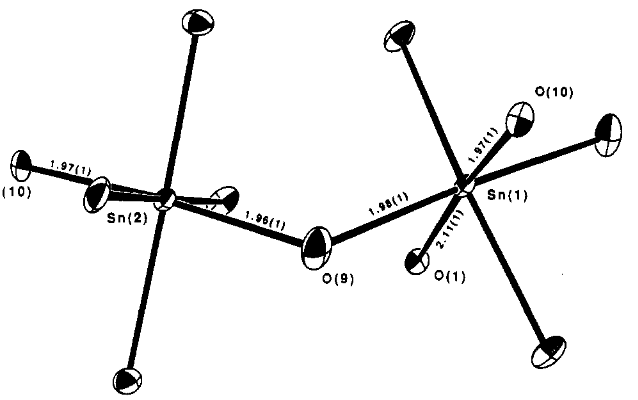

Figure 2. Sn coordination environment in the $KSnOPO_4$ asymmetric unit.

the same radius. The cation–framework interaction is therefore very similar to that seen in KTP, in which coordination numbers of 8 and 9 for K(1) and K(2), respectively, are also seen.

Unlike the case of KTP, the bridging Sn–O distances are nearly identical, and no short Sn–O bonds exist (Figure 2). Some degree of asymmetry in the Sn coordination environment exists, however, and it is evident that $KSnOPO_4$ adopts the less distorted MO_6 coordination environment typified in the compound $KGaPO_4F_{0.7}(OH)_{0.3}$, rather than crystallizing in a centric modification of the KTP structure such as the high-temperature $TlTiOPO_4$ phase.

Optical Properties. The SHG intensity of $KSnOPO_4$ powder from flux is less than that of quartz, though the presence of spurious light induced by laser damage precluded precise measurement, even at low power levels. The powder samples obtained from hydrogels, however, were not damaged even at moderate powder levels. These samples yielded SHG intensities of approximately half that of quartz ($\approx 10^{-4} \times$ KTP's intensity). This result reveals the presence of nonzero $\mathbf{d}_{ijk}$ tensor coefficients in $KSnOPO_4$, which indicates our selection of the acentric starting model during structure refinement is justified.

The UV spectrum of $KSnOPO_4$ shows an absorption edge at 225 nm, corresponding to a ligand-to-metal charge-transfer (LMCT) transition with an E_g of 5.5 eV. In contrast, KTP's absorption edge lies at 350 nm or 3.5 eV. The difference in band gap is due to the presence in KTP of empty 3d orbitals of e_g symmetry into which ligand-to-metal charge transfer may occur. In $KSnOPO_4$, all of the 4d orbitals are filled, and the charge-transfer band consists mainly of 5d orbital character.

Discussion

In the octahedral MO_6 unit, such as that found in KTP isostructures, oxygen $p\pi$ and metal $d\pi$ orbitals mix to form bonding, nonbonding, and antibonding orbitals of g, u, and g symmetries, respectively. The existence of long–short metal–oxygen bonding in KTP can be understood as a stabilization of a distorted ground state formed by mixing orbitals of g and u symmetries. This mixing results in incorporation of a certain amount of charge-transfer excited-state character into the valence-bond orbitals, the amount of which is defined by the mixing coefficients, which are influenced by the magnitudes of E_g and of the overlap integrals. These mixing coefficients determine not only the degree of distortion but the molecular hyperpolarizability β_{ijk} of the MO_6 unit as well.[13,14] On substitution of a d^{10} species, the metal $d\pi$ (e_g) orbitals are filled. Thus, the ground-state orbitals can now mix only with the excited-state metal $d\pi$ orbitals of the next highest quantum number (5d, in the case of $KSnOPO_4$).[4] The band gap energy is increased, and the degree of mixing and thus the charge-transfer character in the ground state are reduced. Less stabilization of the ground state is thus attained on distortion. Consequently, all Sn–O bonds are nearly of the same length, and contribution of the MO_6 unit to $\chi^{(2)}_{ijk}$ is drastically reduced.

In the compound $KSnOPO_4$, all of these predictions of the effects of d^{10} metal ion substitution are realized. The band gap energy E_g is increased, reducing the mixing coefficient between the ground and excited states. As a direct result, the stabilization attained on asymmetric distortion is less, and the Sn–O bonding is much more regular than it is in KTP. Furthermore, the increased band gap results in diminished mixing of excited-state character in the ground-state SnO_6 bonding orbitals, and the optical nonlinearity of the medium is sharply attenuated.

