Cite this: Chem. Commun., 2012, 48, 9595–9597

www.rsc.org/chemcomm

## COMMUNICATION

## Carbon disulfide binding at dinuclear and mononuclear nickel complexes ligated by a redox-active ligand: iminopyridine serving as an accumulator of redox equivalents for the activation of heteroallenes<sup>†</sup>

Amarnath Bheemaraju, Jeffrey W. Beattie, Richard L. Lord, Philip D. Martin and Stanislav Groysman\*

Received 15th June 2012, Accepted 7th August 2012 DOI: 10.1039/c2cc34307j

The dinuclear complex  $Ni_2L^1(\eta^2-CS_2)_2$  (2), featuring iminopyridine ligation, is prepared by COD substitution from  $Ni_2L^1(COD)_2$  (1). Spectroscopic, structural, and theoretical data reveals significant activation of the metal-bound C–S bonds, as well as the different oxidation states of the iminopyridine in 1 (1–) and 2 (0).

Contemporary interest in the chemistry of carbon dioxide is motivated by its detrimental environmental effects combined with a potential to serve as an inexpensive and plentiful  $C_1$  building block in the synthesis of chemicals or fuels.<sup>1,2</sup> Development of the basic chemistry of carbon dioxide is impeded by its low reactivity with metal centers.<sup>3,4</sup> Carbon disulfide is a useful model for carbon dioxide reactivity: it is a liquid, it is slightly more reactive, and it often displays similar binding and activation modes.<sup>5–9</sup> Thus, carbon disulfide chemistry can help shed light on the chemistry of its relatively unreactive congener.

Dinuclear metal complexes tailored for cooperative reactivity<sup>10</sup> present a promising strategy towards activation of small molecules, in particular carbon dioxide.<sup>11</sup> Our synthetic endeavors are focused on the preparation and reactivity studies of dimetallic platforms featuring redox-active chelating units with carbon dioxide and related heteroallenes. We have recently reported dinuclear complexes of Ni(0) with flexible bis(iminopyridine) ligands.<sup>12</sup> The coordination chemistry of these ligands was found to depend on the imino-carbon atom substituent. For the H-substituent, dinuclear complex Ni<sub>2</sub>L<sup>1</sup>(COD)<sub>2</sub> (1) was obtained, whereas a Me-imino carbon atom substituent led to the formation of bis(homoleptic) complexes of (NiL<sup>2</sup>)<sub>2</sub> constitution. Herein, we report the synthesis and the characterization of the dinuclear Ni<sub>2</sub>L<sup>1</sup>(CS<sub>2</sub>)<sub>2</sub> complex obtained by reaction of 1 and CS<sub>2</sub>, and compare it with its mononuclear analogue.

Treatment of a blue-violet THF solution of 1 with two equivalents of carbon disulfide results in an immediate color

Downloaded by Monash University on 14 March 2013 Downloaded by Monash University on 14 March 2013 Downloaded by Monash University on 14 March 2013 Digital Endown on 8 August 2012 on http://pubs.rsc.org | doi:10.1039/C2CC343071 Spect activa Spect activa

change to purple-brown and precipitate formation. Unlike 1, Ni<sub>2</sub>L<sup>1</sup>(CS<sub>2</sub>)<sub>2</sub> (**2**, Fig. 1) has poor solubility in THF, enabling its easy isolation in high yield as a dark purple solid.<sup>‡</sup> Compound **2** has modest solubility in DMF or DMSO. The <sup>1</sup>H NMR spectrum of **2** is consistent with two identical iminopyridine units. We prepared a <sup>13</sup>C-enriched (99% <sup>13</sup>C) sample of **2** and collected its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The <sup>13</sup>CS<sub>2</sub> signal of **2** appears at 268 ppm (see Fig. S3 in the ESI<sup>†</sup>), indicating its substantial activation.<sup>7,9</sup> The IR spectrum of Ni<sub>2</sub>L<sup>1</sup>(CS<sub>2</sub>)<sub>2</sub> shows two prominent signals at *ca*. 1138 cm<sup>-1</sup> and 648 cm<sup>-1</sup> that shift to 1095 cm<sup>-1</sup> and 633 cm<sup>-1</sup> upon substitution by <sup>13</sup>CS<sub>2</sub> (Fig. S24–S27, ESI<sup>†</sup>). These signals are assigned as C=S and C–S stretches, respectively.<sup>9,13</sup> ESI-MS displays a molecular ion peak at *m*/*z* = 581.8, and the signal attributed to CS<sub>2</sub> loss is observed at *m*/*z* = 505.9 (Fig. S22 and S23, ESI<sup>†</sup>).

