Interspin Crossing and Reactivity

Dietmar A. Plattner*

The discussion of reaction mechanisms and pathways is usually based on a single potential energy surface: starting from the reactant minimum the reactive system moves through a transition state and proceeds further to intermediates and/or product minima. Although this concept represents only one aspect of chemical reactivity, it has proven to be a useful tool in rationalizing the greater part of reactions. The success of this concept and its justification, especially in organic chemistry, lies in the fact that organic species generally possess low-spin ground states, and their reactions proceed on a single energy surface (single-state reactivity). Nevertheless, the simple example of the stability of many organic compounds with regard to ground-state triplet O_2 should always remind us of the important consequences of spin states on reactivity. Reactions that involve a change in the spin state and thus occur on two or more potential energy surfaces (and are therefore nonadiabatic processes[1]) have received much attention in recent years. A number of reactions in organic, inorganic, and organometallic chemistry, in which two states of different multiplicities determine the minimum-energy reaction pathway (two-state reactivity), have been confirmed by experimental and computational studies, and it is the aim of the present article to highlight those efforts.

Gas-phase ion chemistry provides a powerful tool for the study of intermediates that are too reactive for a solution-phase characterization. Moreover, information about the intrinsic reactivity of the molecule or reactive system in question is obtained in the gas phase, unperturbed by effects of solvents or aggregation phenomena. Recently, two experimental gas-phase studies have confirmed the possibility of a spin-forbidden proton-transfer reaction, that is, a protonation during which a spin change occurs. The first reaction under consideration is the protonation of F^- by HNO [Eq. (a)][2]).

$$F^- + {}^1(HNO) \rightleftharpoons [FHNO]^- \rightleftharpoons HF + {}^3(NO^-) \qquad (a)$$

The energetics of the ground-state reaction, that is, the reaction with ^{1}HNO, are known from the heats of formation of the ions and molecules (Figure 1). The reaction is exothermic by 8 kcal mol^{-1} and leads to $^3(NO^-)$, since $^1(NO^-)$ is not a bound state. In the study of Brauman and co-workers, the nature of the intermediate complex $[FHNO]^-$ and its reactivity were addressed. $[FHNO]^-$ was synthesized by the reaction of F^- with neopentyl nitrite and then treated with a variety of neutral molecules. The reaction products were monitored in a Fourier transform mass spectrometer. Reactions with alcohols and HCN give F^- transfer, which indicates the structure of the complex is $F^- \cdot HNO$. On the other hand, reaction with NO gives N_2O_2, and the reactions with SF_6, O_2, and SO_2 lead to electron and/or HF transfer as would be expected for the triplet $FH \cdot {}^3(NO)^-$. This dual reactivity is attributed to efficient spin change. The structure of the intermediate complex was assigned by electron photodetachment in an ICR spectrometer. The spectrum shows an onset at about 29 kcal mol^{-1}, which indicates the structure of $[FHNO]^-$ to be $FH \cdot {}^3(NO)^-$ as opposed to $F^- \cdot HNO$. This result is also consistent with high-level ab initio calculations. The calculations show $FH \cdot {}^3(NO)^-$ to be 5 kcal mol^{-1} more stable, with the singlet and triplet curves crossing about 3 kcal mol^{-1} above the singlet minimum. The energy required to reach the curve crossing region is quite low, and—according to the calculations—binding of an alcohol molecule brings the energy of the singlet surface below that of the triplet, which seems to facilitate the spin change in this system.

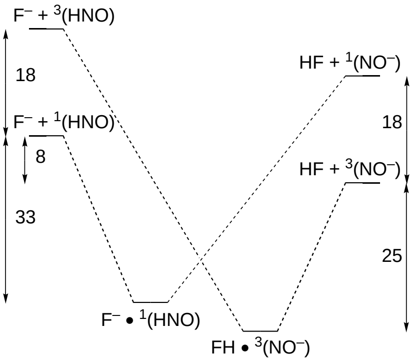

Figure 1. Schematic potential energy diagram for reaction (a). The relative energies are given in kcal mol^{-1}.

