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# Reactions of Ring-Slipped Iron Complexes Derived from $P(=S)Ph$-Bridged [1]Ferrocenophane: Synthesis of Bis(half-sandwich) Heterodinuclear Complexes

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$P(=S)Ph$-bridged [1]ferrocenophane, $[Fe\{(\eta^5\text{-}C_5H_4)_2P(=S)Ph\}]$ (**1**), reacted under UV−vis photoirradiation with $P(OMe)_3$, $P(OMe)_2Ph$, or $PMe_3$ to give respective ring-slipped products. The reaction with $P(OMe)_3$ afforded $[Fe\{(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)P(=S)Ph\}\{P(OMe)_3\}_2]$ (**2a**), while the bulkier $P(OMe)_2Ph$ gave initially the similar complex **2b**, but gradual dissociation of the $\eta^1\text{-}C_5H_4$ moiety took place from the iron center in THF to form $[Fe\{\eta^5\text{-}C_5H_4P(=S)Ph(C_5H_4)\text{-}\kappa S\}\{P(OMe)_2Ph\}_2]$ (**4b**), in which the $\eta^5\text{-}C_5H_4$ ring bearing a $P=S$ pendant group adopted an unprecedented $\eta^5\text{-}\kappa S$ coordination mode and the other $C_5H_4$ group left the coordination sphere of the iron atom. The reaction with $PMe_3$ gave directly the corresponding $\eta^5\text{-}\kappa S$ product **4c** in ether, but its $P=S$ group was replaced in THF with the remaining $PMe_3$ to give $[Fe\{(\eta^5\text{-}C_5H_4)P(=S)Ph(C_5H_4)\}(PMe_3)_3]$ (**3c**) with the $P(=S)Ph(C_5H_4)$ group dangling from the $\eta^5\text{-}C_5H_4$ ring. When **2a** having an $\eta^1\text{-}C_5H_4$ group was allowed to react with $[M(CO)_3(NCMe)_3]$ (M = Mo, W), the iron−molybdenum and −tungsten heterodinuclear complexes $\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2P(=S)Ph\text{-}\kappa S\}[Fe\{P(OMe)_3\}_2]\text{-}[M(CO)_3]$ (M = Mo (**5-Mo**), W (**5-W**)) were obtained, in which the two metal fragments were linked with an $\eta^5\text{-}C_5H_4P(=S)Ph(\eta^5\text{-}C_5H_4)\text{-}\kappa S$ bridge. In addition, **5-Mo** and **5-W** were readily converted in acetonitrile to the respective acetonitrile complexes $\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2P(=S)Ph\}[Fe(NCMe)\{P(OMe)_3\}_2]\text{-}[M(CO)_3]$, with the $P=S$ group giving up coordination to the iron center. A variety of these reaction patterns observed were discussed in terms of steric bulkiness and basicity of the phosphorus ligands concerned.

## Introduction

Dinuclear metal complexes in which two metal centers are held in close proximity have received continuous interest, because a cooperative interaction with a substrate is expected for the two metal centers.[1] A linked bis(cyclopentadienyl) ligand ($C_5H_4-ER_n-C_5H_4{}^{2-}$) is a useful bridging system for the dinuclear bis(half-sandwich)-type complexes, in which each cyclopentadienyl ring holds a respective metal center firmly. A variety of such dinuclear complexes have been reported, but most of them are those whose $ER_n$ group is $CR_2$ or $SiR_2$, simply because free ligands are readily available as alkali-metal salts.[2,3] On the other hand, the phosphorus analogues ($ER_n$ = PR, $P(=O)R$, $P(=S)R$) are considerably limited in number,[4,5] primarily because of the difficulty of preparing a free bridging ligand $(C_5H_5)_2PR$ due to its instability,[6] though some of its derivatives have been reported as noted below. One notable example is a thallium salt, $Tl_2(C_5H_4)_2PPh$, which was prepared and used by Anderson and Lin[7] for the preparation of an *ansa*-zirconocene dichloride derivative, but the toxicity of Tl limits its utility. Other examples classified broadly as a phosphorus-linked bis(cyclopentadienyl) ligand are $(indenyl)_2PPh^{2-}$,[8] $(fluorenyl)_2PPh^{2-}$,[9] and

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[4] Although bis(ferrocenyl)phosphines also have a $C_5H_4-PR-C_5H_4{}^{2-}$ bridge, they are eliminated from the present classification, because the iron center of the ferrocenyl unit is practically inert to substitution and other chemical transformations.

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[6] Mathey, F.; Lampin, J.-P. *Tetrahedron* **1975**, *31*, 2685.

[7] (a) Anderson, G. K.; Lin, M. *Inorg. Chim. Acta* **1988**, *142*, 7−8. (b) Anderson, G. K.; Lin, M. *Organometallics* **1988**, *7*, 2285−2288. The $Tl_2(C_5H_4)_2PPh$ they prepared is not a simple salt of $Tl^+$ but is actually a $Tl^+$ complex whose central metal is readily replaced with transition-metal halides.

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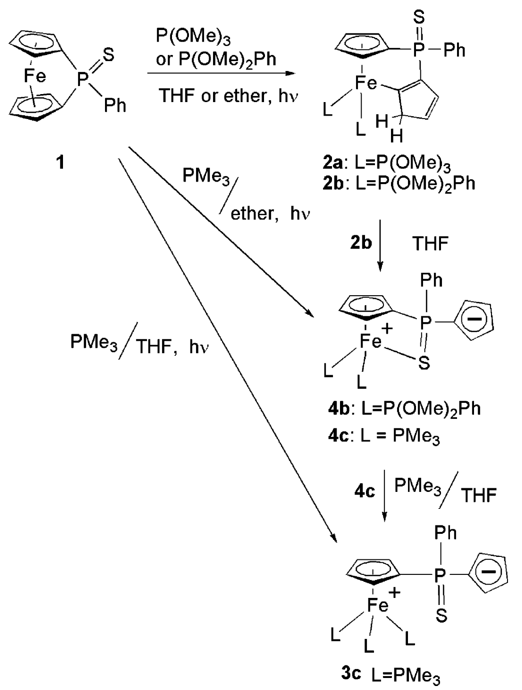
$(C_5Me_4)_2PPh^{2-}$,[10] all of which carry substituents stabilizing the cyclopentadienyl ring electronically and/or sterically.

