Photolytic Ring-Opening Polymerization of Phosphorus-Bridged [1]Ferrocenophane Coordinating to an Organometallic Fragment

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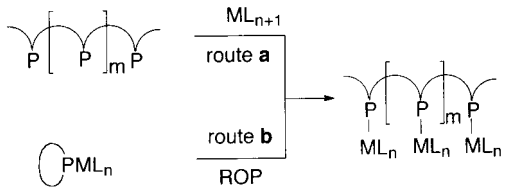
Manganese and tungsten complexes bearing a strained phosphorus-bridged [1]ferrocenophane were prepared by reaction of their appropriate THF complexes with (1,1′-ferrocenediyl)phenylphosphine (**1**). The monomer complexes [Mn(η^5-C_5H_4R)$(CO)_2$(**1**)] (R = Me, H) and [$W(CO)_5$(**1**)] thus obtained were found to undergo a ring-opening polymerization (ROP) upon irradiation with UV−vis light for 10 min in THF or acetonitrile. Because they polymerize in the same manner as the free ligand **1**, with the metallic fragment intact, the photopolymerization reaction is considered applicable to a variety of organometallic fragments bearing **1** as a ligand.

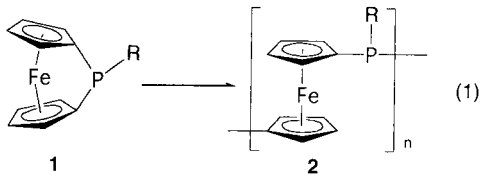
The field of organometallic polymers has attracted considerable interest because of their potential in catalysis and synthesis, and as advanced materials.[1] One important subclass of this field is related to pendant-type polymers, in which organometallic fragments are attached to a polymer backbone.[2] Phosphine polymers have often been used as such a backbone, owing to their versatile ability to bind a variety of metal fragments.[3]

Generally, such a pendant-type organometallic polymer is synthesized through the reaction of a metal fragment with a phosphine polymer prepared in advance (route **a** in Scheme 1). An alternative route is the polymerization of a monomeric complex having a phosphine ligand which possesses a functional group for polymerization (route **b**). The latter method has the advantage of giving a well-defined organometallic polymer, since the primary structure of the polymer can be controlled by designing the monomeric species. In contrast, the phosphine polymer used in route **a** may offer not only monodentate phosphine sites to a metal fragment but also bi-, tri-, and multidentate sites, to give an organometallic polymer with low regularity.

Scheme 1



One of the potential methods for the polymerization of a phosphine ligand is the ring-opening reaction of a strained cyclic substructure. For example, phenylphosphirane and phenylphosphetane (PhP(CH$_2$)$_n$CH$_2$; n = 1, 2) have strained three- and four-membered rings, respectively, which thermally polymerize to give phosphine polymers.[4] Recently, Manners et al. reported that phosphorus-bridged [1]ferrocenophane **1** polymerizes upon heating above 120 °C or upon addition of RLi as the initiator for living anionic polymerization (eq 1).[5,6]



Although the organometallic complexes having these

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(5) (a) Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5503. (b) Honeyman, C. H.; Peckham, T. J.; Massey, J. A.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1996**, 2589. (c) Peckham, T. J.; Massey, J. A.; Honeyman, C. H.; Manners, I. *Macromolecules* **1999**, *32*, 2830. (d) Peckham, T. J.; Lough, A. J.; Manners, I. *Organometallics* **1999**, *18*, 1030.

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strained phosphine ligands are known,[7] none of them successfully polymerizes under the above reaction conditions, probably because severe reaction conditions or reactive species present in the polymerization destroy the monomeric or oligomeric organometallic fragments.[5d]

During the course of our study on the reactivity of phosphorus-bridged [1]ferrocenophane metal complexes,[8] we found that the ring-opening reaction took place upon UV irradiation to give polymers of these complexes. The successful results obtained under mild reaction conditions prompted us to search for a versatile method for the polymerization of the organometallic complexes bearing the strained phosphorus-bridged [1]ferrocenophane.

