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*-$[(NH_3)_5Co\text{–}CN\text{–}Co(NH_3)_4(CN)]^{4+}$, and the last (major), an isomeric $[(NH_3)_5Co\text{–}NC\text{–}Co(NH_3)_4(CN)]^{4+}$ mixture.

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Contribution from the Institute of Organic Chemistry,
Technische Universität Berlin, Strasse des 17. Juni 135,
D-1000 Berlin 12, West Germany

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

Karsten Eller and Helmut Schwarz*

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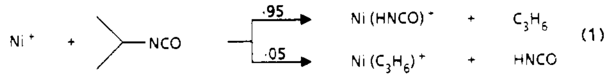
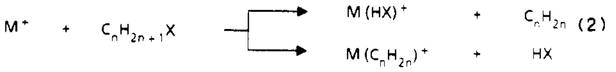
An important motive for the rapidly developing research on the reactions of bare metal ions with organic substrates in the gas phase has been to obtain further insight into the elementary steps of homogeneously and heterogeneously catalyzed processes.[1] Although the bulk of information in gas-phase 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]

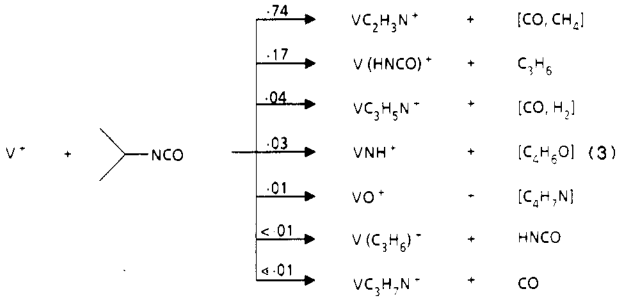


This is another example of the quite common case that reaction of a bare metal ion M^+ with an organic substrate RX leads to an alkene and HX (eq 2). Several mechanisms have been found

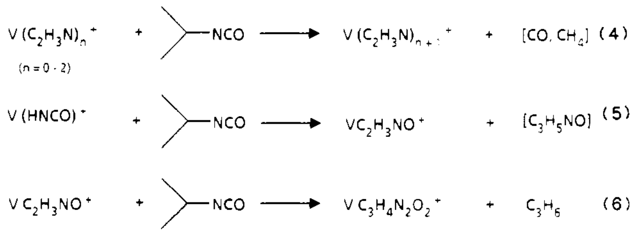


to be operative for different systems.[4] For (1) the presently available data do not permit a mechanistic assignment.

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 $CH_3CN\text{–}V^+$ upon reaction with *i*-PrNCO (eq 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]



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Scheme I

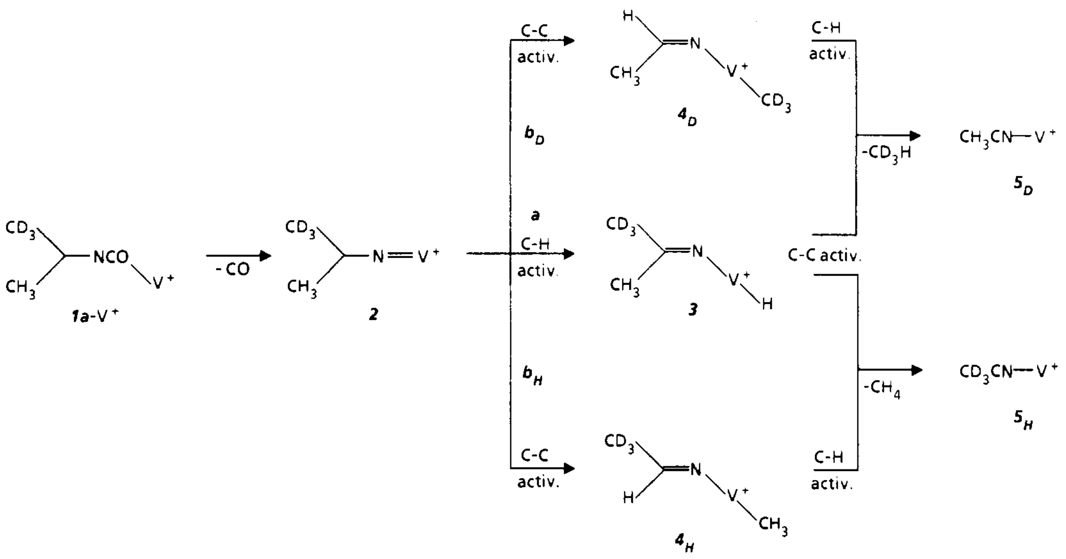

Table I. Reaction Products That Arise from the Reaction of V^+ with the Labeled Isocyanates[a]

reacn products	$CD_3(CH_3)$ CH-NCO (**1a**)	$(CH_3)_2$ CD-NCO (**1b**)
CH_3CNV^+	42	100
CD_3CNV^+	58	
$VHNCO^+$	62	100
$VDNCO^+$	38	
CO, H_2	67	65
CO, HD	33	35

[a] Intensities are given in percents and were normalized to 100% for each neutral, respectively.

