ORGANOMETALLICS

# A new route to metal alkylidene complexes. Synthesis of ylide adducts (CO)4Fe-CH(R)P+Ar3 from aldehydes, triarylphosphines, and [cyclo] (CO)4FeSi(CH3)2CH2CH2Si(CH3)2

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# A New Route to Metal Alkylidene Complexes. Synthesis of Ylide Adducts $(CO)_4Fe^-CH(R)P^+Ar_3$ from Aldehydes, Triarylphosphines, and $(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$

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Chelated disilane complex $(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (**1**) is treated with a variety of aromatic and aliphatic aldehydes (RCHO). Disiloxane $\overline{OSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (**2**), iron carbonyls, and, in the case of benzaldehyde, *trans*-stilbene are formed. When these reactions are conducted in the presence of $P(C_6H_5)_3$ or $P(p\text{-}C_6H_4CH_3)_3$, ylide complexes $(CO)_4Fe^-CH(R)P^+Ar_3$ are isolated in high yields. The displacement of $P(C_6H_5)_3$ from $(CO)_4Fe^-CH(p\text{-}C_6H_4OCH_3)P^+(C_6H_5)_3$ (**4**) by $P(CH_3)_3$ is shown to proceed via a dissociative mechanism. All of these reactions are interpreted as proceeding via reactive alkylidene intermediates $(CO)_4Fe{=}CHR$. Protonation of $(CO)_4Fe^-CH(C_6H_5)P^+(C_6H_5)_3$ (**3**) with $CF_3SO_3H$ affords $C_6H_5CH_2P^+(C_6H_5)_3\,CF_3SO_3^-$. The spectral properties, relative stabilities, and mechanism of formation of the ylide complexes are discussed. It is proposed that the formation of disiloxane **2** constitutes a powerful driving force for the generation of $(CO)_4Fe{=}XL_n$ species from **1** and $O{=}XL_n$ precursors.

## Introduction

Organometallic complexes with metal–carbon double bonds have been of intense recent interest.[3] Previously, we described a number of reactions of transition-metal trialkylsilanes such as $(CO)_5MnSi(CH_3)_3$[4] and *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$[4a,5] with oxygen-containing organic compounds that yield organometallic complexes with metal–carbon *single* bonds. We therefore sought to determine if similar strategies could be used to generate complexes with metal–carbon *double* bonds.

In this paper, we give a detailed account of our studies of the reactions of the chelated bis(silane) $(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (**1**)[6] with aldehydes. In the presence of triarylphosphines, ylide complexes $(CO)_4Fe^-CH(R)P^+Ar_3$ are isolated in high yield. These species are shown to be in facile equilibrium with alkylidene complexes $(CO)_4Fe{=}CHR$. Hence, this transformation constitutes a fundamentally new route to complexes with metal–carbon double bonds. It also provides one of the very few means[4e] for the direct incorporation of aldehydes into organometallic molecules. A portion of this study has been communicated.[4a]

## Results

A rapid reaction occurred when benzaldehyde (1.1 equiv) was added to a 5 °C solution of *cis*-$(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (**1**) in benzene (eq 1). Considerable insoluble material deposited. Analysis by GLC after 2 h showed that cyclic disiloxane $\overline{OSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (**2**)[7] had formed in 95% yield.[8] The only other volatile organic product present in significant quantity was *trans*-stilbene (18–25% of theory). An IR spectrum of the heptane-soluble products showed $Fe_3(CO)_{12}$ and $Fe(CO)_5$.

Disiloxane **2** also formed in 95% yield in reactions of **1** with *p*-methoxybenzaldehyde, *p*-(dimethylamino)benzaldehyde, and octanal. The first two reactions were monitored by $^1H$ NMR in toluene-$d_8$ at −30 and −50 °C, respectively. No low-field resonances attributable to $(CO)_4Fe{=}CHR$ species,[9-12] or resonances due to any other reaction intermediate, were noted.

Brookhart has reported that the iron benzylidene complex $[(\eta\text{-}C_5H_5)Fe(CO)_2({=}CHC_6H_5)]^+$ decomposes to trans-stilbene (50%) over the course of 1 h at 25 °C.[10] Similarly, Casey has found that $(CO)_5W{=}C(C_6H_5)_2$ decomposes in refluxing heptane to, among other products, tetraphenylethylene (35%). In view of these observations, the formation of *trans*-stilbene in eq 1, and the high-yield formation of disiloxane **2** in all of the above reactions, we considered it highly probable that $(CO)_4Fe{=}CHR$ intermediates were being generated from **1**. Hence we conducted trapping experiments.

Reaction of 1.03–1.07 equiv of benzaldehyde with **1** in

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[1] (a) University of Utah. (b) University of California.

[2] To whom correspondence should be addressed at the University of Utah. Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

[3] This literature, which originated with E. O. Fischer, is extensive. Some lead articles are as follows: (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Schrock, R. R. *Science (Washington D.C.)* **1983**, *219*, 13. (c) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491. (d) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *Ibid.* **1982**, *104*, 3761. (e) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258. (f) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *Ibid.* **1983**, *105*, 5804.

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[5] (a) Blakeney, A. J.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *210*, 303. (b) Blakeney, A. J.; Johnson, D. L.; Donovan, P. W.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 4415.

[6] Vancea, L.; Graham, W. A. G. *Inorg. Chem.* **1974**, *13*, 511.

[7] Piccoli, W. A.; Haberland, G. G.; Merker, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 1883.

[8] In all cases, yields are based upon the limiting reactant. Yields determined by GLC and $^1H$ NMR are judged to be accurate within ±5%.

[9] Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

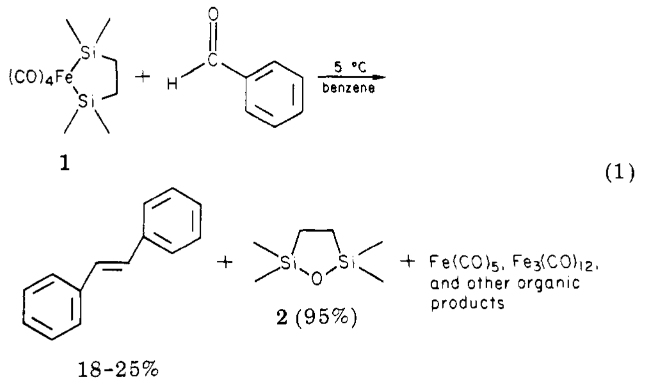
[10] Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

[11] Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.

