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

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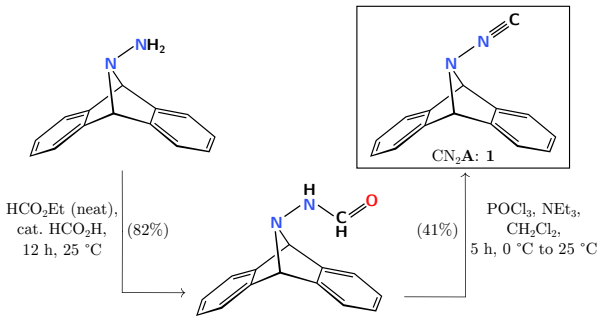
Targeted as an example of a compound composed of a carbon atom together with two stable neutral leaving groups, 7-isocyano-7-azadibenzonorbornadiene, CN_2A (1, A = $C_{14}H_{10}$ or anthracene) has been synthesized and spectroscopically and structurally characterized. The terminal C atom of 1 can be transferred: mesityl nitrile oxide reacts with 1 to produce carbon monoxide, likely via intermediacy of the *N*-isocyanate OCN_2A. Reaction of 1 with $[RuCl_2(CO)(PCy_3)_2]$ leads to $[RuCl_2(CO)(1)(PCy_3)_2]$ which decomposes unselectively: in the product mixture, the carbide complex $[RuCl_2(C)(PCy_3)_2]$ 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 phosphinocarbyne complex.[5] Heppert and coworkers developed a synthesis of a ruthenium carbide complex via CAT from a methylenecyclopropane.[6] Metal carbide complexes have also been obtained through breakdown of carbon monoxide.[7–10]



Scheme 1 Synthesis of **1**.

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**, ON_2**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_2**A** (**1**) was chosen as the synthetic target. Compound **1** is the isocyano bonding isomer of NCN**A** 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_2**A**,[12a] followed by dehydration of the resulting formohydrazide to yield the *N*-isocyanide (Scheme 1, 34% from H_2N_2**A**).†

Notable spectroscopic features that corroborate the formulated structure of **1** are the IR- and Raman NC stretching vibration band (IR: $\tilde{\nu}$ = 2098 cm^{-1} for **1**, $\tilde{\nu}$ = 2060 cm^{-1} for $^{13}CN_2$**A**, **1**-^{13}**C**;

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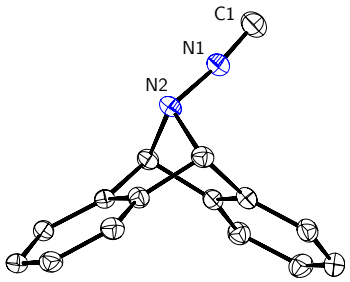

Fig. 1 Molecular structure of **1** drawn with thermal ellipsoids at the 50% probability level and with all H atoms omitted for clarity. Selected distances [Å] and angles [°]: N2-N1 1.381(3), N1-C1 1.164(3), N2-N1-C1 173.3(2).

Raman: $\tilde{\nu}$ = 2093 $cm^{-1}$for **1**) and the ^{13}C NMR resonance corresponding to the terminal carbon (δ = 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]

$$\mathrm{MesCNO} + \mathbf{1} \rightarrow \mathrm{MesCN} + \mathbf{A} + \mathrm{N_2} + \mathrm{CO} \quad (1)$$

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 ^{13}C NMR resonance (δ (^{13}C) = 184.5 ppm, benzene-d_6), and in the gas phase by a redshifted IR vibration band (^{12}CO: $\tilde{\nu}$ = 2132 cm^{-1}, ^{13}CO: $\tilde{\nu}$ = 2101 cm^{-1}).[18] Quantification of CO gas by using [RuCl(Cp*)(PCy_3)] (Cp* = $C_5Me_5^-$) 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}Pr$_2$N-NC with MesCNO yields a triazolidinone,[20] stemming from the expected dimerization of the corresponding isocyanate, *i.e.* ^{i}Pr$_2$N-NCO.†

Direct observation of OCN_2**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 OCN_2**A** upon oxidation of **1** is however further supported by a trapping experiment with ^{t}BuNH$_2$ to yield the corresponding mixed urea (Equation 2).

$$\mathrm{MesCNO} + \mathbf{1} + {}^t\mathrm{BuNH_2} \rightarrow \mathrm{MesCN} + {}^t\mathrm{BuNHC(O)NHN}\mathbf{A} \quad (2)$$

