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

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Targeted as an example of a compound composed of a carbon atom together with two stable neutral leaving aroups. 7-isocyano-7-azadibenzonorbornadiene, CN₂A (1, $A = C_{14}H_{10}$ 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 OCN₂A. Reaction of 1 with [RuCl₂(CO)(PCy₃)₂] leads to [RuCl₂(CO)(1)(PCy₃)₂] which decomposes unselectively: in the product mixture, the carbide complex [RuCl₂(C)(PCy₃)₂] was detected. Upon heating in the solid state or in solution, 1 decomposes to A, N₂ and cyanogen (C₂N₂) 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 (C₃O₂) 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 C₃O₂ in solution, demonstrating the formal insertion of the central C atom of C₃O₂ into a W-phosphine bond, leading to a phosphinocarbyne 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 ($C_{14}H_{10}$, **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, LiN**A**, ON₂**A** and NCN**A** 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 H_2N_2A ,^{12a} followed by dehydration of the resulting formohydrazide to yield the *N*-isocyanide (Scheme 1, 34% from H_2N_2A).[†]

Notable spectroscopic features that corroborate the formulated structure of **1** are the IR- and Raman NC stretching vibration band (IR: $\tilde{v} = 2098 \text{ cm}^{-1}$ for **1**, $\tilde{v} = 2060 \text{ cm}^{-1}$ for ¹³CN₂A, **1**-¹³C;

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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: $\tilde{v} = 2093 \text{ cm}^{-1}$ for 1) and the ¹³C NMR resonance corresponding to the terminal carbon ($\delta = 135.5$ 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

$$MesCNO + 1 \rightarrow MesCN + A + N_2 + CO$$
(1)

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 ¹³C NMR resonance (δ (¹³C) = 184.5 ppm, benzene- d_6), and in the gas phase by a redshifted IR vibration band (¹²CO: $\tilde{v} = 2132 \text{ cm}^{-1}$, ¹³CO: $\tilde{v} = 2101 \text{ cm}^{-1}$).¹⁸ Quantification of CO gas by using $[RuCl(Cp^*)(PCy_3)]$ (Cp^{*} = C₅Me₅⁻) 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 ⁱPr₂N-NC with MesCNO yields a triazolidinone,²⁰ stemming from the expected dimerization of the corresponding isocyanate, *i.e.* ¹Pr₂N-NCO.†

Direct observation of OCN₂A 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, N2 and CO formation occurs rapidly. The intermediacy of the N-isocyanate OCN₂A upon oxidation of 1 is howChemComm Accepted Manuscrip

ever further supported by a trapping experiment with ^tBuNH₂ to yield the corresponding mixed urea (Equation 2).

$$MesCNO + 1 + {}^{t}BuNH_{2} \rightarrow$$

$$MesCN + {}^{t}BuNHC(O)NHNA$$
(2)

Additional backing for transient OCN₂A is given by oxidation of 1 with DMSO and catalytic trifluoroacetic anhydride, an established method for the synthesis of isocvanates from isocvanides.²¹ Subsequent mechanistic steps remain obscure: DFT computations (B3LYP-D3BJ/Def2-TZVP) indicate that unimolecular, concerted fragmentation of OCN_2A 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 OCN₂ which readily decomposes to CO and N₂ 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, N2 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 N2. We identified first a precursor complex to access the known carbido complex [RuCl₂(C)(PCy₃)₂].⁶ To this end, 1 was treated with $[RuCl_2(CO)(PCy_3)_2]$ in THF,²⁶ leading to formation of $[RuCl_2(1)(CO)(PCy_3)_2]$ (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 $[RuCl_2(C_6H_2Me_4)(CNN^iPr_2)] [2.035(2) \text{ Å vs. } 1.947(7) \text{ Å}].^{28}$

Heating a toluene solution of 2 to 100 °C for 3 h led to complete disappearance of the ³¹P 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 [RuCl₂(C)(PCy₃)₂], as identified by its characteristic 13 C NMR resonance at $\delta = 473$ ppm.⁶ Although this reaction was unselective and low-yielding (ca. 15% by ³¹P 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 CN₂ or fragments thereof was studied by thermogravimetric analPublished on 26 September 2017. Downloaded by Gazi Universitesi on 26/09/2017 13:29:42.

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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-Cl 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 $^{\circ}$ 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,Nmicroanalysis 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 $1^{15}N$: ion count of $^{14}N^{15}N$ as a function of temperature; b) Scheme depicting the observed major products with their isotope distributions upon thermal decomposition of $1^{-15}N$. c) Integrated mass spectrum of the evolved gases from $1^{-15}N$ during thermolysis.

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

$$1 \rightarrow A + CN_2$$
 ($\Delta G_{g,298.15K} = 22.57 \text{ kcal} \cdot \text{mol}^{-1}$) (3)

$$\mathbf{1} \to \mathbf{A} + \mathbf{C} + \mathbf{N}_2 \quad (\Delta G_{g,298.15K} = 42.39 \text{ kcal} \cdot \text{mol}^{-1})$$
 (4)

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 ($\tilde{v} = 2662, 2562, 2158 \text{ cm}^{-1}$) 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 ¹³Clabeled isonitrile ($^{13}CN_2A$, **1**- ^{13}C), and featuring a ¹⁵N-labeled bridge ($C^{14}N^{15}NA$, **1**- ^{15}N). Unsurprisingly, the source of carbon of formed cyanogen was the terminal isocyanide carbon. Though rather unexpected was that the evolved gas mixture from **1**- ^{15}N 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 \equiv N bond of **1**, but remains otherwise

speculative. An intuitive pathway involves fragmentation of **1** to **A** and CN₂. CAT from **1** to CN₂ 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 ¹³C NMR analysis of the products revealed formation of minor amounts of unidentified species, together with **A** and cyanogen (δ (¹³C) = 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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An anthracene-based N-isocyanide was synthesized and its reactivity studied. This sensitive compound was structurally characterized as a free species and as a ligand in a ruthenium complex, and underwent C-atom transfer upon treatment with an O-atom donor to evolve CO.