# **Inorganic Chemistry**

# Ligand-Based Reactivity of Oxygenation and Alkylation in Cobalt Complexes Binding with (Thiolato)phosphine Derivatives

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Cite This: https://dx.doi.org/10.1021/acs.inorgchem.9b03740

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ABSTRACT: In our efforts to understand the nature of metal thiolates, we have explored the chemistry of cobalt ion supported by (thiolato)phosphine ligand derivatives. Herein, we synthesized and characterized a square-planar Co<sup>II</sup> complex binding with a bidentate (thiolato)phosphine ligand,  $Co(PS1'')_2$  (1)  $([PS1'']^- = [P (Ph)_2(C_6H_3-3-SiMe_3-2-S)]^{-}$ ). The complex activates  $O_2$  to form a ligand-based oxygenation product,  $Co(OPS1'')_2$  (2) ([OPS1'']<sup>-</sup> = [PO(Ph)<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>-3-SiMe<sub>3</sub>-2-S)]<sup>-</sup>). In addition, an octahedral Co<sup>III</sup> complex with a tridentate bis(thiolato)phosphine ligand, [NEt<sub>4</sub>][Co- $(PS2^*)_2$ ] (3) ([PS2^\*]^2 = [P(Ph)(C\_6H\_3-3-Ph-2-S)\_2]^2), was obtained. Compound 3 cleaves the C-Cl bond in dichloromethane via an S-based nucleophilic attack to generate a chloromethyl thioether group. Two isomeric products, [Co(PS2\*)(PSS<sup>CH<sub>2</sub>Cl\*</sup>)] (4 and 4')  $([PSS^{CH_2Cl_*}]^- = [P(Ph)(C_6H_3-3-Ph-2-S)(C_6H_3-3-Ph-2-SCH_2Cl)]^-),$ were isolated and fully characterized. Both transformations, oxygenation of a Co<sup>II</sup>-bound phosphine donor in 1 and alkylation of a Co<sup>III</sup>bound thiolate in 3, were monitored by spectroscopic methods. These



s Supporting Information

reaction products were isolated and fully characterized. Density functional theory (DFT, the B3LYP functional) calculations were performed to understand the electronic structure of 1 as well as the pathway of its transformation to 2.

# INTRODUCTION

Cobalt ion plays essential roles in several metalloproteins.<sup>1</sup> One such example is cobalt nitrile hydratase, which contains a low-spin Co<sup>III</sup> ion in its active site and catalyzes the conversion of nitriles to amides. The metal center binds to two deprotonated amide nitrogen atoms and three cysteine thiolates, in which the two sulfur atoms are oxidized to sulfenate (SO) and sulfinate (SO<sub>2</sub>).<sup>2</sup> Synthetic analogues of this enzyme have been investigated extensively in the effort to understand the nature of the catalytic site.<sup>3</sup> There is no cobalt containing protein found in nature that binds or activates dioxygen. However, cobalt-substituted hemoglobin has been shown to bind dioxygen reversibly.<sup>4</sup> In addition, cobaltsubstituted dioxygenases display activities similar to native enzymes. Recently, it was found that the Fe<sup>II</sup> center in homoprotocatechuate 2,3-dioxygenase (HPCD) can be replaced by a Co<sup>II</sup> ion with comparable activity. The O<sub>2</sub> adduct of the Co<sup>II</sup> substituted enzyme was characterized as a low-spin Co<sup>III</sup>-superoxide species.<sup>5</sup> Thus, O<sub>2</sub>-dependent chemistry of cobalt complexes has been developed to understand the whole paradigm of dioxygen activation by metalloproteins.6

Metal complexes with noninnocent ligands have offered a diverse chemistry where ligands are not just considered as supporting roles for tuning the steric and electronic feature of metal centers.<sup>7</sup> Instead, the reactivity of metal complexes might be based on ligands that are involved in redox change or chemical tranformation.<sup>8</sup> For instance, metal thiolates might display various sulfur-based reactivity such as the formation of disulfide,<sup>9</sup> the generation of thiyl radical,<sup>10</sup> oxygenation,<sup>11</sup> and alkylation.<sup>12</sup>

The nucleophilic nature of metal bound thiolate has been emphasized, partially due to the finding of thiolate methylation in Zn<sup>II</sup>-dependent proteins.<sup>13</sup> The reactivity is based on a hypothesis of a four-electron destabilizing interaction between sulfur lone pairs and fulfilled metal d orbitals.<sup>14</sup> This chemistry has been well established in many synthetic metal thiolates.<sup>12,15</sup> However, examples are relatively rare showing strong

Received: December 26, 2019



nucleophilicity of metal bound thiolate that activates a weak electrophile such as dichloromethane. They include a *bis*(sulfide)dimolybdenum and a *bis*(thiolate)diiron ligated by cyclopentadienyl ligands.<sup>16</sup> Pd<sup>II</sup>, Ru<sup>II</sup>, and V<sup>III</sup> complexes binding with (thiolato)phosphine ligand derivatives also show the reactivity of dichloromethane activation.<sup>12,15c,17</sup> In addition, a Co<sup>III</sup> center with *bis*-axial cyanide coordination was able to induce in-plane thiolato donors toward dichloromethane.<sup>18</sup>

In cobalt thiolate complexes, several examples of ligandbased reactivity have been reported. They include the interconversion occurring between Co<sup>II</sup> disulfide and Co<sup>III</sup> thiolate.<sup>19</sup> Remarkably, a square-planar Co<sup>II</sup> thiolate displays reactivity toward S-alkylation with CH<sub>3</sub>I.<sup>20</sup> Sequential oxidations of cobalt bound thiolate to sulfenate and sulfinate have been demonstrated in several model complexes.<sup>3c,21</sup> These studies provide implications for post-translational modification of cysteinyl thiolate in cobalt nitrile hydratases.

