Carbon dioxide is expected to be employed as an inexpensive and potential feedstock of C1 sources for the mass production of valuable chemicals and fuel. Versatile chemical transformations of CO2, i.e. insertion of CO2 producing bicarbonate/acetate/formate, cleavage of CO2 yielding μ-CO/μ-oxo transition-metal complexes, and electrocatalytic reduction of CO2 affording CO/HCOOH/CH3OH/CH4/C2H4/C2H6/methylene, were well documented. Herein, we report a novel pathway for the reductive activation of CO2 by the [NiIII(OMe)(P(C6H3-3-SiMe3-2-S)3)] complex, yielding the [NiIII(k¹-OCO⁻¹)(P(C6H3-3-SiMe3-2-S)3)]⁻ complex. The formation of this unusual Ni(III)-mediated reductive activation of CO2 may open a novel pathway promoting the subsequent incorporation of CO2 in the buildup of functionalized products.

**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 C1 sources for the regeneration of valuable chemicals and fuel. Nature developed carbon monoxide dehydrogenase (CODH) to harbor a Ni–Fe cluster for the reversible interconversion between CO2 and CO. To gain insight into the mechanism for the conversion of CO2 to CO in CODH, several Ni–CO2 adducts derived from the reaction of a low-valent Ni complex and CO2 were reported. The direct electrochemical reduction of CO2 affords oxalate, carbon monoxide, formic acid, methanol, methane, and ethylene. To gain insight into the transformation of CO2 at a molecular level, the chemistry of the activation of CO2 via a nucleophilic attack/interaction on the polarized C center, in addition to the reduction of the coordinated CO2 ligand by low-valence transition metal complexes, has grown explosively over past years. The versatile chemical transformations of CO2, i.e. insertion of CO2 producing bicarbonate/acetate/formate, cleavage of CO2 yielding μ-CO/μ-oxo transition-metal complexes, and electrocatalytic reduction of CO2 affording CO/HCOOH/CH3OH/CH4/C2H4/oxalate, were well documented. Here we show a novel pathway for the reductive activation of CO2 by a mononuclear Ni(III) complex [NiIII(OMe)(P(C6H3-3-SiMe3-2-S)3)]⁻. This [NiIII(OMe)]-mediated reduction of CO2 yields the complex Ni(III)₃⁻(OCO⁻¹), evidenced by single-crystal X-ray diffraction, EPR, SQUID, Ni/S K-edge X-ray absorption spectroscopy, and Ni valence-to-core X-ray emission spectroscopy. The inertness of the analogous complexes [NiII(SPh)], [NiIII(CO)], and [NiIII(N2H4)] toward CO2, in contrast, demonstrates that the ionic [NiIII(OMe)] core attracts the binding of weak σ-donor CO2 and triggers the subsequent reduction of CO2 by the nucleophilic [OMe]⁻ in the immediate vicinity. This metal–ligand cooperative activation of CO2 may open a novel pathway promoting the subsequent incorporation of CO2 in the buildup of functionalized products.

**Results and discussion**

**Synthesis and characterization of nickel k¹-OCO complex**

When CO2 was bubbled into the thermally stable [NiIII(OMe)(PS3)]⁻ (1) [PS3 = P(C6H3-3-SiMe3-2-S)3] in THF,
a pronounced color change from blue green to yellow green occurred to yield the O-bound k1-CO2 complex [Ni(k1-OCO)(PS3)]− (2), instead of complexes [Ni(OC(O)CH3)-(PS3)]− or [Ni(OC(O)H)(PS3)]− via the classical insertion or β-H migration mechanisms (Scheme 1a).9,12-16

The accompanied formation of [13C]OMe in the reaction described above was corroborated using the spin-trapping reagent DMPO (ESI Fig. S1†). The IR νOCO stretching peak at 2177 cm−1 (KBr) [νOCO: 2226 cm−1 in THF] exhibited by complex 2 supports the formation of [Ni(k1-OCO)(PS3)]−, which is consistent with the isotopic shift of the IR νOCO stretching peak to 2117 cm−1 (KBr) observed in the 13CO2 labeling experiment (ESI Fig. S2†). The conversion of complex 1 to complex 2 under a CO2 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 CO2 led to the formation of the reported complex [NiII(CO)(PS3)]− accompanied by the release of CO2(g) characterized by IR and GC (Fig. 1).28

