# Photon-, Reductant-, and Oxidant-Induced Substitution of a CO Ligand on *closo*-[$Cp^*_2Fe_3S_2(CO)_3$] ($Cp^* = \eta^5$-$C_5Me_5$)

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Substitution of CO in *closo*-[$Cp^*_2Fe_3S_2(CO)_3$] (**1**) by $PPh_3$ was accelerated upon photolysis or by treatment with reductant or oxidant to give mono($PPh_3$)-substituted clusters. In the redox-induced reaction, [**1**]$^-$ and [**1**]$^+$ were proposed as labile intermediates to substitution of CO.

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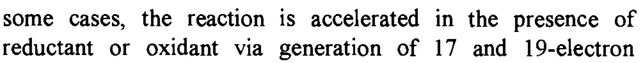
Ligand substitution reactions play an essential role in the catalytic and stoichiometric process.[1] It is usually achieved in the thermal or photochemical conditions. The conventional associative and dissociative mechanisms for such substitution consist of even-numbered 16 and 18-electron intermediates. In some cases, the reaction is accelerated in the presence of reductant or oxidant via generation of 17 and 19-electron species.[2] Their role is only beginning to be understood owing to general instability of the odd-numbered intermediates. To our knowledge, there are relatively limited studies on substitution reactions of transition-metal clusters via 17- and 19-electron intermediates,[3] although the reactivity of clusters has attracted considerable attention.[4] Recently, we reported the synthesis of *closo*-[$Cp^*_2Fe_3S_2(CO)_3$] (**1**) by the thermal reaction of [$Cp^*_2Fe_2(\mu_2$-$S_2)_2$] with iron carbonyls ($Cp^* = \eta^5$-$C_5Me_5$).[5] In this paper, first of all, we examined lability of a carbonyl ligand on cluster **1** in the thermal or photochemical conditions. Moreover, we wish to describe an accelerated substitution of a carbonyl ligand on **1** by $PPh_3$ in the presence of reductant or oxidant. In the reaction, we propose mechanisms involving anionic [**1**]$^-$ and cationic [**1**]$^+$ clusters as labile intermediates, respectively.

First of all, in an attempt to investigate ligand lability of CO on [$Cp^*_2Fe_3S_2(CO)_3$] (**1**), we explored the thermal reaction of **1** with 1 equiv. $PPh_3$ in toluene. The reaction was monitored by the TLC analysis. No reaction was confirmed within 1 day at room temperature. Upon refluxing the solution for 150 min, cluster **1** was converted to mono-substituted [$Cp^*_2Fe_3S_2(CO)_2(PPh_3)$] (**2**) in 56% yield (eq 1). Recrystallization of **2** from $CH_2Cl_2$-hexane afforded analytically pure brown crystals of **2**.[6] The elemental analysis and mass spectral data support the formula [$Cp^*_2Fe_3S_2(CO)_2(PPh_3)$] (**2**). The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 74.7 ppm assigned to a $PPh_3$ ligand. In the $^1H$ NMR spectrum, the signal of two $C_5Me_5$ ligands appears equivalently at 1.39 ppm. The $^{13}C\{^1H\}$ NMR spectrum contains a doublet signal at 211.1 ppm ($J_{CP}$ = 20 Hz) assignable to two chemically equivalent CO ligands. These spectroscopic features imply that phosphorus of the $PPh_3$ ligand is located on the plane consisted of two S atoms and one Fe atom having two CO. The conformation effectively reduces the steric hindrance between two Cp* and $PPh_3$ ligands. Thermolysis of **1** with excess $PPh_3$ in toluene also gave only mono-substituted **2** due to the electronic and steric reasons: Phosphines are known to be much more electron-donating than carbonyls. Thus, the remaining carbonyl ligands in **2** benefit from increased back donation and are more tightly bound to the iron than those in **1**. Furthermore, the coordination sphere around the $Fe(CO)_2(PPh_3)$ fragment is so crowded that there is not enough space for coordination of the additional $PPh_3$ ligand.



