

Communications

Reactions of Phosphorus Electrophiles with $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]^-$: Spectroscopic Evidence for a Phosphinidene Complex

Sir:

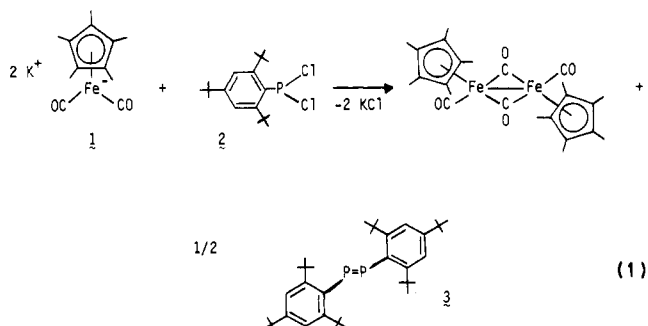
Over the past few years, numerous syntheses of compounds with $\text{P}=\text{C}$ double bonds (diphosphenes) have been reported.¹ These compounds have proven to have a rich chemistry.^{1,2} At the same time, factors that contribute to the stability of complexes with metal-carbon double bonds, $\text{L}_n\text{M}=\text{CRR}'$, have been more precisely defined.³ As a result of our interest in both of these areas,^{1d,k,3d-h} we have undertaken an investigation of the synthesis of phosphinidene complexes, $\text{L}_n\text{M}=\text{PR}$, which contain a metal-phosphorus double bond. Terminal phosphinidene complexes have been implicated as intermediates in elegant trapping experiments conducted by Mathey,⁴ but

no stable examples are known to date.

To complement our studies directed toward the synthesis of rhenium phosphinidene complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{PR})]^+$,⁵ we sought to probe the stability of phosphinidene complexes of less basic L_nM systems. In this communication, we describe reactions of the iron anion $\text{K}^+[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]^-$ (**1**) with two phosphorus electrophiles. Evidence is presented for the generation of a labile $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(=\text{PR})]^+$ species.

The reaction of **1** with an equimolar amount of "super-mesityl" phosphorus dichloride, $(2,4,6\text{-C}_6\text{H}_2(t\text{-C}_4\text{H}_9)_3)\text{PCl}_2$ (**2**),^{1a} in THF was monitored by ³¹P NMR spectroscopy at -78 to -51 °C. Prominent resonances were observed at 492, 371, and 154 (unreacted **2**) ppm (vs. external 85% H_3PO_4). When the NMR probe was warmed to room temperature, the 371 ppm resonance disappeared. A preparative-scale reaction gave $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]_2$ (83% of theory of eq 1) and di-

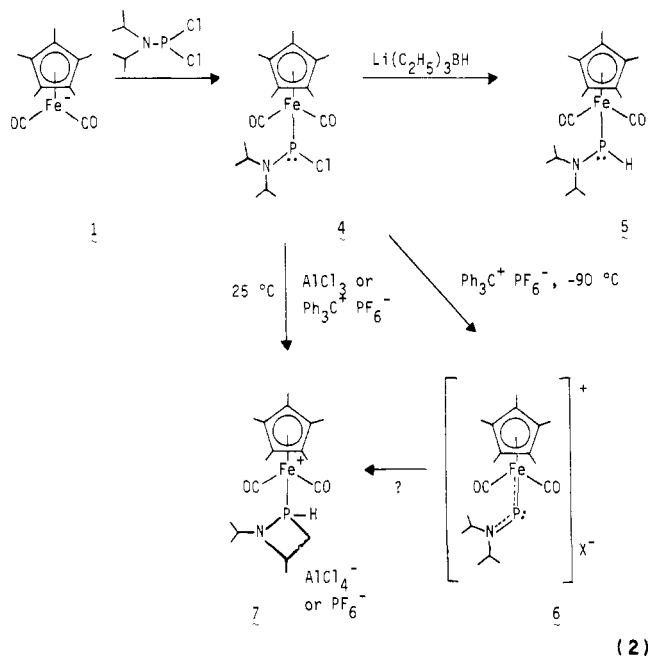
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phosphene **3** (>95% of theory; ³¹P NMR 492 ppm).¹ However, in the absence of any stable iron-phosphorus-bonded products, we decided to attempt the synthesis of a phosphinidene complex with a donor atom substituent. Donor atom substituents often dramatically stabilize complexes with metal-carbon double bonds.³

The reaction of **1** with $(i\text{-C}_3\text{H}_7)_2\text{NPCl}_2$ ⁷ in THF at -78 °C (eq 2) gave, after workup, benzene-soluble yellow-orange crystals of a compound whose microanalysis and mass spectral parent ion were consistent with the formulation $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{PCIN}(i\text{-C}_3\text{H}_7)_2)$ (**4**, 62%).⁸ The ³¹P NMR chemical shift, 346 ppm (THF), was similar to those observed for other

