An Exploding N-Isocyanide Reagent Formally Composed of

Anthracene, Dinitrogen and a Carbon Atom

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Supporting Information

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S.1 Synthetic Details and Characterization of Products

S.1.1 General Information

The synthesis and workup of HC(O)NHNA (or 7-formamido-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene) and of **1** was performed under air employing ACS reagent grade solvents (**A** = 9,10-dihydro-anthracene-9,10-diyl). All other manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N₂. All solvents were obtained anhydrous and oxygen-free by bubble degassing (Ar), purification through columns of alumina and Q5,¹ and storage over molecular sieves.² Deuterated solvents were purchased from Cambridge Isotope Labs, then degassed and stored over molecular sieves for at least 2 days prior to use. Celite 435 (EM Science) and activated charcoal were dried by heating above 250 °C under dynamic vacuum for at least 48 h prior to use. Glassware was oven-dried for at least three hours at temperatures greater than 150 °C. 7-Amino-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (H₂NNA) was prepared as previously described by Carpino and coworkers.³ [RuCl₂(CO)(PCy₃)₂] was prepared as previously described by Moers and coworkers.⁴

NMR spectra were obtained on Varian Inova 300 and 500 instruments equipped with Oxford Instruments superconducting magnets, on a Jeol ECZ-500 instrument equipped with an Oxford Instruments superconducting magnet, or on a Bruker Avance 400 instrument equipped with a Magnex Scientific or with a SpectroSpin superconducting magnet. ¹H NMR and ¹³C NMR spectra were referenced internally to residual solvent signals, ⁵ and ³¹P NMR spectra were referenced externally to 85% aq. H₃PO₄. Variable temperature NMR measurements were calibrated with a methanol or ethylene glycol thermometer.⁶

Electrospray ionization mass spectra (ESI-MS) were acquired on a Micromass Q-TOF ESI spectrometer. Samples were prepared in a glovebox and placed into a 1.5 mL GC vial equipped with a septum to prevent exposure to oxygen and moisture. Prior to injection of the sample, the capillary tubing was flushed with 3 mL of dry acetonitrile. A source temperature of 100 °C and desolvation gas temperature of 150 °C were used.

Attenuated total reflection infrared (ATR-IR) and gas-phase IR spectra (see S.4) were recorded on a Bruker Tensor 37 Fourier transform IR (FTIR) spectrometer.

Raman spectroscopy of **1** and NCNA was performed using a Kaiser Hololab series 5000 Raman Microscope. The Raman scattering was observed via 180° reflectance through the objective and collected by a CCD camera at -60 °C. An excitation wavelength of 785 nm was provided by a solid-state laser through a $100 \,\mu\text{m}$ fiber optic cable. For sample acquisitions, the $10 \times \text{microscope}$ aperture was used along with 4 mW laser power (measured with a photodiode), 3 second exposure times and 100 accumulations. Each spectrum was corrected for dark current and cosmic ray interference using the Hololab software. A crystalline silicon wafer was used as a frequency standard. Several different sample spots were checked for homogeneity of the material. Sample preparation consisted of placing a 5 mg sample on a microscope slide and gently compacting the material to yield a flat, uniform surface. A detailed description of the gas IR cell is given below (see Section S.4).

Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ, USA).

S.1.2 Synthesis of HC(O)NHNA

 H_2 NNA (1.30 g, 6.24 mmol, 1.0 equiv) was suspended in ethyl formate (8.9 mL, 124.80 mmol, 20.0 equiv) and the colorless mixture was stirred for 12 h at ambient temperature. All volatile materials were removed *in vacuo*. The pale-pink residue was suspended in dichloromethane (10 mL) and hexane (50 mL) was added. The flask was cooled for 30 min in an icebath and followed by removal of the supernatant by filtration to isolate a colorless precipitate. The solids were washed with hexanes (10 mL) and dried under vacuum to give the formohydrazide as a colorless crystalline material. Yield: 1.21 g (5.12 mmol, 82 %). N.b.: When a fresh sample of ethyl formate is employed, the addition of a few drops of formic acid is required. Using aged ethyl formate does not require additional catalytic acid.

Elem. Anal. Found(Calc'd) for $C_{15}H_{12}N_2O$: C 75.85 (76.25), H 5.44 (5.12), N 11.77 (11.86). Melting point: 158 °C to 160 °C. ¹H NMR (chloroform-*d*, 500 MHz, 20 °C): 2 rotamers were observed in a ratio of ca. 1:10. Major isomer: δ 8.54 (d, ³*J*_{HH}=10.7 Hz, C(O)*H*, 1H), 7.46-7.40 (m, H_{ar}, 2H), 7.38-7.33 (m, H_{ar}, 2H), 7.13-7.08 (m, H_{ar}, 4H), 6.78 (d, ³*J*_{HH}=10.7 Hz, N*H*, 1H), 5.19 (s, H_{bridgehead}, 2H); Minor isomer: δ 7.89 (s, C(O)*H*), 7.46-7.40 (m, H_{ar}, 2H), 7.38-7.33 (m, H_{ar}, 2H), 7.13-7.08 (m, H_{ar}, 4H), 6.62 (s, N*H*, 1H), 5.24 (s, H_{bridgehead}, 2H). ¹³C NMR (chloroform-*d*, 126 MHz, 20 °C): δ 164.9 (s), 144.2 (s), 144.1 (s), 127.6 (s), 127.2 (s), 124.4 (s), 121.2 (s), 75.0 (s); IR (ATR): amide CO stretching vibration: 1687 cm⁻¹.



Figure S.1: ¹H NMR spectrum (CDCl₃, 500 MHz, 20 °C) of HC(O)NHNA.



Figure S.2: ${}^{13}C{}^{1}H$ NMR spectrum (CDCl₃, 126 MHz, 20 °C) of HC(O)NHNA.

S.1.3 Synthesis of CNNA (1)

