Inorg. Chem. **2003**, *42*, 244–249

Inorganic Chemistry
Article

Migratory Insertion of Hydrogen Isocyanide in the Pentacyano(methyl)cobaltate(III) Anion

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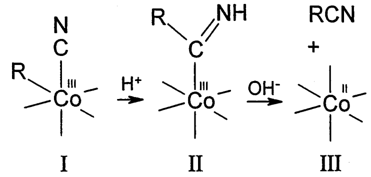
Received May 20, 2002

The preparation of the pentacyano(iminiumacetyl)cobaltate(III) anion and its *N*-methyl and *N*,*N*-dimethyl derivatives is reported. The iminiumacetyl group is formed by migratory insertion of cis hydrogen isocyanide in the pentacyano(methyl)cobaltate(III) anion. The new compounds have been spectroscopically characterized by ^{1}H, ^{13}C, ^{15}N, and ^{59}Co NMR spectroscopy and by absorption spectroscopy. The iminium carbon atoms yield ^{13}C NMR signals at 256.7, 247.7, and 240.4 ppm for the parent iminiumacetyl compound and its *N*-methyl and *N*,*N*-dimethyl derivatives, respectively. The ^{15}N resonance frequencies of the iminium groups and the lack of rotation of the carbon–nitrogen bond both show that this bond is best described as a double bond. The structure of $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$ was determined by X-ray crystallography at 122.0(5) K. The structure displays disorder.

Introduction

Alkylcobaltate(III) anions with five cyano ligands, $[Co(CN)_5(R)]^{3-}$, were among the first synthetically prepared organocobalt(III) compounds.[1a−d] It was early discovered that the alkyl groups (R) in these compounds may react with one of the cyano ligands in acidic solution.[1e] This was inferred from the formation of nitriles (or in some cases carboxylates) upon treatment of pentacyano(alkyl)cobaltate(III) anions with sulfuric acid followed by treatment with strong base (Scheme 1).[1e−g] In order to account for the reaction products it was suggested that this reaction involved an intermediate iminoacylcobaltate(III) anion (Scheme 1, II).[1e] This suggestion was later supported by measurements of the ^{1}H NMR spectra of various pentacyano(alkyl)cobaltate(III) compounds in aqueous sulfuric acid.[1f,g] Release of a nitrile implies a redox reaction, but investigations of the nature of this step have not been performed, and the identity of the cobalt end product (Scheme 1, III) has not been established. The final oxidation state of cobalt is probably +2,[1e] although the elimination reaction also has been suggested to yield cobalt(I).[1f]

Scheme 1. Formation of Nitriles from Treatment of Pentacyano(alkyl)cobaltate(III) Anions with Sulfuric Acid Followed by Strong Base[1e,f]



The analogy between the pentacyanoorganocobalt(III) compounds and the isoelectronic organomanganese(I) pentacarbonyls has been pointed out.[1a,d,f] The methyl cis migration in $[Mn(CO)_5(CH_3)]$, forming acetylmanganese(I) pentacarbonyl in the presence of excess carbon monoxide, has been the subject of detailed studies.[2] One of the key questions has been whether this reaction is a methyl migration or a carbon monoxide insertion. A second question has been the geometry of the (presumably five coordinated) intermediate. Investigations of the isotope distribution in the products have been the major source of information, with the application of ^{13}C NMR being particularly useful.[2b,c] By use of selective ^{13}C labeling of CO in the cis position it was demonstrated