Results and Discussion

The monomer complexes [Mn(η^5-C_5H_4R)$(CO)_2$(**1**)] (**3a**, R = Me; **3b**, R = H) and [$W(CO)_5$(**1**)] (**4**) were prepared by the reaction of **1** with [Mn(η^5-C_5H_4R)$(CO)_2$(THF)] and [$W(CO)_5$(THF)],[7a,9] respectively. The ^{1}H, ^{13}C, and ^{31}P NMR and IR spectra of **3a** and **3b** were consistent with the structures expected, and those of **4** were identical with those reported previously by Seyferth and Withers.[7a] In the $^{13}C\{^1H\}$ NMR spectra of these three complexes, a doublet assignable to the ipso carbons of the ferrocene moiety was observed at considerably high field, i.e., 28.5 ppm (J_{CP} = 15 Hz) (**3a**), 28.3 ppm (J_{CP} = 16 Hz) (**3b**), or 21.1 ppm (J_{CP} = 15 Hz) (**4**), and these doublets are characteristic of the strained [1]ferrocenophane structure.[10]

The molecular structure of **4** was also confirmed by X-ray analysis, as shown in Figure 1, where five CO ligands and **1** form an octahedral geometry around a tungsten center. The W−CO bond trans to the W−P bond is slightly shorter than the other four W−CO bonds, because the former CO ligand receives more effective back-donation than others from the organometallic fragment.[11] The deformation angles α, β, and θ for the strained [1]ferrocenophane unit are defined in Figure 2. The tilt angle α is 25.6°, and the two β angles are 33.6 and 35.5°. Since these deformation parameters are comparable to α = 26.9° and β = 32.3° for the free **1**,[12] it is confirmed that the strain in the [1]ferrocenophane unit is almost intact upon coordination to the metal fragment.

We previously reported the photoreaction of the cationic iron complex [$FeCp(CO)_2$(**1**)]$^+$ (**5**) in CH_2Cl_2.[8] When

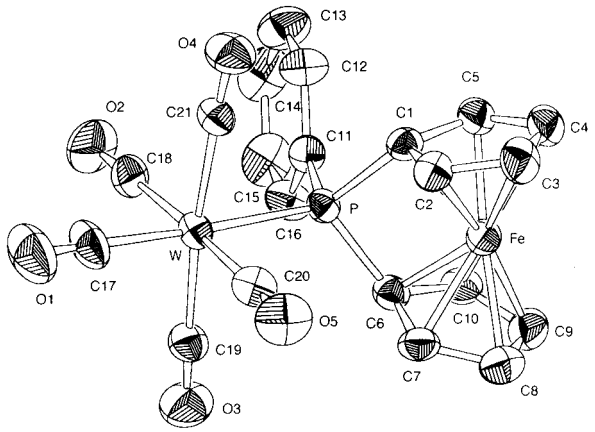


Figure 1. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): W−P = 2.492(1), W−C17 = 2.027(6), W−C18 = 2.040(4), W−C19 = 2.038(4), W−C20 = 2.040(4), W−C21 = 2.050(3), P−C1 = 1.843(3), P−C6 = 1.832(4), P−C11 = 1.814(3); P−W−C17 = 177.0(2), P−W−C18 = 89.5(1), P−W−C19 = 87.1(2), P−W−C20 = 94.1(1), P−W−C21 = 86.1(1), W−P−C1 = 118.0(1), W−P−C6 = 119.6(1), W−P−C11 = 113.9(1), C1−P−C6 = 94.0(2), C1−P−C11 = 103.5(2), C1−P−C6 = 105.0(2).

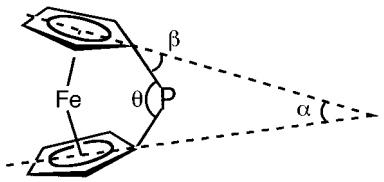
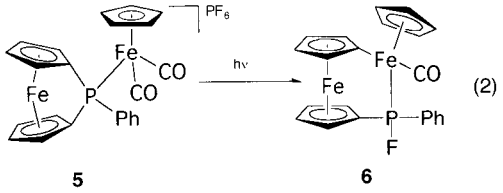


Figure 2. Definition of structural parameters for [1]ferrocenophanes.