**1** **2** 56%

Then, substitution reaction of **1** by $PPh_3$ was also carried out in the photochemical conditions. Photolysis of **1** in the presence of 1 equiv. $PPh_3$ in hexane for 140 min gave **2** in 43% isolated yield. Irradiation of **2** with excess $PPh_3$ in benzene-$d_6$ resulted in decomposition of **2**. Formation of bis- and tris-substituted cluster was not observed. The most reasonable mechanism for the photo-reaction involves the photo-induced promotion of a $d_\pi$ electron into a $d_\sigma$ level corresponding to the M-CO σ* orbital,[7] so that dissociation of CO is accelerated to give a 16-electron moiety.

Especially, in the mononuclear complex, it was reported that substitution reactions were often accelerated by reductant. Sodium benzophenone ketyl[8] was used as a reductant (eq 2). To a THF solution (3 mL) of **1** (0.082 mmol) and $PPh_3$ (0.088 mmol) was added a THF solution of sodium benzophenone ketyl at room temperature in the course of 1 h with stirring and the reaction was monitored by TLC. Cluster **1** disappeared after the addition of 2 equiv. sodium benzophenone ketyl solution (0.17 mmol). Then, volatiles were removed in *vacuo* and the residue was subjected to a silica-gel column chromatography (eluent; hexane : toluene = 2 : 1). The brown fraction was collected and concentrated under reduced pressure to give **2** in 73% yield. Formation of bis- or tris-substituted cluster was not observed at all. Apparently, substitution of a CO ligand in **1** was dramatically accelerated by treatment with sodium benzophenone ketyl as the reductant.[9]

$$\mathbf{1} + PPh_3 \xrightarrow[\text{THF, r. t., 60 min}]{\text{sodium benzophenone ketyl}} \underset{73\%}{\mathbf{2}} \qquad (2)$$

Substitution reaction was also known to be accelerated by oxidation. [$Cp_2Fe$]($PF_6$) was employed as oxidant. To a $CH_2Cl_2$ (5 mL) solution of **1** (0.085 mmol) and $PPh_3$ (0.088 mmol) was added [$Cp_2Fe$]($PF_6$) (0.097 mmol). The mixture was stirred at room temperature for 30 min and volatiles were removed under reduced pressure. The brown residue was washed with water and hexane and extracted with acetnitrile. Removal of the solvent from the extract gave [$Cp^*_2Fe_3S_2(CO)_2(PPh_3)$]($PF_6$) ([**2**]($PF_6$)) in 98% yield (eq 3).[10] Recrystallization of [**2**]($PF_6$) from $CH_3CN$-$Et_2O$ afforded brown crystals suitable for X-ray crystal structure analysis.[11] Crystal structure of the cationic moiety in [**2**]($PF_6$) was shown in Figure 1. Like **1**, the $\{Fe_3S_2\}$ core of [**2**]($PF_6$)

$$\mathbf{1} + PPh_3 \xrightarrow[CH_2Cl_2,\ \text{r.t., 30 min}]{[Cp_2Fe](PF_6)} \underset{98\%}{[\mathbf{2}](PF_6)} \qquad (3)$$

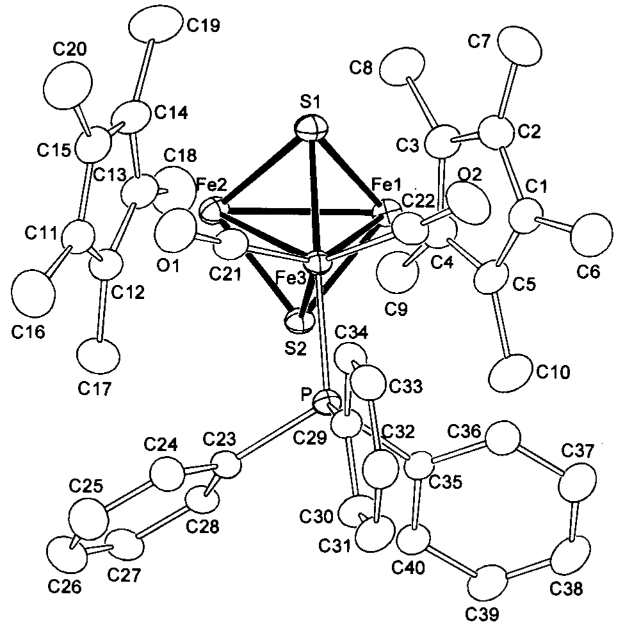
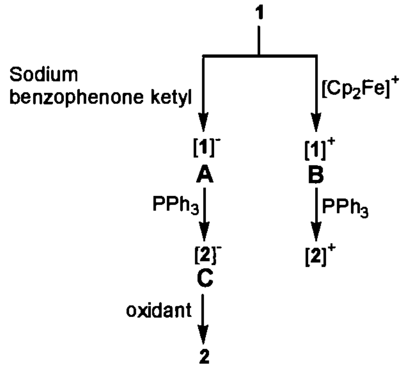


