Studies of the Reaction Behavior of Nitryl Compounds Towards Azides: Evidence for Tetranitrogen Dioxide, N_4O_2

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The reaction behavior of NaN_3, AgN_3, and Me_3SiN_3 towards FNO_2, $ClNO_2$, NO_2SbF_6, and NO_2BF_4 was investigated. At $-30°C$ or below in a solvent-free system sodium azide did not react with $ClNO_2$, NO_2BF_4, or NO_2SbF_6. Below $-30°C$ silver azide did not react either with neat $ClNO_2$. Treatment of Me_3SiN_3 with pure $ClNO_2$ led to the formation of ClN_3, N_2O, and $Me_3SiOSiMe_3$. A mechanism for this reaction has been proposed. Pure chlorine azide was isolated by fractional condensation and identified by its low-temperature Raman spectrum (liquid state). The reaction of $Cp_2Ti(N_3)_2$ with $ClNO_2$ also yielded ClN_3 as the only azide-containing reaction product. Treatment of FNO_2 with NaN_3 at temperatures as low as $-78°C$ always ended in an explosion which was probably due to the formation of FN_3 as one of the reaction products. The reaction of NO_2SbF_6 with NaN_3 in liquid CO_2 ($-55°C \leq T \leq -35°C$) as the solvent afforded a new azide species which was stable at low temperature in solution only and was investigated by means of low-temperature Raman spectroscopy. The obtained vibrational data give strong evidence for the presence of tetranitrogen dioxide, N_4O_2, which can be regarded as nitryl azide (NO_2N_3). The structure and vibrational frequencies of N_4O_2 were computed ab initio at correlated level (MP2/6-31+G*). In liquid xenon ($-100°C \leq T \leq -60°C$) NaN_3 did not react with NO_2SbF_6. A previous literature report on the preparation of N_4O_2 could not be established.

Six molecular oxides of nitrogen (N_2O, NO, N_2O_3, NO_2, N_2O_5 and NO_3; the latter one has not been isolated as a pure compound) and two π^*-π^* bound dimers (N_2O_2 and N_2O_4) have been known for a long time[1,2]. In fact, N_2O, NO, and NO_2 were identified as early as in the 18th century and were amongst the first gaseous compounds to be isolated. Beside their academic interest in terms of structure and bonding the deeper understanding of the very nature and chemistry of binary N–O species is especially important since many of them (i) cause environmental and health problems ("NO_x"), (ii) are physiologically active (NO, N_2O), (iii) represent industrially important intermediate products (NO, NO_2), and (iv) have extensively been used as oxidizers in rocket fuels (N_2O_4, MON-25: 75% N_2O_4/25% NO)[3]. In recent years a large effort has been made in calculating and understanding the bond properties of binary nitrogen oxides[4–8]. Quite recently, we reported on the preparation and characterization of the intrinsically unstable nitrosyl azide N_4O[9]. This led naturally to the attempted synthesis of the nitryl analogous oxide NO_2N_3. In the only communication dealing with this subject dating from 1973 Doyle et al. reported on the "Reaction between Azide and Nitronium Ions" (LiN_3 and NO_2BF_4)[10]. Whereas these authors claimed the existence of N_4O_2 in CCl_4 solution (IR data, CCl_4 solution: 2330 cm^{-1} m, 2185 s, 2165 s, 2070 m, 1609 s; MS: observation of N_2O as the decomposition product) we have been unable to confirm their spectroscopic results.

In the present communication we report on the reaction behavior of inorganic azides towards nitryl compounds. We got strong evidence for the presence of tetranitrogen dioxide, N_4O_2, in the reaction mixture of NO_2SbF_6 and NaN_3 in liquid carbon dioxide. The vibrational frequencies of N_4O_2 have been computed ab initio at correlated level (MP2/6-31+G*) and compare nicely with the experimentally obtained data. Therefore, the previously reported data obviously do not correspond to the claimed N_4O_2.