To contrast complex 2 containing a [NiIII:CO2]− or [NiII:CO2] center, complex [NiIII(NCO)(PS3)]− (4) was synthesized via the reaction of [Ni(OC(O)H)(PS3)]− (3) and K[NCO] to mimic the isolobal [NiIII:CO2] (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 ([PS3]3−) 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 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) Å vs. 1.240(7) Å, found in complex 2 moreover indicates the polarization of CO2 via reductive activation affording a [NiIII:CO2]− species.22,30,31 A similar polarization of CO2 was reported in the O-bound k1-CO2-coordinated complex [[(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.29,31 Besides, complex 2 displays a significantly longer Ni–O bond distance (2.028(3) Å) than those observed in [NiII(L)[pyN(Me2)]]+ complexes (1.857(5) Å for L = HCO3−; 1.817(4) Å for L = HCO3−).32

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 Ni1s-to-Ni3d transition energy. Accordingly, the
The 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^7 Ni(III) center in [Ni^III(L)(PS3)]. The spin quantitation of complex 2 at 300 K (ESI Fig. S7B and S7C) reveals an effective magnetic moment of 1.59 μB, whereas complex 4 exhibits a spin quantitation of 1.59 μB, indicating the presence of a Ni^III complex bearing a 17-valence-electron [CO2]^- ligand.

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]^- by the [CO2]^- 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 resemble the experimental V2C features and, in particular, the trend of the energy shift comparing complexes 2 and 4. The contribution of the 4g^u, 3g^u, and 1π^u orbitals of [NCO]^- and Ni^III=3p orbitals results in the V2C features of complex 4. For complex 2, the absence of transitions from the 3π^u and 1π^g orbitals and an additional transition from the occupied 2π^u orbitals.

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_P 2.028(3); Ni-P 2.122(1); Ni-S 2.221(1), 2.287(1), and 2.285(1); O=C 1.132(6); O=C-C 1.240(7); O=Ni=O_P 176.2(1); O=Ni=O_C 127.0(4); O_C=N=O_C 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=O_P 175.0(1); Ni=N-C 135.1(2); O=C=N-C 177.2(3).

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).
Complexes from the Ni and S K-edge X-ray absorption spectroscopy

| Complexes | Ni_{1s} \rightarrow Ni_{3d} energy (eV) | S_{1s} \rightarrow Ni_{3d} energy (eV) | S_{1s} \rightarrow Ni_{3d} intensity | Relative d-manifold energy shift (eV) |
|-----------|---------------------------------------|---------------------------------------|-----------------------------------|-----------------------------------|
| 1         | 8332.9                                | 2469.7                                | 2470.0                            | 0.29                              | 2472.1                            | 0                                      |
|           | 8333.1                                | 2469.9                                | 2470.5                            | 0.47                              | 2472.1                            | 0.3                                    |
| 4         | 8332.7                                | 2469.5                                | 2470.2                            | 0.33                              | 2472.2                            | 0                                      |
|           | 8333.0                                | 2469.8                                | 2470.4                            | 0.52                              | 2472.3                            | 0.1                                    |

* The peak energy is determined by the minimum of the second derivative. † The peak energy and intensity is determined based on the spectral deconvolution. ‡ The intensity-weighted average energy is given here. § Calculated from the difference of the thiolate peak energy and the intensity-weighted pre-edge peak energy.

The orbit of \([\text{CO}_2]^{2-}\), in addition to the upward shift of the Ni_{3d}–S_{3p} orbitals in complex 2, rationalizes the higher V2C transition energy of complex 2 in comparison with complex 4.