5 is irradiated with UV light in the presence of an F^- source such as PF_6^-, the new complex **6** is formed, though in a limited yield, as a ring-opening product of the phosphorus-bridged [1]ferrocenophane (eq 2). Since



(2)

the fluorinated phosphine ligand in **6** is formed due to the F^- anion present, the products of a similar reaction in the absence of the F^- source are of interest. Thus, the photolysis was carried out with neutral isostructural complexes, [Mn(η^5-C_5H_4R)$(CO)_2$(**1**)] (**3a**, R = Me; **3b**, R = H).

A THF solution of **3a** was irradiated for 10 min with UV light through a Pyrex filter. The $^{31}P\{^1H\}$ NMR spectrum of the THF solution showed that the resonance at 111.1 ppm of the starting **3a** disappeared completely and that a relatively sharp new signal appeared at 74.0 ppm. A similar reaction in acetonitrile gave similar results, whereas those in CH_2Cl_2, 1,2-dichloroethane, benzene, and THF containing CCl_4 as an additive gave rise to complicated $^{31}P\{^1H\}$ NMR spectra.

The product isolated from the THF solution was formulated as **7a** and was characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectra as well as by an elemental

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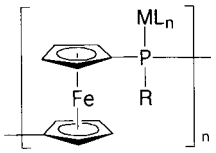
analysis. In the ν(CO) infrared region, two strong peaks

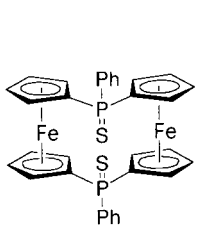


7a, ML$_n$ = Mn(C$_5$H$_4$Me)(CO)$_2$
7b, ML$_n$ = Mn(C$_5$H$_5$)(CO)$_2$
8, ML$_n$ = W(CO)$_5$

were observed at 1926 and 1862 cm^{-1}. These were almost comparable to the peaks at 1930 and 1864 cm^{-1} of the starting **3a**, indicating not only that neither of the two carbonyl groups left the manganese moiety but also that the electronic environments of the two carbonyl groups were similar in **3a** and **7a**. The ^{1}H NMR spectrum showed considerably broad resonances, but their integrated intensities agreed with those expected for the Ph, Me, and three C_5H_4 groups. In the ^{31}P{^{1}H} NMR spectrum, the resonance shifted from 111.1 ppm for the starting **3a** to 74.0 ppm. This upfield shift is characteristic of the polymerization of the phosphorus-bridged [1]ferrocenophane. For example, the resonance of **1** shifts from 13.3 ppm to −31.7 ppm in the thermal and living anionic ring-opening polymerization (eq 1),[5a,6] and for the cationic phosphenium-bridged [1]ferrocenophane, the resonance shifts from 37.5 to 23.8 ppm.[5d] Elemental analysis of **7a** supported a formula identical with that of the starting **3a**. GPC indicated that the product possessed an approximate weight-average molecular weight (M_w) of 3700 and a number-average molecular weight (M_n) of 2000. The molecular weight distribution was wide, from 450 to 2.0×10^4, with a polydispersity of 1.9. The results for **3b** were essentially the same as those for **3a**, though the product **7b** had higher molecular weights ($M_w = 2.2 \times 10^4$ and $M_n = 2.2 \times 10^4$) than **7a**. The better result attained for **7b** may be due to the purity of **3b** being higher than that of **3a**.

Next, to examine the applicability of the present photolytic polymerization, the reaction was carried out with complex **4** and with the free ligand as well. A THF solution of **4** was irradiated for 10 min in a manner similar to that above. The ^{31}P{^{1}H} NMR of this solution consisted of a major singlet at −1.1 ppm with ^{183}W satellites, $J_{WP} = 249$ Hz, and a trace of minor resonaces at a higher field. The major product was characterized as **8** by the IR and ^{1}H, ^{13}C, and ^{31}P NMR spectra. The single resonance in ^{31}P{^{1}H} NMR shifted to a field 27.0 ppm higher than that of **4**. The three ν(CO) infrared bands at 2070, 1978, and 1932 cm^{-1} were almost identical with those at 2072, 1985, and 1942 cm^{-1} of **4**, respectively, indicating the presence of the W(CO)$_5$ fragment. The estimated molecular weights of **8** were as follows: $M_w = 3.0 \times 10^4$ and $M_n = 1.8 \times 10^4$.

