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# [Ni<sup>III</sup>(OMe)]-mediated reductive activation of CO<sub>2</sub> affording a Ni( $\kappa^1$ -OCO) complex†

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Carbon dioxide is expected to be employed as an inexpensive and potential feedstock of C<sub>1</sub> sources for the mass production of valuable chemicals and fuel. Versatile chemical transformations of CO<sub>2</sub>, *i.e.* insertion of CO<sub>2</sub> producing bicarbonate/acetate/formate, cleavage of CO<sub>2</sub> yielding  $\mu$ -CO/ $\mu$ -oxo transition-metal complexes, and electrocatalytic reduction of CO<sub>2</sub> affording CO/HCOOH/CH<sub>3</sub>OH/CH<sub>4</sub>/C<sub>2</sub>H<sub>4</sub>/oxalate were well documented. Herein, we report a novel pathway for the reductive activation of CO<sub>2</sub> by the [Ni<sup>III</sup>(OMe)(P(C<sub>6</sub>H<sub>3</sub>-3-SiMe<sub>3</sub>-2-S)<sub>3</sub>)]<sup>-</sup> complex, yielding the [Ni<sup>III</sup>( $\kappa^1$ -OCO<sup>-</sup>)(P(C<sub>6</sub>H<sub>3</sub>-3-SiMe<sub>3</sub>-2-S)<sub>3</sub>)]<sup>-</sup> complex. The formation of this unusual Ni<sup>III</sup>( $\kappa^1$ -OCO<sup>-</sup>) complex was characterized by single-crystal X-ray diffraction, EPR, IR, SQUID, Ni/S K-edge X-ray absorption spectroscopy, and Ni valence-to-core X-ray emission spectroscopy. The inertness of the analogous complexes [Ni<sup>III</sup>(SPh)], [Ni<sup>III</sup>(CO)], and [Ni<sup>II</sup>(N<sub>2</sub>H<sub>4</sub>)] toward CO<sub>2</sub>, in contrast, demonstrates that the ionic [Ni<sup>III</sup>(OMe)] core attracts the binding of weak  $\sigma$ -donor CO<sub>2</sub> and triggers the subsequent reduction of CO<sub>2</sub> by the nucleophilic [OMe]<sup>-</sup> in the immediate vicinity. This metal–ligand cooperative activation of CO<sub>2</sub> may open a novel pathway promoting the subsequent incorporation of CO<sub>2</sub> in the buildup of functionalized products.

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## Introduction

Carbon dioxide, the waste from human activity embodying the nature of high thermodynamic stability and chemical inertness, is expected to be employed as an inexpensive and potential feedstock of C<sub>1</sub> sources for the regeneration of valuable chemicals and fuel.<sup>1,2</sup> Nature developed carbon monoxide dehydrogenase (CODH) to harbor a Ni–Fe cluster for the reversible interconversion between CO<sub>2</sub> and CO.<sup>3–5</sup> To gain insight into the mechanism for the conversion of CO<sub>2</sub> to CO in CODH, several Ni–CO<sub>2</sub> adducts derived from the reaction of a low-valent Ni complex and CO<sub>2</sub> were reported.<sup>6–9</sup> The direct electrochemical reduction of CO<sub>2</sub> affords oxalate, carbon monoxide, formic acid, methanol, methane, and ethylene.<sup>10</sup> To gain insight into the transformation of CO<sub>2</sub> at a molecular level, the chemistry of the activation of CO<sub>2</sub> *via* nucleophilic attack/interaction on the polarized C center, in addition to the reduction of the coordinated CO<sub>2</sub> ligand by low-valence

