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An Exploding *N*-Isocyanide Reagent Formally Composed of Anthracene, Dinitrogen and a Carbon Atom[†]

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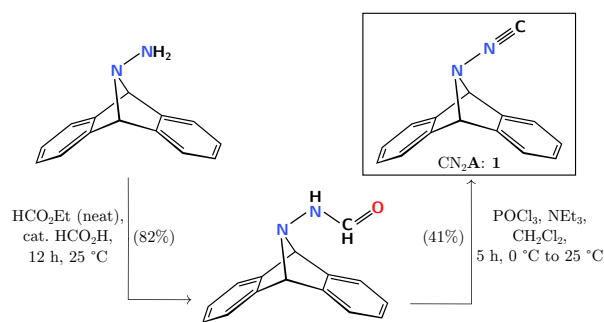
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Targeted as an example of a compound composed of a carbon atom together with two stable neutral leaving groups, 7-isocyano-7-azadibenzonorbornadiene, CN_2A (**1**, $\text{A} = \text{C}_{14}\text{H}_{10}$ or anthracene) has been synthesized and spectroscopically and structurally characterized. The terminal C atom of **1** can be transferred: mesityl nitrile oxide reacts with **1** to produce carbon monoxide, likely via intermediacy of the *N*-isocyanate OCN_2A . Reaction of **1** with $[\text{RuCl}_2(\text{CO})(\text{PCy}_3)_2]$ leads to $[\text{RuCl}_2(\text{CO})(\text{1})(\text{PCy}_3)_2]$ which decomposes unselectively: in the product mixture, the carbide complex $[\text{RuCl}_2(\text{C})(\text{PCy}_3)_2]$ was detected. Upon heating in the solid state or in solution, **1** decomposes to **A**, N_2 and cyanogen (C_2N_2) as substantiated using molecular beam mass spectrometry, IR and NMR spectroscopy techniques.

Carbon atom transfer (CAT) remains a non-trivial synthetic problem. CAT chemistry was observed and studied via electric arc-generated C,¹ and is likely commonly occurring in space,² but the lack of suitable CAT reagents has hindered the development of such reactivity in solution chemistry. Notable exceptions exist: Shevlin reported on the thermal decomposition of a tetrazolyl diazonium salt, proposing C atom generation and unselective transfer reactions to ethylene and ethylene oxide.³ Willis and Bayes showed that upon irradiation carbon suboxide (C_3O_2) inserts in the gas phase into ethylene, propylene and butenes with concomitant CO loss to form the corresponding allenes.⁴ Hillhouse and coworkers investigated the coordination chemistry of C_3O_2 in solution, demonstrating the formal insertion of the central C atom of C_3O_2 into a W-phosphine bond, leading to a phosphinocarbene complex.⁵ Heppert and coworkers developed a synthesis of a ruthenium carbide complex via CAT from a methylenecy-



Scheme 1 Synthesis of **1**.

clopropane.⁶ Metal carbide complexes have also been obtained through breakdown of carbon monoxide.^{7–10}

In the present work we set out to synthesize a carbon source which like carbon suboxide could potentially transfer a C atom with release of a pair of stable, neutral leaving groups. Incorporation of a latent anthracene molecule ($\text{C}_{14}\text{H}_{10}$, **A**) which is readily released upon heating has been shown to be a fruitful strategy for mild thermal release of reactive fragments.¹¹ Group transfer reactions and small molecule release coupled with **A** formation from 7-pnicta-dibenzonorbornadiene-scaffolds have been shown to be especially efficient.¹² For example, LiNA, ON_2A and NCNA were employed as N-mono-anion, O-atom and NCN -group transfer reagents to transition metal centers, respectively.¹³ Herein we present the design and synthesis of a new type of CAT reagent.