In the course of our studies on a ring-opening reaction of the phosphorus-bridged [1]ferrocenophane **1**,[11] **1** was found to give the ring-slippage product **2** upon photoirradiation.[11e] Since **2** has an $\eta^1$-$C_5H_4$ moiety available for $\eta^5$ coordination toward a second metal fragment, it is considered to be a promising precursor for the preparation of $C_5H_4{-}P({=}S)R{-}C_5H_4{}^{2-}$-bridged heterodinuclear complexes. In addition, a P=S group of the P(=S)R linker can work as a Lewis base, in contrast with the usual $C_5H_4{-}ER_2{-}C_5H_4{}^{2-}$ systems ($ER_2 = CR_2$, $SiR_2$), for which no such additional functionality is expected. Here, we report a novel synthetic route to $C_5H_4{-}P({=}S)R{-}C_5H_4{}^{2-}$-bridged heterodinuclear complexes which have a $C_5H_4{-}P{=}S$ moiety adopting an unprecedented $\eta^5$-$\kappa S$ coordination mode.

## Results and Discussion

**Ring-Slippage Reaction**. The P(=S)Ph-bridged [1]ferrocenophane **1** suffers severe steric strain,[12] because the two $C_5H_4$ rings are bridged with a single phosphorus atom. Upon photoirradiation of **1** in the presence of an excess amount of phosphite or phosphine, ring slippage of one of the $C_5H_4$ rings takes place to relieve the steric strain (Scheme 1).[11e,13] The structure of the slipped ring depends on the phosphorus ligand used, as follows. Photolysis in the presence of $P(OMe)_3$ in THF gives the piano-stool-type iron complex **2a**, bearing an $\eta^1$-$C_5H_4$ group and two $P(OMe)_3$ ligands as legs, whereas the corresponding photolysis with $PMe_3$ gives the complex **3c**, bearing three $PMe_3$ legs with the $P({=}S)PhC_5H_4$ group dangling from the $\eta^5$-$C_5H_4$ group bound to the metal center.[11e] To obtain more information controlling the reaction patterns, a similar reaction was carried out using $P(OMe)_2Ph$. The cone angles of $P(OMe)_2Ph$, $P(OMe)_3$, and $PMe_3$ and p$K_a$ values of their conjugate acids are 120, 107, and 118° and 2.6, 2.6, and 8.65, respectively;[14,15] $P(OMe)_2Ph$ has a basicity similar to that of $P(OMe)_3$ but has a large cone angle comparable to that of $PMe_3$.

**Scheme 1**



After photoirradiation of a THF solution of **1** in the presence of $P(OMe)_2Ph$, a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed major signals at 208.8 and 30.6 ppm and minor signals at 205.8 and 204.1 ppm (AB quartet, $J_{PP} = 124$ Hz) and at 28.5 ppm. The major signals decreased significantly in intensity after several hours, while the minor signals increased. This change was found to be suppressed almost completely in a less polar solvent such as ether. Thus, the product **2b**, giving the major signals, was isolated successfully by a separate reaction in ether. The molecular structure of **2b** was determined by X-ray analysis, as shown in Figure 1, where the $C_5H_4{-}P({=}S)Ph{-}C_5H_4{}^{2-}$ moiety adopts a coordination mode similar to that in **2a** reported previously,[11e] and the iron fragment adopts a piano-stool geometry with $\eta^5$-$C_5H_4$, $\eta^1$-$C_5H_4$, and two $P(OMe)_2Ph$ groups as ligands. Positions of the two C=C bonds in the $\eta^1$-$C_5H_4$ ring were readily assigned on the basis of the geometrical parameters; summations of bond angles around C6 and C7 atoms are 359.1 and 360.0°, respectively, and the C6−C7 and C9−C10 bond lengths are 1.378(2) and 1.335(3) Å, respectively, which are significantly smaller than those of the other three C−C bonds in the $\eta^1$-$C_5H_4$ ring. These structural characteristics are consistent with the right-hand structure in Figure 1 and are similar to those of **2a**.[11e] However, notable structural differences were found between **2a** and **2b** in bond angles around the iron center; the P−Fe−P angle of 101.02(2)° in the $P(OMe)_2Ph$ complex **2b** is larger than the corresponding angle of 95.67(7)° in the $P(OMe)_3$ analogue **2a**, whereas the two P−Fe−C7($\eta^1$-$C_5H_4$) angles of 88.87(5) and 93.60(5)° in **2b** are smaller than those of 93.3(2) and 95.3(2)° in **2a**. These differences indicate that the two bulkier $P(OMe)_2Ph$ ligands in **2b** bring about a severe steric congestion around the iron center to exert a larger steric demand on the $\eta^1$-$C_5H_4$ ring, which is probably responsible for the spontaneous dissociation of the $\eta^1$-$C_5H_4$ ring from the iron center in a polar solvent (vide infra). Since **2b** dissolved in $CDCl_3$ also transformed gradually to **4b**, which gave the minor $^{31}P$ NMR signals in the reaction mixture mentioned above, we were obliged to measure the $^1H$ NMR spectrum of **2b** contaminated with **4b** in $CDCl_3$. However, the signals at 3.09 and 3.22 ppm and at 6.46 and 6.53 ppm were identified as those due to the $CH_2$ and two olefin protons, respectively, of the $\eta^1$-$C_5H_4$ ring in **2b**, though several signals of **2b** overlapped with those of **4b**. These assignments are consistent with the X-ray structure of the $\eta^1$-$C_5H_4$ ring found in **2b**.

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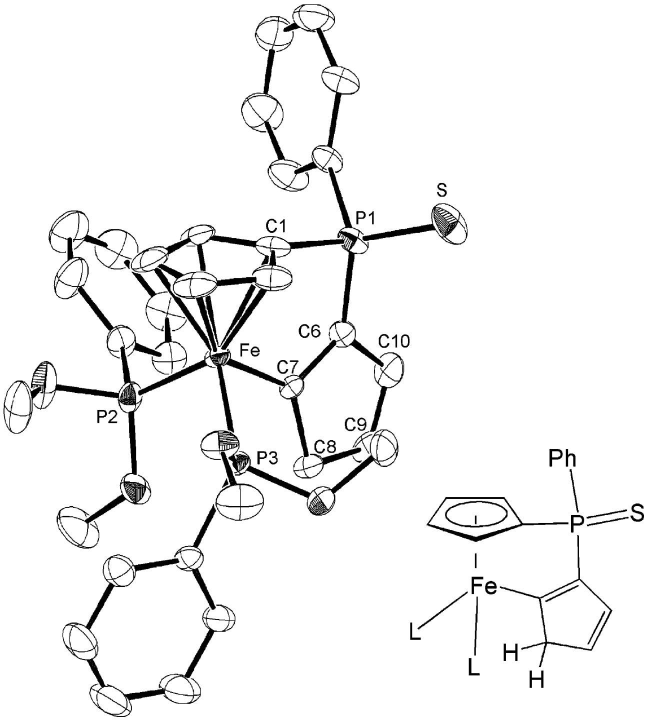
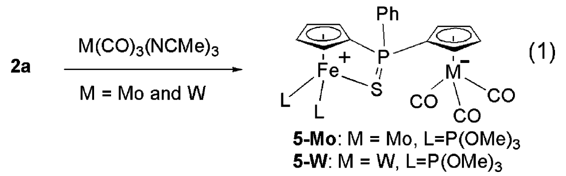


