zyloxide transesterification followed by reduction ($LiAlH_4$) to the alcohol **14b**, $[\alpha]^{22}_D$ +43.3° (*c* 0.78, CCl_4), whose absolute configuration has been previously established, $[\alpha]^{22}_D$ +41.0° (*c* 1.94, CCl_4).[2]

From a mechanistic standpoint the actual structure of the Lewis acid–dienophile complex is of considerable interest. We are currently operating on the premise that the complexed ion pair **17** is the putative species exhibiting good levels of π-facial selectivity during the cycloaddition process. The stereochemical course of all preceeding cycloadditions can be readily rationalized assuming that the C_4 substituent, R_2, directs the cycloaddition process to the opposite face of the cisoid dienophile complex **17**.

Acknowledgment. This research was supported by the National Science Foundation and the Eli Lilly Co.

Supplementary Material Available: Synthesis of **1a,b**, **2a,b**, and **3a,b** and experimental conditions for individual diastereomer resolutions (11 pages). Ordering information is given on any current masthead page.

Alkynyl Sulfenylation. A Direct Approach for Nucleophilic Addition and Substitution of Olefins by Carbanions

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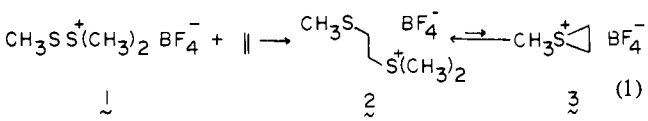
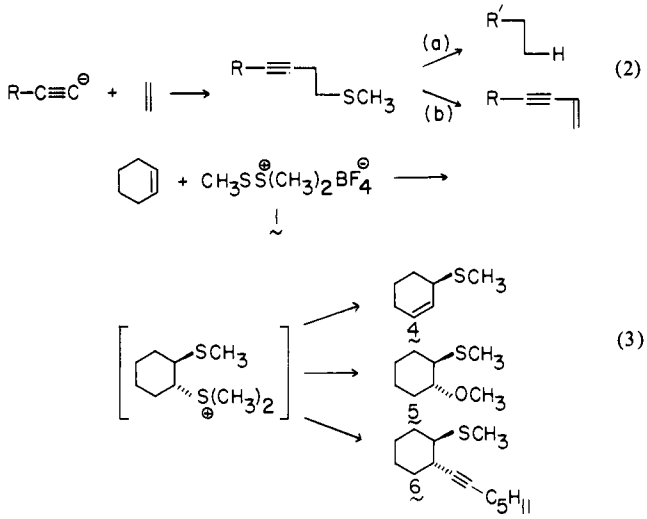
In exploring the concept of nucleophilic addition and substitution of olefins initiated by DMTSF (**1**), the question of the choice of nucleophile is of paramount importance.[1-4] The difficulty arises from the fact that the species present is the adduct **2**, which must be coaxed to solvolyze to the episulfonium ion **3** prior to nucleophilic attack. Thus, the nature of the nucleophile that can



(1)

exercise such discrimination without simply decomposing **2** becomes critical. Use of simple carbon nucleophiles would appear to be incompatible with such a reaction because of their basicity. Nevertheless, the importance of such carbon–carbon bond-forming reactions in organic synthesis and the importance of acetylenes for further structural elaboration[5] led us to examine an alkynyl sulfenylation as in eq 2. However, we were not surprised that use of a plethora of nucleophilic acetylide species failed. To illustrate (see eq 3), simple acetylide anions either failed to react



(2)

(3)

or produced complex mixtures or the elimination product **4**. In fact, with lithium heptynylide, this sequence constitutes a useful allylic sulfenylation. Attenuating the basicity but hopefully retaining nucleophilicity with boron compounds led to complex mixtures with trialkyl "ate" complexes (in part due to the oxidative workup required), preferential transfer of a methoxy group to give **5** (67% yield) with trimethyl borate "ate" complexes, or elimination to **4** in addition to **6** (43% yield) if a poorer migrating group, isopropoxy, is substituted for methoxy. Believing that use of a reagent that could complex dimethyl sulfide would facilitate formation of the reactive episulfonium salt intermediate and still possess a nucleophilic acetylide led us to explore the aluminum derivatives of acetylides.[6] The "ate" complex with triethylaluminum and lithium heptynylide (reagent B) gave up to 92% yields of **6** but with some competing ethyl transfer (0–20%). The dialkynylethylalane (reagent A, from 2 equiv of lithium heptynylide and 1 equiv of $(C_2H_5)_2AlCl$) and the lithium dialkynyldiethylaluminate (from 2 equiv of lithium heptynylide and 1 equiv of $(C_2H_5)_2AlCl$) gave clean reaction to produce **6** in 63% and 88% distilled yields, respectively.[7] Table I summarizes the results.[8]

