The Synthesis of Mononuclear Cyanocobalt(III) Complexes

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1 Introduction*

Our understanding of mechanism in metal-complex chemistry has developed in the past twenty years by the study of a relatively small number of systems. Cobalt complexes occupy a prominent place in most accounts, being accorded in one case[1] the ultimate philosophical accolade[2] of 'paradigm'. The S_N1–S_N2 dichotomy originally prompted a search[3] for 'typical limiting S_N1 systems'[1] and two of the small number established are cyanocobalt complexes, —$Co(CN)_4(SO_3)(OH_2)^{3-}$ and $Co(CN)_5(OH_2)^{2-}$. The latter case seems less reliably established how than it was at first supposed[4] but, nevertheless, the original idea remains plausible. The search was concentrated on cyanide systems because a strongly π-acid high-field ligand such as the cyanide ion might be expected to promote a limiting dissociative mechanism by selectively weakening[5] the metal-ligand bond *trans* to it and by stabilizing the five-co-ordinate intermediate[6] formed.

The purpose of this review is to survey the various means of synthesis of mononuclear cyanocobalt(III) complexes so as to assist the further study of their mechanistic chemistry and associated properties. An excellent general text on the cyano-complexes of the transition metals[7] includes most of the synthetic literature up to 1974. The present review covers, it is hoped, all the significant synthetic approaches published up to 1981 and also includes some work from 1982. The

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* Abbreviation used in this review: acac, acetylacetonate anion; β-ala, β-alanine anion; bip 2,2′-dipyridine; cyen, 1,2-cyoclohexanediamine; dien, diethylenetriamine; dmf, dimethyl formamide; dmgH, dimethyl glyoxime monoanion; dpe, 1,2-(bisdiphenylphosphino)ethane; dtc, dimethyldithiocarbamate anion; edda, ethylenediamine diacetate anion; en, ethylenediamine; gly, glycine anion; malo, malonate dianion; ox, oxalate dianion; phen, 1,10-phenanthroline; pn, propylenediamine; py, pyridine; thio, thiourea; tetars, $(CH_3)_2As(CH_2)_3As(Ph)(CH_2)_2As(Ph)(CH_2)_3As(CH_3)_2$; tn, trimethylenediamine; trien, triethylenetetramine; vpp, *cis*-1,2-(bisdiphenylphosphino)ethylene; xan, methyl xanthate anion.

[1] C. H. Langford and V. S. Sastri in 'M.T.P. Int. Review of Science; Inorganic Chemistry, Ser. 1, vol. 9, Reaction Mechanisms in Inorganic Chemistry, ed. M. L. Tobe, Butterworths, London, 1972, p. 203.

[2] T. S. Kuhn, 'The Structure of Scientific Revolutions', University of Chicago Press, Chicago, 1970.

[3] J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta Rev.*, 1971, **5**, 7.

[4] A. Haim, *Inorg. Chem.*, 1982, **21**, 2887.

[5] P. J. Toscano and L. G. Marzilli, *Inorg. Chem.*, 1979, **18**, 421.

[6] M. A. Tobe, "Inorganic Reaction Mechanisms', Nelson, London, 1972.

[7] A. G. Sharpe, 'The Chemistry of the Cyano Complexes of the Transition Metals', Academic Press, New York, 1976.

reference material is also summarized in tables which have been arranged according to the number of cyanide ligands in the complex and also by means of the identity of the other principal constituents. The methods are discussed and classed in terms of the basic mechanistic principles[6] controlling the products of oxidation and substitution in cobalt chemistry.

2 Synthesis by the Oxidation of Cobalt(I) and Cobalt(II) Complexes

A. Cobalt(I) or (II) by Dioxygen or Hydrogen Peroxide.—Cobalt(I) oxidation by dioxygen or hydrogen peroxide has not generally been used to synthesize cobalt(III) complexes. However, in one case the approach has been found to be successful.[8] Air oxidation of π-$C_5H_5Co(CO)_2L$, L = CO or PPh_3, in alcoholic potassium cyanide gives π-$C_5H_5Co(CN)_3^-$ or π-$(C_5H_5)Co(CN)_2PPh_3$, in good yield, ($\sim$50%).

Cobalt(II) complexes are more frequently used. For instance, the anion $Co(CN)_6{}^{3-}$ is the simplest cyano-complex to prepare since it is made by boiling cobalt(II) cyanide in excess aqueous potassium cyanide[9] in the presence of air. A limited number of substituted complexes can be made in a similar way. The restricted range of the method is due to the extreme stability of the $Co(CN)_5{}^{3-}$ anion, which generally forms to the exclusion of any other when the molar ratio of cyanide to cobalt is greater than or equal to five. The product of oxidation is then frequently contaminated with $Co(CN)_6{}^{3-}$ derived from $Co(CN)_5{}^{3-}$ oxidation. However, providing the relative concentration of cyanide is low enough and the competing ligand forms a strong bond with cobalt, mixed complexes can be prepared.

Both $Co(CN)_4(bip)^-$ and $Co(CN)_2(phen)_2{}^+$ are formed[10] by the aerial oxidation of an aqueous alcoholic solution containing the stoicheiometric proportions of cobalt(II) acetate, potassium cyanide, and the appropriate amine. $Co(CN)_4en^-$ is likewise formed[11] by oxidizing a solution of cobalt(II), cyanide, and ethylenediamine in the molar proportions 1 : 4 : 3. The dimer $Co(CN)_5SO_2Co(CN)_5{}^{6-}$, made[12] from $Co(CN)_5{}^{3-}$ and sulphur dioxide in water, has been used as an intermediate in the preparation[13] of $Co(CN)_5(NH_3)^{2-}$ by oxidation with hydrogen peroxide in the presence of ammonia.

Carbon monoxide apparently causes[14] disproportionation of $Co(CN)_5{}^{3-}$ in dilute (<0.1M) solution to $Co(CN)_6{}^{3-}$ and $Co(CN)_3(CO)_2{}^{2-}$. No identifiable cyanocarbonyl cobalt(III) complexes were isolated from the mixture after oxidation. However, a later report[15] contains infra-red evidence that $Co(CN)_5(CO)^{2-}$

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[8] J. A. Dineen and P. L. Pauson, *J. Organomet. Chem.*, 1974, **71**, 77.

[9] J. H. Bigelow, *Inorg. Synth.*, 1946, **2**, 225.

[10] L. Cambi and E. Paglia, *J. Inorg. Nucl. Chem.*, 1958, **8**, 249.

[11] R. Ripan, A. Farcas, and O. Piringer, *Z. Anorg. Allg. Chem.*, 1966, **346**, 221.

[12] A. A. Vlcek and F. Basolo, *Inorg. Chem.*, 1966, **5**, 156.

[13] L. Cambi and E. Paglia, *Gazz. Chim. Ital.*, 1958, **88**, 691.

[14] J. Halpern, G. Guastalla, and J. Bercaw, *Coord. Chem. Rev.*, 1972, **8**, 167.

