

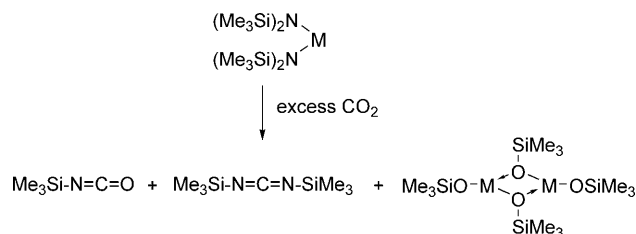
Insertion of Carbon Dioxide into Main-Group Complexes: Formation of the $[\text{N}(\text{CO}_2)_3]^{3-}$ Ligand**

Diane A. Dickie, Marie V. Parkes, and Richard A. Kemp*

Under mild conditions CO_2 is found to react with $[\text{Sr}\{\text{N}(\text{PPh}_2)_2\}_2](\text{THF})_3$ (**1**) to oxidatively cleave PPh_2 groups from N, resulting in the previously unknown ligand $[\text{N}(\text{CO}_2)_3]^{3-}$ coordinated to a Sr_6 backbone. Overall, the Sr_6 framework chemically fixates twelve molar equivalents of CO_2 , half by the formation of two $[\text{N}(\text{CO}_2)_3]^{3-}$ ligands and the other half by CO_2 insertion to form the unprecedented phosphanyl-substituted carbamate $\text{O}_2\text{CN}(\text{PPh}_2)_2$.

The reaction chemistry of carbon dioxide to form valuable chemicals has garnered significant attention for several decades. With interests extending from the economic desire to convert a “useless” C_1 source into higher-valued products to the desire to mitigate global warming, CO_2 fixation studies span an enormous range.^[1] More specifically, we^[2] and others^[3] have previously studied the reaction chemistry of CO_2 with main-group metal amides to yield organic isocyanates and carbodiimides as products. Previous reactions of these main-group complexes with CO_2 have utilized silyl-containing amido groups as ligands. It has been postulated that the major driving force to produce the organic products is the migration of the silyl group to form a strong Si–O bond subsequent to CO_2 insertion into the metal–nitrogen bond.^[3c]

As part of our efforts in this area we have been interested in expanding the different types of amido ligands that can be utilized in reactions analogous to that shown in Scheme 1. More specifically, we focused on replacing the SiMe_3 groups with PR_2 substituents to prepare either phosphanyl-substituted isocyanates or bis(phosphanyl)carbodiimides. These phosphorus-containing organic products are relatively rare compounds that are of interest in a variety of reactions, including novel heterocycle preparations, or as possible cross-linking agents or biologically active compounds.^[4] Despite significant use in transition-metal^[5] and now lanthanide chemistry,^[6] the $\text{N}(\text{PPh}_2)_2$ fragment is relatively unexplored as a ligand in main-group chemistry.^[7] Part of the reason for this may be the tendency for the $\text{N}(\text{PPh}_2)_2$ ligand to undergo oxidative scrambling reactions in many cases, resulting in

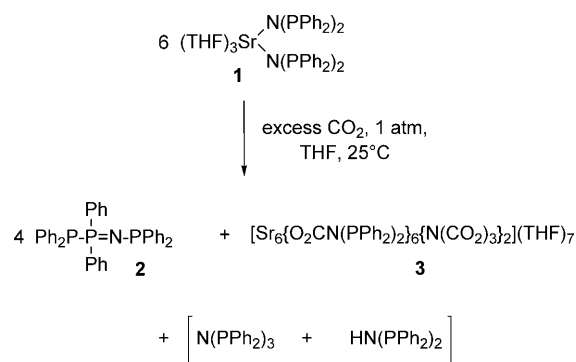


Scheme 1. Production of isocyanates and/or carbodiimides using divalent main-group metal bis(silylamides) ($\text{M} = \text{Ge}, \text{Sn}$).^[3c]

cleavage of the ligand and oxidation of the P atom to yield a polyphosphazene product. Interestingly, the conditions required in these reactions to scramble the $\text{N}(\text{PPh}_2)_2$ ligand are typically quite forcing (e.g., boiling toluene for 5–60 h).^[8]