**Figure 1.** ORTEP drawing of **2b** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Fe−C7 = 1.9791(16), Fe−C1 = 2.0886(17), Fe−P2 = 2.1392(5), Fe−P3 = 2.1530(5), S−P1 = 1.9602(7), P1−C6 = 1.7627(18), P1−C1 = 1.8063(19), C6−C10 = 1.466(2), C6−C7 = 1.378(2), C7−C8 = 1.527(2), C8−C9 = 1.504(3), C9−C10 = 1.335(3); P2−Fe−P3 = 101.02(2), C7−Fe−P2 = 88.87(5), C7−Fe−P3 = 93.60(5), C6−P1−C1 = 98.38(8), P1−C1−Fe = 115.15(9), C7−C6−P1 = 117.69(13), C7−C6−C10 = 112.31(16), C10−C6−P1 = 129.10(14), C6−C7−Fe = 122.89(12), C8−C7−Fe1 = 132.78(12), C6−C7−C8 = 104.33(14).

**4b** was isolated after a THF solution of **2b** was allowed to stand for several hours (Scheme 1). $^{31}P\{^1H\}$ NMR signals of **4b** were found to be shifted as a whole only slightly upfield compared with those of **2b** as stated above, suggesting a structural resemblance of **4b** to **2b** around the phosphorus atom. Notable differences between them in the $^1$H NMR spectra were discerned with respect to the signals assigned to the slipped $C_5H_4$ ring; the $CH_2$ signals of the $\eta^1$-$C_5H_4$ ring observed in **2b** disappeared completely in **4b**, while the total intensity of the olefinic proton signals around 6.0−6.5 ppm increased from 2H to 4H. In addition, $^{13}C\{^1H\}$ NMR signals of the olefinic carbons appearing at 113.6 and 115.3 ppm in **4b** could be assigned to the anionic $C_5H_4^-$ freed from coordination, judging from their chemical shifts close to 109.9 and 114.6 ppm of the $C_5H_4^-$ group in the complex **3c** reported previously[11e] and to the 114.3 and 116.9 ppm signals of $Ph_3P^+{-}C_5H_4^-$.[16] In contrast, the chemical shift of the ipso carbon of the $C_5H_4^-$ group showed some difference among the above three compounds: 105.2, 88.7, and 127 ppm, respectively. These spectral data indicate that one of the $C_5H_4$ rings in **4b** has completely dissociated from the iron center, the resulting vacant coordination site having been occupied probably with a sulfur atom of the P=S group. Although, to our knowledge, **4b** seems to provide the first example of an $\eta^5$-$\kappa S$ coordination mode with a P=S pendant attached to the $\eta^5$-$C_5H_4$ ring,[17] a similar coordination mode is definitely established in the dinuclear complexes **5-Mo** and **5-W**, which be described in the next section (vide infra).

The driving force for the facile dissociation of the $\eta^1$-$C_5H_4$ ring in **2b** to form **4b** in THF is considered to be the steric demand exerted by the two $P(OMe)_2Ph$ ligands as mentioned above. In fact, $P(OMe)_3$ in **2a** having basicity comparable to, but a cone angle smaller than, those of $P(OMe)_2Ph$ does not induce such dissociation in THF at room temperature. Because $PMe_3$ has a cone angle comparable to that of $P(OMe)_2Ph$, the $PMe_3$ analogue (**4c**) of **4b** is expected to be formed when **1** is allowed to react with $PMe_3$. **4c** was actually obtained directly by the photolysis of **1** in ether containing excess $PMe_3$, where immediate precipitation of **4c** took place, enabling us to isolate **4c** (Scheme 1). However, when the photolysis was carried out in THF, the free $PMe_3$ ligand present gradually replaced the coordinating P=S group in **4c** to eventually give **3c** with the coordination-free $P(=S)Ph(C_5H_4)$ group dangling from the $\eta^5$-$C_5H_4$ ring, as stated earlier (Scheme 1). However, a complex having an $\eta^1$-$C_5H_4$ ring, that is, the $PMe_3$ analogue (**2c**) of **2a**, was not observed. It is likely that **2c** was once formed also in this case, but probably it immediately transformed to **4c** through the more facile dissociation of the $\eta^1$-$C_5H_4$ ring in **2c** compared to that in **2a**. Since the steric demand of $PMe_3$ is comparable to that of $P(OMe)_2Ph$, as judged from their similar cone angles, a much greater donating ability of the two $PMe_3$ ligands is considered to be one of the probable factors which contribute additionally to the more facile dissociation in **2c**.

**Preparation of Heterodinuclear Complexes.** The ring-slippage product **2a** was allowed to react with $M(CO)_3(NCMe)_3$ (M = Mo, W) in THF (eq 1).



In the IR spectrum of the resulting product, $\nu$(CO) absorptions were observed at 1914 and 1806 $cm^{-1}$ for M = Mo and at 1907 and 1802 $cm^{-1}$ for M = W, indicating the $C_5H_4$ group adopting an $\eta^5$ coordination mode to the $M(CO)_3$ fragment.[18] Structures of the products **5-Mo** and **5-W** were determined by X-ray analysis, as shown in Figures 2 and 3, respectively, where the Fe fragment and the Mo or W fragment are linked through an $(\eta^5\text{-}C_5H_4)_2P(=S)Ph^{2-}$ bridging ligand. Bitterwolf et al. reported a similar $\eta^1$- to $\eta^5$-$C_5H_4$ conversion, in which $Ru(CO)_2(\eta^5{:}\eta^1\text{-}C_5H_4CR_2C_5H_4)$ reacted with $M(CO)_3(NCMe)_3$ (M = Mo, W), to give a heterodinuclear complex having a direct Ru-M bond, i.e., $(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4CR_2C_5H_4)[Ru(CO)_2][M(CO)_3]$.[19] In **5-Mo** and **5-W**, the Fe atom is not bonded to the Mo or W atom, resulting in a zwitterionic dinuclear structure. The absence of a Fe−M bond in **5-Mo** and **5-W** is attributable to the steric bulkiness of the $P(OMe)_3$ ligands on the Fe fragment, which blocks a close