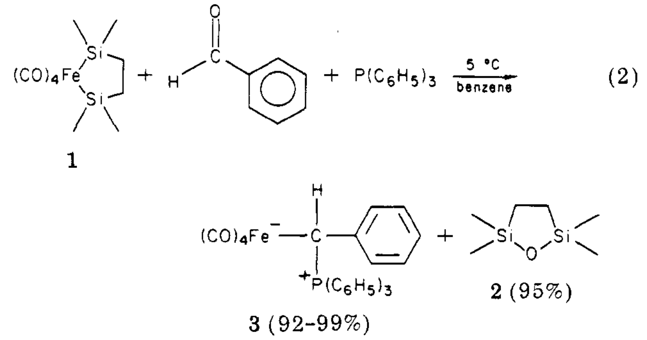
[12] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

[13] Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

0276-7333/83/2302-1846$01.50/0



the presence of 1.0–1.1 equiv of $P(C_6H_5)_3$ at 5 °C for 2 h gave, after workup, ylide complex $(CO)_4Fe^-CH(C_6H_5)P^+(C_6H_5)_3$ (**3**) as fine yellow crystals in 92–99% yields (eq 2). Disiloxane **2** was also detected by GLC

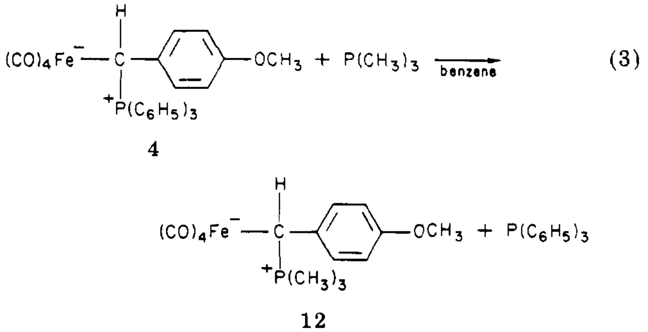


(95%). Complex **3** was characterized by IR and NMR spectroscopy as summarized in Table I and by microanalysis. The zwitterion was indefinitely stable in the solid state but slowly decomposed upon standing in benzene to $(CO)_4FeP(C_6H_5)_3$ (2051 (m), 1978 (m), 1947 (vs) cm$^{-1}$) and $(CO)_3Fe(P(C_6H_5)_3)_2$ (1886 (vs) cm$^{-1}$), as assayed by IR spectroscopy.[14]

The low-temperature reaction of equimolar quantities of **1**, benzaldehyde, and $P(C_6H_5)_3$ in $CD_2Cl_2$ was $^1H$ NMR monitored. An identical, side-by-side experiment was conducted without $P(C_6H_5)_3$. Both reactions proceeded at the same rate. Products slowly began to appear upon warming to −10 °C. No intermediates were observed.

The transformation depicted in eq 2 proved general for a variety of aromatic and aliphatic aldehydes, as summarized in entries 2–9 of Table I. In some reactions, $P(p\text{-}C_6H_4CH_3)_3$ was used in place of $P(C_6H_5)_3$ to enhance the crystallinity of the ylide complex. The *p*-(dimethylamino)phenyl- and cyclohexyl-substituted ylides **5** and **10** (entries 3, 8) were less stable in solution than **3**.

Ylide complexes $L_nM^-{-}CXYP^+R_3$ have commonly been prepared by the equilibrium addition of a phosphine, $PR_3$, to a carbene complex, $L_nM{=}CXY$.[9,15] Hence, the accessibility of $(CO)_4Fe{=}CHR$ intermediates from adducts **3**–**11** was probed. Zwitterion **4** was treated with 1 equiv of $P(CH_3)_3$ in $C_6D_6$ (eq 3). *Complete* conversion to $(CO)_4Fe^-CH(p\text{-}C_6H_4OCH_3)P^+(CH_3)_3$ (**12**) was observed by $^1H$ NMR over the course of several hours at room temperature. The new ylide complex **12** was an oil and could not be separated from byproduct $P(C_6H_5)_3$. However, it



could be characterized by IR and $^1H$ and $^{31}P$ NMR spectroscopy.

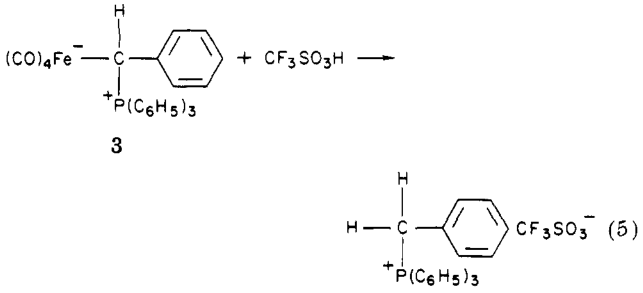
The rate of disappearance of **4** in eq 3 was monitored by $^1H$ NMR at 35.5 °C through 2.3 $t_{1/2}$ under the conditions summarized in Table II. The rate law

$$d[4]/dt = -k_{obsd}[4][P(CH_3)_3]^0 \tag{4}$$

was followed. Hence, phosphine substitution occurs via a *dissociative* mechanism.

Casey and Brookhart have shown that $(CO)_5W{=}CHC_6H_5$ and $[(\eta\text{-}C_5H_5)Fe(CO)_2({=}CHC_6H_5)]^+$ react with a variety of olefins to give phenylcyclopropanes.[9,16] Isobutylene was found to be the most reactive substrate. Thus, eq 1 was repeated at −78 °C in the presence of a large excesss of isobutylene. The major phenyl-containing product was again *trans*-stilbene (18%). No 1,1-dimethyl-2-phenylcyclopropane was found. A 5% yield would have been detected. Similarly, no reaction occurred when **3** was treated with a large excess of isobutylene at −20 °C (9 h) and then room temperature (15 h).

