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Astrochemistry by transition metals? The selected cases of $[FeN]^+$, $[FeNH]^+$ and $[(CO)_2FeN]^+$]: pathways toward CH_3NH_2 and HNCO†

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Transition Metals (TM) are proposed to play a role in astrophysical environments in both gas and solid state astrochemistry by co-determining the homogeneous/heterogeneous chemistry represented by the gas/gas and gas/dust grain interactions. Their chemistry is function of temperature, radiation field and chemical composition/coordination sphere and as a consequence, dependent from the astrophysical object where TM are localized. Here five main categories of TM compounds are proposed and classified as: **a)** pure bulk and clusters; **b)** TM naked ions; **c)** TM oxides/minerals or inorganic; **d)** TM-L (L = ligand) with L = (σ and/or π)-donor/acceptor species like H/H_2, N/N_2, CO, H_2O and **e)** TM-organoligands such as C_p, PAH, R_1=•=•=R_2. Each of the classes is correlated to their possible localization within astrophysical objects. Because of this variety coupled with their ability to modulate reactivity and regio/enantioselectivity by ligand sphere composition, TM compounds can introduce a *fine organic synthesis* in astrochemistry. For the selection of small TM parental compounds to be analyzed as first examples, by constraining the TM and the second element/molecule on the basis of their cosmic abundances and mutual reactivity, Fe atoms coupled with N and CO are studied by developing the chemistry of $[FeN]^+$, $[FeNH]^+$ and $[(CO)_2FeN]^+$. These molecules, due to their ability to perform C-C and C-H bond activations, are able to open the pathway toward the nitrogenation/amination and carbonylation of organic substrates. By considering the simplest organic substrate CH_4, the parental reaction schemes (gas phase, T=30 K): **I)** $[FeN]^+ + CH_4 + H \rightarrow [Fe]^+ + H_3C\text{-}NH_2$; **II)** $[FeNH]^+ + CH_4 \rightarrow [Fe]^+ + H_3C\text{-}NH_2$ and **III)** $[(CO)_2FeN]^+ + H \rightarrow [FeCO]^+ + HNCO$ are analyzed by theoretical methods (B2PLYP double hybrid functional/TZVPPP basis set). All reactions are thermodynamically favored and first step transition states can follow a minimal energy path by spin crossing, while H extraction in reaction **II** shows very high activation energies. The need to overcome high activation energy barriers underlines the importance of molecular activation by radiation and particle collision. TM chemistry is expected to contribute to the known synthesis of organic compounds in space leading towards a new direction in the astrochemistry field whose qualitative (type of compounds) and quantitative contribution must be unraveled.

1 Introduction: the chemistry age

The Universe can be seen as an immense heterogeneous non-equilibrium chemical reactor whose richness, variety and complexity can still surprise a curious Scientist. At small scales the Universe has been always conceived as a heterogeneous entity due to the presence of well localized mass objects with radiation/radiationless emission characters and, as a consequence, with the Universe locally characterized by a heterogeneous and non-isotropic distribution of matter and energy, it's thermodynamical equilibrium is far to be achieved. Under such a non-equilibrium regime chemistry can efficiently operate. Nowadays thanks to the development of sophisticated observational techniques[1] supported by a series of theoretical and experimental developments[2–4], the detection of a complex inorganic/organic chemistry gave birth to the cosmochemistry/astrochemistry[2–4] research fields. However despite the exponentially increasing interest in the physical-chemistry and synthesis of inorganic/organic compounds in space[5], transition metals (TM) have not yet been included as active elements contributing to the synthetic pathways. In the present work the contribution of TM to astrochemistry is envisaged and proposed by showing: **a)** TM genesis and their amount produced during Universe evolution; **b)** TM localization within astrophysical objects; **c)** a classification based on five main groups of TM differentiated by chemical characteristics and aggregation states is suggested and correlated to the known observational and theoretical data; **d)** applying a series of selection rules, the chemistry of iron nitride compounds based on the reactions **I)** $[FeN]^+ + CH_4 + H \rightarrow [Fe]^+ + H_3C\text{-}NH_2$; **II)** $[FeNH]^+ + CH_4 \rightarrow [Fe]^+ + H_3C\text{-}NH_2$ and **III)** $[(CO)_2FeN]^+ + H \rightarrow [FeCO]^+ + HNCO$ is analyzed by means of DFT methods and experimental data, when possible; **e)** finally a general

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conclusion on the potential contribution of TM in the synthesis of organic compounds in space is reported.