[15] Yu. P. Nazarenko, V. V. Zhilinskaya, C. A. Kozlov, and K. B. Yatsimirskii, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1978, **23**, 1693.

may be prepared from the oxidation of the much stronger solutions that were used in the earlier preparations said to form[16] $Co(CN)_5(CO)^{3-}$

The direct preparation of cyanophosphine complexes appears practicable in theory but it is complicated by the formation of phosphine oxides. Mixed low-spin cyanophosphine cobalt(II) complexes are readily prepared in solution from CoX_2P_2, (X = halogen, P = phosphine), by cyanide–halide exchange in the presence of excess phosphine using an anion exchange column.[17] The presence of an excess of cyanide in solution will cause the complexes to decompose forming $Co(CN)_5{}^{3-}$ but in excess phosphine $Co(CN)_2P_3$ is stable. Unfortunately aerial oxidation of cobalt(II) phosphine complexes will probably yield phosphine oxide rather than a cobalt(III) complex,[18] leading eventually to mixed phosphine–phosphine oxide complexes.[19] Consistent with this, the cyanocobalt complex $Co(CN)_2(PMe_2Ph)_3$ catalytically oxidizes[20] excess PMe_2Ph in benzene to Me_2PhPO, so it is unlikely that monodentate tertiary phosphine cyanocobalt(III) complexes could be made by this route. The polydentate phosphine and arsine ligands do not oxidize so readily and their cobalt(II) complexes pass cleanly to the corresponding cobalt(III) compounds.[21] Only two applications of this method to a cyanocomplex seem to have appeared, $Co(CN)_2(dpe)_2{}^-$ [22] and $Co(CN)_2(vpp)_2{}^-$.[23] The intermediate peroxo-complex[22] forms the final product by oxidizing the solvent methanol to formaldehyde.

The preparation of cyanocobaloximes has been recommended[24] by direct oxidation of mixtures of dimethyl glyoxime, potassium cyanide, and cobalt(II) chloride but although this method is successful for $Co(dmgH)_2(CN)_2{}^-$, very poor yields of $Co(dmgH)_2(CN)(X)^-$ are obtained[25] when the stoicheiometric amount of the second substituent X^- is included in the reaction mixture. As with the other direct oxidation preparations, only the most stable grouping of ligands can survive displacement by the cyanide ion. In most cases the explanation probably lies in rapid Co^{II}–Co^{III} electron transfer[26,27] reactions, which effectively catalyse the substitution of ligands in the initially formed Co^{III} complex by cyanide ions during the oxidation.

One of the most successful early syntheses of mixed cyanocobalt(III) complexes is based on the oxidation of a mixture of cold concentrated sodium cyanide and an aqueous solution of cobalt acetate saturated with sulphur dioxide.[28] The product crystallizing first, *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$, possibly forms *via* the initially formed

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[16] W. Manchot and H. Gall, *Chem. Ber.*, 1926, **59**, 1056.

[17] P. Rigo, M. Bressan, and A. Turco, *Inorg. Chem.*, 1968, **7**, 1460.

[18] K. A. Jensen, B. Nygaard, and C. Th. Pedersen, *Acta Chem. Scand.*, 1963, **17**, 1126.

[19] J. Rimbault and R. Hugel, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 1.

[20] J. Halpern, B. L. Goodall, G. P. Ghare, H. S. Lin, and J. J. Pluth, *J. Am. Chem. Soc.*, 1975, **97**, 2301.

[21] C. A. McAuliffe and W. Levason, 'Phosphine, Arsine, and Stibine Complexes of the Transition Elements', Elsevier, Amsterdam, 1979, p. 331.

[22] P. Rigo, M. Bressan, B. Corrain, and A. Turco, *J. Chem. Soc., Chem. Commun.*, 1970, 598.

[23] P. Rigo and M. Bressan, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1812.

[24] G. N. Schrauzer, *Inorg. Synth.*, 1968, **11**, 61.

[25] A. L. Crumbliss and P. L. Gauss, *Inorg. Chem.*, 1976, **15**, 737.

[26] L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, 1972, **11**, 2050.

[27] J. P. Birk and J. Halpern, *J. Am. Chem. Soc.*, 1968, **90**, 305.

[28] P. Ray and S. C. Chackrabarty, *Z. Anorg. Allg. Chem.*, 1933, **211**, 173.

dimer $Co(CN)_5SO_2Co(CN)_5^{6-}$.[12] A second product $Co(CN)_5(SO_3)^{4-}$ may be precipitated from the reaction mixture on standing, but it is hard to obtain pure.

B. Cobalt(I) and (II) by Halogens, Pseudohalogens, or Halides.—A wide range of cobalt(I) complexes may be prepared when some of the ligands are of the high-field type. Oxidative addition by either halogens or pseudohalogens then converts them into substituted cyano-complexes.

Both $(\pi\text{-}C_3H_4R)Co(CN)_4^{2-}$ and $(\sigma\text{-}C_3H_4R)Co(CN)_5^{3-}$, (R = H or Me), have been prepared[29] from the corresponding tricarbonylcobalt(I)

$$e.g.\ (\pi\text{-}C_3H_4R)Co(CO)_3 \xrightarrow[-20\,^{\circ}C,\ \text{tetrahydrofuran}]{I_2,\ 4KCN} (\pi\text{-}C_3H_4R)Co(CN)_4^{2-} + 3CO + 2KI$$

The initial step is an oxidative addition to form $(\pi\text{-}C_3H_4R)CoI_2(CO)_2$ followed by iodide and carbon monoxide substitution. Readily available phosphine-substituted allyl complexes, {*e.g.* $(\pi\text{-}C_3H_4)Co(CO)_2(PPh_3)$}, produce the corresponding phosphine-substituted cyano-complexes. An analogous reaction occurs for the cyclopentadienyldicarbonylcobalt(I) complexes,[30] giving $(\pi\text{-}C_5H_5)Co(CN)_3^-$ and $(\pi\text{-}C_5H_5)Co(CN)_2L$, (L = PPh_3, PMe_2Ph, or py). The initial oxidative addition step has been used with the latter complexes and XCN[31] or $S(CN)_2$,[32] (X = Br or I), to give cyano-complexes directly.

$$(\pi\text{-}C_5H_5)Co(CO)_2 + S(CN)_2 \xrightarrow{\text{Ether},\ -20\,^{\circ}C} (\pi\text{-}C_5H_5)Co(CO)(CN)(SCN) + CO$$

A similar approach seems quite practicable with other low-spin Co^I carbonyl complexes. For instance, although $Co(CN)_3(CO)_2^{2-}$ is unstable in solution,[33] a range of its phosphine derivatives have been prepared, $Co(PR_3)_2(CN)(CO)_2$,[14,34] $Co(PR_3)(CN)_2(CO)_2^-$,[14] and $Co(PR_3)_2(CN)_2(CO)^-$,[14] all of which could be used to produce a variety of carbonyl phosphine cyano-complexes.