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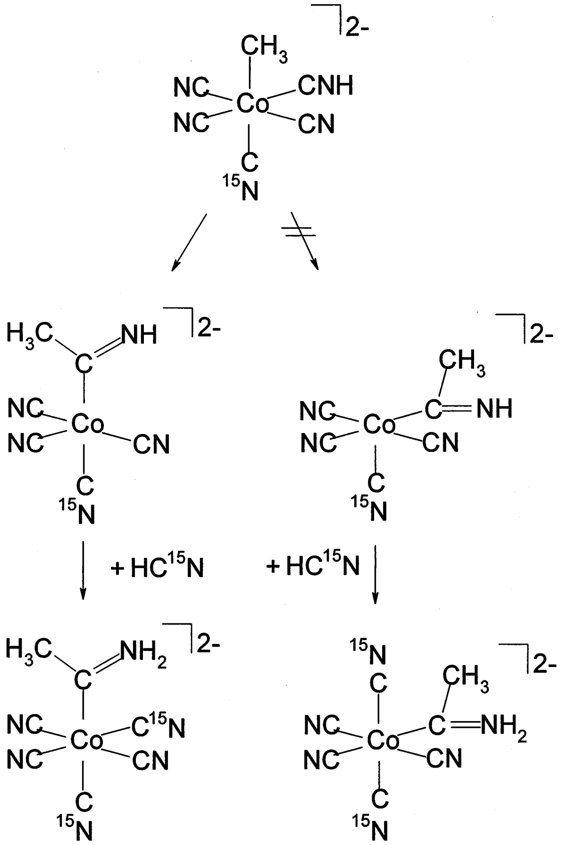
10.1021/ic020353u CCC: $25.00

that the insertion reaction is a methyl cis migration.[2b,c] The rearrangement of the pentacyano(alkyl)cobalt(III) compounds in acidic solution may proceed analogously, raising the quest for methods to distinguish hydrogen isocyanide insertion from methyl migration.

It is here shown that the neutral carbon-bonded iminiumacetyl ligand ($-C(CH_3)=NH_2$) is formed upon acidification of an aqueous solution of $[Co(CN)_5(CH_3)]^{3-}$. The iminiumacetyl ligand is, to our knowledge, unprecedented in organocobalt(III) chemistry, whereas there are many examples known of transition metals in low oxidation states having 1-aminoalkylidene ($=C(R)NH_2$) groups as ligands.[10] The preparation of the pentacyano(iminiumacetyl)cobaltate(III) anion (the end product in Scheme 2) and the N-methylation of the iminium group are reported. The migratory insertion of cis hydrogen isocyanide has been studied by ^1H, ^{13}C, ^{15}N, and ^{59}Co NMR using ^{13}C- or ^{15}N-cyanide. The product and its methyl derivatives are isoelectronic with the corresponding 1-aminoethylidenepentacarbonylchromium(0) compounds, and the NMR spectroscopic data are discussed in this context. The crystal structure of $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$ has been determined from low-temperature X-ray diffraction data.

Scheme 2. Isotope Distributions in the Pentacyano(iminiumacetyl)cobaltate(III) Anion upon Migratory Insertion of Cis Hydrogen Isocyanide (Left) or Methyl Cis Migration (Right) Assuming a Square-Pyramidal Intermediate Which Is Rigid over the Time Scale of the Reaction



Experimental Section

Materials. Deuterium oxide (99.8% D), dimethyl sulfoxide-d_6 (99.9% D), potassium cyanide-^{13}C (99% atom ^{13}C), and potassium cyanide-^{15}N (98% atom ^{15}N) were obtained from Sigma. Tetraethylammonium cyanide was obtain from Aldrich. Tetraethylammonium pentacyanomethylcobaltate(III) was prepared from pentaamminemethylcobaltate(III) nitrate and tetraethylammonium cyanide as previously reported.[3] The ^{13}C- or ^{15}N-labeled preparations were obtained by partly substituting labeled potassium cyanide for tetraethylammonium cyanide.

Instrumentation. NMR spectra were measured at 14.09 T on a Varian Unity Inova 600 NMR spectrometer equipped with a 5 mm broadband tunable probe. Deuterated solvents were used to provide a deuterium lock. ^1H and ^{13}C chemical shift values (δ) are reported in parts per million relative to the methyl group of internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in aqueous solution or tetramethylsilane (TMS) in dmso. ^{15}N chemical shift values are reported in parts per million relative to 0.3 M CH_3NO_2 in D_2O ($\delta = 2.0$ ppm).[4] Potassium hexacyanocobaltate(III) was used as a standard for ^{59}Co NMR.

UV−visible absorption spectra were recorded with a Shimadzu MPS-2000 spectrophotometer.

Elemental analyses were made at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen.