A well-established method for the synthesis of alkyl isocyanides is the reaction of alkyl halides with silver cyanide.⁷ However, CNNA (1) could not be prepared via this route: reaction of BrNA with AgCN yields the bonding isomer NCNA.⁸ Compound 1 was thus prepared by modification of the reported procedures for the synthesis of N-isocyanides.^{9,10} An off-white suspension of HC(O)NHNA (2500 mg, 10.58 mmol, 1.0 equiv) in dichloromethane (20 mL) was cooled to 0 °C and triethylamine (4.42 mL, 31.74 mmol, 3.0 equiv) was added. After stirring for 5 min at 0 °C, POCl₃ (1.48 mL, 15.87 mmol, 1.5 equiv) was slowly added. Stirring was maintained for 5 h at icebath temperature. During this time the color of the reaction mixture changed gradually to orange, then red-brown to brown. Na₂CO₃ (2135 mg) in water (20 mL) was added. The mixture was stirred for further 30 min at 0 °C, then the coldbath was removed and the reaction media allowed to warm up to ambient temperature over 30 min. Dichloromethane (20 mL) and water (20 mL) were added, and the aqueous phase was separated. The aqueous phase was extracted with dichloromethane (20 mL). The combined organic layers were washed with a saturated aqueous sodium carbonate solution ($2 \times 10 \text{ mL}$), dried over MgSO₄, filtered, and all volatile materials were removed to yield an orange-brown residue. This residue was solubilized in dichloromethane (ca. 15 mL) and Celite (a volume of ca. 10 mL) was added. All volatile materials were removed in vacuo. The powdery residue was added on top of a silica gel column (height: ca. 15 cm, diameter: ca. 4 cm, 60 g of silica gel, deactivated with hexanes/Et₃N (10:1, 400 mL) and rinsed with hexanes (500 mL). The column was then quickly eluted with hexanes/EtOAc (10:1). The first 300 mL contained only anthracene, the following 1200 mL contained **1** in colorless to pale orange fractions; removal of all volatile material of the latter fractions gave 1 as a pale-yellow, almost colorless solid. Yield: 954 mg, 4.37 mmol, 41 %. Small, pale-yellow crystalline needles suitable for an X-ray diffraction analysis were grown by storing a concentrated solution of 1 in ethanol for 12 h at -30 °C. 1 decomposes in the course of hours in solutions of benzene, chloroform, dichloromethane, acetonitrile, ethyl acetate, tetrahydrofuran or diethyl ether and is best prepared in small batches, swiftly worked up, stored under nitrogen in the cold and used shortly after preparation. Upon standing or less careful workup, the material undergoes a color change to yellow, then to orange. The corresponding ¹H NMR data indicate formation of minor amounts of unidentified species. Terminal-¹³C-labeled 1 (1-¹³C) and bridgehead-¹⁵N-labeled 1 (1-¹⁵N) were prepared analogously as described above by employing the corresponding labeled starting materials.^{11–13}

CAUTION! This N-isocyanide is an energetic compound. It was not found to be shock-sensitive, but

violently decomposes upon heating (see main text of this paper and below). While we encountered no issues in the synthesis and handling of this material up to quantities of ca. 500 mg, we cannot exclude a different behavior at increased scale.

Elem. Anal. Found(Calc'd) for $C_{15}H_{10}N_2$: C 82.44 (82.55), H 4.83 (4.62), N 12.71 (12.84). ¹H NMR (chloroform-*d*, 500 MHz, 20 °C) δ 7.45 (m, 2H, H_{ar}), 7.35 (m, 2H, H_{ar}), 7.11 (m, 4H, H_{ar}), 5.60 (s, 2H, H_{bridgehead}); ¹H NMR (benzene-*d*₆, 400 MHz, 20 °C) δ 6.95 (m, 2H, H_{ar}), 6.79 (m, 2H, H_{ar}), 6.74 (m, 2H, H_{ar}), 6.70 (m, 2H, H_{ar}), 4.86 (s, 2H, H_{bridgehead}); ¹³C{¹H} NMR (chloroform-*d*, 126 MHz, 20 °C): δ 144.6 (s, C_{ipso}), 142.4 (s, C_{ipso}), 135.5 (s, CN), 127.2 (s, CH_{ar}), 127.2 (s, CH_{ar}), 123.8 (s, CH_{ar}), 121.7 (s, CH_{ar}), 75.9 (s, CH_{bridgehead}); IR (ATR): isocyanide stretching vibration of **1**: 2098 cm⁻¹, isocyanide stretching vibration of **1**: 2093 cm⁻¹.



Figure S.3: ¹H NMR spectrum (chloroform-d, 500 MHz, 20 °C) of **1**.



Figure S.4: ¹H NMR spectrum (benzene- d_6 , 400 MHz, 20 °C) of **1**.



Figure S.5: ¹³C{¹H} NMR spectrum (chloroform-*d*, 126 MHz, 20 °C) of **1**.



Figure S.6: Superposed infrared spectra (ATR) of 1 (blue) and its bonding isomer NCNA (red).



Figure S.7: Superposed Raman spectra of 1 (blue) and its bonding isomer NCNA (red).

S.1.4 Comments on Stability and Reactivity of 1

N-isocyanides are in general unstable species and **1** is no exception.¹⁴ In solution, **1** decomposes rapidly at ambient temperature and slower at -30 °C to small amounts of anthracene and unidentified, insoluble, bright yellow products, likely due to intermolecular reactivity.⁹ In the solid state, slow decomposition was observed at -30 °C.

C-atom transfer was attempted with a range of main-group compounds and transition-metal complexes which was in most cases unsuccessful. Among these trials were for example the reaction with phosphines to give carbodiphosphoranes, the reaction with *N*-heterocyclic carbenes to give vinylidenes or dimers thereof, and the reaction with 3,5-di-*tert*-butyl-1,2-benzoquinone to give an *O*,*O*-heterocyclic carbene or a dimer thereof. Simple coordination to transition-metal fragments to form isocyanide complexes failed in certain cases: for example the coordination to the tungsten pentacarbonyl fragment, using either [W(CO)₅(THF)] or [W(CO)₅(MeCN)] led to immediate decomposition to anthracene and an unidentified black precipitate. Coordination to gold(I) was attempted: although cationic complexes of the type [Au(PR₃)(isocyanide)]⁺ are commonly stable species, ¹⁵ reaction of **1** with [Au(NTf₂)(PPh₃)] led to intractable mixtures and deposition of elemental gold. The attempted reaction of **1** with [Mo(N(R)Ar)₃] (R = *t*Bu, Ar = 3,5-Me₂C₆H₃) to form [Mo(N(R)Ar)₃(**1**)] as a potential precursor to the known carbide anion [CMo(N(R)Ar)₃]⁻, ¹⁶ seemed instead to lead immediately to the cyanide bridged dimeric complex [(Mo(N(R)Ar)₃)₂(CN)]. **1** reacts with methylene triphenylphosphorane, but instead of the envisioned vinylidenephosphorane, the formation of Ph₃P=CH(CN) was observed. Cleavage of the rather weak N–NC bond in **1** is likely the common entrypoint in these transformations. Successful C-atom transfer reactions are described below.

S.1.5 Thermal Decomposition of 1

The thermal decomposition of **1** was studied in the solid state and in solution:

S.1.5.1 Thermogravimetric Analyis

The platinum pan of a TGA Q500 V20.10 Build 36 instrument was charged with **1** (ca. 3 mg). The temperature was slowly increased to 400 °C at a rate of 3 °C min⁻¹ using N₂ as the carrier gas. A large mass loss was observed at about 75 °C (Figure S.8). The structural isomer 7-cyano-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-

2,5-diene (NCNA) was analyzed (up to $800 \,^{\circ}$ C) for comparative purposes.⁸ A slow, gradual mass loss was observed for this compound (Figure S.9).



