that the resulting disilene adds a polysilyl radical generated in reaction 2, at the less hindered chain end:

$$\text{R-}\dot{\text{S}}\text{i—RR}'\text{Si—RR}'\text{Si-} \rightarrow \text{-RR}'\underset{\cdot}{\text{S}}\text{i—SiR=SiRR}' \xrightarrow{\cdot\text{SiRR}'\text{-}} \text{-RR}'\text{Si—}\dot{\text{S}}\text{iR—SiRR}'\text{—SiRR}'\text{-} \quad (4)$$

Note that C=C bonds are already believed to undergo a similar attack in the olefin polymerization process;[8] Si=Si bonds should be no less reactive. Mechanism 4 is consistent with the observation that the ESR spectrum of an irradiated mixture of an α-deuteriated and a α-^{13}C-labeled poly(di-*n*-hexylsilane) equals the sum of the spectra of each polymer irradiated individually.

In summary, we have established the structure of the persistent radicals formed by the irradiation of solutions of poly(dialkylsilane)s and have proposed a mechanism for their formation. We propose that the photochemistry of alkylated polysilanes involves at least three distinct primary reactions: monomer extrusion (eq 1), homolytic chain cleavage (eq 2), and chain cleavage by reductive elimination (eq 3).

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Synthesis of Iron Arylphosphonate Complexes

Dorothy H. Gibson,* Tek-Sing Ong, Ming Ye,
Jaime O. Franco, and Kathryn Owens

Department of Chemistry, University of Louisville
Louisville, Kentucky 40292

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Summary: Reactions of cationic iron complexes bearing aryl phosphite ligands, $(\eta\text{-}C_5H_5)Fe(CO)_2(L)^+BF_4^-$ [L = $P(OPh)_3$ or $P(O\text{-}p\text{-tolyl})_3$] and $(\eta\text{-}C_5Me_5)Fe(CO)_2[P(OPh)_3]^+BF_4^-$, with aqueous base give the corresponding phosphonate complexes quickly and in good yields. Alternatively, $(\eta\text{-}C_5H_5)Mo(CO)_3[P(OEt)_3]^+BF_4^-$ and *trans*-$Mn(CO)_4[P(OPh)_3]_2{}^+BF_4^-$ give hydrides under the same reaction conditions. A pathway involving intramolecular oxygen transfer from intermediate metallocarboxylate anions is suggested to account for the results with the iron compounds.

Interest in transition-metal phosphonate complexes is derived, in part, from the presence of a pentavalent phosphorus ligand covalently bound to the metal center. The main synthetic route to the compounds results from nucleophilic displacement by a halide ion on a phosphite cation complex in an Arbuzov-like reaction.[1] However, the method is successful only for alkyl phosphite complexes; it is not successful for the synthesis of aryl phosphonates because of the reluctance of an unactivated aromatic nucleus to undergo nucleophilic addition or displacement. As part of a general study of the reactions of metal carbonyl cations toward hydroxylic bases,[2] we have determined that a series of iron carbonyl cations bearing aryl phosphite ligands are readily converted to the corresponding phosphonates by the action of KOH in acetone–water. The cations and their phosphonate products are identified:

cation	phosphonate
$(\eta\text{-}C_5H_5)Fe(CO)_2[P(OR)_3]^+BF_4^-$	$(\eta\text{-}C_5H_5)Fe(CO)_2[P(O)(OR)_2]$
1a,b	**2a,b**
$(\eta\text{-}C_5Me_5)Fe(CO)_2[P(OPh)_3]^+BF_4^-$	$(\eta\text{-}C_5Me_5)Fe(CO)_2[P(O)(OPh)_2]$
3	**4**

a, R = phenyl; **b**, *p*-tolyl

The reactions are complete after a few minutes at 0 °C, and product yields range from 61 to 75%; the phosphonate complexes have been characterized[3] by elemental analysis and by IR and NMR spectroscopy; their NMR spectral properties are summarized in Table I.

Since hydrolysis (or methanolysis) of uncoordinated (aryloxy)phosphonium ions occurs by direct attack on the phosphorus atom,[4] we felt that additional probes of these and other cations with phosphite ligands were needed to try to establish the nature of the reactions. Reaction of **1a** with sodium methoxide in methanol gave the methyl ester $(\eta\text{-}C_5H_5)Fe(CO)[P(OPh)_3]COOCH_3$ (**5**).[5] Compound **6**, $(\eta\text{-}C_5H_5)Mo(CO)_3[P(OEt)_3]^+BF_4^-$, was slowly converted to the alkyl phosphonate $(\eta\text{-}C_5H_5)Mo(CO)_3[P(O)(OEt)_2]$ (**7**)[6] by reaction with Et_4NBr, as expected. Reaction of **6** with aqueous base, in the same manner as the iron cations above, gave the hydride $(\eta\text{-}C_5H_5)Mo(CO)_2[P(OEt)_3]H$ (**8**).[7] However, reaction of **6** with methoxide in methanol afforded *trans*-$(\eta\text{-}C_5H_5)Mo(CO)_2[P(OEt)_3]COOCH_3$ (**9**),[8] indicating that the initial product of hydroxide addition to the cation was probably the corresponding trans metallocarboxylic acid. Thermal or base-catalyzed decarboxylation of an intermediate metallocarboxylic acid could be expected to give the hydride product.[2,9] Similarly, *trans*-$Mn(CO)_4[P(OPh)_3]_2{}^+BF_4^-$ (**10**) yields *mer,trans*-$HMn(CO)_3[P(OPh)_3]_2$ (**11**)[10] when treated with aqueous

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(1) See: Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577 for a recent review of these complexes.