Preparations. Tetraethylammonium Pentacyano(iminiumacetyl)cobaltate(III) (1). A 1.0 mL (17.5 mmol) amount of acetic acid was added to a solution of tetraethylammonium pentacyano(methyl)cobaltate(III) (1.0 g, 1.68 mmol) and tetraethylammonium cyanide (1.0 g, 6.0 mmol) in water (5 mL) at 0 °C. The flask was closed, and the solution was stirred at room temperature for 5 days. Acetone (90 mL) was then added to the mixture, and the stirring was continued for 3 days, during which a white solid precipitate formed. The solid was filtered off, washed with acetone followed by washing with diethyl ether, and air-dried. Recrystallization was performed by dissolving the crude product in a 1:10 mixture of acetic acid and acetonitrile (10 mL) and filtering, followed by addition of acetone (100 mL) to the filtrate. After stirring for 24 h, the off-white powder was filtered off and washed with acetone followed by washing with diethyl ether, and stored desiccated. Yield: 0.6 g (72%). Anal. Calcd for $CoC_{23}H_{45}N_8$: C, 56.08; H, 9.21; N, 22.75. Found: C, 55.39; H, 9.19; N; 22.55.

Tetraethylammonium Pentacyano((*E*)-*N*-methyliminiumacetyl)cobaltate(III) Dihydrate (2). A solution of 0.493 g (1 mmol) of **1** in water (1.0 mL) was added to a solution of iodomethane (1.0 g, 7.0 mmol) in acetonitrile (20 mL) at 0 °C. To this mixture

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Table 1. Crystal Data and Structure Refinement for $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$

identification code	$(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$
empirical formula	$C_{62}H_{63}As_2CoN_6$
fw (g/mol)	1100.95
temp (K)	122(2)
wavelength (Å)	0.71073
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimens	
a (Å)	10.724(2)
b (Å)	11.070(2)
c (Å)	12.923(3)
α (deg)	65.01(2)
β (deg)	82.11(2)
γ (deg)	73.36(2)
vol ($Å^3$)	1332.1(5)
Z, calcd density (Mg/m^3)	1, 1.372
absorption coeff (mm^{-1})	0.400
reflns collected/unique (cryst class)	16006/9626 [$R_{int} = 0.031$]
final *R* indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0392$, $R_w(F^2) = 0.0949$
R indices (all data)	$R_1 = 0.0505$, $R_w(F^2) = 0.1015$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

was added a 35% solution of tetraethylammonium hydroxide in water (0.5 mL, 1.2 mmol). The temperature was slowly increased to room temperature, and the mixture was stirred further at this temperature for 30 min. The reaction mixture was filtered, and the filtrate was slowly added to diethyl ether (100 mL) with stirring. The solution was decanted off, and the oily precipitate was dried in vacuo. Then 2-propanol (15 mL) was added to the precipitate. After this mixture was stirred for 1 h, the white solid was filtered off using a sintered glass funnel (No. 4), and the filtrate was slowly added to diethyl ether (100 mL) with stirring, whereby **2** precipitated. The off-white solid was collected by filtration, washed with diethyl ether, and air-dried. Yield: 0.26 g (48%). Anal. Calcd for $CoC_{24}H_{51}N_8O_2$: C, 53.12; H, 9.47; N, 20.65. Found: C, 53.57; H, 10.00; N, 20.63.

Tetraethylammonium Pentacyano(*N*,*N*-dimethyliminiumacetyl)cobaltate(III) Hydrate (3). A 0.493 g (1 mmol) amount of **1** was added to a solution of iodomethane (1.0 g, 7.0 mmol) in acetonitrile (12 mL) at 0 °C. To this mixture was added a 35% solution of tetraethylammonium hydroxide in water (1.0 mL, 2.4 mmol). After stirring for 30 min at room temperature, the reaction mixture was worked up as described above. Yield: 0.3 g (56%). Anal. Calcd for $CoC_{25}H_{51}N_8O$: C, 55.74; H, 9.54; N, 20.80. Found: C, 55.75; H, 9.71; N, 20.82.

X-ray Crystallography. Crystals of $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$ were grown by diffusion of a solution of $(Et_4N)_3[Co(CN)_5(CH_3)]$ in acetonitrile into a saturated acetonitrile solution of tetraphenylarsonium chloride.