Metal-assisted activation of  $CS_2$  has often resulted in its further reactivity, culminating in disproportionation or C–C coupling.<sup>5,6,14</sup> Compound **2** is sparingly soluble, can be isolated in high yield, and demonstrates no decomposition in solution over 24 hours as judged by its <sup>1</sup>H NMR spectrum. We have also prepared a mononuclear analogue of **2**, compound **4**. Compound **4** was obtained by the reaction of **3** (prepared from *N*-benzyliminopyridine<sup>15</sup> and Ni(COD)<sub>2</sub>, see ESI† for details) with 1 equiv. of  $CS_2$ . Spectroscopic data for **3** and **4** are similar to the spectroscopic data for **1** and **2** (Fig. S4–S6, ESI†). Compound **4** has significantly higher solubility in THF, DMF and DMSO. Surprisingly, **4** is not stable in solution for prolonged periods



Fig. 1 Reactivity of 1 and 3 with CS<sub>2</sub>.

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA. E-mail: groysman@chem.wayne.edu;

Tel: +1 313 577 2689

<sup>†</sup> Electronic supplementary information (ESI) available: Full experimental procedures, NMR spectra, and X-ray data. CCDC 887355–887357. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc34307j



**Fig. 2** (a): X-ray structure of **2**; (b): X-ray structure of **3**. (c): X-ray structure of **4**. The structures are drawn with 50% probability ellipsoids. Relevant bond distances are shown. The structure of **4** contains two crystallographically independent molecules showing different CS bond metrics.

of time, undergoing facile decomposition to unidentified products, as evidenced by <sup>1</sup>H NMR spectroscopy (see ESI<sup>†</sup>).

2 can be recrystallized from DMSO-ether. The X-ray structure of  $Ni_2L^1(CS_2)_2$  is presented in Fig. 2.§ This structure is one of the few examples of a group 10 carbon-disulfide complex.<sup>5,6,9,16</sup> The first example, Pt(PPh<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>), was reported by Wilkinson and coworkers,16a and the structure of  $Ni(dtbpe)(CS_2)$  (dtbpe = 1.2-bis(di-tert-butylphosphino)ethane) was recently reported by Hillhouse and co-workers.<sup>9</sup> The structures of 2 and 4 provide the first examples involving a non-phosphine ligated group 10 metal CS<sub>2</sub> complex. The metal coordination geometry is nearly square-planar. Side-on coordination of CS<sub>2</sub> leads to a significant difference in the bound vs. unbound CS<sub>2</sub> bonds (C3–S2 = 1.59(1) Å, C3-S1 = 1.70(1) Å). Inspection of the relevant C-C bonds in the imino-pyridine ligand backbone (C1–C2 = 1.45(1) Å; C1-N1 = 1.27(1) Å) reveals fully oxidized iminopyridine ligand. The structure of the mononuclear analogue 4¶ (ESI<sup>†</sup>) confirms the overall structural features of CS<sub>2</sub> ligation and the iminopyridine ligand redox state. The unit cell contains two independent molecules of 4 (4a and 4b) showing a variability in the C-S/C=S metrics: 1.69(1)/1.62(1) Å are observed for 4a and 1.74(1)/1.55(1) Å are detected for 4b. However, relevant iminopyridine metrics are almost identical for 4a, 4b and 2, and are consistent with the fully oxidized iminopyridine: C1-C2 =1.47(1) Å; C1–N1 = 1.27(1) Å for **4a** and C1–C2 = 1.45(1) Å; C1-N1 = 1.27(1) A for 4b. Density functional theory calculations for 4 are consistent with C-S/C=S bond lengths of 1.706/1.634 Å and iminopyridine metrics of C1–C2 = 1.458 Å and C1–N1 = 1.303 Å. Unlike the electronic structure we reported for the iminopyridine/COD and bis(iminopyridine) complexes,<sup>12</sup> 4 has Ni<sup>II</sup> and an oxidized iminopyridine ligand as evidenced by the orbital diagram in Fig. 3 (the electronic structure for the dinickel complex 2 is the same as for the