Cooke and Collman have shown that iron anions $(CO)_4Fe^-R$ liberate alkanes RH when treated with acid.[17] Hence, 3.1 equiv of $CF_3SO_3H$ was added to ylide complex **3** in $CD_3CN$. The yellow color of the reaction was immediately discharged. The reaction was stirred overnight, after which time $^1H$ NMR analysis showed $C_6H_5CH_2P^+(C_6H_5)_3\ CF_3SO_3^-$ to be present in spectroscopically quantitative yield. Product identity was confirmed by $^{31}P$ NMR and comparison to an authentic sample.



Finally, reactions of **1** with substrates other than those listed in Table I were briefly examined. Crotonaldehyde, **1**, and $P(C_6H_5)_3$ yielded what appeared to be a mixture of ylide complexes. The reaction of α-methylbutyraldehyde, **1**, and $P(C_6H_5)_3$ or $P(p\text{-}C_6H_4CH_3)_3$ gave an extremely unstable product which upon attempted characterization yielded $(CO)_3Fe(PAr_3)_2$. The reaction of cyclohexanone and **1** gave disiloxane **2** in 95% GLC yield. When this reaction was conducted in the presence of $P(C_6H_5)_3$, only $(CO)_4FeP(C_6H_5)_3$ and $(CO)_3Fe(P(C_6H_5)_3)_2$ were detected.

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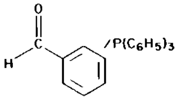
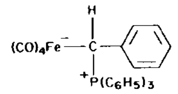
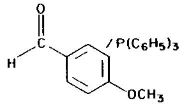
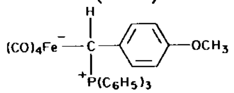
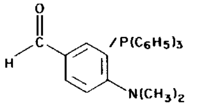
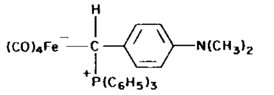
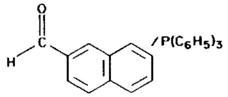
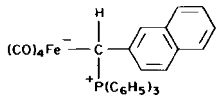
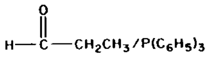
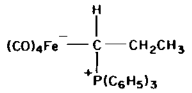
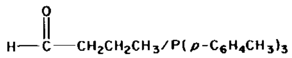
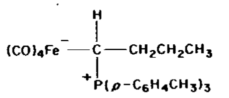
(14) (a) Clifford, A. F.; Mukherjee, A. K. *Inorg. Synth.* **1966**, *8*, 185. (b) Reckziegel, A.; Bigorgne, M. *J. Organomet. Chem.* **1965**, *3*, 341.

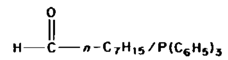
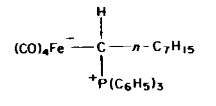
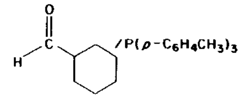
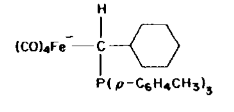
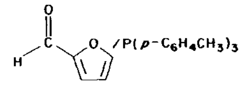
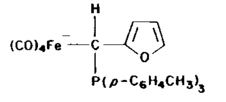
(15) (a) Fischer, H.; Fischer, E. O.; Kreiter, C. G.; Werner, H. *Chem. Ber.* **1974**, *107*, 2459. (b) Kreissl, F. R.; Held, W. *Ibid.* **1977**, *110*, 799. (c) Fischer, H. *J. Organomet. Chem.* **1979**, *170*, 309. (d) Choi, H. S.; Sweigart, D. A. *Ibid.* **1982**, *228*, 249. (e) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(16) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802.

(17) (a) Cooke, M. P. *J. Am. Chem. Soc.* **1970**, *92*, 6080. (b) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

**Table I.** Spectroscopic Characterization of Ylide Complexes $(CO)_4Fe^-CH(R)P^+Ar_3$ Prepared from $(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (1), Aldehydes, and $PAr_3$

