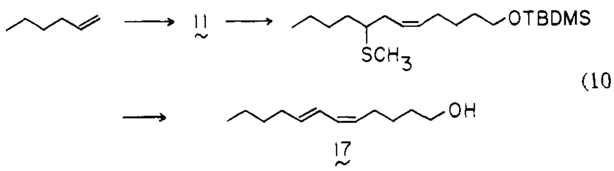

(10)

substituted olefins and with high chemo-, regio-, and diastereoselectivity. The anti-Markovnikov orientation even with a trisubstituted double bond is particularly noteworthy and suggests that, in the opening of the presumed episulfonium ion intermediate, bond formation and cleavage occur more nearly to the same extent at the transition state regardless of the olefin substitution, unlike other olefin additions. The importance of vinylacetylenes themselves (e.g., histrionicotoxins) and their use as intermediates for the stereocontrolled synthesis of dienes attaches additional interest to this olefin elaboration method.

Acknowledgment. We thank the National Science Foundation for their generous support of our program.

Registry No. 1, 5799-67-7; **3**, 90108-00-2; **4**, 34046-61-2; **5**, 41578-02-3; **6**, 90108-01-3; **7**, 628-71-7; **8**, 90108-02-4; **9**, 90108-03-5; **10**, 90108-04-6; **11**, 90108-05-7; **12a**, 5617-41-4; **12b**, 10483-56-4; **13**, 90108-06-8; **14a**, 90108-07-9; **14b**, 90108-09-1; **15**, 90108-09-1; **16**, 90108-10-4; **17**, 72922-18-0; TDMSOCH$_2$C≡CH, 76782-82-6; TBDMSO(CH$_2$)$_4$C≡CH, 73448-13-2; Et$_2$AlCl, 96-10-6; Et$_3$Al, 97-93-8; cyclohexene, 110-83-8; methylenecyclopentane, 1528-30-9; 1-methyl-1-cyclohexene, 591-49-1; (*E*)-dec-5-ene, 7433-56-9; (*Z*)-dec-5-ene, 7433-78-5; methyl undec-10-enoate, 111-81-9; 1-hexene, 592-41-6; 1-(methylthio)-1-(oct-2-yn-1-yl)cyclopentane, 90108-11-5; methyl 3-(methylthio)undec-5-ynoate, 90108-12-6; *trans*-1-[3-(*tert*-butyldimethylsiloxy)-1-propynyl]-2-(methylthio)cyclohexane, 90108-13-7; 1-(1-heptynyl)cyclohexene, 90108-14-8; (*E*)-1-(*tert*-butyldimethylsiloxy)dodec-7-en-5-yne, 90108-15-9; (*Z*)-1-(*tert*-butyldimethylsiloxy)dodec-7-en-5-yne, 90108-17-1; (*Z*)-1-(*tert*-butyldimethylsiloxy)-8-(methylthio)dodec-5-ene, 90108-16-0; lithium triethylheptynylaluminate, 90108-18-2; lithium diethyldiheptynylaluminate, 90108-19-3; 1-lithio-1-heptyne, 42017-07-2.

Isolation and Characterization of $(PNP)_2Co(CN)_4$, an Unusual Square-Planar Cobalt(II) Complex

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Received February 13, 1984

Cyanide ion is regarded as promoting the formation of higher coordination numbers in transition-metal complexes.[1] Thus it is not surprising that, although good evidence for loss of CN^- from $Co(CN)_5^{3-}$ in solution has been presented,[2,3] no simple monomeric $Co(CN)_4^{2-}$ species has yet been isolated in the solid state. It occurred to us that, since many cyanide complexes are anionic, appropriate variation of counterions would permit stabilization of different geometries or coordination numbers. We now report the successful synthesis and characterization of $(PNP)_2Co(CN)_4$ (**1**),[4] a simple, monomeric, coordinately unsaturated Co(II) complex. This has proven to be a very rare example of low-spin, square-planar Co(II) with unidentate ligands,[5] in fact to our knowledge, the first with only a *single* type of unidentate ligand.

Anhydrous $CoCl_2$ reacts with 4 equiv of (PNP)CN in dimethylformamide solution to produce a green solution from which pale blue $(PNP)_2Co(CN)_4$ can be crystallized by cooling. Compound **1** is isolated as a DMF solvate. Drying at 80 °C in vacuo produces solvent-free material as a pale blue, air-sensitive powder. Satisfactory analytical data was obtained on a sample recrystallized from DMF and dried as above, mp 227.5–229 °C (corrected). Anal. ($C_{76}H_{60}N_6P_4Co$) C, H, N, Co (Pascher Mikroanalytische Laboratorium, Bonn). The infrared spectrum of the unsolvated solid (Nujol mull) shows bands at 2100 (sh, s) and 2095 (s) ($\nu_{C\equiv N}$) and 397 cm^{-1} (ν_{Co-C}). The magnetic moment of **1** in the solid state was found to be 2.15 μ_B.[6] Solution spectral and magnetic data are solvent and concentration dependent; the resultant equilibria are currently under investigation. The magnetic moment of **1** in acetonitrile (1.25×10^{-1} M) is 2.52 μ_B.[7] Infrared spectral data for varying ratios of cobalt to added cyanide in acetonitrile solution are in Table I; the IR spectrum of **1** in DMF or CH_3CN solution is similar to the 1:4 Co:CN solution. Only one cyanide absorption, at 2096 cm^{-1}, was detected for **1** in CH_2Cl_2 solution.