Here, it was considered interesting to determine whether the present photolytic ring-opening reaction requires the coordination of **1** to an organometallic fragment. Thus, the free **1** was irradiated in THF. The ^{31}P{^{1}H} NMR spectrum of the products showed a major singlet at −31.6 ppm with several minor signals. The chemical shift of the major signal was almost identical with that reported for the polymer **2** prepared by eq 1. After sulfurization of the products with elemental sulfur, the products having a major singlet at 38.2 ppm in ^{31}P{^{1}H} NMR were separated with a preparative-scale GPC column and then examined using an analytical GPC column. The estimated molecular weights were as follows: $M_w = 1.1 \times 10^4$ and $M_n = 1.9 \times 10^3$. Other sulfurized products having minor signals were separated further by the preparative GPC column using a recycling mode. Finally, a dimer (**9**) and a trimer (**10**) of **1** were separately isolated as crystalline materials. X-ray structural analyses indicated that they have cyclic structures.[13]



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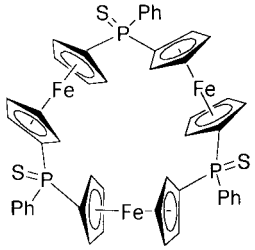

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The polymer **2** obtained by the photolysis of **1** was treated with [W(CO)$_5$(THF)]. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture consisted of a broad multiplet at 0.0 ppm, which is close to that observed for **8**. In addition, another multiplet was observed at 16 ppm. The results indicated that the polymer prepared from **2** and [W(CO)$_5$(THF)] has lower regularity than **8**, probably because the phosphine sites in **2** act not only as monodentate sites but also as bi-, tri-, and multidentate sites.[6]

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were dried and purified by distillation: CH_2Cl_2, 1,2-dichloroethane, and CH_3CN were distilled from P_2O_5, benzene and THF were distilled from sodium/benzophenone, and hexane was distilled from sodium metal. These purified solvents were stored under an N_2 atmosphere. Other reagents were used as received. **1** and [W(CO)$_5$(**1**)] (**4**) were prepared according to previously described methods.[5a,7a,14]

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. NMR spectra were recorded on a JEOL LA-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were reported relative to Me_4Si and were determined by reference to the residual solvent peaks. ^{31}P NMR chemical shifts were reported relative to H_3PO_4 (85%) used as an external reference. Elemental analyses were performed with a Perkin-Elmer 2400CHN elemental analyzer.

Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission lines (nm) used and their relative intensities (in parentheses) were as follows: 577.0 (69), 546.1 (82), 435.8 (69), 404.7 (42), 365.0 (100), 334.1 (7), 312.6 (38), and 302.2 (9). Gel permeation chromatography (GPC) analyses were run on a Shodex GPC-System 11 instrument using a Shodex KF803L column (exclusion limit 7×10^4) for **7a** and on a Tosoh model SC-8010 using columns of TSKgel G5000H, G4000H, G3000H, and G2000H (exclusion limits: 4×10^6, 4

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(13) Full details of these structures will be reported elsewhere.

(14) The synthesis of **1** has been previously described. See: (a) Seyferth, D.; Withers, H. P., Jr. *J. Organomet. Chem*. **1980**, *185*, C1. (b) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem*. **1980**, *193*, 345.

$\times 10^5$, 6×10^4, and 1×10^4, respectively) for sulsurized **2**, **7b**, and **8**. The molecular weights were estimated on the basis of a comparison to polystyrene and poly(methyl methacrylate) standards for the former and the latter apparatuses, respectively. Preparative-scale GPC was performed with a recycling HPLC system (Japan Analytical Industry Model LC-908) with JAIGEL-1H (20 mm i.d. × 600 mm; exclusion limit 1.0×10^3) and JAIGEL-2H (20 mm i.d. × 600 mm; exclusion limit 5.0×10^3) columns.