An example of an organic conjugate acid–base pair with different spin multiplicities was studied by Hu, Hill, and Squires.[3] They synthesized a so-called distonic[4] carbene ion, that is, a species where the charged and the carbenic moieties are formally separate, in a flowing afterglow-triple-quadrupole apparatus by the reaction sequence shown in Scheme 1. The chemical reactivity of the (3-oxyphenyl)methylene anion **1** is indicative of a singlet ground state: the ion reacts with NO_2 to yield the 3-oxybenzaldehyde anion, abstracts sulfur from CS_2 and COS, and undergoes cycloadditions with electron-deficient olefins. Calculations at the B3LYP/cc-pVTZ level also predict a singlet ground state for **1**, with the lowest triplet 3 kcal mol^{-1} higher in energy, but a triplet ground state for the conjugate acid **2** with a singlet–triplet gap of 6.4 kcal mol^{-1} (the protonation at the oxygen atom is kinetically favored with respect to carbon protonation to give **3**). The proton affinity of **1** was determined experimentally by collision induced dissociation (CID) of clusters with different phenols to be 343.0 ± 0.5 kcal mol^{-1}, which is in excellent

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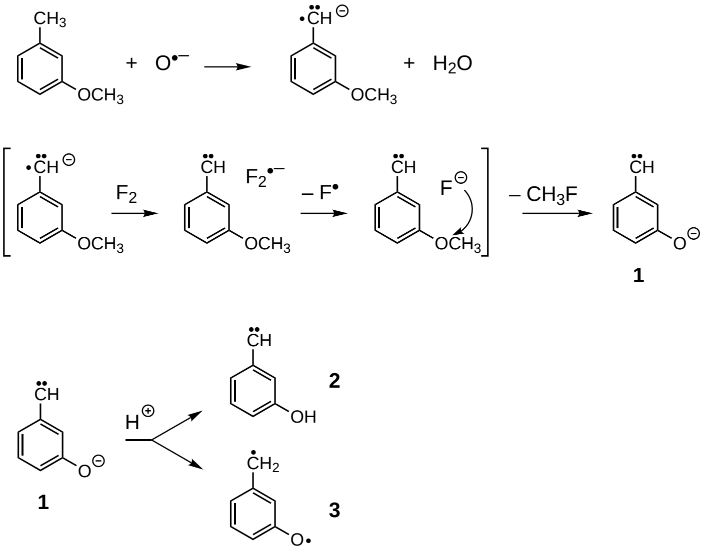
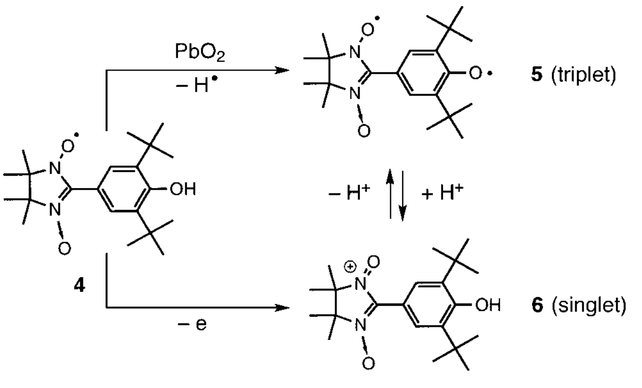
[*] Dr. D. A. Plattner
Laboratorium für Organische Chemie der
Eidgenössischen Technischen Hochschule (ETH) Zürich
Universitätstrasse 16, CH-8092 Zürich (Switzerland)
Fax: (+41) 1-632-1280
E-mail: plattner@org.chem.ethz.ch



Scheme 1. Synthesis of the distonic carbene ion **1** and the subsequent protonated products as an example of an organic acid–base pair with interspin crossing.

agreement with the calculated value for a S→T proton transfer. These results suggest that the spin barrier for the proton transfer in the cluster of **1** with the phenol must be small and that intersystem crossing is an efficient process.

Another example of an organic acid–base pair with different spin multiplicities was recently described by Sawaki et al.[5] The cross-conjugated phenoxyl-nitronyl nitroxide biradical **5,** prepared by PbO_2 oxidation of the corresponding phenol-substituted radical **4** (Scheme 2), has a triplet ground state according to ESR spectroscopy. Upon protonation the closed-shell cation **6** is formed, which can also be prepared independently by one-electron oxidation of **4**. Thus, the spin state of the system can be controlled by altering the pH of the solution. This observation may lead to applications as pH sensors that respond to changes in magnetic properties.



Scheme 2. Another example of an organic acid–base pair with interspin crossing.

