



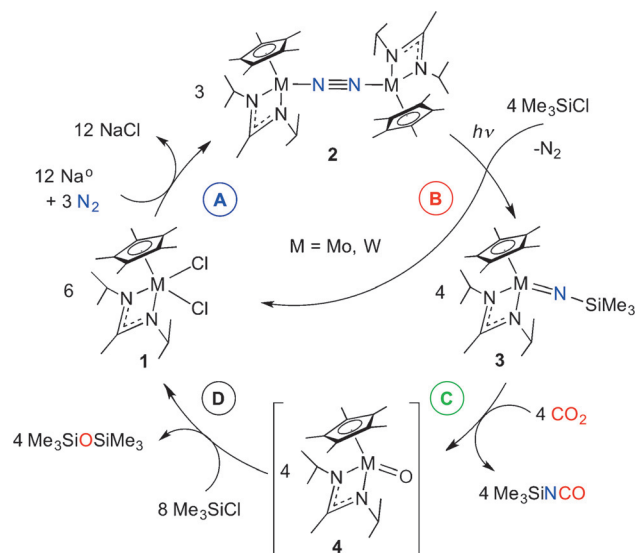
Metal-Mediated Production of Isocyanates, $R_3EN=C=O$ from Dinitrogen, Carbon Dioxide, and R_3ECl^{**}

Andrew J. Keane, Wesley S. Farrell, Brendan L. Yonke, Peter Y. Zavalij, and Lawrence R. Sita*

Abstract: A highly efficient and versatile chemical cycle has been developed for the production of isocyanates through the molecular fixation of N_2 , CO_2 and R_3ECl ($E = C, Si, \text{ and } Ge$). Key steps include a ‘one-pot’ photolytic N–N bond cleavage of a Group 6 dinuclear dinitrogen complex with in situ trapping by R_3ECl to provide a metal terminal imido complex that can engage in simultaneous nitrene-group transfer and oxygen-atom transfer to generate an intermediate metal terminal oxo complex with release of the isocyanate product. Reaction of the oxo complex with additional equivalents of R_3ECl regenerates a metal dichloride that is the precursor for dinuclear dinitrogen starting material.

One of the ultimate objectives of exploring metal-mediated nitrogen (N_2) fixation is to develop more energy-efficient and atom-economical routes to high-value nitrogen-based chemicals in a manner that generates little or no waste by-products.^[1] In this regard, heterocumulenes, comprising isocyanates ($RN=C=O$) and carbodiimides ($RN=C=NR'$), are ideal synthetic targets since the overall free-energy penalty associated with breaking the exceptionally strong triple bond of N_2 can be partially offset through the compensating formation of N–C double bonds within these products. To date, some progress has been made towards the development of N_2 fixation cycles that generate small molecules containing N–C single and multiple bonds; however, the challenge of coupling high chemical efficiency with synthetic versatility has not yet been demonstrated.^[2–6] Herein, we report a versatile and atom-economical chemical cycle that formally converts N_2 , carbon dioxide (CO_2), and a Group 14 element alkyl- or aryl-substituted chloride, R_3ECl , into a set of isocyanate derivatives, $R_3EN=C=O$, for $E = C, Si, \text{ and } Ge$.

Scheme 1 provides a summary of the new N_2 fixation cycle, exemplified using Me_3SiCl , that comprises four separate chemical processes involving: Step A) dinuclear coordination of N_2 through reduction of a metal dichloride ($1 \rightarrow 2$), Step B) photolytic $N \equiv N$ bond cleavage and N-atom functionalization to form a terminal metal imido ($2 \rightarrow 3$), Step C)



Scheme 1. Complete N_2 fixation cycle for production of Me_3SiNCO . See text for descriptions of Steps A–D.

Me_3SiNCO generation through simultaneous nitrene group transfer (NGT) and oxygen-atom transfer (OAT) from carbon dioxide (CO_2) to produce an intermediate metal terminal oxide ($3 \rightarrow 4$), and Step D) regeneration of the starting metal dichloride through OAT with concomitant formation of $Me_3SiOSiMe_3$ ($4 \rightarrow 1$).