Figure S.8: Thermogravimetric analysis of 1



Figure S.9: Thermogravimetric analysis of NCNA

S.1.5.2 MBMS Analysis

The molecular beam mass spectrometer (MBMS) apparatus has been previously described elsewhere.¹⁷ Briefly, the apparatus consists of two high vacuum chambers designated the source and detection chamber. The source chamber consists of a sample holder suspended in the middle of the vacuum chamber. The sample holder is a ceramic cup directed at a 1 mm-diameter skimmer from the source chamber to the detection chamber. The ceramic cup is loaded with 10 mg to 15 mg of sample, restrained with a stainless steel screen (98% open area, Unique Wire Weaving Co), resistively heated and the temperature is monitored with a K-type thermocouple reader. Once gases are evolved from the sample, they pass unimpeded through a 1 mm-diameter skimmer from the source chamber to the detection chamber, creating a molecular beam. The molecular beam is then sent to the entrance of an axially oriented Extrel MAX500 Mass Spectrometer (Extrel Core Mass Spectrometers), where the beam is ionized by EI (Electron impact, 70 eV), mass separated by a quadrupole and detected by a Faraday cup. The masses of interest are monitored as a function of temperature and are baseline corrected for background signal.

Upon heating of a sample of **1**, a very sharp mass release was observed. An integrated mass spectrum of the gases indicates that the primary gas evolved (ignoring N_2) is cyanogen (Figure S.10 a). The ratio of cyanogen to dinitrogen can be estimated and is approximately 3:10. The amount of detected **A** is unexpectedly small. In general, a temperature offset for less volatile fragments (like **A**) was commonly observed in our previous MBMS studies. The small amount of anthracene observed here may be thus due to the vast difference in vapor pressure between dinitrogen and cyanogen *vs* **A**. Heating the sample to higher temperatures in order to observe larger amounts of **A** proved not feasible due to detector saturation of the copious amounts of released dinitrogen. Fragments belonging to dichloromethane were detected from trace dichloromethane present in the sample (the sample of **1** was transferred beforehand to a storage flask in dichloromethane solution. Even after extensive drying, traces of CH₂Cl₂ remained). MBMS analysis of **1**-¹³C indicated that the carbon source for cyanogen is entirely the terminal isocyanide carbon atom (Figure S.10 b). MBMS analysis of **1**-¹⁵N indicated that almost all of the evolved dinitrogen is ¹⁴NCC¹⁵N (Figure S.10 c).



Figure S.10: Masses observed during MBMS analysis of 1 (a), $1^{-13}C$ (b) and $1^{-15}N$ (c).

S.1.5.3 IR Spectrum of Evolved Gases Upon Decomposition and Analysis of the Residue

The gases evolving upon thermal degradation of **1** were analyzed using a gas IR cell (described in section Figure S.18): A small amount of **1** (ca. 10 mg) was placed in the glass pocket of the cell which was subsequently sealed, put under static vacuum and a blank spectrum was recorded. The glass pocket was heated with an oilbath (at ca. 100 °C) or a heat gun until the material violently decomposed and the spectrum of the evolved gases was recorded, indicating the formation of cyanogen by comparison with reported data.¹⁸



Figure S.11: Detail of the IR spectrum of the gases formed upon thermal decomposition of 1, containing cyanogen (red annotations). The observed CO_2 , stems likely from the atmosphere surrounding the gas-IR cell (black annotations).

The remaining residue, a brown solid, was analyzed by elemental analysis. This material contained nitrogen [Found: C: 87.45, H: 5.55, N: 4.57, expected for anthracene ($C_{14}H_{10}$): C: 94.34, H: 5.66]. The residue was soluble in benzene (yellow-orange solution) and ¹H NMR spectroscopy revealed anthracene as the major solid decomposition product (see Figure S.12).



Figure S.12: ¹H NMR spectrum (benzene- d_6 , 300 MHz, 20 °C) of the solid residue obtained after thermal decomposition of **1**.

S.1.5.4 Analysis of Pressure Increase Upon Decomposition

In order to illustrate the explosion-like behavior of **1** upon heating, the pressure increase upon thermal decomposition was monitored. The experimental setup consisted of a round-bottom flask (10 mL) equipped with a rubber septum. The septum was pierced and the outer tube of a 1 mL-plastic syringe was put through the hole so that the needle-connection part of the syringe tube was located on the exterior of the flask. The syringe tubing was then connected directly (without any additional tubing) to a GPS-BTA gas pressure sensor (Vernier). Pressure changes over time were monitored and recorded using the Vernier Logger Lite software. A calibration curve was established: after assembly of the setup and equilibration, known amounts of air (0.25 mL, 0.50 mL, 0.75 mL and 1.00 mL) were introduced into the closed system via the rubber septum using a 1 mL-syringe equipped with a needle. The changes in pressure upon addition of air were recorded. On the assumption that air behaves as an ideal gas (with T = 298 K, p = 1031 mbar), the added volumes of air correspond to the amounts of gas given in Table S.1. Plotting the observed pressure difference over the amount of added gas results in a calibration curve ($\Delta n \pmod{1 = \frac{\Delta p \pmod{1}}{1795.38}}$) which is used for estimating the amount of gas evolved upon thermal degradation of 1 (Figure S.13).

V added gas Amount added gas		Pressure change upon addition	
(mL)	(mmol)	(mbar)	
0.25	0.0101	71.0 (± 3.7)	
0.50	0.0202	57.0 (± 2.9)	
0.75	0.0303	33.0 (± 2.2)	
1.00	0.0404	23.0 (± 2.6)	





Figure S.13: Calibration curve established for the pressure change analysis upon decomposition of 1.

A sample of **1** (5.0 mg, 0.023 mmol) was placed into the round-bottom flask, which was then sealed as described above. The sample was heated with a heat gun, leading to its vigorous decomposition, accompanied by a sharp increase in pressure (Figure S.14). Upon cooling to 25 °C the pressure slowly equilibrated. The experiment was performed in triplicate. The estimated amounts of released gas are given in Table S.2. Theoretically, 1 equiv of **1** could yield 0.5 equiv of N₂ and 0.5 equiv of cyanogen. If this were the correct stoichiometry for the thermal decomposition of **1**, the yield of gaseous products is about 61 %.



Figure S.14: Observed pressure increase in a closed system upon thermal decomposition of **1** in the solid state

Run	Mass CN ₂ A	Amount CN ₂ A	Pressure change upon addition	Amount gas
	(mg)	(mmol)	(mbar)	(mmol)
1	5.0	0.023	27	0.015
2	5.0	0.023	25	0.014
3	5.0	0.023	23	0.013
avg	5.0	0.023	25	$0.014 {\pm} 0.002$

Table S.2: Estimation of amount of released gases upon thermal decomposition of 1.

S.1.5.5 Decomposition in Solution

A solution of 1^{-13} C (10 mg, 0.046 mmol) in C₆D₆ was heated for ca. 3 h in an oilbath at about 75 °C. Analysis by ¹H NMR spectroscopy indicated formation of anthracene as the major product, together with minor unidentified species. Analysis by ¹³C{¹H} NMR spectroscopy revealed generation of cyanogen, identified by its characteristic resonance at 95.2 ppm.¹⁹ In addition, the reaction was monitored in a separate exper-

iment by ¹H NMR spectroscopy: A solution of **1** (10 mg, 0.046 mmol) and hexamethylbenzene (2.5 mg, 0.015 mmol) as internal standard in benzene- d_6 (0.8 mL) was transferred to an NMR tube. The tube was sealed, and immediately placed in a preheated NMR probe (calibrated to be at 70 °C). After thermal equilibration, locking and shimming (ca. 10 min, the decreasing concentration of **1** was measured by acquiring single-scan ¹H NMR spectra over 3 to 4 half-lives every 2.5 min and integrating the bridgehead-proton signal of **1** against the methyl resonance of hexamethylbenzene. The experiment was conducted in triplicate. The obtained data were found to fit a second-order decay ($k_{obs} = (4.3 \pm 1.2) \times 10^{-2} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$ at 70 °C in benzene).