7-isocyano-7-azadibenzonorbornadiene CN_2A (**1**) was chosen as the synthetic target. Compound **1** is the isocyano bonding isomer of NCNA and can be envisioned to fragment into **A**, dinitrogen and a C atom. The synthesis of **1** was achieved by formylation of Carpino's hydrazine $\text{H}_2\text{N}_2\text{A}$,^{12a} followed by dehydration of the resulting formohydrazide to yield the *N*-isocyanide (Scheme 1, 34% from $\text{H}_2\text{N}_2\text{A}$).[†]

Notable spectroscopic features that corroborate the formulated structure of **1** are the IR- and Raman NC stretching vibration band (IR: $\tilde{\nu} = 2098 \text{ cm}^{-1}$ for **1**, $\tilde{\nu} = 2060 \text{ cm}^{-1}$ for $^{13}\text{CN}_2\text{A}$, **1**- ^{13}C ;

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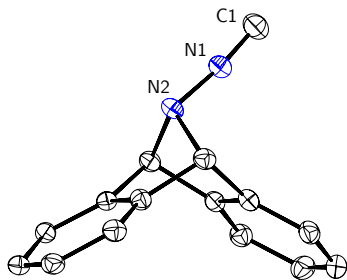
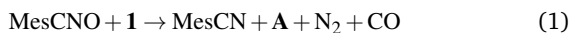


Fig. 1 Molecular structure of **1** drawn with thermal ellipsoids at the 50% probability level and with all H atoms omitted for clarity. Selected distances [Å] and angles [°]: N2-N1 1.381(3), N1-C1 1.164(3), N2-N1-C1 173.3(2).

Raman: $\tilde{\nu} = 2093 \text{ cm}^{-1}$ for **1**) and the ^{13}C NMR resonance corresponding to the terminal carbon ($\delta = 135.5 \text{ ppm}$). These data are typical of other known *N*-isocyanides.¹⁴ The metrical parameters of the molecular structure of **1** obtained from an X-ray diffraction analysis (Fig. 1) compare well with those reported for structurally characterized *N*-isocyanides.¹⁵

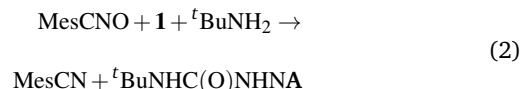
CAT reactivity of **1** was studied: we targeted the release of carbon monoxide from **1** by its oxidation, as the expulsion of a CO molecule should favor the transfer process. CO formation from elemental, electric arc-generated carbon was previously investigated by Skell and coworkers.^{1a} Our group previously performed an in-depth study of the oxidation of phosphines and carbenes with mesityl nitrile oxide (MesCNO) showing that this compound acts as an efficient and mild O-atom transfer agent.¹⁶ **1** was thus subjected to reaction with MesCNO in benzene solution at 25 °C (Equation 1).¹⁷



Monitoring the reaction for several hours by ^1H NMR spectroscopy indicated the formation of **A** over time, together with unidentified species. Gas evolution was observed and analysis of the headspace gases by gas IR spectroscopy revealed the presence of CO. By employing **1**- ^{13}C we confirmed the origin of C in the produced CO in solution by its characteristic ^{13}C NMR resonance ($\delta (^{13}\text{C}) = 184.5 \text{ ppm}$, benzene- d_6), and in the gas phase by a redshifted IR vibration band (^{12}CO : $\tilde{\nu} = 2132 \text{ cm}^{-1}$, ^{13}CO : $\tilde{\nu} = 2101 \text{ cm}^{-1}$).¹⁸ Quantification of CO gas by using $[\text{RuCl}(\text{Cp}^*)(\text{PCy}_3)]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5^-$) as a chemical trap indicated a yield of 27% for CO generation from **1**.¹⁹ The precise pathway for CO generation is unclear, but the oxidation of **1** likely involves an intermediate *N*-isocyanate, as the reaction of the model *N*-isocyanide $^i\text{Pr}_2\text{N}-\text{NC}$ with MesCNO yields a triazolidinone,²⁰ stemming from the expected dimerization of the corresponding isocyanate, i.e. $^i\text{Pr}_2\text{N}-\text{NCO}$.†