Results and Discussion

Neat $ClNO_2$ NO_2BF_4, or NO_2SbF_6 do not react with NaN_3 or AgN_3 at temperatures as low as $-30°C$ or below. Therefore, we studied the reactivity of Me_3SiN_3 towards $ClNO_2$ in order to generate NO_2N_3 [Eq. (1)].

$$Me_3SiN_3 + ClNO_2 \xrightarrow{?} Me_3SiCl + NO_2N_3 \qquad (1)$$

However, we were surprised to find that ClN_3, N_2O, Me_3SiCl, and $Me_3SiOSiMe_3$ had been formed in this reaction [Eq. (2)] (so far we have been unable to prove the formation of either N_3O_3 and/or NO/NO_2 as side products).

$$3\,Me_3SiN_3 + 3\,ClNO_2 \rightarrow Me_3SiCl + Me_3SiOSiMe_3 + 2\,N_2O + 2\,ClN_3 + \text{"}N_2O_3\text{"} \qquad (2)$$

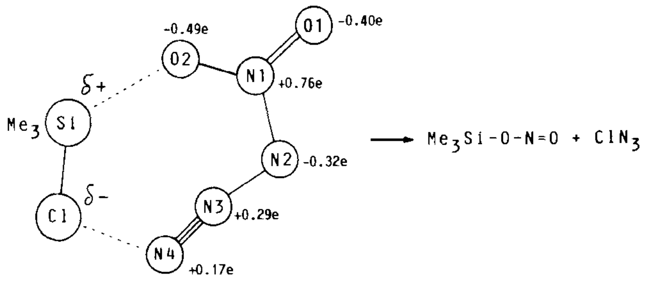
Presumably NO_2N_3 is initially formed but partly decomposes to the more thermodynamically stable (and experimentally detected) N_2O and also reacts with Me_3SiCl to give Me_3SiONO which itself is unstable with respect to the experimentally observed siloxane [Eqs. (3–7), Eq. (7) corresponds to Eq. (2)].

$$\begin{array}{rll}
3\,Me_3SiN_3 + 3\,ClNO_2 & \rightarrow 3\,Me_3SiCl + 3\,NO_2N_3 & (3)\\
2\,Me_3SiCl + 2\,NO_2N_3 & \rightarrow 2\,Me_3SiONO + 2\,ClN_3 & (4)\\
2\,Me_3SiONO & \rightarrow Me_3SiOSiMe_3 + \text{“}N_2O_3\text{”} & (5)\\
NO_2N_3 & \rightarrow 2\,N_2O & (6)
\end{array}$$

$$3\,Me_3SiN_3 + 3\,ClNO_2 \rightarrow Me_3SiCl + Me_3SiOSiMe_3 + 2\,N_2O + 2\,ClN_3 + \text{“}N_2O_3\text{”} \qquad (7)$$

Due to the bond polarities (cf. Figure 4) it is unlikely that Me_3SiN_3 reacts with $ClNO_2$ directly to give ClN_3. However, Me_3SiCl and NO_2N_3 once generated according to Eq. (3) may very well react yielding ClN_3 (for structure and Lewis representation of ClN_3 see ref.[11]) and metastable Me_3SiONO [cf. Eq. (4) and (5)] (Scheme 1).

Scheme 1. Reaction of Me_3SiCl with NO_2N_3 (charges at NO_2N_3 correspond to NBO charges, see below)



The formation of Me_3SiCl and $Me_3SiOSiMe_3$ from Me_3SiN_3 was followed by time-dependent ^1H-NMR spectroscopy (Figure 1). The spectra indicate that initially only Me_3SiCl was formed which partly reacts to give $Me_3SiOSiMe_3$. As the NMR reaction was carried out on a stoichiometric scale integration of the peaks of the final products clearly points to an equimolar ratio of Me_3SiCl (9H) and $Me_3SiOSiMe_3$ (18H).

Experimentally, it seems to be almost impossible to distinguish between a N4 or a N2 attack of the chlorine (from Me_3SiCl) at the azide unit (cf. Scheme 1) since all preparations known for isotopically labeled azides proceed via ionic NaN_3[12]. Therefore, it is only possible to prepare a 1:1 mixture of $O_2N\mathit{N}NN$ and $O_2NNN\mathit{N}$ ($\mathit{N} = {}^{15}N$) or fairly pure $O_2NN\mathit{N}N$.

It is worthwhile to mention that from a reaction according to Eq. (7) highly explosive chlorine azide was isolated as a pure compound on a preparative scale[13]. The obtained IR and Raman spectra compare nicely with earlier reports on this compound and might indicate a preparative use of this route (Figure 2)[14]. Moreover, ClN_3 was unambiguously identified by its mass spectrum. The basis peak is represented by the fragment ion ClN^+ which is in agreement with experimental observations[15] and quantum-mechanical computations[16] that the dissociation of ClN_3 into N_2 and ClN is exothermic and highly favorable.

