Nitrile regio-synthesis by Ni centers on a siliceous surface: implications in prebiotic chemistry

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“Nitrile regio-synthesis by Ni centers on a siliceous surface: implications in prebiotic chemistry”†

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By means of quantum chemistry (PBE0/def2-TZVPP; DLPNO-CCSD(T)/cc-pVTZ) and small, but reliable models of Polyhedral Oligomeric Silsesquioxanes (POSS), an array of astrochemically-relevant catalysis products, related to prebiotic and origin of life chemistry, has been theoretically explored. In this work, the heterogeneous phase hydrocyanation reaction of an unsaturated C=C bond (propene) catalyzed by a Ni center complexed to a silica surface is analyzed. Of the two possible regioisomers, the branched iso-propyl-cyanide is thermodynamically and kinetically preferred over the linear n-propyl-cyanide (T=200 K). The formation of nitriles based on a regioselective process has profound implications on prebiotic and origin of life chemistry, as well as deep connections to terrestrial surface chemistry and geochemistry.

Unraveling heterogeneous phase astrochemistry and catalysis (solid-gas/solid-solid) starting with the "dirty ice" hypothesis of van Hulst[1], is of crucial importance in the formation of complex organic molecules (COM)[2–7]. The composition of the heterogeneous phase spans from pure H_2O or CO ices and their mixtures[8], to inorganic compounds such as SiC[9], TiO_2[5], olivine[10], forsterite[11,12], enstatite[12] and aluminosilicates[13,14]. The presence of organic material in astrophysical objects[15] as well as in the Solar System[16], is well established. In the Solar System, data acquired by direct spectroscopic analysis *via* interplanetary probes or terrestrial-based observations reveal a complex organic chemistry[16]. In particular, the chemical complexity of meteoric samples shows an elegant CHNOS organic chemistry[17]. To further enrich our understanding of heterogeneous phase astrochemistry, we have developed an interest in the role of transition metals (TM) such as Fe[18] and Ni and "chemical defects". "Chemical defects" such as atoms on a mineral surface displaying free valences were shown to develop a fascinating catalytic chemistry with the formation of organic molecules and/or polymers starting from simple molecules/atoms (HCN, CO, H)[19,20]. Of particular interest are *regio/enantio-selective* chemical processes due to their direct involvement in prebiotic chemistry with the regioselective processes attracting less scientific attention. An efficient way to get a regioselective chemistry is the use of organometallic catalysts based on early and late transition metals, as is well known in industrial and laboratory chemistry[21]. The aim of the present study is to understand if and how a Ni atom complexed to a silica surface is catalytically active with organic substrates inducing regioselective reactions. The selection of Ni is based on its cosmic abundance (after Fe the most abundant TM in space) and on its known ability to perform regioselective hydrocyanation of unsaturated double carbon bonds[22]. It should be mentioned that Ni atoms can be present also on minerals not correlated to the Ni mineral class. This hypothesis has a long standing tradition, where rare elements are ubiquitously present on rock forming minerals (10 to 1000s parts-per-million) and possibly responsible for the origin of Life and metabolism due to their catalytic activity[23]. The astrochemical model here proposed benefits from the catalytic properties of a Ni atom bound to a silica surface performing a hydrocyanation reaction on a propene molecule. In this study, propene is the minimally-sized substrate needed to form two regioisomers, linear n-propyl-cyanide (l) and branched iso-propyl-cyanide (b) (see Fig. 1).

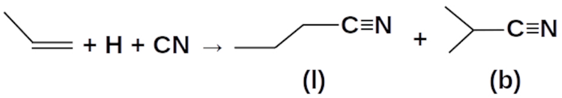

Fig. 1 Non-stoichiometric reaction scheme of propene hydrocyanation displaying the two regio-products: linear (l); n-propyl-cyanide and branched (b); iso-propyl-cyanide.