(Thiolato)phosphine ligand derivatives have shown a noninnocent nature in several well-defined metal complexes.<sup>12,15c,22</sup> From this perspective, the reactivity of cobalt complexes with several (thiolato)phosphine derivatives were explored (Chart 1). In this particular study, a four-coordinate



square-planar Co<sup>II</sup> complex, Co(PS1")<sub>2</sub> (1) ([PS1"]<sup>-</sup> =  $[P(Ph)_2(C_6H_3-3-SiMe_3-2-S)]^-$ ), and an octahedral Co<sup>III</sup> thiolate complex,  $[NEt_4][Co(PS2^*)_2]$  (3) ( $[PS2^*]^{2^-} = [P(Ph)(C_6H_3-3-Ph-2-S)_2]^{2^-}$ ), were isolated and characterized. Complex 1 activates O<sub>2</sub>, leading to a ligand-based oxygenation where metal-bound phosphine donor converts to phosphine oxide, as shown in Scheme 1. Complex 3 showed a strong nucleophilicity of bound thiolate that activates the C–Cl bond in dichloromethane, as shown in Scheme 2.



Scheme 2

### RESULTS AND DISCUSSION

**Syntheses and Characterization of [Co(PS1'')\_2] (1).** A square-planar Co<sup>II</sup> thiolate complex,  $[Co(PS1'')_2]$  (1), was obtained from a reaction of CoCl<sub>2</sub> and  $[PS1'']^-$  ( $[PS1'']^- = [P(Ph)_2(C_6H_3-3-SiMe_3-2-S)]^-$ ) in a 1:2 ratio. The obtained orange precipitate was recrystallized from dichloromethane and methanol to give a crystalline solid of 1 (79% yield). The elemental analysis is consistent with the formula of Co(PS1'')<sub>2</sub> (1). The ESI-MS data gives a set of peaks at 789.13 m/z, and its isotope pattern is in agreement with the calculated one of 1 (Figure S1). The structure resolved from X-ray crystallographic data contains a four-coordinate Co<sup>II</sup> ion superimposed with a crystallographic inversion center (Figure 1). The metal ion



Figure 1. Thermal ellipsoid plots (35% probability) of 1 (A) and 3-2CH<sub>3</sub>OH·0.5THF (B). The H atoms, cation, and solvated molecules are omitted for clarity.

binds to two bidentate PS1" ligands and has a square-planar geometry with a  $\tau_4$  value of 0.00, where the  $\tau_4$  value is an index of distortion between  $T_d$  and  $D_{4h}$ , ranging from 1.00 to 0.00 from a tetrahedron to a square planar, respectively.<sup>23</sup> Two phosphine or two thiolato donors are *trans* to each other. The Co<sup>II</sup>–S distance is 2.1518(7) Å, similar to those in a reported square-planar Co<sup>II</sup> thiolate (Co–S<sub>ave</sub> = 2.168 Å).<sup>20</sup>

Complex 1 dissolved in  $CH_2Cl_2$  showed an orange color. The electronic spectrum of complex 1 displays three intense bands at 391 nm ( $\varepsilon = 6.48 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), 427 nm ( $\varepsilon = 5.08 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), and 520 nm ( $\varepsilon = 4.81 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), likely associated with charge-transfer transition (Figure S2). A weaker band appears at 822 nm (7.28  $\times 10^1 \text{ M}^{-1}\text{cm}^{-1}$ ) might be attribited to d-d transition. The noninnocent nature of (benzenethiolato)phosphine derivatives was found in vanadium and ruthium complexes, where the electronic structures of metal-thiyl radical species were also considered.<sup>10a,24</sup> A characteristic intense band appearing at the NIR region for the reported metal thiyl radical species is absent in complex 1, indicating the electronic structure of 1 should be viewed as a



https://dx.doi.org/10.1021/acs.inorgchem.9b03740 Inorg. Chem. XXXX, XXX, XXX–XXX

Co(II)-thiolate species rather than a Co(I)-thivl radical species.<sup>10a,24</sup> The calculation data is in agreement with the findings (vide infra). The magnetic data of 1 was measured with a SQUID magnetometer in a 1 T applied magnetic field and at a temperature range of 1.8-300 K (Figure S3). The obtained  $\mu$  value of 1.81  $\mu_{\rm B}$  at 50 K and 2.07  $\mu_{\rm B}$  at 300 K is close to the spin-only value for a ground state S = 1/2 (1.73)  $\mu_{\rm R}$ ), indicating a low-spin d<sup>7</sup> configuration present in a squareplanar geometry. The <sup>1</sup>H NMR spectrum gave resonance peaks at the paramagnetic region (23.73 and -18.88 ppm) associated with three protons in benzenethiolate of the PS1" ligand (Figure S4). The X-band EPR spectra of 1 was measured at 77 K in 2-MeTHF (Figure S5). It displays rhombic signals with a large anisotropy in g values, which is a characteristic feature for square-planar low-spin Co(II) species.<sup>25</sup> The fits gave the parameters with g values of 2.9, 1.98, and 1.975 and A values of 220, 30, and 10 MHz, respectively. The pattern of  $g_1 > g_2 \sim g_3$ with a  $g_3$  value less than 2 is an indication of having an unpaired electron in a  $d_{vz}$  orbital rather than a  $d_z^2$  orbital.<sup>26</sup> The finding is further confirmed by density functional theory (DFT) calculations (vide infra).