1.1 The Universe chemical evolution: main period elements and transition metals *genesis*

The elements beyond the ones synthesized during the Big Bang ^{1}H, ^{3}He, ^{4}He[6–8] (^{6}Li, ^{9}Be, ^{10}B and ^{11}B are continuously synthesized by cosmic rays *spallation* processes[9]) are born in the stellar hot cores or during the complex star death phenomena. Depending on their mass and metallicity (in astrophysics all elements but H and He are classified as ”metals”) stars show a characteristic evolution pattern as classically depicted by the Hertzsprung-Russell temperature-luminosity diagram[10]. The first light of a star starts with the H burning phase where He is produced based on a proton-proton (pp) chain or on CNO-cycles. When the hydrogen core is exhausted and enriched in He, hydrogen burning continues in a shell embedding the same He ashes and the following gravitational contraction increases the core temperatures enough to ignite He (*Asymptotic Giant Branch* (AGB) stage). Depending on the star mass this process can proceed till the synthesis of ^{56}Fe in an *onion* layered structure[11], where a series of shell burnings made of ^{4}He, ^{12}C, ^{20}Ne, ^{16}O and ^{28}Si are concentrically organized around a central ^{28}Si/^{56}Fe core. The AGB stars are believed to be the main sources of carbon and nitrogen in the Universe as well as of some of the heavier nuclides[12,13]. In particular the *Thermal Pulsating Asymptotic Giant Branch* (TP-AGB) period is characterized by a series of dredge up phenomena, allowing the star to mix the rich C, N and O deep layers up to the surface, experiencing a significant mass loss via strong stellar winds, thereby enriching the interstellar medium with the products of their nucleosynthesis[14]. Elements heavier than ^{56}Fe are to a large fraction created in the explosive nucleosynthesis such as the r-process (rapid neutron capture)[15] and rp-process (rapid proton capture)[14] while the s-process (slow neutron capture) is responsible for the nucleosynthesis in the stellar core[16,17] with the latter bearing the fundamental role of the synthesis of about half of the elements heavier than ^{56}Fe. Specifically, explosive nucleosynthesis is characterized by p-, ν-, νp-, α- and r-processes referring to core-collapse supernovae (type II, Ib, Ic) of outstanding importance as they are predicted to be the most prolific sources of Galactic elements[18]. In fact, the explosive nucleosynthesis process is predicted to be the source of the majority of nuclides with $A > 12$. To give an idea of the amounts of the Fe group metals (first row TM) involved in a supernova explosion like SN 1987A, a total of $\sim$0.07 $M_{\odot}$ of ^{56}Co in the ejecta was calculated[19], while an estimate for the ^{56}Ni masses deduced from 17 type Ia supernovae sets a range of 0.1-1.0 $M_{\odot}$[20]. The relative TM abundances have been estimated based on observation as well as calculated (refractory elements are not yet easily detectable) on evolutionary models of star/galaxies[21,22]. TM such as Fe, Co, Ni show fractional abundances of $\sim$1-10^{-2} toward Si. Higher atomic weight TM can be set with Si fractional abundances comprised between the Pb peak and the Fe peak at $10^{-5} < \mathrm{TM} < 1$. As will be reported in the next section all the heavy and refractory-elements are expected to be partially depleted[23] and condensed into dust grains, resulting in an interesting concentration of active TM for a further complex chemistry.

2 Complex chemistry in action

Following the classification made by the US National Research Council Astro 2010 Survey on Astronomy and Astrophysics[24] the two categories **I)** Planetary systems and star formation and **II)** Stars, stellar evolution and dust grain formation, will be considered. In this cases the fundamental chemistry/physics set by gas/gas and gas/dust grains interactions[25,26] takes place with TM proposed to play a role in the overall chemistry.

I) Planetary systems and star formation. In molecular clouds a rich carbon based chemistry[27] has been detected with the presence of molecular anions[28] and complex polycyclic aromatic hydrocarbons (PAHs), carbon chains and fullerenes as part of an extended size distribution of interstellar dust[29,30]. In dark cold ($\sim$10 K) interstellar clouds an unsaturated (C_nH) or bare carbon chemistry has been found[27,31] coupled with a N, S and O organic chemistry[32] while in *hot cores* and *corinos*; *i.e* warm objects with temperatures of 100-300 K and associated with low mass protostars or heavy young stellar objects; a rich organic chemistry (simple alcohols, esters, ethers, nitriles) is shown[33]. The elegant *hot cores* and *corinos* organic chemistry is probably due to the involvement of the dust surface as a catalytic site and the organic products are then desorbed or evaporated into the gas-phase[33–35]. Looking to our Solar System, the Murchison meteorite classified as a carbon rich carbonaceous chondrite is the example prototype of the complex organic chemistry of non-terrestrial origin[36]. The Murchison carbon content is characterized by a 70 % in weight fraction by a macromolecular insoluble organic matter of high aromaticity, with the remaining soluble fraction containing several hundreds of characterized organic molecules[37]. Late estimates based on sophisticated techniques such as Electrospray ionization (ESI) Fourier transform ion cyclotron resonance/mass spectrometry (FTICR/MS) extend this number to 10^{4} different molecular compositions and 10^{6} possible diverse structures[36]. In pre-stellar cores, where the stellar birth starts characterized by low temperatures $\sim$10 K and relatively high density during the isothermal collapse, a depletion of heavier molecules on dust particles has been suggested[38] followed by deuterium fractionation. In protoplanetary disks the detection of CO in gas-phase has been explained by photodesorption[39] and the presence of complex molecules is a function of the temperature gradient (distance from the central star and distance from the disk mid-plane). Directly linked to the proto-planetary disks, solar system comets show the composition of the primordial solar nebulae with many organic species[40]. Furthermore with a similarity between the cometary ice grains[41] and the interstellar counterpart[42], the chemical composition of the cometary one rich in H_2O, CO_2, CO, CH_3OH, hydrocarbons, nitrogen and sulfur containing compounds, minerals and silicates, allows an important look on the interstellar ice-grain chemistry where radiation processing of organic molecules on ice surfaces is suggested[25,43–45].

II) Stars, stellar evolution and dust grain formation. After their nuclear synthesis, elements undergo a series of chemical and physical processes. In general, low-mass AGB stars are predicted to be the most prolific sources of dust in the Galaxy together with the *novae* phenomenon, frequently revealing dust forming episodes in the ejecta[46] creating a perfect condition for gas and dust chemistry development[4]. Close to the stellar photosphere, chemical species as well as dust condensates are formed under thermodynamic equilibrium in concentric shells centered on the mother star defined by large temperature, density and radiation gradients[47]. As a consequence circumstellar envelopes can be well defined as *chemical factories*. For example in the C-rich shell of the AGB star IRC + 10216, have been found over 70 different chemical compounds[48,49]. Most importantly refractory-element-bearing species (Si, P and metals) are predicted to be in some sort of mineral grain[50], supported by condensation models predicting that dust in circumstellar shells takes on several forms, depending on whether the environment is oxygen or carbon-rich[51]. For example considering a TM such as Fe, its presence together with its FeS derivative has been proposed to be included in interstellar silicates[52]. However, based on millimeter observations, refractory elements in circumstellar environments are not all contained in dust grains. Nine Si containing molecules have been found in circumstellar shells together with eleven molecules containing metals[53]. In C-rich envelopes, metals are present as halides (NaCl, KCl, AlF and AlCl) or metal cyanides (MgCN, AlNC, MgNC, KCN and NaCN[54], while in O-rich shells, oxides and hydroxides such as AlO and AlOH dominate[55] with Al proposed to be condensed in Al_2O_3. The presence of AlO and AlOH indicates that photospheric shocks are likely disrupting grains. In C-rich shells, silicon is primarily present as SiC, while in O-rich objects in oxide condensates. Phosphorus is probably present in the form of *schreibersite*, $(Fe,Ni)_3P$, while magnesium is contained in silicon and aluminum oxides in O-rich shells and primarily as MgS in C-rich shells. Interestingly few molecules containing phosphorous have been observed in the ISM (Interstellar Medium). Phosphorus-containing molecules seem to be relatively abundant in circumstellar shells, underlined by the discoveries of CCP, PN, HCP, PO and, probably, PH_3[56]. Furthermore carbonaceous dust outflows of late-type stars and silicates in envelopes of late-type stars give fundamental contributions to the dust presence in ISM. Carbonaceous dust particles are primarily formed by a combustion-like process where small carbon chains form PAHs nucleate into larger-size PAHs and, ultimately, into nanoparticles[57], while silicates are mostly found in the amorphous state[58] though some silicates in crystalline form have been observed in (post-)AGB stars and in disks around Herbig Ae/Be stars, T-Tauri stars and brown dwarfs[59]. The detection of silicate dust grains containing O, Si, Fe and Mg, as well as some Ca and Al, provides an important clue on dust chemical composition[53].