From recent experimental and computational studies, two-state reactivity also accounts for the notorious elusiveness of C_2O_2 (ethylenedione).[6] Singlet C_2O_2 is of course a classic example of an unbound species, a consequence of the extraordinary large singlet–triplet gap of CO (139.1 kcal mol^{-1}[7]). Ab initio calculations predict triplet C_2O_2 ($^3\Sigma_g^-$) to be thermochemically stable with respect to the spin-allowed dissociation into CO ($^1\Sigma_g^+$) and CO ($^3\Pi$) (Figure 2).[8, 9] A "complete" mass spectrometric study was performed to elucidate the stability of triplet C_2O_2:[8] all possible neutralization–reionization and charge-reversal experiments were conducted starting from $C_2O_2^{\bullet +}$ and $C_2O_2^{\bullet -}$, respectively. In no case was it possible to obtain a recovery signal in a neutralization–reionization experiment. On the other hand, charge reversal is quite an efficient process in this experimental setup. The energetics of the charge-reversal experiment suggest that the appearance of the recovery signal is a result of a double electron transfer in a single collision (with Xe) and rule out a two-step mechanism. Stepwise electron transfer, however, would be expected to be observed if the neutral C_2O_2 molecule were to have a lifetime above 30 ns. The successful charge-reversal experiments also rule out Franck–Condon effects as the reason for the failure to observe neutral C_2O_2. These results suggest that triplet ethylenedione is an intrinsically unstable molecule. The mechanism proposed to account for the short lifetime of C_2O_2 is outlined in Figure 2: the bound triplet state proceeds via efficient curve crossing from the triplet to the singlet surface followed by fast dissociation. Support for this view comes from the location of the minimum-energy crossing point (MECP) of the two surfaces and the calculation at the MP2/cc-pVDZ level of theory of the magnitude of the spin-orbit coupling element H_{SO} at the MECP. The structure of the MECP is fairly close to that of the triplet minimum, and its energy is only about 3 kcal mol^{-1} above the triplet minimum (Figure 2).[10] The low-lying MECP is mainly responsible for the very short lifetime of triplet C_2O_2, which is estimated to be in the low nanosecond regime.

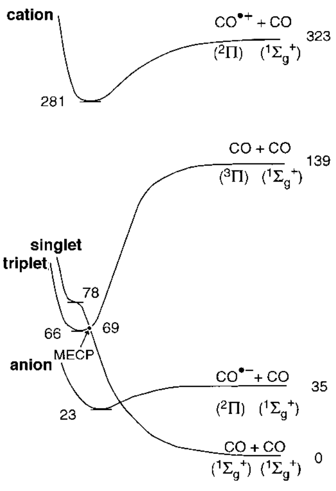


Figure 2. Schematic representation of the potential energy surfaces of the cationic, neutral, and anionic states of C_2O_2. The energies shown [kcal mol^{-1}] were obtained from calculations at the CCSD(T) level of theory.

A similar combined experimental/theoretical approach was taken by the Schwarz group to establish the mechanism of the unimolecular decay of the triplet methoxy cation.[11] Two pathways have so far been proposed in the literature: a) a stepwise reaction, namely a hydrogen shift concurrent with spin change to form $^1(CH_2OH^+)$, which then eliminates H_2 [Eq. (b)];[12] and b) a concerted pathway that involves simultaneous spin change and [1,1] elimination of H_2 from $^3(CH_3O^+)$ [Eq. (c)].[13] The kinetic isotope effect observed in

$$^3(CH_3O^+) \rightarrow {}^1(CH_2OH^+) \rightarrow {}^1(HCO^+) + H_2 \qquad (b)$$

$$^3(CH_3O^+) \rightarrow {}^1(HCO^+) + H_2 \qquad (c)$$

the MS experiments for the decay of $^3(CH_2DO^+)$ is not consistent with a stepwise mechanism. Instead, the $[H_2]/[HD]/[D_2]$ branching ratio is indicative of the concerted pathway. The calculated location of both MECPs and the calculation of the spin–orbit coupling constant H_{SO} for both reactions indicate that the concerted mechanism is somewhat favored over the stepwise pathway.