Four-coordinate Co<sup>II</sup> complexes are mostly stabilized in a tetrahedral geometry; complexes with a square-planar structure are relatively few. Where a square-planar geometry is found, its underlying structure is determined by different ligand substituents or through a second coordination sphere interaction.<sup>25c,27</sup> In Co<sup>II</sup> thiolate complexes, most geometries are also tetrahedral.<sup>28</sup> Precisely three examples with a squareplanar configuration exist in the literature: Co<sup>II</sup>L where L is a bipyridine-*bis*(thiolato) ligand;<sup>20</sup> bis(maleonitrile-dithiolato)-Co<sup>II</sup>;<sup>29</sup> bis(dithioacetylacetonato)Co<sup>II</sup> complexes.<sup>30</sup> The structure of a zinc(II) complex with two PS1" ligands,  $[Zn(PS1")_2]$ , was reported in the literature.<sup>31</sup> It has a tetrahedral geometry, further implying that an unusual square-planar geometry adopted in 1 is not attributed to the ligand constrain or steric effect from a bulky trimethylsilyl substituent in the PS1" ligand. Density functional theory (DFT, the B3LYP functional) calculations were performed to provide more insights for interpreting the unusual geometry adopted in 1 as well as have an understanding of its electronic structure. Our calculations show that 1 has a doublet ground state with a square-planar geometry around Co. The only unpaired electron is localized at the metal center (spin density = 1.15 lel, Mulliken analysis), indicating that the electronic structure of 1 is  $\text{Co}^{2+}[(\text{PS1}'')_2]^{2-1}$ rather than  $\operatorname{Co}^{1+}[(\operatorname{PS1}'')_2]^{\bullet 1-}$ . In contrast, the quartet state of 1 adopts a tetrahedral conformation and is 8.6 kcal/mol higher in energy with most of its three unpaired electrons localized at Co (spin density = 2.63 lel). The electron spin-density plots for both configurations are shown in Figures 2 and S6, respectively. Furthermore, a single point calculation based on the optimized structure of the pure doublet state was performed to obtain a broken-symmetry doublet state with two  $\alpha$  unpaired electrons localized at Co and one  $\beta$  unpaired electron localized on the ligand (Figure S7). However, we find that this broken-symmetry doublet state is 30.0 kcal/mol higher in energy than the pure doublet state. Importantly, the optimization of this broken-symmetry doublet state led to the pure doublet state. These calculations indicate that the supporting ligand prefers to be innocent and Co prefers to have a +2 oxidation state.

**Oxygenation of Bound Phosphine Donor in**  $[Co^{II}(PS1'')_2]$  (1). The addition of dioxygen to a  $CH_2Cl_2$  solution of 1 at room temperature causes a slow color change



Figure 2. Electron spin-density plot of 1 in a doublet state with a square-planar geometry. Top view (left); side view (right).

from orange to bluish green. This solution was layered with methanol, and a navy blue crystalline solid of  $[Co^{II}(OPS1'')]_2$ (2)  $([OPS1'']^- = [OP(Ph)_2(C_6H_3-3-SiMe_3-2-S)]^-)$  was precipitated (93% yield) (Scheme 1). Alternatively, a synthetic method for generating complex 2 can be completed through the reaction of CoCl<sub>2</sub> and Li[OPS1"] in methanol. The solvent was removed from the reaction mixture, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> followed by layering CH<sub>3</sub>OH. The crystalline solid of complex 2 was produced at 90% yield (based on CoCl<sub>2</sub>). The elemental analysis is consistent with the molecular formula of 2. The ESI-MS data displays a set of peaks at 821.12  $m/z_1$  and its isotope pattern is in agreement with the calculated one of 2 (Figure S8). The X-ray crystallographic structure of complex 2 was reported previously in the literature,<sup>32</sup> where crystals were obtained by electrochemical oxidation of a sacrificial cobalt anode in the presence of the  $[OPS1'']^-$  ligand solution. The analogue of 2,  $Co^{II}(OPS1)_2$  ([OPS1]<sup>-</sup> = [OP(Ph)\_2(C\_6H\_4-2-S)]<sup>-</sup>, obtained from a reaction of  $CoCl_2$  with PS1 ligand ([PS1]<sup>-</sup> =  $[P(Ph)_2(C_6H_4-2-S)]^-)$  was also reported.<sup>33</sup> In both reported works, only X-ray structures were described and other physical properties were not investigated. The structural parameters of complex 2 that we have obtained are similar to those previously reported.<sup>32</sup> According to the data, one asymmetric unit contains two molecules and each molecule has a distorted tetrahedral Co<sup>II</sup> center formed from bonds with two bidentate OPS1" ligands with  $\tau_4$  values of 0.77 and 0.81, respectively. The average Co-S and Co-O bond distances are 2.276 and 1.976 Å, respectively. The Co-S distances are approximately 0.1 Å longer than those in complex 1. The magnetic data of 2 measured by a SQUID magnetometer gave  $\mu$  values of 4.11  $\mu_{\rm B}$ that is slightly higher than the spin-only value (3.87  $\mu_{\rm B}$ ) for a configuration with a ground state S = 3/2, likely due to orbital contribution (Figure S9). Complex 2 gives no EPR signal at room temperature and 77 K, likely due to the fast spin-lattice relaxation.<sup>34</sup> However, it gives signals at 4 K with g = 4.80, 2.75, and 2.01, implying a S = 3/2 configuration of the Co(II) center (Figure S10). The <sup>1</sup>H NMR spectrum taken in  $CD_2Cl_2$ gave paramagnetic shifts at 43.06, 33.63, and -13.50 ppm, associated with three protons of the benzenthiolato group in 2 (Figure S11).

The isolation of complex 2 by the reaction of 1 with dioxygen unequivocally indicates that the square-planar  $Co^{II}$  center in 1 activates dioxygen to form the ligand oxygenation product, OPS1". The reaction can be monitored by UV–vis–NIR and NMR spectroscopies. The spectrum of 1 was taken every hour for a 18 h period in a dioxygen atmosphere. As shown in Figure 3, the spectrum gradually changed to the one similar to that of complex 2 (Figure 3, inset). Two isosbestic



**Figure 3.** Variation of the UV–vis–NIR spectrum of  $[Co(PS1'')_2]$ (1) in CH<sub>2</sub>Cl<sub>2</sub> (1.3 × 10<sup>-4</sup> M) in a O<sub>2</sub> atmosphere. The spectrum was taken over an 18 h period: initial (red line) and final (blue line) spectra. Inset: The UV–vis–NIR spectrum of  $[Co(OPS1'')_2]$  (2) in CH<sub>2</sub>Cl<sub>2</sub>.

points at 378 and 560 nm were observed, implying no detectable intermediates. According to the absorbance of the final spectrum, the formation yield of 2 is nearly quantitative (~95%). In addition, the transformation is also clearly evidenced by following the reaction with <sup>1</sup>H NMR measurements (Figure S12). The spectrum taken under an  $O_2$  atmosphere showed the characteristic peaks of 1 at 23.73 and -18.88 ppm that gradually disappeared as well as the appearance of peaks at 43.06, 33.63, and -13.50 ppm (Figure S12A). In addition, the peaks at 0 to -10 ppm associated with trimethylsilane groups of ligands display the same growth and decline during the reaction (Figure S12B).