**Figure 1.** Crystal structure of the cationic moiety in $[Cp^*_2Fe_3S_2(CO)_2(PPh_3)](PF_6)$ ($[\mathbf{2}](PF_6)$). Selected bond lengths (Å) and bond angles (deg); Fel-Fe2 2.663(1), Fel-Fe3 2.622(1), Fe2-Fe3 2.596(1), Fel-S1 2.166(1), Fel-S2 2.141(2), Fe2-S1 2.153(1), Fe2-S2 2.145(1), Fe3-S1 2.291(1), Fe3-S2 2.245(1); Fe2-Fel-Fe3 58.52(2), Fel-Fe2-Fe3 59.80(2), Fel-Fe3-Fe2 61.38(2), S1-Fel-S2 94.01(5), S1-Fe2-S2 94.25(5), S1-Fe3-S2 87.97(4).

adopts a trigonal bipyramidal geometry where three iron atoms are bicapped by two $\mu_3$-S ligands. The three Fe-Fe interatomic distances Fe(1)-Fe(2) [2.663(1) Å], Fe(2)-Fe(3) [2.596(1) Å], Fe(1)-Fe(3) [2.622(1) Å] are lying in the normal range expected for the Fe-Fe single bond. However, they were somewhat shorter than those in **1** [2.704(1), 2.601(1), 2.648(1) Å] due to the increasing total bond order (0.5) of Fe-Fe via one electron oxidation. Each of the Fel and Fe2 atoms has an Cp* ligand, and the Fe3 atom has two carbonyl and one $PPh_3$ ligands. Two Cp* ligands adopts a staggered configuration due to the steric repulsion between them (C9···C18 3.661(10) Å). The phosphorous atom of the $PPh_3$ ligand is located on the plane of S1-Fe3-S2 to reduce the steric hindrance between two Cp* and one $PPh_3$ ligands (C6···C36 3.758(9) Å, C17···C28 3.744(7) Å).



Scheme 1.

Possible mechanisms for the substitution reactions in eqs 2 and 3 were illustrated in Scheme 1. The mechanisms involve a monoanionic cluster $[Cp^*_2Fe_3S_2(CO)_3]^-$ (**A**) and a monocationic cluster $[Cp^*_2Fe_3S_2(CO)_3]^+$ (**B**). The cyclic voltammogram of **1** exhibits one reversible and one quasi-reversible one-electron redox at +0.32 and −1.49 V vs SCE, respectively, in $CH_2Cl_2$ solution containing 0.1 M $n$-$Bu_4NBF_4$ as supporting electrolyte. The resting potential was around −0.15 V vs SCE. These results indicate the existence of **A** and **B**. In the case of reductant-induced substitution, the intermediate **A** results from reduction of **1**. As **A** possesses an electron in Fe-CO $\sigma^*$ antibonding orbital, it causes substitution of CO by $PPh_3$ to give **C**, followed by oxidation to give **2**. The oxidant is tentatively assumed to be **1** itself or $O_2$. In the case of oxidant-promoted substitution, cluster **1** loses an electron from M-CO $\pi$ bonding orbital to give **B**. Intermediate **B** undergoes substitutuion of CO by $PPh_3$ to give $[\mathbf{2}]^+$.

This paper revealed that carbonyl substitution in cluster **1** was accelerated upon photolysis or by treatment with reductant or oxidant. In the reductant- and oxidant-induced substitution reactions, anionic $[Cp^*_2Fe_3S_2(CO)_3]^-$ (**A**) and cationic $[Cp^*_2Fe_3S_2(CO)_3]^+$ (**B**) intermediates were proposed as key intermediates, respectively. Isolation of **A** and **B** is now in progress.