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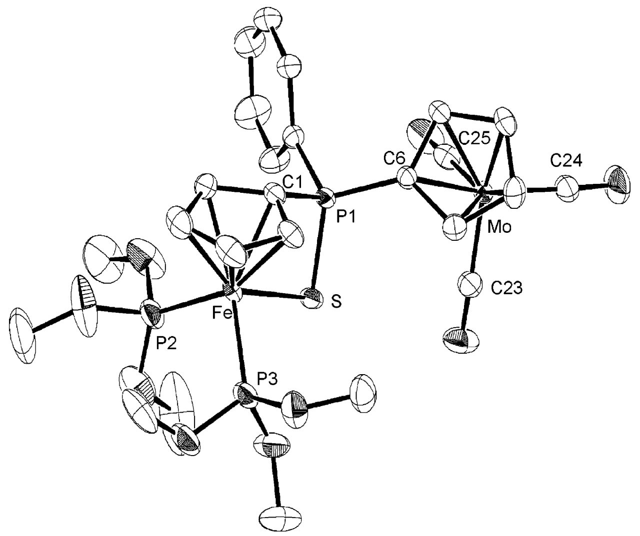

**Figure 2.** ORTEP drawing of **5-Mo** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Mo−C23 = 1.933(3), Mo−C24 = 1.945(3), Mo−C25 = 1.945(3), Fe−C1 = 2.060(3), Fe−P3 = 2.1415(8), Fe−P2 = 2.1501(9), Fe−S = 2.3646(8), S−P1 = 2.0075(9), P1−C6 = 1.756(3), P1−C1 = 1.797(3), P1−C11 = 1.801(3); P3−Fe−P2 = 94.34(3), P3−Fe−S = 93.66(3), P2−Fe−S = 94.29(3), P1−S−Fe = 83.20(3), C6−P1−C1 = 111.89(13), C6−P1−S = 113.41(9), C1−P1−S = 97.42(9).

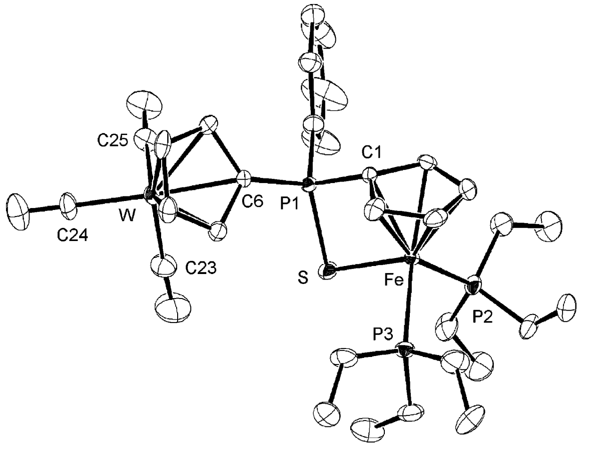

**Figure 3.** ORTEP drawing of **5-W** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): W−C24 = 1.947(6), W−C25 = 1.964(6), W−C23 = 1.970(7), Fe−C1 = 2.058(6), Fe−P3 = 2.1431(16), Fe−P2 = 2.1446(17), Fe−S = 2.3820(17), S−P1 = 1.999(2), P1−C6 = 1.758(6), P1−C1 = 1.787(6), P1−C11 = 1.793(6); P3−Fe−S = 93.24(7), P2−Fe−S = 95.22(7), P1−S−Fe = 83.40(7), C6−P1−C1 = 109.2(3), C6−P1−S = 114.5(2), C1−P1−S = 97.78(19).

approach of the two metal centers. The coordination site from which the $\eta^1$-$C_5H_4$ group has dissociated is now occupied with a sulfur atom of the P═S group, as seen in Figures 2 and 3. Cyclopentadienyl ligands bearing a pendant group capable of coordinating to the metal center have been intensively investigated in the past decade with reference to the potential utility of their metal complexes as so-called "constrained geometry" catalysts for olefin polymerization.[17] However, no example adopting the $\eta^5$-$\kappa S$ coordination mode is known to date, which is found for the first time in **5-Mo** and **5-W**, and probably in **4b** and **4c** as well. Similar dinuclear complexes are expected to be formed when **2b** is used in place of **2a**. **4b** and **4c** should also serve as a precursor of them.

The Mo or W fragment obviously constitutes the anionic part of the zwitterionic dinuclear complexes **5-Mo** and **5-W**, as evidenced by their $\nu$(CO) absorptions being comparable in wavenumber to those reported for the anionic carbonyl complexes $[MCp(CO)_3]^-$ (M = Mo, W).[18] The cationic charge is thus located formally at the iron center, but the highly polarized P−S bond renders such a simple formalism fruitless. An exact nature of the P−S bond in $R_3P{=}S$ has been a subject of controversy.[20] On the basis of recent theoretical studies, the bond is considered as a highly polarized $\sigma$-bond with a strong electrostatic attraction between $P^{\delta+}$ and $S^{\delta-}$ atoms,[21] and thus the cationic charge is delocalized to some extent to the bridging P atom in **5-Mo** and **5-W**.