Oxidative addition reactions have also been used with $Co(CN)_5^{3-}$, although the isolation of pure products has usually been difficult. Bromine and iodine have been used[35] to make $Co(CN)_5Br^{3-}$ and $Co(CN)_5I^{3-}$, but the problem of purification has made alternative routes preferable. Organic halides have been used to make organopentacyano-complexes,[36] although again the isolation of pure products is always difficult and frequently the desired product is formed in poor yield[37] because a second reaction path is possible.

$$2Co(CN)_5^{3-} + RCH_2CH_2X \longrightarrow RCH_2CH_2Co(CN)_5^{3-} + Co(CN)_5X$$

$$2Co(CN)_5^{3-} + 2RCH_2CH_2X \longrightarrow RCH{=}CH_2 + RCH_2CH_3 + 2Co(CN)_5X$$

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[29] J. A. Dineen and P. L. Pauson, *J. Organomet. Chem.*, 1974, **71**, 87.
[30] J. A. Dineen and P. L. Pauson, *J. Organomet. Chem.*, 1972, **43**, 209.
[31] M. Moran, *Z. Naturforsch., Teil B*, 1981, **36**, 431.
[32] M. Moran, A. Ibanez, and J. R. Masaguer, *Z. Naturforsch.*, Teil B, 1982, **37**, 292.
[33] A. Farcas and D. Lupu, *J. Inorg. Nucl. Chem.*, 1975, **37**, 837.
[34] M. Bressan, B. Corain, P. Rigo, and A. Turco, *Inorg. Chem.*, 1970, **9**, 1733.
[35] A. W. Adamson, *J. Am. Chem. Soc.*, 1956, **78**, 4260.
[36] J. Kwiatek, *Catal. Rev.*, 1967, **1**, 37.
[37] P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, 1969, **91**, 582.

The successful syntheses using this method have involved organoligands that cannot disproportionate, *e.g.* $(CN)_5CoCH_2C_5H_5N$,[38] $(CN)_5CoCH_2Ph$,[39] but the numerous other compounds[36] appearing in the literature occur as grossly impure mixtures in the solid or the dissolved state.

The use of alkyl halides or cyanides with cobalt(I) complexes has never been exploited, but it does seem to offer a potential method for making mixed cyanocobalt complexes.

C. Cobalt(II) by Metal Complexes.—The substitution of ammine ligands by cyanide ions in $Co(NH_3)_5X^{2+}$ may be catalysed by cobalt(II) *via* a fast inner-sphere electron transfer *via* the bridging ligand X.

$$\mathrm{CoX(NH_3)_5} \xrightarrow[\mathrm{CN^-\ in\ water}]{\mathrm{Co^{2+}}} \mathrm{Co(CN)_5X} + 5\mathrm{NH_3}$$

The success of the reaction path depends on the ability of X to bridge the cobalt(II) and (III) centres, so that the reaction cannot be universally applicable. In cases where the species X is less efficient, the competing[40] outer-sphere electron-transfer,

$$\mathrm{CoX(NH_3)_5{}^{2+}} \xrightarrow[\mathrm{CN^-\ in\ water}]{\mathrm{Co^{2+}}} \mathrm{Co(CN)_6{}^{3-}} + 5\mathrm{NH_3} + \mathrm{X^-}$$

can become of comparable, or greater, rate. The method has been successful[35,40–42] for X = Cl^-, Br^-, I^-, $NO_2{}^-$, $N_3{}^-$, NCS^-, $NCSe^-$, or OH^-. The difficulties of product isolation make the method unsuitable[42] for $Co(CN)_5(OH)^{3-}$. The $Co(CN)_5{}^{3-}$-catalysed cyanide-ion substitution already mentioned,[27]

$$\mathrm{Co(CN)_5X} \xrightarrow[\mathrm{CN^-\ in\ water}]{\mathrm{Co^{2+}}} \mathrm{Co(CN)_6{}^{3-}} + \mathrm{X^-}$$

can lead to the products being contaminated with $Co(CN)_6{}^{3-}$.

$Hg(SCN)^{2-}$ has also been used as the oxidant for $Co(CN)_5{}^{3-}$. The original purpose of the change was to produce the linkage isomer $Co(CN)_5(NCSe)^{3-}$ since it was supposed that the $Co(CN)_5{}^{3-}$ ion would preferentially attack the uncomplexed nitrogen atom in the bidentate $SeCN^-$ ion.[41] However, it was subsequently found[43] that the preferred bridge was still the selenium atom and $Co(CN)_5(SeCN)^{3-}$ was formed. In the same way, parallel studies using $Co(NH_3)_5(NCS)^{2+}$ and $Co(NH_3)_5(SCN)^{2+}$ showed that the preferred bridge[43] for electron transfer to $Co(CN)_5{}^{3-}$ was always the sulphur atom. The linkage isomers of thiocyanate and selenocyanate are most readily prepared by conversion of the sulphur or selenium into the corresponding nitrogen-bonded forms by the use of counter ion or solvent effects,[44] which can entirely reverse the stability order of the isomers in solution.

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[38] M. D. Johnson, M. L. Tobe, and L.-Y. Wong, *J. Chem. Soc.* (*A*), 1967, 491.

[39] J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, 1964, **86**, 2311.

[40] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, 1963, **85**, 2517.

[41] J. L. Burmeister and M. Y. Al-Janabi, *Inorg. Chem.*, 1965, **4**, 962.

[42] V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1975, **14**, 401.

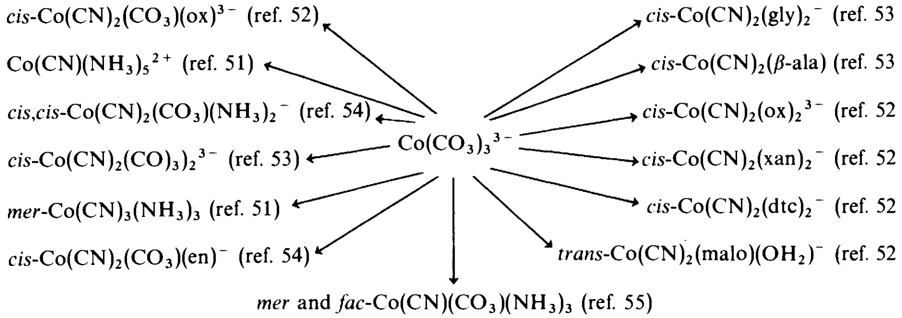
[43] J. B. Melpolder and J. L. Burmeister, *Inorg. Chim. Acta*, 1975, **15**, 91.

[44] D. F. Gutterman and H. B. Gray, *J. Am. Chem. Soc.*, 1971, **93**, 3364.

3 Synthesis by Cyanide Ion Substitution in Cobalt(III) Complexes

The predominant mechanism of substitution in cobalt(III) complexes seems[1] to be of the I_d type and this is reflected in the strategy of cyano-complex synthesis by substitution. Ligands are introduced so as to labilize those in the *trans* position selectively and thus construct the desired product. The '*trans*' sequence can vary depending on the family of complex but a rough general sequence does apply[5,45] and is often described for particular cases, *e.g.* for the $Co(dmgH)_2XY^-$ system.[46] The ligand high in the *trans* series usually is also the strongly bonded, so that the desired product is built up by inserting first the ligands high in the order.