Low-temperature X-ray diffraction data of $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$ were collected with a CAD4 diffractometer using graphite (002) monochromated Mo Kα radiation. The temperature was set to 122 K, adjusted by the tetragonal to orthorhombic phase transition of KH_2PO_4 at this temperature. The cell dimensions were determined from 20 reflections in the θ range 17.93−20.50°. Data were collected for 16548 reflections, including standards in the octants $\pm h, \pm k, \pm l$ ($1° < \theta < 32.5°$). The intensities of five standard reflections were measured every 10000 s. The data set showed a small systematic decrease of 2%, for which it was corrected using a polynomial fit to third order. Table 1 lists the crystal data and the final refinement results. Data reduction, including corrections for Lorentz, polarization, and absorption effects, were done using the DREADD program suite.[5a] The absorption correction was performed with the Gaussian integration procedure.

Table 2. Selected Bond Distances (Å) for the Anion in $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]^a$

bond	distance	bond	distance
Co−C31	1.900(2)	C31−N1	1.159(2)
$Co-C32^3$	1.903(2)	C32−N2	1.161(2)
$Co-C33B^1$	1.930(4)	C33B−N3	1.156(3)
$Co-C33A^1$	2.050(5)		

[a] Symmetry transformations used to generate equivalent atoms: (1) $x + 1, y, z$; (2) $-x + 1, -y, -z$; (3) $-x + 1, -y, -z + 1$; (4) $x, y, z - 1$; (5) $-x, -y, -z$.

The Laue symmetry of the diffraction pattern is −1, consistent with the space groups $P1$ or $P\bar{1}$. With one formula per unit cell and the space group $P\bar{1}$, cobalt and nitrogen of the tetraethylammonium ion must be placed at inversion centers, which implies disorder of both moieties. The structure could be determined in either space group by direct methods (SHELXS-86)[5b] and was subsequently refined using SHELXL-97[5c] by minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$; 9626 unique reflections were used in the refinement of the 404 parameters. The conventional R_1 value was calculated from 8194 reflections with $|F_o| > 4\sigma(|F_o|)$.

Refinements in either $P1$ or $P\bar{1}$ resulted in disorder of the anion and of the tetraethylammonium ion. In the latter cation this corresponds to an ammonium ion with two centrosymmetrically related sets of ethyl groups. The disorder of the anion makes it impossible to distinguish the carbon atoms of the cyano group in the trans position to the methyl group and the carbon atom of the methyl group, implying that the nitrogen of this cyano group should be introduced with an occupancy of 0.5. The best description was found to be in $P\bar{1}$, where this disorder is described by the inversion symmetry. We performed the refinement by restraining the CN bond of the trans cyano group to be 1.16 Å. In this way we have introduced two carbon atoms in slightly different positions.

The positions of the hydrogen atoms of the ordered Ph_4As^+ ion appeared clearly in the difference electron density calculated after anisotropic atomic displacement parameters were introduced for non-hydrogen atoms. The positional parameters of all hydrogen atoms of this cation were included in the refinement while those of the disordered tetraethylammonium ion were introduced in idealized positions. The thermal parameters were made equal to U_{eq} of the parent C or N atom multiplied by 1.2 or 1.5, respectively.

Diffraction data collected on $(PPN)_2[Co(CN)_5(C(CH_3){=}NH_2)]$ were too poor to allow for an accurate structure determination ($PPN^+ = \mu$-nitrido-bis(triphenylphosphorus)(1+)).

Results and Discussion

Syntheses. The reaction of the pentacyano(methyl)cobaltate(III) anion in acetate buffer with an excess of cyanide results in the formation of **1** as the only product as revealed by ^1H, ^{13}C, ^{15}N, and ^{59}Co NMR spectroscopic measurements (cf. Scheme 2). Elemental analysis and ^1H NMR (Table 3) show that the imino group is protonated. In an aqueous acetonitrile solution the imino group reacts readily with iodomethane to give the corresponding *N*-methyl and *N*,*N*-dimethyl compounds. However, NMR spectroscopy showed that preparations of **2** contain detectable amounts of both **1** and **3** as impurities. Preparations of **2** afforded only *one* monomethyl isomer as revealed by NMR.

