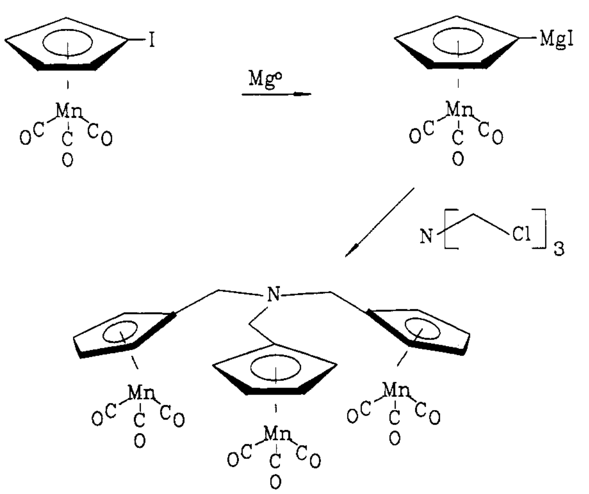
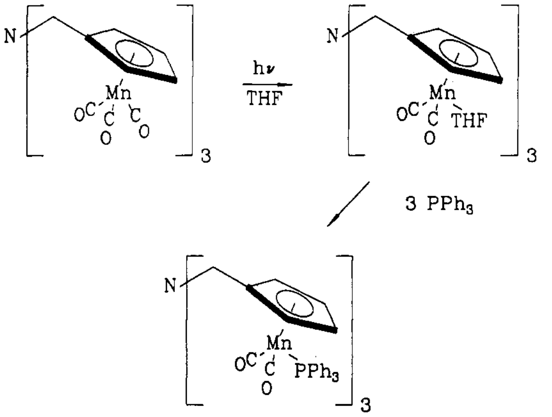


(2)

$[Mn(CO)_3]_3$ shows three chemically distinct carbons in the Cp ring resulting from ring substitution. The melting point for $TCp[Mn(CO)_3]_3$ in an evacuated capillary is 97–98 °C though no visible change in the yellow melt occurs until ca. 260 °C when it begins to darken.

Irradiation of $TCp[Mn(CO)_3]_3$ in THF at −90 °C with a 100-W mercury lamp generates $TCp[Mn(CO)_2(THF)]_3$[12] cleanly based on the IR spectrum. Obtaining the THF derivative subjects this TCp manganese trimer to the extraordinarily rich chemistry[12] of the $CpMn(CO)_2$ fragment. As a preliminary test, $TCp[Mn(CO)_2(THF)]_3$ was treated with a twofold excess of PPh_3 which gave $TCp[Mn(CO)_2(PPh_3)]_3$ in 35% unoptimized yield (eq 3).[13] Purification was performed by preparative TLC as described above for $TCp[Mn(CO)_3]_3$ but in the inert atmosphere of a glovebox eluting with 20% ethyl acetate in hexane.



(3)

In a manner analogous to that for $(\eta^5\text{-}C_5H_4I)Mn(CO)_3$, $(\eta^5\text{-}C_5H_4I)Re(CO)_3$ was prepared as a tan solid (89%) from $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (0.63 mmol), n-BuLi in hexanes (0.65 mmol), and iodine (0.65 mmol).[14] The Grignard reagent $(C_5H_4MgI)Re(CO)_3$ is formed from $(C_5H_4I)Re(CO)_3$ (0.35 mmol) and excess magnesium dust as performed above for the manganese analogue. The Grignard is then combined with $N(CH_2Cl)_3$[10] (0.12 mmol) to obtain the trirhenium TCp complex $TCp[Re(CO)_3]_3$[15] in 22% yield also following the method used for $TCp[Mn(CO)_3]_3$.

Three or more Cp rings in a single molecule appear in an unusual collection of substances: metal sulfide cubanes,[16] f-element complexes,[17] and numerous metal clusters.[18] Our continuing studies are aimed at generalizing syntheses to TCp analogues of these compounds and exploring the effects of TCp on their reactivities.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for the support of this research. We thank J. M. Kessler for synthetic assistance.

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[12] Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1. Fong, R. H.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468.