The importance of nitriles in chemistry, synthetic and prebiotic chemistry is well known, being fundamental building blocks for the synthesis of carboxylic acids, amines, amides and as interme-

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diates in the Strecker reaction (amino acid synthesis). For example, simple organic/prebiotic building blocks can be synthesized by nitriles hydrolysis, with the formation of carboxylic acids. In the presence of low water activity, primary amides are the main products. By reduction, primary or tertiary amides are synthesized and the electrophilic carbon center can undergo a nucleophilic attack. Most importantly, the various products (carboxylic acids, amides, imino-esters) will maintain the original l (linear) or b (branched) alkyl skeleton determining a possible excess of linear or branched carboxylic acids, amides and amino-esters. The POSS model (POSS: partially condensed silsesquioxane of formula [$H_7Si_7O_9(OH)_3$]) used in the present work (see Fig. 2) is a small silica cluster, but was extensively used to analyze the heterogeneous phase catalytic mechanisms of silica surfaces on both the theoretical and experimental levels[24–28].

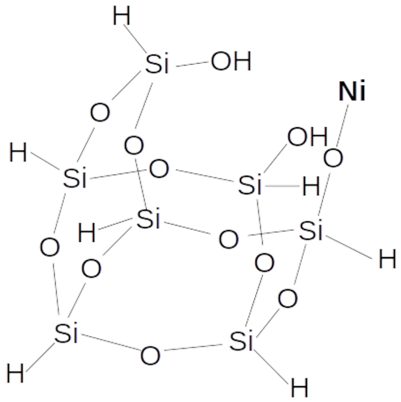

Fig. 2 Ni bound to the POSS model.

The adoption of the POSS model is due to: **a)** its ability to easily model "chemical defects" on siliceous surfaces. In particular, our research focuses on the $[SiO]_x$ matrix common to all siliceous minerals of astrochemical interest where silanol (SiOH) groups are present, as suggested by the 3.2 μm band detected on the nucleus surface of comet 67P/Churyumov–Gerasimenko[29] and as found by H_2^+ irradiation of the major minerals of carbonaceous chondrites[30]. Furthermore, SiOH groups lead to the astrochemistry of siloxyl ($SiO^\bullet$)[19,20,31] and sylil ($Si^\bullet$) radical defects or if the SiOH acid/base properties must be considered, as known in zeolites; **b)** a transition metal-containing POSS is a model of heterogeneous phase catalysts[25] and was used by us to model the formation of H_2 from atomic H on a Fe^+[18]; **c)** finally, the selected POSS with only 29 atoms allows a powerful synergy between DFT and high-level *ab initio* methods to get accurate thermodynamic and activation energy data involved in the synthesis of astro-inorganic/organic compounds[19,20,31]. The formation of reactive free metal sites such as Fe or Ni can be the result of a "space-weathering" mechanism[32–34] *i.e.* photon processing, solar/stellar wind, cosmic rays, magnetospheric and micrometeoroid bombardment. Furthermore, the detection of neutral atomic Fe and Ni in the coma of the comet C/1996 B2 (Hyakutake)[35] as well as on other 20 comets[36] raises the question not only of the associated formation mechanisms of the two TMs, but what chemistry can be developed once Fe and/or Ni remain bound to the rocky surface displaying free valences. Regarding the selected Ni ligand sphere (Fig. 2), similarly to the Fe-POSS model[18], H can react with the siloxo groups bonded to the Ni center by the sequence:
$(SiO)_3Ni+H \rightarrow (SiO)_2Ni\text{-}(SiOH)+H \rightarrow (SiO)Ni\text{-}(SiOH)_2+H \rightarrow Ni(SiOH)_3$
to give a variety of Ni atoms differently coordinated. However, the selected Ni ligand sphere anchors Ni to the silica surface while allowing geometrical flexibility to ligate molecules *i.e.* propene, H, CN. Ni(I) is known mainly as an catalytic intermediate, though recent research has amplified its importance[37]. The proposed Ni-based propene hydrocyanation mechanism on a silicate surface is shown in Fig. 3.