The importance of spin state for the reactivity of organometallic compounds has been the subject of controversy for a long time, but it has only recently become feasible to study this problem quantitatively. It has long been recognized that different coordinatively unsaturated organometallic fragments display highly variable reactivities. For example, pulsed UV photolysis of $[Fe(CO)_5]$ leads to the formation of the unsaturated species $[Fe(CO)_x]$ ($x = 2-4$), which show quite different reactivities in the recombination reaction with CO.[14, 15] While the reactions of $[Fe(CO)_2]$ and $[Fe(CO)_3]$ with CO proceed at near gas kinetic rates, the reaction of $[Fe(CO)_4]$ is about three orders of magnitude slower, with an activation energy of about 2.5 kcal mol^{-1}.[15] This unexpected behavior was explained by the spin change in the reaction since ground-state $[Fe(CO)_4]$ is high spin (triplet[16]), whereas ground-state $[Fe(CO)_5]$ is low spin. Significant spin changes also occur in the sequential addition of CO to Mn^+ to form $[Mn(CO)_6]^+$, and the CO exchange rates of the unsaturated fragments were discussed in terms of the requirements for spin conservation in ligand exchange reactions.[17, 18]

While "spin-blocking" in typical organometallic two-electron reactions has often been claimed to explain unusual reactivity (for a recent example see ref. [19]), no barrier has been observed in ligand-binding reactions that convert 16e ground-state triplet complexes to diamagnetic 18e singlet products.[20, 21] Speculation regarding the spin-forbiddenness of certain organometallic reactions remains difficult to justify without benefit of reliable information on the exact value of the energy difference between the ground and lowest excited state and the energy required to reach the curve crossing point(s). Recently, the significance of two-state reactivity for organometallic reactions was addressed quantitatively. During the last decade, the dependence of reactivity of bare transition metal cations on the spin state has been demonstrated in a series of cleverly devised experiments.[22, 23] For example, Fe^+ in the quartet excited state (^4F) is about 70 times more reactive than the sextet ground state (^6D) in the reaction with H_2. It is no exaggeration to claim that in atomic transition metal ion chemistry each electronic state is potentially a different chemical.

The state-specific reactivity of metal–oxo complexes has received much attention recently. At the beginning of this development is the finding that OsO^+ and FeO^+ can activate CH_4, a process of utmost importance for the functionalization of hydrocarbons.[24–27] Subsequently, the reaction of FeO^+ with H_2 was studied and was found to have a surprisingly low efficiency. Although an exothermic, spin-allowed process, the reaction is very inefficient and occurs only once in every 100–1000 collisions.[28, 29] This unexpected behavior stimulated a series of experimental and computational studies directed at the elucidation of the electronic structures and gas-phase reactivities of late, first-row transition metal oxide cations MO^+ (M = Mn, Fe, Co, Ni, Cu).[30–34] Two recent computational studies have proven the validity of the two-state reactivity scheme for metal–oxo cations. Danovich and Shaik calculated the amount of spin–orbit coupling along the pathway for the reaction $FeO^+ + H_2 \rightarrow Fe^+ + H_2O$.[33] The low-energy path involves two spin-inversion junctions between the sextet and quartet series: one near the FeO^+/H_2 cluster at the entrance channel, and one near the Fe^+/H_2O cluster at the exit channel. The spin–orbit coupling matrix elements are relatively large at the entrance channel, and they decrease steadily along the insertion pathway, going to nearly zero at the exit channel between the ^6D ground state and the ^4F excited state. The overall reaction efficiency is found to be limited by the spin–orbit coupling at the spin-inversion junctions, which is in good agreement with the experimental data by Schwarz and Armentrout.[28, 29] A similar picture has been derived from hybrid Hartree–Fock/density functional calculations (B3LYP) on the system $MO^+ + CH_4$ (M = Fe, Mn, Co).[34] In the case of FeO^+ and CoO^+, a low-energy reaction pathway is opened by a crossing of the sextet and quartet surfaces at the entrance channel, that is, between the reactant complex $OM^+(CH_4)$ and the transition state of the insertion step (Figure 3). It is important to note that $HO{-}M^+{-}CH_3$ is not formed by a mechanism that involves direct hydrogen abstraction by MO^+, but that CH_4 is activated through the simultaneous formation of M–C as well as M–H bonds. Another crossing occurs in the exit channel when $M^+(CH_3OH)$ dissociates. The situation is different for MnO^+, where only one surface crossing occurs in the exit channel between the high-spin septet and the low-spin quintet surface. The energies obtained for the transition states compare very well with experimentally reported reaction efficiencies and product branching ratios, which thus suggests that two-state reactivity is indeed operative in these reactions.