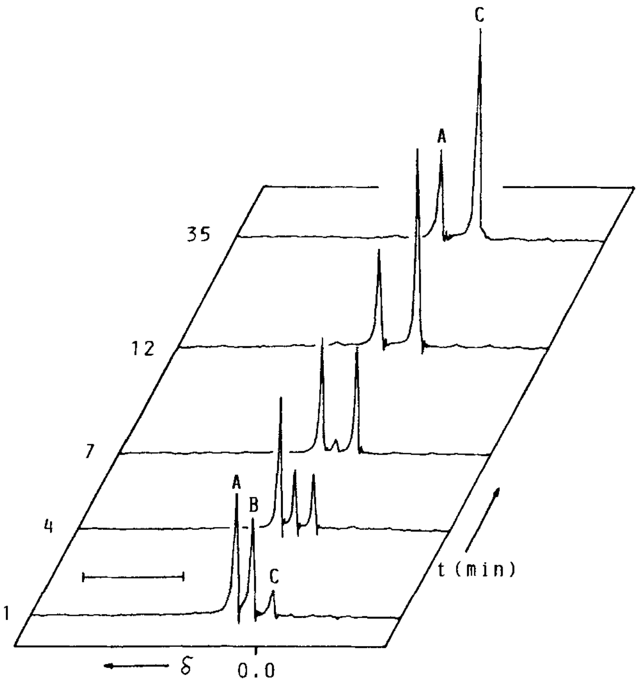


Figure 1. Time-dependent ^1H-NMR spectra recorded on a 1:1 stoichiometric reaction mixture of $ClNO_2$ and Me_3SiN_3 (cf. [Eq. (7)] (sample temperature 0°C; $t = 0$ corresponds to warming up the sample from -196 to 0°C; A: Me_3SiCl, B: Me_3SiN_3, C: $Me_3SiOSiMe_3$)

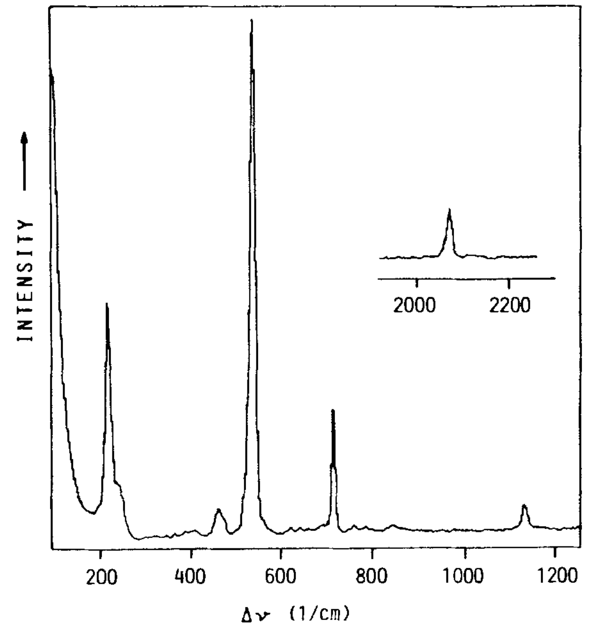


Figure 2. Raman spectrum of ClN_3 obtained according to Eq. (7) (647.09 nm, -90°C, 40 mW, 0.5 s/point, 2 scans)

Since NO_2N_3 was shown to be unstable in the condensed phase at higher temperatures and it also seemed to react with Me_3SiCl (see above) we tried to avoid the formation of reactive by-products and treated NO_2SbF_6 with NaN_3 in CO_2 solution [Eq. (8)].

$$NO_2SbF_6 + NaN_3 \xrightarrow{CO_2\,(l),\ -50^\circ C} NaSbF_6 + NO_2N_3 \qquad (8)$$