[13] **$N[CH_2(C_5H_4)Mn(CO)_2PPh_3]_3$**: IR (cm^{-1}, THF, ν(CO)) 1933 (s), 1870 (s); ^1H NMR ($CDCl_3$) δ 7.5–7.3 (m, 45, C_6H_5), 4.27 (br, 6, Cp), 4.07 (br, 6, Cp), 3.17 (br, 6, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 232.5 (d, J_{CP} = 24 Hz, CO), 138.3 (d, J_{CP} = 40 Hz), 132.9 (d, J_{CP} = 10 Hz), 128.9 (d, J_{CP} = 82 Hz), 128.1 (d, J_{CP} = 9 Hz), 98.1 (s), 83.5 (s), 83.3 (s), 50.9 (s); $^{31}P\{^1H\}$ NMR (C_6D_6, relative to PPh_3 at δ −6.0) δ 92.3 (s). Anal. Calcd for $C_{78}H_{63}Mn_3NO_6P_3$: C, 68.48; H, 4.64. Found: C, 68.94; H, 5.22.

[14] This is the preferred route to $(\eta^5\text{-}C_5H_4I)Re(CO)_3$ when compared to other literature methods: Herrmann, W. A. *Chem. Ber.* **1978**, *111*, 2458.

[15] **$N[CH_2(C_5H_4)Re(CO)_3]_3$**: IR (cm^{-1}, hexanes, ν(CO)) 2029 m, 1945 s; ^1H NMR ($CDCl_3$) δ 5.33 (s, 12, C_5H_4), 3.45 (s, 6, CH_2); ^{13}C NMR ($CDCl_3$) δ 193.6 (s, CO) [104.5 (s), 84.8 (d, J_{CH} = 179 Hz), 84.4 (d, J_{CH} = 184 Hz), C_5H_4R], 50.5 (t, J_{CH} = 137 Hz, CH_2). Anal. Calcd for $C_{27}H_{18}NO_9Re_3$: C, 30.62; H, 1.71. Found: C, 30.32; H, 1.74.

[16] Darkwa, J.; Lockemeyer, J. R.; Boyd, P. D. W.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 141.

[17] Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42.

[18] Barnes, C. E.; Dial, M. R. *Organometallics* **1988**, 7, 782 and references therein. Raithby, P. R. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 2.

Photodegradation of Poly(dialkylsilane)s in Solution: The Persistent Radicals Have an Unexpected Structure

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Received August 15, 1988

Summary: The structure of the initial persistent radicals observed upon UV irradiation of poly(dialkylsilane)s $(R_2Si)_n$ in solution, at any wavelength absorbed, is $-SiR_2-\dot{S}iR-SiR_2-$ as determined by EPR and ENDOR spectroscopy. A mechanism proposed for their formation consists of several steps, initiated by a new photochemical chain-breaking process, reductive elimination on a Si–Si–C unit, with the formation of trialkylsilyl terminal groups. The presence of such terminal groups in the irradiated product was established by GC–MS analysis after exhaustive irradiation at 254 nm.

Polysilanes[2] $(RR'Si)_n$ are of interest as photoresists.[3,4] They photodegrade both in the neat solid[4,5] and in solu-

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[1] (a) The University of Texas. (b) IBM Research Laboratories. (c) This project was initiated at the University of Utah.

[2] West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

[3] Miller, R. D.; Rabolt, J. F.; Sooriyakumaran, R.; Fleming, W.; Fickes, G. N.; Farmer, B. L.; Kuzmany, H. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allock, J., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 4. Miller, R. D.; McKean, D. R.; Hofer, D.; Willson, C. G.; West, R.; Trefonas, III, P. T. In *Materials for Microlithography*; Thompson, L. F., Willson, C. G., Fréchet, J. M. J., Eds.; ACS Symposium Series 266; American Chemical Society: Washington, DC, 1984; Chapter 3.

[4] Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Proc. SPIE, Adv. Resist Technol. Process. II* **1985**, *539*, 166.

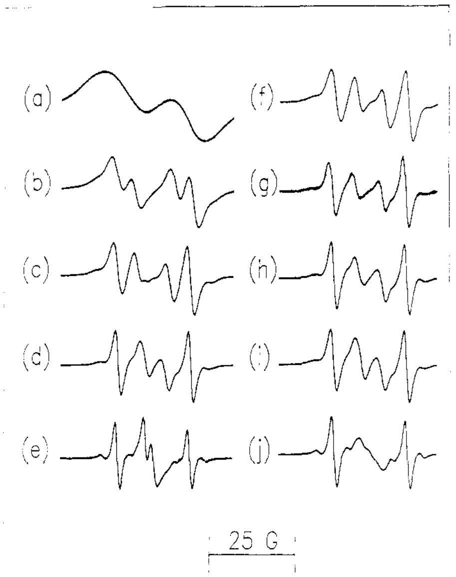


Figure 1. The EPR spectra of irradiated polysilanes $(R_2Si)_n$ in n-octane (a–c in n-pentane): a–e, R = 4-methylpentyl (a, 200 K; b, 220 K; c, 260 K; d, 300 K; e, 350 K); f, R = n-$C_{14}H_{29}$; g, R = n-$C_{10}H_{21}$; h, R = n-C_8H_{17}; i, R = n-C_6H_{13}; j, R = n-C_4H_9; 300 K.