Collision-induced dissociation[6] (CID) spectra of $VC_2H_3N^+$ were dominated by signals for the loss of the complete C_2H_3N unit with exclusive formation of V^+ for low energies and weak signals for the loss of 15, 26, and 27 mass units under the highest energies accessible. These findings point very much to a complex that consists of acetonitrile and V^+, with the losses being $CH_3^\bullet$, $CN^\bullet$, and HCN, and therefore completely in keeping with the expectations.

Further insight into the mechanism that leads to the formation of this complex can be gained from the study of the deuterated isocyanates $CD_3(CH_3)CH$-NCO (**1a**, Scheme I) and $(CH_3)_2C$-D-NCO (**1b**). The products that arise from the reaction of **1a** and **1b** with V^+ are given in Table I and can best be interpreted in terms of the mechanism presented in Scheme I for **1a**-V^+. The first step most likely proceeds via loss of CO and produces the nitrene complex **2**, in which either a C–H (path a) or a C–C bond (path b) can be activated. Further rearrangement by C–C (part a) or C–H bond activation (path b) is followed by reductive elimination of CX_3H (X = H, D) and produces the observed complexes **5**. The observation of a combined loss of CO/H_2 might point to path a, where **3** could rearrange by further C–H activation, although, as evidenced by the label distribution, this process seems to be more complicated and must not necessarily proceed via **3**. Several arguments led us to propose this mechanism in lieu of other conceivable alternatives. First of all, albeit extremely less intense, loss of CO is observed as well, thus demonstrating the principal feasibility of this step. Yet, the structure of the $VC_3H_7N^+$ ion could not be further probed and ejection experiments were inconclusive. Nevertheless, the absence of any scrambled products speaks against involvement of the methyl C–H bonds and clearly proves the formal presence of a 1,1-elimination. Furthermore, a nitrene structure such as **2**, which is very likely involved in the surface-catalyzed process[2] and which is also a common intermediate in the condensed-phase chemistry of isocyanates reacting with transition-metal complexes,[7-9] has been observed previously in gas-phase reactions of V^+.[10,11]

In addition, the binding energy (BE) of the simplest nitrene, $HN{=}V^+$, has been determined to be quite strong, namely 99 ± 4 kcal mol^{-1}.[11] Similar high binding energies have been found for other early-transition-metal ions, especially for Ti^+, which also gives rise to combined loss of CO/CH_4, while Fe^+, as a representative of groups 8–10, has been found to possess a much weaker binding energy ($D(HN{=}Fe^+)$ = 54 ± 14 kcal mol^{-1}).[10] The finding that metal ions with high BE's for nitrenes (V^+, Ti^+) *can react* to form acetonitrile/M^+ complexes and those with substantially weaker BE's (Fe^+, Co^+, Ni^+) are *unable* to do so strongly supports the presented mechanism, which is indeed strictly analogous to the solution studies with Ni_x/C_∞.[2] Further support can also be gained from the generalization stated in the early review:[7] "...the RN=CO bond of organic isocyanates is not so readily broken, and carbon monoxide is displaced only in the reactions which lead to the formation of stable derivatives of the nitrene ... ligand." It is thus conceivable that the crucial factor of the binding energies can be directly transcribed into the condensed-phase studies. A conclusion derived therefrom would then be that catalysts with high binding energies for surface nitrenes should work best in the formation of acetonitrile.

Experimental Section

The experiments were performed by using a Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an external ion source;[12] the instrument and further details

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of its operation have been previously described.[13] Briefly, metal ions were generated by laser desorption/ionization by focusing the beam of a Nd:YAG laser (Spectron Systems, 1064 nm) onto a high-purity rod of the desired transition metal, which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electric potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (Balzers TPU 330 for source and cell, respectively, and Balzers TPU 50 in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. The metal's most abundant isotope is isolated by using FERETS[14] and allowed to react with the substrate, which is present with a constant pressure of the order of 10^{-8} mbar; reaction times are typically 1-10 s. For collisional cooling of eventually formed excited states and removal of kinetic energy remaining from the transfer, as well as for CID experiments,[6] argon was present as a buffer gas with a constant pressure of $(1-5) \times 10^{-7}$ mbar, as measured with an uncalibrated ionization gauge (Balzers IMG 070). All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer; broad-band spectra were recorded with a fast ADC, digitized as 64K or 128K data points and zero-filled[15] to 256K before Fourier transformation. Reaction products were unambiguously identified by double-resonance and MS/MS techniques.[5]

The isocyanates were synthesized and fully characterized by using established procedures, purified by preparative gas chromatography, and carefully degassed by multiple freeze-pump-thaw cycles immediately before the experiments. The label content was determined with NMR and mass spectrometry techniques.