We have carried out preliminary reactivity studies involving **2**. Treatment of **2** with PPh<sub>3</sub> at RT for 24 h does not lead to S-atom transfer to the phosphine (Fig. S19 and S20, ESI†). Treatment of <sup>13</sup>C-labelled **2** (**2**-<sup>13</sup>CS<sub>2</sub>) with unlabelled CS<sub>2</sub> has resulted in exchange, forming free <sup>13</sup>CS<sub>2</sub> (192 ppm in DMSO-d<sub>6</sub>) and **2**-CS<sub>2</sub> (no <sup>13</sup>C NMR signal at 268 ppm). Cyclic voltammetry of **2** has demonstrated several irreversible features, most notably an irreversible oxidation around -0.25 V (*vs.* FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup>, see Fig. S29, ESI†). For comparison, this feature was absent in the voltammogram of **1** (Fig. S30, ESI†). The presence of this oxidation wave prompted us to investigate chemical oxidation of **2**.



Fig. 3 Frontier orbital diagram of 4. Doubly occupied and unoccupied orbitals represented by bold and normal lines, respectively.

mononickel complex 4 and is presented in the ESI<sup>†</sup> in Fig. S28).

The LUMO (81) shows the completely unoccupied  $\pi^*$  orbital of

the iminopyridine ligand, and the LUMO + 3 (84) shows the

antibonding orbital between Ni– $d_{x^2-v^2}$  and the activated CS<sub>2</sub>. In

addition, there are two doubly occupied orbitals, 78 and 80,

which correspond to in- and out-of-phase combinations

between  $d_{z^2}$  and a sulfur p-orbital and therefore only count as one metal-based orbital, confirming the Ni<sup>II</sup> oxidation state. We

Treatment of a deep-purple solution of **2** in DMSO-d<sub>6</sub> with 2 equiv. of  $[FeCp_2](PF_6)$  led to an immediate color change to yellow, followed by a slow decay to purple. <sup>1</sup>H NMR of the resulting solution indicated formation of FeCp<sub>2</sub>, along with a trace amount of **2**. Formation of free <sup>13</sup>CS<sub>2</sub> was observed by <sup>13</sup>C NMR spectrum. Addition of two more equivalents of  $[FeCp_2](PF_6)$  has led to a significant increase in the free <sup>13</sup>CS<sub>2</sub> as indicated by <sup>13</sup>C NMR spectrum. Based on these experiments, we propose that the oxidation of **2** releases CS<sub>2</sub> instead of its functionalization. Compound **4** displays similar behavior, releasing CS<sub>2</sub> upon treatment with  $[FeCp_2](PF_6)$ .

In summary, we report synthesis and characterization of the dinuclear  $L^1Ni_2(CS_2)_2$  complex featuring square planar Ni centers ligated by iminopyridine chelates. Spectroscopic, theoretical and structural investigation of the dinuclear  $CS_2$  complex **2** and its mononuclear analogue **4**, and their COD-ligated counterparts **1** and **3**, reveal that the iminopyridine serves as a redox accumulator, moderating redox changes in Ni upon binding of a heteroallene. Our preliminary experiments targeting oxidative modification of bound  $CS_2$  have resulted in  $CS_2$  release in both **2** and **4**. We are currently preparing related  $CO_2$  complexes, and investigating their reactivity. In addition, other dinucleating ligands are being designed, to enable more reactive heteroallene adducts.

We thank Wayne State University for funding. SG thanks Prof. H. B. Schlegel for helpful discussions. AB thanks Bashar Ksebati and Lew Hryhorczuk for the experimental assistance. The computational resources were provided by the WSU Grid.