For Step A in Scheme 1, we have previously reported that chemical reduction of the Group 6 M^{IV} dichlorides, $[Cp^*M\{N(iPr)C(Me)N(iPr)\}Cl_2]$ ($Cp^* = \eta^5-C_5Me_5$, **1a** ($M = Mo$) and **1b** ($M = W$)), using sodium amalgam (0.5% NaHg) provides excellent yields of the corresponding diamagnetic dinuclear ‘end-on-bridged’ dinitrogen complexes, $[(Cp^*M\{N(iPr)C(Me)N(iPr)\})_2(\mu-\eta^1:\eta^1-N_2)]$ **2a** ($M = Mo$) and **2b** ($M = W$), respectively.^[7] Importantly, while both **2a** and **2b** were determined to be thermally robust in hydrocarbon solution up to temperatures of at least $100^\circ C$, during the course of subsequent investigations, it was discovered that both of these compounds are light sensitive in hydrocarbon (e.g. benzene or methylcyclohexane) solution. Following this lead, preliminary photolysis experiments were conducted with a $[D_6]$ benzene solution of **2** that was sealed under Ar within a Pyrex J-Young-NMR tube and irradiated using a Rayonet carousel of medium-pressure Hg lamps.^[8] A series of 1H NMR spectra taken at timed intervals then revealed the complete disappearance of **2a** after 48 h of irradiation with concomitant formation of new paramagnetic species. In the case of **2b**, a similar set of 1H NMR spectra showed that photoconversion

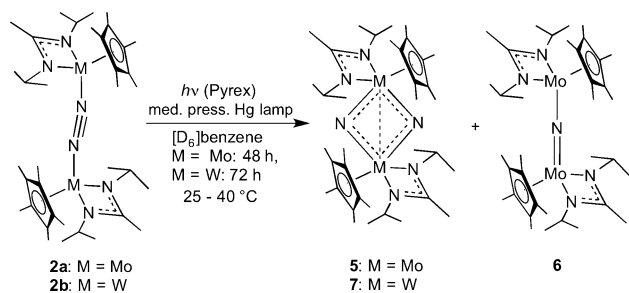
[*] A. J. Keane, W. S. Farrell, B. L. Yonke, P. Y. Zavalij, Prof. L. R. Sita
Department of Chemistry and Biochemistry
University of Maryland
College Park, MD 20742 (USA)
E-mail: lsita@umd.edu

[**] Funding for this work was partially provided by the Department of Energy, Basic Energy Sciences (DE-SC0002217) and the National Science Foundation (CHE-1361716). $E = C, Si, \text{ and } Ge$.

Supporting information (complete experimental details) for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201502293>.

to a single new diamagnetic product occurred quite cleanly up to about 50 % conversion. However, the much longer time required for complete conversion of **2b** (ca. 72 h) resulted in a subsequent small degree of photodegradation of this initial product. Following the course of photolysis of a solution of **2a** in methylcyclohexane ($c = 0.86$ mm) by UV/Vis spectroscopy did not produce a well-defined isosbestic point from an overlay of electronic spectra taken at timed intervals, thereby indicating formation of more than one photoproduct. On the other hand, a similar UV/Vis spectroscopic investigation of the photolysis of **2b** under identical conditions now produced well-resolved isosbestic points at 430, 583, and 761 nm after a relatively short period of time (e.g. <9 h). However, consistent with the photodegradation observed by ^1H NMR spectroscopy, these isosbestic points became less resolved upon continued irradiation of **2b**.^[8]

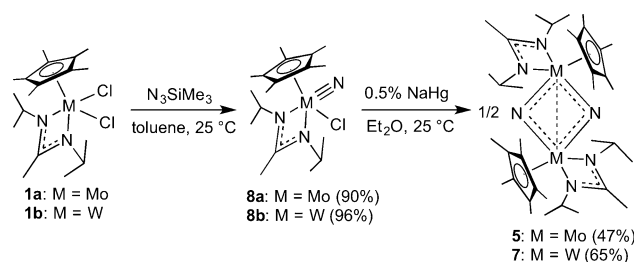
Fortunately, large-scale photolysis of **2a** provided crystalline material directly from the reaction mixture on two different occasions, and when subjected to single-crystal X-ray analyses, two different photoproducts were identified, with these being the formal Mo^{V} (d^1), Mo^{V} (d^1) bis(μ -nitrido) complex, $[\{\text{Cp}^*\text{Mo}[\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})](\text{N})\}_2]$ (**5**), and the formal Mo^{III} (d^3), Mo^{IV} (d^2) mono(μ -nitrido) complex, $[\{\text{Cp}^*\text{Mo}[\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})]\}_2(\text{N})]$ (**6**), that are shown in Scheme 2.^[8] The occurrence of both **5** and **6** as photolysis



Scheme 2. Photolysis of compounds **2a** and **2b**.

products is consistent with reported observations of competing $\text{N}\equiv\text{N}$ bond cleavage and N_2 extrusion reaction pathways in the photolysis of dimolybdenum $\mu\text{-N}_2$ complexes.^[9,10] Finally, although crystalline material could not be isolated in the case of large-scale photolysis of **2b**, the structure of the new diamagnetic photoproduct observed by ^1H NMR spectroscopy was tentatively assigned as being the corresponding dinuclear bis(μ -nitrido) complex $[\{\text{Cp}^*\text{W}[\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})](\text{N})\}_2]$ (**7**).