The ^1H chemical shifts (Table 3) were assigned on basis of nuclear Overhauser effects (NOE). In **3**, irradiation of the $C-CH_3$ signal at 2.76 ppm gave a large NOE at 3.48 ppm and no NOE at 4.00 ppm. Therefore the signal at 3.48 ppm

Table 3. NMR and Absorption Spectroscopic Data for Aqueous Solutions of the Pentacyano(iminiumacetyl)cobaltate(III) Anion and Its N-Methylated Derivatives at 20 °C

anion	$\delta(\mathrm{C{-}C}H_3)$/ ppm	$\delta(\mathrm{N{-}C}H_3)$/ ppm	$\delta(\mathrm{N{-}}H)$/ ppm	$\delta(\mathrm{C{-}}C\mathrm{H_3})$/ ppm	$\delta(\mathrm{N{-}}C\mathrm{H_3})$/ ppm	$\delta(C\mathrm{{=}N})$/ ppm	$\delta(C\mathrm{{\equiv}N})$/ ppm	$\delta(\mathrm{C{=}}N)$/ ppm	$\delta(\mathrm{C{\equiv}}N)$/ ppm	$\delta(\mathrm{Co})$/ ppm	λ_{max}/nm (ϵ/M^{-1} cm^{-1})
$[\mathrm{Co(CN)_5(C(CH_3){=}NH_2)}]^{2-}$	2.81		10.53[b]	40.7		256.7	146.4	−175.9	−97.05 (trans)	60	309
			9.66[b]						−96.95 (cis)		(233)
$[\mathrm{Co(CN)_5(C(CH_3){=}NHCH_3)}]^{2-}$	2.70	3.29 (*E*)[a]	10.35[b]	38.3	35.1	247.7	146.6	−176.4	−96.4 (trans)	130	312
									−96.1 (cis)		(223)
$[\mathrm{Co(CN)_5(C(CH_3){=}N(CH_3)_2)}]^{2-}$	2.76	3.48 (*E*)[a]		41.6	47.6	240.4	146.7	−175.8	−96.9 (trans)	260	314
		4.00 (*Z*)[a]			56.7				−94.4 (cis)		(271)

[a] The assignments to *E* and *Z* are based upon NOE difference spectroscopy. [b] In dmso-d_6.

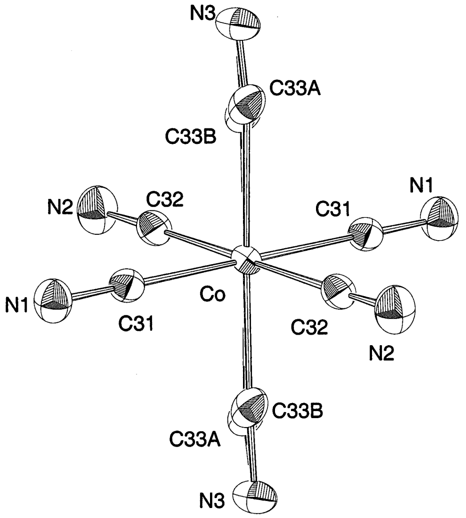

Figure 1. ORTEPII[5d] 50% probability plots of the anion in $(\mathrm{Et_4N})(\mathrm{Ph_4As})_2[\mathrm{Co(CN)_5(CH_3)}]$.

was assigned to the *E* methyl group. Irradiation of the two other methyl ^{1}H resonance signals confirmed this assignment. In **2**, irradiation of the $\mathrm{C{-}C}H_3$ signal at 2.70 ppm gave a large NOE at 3.29 ppm and vice versa. Therefore **2** was assigned to be the *E* isomer. The tetraethylammonium salts of the new compounds are soluble in water and in coordinating organic solvents, giving colorless to pale yellow solutions.