A. Carbonate.—The 'Field–Durrant' solution[47] is one of the most useful aids to cobalt(III)-complex synthesis. It contains a mixture of mononuclear and dinuclear carbonato-complexes[48] but behaves as if it consisted of $Co(CO_3)_3{}^{3-}$. The ease of substitution of each carbonate ligand diminishes as successive ligands are removed[49] so that the selective preparation of cobalt(III) complexes with three distinct ligand types becomes possible.[47] The chemistry and applications of the carbonato-cobalt(III) complexes have been very thoroughly reviewed[50] for the period before 1968. In the case of cyano-complex synthesis it is possible to control the numbers of cyanide and other ligands by regulating the relative concentrations added to the Field–Durrant preparation and the severity of the treatment, *i.e.* through temperature, time or, unusually, by the addition of an active carbon catalyst[51] in the synthesis of $Co(CN)(NH_3)_5{}^{2+}$ and $Co(CN)_3(NH_3)_3$.



Scheme 1

These preparations are all one-pot processes (Scheme 1). The Field–Durrant solution is treated with the correct proportion of potassium cyanide and, after the

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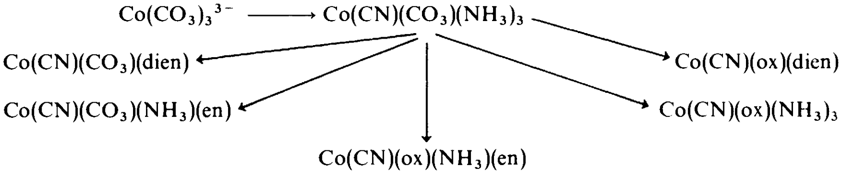
[45] T. P. Das Gupta in 'M.T.P. Int. Review of Science; Inorganic Chemistry, Ser. 2, vol. 9, Mechanisms of Octahedral Substitution,' ed. M. L. Tobe, Butterworths, London, 1974, p. 66.
[46] G. P. Syrtsova, *Russ. J. Inorg. Chem.* (Engl. Transl.), 1974, **19**, 423.
[47] M. Shibata, *Proc. Japan. Acad.*, 1974, **50**, 779.
[48] G. Davies and Y.-W. Hung, *Inorg. Chem.*, 1976, **13**, 764.
[49] J. F. Glenister, K. E. Hyde, and G. Davies, *Inorg. Chem.*, 1982, **21**, 2331.
[50] C. R. Pinz-MacColl, *Coord. Chem. Rev.*, 1969, **4**, 147.
[51] M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, 1964, **3**, 1573.

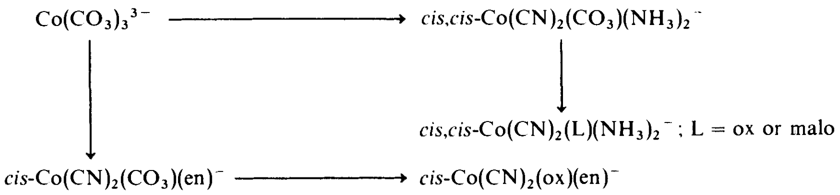
red colour of $Co(CN)_2(CO_3)_2{}^{3-}$ has developed, the required amount of the remaining ligand. Some of the earlier preparations[51] give crystals of the desired compound in reasonable yield directly from the reactant solution, *e.g.* $Co(CN)_3(NH_3)_3$, 17%; $Co(CN)(NH_3)_5{}^{2+}$, 50%; $Co(CN)_2(CO_3)_2$, 60%. The later applications contain lengthy purification and column chromatographic separations which frequently reduce over-all yields to the order of 1% or even less.[52,54,55]

The Field–Durrant method has been further extended[55] to generate intermediates used to produce a monocyano-series (Scheme 2)



Scheme 2

and a dicyanodiammino-series (Scheme 3).[54]



Scheme 3

The monocyano-compounds[55] were isolated as pure geometrical isomers and the optically active dicyano-compounds were all resolved.[54] A high yielding direct synthesis[56] of $Co(CO_3)(en)_2{}^+$ provides an efficient route[57] to *cis*-$Co(CN)_2(en)_2{}^+$ while a similar preparation of $Co(CO_3)(trien)^+$ gives[58] *cis*-$Co(CN)_2(trien)^+$.

B. Sulphite.—The first sulphite ligand in *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ is readily replaced and the complex has been used to make[59] $Co(CN)_5(SO_3)^{4-}$ but the more interesting application lies in the formation[60] of *cis*-$Co(CN)_4(SO_3)_2{}^{5-}$ *via*

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[52] S. Fujinami and M. Shibata, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3443.
[53] S. Fujinami and M. Shibata, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2939.
[54] T. Ito and M. Shibata, *Inorg. Chem.*, 1977, **16**, 108.
[55] S. Nakashima and M. Shibata, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3128.
[56] J. Springbørg and C. E. Shäfter, *Inorg. Synth.*, 1973, **14**, 63.
[57] K. Kuroda, *Nippon Kagaku Zasshi*, 1968, **89**, 720. *Chem. Abstr.*, 1968, **69**, 102621r.
[58] K. Kuroda and P. S. Gentile, *Inorg. Nucl. Chem. Lett.*, 1967, **3**, 151.
[59] K. F. Muller and R. A. D. Wentworth, *Inorg. Chem.*, 1976, **15**, 1467.
[60] H. Siebert, C. Siebert, and S. Thym, *Z. Anorg. Allg. Chem.*, 1971, **383**, 165.

$Co(SO_3)_3{}^{3-}$. The latter is produced as a slurry from $Co(NO_2)_6{}^{3-}$ and sodium sulphite and the product is obtained in a single stage by heating the slurry with potassium cyanide. The final product is $Co(CN)_6{}^{3-}$ but if heating is stopped when the last of the slurry has dissolved, a 13% yield of *cis*-$Co(CN)_4(SO_3)_2{}^{5-}$ is obtained. The general resemblance to the Field–Durrant reactions suggest that this method might also be extended to produce mixed cyano-complexes containing two other ligands.

C. Halide.—The substitution of halide by cyanide ions usually occurs very readily and it has been much used since the direct synthesis of mixed halo-complexes from cobalt(II) salts is far easier than that of the corresponding cyano-complexes.

The use of the di-iodo-derivatives of π-allyl or π-cyclopentadienyl cobalt(III) to give the dicyano-complexes has been quoted previously in Section 2B.

The high hydroxide-ion concentration encountered in aqueous cyanide solutions leads to the base-catalysed[6] decomposition of the ammino- and ethylenediamino-complexes of cobalt(III), but three methods of avoiding this have been devised. In one case[61] a suspension of silver cyanide is stirred with hot aqueous *trans*-$CoCl_2(en)_2{}^+$ or, alternatively, a hot dimethyl sulphoxide[62] solution of potassium cyanide is used. The product $Co(CN)_2(en)_2{}^+$ has the *cis*-configuration using the first method but remains substantially *trans* using the second. The rates of homogeneous cyanide substitution in these systems make it almost certain that the first method is actually an example of surface catalysis in view of the extremely small cyanide ion concentration present, ($\sim 10^{-6}$M). Isomerization generally accompanies the first process, apart from the case of *trans*-$Co(CN)(SO_3)(en)_2$,[61] and it also apparently can occur in dimethyl sulphoxide,[63] although to a smaller extent. The third method is more limited in potential since it depends on the *trans*-activating effect of the sulphite ligand. In the single case[64] reported, *cis*- and *trans*-$Co(CN)(SO_3)(en)_2$ were separately crystallized from an aqueous mixture of *trans*-$CoCl(SO_3)(en)_2$ and potassium cyanide. The method of selective *trans*-labilization by cyanide or sulphite ligands is, however, commonly encountered in other cyano-complex syntheses.