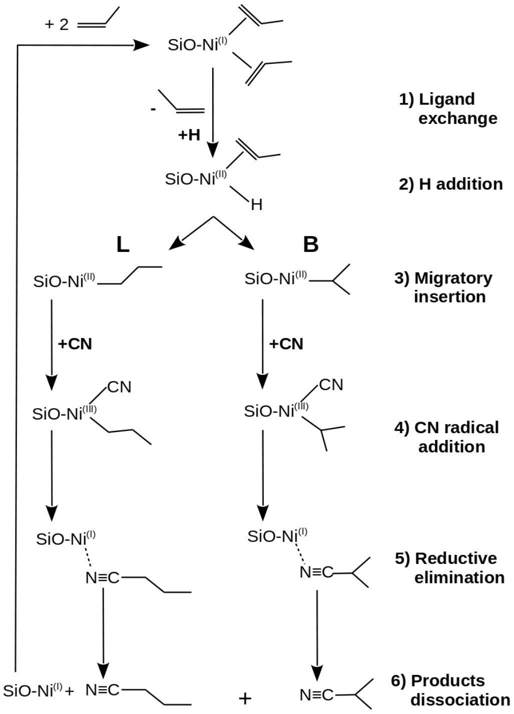

Fig. 3 The proposed six elementary steps of propene hydrocyanation on a Ni atom bond to a silica surface.

Differing from laboratory and industrial chemistry, where HCN undergoes to a $2e^-$ oxidative addition to form a hydrido-cyanide complex[22], the sequential reaction of atomic H, the most abundant atom in the Universe and the $^\bullet$CN radical, highly abundant in the ISM (inter-stellar medium)[38], cometary coma[39,40] and Titan's atmosphere[41], was considered. Radical reactions are generally characterized by low activation energies opening the possibility to synthesize new compounds at relatively low temperatures. The selected T=200 K is a lower bound for HCN polymerization to progress efficiently (see later analysis on the chemical kinetics). In Fig. 4 the computed PES is reported (see ESI†), while in Fig. 5 the minima are depicted.

To find the minima, the conformational space of all compounds was manually analyzed, together with the spin multiplicity (see ESI†). As expected, low spin compounds are the most stable. The energy difference between high-low spin $\Delta_{hs-ls} \geq 26.0$ kcal/mol,

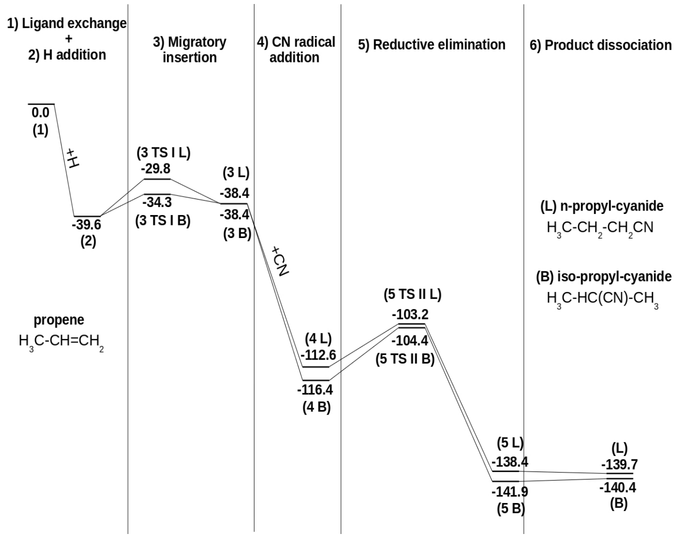

Fig. 4 Calculated PES (ΔG, kcal/mol, T=200 K) of propene hydrocyanation calculated by the ORCA program[42]. Geometry optimizations/entropy corrections: PBE0/def2-TZVPP[43–45]; single point corrections: DLPNO-CCSD(T)/cc-pVTZ[46–49]. Only DLPNO-CCSD(T) corrected energies are reported (see ESI†). All compounds are in the lower spin state (see ESI†).