tion.[6,7] In solution, photoproduced silylenes RR′Si: are trapped with Et_3SiH,[6] and the formation of polysilyl radicals has been deduced from the presence of terminal Si–H bonds in the products of exhaustive irradiation at 254 nm, $H(SiRR')_nH$ (n = 2, 3),[6] and from the ability of irradiated polysilanes to induce polymerization of olefins.[8] The favored interpretation is silylene extrusion (eq 1) competing with homolytic cleavage (eq 2). Both of these processes are known[9,10] in short-chain oligosilanes:

$$\text{-SiRR'-SiRR'-SiRR'-} \xrightarrow{h\nu} \text{-SiRR'-SiRR'-} + \text{RR'Si:} \tag{1}$$

$$\text{-SiRR'-SiRR'-SiRR'-} \xrightarrow{h\nu} \text{-SiRR'-SiRR'}\cdot + \cdot\text{SiRR'-} \tag{2}$$

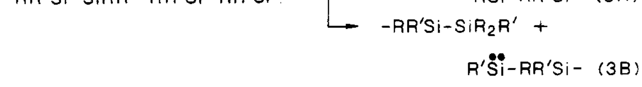
Polysilane (MW > 10^6) solutions in deoxygenated n-alkanes or cyclohexane exhibit EPR signals from the outset of irradiation with UV light from a variety of sources (lamp or pulsed laser, λ = 248–330 nm). The radical yield (DPPH standards) is only a few percent of the total number of the Si–Si bonds broken, as estimated from a decrease in the UV absorption intensity. The radicals are stable for hours or days. Surprisingly, we find that they are formally derived from the polymer by Si–C bond cleavage, $-RR'Si-\dot{S}iR-SiRR'-$ and $-RR'Si-\dot{S}iR'-SiRR'$, in comparable amounts.

The spectra of the radicals from $(R_2Si)_n$, R = alkyl other than methyl, are temperature-dependent. Poor solubility at low temperatures and decay at high temperatures limit the observation of spectral changes. The case where we approached the full range from the low temperature to the high temperature limit most closely was R = 4-methylpentyl. Figure 1 makes it clear that at low temperatures the spectrum resembles a doublet of doublets (eventually, effects of slow rotational averaging interfere) and at high temperatures a triplet. Similar spectra were obtained for all choices of R; an increase in the length of R has the same effect as a decrease in temperature. We attribute the observed temperature and structural dependence to hindered libration about the ·Si–CH′H″ bond at the presumably nearly planar tricoordinate silicon, with C–H′ or C–H″ preferably close to normal to the plane. At low temperatures, or when R is long, the two α protons are distinctly inequivalent.

In the following, we quote the numerical values obtained for R = hexyl. The evidence for the assignment of the local structure as $(-C^{\beta}{}_2Si^{\alpha})_2\dot{S}i^{i}-C^{\alpha}H^{\alpha'}H^{\alpha''}CH^{\beta}{}_2CH^{\gamma}{}_2-$ is as follows: (a) g = 2.004 72 (3) (absolute measurement), compatible only with disilylsilyl or trisilylsilyl radicals;[11] (b) ^{29}Si satellites, a_{α} = 5.8 (2) G (2 Si), a_i = 75 (1) G (weak, presumably due to large anisotropy combined with incomplete motional averaging), assigned to $-Si^{\alpha}-\dot{S}i^{i}-Si^{\alpha}-$; (c) proton coupling, $a_{\alpha'} \simeq$ 11 G (1 H) and $a_{\alpha''} \simeq$ 3 G (1 H) near the low-temperature limit and a_{α} = 6.99 (2) G (2 H) extrapolated to the high-temperature limit, and from ENDOR, a_{β} = 0.34 (1) G and a_{γ} = 0.13 (1) G, with sgn a_{α} = sgn a_{γ} = −sgn a_{β} established by TRIPLE resonance (these couplings are assigned to $-CH^{\gamma}{}_2-CH^{\beta}{}_2-CH^{\alpha'}H^{\alpha''}-Si\cdot$ and are affected in the expected manner by full deuteriation of the initial polymer in the positions α or β); (d) the spectrum obtained on a polymer ^{13}C-labeled at all α-carbons is poorly resolved and compatible with splitting by five ^{13}C atoms ($a \simeq$ 4 G), and ENDOR yields a_{β} = 4.12 (5) G, assigned to $-C^{\beta}{}_2Si-\dot{S}iC^{\alpha}-SiC^{\beta}{}_2-$.