**References and notes**

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6 Data for **2**: $^1$H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 30 H, Cp*), 7.31, 7.50 (m, 15H, Ph). $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 11.3 ($C_5(CH_3)_5$), 89.3 ($C_5(CH_3)_5$), 127.8 (d, $^4J_{CP}$ = 9.4 Hz, $m$-Ph), 129.3 (d, $^5J_{CP}$ = 2.1 Hz, $p$-Ph), 133.4 (d, $^3J_{CP}$ = 9.8 Hz, $o$-Ph), 138.9 (d, $^2J_{CP}$ = 41 Hz, *ipso*-Ph), 211.1 (d, $^2J_{CP}$ = 20 Hz, CO). $^{31}$P NMR (121.5 MHz, $CDCl_3$) δ 74.7. IR (KBr pellet) $\tilde{\nu}$/cm$^{-1}$ 1938, 1894 ($\nu_{CO}$). MS (FAB, Xe, $m$-nitrobenzyl alcohol matrix) $m/z$ 820 (19, $M^+$), 764 (100, $M^+$−2CO). Anal. Found: C, 58.17; H, 5.41%. Calcd for $C_{40}H_{45}Fe_3O_2PS_2$: C, 58.56; H, 5.53%.
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8 THF solution of sodium benzophenone ketyl was prepared by refluxing benzophenone (173 mg, 0.949 mmol) and sodium (100 mg, 4.3 mmol) in THF (20 mL) for 75 min before use.
9 The reaction of **1** with $PPh_3$ in THF was carried out at room temperature. The TLC analysis revealed that **1** was inert to substitution of CO in THF at room temperature in the absence of reductant.
10 Data for $[\mathbf{2}](PF_6)$: $^1$H NMR (300 MHz, $CDCl_3$) δ -9.88 (s, 30 H, Cp*, $W_{1/2}$ = 16 Hz), 6.01, 6.53, 7.50 (br. m, 15H, Ph). $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 16.3 ($C_5(CH_3)_5$), 125.9, 133.7, 134.6, 147.1 (Ph). $^{31}$P NMR (121.5 MHz, $CDCl_3$) δ -4.0 (br., $PPh_3$, $W_{1/2}$ = 40 Hz), -143.9 (sep, $^1J_{PF}$ = 288 Hz, $PF_6^-$). IR (KBr pellet) $\tilde{\nu}$/cm$^{-1}$ 1984, 1938 (s, $\nu_{CO}$), 839 (s, $\nu_{P\text{-}F}$), 557 (m, $\delta_{P\text{-}F}$). MS (FAB, Xe, $m$-nitrobenzyl alcohol matrix) $m/z$ 820 (52, $M^+$), 764 (100, $M^+$−2CO). Anal. Found: C, 50.07; H, 4.60%. Calcd for $C_{40}H_{45}Fe_3O_2PS_2$: C, 49.77; H, 4.70%.
11 Crystallographic data for $[\mathbf{2}](PF_6)$: $C_{40}H_{45}Fe_3O_2PS_2$, $M$ = 965.41, *monoclinic*, space group $P2_1/a$ (variant No.14), $a$ = 19.768(3) Å, $b$ = 18.698(2) Å, $c$ = 11.950(2) Å, $\beta$ = 107.98(2)°, $V$ = 4202(1) Å$^3$, $Z$ = 4, $D_c$ = 1.53 gcm$^{-3}$, $\mu$(Mo-K$\alpha$) = 12.83 cm$^{-1}$. The structure was solved by direct methods and refined by block diagonal least-squares methods using UNICS III. Hydrogen atoms on the phenyl groups were caluculated and fixed. All non-hydrogen atoms were refined anisotropically. 12717 unique reflections were collected by $\omega$-2$\theta$ scan in the range 3°<2$\theta$<60°, with 8847 ($|F_o| > 3\sigma(F_o)$) used in calculations. The final reliability factors converged $R$ = 0.057 and $R_w$ = 0.091.