Figure S.15: Thermal decay of 1 at 70 °C in benzene- d_6 : Plot of the concentration of 1 over time.



Figure S.16: Thermal decay of 1 at 70 °C in benzene- d_6 : Plot of the the natural logarithm of the concentration of 1 over time, indicating a nonlinear relationship and thus non-first-order behavior.



Figure S.17: Thermal decay of 1 at 70 °C in benzene- d_6 : Plot of the the inverse concentration of 1 over time, indicating a linear relationship and thus a second-order rate law.

S.1.6 Reaction of 1 with MesCNO

A solution of mesitylnitrile oxide (10.0 mg, 0.062 mmol, 1.3 equiv) in C_6D_6 (0.7 mL) was slowly added to **1** (10.0 mg, 0.046 mmol, 1.0 equiv) in a scintillation vial at 25 °C. The bright yellow-orange solution was stirred for 2 min and transferred to an NMR tube which was sealed with a rubber septum. The evolution of small gas bubbles was observed in the tube. Analysis by ¹H NMR revealed the formation of anthracene and mesitylnitrile. After complete conversion was achieved (ca. 8 h), the headspace gases of the tube were

transferred into a gas-IR-cell. The infrared spectrum of the evolved gases indicated the presence of carbon monoxide gas. The experiment was performed as well with $1-{}^{13}C$, showing the formation of ${}^{13}CO$ (Figure S.18).



Figure S.18: Infrared spectra of the headspace gases from the reaction of mesitylnitrile oxide with 1 and 1^{-13} C, respectively. The band centered at 2287.8 cm⁻¹ is attributed to C₆D₆.²⁰

Carbon monoxide generation from **1** and mesityl nitrile oxide was also indirectly shown and quantified by formation of $[RuCl(Cp^*)(CO)(PCy_3)]$ from $[RuCl(Cp^*)(PCy_3)]$.²¹ A sample of compound **1** (10.0 mg, 0.046 mmol, 1.0 equiv) was placed into a scintillation vial (OD: 1 cm) equipped with a magnetic stirbar. This vial was placed into a second, larger vial (OD: 3 cm) containing a solution of $[RuCl(Cp^*)(PCy_3)]$ (25.3 mg, 0.046 mmol, 1.0 equiv) in THF (1 mL). A solution of mesityl nitrile oxide (8.1 mg, 0.050 mmol, 1.1 equiv) in THF (1 mL) was added to **1** in the inner vial and the the surrounding vial was quickly capped with a screw-cap featuring a Teflon liner. The mixture was stirred for 24 h, an aliquot (0.7 mL) of the solution in the outer vial was transferred to an NMR tube and analyzed by ³¹P NMR. The experiment was conducted in triplicate. According to the relative ratio of $[RuCl(Cp^*)(PCy_3)]$ and $[RuCl(Cp^*)(CO)(PCy_3)]$ the yield of CO generation from **1** was 27 %.



Figure S.19: ³¹P{¹H} NMR spectrum (THF, 162 MHz, 20 °C) of the mixture of [RuCl(Cp^{*})(PCy₃)] (40.61 ppm) and [RuCl(Cp^{*})(CO)(PCy₃)] (51.74 ppm) as a result of trapping CO evolved from the reaction of **1** with MesCNO.

The yield of formed anthracene upon reaction of **1** with mesityl nitrile oxide was determined in a separate experiment. A sample of compound **1** (10.0 mg, 0.046 mmol, 1.0 equiv) was dissolved in a stock solution of C_6Me_6 in benzene- d_6 (internal standard, $c = 1.51 \text{ g mL}^{-1}$, 0.7 mL). This solution was added to mesityl nitrile oxide (7.4 mg, 0.046 mmol, 1.0 equiv). The mixture was immediately transferred to an NMR tube which was sealed, kept for 18 h at 25°C and then analyzed by ¹H NMR spectroscopy. The yield of anthracene was calculated to be 28 % by determining the ratio of integrations for the methyl resonance of the internal standard C_6Me_6 and the for the 9,10-CH resonance of anthracene, in line with the yield of released CO.



Figure S.20: ¹H NMR spectrum (benzene- d_6 , 400 MHz, 20 °C) of the mixture of **1** with mesityl nitrile oxide with hexamethylbenzene (internal standard).

S.1.7 Trapping of OCNNA with ^tBuNH₂: Synthesis of ^tBuNHC(O)NHNA with ^tBuNH₂

In order to probe for the possible intermediacy of OCNNA resulting from the oxidation of **1** with MesCNO, this reaction was performed in the presence of an amine, aiming at the formation of the corresponding, isolable urea compound (Scheme Scheme 1 a).



Scheme 1: a) Synthesis of 'BuNHC(O)NHNA via trapping of intermediate OCNNA; b) Independent synthesis employing H_2NNA and 'Bu NCO.

A solution of MesCNO (7.5 mg, 0.046 mmol, 1.0 equiv) in benzene- d_6 (0.4 mL) was slowly added at 25 °C to a solution of **1** (10.0 mg, 0.046 mmol, 1.0 equiv) in benzene- d_6 (0.4 mL). The mixture was transferred to an NMR tube containing ^{*t*}BuNH₂ (34.0 mg, 0.46 mmol, 10.0 equiv). The initially clear yellow,

homogeneous mixture turned bright yellow and heterogeneous. A colorless, thick precipitate deposited. After 16 h at 25 °C, the precipitate was isolated by filtration, dissolved in chloroform-*d* and analyzed by ¹H NMR, indicating the formation of ^{*t*}BuNHC(O)NHNA.

^{*t*}BuNHC(O)NHNA was prepared independently by reaction of Carpino's hydrazine with ^{*t*}BuNCO (Scheme 1 b): A solution of H_2 NNA (100.0 mg, 0.48 mmol, 1.0 equiv) in CHCl₃ (1.5 mL) was added at 25 °C to a solution of ^{*t*}BuNCO (52.0 mg, 0.53 mmol, 1.1 equiv) in CHCl₃ (1.0 mL). The reaction mixture was stirred for 24 h at this temperature. All volatile materials were removed under vacuum and the resulting pale yellow solid was washed with benzene (3 × 3 mL to give ^{*t*}BuNHC(O)NHNA as a colorless solid which was brought to constant mass. Yield: 92.0 mg (0.30 mmol, 62 %).