Although hydroxide catalysed solvolysis occurs in other amine complexes, the direct use of aqueous cyanide solutions is still possible. The absence of ionizable amine protons in phenanthrolene and bipyridine makes base-catalysed solvolysis unknown for their complexes, so that *cis*-$Co(CN)ClL_2{}^+$ may be safely made from $CoCl_2L_2$, L = phen or bip.[63] Despite this the silver cyanide or non-aqueous cyanide methods have been used in the synthesis of mono- and di-cyano mixed complexes of bip[61,65,66] and phen[61,66] as well as cyen,[67] pn,[67] and tn.[68,69] The

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[61] N. Maki and S. Sakuraba, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1908.

[62] M. Muto, T. Baba, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2918.

[63] T. Kashiwabara, T. Yamanaka, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3631.

[64] I. B. Baranovskii and A. V. Babaeva, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 1964, **9**, 1168.

[65] N. Maki, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2275.

[66] N. Maki, J. Hamazaki, and S. Sakuraba, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 1735.

[67] T. Kashiwabara, T. Yamanaka, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3631.

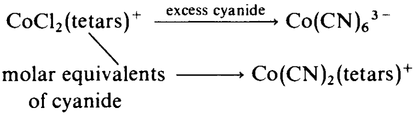
[68] H. Kawaguchi and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2103.

[69] H. Kawaguchi and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3453.

synthesis of *trans*-isomers containing two cyanide ligands can usually be achieved, even in difficult cases,[61] by a step-wise substitution. In one case the silver cyanide method was modified by using silver oxide suspended in methanol to remove the chloride ligand from *trans*-$CoCl_2(tn)_2^+$ followed by the addition of potassium cyanide to give *trans*-$Co(CN)_2(tn)_2^+$ in good yield.[69]

The same methods may also be used to synthesize cyanodimethylglyoxime complexes,[61] but direct substitution has also been used[70,71] in aqueous methanol. It is worth noting in this context that just as $Co(CN)_6^{3-}$ contaminates $Co(CN)_5X^{3-}$ made[72] from $CoX(NH_3)_5^{2+}$, so also does $Co(dmgH)_2(CN)_2^-$ form preferentially in syntheses of $Co(dmgH)_2(CN)(B)$, B = amine ligand, made from $Co(dmgH)_2Cl(B)$.[73] This may be suppressed by adding $BrCCl_3$ to oxidize any cobalt(II) present, since it is this ion which is thought to catalyse[26] the dicyano-complex formation. A further method of avoiding the problem is outlined in Section 3D below.

Halide replacement is clearly a method which may be widely applied to stable compounds, but even labile systems can be converted into the cyano-form provided the cyanide ion concentration is carefully controlled (Scheme 4).[74]



Scheme 4

D. Ammonia and Amines.—The catalysed substitution of ammonia by the cyanide ion is more correctly classified as synthesis by cobalt(II) oxidation, but the substitution of ammonia in pentamminocobalt(III) complexes will often proceed without the addition of cobalt(II). The first pentacyanocobalt(III) synthesis,[75] that of $Co(CN)_5(S_2O_3)^{4-}$, occurred immediately on addition of concentrated potassium cyanide solution. The unsubstantiated suspicion remains[35] that a trace of cobalt(II) is formed by ligand reduction of the cobalt(III) complex. The complex $Co(CN)_5X^{3-}$, X = Cl or Br, is readily made[35] without added cobalt(II) but a common impurity in this method of synthesis[72] is $Co(CN)_6^{3-}$ and this suggests that the catalysed path[40] may be operating. The problem is reduced by a synthetic route[72] *via* $Co(CN)(SO_3)(NH_3)_4$,[76] which yields $Co(CN)X(NH_3)_4^+$. The latter can be more easily converted into $Co(CN)_5X$ by treatment with the stoicheiometric amount of potassium cyanide aided by the addition of active charcoal catalyst.

The catalytic effect of charcoal has also been used[77] to promote amine or

[70] A. L. Crumbliss and P. L. Gauss, *Inorg. Chem.*, 1975, **14**, 486.

[71] A. V. Ablov and G. P. Syrtsova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1965, **10**, 1079.

[72] N. Maki, *Inorg. Chem.*, 1974, **13**, 2180.

[73] W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, 1974, **13**, 1564.

[74] B. Bosnich and W. G. Jackson, *Inorg. Chem.*, 1974, **13**, 1121.

[75] P. R. Ray, *Quart. J. Indian Chem. Soc.*, 1927, **4**, 325. D. Bannerjea and T. P. Das Gupta, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1021.

[76] H. Siebert, *Z. Anorg. Allg. Chem.*, 1964, **327**, 63.

[77] K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem.*, 1968, **7**, 1165.

diamine substitution by cyanide ligands to give, $Co(CN)(NH_3)_5^{2+}$,[77] $Co(CN)_2(N_4)$,[77] $\{N_4 = (NH_3)_4$ or $(en)_2\}$, $Co(CN)_2(O_2N_2)$,[78] $(O_2N_2 =$ gly or edda), $Co(CN)_3(N_3)$,[77] $\{N_3 = (NH_3)_3$ or dien$\}$. The separation of the various isomeric forms of these complexes depends on the use of preparative ion-exchange chromatography.

The necessity for catalysis may be avoided and the specificity improved if a stepwise synthesis is adopted in which the nitrogen ligand is activated by a suitable *trans*-ligand. The synthesis of $Co(CN)(SO_3)(NH_3)_4$ mentioned above[76] uses this method. The initial preparation of $Co(SO_3)(NH_3)_5^+$ by cobalt(II) oxidation is followed by cyanide ion substitution in the same reaction mixture, replacing the *trans*-ammonia ligand to give *trans*-$Co(CN)(SO_3)(NH_3)_4$, (70% yield). The dissociative and *trans*-activated nature of this reaction have been established[79] and the pattern[80] is found to extend to *cis*-$Co(SO_3)_2(NH_3)_4^-$. The synthetic potential of the latter compound, which may be readily obtained by the oxidation[81] of cobalt(II) in the appropriate ligand mixture, has been exploited[82] to give *trans*, *N*-$Co(CN)_2(SO_3)_2(NH_3)_2^{3-}$. Heating produces another but unidentified isomer.[83] Substitution of ammino-ligands *trans* to a bidentate amine also occurs in the synthesis[84] of $Co(CN)_4(N_2)^-$ from *trans*-$CoCl_2(NH_3)_2(N_2)^+$, $N_2 =$ en, pn, or tn. This route to the tetracyano-series seems unattractive, however, since the starting materials are not easy to make.[81,84] Both ammonia and pyridine complexes, $Co(dmgH)_2(SCN)N$, $N = NH_3$ or py, have been used as intermediates in the synthesis[85] of $Co(dmgH)_2(CN)(SCN)^-$. This method selectively produces monocyanocobaloximes uncontaminated by the dicyano-complexes usually produced. The same technique has been used to prepare[86] $Co(dmgH)_2(CN)R$ where R is an alkyl, alkenyl, or alkynyl ligand.