[Mn(η^5-C_5H_4Me)$(CO)_2$(1)] (3a). [Mn(η^5-C_5H_4Me)$(CO)_3$] (0.50 mL, 0.69 g, 3.16 mmol) and THF (100 mL) were added to a Pyrex Schlenk tube, and the solution was irradiated with the 400 W mercury arc lamp at 0 °C for 2.5 h. The IR spectra of the solution indicated that almost half of the initial amount of the starting tricarbonyl complex remained in the solution, but further irradiation did not improve the yield of the product [Mn(η^5-C_5H_4Me)$(CO)_2$(THF)]. To the solution thus obtained was added **1** (340 mg, 1.16 mmol). After the mixture was stirred for 7 h, the solvent was removed in vacuo. The residue was washed three times with hexane (15 mL) and dried in vacuo to give a reddish brown powder of **3a**. Yield: 1.034 g (89% based on **1**). IR (ν_{CO}, cm^{-1}, in THF): 1930, 1864. ^1H NMR (δ, in C_6D_6): 1.68 (s, 3H, Me), 4.00 (m, 4H, Cp′ and Fc), 4.09 (m, 2H, Cp′), 4.16 (m, 2H, Fc), 4.31 (m, 2H, Fc), 5.24 (m, 2H, Fc), 7.05−7.20 (m, 3H, *m*- and *p*-Ph), 7.55−7.70 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (δ, in C_6D_6): 13.40 (s, Me), 28.55 (d, $J_{PC} = 15.0$ Hz, *i*-Fc), 76.70 (s, Fc), 76.90 (d, $J_{PC} = 19.8$ Hz, Fc), 78.02 (d, $J_{PC} = 3.7$ Hz, Fc), 78.61 (d, $J_{PC} = 8.1$ Hz, Fc), 82.06 (s, Cp′), 82.94 (s, Cp′), 98.38 (s, Cp′), 128.78 (d, $J_{PC} = 9.0$ Hz, Ph), 129.30 (d, $J_{PC} = 2.9$ Hz, *p*-Ph), 129.41 (d, $J_{PC} = 9.9$ Hz, Ph), 140.50 (d, $J_{PC} = 42.2$ Hz, *i*-Ph), 233.04 (d, $J_{PC} = 24.1$ Hz, CO). $^{31}P\{^1H\}$ NMR (δ, in C_6D_6): 110.5.

[MnCp$(CO)_2$(1)] (3b). 3b was prepared from [MnCp$(CO)_3$] (400 mg, 1.96 mmol) and **1** (300 mg, 1.02 mmol) in a manner similar to that used for **3a**. **3b** (329 mg) thus obtained was suspended in hexane (100 mL), and CH_2Cl_2 (17 mL) was added. After filtration, the solvents of the filtrate were removed in vacuo, and the residue was dried in vacuo to give a reddish brown powder of **3b**. Yield: 297 mg (62% based on **1**). Anal. Calcd for $C_{23}H_{18}FeMnO_2P$: C, 59.01; H, 3.88. Found: C, 59.24; H, 4.13. IR (ν_{CO}, cm^{-1}, in THF): 1932, 1868. ^1H NMR (δ, in C_6D_6): 3.98 (br, 2H, Fc), 4.10 (m, 5H, Cp), 4.15 (br, 2H, Fc), 4.30 (br, 2H, Fc), 5.22 (br, 2H, Fc), 7.05−7.20 (m, 3H, *m*- and *p*-Ph), 7.55−7.70 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (δ, in CD_2Cl_2): 28.31 (d, $J_{PC} = 16.1$ Hz, *i*-Fc), 76.72 (s, Fc), 76.81 (d, $J_{PC} = 19.2$ Hz, Fc), 77.15 (d, $J_{PC} = 4.5$ Hz, Fc), 78.49 (d, $J_{PC} = 8.7$ Hz, Fc), 82.76 (s, Cp), 129.09 (d, $J_{PC} = 9.3$ Hz, Ph), 129.45 (d, $J_{PC} = 9.3$ Hz, Ph), 129.90 (d, $J_{PC} = 2.5$ Hz, Ph), 140.01 (d, $J_{PC} = 43.5$ Hz, *i*-Ph), 232.82 (d, $J_{PC} = 24.8$ Hz, CO). $^{31}P\{^1H\}$ NMR (δ, in C_6D_6): 110.5.