## Notes and references

‡ Synthesis of **2**. A 1.5 M THF solution of CS<sub>2</sub> (0.15 mL, 0.231 mmol) was added to a 5 mL violet-blue THF solution of Ni<sub>2</sub>(L<sup>1</sup>)(COD)<sub>2</sub> (**1**, 75 mg, 0.115 mmol). A precipitate was obtained after the addition of CS<sub>2</sub>. The reaction was stirred for 15 min, and the solid was separated from the reaction mixture and washed with ether. Removal of the supernatant followed by drying resulted a purple brown solid (60 mg, 88%). The <sup>13</sup>C-labeled sample was prepared in an identical fashion. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$  9.44 (d, J = 4.8, 2H), 8.90 (s, 2H), 8.23 (t, J = 7.6 Hz, 2H), 7.96 (d, J = 8.0, 2H), 7.90 (t, J = 6.4, 2H), 7.51 (s, 4H), 5.23 (s, 4H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75 MHz)  $\delta$  267.87 (<sup>13</sup>CS<sub>2</sub>). MS (ESI) calcd for [Ni<sub>2</sub>(L<sup>1</sup>)(CS<sub>2</sub>)]<sup>+</sup> 581.9, found 581.8; [Ni<sub>2</sub>(L<sup>1</sup>)(CS<sub>2</sub>)]<sup>+</sup> 505.9, found 505.8. IR (cm<sup>-1</sup>, <sup>12</sup>CS)<sup>13</sup>CS signals): 1138/1095 (s), 648/633 (s). Anal. calcd for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>Ni<sub>2</sub>S<sub>4</sub>: C, 45.24; H, 3.11; N, 9.59. Found: C, 44.97; H, 3.27 N, 9.32.

§ Crystal data for **2**. C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>NiS<sub>2</sub>, M = 292.03, monoclinic, space group  $P2_1/n$ , a = 7.2464(7) Å, b = 10.7305(9) Å, c = 14.446(1) Å,  $\beta = 94.265(5)^{\circ}$ , V = 1120.14(17) Å,  $D_c = 1.732$  g cm<sup>-1</sup>, Z = 4,  $\mu = 2.073$  mm<sup>-1</sup>, T = 100(2), 1920 unique reflections,  $R_1(I > 2\sigma(I)) = 0.0695$ ,  $wR_2(I > 2\sigma(I)) = 0.1731$ , GOF = 1.071.

¶ Crystal data for **4**.  $C_{28}H_{24}N_4N_{12}S_4$ , M = 662.17, triclinic, space group  $P\bar{I}$ , a = 8.7358(7) Å, b = 9.5434(7) Å, c = 17.008(1) Å,  $\alpha = 98.210(5)^\circ$ ,  $\beta = 98.742(5)^\circ$ ,  $\gamma = 96.563(5)^\circ$ , V = 1373.60(19) Å,  $D_c = 1.601$  g cm<sup>-1</sup>, Z = 2,  $\mu = 1.701$  mm<sup>-1</sup>, T = 100(2), 5945 unique reflections,  $R_1(I > 2\sigma(I)) = 0.0712$ ,  $wR_2(I > 2\sigma(I)) = 0.2004$ , GOF = 1.030.

|| See ESI† for calculations details.

\*\* Crystal data for **3**.  $C_{21}H_{24}N_2Ni$ , M = 363.13, monoclinic, space group C2/c, a = 25.286(3) Å, b = 7.3278(6) Å, c = 21.348(2) Å,  $\beta = 120.423(8)^{\circ}$ , V = 3411.0(6) Å,  $D_c = 1.414$  g cm<sup>-1</sup>, Z = 8,  $\mu = 1.141$  mm<sup>-1</sup>, T = 100(2), 6713 unique reflections,  $R_1(I > 2\sigma(I)) = 0.0258$ ,  $wR_2(I > 2\sigma(I)) = 0.0710$ , GOF = 1.046.