Note Added in Review. Voronkova and Yanovskii have recently reported an anomaly in the dielectric susceptibility of $KSnOPO_4$ between 900 and 1000 °C, which can be explained by a second-order ferroelectric-to-paraelectric phase transition with a Curie temperature between 1040 and 1100 °C.[15] The ferroelectric behavior of $KSnOPO_4$ is further evidence that this compound crystallizes in the acentric space group $Pna2_1$, and not in either $Pnam$ or $Pnan$.

Acknowledgment. This work was supported by the National Science Foundation. We also thank a reviewer for helpful suggestions concerning the structure refinement.

Supplementary Material Available: Listings of anisotropic thermal parameters and all bond distances within 3.3 Å (2 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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Isocyanocobalt(III) Species: Identification of the Elusive $[(NH_3)_5Co-NC]^{2+}$ Ion

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Cyanide ion binds metal ions through its carbon atom almost without exception.[1] Binding through nitrogen is rarer, but nonetheless well-established—for the bridging mode (where it is essentially enforced)[2,3] and for the terminally bound NC^-.[4] The latter isocyano ions can be synthesized by kinetic routes for the inert transition-metal ions by using CN^- blocked at carbon with, for example, H^+,[6] BR_3 and BH_3 in particular,[6-8] and Ag^+.[4] They can also be prepared in favorable cases by inner-sphere electron transfer with CN^- bridge transferral.[5]

The C- and N-bonded linkage isomers for pentacyanocobalt(III),[9] pentaaquachromium(III),[5] and pentaammineruthenium(II)[6] have been described. Of these, the N-bonded CN^- mode seems secure for Cr(III)[5] and Ru(II),[6] but there is controversy for the Co(III) system.[9,10] This note is concerned with the stability and lability of cyanide N-bonded to cobalt(III).

The existence of the transient $[(CN)_5Co-NC]^{3-}$ ion was originally reported for the $[(CN)_5)Co]^{2-}$ ion reduction of

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$[(NH_3)_5Co–CN]^{2+}$, which yields ultimately $[(CN)_5Co–CN]^{3-}$ and Co(II).[9] The observed rate law and the observation of CN^- bridge transfer establish inner-sphere electron transfer, but the apparent observation[9] of the putative $[(CN)_5Co–NC]^{3-}$ ion en route to $[(CN)_5Co–CN]^{3-}$ could not be reproduced.[10] It has been suggested that the ion is formed but the isomerization of the isocyano ion to the C-bonded form is catalyzed by an inner-sphere electron-transfer process involving $[(CN)_6Co]^{4-}$.[10]

Both *trans*-$[(dmg)_2(OH_2)Co–NC]$ and *trans*-$[(dmg)_2(OH_2)$-$Co–CN]$ have been characterized by single-crystal X-ray structures.[4] The difficulty of distinguishing C from N by the X-ray diffraction technique coupled with the report that they are isomorphous with very similar structural parameters renders this work dubious; however the isomers are distinguished by IR spectroscopy in solution. At least in the solid state, the isocyano to cyano isomerization does not appear to be extremely rapid, although the conversion has been observed.[4]

Results and Discussion

We have attempted to generate the previously unknown isocyano $[(NH_3)_5Co–NC]^{2+}$ ion by selenium extrusion reactions from $[(NH_3)_5Co–NCSe]^{2+}$. In Me_2SO, triphenylphosphine reacts rapidly with the N-bonded[11,12] selenocyanate complex to give a yellow solution characteristic of CN^- bonded to Co(III). The same reagent did not react with the O and S analogues $[(NH_3)_5Co–NCO]^{2+}$ [13] and $[(NH_3)_5Co–NCS]^{2+}$,[14] nor the Se-bonded[11] linkage isomer $[(NH_3)_5Co–SeCN]^{2+}$. These observations suggested a reaction involving preferred attack at the remote Se center:

$$[(NH_3)_5Co–NCSe]^{2+} \xrightarrow[P(C_6H_5)_3]{Me_2SO} [(NH_3)_5Co–NC]^{2+} + (C_6H_5)_3P–Se$$