Isotopic labeling studies were used to understand the path of  $O_2$  addition to complex 1. The reaction with a mixture of  ${}^{16}O_2$ 

and <sup>18</sup>O<sub>2</sub> in a 1:1 ratio was monitored by ESI-MS. As shown in Figure S13, [Co(PS1'')(OPS1'')] formed and then disappeared, followed by the formation of the product,  $[Co(OPS1'')_2]$ . The analysis of isotope distribution of the intermediate species is consistent with the theoretic pattern of  $[1 + {}^{16}O]$  and  $[1 + {}^{18}O]$  in a 50:50 ratio. The composition for the final product agrees with the theoretic pattern of  $[1 + {}^{16}O]$ ,  $[1 + {}^{216}O]$ , and  $[1 + {}^{218}O]$  in a 50:25:25 ratio. The observation implies that the addition of the O atom is stepwise and likely involves an intermolecular path. The DFT calculation was performed to interpret this finding (vide infra).

The addition of  $O_2$  to the solution of 1 does not cause an instant color change between room temperature and -40 °C. However, the solution changed to a deep greenish-brown immediately when the temperature progressed down to -80°C. While the temperature was raised, complex 1 was recovered. The process was reversible and recorded by UVvis-NIR spectra (Figure S14). It has been reported in some Co(II) complexes that  $O_2$  coordination is thermodynamically unfavorable and often only observed at a very low temperature.<sup>6d,35</sup> This transit intermediate observed at low temperature is likely associated with the O2 adduct of 1,  $[Co(PS1'')_2(O_2)]$ , as found in many other cobalt systems.<sup>6d,35,36</sup> The X-band EPR measurements were performed at 77 K to characterize this transit intermediate (Figure S15). The spectrum of complex 1 with the addition of dioxygen in frozen 2-MeTHF display a S = 1/2 signal with resolved hyperfine coupling splitting to <sup>59</sup>Co and <sup>31</sup>P. The best fit gave parameters of  $g_1 = 2.036$ ,  $g_2 = 2.018$ , and  $g_3 = 2.010$  ( $|A_1| = 38$ MHz,  $|A_2| = 13$  MHz,  $|A_3| = 56$  MHz for <sup>59</sup>Co;  $|A_1| = 10$  MHz,  $|A_3| = 10$   $A_2$  = 21 MHz,  $|A_3|$  = 26 MHz for <sup>31</sup>P). A small magnetic anisotropy observed in the spectrum compared to the data of 1 clearly indicates an  $O_2$  interaction to the Co(II) center, which produces an effective axial ligand field.<sup>37</sup> Furthermore, the magnitude of <sup>59</sup>Co hyperfine coupling constants are relatively



Figure 4. DFT calculations for pathways of 1 reacting with  $O_2$  to form 2. The ground state multiplicity for each stationary point along the pathway is marked as D for doublet states, Q for quartet states, and Qui for quintet states.

small, implying that an unpaired electron density mainly localizes in the bound  $O_2^-$  moiety. Thus, the electronic structure of the  $O_2$  adduct of 1,  $[Co(PS1'')_2(O_2)]$ , should be considered as a Co(III)-superoxide species.<sup>5b,6d,35,38</sup>

To understand whether the oxidation process of phosphine donor to phosphine oxide in 1 is mediated by the Co<sup>II</sup> center, the reactivity of Zn<sup>II</sup> analogue with dioxygen was explored.  $Zn^{II}(PS1'')_2$  and  $Zn^{II}(OPS1'')_2$  were prepared by following literature procedures.<sup>31</sup> The reactivity of Zn<sup>II</sup>(PS1")<sub>2</sub> with dioxygen was monitored by NMR measurements. As shown in Figures S16 and S17, the addition of dioxygen to a solution of  $Zn^{II}(PS1'')_2$  does not cause any change in the <sup>1</sup>H and <sup>31</sup>P NMR spectra, implying no formation of Zn<sup>II</sup>(OPS1")<sub>2</sub>. In addition, H[PS1"] in solution at a dioxygen atmosphere is stable at least for 1 day, as recorded at NMR spectra (Figures S18 and S19). Thus, the Co<sup>II</sup> center was involved in the activation of dioxygen, leading to the oxygenation of a bound phosphine donor in 1. Similar chemistry has been observed in a low-spin tetrahedral Co(II) system, [PhBP3]CoI ([PhBP<sub>3</sub>] =  $[PhB(CH_2PPh_2)_3]^{-}).^{39}$ 

DFT calculations were conducted to understand how 1 is oxidized by O<sub>2</sub> to form 2. We find that O<sub>2</sub> first coordinates with 1 to form 1-O<sub>2</sub> with  $\Delta G = 3.7$  kcal/mol (Figure 4). This is followed by insertion of the entire O<sub>2</sub> into Co–P to form 1-OO with a Co-OO-P moiety ( $\Delta G^{\ddagger} = 17.4$  kcal/mol and  $\Delta G =$ -15.7 kcal/mol). In the next step, a structural rearrangement takes place in 1-OO to form 1-O(O) with  $\Delta G^{\ddagger} = 4.7$  kcal/mol and  $\Delta G = -33.0$  kcal/mol. The oxo group of 1-O(O) has a strong radical character (spin density = 0.98 lel), suggesting that this intermediate is very reactive. Indeed, all possible subsequent reactions for 1-O(O) are very facile. The insertion of oxo of 1-O(O) into the other Co–P forms 2 with  $\Delta G^{\ddagger} =$ 2.7 kcal/mol and  $\Delta G = -71.4$  kcal/mol.