Recently, Roesky reported the preparation and structural characterization of the heavier Group 2 elements (Sr, Ba) containing this $\text{N}(\text{PPh}_2)_2$ ligand.^[9] Concurrent with Roesky's work, in our own laboratory we had prepared and characterized the lighter Group 2 element (Mg, Ca) complexes of the same ligand,^[10] both of which were essentially isostructural to the Sr salt prepared by Roesky.^[9]

Based on this background we examined the reaction of CO_2 with these compounds, including the highly ionic complex **1**. The reaction of **1** with CO_2 is shown in Scheme 2. Bubbling an excess of dry CO_2 at room temperature through a solution of **1** in THF led to a rapid reaction, as evidenced by the complete disappearance of the signal in the ^{31}P NMR spectrum of **1** in less than 15 min. ^{31}P NMR spectroscopic analysis of the product solution indicated a mixture of P-containing compounds. Easily identifiable by their ^{31}P NMR chemical shifts were **2**, a compound prepared previously by Nöth using a direct synthesis,^[11] and trace amounts of $\text{N}(\text{PPh}_2)_3$ ^[12] and $\text{HN}(\text{PPh}_2)_2$.^[11] It was thus obvious to us that the expected reaction analogous to Scheme 1 had not occurred, or at least not cleanly.



Scheme 2. Synthesis of compounds **2** and **3**.

[*] Dr. D. A. Dickie, M. V. Parkes, Prof. R. A. Kemp
Department of Chemistry and Chemical Biology
University of New Mexico, Albuquerque, NM 87131 (USA)
E-mail: rakemp@unm.edu

[**] We thank the Natural Science and Engineering Research Council of Canada (Post-Doctoral Fellowship to D.D.), the National Science Foundation (Grants CHE-0213165 and CHE-0443580) and the Sandia LDRD Program (Grants 105932 and 113486) for funding this work. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000. We also thank Dr. E. N. Duesler and Prof. A. L. Rheingold for aid in the X-ray structure analysis.

Upon prolonged standing, the reaction mixture from Scheme 2 deposited **3** as colorless single crystals suitable for X-ray analysis.^[13] The X-ray structure of **3** is shown in Figure 1. It consists of a hexanuclear strontium backbone held

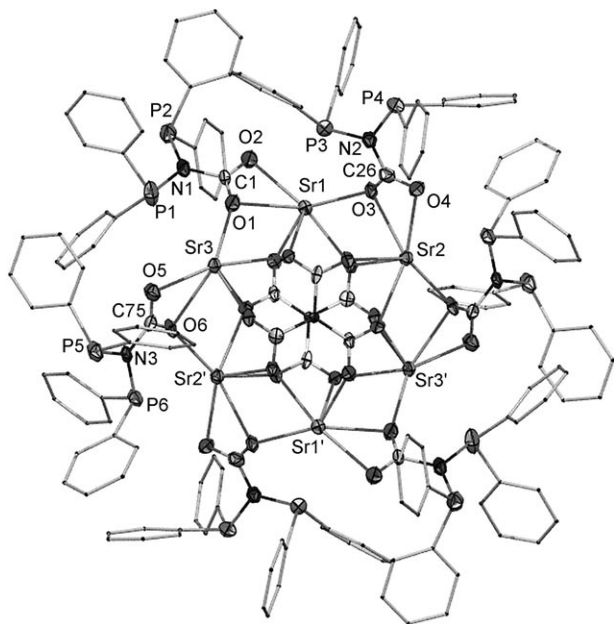


Figure 1. X-ray crystal structure of **3**. Thermal ellipsoids are set at the 50% probability level. For clarity, hydrogen atoms and THF molecules have been removed, and the phenyl rings are shown as stick drawings. The periphery of the molecule consists of one $\text{O}_2\text{C}[\text{N}(\text{PPh}_2)_2]$ group per Sr atom. The core of the structure (shown in more detail in Figure 2) consists of two symmetry-related $[\text{N}(\text{CO}_2)_3]^{3-}$ fragments coordinated to six Sr atoms.