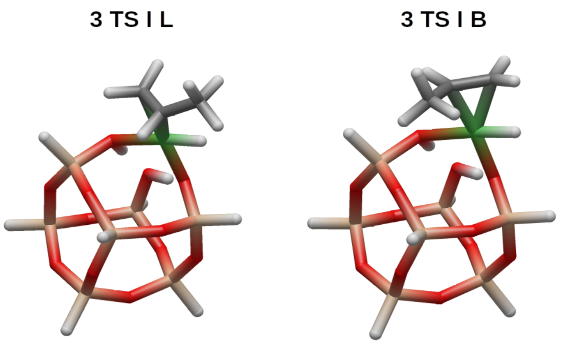
3 TS I L **3 TS I B**

Fig. 5 All atom models of the two important TSs: **3 TS I B** and **3 TS I L**, determining the splitting into two reaction channels L and B, as reported in Fig. 3 and Fig. 4. For a detailed view of all the elementary steps see ESI†.

which makes the PES spin crossing thermally forbidden at T=200 K. In the 1st step, *ligand exchange*, the Ni center is bound to two propene molecules to saturate the Ni ligand sphere near to the canonical 18 e^-. Obviously, the Ni ligand sphere depends on which organic (COM, CH_3OH, C_2H_5OH) or inorganic (H_2O, CO, NH_3) phase covers the mineral surface. Here, we have hypothesized an environment relatively rich in H, CN, CO and unsaturated organic substrates as observed in patches on 67P/Churyumov-Gerasimenko and other comets[50–52]. In the 2nd reaction step, *H addition*, one propene molecule must be replaced by an atomic H resulting in a $1e^-$ change. The total reaction is energetically favored by ΔG=-39.6 kcal/mol with a barrierless addition of H to the Ni center (see ESI†). Most importantly, the H addition is the splitting point determining two pathways for the formation of the linear n-propyl-cyanide (l) or branched iso-propyl-cyanide (b) (see Fig. 5). The propene ligand can rotate around the Ni-(C=C) axis, leading to two conformers in which either the terminal CH or CH_2 are closer to the Ni-hydride. This change forms the two regioisomeric transition states **3 TS I B** ($\Delta G^\dagger$=5.3 kcal/mol) and **3 TS I L** ($\Delta G^\dagger$=9.8 kcal/mol), showing a clear preference for the branched form. The migratory insertion products, **3 B** and **3 L** are both characterized by a Ni-H agostic interaction[53] with the hydrogen of the transferred hydride. The agostic interaction is underlined by a slight uphill thermodynamics of ΔG=1.2 kcal/mol (isoenergetic at the DLPNO-CCSD(T) level of theory) compared to the initial compound **2**. The isomerization reaction connecting the branch **3 B** to the linear **3 L**, was also analyzed. However, a $\Delta G^\dagger$ value of 29.3 kcal/mol at the considered T forbids the isomerization. The 4th reaction step, *CN radical addition* (similarly to the H oxidative addition is a $1e^-$ change) is barrierless (see ESI†) with favorable thermodynamics of ΔG=-74.3 kcal/mol for the linear **4 L** and ΔG=-78.0 kcal/mol for the branched **4 B**, determining a slight thermodynamic preference of the b over the l isomer of ΔΔG=-3.7 kcal/mol. The 5th reaction step, *reductive elimination*, involves the cyanide transfer to the substrate and is characterized by the two TSs **5 TS II B** and **5 TS II L** and the two b and l products, **5 B** and **5 L**, respectively. In both pathways, the thermodynamics are downhill for reaction products **5 L**, (ΔG=-35.2 kcal/mol) and **5 B** (ΔG=-37.5 kcal/mol). However, **5 TS II L** is characterized by an activation energy of $\Delta G^\dagger$=9.5 kcal/mol while **5 TS II B** has an activation energy of $\Delta G^\dagger$=12.0 kcal/mol. Finally, the dissociation steps for both products are near thermodynamical neutrality (at the DLPNO-CCSD level of theory). It should be underlined that compound **5 B**, with the cyanide nitrogen coordinated to Ni, (ΔG=25.3 kcal/mol) can be an interesting reactive intermediate. In fact, in presence of organics such as aldehydes (R-CHO) or ketones (R_1R_2CO), cyanohydrins can be formed. By kinetic modeling[54,55] at T=200 K, ‡ the estimated reaction time (step 1 to 5) is t≈20 seconds while by increasing the temperature tote T=300 K, t≈10^{-3} seconds (see ESI†). The total reaction time is determined by the formation of the final product **5 B** surmounting **5 TS II B**, while due to the low energy barrier of **3 TS I B**, intermediate **3 B** is formed within 10^{-3} sec. The considered range of temperatures can be experienced, for example, by astronomical objects, especially comets, where temperature rises periodically by surface heating due to strong orbital eccentricity while approaching the central star, like the Sun, or by dust particles and greater bodies (asteroids, planetoids) in the stable as well as turbulent phase of a proto-planetary disc and planetary system evolution. Finally, the resulting regioexcess re%=0.99 of the b isomer (see ESI†) defines the POSS-Ni system as an efficient catalyst in the synthesis of branched alkylnitriles, rationalized by the free energy diagrams in Fig. 4. In fact, the b isomer is always thermodynamically preferred and the rate determining step can be associated to the **3 TS I L** and **3 TS I B** pairs, where the $\Delta G^\dagger_{l-b}$=4.5 kcal/mol implies a ≈10^5 faster reactivity of the **3 TS I B** compared to **3 TS I L.** §. The second TS pair **5 TS II L** and **5 TS II B**, though show a $\Delta G^\dagger_{l-b}$=-2.5 kcal/mol, resulting in a