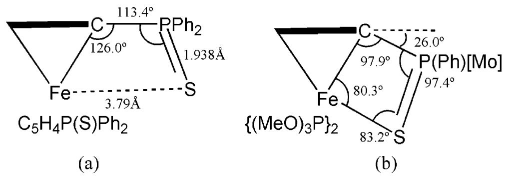

**Figure 4.** Geometrical parameters relevant to the P═S pendant group in $dppfS_2$ (a) and **5-Mo** (b).

The coordination of the pendant P═S group to the iron center forms a four-membered ring comprised of Fe, C(*ipso*-Cp), P(bridge), and S atoms in **5-Mo** and **5-W**. Bond angles within the ring are summarized in Figure 4 for **5-Mo**, where the corresponding angles for the related ferrocene derivative $[Fe\{C_5H_4P(S)Ph_2\}_2]$ (abbreviated as $dppfS_2$) are also given for comparison.[22] In $dppfS_2$, the Fe−C(Cp)−P and C(Cp)−P−S angles are 126.0 and 113.4°, respectively, and the S atom is separated by ca. 3.79 Å from the iron center. The corresponding angles (97.9 and 97.4°) in **5-Mo** are significantly reduced as compared with those of $dppfS_2$ so as to form the Fe−S bond. As a result, the bridging P atom is displaced from the $\eta^5$-$C_5H_4$ ring plane toward the iron center considerably, the displacement angle being 26.5°, comparable to those of the highly strained complex **1**, in which the two $\eta^5$-$C_5H_4$ rings of the ferrocene unit are linked with one P atom.[12a] Such steric strain is also inferred from the $^{13}C\{^1H\}$ NMR spectrum of the ipso carbon atom of the $\eta^5$-$C_5H_4$ group on the iron atom;[23] **Mo-5**, **W-5**, **4c**, and **1**, all suffering the strain, show the signals at 69.0, 68.4, 71.5, and 28.9 ppm, respectively, while the strain-free **2a**, **3c**, and **6-W** (vide infra) show the carbon atom at a lower field (114.4, 96.2, and 92.8 or 94.0 ppm, respectively).[24] Such steric strain built into **5-Mo** is probably responsible for its spontaneous ring-opening reaction taking place in neat MeCN (vide infra). The P═S bond (2.008(1) Å) in **5-Mo** is longer by 0.042 Å than that of **2a**,[11e] indicating reduced electrostatic interaction between the $P^{\delta+}$ and $S^{\delta-}$ atoms in **5-Mo**, as is generally observed upon coordination of $R_3P{=}S$ to a metal fragment.[25] The structural

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(21) (a) Chesnut, D. B. *J. Phys. Chem. A* **2003**, *107*, 4307−4313. (b) Dobado, J. A.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 8461−8471.

(22) Fang, Z.-G.; Hor, T. S. A.; Wen, Y.-S.; Liu, L.-K.; Mak, T. C. W. *Polyhedron* **1995**, *14*, 2403−2409.

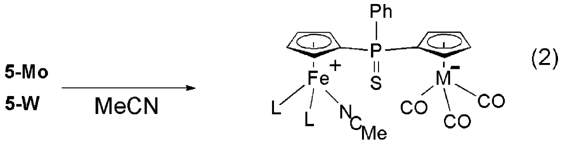
(23) For example: Resendes, R.; Nelson, J. M.; Fischer, A.; Jakle, F.; Bartole, A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2001**, *123*, 2116−2126.

(24) The corresponding signal was not detected for **4b** and **6-Mo** because of its inherently low intensity and their low solubility.

(25) (a) Saak, W.; Pohl, S. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 813−817. (b) Saak, W.; Haase, D.; Pohl, S. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 289−294.

characteristics of **5-W** are naturally similar to those of **5-Mo**, in particular with respect to the Fe−C(Cp)−P−S four-membered ring.

The pendant P═S group of **5-Mo** and **5-W** was found to dissociate spontaneously from the iron center when they were dissolved in MeCN. The resulting vacant coordination site was occupied with MeCN to form **6-Mo** and **6-W** (eq 2).



(2)

**6-Mo**: M = Mo
**6-W**: M = W

In the $^{31}P\{^1H\}$ NMR spectrum, signals of **6-Mo** appeared at slightly higher fields than those of **5-Mo**. The $^1H$ NMR signals at 2.38 ppm and the $^{13}C\{^1H\}$ signals at 6.7 and 135.0 ppm observed in **6-Mo** were assigned to the MeCN ligand coordinating to the iron center, as judged from the corresponding chemical shifts, 2.39 ppm in the $^1H$ NMR spectrum and 4.29 and 135.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum of the related $[FeCp\{P(OMe)_3\}_2(NCMe)]^+$.[26] Other signals in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **5-Mo** and **6-Mo** indicate that the two $P(OMe)_3$ groups on Fe and the three CO groups on Mo stay almost intact in the present ring-opening reaction in eq 2. Similar spectral changes were observed between **5-W** and **6-W**.

A driving force for the facile substitution of the P═S group with MeCN in **5-Mo** and **5-W** is probably the strain built into the four-membered ring shown in Figure 4. $Ph_3P{=}S$ is known to possess a strong donation ability comparable to that of $PPh_3$, MeCN, CO, or $C_2H_4$.[20d] In addition, several examples of the reversed substitution have been reported; that is, MeCN coordinating to a metal fragment is readily replaced with $Ph_3P{=}S$, indicative of the latter having a stronger coordination ability than MeCN.[27] Thus, the spontaneous substitution with MeCN observed in **5-Mo** and **5-W** is attributable to the aforementioned severe ring strain, which is relieved upon the substitution. In other words, the dissociation of the $\eta^1$-$C_5H_4$ ring and the subsequent formation of the unstable four-membered ring in Scheme 1 or eq 1 must be substantiated by the stabilization gained by the accompanying transformation of the nonaromatic $\eta^1$-$C_5H_4$ ring to the more stable aromatic $C_5H_4$ ring. The $\eta^5$ coordination of the latter $C_5H_4$ ring to the $M(CO)_3$ fragment also adds to the stabilization of **5-Mo** or **5-W** in eq 1. The Fe−S bond is maintained in **5-Mo**, **5-W**, **4b**, and **4c** unless a competing ligand such as phosphine or MeCN is present.

## Experimental Section

**General Remarks**. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were dried and distilled from sodium (hexane), sodium/benzophenone (ether and THF), or $P_2O_5$ (acetonitrile). These purified solvents were stored under an $N_2$ atmosphere. $P(OMe)_2Ph$[28] and $[M(CO)_3(NCMe)_3]$ (M = Mo, W)[29] were prepared according to previously described methods. Other reagents were used as received.

NMR spectra were recorded on a JEOL LA-300 spectrometer. $^1H$ 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, but satisfactory results could not be obtained for **4b**, **5-Mo**, **6-Mo**, and **6-W**.

Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission lines used (nm) and their relative intensities (in parentheses) are 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).