| entry | aldehyde/$PAr_3$ | product (yield) | IR,[a] $cm^{-1}$ | $^1H$ NMR,[b] $\delta$ | $^{13}C$ NMR,[b] ppm | $^{31}P$ NMR,[b] ppm |
|---|---|---|---|---|---|---|
| 1 |  | <br>3 (99%) | 2023 (m), 1930 (m), 1905 (vs) | 7.63-6.90 (m, 20 H), 4.06 (d, $J_{H-P}$ = 12.7 Hz, 1 H)[c] | 218.86 (d, $J_{C-P}$ = 3.7 Hz, CO), $PPh_3$ at 134.85 (d, $J$ = 8.5 Hz), 133.41 (d, $J$ = 2.2 Hz), 129.54 (d, $J$ = 11.2 Hz), 126.16 (d, $J$ = 82.0 Hz), other Ph obscured, 11.30 (d, $J$ = 24.2 Hz, FeCH)[c] | 28.93 (30.05)[c] |
| 2 |  | <br>4 (99%) | 2022 (m), 1927 (m), 1901 (vs) | 7.85-6.65 (m, 19 H), 4.35 (d, $J_{H-P}$ = 13.1 Hz, 1 H), 3.31 (s, 3 H) | 219.03 (d, $J_{C-P}$ = 3.5 Hz, CO), $PPh_3$ at 134.93 (d, $J$ = 7.5 Hz), 133.38 (s), 129.53 (d, $J$ = 12.1 Hz), 126.22 (d, $J$ = 81.8 Hz), $C_6H_4OCH_3$ (partly obscured) at 169.39 (s), 139.91 (s), 54.93 (s, $OCH_3$), 10.51 (d, $J$ = 21.9 Hz, FeCH) | 28.77 |
| 3 |  | <br>5 (50%) | 2021 (m), 1925 (m), 1895 (vs) | 7.73-6.43 (m, 19 H), 4.37 (d, $J_{H-P}$ = 13.2 Hz, 1 H), 2.50 (s, 6 H) (4.08, 2.85[c]) | 219.26 (d, $J_{C-P}$ = 2.8 Hz, CO), $PPh_3$ at 135.03 (d, $J$ = 8.1 Hz), 133.32 (s), 129.53 (d, $J$ = 10.9 Hz), 126.53 (d, $J$ = 81.7 Hz), $C_6H_4N(CH_3)_2$ (partly obscured) at 113.87 (s), 40.41 (s, $NCH_3$), 10.54 (d, $J$ = 20.4 Hz, FeCH) | 28.21 |
| 4 |  | <br>6 (98%) | 2029 (m), 1928 (m), 1909 (vs), 1900 (vs) | 7.81-7.20 (m, 22 H), 4.20 (d, $J_{H-P}$ = 12.3 Hz, 1 H)[c] | 218.06 (d, $J_{C-P}$ = 3.5 Hz, CO), $PPh_3$ at 134.69 (d, $J$ = 7.6 Hz), 133.57 (d, $J$ = 2.3 Hz), 129.59 (d, $J$ = 11.1 Hz), 125.72 (d, $J$ = 82.9 Hz), naphthyl (partly obscured) at 145.16, 135.35, 128.64, 128.06, 127.69, 126.38, 125.01 (all s), 11.06 (d, $J$ = 25.8 Hz, FeCH)[c] | 29.75[c] |
| 5 | <br>$H{-}C({=}O){-}CH_2CH_3/P(C_6H_5)_3$ | <br>$(CO)_4Fe^-{-}CH(CH_2CH_3){-}P^+(C_6H_5)_3$<br>7 (70%) | 2023 (m), 1923 (m), 1901 (vs) | 7.97-7.03 (m, 15 H), 2.50-1.40 (m, 6 H) | 219.86 (d, $J_{C-P}$ = 3.5 Hz, CO), $PPh_3$ at 134.16 (d, $J$ = 8.4 Hz), 132.91 (d, $J$ = 2.3 Hz), 129.58 (d, $J$ = 11.1 Hz), 125.77 (d, $J$ = 81.8 Hz), 28.06 (s, $CH_2$),[d] 16.99 (d, $J$ = 20.8 Hz, $CH_3$),[d] 1.93 (d, $J$ = 13.6 Hz, FeCH)[d] | 34.47 |
| 6 | <br>$H{-}C({=}O){-}CH_2CH_2CH_3/P(p\text{-}C_6H_4CH_3)_3$ | <br>$(CO)_4Fe^-{-}CH(CH_2CH_2CH_3){-}P^+(p\text{-}C_6H_4CH_3)_3$<br>8 (51%) | 2053 (w), 2024 (m), 1927 (m), 1899 (vs)[e] | 7.70-6.80 (m, 12 H), 2.50-0.10 (m, 17 H) | 219.33 (d, $J_{C-P}$ = 3.5 Hz, CO), $P(p\text{-}C_6H_4CH_3)_3$ at 143.56 (d, $J$ = 2.4 Hz), 133.87 (d, $J$ = 8.5 Hz), 130.18 (d, $J$ = 12.1 Hz), 122.26 (d, $J$ = 84.1 Hz), 21.64 (s, $CH_3$), 36.52 (s, FeCC), 24.68 (d, $J$ = 19.5 Hz, $CH_2CH_3$), 14.19 (s, $CH_3$), −0.44 (d, $J$ = 14.3 Hz, FeCH)[c] | 34.13 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 7 |  |  <br>9 (85%) | 2021 (m), 1924 (m), 1901 (vs) | 7.85-6.80 (m, 15 H), 2.53 (m, 1 H), 1.95 (m, 2 H), 1.25 (m, 10 H), 0.88 (t, $J_{H-H}$ = 6.0 Hz, 3 H) | 219.92 (d, $J_{C-P}$ = 3.6 Hz, CO), PPh$_3$ at 134.21 (d, *J* = 8.4 Hz), 132.97 (d, *J* = 2.2 Hz), 129.60 (d, *J* = 11.1 Hz), 125.84 (d, *J* = 81.8 Hz), *n*-$C_7H_{15}$ at 34.92 (s), 32.41 (s), 32.18 (d, *J* = 18.4 Hz, FeCC*C*), 30.31 (s), 29.81 (s), 23.17 (s), 14.39 (s, $CH_3$), 0.31 (d, *J* = 13.5 Hz, FeCH) | 34.70 |
| 8 |  |  <br>10 (42%) | 2052 (w), 2024 (m), 1927 (m), 1896 (vs)[e] | 7.69 (d of d, $J_{H-P}$ = 11.4 Hz, $J_{H-H}$ = 8.7 Hz, 6 H, ortho to P), 6.91 (d of d, $J_{H-P}$ = 3.0 Hz, $J_{H-H}$ = 8.7 Hz, 6 H, meta to P), 2.77 (d, $J_{H-P}$ = 18.0 Hz, 1 H), 1.87 (s, 9 H), 1.80-0.00 (m, 11 H) | 219.60 (d, $J_{C-P}$ = 3.6 Hz, CO), P(*p*-$C_6H_4CH_3$)$_3$ at 143.15 (s), 133.84 (d, *J* = 8.5 Hz), 129.63 (d, *J* = 12.1 Hz), 122.94 (d, *J* = 83.0 Hz), 21.30 (s, $CH_3$), $C_6H_{11}$ at 41.83 (s), 36.42 (d, *J* = 18.2 Hz), 34.65 (s), 26.97 (s), 26.53 (s), 25.52 (s),[f] 8.54 (d, *J* = 12.4 Hz, FeCH)[c] | 32.79 |
| 9 |  |  <br>11 (93%) | 2030 (s), 1928 (s), 1916 (m), 1902 (s) | 7.59 (d of d, $J_{H-P}$ = 11.4 Hz, $J_{H-H}$ = 8.7 Hz, 6 H, ortho to P), 6.90 (d of d, $J_{H-P}$ = 3.0 Hz, $J_{H-H}$ = 8.7 Hz, 6 H, meta to P), 7.01 (s, 1 H of $C_4H_3O$), 6.07 (m, 2 H of $C_4H_3O$), 4.43 (d, $J_{H-P}$ = 14.4 Hz, 1 H) | 219.00 (d, $J_{C-P}$ = 3.7 Hz, CO), P(*p*-$C_6H_4CH_3$)$_3$ at 144.24 (d, *J* = 2.3 Hz), 134.82 (d, *J* = 9.4 Hz), 130.31 (d, *J* = 12.2 Hz), 122.49 (d, *J* = 86.7 Hz), 21.33 (s, $CH_3$), $C_4H_3O$ at 169.31 (s), 139.46 (s), 112.01 (s), 103.67 (d, *J* = 9.5 Hz), 2.43 (d, *J* = 27.1 Hz, FeCH) | 28.30 |