Besides the monomolecular reaction, 1-O(O) could react with another Co complex. The coordination of 1-O(O) with another 1 forms [1-O]-O-[1] with  $\Delta G = -26.8$  kcal/mol. Then, the bridged O inserts into Co-P of the [1] moiety to form two isolated 1-Os with  $\Delta G^{\ddagger} = 9.1$  kcal/mol and  $\Delta G =$ -37.8 kcal/mol. Alternatively, 1-(0)O could coordinate with a 1-O to form [1-O]-O-[1-O] with  $\Delta G = -37.6$  kcal/mol. This is followed by a fast insertion of the bridged O into one of the 1-O moieties to form 1-O plus 2 with  $\Delta G^{\ddagger} = -0.4$  kcal/mol and  $\Delta G = -33.8$  kcal/mol, where  $\Delta G^{\ddagger}$  is negative due to the inclusion of the ZPVE correction and is an indication that there is no barrier for this elementary step. Overall, we find that the 1-O(O) prefers to proceed through the bimolecular reactions. This explains why two oxygens in 2 could come from two different O<sub>2</sub> molecules, as evidenced by isotope labeling studies. The rate-determining step for the oxidation of 1 by  $O_2$ to **2** is the insertion of  $O_2$  into Co-P of **1**.

Syntheses and Characterization of  $[NEt_4][Co(PS2^*)_2]$ (3). A six-coordinate  $Co^{III}$  complex,  $[NEt_4][Co(PS2^*)_2]$  (3)  $([PS2^*]^{2-} = [P(Ph)(C_6H_3-3-Ph-2-S)_2]^{2-})$ , was obtained from a reaction of  $CoCl_2$  and  $[PS2^*]^{2-}$  in methanol with a 1:2 ratio. The addition of the cation, tetraethylammonium, to the reaction mixture gave a brown precipitate. The solid was recrystallized from THF and methanol to give crystals of 3- $2CH_3OH \cdot 0.5THF$  in a 75% yield. The formula is confirmed by elemental analysis. The ESI-MS data gives a set of peaks at  $1011.09 \ m/z$ , and its isotope pattern is consistent with the calculated one of  $[Co(PS2^*)_2]^-$  (the anion of 3) (Figure S20). Dissolving complex 3 in  $CH_3CN$  yielded a reddish brown solution and showed an absorption band at 483 nm ( $\varepsilon = 2.35$  ×  $10^3 \text{ M}^{-1}\text{cm}^{-1}$ ) in the UV-vis-NIR spectrum (Figure S21). The diamagnetic nature of complex 3 is revealed by the <sup>1</sup>H NMR spectrum through resonance peaks appearing at the range of 0–10 ppm (Figure S22), further indicating a low-spin d<sup>6</sup> configuration. The <sup>31</sup>P NMR spectrum gives two peaks at 82.33 and 88.71 ppm attributed to two nonequivalent bound phosphine donors (Figure S23). The structure of 3 was well resolved by X-ray crystallography. It contains a distorted octahedral Co<sup>III</sup> center bound by two tridentate [PS2\*]<sup>2-</sup> ligands (Figure 1). Two phosphine atoms are in the *cis* position. The average distance of the Co–S bonds is 2.286 Å.

Alkylation of Bound Thiolate in [NEt<sub>4</sub>][Co(PS2\*)<sub>2</sub>] (3). Dissolving complex 3 in CH<sub>2</sub>Cl<sub>2</sub> yielded a reddish-brown solution initially, but the color slowly changed to violet in several days. This violet solution was layered with methanol to give crystalline solids of two isomeric products, [Co(PS2\*)- $(PSS^{CH_2Cl*})]$  (4 and 4') ( $[PSS^{CH_2Cl*}]^- = [P(Ph)(C_6H_3-3-Ph 2-S(C_6H_3-3-Ph-2-SCH_2Cl)]^{-}$ , in a 68% total yield (Scheme 2). The ESI-MS data of these products show a set of peaks at 1060.09 m/z, consistent with the theoretical isotope pattern of 4 and 4'. The formula agrees with the measurement of elemental analysis. Attempts to separate 4 and 4' by recrystallization with various solvent systems were not successful. Two types of crystals were identified in the precipitated solid, and both were measured by X-ray crystallography; the major product has a needle shape and gave the structure of 4, and the minor one has a block-like appearance and yielded the structure of 4'. Both structures contain Co<sup>III</sup> centers ligated by one [PS2\*]<sup>2-</sup> ligand and one  $[PSS^{CH_2Cl_*}]^-$  ligand, where one of the thiolato groups has been alkylated by the chloromethyl group to form a thioether moiety (Figure 5). The metal centers both adopt an octahedral



Figure 5. Thermal ellipsoid plots (35% probability) of  $4 \cdot SCH_3OH$  (A) and  $4' \cdot CH_2Cl_2$  (B). The H atoms and solvated molecules are omitted for clarity.

geometry by binding with two phosphine donors, three thiolato groups, and one chloromethyl thioether. The two structures are isomeric; the thioether group is *trans* to the thiolate in 4 while in 4' it is *trans* to the phosphine donor. The average distances of Co–S bonds in both structures are 2.267 and 2.275 Å, respectively, similar to that in 3. Notably, the Co–S bond distances decrease slightly upon alkylation; for example, Co–S<sub>4</sub> = 2.2754 Å in 3 changes to 2.266(1) Å in 4; Co–S<sub>3</sub> = 2.3103(5) Å in 3 changes to 2.295(1) Å in 4'. The comparable distances of Co–S<sub>thiolate</sub> and Co–S<sub>thioether</sub> bonds have been found in the alkylation of other metal thiolates and

well discussed by the Grapperhaus group.<sup>15c</sup> The variation of metal-sulfur bond distance is due to two types of orbital interaction upon alkylation of metal-bound thiolate to thioether; (1) the  $\pi^*$ -bonding interaction between metal and sulfur decreases, leading to a shortened M–S bond, and (2) the  $\sigma$ -bonding interaction is less for the thioether donor compared to thiolate, resulting in the elongation of the M–S bond. Consequently, these two competing factors compensate each other, giving rise to similar Co–S bond distances upon alkylation.