Description of the Crystal Structure. The crystal structure determination of $(\mathrm{Et_4N})(\mathrm{Ph_4As})_2[\mathrm{Co(CN)_5(CH_3)}]$ showed that the structure is disordered. However, it was possible to make a description of the disorder that justifies the bond lengths and angles that are listed in Table 2. An ORTEP drawing of the $[\mathrm{Co(CN)_5(CH_3)}]^{3-}$ anion is shown in Figure 1. Due to the disorder in $[\mathrm{Co(CN)_5(CH_3)}]^{3-}$ of the methyl group and the *trans* cyano group, we shall not draw any conclusions about the trans influence of the methyl group on the cobalt−cyanide distance, but with 1.930(4) Å it seems to be somewhat longer than the cobalt−cyanide distances (1.900(2) and 1.903(2) Å) of the cis cyano groups. These cobalt−cyanide bond lengths are similar to those in the $[\mathrm{Co(CN)_5(CF_2CHF_2)}]^{3-}$ anion, which were reported to be 1.927 and 1.894 Å for the trans and cis cyano groups, respectively.[7a] In the related dinuclear $[(\mathrm{NC})_5\mathrm{CoC(COOCH_3){=}C(COOCH_3)Co(CN)_5}]^{6-}$ anion a bond length of 1.921(3) Å was found for the trans cyano group, while those of the cis cyano groups varied from 1.895(3) to 1.909(3) Å.[7b]

Absorption Spectra. The near UV spectra are characterized by a single absorption (Table 3). The values for λ_{max} are in the range 309−314 nm and are thus only 5−10 nm lower than that transition in the corresponding chromium(0) compounds, which has been assigned to a d−d transition.[6] In analogy with $\delta(^{53}\mathrm{Cr})$ for the latter class of compounds,[6] one might expect $\delta(^{59}\mathrm{Co})$ to correlate with λ_{max}. Even if this is in fact the case (Table 3), it should be noted that variations in λ_{max} are not great and that the data set is not big enough to make any firm conclusion.

NMR Spectroscopic Characterization. The NMR spectroscopic data of the iminiumacetylcobaltate(III) anions are given in Table 3. The ^{13}C and ^{15}N resonance lines for these coordination compounds are generally broad due to scalar coupling to ^{59}Co ($I = 7/2$).[3,9b]

A unique NMR spectroscopic characteristic of **1**, **2**, and **3** is the high ^{13}C resonance frequency of the cobalt(III)-bonded carbon atom of the iminium group. This frequency decreases monotonically upon successive methylation of the iminium nitrogen atom. The ^{59}Co chemical shifts show the opposite trend, that is, methylation gives a decreased shielding of the ^{59}Co nucleus. These trends match the variation in the ^{13}C and ^{53}Cr chemical shifts of $[\mathrm{Cr(CO)_5(C(CH_3)NRR')}]$, which for $\mathrm{R = R' = H}$ are $\delta(^{13}\mathrm{C}) = 292.0$ ppm and $\delta(^{53}\mathrm{Cr}) = 103$ ppm, for $\mathrm{R = H}$, $\mathrm{R' = CH_3}$ (the *E* isomer) are $\delta(^{13}\mathrm{C}) = 282.0$ ppm and $\delta(^{53}\mathrm{Cr}) = 136$ ppm, and for $\mathrm{R = R' = CH_3}$ are $\delta(^{13}\mathrm{C}) = 274.3$ ppm and $\delta(^{53}\mathrm{Cr}) = 165$ ppm.[6] It is noteworthy that the ^{13}C chemical shifts of the iminium carbon nuclei in the iminiumacetylcobaltate(III) compounds are only about 30 ppm lower than in the corresponding 1-aminoethylidenechromium(0) compounds. Combined with knowledge from the above listed ^{59}Co and ^{53}Cr NMR spectroscopic data, this suggests an electronic resemblance of these two classes of compounds.

The ^{15}N chemical shift of the iminium nitrogen (Table 3) is typical for iminium groups, which resonate at about −180 to −280 ppm.[4] By comparison, enamines resonate in the

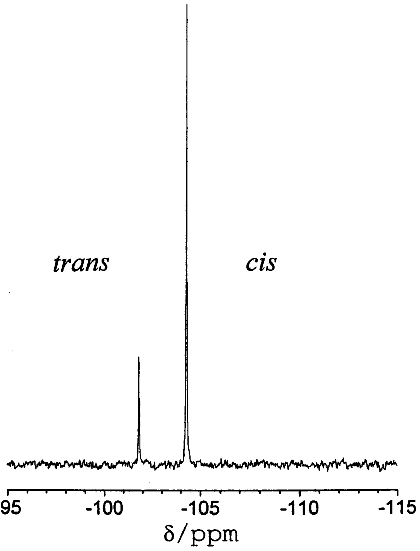

Figure 2. ^{15}N NMR spectrum of 20 mM tetraethylammonium pentacyano(methyl)cobaltate(III) in D_2O (50% ^{15}N).