3 TM chemistry in dust particles and gas phase: new chemical pathways

The previous Sections reported a condensed synthesis on the origin and composition of the known inorganic as well as organic compounds. However the complex chemistry that has been found in space can reasonably contain; in some part and under opportune conditions; a contribution of TM for which vast knowledge on their chemical-physical behavior has been acquired due to their fundamental role in both industrial and research applications. In fact the occupied d orbitals make TM elements and their derivatives possible important players in astrochemistry and astrocatalysis both in gas phase as well as in solid state. First pioneering proposals regarding TM involvement in space chemistry/catalysis was suggested by Irikura back in 1980-1990[60], Prasad[61], Bohme[62] and Klotz[63]. In space TM are detected in the gas phase within supernova remnants with an overwhelming presence of Fe^{+n}, Ni^{+n} and Co^{+n} or in star atmospheres and envelopes as FeO[64], FeCN[65] and TiO/TiO_2[66]. However for 4d and 5d TM with cosmic fractional abundances of 10^{-2}-10^{-5} compared to Si, their line spectra resolution and assignment is difficult due to spectral complexity. As a consequence though there is little knowledge on their exact chemical/structural nature and localization once leaving their mother star, it is possible to build an educated guess based on the known TM chemical-physical characters as depicted in Table 1.

The chemical reactions in which TM are possibly actively involved can be selected by imposing constrains on the thermodynamic (exothermic reactions) as well as kinetic (low transition states, activation by UV or charged particles) levels, resulting in the chemical reaction typologies as ion-ion, ion-neutral molecule and radical. In the next lines follows a short synthesis on the possible role of each of the categories reported in Table 1.

a) Pure bulk TM and TM clusters. As pure, TM can exist in two different forms, as *bulk* where the number of atoms

Table 1 The TM chemical nature, type and occurrence does not consider planet chemistry but only objects as defined in Section 2. The term *dust* refers to a model of a dust grain with a central solid core surrounded by ice (H_2O, CO, CH_3OH)[25], while *inclusions* are intended as small solid fragments enclosed in the dust grain within the silicate core or covering ice

Chemical Nature	Type	Occurrence
Pure Metals	Bulk	as Inclusions or Dust
	Clusters	as Inclusions in Gas Phase
	Naked Ions	Included in Gas Phase
Metal Compounds	Inorganic as Minerals	as Inclusions or Dust
Metal Compounds with Ligands	H/H_2, N/N_2, CO, H_2O	as Inclusions in Gas Phase
	Organo-Ligands	as Inclusions in Gas Phase

constituting the agglomerate is greater than what is defined as a *cluster*. TM clusters possess a size ranging from a few to several hundred thousand atoms, representing an intermediate stage in the transition from small molecules to solids, showing a characteristic differential reactivity and stereo/regio selectivity compared to the parent bulk TM[67]. Till now, though not directly considered for their chemical reactivity, formation kinetics of small clusters made of Si, Mg and Fe have been considered in the attempt to calculate dust formation in the early universe by SN ejecta derived from population III stars[68]. A further valid process of cluster formation can consider the *Mond* process where the reaction: $[TM(CO)_n]_m \rightarrow TM_m + CO_{m*n}]$ takes place in the gas-phase. When considering pure bulk TM, it is reasonable to hypothesize their contribution to the chemical composition of space dust. In general dust is defined to be formed by a silicate based material or following the Goldschmidt classification[69] by *litophile* elements. However a core of pure TM or alloy(s) can be constituted by *siderophile elements*[69] where, for example, pure dust-bulks of TM *siderophile* like Fe and Ni can be easily obtained by a *Mond* process. This growth process is well different in type, scale and dimension from the process taking place in a disk-planetary object. For example meteoric bulk iron is derived from M-type asteroids, asteroids large enough to melt and differentiate with the *siderophile elements* sinking into the core while leaving *litophile* elements in the crust[70,71]. Finally and most importantly regarding their chemical reactivity, solid metals as well as their oxides can be activated by microwave, UV and electrons developing a C-C and C-H activation[72] (see next paragraphs);

b) TM naked ions. TM naked ions have been proposed to be involved in the destruction/formation of CO[61], formation of HCO[61] and co-involved in the formation of PAH[62]. However TM naked ions are known to activate C-C and C-H bonds in gas phase acting on a substrate such as CH_4 or higher saturated/insaturated hydrocarbons[73]. Huge efforts have been applied to the analysis and mechanistic understanding of these industrially and scientifically interesting reactions where different TM and some actinides at different charged states ($[TM]^{-/0/n+}$) have been reacted in the gas phase with alkanes[73]. For example Fe^+ or Pt^+ can oxidize CH_4 obtaining a series of organic molecules such as CH_3OH, CH_3CH_2OH, H_2CO and HCOOH and a first structural and electronic characterization of the complex corresponding to the oxidative addition of Zn to methane (H-Zn-CH_3) has been performed[74]. The interest of such compounds within the astrophysical contest can be found in their ability to perform an "*easy*" C-C and C-H bond activation when in electronically excited states[72], a condition that can be easily obtained in some environments, especially in planetary systems and star formation zones[34];