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‡ Kinetic constants were obtained by the computational data and deduced by the Eyring relation

§ At T=200 K for a ten-fold increase in the kinetics, the term RT*ln10=0.91 kcal/mol

$\approx$500 times faster reactivity of **5 TS II L**, due to the extremely low population of **4 L** compared to **4 B**, which causes the b isomer to be the main product. A comparison with the same reaction (propene+$^{\bullet}$CN+H) conducted without the help of the Ni catalyst, was analyzed (see ESI†). No barriers have been found and ΔG_{l-b}=0.7 kcal/mol at T=200 K gives a 14.5% population of the linear isomer, which is $\approx 10^4$ higher compared to the Ni catalyzed reaction (Markovnkov addition). In conclusion, the proposed Ni based C=C hydrocyanation is able to stabilize highly reactive radical species, such as H and $^{\bullet}$CN, coordinated to the Ni atom in a regio-selective hydrocyanation in the heterogeneous phase, while maintaining and enhancing the regio-character of the corresponding homogeneous gas-phase reaction.

The potential implications of the reported findings are beyond the regioexcess of nitriles, affecting prebiotic, origin of life, and terrestrial geochemistry by opening, conceptually, new possible synthetic pathways. For example, the proposed Ni catalyzed [-C=C-] hydrocyanation can be involved in the excess of branched fatty acids (mono- and di carboxylic) or amines, as found in some meteorites[56–59], being both carboxyl acids and amines easily obtained by nitriles. Finally, *astro-regiochemistry* can result in a wide chemical variety of products with the regioexcess dependent from the physico-chemical conditions in both heterogeneous and homogeneous phases[60] *i.e.* strongly dependent on astrophysical environments.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 H. C. van de Hulst, *Res. Astr. Obs. Utrecht., part 2*, 1949, **11**, 1–50.
2 H. M. Cuppen, C. Walsh, T. Lamberts, D. Semenov, R. T. Garrod, E. M. Penteado and S. Ioppolo, *Space Sci. Rev.*, 2017, **212**, 1–58.
3 Q. Li, B. S. Liu, P. J. Sarre and A. S.-C. Cheung, *Proc. Int. Astron. Union*, 2017, **13**, 320–325.
4 M. d'Ischia, P. Manini, M. Moracci, R. Saladino, V. Ball, H. Thissen, R. A. Evans, C. Puzzarini and V. Barone, *Int. J. Mol. Sci.*, 2019, **20**, 4079.
5 G. A. Cruz-Diaz, A. Ricca and A. L. Mattioda, *ACS Earth Space Chem.*, 2020, **4**, 1730–1742.
6 A. Rimola, S. Ferrero, A. Germain, M. Corno and P. Ugliengo, *Minerals*, 2021, **11**, 26.
7 J. Lasne, *ACS Earth Space Chem.*, 2021, **5**, 149–162.
8 C. K. Materese, P. A. Gerakines and R. L. Hudson, *Acc. Chem. Res.*, 2021, **54**, 280–290.
9 T. Q. Zhao, Q. Li, B. S. Liu, R. K. E. Gover, P. J. Sarre and A. S.-C. Cheung, *Phys. Chem. Chem. Phys.*, 2016, **18**, 3489–3496.