[a] In THF unless noted. [b] In $C_6D_6$ unless noted. [c] In $CDCl_3$. [d] Assignment based upon the $^1H$ coupled spectrum obtained with the gated decoupler on during the pulse delay and off during the acquisition. [e] In $C_6H_6$. [f] Note that two pairs of the $C_6H_{11}$ carbons are diastereotopic; hence up to six ring $^{13}C$ NMR resonances are expected.

The reaction of acetone, **1**, and $P(C_2H_5)_3$ gave a similar result.

## Discussion

We consider the high-yield formation of disiloxane **2** in eq 1 to be evidence for the simultaneous generation of a species of empirical formula $(CO)_4FeCHC_6H_5$, such as $(CO)_4Fe{=}CHC_6H_5$. When this reaction is conducted in the presence of $P(C_6H_5)_3$ (eq 2), the rate is unaffected. Under these conditions, ylide complex **3**, which is an adduct of $(CO)_4Fe{=}CHC_6H_5$ and $P(C_6H_5)_3$, is isolated in high yield. A mechanism which encompasses these observations, and others given above, is shown in Scheme I.

The initial step of Scheme I is the insertion of the benzaldehyde carbonyl group into an iron–silicon bond of **1**. Although the resulting intermediate **13** contains a seven-membered ring, a strong silicon–oxygen bond (106–127 kcal/mol)[18] is formed. Furthermore, this insertion has good chemical precedent in the reactions of $(CO)_5MnSi(CH_3)_3$ and *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ with benzaldehyde to give $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$[4c,e] and $(CO)_4Fe[Si(CH_3)_3]CH(C_6H_5)OSi(CH_3)_3$,[5b] respectively. Importantly, the latter compound, which lacks the chelate ring of **13**, undergoes only iron–carbon bond homolysis at room temperature.

Intermediate **13** could subsequently extrude disiloxane **2** via several possible pathways. For instance, we have shown that manganese–silicon and iron–silicon bonds can be heterolytically cleaved by attack of ether oxygens upon silicon.[4b,e,5] Hence, the ether oxygen in **13** could displace the remaining silicon from iron.

The overall thermodynamics for **1** + benzaldehyde → **2** + $(CO)_4Fe{=}CHC_6H_5$ (steps a and b, Scheme I) can be estimated. The carbon–oxygen double bond in benzaldehyde is worth on the order of 175 kcal/mol.[19] The two silicon–oxygen bonds in **2** likely provide at least 225 kcal/mol of driving force.[18] Direct measurements of metal–trialkylsilyl bond strengths have not yet been made. However, the iron–silicon bond in $(\eta\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_2CH_2Br$ has been shown to be no more than 5–7 kcal/mol stronger than the iron–carbon bond in $(\eta\text{-}C_5H_5)Fe(CO)_2CH_2Si(CH_3)_2Br$.[20] Therefore, in view of current estimates of first-row transition-metal–carbon bond strengths,[21] the iron–silicon bonds in **1** are unlikely to be worth much more than 30 kcal/mol each. On the basis of the calculated Fe=C bond strength in $(CO)_4Fe{=}CHOH$[22] and recent determinations of rotational barriers about $L_nM{=}CHR$ bonds,[23] the iron–carbon double bond in $(CO)_4Fe{=}CHC_6H_5$ is unlikely to be significantly stronger than 35 kcal/mol. Thus, an approximate $\Delta H$ for steps a and b of Scheme I is −15 kcal/mol. This suggests that $L_nX{=}O$ double bonds considerably stronger than the C=O bond of benzaldehyde might be cleaved by **1**, thus providing a novel and direct entry into a variety of $(CO)_4Fe{=}XL_n$ species.

Our inability to trap $(CO)_4Fe{=}CHC_6H_5$ with isobutylene is surprising in view of Casey's and Brookhart's results.[9,16]

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(18) (a) Ebsworth, E. A. V. In "Organometallic Compounds of the Group IV Elements"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part 1, pp 46–50. (b) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(19) Cottrell, T. L. "The Strengths of Chemical Bonds", 2nd ed.; Butterworths: London, 1958; p 275.

(20) Windus, C.; Sujishi, S.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1951.

(21) (a) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

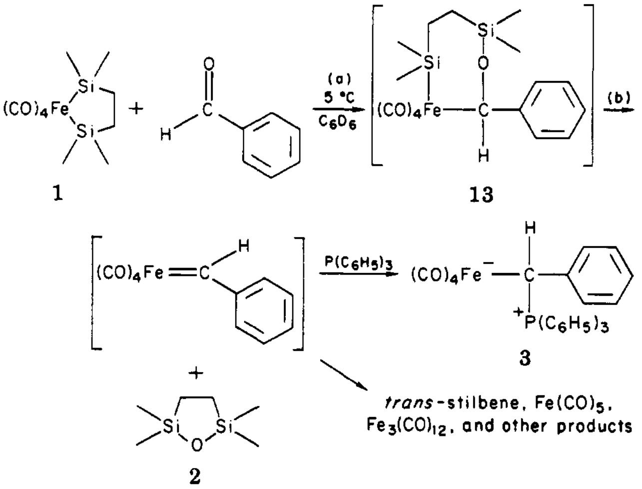
(22) Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1983**, *105*, 426.

(23) See citations in ref 3f and 12 and: Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.