transition metal complexes, has grown explosively over past years.<sup>11</sup> The versatile chemical transformations of CO<sub>2</sub>, *i.e.* insertion of CO<sub>2</sub> producing bicarbonate/acetate/formate,<sup>12–18</sup> cleavage of CO<sub>2</sub> yielding  $\mu$ -CO/ $\mu$ -oxo transition-metal complexes,<sup>19–23</sup> reduction of CO<sub>2</sub> affording CO/HCOOH/CH<sub>3</sub>OH/CH<sub>4</sub>/C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/methylene, and electrocatalysis of CO<sub>2</sub> converting it into oxalate, were well documented.<sup>24–26</sup> The direct electrochemical reduction or electrocatalytic transformation of CO<sub>2</sub> for the mass production of valuable chemicals and fuel, however, relies on the consumption of sustainable electric potential energy. Here we show a novel pathway for the reductive activation of CO<sub>2</sub> by a mononuclear Ni(III) complex [Ni<sup>III</sup>(OMe)(P(C<sub>6</sub>H<sub>3</sub>-3-SiMe<sub>3</sub>-2-S)<sub>3</sub>)].<sup>27</sup> This [Ni<sup>III</sup>(OMe)]-mediated reduction of CO<sub>2</sub> yields the complex Ni<sup>III</sup>( $\kappa^1$ -OCO<sup>-</sup>), evidenced by single-crystal X-ray diffraction, EPR, SQUID, Ni/S K-edge X-ray absorption spectroscopy, IR and Ni valence-to-core X-ray emission spectroscopy. The ionic [Ni<sup>III</sup>(OMe)] core provides a kinetic pathway to induce the binding of CO<sub>2</sub> and trigger the subsequent reduction of CO<sub>2</sub> by the nucleophilic [OMe]<sup>-</sup> in the immediate vicinity. The covalent [Ni<sup>III</sup>(SPh)] core as well as Ni(II) center in complexes [Ni<sup>II</sup>(L)(P(C<sub>6</sub>H<sub>3</sub>-3-SiMe<sub>3</sub>-2-S)<sub>3</sub>)]<sup>-</sup> (L = CO or N<sub>2</sub>H<sub>4</sub>), in contrast, are inert toward CO<sub>2</sub>.<sup>28</sup>

## Results and discussion

### Synthesis and characterization of nickel $\kappa^1$ -OCO complex

When CO<sub>2(g)</sub> was bubbled into the thermally stable [Ni<sup>III</sup>(OMe)(PS<sub>3</sub>)]<sup>-</sup> (**1**) (PS<sub>3</sub> = P(C<sub>6</sub>H<sub>3</sub>-3-SiMe<sub>3</sub>-2-S)<sub>3</sub>) in THF,<sup>27</sup>

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a pronounced color change from blue green to yellow green occurred to yield the O-bound  $\kappa^1$ -CO<sub>2</sub> complex [Ni( $\kappa^1$ -OCO)(PS<sub>3</sub>)]<sup>-</sup> (2), instead of complexes [Ni(OC(O)OCH<sub>3</sub>)-(PS<sub>3</sub>)]<sup>-</sup> or [Ni(OC(O)H)(PS<sub>3</sub>)]<sup>-</sup> *via* the classical insertion or  $\beta$ -H migration mechanisms (Scheme 1a).<sup>9,12-16</sup>

The accompanied formation of [·OMe] in the reaction described above was corroborated using the spin-trapping reagent DMPO (ESI Fig. S1†).<sup>29</sup> The IR  $\nu_{\text{OCO}}$  stretching peak at 2177 cm<sup>-1</sup> (KBr) ( $\nu_{\text{OCO}}$ : 2226 cm<sup>-1</sup> in THF) exhibited by complex 2 supports the formation of [Ni( $\kappa^1$ -OCO)(PS<sub>3</sub>)]<sup>-</sup>, which is consistent with the isotopic shift of the IR  $\nu_{\text{OCO}}$  stretching peak to 2117 cm<sup>-1</sup> (KBr) observed in the <sup>13</sup>CO<sub>2</sub> labeling experiment (ESI Fig. S2†). The conversion of complex 1 to complex 2 under a CO<sub>2</sub> atmosphere was also monitored by UV-vis spectrometry; the intense bands at 419 and 605 nm disappeared with the simultaneous formation of absorption bands at 425 and 610 nm (THF) (ESI Fig. S3†). The green needle crystals of complex 2 were isolated when complex 2 was recrystallized from THF-diethyl ether at room temperature. As shown in Scheme 1b, treatment of complex 2 with CO<sub>(g)</sub> led to the formation of the reported complex [Ni<sup>II</sup>(CO)(PS<sub>3</sub>)]<sup>-</sup> accompanied by the release of CO<sub>2(g)</sub> characterized by IR and GC (Fig. 1).<sup>28</sup>