Elem. Anal. Found(Calc'd) for $C_{19}H_{21}N_3O$: C 73.69 (74.24), H 6.65 (6.89), N 13.60 (13.67). Melting point: 158 °C to 160 °C. ¹H NMR (chloroform-*d*, 500 MHz, 20 °C) δ 7.38 (m, 2H, H_{ar}), 7.32 (m, 2H, H_{ar}), 7.07 (m, 4H, H_{ar}), 5.96 (s br, 1H, H_{NH}), 5.46 (s br, 1H, H_{NH}), 5.12 (s, 2H, H_{bridgehead}), 1.32 (s, 9H, H_{'Bu}); ¹³C{¹H} NMR (chloroform-*d*, 126 MHz, 20 °C): δ 157.03 (s, C_{C=O}), 145.22 (s, C_{ipso}), 144.69 (s, C_{ipso}), 127.01 (s, CH_{ar}), 126.30 (s, CH_{ar}), 124.43 (s, CH_{ar}), 121.13 (s, CH_{ar}), 74.28 (s, CH_{bridgehead}), 50.19 (s, *C*(CH₃)₃), 29.52 (s, C(*CH*₃)₃); IR (ATR): 3384 cm⁻¹, 3173 cm⁻¹, 3071 cm⁻¹, 2958 cm⁻¹, 2867 cm⁻¹, 1666 cm⁻¹, 1512 cm⁻¹, 1456 cm⁻¹.



Figure S.21: ¹H NMR spectrum (CDCl₃, 300 MHz, 20 °C) of ^{*t*}BuNHC(O)NHNA from the reaction of **1** with MesCNO and ^{*t*}BuNH₂.



Figure S.22: ¹H NMR spectrum (chloroform-*d*, 500 MHz, 20 °C) of ^{*t*}BuNHC(O)NHNA prepared via reaction of H_2 NNA with ^{*t*}BuNCO.



Figure S.23: ¹³C{¹H} NMR spectrum (benzene- d_6 , 126 MHz, 20 °C) of ^{*t*}BuNHC(O)NHNA prepared via reaction of H₂NNA with ^{*t*}BuNCO.

S.1.8 Reaction of ^{*i*}Pr₂N–NC with MesCNO

In order to gain additional evidence for the intermediacy of an *N*-isocyanate in the above reaction (see S.1.6), the previously reported *N*-isocyanodiisopropylamine was oxidized with MesCNO.^{9,10} The corresponding *N*-isocyanate (which cannot – unlike oxidized **1** – easily release N₂ and CO) is known to dimerize and yield a stable triazolidinedione (Scheme 2).²² A solution of MesCNO (128.0 mg, 0.79 mmol, 1.0 equiv) in benzene (1.5 mL) was added to a solution of ^{*i*}Pr₂N–NC (100.0 mg, 0.79 mmol, 1.0 equiv) in benzene (1.5 mL). The mixture was stirred at 25 °C for 48 h. All volatile materials were removed *in vacuo* to yield a brown-orange oily residue. The residue was solubilized in pentane (as little as possible, ca. 2 mL), filtered and the resulting solution placed in the freezer for 14 h. The formed yellow precipitate was isolated, washed with cold pentane (2 × 0.5 mL) and dried under vacuum to give 4-(diisopropylamino)-1-isopropyl-1,2,4-triazolidine-3,5-dione in about 90 % purity (traces of MesCNO and MesCN were observed by ¹H NMR to be present). Yield: 29.0 mg (0.12 mmol, 30 %). The ¹H NMR-spectroscopic and mass spectrometric data are in accordance with those previously reported.²² Performing the reaction in an NMR tube and monitoring by ¹H NMR spectroscopy allowed for the detection of propene (the coproduct of this reaction due to the

spontaneous loss of an isopropyl group).



Scheme 2: Synthesis of a triazolidinedione by oxidation of an *N*-isocyanide with MesCNO: indirect evidence for the intermediacy of an *N*-isocyanate.



Figure S.24: ¹H NMR spectrum (CDCl₃, 400 MHz, 20 °C) of 4-(diisopropylamino)-1-isopropyl-1,2,4-triazolidine-3,5-dione from the oxidation and subsequent dimerization of iPr_2N-NC .

S.1.9 Reaction of 1 with DMSO and TFAA

The oxidation of **1** was also performed as described for the synthesis of isocyanates from common isocyanides with DMSO and catalytic trifluoroacetic anhydride (TFAA).²³ Under N₂, a solution of **1** (20.0 mg, 0.092 mmol, 1.0 equiv) and DMSO (7.2 μ L, 0.101 mmol, 1.1 equiv) in dichloromethane (1.0 mL) was cooled to -60 °C. TFAA (0.7 μ L, 0.0046 mmol, 0.05 equiv) was added and the mixture was stirred for 5 min at -60 °C, then for further 5 min at 25 °C. The headspace gases of the reactor were transferred into a gas-IRcell. The infrared spectrum of the evolved gases indicated the presence of carbon monoxide. The yield of CO generation from **1** (ca. 9 %) was quantified analogously to the procedure described above using [RuCl(Cp*)(PCy₃)] (S.1.6).

S.1.10 Synthesis of $[RuCl_2(CO)(1)(PCy_3)_2]$ (2)

A solution of **1** (30.0 mg, 0.138 mmol, 1.05 equiv) in THF (5 mL) was quickly added at ambient temperature to an orange suspension of $[RuCl_2(CO)(PCy_3)_2]$ (100.0 mg, 0.131 mmol, 1.0 equiv) in THF (5 mL). The mixture was stirred for 30 min during which time the initially orange-red suspension became homogeneous and turned to a red color. All Volatile materials were removed under vacuum, leaving behind a red oily residue. Pentane (2 mL) was added and removed under vacuum to give a red solid which was washed with pentane/THF (4:1, 3 × 2 mL). The remaining yellow residue was dried under vacuum to give the title compound. Yield: 91.2 mg (0.093 mmol, 71 %). Crystals suitable for an X-ray diffraction analysis were grown at -30 °C. ¹³C-labeled **2** was prepared analogously by employing **1**-¹³C.

Elem. Anal. Found(Calc'd) for $C_{52}H_{76}Cl_2N_2OP_2Ru$: C 63.60 (63.79), H 7.53 (7.82), N 2.64 (2.86). ¹H NMR (chloroform-*d*, 500 MHz, 20 °C) δ 7.38 (m, br, 4H, H_{ar}), 7.12 (m, 4H, br, H_{ar}), 5.72 (s, 2H, H_{bridgehead}), 2.30 (m, 6H, H_{Cy}), 1.98 (m, 12H, H_{Cy}), 1.78 (m, 12H, H_{Cy}), 1.64 (m, 6H, H_{Cy}), 1.55 (m, 12H, H_{Cy}), 1.24 (m, 18H, H_{Cy}); ¹³C NMR (chloroform-*d*, 126 MHz, 20 °C): δ 206.0 (t, ³*J*_{PC} = 12.3 Hz, *CO*), 145.4 (s, br, C_{q-ar}), 143.1 (t, ³*J*_{PC} = 14.4 Hz, *CN*), 142.4 (s, br, C_{q-ar}), 127.3 (s, br, CH_{ar}), 123.4 (s, br, CH_{ar}), 121.5 (s, br, CH_{ar}), 75.2 (s, CH_{bridgehead}), 34.3 (t, ¹*J*_{PC} = 8.6 Hz, CH_{Cy}), 29.17 (s, CH_{2-Cy}), 28.10 (s, CH_{2-Cy}), 26.49 (s, CH_{2-Cy}); ³¹P{¹H} NMR (chloroform-*d*, 203 MHz, 20 °C): δ 24.5.