Preparation of 7a by Photolysis. 3a (210 mg, 0.436 mmol) and THF (10 mL) were added to a Pyrex Schlenk tube, and the solution was irradiated for 10 min at 0 °C with the mercury arc lamp. After filtration to remove a small quantity of precipitates, the solvent was removed. The residue was recrystallized from $CHCl_3$/hexane to give a brown powder (211 mg, 90%) as a hemisolvate of $CHCl_3$ per one monomer unit. $M_w = 3.7 \times 10^3$. $M_n = 2.0 \times 10^3$. $M_w/M_n = 1.85$. Anal. Calcd for $[\{C_{24}H_{20}FeMnO_2P\}\cdot 0.5CHCl_3]_n$: C, 54.31; H, 3.81. Found: C, 54.51; H, 3.85. IR (ν_{CO}, cm^{-1}, in THF): 1926, 1862. ^1H NMR (δ, in $CDCl_3$): 1.91 (br, 3H, Me), 3.6−4.6 (br, 12H, Cp′ and Fc), 7.2−7.8 (br, 5H, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 13.74 (s, Me), 72.1−74.1 (m, Fc), 81.66 (s, Cp′), 83.21 (s, Cp′), 84.65 (d, $J_{PC} = 43.5$ Hz, *i*-Fc), 98.52 (s, Cp′), 127.25 (br, Ph), 128.83 (br, Ph), 131.65 (br, Ph), 140.61 (d, $J_{PC} = 41.0$ Hz, *i*-Ph), 233.12 (d, $J_{PC} = 23.6$ Hz, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 74.5.

Preparation of 7b by Photolysis. 3b (250 mg, 0.53 mmol) and THF (13 mL) were added to a Pyrex Schlenk tube, and the solution was irradiated for 10 min at 0 °C with the mercury arc lamp. After a workup similar to that used for **7a**, a brown powder (186 mg, 74%) was obtained. $M_w = 2.2 \times 10^4$. $M_n = 1.1 \times 10^4$. $M_w/M_n = 1.96$. IR (ν_{CO}, cm^{-1}, in THF): 1929, 1864. ^1H NMR (δ, in CD_2Cl_2): 3.91 (d, 2H, Fc), 4.26 (s, 5H, Cp), 4.2−4.5 (m, 6H, Fc), 7.32 (br, 3H, Ph), 7.63 (br, 2H, Ph). $^{13}C\{^1H\}$ NMR (δ, in CD_2Cl_2): 72.6−75.0 (m, Fc), 83.00 (br, Cp), 84.92 (dm, $J_{PC} = 44.1$ Hz, *i*-Fc), 127.71 (dm, $J_{PC} = 9.3$ Hz,Ph), 129.37 (m, Ph), 132.13 (m, Ph), 140.82 (m, *i*-Ph), 233.30 (dm, $J_{PC} = 24.8$ Hz, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 73.7.

Preparation of 8 by Photolysis. 4 (194 mg, 0.31 mmol) and THF (8 mL) were added to a Pyrex Schlenk tube, and the solution was irradiated for 10 min at 0 °C with the mercury arc lamp. After a workup similar to that used for **7a**, a brown powder (155 mg, 80%) was obtained. $M_w = 3.0 \times 10^4$. $M_n = 1.8 \times 10^4$. $M_w/M_n = 1.71$. IR (ν_{CO}, cm^{-1}, in THF): 2070, 1978, 1932. ^1H NMR (δ, in $CDCl_3$): 3.5−4.8 (br, 8H, Fc), 7.31 (br, 5H, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 72.5−75.5 (m, Fc), 82.5 (m, *i*-Fc), 128.00 (m, Ph), 129.59 (m, Ph), 130.11 (m, Ph), 138.17 (m, *i*-Ph), 197.47 (br, CO). $^{31}P\{^1H\}$ NMR (δ, in THF): −1.10 ($J_{wp} = 249$ Hz).