The reaction is stereospecific (entries 1, and 3–6). The trans addition stems from the spectroscopic data, reasonable analogy

(1) For other types of nucleophiles, see: (a) Trost, B. M.; Shibata, T. *J. Am. Chem. Soc.* **1982**, *104*, 3225. (b) Trost, B. M.; Shibata, T.; Martin, S. J. *Ibid.* **1982**, *104*, 3228. (c) Caserio, M. C.; Kim, J. K. *Ibid.* **1982**, *104*, 3231.

(2) For reviews on episulfonium ions, see: Schmid, G. H. *Top. Sulfur Chem.* **1977**, *3*, 101. Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 282. For leading references to metal-initiated nucleophilic attack on olefins see ref 1a.

(3) For independent investigations of the application of the adducts of benzenesulfenyl chloride and olefins, see: Ibragimov, M. A.; Smit, W. A. *Tetrahedron Lett.* **1983**, *24*, 961. Patel, S. K.; Paterson, I. *Ibid.* **1983**, *24* 1315. Alexander, R. P.; Paterson, I. *Ibid.* **1983**, *24*, 5911.

(4) DMTSF = *d*imethyl(*m*ethylthio)*s*ulfonium *f*luoroborate. Meerwein, H.; Zenner, K. F.; Gipp, R. *Liebigs Ann. Chem.* **1965**, *688*, 67. Helmkamp, G. K.; Cassey, H. N.; Olsen, B. A.; Pettitt, D. J. *J. Org. Chem.* **1965**, *30*, 933. Smallcombe, S. H.; Caserio, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 5826.

(5) For a review, see: Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. Negishi, E. "Organometallics in Organic Synthesis"; Wiley Interscience: New York, 1980; Vol. 1, Chapter 5. For some very recent examples, see: Miller, R. B.; Al-Hassan, M. I. *Tetrahedron Lett.* **1983**, *24*, 2055. Yoshida, T. *Chem. Lett.* **1982**, 293. Pelter, A.; Singarem, S.; Brown, H. C. *Tetrahedron Lett.* **1983**, *24*, 1433. Brown, H. C.; Basavarah, D. *J. Org. Chem.* **1982**, *47*, 5407, 3808, 3806.

(6) Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3941. Negishi, E.; Baba, S. *J. Am. Chem. Soc.* **1975**, *97*, 7385. Also see: Fried, J.; Sih, J. C. *Tetrahedron Lett.* **1973**, 3899. Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520.

(7) Typical procedures: (Reagent A) In a centrifuge tube, 0.728 mL (1.31 mmol) of a 1.8 M solution of diethylaluminum chloride in toluene was added to 1-lithio-1-heptyne (from 252 mg, 2.62 mmol of 1-heptyne and 1.69 mL, 2.62 mmol, of a 1.55 M solution of *n*-butyllithium in hexane) and 0.2 mL of dry THF. The resultant suspension was centrifuged to settle the lithium chloride. In a separate flask, cyclohexene (54 mg, 0.657 mmol) was added to 128.5 mg (0.655 mmol) of DMTSF in 0.8 mL of 1,2-dichloroethane at room temperature. After 15 min, the aluminate solution was cannulated away from the lithium chloride into the resultant mixture. After the mixture was heated for 2 h at 80 °C, the solution was diluted with methylene chloride, washed with aqueous sodium bisulfate and then sodium bicarbonate, and dried. After concentration, the crude product was distilled in a Kugelrohr apparatus to give 129 mg (88%) of product. (Reagent B) To 1.8 mL (2.79 mmol) of *n*-butyllithium in hexane (1.55 M) and 0.1 mL of THF at 0 °C was added 593 mg (2.79 mmol) of 1-*tert*-butyldimethylsiloxy-5-hexyne. After 15 min of stirring at room temperature, the solution was recooled to 0 °C and 1.47 mL (1.9 M, 2.79 mmol) of triethylaluminum in toluene added. In a separate flask, a solution of 118 mg (1.40 mmol) of 1-hexene in 1.4 mL of 1,2-dichloroethane was stirred at room temperature with 274 mg (1.40 mmol) of DMTSF for 90 min. The solution of the DMTSF/olefin adduct, cooled to 0 °C, was cannulated into a solution of the aluminate also at 0 °C. After the mixture was stirred for 3 h at room temperature, slow addition of aqueous sodium bisulfate quenched the reaction. Partitioning between ether and water was followed by washing the ether layer with aqueous sodium bisulfate and saturated aqueous sodium bicarbonate and then drying ($MgSO_4$). Evaporation of the solvent in vacuo and Kugelrohr distillation gave two fractions. The first fraction, bp 60–80 °C (0.1 mm), yielded 421 mg (71% recovery) of starting alkyne which accounts quantitatively for all the alkyne. Fraction two, bp 90–140 °C (0.1 mm), yielded 255.6 mg (53%) of 1-*tert*-butyldimethylsiloxy-8-methylthiododec-5-yne.