To have adequate supplies of **5** and **7** for more extensive characterization and chemical reactivity studies, an alternative synthetic route to these photoproducts was devised. Thus, as Scheme 3 shows, reaction of the M^{IV} dichlorides **1a** and **1b** with a slight excess of trimethylsilylazide, N_3SiMe_3 , in toluene solution at room temperature provided excellent yields of the corresponding M^{VI} terminal nitrido, chlorides, $[\text{Cp}^*\text{M}[\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})](\text{N})\text{Cl}]$ **8a** ($\text{M} = \text{Mo}$) and **8b** ($\text{M} = \text{W}$).^[8,10] The molecular structures of **8a** and **8b** were confirmed by single-crystal X-ray analyses which revealed solid-state structural similarities with the reported pair of M^{VI} nitrido,



Scheme 3. Alternative synthesis of **5** and **7**.

trimethylsiloxy complexes, $[\text{Cp}^*\text{M}[\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})](\text{N})(\text{OSiMe}_3)]$ ($\text{M} = \text{Mo}$ and W).^[8,11]

As presented in Scheme 3, chemical reduction of **8a** and **8b** in diethyl ether (Et_2O) solution using a slight excess of 0.5 % NaHg provided good yields of the dinuclear bis(μ -nitrido) complexes **5** and **7** as analytically pure crystalline materials. As Figure 1 presents, single-crystal X-ray analyses

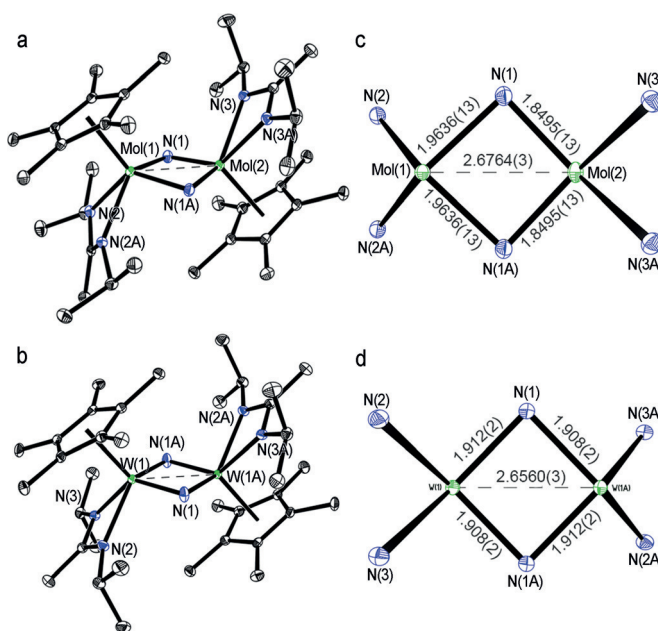


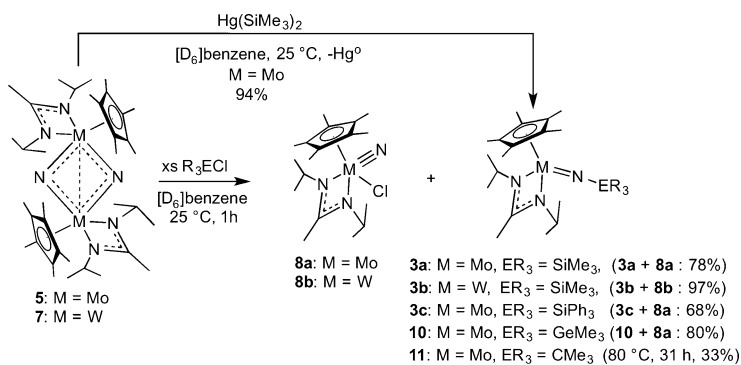
Figure 1. Molecular structures (thermal ellipsoids set at 30 % probability) of a) **5** and b) **7**. Hydrogen atoms have been removed for the sake of clarity. Selected geometric parameters for the M_2N_2 cores of **5** and **7** are provided in (c) and (d) respectively.