together by six bridging phosphanyl-modified carbamate ligands $\text{O}_2\text{CN}(\text{PPh}_2)_2$, formed by CO_2 insertion into the Sr–N bond of a $\text{N}(\text{PPh}_2)_2$ ligand. While the primary bonding mode of the new ligand is η^2 -chelating to Sr through the O–C–O linkage of the carbamate, one of the O atoms also acts as a bridge to an adjacent Sr atom. Similarly, one of the P atoms of the ligand provides an additional chelating arm to the same adjacent Sr atom in the Sr_6 backbone. This connectivity is repeated around the ring. The Sr_6 backbone itself can be visualized as the chair form of cyclohexane. Furthermore, one molecule of THF is also coordinated to each Sr atom, and one additional THF molecule is present but disordered within the crystal lattice.

The atomic structure of the core of **3** is shown in more detail in Figure 2. Remarkably, two $\text{N}(\text{PPh}_2)_2$ ligands have reacted with CO_2 to cleave the PPh_2 groups from nitrogen and formally insert three molar equivalents of CO_2 , resulting in the formation of two unprecedented, symmetry-related $[\text{N}(\text{CO}_2)_3]^{3-}$ ligands linked to the Sr_6 backbone. A search of the Cambridge Crystallographic Database (August 2008 update) found no structure containing the $[\text{N}(\text{CO}_2)_3]^{3-}$ fragment. The extraordinary reactivity of **1** towards CO_2 , resulting in facile CO_2 -induced cleavage of the $\text{N}(\text{PPh}_2)_2$ ligand at ambient temperature and pressure within minutes, is highly unexpected and unusual. $[\text{N}(\text{CO}_2)_3]^{3-}$ can be viewed as the trianion

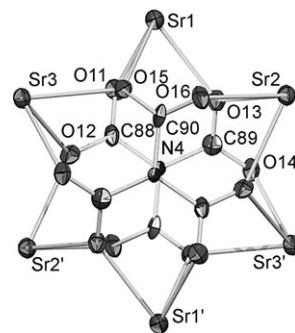


Figure 2. X-ray crystal structure of the core of **3**. Thermal ellipsoids are set at the 50% probability level.

derived from deprotonation of the hypothetical $\text{N}(\text{CO}_2\text{H})_3$ molecule.^[14] While the parent triprotic acid complex is unknown, organic esters of the formula $\text{N}(\text{CO}_2\text{R})_3$ (where $\text{R} = \text{Et}$, $t\text{Bu}$, or substituted cyclohexyl derivatives) have been prepared by conventional synthetic routes that do not involve direct insertions of CO_2 .^[15]

Complex **3** was further characterized by other spectroscopic methods. Due to its insolubility in common organic solvents, a solid-state ^{31}P NMR spectrum of **3** was obtained instead. It cleanly showed a single, relatively sharp resonance at 36.5 ppm, indicating that the P atoms are equivalent, or very nearly so, in the solid state. The infrared spectrum contained stretches at 1659 and 1603 cm^{-1} , indicating the presence of the carboxylate moiety.

After identification of **3**, a possible explanation for the formation of the $\text{N}(\text{PPh}_2)_3$ byproduct can be postulated. Ellermann et al. have seen that $\text{N}(\text{PPh}_2)_3$ can arise from disproportionation of the $[\text{N}(\text{PPh}_2)_2]^-$ ion, which also results in a $\{\text{N}-\text{PPh}_2\}$ nitrene intermediate.^[8a] We believe that the $[\text{N}(\text{PPh}_2)_2]^-$ ion can be transiently generated during the formation of **3**, thus leading to the possibility for undesired conversion of our starting material into $\text{N}(\text{PPh}_2)_3$, thereby decreasing the yield of **3**.