(8) All new compounds have been fully characterized by spectral means and have satisfactory combustion analysis or high-resolution peak matching.

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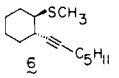
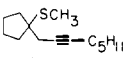
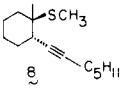
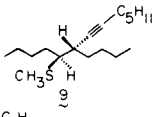
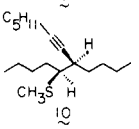
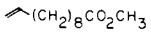
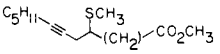
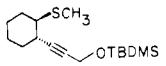
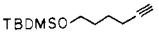
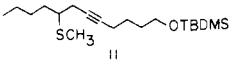
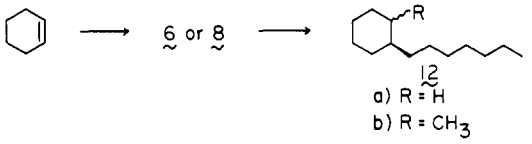
Table I. Alkynl Sulfenylation of Olefins

entry	olefin[a]	alkyne	reagent	solvent ratio[b] (Cl Cl / THF)	temp[c]	time[c]	product[d]	isolated yield[e]
1		$^{n}C_5H_{11}C{\equiv}CH$ **7**	A	4/1	80 °C	2 h	 **6**	88%
2		**7**	B	5/1	rt	45 min		86%
3		**7**	B	5/1	rt	35 min	 **8**	86%
4		**7**	A	4/1	rt	1 h	 **9**	74%
5		**7**	A	5/1	0 °C	45 min	 **10**	83%
6		**7**	A	5/1	0 °C	1 h		54%
7		$TBDMSOCH_2C{\equiv}CH$	B	5/1	40 °C	40 min		72%
8		TBDMSO 	B	14/1	rt	3 h	 **11**	53%

[a] Normally a 2:1 ratio of the reagent to the olefin is employed. [b] Toluene and hexane derived from the organoaluminum and *n*-butyllithium, , respectively, are also present. The given ratio is for the added solvents at the final stage of reaction. [c] Time and temperature at the final stage of reaction, rt = room temperature. [d] All new compounds have been fully characterized. In each case, spectroscopy including ^{13}C NMR and chromatography (TLC and GC), indicate a single regio- and/or stereoisomer was present. [e] The products have been purified either by chromatography or distillation. [f] In this case, a byproduct, whose structure has not been deduced, contaminates the major product.

to additions to episulfonium ions, and subsequent chemistry (vide infra). The reaction is completely regioselective (entries 2, 3, 6, and 8) leading to an anti-Markovnikov addition even in the case of a trisubstituted olefin (entry 3) in contrast to other reactions of episulfonium salts. Preliminary results indicate good chemoselectivity too (entries 6–8).

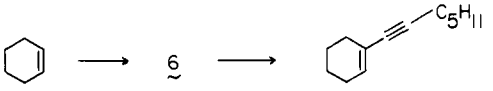
The equivalent of nucleophilic addition to a double bond was explicitly demonstrated in the case of **6** and **8**, which, upon exposure to W-2 or W-5 Raney nickel in refluxing ethanol, gave **12** in 87% and 84% yield, respectively (eq 4). The presence of



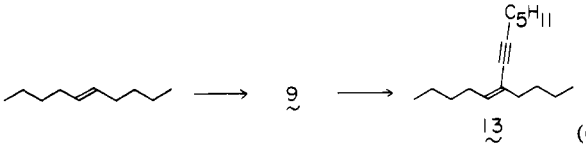
(4)

a doublet for the ring methyl group in **12b** also establishes the regiochemistry of the addition to 1-methylcyclohexene.