The <sup>1</sup>H NMR spectra show two sets of absorption peaks associated with methylene groups in chloromethyl thioether derived from 4 and 4' (Figures 6A and S24). Two protons are



**Figure 6.** (A) <sup>1</sup>H NMR spectrum of 4 and 4' in  $CD_2Cl_2$  at a range of 4.50 to 4.00 ppm. (B) The <sup>31</sup>P NMR spectrum of 4 and 4' in  $CD_2Cl_2$  at a range of 120 to 60 ppm. Resonance peaks associated with 4 ( $\blacktriangle$ ) and 4' ( $\spadesuit$ ).

diastereotopic and give two sets of doublets for each species: 4.35 and 4.14 ppm for 4 with  ${}^{2}J_{H-H} = 10.36$  Hz; 4.39 and 4.08 ppm for 4' with  ${}^{2}J_{H-H} = 10.15$  Hz. According to the ratio of intensity, the composition of 4 and 4' is around 5:1. The  ${}^{31}P$  NMR data gives two resonance peaks at 91.58 and 85.02 ppm, attributed to two nonequivalent phosphines in 4 (Figure 6B). The set of peaks at 86.10 and 81.34 ppm are associated with those in 4'.

The conversion of 3 reacting with CH<sub>2</sub>Cl<sub>2</sub> to give 4 and 4' was monitored by UV-vis-NIR spectra. As shown in Figure 7, the electronic spectrum of 3 in CH<sub>2</sub>Cl<sub>2</sub> shows an absorption at 483 nm initially, but slowly changes to the one with a broad band between 500 and 600 nm. The final spectrum resembles the one obtained from the mixtures of 4 and 4' in  $CH_2Cl_2$ . The conversion of 3 to 4 and 4' is marked by an isosbestic point at 575 nm. Isotope studies combined with ESI-MS spectrometric investigations concur with our results. The molecular ion peaks of the reaction products have isotopic distributions at 1060.09  $m/z_1$  consistent with the theoretic pattern of  $[Co(PS2^*) (PSS^{CH_2Cl_*})$ ] (4 and 4') (Figure S25A). When complex 3 reacts with CD<sub>2</sub>Cl<sub>2</sub> instead of CH<sub>2</sub>Cl<sub>2</sub>, the isolated products show a molecular ion peak at 1062.09 m/z with the isotope distribution in agreement with the theoretic one of [Co-(PS2\*)(PSS<sup>CD2Cl\*</sup>)] (Figure S25B). It is clear that the chloromethyl moiety of thioether group in 4 and 4' is from the activation of the C–Cl bond in  $CH_2Cl_2$ .

The formation of 4 and 4' from the reaction of 3 with  $CH_2Cl_2$  indicates that the C–Cl bond is activated by  $Co^{III}$ -



Figure 7. Variation in UV–vis–NIR spectrum of 3 in  $CH_2Cl_2$ . The spectrum was monitored over a 70 h period: the initial (red line) and the final (blue line) spectra. Inset: the UV–vis–NIR spectrum of 4 and 4' in  $CH_2Cl_2$ .

bound thiolate via a nucleophilic reaction. To confirm the nucleophilic nature of the bound thiolate in 3, the reactions with other strong electrophiles such as benzyl chloride and methyl iodide were carried out and monitored by UV–vis–NIR spectra (Figures S26 and S27). With 100 equiv of methyl iodide, the reaction proceeded immediately, and with benzyl chloride, the reaction completes at around 7 h. The final spectra of the two reactions were alike. The ESI-MS analysis of the reaction products indicates dialkylation species of 3,  $[3 + 2CH_3]^{+1}$  and  $[3 + 2CH_2Ph]^{+1}$ , respectively (Figures S28 and S29).

The  $Co^{II}$ -bound thiolate in complex 1 does not show nucleophilicity toward dichloromethane or stronger electrophiles such as benzyl chloride. Even with the addition of 100 equiv of reactive alkylating reagent, CH<sub>3</sub>I, the reaction does not proceed for several hours (Figure S30), in contrast to a literature example of a square-planar Co<sup>II</sup> thiolate that undergoes S-alkylation with CH<sub>3</sub>I.<sup>20</sup>

# CONCLUSIONS

In summary, we have isolated and characterized a fourcoordinate Co<sup>II</sup> complex with a P<sub>2</sub>S<sub>2</sub> coordination environment. The structure of the Co<sup>II</sup> center adopts a square-planar geometry, which is unusual relative to a pseudotetrahedron. The finding is supported by the DFT calculations that 1 has a doublet ground state with a square-planar geometry around Co. Importantly, the complex activates dioxygen and leads to a ligand-based oxygenation product: a distorted tetrahedral Co<sup>II</sup> complex binding with two (thiolato)phosphine oxides. Such a metal-mediated oxo transformation derived from dioxygen to the substrate is unprecedented in a well-defined square-planar Co<sup>II</sup> complex. In addition, a low-spin octahedral Co<sup>III</sup> complex binding to two tridentate *bis*(thiolato)phosphine ligands was obtained. The bound thiolato group of this complex shows a strong nucleophilic reactivity to activate CH<sub>2</sub>Cl<sub>2</sub>, which is a weak electrophile. The reaction leads to the formation of Co<sup>III</sup> complexes containing a chloromethyl thioether moiety. It has been well addressed by Ashby and Enemark that the nucleophilicity of bound sulfur in metal thiolates is attributed to a four-electron destabilizing interaction of lone pairs on thiolate sulfur and fulfilled metal d orbitals.<sup>14</sup> This hypothesis has been further elaborated by Grapperhaus and co-workers

that the reactivity is enhanced when the metal d and sulfur p orbitals have comparable energy and good overlap.<sup>10c,40</sup> Thus, for low-spin octahedral Co<sup>III</sup> in complex **3**, the small ionic radii and fulfilled  $t_{2g}$  electrons might lead to a significant metal–sulfur  $\pi$ -antibonding orbital interaction and large electron repulsion, consequently resulting in a strong nucleophilicity.