[N.B. CO_2 is a particularly nice solvent for Raman spectroscopy in solution since it only shows two sharp peaks at 1387 and 1286 cm^{-1} (Fermi resonance of ν_1 with $2\nu_2$[17]).] The low-temperature Raman spectrum obtained from a reaction mixture according to Eq. (8) unambiguously indicated the formation of a new azide-containing species (see Experimental) and was consistent with the generation of nitryl azide (Figure 3). To support our vibrational data of NO_2N_3, the structure and vibrational frequencies were computed ab initio. The geometries were fully optimized at the HF level and at correlated level according to the Møller-Plesset second-order perturbation theory [RMP(FC)]. Since the HF calculation predicted an unreliable, short terminal N3–N4 bond length (1.079 Å), the vibrational frequencies were computed at the correlated RMP2 level (6-31+G*). [N.B. The HF/6-31+G* structural parameters are: O1–N1 1.172, O2–N1 1.191, N1–N2 1.389, N2–N3 1.275, N3–N4 1.079 Å and O1–N1–O2 127.2, O1–N1–N2 113.6, O2–N1–N2 119.2, N1–N2–N3 108.8, N2–N3–N4 172.8° (C_s *trans*-bent structure)]. Table 1 shows the computed, scaled[25], and observed frequencies and their assignments.

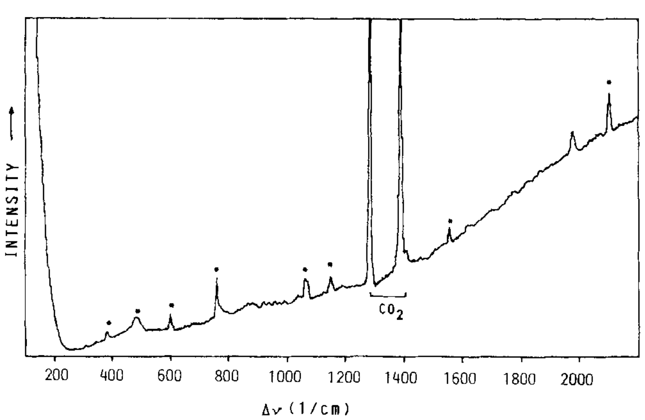


Figure 3. Raman spectrum of a reaction mixture of NaN_3 and NO_2SbF_6 in CO_2 solution (647.09 nm, −49°C, 40 mW, 0.5 s/point, 2 scans; * azide species)

Table 1. Computed (MP2) and experimentally observed vibrational frequencies [cm^{-1}] of N_4O_2

Calcd.[a]	Scaled (F = 0.90)	Raman (Int.)[b]	Assignment
2321 (322)	2089	2107 (8)	$\nu_{as}NNN$
1806 (186)	1625	1556 (2)	$\nu_{as}ONO$
1294 (255)	1165	1151 (3)	$\nu_{s}ONO$
1163 (258)	1047	1060 (10)	$\nu_{s}NNN$
865 (191)	779	758 (8)	δN_4O_2
773 (29)	696	[c]	δN_4O_2
711 (7)	640	605 (3)	γN_4O_2
533 (17)	480	485 (7)	δN_4O_2
472 (12)	425	[c]	δN_4O_2
456 (3)	410	395 (2)	γN_4O_2
191 (0.3)	172	[d]	
95 (0.01)	86	[d]	

[a] MP2/6-31+G*; the calculated intensities (in parentheses) refer to IR intensities. – [b] 647 nm, 40 mW, −48°C, 0.5 s integration time, 2 scans. – [c] Not observed. – [d] Strong tailing of the laser line up to 200 cm^{-1}.

In agreement with the experimental spectroscopic results, the ab initio computation also shows a planar C_s N_4O_2 structure (Figure 4). All structural parameters of the (*trans*-bent) N_3 unit in N_4O_2 are in good agreement with other covalent azides[18]. Therefore, also the interpretation of N_4O_2 as *nitryl azide* seems to be justified. The computed N–O bond distances in N_4O_2 of 1.223 and 1.235 Å are slightly longer than in N_2O (1.186 Å)[19] and in $ClNO_2$ (1.20 Å)[1]. The NLMO bond orders (BO) as well as the total bond orders (ΣBO) of N_4O_2 and of N_4O for comparison are summarized in Table 2[20]. Another remarkable difference to the bond situation in N_4O where the cyclic aromatic 6π isomer (isoelectronic to N_5^-) was calculated to be most favorable[9] is the fact that the most stable cyclic derivative of N_4O_2 (O–NONNN, C_s) was computed to be 17 kcal mol^{-1} less stable than the observed chain-like species (RHF/6-31+G*). In fact, at correlated level (RMP2/6-31+G*) the cyclic isomer does not represent a local minimum, and the planar chain-like C_s isomer was found to be a true minimum (see above). The preference of the (experimentally observed) *trans*-bent O_2N-N_3 isomer can be rationalized by a high degree of π delocalization in the planar molecule and a lower degree of π delocalization in the cyclic N_4O_2 isomer (C_s) compared with the cyclic N_4O (C_{2v}) derivative.