Table II. Summary of Rate Data for Equation 3 in $C_6D_6$ at 35.5 °C

| run | $[4]_0$, mmol/L | $[P(CH_3)_3]_0$, mmol/L | $10^4k_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| 1 | 58.2 | 58.2 | 3.61 ± 0.16 |
| 2 | 58.2 | 3 × 58.2 | 3.69 ± 0.10 |
| 3 | 58.2 | 6 × 58.2 | 3.79 ± 0.10 |
| 4 | 58.2 | 10 × 58.2 | 3.67 ± 0.10 |
| 5 | 0.5 × 58.2 | 58.2 | 3.99 ± 0.31 |

Scheme I. Proposed Pathway for the Reaction of 1 with Benzaldehyde



Thermal decomposition must be preferred over cyclopropane formation. It should also be emphasized that an alternative route from 1, benzaldehyde, and $P(C_6H_5)_3$ to ylide complex 3, which does not pass through $(CO)_4Fe{=}CHC_6H_5$, may exist.

Ylide complexes 3–11 exhibit the expected spectroscopic properties (Table I). The IR spectra closely resemble those reported by Siegl and Collman for alkyls $[(C_6H_5)_3P]_2N^+(CO)_4Fe^-R$.[24] The $H_\alpha$ NMR chemical shifts and $J_{^1H-^{31}P}$ values are close to those found by Casey for $(CO)_5W^-CH(C_6H_5)P^+(C_6H_5)_3$ ($\delta$ 3.82 ($J$ = 15.6 Hz)).[9] This compound was synthesized by trapping the observable benzylidene $(CO)_5W{=}CHC_6H_5$ with $P(C_6H_5)_3$ at −78 °C. The $C_\alpha$ $^1J_{^{13}C-^{31}P}$ in 3–11 (12–27 Hz) are quite low for directly bonded couplings. Interestingly, assignments made via the $^1H$-coupled $^{13}C$ NMR spectrum of 7 indicate that for the ylide chain $^3J_{^{13}C-^{31}P} > {}^1J_{^{13}C-^{31}P} > {}^2J_{^{13}C-^{31}P}$.

The most straightforward interpretation of the rate expression for eq 3 (eq 4) is that initial $P(C_6H_5)_3$ dissociation from 4 occurs to give $(CO)_4Fe{=}CH(p\text{-}C_6H_4OCH_3)$. The equilibrium $L_nM{=}CXY + PR_3 \rightleftharpoons L_nM^-\text{-}CXYP^+R_3$ has been shown to be influenced by (1) the basicity of the phosphine, (2) the Lewis acidity of the carbene carbon, and (3) steric effects.[15a-d] Hence in eq 3, the less basic phosphine is displaced. Interestingly, alkoxy-substituted carbene complexes $L_nM{=}C(OR)R$ are reluctant to form $P(C_6H_5)_3$ adducts, presumably due to their lower Lewis acidity.[3a,15a-d] The lower solution stability of p-(dimethylamino)phenyl-substituted ylide 5 is also probably due to decreased $C_\alpha$ Lewis acidity.[15c]

The absence of ylide complex products from the reaction of 1, ketones, and phosphines is probably due to a combination of steric and electronic factors; any $(CO)_4Fe{=}CR_2$ intermediate would be bulkier and of lower Lewis acidity than $(CO)_4Fe{=}CHR$. It also appears, due to the instability of cyclohexyl-substituted ylide complex 10 and the initial product from 1, $PAr_3$, and α-methylbutyraldehyde, that $C_\beta$ branching decreases ylide complex stability.

Finally, the reaction shown in eq 5 is most plausibly interpretated as proceeding via initial protonation on iron to give a $(CO)_4FeHR$ intermediate, followed by reductive elimination. Thus, this series of ylide complexes behaves, to some extent, like the corresponding unfunctionalized iron alkyls.[17]

## Conclusion

This study has provided a facile and novel entry into a variety of ylide complexes $(CO)_4Fe^-CH(R)P^+Ar_3$. The synthetic strategy employed is potentially of broad generality for the generation of $(CO)_4Fe{=}XL_n$ and other species with multiple bonds to metals. Extensions of this strategy, and the chemical properties of the new ylide complexes, are under active investigation.

## Experimental Section

**General Remarks.** All reactions were carried out under an inert atmosphere. Solvents were dried and deoxygenated as previously described.[4a,d,5] Silane 1 and disiloxane 2 were prepared by published methods.[6,7] Aldehydes were obtained from common commercial sources and were purified by standard procedures.[25] Phosphines, $C_6H_5CH_2P^+(C_6H_5)_3Cl^-$, and $CF_3SO_3H$ were obtained from Aldrich or Strem Chemicals. Triarylphosphines were recrystallized from 1:1 methanol/benzene, and $CF_3SO_3H$ was distilled prior to use. Isobutylene (Phillips) was used without purification.

All $^1H$ NMR data were obtained at 90–200 MHz, and all $^{13}C$ NMR data were obtained at 50–75 MHz, unless noted. Spectra were referenced to internal $(CH_3)_4Si$. $^{31}P$ NMR spectra were obtained on a Varian FT-80 spectrometer and were referenced to external 85% $H_3PO_4$. IR spectra were obtained on Perkin-Elmer Model 521 and 1500 (FT) spectrometers. GLC analyses were performed as previously described.[4c,8] Microanalyses were conducted by Schwartzkopf.

**Reaction of 1 with Benzaldehyde.** A 5-mm NMR tube was charged with 281 mg (0.90 mmol) of 1 and 0.50 mL of benzene-$d_6$ in a glovebox and capped with a septum. The tube was removed from the box and cooled to 5 °C. Then benzaldehyde (100 μL, 1.06 mg, 1.00 mmol) was injected by syringe. Considerable insoluble material formed rapidly. A $^1H$ NMR spectrum (60 MHz) showed only severely broadened resonances. GLC analysis was conducted after 2 h at 5 °C and included coinjection with authentic product samples. Data are given in the results section. In separate experiments, the formation of disiloxane 2 was confirmed by $^1H$ NMR.