of **5** and **7** served to confirm the dinuclear bis(μ -nitrido) molecular structures of these two compounds in the solid state.^[8] For the Group 6 metals, only one experimental example of the formal M^{V} (d^1), M^{V} (d^1) ground state electronic configuration that is suggested by the $\{\text{M}(\mu\text{-N})\}_2$ four-membered ring core of **5** and **7** has been reported for $\text{M} = \text{Cr}$.^[12] For $[\{(\text{iPr}_2\text{N})_2\text{Cr}(\mu\text{-N})\}_2]$, variable temperature NMR spectroscopy and SQUID data support the conclusion that the two Cr^{V} metal centers are antiferromagnetically coupled in solution and the solid-state, while a crystallographic analysis reveals a rhomboid structure for the $\{\text{Cr}(\mu\text{-N})\}_2$

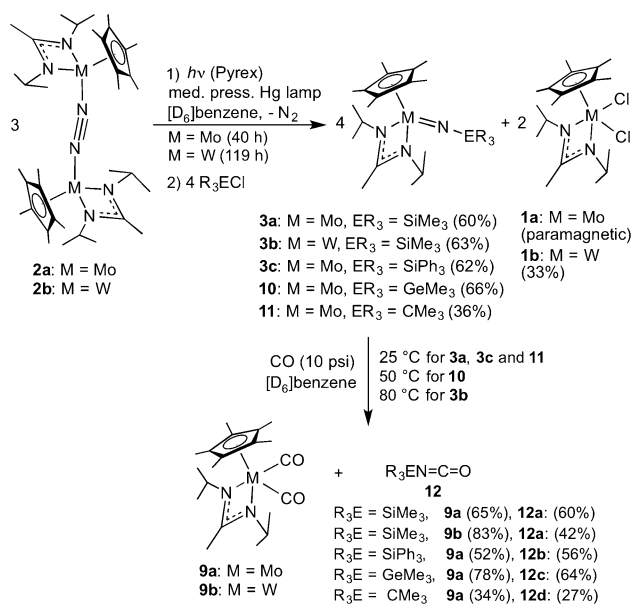
$\text{N})_2$ core with a pair of 'long' and 'short' Cr–N bond lengths of 1.743(3) Å and 1.730(3) Å, respectively. For **5** and **7**, the exact nature of the ground-state electronic configuration for each compound is far less certain. The detailed crystallographic analyses of the data for **5** and **7** establish, with a very high degree of confidence, that the two bridging first-row elements are indeed nitrogen in each case—thereby ruling out any possible structural artefact that might be introduced with partial or full occupancy by adventitious inclusion of oxygen in these positions.^[8] Variable temperature ^1H NMR (500 MHz, $[\text{D}_8]\text{toluene}$, 213–354 K) spectra establish that while **7** is diamagnetic in solution, it is engaged in a dynamic structural process.^[8] Geometric parameters for the $\{\text{W}(\mu\text{-N})\}_2$ core of **7** are also consistent with a W–W bonding interaction in the solid-state (see Figure 1). In contrast, the corresponding $\{\text{Mo}(\mu\text{-N})\}_2$ core of **5** displays a striking asymmetry with a pair of 'long' Mo(1)–N(1A) bonds of 1.9636(13) Å being associated with the Mo(1) center and a pair of 'short' Mo(2)–N(1A) bonds of 1.8495(13) Å being assigned to the Mo(2) center. Preliminary magnetic data obtained using a SQUID magnetometer strongly supports a diamagnetic closed-shell electronic configuration in the solid-state.^[8] On the other hand, variable temperature NMR and EPR spectra recorded for solutions of **5** are indicative of paramagnetic character. Additional detailed experimental and computational investigations of the molecular and electronic structures of **5** and **7** are clearly warranted and the results of these studies will be reported in due course.