Preparation of 2 by Photolysis. A solution of **1** (495 mg, 1.69 mmol) in THF (40 mL) was irradiated for 10 min at 0 °C with the mercury arc lamp. A considerable amount of the resulting precipitates was separated by filtration and dried in vacuo to give **2a** (60 mg). Since the **2a** thus obtained was insoluble in common solvents, characterization by NMR spectra could not be performed.

The solvent of the filtrate was removed in vacuo to give the orange residue **2b** (477 mg). $^{31}P\{^1H\}$ NMR (δ, in THF) (relative intensities are in parentheses): −23.27 (15), −26.33 (25), −26.78 (5), −29.44 (5), −30.39 (9), −31.56 (100), −35.96 (4), and −36.87 (10).

Reaction of 2 with Sulfur. To a suspension of **2a** in THF (10 mL) was added elemental sulfur (30 mg). Though the suspension was stirred for 2 days, most of the **2a** remained as an unreacted solid. The $^{31}P\{^1H\}$ NMR spectrum of the supernatant solution showed signals of a trace of sulfurized products at 36.4 and 39.6 ppm.

2b was suspended in CH_2Cl_2 (15 mL), and elemental sulfur (200 mg) was added. After the mixture was stirred for 3 h, a homogeneous solution was obtained and then the solvent was removed in vacuo. The residue dissolved in $CHCl_3$ was separated into two fractions by preparative GPC columns. A fraction with higher molecular weight (273 mg after workup) was examined using analytical GPC columns. $M_w = 1.1 \times 10^4$. $M_n = 1.9 \times 10^3$. $M_w/M_n = 5.71$. $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$) (relative intensities are in parentheses): 38.18 (100) and 31.88 (4).

The other fraction (318 mg after workup) was loaded again into the preparative GPC column and separated further by a recycling mode. Five peaks were observed at the first cycle. After several recyclings, dimeric product **9** was isolated from the fifth fraction and trimer **10** from the third fraction.

9 (16 mg): ^1H NMR (δ, in $CDCl_3$) 4.56 (br, 4H, Fc), 4.67 (br, 8H, Fc), 5.42 (br, 4H, Fc), 7.15−7.30 (m, 6H, Ph), 7.40 (m, 4H, Ph); $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$) 37.66.

10 (40 mg): ^1H NMR (δ, in $CDCl_3$) 3.95 (br, 3H, Fc), 4.37 (br, 3H, Fc), 4.68 (br, 3H, Fc), 4.84 (br, 6H, Fc), 5.34 (br, 3H, Fc), 5.52 (br, 3H, Fc), 5.72 (br, 3H, Fc), 7.41−7.54 (m, 9H, Ph), 7.85 (m, 6H, Ph); $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$) 39.13.

X-ray Crystallography. Crystal data and refinement details were as follows: formula $C_{21}H_{13}FeO_5PW$, $M_r = 616.00$, $0.60 \times 0.35 \times 0.25$ mm^3, $a = 14.3180$ (4) Å, $b = 7.1650$ (4) Å, $c = 19.9040$ (4) Å, $\beta = 98.868$ (1)°, $V = 2017.51$ (7) $Å^3$, $\rho_{calcd} = 2.028$ g cm^{-3}, $\mu = 65.31$ cm^{-1}, $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\ 69$ Å, $T = 300$ K, $R = 0.040$, $R_w = 0.068$, GOF = 1.37, maximum residual positive and negative electron densities 2.50 and −2.37 e $Å^{-3}$, respectively, situated in close proximity to the W atom.

A suitable crystal of **4** was mounted on a glass fiber. All measurements were made on a Mac Science DIP2030 imaging plate area detector. The data were collected to a maximum 2θ

value of 55.8°. Cell parameters and intensities for the reflection were estimated using the program packages of MacDENZO.[15] A total of 5087 reflections were collected, and 4572 reflections ($I > 3.00\sigma(I)$) were used for the final refinement. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corp.[16]

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Supporting Information Available: Tables giving positional and thermal parameters, crystallographic data, and bond lengths and angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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