The formation of $(C_6H_5)_3PSe$ as the only phosphorus-containing species was established by ^{31}P and ^{77}Se NMR spectroscopy. However the ^1H, ^{59}Co, and ^{13}C NMR spectra indicated the presence of several Co(III) products. Ion-exchange chromatography revealed the regular C-bonded CN^- species $[(NH_3)_5Co–CN]^{2+}$ as the only 2+ ion, as shown by its visible[10,15] and ^1H[16] and ^{13}C NMR spectra. Interestingly, this was the minor product, and apart from a little $[Co(NH_3)_6]^{3+}$, two more highly charged ions (≥4+) were removed from the column and crystallized. These appear to be isomeric cyanide-bridged complexes, with one fragment being a pentaamminecobalt(III) species and the other a cyanotetraamminecobalt(III) moiety, with the terminal CN^- cis or trans to the CN^- bridge (*cis*-$[(NH_3)_5Co–CN–Co(NH_3)_4(CN)]^{4+}$ and an isomeric $[(NH_3)_5Co–NC–Co(NH_3)_4(CN)]^{4+}$ mixture). The nonbridging cyanide ions appear to be C-bonded. These conclusions come from a comparison of the FT-IR and ^1H and ^{13}C NMR spectra for Me_2SO solutions with those for the monomeric $[(NH_3)_5Co–CN]^{2+}$ and dimeric $[(NH_3)_5Co–CN–Co(NH_3)_5]^{5+}$ standards (Table I).

The multiplicity of products suggests scrambling caused by the presence of trace Co(II), perhaps generated by the triphenylphosphine and facilitated by the CN^- ion, i.e., electron-transfer-mediated scrambling, which is typical Co(III)/Co(II)/CN^- chemistry.[17]

We therefore moved to another and hopefully less reducing selenium-extruding reagent, namely the CN^- ion itself. The reaction with $[(NH_3)_5Co–NCSe]^{2+}$ was strikingly rapid and remarkably clean. By using approximately the stoichiometric amount of KCN in Me_2SO solution, we observed only starting material and $[(NH_3)_5Co–CN]^{2+}$ by either ^1H (Figure 1) or ^{13}C NMR spectroscopy. The other product was of course free $SeCN^-$ ion, observed in both the ^{13}C and ^{77}Se NMR spectra, and it remained to discover whether in fact the CN^- ion had attacked

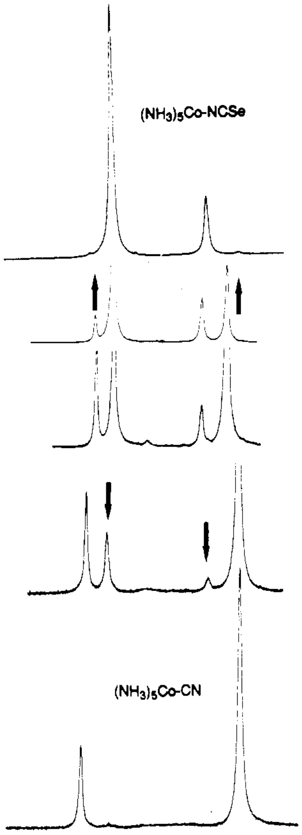

Figure 1. ^1H NMR spectra for the reaction between $[(NH_3)_5Co–NCSe]^{2+}$ and CN^- in Me_2SO-d_6 at 25 °C.