A preliminary screen of the chemical reactivity of **5** and **7** revealed that addition of a slight excess of Me_3SiCl to a benzene solution of these compounds rapidly produced an excellent yield of a 1:1 mixture of the corresponding mononuclear nitrido, chlorides, **8a** and **8b**, respectively, along with the previously reported Mo^{IV} terminal imido complexes, $[\text{Cp}^*\text{M}\{\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})\}(\text{NSiMe}_3)]$ **3a** ($\text{M} = \text{Mo}$) and **3b** ($\text{M} = \text{W}$),^[13] according to Scheme 4.^[8,14,15] More interestingly, as Scheme 4 further presents, replacement of Me_3SiCl with the trisubstituted Group 14 chlorides, Ph_3SiCl , Me_3GeCl , and Me_3CCl provided the corresponding Mo^{IV} imido complexes, **3c**, **10**, and previously reported **11**^[13] in modest to excellent yields. Thus, with the isolation of analytically pure **10** and solid-state characterization achieved through a single-crystal X-ray analysis,^[8] the collection of compounds, **11**, **3a**, and **10**, now establish an unprecedented Group 14 vertical series of isostructural metal imido congeners.^[10,16] Finally, in support of the hypothesis that reaction of **5** with Me_3SiCl proceeds through chloride-atom abstraction and capture of a trimethylsilyl radical to produce **8a** and **3a**, respectively, use of one equivalent of bis(trimethylsilyl)mercury, $\text{Hg}(\text{SiMe}_3)_2$,^[17] now led to a near quantitative yield of **3a** (Scheme 4).

With respect to the development of Step B in Scheme 1, the chemical transformations presented in Scheme 2 and Scheme 4 raised the possibility of being able to directly convert **2**→**3** by photolyzing **2** in the presence of excess equivalents of Me_3SiCl .^[6] In practice, while this hypothesis proved to be correct, its experimental verification yielded yet another surprise. More specifically, in addition to the



Scheme 4. Functionalization of **5** and **7**. Yields are based on durene as an internal standard.



Scheme 5. Photolysis of **2** in the presence of excess equivalents of R_3ECl and subsequent nitrene-group transfer from **3**, **10**, and **11** to CO. Yields of products are relative to **2** and based on durene as an internal standard.^[8]

expected terminal imido product **3**, this 'one-pot' photo-conversion of **2** now provided the corresponding metal dichloride **1** as the co-product with no **8** being observed (Scheme 5). Importantly, results obtained from five separate experiments conducted with **2b** firmly established a reproducible yield for **3b** of $63 \pm 1\%$ and for **1b** of $33 \pm 1\%$. On the strength of these data in which up to 96 % of the metal can be accounted for based on the stoichiometry of Scheme 5, it is reasonable to propose a formal mechanism in which one equivalent of the dinuclear $\mu\text{-N}_2$ starting material **2** is efficiently acting as an internal trap for the total of four chlorine atoms that are being generated. Finally, one of the most exciting consequences of Scheme 5 is that we had already reported NGT using CO as a substrate. Namely, treatment of the terminal imido complexes **3a** and **3b** with CO (10 psi) as shown in this scheme, provides an excellent yield of Me_3SiNCO and the corresponding Group 6 M^{II}

bis(carbonyl) complexes, $[\text{Cp}^*\text{M}\{\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})\}(\text{CO})_2]$ **9a** (M = Mo) and **9b** (M = W), respectively.^[13]

The versatility of the N_2 fixation process established by the chemistry in Scheme 5 was explored further. To begin, chemical reduction of **1a** under an atmosphere of isotopically labeled $^{15}\text{N}_2$ (98%) first provided (^{15}N) -**2a** that was then photolyzed to first provide (^{15}N) -**3a**, which was then reacted with isotopically labeled ^{13}CO (99%) to produce double isotopically labeled $[(^{15}\text{N}, ^{13}\text{C})\text{-Me}_3\text{SiNCO}]$ in high yield.^[8] The series of heteronuclear (^{13}C , ^{15}N , and ^{29}Si) NMR spectra obtained for this product (Figure 2) serve to establish the

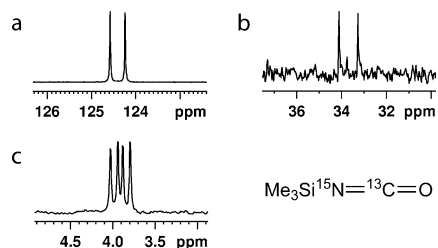
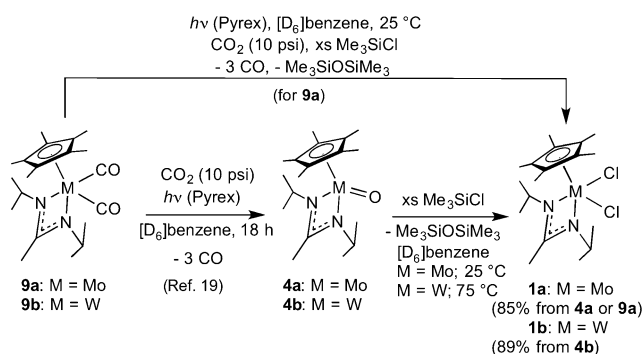