range typical for organic amines, namely, from about −280 to −380 ppm.[4] The ^{1}H resonances in dmso-d_6 of the iminium group in pentacyano(iminiumacetyl)cobaltate(III) consist of *two* distinct signals at 10.53 and 9.66 ppm. Similarly, both the ^{1}H and ^{13}C NMR spectra of pentacyano(*N*,*N*-dimethyliminiumacetyl)cobaltate(III) show two different resonance lines from the two methyl groups. There is no indication of coalescence at elevated temperatures in dmso-d_6 when heated to 60 °C. This shows that the carbon−nitrogen bond in the iminiumacetyl group is best described as a double bond.

In the pentacyano(methyl)cobaltate(III) anion the ^{15}N resonance signals of the cis and trans cyano ligands are clearly different (Figure 2). The ^{13}C resonance frequency of the trans cyano ligand is likewise higher (by 1.9 ppm) than that of the cis cyano ligands.[3,8] By contrast, the ^{13}C resonance lines of the cis and trans cyano groups in **1** are not resolved. Only a single broad line is observed positioned at 146.4 ppm. The ^{15}N NMR spectrum, however, contains separate signals for the cis and trans cyano groups at −96.95 and −97.05 ppm, respectively (Figure 3A). When compared to pentacyano(methyl)cobaltate(III), the ^{13}C atoms of the cyano groups become more shielded and the ^{15}N atoms become less shielded in **1**. A similar inverse relationship has been observed in cyanocobalt(III)corrins and has been ascribed to variations in $d\pi{-}p\pi$ back-bonding.[9a]

The NMR spectra of **1**, **2**, and **3** indicate a free rotation of the iminiumacetyl group around the cobalt−carbon bond and at the same time a significant hindrance toward rotation around the carbon−nitrogen bond. It is well-known that the barrier toward rotation of the carbon−nitrogen bond in 1-aminoalkylidenechromium(0) compounds is much higher than that of the carbon oxygen bond in the corresponding 1-alkoxyalkylidene compounds.[10]

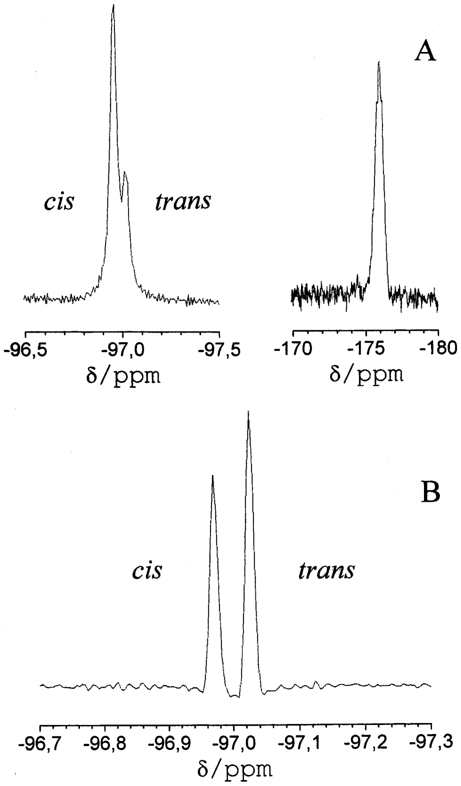

Figure 3. (A) ^{15}N NMR spectrum of the pentacyano(iminiumacetyl)cobaltate(III) anion (0.2 M) in acetate buffer (D_2O) (approximately 50% ^{15}N). (B) ^{15}N NMR spectrum of the pentacyano(iminiumacetyl)cobaltate(III) anion (0.2 M) in acetate buffer (D_2O). The reaction mixture was prepared from tetraethylammonium pentacyanomethylcobaltate(III) (natural abundance ^{15}N) using a 10-fold excess of $KC^{15}N$ (98% ^{15}N). Resolution enhancement was employed to emphasize the separation of the signals from cis and trans cyano groups. The 1:1 ratio of intensities of the signals from the cis cyano groups and the trans cyano group is consistent with a migratory insertion of cis hydrogen isocyanide according to Scheme 2.