Direct observation of $\text{OCN}_2\mathbf{A}$ was not realized: monitoring the reaction of MesCNO with **1** at low temperature (−60 °C to 25 °C) in THF- d_8 by ^1H NMR spectroscopy indicated that formation of **A** and MesCN started at 0 °C. No intermediate species was detected, suggesting that the oxidation is the rate-determining step and subsequent **A**, N_2 and CO formation occurs rapidly. The intermediacy of the *N*-isocyanate $\text{OCN}_2\mathbf{A}$ upon oxidation of **1** is how-

ever further supported by a trapping experiment with $^t\text{BuNH}_2$ to yield the corresponding mixed urea (Equation 2).



Additional backing for transient $\text{OCN}_2\mathbf{A}$ is given by oxidation of **1** with DMSO and catalytic trifluoroacetic anhydride, an established method for the synthesis of isocyanates from isocyanides.²¹ Subsequent mechanistic steps remain obscure: DFT computations (B3LYP-D3BJ/Def2-TZVP) indicate that unimolecular, concerted fragmentation of $\text{OCN}_2\mathbf{A}$ on the singlet surface to CO, N_2 and **A** is linked to a high barrier (ca. 37 kcal·mol^{−1}) which does not conform with the experimental ease of reaction at ambient temperature.† The detection of the fleeting triplet OCN_2 which readily decomposes to CO and N_2 was claimed,²² and this species may be involved in a radical mechanism. A different potential route, in analogy to the commonly observed *N*-isocyanate chemistry,²⁰ is the occurrence of fast dimer formation and its subsequent collapse to yield **A**, N_2 and CO. Due to concurrent decomposition pathways, performing a kinetic analysis on the reaction of **1** with MesCNO proved unsuccessful.

Molecular terminal metal carbido complexes remain comparatively rare and their syntheses limited to only a few routes.^{6,9,10,23–25} We reasoned that **1** bound to a transition metal fragment might be a suitable precursor for accessing carbido complexes by thermal loss of **A** and N_2 . We identified first a precursor complex to access the known carbido complex $[\text{RuCl}_2(\text{C})(\text{PCy}_3)_2]$.⁶ To this end, **1** was treated with $[\text{RuCl}_2(\text{CO})(\text{PCy}_3)_2]$ in THF,²⁶ leading to formation of $[\text{RuCl}_2(\mathbf{1})(\text{CO})(\text{PCy}_3)_2]$ (**2**). An X-ray diffraction analysis of crystals grown from a chloroform/pentane solution of **2** revealed the structure of this compound featuring an all-*trans* octahedral arrangement (Figure 2). The NNC angle in **2** deviates by ca. 15 ° from the quasi-linear geometry found in **1**. The origin of this effect is certainly the backbonding from Ru to C1,²⁷ although concomitant rehybridization at N1 must be minimal as the bond distances of the *N*-isocyanide group in **2** do not change significantly compared to **1**, i.e. the C1-N1 linkage remains a triple bond. The Ru-C1 distance is slightly longer than in the single structurally characterized Ru(II) *N*-isocyanide complex $[\text{RuCl}_2(\text{C}_6\text{H}_2\text{Me}_4)(\text{CNN}^i\text{Pr}_2)]$ [2.035(2) Å vs. 1.947(7) Å].²⁸

Heating a toluene solution of **2** to 100 °C for 3 h led to complete disappearance of the ^{31}P NMR signal corresponding to the starting material and to the appearance of signals due to several new species, among them the previously reported carbide complex $[\text{RuCl}_2(\text{C})(\text{PCy}_3)_2]$, as identified by its characteristic ^{13}C NMR resonance at $\delta = 473 \text{ ppm}$.⁶ Although this reaction was unselective and low-yielding (ca. 15% by ^{31}P NMR spectroscopy) due to the harsh reaction conditions required to induce the carbide complex formation, this route presents an initial demonstration for the rational installation of a single C atom onto a transition metal complex using **1**.