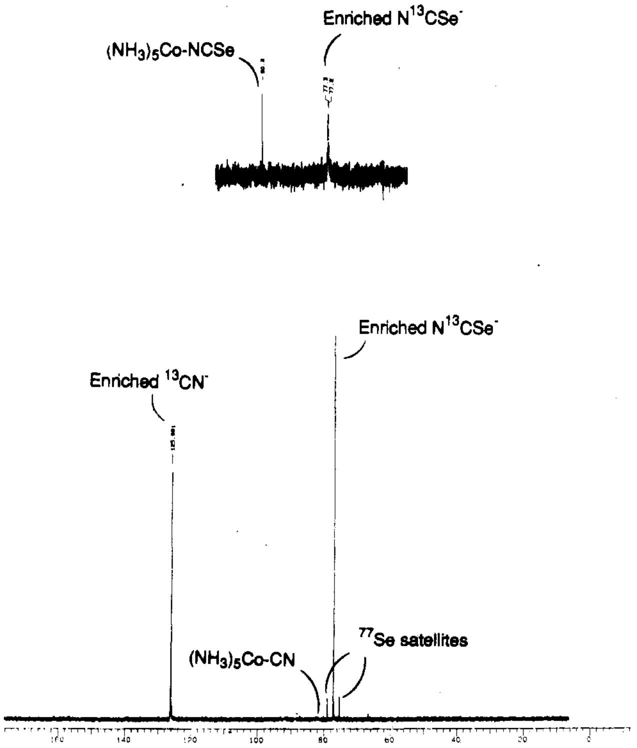

Figure 2. ^{13}C NMR spectra showing the uptake of ^{13}C from $^{13}CN^-$ into the bound $NCSe^-$ of $[(NH_3)_5Co–NCSe]^{2+}$ with release of $N^{13}CSe^-$ and formation of unenriched $[(NH_3)_5Co–CN]^{2+}$ in Me_2SO at 25 °C. The upper spectrum represents only about 5% reaction, while the lower is for complete reaction and it shows the residual $^{13}CN^-$.

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Table I. ^{1}H, ^{13}C, ^{77}Se, and ^{31}P NMR and FT-IR Spectral Data for $[(NH_3)_5CoX]^{n+}$ Complexes and Free Ligands

complex	NMR: δ (Me_2SO-d_6)					FT-IR (Me_2SO) ν^e
	$^{13}C^a$	$^1H^b$		$^{77}Se^c$	$^{31}P^d$	
$[(NH_3)_5Co{-}CN]^{2+}$	82.91	2.92	3.76			2132 (mw)
$[(NH_3)_5Co{-}NC]^{2+}$		3.66	3.17			
$[(NH_3)_5Co{-}Co{-}NCSe]^{2+}$	90.28 (J_{Se-C} = 284 Hz)	3.65	3.07	−1529.6		2115 (s)
$[(NH_3)_5Co{-}NH_3]^{3+}$		3.22	3.22			
$[(NH_3)_5Co{-}CN{-}Co(NH_3)_5]^{5+}$	104.10	3.57	3.23			2209 (m)
		2.94	3.85			
cis-$[(NH_3)_5Co{-}CN{-}Co(NH_3)CN]^{4+}$	105.95	3.58 (12)	3.22 (3)			2200 (m)
	80.66	3.54 (3)	2.56 (6)			2135 (mw)
			3.40 (3)			
$[(NH_3)_5Co{-}NC{-}Co(NH_3)_5(CN)]^{4+}$	105.00	3.59[f]	3.52			2194 (m)
(mixture)	78.6, 77.6	3.24	3.18			2137 (mw)
	114.1	3.17	3.09			
CN^-	126.75					2154 (w, br)
$SeCN^-$	77.17 (J_{Se-C} = 270 Hz)			−1570.1		2057 (w)
						2063 (s)
$P(C_6H_5)_3$					0 (ref)	
$(C_6H_5)_3PSe$					41.73 (J_{PSe} = 722 Hz)	

[a] ppm downfield from central Me_2SO-d_6 peak (39.37 ppm relative to TMS). [b] ppm downfield from TMS; except where noted otherwise, the first signal is cis NH_3 (12 H), and the second, trans NH_3 (3 H). [c] ppm downfield from external H_2SeO_3 in D_2O. [d] ppm downfield from $P(C_6H_5)_3$. [e] In cm^{-1}; s = strong, w = weak, m = medium, br = broad. [f] Relative intensities nonstoichiometric; isomer mixture.

the Se or the Co center, since by the former route the isocyano complex results and by the latter either the cyano or isocyano species, depending upon the mechanism.