10 Q. Li, B. S. Liu, P. J. Sarre and A. S.-C. Cheung, *Proc. Int. Astron. Union*, 2017, **13**, 320–325.
11 Q. Li, W. Dai, B. S. Liu, P. J. Sarre, M. H. Xie and A. S.-C. Cheung, *Mol. Astrophys.*, 2018, **13**, 22–29.
12 E. M. Valencia, C. J. Worth and R. C. Fortenberry, *Mon. Not. R. Astron. Soc.*, 2019, **492**, 276–282.
13 E. S. Doerksen and R. C. Fortenberry, *ACS Earth Space Chem.*, 2020, **4**, 812–817.
14 R. C. Fortenberry, *Mol. Astrophys.*, 2020, **18**, 100062.
15 M. Guélin and J. Cernicharo, *Front. Astron. Space Sci.*, 2022, **9**, 1–16.
16 Z. Martins, Q. H. S. Chan, L. Bonal, A. King and H. Yabuta, *Space Sci Rev 216, 54 (2020)*, 2020, **216**, 54.
17 S. Islam and M. W. Powner, *Chem*, 2017, **2**, 470–501.
18 M. Fioroni and N. J. DeYonker, *ChemPhysChem*, 2016, **17**, 3390–3394.
19 M. Fioroni and N. J. DeYonker, *Front. Chem.*, 2021, **8**, 621898.
20 M. Fioroni and N. J. DeYonker, *Mon. Not. R. Astron. Soc.*, 2022, **512**, 1629–1638.
21 E. P. Beaumier, A. J. Pearce, X. Y. Xin Yi See and I. A. Tonks, *Nat. Rev. Chem.*, 2019, **3**, 15–34.
22 K. Liu, S. Zhang and M. Han, *Catalysts*, 2020, **10**, 818.
23 R. M. Hazen and S. M. Morrison, in *Mineralogical Environments of the Hadean Eon: Rare Elements Were Ubiquitous in Surface Sites of Rock-Forming Minerals*, ed. A. Neubeck and S. McMahon, Springer International Publishing, Cham, 2021, pp. 43–61.
24 F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741–1748.
25 E. A. Quadrelli and J.-M. Basset, *Coord. Chem. Rev.*, 2010, **254**, 707 – 728.
26 D. P. Estes, G. Siddiqi, F. Allouche, K. V. Kovtunov, O. V. Safonova, A. L. Trigub, I. V. Koptyug and C. Copéret, *J. Am. Chem. Soc.*, 2016, **138**, 14987–14997.
27 M. K. Assefa, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2020, **142**, 8738–8747.
28 T. W. Dijkstra, R. Duchateau, R. A. van Santen, A. Meetsma and G. P. A. Yap, *J. Am. Chem. Soc.*, 2002, **124**, 9856–9864.
29 V. Mennella, M. Ciarniello, A. Raponi, F. Capaccioni, G. Filacchione, T. Suhasaria, C. Popa, D. Kappel, L. Moroz, V. Vinogradoff, A. Pommerol, B. Rousseau, I. Istiqomah, D. Bockelee-Morvan, R. W. Carlson and C. Pilorget, *Astrophys. J.*, 2020, **897**, L37.
30 Y. Nakauchi, M. Abe, M. Ohtake, T. Matsumoto, A. Tsuchiyama, K. Kitazato, K. Yasuda, K. Suzuki and Y. Nakata, *Icarus*, 2021, **355**, 114140.
31 M. Fioroni, A. K. Tartera and N. J. DeYonker, *J. Phys. Chem. A*, 2018, **122**, 9100–9106.
32 C. J. Bennett, C. Pirim and T. M. Orlando, *Chem. Rev.*, 2013, **113 12**, 9086–9150.
33 M. Murri, G. Capitani, M. Fasoli, A. Monguzzi, A. Calloni, G. Bussetti, N. Malaspina and M. Campione, *ACS Earth Space Chem.*, 2022, **6**, 197–206.