To contrast complex 2 containing a [Ni<sup>III</sup>:CO<sub>2</sub>·<sup>-</sup>] or [Ni<sup>II</sup>:CO<sub>2</sub>] center, complex [Ni<sup>III</sup>(NCO)(PS<sub>3</sub>)]<sup>-</sup> (4) was synthesized *via* the reaction of [Ni(Cl)(PS<sub>3</sub>)]<sup>-</sup> (3) and [K][NCO] to mimic the isolobal [Ni<sup>III</sup>:CO<sub>2</sub>] (Scheme 1c). Fig. 2 displays ORTEP plots of complexes 2 and 4, with the selected bond distances and angles given in the caption. The strain effect of the chelating ligand ([PS<sub>3</sub>]<sup>3-</sup>) in the coordination sphere of complexes 2 and 4 explains that the Ni is in a distorted trigonal bipyramidal geometry with three thiolates locating equatorial positions and the phosphorus is occupying an axial position trans to the [OCO] and [NCO] ligands. In contrast to the linear N-C-O (177.2(3)°) bond observed in complex 4, complex 2 displays a bent O-C-O bond with a bond angle of 171.7(7)°. Compared to the similar O-C and N-C bond distances of 1.200(3) and 1.181(3) Å in complex 4, the dramatic difference (~0.1 Å) in O-C bond lengths, 1.132(6) vs. 1.240(7) Å, found in complex 2 moreover indicates the polarization of CO<sub>2</sub> *via* reductive activation affording a [Ni<sup>III</sup>:CO<sub>2</sub>·<sup>-</sup>] species.<sup>22,30,31</sup> A similar polarization of CO<sub>2</sub> was reported in the O-bound  $\kappa^1$ -CO<sub>2</sub>

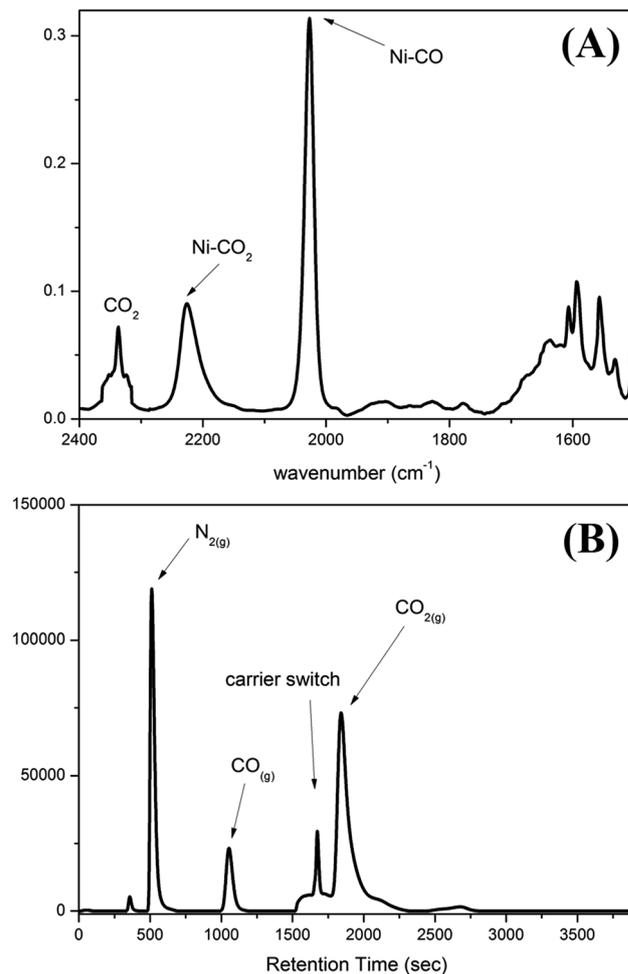
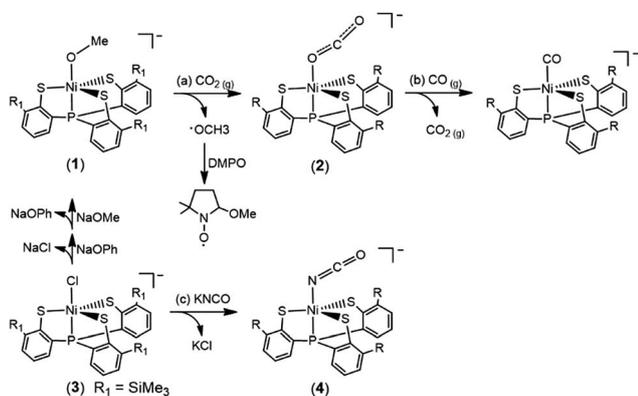