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- (7) Prepared from PCl_3 and $\text{HN}(i\text{-C}_3\text{H}_7)_2$ (2 equiv) in benzene by a modification of the procedure of: Ivanova, Z. M. *Zh. Obshch. Khim.* **1965**, *35*, 165.
- (8) Full characterization of this compound is provided in the supplementary material.



phosphide complexes with electron-withdrawing substituents.⁹ At temperatures ≤ -50 °C, **4** exhibited *four* CH₃ and *two* CH ¹H NMR and ¹³C NMR resonances, and two CO ¹³C NMR resonances. At higher temperatures, pairwise coalescence was observed; at 25 °C, only *one* CH₃ ¹H NMR resonance remained. This behavior may be rationalized by nitrogen and phosphorus atom inversions, coupled with phosphorus–nitrogen bond rotation.¹⁰

Additional support for the structure of **4** was provided by its reaction (THF, 25 °C) with Li(C₂H₅)₃BH (eq 2). Workup and sublimation gave the phosphide complex (η^5 -C₅Me₅)Fe(CO)₂(PHN(*i*-C₃H₇)₂) (**5**) in 49% yield. The presence of a phosphorus–hydrogen bond was clearly indicated by coupling in the ³¹P NMR (72 ppm, d, $J_{\text{PH}} = 166$ Hz) and ¹H NMR (δ 6.17, d, $J_{\text{HP}} = 167$ Hz) spectra (C₆D₆). Except for the higher field ³¹P NMR chemical shift, the spectroscopic features of **5** were very similar to those of **4**.⁸

The abstraction of Cl⁻ from **4** was attempted. Treatment of a toluene solution of **4** with AlCl₃ rapidly gave a yellow powder. The ²⁷Al NMR spectrum of this material (CH₂Cl₂) indicated the presence of an AlCl₄⁻ anion (102.74 ppm, $w_{1/2} < 23$ Hz),¹¹ and the IR $\nu_{\text{C=O}}$ suggested an iron cation.⁸ However, the hoped-for phosphinidene structure [$(\eta^5$ -C₅Me₅)Fe(CO)₂(\rightarrow P \leftarrow N(*i*-C₃H₇)₂)]⁺AlCl₄⁻ (**6**·AlCl₄⁻) was readily excluded by the phosphorus–hydrogen bond evident from coupling in the ³¹P NMR (121 ppm, d, $J_{\text{PH}} = 439$ Hz) and ¹H NMR (δ 7.90 d, $J_{\text{HP}} = 437$ Hz) spectra (CH₂Cl₂/CD₂Cl₂). Furthermore, the ¹H and ¹³C NMR spectra clearly showed that one isopropyl group had reacted. On this basis, the product was assigned the isomeric cyclic structure [$(\eta^5$ -C₅Me₅)Fe(CO)₂(PHN(*i*-C₃H₇)(CH(CH₃)CH₂))]⁺AlCl₄⁻ (**7**·AlCl₄⁻, 60%; eq 2).⁸ Correct Al, Cl, and N (and reasonably good C, H) analyses were obtained for this material, but NMR and IR spectra indicated the presence of three components (two major and one very minor), the relative ratios of which were not appreciably affected by CH₂Cl₂/ether recrystallization. In accord with the presence of asymmetric carbon, phosphorus, and nitrogen atoms, these were assigned to diastereomers of **7**·AlCl₄⁻.

Since R₂P⁺ species are known to undergo C–H bond insertion^{2f,12} and exhibit extreme downfield ³¹P NMR chemical shifts,¹³ the reaction of **4** with AlCl₃ was monitored by ³¹P NMR in CD₂Cl₂ at –84 °C. The ³¹P NMR resonance of **4** was immediately (≤ 5 min) replaced by a weak 122 ppm resonance, tentatively assigned to **7**·AlCl₄⁻. No other ³¹P NMR resonances were visible in the range 0–1100 ppm. Hence we sought other conditions for the detection of phosphinidene complex **6**.