The Co<sup>II</sup> center in 1 induces dioxygen activation and leads to the oxygenation of phosphine donors. Such Co<sup>II</sup>-mediated dioxygen cleavage has also been seen in a well-defined squareplanar complex and in a complex with NN<sub>3</sub> tripodal ligand that provides an intramolecular H-bonding interaction.<sup>41</sup> Furthermore,  $Co^{II}$  complexes,  $[Co(PEt_3)_2Cl_2]$  and  $[Co(acac)_2]$ , catalyzing phosphine oxidation with dioxygen have been documented.<sup>42</sup> ESI-MS data combined with isotope labeling studies show that the addition of the O atom is stepwise and likely involves an intermolecular path. The DFT calculation provides a feasible reaction pathway that the first oxygenation occurs in a single cobalt center, followed by the second oxygenation with a dicobalt transition state. Although  $[Co(O_2)]^{2+}$  and  $[Co(O)]^{2+}$  metastable species have been identified in Co complexes with other ligand systems,<sup>36,43</sup> efforts for isolating such intermediates in this system are continuing in our laboratory.

#### EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under an atmosphere of dinitrogen with a standard Schlenk technique or glovebox. Ligands,  $[P(Ph)_2(C_6H_3-3-SiMe_3-2-SH)]$ ,  $[PO-(Ph)_2(C_6H_3-3-SiMe_3-2-SH)]$ , and  $[P(Ph)(C_6H_3-3-Ph-2-SH)_2]$ , were synthesized according to the literature procedures.<sup>44</sup> Solvents were dried and distilled by standard procedures. Otherwise, all starting materials were obtained commercially and used without further purification.

Physical Methods. Electronic spectra were recorded in the range of 300-1100 nm on a Hewlett-Packard 8453 spectrometer. NMR spectra were obtained on a Bruker AMX400 and Bruker AVIIIHD700X. The samples were prepared in a sealed NMR tube under a nitrogen atmosphere in a glovebox. <sup>1</sup>H NMR was referenced to the residual proton peaks of the solvents. <sup>31</sup>P NMR was referenced to -6 ppm of PPh<sub>3</sub> as external standard. Elemental analyses were measured with an Elementar vario EL III. The electrospray ionization (ESI) mass data were taken in CH<sub>2</sub>Cl<sub>2</sub> or THF with the LTQ Orbitrap XL, Thermo-Fisher spectrometer. The magnetization data was recorded on a SQUID magnetometer (Quantum Design MPMS SQUID VSM System) with an external 1 T magnetic field at a temperature range of 1.8 to 300 K. The susceptibility data were corrected for diamagnetic contributions by using Pascal constants. EPR samples of 1 and 2 were prepared under a nitrogen atmosphere in a glovebox. The sample of 1 reacting with dioxygen was obtained by purging  $O_2$  into the 2-MeTHF solution of 1. The spectra of 1 in both a N<sub>2</sub> and O<sub>2</sub> atmosphere were obtained at the X band by using a Bruker ELEXSYS E580 spectrometer at 77 K. The measurement parameters were as follows: microwave frequency, 9.65 GHz; modulation amplitude, 3 G; modulation frequency, 100 kHz; power, 15 mW. The spectrum of 2 was recorded at 4 K with a microwave frequency of 9.62 GHz, modulation amplitude of 10 G, and power of 2 mW. Spectral analysis and simulations were performed using the EasySpin program.<sup>45</sup>

X-ray Structure Determination. Crystallographic data and refinement parameters of 1, 3·2CH<sub>3</sub>OH·0.5THF, 4·5CH<sub>3</sub>OH, and 4'·CH<sub>2</sub>Cl<sub>2</sub> are summarized in Tables S1–S4. Selected bond lengths and angles are listed in Tables S5–S8. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. Diffraction measurements were performed with a Nonius Kappa diffractometer equipped with a CCD detector. Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on F2. A

SADABS absorption correction was made.<sup>46</sup> The SHELXTL structural refinement program was employed.<sup>47</sup> All non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were calculated using the riding model. CCDC 1574445, CCDC 1574262, CCDC 1574279, and CCDC 1574278 contain the supplementary crystallographic data of 1, 3, 4, and 4', respectively, for this paper.

**Synthesis of [Co(PS1**")<sub>2</sub>] (1). H[PS1"] (0.1 g, 0.273 mmol) and lithium (0.0028 g, 0.403 mmol) were dissolved in CH<sub>3</sub>OH to generate a solution. The addition of a methanol solution of CoCl<sub>2</sub> (0.0177 g, 0.136 mmol) to the reaction mixture produced an orange precipitate. The obtained solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH to give reddish-orange crystals with a yield of 79% (based on CoCl<sub>2</sub>). Anal. Calcd for C<sub>42</sub>H<sub>44</sub>P<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>Co: C, 63.86; H, 5.61; S, 8.12. Found: C, 63.22; H, 5.54; S, 8.07. <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  23.73 (2H, Ph), 12.41 (3H, Ph), 11.26 (5H, Ph), 9.37 (4H, Ph), 6.46 (8H, Ph), 1.49 (1H, Ph), 0.09 (2H, Ph), -4.35 (18H, Si(CH<sub>3</sub>)<sub>3</sub>), -18.88 (1H,Ph) ppm. UV-vis-NIR in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda$ , nm;  $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 391 (6.48 × 10<sup>3</sup>), 427 (5.08 × 10<sup>3</sup>), 520 (4.81 × 10<sup>3</sup>), 822 (7.28 × 10<sup>1</sup>). ESI-MS: calcd for C<sub>42</sub>H<sub>44</sub>CoP<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> 789.12, found 789.13.