Fig. 1 (A) IR spectra for the transformation of complex 2 to [Ni<sup>II</sup>(CO)(PS<sub>3</sub>)]<sup>-</sup> in THF. The decrease in the intensity of the IR  $\nu_{\text{CO}_2}$  peak at 2226 cm<sup>-1</sup> exhibited by complex 2 with the simultaneous formation of an IR  $\nu_{\text{CO}}$  peak at 2027 cm<sup>-1</sup> indicated the formation of complex [Ni<sup>II</sup>(CO)(PS<sub>3</sub>)]<sup>-</sup>. (B) GC chromatogram, derived from the sample collected from the headspace of the tube containing the reaction solution of complex 2 and CO<sub>(g)</sub>, indicating the release of CO<sub>2(g)</sub> during the transformation of complex 2 to [Ni<sup>II</sup>(CO)(PS<sub>3</sub>)]<sup>-</sup>.

coordinated complex [([<sup>Ad</sup>ArO]<sub>3</sub>tacn)-U<sup>IV</sup>(CO<sub>2</sub>·<sup>-</sup>)] ([<sup>Ad</sup>ArOH]<sub>3</sub>-tacn = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane), O-C = 1.122(4) and 1.277(7) Å, with the linear U-O-C and O-C-O bonds stabilized by the sterically encumbering ligand framework.<sup>30,31</sup> Besides, complex 2 displays a significantly longer Ni-O bond distance (2.028(3) Å) than those observed in [Ni<sup>II</sup>(L)(pyN<sub>2</sub>Me<sub>2</sub>)]<sup>1-</sup> complexes (1.857(5) Å for L = HCO<sub>2</sub><sup>-</sup>; 1.817(4) Å for L = HCO<sub>3</sub><sup>-</sup>).<sup>32</sup>

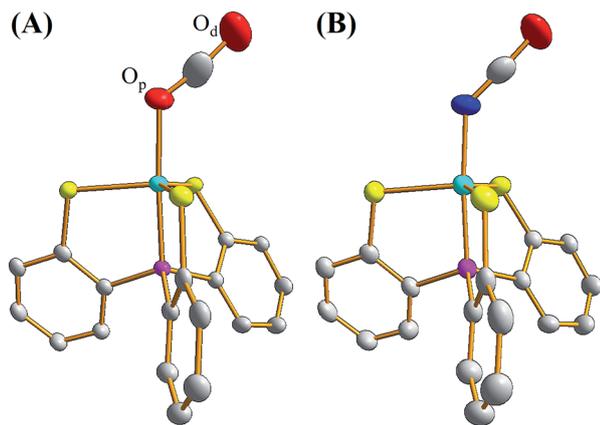
### X-ray absorption/emission spectrum

A Ni and S K-edge X-ray absorption spectroscopic (XAS) study of complex 2 was further attempted to investigate its electronic structure using complexes 1 and 4 as reference complexes. As shown in Fig. 3A, the Ni K-edge XAS of complex 2 (8333.1 eV) together with analogous complexes 1 (8332.9 eV) and 4 (8332.7 eV) shows a similar Ni<sub>1s</sub>-to-Ni<sub>3d</sub> transition energy. Accordingly, the



Scheme 1





**Fig. 2** ORTEP drawing schemes of (A) complex 2 and (B) complex 4 with thermal ellipsoids drawn at a 50% probability level. The Ni, P, S, O, N, and C atoms are shown as light blue, purple, yellow, red, blue, and white ellipsoids. The H atom and TMS group are omitted for clarity. Selected bond distances (Å) and angles (°) for complex 2: Ni–O<sub>p</sub>, 2.028(3); Ni–P, 2.122(1); Ni–S, 2.221(1), 2.287(1), and 2.285(1); O<sub>p</sub>–C, 1.132(6); O<sub>d</sub>–C, 1.240(7); O–Ni–P, 176.2(1); Ni–O–C, 127.0(4); O<sub>p</sub>–C–O<sub>d</sub>, 171.7(7). Selected bond distances (Å) and angles (°) for complex 4: Ni–N, 1.933(2); Ni–P, 2.120(1); Ni–S, 2.226(1), 2.286(1), and 2.291(1); O–C, 1.200(3); N–C, 1.181(3); N–Ni–P, 175.0(1); Ni–N–C, 135.1(2); O–C–N, 177.2(3).