c) TM oxides/minerals or inorganic compounds. This term defines all TM *minerals* from simple TMX_y, where X is a generally non-metal element like N,O or S to more complex compounds like *schreibersite* $(Fe,Ni)_3P$ or *kamacite* α-(Fe,Ni) found in meteorites, to mention few. Interestingly some minerals characterized by a layer structure working as simple support or matrix for the TM, for example in manganates where Ni or other TM are inter-layered, show a strong catalytic activity comparable to the same free amount of TM contained within the layers[75]. A structurally simple but extremely important subclass is constituted by TM oxides and as reported in the following section in the solid state can react with hydrocarbons by use of microwave, UV and electrons for C-C, C-H[72] bond activation. Specifically in gas phase they can activate CH_4 leading to three different products: CH_3OH, metal hydroxides via loss of a $[CH_3]\cdot$ and formation of $[TM{=}CH_2]^+$

concomitant with H_2O as a neutral product. They can also react with higher saturated hydrocarbons, ethene and higher alkynes[76];

d) Metal-(L)igand compounds (L = H/H_2, N/N_2, CO, H_2O). This simple and space abundant L species can potentially form a classical metal-ligand (TM-L) bond with important catalytic activity in the synthesis of organic compounds. In fact the ability of many of the TM to interact with σ/π-donor/acceptor species gives many of the resulting compounds catalytic activity. For example simple abundant molecules like CO or H_2/H produce carbonyl and hydride derivatives opening the pathway toward CO and H addition chemistry. In the past (1992) some $Fe(CO)_5N$ and $Fe(CO)_5H$ studies were performed with interesting applications in space chemistry[60,77]. A further possible role can be their involvement as *sink compounds*. Because CO and H_2 can sublimate at extremely low temperatures both can be retained as TM-CO and TM-H_2 within the dust grain and at higher temperatures, for example in a *corinos*, starting the addition reactions to organic substrates or, if not reacting, simply to be released as H_2 and CO;

e) Metal-organoligands. Just as an example the TM-L bond with organic species like $H_2C{=}CH_2$, C_{60}, $R_1{=}\bullet{=}\bullet{=}R_2$, PAH can be well foreseen. The first organometallic compound was proposed back in the 1992[78] where Fe and Ru were suggested to interact with coronenes molecules possibly involved in the olygomerization of acetylene molecules and responsible for TM depletion[79]. More recently theoretical calculations and experimental data on $[C_pFeC_{24}H_{12}]^+$ and $[C_p{}^*FeC_{24}H_{12}]^+$ complexes have been published[80] confirming the possible importance and interest of organometallic chemistry in space. All the previous categories can be easily *mixed*. For example mixing the **d)** and **e)** categories, the resulting ML_CL_i compounds; to be found for example on the surface of carbon agglomerates, where L_C = organic and L_i = CO, H_2O, H_2; enhance the insertion probabilities of the L_i σ-type ligands into organic molecules.

In short, the five main TM compound categories and mixed ones previously listed and discussed in Table 1 show a potential that can contribute to the gas/gas and gas/dust grain chemistry, itself a function of the temperature and radiation field within the astrophysical object considered[34].

3.1 Computational details

All calculations were performed with the ORCA software (vs. 2.9.1)[81] by setting the B2PLYP double-hybrid functional level of theory[82,83]. In case of the $[FeN]^+$ and $[FeNH]^+$ system (see Section 3.2), the triple ζ-basis TZV[84,85] with polarization and diffuse functions (the Ahlrichs polarization and diffuse functions were obtained from the TurboMole basis set library under ftp.chemie.uni-karlsruhe.de/pub/basen) on all atoms were used: Fe = TZV(2f/sppd); C,N,O = TZV(2d/sp) and H = TZV(p/s) where TZV(x/y) refers to the character of the polarization functions x and diffuse functions y. For the $[(CO)_2FeN]^+$ species (see Section 3.3), the Fe atom was described by using an ECP (Effective Core Potential) LANLTZ(f)[86–88] while on all non-metallic atoms the previous cited triple ζ-basis set TZV[84,85] with polarization and diffuse functions was used. To determine the probability of the intersystem crossing, a demanding spin-orbit coupling (SOC) constants would be required[89,90]. Here a scheme for determining the existence of a minimum energy crossing point (MECP) between the calculated spin surfaces is used as implemented in Orca 2.9.1[81] based on the algorithm of Harvey *et al.*[91]. To test if the computed structures represent a minimum or a transition state, frequency calculations were performed on all calculated models at T=30 K and the obtained ZPE (Zero Point Energies) and entropies were used to deduce the potential energy surfaces diagrams (PES).

3.2 Model System I. The case of $[FeN]^+$ and $[FeNH]^+$: paths toward CH_3NH_2

The inclusion of TM chemistry within the astrochemistry field results in an *explosion* of new possible chemical pathways. As previously reported, a first pioneering proposal considering the TM contribution to astrochemistry can be dated back to the decade 1980-1990[60–62]. The idea, as later underlined by Mestdagh[77] was straightforwardly based on the observation that free atoms like H are important components of the interstellar medium. As a consequence, considering that TM can be potentially easily photoionized to cations, the reaction between TM^{+n} and the abundant H, N or CO is easily achieved[77]. Due to the TM chemical richness and variety, a detailed analysis of the five categories previously analyzed would result in a cumbersome task. However by an educated guess a restricted number of TM compounds can be selected showing their potential contribution. First selection rules must reasonably consider variables such as: **a)** cosmic abundances of the elements; **b)** thermodynamic (exothermic reactions) as well as kinetic (low transition states, activation by UV or charged particles, charged and radical states); **c)** structural simplicity of the systems involving some already known data derived by experimental or theoretical calculations and **d)** the specific chemistry based on the development of a heteroatom organic chemistry. The most abundant elements after H and He are (ordered by a decreasing scale) O, C, Ne, Fe, N, Si, Mg, S, all elements able to develop an organic HCONS chemistry and dust-grain inorganic chemistry. By taking into account molecular simplicity, reactivity and abundances, TM oxides $[TM_mO_y]^{+n}$ and TM nitrides $[TM_mN_y]^{+n}$ possess an interesting chemistry[73,92,93] that can be (co)-involved in the synthesis of organic compounds in the gas phase or as inclusions within/on the surface of dust grains.