**Reaction of 1 with p-Methoxybenzaldehyde and p-(Dimethylamino)benzaldehyde.** The following experiment is representative. Additional details are provided elsewhere.[26]

A 5-mm NMR tube was charged with 79 mg (0.25 mmol) of 1 in a glovebox and capped with a septum. The tube was removed from the box and cooled to 5 °C. Then toluene-$d_8$ (0.25 mL) was added by syringe. The tube was shaken and cooled to −78 °C. A toluene-$d_8$ solution of p-(dimethylamino)benzaldehyde (37 mg, 0.25 mmol) was then slowly added in a manner that allowed it to be considerably cooled on the wall of the tube before it came into contact with the solution of 1. The tube was then transferred to a −50 °C Bruker WP-200 NMR probe. $^1H$ NMR monitoring showed the formation of siloxane 2 over the course of 2 h. However, no resonances ascribable to $(CO)_4Fe{=}CH(p\text{-}C_6H_4N(CH_3)_2)$ or other intermediates were observed. The reaction was allowed to warm to room temperature, whereupon GLC analysis indicated a 95% yield of 2. No other volatile organic products were formed in significant quantities.

**Preparation of $(CO)_4Fe^-CH(C_6H_5)P^+(C_6H_5)_3$ (3).** A solution of 1 (408 mg, 1.31 mmol) and $P(C_6H_5)_3$ (367 mg, 1.40 mmol) in 3 mL of benzene was cooled to 5 °C. Then 142 μL (149 mg, 1.40

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[24] Siegl, W. O.; Collman, J. P. J. Am. Chem. Soc. 1972, 94, 2516.

[25] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1980.

[26] Johnson, D. L. Ph.D. Thesis, UCLA, 1980.

mmol) of benzaldehyde was added, and the reaction was magnetically stirred for 1.5 h at 5 °C. Then 6 mL of heptane was added. Fine yellow crystals formed, which were isolated by filtration, washed with heptane, and dried in vacuo. Thus obtained was 672 mg (1.29 mmol, 99%) of **3**, dec pt 115–120 °C. Anal. Calcd for $C_{29}H_{21}FeO_4P$: C, 66.94; H, 4.07; Fe, 10.73; P, 5.95. Found: C, 67.07; H, 4.68; Fe, 11.33; P, 6.18.

**Preparation of $(CO)_4Fe^-CH(p\text{-}C_6H_4OCH_3)P^+(C_6H_5)_3$ (4).** A solution of **1** (124 mg, 0.40 mmol) and $P(C_6H_5)_3$ (108 mg, 0.41 mmol) in 3 mL of benzene was cooled to 5 °C. Then 49 $\mu$L (54 mg, 0.40 mmol) of *p*-anisaldehyde was added, and the reaction was magnetically stirred for 2 h at 5 °C. Then 6 mL of heptane was added. Yellow crystals formed, which were isolated by filtration, washed with 3 × 6 mL of heptane, and dried in vacuo. Thus obtained was 217 mg (0.39 mmol, 99%) of **4**, dec pt 94–110 °C. Anal. Calcd for $C_{30}H_{23}FeO_5P$: C, 65.47; H, 4.21; Fe, 10.15; P, 5.63. Found: C, 65.28; H, 4.25; Fe, 10.02; P, 5.80.

**Preparation of $(CO)_4Fe^-CH(p\text{-}C_6H_4N(CH_3)_2)P^+(C_6H_5)_3$ (5).** A solution of **1** (223 mg, 0.71 mmol) and $P(C_6H_5)_3$ (189 mg, 0.72 mmol) in 3 mL of benzene was cooled to 5 °C. Then 107 mg (0.72 mmol) of *p*-(dimethylamino)benzaldehyde was added, and the reaction was magnetically stirred for 2 h at 5 °C. To the resulting brown homogeneous solution was added 6 mL of heptane. A yellow precipitate formed, which was isolated by filtration and recrystallized from benzene/heptane. Thus obtained was 200 mg (0.36 mmol, 50%) of **5** as fine yellow crystals, dec pt 115–125 °C.

**Preparation of $(CO)_4Fe^-CH(2\text{-naphthyl})P^+(C_6H_5)_3$ (6).** Yellow crystalline **6**, dec pt 121–126 °C, was prepared in a manner identical with that for **2** in 98% yield (470 mg, 0.82 mmol) from 262 mg (0.84 mmol) of **1**, 223 mg (0.85 mmol) of $P(C_6H_5)_3$, and 133 mg (0.85 mmol) of 2-naphthaldehyde.

**Preparation of $(CO)_4Fe^-CH(CH_2CH_3)P^+(C_6H_5)_3$ (7).** Yellow crystalline **7**, mp 130 °C (dec ca. 131 °C), was prepared in a manner identical with that for **3** in 70% yield (158 mg, 0.34 mmol) from 150 mg (0.48 mmol) of **1**, 140 mg (0.53 mmol) of $P(C_6H_5)_3$, and 34.4 $\mu$L (28 mg, 0.48 mmol) of propionaldehyde.

**Preparation of $(CO)_4Fe^-CH(CH_2CH_2CH_3)P^+(p\text{-}C_6H_4CH_3)_3$ (8).** A solution of **1** (129 mg, 0.41 mmol) and $P(p\text{-}C_6H_4CH_3)_3$ (128 mg, 0.42 mmol) in 1 mL of benzene was cooled to 5 °C. Then 37 $\mu$L (30 mg, 0.42 mmol) of butyraldehyde was added, and the reaction was magnetically stirred for 4.5 h at 5 °C. Then 5 mL of heptane was added, and the reaction mixture was concentrated in vacuo. A yellow precipitate formed, which was recrystallized from heptane and dried in vacuo to give 112 mg (0.21 mmol, 51%) of **8** as fine yellow crystals, mp 99–101 °C dec.

**Preparation of $(CO)_4Fe^-CH(n\text{-}C_7H_{15})P^+(C_6H_5)_3$ (9).** Yellow crystalline **9**, dec pt 112–115 °C, was prepared in a manner identical with that for **3** in 85% yield (320 mg, 0.54 mmol) from 201 mg (0.64 mmol) of **1**, 171 mg (0.65 mmol) of $P(C_6H_5)_3$, and 102 $\mu$L (83 mg, 0.65 mmol) of octanal. Anal. Calcd for $C_{30}H_{31}FeO_4P$: C, 66.41; H, 5.76; Fe, 10.30; P, 5.71. Found: C, 66.63; H, 5.98; Fe, 10.49; P, 5.81.