The two-state reactivity paradigm was recently applied to the hydroxylation of alkanes by cytochrome P-450.[35] The detailed mechanism of alkane hydroxylation by cytochro-

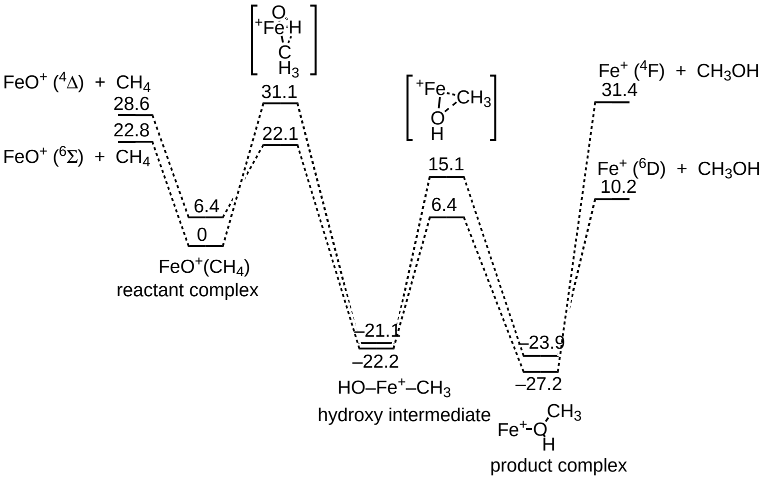


Figure 3. Schematic potential energy diagram for the reaction $FeO^+ + CH_4 \rightarrow Fe^+ + CH_3OH$ in the sextet and quartet states. Relative energies are given in kcal mol^{-1}.

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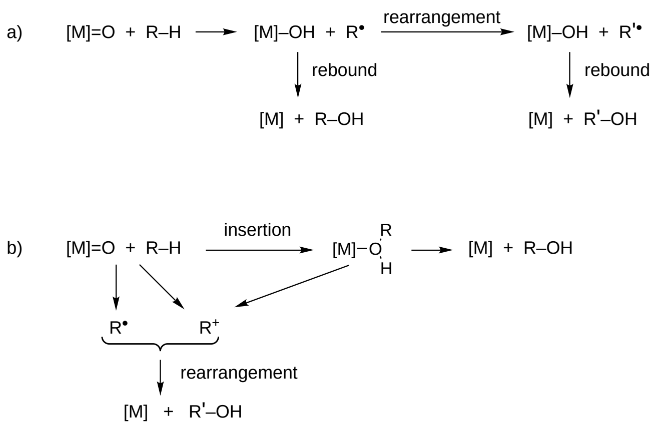
me P-450 is still the subject of much debate, which has been further stimulated by the recent experiments by Newcomb and co-workers[36] (Scheme 3): the rebound mechanism (Scheme 3 a), which involves the formation of alkyl radicals, is not entirely consistent with the lifetimes of the putative radical intermediates. Newcomb has therefore suggested a concerted oxene-insertion mechanism where the occurrence of radicals and carbocations is the result of a minor pathway (Scheme 3 b). The problem with the latter mechanism is that the ferryl complex (bare FeO^+ as well as the FeO moiety in the active form of cytochrome P-450) has a high-spin ground state that does not react with C–H or C–C bonds in a concerted manner,[37] but favors stepwise reactions such as hydrogen abstraction. The low-spin state, on the other hand, is prone to concerted mechanisms with only a low barrier to the insertion product $R{-}Fe^+{-}OH$, which, in addition, is also more stable than the high-spin analogue. However, initial excitation is not necessary in order to switch to the low-spin surface. Two-state reactivity will be operative if spin inversion occurs on the way to the intermediate, and the reaction efficiency is then determined by the probability of spin inversion at the crossing junction. The amount of concerted versus radical mechanism in this mechanistic scheme is simply modulated by the spin-inversion probability.



Scheme 3. a) The rebound mechanism for alkane hydroxylation by cytochrome P-450; b) the concerted oxene-insertion mechanism proposed by Newcomb and co-workers.