The thermal stability of **1** and the potential release of **A** and CN_2 or fragments thereof was studied by thermogravimetric anal-

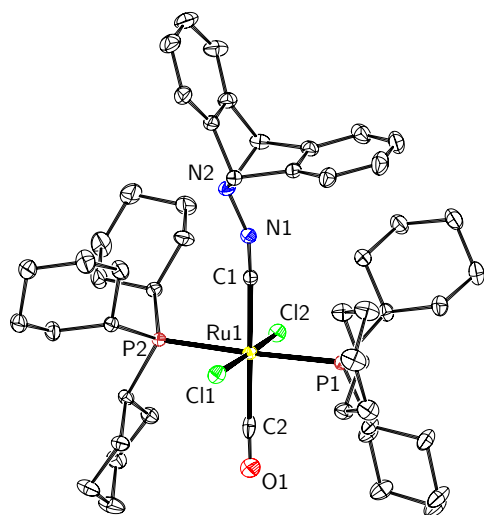


Fig. 2 Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level and with all H atoms and solvent molecules of crystallization omitted for clarity. Selected distances [Å] and angles [°]: Ru1-C2 1.933(3), Ru1-C1 2.035(2), Ru1-P1 2.4221(5), Ru1-Cl1 2.4236(6), Ru1-Cl2 2.4339(6), Ru1-P2 2.4464(5), C2-O1 1.089(3), C1-N1 1.160(3), N1-N2 1.385(2), C1-N1-N2 158.6(2), C2-Ru1-C1 174.85(10), Cl1-Ru1-Cl2 176.16(2), P1-Ru1-P2 175.45(2).

ysis (TGA). A rapid, very significant mass loss, suggestive of explosive behavior of the compound, was observed at around 80 °C.† Following this process visually by heating a sample of **1** (5 mg) to 80 to 120 °C under air, under N₂ or under vacuum in a transparent flask indeed resulted in observation of a mild blast, rocketing solid material through the entire volume of the container. Although energetic materials containing only C, H and N are not uncommon,²⁹ the decomposition behavior of **1**, despite its low N content (12.7%) is remarkable. While we experienced no hazards in the course of working with compound **1** (at least up to a scale of 500 mg), and it did not exhibit shock-sensitivity, we recommend the exercise of due caution if working with this heat-sensitive explosive reagent. The remaining recovered solid residue was shown by NMR spectroscopic means to be predominantly composed of **A** next to minor unidentified species (C,H,N-microanalysis revealed that the residue contained about 4.6% of N). By measuring the pressure increase upon decomposition in a closed vessel, the amount of released gases per mole of employed **1** was determined to be 0.61 mol.†

Molecular beam mass spectrometry (MBMS) allowed for the identification of the evolved, volatile compounds during the thermal decomposition of **1**. In line with the TGA, copious amounts of gases were detected upon heating **1** in the MBMS source vacuum chamber (to ca. 110 °C). These gases were primarily composed of cyanogen (NC–CN) or an isomer of identical mass, and dinitrogen.† No evidence for formation of CN₂ or any C allotrope was found. This result is in line with gas-phase free energy of formation calculations using a modified ccCA procedure,³⁰ predicting that fragmentation of **1** into either CN₂ and **A** (Equation 3) or C,