Complex \([\text{Ni} (\text{L}) (\text{P} (\text{C}_6\text{H}_3-3\text{-SiMe}_3-2\text{-S})_3)]^\text{−}\), 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 Ni^{III}; L = CO, N_{2}H_{4} for Ni^{II}). To dissect the unique reactivity of \([\text{Ni}^{III}(\text{OMe})(\text{PS}_3)]^-\) (1) toward CO\(_2\) activation, the addition of CO\(_2\) into a THF solution of the representative Ni^{III}-chalcogenate complex \([\text{Ni}(\text{SPh})(\text{PS}_3)]^-\) was investigated. In contrast to the reaction of complex 1 and CO\(_2\) yielding complex 2, complex \([\text{Ni}^{III}(\text{SPh})(\text{PS}_3)]^-\) is inert toward CO\(_2\). In addition, despite the potential reduction power of the Ni^{II} center in combination with the labile nature of the CO or N\(_2\)H\(_4\) ligand, neither complex \([\text{Ni}^{III}(\text{CO})(\text{PS}_3)]^-\) nor complex \([\text{Ni}^{III}(\text{N}_{2}\text{H}_4)(\text{PS}_3)]^-\) showed a reaction toward CO\(_2\) when the THF solution of these Ni complexes was treated with CO\(_2\), respectively, at ambient temperature for 3 days. As shown in ESI Fig. S4† and Table 1, the covalent character of the \([\text{Ni}^{III}(\text{SPh})]\) core, compared to the \([\text{Ni}^{III}(\text{OMe})]\) core, derived from the σ/π-electron-donating nature of the coordinated phenylthiolate ligand, rationalizes the inertness of \([\text{Ni}^{III}(\text{SPh})(\text{PS}_3)]^-\) toward CO\(_2\)\(^{33,34}\). Despite the labile nature of CO and N\(_2\)H\(_4\), the inert reactivity of the Ni^{II} center toward CO\(_2\) demonstrates that the lowered Ni_{3d} manifold orbitals in Ni^{III} complex 1 attracts the binding of weak σ-donor CO\(_2\) and triggers the subsequent reduction of CO\(_2\) by the nucleophilic \([\text{OMe}]^-\) in the immediate vicinity. The reactivity of complex 1 toward CO\(_2\), affording an O-bound \([\text{Ni}^{III}(\text{CO}_2)\text{–}\text{OMe}]^-\) species, unveils a novel strategy for the immobilization and reductive activation of CO\(_2\) contrary to the typical interaction of unoccupied CO\(_2\) 2π\(_u\) orbitals with filled high-lying metal d orbitals in low-valence metal complexes.\(^{38,39}\) Theoretically, lowering the energy of the 2π\(_u\) (6a\(_1\)) (LUMO) orbital on CO\(_2\) for interaction with nickel orbitals binding by way of the O=\(\equiv\)C– unit may be responsible for the coordinated CO\(_2\) reduction and the nonlinearity of the triatomic CO\(_2\) molecule which contains 17 valence electrons, as reported by McGlynn and co-workers.\(^{37}\) 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 CO\(_2\).

**Conclusions**

Complex 1, with the inherent combination of an electrophilic \([\text{Ni}^{III}(\text{PS}_3)]^-\) core and a properly positioned \([\text{OMe}]^-\) nucleophile, was employed to provide an optimum electronic condition to trap and activate CO\(_2\) to afford complex 2, containing the O-coordinated \([\kappa^3\text{CO}_2\text{–}\text{OMe}]^-\) ligand. The Ni^{III}-mediated reduction of CO\(_2\) by an adjacent \([\text{OMe}]^-\) ligand immobilizes CO\(_2\) in the form of \([\text{Ni}^{III}(\text{CO}_2\text{–}\text{OMe})]\) and may open a novel CO\(_2\) activation pathway promoting the subsequent incorporation of CO\(_2\) in the buildup of functionalized products.

---

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

---

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

We gratefully acknowledge the support on the hardware and software from staff at BL-16A and BL-17C of NSRRC, and BL 6-2 of SLAC. Authors thank Ms Pei-Lin Chen for single-crystal X-ray structural determinations, Mr Yu-Huan Lu and Prof Hsin-Tsung Chen for the help on theoretical calculation. We also thank the Ministry of Science and Technology (Taiwan) for the financial support.