Formation of a new carbon−carbon bond via an intermediate iminiumacetylcobalt(III) moiety occurs with relative ease and thus formed the basis of a proposal to utilize this insertion reaction as a new synthesis of nitriles.[1d,e] It is therefore of interest to investigate the mechanism of this reaction. The adopted approach was that of isotope labeling, which previously had been applied successfully in the investigations of the rearrangement of $[Mn(CO)_5(CH_3)]$.[2]

Migratory Insertion of Cis Hydrogen Isocyanide. In acidic aqueous solution the pentacyano(methyl)cobaltate(III) anion becomes protonated, and the conjugate acid has been reported to have pK_a 2.7 ± 0.1 as determined by absorption spectroscopy.[1f] The mechanism of the subsequent rearrangement has been the subject of discussion, and it has been proposed either to be a methyl migration[1e] or to be a hydrogen isocyanide insertion.[1f] The problem can be approached in a direct way by selective labeling of the cyano ligands either in the trans position or in the cis position (Scheme 2). In acetate buffer (pH 4.8), exchange of the trans cyano group is much faster than the formation of **1**. The use of nonlabeled pentacyano(methyl)cobaltate(III) and addition of excess ^{15}N-cyanide effectively results in selective labeling of the trans position ($\delta(^{15}N) = -101.9$ ppm, cf. Figure 2) of pentacyano(methyl)cobaltate(III). No detectable exchange of cis cyano groups ($\delta(^{15}N) = -104.2$ ppm) occurs under the same conditions. The use of a 5-fold excess of ^{15}N-cyanide ensures that the free cyanide is labeled to more than 80%. The isotope distribution upon either methyl group cis migration or migratory insertion of cis hydrogen isocyanide is shown in Scheme 2.

In the present case, both ^{13}C and ^{15}N NMR spectra using labeled pentacyano(methyl)cobaltate(III) and nonlabeled cyanide or vice versa show unequivocally that the iminium group results from the reaction of the methyl group with a *coordinated* cyanide. For example, if nonlabeled pentacyano(methyl)cobaltate(III) is used together with ^{13}C-labeled free cyanide, then *no* ^{13}C-labeled cyanide is incorporated in the iminiumacetyl group. Furthermore, from the isotopic distribution it is clear that the iminiumacetyl group is formed by a hydrogen isocyanide cis migration. This is evident from the fact that using ^{15}N-labeled free cyanide in combination with nonlabeled pentacyano(methyl)cobaltate(III) yields two ^{15}N resonance signals of equal intensity, one signal at the frequency of the cis cyano groups and one signal at the frequency of the trans cyano group (Figure 3B).

Conclusion

The insertion reaction that transfers a methyl group coordinated to cobalt(III) in $[Co(CN)_5(CH_3)]^{3-}$ to one of the cyano groups has been shown to be a migratory insertion of cis hydrogen isocyanide as evidenced by the isotope distribution in the end product. The trans influence of the methyl group in $[Co(CN)_5(CH_3)]^{3-}$ facilitates the selective ^{13}C or ^{15}N isotope labeling of the trans cyano ligand in acidic solution. The insertion reaction yields a carbon-bonded iminiumacetyl ligand. The NMR spectroscopic properties of the new pentacyano(iminiumacetyl)cobaltate(III) compounds resemble those of the isoelectronic aminoethylidenepentacarbonylchromium(0) compounds.

Acknowledgment. We are grateful to Flemming Hansen for his help with collection of X-ray diffraction data and to Henning O. Sørensen for computational support. Financial support by the Danish Natural Science Research Council and the Carlsberg Foundation is gratefully acknowledged. The Centre for Crystallographic Studies is funded by the Danish National Research Foundation.

Supporting Information Available: NOE difference spectra of **2** and **3** (Figures S1−S5), ^{59}Co spectrum of **1** (Figure S6), and absorption spectra of **1** and **3** (Figure S7). X-ray crystallographic files, in CIF format, for $(Et_4N)(Ph_4As)_2[Co(CN)_5(CH_3)]$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020353U