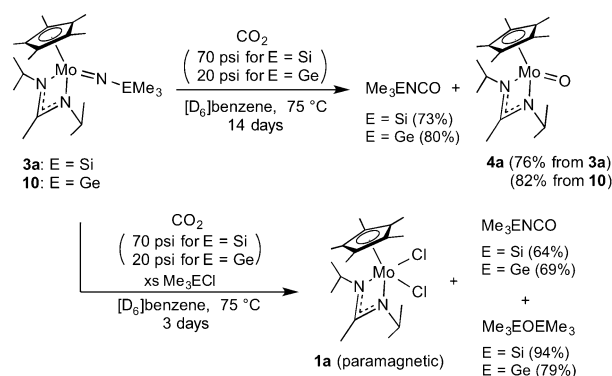
Figure 2. Partial heteronuclear NMR spectra for $[(^{15}\text{N}, ^{13}\text{C})\text{-Me}_3\text{SiNCO}]$. a) $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, $[\text{D}_6]\text{benzene}$): $\delta = 124.41$ ppm; $J(^{13}\text{C}-^{15}\text{N}) = 42.8$ Hz, b) ^{15}N NMR (50.68 MHz, $[\text{D}_6]\text{benzene}$, neat MeNO_2 as external standard): $\delta = 33.48$ ppm; $J(^{15}\text{N}-^{13}\text{C}) = 42.8$ Hz., c) ^{29}Si DEPT-35 NMR (99.36 MHz, 4.67% natural abundance ^{29}Si , $[\text{D}_6]\text{benzene}$, neat Me_4Si as external standard): $\delta = 3.91$ ppm; $J(^{29}\text{Si}-^{15}\text{N}) = 14.7$ Hz, $J(^{29}\text{Si}-^{13}\text{C}) = 8.5$ Hz.

efficiency and extent of double isotopic incorporation.^[8] Similar results were obtained upon substitution of Me_3SiCl with the other R_3ECl derivatives Ph_3SiCl , Me_3GeCl , and Me_3CCl in the photolysis of **2a** (Scheme 5) to respectively provide the corresponding terminal imido complexes **3c**, **10**, and **11**.^[8,13] Finally, treatment of **3c** and (^{15}N) -**10**, and (^{15}N) -**11** with ^{13}CO yielded $[(^{15}\text{N}, ^{13}\text{C})\text{-Ph}_3\text{SiNCO}]$ and $[(^{15}\text{N}, ^{13}\text{C})\text{-Me}_3\text{GeNCO}]$, and $[(^{15}\text{N}, ^{13}\text{C})\text{-Me}_3\text{CNCO}]$ respectively (Scheme 5), and the structural identities of these heterocumulene products were confirmed by ^1H , ^{13}C , and ^{15}N NMR spectra and comparison with literature values.^[8,18]

To complete the formal catalytic cycle for N_2 fixation presented in Scheme 1, a step is required to recycle the metal bis(carbonyl) complexes **9** back to the starting metal dichlorides **1**. Gratifyingly, this goal could be realized by relying on our reported catalytic OAT process involving CO_2 and a Group 6 $\text{M}^{\text{II}}/\text{M}^{\text{IV}}$ redox couple. More specifically, as presented in Scheme 6, photolysis of **9a** and **9b** in the presence of CO_2 cleanly provides the corresponding mononuclear terminal oxo complexes **4a** (M = Mo) and **4b** (M = W).^[19] In the present work, it was determined that both **4a** and **4b** react with excess equivalents of Me_3SiCl in benzene solution to produce one equivalent of hexamethyldisiloxane, $\text{Me}_3\text{Si-O-SiMe}_3$, and the desired respective products **1a** and **1b** (see Scheme 6).^[8,20] Even more satisfying, the **9a**→**1a** transformation could be achieved by simply photolyzing **9a** in the presence of CO_2 and excess equivalents of Me_3SiCl , to directly produce **1a** in high yield and without the need to isolate the intermediate terminal oxo complex **4a**.