The abstraction of Cl⁻ from **4** was attempted with other reagents. When the reaction of **4** with Ph₃C⁺PF₆⁻ was monitored by ³¹P NMR at –90 °C, a downfield resonance at 954 ppm appeared immediately (≤ 5 min), together with resonances at 188 and 122 ppm. These signals remained unchanged over the course of 1.5 h at –90 °C and were integrated (with use of a long pulse delay) in a 1.6:1.1:1.0 ratio. The 954 ppm resonance was not proton coupled, but the 188 and 122 ppm resonances were, with J_{PH} of 20 and 447 Hz, respectively; the latter was assigned to one diastereomer of **7**·PF₆⁻. Above –68 °C, the 954 ppm resonance disappeared rapidly, but without the appearance of a new resonance or a marked increase in intensity of existing resonances. Finally, in a preparative-scale reaction, **4** was treated with Ph₃C⁺PF₆⁻ at room temperature. Complex **7**·PF₆⁻ was subsequently isolated from CH₂Cl₂/ether in 35% yield as a ca. 4:4:1 mixture of three diastereomers: ³¹P NMR (CD₂Cl₂, –30 °C) 184 ($J_{\text{PH}} = 459$ Hz), 152 ($J_{\text{PH}} = 456$ Hz), and 124 ($J_{\text{PH}} = 437$ Hz) ppm.⁸

We interpret the reactions of **4** with Ph₃C⁺PF₆⁻ and AlCl₃ as follows. First, we suggest that the 954 ppm ³¹P NMR resonance is due to phosphinidene complex **6**·PF₆⁻.¹⁴ This constitutes the first spectroscopic evidence for a phosphinidene complex of the type L_nM=PR. However, some **7** also forms at very low temperatures, and thus we cannot unequivocally determine whether **6** subsequently cyclizes to **7**. Both AlCl₃ and Ph₃C⁺PF₆⁻ can serve as one-electron oxidants.¹⁵ Hence, it is possible that some **7** might arise from radical byproducts and/or precursors to **6**. The presence of radical species could also account for the apparent lack of mass balance in our NMR-monitored reactions. Finally, the decomposition chemistry of **6** could also depend markedly upon solvent (e.g., CH₂Cl₂ vs. toluene) and temperature.

In summary, this study, together with those of Mathey,⁴ provides good evidence for the generation of metal phosphinidene complexes, L_nM=PR, as reaction intermediates. However, stable examples of this class of compounds are still lacking. Our results suggest that the use of yet more basic L_nM moieties, and “cyclization-resistant” phosphorus substituents, should be investigated.

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Registry No. 1, 59654-59-0; 2, 79074-00-3; 3, 79073-99-7; 4, 92220-44-5; 5, 92220-45-6; 6·PF₆⁻, 92220-47-8; 7·AlCl₄⁻, 92220-49-0; 7·PF₆⁻, 92220-50-3; (*i*-C₃H₇)₂NPCl₂, 921-26-6; Li(C₂H₅)₃BH, 22560-16-3; AlCl₃, 7446-70-0; Ph₃C⁺PF₆⁻, 437-17-2.

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Supplementary Material Available: Spectroscopic and physical characterization of 4, 5, and 7 (4 pages). Ordering information is given on any current masthead page.

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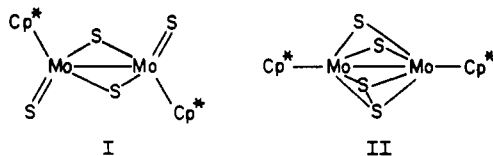
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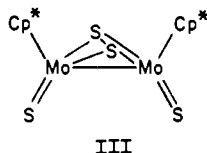
Photochemical Isomerization of $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ ($\text{Cp}^* = \eta^5\text{-(CH}_3)_5\text{C}_5\text{}$) to $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$ and $[\text{Cp}^*\text{MoS}]_2(\mu\text{-S}_2)$

Sir:

As part of our continuing study^{1,2} of the ligand-to-metal charge-transfer (LMCT) photochemistry of organometallic sulfide complexes, we investigated the reactivity of the $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ complex. This molecule is one of three known isomers with the formula $\text{Cp}^*_2\text{Mo}_2\text{S}_4$, the others being formulated as $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$ and $[\text{Cp}^*\text{MoS}]_2(\mu\text{-S}_2)$.³ The $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ and $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$ isomers have been structurally characterized, and their structures are shown as I and II, respectively.³ The $[\text{Cp}^*\text{MoS}]_2(\mu\text{-S}_2)$ complex has



not been structurally characterized, but the structure III has



been proposed on the basis of chemical reactivity.³ In this communication we report the stepwise photochemical interconversions of the three isomers.

Irradiation ($\lambda > 450$ nm) of $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ in chloroform solution (~ 2 mM) causes a color change from orange to green.⁴ An NMR spectrum of the green solution shows two new resonances in the Cp^* region at δ 2.21 and 2.03, corresponding to isomers II and III, respectively. In addition, monitoring the reaction by electronic absorption spectroscopy shows that the intense $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ band at 446 nm (Figure 1a) decreases in intensity while new bands appear at 620 and 790 nm (Figure 1b-d, Figure 2). Similar electronic spectral changes are observed in benzene, acetonitrile, and tetrahydrofuran solutions. Infrared spectroscopy is less in-