The spectra of radical mixtures from the irradiation of $(RR'Si)_n$ (R ≠ R′) are easily separable in two simple cases, both temperature independent. The EPR of $-SiRR'-\dot{S}iR-SiRR'$ (R = methyl, R′ = hexyl) shows a_{α} = 9.4(2) G (3 H); that of R = cyclohexyl and R′ = methyl shows two doublets attributed to two distinct conformers: one with $a_{\alpha'}$ = 15.5(2) G (1 H), the other with $a_{\alpha''}$ = 2.6 (2) G (1 H). These results are compatible with the methyl rotation being always fast and the cyclohexyl rotation negligible.

The mechanism by which the persistent radicals are formed is not a simple C–Si bond dissociation to yield R·, since the alkanes RH and R′H were not detectable among the products by GC–MS analysis. A key hint is provided by a GC–MS analysis after exhaustive 248-nm irradiation: about 10–15% of the volatile products contain terminal trialkylsilyl groups. E.g., for R = cyclohexyl, R′ = methyl: $H(RR'Si)_2H$ (49%), $H(RR'Si)_3H$ (19%), $R_2R'SiH$ (2%), $R'_2RSiRR'SiH$ (5%), and $R_2R'SiRR'SiH$ (7%). This suggests that a photochemical chain-breaking reductive elimination (eq 3), analogous to the thermal decomposition



$$\text{-RR'Si-SiRR'-RR'Si-RR'Si-} \xrightarrow{h\nu} \text{-RR'Si-SiRR}_2\text{'} + \text{R}\ddot{\text{S}}\text{i-RR'Si-} \tag{3A}$$

$$\text{-RR'Si-SiRR'-RR'Si-RR'Si-} \xrightarrow{h\nu} \text{-RR'Si-SiR}_2\text{R'} + \text{R'}\ddot{\text{S}}\text{i-RR'Si-} \tag{3B}$$

of disilanes,[12] contributes to the photodegradation of molecular weight. An attempt to trap an alkylsilylene-terminated polysilane with Et_3SiD was unsuccessful (no Si–D in IR), presumably due to a disilylsilylene to silyldisilene rearrangement, known to be facile.[13] We propose

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(5) Magnera, T. F.; Balaji, V.; Michl, J.; Miller, R. D. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood, Ltd.: Chichester, 1988; Chapter 45. Magnera, T. F.; Balaji, V.; Michl, J.; Miller, R. D.; Sooriyakumaran, R. *Macromolecules*, in press.

(6) Trefonas, III, P.; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.

(7) Michl, J.; Downing, J. W.; Karatsu, T.; Klingensmith, K. A.; Wallraff, G. M.; Miller, R. D. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allock, J., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 5, p 61.

(8) West, R.; Wolff, A. R.; Peterson, D. J. *J. Radiat. Curing* **1986**, *13*, 35.

(9) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

(10) Ishikawa, M.; Takaoka, T.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 333.

(11) Cooper, J.; Hudson, A.; Jackson, R. A. *Mol. Phys.* **1972**, *23*, 209.

(12) Walsh, R. *Organometallics* **1988**, *7*, 75 and references therein.

(13) Sakurai, H.; Nakadaira, Y.; Sakaba, H. *Organometallics* **1983**, *2*, 1484. Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 1320.

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

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

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).

Acknowledgment. This project was supported by the U.S. National Science Foundation (CHE 8796257) and by IBM Corp. (707312).

Synthesis of Iron Arylphosphonate Complexes

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Received August 19, 1988

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**
a, R = phenyl; **b**, *p*-tolyl	
$(\eta\text{-}C_5Me_5)Fe(CO)_2[P(OPh)_3]^+BF_4^-$	$(\eta\text{-}C_5Me_5)Fe(CO)_2[P(O)(OPh)_2]$
3	**4**

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.

0276-7333/88/2307-2569$01.50/0