Scheme 6. Synthesis of Group 6 metal dichlorides by oxygen atom transfer.^[8]



Scheme 7. Synthesis of Group 6 metal dichlorides by nitrene-group transfer/oxygen-atom transfer with CO_2 and Me_3ECl . Yields are based on durene as an internal standard.^[8]

Although Scheme 5 and Scheme 6 comprise a formal N_2 fixation chemical cycle for production of Group 14 isocyanates, the overall process requires both CO and CO_2 , as well as photolysis. Accordingly, to provide a more efficient path, the direct reaction of **3a**, **3b**, and **10** with CO_2 and Me_3ECl (E = Si and Ge) was investigated. As Scheme 7 reveals, when a solution of **3a** in $[\text{D}_6]\text{benzene}$ was heated under CO_2 pressure (70 psi) at 75°C for 14 days within a thick-walled sealed NMR tube, conversion into **4a** (76% yield) and Me_3SiNCO (73% yield) occurred as established by ^1H NMR spectroscopy and an internal standard (durene).^[8] Under lower CO_2 pressure (20 psi), compound **10** was observed to convert even more efficiently at the same temperature into **4a** and Me_3GeNCO in 82% and 80% respective yields after a total of 14 days. To our knowledge, these results provide the first documentation of simultaneous NGT and OAT involving CO_2 and a Group 6 metal imido as substrates.^[21] A final consideration was to determine if **3a** and **10** could be directly converted into **1a** by simply heating under CO_2 pressure in the presence of excess equivalents of Me_3SiCl and Me_3GeCl , respectively. Fortunately, as shown in Scheme 7, this goal was achieved in a surprisingly easy manner and in high yield.^[8]

To test the validity of combining the NGT and OAT processes of Scheme 5–7 to provide complete N_2 fixation cycles for production of isocyanates, fixed amounts of **2a** and **2b** were carried through in one-pot fashion to provide these

dinuclear μ -N₂ starting materials in 50% recovered yields when CO was employed (Scheme 6) and a 82% yield of the dichloride **1a** was isolated when CO₂ was used for simultaneous NGT and OAT according to Scheme 7.^[8]

In summary, the present work establishes a highly efficient and versatile chemical cycle for the production of isocyanates from N₂, CO₂, and R₃ECI, and one that proceeds under relatively mild conditions. We are currently investigating further refinements to this chemical cycle that would permit it to proceed in true catalytic fashion.

Keywords: nitrene-group transfer · nitrogen fixation · oxygen-atom transfer · small-molecule activation

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10220–10224
Angew. Chem. **2015**, *127*, 10358–10362