Figure S.25: ¹H NMR spectrum (CDCl₃, 500 MHz, 20 $^{\circ}$ C) of **2**.



Figure S.26: ${}^{13}C{}^{1}H$ NMR spectrum (CDCl₃, 126 MHz, 20 °C) of **2**.



Figure S.27: ${}^{31}P{}^{1}H$ NMR spectrum (CDCl₃, 203 MHz, 20 °C) of **2**.

S.1.11 Thermal decomposition of [RuCl₂(CO)(1)(PCy₃)₂]

A solution of 2^{-13} C (69.0 mg, 0.07 mmol) in toluene- d_8 (0.7 mL) in a J. Young NMR tube was heated for 180 min to 100 °C. The contents of the tube were analyzed by ¹H NMR, ¹³C NMR and ³¹P NMR spectroscopy, revealing a complex mixture of several species. Among the formed products, the previously reported carbide complex was identified on the basis of its characteristic ³¹P NMR and ¹³C NMR shifts (δ 32 ppm and 473 ppm, respectively).^{24,25}



Figure S.28: ¹H NMR spectrum (CDCl₃, 400 MHz, 20 °C) of the reaction mixture resulting from the thermal decomposition of **2**.



Figure S.29: ¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz, 20 °C) of the reaction mixture resulting from the thermal decomposition of **2**.



Figure S.30: ${}^{31}P{}^{1}H$ NMR spectrum (CDCl₃, 203 MHz, 20 °C) of the reaction mixture resulting from the thermal decomposition of **2**.

S.2 X-Ray Diffraction Studies

S.2.1 Data acquisition

The crystals were mounted in hydrocarbon oil on a nylon loop or a glass fiber. Low-temperature (100 K) data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo K α radiation ($\lambda = 0.71073$ Å) with ϕ - and ω -scans. A semi-empirical absorption correction was applied to the diffraction data using SADABS.²⁶ All structures were solved by intrinsic phasing using SHELXT²⁷ and refined against F^2 on all data by full-matrix least squares with SHELXL-2015²⁸ using established methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Descriptions of the individual refinements follow below and details of the data quality and a summary of the residual values of the refinements for all structures are given in Table S.3. Further details can be found in the form of .cif files available from the CCDC.

Table S.3: Crysta	ullographic Data for 1 and [RuCl ₂ (0	CO)(1)(PCy ₃) ₂]
	1	[RuCl2(CO)(1)(PCy3)2]
Reciprocal Net code / CCDC	X8_17056 / CCDC 1566922	X8_16184 / CCDC 1566923
Empirical formula, FW (g/mol)	$C_{15}H_{10}N_2$, 218.25	$C_{53}H_{77}Cl_5N_2OP_2Ru, 1098.42$
Color / Morphology	Colorless / Needle	Yellow / Block
Crystal size (mm ³)	$0.350\times0.070\times0.070$	$0.262 \times 0.082 \times 0.062$
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Monoclinic, P2 ₁	Monoclinic, Cc
Unit cell dimensions (Å, °)	$a = 8.291(2), \alpha = 90$	$a = 25.9247(8), \alpha = 90$
	$b = 6.1867(15), \beta = 106.880(4)$	$b = 13.1773(4), \beta = 124.2610(10)$
	$c = 11.241(3), \gamma = 120$	$c = 19.0154(6), \ \gamma = 90$
Volume ($Å^3$)	551.8(2)	5368.8(3
Ζ	2	4
Density (calc., g/cm ³)	1.314	1.359
Absorption coefficient (mm ⁻¹)	0.079	0.639
F(000)	228	2304
Theta range for data collection (°)	1.893 to 30.524	1.814 to 32.040
Index ranges	$-11 \le h \le 11, -8 \le k \le 8,$	$-38 \le h \le 38, -19 \le k \le 19,$
	$-16 \le l \le 16$	$-38 \le l \le 19$
Reflections collected	23562	89774
Independent reflections, Rint	3361, 0.0697	16154, 0.0328
Completeness to θ_{\max} (%)	2.66	100.0
Absorption correction	Semi-empirical from equiv.	Semi-empirical from equiv.
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / Restraints / Parameters	3361 / 1 / 154	16154 / 152 / 614
Goodness-of-fit ^a	0.996	1.019
Final <i>R</i> indices ^{<i>b</i>} $[I > 2\sigma(I)]$	$R_1 = 0.0453, wR_2 = 0.1042$	$R_1 = 0.0253, wR_2 = 0.0568$
R indices ^b (all data)	$R_1 = 0.0575, wR_2 = 0.1112$	$R_1 = 0.0272, wR_2 = 0.0578$
Largest diff. peak and hole $(e \cdot \text{\AA}^{-3})$	0.218 and -0.273	0.992 and -0.350
^{<i>a</i>} GooF = $\sqrt{\frac{\Sigma[w(F_c^2 - F_c^2)^2]}{(n-p)}} \ b R_1 = \frac{\Sigma[F_o - F_c]}{\Sigma[F_o]}; w$	${}^{I}\!R_2 = \sqrt{rac{\Sigma[w(F_o^2 - F_o^2)^2]}{\Sigma[w(F_o^2)^2]}}; w = rac{1}{\sigma^2(F_o^2) + (aP)^2 + bP}$	$;; P = rac{2F_c^2 + \max(F_o^2, 0)}{3}$

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S.3 Computational Details

S.3.1 General Information

All calculations were performed with the ORCA 4.0.0 quantum chemistry package from the development team at the University of Bonn.^{29,30} Tables of Cartesian coordinates for all computed structures are provided in separate files on the website linked to this article.

S.3.2 Enthalpy of Formation Calculations

The enthalpy of formation calculations were performed using a modified "correlation-consistent composite approach" (ccCA) methodology.^{31,32} Our approach compiled the results of seven individual calculations together into a projected enthalpy value for the molecule of study. The seven calculations (and the appropriate ORCA keywords) are listed below:

- B3LYP³³/6-31G(d)³⁴ optimization and frequency calculation: B3LYP 6-31G(d) TightSCF Opt Freq
- MP2/cc-pVTZ³⁵ single point calculation at the B3LYP/6-31G(d) geometry: MP2 cc-pVTZ FrozenCore TightSCF
- MP2/aug-cc-pVTZ³⁶ single point calculation at the B3LYP/6-31G(d) geometry: MP2 aug-cc-pVTZ FrozenCore TightSCF
- MP2/aug-cc-pVDZ³⁶ single point calculation at the B3LYP/6-31G(d) geometry: MP2 aug-cc-pVDZ FrozenCore TightSCF
- DLPNO-CCSD(T)³⁷⁻⁴³/cc-pVTZ^{35,44} single point calculation at the B3LYP/6-31G(d) geometry: DLPNO-CCSD(T) cc-pVTZ cc-pVTZ/C VeryTightSCF
- 6. MP2(full)/aug-cc-pCVTZ^{36,45} single point calculation at the B3LYP/6-31G(d) geometry: MP2 aug-cc-pCVTZ NoFrozenCore TightSCF using the aug-cc-pVTZ basis set on H, specified with a %basis NewGTO H "aug-cc-pVTZ" end end block
- 7. MP2(DKH2)/cc-pVTZ-DK⁴⁶ single point calculation at the B3LYP/6-31G(d) geometry: MP2 cc-pVTZ-DK DKH2 FrozenCore TightSCF