E. Miscellaneous Ligands.—In practice probably any ligand system could be replaced by the cyanide ion, but apart from the well-defined groups already mentioned, there remain a few examples which have been often used in a limited range of compounds. The substitution, for instance, of carbonyl ligands is uncommon but has already been mentioned[8,39,30] in the preparation of the cyano-complexes of π-cyclopentadienyl and π-allyl cobalt(III), (Sections 2A and 2B).

Thiosulphate complexes have been used as cyano-precursors both because of their ease of substitution and because of their *trans*-directing influence. The complex *cis*-$Co(CN)_2(en)_2^+$ may be made directly[87] from the easily prepared

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[78] A. L. Poznjak and V. I. Pawlowskii, *Z. Anorg. Allg. Chem.*, 1980, **465**, 159.
[79] J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Am. Chem. Soc.*, 1966, **88**, 3877.
[80] L. Richards and J. Halpern, *Inorg. Chem.*, 1976, **15**, 2571.
[81] J. C. Bailar Jr. and D. F. Peppard, *J. Am. Chem. Soc.*, 1940, **62**, 105.
[82] A. V. Babaeva and I. B. Baranovskii, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1962, **7**, 404.
[83] K. Ohkawa, F. Fujita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1715.
[84] K. Ohkawa, F. Fujita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 66.
[85] A. L. Crumbliss and P. L. Gauss, *Inorg. Chem.*, 1976, **15**, 737.
[86] D. Dodd and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, 1973, 1218.
[87] P. Ray and B. Sarma, *J. Indian Chem. Soc.*, 1951, **28**, 59.

$Co(S_2O_3)_2(en)_2^-$ by treatment with aqueous potassium cyanide. The same method has really been used in making[68,84] *cis*-$Co(CN)_2(N_2)$, N_2 = pn or tn, from the primary complexes[88,89] $CoCl_2(N_2)$ since the thiosulphato-complex was formed, although not isolated, and was immediately converted in the original reaction mixture into the cyano-product by the addition of potassium cyanide.

Cyanodimethylglyoxime complexes have been made by the displacement of a variety of ligands, for instance[46]

$$Co(dmgH)_2(NO_2)_2^- \xrightarrow{CN^-} Co(dmgH)_2(CN)(NO_2)^- \xrightarrow{X^-} Co(dmgH)_2(CN)X^-$$

The *trans*-directing influence of the cyanide ion and the difference in the ease of displacement of the nitro-ligands ensures the success of the method. An alternative approach, mentioned earlier, is essentially similar but depends instead on the sequential displacement of pyridine by cyanide and then thiocyanate by a base, L.[85]

$$Co(dmgH)_2(SCN)(py) \xrightarrow{CN^-} Co(dmgH)_2(SCN)(CN)^- \xrightarrow{L} Co(dmgH)_2(CN)L$$

Finally the use of an active carbon catalyst seems capable of labilizing apparently highly stable systems to substitution. The complex $Co(CN)_2(acac)_2^-$ may be made[90] in 47% yield from $Co(acac)_3^{3+}$ by stirring for 6 hours at 0 °C with the catalyst. Mixed complexes such as *cis*- or *trans*-$Co(CN)(py)(acac)_2$ may also be made by using a suitable ligand mixture and the carbon catalyst, but the yields become much lower, (*cis* 4%, *trans* 2%).

4 Synthesis by Ligand Substitution in Cyanocobalt(III) Complexes

The cobalt–cyanide bond is usually the strongest of those binding monodentate ligands to the cobalt centre, so that the cyano-grouping, once it is formed, tends to move unaltered through reaction sequences save perhaps for geometrical rearrangement. Consequently the cyano-systems generated by the methods already described may be modified by ligand exchange to produce families of related cyano-complexes. The ligands to be replaced broadly cover those already mentioned in Section 3 with the addition of water and the cyanide ion itself.

A. Carbonate.—The exploitation of the Field–Durrant solution of $Co(CO_3)_3^{3-}$ has already been described in Section 3A above, in which hetero-substituted mono[52,55] and dicyano[52,54] complexes were produced.

B. Sulphite.—The sulphite ligand has the useful property of usually being labile in acid solution but of being highly stable in alkaline solution and of having a strongly *trans*-labilizing effect. These properties are fully utilized in the synthesis[61] of *trans*-$Co(CN)_2(en)(NH_3)_2$.

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[88] A. Werner and A. Frohlich, *Ber.*, 1907, **40**, 2228.
[89] A. Werner and G. Lindenberg, *Ann.*, 1912, **386**, 271.
[90] L. J. Boucher, C. G. Coe, and D. R. Herrington, *Inorg. Chim. Acta*, 1974, **11**, 123.

$$\mathrm{Co^{2+}} \xrightarrow[\mathrm{O_2}]{\mathrm{NH_3}} \mathrm{Co(OH_2)(NH_3)_5{}^{3+}} \xrightarrow{\mathrm{SO_3{}^{2-}}} \mathrm{Co(SO_3)(NH_3)_5{}^{+}} \xrightarrow{\mathrm{CN}} trans\text{-}\mathrm{Co(SO_3)(CN)(NH_3)_4} \quad (1)$$

$$\begin{tikzcd} trans\text{-}\mathrm{Co(SO_3)(CN)(NH_3)_4} \arrow[r, "\mathrm{en}"] & trans,cis(N,N)\text{-}\mathrm{Co(CN)(SO_3)(en)(NH_3)_2} \quad (2) \arrow[d, "\mathrm{HCl}"'] \\ trans\text{-}\mathrm{Co(CN)_2(en)(NH_3)_2{}^{+}} & trans,cis(N,N)\text{-}\mathrm{Co(CN)Cl(en)(NH_3)_2{}^{+}} \arrow[l, "\text{KCN in}"', "\text{dimethyl sulphoxide}"] \end{tikzcd}$$

$$(3)$$

$$(4)$$

Stages (1) and (4) have already been mentioned in Section 3D and 3C respectively, but stage (3) provides an example of sulphite and cyanide ion promoted substitution of two ammine ligands *trans* to them. The direct substitution of sulphite by cyanide is achieved by the acid substitution by chloride in stage (3) followed by its replacement in stage (4). Similar techniques have been used to synthesize[91] *cis*-$\mathrm{Co(CN)X(en)_2{}^{+}}$, X = Cl or Br, *via* $\mathrm{Co(CN)_2(SO_3)_2(NH_3)_2{}^{3-}}$. *trans*-$\mathrm{Co(CN)_4(SO_3)_2{}^{5-}}$ can be used[28] to prepare[92, 93] *trans*-$\mathrm{Co(CN)_4L_2{}^{-}}$, L = $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$, by refluxing with the tertiary phosphine or arsine in glacial acetic acid.