Synthesis of  $[Co(OPS1'')_2]$  (2). For Method A,  $[Co(PS1'')_2]$  (1) (0.100 g, 0.127 mmol) was dissolved in CH2Cl2, and purging dioxygen to the solution for 30 s caused the color to gradually change from orange to bluish-green. The solution was concentrated by vacuum and layered with CH<sub>3</sub>OH. A crystalline solid of  $[Co^{II}(OPS1'')_2]$  (2) was produced after a few days (0.105 g, 0.118) mmol, ca. 93% based on 1). For Method B, H[OPS1"] (0.100 g, 0.261 mmol) and lithium (0.0022 g, 0.317 mmol) were dissolved in CH<sub>3</sub>OH to generate a solution. The addition of a CH<sub>3</sub>OH solution of CoCl<sub>2</sub> (0.017 g, 0.131 mmol) to the reaction mixture gave a bluishgreen precipitate that was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH (0.193 g, 0.108 mmol, ca. 90% based on CoCl<sub>2</sub>). Anal. Calcd for C42H44P2O2S2Si2Co: C, 61.37; H, 5.40; S, 7.80. Found: C, 61.16; H, 5.52; S, 7.82. <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ 43.06 (2H, Ph), 33.63 (2H, Ph), 9.01 (10H, Ph), 7.72 (6H, Ph), 0.21 (4H, Ph), -5.84 (18H, Si(CH<sub>3</sub>)<sub>3</sub>), -13.50 (2H,Ph) ppm. UV-vis-NIR in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda$ , nm;  $\epsilon$ ,  $M^{-1}$  cm<sup>-1</sup>): 363 (6.75 × 10<sup>3</sup>), 413 (1.73 × 10<sup>3</sup>), 427 (1.50 × 10<sup>3</sup>), 556  $(4.16 \times 10^2)$ , 616  $(3.17 \times 10^2)$ , 676  $(1.56 \times 10^2)$ . ESI-MS: calcd for C<sub>42</sub>H<sub>44</sub>CoO<sub>2</sub>P<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> 821.11, found 821.12.

**Synthesis of [N(C\_2H\_5)\_4][Co<sup>III</sup>(PS2\*)\_2] (3).**  $H_2[PS2*]$  (0.1000 g, 0.209 mmol) and lithium (0.0032 g, 0.461 mmol) were reacted to generate a clear solution. After the addition of  $CoCl_2$  (0.0136 g, 0.105 mmol) in methanol, the solution color changed to reddish-brown. The addition of the cation,  $[N(C_2H_5)_4]Br$  (0.0221 g, 0.105 mmol), in CH<sub>3</sub>OH to the reaction mixture gave a brown precipitate. The solid was recrystallized from THF and methanol to give crystals of 3· 2CH<sub>3</sub>OH·0.5 THF after 10–14 days (0.090 g, 0.079 mmol, ca. 75% based on CoCl<sub>2</sub>). Anal. Calcd for  $C_{72}H_{74}CoNO_{2.5}P_2S_4$ : C, 69.60; H, 6.00; N, 1.13; S, 10.32. Found: C, 70.69; H, 5.83; N, 1.12; S, 10.65. <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  6.60–7.90 (42H, Ph), 2.56 (8H, N(C<sub>2</sub>H<sub>3</sub>)<sub>4</sub>), 0.68 (12H, N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) ppm. <sup>31</sup>P NMR in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  82.33, 88.71 ppm. UV–vis–NIR in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda$ , nm;  $\varepsilon$ ,  $M^{-1}$  cm<sup>-1</sup>): 483 (2.35 × 10<sup>3</sup>). ESI-MS: calcd for  $[C_{60}H_{42}CoP_{3}S_4]^{-1}$  1011.10, found 1011.09.

<sup>11</sup><sup>3)</sup>. ESI-MS: calcd for  $[C_{60}H_{42}CoP_2S_4]^-$  1011.10, found 1011.09. **Synthesis of [Co^{III}(PS2^\*)(PSS^{CH\_2CI\_\*})](4 \text{ and } 4').** $<math>[N(C_2H_5)_4]^ [Co^{III}(PS2^*)_2]$  (3) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and layered with CH<sub>3</sub>OH. A violet black crystalline solid of Co(PS2^\*)(PSS^{CH\_2CI\_\*}) (4 and 4') was produced after 3 days with a 68% yield. Anal. Calcd for  $C_{61}H_{44}ClCoP_2S_4$ : C, 69.01; H, 4.18; S, 12.08. Found: C, 68.13; H, 4.26; S, 11.90. <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  6.70–7.80 (42H, Ph), 4.39 (d, 1H, <sup>2</sup>J<sub>H-H</sub> = 10.15 Hz, CH<sub>2</sub>Cl, 4'), 4.35 (d, 1H, <sup>2</sup>J<sub>H-H</sub> = 10.36 Hz, CH<sub>2</sub>Cl, 4), 4.14 (d, 1H, <sup>2</sup>J<sub>H-H</sub> = 10.36 Hz, CH<sub>2</sub>Cl, 4), 4.08 (d, 1H, <sup>2</sup>J<sub>H-H</sub> = 10.15 Hz, CH<sub>2</sub>Cl, 4') ppm. <sup>31</sup>P NMR in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  91.58 (4), 86.10 (4'), 85.02 (4), 81.34 (4') ppm. ESI-MS: calcd for  $C_{61}H_{44}ClCoP_2S_4$  1060.08, found 1060.09.

**Computational Details.** The B3LYP functional combined with the LACVP\*\* basis set (LanL2DZ for Co and 6-31G\*\* for the others) was used for the geometry optimizations and the zero-point vibrational energy (ZPVE). To obtain more accurate electronic energies, single point energy calculations using a larger basis set (LACV3P++\*\*, LanL2TZ for Co, and 6-311++G\*\* for the others) with Grimme's D3 empirical correction were performed on the B3LYP/LACVP\*\* optimized structures. All the calculations were performed using the Gaussian 16 package. The energies discussed here are Gibbs free energies obtained using the equation as follows for nonlinear molecules:

$$G_{298K} = E_{elec} + ZPVE + 4kT + \sum_{\nu} \frac{h\nu}{e^{h\nu/kT} - 1}$$
$$- T \times (S_{trans} + S_{rot} + S_{vib})$$

4kT is replaced by 3.5kT for  $O_{2(g)}$ .

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03740.

Additional characterization, spectra, and crystallographic data (PDF)

## **Accession Codes**

CCDC 1574262, 1574278, 1574279, and 1574445 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology in Taiwan (MOST 107-2113-M-006-003, 107-2113-M-006-008-MY2, and 108-2113-M-007-029) and National Cheng Kung University in Taiwan. We thank Mr. Ming-Feng Chen and Mr. Tsung-Lun Kan in the Establishment of the Instrument Development Center at National Cheng Kung University for assisting with the measurements of ESI-MS data and NMR data.

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