**$[Fe\{(\eta^5\text{-}C_5H_4)(\eta^1\text{-}C_5H_4)P({=}S)Ph\}\{P(OMe)_2Ph\}_2]$ (2b). 1**[12] (94 mg, 0.29 mmol), ether (20 mL), and $P(OMe)_2Ph$ (0.45 mL, 2.84 mmol) were added to a Pyrex Schlenk tube, and the solution was irradiated with a 400 W mercury arc lamp at 0 °C for 30 min. The yellow precipitate that formed was separated by decantation and washed with hexane. The residue was dried in vacuo to give **2b** as a yellow powder (154 mg, 80%). $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 3.09 (d, $J_{HH}$ = 24.3 Hz, 1H, $CH_2$), 3.22 (d, $J_{HH}$ = 24.3 Hz, 1H, $CH_2$), 3.18 (m, 3H, OMe), 3.45 (m, 3H, OMe), 3.55 (m, 6H, OMe), 3.78 (br, 1H, $\eta^5$-$C_5H_4$), 4.09(br, 1H, $\eta^5$-$C_5H_4$), 5.72 (br, 1H, $\eta^5$-$C_5H_4$), 6.46 (m, 1H, $\eta^1$-$C_5H_4$), 6.53 (m, 1H, $\eta^1$-$C_5H_4$). Other signals overlapped with those of **4b**. $^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 32.5 (s, P(S)Ph), 209.5 (s, $P(OMe)_2Ph$). Anal. Calcd for $C_{32}H_{35}FeO_4P_3S$: C, 57.84; H, 5.31. Found: C, 57.85; H, 5.26.

**$[Fe\{\eta^5\text{-}C_5H_4P({=}S)Ph(C_5H_4)\text{-}\kappa S\}\{P(OMe)_2Ph\}_2]$ (4b).** A solution of **2b** (26 mg, 0.04 mmol) in THF (8 mL) was stirred for several hours. After almost complete conversion of **2b** to **4b** was confirmed by monitoring the $^{31}P\{^1H\}$ NMR signals, the solution was reduced in volume to 1 mL, and then the product was precipitated by addition of hexane (10 mL). The product was separated by decantation and washed with hexane. The residue was dried in vacuo to give yellow **4b** in almost quantitative yield. $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 3.39 (d, $J_{PH}$ = 10.1 Hz, 3H, OMe), 3.40 (d, $J_{PH}$ = 10.1 Hz, 3H, OMe), 3.51 (d, $J_{PH}$ = 10.1 Hz, 3H, OMe), 3.58 (d, $J_{PH}$ = 10.3 Hz, 3H, OMe), 3.58 (br, 1H, $\eta^5$-$C_5H_4$), 3.92 (br, 1H, $\eta^5$-$C_5H_4$), 4.15 (br, 1H, $\eta^5$-$C_5H_4$), 4.77 (br, 1H, $\eta^5$-$C_5H_4$), 6.12 (m, 2H, $C_5H_4^-$), 6.25 (m, 2H, $C_5H_4^-$), 7.29 (m, 2H, Ph), 7.37−7.63 (m, 9H, Ph), 7.81 (m, 2H, Ph), 7.94 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta$ 53.0 (d, $J_{PC}$ = 6 Hz, OMe), 53.1 (d, $J_{PC}$ = 9 Hz, OMe), 53.3 (d, $J_{PC}$ = 8 Hz, OMe), 53.7 (d, $J_{PC}$ = 6 Hz, OMe), 79.4 (d, $J_{PC}$ = 9 Hz, $\eta^5$-$C_5H_4$), 81.4 (m, 2C, $\eta^5$-$C_5H_4$), 85.0 (d, $J_{PC}$ = 9 Hz, $\eta^5$-$C_5H_4$), 105.2 (d, $J_{PC}$ = 97 Hz, *ipso*-$C_5H_4^-$), 113.6 (d, $J_{PC}$ = 19 Hz, $C_5H_4^-$), 115.3 (d, $J_{PC}$ = 18 Hz, $C_5H_4^-$), 127.9 (d, $J_{PC}$ = 13 Hz, 2C, Ph), 128.0 (d, $J_{PC}$ = 14 Hz, Ph), 129.2 (d, $J_{PC}$ = 10 Hz, Ph), 129.7 (s, Ph), 130.2 (d, $J_{PC}$ = 9 Hz, Ph), 130.2 (s, Ph), 131.5 (d, $J_{PC}$ = 3 Hz, Ph), 131.8 (d, $J_{PC}$ = 11 Hz, Ph), 139.3 (d, $J_{PC}$ = 97 Hz, *ipso*-Ph), 140.2 (d, $J_{PC}$ = 96 Hz, *ipso*-Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 31.2 (s, P(S)Ph), 205.0 (d, $J_{PP}$ = 124 Hz, $P(OMe)_2Ph$), 206.9 (d, $J_{PP}$ = 125 Hz, $P(OMe)_2Ph$).

**$[Fe\{\eta^5\text{-}C_5H_4P({=}S)Ph(C_5H_4)\text{-}\kappa S\}(PMe_3)_2]$ (4c). 1** (117 mg, 0.36 mmol) and an ether solution of $PMe_3$ (0.212 mol/L, 17 mL, 3.60 mmol) were added to a Pyrex Schlenk tube, and the solution was irradiated with a 400 W mercury arc lamp at 0 °C for 20 min. The pale green precipitate that formed was separated by decantation and washed with ether. The residue was dried in vacuo to give **4c** as a pale green powder (160 mg, 93%). $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 1.39 (d, $J_{PH}$ = 8 Hz, 9H, $PMe_3$), 1.61 (d, $J_{PH}$ = 8 Hz, 9H, $PMe_3$), 3.49 (br, 1H, $\eta^5$-$C_5H_4$), 3.80 (br, 1H, $\eta^5$-$C_5H_4$), 4.27 (br, 1H, $\eta^5$-$C_5H_4$), 5.01 (br, 1H, $\eta^5$-$C_5H_4$), 6.29 (m, 4H, $C_5H_4^-$), 7.51−7.65 (m, 3H, Ph), 8.05 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta$ 20.9 (dd, $J_{PC}$ = 22 Hz, $J_{PC}$ = 3 Hz, $PMe_3$), 21.2 (dd, $J_{PC}$ = 22 Hz, $J_{PC}$ = 3 Hz, $PMe_3$), 71.5 (d, $J_{PC}$ = 86 Hz, *ipso*-$\eta^5$-$C_5H_4$), 76.0 (d, $J_{PC}$ = 9 Hz, $\eta^5$-$C_5H_4$), 77.3 (d, $J_{PC}$ = 6 Hz, $\eta^5$-$C_5H_4$), 77.5 (d, $J_{PC}$ = 5 Hz, $\eta^5$-$C_5H_4$), 80.0 (d, $J_{PC}$ = 9 Hz,