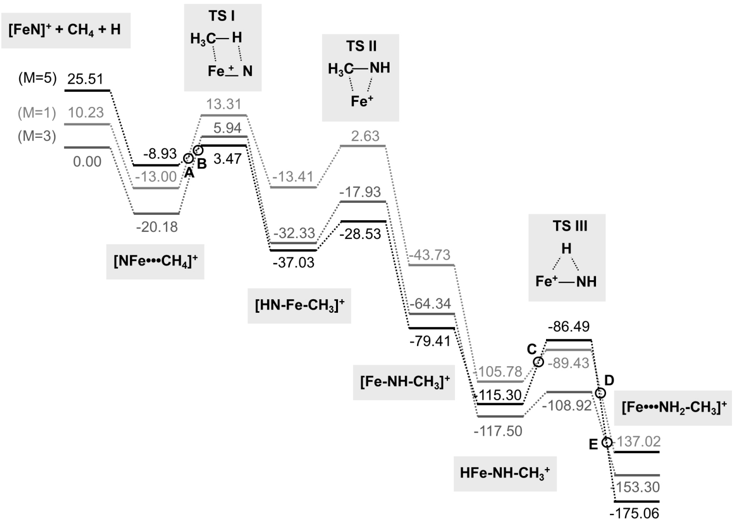

Fig. 1 $[FeN]^+$ activating the C-H bond of CH_4. PES are calculated at T=30 K with $[FeN]^+$ in the singlet (light gray line), triplet (gray line) and quintet (black line) states changing in doublet, quartet and sextet states after H addition to the Fe center. In the process: $[Fe^{***}NH_2CH_3]^+ \rightarrow [Fe]^+ + H_3C\text{-}NH_2$ the investment in energy is 78.24, 50.92 and 45.50 kcal/mol in the doublet, quartet and sextet states, bringing the overall reaction thermodynamics to -58.78, -102.38 and -129.56 kcal/mol, respectively. The circles are the considered calculated important MECP.

However a word of caution should be addressed. Though the applied selection rules are reasonable, the real amount of TM oxides and TM nitrides produced in star envelopes or SN outbursts must be in the future better analyzed as well as their partition in the gas and solid state phases must be understood considering condensation models functional of the astrophysical object. This can be reached by introducing detailed physical and chemical kinetic variables as used, for example, in kinetic models for the condensation of carbon dust[94] or by introducing elegant non-steady-state formulations for the analysis of small clusters and grains growth (C and $MgSiO_3$) in the ejecta of supernovae[95]. From the observational point of view the TM oxides presence is confirmed by the detection of FeO, TiO/TiO_2[66] and CrO[96] all spectroscopically assigned (though FeO has to be confirmed) while TM nitrides have been not yet assigned though SiN[97,98] and PN[99] have been detected. Because of the reactivity, the attention can be restricted to the singly charged states as $[FeO]^+$ and $[FeN]^+$, although the electronically excited states of the same compounds or even of the neutral form can be strongly reactive toward organic substrates. In fact in gas phase: **I)** electronically excited naked TM ions are able to dehydrogenate CH_4[93] through a reaction sequence: $TM^+ + CH_4 \rightarrow TM(CH_2)^+ + H_2$; **II)** if thermalized only 5d naked TM ions can dehydrogenate CH_4; **III)** however thermalized ligated $[TMO_y]^{+n}$ react with CH_4, small alkanes and alkenes with a series of products like (for a singly charged cation): **IIIa)** $[TM]^+$ + R-OH; **IIIb)** $[TM\text{-}OH]^+ + R\cdot$ and **IIIc)** $[TM{=}CH_2]^+ + H_2O$, strongly dependent from the TM if a (late) 3d, or if a 4d/5d and oxidation state[92,100]. The reaction tree previously described has been already analyzed considerably well for a series of 3d, 4d and 5d TM though only at lower oxidation states[72,92]. Furthermore and importantly the number of ligands (L) on the iron center, especially with closed shell CO ligands can determine, for example, the *carbene* or *alkylidine* character of $Fe(CH_2)^+$ as well as the selectivity toward the C-C or C-H as known for the TM^+ or TMO^+ species[100]. Another important reaction follows the scheme: **IV)** $TM(CH_2)^+ + NH_3 \rightarrow$(C-N) were nitrogen addition is obtained through a TM carbene. The C-N products can be achieved only using 5d thermalized TM. In case of Fe, its carbene is not active toward ammonia, while its nitrido form $[FeN]^+$ allows access to the amination of organic substrates, as suggested by Schröder and Schwanz[100]. Nitrido-iron compounds are extremely reactive species and few laboratory compounds ligand stabilized were isolated at low temperatures after thermal or photochemical oxidative elimination of molecular nitrogen from an azide complex obtaining Fe(IV), Fe(V), Fe(VI)[93,101,102], while the most simple $[FeN]^+$ has not been produced in sufficient amount for experimental analysis[77,100]. However recently the synthesis of organo-iron nitrido compounds stable at normal conditions have been obtained[103–105] due to their importance as intermediates in some chemical and biological reactions[106] for nitrogen fixation. The parental inorganic compounds Fe_2N (capable of slowly reacting with water emitting NH_3 fumes) and FeN have attracted some attention due to their important technological applications (steel nitridation as well as its colloidal solutions to obtain ferrofluids)[107,108].