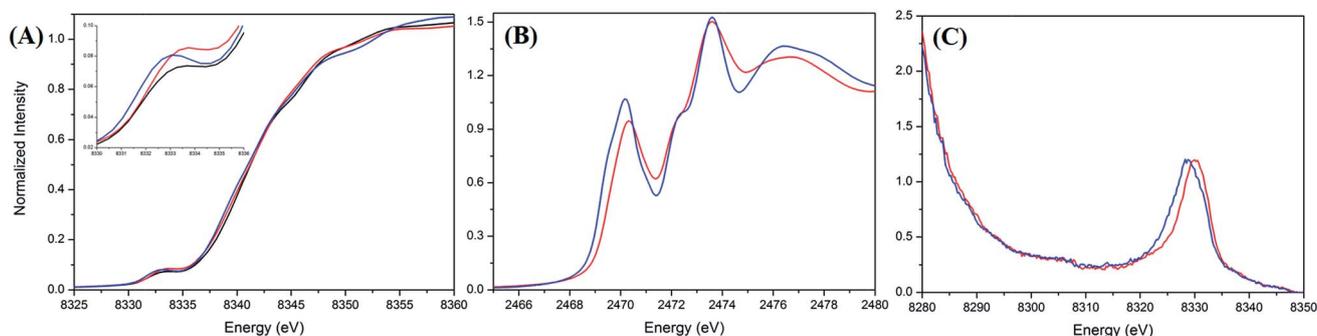
formal oxidation state of Ni in complex 2 is similar to those of complexes 1 and 4, which are generally known as a L ligand bound to a d<sup>7</sup> Ni(m) center in [Ni<sup>III</sup>(L)(PS<sub>3</sub>)]<sup>−</sup>.<sup>28</sup> Fig. 3B and ESI Fig. S4† depict the S K-edge XAS spectra of complexes 1, 2, and 4, whereas ESI Fig. S5† shows the calculated S K-edge XAS spectra and spectral deconvolution. As shown in Table 1, the intensity-weighted average energy of the S<sub>1s</sub>-to-Ni<sub>3d</sub> transitions in combination with the S<sub>1s</sub>-to-S<sub>C-S</sub> transition energy demonstrate that the Ni<sub>3d</sub> manifold orbital energy of complex 2 is 0.3 eV higher than those of complexes 1 and 4.<sup>33,34</sup> With further regard to the Ni<sub>1s</sub>-to-Ni<sub>3d</sub> pre-edge transition energy observed in the Ni K-edge XAS, Ni Z<sub>eff</sub> of complexes 1, 2, and 4 are all comparable. That is, the Ni and S K-edge XAS study supports the [Ni<sup>III</sup>:CO<sub>2</sub>]<sup>•−</sup> electronic structure in complex 2. As shown in Fig. S6,† the cyclic voltammogram of a 2 mM solution of complex 4 in CH<sub>3</sub>CN indicates a reversible interconversion between Ni<sup>III</sup>/Ni<sup>II</sup> at E<sub>1/2</sub> = −0.58 V and an

irreversible oxidation at E<sub>pa</sub> = −0.21 V, whereas complex 2 exhibits a reversible interconversion between Ni<sup>III</sup>/Ni<sup>II</sup> at E<sub>1/2</sub> = −0.70 V and an irreversible oxidation at E<sub>pa</sub> = −0.29 V (vs. Fc/Fc<sup>+</sup>).