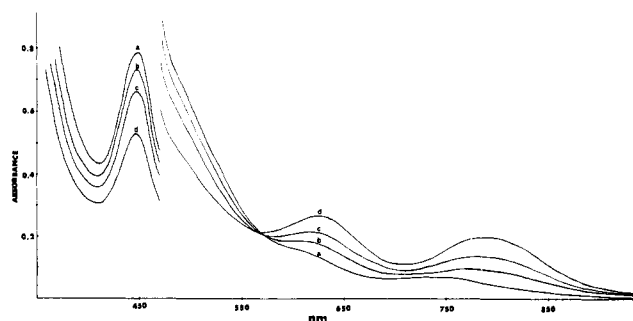


Figure 1. Electronic absorption spectral changes upon photolysis ($\lambda > 450$ nm) of $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ (I) in chloroform solution (a) before irradiation (0.26 mM), (b) after 2-min irradiation, (c) after 7-min irradiation, and (d) after 15-min irradiation (absorbance $\times 2$ at $\lambda < 470$ nm).

formative, but it shows a decrease in the $\nu(\text{Mo}=\text{S})$ band of the starting material at 486 cm^{-1} .³ A comparison of the spectral and color changes described above to the data in Table I shows that all of the changes are consistent with the photochemical conversion of isomer I to isomers II and III. The quantum yield of disappearance for isomer I ($\lambda = 436$ nm) in the reaction above is 1×10^{-3} .⁷

In order to determine which isomer results from the irradiation of isomer I, we synthesized isomers II and III^{3b} and irradiated each. The electronic spectrum of each isomer is shown in Figure 2. When II is irradiated ($\lambda > 450$ nm) in chloroform-*d*, the NMR spectral changes are consistent with the initial formation of III ($\Phi(\text{disappearance}, 436\text{ nm}) = 3 \times 10^{-3}$).⁸ Continued irradiation eventually yields small amounts of I. Isomer III initially yields I on irradiation ($\lambda > 450$ nm) ($\Phi(\text{appearance}, 436\text{ nm}) = 2 \times 10^{-3}$).⁹ Prolonged irradiation of the reaction solution eventually yields some of

- (4) All preparative and photochemical reactions were done under an argon or nitrogen atmosphere. Solvents were dried with the appropriate drying agent and distilled under nitrogen.⁵ Literature methods were used to synthesize isomers I,^{3a} II, and III.^{3b} Electronic absorption spectra were recorded on a Cary 17 spectrophotometer in 1-cm quartz cuvettes of ~ 3 -mL cell volume. ¹H NMR spectra were obtained on a Varian XL 200 or a Bruker WM 250 instrument. Infrared spectra were obtained on a Perkin-Elmer 983 spectrophotometer equipped with a Perkin-Elmer data station. A 200-W Oriel high-pressure mercury arc lamp was used for the photochemical experiments. Corning glass cutoff filters (3-72, $\lambda > 450$ nm; 3-70, $\lambda > 490$ nm; 2-61, $\lambda > 610$ nm; 3-68 + 7-39, $\lambda > 700$ nm) and a 436-nm interference filter from Edmund Scientific were used to isolate the wavelengths of irradiation. For quantum yield measurements, solutions were irradiated at room temperature in 1.0-cm quartz cells and were stirred during irradiation. Each isomer was irradiated at 436 nm, and the spectral change was monitored at 446 nm for I and III and at 800 nm for II. The lamp intensity was measured by Reinecke's salt actinometry.⁶ Photochemical experiments monitored by proton NMR or infrared were done as follows. (a) ¹H NMR: 1-2 mM solutions of each isomer in CDCl_3 were irradiated (directly in the NMR tube) in an ice-water bath for short time intervals (1-5 min). The spectrum was recorded after each irradiation. Typical irradiation times were 12 min for I, 25 min for II, and 14 min for III. (b) Infrared: A 2 mM solution of I in CHCl_3 was irradiated for 12 min in a 6 mm path length polyethylene cell.
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- (7) The photochemistry of I is wavelength dependent. When a 5.4×10^{-4} M solution of I in CHCl_3 is irradiated in the two lowest energy absorption bands ($\lambda > 700$ nm, ~ 2 h), there was a very slight decrease in the absorbance at 750 nm, but the bands due to isomer II did not appear. However, irradiation of I in CHCl_3 at wavelengths ranging from $\lambda > 610$ to $\lambda > 330$ nm leads to the efficient formation of II (~ 5 min; $\lambda > 330$ nm; ~ 15 min, $\lambda > 610$ nm).
- (8) The thermal conversion of isomer II to III requires stirring at 45°C for 3 days.^{3b} A control reaction showed that there is no thermal conversion of II to III under the conditions used in our photochemical experiment.⁴
- (9) The extinction coefficient of isomer III at 446 nm is approximately two-thirds that of isomer I (see Table I). Thus as III is irradiated and I grows in, the absorbance increases at 446 nm.

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