The sulphite complexes have often been used to generate cyanoaquo-complexes by acid hydrolysis[64,94] although the method can produce polynuclear cyanide-bridged species.[95,96] Sulphite hydrolysis followed immediately by aquo-substitution, however, has been successful. Acid hydrolysis of $\mathrm{Co(CN)_4(SO_3)_2{}^{5-}}$ followed by autoclaving the crude product in concentrated ammonia for 4 hours at 100 °C produces *fac*-$\mathrm{Co(CN)_3(NH_3)_3}$.[97] Drastic treatment of this sort is known to break down the polynuclear products of hydrolysis.[95]

C. Halide.—Halide substitution is little used although certainly quite practicable. A two-stage version of the process which really involves an intermediate aquo-complex has been used to form[98] *cis*-$\mathrm{Co(CN)X(en)_2{}^{+}}$ and *trans*-$\mathrm{Co(CN)(NO_2)(en)_2{}^{+}}$. The halide is removed by stirring the corresponding monocyanohalo-complex with silver oxide, filtering, and then adding ammonia or KX, X = $\mathrm{OH^-}$, $\mathrm{I^-}$, or $\mathrm{NO_2{}^-}$. Straightforward single-step substitution has also been used[99] in making $\mathrm{Co(CN)_5(SO_3)^{4-}}$ from $\mathrm{Co(CN)_5Br^{3-}}$ and $\mathrm{Co(CN)(SO_3)(N_2)}$, $\mathrm{N_2}$ = bip or phen, from[100] $\mathrm{Co(CN)Cl(N_2)}$. The same starting compound or the chloro-equivalent reacts with triphenyl phosphine in glacial acetic acid to give[101] $\mathrm{Co(CN)_5(PPh_3)^{2-}}$. The same medium, on the other hand, used with $\mathrm{Co(CN)_5I}$ produces the substitution of a cyanide as well as a halide ligand to form[92] $\mathrm{Co(CN)_4L_2{}^{-}}$, L = $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$, $\mathrm{PPh_3}$ or $\mathrm{L_2}$ = dpe.

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[91] H. Ohkawa, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1715.

[92] K. Kashiwabara, K. Katoh, and T. Ohishi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 149.

[93] N. Maki and K. Ohshima, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3970.

[94] P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 611.

[95] N. Maki, *Inorg. Chim. Acta*, 1975, **13**, L7.

[96] N. Maki and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2450.

[97] H. Siebert, *Z. Anorg. Allg. Chem.*, 1971, **380**, 30.

[98] K. Ohkawa, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2830.

[99] J. Fujita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 1281.

[100] G. Schiavon and F. Marchetti, *Inorg. Chim. Acta*, 1979, **33**, L101.

[101] K. Watanabe, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1150.

D. Ammonia.—Substitutions involving ammonia are usually made before the insertion of the cyanide ligands but in a few cases the order has been reversed. The geometric and optical isomers of $Co(CN)(NH_3)(pn)_2{}^{2+}$ have been isolated from the carbon-catalysed substitution[102] of $Co(CN)(NH_3)_5{}^{2+}$ using cation-exchange chromatography. The synthesis of $Co(CN)_5X^{3-}$ from $Co(CN)X(NH_3)_4{}^{+}$ by carbon-catalysed ammonia-substitution[70] has already been mentioned in Section 3D.

Trans-promoted ammonia-substitution has also been used in cyano-complexes. Reference was made in Section 4B to the formation[61] of *trans*-$Co(CN)(SO_3)(en)(NH_3)_2$ by replacement of the two trans-activated ammine ligands in $Co(CN)(SO_3)(NH_3)_4$. A related substitution occurs in forming[91] $Co(CN)(SO_3)(en)_2$ from $Co(CN)_2(SO_3)_2(NH_3)_2{}^{3-}$ but the conditions must be extreme[103] for this unusual simultaneous cyanide, sulphite, and ammonia replacement to be successful. The preparation has been shown to be capable of yielding[104] $Co(CN)(en)(NH_3)_3{}^{2+}$.

E. Cyanide.—The modification of cyano-complexes by cyano-ligand substitution is normally not practicable due to the strength of the cyano-bond. However, in addition to the occasional examples already quoted[40,61,91,103] and the formation[92] of $Co(CN)(acac)_2PMe_3$ from $Co(CN)_2(acac)_2{}^{-}$, two approaches have been successful. The cyanide ligand may be removed either by thermal dissociation after protonation or by photolysis.

The weakening of the cyanide bond after ligand protonation may explain the cyanide substitution already referred to in Section 4E where $Co(CN)_4L_2{}^{-}$ was produced from $Co(CN)_5I^{3-}$ and the phosphine ligand L by heating in glacial acetic acid.[92,101] The hydrolysis of the cyano-ligand in strongly acid media was known many years earlier[105] but it has become clear subsequently that such conditions lead to the formation of cyano-bridged polymers and highly impure products. It is quite likely that the uncharacterized intermediate formed in the synthesis of *fac*-$Co(NH_3)_3(CN)_3$[97] referred to in Section 4B contained aquo-ligands introduced by the acid hydrolysis of a cyanide group. The same principle has been applied with greater success in the solid state. The phosphonium acid salt $(Ph_4P)H_2\{Co(CN)_6\}$ yields $(Ph_4P)\{Co(CN)_4(PPh_3)_2\}$ on heating[106] with triphenylphosphine at 210—220 °C under nitrogen. The low co-ordination intermediates $Co(CN)_4{}^{-}$ and $Co(CN)_5{}^{2-}$ may also be prepared in the solid state from the acid salts $(PPh_4)H_2\{Co(CN)_6\}$ and $\{Ph_3P(CH_2)_3PPh_3\}H\{Co(CN)_6\}$. These intermediates react in dimethyl formamide with amines and triphenylphosphine to yield tetra- and penta-cyano-complexes such as $Co(CN)_4(bip)^{-}$ or $Co(CN)_5(bip)^{2-}$, the bipyridyl ligand being monodentate in the second case.

Photolytic synthesis has so far been limited to producing solvolytic adducts. The

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[102] K. Kashiwabara and S. Suzuki, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3329.

[103] M. L. Tobe and C. K. Williams, *Inorg. Chem.*, 1976, **15**, 918.

[104] A. R. Norris, *Can. J. Chem.*, 1974, **52**, 477.

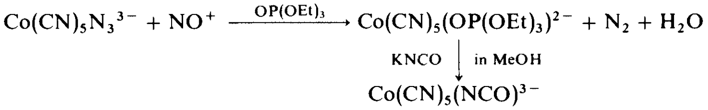
[105] P. Ray and N. K. Dutt, *Z. Anorg. Allg. Chem.*, 1937, **234**, 65.

[106] S. Papp and S. Czegledi, *Z. Naturforsch., Teil B*, 1977, **32**, 167.

aquo-ions $Co(CN)_5(OH_2)^{2-}$ and $Co(CN)_4(OH_2)_2^-$ are difficult to isolate as solids without producing cyano-bridged polymers but they may readily be prepared[42,107] in aqueous solution by photolysis with a pyrex filtered low-pressure mercury arc. Non-aqueous solvates $Co(CN)_5S^{2-}$ may also be made,[108] S = MeOH, EtOH, MeCN, or dmf.