Finally, we note that this novel reaction behavior and chemical conversion of CO_2 to $[\text{N}(\text{CO}_2)_3]^{3-}$ does not appear to be limited to Sr complexes. We have observed rapid reactions of CO_2 with the lighter Group 2 complexes $[\text{Mg}\{\text{N}(\text{PPh}_2)_2\}](\text{THF})_2$ and $[\text{Ca}\{\text{N}(\text{PPh}_2)_2\}](\text{THF})_3$, and full characterization of these products is currently underway. Initial results suggest that the Ca salt behaves virtually identically to **1**, while the Mg complex reacts differently. This is not entirely unexpected, as the much smaller Mg cation is likely unable to accommodate the eight bonds seen the Sr-containing product **1**.

Experimental Section

All manipulations were carried out in an argon-filled glovebox or using standard Schlenk techniques. The ligand $\text{HN}(\text{PPh}_2)_2$ ^[11] and the starting complex $[\text{Sr}\{\text{N}(\text{PPh}_2)_2\}](\text{THF})_3$ (**1**)^[9] were synthesized according to literature procedures.

3: Carbon dioxide was bubbled into a colorless solution of **1** (0.75 g, 0.24 mmol) in anhydrous THF (ca. 10 mL). After 15 min, the solution was purged with argon and left undisturbed at room temperature. Colorless, needle-like crystals of **3** grew over a period of weeks and were isolated by decanting the solvent. Yield: 0.067 g

(15% based on Sr). Mp = 177–178°C. Elemental analysis (%) for $C_{184}H_{176}N_8O_{31}P_{12}Sr_6$ calcd: C 56.77, H 4.56, N 2.88; found: C 56.95, H 4.50, N 2.88. IR: $\tilde{\nu}$ = 1659 (vs), 1603 (s), 1432 (m), 1384 (m), 1308 (m), 1272 (s), 1018 (m), 815 (m), 738 (m), 692 cm^{-1} (m). CP-MAS ^{31}P NMR (101 MHz): δ = 36.5 ppm. Byproducts including $Ph_2P-N-PPH_2$ (**2**), $N(PPH_2)_3$, and $HN(PPH_2)_2$ were identified by ^{31}P NMR spectra of the crude reaction mixture but were not isolated.

Received: August 26, 2008

Published online: October 20, 2008

Keywords: carbon dioxide · CO_2 fixation · main-group elements · N ligands · strontium