(2) See: Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* **1987**, *109*, 7191 and references cited therein.

(3) Compound **2a**: mp 140–141 °C; IR (CH_2Cl_2) ν_{CO} 2050 (s), 1992 (s), 1587 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_5PFe$: C, 55.64; H, 3.69; P, 7.55. Found: C, 55.28; H, 3.72; P, 7.32. Compound **2b**: mp 125–126 °C; IR (CH_2Cl_2) ν_{CO} 2043 (s), 1988 (s), 1605 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{19}O_5PFe$: C, 57.56; H, 4.37; P, 7.07. Found: C, 57.89; H, 4.21; P, 6.85. Compound **4**: mp 113–114 °C; IR (CH_2Cl_2) ν_{CO} 2023 (s), 1970 (s), 1589 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{25}O_5PFe$: C, 60.02; H, 5.25. Found: C, 59.90; H, 5.29. A sample of compound **1a** was dissolved in cold (0 °C) acetone/water (50:50) which contained 1.2 molar equiv of KOH. This mixture became red immediately; it was maintained, with stirring, at 0 °C for an additional 5 h, and the product began to precipitate during this time. The mixture was allowed to stand, overnight, at 0 °C to effect complete precipitation; the product was then collected by filtration and dried, in a desiccator, under vacuum. The crude product was recrystallized from CH_2Cl_2/pentane (30:70) to afford yellow needles (71% yield).

(4) Hudson, H. R. *Top. Phosphorus Chem.* **1983**, *11*, 339.

(5) Compound **5**: IR (CH_2Cl_2) ν_{CO} 1966 (s), 1610 (m, sh), 1590 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2, −24 °C) δ 7.30 (m), 4.20 (s), 3.48 (s); ^{13}C NMR (CD_2Cl_2, −24 °C) δ 216.97 (d, J_{PC} = 42.6 Hz), 209.22 (d, J_{PC} = 49.8 Hz), 151.19 (d, J_{PC} = 8.4 Hz), 129.72 (s), 125.15 (s), 121.66 (d, J_{PC} = 4.4 Hz), 83.65 (s), 51.23 (s); ^{31}P NMR (CD_2Cl_2, −24 °C) δ 176.47.

(6) Compound **7**: mp 40–41 °C; IR (CH_2Cl_2) ν_{CO} 2037 (s), 1946 (s, br) cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_6PMo$: C, 37.72; H, 3.96. Found: C, 37.19; H, 3.97. The compound darkens upon standing at room temperature, especially when exposed to light.

(7) Compound **8**: ^{1}H NMR (CD_2Cl_2) δ 5.28 (s), 3.86 (quintet), 1.26 (t, J = 7.1 Hz), −6.60(d, J_{PH} = 60.6 Hz).

(8) Compound **9**: IR (Nujol) ν_{CO} 1954 (s), 1872 (vs), 1622 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2, −10 °C) δ 5.27 (s), 3.95 (quintet), 3.44 (s), 1.28 (t, J = 7.0 Hz); ^{13}C NMR (CD_2Cl_2, −10 °C) δ 235.70 (d, J_{PC} = 36.9 Hz), 208.14 (d, J_{PC} = 14.8 Hz), 94.01 (s), 61.79 (d, J_{PC} = 5.4 Hz), 50.88 (s), 16.08 (d, J_{PC} = 6.0 Hz). The ratio of the two low-field carbon resonances was 2:1, respectively.

(9) See: (a) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1987**, *28*, 139. (b) Bennett, M. A. *J. Mol. Catal.* **1987**, *41*, 1 for recent reviews of the characteristics of metallocarboxylic acids.

(10) The spectral properties of compound **11** were identical with those reported previously: Berke, H.; Weiler, G. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1984**, *39B*, 431.