The results of these calculations are compiled into a ccCA energy E_{ccCA} using the following equations: ^{31,32}

$$E_{\rm ccCA} = E[MP2/aug-cc-pV\infty Z] + \Delta E_{\rm CC} + \Delta E_{\rm CV} + \Delta E_{\rm DKH2} + 0.9854E[ZPE] + k_{\rm B}T$$
(1)

$$\Delta E_{\rm CC} = E[\rm DLPNO-CCSD(T)/cc-pVTZ] - E[\rm MP2/cc-pVTZ]$$
(2)

$$\Delta E_{\rm CV} = E[\rm MP2(full)/aug-cc-pCVTZ] - E[\rm MP2/aug-cc-pVTZ]$$
(3)

$$\Delta E_{\text{DKH2}} = E[\text{MP2}(\text{DKH2})/\text{cc-pVTZ-DK}] - E[\text{MP2}/\text{cc-pVTZ}], \qquad (4)$$

where $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature (298.15 K), and *E*[ZPE] is the non-thermal zero point correction to the internal energy. The notation *E*[*X*] represents the final single point energy of calculation *X*. The *E*[MP2/aug-cc-pV∞Z] entry is the MP2 single point energy extrapolated to the basis set limit using the following formula, where the SCF energies and MP2 corrections are taken separately from the aug-cc-pVTZ (step 3) and aug-cc-pVDZ (step 4) calculations:^{47–49}

$$E[MP2/aug-cc-pV\infty Z] = \left(\frac{e^{4.300\sqrt{3}}SCF[aug-cc-pVTZ] - e^{4.300\sqrt{2}}SCF[aug-cc-pVDZ]}{e^{4.300\sqrt{3}} - e^{4.300\sqrt{2}}}\right) + \left(\frac{3^{2.510}MP2[aug-cc-pVTZ] - 2^{2.510}MP2[aug-cc-pVDZ]}{3^{2.510} - 2^{2.510}}\right), \quad (5)$$

The E_{ccCA} value was converted to an enthalpy of formation by calculating the enthalpy of atomization and then converting this into the final value using the atomic heats of formation. Thus, the E_{ccCA} values for individual atoms were calculated. The E_{ccCA} values for individual non-hydrogen atoms were calculated using steps 2–6 on triplet C, quartet N, triplet O, and doublet F, where E[ZPE] = 0 for an atom. For hydrogen, there is only one electron and one orbital, such that $\Delta E_{CC} = 0$ and $\Delta E_{CV} = 0$ and that MP2 = HF, meaning the MP2 portion of the formula for extrapolation to the complete basis set limit can be ignored.

Although experimentally derived heats of formation would ideally be used to convert these atomization energies into enthalpies of formation, calculations on individual atoms are notoriously difficult and often unreliable. When using experimental gaseous atomic heats of formation, the mean absolute deviation among a 51 molecule test set (Table S.4) was 4.20 kcal/mol; these values were $\Delta H_f(H) = 52.10$ kcal/mol, $\Delta H_f(C) =$ 171.29 kcal/mol, $\Delta H_f(N) = 112.97$ kcal/mol, $\Delta H_f(O) = 59.55$ kcal/mol, and $\Delta H_f(F) = 18.97$ kcal/mol. Instead, these values were obtained by a least-squared linear regression among the 51 molecule test set (Table S.4). The fitted values of $\Delta H_f(g, 298.15 \text{ K})$ were $\Delta H_f(H) = 52.39$ kcal/mol, $\Delta H_f(C) = 170.01$ kcal/mol, $\Delta H_{\rm f}({\rm N}) = 111.60$ kcal/mol, $\Delta H_{\rm f}({\rm O}) = 58.46$ kcal/mol, and $\Delta H_{\rm f}({\rm F}) = 19.36$ kcal/mol with $R^2 = 0.999999924$ and adjusted $R^2 = 0.97826004$. With these fitted values, the mean absolute deviation among the test set was 0.83 kcal/mol.

Calculation of the heat of formation proceeds in two steps. First, an intermediate atomization energy is calculated by taking the difference between E_{ccCA} of the molecule of interest and the sum of the E_{ccCA} values for its constituent atoms. Second, the fitted heats of formation for each gaseous atom are added to the atomization energy. For example, in order to calculate the heat of formation for methane:

$$E(CH_4) = E_{ccCA}(CH_4) - \sum E_{ccCA}(atoms)$$

= $E_{ccCA}(CH_4) - [E_{ccCA}(C, {}^{3}P) + 4E_{ccCA}(H, {}^{2}S)]$
= $(-40.48205571) - [(-37.85229385) + 4(-0.499049887)]$
= -0.6335623 Hartrees = -397.57 kcal/mol

$$\Delta H_{f}(CH_{4}) = E(CH_{4}) + \sum \Delta H_{f}(atoms)$$

$$= E(CH_{4}) + [\Delta H_{f}(C, {}^{3}P) + 4\Delta H_{f}(H, {}^{2}S)]$$

$$= (-397.57) + (170.01) + 4(52.39) = -17.98 \text{ kcal/mol}$$

Thus, the calculated enthalpy of formation is $\Delta H_f(CH_4, 298.15 \text{ K}) = -17.98 \text{ kcal/mol}$, which agrees closely with the experimental value of -17.9 kcal/mol.

The ccCA calculations were then run on singlet CNNA, triplet CNN, and singlet ONNA. The values were $\Delta H_{f(g,calc)}(CNNA) = 161.22 \text{ kcal/mol}, \Delta H_{f(g,calc)}(^3CNN) = 137.33 \text{ kcal/mol}, and \Delta H_{f(g,calc)}(ONNA) = 111.97 \text{ kcal/mol}$. These results were used to calculate energies of the reactions tabulated in Table S.5. The free energies were determined using entropic contributions taken from the B3LYP/6-31G(d) frequency calculation in step 1. The enthalpy of reaction for CNNA fragmenting into anthracene, dinitrogen, and one-sixtieth buckminsterfullerene was found to be $\Delta H_{f(g,calc)}(ONNA) = -97.73 \text{ kcal/mol}$.