Considering the existence of $[FeN]^+$ in astrophysical environments, its presence in certain stars[109] has been suggested but not further confirmed, though the importance of the neutral [FeN] was addressed in an experimental work to determine the rotational constants[110]. Laboratory production of the neutral form of [FeN] was obtained by direct combination of iron vapor with low pressure N_2 under high temperature/electric discharge conditions[110] or by laser ablation resulting in the production of ”exotic” iron-nitride species like NFeN, $Fe(N_2)$, $Fe(NN)_x$ with x = 1-5, and $Fe(NN)_3^-$ [111,112]. The positively charged counterpart $[FeN]^+$ was obtained from iron carbonyl precursors in presence of atomic nitrogen, with the bare Fe^+ characterized by a too low cross section to react efficiently with N_2 under laboratory conditions to produce a detectable amount of product[77]. The same trend was observed by using atomic nitrogen since collisional stabilization of short-lived intermediates and radiative association is not efficient[60]. As shown later (see Section 3.3) iron carbonyl precursors open an interesting new reaction channel coupled with the role to obtain the high reactive $[FeN]^+$ by an equilibrium scheme like $[Fe(CO)_mN]^+ \rightleftharpoons [FeN]^+ + mCO$ (m=1 or 2), with the low efficient direct reaction of Fe^+ with atomic and molecular nitrogen giving a certain contribution. To better understand reactivity and behavior of a ”hungry” 13 e^- $[FeN]^+$ system, a computational approach analyzing the reaction scheme $[FeN]^+ + CH_4 + H \rightarrow [Fe]^+ + H_3C\text{-}NH_2$ in gas phase was used (Figure 1). The methane molecule was obviously selected for its low number of atoms, it is the archetypal molecule for alkanes reactions and it’s certified presence in space[25], while the 30 K reference temperature was considered as a representative upper limit existing within a molecular cloud (see Section 2). Furthermore the methylamine product shares its importance,as it is a possible precursor of the simplest aminoacid glycine[113,114]. The overall reaction scheme proceeds through four inter-media and three transition states characterizing the H abstraction (TS I), methyl transfer (TS II) and substrate hydrogenation (TS III) (see Figure 1). Most importantly Figure 1 shows two main features: the strong thermodynamic driving force favoring the reaction products and the many crossing seams between the potential energy surfaces at different spin states. The crossing between different potential energy surfaces at different spin states is not a newcomer especially within first row TM complexes, as known for $[FeO]^+$ [115] and many other species differing in the metal center (Co, Ni), ligand type and substrate[73]. The reason for this finding is the ability of first row transition metals to possess large exchange constants between the 3d-orbitals so to be characterized by a large spin-orbit coupling allowing spin-forbidden reactions bypassed by inter-system crossings[73]. The most important spin-crossing is located near TS I, determining the H oxidative addition to Fe (see Figure 1). Here the quintet surface crosses the singlet (circle A) and triplet (Circle B). This hopping permits to lower the energy to 23.65 and 16.47 kcal/mol against the 26.12 and 26.31 kcal/mol for the singlet and triplet states,respectively. The second energetic barrier is characterized by the methyl transfer to NH_2 (TS II) reporting energies of 8.5 kcal/mol (quintet), 14.40 kcal/mol (triplet) and 16.04 kcal/mol (singlet). In the next reaction step, though a H can directly react with the $H_3C\text{-}NH$ residue, the reductive elimination of one hydrogen when captured by the Fe center is considered. Here a series of hopping takes place. A first hopping is placed between the doublet and sextet surfaces near TS II (circle C). Here the doublet, quartet and sextet surfaces (due to the H addition) show a barrier of 16.35, 8.58 and 28.81 kcal/mol, respectively, while the doublet-sextet hopping permits the energy to be lowered from 28.81 to 25.87 kcal/mol. The second series of most important hopping determining the final thermodynamic state is placed where the sextet surface crosses both the doublet (circle D) and quartet (circle E) surfaces. Due to the hopping phenomenon, the system has multiple ”choices” where the local thermodynamic and energy barriers will determine the most populated pathway toward the products. Finally because of the temperature within a molecular cloud (10-30 K) or even in *hot cores* and *corinos* (100-300 K), the reaction does not efficiently proceed if energy is not obtained by radiation or charged particles, a possibility experimentally observed in a different series of TM naked ions and compounds[72]. If the iron-nitride $[FeN]^+$ ion is present in space, its hydrogenated form $[FeNH]^+$ can be expected. Due to its known reactivity working as imino transfer agent toward O_2, H_2O, H_2, ethene, benzene, ethane, propane though quite inefficient toward CH_4 [116,117], $[FeNH]^+$ has been extensively analyzed[117]. In Figure 2 the PES computed at three different multiplicities based on the reaction scheme: $[FeNH]^+ + CH_4 \rightarrow [Fe]^+ + H_3C\text{-}NH_2$ is reported.

As found for the previous $[FeN]^+$ case, the overall thermodynamic (till the $[Fe{*}{*}{*}NH_2CH_3]^+$ product) shows a nice downfall cascade toward the products. However the first transition state TS I, corresponding to the H abstraction from CH_4 is very high for all the three spin surfaces on the order of $\approx$ 41 kcal/mol. Though the spin crossing would permit a small reduction in the energy barrier (0.97 kcal/mol), its late action involving the methyl transfer near to TS II and the final product (circles A and B) reduces its importance due to the previous determining step corresponding to TS I. These results can explain the experimental findings showing the low reactivity of $[FeNH]^+$ toward methane[116]. Obviously though $[FeNH]^+$ does not show a reactivity toward CH_4 here considered as an alkane prototype, other longer chain alkanes, aromatics, water and oxygen can efficiently react underlining its possible role as imino-transfer agent[116,117]. Regarding further reaction schemes to be considered in the astrochemistry field, it would be interesting to increase the number of elements coupled to Fe where a possible *paper chemistry* on the

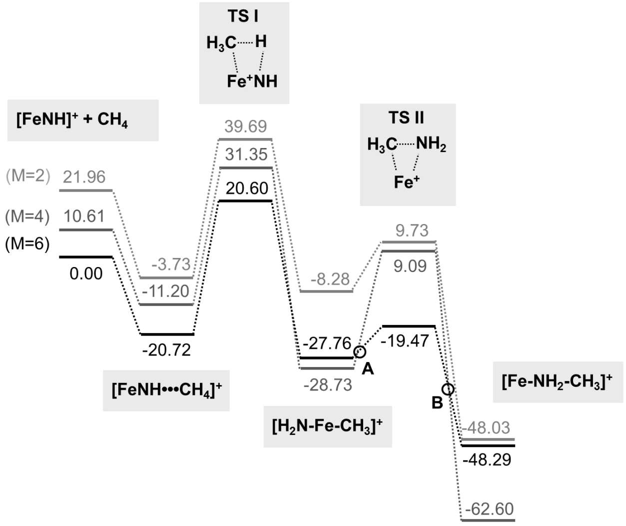

Fig. 2 $[FeNH]^+$ activating the C-H bond of CH_4. PES are calculated at T=30 K with $[FeNH]^+$ in the doublet (light gray line), quartet (gray line) and sextet (black line) states. Considering the un-coordination process (see caption in Figure 1), the overall reaction thermodynamics is +30.21, -11.68 and -2.75 kcal/mol in the doublet, quartet and sextet states, respectively. The circles are the considered calculated important MECP.