The mechanism was resolved by using ^{13}C NMR experiments and ^{13}C-enriched KCN. These spectra (Figure 2) were obtained by gradually introducing small amounts (<1 equiv) of $K^{13}CN$ into a concentrated Me_2SO-d_6 solution of $[(NH_3)_5Co{-}NCSe](ClO_4)_2$. A signal due to $Se^{13}CN^-$ quickly appeared, even at very small reaction times. The resonance due to (unenriched) $[(NH_3)_5Co{-}NCSe]^{2+}$ disappeared and could hardly be seen relative to $SeCN^-$ even at equimolar concentrations. Experiments with natural-abundance free $SeCN^-$, its N-bonded complex, and $[(NH_3)_5Co{-}CN]^{2+}$ showed comparable C-signal strengths for equivalent concentrations. Furthermore, only after more than 1 equiv of $^{13}CN^-$ had been added did the signal due to free CN^- appear, while the strength of the signal due to the sole cobalt-containing product always corresponded to natural-abundance ^{13}C. The above observations are therefore consistent with *all* of the label originally in free CN^- appearing in liberated $SeCN^-$. A control experiment using free $SeCN^-$ and enriched $^{13}CN^-$ indicated that the enrichment appearing in $SeCN^-$ did not arise by a subsequent and more rapid substitution process, i.e., $[(NH_3)_5Co{-}NCSe]^{2+}$ with $^{13}CN^-$ first giving $[(NH_3)_5Co(^{13}CN)]^{2+}$ and $SeCN^-$, and then the free $SeCN^-$ exchanging its CN^- with introduced $^{13}CN^-$. This is clear also from the fact that the $[(NH_3)_5Co{-}CN]^{2+}$ product is unlabeled; moreover, the cyano product does not rapidly exchange bound with free CN^-.

The $NCSe^-$ ligand is known[11] to be N-bonded, and the attack by CN^- at the Se center converts this to NC^- while still on the metal; these facts require the formation of the isocyano complex. Yet we observe, by NMR spectroscopy, only the C-bonded isomer. It would seem that the isocyano to cyano rearrangement is very rapid at ambient temperature in Me_2SO solution under the conditions.

The following scheme suggests an obvious way of at least observing, if not isolating, the elusive isocyano complex:

$$[(NH_3)_5Co{-}NCSe]^{2+} \xrightarrow[Me_2SO]{CN^-} \underset{+\ SeCN^-}{[(NH_3)_5Co{-}NC]^{2+}} \rightarrow [(NH_3)_5Co{-}CN]^{2+}$$

The first step could be rendered fast relative to the second by operating at high $[CN^-]$, and the transient isocyano species could be observed spectrophotometrically by using a stopped-flow apparatus if necessary. KCN did not have the desired solubility in Me_2SO, and so we tried H_2O as solvent. Although CN^- is undoubtedly a poorer nucleophile in this solvent, the compensation was that we could employ $edta^{n-}$ to trap adventitious Co(II) and perhaps prevent a redox-catalyzed N- to C-bonded rearrangement. As it transpired, with $[CN^-]$ = 0.1 M (or even 0.01 M) and $[Li_3edta]$ = 0.01 M, the $[(NH_3)_5Co{-}NCSe]^{2+}$ species (λ_{max} = 492 nm) was very rapidly consumed (seconds, 25 °C), and the yellow-orange product had an absorption spectrum showing λ_{max} = 459 nm, consistent with N- rather than C-bonding ($[(NH_3)_5Co{-}CN]^{2+}$ shows λ_{max} = 438 nm in H_2O; $[(NH_3)_6Co]^{3+}$ shows λ_{max} = 474 nm). Furthermore, this species eventually rearranged quantitatively to $[(NH_3)_5Co{-}CN]^{2+}$, as shown by visible and ^{1}H NMR spectroscopy, but only very slowly (hours, 25 °C) compared to its apparently very rapid rate in Me_2SO. The experiment was repeated omitting the $edta^{n-}$, and the results were *usually* the same (significantly, direct conversion to $[(NH_3)_5Co{-}CN]^{2+}$ was occasionally observed).

These observations prompted a direct attack on the synthesis of a salt of $[(NH_3)_5Co{-}NC]^{2+}$. The $[(NH_3)_5Co{-}NCSe](ClO_4)_2$[11] complex was added slowly with stirring to an aqueous CN^- solution containing Li_3edta at ca. 20 °C. The addition of $NaClO_4$ and $LiNO_3$ yielded a yellow-orange crystalline salt of $[(NH_3)_5Co{-}NC]^{2+}$. Its ^{1}H NMR spectrum in Me_2SO and visible spectrum (λ_{max} = 459 nm) is diagnostic of the CoN_6 skeleton. Furthermore, the chemical shifts for the cis- and trans-NH_3 protons of the known $[(NH_3)_5Co{-}CN]^{2+}$ (δ 2.92, 12 H; δ 3.76, 3 H) and new $[(NH_3)_5Co{-}NC]^{2+}$ (δ 3.66, 12 H; δ 3.17, 3 H) complexes closely match those observed for each "half" of the cyanide-bridged dimer $[(NH_3)_5Co{-}NC{-}Co(NH_3)_5]^{5+}$ in Me_2SO-d_6 (δ 2.92, 12 H; δ 3.85, 3 H; δ 3.57, 12 H; δ 3.23, 3 H). Moreover heating the new isocyano species in the NMR tube quickly yielded signals for the cyano linkage isomer.

