structure of the m/z 156 ions, must revert to 1 in the collision–addition with D_2 because the available evidence shows that 17- and 18-electron metal complex negative ions do not react with H_2 or D_2 in the gas phase.[17] The suggested mechanism of the D_2 reactions is shown in Scheme I. Confirmation for the iron–carbene structure 1 was obtained when the reaction of $(OC)_2Fe^{\bullet -}$ with CD_3OCH_3 formed only $(OC)_2Fe{=}CDOCH_3^{\bullet -}$ (m/z 157) and $(OC)_2Fe{=}CHOCD_3^{\bullet -}$ (m/z 159). The absence of reaction of the adduct at m/z 158 (eq 4a) with D_2 is consistent with the 17-electron structure $(OC)_2Fe(H_2)({=}CHOCH_3)^{\bullet -}$ for these ions and rules out the 15-electron structures of the Lewis complex $((OC)_2Fe^{-}(O^{+}(CH_3)_2))^{\bullet -}$ and $(OC)_2Fe(H)(CH_2OCH_3)^{\bullet -}$ where addition, substitution for the ether molecule, or H/D exchange could occur.

The results of the reaction of $(OC)_2Fe^{\bullet -}$ with $(CH_3)_2O$ are the first example of α-hydrogen migration in a gas-phase transition-metal–alkyl negative ion complex. The availability of the 15-electron Fischer-type carbene complex $(OC)_2Fe{=}CHOCH_3^{\bullet -}$ for study is the bonus of this investigation.

Acknowledgment. We gratefully acknowledge the support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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[17] (a) McDonald, R. N.; Schell, P. L.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 5578. (b) Jones, M. T. Ph.D. Thesis, Kansas State University, 1987.

Palladium-Catalyzed Alkyne–Oxalate Ester Reaction. A Formal Carbon–Carbon Bond Cleavage Process

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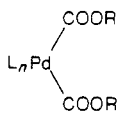
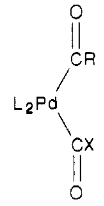
Summary: Terminal alkynes react with oxalate esters in the presence of bis(dibenzylideneacetone)palladium or palladium acetate and 1,4-bis(diphenylphosphino)butane, at 100 °C and 82 atm of carbon monoxide, to give trans-α,β-unsaturated esters and diynes. This carbon–carbon bond cleavage reaction may be proceeding by oxidative addition of the oxalate ester to palladium.

The palladium complex catalyzed oxidative coupling of carbon monoxide and alcohols to oxalate esters is a reaction of considerable interest.[2,3] It is believed that the oxalate ester arises by reductive elimination from a palladium dicarboxylate such as 1.



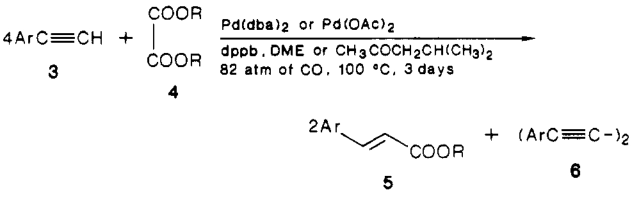
1



2

Another area which has been the subject of numerous studies in recent years is the palladium[4] and cobalt[5] catalyzed double carbonylation of halides to α-keto acids, esters, and amides. Investigations by Yamamoto and coworkers[4] indicate that the α-dicarbonyl compound is formed by reductive elimination from a acylmetal carboxylic acid, ester or amide (2, X = OH, OR, NR_2). It seemed conceivable to us that, under appropriate conditions, one could attain oxidative addition of the carbon–carbon bond of oxalate esters to palladium resulting in the generation of 1, i.e. the reverse of the above processes. This communication describes the interesting palladium-catalyzed reaction of alkynes and oxalate esters.

No reaction occurs when a mixture of phenylacetylene (3, Ar = Ph) and diethyl oxalate (4, R = C_2H_5) in 1,2-dimethoxyethane (DME) is treated with a catalytic quantity of bis(dibenzylideneacetone)palladium(0) and 82 atm of carbon monoxide, at 100 °C for 3 days. However, the presence of 1,4-bis(diphenylphosphino)butane (dppb) results in the generation of *trans*-methyl cinnamate (5, Ar



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[1] Killam Research Fellow, 1986–1988.

[2] Dekleva, T. W.; Forster, D. *Adv. Catal.* **1986**, *34*, 81 and references cited therein.

[3] Morris, G. E.; Oakley, D.; Pippard, D. A.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1987**, *410*, 411.

[4] Son, T.; Yanagihara, H.; Ozawa, F.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1251 and references cited therein.

[5] Foa, M.; Francalanci, F. *J. Mol. Catal.* **1987**, *41*, 89 and references cited therein.

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