**Preparation of $(CO)_4Fe^-CH(c\text{-}C_6H_{11})P^+(p\text{-}C_6H_4CH_3)_3$ (10).** Yellow powder **10**, dec pt 58–62 °C, was prepared in a manner identical with that for **8** in 42% yield (107 mg, 0.19 mmol) from **1** (142 mg, 0.45 mmol), $P(p\text{-}C_6H_4CH_3)_3$ (138 mg, 0.45 mmol), and cyclohexanecarboxaldehyde (55 $\mu$L, 50 mg, 0.45 mmol).

**Preparation of $(CO)_4Fe^-CH(2\text{-furyl})P^+(p\text{-}C_6H_4CH_3)_3$ (11).** Yellow crystalline **11**, dec pt 120–135 °C, was prepared in a manner identical with that for **3** in 93% yield (175 mg, 0.32 mmol) from **1** (107 mg, 0.34 mmol), furfural (29 $\mu$L, 34 mg, 0.35 mmol), and $P(p\text{-}C_6H_4CH_3)_3$ (107 mg, 0.35 mmol).

**Reaction of 1 with Benzaldehyde and Isobutylene.** A Schlenk flask was charged with **1** (113 mg, 0.36 mmol), $CH_2Cl_2$ (2.0 mL), and a stir bar and was cooled in a liquid nitrogen bath. Then benzaldehyde (38 $\mu$L, 39 mg, 0.37 mmol) was added. The flask was evacuated, and ca. 9 mmol of isobutylene gas was introduced. The reaction was warmed to −78 °C and stirred for 1 h. It was subsequently warmed to −40 °C (1 h), −10 °C (1 h), 0 °C (1 h), and room temperature (3 h). Subsequent GLC analysis showed *trans*-stilbene (18%) and disiloxane **2** (74%) to be present, but no 1,1-dimethyl-2-phenylcyclopropane (<5%). An IR spectrum indicated $Fe_3(CO)_{12}$ (2048 (s), 2028 (sh) cm$^{-1}$) to be the major iron-containing product. Additional analysis (column chromatography, $^1H$ NMR) gave no evidence for a cyclopropane product.

**Preparation of $(CO)_4Fe^-CH(p\text{-}C_6H_4OCH_3)P^+(CH_3)_3$ (12).** A Schlenk flask was charged with **4** (17.3 mg, 0.031 mmol), $P(CH_3)_3$ (2.4 mg, 0.031 mmol), and benzene-$d_6$ (1.0 mL). An aliquot was transferred to a 5-mm septum-capped NMR tube. After several hours, starting material $^1H$ and $^{31}P$ NMR resonances were absent; only resonances ascribable to **12** and $P(C_6H_5)_3$ ($^{31}P$, −5.86 ppm) were present. The contents of the Schlenk flask and NMR tube were combined. The solvent was removed to give a yellow oil from which neither component could be induced to crystallize. The rate constants in Table II were obtained from similar experiments employing procedures previously described.[12,15e] Data on **12**: $^1H$ NMR ($\delta$ $C_6D_6$) 0.77 (d, $J_{H-P}$ = 12.0 Hz, 9 H), 2.64 (d, $J_{H-P}$ = 14.0 Hz, 1 H), 3.36 (s, 3 H), 6.6–7.5 (m, 4 H); $^{31}P$ NMR ($\delta$, $C_6D_6$) 30.04 ppm; IR (cm$^{-1}$, $C_6D_6$) 2024 (m), 1941 (m), 1910 (vs).

**Reaction of 3 with $CF_3SO_3H$.** A Schlenk flask was charged with **3** (8.0 mg, 0.015 mmol), toluene internal standard (2 $\mu$L), and $CD_3CN$ (1.0 mL). Two 0.5-mL aliquots of this solution were transferred to two separate septum-capped 5-mm NMR tubes. The $^1H$ NMR spectrum of one tube was recorded. The other tube was treated with $CF_3SO_3H$ (2 $\mu$L, 3.4 mg, 0.023 mmol). The solution turned from yellow to colorless and was allowed to stand overnight. NMR spectra showed **3** to be consumed, and the characteristic $^1H$ (and $^{31}P$) resonances of $C_6H_5CH_2P^+(C_6H_5)_3$ to be present in quantitative yield vs. the toluene standard: $^1H$ NMR ($\delta$, $CD_3CN$) 4.62 (d, $J_{H-P}$ = 15.0 Hz, 2 H), 6.8–8.0 (m, 20 H); $^{31}P$ NMR ($CD_3CN$) 22.15 ppm. These values corresponded closely to those of an authentic sample of $C_6H_5CH_2P^+(C_6H_5)_3PF_6^-$, which was obtained as a white powder from the addition of $NH_4^+PF_6^-$ (41.9 mg, 0.257 mmol) to an aqueous solution (20 mL) of $C_6H_5CH_2P^+(C_6H_5)_3Cl^-$ (100 mg, 0.257 mmol).

**Acknowledgment.** We thank the National Science Foundation for support of this research. FT NMR spectrometers utilized in this study were provided by NSF departmental instrumentation grants.

**Registry No.** 1, 43198-13-6; **2**, 7418-20-4; **3**, 72098-96-5; **4**, 87412-14-4; **5**, 87412-15-5; **6**, 87412-16-6; **7**, 87412-17-7; **8**, 87412-18-8; **9**, 87412-19-9; **10**, 87412-20-2; **11**, 87412-21-3; **12**, 87412-22-4; $C_6H_5CH_2P^+(C_5H_5)_3PF_6^-$, 87412-23-5; $P(C_6H_5)_3$, 603-35-0; $P(p\text{-}C_6H_4CH_3)_3$, 1638-95-5; benzaldehyde, 100-52-7; *p*-anisaldehyde, 123-11-5; *p*-(dimethylamino)benzaldehyde, 100-10-7; 2-naphthaldehyde, 66-99-9; propionaldehyde, 123-38-6; butyraldehyde, 123-72-8; octanal, 124-13-0; cyclohexanecarboxaldehyde, 2043-61-0; furfural, 98-01-1; isobutylene, 115-11-7.