reactivity of $[FeX]^{+n}$ with X = N,O,S,P toward higher alkanes (C_2H_6, C_3H_8) and alkenes ($H_2C{=}CH_2$) as well as aromatic compounds, can be proposed[76]. For example an abundant iron compound with an interesting organic chemistry is $[FeS]^{+n}$ (its abundances have been calculated in the ejecta of SNe Ia[118] and SNe III[68,119]) determining the development of the sulfur organic chemistry such as thiols (C_nH_{2n+1}-SH)[120].

3.3 Model System II. The case of $[(CO)_2FeN]^+$: a path toward HNCO and HOCN

As reported in Section 3 and 3.2 the classes of TM-Ligand compounds where ligand L is represented by L_i = H/H_2, N/N_2, CO, H_2O (class (d) in Section 3) or organic as L_C = C_p, PAH (class (e) in Section 3) can be "mixed" resulting in organometallic TML_CL_i species often showing interesting chemical reactivities in both the homogeneous[121] and heterogeneous[122] phases. By applying the assumptions and selection rules (see Section 3.2) as developed for the $[FeN]^{+n}$ case, the general group represented by the iron organometallic compounds (FeL_CL_i) can be of chemical interest[123]. $[Fe]^+$ ions have been proposed to be the principal charge-carriers within dense clouds and the formation of Fe containing molecules such as $[FeCO]^{0/+n}$ and simple organo-compounds with the short chain abundant interstellar hydrocarbons such as C_2H_2 and C_4H_2 were suggested and analyzed in laboratory[123]. Focusing on the L_i ligands, simple and abundant molecules like CO or H_2/H producing carbonyl and hydride derivatives opening the pathway toward CO and H addition chemistry. In fact because carbon monoxide is one of the most abundant molecules in space used, for example, as reference tracer of the ISM being excited already at very low temperatures[124], simple carbonyl derivatives such as $[FeCO]^{0/+n}$[123] and $[Fe(CO)_m]^{0/+n}$ or the correlated nitrido and hydride carbonyl derivatives such as $[Fe(CO)_mN]^+$ and $[Fe(CO)_mH]^+$ can contribute to the synthesis of organo-compounds. First interest (1992) toward the $[Fe(CO)_mN]^+$ (m=1-2) and $[Fe(CO)_mH]^+$ (m=1-4) as chemical species relevant in astrochemical synthesis was shown as mentioned by Mestdagh[77,125]. Hereby the attention was focused on the 17 e^- species $[Fe(CO)_2N]^+$ resulting in the general reaction scheme (internal carbonyl addition): $[Fe(CO)_2N]^+ \rightarrow [FeCO]^+ + HNCO$ (isocyanic acid). Similarly a Mo and V nitrido organometallic compound was reported for the synthesis of cyanide *via* external addition of CO[126]. Isocyanic acid was first detected in Sgr B2 giant molecular cloud[127] with its isomer HCNO (fulminic acid) dating its discovery quite recently (2008)[128]. Furthermore the HNCO product itself has a rich following organic chemistry reacting promptly with primary amines giving carbamides through a carbamylation reaction: $HNCO + RNH_2 \rightarrow RNHC(O)NH_2$. In Figure 3 the PES calculated at 30 K, considered as an upper limit temperature within a molecular cloud is shown. Thermodynamically the reaction is strongly favored showing a nice energy down-cascade from the reactants to the products while the determining step is characterized by the transition state corresponding to the carbonyl addition (TS I). Here the first important spin crossing is placed between the reactant $[(CO)_2FeN]^+$ and TS

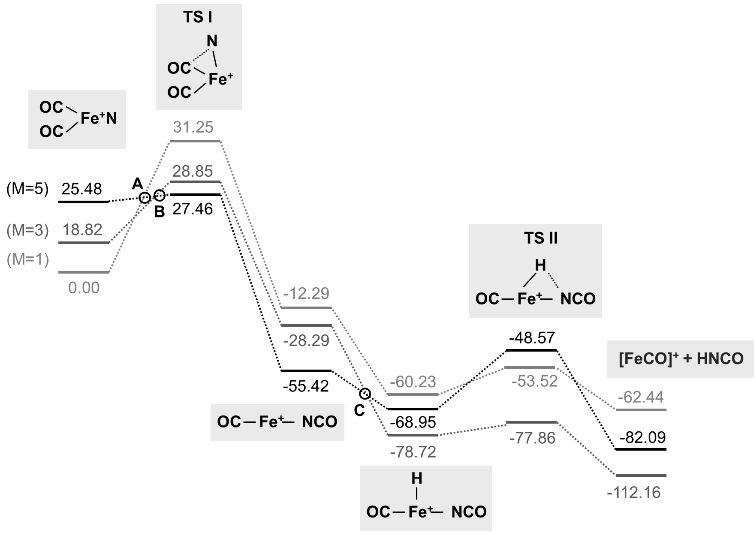

Fig. 3 Calculated CO insertion reaction path for the $[(CO)_2FeN]^+$ species. PES calculated at T=30 K with $[Fe(CO)_2N]^+$ in the singlet (light gray line), triplet (gray line) and quintet (black line) states changing to doublet, quartet and sextet states after H addition to the Fe center. The circles are the considered calculated important MECP.