It is now clear that the rearrangement in Me_2SO, as in H_2O, is quite slow. The failure to directly observe the isocyano ion by using Se extrusion reactions for Me_2SO as solvent we attribute to ligand scrambling and catalyzed isomerization, probably induced by trace $[Co^{II}(CN)_6]^{4-}$. Note that the rearrangement, if redox-catalyzed, cannot be a $[Co^{II}(CN)_5]^{3-}$ inner-sphere process as suggested[10] for the pentacyano system, obviously since the product is $[(NH_3)_5Co^{III}CN]^{2+}$ rather than $[(CN)_5Co^{III}CN]^{3-}$. Indeed, it is difficult to suggest a plausible mechanism for the catalysis, since we know the CN^- involved in the ligand "turnover" never leaves the metal ion.

A study of the spontaneous, induced, redox-catalyzed and base-catalyzed reactions of the isocyanopentaamminecobalt(III) ion now seems warranted, and the classic pentacyanocobalt(III) system[9,10] could stand reexamination, since the authentic isocyano linkage isomer would now seem to be accessible.

Experimental Section

NMR spectra (^{1}H, ^{13}C, ^{77}Se, ^{59}Co, ^{31}P) were obtained on a Varian FX300 spectrometer at 25 °C with a 5-mm broad-band probe. Infrared spectra were recorded for Me_2SO solutions on an FT-IR instrument. The syntheses of $[(NH_3)_5CoCN](ClO_4)_2$,[15] $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$,[18] $[(NH_3)_5CoNCSe]Br_2$,[19] $[(NH_3)_5CoNCSe](ClO_4)_2$,[11,19] $[(NH_3)_5CoSeCN]Cl(ClO_4)$,[11] $[(NH_3)_5CoSeCN](ClO_4)_2$,[11] $[(NH_3)_5CoSCN](ClO_4)_2$,[20] and $[(NH_3)_5CoNCS](ClO_4)_2$[20] are described elsewhere. $K^{13}CN$ (MSD isotopes; 99.2 atom %) was a gift from Dr. S. B. Wild. All other chemicals were AnalaR grade or its equivalent.

The isocyano complex was prepared from $[(NH_3)_5CoNCSe](ClO_4)_2$[11] (ca. 0.1 g), which was added slowly with stirring to an aqueous solution (5–10 mL) containing Li_3edta (0.01 M) and NaCN (ca. 0.1–0.5 M) at ca. 20 °C. Much of the insoluble starting material dissolved through reaction. Filtration followed by addition of $NaClO_4$ and $LiNO_3$ to the filtrate yielded crystals of yellow-orange $[(NH_3)_5CoNC]ClO_4(NO_3)$ (ca. 0.05 g).

The lemon-colored $[(NH_3)_5CoNCCo(NH_3)_5](ClO_4)_5$ dimer was synthesized in high yield by heating $[(NH_3)_5CoCN](ClO_4)_2{\cdot}0.5H_2O$[15] (1.0 g) and excess $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$[18] (3.1 g, 2 equiv) in sulfolane (3 h, 90 °C); it was purified by chromatography on SP-Sephadex C-25, with 2 M NaO_2CCH_3 as eluant, and crystallized by neutralization using 70% $HClO_4$.

A deep orange-brown solution of $[(NH_3)_5CoNCSe](ClO_4)_2$ (1.0 g) in Me_2SO (10 mL) was treated with a 1 molar excess of triphenylphosphine (1.16 g; 2 equiv), whereupon it rapidly became yellow. After 5 min of stirring, the complex was precipitated with excess 2-propanol and ether. On settling, the solvent was decanted from the sticky yellow solid, which was dissolved in water. The resulting solution was then sorbed onto and eluted (0.5, 1 then 2 M NaO_2CCH_3) from SP-Sephadex C25 cation-exchange resin. Three yellow bands were taken from the column and neutralized with $HClO_4$ (70%), and the solutions were reduced in volume by freeze-drying. Each component crystallized readily. The first and minor band proved to be $[(NH_3)_5CoCN](ClO_4)_2$, the second (major) band, *cis*-$[(NH_3)_5Co{-}CN{-}Co(NH_3)_4(CN)]^{4+}$, and the last (major), an isomeric $[(NH_3)_5Co{-}NC{-}Co(NH_3)_4(CN)]^{4+}$ mixture.