The values in Table S.5 for ONNA were found to be similar to the experimentally known values of $\Delta H =$ 39.5 kcal/mol for N₂O_(g) \rightarrow N_{2(g)} + O_(g), $\Delta H =$ 9.2 kcal/mol for ONNA_(s) \rightarrow A_(s) + N_{2(g)} + O_(g), and $\Delta H =$ 8.0 kcal/mol for ONNA_(toluene) \rightarrow A_(toluene) + N_{2(g)} + O_(g).⁵⁰ The moderate agreement is satisfying because the change from condensed to gaseous media is known to have a large impact on enthalpy of formation; e.g. $\Delta H_f(\mathbf{A}_{(s)}) =$ 28.9 kcal/mol, $\Delta H_f(\mathbf{A}_{(toluene)}) =$ 33.9 kcal/mol, and $\Delta H_f(\mathbf{A}_{(g)}) =$ 53.3 kcal/mol.

Molecule	$\Delta H_{ m f(g,exp)}{}^{ab}$	$\Delta H_{\mathrm{f}\mathrm{(g,calc)}}^{b}$	Molecule	$\Delta H_{\mathrm{f}\mathrm{(g,exp)}^{ab}}$	$\Delta H_{\mathrm{f}\mathrm{(g,calc)}}{}^{b}$
methane	-17.9	-17.98	ozone	34.1	36.35
ammonia	-11.0	-10.98	oxirane	-12.6	-13.69
water	-57.8	-59.02	cyclopropane	12.7	13.01
hydrogen fluoride	-65.1	-65.50	cyclopropanone	3.8	3.82
hydrogen cyanide	31.5	30.37	cyclopropyl cyanide	43.7	44.07
carbon monoxide	-26.4	-27.60	methyloxirane	-22.6	-23.48
acetonitrile	17.7	16.97	oxetane	-19.3	-19.72
benzene	19.8	20.06	propiolactone	-68.4	-68.47
naphthalene	35.9	35.69	cyclobutene	37.5	38.54
anthracene	53.3	54.80	norbornane-7-one	-32.0	-34.52
formaldehyde	-27.7	-26.98	styrene	35.1	35.64
acetone	-52.2	-52.42	phenylcyclopropane	36.0	37.38
urea	-56.3	-54.75	adamantane	-32.1	-31.43
methyl isocyanide	39.1	41.70	nitrous oxide	19.6	19.34
difluoromethane	-107.8	-107.55	1-norbornyl isocyanide	39.6	37.75
ethane	-20.1	-20.10	1-norbornyl cyanide	18.0	16.51
ethylene	12.5	12.28	acenaphthene	37.5	37.17
acetylene	54.3	51.77	isobutane	-32.1	-31.72
methanol	-49.0	-48.87	cyclopentadiene	33.2	31.96
norbornane	-13.1	-12.36	cyclopentene	8.5	8.62
norbornene	21.5	20.08	cyclopentane	-18.3	-17.46
norbornadiene	57.4	57.82	neopentane	-40.1	-39.30
dihydrogen	0	-0.51	fulvene	53.6	51.67
dinitrogen	0	-0.19	1,3-cyclohexadiene	25.0	25.92
dioxygen (triplet)	0	-0.59	1,4-cyclohexadiene	24.0	25.59
difluorine	0	-0.05	Mean Absolute Deviation	•.	0.83
^a Values taken from the "	Active Thermoche	smical Tables, Ve	rsion 1.118" ^b Units of kcal/mol		

Table S.4: Set of 51 Molecules for Calibration of Modified ccCA Method

Reaction	$\Delta H_{(g)}{}^a$	$\Delta G_{\rm (g,\ 298.15K)}{}^a$
$CNNA_{(g)} \rightarrow CNN_{(g)} + A_{(g)}$	30.92	22.57
$\text{CNN}_{(g)} \rightarrow \text{C}_{(g)} + \text{N}_{2(g)}$	32.48	19.83
$\text{CNNA}_{(g)} \xrightarrow{\sim} \text{C}_{(g)} + \text{N}_{2(g)} + \text{A}_{(g)}$	63.39	42.39
$ONNA_{(g)} \rightarrow ONN_{(g)} + A_{(g)}$	-37.82	-46.54
$ONN_{(g)} \rightarrow O_{(g)} + N_{2(g)}$	38.92	25.34
$\mathbf{ONNA}_{(g)} \rightarrow \mathbf{O} + \mathbf{N}_{2(g)} + \mathbf{A}_{(g)}$	1.10	-21.20
^a Units of kcal/mol		

Table S.5: Energies of Fragmentation

S.3.3 Transition States for Unimolecular Decomposition of OCN₂A

These calculations were performed using ORCA keywords B3LYP D3BJ Def2-TZVP TightSCF Grid5 FinalGrid6 0pt Tight0pt Freq. This indicates the B3LYP density functional³³ with the Def2-TZVP basis set^{51,52} in combination with D3(BJ) dispersion correction.⁵³ In all cases, computed electronic energies were corrected for zero-point energy, thermal energy, and entropic effects to obtain the enthalpy and free energy (all free energies reported at 298.15 K). The results are illustrated in Figure S.31. The stationary points had no vibrational modes with an imaginary frequency, and transition states had one. The only exception was the encounter complex of carbon monoxide, dinitrogen, and anthracene, which had a spurious, weak imaginary vibration of -35.53i cm⁻¹ that corresponded to a twisting of the carbon monoxide molecule. A transition state for initial fragmentation of both C–N bonds could not be located. Bimolecular reaction pathways were not computationally investigated.



Figure S.31: The barrier to direct CO release *via* N=C bond scission. ΔU corresponds to the potential energy.

S.4 Construction and Use of a Gas-IR cell

In order to analyze by gas-phase IR spectroscopy the gases evolved from **1** upon thermal decomposition and the reaction of **1** with oxidants, a gas-IR cell was employed. The cell was constructed from 1" OD, 0.6875" ID heavy-walled borosilicate glass tubing (Chemglass Life Sciences). An 8" length of tubing was cut and two glass stopcock valves were attached to the two ends. The two openings of the tube were closed with calcium fluoride windows (Edmund optics, 47-683, 25 mm diameter, 3 mm thickness) using epoxy glue. The epoxy is a special blend (Epotek, 353ND) for attaching optic devices to glass and was cured at 150 °C for 1 hour. The calcium fluoride windows have high transparency from 80 000 cm⁻¹ to 1000 cm⁻¹. A schematic drawing and a photo of the cell are shown below (Figure S.32 and Figure S.33, respectively).

During routine usage, the cell was usually attached between a reaction vessel and a Schlenk line. The cell was evacuated and the gases were then pulled into the cell from the reaction vessel by static vacuum.

A slightly modified cell, which is mostly identical to the one described above, but features an additional 14/20 ground-glass joint and a small glass pocket directly below the joint on the opposite side of the tube was employed as well. Gases were introduced into the nitrogen-purged cell compartment through a rubber septum using a syringe with a needle, or were generated directly in the evacuated cell by thermal decomposition of a solid sample (about 10 mg) placed into the glass pocket. A photo of this cell is shown below (Figure S.34).



Figure S.32: A schematic of the gas IR cell.



Figure S.33: A photograph of the gas IR cell.



Figure S.34: A photograph of the modified gas IR cell used for the generation and analysis of gases evolving from a solid sample (placed into the glass pocket) by thermal decomposition.

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