- [1] a) K. C. MacLeod, P. L. Holland, *Nat. Chem.* **2013**, *5*, 559–565; b) N. Khoenkhon, B. de Bruin, J. N. H. Reek, W. I. Dzik, *Eur. J. Inorg. Chem.* **2015**, 567–598.
- [2] For formation of a carbodiimide product from N₂ and CO through a series of transformations that do not constitute a chemical cycle, see: S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2013**, *135*, 11373–11383.
- [3] For a chemical cycle for formation of KNCO from N₂ and CO, see: a) Y. Ishida, H. Kawaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 16990–16993; For related work, see: b) J. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 446–447; c) A. F. Cozzolino, J. S. Silvia, N. Lopez, C. C. Cummins, *Dalton Trans.* **2014**, 43, 4639–4652.
- [4] For development of a chemical cycle for formation of organonitriles from N₂ and acid chlorides, see: a) J. J. Curley, E. L. Sceats, C. C. Cummins, *J. Am. Chem. Soc.* **2006**, *128*, 14036–14037; b) J. S. Figueroa, N. A. Piro, C. R. Clough, C. C. Cummins, *J. Am. Chem. Soc.* **2006**, *128*, 940–950.
- [5] For metal-mediated N₂ fixation leading to other small molecule products, see: a) P. Sobota, Z. Janas, *J. Organomet. Chem.* **1984**, *276*, 171–176; b) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Angew. Chem. Int. Ed.* **2007**, *46*, 2858–2861; *Angew. Chem.* **2007**, *119*, 2916–2919; c) D. J. Knobloch, H. E. Toomey, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, *130*, 4248–4249; d) D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 10553–10564; e) D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 15340–15350; f) S. P. Semproni, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2011**, *133*, 10406–10409.
- [6] For catalytic formation of N(SiMe₃)₃ from N₂ and Me₃SiCl, see: a) K. Shiina, *J. Am. Chem. Soc.* **1972**, *94*, 9266–9267; b) H. Tanaka, K. Arashiba, S. Kuriyama, A. Sasada, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2014**, *5*, 3737–3747.
- [7] P. P. Fontaine, B. L. Yonke, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2010**, *132*, 12273–12285.
- [8] Experimental details are provided in the Supporting Information.
- [9] a) E. Solari, C. Da Silva, B. Iacono, J. Hesschenbrouck, C. Rizzoli, R. Scopelliti, C. Floriani, *Angew. Chem. Int. Ed.* **2001**, *40*, 3907–3909; *Angew. Chem.* **2001**, *113*, 4025–4027; b) J. J. Curley, T. R. Cook, S. Y. Reece, P. Müller, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9394–9405; c) H. Kunkely, A. Vogler, *Angew. Chem. Int. Ed.* **2010**, *49*, 1591–1593; *Angew. Chem.* **2010**, *122*, 1636–1638; d) A. S. Huss, J. J. Curly, C. C. Cummins, D. A. Blank, *J. Phys. Chem. B* **2013**, *117*, 1429–1436; e) C. Rebreyend, B. de Bruin, *Angew. Chem. Int. Ed.* **2015**, *54*, 42–44; *Angew. Chem.* **2015**, *127*, 42–44; f) T. Miyazaki, H. Tanaka, Y. Tanabe, M. Yuki, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2014**, *53*, 11488–11492; *Angew. Chem.* **2014**, *126*, 11672–11676.
- [10] R. A. Eikey, M. M. Abu-Omar, *Coord. Chem. Rev.* **2003**, *243*, 83–124.
- [11] B. L. Yonke, J. P. Reeds, P. Y. Zavalij, L. R. Sita, *Z. Anorg. Allg. Chem.* **2015**, *641*, 61–64.
- [12] A. L. Odom, C. C. Cummins, *Organometallics* **1996**, *15*, 898–900.
- [13] B. L. Yonke, J. P. Reeds, P. P. Fontaine, P. Y. Zavalij, L. R. Sita, *Organometallics* **2014**, *33*, 3239–3242.
- [14] Z. J. Tonzetich, R. R. Schrock, K. M. Wampler, B. C. Bailey, C. C. Cummins, P. Müller, *Inorg. Chem.* **2008**, *47*, 1560–1567.
- [15] For recent examples of nitride-functionalization, see: a) C. R. Clough, P. Müller, C. C. Cummins, *Dalton Trans.* **2008**, 4458–4463; b) J. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* **2010**, *132*, 2169–2171; c) J. J. Scepaniak, R. P. Bontchev, D. L. Johnson, J. M. Smith, *Angew. Chem. Int. Ed.* **2011**, *50*, 6630–6633; *Angew. Chem.* **2011**, *123*, 6760–6763; d) P. J. J. Curley, A. F. Cozzolino, C. C. Cummins, *Dalton Trans.* **2011**, *40*, 2429–2432; e) P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2014**, *53*, 10412–10415; *Angew. Chem.* **2014**, *126*, 10580–10583; f) I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881–6883.
- [16] K. Weber, K. Korn, A. Schorm, J. Kipke, M. Lemke, A. Khvorost, K. Harms, J. Sundermeyer, *Z. Anorg. Allg. Chem.* **2003**, *629*, 744–754.
- [17] J. Arnold, T. D. Tilley, A. L. Rheingold, S. J. Geib, *Organometallics* **1987**, *6*, 473–479.
- [18] M. H. Palmer, *J. Mol. Struct.* **2004**, *692*, 43–56.
- [19] a) B. L. Yonke, J. P. Reeds, P. Y. Zavalij, L. R. Sita, *Angew. Chem. Int. Ed.* **2011**, *50*, 12342–12346; *Angew. Chem.* **2011**, *123*, 12550–12554; b) J. P. Reeds, B. L. Yonke, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2011**, *133*, 18602–18605.
- [20] J. H. Shin, W. Savage, V. J. Murphy, J. B. Bonanno, D. G. Churchill, G. Parkin, *J. Chem. Soc. Dalton Trans.* **2001**, 1732–1753.
- [21] a) A. J. Blake, J. M. McInnes, P. Mountford, G. I. Nikonov, D. Swallow, D. J. Watkin, *J. Chem. Soc. Dalton Trans.* **1999**, 379–392; b) P. Royo, J. Sánchez-Nieves, *J. Organomet. Chem.* **2000**, *597*, 61–68; c) U. J. Kilgore, F. Basuli, J. C. Huffman, D. J. Mindiola, *Inorg. Chem.* **2006**, *45*, 487–489; d) Z. J. Tonzetich, R. R. Schrock, P. Müller, *Organometallics* **2006**, *25*, 4301–4306.

Received: March 11, 2015

Published online: June 26, 2015