F. Water.—The aquo-complexes have not infrequently been used as convenient intermediates for the synthesis of a family of products, *e.g.* $Co(CN)_5L^{3-}$,[109] L = py, NH_3, NCS, or N_2H_4; $Co(CN)L(NH_3)_4^+$,[96] L = I, N_3, NO_2, SCN, NO, py, NH_2Et, or NH_2Me; $Co(CN)L(NH_3)_4$,[96] L = S_2O_3 or CO_3. Frequently, as was mentioned in Section 3E, substitution *via* the aquo-complex is used without the intermediate actually being isolated.

G. Miscellaneous Ligands.—Very few reactions have been used beyond the classes already covered although it seems probable that standard techniques from other families of cobalt complexes could be applied. For example, the unstable isocyanato-complex $Co(CN)_5(NCO)^{3-}$ is synthesized from the azido-derivative[110] using a technique developed for the synthesis of substituted ammino-cobalt(III) complexes (Scheme 5).[111]



$$\begin{tikzcd}
Co(CN)_5N_3^{3-} + NO^+ \arrow[r, "OP(OEt)_3"] & Co(CN)_5(OP(OEt)_3)^{2-} + N_2 + H_2O \arrow[d, "KNCO"', "\text{in MeOH}"] \\
 & Co(CN)_5(NCO)^{3-}
\end{tikzcd}$$

Scheme 5

Providing the incoming ligand is a sufficiently effective nucleophile, apparently stable ligand systems can still be disrupted. Acetylacetonate may be thermally displaced from $Co(CN)_2(acac)_2^-$ [90] to yield[92] $Co(CN)_2(acac)P_2$, $P_2 = (PPh_3)_2$, $(PMePh_2)_2$, $(PMe_2Ph)_2$, $(PMe_3)_2$, or dpe. The method does depend on ion-exchange chromatography to isolate the products from the reaction mixture, but the reactions are nevertheless reasonably selective with yields around 20%.

Dimethyl glyoxime complexes, $Co(dmgH)_2(CN)X^-$, readily exchange any ligand X with a free nucleophile in solution provided the incoming ligand is at least of comparable nucleophilicity compared to the ligand it displaces.[71]

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[107] L. Viaene, J. D'Olieslager, and S. De Jaegere, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2435.

[108] K. Nakamaru, K. Jin, A. Tazawa, and M. Kanno, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3486.

[109] R. Barca, J. Ellis, M.-S. Tsao, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 243.

[110] M. A. Cohen, J. B. Melpolder, and J. L. Burmeister, *Inorg. Chim. Acta*, 1972, **6**, 188.

[111] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, 1966, **5**, 1091.

Table 1 $Co(CN)L_1L_2L_3L_4L_5$

Main substituent	*Other groups*	*References*[a]
acac	PMe_3	92(4E).
acac	py	90(3E and 4G).
ammonia or en	halide, N_3, NO_2, S_2O_3, SCN, NO, py, NH_2Et, NH_2Me, OH_2, OH, NO_2, SO_3	51(3A), 55(3A and 4A), 61(3C and 4B, D, and E), 64(3C), 76(3D), 77(3D), 82(3D and E), 87(3E), 91(4D and E), 96(4B and F), 98(4C), 103(4D and E), 104(4D).
bip	Cl, SO_3	100(4C).
cyclopentadiene	CO, NCR, PR_3	30(2B and 3E), 31(2B), 32(2B).
dmgH	SO_3, NH_3, Cl, H_2O, SCN, py, $PhNH_2$	46(3A and E), 61(3C and 4B, D and E), 70(3C), 71(3C and 4G), 73(3C), 85(3D and E), 86(3D).
malo	OH_2	52(3A and 4A).
pn	NH_3	102(4D).
tn	SO_3	68(3C and E).

[a] The sections in which each reference is mentioned in this review are given in brackets

Table 2 $Co(CN)_2L_1L_2L_3L_4$

Main substituent	*Other groups*	*References*[a]
acac	none, py, PR_3	90(3E, 4G), 92(4B, C, E, and F).
β-ala	none	53(3A).
ammonia	CO_3, en, ox, none, mal, SO_3	54(3A, 4A), 61(3C and 4B, D and E), 77(3D), 82(3D and E).
bip	none	10(2A), 66(3C), 61(3C and 4B, D, and E).
carbonate	none	52(3A and 4A).
cyclopentadiene	CO, NCR, PPh_3	8(2A and 3E), 30(2B and 3E).
cyen	none	63(3C).
dmgH	H_2O, I, none, NO_2, OH, $PhNH_2$, py, SCN, S_2O_3, thio	47(3A and E), 61(3C and 4B, D, and E), 70(3C), 71(3C and 4G).
dpe	none	22(2A).
dtc	none	52(3A and 4A).
edda	none	79(3D).
en	CO_3, ox, none	54(3A and 4A), 57(3A), 61(3C and 4B, D, and E), 62(3C), 77(3D), 83(3D), 84(3D and E), 87(3E).
gly	none	53(3A).
ox	CO_3, H_2O, none	52(3A and 4A).
phen	none	10(2A), 66(3C), 61(3C and 4B, D, and E).
pn	none	61(3C and 4B, D, and E), 63(3C), 84(3D and E).
tetars	none	74(3C).
tn	none	68(3C and E), 69(3C), 84(3D).
trien	none	58(3A).
vpp	none	23(2A).
xan	none	52(3A and 4A).

[a] The sections in which each reference is mentioned in this review are given in the brackets

Table 3 $Co(CN)_3L_1L_2L_3$

Main substituent	*Other groups*	*References*[a]
ammonia	en, none	51(3A), 61(3C and 4B, D, and E), 77(3D), 97(4B and E).
cyclopentadiene	none	8(2A and 3E), 30(2B and 3E), 29(2B and 3E).
dien	none	77(3D).

[a] The sections in which each reference is mentioned in this review are given in the brackets

Table 4 $Co(CN)_4L_1L_2$

Other groups	*References*[a]
π-allyl	29(2B)
$AsPh_3$	93(3B)
π-crotyl	29(2B)
bip	10(2A), 106(4E)
en	11(2A), 84(3D), 106(4E)
phen	106(4E)
pn	84(3D)
PPh_3	93(4B), 101(4C)
PR_3	92(4B, C, E, and F)
SO_3	28(2A), 60(3B)

[a] The sections in which each reference is mentioned in this review are given in the brackets

Table 5 $Co(CN)_5L_1$

Other groups	*References*[a]
ammonia	10(2A), 109(4F)
alkyl, alkenyl, alkynyl, or aryl	29(2B), 36(2B), 38(2B), 39(2B)
CO	15(2A)
CO_3, $MeNH_2$, $EtNH_2$, NO, N_3	72(3C and D)
EtOH, MeOH, MeCN, dmf	108(4E)
halide	72(3C and D), 35(2C and D)
H_2O	42(2C), 107(4E)
NCS, NCSe	44(2C)
NCO	110(4G)
NO_2	72(3C and D), 99(4C)
PPh_3	72(3C and D), 101(4C and E), 106(4E)
py	72(3C and D), 108(4E)
SCN, SeCN	72(3C and D), 41(2C), 43(2C)
SO_3	72(3C and D), 99(4C)
S_2O_3	75(3D), 72(3C and D)

[a] The sections in which each reference is mentioned in this review are given in the brackets