With regard to complex 4 as an isolobal equivalent to [Ni<sup>III</sup>:CO<sub>2</sub>], complex 2 is a Ni<sup>III</sup> complex bearing a 17-valence-electron [CO<sub>2</sub>]<sup>•−</sup> ligand. The significantly lower intensity of the second S<sub>1s</sub>-to-Ni<sub>3d</sub> transition peak observed in the S K-edge XAS spectrum of complex 2, compared to that of complex 4, discloses that the one extra electron shared by the axial Ni<sub>3d</sub> orbital and 2π<sub>u</sub><sup>\*</sup> orbital of CO<sub>2</sub> leads to a strengthening of the Ni<sup>III</sup>–CO<sub>2</sub><sup>•−</sup> bond and stabilizes the coordination of κ<sup>1</sup>-[CO<sub>2</sub>]<sup>•−</sup> toward the Ni<sup>III</sup> center (Fig. 3B and Table 1). As observed in complex [Ni<sup>III</sup>(L)(PS<sub>3</sub>)]<sup>−</sup> (L = OMe, SEt, SPh), complex 4 displays an EPR silence at 300 K, an axial signal at g = 2.27 and 2.04 at 77 K, and an effective magnetic moment of 1.74 μ<sub>B</sub> at 300 K (Fig. 4C and S7A†).<sup>27,28,35</sup> The stabilization of the [CO<sub>2</sub>]<sup>•−</sup> radical through coordination to the Ni<sup>III</sup> center in complex 2 was further evidenced by EPR spectroscopy.

As shown in Fig. 4A and B, the EPR spectrum of complex 2 at 77 K apparently resembles a combination of the typical EPR signal of [Ni<sup>III</sup>(L)(PS<sub>3</sub>)]<sup>−</sup> (g = 2.31, 2.03, and 2.00) and the [CO<sub>2</sub>]<sup>•−</sup> radical with a contribution of Ni<sub>3d</sub> leading to the observed g anisotropy (Fig. 4A and B).<sup>36</sup> The spin quantitation of complex 2, using complex 4 as a reference, demonstrates that the electronic structure of complex 2 is best described as a resonance hybrid between [Ni<sup>III</sup>:CO<sub>2</sub>]<sup>•−</sup> and [Ni<sup>II</sup>:CO<sub>2</sub>], which is supported by the effective magnetic moment of 1.59 μ<sub>B</sub> exhibited by complex 2 at 300 K (ESI Fig. S7B and S7C†).

The experimental valence-to-core X-ray emission (V2C XES) spectra of complexes 2 and 4 are presented in Fig. 3C. In comparison with complex 4, the broad V2C transition peak of complex 2 at 8330.0 eV shifts from 8328.8 eV upon replacement of the [NCO]<sup>−</sup> by the [CO<sub>2</sub>]<sup>•−</sup> ligand. DFT calculation was further pursued to verify the nature of the V2C transition(s). As shown in ESI Fig. S8A and S8B,† the DFT calculated V2C XES spectra resembles the experimental V2C features and, in particular, the trend of the energy shift comparing complexes 2 and 4. The contribution of the 4σ<sub>g</sub>, 3σ<sub>u</sub>, and 1π<sub>g</sub> orbitals of [NCO]<sup>−</sup> and Ni<sub>3d</sub>-S<sub>3p</sub> orbitals results in the V2C features of complex 4.<sup>37</sup> For complex 2, the absence of transitions from the 3σ<sub>u</sub> and 1π<sub>g</sub> orbitals and an additional transition from the occupied 2π<sub>u</sub>



**Fig. 3** (A) Ni K-edge X-ray absorption spectra of complexes 1 (black), 2 (red), and 4 (blue). (B) S K-edge X-ray absorption and (C) Ni valence-to-core X-ray emission spectra of complexes 2 (red) and 4 (blue).



**Table 1**  $\text{Ni}_{1s} \rightarrow \text{Ni}_{3d}$ ,  $\text{S}_{1s} \rightarrow \text{Ni}_{3d}$ ,  $\text{S}_{1s} \rightarrow \text{S}_{C-S}^*$  transition energy and  $\text{S}_{1s} \rightarrow \text{Ni}_{3d}$  transition intensity of complexes **1**, **2**, **4**, and  $[\text{Ni}(\text{SPh})(\text{PS}_3)]^-$ , derived from the Ni and S K-edge X-ray absorption spectroscopy