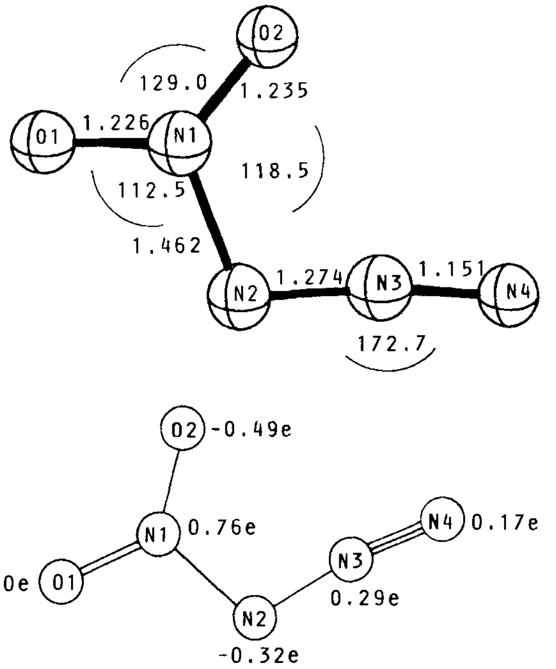


Figure 4. Top: RMP2-optimized geometry (distances in Å, angles in °); bottom: Lewis representation with natural bond orbital (NBO)[20,27,28] charges for N_4O_2

It is also interesting to compare N_4O_2 with the isoelectronic carbonyl azide $FC(O)-N_3$, the structure of which was studied by gas electron diffraction and ab initio calculations[21]. $FC(O)-N_3$ exists in the gas phase as a mixture of two planar conformers (C_s symmetry), with the *cis* form (carbonyl C=O in the *cis* position with respect to the N=N bond) being slightly lower in energy than the *trans* rotamer (ΔE = 1.4 ± 0.1 kcal mol^{-1}).

According to our experimentally observed Raman data for NO_2N_3 and due to the ab initio computed frequencies for this nitryl azide we do not support the data previously reported[10]. However, we have so far been unable to isolate

Table 2. NLMO bond orders (BO) and total bond orders (ΣBO)

	BO(N1−N2)	BO(N2−N3)	BO(N3−N4)	ΣBO(N2)	ΣBO(N3)	ΣBO(N4)
$ON{-}N_3$	0.99	0.99	2.52	1.70	3.54	2.29
$O_2N{-}N_3$	0.92	0.97	2.50	1.56	3.48	2.30

this compound from solution, and a pure compound consisting of N_4O_2 is still yet to be prepared that is likely not possible, as this intrinsically unstable material dissociates to the more thermodynamically stable N_2O [Eq. (9)] [after correction of ZPE contributions, temperature correction for H by means of C_p and inclusion of the work term; $ZPE(N_4O_2) = 13.76$ kcal mol^{-1}, scaled by 0.90]. With $\Delta H^0_{298}(N_2O) = +19.6$ kcal mol^{-1}[22] the standard heat of formation for N_4O_2 can be calculated to be $\Delta H^0_{298}(N_4O_2) = +98$ kcal mol^{-1}.

$$N_4O_2(g) \rightarrow 2\,N_2O(g)\ \Delta_R H^0(298\text{ K, MP2}) = -58.9\text{ kcal mol}^{-1} \quad (9)$$

In conclusion, for the first time the existence of covalently bound tetranitrogen dioxide, N_4O_2, which can be regarded as nitryl azide, has been established by means of vibrational spectroscopy (Raman) in combination with correlated quantum mechanical ab initio computations. Moreover, the formation of chlorine azide on a preparative scale in the reaction of $ClNO_2$ with Me_3SiN_3 is reported. A likely mechanism of this reaction is proposed.