The equivalent of nucleophilic substitution of an olefin was explicitly demonstrated in the case of **6**, **9**, **10**, and **11** (eq 5–8).



(5)



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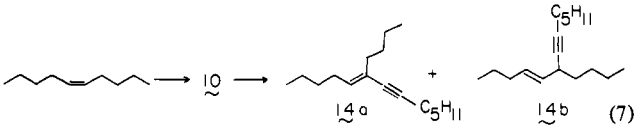
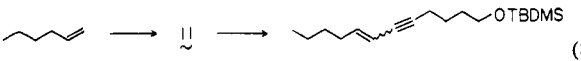


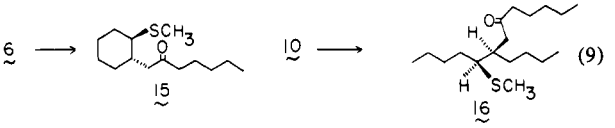
(7)



(8)

Eliminations were accomplished either by oxidation to the sulfoxide followed by heating in a sealed tube at 140–220 °C ($CaCO_3$, $C_2H_5OCH{=}CH_2$)[9] [eq 6 and 7 (**14a**:**14b** 2:1)] or by alkylation–elimination [$CF_3SO_3CH_2CO_2C_2H_5$, CH_3CN then DBU[10] eq 5, 7 (**14a**:**14b** 5:1), and 8]. Since both eliminations are known to be cis, the elimination products provide chemical evidence for the stereochemistry of the alkynyl sulfenylation.

The versatility of this approach also derives from the versatility of the acetylene. One illustration is the net hydration of the acetylene to a ketone. While mercury-based methods proved less than satisfactory, hydroboration–oxidation[11] of **6** and **10** gave the ketones **15** and **16** in 91% and 79% yields, respectively (eq 9).

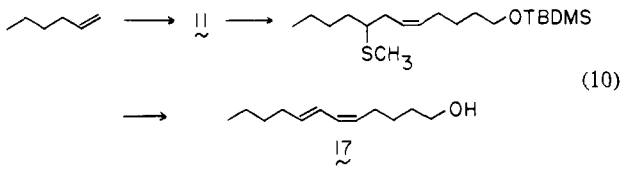


(9)

A short synthesis of the sex pheromone of *Malacosoma disstria* (forest tent caterpillar) **17**[12] from 1-hexene utilizes the adduct **11** (eq 10). Since elimination at the stage of the acetylene gave an *E*,*Z* mixture (eq 8), an alternative was sought. By an increase in the effective steric bulk of the alkyl group, enhanced stereoselectivity should result. Indeed, reduction of **11** (H_2, Lindlar's catalyst, hexane, 99%) followed by elimination (i, TfO $CH_2CO_2C_2H_5$, CH_3CN; ii, DBU, 46 °C; iii, $(C_4H_9)_4NF$, THF; 69% overall) proceeds stereoselectively to give the desired diene (eq 10) with high (>98%) stereocontrol.

This direct elaboration of olefins with nucleophiles has several notable merits. The activating sulfur conjunctive reagent, DMTSF, is a readily available, crystalline solid that can be stored indefinitely. The reactions work well with mono-, di-, and tri-

(9) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887 and references therein. For reviews, see: Trost, B. M. *Acc. Chem. Res.* **1978**, *11*, 453; *Chem. Rev.* **1978**, 363.
(10) Vedejs, E.; Engler, D. A. *Tetrahedron Lett.* **1976**, 3487.
(11) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 3222.
(12) Chisholm, M. D., Underhill, E. W.; Steck, W.; Slessor, K. N.; Grant. G. G. *Environ. Entomol.* **1980**, *39*, 287.



(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; $TDMSOCH_2C{\equiv}CH$, 76782-82-6; $TBDMSO(CH_2)_4C{\equiv}CH$, 73448-13-2; Et_2AlCl, 96-10-6; Et_3Al, 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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