Complexes	$\text{Ni}_{1s} \rightarrow \text{Ni}_{3d}$ energy <sup>a</sup> (eV)	$\text{S}_{1s} \rightarrow \text{Ni}_{3d}$ energy <sup>b</sup> (eV)			$\text{S}_{1s} \rightarrow \text{Ni}_{3d}$ intensity <sup>b</sup>		$\text{S}_{1s} \rightarrow \text{S}_{C-S}^*$ energy <sup>b</sup> (eV)	Relative d-manifold energy shift <sup>d</sup> (eV)
		1 <sup>st</sup> peak	2 <sup>nd</sup> peak	Avg <sup>c</sup>	1 <sup>st</sup> peak	2 <sup>nd</sup> peak		
<b>1</b>	8332.9	2469.7	2470.4	2470.0	0.29	1.34	2472.1	0
<b>2</b>	8333.1	2469.9	2470.5	2470.3	0.47	1.15	2472.1	0.3
<b>4</b>	8332.7	2469.5	2470.2	2470.1	0.33	1.77	2472.2	0
$[\text{Ni}(\text{SPh})(\text{PS}_3)]^-$	8333.0	2469.8	2470.4	2470.3	0.52	1.91	2472.3	0.1

<sup>a</sup> The peak energy is determined by the minimum of the second derivative. <sup>b</sup> The peak energy and intensity is determined based on the spectral deconvolution. <sup>c</sup> The intensity-weighted average energy is given here. <sup>d</sup> Calculated from the difference of the thiolate peak energy and the intensity-weighted pre-edge peak energy.

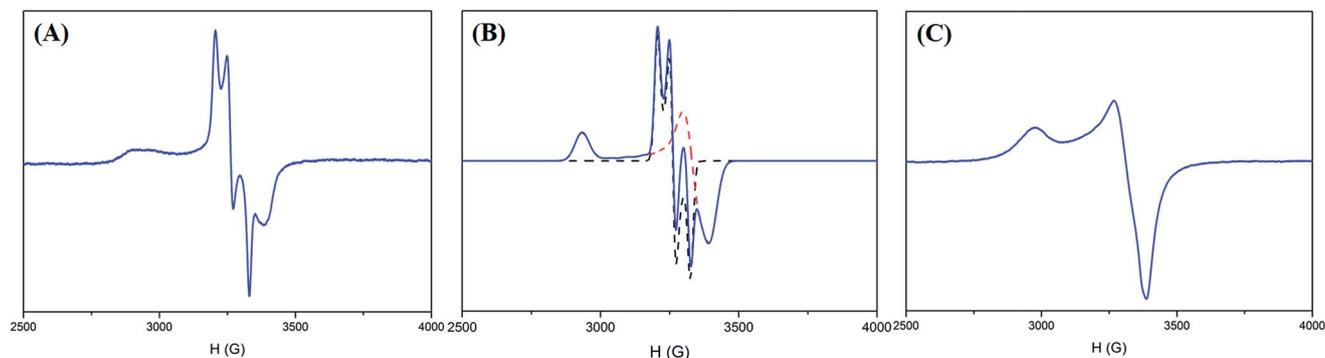
orbital of  $[\text{CO}_2]^-$ , in addition to the upward shift of the  $\text{Ni}_{3d}$ - $\text{S}_{3p}$  orbitals in complex **2**, rationalizes the higher V2C transition energy of complex **2** in comparison with complex **4**.