Table I. IR Data for Solutions of $CoCl_2$ in Acetonitrile to Which Increasing Amounts of (PNP)CN Are Added[a]

Co:CN$^-$	color	IR,[b] cm^{-1}
3	deep blue	2131 (w), 2120 (w), 2096 (s), 2089 (m)
4	blue-black	2131 (vw), 2099 (m), 2090 (s), 2071 (w)
5	olive-green	2090 (m), 2072 (s)
6	yellow	2090 (w), 2072 (s)

[a] Compare $(PNP)_3Co(CN)_5$ ν_{CN} 2072 cm^{-1}, $K_3Co(CN)_6$ ν_{CN} 2131, 2128 cm^{-1} (mineral oil mulls). [b] IR solutions 1.75×10^{-2} M.

The only previously reported solid apparently containing the $Co(CN)_4^{2-}$ anion is $K_2Co(CN)_4$, isolated from liquid ammonia.[8] The spectroscopic properties of this material clearly indicate its polymeric nature. Monomeric $Co(CN)_4^{2-}$, as well as $Co(CN)_3(solvent)^-$, have been observed in solution, but not isolated.[3,9] Compound **1** has properties distinctly different from those of $K_2Co(CN)_4$ with solubility and spectral data suggestive of a stable form of monomeric $Co(CN)_4^{2-}$. The magnetic moment of **1** rules out a tetrahedral coordination geometry. Although all known $Co(II)L_4$ species (L = unidentate ligand) exist in a tetrahedral configuration, the possibility of cyanide inducing a square-planar coordination geometry should not be unexpected since cyanide is a very strong field ligand (cf. $Ni(CN)_4^{2-}$). Square-planar Co(II) complexes with macrocyclic ligands exhibit magnetic moments in the range 2.1–2.8 μ_B,[10] suggesting such a structure for the solid. The cobalt(II) bis(dithioacetylacetonate) complex, $Co(SacSac)_2$, has a magnetic moment of 2.35 μ_B[11] and has been shown to be square planar by X-ray crystallography.[12] The IR data for **1** indicate only the presence of terminal cyanide groups in the solid state, thus precluding the possibility of bridging cyanides bonded to a low-spin octahedral Co(II) center.[13]

The IR data in Table I are consistent with the idea that in a coordinating solvent, such as acetonitrile, the $[Co(CN)_4]^{2-}$ anion participates in a dynamic equilibrium:

$$[Co(CN)_2(CH_3CN)_2] \rightleftharpoons [Co(CN)_3CH_3CN]^- \rightleftharpoons [Co(CN)_4]^{2-} \rightleftharpoons [Co(CN)_5]^{3-}$$

Consistent with this, the electronic spectrum of **1** is dominated

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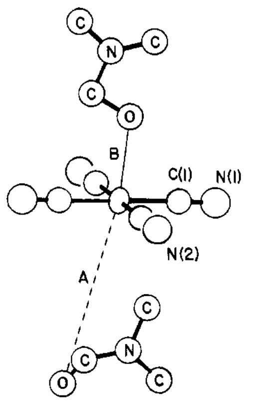

Figure 1. View of the $Co(CN)_4^{2-}$ molecular anion and the associated pair of disordered DMF molecules (see text). Co–O distances are indicated by letter (*A*, 5.89; *B*, 2.64 Å).

by absorptions assigned to the known *tetrahedral* $[Co(CN)_3CH_3CN]^-$ anion.[14]