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Reaction of Isopropyl Isocyanate with Bare Vanadium(I) Cations Leading to Combined Decarbonylation/Demethanation

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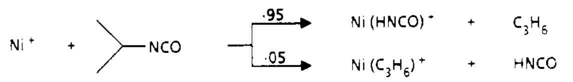
An important motive for the rapidly developing research on the reactions of bare metal ions with organic substrates in the gas phase has been to obtain further insight into the elementary steps of homogeneously and heterogeneously catalyzed processes.[1] Although the bulk of information in gas-phase organometallic chemistry is steadily growing and the mechanisms operative are much better understood now than in the earlier studies, direct relationship to catalytic processes is scarce. This is partly due to the fact that only few systems have been studied for which analogous counterparts exist in the condensed phase.

For that particular reason we picked up a specific reaction that has been studied in more detail by Bock and Breuer,[2] namely the thermal decomposition of isopropyl isocyanate (*i*-PrNCO) to carbon monoxide, methane, and acetonitrile, which is catalyzed by Ni_x clusters on carbon support (Ni_x/C_∞). This reaction is quite unusual, as it involves the intermediacy of surface-bound nitrenes, which split off methane to form the thermodynamically favorable acetonitrile. *Un*catalyzed pyrolysis of *i*-PrNCO at higher temperatures gives rise only to propene and HNCO.[2] It was thus quite surprising to learn that bare Ni^+ ions yielded exclusively the complexes $Ni(HNCO)^+$ and $Ni(C_3H_6)^+$ upon reaction with *i*-PrNCO in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (eq 1).[3]



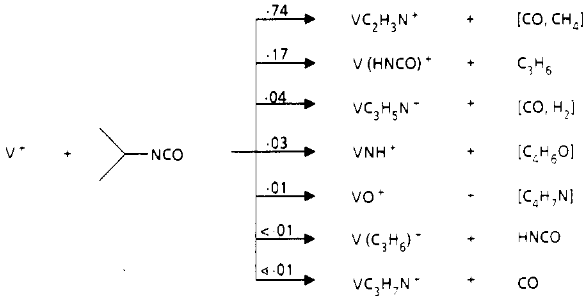
(1)

This is another example of the quite common case that reaction of a bare metal ion M^+ with an organic substrate RX leads to an alkene and HX (eq 2). Several mechanisms have been found

$$M^+ + C_nH_{2n+1}X \longrightarrow \begin{cases} M(HX)^+ + C_nH_{2n} \\ M(C_nH_{2n})^+ + HX \end{cases} \quad (2)$$

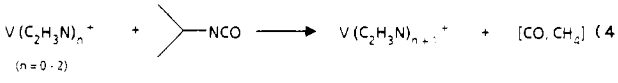
to be operative for different systems.[4] For (1) the presently available data do not permit a mechanistic assignment.

Interestingly, a screening of the various first-row transition-metal ions Ti^+–Zn^+ revealed that the solid-state process,[2] i.e. the generation of CO, CH_4, and CH_3CN, seems to be operative only for early transition-metal ions (i.e., Ti^+ and V^+). The account of the detailed study of all metal ions will form the subject of a further publication; here we will report only the results obtained for V^+, which gave, in high yield, rise to $CH_3CN{-}V^+$ upon reaction with *i*-PrNCO (eq 3).



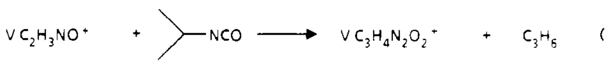
(3)

It might be possible that the amount of $VC_3H_6^+$ is somewhat underestimated due to very rapid secondary reactions and that the VO^+ ions arise from the reaction with the ever-present background water, but obviously the formation of the acetonitrile complex is the most favored decomposition pathway in the case of vanadium. Secondary and tertiary reactions of the main products could be established with double-resonance techniques (eqs 4–6).[5]



(4)

(5)



(6)

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