Complex  $[\text{Ni}(\text{L})(\text{P}(\text{C}_6\text{H}_3-3-\text{SiMe}_3-2-\text{S})_3)]^-$ , embedded in a distorted trigonal bipyramidal geometry, features a wealth of chemical reactivity tailored by the oxidation state of Ni and coordinating ligand L (L = OPh, SPh, SePh and Cl for  $\text{Ni}^{\text{III}}$ ; L = CO,  $\text{N}_2\text{H}_4$  for  $\text{Ni}^{\text{II}}$ ).<sup>27,28,35</sup> To dissect the unique reactivity of  $[\text{Ni}^{\text{III}}(\text{OMe})(\text{PS}_3)]^-$  (**1**) toward  $\text{CO}_2$  activation, the addition of  $\text{CO}_2$  into a THF solution of the representative  $\text{Ni}^{\text{III}}$ -chalcogenate complex  $[\text{Ni}(\text{SPh})(\text{PS}_3)]^-$  was investigated. In contrast to the reaction of complex **1** and  $\text{CO}_2$  yielding complex **2**, complex  $[\text{Ni}^{\text{III}}(\text{SPh})(\text{PS}_3)]^-$  is inert toward  $\text{CO}_2$ . In addition, despite the potential reduction power of the  $\text{Ni}^{\text{II}}$  center in combination with the labile nature of the CO or  $\text{N}_2\text{H}_4$  ligand, neither complex  $[\text{Ni}^{\text{II}}(\text{CO})(\text{PS}_3)]^-$  nor complex  $[\text{Ni}^{\text{II}}(\text{N}_2\text{H}_4)(\text{PS}_3)]^-$  showed a reactivity toward  $\text{CO}_2$  when the THF solution of these Ni complexes was treated with  $\text{CO}_2$ , respectively, at ambient temperature for 3 days. As shown in ESI Fig. S4† and Table 1, the covalent character of the  $[\text{Ni}^{\text{III}}(\text{SPh})]$  core, compared to the  $[\text{Ni}^{\text{III}}(\text{OMe})]$  core, derived from the  $\sigma$ -/ $\pi$ -electron-donating nature of the coordinated phenylthiolate ligand, rationalizes the inertness of  $[\text{Ni}^{\text{III}}(\text{SPh})(\text{PS}_3)]^-$  toward  $\text{CO}_2$ .<sup>33,34</sup> Despite the labile nature of CO and  $\text{N}_2\text{H}_4$ , the inert reactivity of the  $\text{Ni}^{\text{II}}$  center toward  $\text{CO}_2$  demonstrates that the lowered  $\text{Ni}_{3d}$  manifold orbitals in  $\text{Ni}^{\text{III}}$  complex **1** attracts the binding of weak  $\sigma$ -donor  $\text{CO}_2$  and triggers the subsequent reduction of  $\text{CO}_2$  by the nucleophilic

$[\text{OMe}]^-$  in the immediate vicinity. The reactivity of complex **1** toward  $\text{CO}_2$ , affording an O-bound  $[\text{Ni}^{\text{III}}:\text{CO}_2]^-$  species, uncovers a novel strategy for the immobilization and reductive activation of  $\text{CO}_2$ , contrary to the typical interaction of unoccupied  $\text{CO}_2$   $2\pi_u^*$  orbitals with filled high-lying metal d orbitals in low-valence metal complexes.<sup>38,39</sup> Theoretically, lowering the energy of the  $2\pi_u^*$  ( $6a_1$ ) (LUMO) orbital on  $\text{CO}_2$  for interaction with nickel orbitals binding by way of the O=C- unit may be responsible for the coordinated  $\text{CO}_2$  reduction and the nonlinearity of the triatomic  $\text{CO}_2$  molecule which contains 17 valence electrons, as reported by McGlynn and co-workers.<sup>37</sup> These results illustrate aspects of how a coordinated ligand and the electronic state of the nickel center work in concert to trigger coordination and activation of  $\text{CO}_2$ .

## Conclusions

Complex **1**, with the inherent combination of an electrophilic  $[\text{Ni}^{\text{III}}(\text{PS}_3)]$  core and a properly positioned  $[\text{OMe}]^-$  nucleophile, was employed to provide an optimum electronic condition to trap and activate  $\text{CO}_2$  to afford complex **2**, containing the O-coordinated  $[\kappa^1\text{-CO}_2]^-$  ligand. The  $\text{Ni}^{\text{III}}$ -mediated reduction of  $\text{CO}_2$  by an adjacent  $[\text{OMe}]^-$  ligand immobilizes  $\text{CO}_2$  in the form of  $[\text{Ni}^{\text{III}}:\text{CO}_2]^-$  and may open a novel  $\text{CO}_2$  activation pathway promoting the subsequent incorporation of  $\text{CO}_2$  in the buildup of functionalized products.



**Fig. 4** (A) EPR spectrum of complex **2** at 77 K, (B) simulated EPR spectrum (blue) of complex **2** combining  $[\text{Ni}^{\text{III}}(\text{L})(\text{PS}_3)]^-$  (dashed red line) and the  $[\text{CO}_2]^-$  radical (dashed black line), and (C) EPR spectrum of complex **4** at 77 K.



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