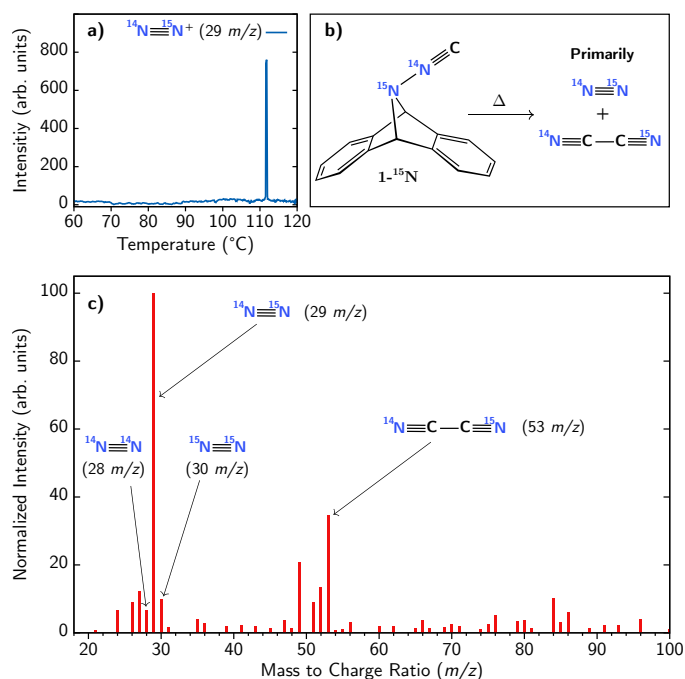
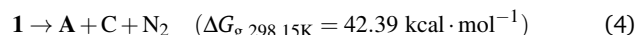
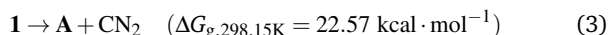


Fig. 3 a) Molecular beam mass spectrometry (MBMS) of **1-¹⁵N**: ion count of ¹⁴N¹⁵N as a function of temperature; b) Scheme depicting the observed major products with their isotope distributions upon thermal decomposition of **1-¹⁵N**. c) Integrated mass spectrum of the evolved gases from **1-¹⁵N** during thermolysis.

N₂ and **A** (Equation 4) are endergonic processes.†



The formation of NC–CN was confirmed by heating a sample of **1** in a gas IR cell and subsequent detection in the IR spectrum on the basis of its diagnostic vibrations ($\tilde{\nu} = 2662, 2562, 2158 \text{ cm}^{-1}$) and hence excluding isocyanogen as the ultimate product, although it may be involved, like thermally unstable diisocyanogen, as an intermediate species.³¹ Like the primary explosive mercury fulminate, *N*-isocyanide **1** is a rare example of a compound able to detonate with evolution of cyanogen gas.³²

In order to gain insight into the mechanism of NC–CN formation, we conducted the MBMS analysis employing **1** with a ¹³C-labeled isonitrile (¹³CN₂**A**, **1-¹³C**), and featuring a ¹⁵N-labeled bridge (C¹⁴N¹⁵NA, **1-¹⁵N**). Unsurprisingly, the source of carbon of formed cyanogen was the terminal isocyanide carbon. Though rather unexpected was that the evolved gas mixture from **1-¹⁵N** contained almost exclusively ¹⁴N,¹⁵N cyanogen and ¹⁴N,¹⁵N dinitrogen (Figure 3).

This finding eliminates several mechanistic scenarios for the formation of cyanogen such as homolytic N–N bond cleavage and subsequent recombination of cyano-radicals or a rearrangement involving two molecules of **1** via a cyclic intermediate or transition state to account for the observed products. The precise pathway for ¹⁴N,¹⁵N cyanogen and ¹⁴N,¹⁵N dinitrogen formation demands cleavage of a C≡N bond of **1**, but remains otherwise

speculative. An intuitive pathway involves fragmentation of **1** to **A** and CN_2 . CAT from **1** to CN_2 and subsequent rearrangement to cyanogen may account for the observed isotopic distribution.

The decomposition of **1** was studied as well in solution: Heating a solution of **1** in benzene- d_6 to 70 °C over ca. 3 h led to complete disappearance of the starting material. Kinetic analysis by ^1H NMR spectroscopy indicated that the decomposition occurs via a bimolecular mechanism, as a second-order dependence on the concentration of **1** was found. No intermediate was observed. ^1H and ^{13}C NMR analysis of the products revealed formation of minor amounts of unidentified species, together with **A** and cyanogen (δ (^{13}C) = 95.2 ppm) as the major products.³³

In conclusion, synthesis and reactivity studies of *N*-isocyanide **1** allowed establishment of a proof of concept for the transfer of a lone carbon atom. Thermal decomposition of **1** led to cyanogen formation.

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