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**Table 1. Crystallographic Data**

| | **2a** | **5-Mo** | **5-W** |
|---|---|---|---|
| formula | $C_{32}H_{35}FeO_4P_3S$ | $C_{25}H_{31}FeMoO_9P_3S$ | $C_{25}H_{31}FeO_9P_3SW$ |
| cryst color | orange | red | red |
| cryst syst | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/n$ (No. 14) | $P2_1/c$ (No. 14) | $P2_12_12_1$ (No. 19) |
| $a$ (Å) | 13.6210(2) | 9.7390(1) | 9.7430(1) |
| $b$ (Å) | 16.9900(3) | 21.0770(2) | 13.2490(1) |
| $c$ (Å) | 14.0890(2) | 14.9500(1) | 23.1550(2) |
| $\alpha$ (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 107.170(1) | 90.583(1) | 90 |
| $\gamma$ (deg) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 3115.18(8) | 3068.61(5) | 2988.96(5) |
| $Z$ | 4 | 4 | 4 |
| temp (K) | 200 | 200 | 200 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 0.741 | 1.154 | 4.610 |
| no. of rflns | | | |
| measd | 7068 | 6857 | 6824 |
| obsd ($I > 2\sigma(I)$, $2\theta < 55°$) | 6410 | 6816 | 6778 |
| no. of variables | 511 | 368 | 368 |
| R1 | 0.0390 | 0.0388 | 0.0397 |
| wR2 ($I > 2\sigma(I)$)[a] | 0.0815 | 0.0988 | 0.1046 |
| Flack param | | | 0.370 (8) |
| largest diff peak(e/Å$^3$) | 0.33 (0.879 Å from P1) | 1.95 (1.420 Å from P1) | 2.85 (0.779 Å from W) |
| $a/b$ | 0.0361/2.6791 | 0.0459/6.6913 | 0.0730/13.6135 |

[a] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

$\eta^5$-$C_5H_4$), 96.5 (d, $J_{PC}$ = 105 Hz, *ipso*-$C_5H_4^-$), 113.2 (d, $J_{PC}$ = 19 Hz, $C_5H_4^-$), 114.6 (d, $J_{PC}$ = 17 Hz, $C_5H_4^-$), 128.1 (d, $J_{PC}$ = 12 Hz, Ph), 131.4 (d, $J_{PC}$ = 11 Hz, Ph), 131.7 (d, $J_{PC}$ = 2 Hz, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 25.0 (d, $J_{PP}$ = 69 Hz, $PMe_3$), 26.0 (d, $J_{PP}$ = 69 Hz, $PMe_3$), 34.6 (s, P(S)Ph). Anal. Calcd for $C_{32}H_{35}FeO_4P_3S$: C, 55.48; H, 6.56. Found: C, 55.52; H, 6.52.

**{$\mu$-$\eta^5$:$\eta^5$-$(C_5H_4)_2P(=S)Ph$-$\kappa S$}[Fe{P(OMe)$_3$}$_2$][Mo(CO)$_3$] (5-Mo). 2a**[11e] (115 mg, 0.20 mmol), $Mo(CO)_3(NCMe)_3$ (61 mg, 0.20 mmol), and THF (15 mL) were added to a Pyrex Schlenk tube, and the solution was stirred for 3 h. After the solvent and volatile species were removed under reduced pressure, the residue was recrystallized from THF/hexane and washed with hexane. The product was dried in vacuo to give **5-Mo** as a brown powder (139 mg, 92%). $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 3.57 (t, $J_{PH}$ = 5.1 Hz, 9H, OMe), 3.75 (t, $J_{PH}$ = 5.1 Hz, 9H, OMe), 3.96 (br, 1H, $C_5H_4$), 4.33 (br, 1H, $C_5H_4$), 4.76 (br, 1H, $C_5H_4$), 5.15 (br, 1H, $C_5H_4$), 5.31 (br, 2H, $C_5H_4$), 5.36 (br, 2H, $C_5H_4$), 7.55−7.72 (m, 3H, Ph), 8.07 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta$ 52.6 (s, OMe), 53.0 (s, OMe), 69.0 (d, $J_{PC}$ = 89 Hz, *ipso*-$C_5H_4$), 79.9 (d, $J_{PC}$ = 17 Hz, $C_5H_4$), 80.2 (s, $C_5H_4$), 80.7 (d, $J_{PC}$ = 14 Hz, $C_5H_4$), 82.9 (d, $J_{PC}$ = 96 Hz, *ipso*-$C_5H_4$), 84.2 (d, $J_{PC}$ = 9 Hz, $C_5H_4$), 89.8 (d, $J_{PC}$ = 13 Hz, $C_5H_4$), 90.7 (d, $J_{PC}$ = 13 Hz, $C_5H_4$), 93.4 (d, $J_{PC}$ = 15 Hz, $C_5H_4$), 94.4 (d, $J_{PC}$ = 16 Hz, $C_5H_4$), 126.8 (d, $J_{PC}$ = 87 Hz, *ipso*-Ph), 128.5 (d, $J_{PC}$ = 13 Hz, Ph), 131.3 (d, $J_{PC}$ = 12 Hz, Ph), 133.3 (s, Ph), 230.7 (s, CO). $^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 38.1 (s, P(S)Ph), 178.4 (s, P(OMe)$_3$).

**{$\mu$-$\eta^5$:$\eta^5$-$(C_5H_4)_2P(=S)Ph$-$\kappa S$}[Fe{P(OMe)$_3$}$_2$][W(CO)$_3$] (5-W). 2a** (118 mg, 0.210 mmol), $W(CO)_3(NCMe)_3$ (75 mg, 0.19 mmol), and THF (15 mL) were added to a Pyrex Schlenk tube, and the solution was stirred for 3 h. After the solvent and volatile species were removed under reduced pressure, the residue was washed with ether and dried in vacuo to give **5-W** as a brown powder (117 mg, 73%). $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 3.57 (t, $J_{PH}$ = 5.3 Hz, 9H, OMe), 3.75 (t, $J_{PH}$ = 5.3 Hz, 9H, OMe), 3.97 (br, 1H, $C_5H_4$), 4.32 (br, 1H, $C_5H_4$), 4.77 (br, 1H, $C_5H_4$), 5.09 (br, 1H, $C_5H_4$), 5.32 (m, 4H, $C_5H_4$), 7.55−7.72 (m, 3H, Ph), 8.06 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta$ 52.8 (s, OMe), 53.2 (s, OMe), 68.4 (d, $J_{PC}$ = 90 Hz, *ipso*-$C_5H_4$), 80.0 (d, $J_{PC}$ = 16 Hz, $C_5H_4$), 80.3 (d, $J_{PC}$ = 10 Hz, $C_5H_4$), 81.1 (d, $J_{PC}$ = 14 Hz, $C_5H_4$), 81.3 (d, $J_{PC}$ = 96 Hz, *ipso*-$C_5H_4$), 84.2 (d, $J_{PC}$ = 10 Hz, $C_5H_4$), 87.6 (d, $J_{PC}$ = 12 Hz, $C_5H_4$), 88.4 (d, $J_{PC}$ = 12 Hz, $C_5H_4$), 90.4 (d, $J_{PC}$ = 14 Hz, $C_5H_4$), 91.4 (d, $J_{PC}$ = 15 Hz, $C_5H_4$), 126.4 (d, $J_{PC}$ = 88 Hz, *ipso*-Ph), 128.7 (d, $J_{PC}$ = 14 Hz, Ph), 131.5 (d, $J_{PC}$ = 12 Hz, Ph), 133.6 (s, Ph), 220.9 (s, $J_{CW}$ = 198 Hz, CO). $^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 37.4 (s, P(S)Ph), 178.2 (s, P(OMe)$_3$). Anal. Calcd for $C_{25}H_{31}FeO_9P_3SW$: C, 35.74; H, 3.72. Found: C, 35.48; H, 3.69.