I. Thanks to it, the lower singlet spin state showing an activation barrier of 31.25 kcal/mol is reduced to 27.46 kcal/mol (circle A) by crossing the quintet surface. Another hopping is placed between the triplet and quintet surfaces (circle B). Interestingly in the higher energy triplet and quintet states the TS I energy barriers are only 10.03 and 1.98 kcal/mol, respectively. The second transition state (TS II) characterizes the hydrogenation step (only when an H is captured by Fe). The lowest energy barrier lays on the triplet surface (1.16 kcal/mol), while the singlet shows a barrier of 6.71 kcal/mol and the quintet a quite high 20.48 kcal/mol. Here a second spin-crossing gives (circle C) the possibility to cross from the quintet to the singlet surfaces characterized by a very low energy barrier and the lowest thermodynamic pathway. Interestingly the final product HNCO can isomerize to HOCN (cyanic acid) by a mechanism as reported for the cation $HCNH^+$. In fact similarly to $HCNH^+$, which represents a key intermediate in ion-molecule reactions forming HNC *via* dissociative electron recombination in cold dense interstellar molecular clouds[129,130], $HNCOH^+$ can play the same role[129,130] opening a channel toward the synthesis of isocyanic and cyanic acid by an iron nitride carbonyl species. Such species can contribute to the formation of the two acids in parallel with other reactions as shown by recent gas-grain model estimating the abundances in cold and warm sources[131] of all the four isomers as isocyanic acid (HNCO), cyanic acid (HOCN), fulminic acid (HCNO) and isofulminic acid (HONC).

4 Conclusions

The aim of the present study is to propose the role held by transition metals (TM) and their related fine and rich chemistry within the astrochemistry field. The *"premissa"* is based on two main assumptions: **I)** TM cosmic abundances and **II)** TM chemical reactivity. In fact based on the actual chemical knowledge, TM contribution can be foreseen in both gas and solid state chemistry and homogeneous/heterogeneous catalysis by developing a net of chemical reactions by gas/gas and gas/dust grain interactions. To distinguish their chemistry; function of their physical state, state of aggregation and coordination sphere; TM compounds have been classified in five main groups, respectively: **a)** pure bulk and clusters; **b)** TM naked ions; **c)** TM oxides/minerals or inorganic; **d)** TM-L (L = ligand) with L = (σ and/or π)-donor/acceptor species like H/H_2, N/N_2, CO, H_2O and **e)** TM-organoligands such as C_p, PAH, R_1=•=•=R_2. Placing TM in space and correlating the actual observational data with the aforementioned proposed five groups, their reactivity is function of the temperature, radiation field (both or singly (co)-determining the important excited states) and chemical composition and consequently, dependent from the astrophysical object in which TM are localized. However even a simple analysis of the five aforementioned categories would lead to a cumbersome task. As a consequence some simple selection rules have been applied to choose the systems to be analyzed: **a)** the cosmic abundances of the elements; **b)** thermodynamic (exothermic reactions) as well as kinetic (low transition states or activation by UV/charged particles, charged and radical states); **c)** structural simplicity and **d)** specific chemistry based on the development of a HCNO organic chemistry. Following the aforementioned selection rules TM compounds showing an active HCNO chemistry are the naked TM themselves or characterized by the general formula: $[TM_mX_y]^{+n}$ with +n=total charge and X representing a second non-metallic element. To limit further the working example, the focus was applied to the chemistry of the iron nitride compounds $[FeN]^+$, $[FeNH]^+$ and the related carbonyl derivate $[(CO)_2FeN]^+$ able to perform C-C and C-H bond activations resulting in organic C-N compounds. Theoretical calculations have been conducted on three main model reactions: $[FeN]^+ + CH_4 + H \rightarrow [Fe]^+ + H_3C\text{-}NH_2$, $[FeNH]^+ + CH_4 \rightarrow [Fe]^+ + H_3C\text{-}NH_2$ and $[Fe(CO)_2N]^+ \rightarrow [FeCO]^+ + HNCO$. In all three cases the intersection between the different free energy surfaces (spin crossing) calculated at different spin states helps the reaction to follow a minimal energy path. The reactions products such as methylamine and isocyanic acid can further determine a rich following organic chemistry with methylamine being a possible precursor of the simplest aminoacid glycine while isocyanic acid can react with primary amines through a carbamylation reaction: $HNCO + RNH_2 \rightarrow RNHC(O)NH_2$. In general when 3^{rd} row TM as Fe, Co and Ni are involved in the reaction, the spin crossing phenomenon is expected to play a major role ”minimizing” the synthetic pathway toward the resulting products. The simplicity of the model chemistry based only on Fe nitrido compounds suggests the enormous potential that such new chemical actors may introduce to the astrochemistry field. Obviously there is still a long way to the top before the effects and contributions of TM to space chemistry are unraveled. For example other important metals such as Co and Ni (together with Fe are the main metallic element products from supernova outbursts) and non-metallic elements such as S can introduce an ulterior sophisticated chemistry. Most importantly the real amount of $[FeN]^{+1}$, $[Fe(CO)_2N]^+$ or $[TM\text{-}X]^{+n}$ and $[TM(CO)_mX]^{+n}$ with X=O,N,P,S produced in the ejecta of supernovae or late type stars must be calculated as well as it must be understood their partition in the gas and solid state phases by condensation models functional of the astrophysical object considered. From the chemical point of view excited states seem to be important as irradiation is one of the main physical phenomena able to overcome the energy barriers involved in the transition states, while from the experimental point of view, at the best of my knowledge, no experiments have been conducted to check the effect of transition metals by irradiating a TM ”dirty ice”. Once amount, physical state, chemical character and reactivity of the TM compounds are better understood, their chemistry can be added to the already complex network models developed to understand the complex physical-chemistry of the gas/grain interactions. Finalizing, the preamble is promising and TM *fine chemistry* have a high probability to add their contribution to the known synthesis of organic compounds opening a new perspective in the astrochemistry field whose qualitative (type of compounds determined by the coordination sphere affecting the reactivity and selectivity) and quantitative contribution must be unraveled.

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Graphical Abstract

Astrochemistry by transition metals? The selected cases of $[FeN]^+$, $[FeNH]^+$ and $[(CO)_2FeN]^+$: pathways toward CH_3NH_2 and HNCO

Marco Fioroni

Transition metals are proposed to play an active role in the synthesis of organic compounds containing heteroatoms in astrochemistry.