- 1 M. Arresta and A. Dibenedetto, in *Carbon Dioxide Recovery* and *Utilization*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2010, p. 211.
- 2 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
- 3 J. Mascetti, in *Carbon Dioxide as a Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, Germany, 2010, p. 55.
- 4 For selected examples of structurally characterized M-CO<sub>2</sub> complexes, see: (a) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni and M. Manassero, J. Chem. Soc., Chem. Commun., 1975, 636; (b) G. Fachinetti, C. Floriani and P. F. Zanazzi, J. Am. Chem. Soc., 1978, 100, 7405; (c) J. S. Field, R. J. Haines, J. Sundermeyer and S. F. Woollam, J. Chem. Soc., Chem. Commun., 1990, 985; (d) T.-F. Wang, C.-C. Hwu, C.-W. Tsai and K.-J. Lin, Organometallics, 1997, 16, 3089; (e) C. H. Lee, D. S. Laitar, P. Mueller and J. P. Sadighi, J. Am. Chem. Soc., 2007, 129, 13802; (f) C. C. Lu, C. T. Sauoma, M. W. Day and J. C. Peters, J. Am. Chem. Soc., 2007, 129, 4; (g) J. C. Calabrese, T. Herskovitz and J. B. Kinney, J. Am. Chem. Soc., 1983, 105, 5914.
- 5 (a) J. A. Ibers, Chem. Soc. Rev., 1982, 11, 57; (b) K. K. Pandey, Coord. Chem. Rev., 1995, 140, 37.
- 6 W. Poppitz, Z. Anorg. Allg. Chem., 1982, 489, 67.
- 7 P. Haack, C. Limberg, T. Tietz and R. Metzinger, *Chem. Commun.*, 2011, **47**, 6374.
- 8 E. M. Matson, W. P. Forrest, P. E. Fanwick and S. C. Bart, J. Am. Chem. Soc., 2011, 133, 4948.
- 9 J. S. Anderson, V. M. Iluc and G. L. Hillhouse, *Inorg. Chem.*, 2010, **49**, 10203.
- For selected recent references, see: (a) D. E. Herbert and O. V. Ozerov, *Organometallics*, 2011, **30**, 6641; (b) A. R. Fout, Q. Zhao, D. J. Xiao and T. A. Betley, *J. Am. Chem. Soc.*, 2011, **133**, 16750; (c) T. C. Davenport and T. D. Tilley, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 12205.
- For selected recent references, see: (a) D. P. Hruszkewycz, J. Wu, J. C. Green, N. Hazari and T. J. Schmeier, *Organometallics*, 2012, **31**, 470; (b) J. P. Krogman, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2011, **133**, 14582.
- 12 A. Bhemaraju, R. L. Lord, P. Müller and S. Groysman, Organometallics, 2012, 31, 2120.
- 13 DFT calculations agree with these assignments.
- 14 (a) M. G. Mason, P. N. Swepston and J. A. Ibers, *Inorg. Chem.*, 1983, **22**, 411; (b) C. Bianchini, C. Mealli, A. Meli and M. Sabat, *Inorg. Chem.*, 1984, **23**, 4125; (c) J. J. Maj, A. D. Rae and L. F. Dahl, *J. Am. Chem. Soc.*, 1982, **104**, 4278.
- 15 E. C. Volpe, P. T. Wolczanski and E. B. Lobkovsky, Organometallics, 2010, 29, 364.
- 16 For the structures of Group 10 CS<sub>2</sub> complexes, see: (a) M. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae and G. Wilkinson, Chem. Commun., 1967, 92; (b) C. Bianchini, D. Masi, C. Mealli and A. Meli, Inorg. Chem., 1984, 23, 2838; (c) D. H. Farrar, R. R. Gukathasan and S. A. Morris, Inorg. Chem., 1984, 23, 3258; (d) P. Leoni, M. Pasquali, L. Fadini, A. Albinati, P. Hofmann and M. Metz, J. Am. Chem. Soc., 1997, 119, 8625; (e) T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi and N. Hagihara, Bull. Chem. Soc. Jpn., 1968, 41, 296.
- 17 (a) C. C. Lu, E. Bill, T. Weyhermüller, E. Bothe and K. Wieghardt, J. Am. Chem. Soc., 2008, **130**, 3181–3197; (b) C. C. Lu, S. DeBeer George, T. Wehermüller, E. Bill, E. Bothe and K. Wieghardt, Angew. Chem., 2008, **120**, 6484.
- 18 (a) T. W. Myers and L. A. Berben, J. Am. Chem. Soc., 2011, 133, 11865; (b) T. W. Myers, N. Kazem, S. Stoll, R. D. Britt, M. Shanmugam and L. A. Berben, J. Am. Chem. Soc., 2011, 133, 8662; (c) T. W. Myers and L. A. Berben, Inorg. Chem., 2012, 51, 1480.
- 19 N. A. Ketterer, H. Fan, K. J. Blackmore, X. Yang, J. W. Ziller, M.-H. Baik and A. F. Heyduk, *J. Am. Chem. Soc.*, 2008, **130**, 4364.
- 20 (a) K. G. Caulton, Eur. J. Inorg. Chem., 2012, 435; (b) P. J. Chiric, Forum on Redox-Active Ligands, Inorg. Chem., 2011, 50, 9737.