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Experimental

The reactions were carried out in glass vessels in an inert gas atmosphere (N_2, dry box). – NaN_3 (Aldrich) and $NaNO_2$ (Merck) were dried over P_4O_{10} and used without further purification. NO_2BF_4, NO_2SbF_6, and Me_3SiN_3 (all Aldrich) were used as supplied. $ClNO_2$ (from HNO_3 and HSO_3Cl) and FNO_2 (from N_2O_4 and F_2 or from $NaNO_2$ and F_2) were prepared by standard procedures and were purified by fractional distillation ($ClNO_2$) or fractional condensation (FNO_2), respectively[1]. AgN_3 and $Cp_2Ti(N_3)_2$ were prepared as described previously[23].

IR: Perkin Elmer 580 B or Nicolet Magna. – Raman: Jobin Yvon Ramanor U 1000, Spectra Physics krypton ion laser (647.09 nm). – ^{1}H-NMR: Varian EM 360 (60 MHz), referred to $SiMe_4$. – MS: Varian MAT 311 A (electron impact, 70 eV).

Caution: At −35°C CO_2 has a vapor pressure of 12 bar. Appropriate safety precautions should be taken.

Computational Methods: The computations were carried out with the Gaussian 92 program by using the 6-31+G* basis set for nitrogen and oxygen[24]. The geometry of N_4O_2 was fully optimized at the HF level and at the electron-correlated second-order Møller-Plesset level [MP2 (full)] by employing standard procedures[25].

Reaction of Me_3SiN_3 with $ClNO_2$: Gaseous $ClNO_2$ (0.61 g, 7.54 mmol) was condensed from a calibrated stainless vacuum line at −196°C onto Me_3SiN_3 (0.87 g, 7.54 mmol). The mixtúre was warmed to −75°C and allowed to react for 1 h. The products were separated by fractional condensation (see below) yielding three fractions which were identified by mass spectrometry and by vibrational (IR, Raman) or NMR spectroscopy.

Fraction 1 (b.p. ≤ −85°C): MS, *m/z* (%): 44 (100) [N_2O^+], 32 (<0.2) [O_2^+], 30 (14)[NO^+], 28(9) [N_2^+. – Raman (647 nm, −100°C, 40 mW): Δν (Int.) = 2224 cm^{-1} (4) [ν_1-N_2O], 1284 (10) [ν_3-N_2O][26]. – IR (gas, 20°C): ν = 2225 cm^{-1} s ($\nu_1 N_2O$), 1882 w (νNO), 1275 vs ($\nu_3 N_2O$), 588 m ($\nu_2 N_2O$). – ^{1}H NMR (60 MHz, solvent $CDCl_3$): No resonance signal.

Fraction 2 (−60°C ≤ b.p. ≤−10°C): MS, *m/z* (%): 77/79 (65) [ClN_3^+], 49/51 (100) [ClN^+], 42 (50) [N_3^+], 35/37 (45) [Cl^+], 32 (≤1) [O_2^+], 28 (50) [N_2^+]. – Raman (647 nm, −90°C, 40 mW): Δ (Int.) = 2068 cm^{-1} (1) ($\nu_{as}N_3$, ClN_3), 1136 (0.5) ($\nu_{sym}N_3$, ClN_3), 719 (3) (γClN, ClN_3), 542 (10) (δN_3, ClN_3), 467 (0.5), 222 (5) (δClNN, ClN_3); (see also Figure 2). – IR (gas, 20°C): ν = 2070 cm^{-1} s ($\nu_{as}N_3$, ClN_3), 1140 vs ($\nu_{sym}N_3$, ClN_3), 718 s (γClN, ClN_3). – ^{1}H NMR (60 MHz, solvent $CDCl_3$): No resonance signal.

Fraction 3 (b.p. >15°C): ^{1}H NMR (60 MHz, solvent $CDCl_3$): 0.37 (9H, s, Me_3SiCl), 0.02 (18H, s, $Me_3SiOSiMe_3$). – MS, *m/z* 162 [$Me_3SiOSiMe_3^+$], 108/110 [Me_3SiCl^+].

In order to follow the reaction of Me_3SiN_3 with $ClNO_2$ affording Me_3SiCl and $Me_3SiOSiMe_3$ time-dependent ^{1}H-NMR spectra were recorded (see Figure 1).