Owing to the unusual stereochemistry suggested by our spectral and magnetic measurements and the ambiguity of the spectral measurements resulting from the aforementioned equilibria, we decided to carry out an X-ray structure determination on the salt. Very small single crystals could be obtained only from DMF solution. The crystals are monoclinic, space group $P2_1/c$, with $a = 11.188$ (3) Å, $b = 12.423$ (4) Å, $c = 29.142$ (9) Å; $\beta = 98.31$ (3)°. The observed density,[15] 1.26 (1) g cm^{-3}, implied that DMF solvate was contained in the crystals; the resultant formulation is $(PNP)_2Co(CN)_4 \cdot 4DMF$ (for $Z = 2$, $d_{calcd} = 1.270$). Full-matrix least-squares refinement of positional and thermal parameters for all atoms, using 2025 data for which $F > 3.92\sigma(F)$ and $2\theta_{Mo\ K\alpha} < 40°$, gave $R = 0.084$ and $R_w = 0.105$. The structure of the anion (Figure 1) consists of a crystallographically centrosymmetric square-planar $Co(CN)_4^{2-}$ moiety, associated with a pair of disordered DMF molecules. This disorder is such that the NC_3 skeleton of the DMF is similar for each molecule, but the oxygen atoms occupy two different positions of equal probability. In one (A) the Co–O distance is 5.89 Å, while in the other (B), a significant contact, 2.64 (3) Å, occurs. This interaction represents a bond order of ~0.1, as discussed by Raymond et al.[16] The shortest distances from Co to the P and N atoms of the PNP cation are ~9 Å. This suggests formulation of the complex as square-planar $Co(CN)_4^{2-}$ *weakly coordinated*[16] to one DMF molecule. The remaining DMF molecules in the unit cell, which arise from one symmetry-independent DMF, are ordered and do not approach the Co atom. The Co–C(1) and –C(2) distances (1.869 (15), 1.875 (14) Å, respectively) are among the shortest observed for Co(II)–CN distances;[16,17] the C(1)–Co–C(2) angle is 91.1 (6)°.[18]

Besides being a textbook demonstration of the great ligand field strength of cyanide, the existence and structure of $(PNP)_2Co(CN)_4$ emphasizes the complexity of cobalt–cyanide chemistry. The sensitivity of the catalytically active[19] $Co(II)–CN^-$ system to counterion (as well as to solvent[3,10]) predicts a significant dependence of reactivity on counterion. This and the effects of other choices of counterion are under active study in our laboratory.

Acknowledgment. We thank Professor R. Holm and Dr. J. J. Girerd (Harvard) for their kind assistance in measurement of the solid-state magnetic moment data. This research was supported by the National Science Foundation under Grant CHE-8209006, the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Three tables of atomic coordinates, temperature factors, and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(14) ESR, electrochemical, and magnetic moment data provide good evidence for the existence of this species.[3,9]

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(18) Other distances and angles in the anion: N(1)–C(1), 1.15 (2); N(2)–C(2), 1.17 (2) Å; C(1)–Co–O(1B), 90.6 (9)°; C(2)–Co–O(1B), 92.8 (8)°; Co–C(1)–N(1), 178 (1)°; Co–C(2)–N(2), 177 (1)°.

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N-Bromodifluoromethanimine

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The fascinating chemistry of the simple imines $CF_2{=}NX$ ($X = F, Cl$) has provided routes to many novel fluorinated materials.[1-5] These compounds have also provided an opportunity to compare the reactivities of the carbon–nitrogen double bonds affected only by the halogen substituent on nitrogen and to compare the reactivities of the N–X bonds. Perfluoromethanimine is considerably more electrophilic than $CF_2{=}NCl$, but the N—X bond in the latter is considerably more reactive.

In the course of research with $CF_2{=}NX$ ($X = Cl, F$), we became increasingly interested in preparing the *N*-bromo analogue. It was obvious that the latter would have the most reactive N–X bond and would represent an extremely useful synthon. However, all attempts to prepare it by methods analogous to the preparation of $CF_2{=}NCl$[6] and $CF_2{=}NF$[7] failed. We speculated that the fluoride-promoted oxidation of $FC{\equiv}N$ by Br_2 might yield the desired compound. However, $FC{\equiv}N$ is quite difficult to prepare,[8] and this reaction remained untried until an unexpected source of $FC{\equiv}N$ became available. Pyrolysis of $CF_3CF_2CF{=}NBr$ at 450 °C gives $FC{\equiv}N$ and C_2F_5Br in excellent yield.[9] This provided the needed $FC{\equiv}N$, and our first attempt at the preparation of $CF_2{=}NBr$ was successful.

$$FC{\equiv}N + MF \rightarrow F_2C{=}N^-M^+ \xrightarrow{Br_2} F_2C{=}NBr + MBr \qquad M = K, Rb, Cs$$

Some of the $CF_2{=}NBr$ is further oxidized to CF_3NBr_2, which was previously prepared from the metal fluoride catalyzed conversion of CF_3NClBr to CF_3NBr_2 by Br_2.[4]

$$CF_2{=}NBr + MF \rightarrow CF_3NBr^-M^+ \xrightarrow{Br_2} CF_3NBr_2 + MBr$$

In a typical reaction, a 100-mL flask fitted with a glass–Telfon valve is charged with 15 mmol of active KF in a drybox.[10] The

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(10) Both CsF and RbF are effective in this reaction. However, KF appears to give higher yields. Metal fluorides are activated by fusing in a platinum crucible, followed by grinding to a fine powder in a ball mill under very anhydrous conditions. No reaction was observed with NaF.

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