- [1] a) M. Aresta, A. Dibenedetto, *Dalton Trans.* **2007**, 2975–2992; b) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, 107, 2365–2387; c) R. Zevenhoven, S. Eloneva, S. Teir, *Catal. Today* **2006**, 115, 73–79; d) J. Louie, *Curr. Org. Chem.* **2005**, 9, 605–623; e) D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* **2003**, 103, 3857–3897; f) W. Leitner, *Coord. Chem. Rev.* **1996**, 153, 257–284.
- [2] a) Y. Tang, A. M. Felix, V. W. Manner, L. N. Zakharov, A. L. Rheingold, B. Moasser, R. A. Kemp, *ACS Symp. Ser.* **2006**, 917, 410–421; b) Y. Tang, A. M. Felix, B. J. Boro, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Polyhedron* **2005**, 24, 1093–1100; c) Y. Tang, W. S. Kassel, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Inorg. Chem.* **2005**, 44, 359–364; d) Y. Tang, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Organometallics* **2004**, 23, 4788–4791.
- [3] a) K.-C. Yang, C.-C. Chang, C.-S. Yeh, G.-H. Lee, S.-M. Peng, *Organometallics* **2001**, 20, 126–137; b) R. Xi, L. R. Sita, *Inorg. Chim. Acta* **1998**, 270, 118–122; c) L. R. Sita, J. R. Babcock, R. Xi, *J. Am. Chem. Soc.* **1996**, 118, 10912–10913; d) J. R. Babcock, L. Liable-Sands, A. L. Rheingold, L. R. Sita, *Organometallics* **1999**, 18, 4437–4441; e) U. Wannagat, H. Kuckertz, C. Krüger, J. Pump, *Z. Anorg. Allg. Chem.* **1964**, 333, 54–60.
- [4] a) G. Veneziani, P. Dyer, R. Réau, G. Bertrand, *Inorg. Chem.* **1994**, 33, 5639–5642; b) G. Veneziani, R. Réau, F. Dahan, G. Bertrand, *J. Org. Chem.* **1994**, 59, 5927–5929; c) A. Weisz, K. Utvary, *Monatsh. Chem.* **1968**, 99, 2498–2503; d) N. A. Polezhaeva, Yu. M. Volodina, V. G. Sakhibullina, D. B. Krivolapov, A. T. Gubaidullin, V. A. Naumov, V. I. Galkin, R. A. Cherkasov, *Russ. J. Gen. Chem.* **2000**, 70, 854–858; e) R. I. Tarasova, N. I. Sinitsyna, R. R. Mukhamedieva, *Russ. J. Gen. Chem.* **1997**, 67, 1597–1601.
- [5] a) P. Bhattacharyya, J. D. Woollins, *Polyhedron* **1995**, 14, 3367–3388; b) J. Ellermann, J. Utz, F. A. Knoch, M. Moll, *Z. Anorg. Allg. Chem.* **1996**, 622, 1871–1878; c) M. L. Cole, G. B. Deacon, P. C. Junk, K. Konstantas, P. W. Roesky, *Eur. J. Inorg. Chem.* **2005**, 1090–1098.
- [6] M. T. Gamer, P. W. Roesky, *Inorg. Chem.* **2004**, 43, 4903–4906, and references therein.
- [7] a) H. Schmidbaur, S. Lauteschläger, B. Milewski-Mahrle, *Chem. Ber.* **1983**, 116, 1403–1410; b) A. Winkler, W. Bauer, F. W. Heinemann, V. Garcia-Montalvo, M. Moll, J. Ellermann, *Eur. J. Inorg. Chem.* **1998**, 437–444.
- [8] a) J. Ellermann, J. Sutter, F. A. Knoch, M. Moll, *Angew. Chem.* **1993**, 105, 763–764; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 700–701; b) J. Ellermann, J. Sutter, C. Schelle, F. A. Knoch, M. Moll, *Z. Anorg. Allg. Chem.* **1993**, 619, 2006–2014; c) J. Ellermann, P. Gabold, C. Schelle, F. A. Knoch, M. Moll, W. Bauer, *Z. Anorg. Allg. Chem.* **1995**, 621, 1832–1843; d) M. Dotzler, A. Schmidt, J. Ellermann, F. A. Knoch, M. Moll, *Polyhedron* **1996**, 15, 4425–4433.
- [9] P. W. Roesky, *Inorg. Chem.* **2006**, 45, 798–802.
- [10] “Main Group Metal Amide Complexes and Their Reactivity with Small Molecules”: A. M. Felix, Ph.D. Dissertation, University of New Mexico, Albuquerque, **2007**.
- [11] H. Nöth, L. Meinel, *Z. Anorg. Allg. Chem.* **1967**, 349, 225–240.
- [12] J. Ellermann, W. Wend, *J. Organomet. Chem.* **1985**, 281, c29–c32.
- [13] Crystal data for **3** at 225(2) K with $Mo_{K\alpha}$ radiation (λ = 0.70173 Å): M_r = 477.83, triclinic, space group $P\bar{1}$, a = 14.027(3), b = 19.591(4), c = 21.124(5) Å, α = 80.80(2)°, β = 70.761(13)°, γ = 77.969(13)°, Z = 8, R_1 = 0.0883. One molecule of disordered THF was present for each Sr_6 cluster, and this solvent was modelled using SQUEEZE. CCDC 684318 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [14] We note that there is one patent application reference in the literature to $N(CO_2H)_3$. However, in reading the patent it appears to us that this compound has never actually been prepared. See: J. Roussilhe, C. G. Goumont, EP 733945A1 19960925, **1996**.
- [15] a) C. F. H. Allen, A. Bell, *Org. Synth. Coll. Vol. III.* **1953**, 415–416; b) F. Degerbeck, L. Grehn, U. Ragnarsson, *Acta. Chem. Scand.* **1993**, 47, 896–898; c) S. Hajra, M. Bhowmick, B. Maji, D. Sinha, *J. Org. Chem.* **2007**, 72, 4872–4876.