Two-state reactivity is a governing factor in many reactions when the adjacency of excited-state surfaces makes it necessary to expand the single-surface representation. The transition probability between the surfaces of different multiplicities is of the same fundamental importance as are transition structures, their entropic requirements, and the associated barrier heights in the classical kinetic model. In the future, new experimental examples of two-state reactivity will undoubtedly emerge, which will highlight the need for a deeper understanding and more precise calculations of spin-inversion probabilities in polyatomic molecules in order to establish this concept alongside the classical reactivity paradigms.

German version: *Angew. Chem.* **1999**, *111*, 86–90

Keywords: gas-phase chemistry · ion chemistry · mass spectrometry · spin-forbidden reactions

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[37] The comparison of the MO diagram for FeO^+ with the elecronic configuration of the triplet ground state of O_2 reveals that both molecules exhibit a similar bonding situation (see ref. [31]). Ground-state triplet oxygen reacts with closed-shell molecules through radical mechanisms, whereas the first excited state $^1\Delta_g$ readily undergoes concerted reactions such as cycloadditions.

Parent Substances of Inorganic Chemistry: Homoleptic Pnictogenyl Compounds of Group 14, $E(ZR_2)_4$

Norbert W. Mitzel*

A new parent substance of inorganic nonmetal chemistry has been prepared and structurally characterized: the simplest compound containing a SiP_4 unit, tetraphosphanylsilane, $Si(PH_2)_4$.[1] Driess and Monsé achieved the synthesis of this compound by treating lithium tetraphosphanylalanate, $Li[Al(PH_2)_4]$, with $SiCl_4$; Boese and Bläser have grown a single crystal at low temperatures and determined its structure (Figure 1). Thus, $Si(PH_2)_4$ is the first example of the successful synthesis of an $E(ZH_2)_4$ compound (E = C, Si, Ge, Sn, Pb; Z = N, P, As, Sb, Bi), that is an EZ_4 fragment without organic substituents. $Ge(PH_2)_4$ was also prepared, but was so far only detected by means of GC/MS analysis. The simplest representative of an Si–P compound, H_3SiPH_2, had already been prepared in 1955 by G. Fritz,[2] while $HSi(PH_2)_3$ was described in 1968.[3]

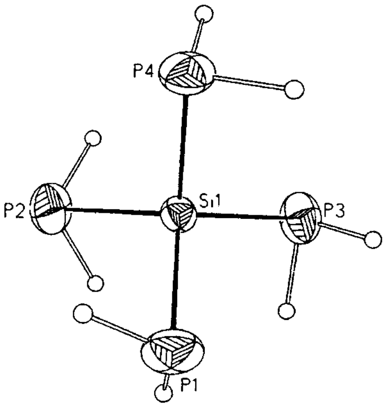

Figure 1. Molecular structure of $Si(PH_2)_4$.

The synthesis of compounds without organic substituents is of importance because their existence allows conclusions to be drawn regarding the inherent stability of the core structure and allows an assessment of the influence of the stabilization by more or less space-filling organic substituents, which is important for the synthesis of derivatives. Moreover, since in most cases direct comparisons with the results of high-level quantum chemical calculations is only possible for the simplest unsubstituted systems, such studies serve to confirm theoretical methods and allow for their further development.

Recently the research on $E(ZR_2)_4$ compounds was intensified. On the one hand, attempts were made to apply such compounds as precursors for new IV/V materials, on the other to provide representative objects for structural studies. The presence of four donor centers in these molecules makes them attractive as ligands for complex chemistry and for the design of supramolecular aggregates.

Many compounds of the type $E(ZR_2)_4$ are unknown. Despite numerous attempts, no synthetic pathway to a neutral compound $C(PR_2)_4$ has been found. The same applies for analogous compounds of arsenic, antimony, and bismuth. Some silicon phosphanides have been prepared, for example, tetrakis(*tert*-butyl)-1,2,4,5-tetraphosphasilaspiro[2.2]pentane.[4] Compounds with $SiAs_4$, $SiSb_4$, and $SiBi_4$ units, however, have not been documented so far. $Sn(SbPh_2)_4$ is known as an example from tin chemistry.[5]

The only class of compounds with numerous members in this context are the element amides, while compounds containing CN_4 units are rare, but of actual interest. Plenty

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[*] Dr. N. W. Mitzel
Anorganisch-chemisches Institut der
Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Fax: (+49) 89-289-13125
E-mail: n.mitzel@lrz.tum.de

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