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Table I. NMR Spectral Data for Phosphonate Complexes

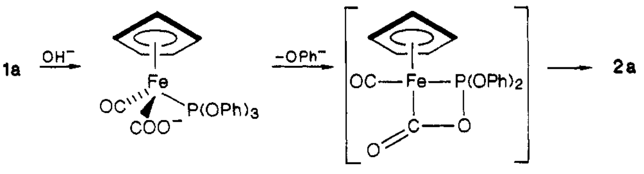
compd (solvent)	^{1}H NMR[a]	^{13}C NMR[a]	^{31}P NMR[b]
2a (CD_2Cl_2)	7.25 (m) 5.00 (s)	210.86 (d, J_{PC} = 41.2 Hz) 152.06 (d, J_{PC} = 10.8 Hz) 129.53 (s) 124.07 (s) 121.34 (d, J_{PC} = 4.1 Hz) 85.98 (s)	109.40
2b (acetone-d_6)	7.12 (m) 5.21 (s) 2.26 (s)	212.66 (d, J_{PC} = 41.1 Hz) 151.54 (d, J_{PC} = 11.1 Hz) 133.80 (s) 130.63 (s) 122.05 (d, J_{PC} = 3.4 Hz) 87.36 (s) 20.91 (s)	106.66
4 (acetone-d_6)	7.23 (m) 1.94 (s)	214.36 (d, J_{PC} = 39.8 Hz) 154.12 (d, J_{PC} = 13.1 Hz) 129.64 (s) 123.67 (s) 121.76 (d, J_{PC} = 4.2 Hz) 99.23 (s) 9.62 (s)	116.96
4 (CD_2Cl_2)	7.29 (m) 1.94 (s)	213.57 (d, J_{PC} = 39.6 Hz) 153.28 (d, J_{PC} = 14.1 Hz) 129.33 (s) 123.46 (s) 121.50 (d, J_{PC} = 4.3 Hz) 98.70 (s) 9.71 (s)	117.11
7 ($CDCl_3$)	5.56 (s) 4.04 (m) 1.27 (t, J = 7.06 Hz)	232.40 (d, J_{PC} = 8.3 Hz) 224.52 (d, J_{PC} = 39.4 Hz) 93.14 (s) 60.12 (d, J_{PC} = 9.3 Hz) 16.37 (d, J_{PC} = 6.2 Hz)	97.34

[a] Chemical shift positions in ppm relative to TMS. [b] Chemical shift positions in ppm relative to external H_3PO_4.

base and the ester *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2COOCH_3$ (**12**)[11] after reaction with methoxide in methanol.

Since the triphenylphosphine analogue of **1a,b** yields the metallocarboxylic acid when treated with 1 equiv of KOH in aqueous acetone and the metallocarboxylate anion $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-K^+$ (**13**) is formed when 2 equiv of base are used,[2] it is reasonable to expect that metallocarboxylate anions are formed as intermediates in reactions of cations **1a,b** and **3** conducted under similar conditions. Furthermore, anion **13** reacts with **1a** in CH_2Cl_2 solution to provide phosphonate **2a** and $(\eta\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+BF_4^-$ as the only organometallic products. However, reaction of **13** with manganese cation **10**, followed by addition of methyl iodide, gave the same iron cation together with *mer,trans*-$CH_3Mn(CO)_3[P(OPh)_3]_2$[12] as the only organometallic products.

On the basis of all of these results, we suggest the following intramolecular pathway, illustrated for **1a**, to account for the formation of the iron phosphonate products:



The pathway is consistent with the known ability of metallocarboxylate anions to transfer oxygen (or oxide) intra- or intermolecularly.[2,13,14]

Such a reaction pathway would require that the intermediate metallocarboxylate anion have a significant lifetime and that the carboxylate ligand must be stereochemically oriented in such a way to deliver the oxygen to the phosphorus atom; i.e., a cis relationship between the carboxylate and phosphite ligands would be preferred. The failure of cation **6** to yield a phosphonate product can be attributed to its preference for trans addition of oxygen nucleophiles. Although cation **10** can yield only products having cis relationships of carboxyl and phosphite ligands, no phosphonate product resulted from this system. Either the initially formed metallocarboxylic acid decarboxylates quite readily or, as suggested by the reaction between **10** and **13**, the metallocarboxylate anion decarboxylates before being able to transfer oxygen to one of the phosphite ligands (or, alternatively, metal–carbon bond breaking may be concerted with O–H bond breaking in the reaction of base with the intermediate metallocarboxylic acid as suggested previously for another system[15]).

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(11) Compound **12**: IR (CH_2Cl_2) ν_{CO} 2060 (vw), 1980 (vs), 1955 (m), 1610 (w, sh), 1590 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2, −8 °C) δ 7.21 (m), 3.07 (s); ^{13}C NMR (CD_2Cl_2, −8 °C) δ 213.2 (t, J_{PC} = 30.9 Hz), 210.9 (t, J_{PC} = 45.6 Hz), 151.4 (t, J_{PC} = 5.2 Hz), 129.8 (s), 125.1 (s), 121.1 (s), 51.2 (s). Integration gave a ratio of approximately 3:1 for the two low-field carbon resonances, indicating that the carboxyl resonance was obscured beneath the signal at δ 213.2.

(12) The spectral properties of this product were identical with those reported previously: Maples, P. K.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1968**, *90*, 6645.

(13) (a) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 1764. (b) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797. (c) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794. (d) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467. (e) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

(14) Oxygen transfers from metal-bound CO_2 to coordinated phosphine ligands have been suggested previously; see: Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698. Bianchini, C.; Meali, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 2731.

(15) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982.