Notes and references

1. T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
2. D. J. Darenbourg, *Chem. Rev.*, 2007, **107**, 2388.
3. J.-H. Jeoung and H. Dobbek, *Science*, 2007, **318**, 1461.
4. M. Can, F. A. Armstrong and S. W. Ragsdale, *Chem. Rev.*, 2014, **114**, 4149.
5. J. Fesseler, J.-H. Jeoung and H. Dobbek, *Angew. Chem.*, 2015, **54**, 8560.
6. M. Aresta, C. F. Nobile, V. G. Albano, E. Forni and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 1975, 636.
7. J. S. Anderson, V. M. Iluc and G. L. Hillhouse, *Inorg. Chem.*, 2010, **49**, 10203.
8. Y.-E. Kim, J. Kim and Y. Lee, *Chem. Commun.*, 2014, **50**, 11458.
9. Y.-E. Kim, S. Oh, S. Kim, O. Kim, J. Kim, S. W. Han and Y. Lee, *J. Am. Chem. Soc.*, 2015, **137**, 4280.
10. C. Costentin, M. Robert and J. M. Saveant, *Chem. Soc. Rev.*, 2013, **42**, 2423.
11. M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975.
12. A. Looney, R. Han, K. Mcneill and G. Parkin, *J. Am. Chem. Soc.*, 1993, **115**, 4690.
13. O. R. Allen, S. J. Dalgaro, L. D. Field, P. Jensen, A. J. Turnbull and A. C. Willis, *Organometallics*, 2008, **27**, 2092.
14. A. Jana, D. Ghoshal, H. W. Roessky, I. Objartel, G. Schwab and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288.
15. S. F. Yin, J. Maruyama, T. Yamashita and S. Shimada, *Angew. Chem.*, 2008, **47**, 6590.
16. B. Kersting, *Angew. Chem.*, 2001, **40**, 3987.
17. M. Vogt, A. Nerush, Y. Diskin-Posner, Y. Ben-David and D. Milstein, *Chem. Sci.*, 2014, **5**, 2043.  
18. G. A. Filonenko, M. P. Conley, C. Copéret, M. Lutz, E. J. M. Hensen and E. A. Pidko, *ACS Catal.*, 2013, **3**, 2522.
19. C. C. Lu, C. T. Saouma, M. W. Day and J. C. Peters, *J. Am. Chem. Soc.*, 2007, **129**, 4.
20. M. T. Whited and R. H. Grubbs, *J. Am. Chem. Soc.*, 2008, **130**, 5874.
21. B. C. Fullmer, H. J. Fan, M. Pink and K. G. Caulton, *Inorg. Chem.*, 2008, **47**, 1865.
22. I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242.
23. S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 12536.
24. J. G. Rebelein, Y. Hu and M. W. Ribbe, *Angew. Chem.*, 2014, **53**, 11543.
25. R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313.
26. G. H. Jin, C. G. Werncke, Y. Escudiee, S. Sabo-Etienne and S. Bontemps, *J. Am. Chem. Soc.*, 2015, **137**, 9563.
27. T.-W. Chiou and W.-F. Liaw, *Inorg. Chem.*, 2008, **47**, 7908.
28. C.-M. Lee, Y.-L. Chuang, C.-Y. Chiang, G.-H. Lee and W.-F. Liaw, *Inorg. Chem.*, 2006, **45**, 10895.
29. N. A. M. Azman, S. Peiro, L. Fajari, L. Julia and M. P. Almajano, *J. Agric. Food Chem.*, 2014, **62**, 5743.
30. I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. A Meyer, *Science*, 2004, **305**, 1757.
31. W. J. Evans, C. A. Seibel and J. W. Ziller, *Inorg. Chem.*, 1998, **37**, 770.
32. D. G. Huang and R. H. Holm, *J. Am. Chem. Soc.*, 2010, **132**, 4693.
33. T.-T. Lu, S.-H. Lai, Y.-W. Li, I.-J. Hsu, L.-Y. Jang, J.-F. Lee, I.-C. Chen and W.-F. Liaw, *Inorg. Chem.*, 2011, **50**, 5396.
34. E. I. Solomon, B. Hedman, K. O. Hodgson, A. Dey and R. K. Szilagyi, *Coord. Chem. Rev.*, 2005, **249**, 97.
35. C.-M. Lee, C.-H. Chen, S.-C. Ke, G.-H. Lee and W.-F. Liaw, *J. Am. Chem. Soc.*, 2004, **126**, 8406.
36. J. H. Lunsford and J. P. Jayne, *J. Phys. Chem.*, 1965, **69**, 2182.
37. J. W. Rabalais, J. M. McDonald, V. Scherr and S. P. Meglynn, *Chem. Rev.*, 1971, 71, 73.
38. X. L. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
39. D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063.