34 M. Anand, L. A. Taylor, A. Nazarov, Mikhail, J. Shu, H.-K. Mao and J. Hemley, Russel, *Proc. Natl. Acad. Sci. U.S.A.*, 2004, **101**, 6847–6851.
35 S. J. Bromley, B. Neff, S. D. Loch, J. P. Marler, J. Országh, K. Venkataramani and D. Bodewits, *Planet. Sci.*, 2021, **2**, 228.
36 J. Manfroid, D. Hutsemékers and E. Jehin, *Nature*, 2021, **593**, 372–374.
37 C.-Y. Lin and P. P. Power, *Chem. Soc. Rev.*, 2017, **46**, 5347–5399.
38 Borget, Fabien, Müller, Sandra, Grote, Dirk, Theulé, Patrice, Vinogradoff, Vassilissa, Chiavassa, Thierry and Sander, Wolfram, *Astron. Astrophys.*, 2017, **598**, A22.
39 Hänni, N., Altwegg, K., Balsiger, H., Combi, M., Fuselier, S. A., De Keyser, J., Pestoni, B., Rubin, M. and Wampfler, S. F., *Astron. Astrophys.*, 2021, **647**, A22.
40 N. Hänni, K. Altwegg, B. Pestoni, M. Rubin, I. Schroeder, M. Schuhmann and S. Wampfler, *Mon. Not. R. Astron. Soc.*, 2020, **498**, 2239–2248.
41 K. Willacy, M. Allen and Y. Yung, *Astrophys. J.*, 2016, **829**, 79.
42 F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108.
43 J. P. Perdew, M. Ernzerhof and K. Burke, *J. Chem. Phys.*, 1996, **105**, 9982–9985.
44 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
45 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
46 C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.
47 C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.
48 N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2006, **125**, 074110.
49 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
50 M. Läuter, T. Kramer, M. Rubin and K. Altwegg, *ACS Earth Space Chem.*, 2022, **6**, 1189–1203.
51 F. Goesmann, H. Rosenbauer, J. H. Bredehöft, M. Cabane, P. Ehrenfreund, T. Gautier, C. Giri, H. Krüger, L. L. Roy, A. J. MacDermott, S. McKenna-Lawlor, U. J. Meierhenrich, G. M. Munõz Caro, F. Raulin, R. Roll, A. Steele, H. Steininger, R. Sternberg, C. Szopa, W. Thiemann and S. Ulamec, *Science*, 2015, **349**, aab0689.
52 A. J. McKay and N. X. Roth, *Life*, 2021, **11**, 37.
53 M. Brookhart, M. L. H. Green and G. Parkin, *Proc.Nat. Acad. Sci. USA*, 2007, **104**, 6908–6914.
54 D. L. Bunker, B. Garrett, T. Kliendienst and G. S. Long III, *Combustion and Flame*, 1974, **23**, 373–379.
55 D. T. Gillespie, *J. Comput. Phys.*, 1976, **22**, 403–434.
56 J. C. Y. Lai, B. K. Pearce, R. E. Pudritz and D. Lee, *Icarus*, 2019, **319**, 685–700.
57 *Meteorites and the Early Solar System II*, ed. D. S. Lauretta and J. H. Y. McSween, University of Arizona Press, 2006.
58 J. C.-Y. Lai, B. K. Pearce, R. E. Pudritz and D. Lee, *Icarus*, 2019, **319**, 685–700.
59 S. Pizzarello, S. K. Davidowski, G. P. Holland and L. B. Williams, *Proc. Nat. Acad. Sci. USA*, 2013, **110**, 15614–15619.
60 D. Loffreda, F. Delbecq, F. Vigné and P. Sautet, *J. Am. Chem. Soc.*, 2006, **128**, 1316–1323.