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Contribution from the Department of Chemistry,
Rice University, Houston, Texas 77251

Synthesis and Characterization of Bis(trifluoromethyl)gold μ-Halide Dimers: X-ray Structural Characterization of $[Au(CF_3)_2(\mu-I)]_2$

John L. Margrave,* Kenton H. Whitmire,* Robert H. Hauge, and Nathan T. Norem

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Perfluoroalkyl complexes of metal atoms have received attention owing to the importance of fluorocarbons in important materials applications. For example, trifluoromethyl metal complexes often show enhanced volatility, which make them potentially useful in vapor deposition studies. Gold complexes hold particular interest because of desirable electrical properties of gold for electronics manufacture. In spite of this, very few (trifluoromethyl)gold complexes have been reported. In 1976 Johnson and Puddephatt synthesized the first (trifluoromethyl)gold complexes by the oxidative addition CF_3I to methylgold phosphine complexes.[1] These products were characterized by ^{19}F NMR spectroscopy but were not isolated. It has only been with the recent combination of metal vapor techniques and radio frequency discharge generated plasmas of C_2F_6 that Lago et al. have succeeded in preparing compounds that have more than one trifluoromethyl group attached to a metal.[2] Unstable $Au(CF_3)_3$ synthesized from gold vapors and plasma-generated trifluoromethyl radicals at −196 °C is stabilized by addition of PMe_3.[3] More recently, Fackler, Lagow, and co-workers have prepared CF_3 derivatives of gold(II) ylide complexes by exchange reactions between $Cd(CF_3)_2(glyme)$ and $[Au(CH_2)_2PPh_2]_2Br_2$.[4] Sanner, Sacher, and Droege have stabilized (trifluoromethyl)gold halide complexes with PMe_3, PEt_3, and PPh_3.[5] In this paper we report the vapor deposition synthesis of the dimeric bis(trifluoromethyl)gold(III) bromide and iodide complexes and the X-ray structural characterization of the iodide complex.

Table I. Crystallographic Data Collection Parameters for Compound Ib

emp formula	$Au_2C_4F_{12}I_2$	fw	923.77
space group	$P2_1/n$ (*no.* 14)	T, °C	23
a, Å	7.5963 (8)	λ(Mc Kα), Å	0.71069
b, Å	7.295 (1)	ρ, g/cm^3	4.31
c, Å	13.057 (1)	μ, cm^{-1}	257.62
β, deg	100.710 (7)	T_{max}/T_{min}	1.000/0.2847
V, Å^3	711.0 (1)	R^a	0.039
Z	2	$R_w{}^a$	0.053

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w\{|F_o| - |F_c|\}^2/\sum w|F_o|^2]^{1/2}$. The function minimized during least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$.

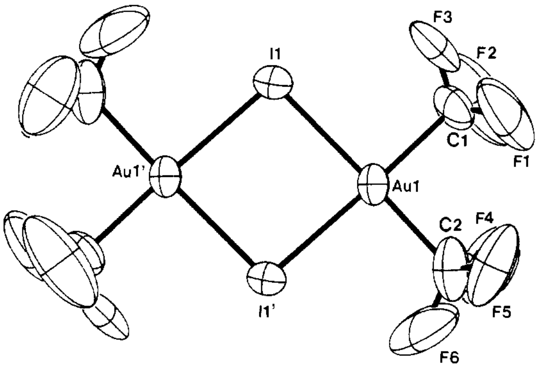

Figure 1. ORTEP diagram of $[Au(CF_3)_2(\mu-I)]_2$, showing 50% anisotropic thermal ellipsoids and atom labeling.

Experimental Section

Synthesis of $[Au(CF_3)_2(\mu-X)]_2$ (X = Br (Ia), I (Ib)). A typical reaction consisted of cocondensation of about 0.75 g (3.81 mmol) of gold with about 50 g (335.8 mmol) of bromotrifluoromethane over a period of about 1.5 h in an apparatus that has been previously described.[6] The bell jar upon which the reagents were condensed was then washed with diethyl ether (total volume ~400 mL) from which 250 mg (16%) of the $[Au(CF_3)_2(\mu-Br)]_2$ was isolated. A similar procedure was followed by using CF_3I and gold (100:1) with a yield of 8%. The compounds Ia and Ib are sublimable (room temperature 10^{-2} Torr) orange to brownish orange solids with melting points 90–94 °C (Ia) and 136–137 °C (Ib). Mass spectra showed the parent ions in both cases (Ia, *m/e* 832; Ib *m/e* 924). ^{19}F NMR: $\delta = -71.4$ (Ia), −73.7 ppm (Ib) (CF_3CO_2H reference). Both compounds are moderately air and light sensitive. Recrystallization from pentane gave diamond-shaped crystals suitable for X-ray diffraction.

X-ray Analyses of Ia and Ib. X-ray diffraction data for both Ia and Ib were collected on a Rigaku AFC5S fully automated single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation.

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