**{$\mu$-$\eta^5$:$\eta^5$-$(C_5H_4)_2P(=S)Ph$}[Fe(NCMe){P(OMe)$_3$}$_2$][Mo(CO)$_3$] (6-Mo). 5-Mo** (30 mg, 0.04 mmol) was dissolved in acetonitrile (3 mL). After the mixture was stirred for several hours, the solvent was removed under reduced pressure. The residue was recrystallized from THF/hexane and then washed with hexane. The product was dried in vacuo to give **6-Mo** quantitatively as a yellow powder. $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 2.38 (s, 3H, $CH_3CN$) 3.46 (br, 1H, $C_5H_4$), 3.56 (t, $J_{PH}$ = 5.5 Hz, 9H, OMe), 3.76 (t, $J_{PH}$ = 5.3 Hz, 9H, OMe), 4.56 (br, 1H, $C_5H_4$), 4.95 (br, 1H, $C_5H_4$), 5.23 (br, 2H, $C_5H_4$), 5.34 (br, 1H, $C_5H_4$), 5.62 (br, 1H, $C_5H_4$), 6.05 (br, 1H, $C_5H_4$), 7.50 (m, 3H, Ph), 8.25 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta$ 6.7 (s, $CH_3CN$), 52.8 (m, OMe), 53.3 (m, OMe), 69.9 (d, $J_{PC}$ = 11 Hz, $C_5H_4$), 79.7 (d, $J_{PC}$ = 10 Hz, $C_5H_4$), 85.7 (d, $J_{PC}$ = 12 Hz, 2C, $C_5H_4$), 85.9 (d, $J_{PC}$ = 10 Hz, 2C, $C_5H_4$), 88.1 (d, $J_{PC}$ = 11 Hz, $C_5H_4$), 90.3 (d, $J_{PC}$ = 12 Hz, $C_5H_4$), 93.6 (d, $J_{PC}$ = 15 Hz, $C_5H_4$), 94.3 (d, $J_{PC}$ = 13 Hz, $C_5H_4$), 127.9 (d, $J_{PC}$ = 12 Hz, Ph), 131.3 (s, Ph), 132.4 (d, $J_{PC}$ = 11 Hz, Ph), 135.0 (s, $CH_3CN$), 232.8 (s, CO).$^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 30.9 (s, P(S)Ph), 176.6 (s, P(OMe)$_3$).

**{$\mu$-$\eta^5$:$\eta^5$-$(C_5H_4)_2P(=S)Ph$}[Fe(NCMe){P(OMe)$_3$}$_2$][W(CO)$_3$] (6-W).** The preparation of **6-W** was carried out in a manner similar to that described above for **6-Mo**, using **5-W** (25 mg 0.03 mmol). $^1H$ NMR (300.4 MHz, $CDCl_3$): $\delta$ 2.39 (s, 3H, $CH_3CN$), 3.48 (br, 1H, $C_5H_4$), 3.53 (t, $J_{PH}$ = 5.3 Hz, 9H, OMe), 3.76 (t, $J_{PH}$ = 5.3 Hz, 9H, OMe), 4.55 (br, 1H, $C_5H_4$), 4.93 (br, 1H, $C_5H_4$), 5.18 (br, 2H, $C_5H_4$), 5.30 (br, 1H, $C_5H_4$), 5.53 (m, 1H, $C_5H_4$), 5.92 (br, 1H, $C_5H_4$), 7.51 (m, 3H, Ph), 8.23 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta$ 6.6 (s, $CH_3CN$), 52.9 (s, OMe), 53.4 (s, OMe), 70.1 (d, $J_{PC}$ = 9 Hz, $C_5H_4$), 79.7 (d, $J_{PC}$ = 10 Hz, $C_5H_4$), 85.9 (d, $J_{PC}$ = 11 Hz, 2C, $C_5H_4$), 86.4 (d, $J_{PC}$ = 11 Hz, $C_5H_4$), 88.1 (d, $J_{PC}$ = 12 Hz, $C_5H_4$), 90.9 (d, $J_{PC}$ = 14 Hz, $C_5H_4$), 91.6 (d, $J_{PC}$ = 12 Hz, $C_5H_4$), 92.8 (d, $J_{PC}$ = 91 Hz, *ipso*-$C_5H_4$), 94.0 (d, $J_{PC}$ = 104 Hz, *ipso*-$C_5H_4$), 128.0 (d, $J_{PC}$ = 12 Hz, Ph), 131.4 (d, $J_{PC}$ = 2 Hz, Ph), 132.5 (d, $J_{PC}$ = 11 Hz, Ph), 132.7 (d, $J_{PC}$ = 88 Hz, *ipso*-Ph), 135.2 (s, $CH_3CN$), 223.3 (s, $J_{CW}$ = 199 Hz, CO). $^{31}P\{^1H\}$ NMR (121.5 MHz, in $CDCl_3$): $\delta$ 30.6 (s, P(S)-Ph), 175.9 (s, P(OMe)$_3$).

**X-ray Crystallography.** Suitable crystals of **2b**, **5-Mo**, and **5-W** were mounted separately on a glass fiber. All measurements were made on a Mac Science DIP2030 imaging plate area detector. The data were collected to a maximum 2$\theta$ value of 55.8°. Cell parameters and intensities for the reflections were estimated using the program packages of HKL.[30] The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions. All calculations were performed using a SHELXL-97 crystallographic software package.[31] Details of the data collection and refinement are given in Table 1, and bond distances and angles, atomic coordinates, and anisotropic thermal parameters are given as Supporting Information.

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**Supporting Information Available:** Full crystallographic data given in as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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