Additional backing for transient OCN_2**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 OCN_2**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 [$RuCl_2$(C)(PCy_3)$_2$].[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^{i}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 [$RuCl_2$(C)(PCy_3)$_2$], as identified by its characteristic ^{13}C NMR resonance at δ = 473 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-

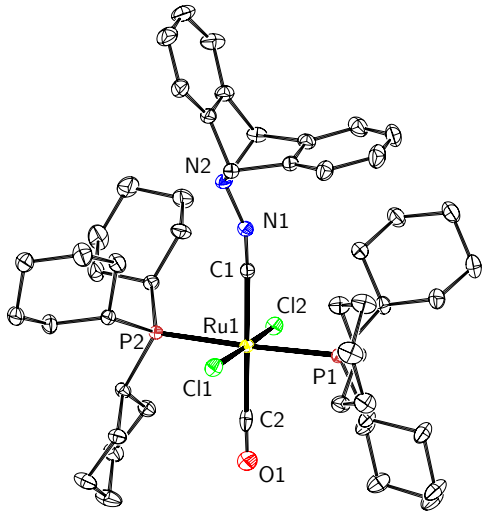

Fig. 2 Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level and with all H atoms and solvent molecules of crystallization omitted for clarity. Selected distances [Å] and angles [°]: Ru1-C2 1.933(3), Ru1-C1 2.035(2), Ru1-P1 2.4221(5), Ru1-Cl1 2.4236(6), Ru1-Cl2 2.4339(6),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

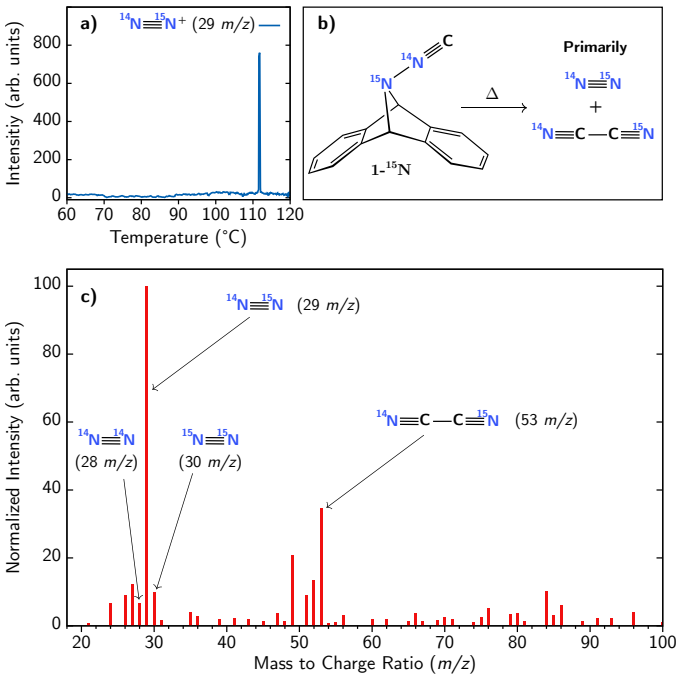

Fig. 3 a) Molecular beam mass spectrometry (MBMS) of **1-^{15}N**: ion count of $^{14}N^{15}N$ as a function of temperature; b) Scheme depicting the observed major products with their isotope distributions upon thermal decomposition of **1-^{15}N**. c) Integrated mass spectrum of the evolved gases from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

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 N_2 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 CN_2 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 CN_2 and **A** (Equation 3) or C, N_2 and **A** (Equation 4) are endergonic processes.†

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

$$\mathbf{1} \rightarrow \mathbf{A} + C + N_2 \quad (\Delta G_{g,298.15K} = 42.39\ \text{kcal}\cdot\text{mol}^{-1}) \tag{4}$$

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 ($\tilde{\nu}$ = 2662, 2562, 2158 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 ^{13}C-labeled isonitrile ($^{13}CN_2$**A**, **1-^{13}C**), and featuring a ^{15}N-labeled bridge ($C^{14}N^{15}N$**A**, **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 $^{14}N,^{15}N$ cyanogen and $^{14}N,^{15}N$ 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 $^{14}N,^{15}N$ cyanogen and $^{14}N,^{15}N$ 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 ^{1}H 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. ^{1}H 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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