Reaction of NaN_3 with FNO_2: Gaseous FNO_2 (0.49 g, 7.54 mmol) was condensed from a calibrated stainless steel vacuum line at −196°C onto NaN_3 (0.49 g, 7.54 mmol). The reaction mixture was warmed to −115°C (m.p. of FNO_2 −166°C). At this stage the reaction vessel exploded heavily. Two attempts were made to treat FNO_2 with NaN_3 in this way.

Reaction of $Cp_2Ti(N_3)_2$ with $ClNO_2$: In two separate reactions gaseous $ClNO_2$ (0.61 g, 7.54 mmol, 1:1 stoichiometry; 1.23 g, 15.08 mmol, 1:2 stoichiometry) was condensed from a calibrated stainless steel vacuum line at −196°C onto $Cp_2Ti(N_3)_2$ (1.98 g, 7.54 mmol). The reaction mixture was warmed to −50°C and allowed to react for 1 h. Volatile products were separated by fractional condensation, and ClN_3 was found by Raman spectroscopy to be the only azide-containing product from these reactions (both stoichiometries). The ^{1}H-NMR spectrum of the solid residue indicated in both cases a complex mixture of unreacted $Cp_2Ti(N_3)_2$, generated $Cp_2TiCl(N_3)$ and Cp_2TiCl_2 and further unidentified titanocene species. – Raman (647 nm, −90°C, 40 mW, 1:1 stoichiometry): Δν (Int.) = 2074 cm^{-1} (1) ($\nu_{as}N_3$, ClN_3), 1285 (4) ($\nu_3 N_2O$, N_2O), 1136 (1) ($\nu_{sym}N_3$, ClN_3), 791 (1) ($\nu_1 ClNO_2$, $ClNO_2$), 719 (3) (γClN, ClN_3), 542 (6) (δN_3, ClN_3), 414 (2) ($\nu_2 ClNO_2$, $ClNO_2$), 373 ($\nu_5 ClNO_2$, $ClNO_2$), 223 (4) (δClNN, ClN_3).

Reaction of NO_2SbF_6 with NaN_3 in CO_2: This reaction was carried out in a thick-walled 5-mm Raman tube (Pyrex glass). Carbon dioxide (ca. 0.5 ml of liquid) was condensed at −196°C onto a mixture of NO_2SbF_6 (0.100 g, 0.35 mmol) and NaN_3 (0.023 g, 0.35 mmol). The glass tube was flame-sealed and warmed to −50°C. The reaction mixture was allowed to react at this temp. for 2 h. After it had been warmed to −35°C for 30 min it was recooled to −50°C and subsequently allowed to react for another 4 h. Raman spectra of the reaction mixture were recorded at low temperature. − Raman (647 nm, −48°C, 50 mW): $\Delta\nu$ (Int.) = 2107 cm^{-1} (8) ($\nu_{as}N_3$, N_4O_2), 1386 and 1280 (out of scale, CO_2 Fermi resonance), 1556 (2) ($\nu_{as}ONO$, N_4O_2), 1151 (3) (ν_sONO, N_4O_2), 1060 (10) (ν_sN_3, N_4O_2), 758 (8) (δN_4O_2, N_4O_2), 605 (3) (δN_4O_2, N_4O_2), 485 (7, br) (δN_4O_2, N_4O_2), 395 (2) (γN_4O_2, N_4O_2) (see also Figure 3).

In another experiment we did not seal the glass reaction tube but used a stainless steel needle valve and only 0.1 ml of liquid CO_2. After the experiment gas phase IR spectra were recorded and N_2O was shown to be the only detectable species besides CO_2 (N_2O: ν_1 = 2225 cm^{-1})[26].

Reaction of NO_2SbF_6 with NaN_3 in Xe: This reaction was carried out in analogy to the reaction in liquid CO_2. However, in this case the reaction mixture was kept at −100°C for 6 h and allowed to react at −75°C for 1 h. (For safety reasons the glass reaction tube was not exposed to a higher pressure than the vapor pressure of Xe at −75°C.) Raman spectra of the reaction mixture were recorded at −100°C. Only traces of an azide and some N_2O were detected. − Raman (647 nm, −110°C, 50 mW): $\Delta\nu$ 2130 cm^{-1} ($\nu_{as}N_3$).

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