Allyl- and Propadienyl-cobaloximes: Character and Reactions with Tetracyanoethylene

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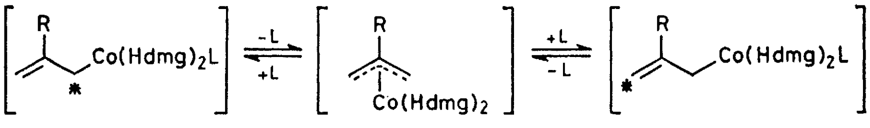
The temperature-dependent ^1H n.m.r. spectra of allylcobaloximes show characteristics of a dynamic process in which interchange between the two possible σ-allylcobaloxime complexes takes place. This is ascribed to two processes: allylaquabis(dioximato)cobalt(III) complexes undergo a unimolecular reaction which involves a transient η-allylcobaloxime formed after loss of the axial aqua-ligand; allylbis(dioximato)pyridinecobalt(III) complexes undergo a bimolecular reaction in which an S_H2' attack of a cobaloxime(II) complex (present as impurity) attacks the δ-carbon of the allyl group and displaces cobaloxime(II) from the α-carbon. The latter mechanism may also operate with the allylaquabis(dioximato)cobalt(III) complexes. Under conditions where the η-allylcobaloximes are not formed, *i.e.* in the presence of an appropriate axial ligand, the σ-allylcobaloximes react with $C_2(CN)_4$ to give 3,3,4,4-tetracyanocyclopentylcobaloximes. The formation of *trans*-bis(dimethylglyoximato)imidazole-(3,3,4,4-tetracyano-2-phenylcyclopentyl)cobalt(III) from the reaction of *trans*-cinnamylbis(dimethylglyoximato)-imidazolecobalt(III) with $C_2(CN)_4$ indicates that the cycloaddition involves a σ–π–σ *antarafacial* migration of the cobalt from the α- to the β-carbon of the allyl group.

THE chemistry of allylmetal complexes has been of interest for many years because of their value in organic synthesis and the possible variations in bonding of the allyl group to the metal.[1] We noted previously that the allylcobaloximes exist predominantly as the σ-bonded complexes,[2] but further studies showed that the n.m.r. spectra were not straightforward, indicating more complex behaviour sensitive to the nature of the axial ligand and to the nature of other materials present.[3]

This paper presents a more detailed account of the character of allyl- and propadienyl-cobaloximes in solution, and of their reactions with tetracyanoethylene which has been shown to undergo cycloaddition reactions with a number of other σ-allyl complexes of transition metals.[4,5] The corresponding reactions of propadienylcobaloxime with $C_2(CN)_4$ and with hexafluoroacetone are also described.

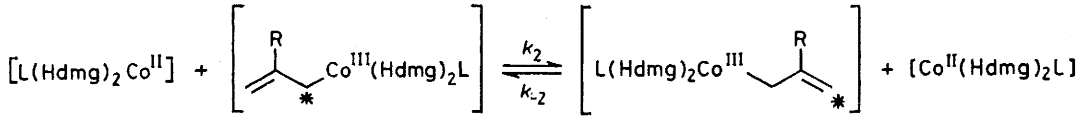
RESULTS AND DISCUSSION

Character of Allylcobaloximes in Solution.—The temperature dependence of the ^1H n.m.r. spectra of allylaquabis(glyoximato)cobalt(III) complexes in $CDCl_3$–CD_3OD mixtures show characteristics of a dynamic equilibrium involving rapid interchange between the two possible σ-bonded species, *e.g.* (1a) and (1b). For example, the spectrum of allylaquabis(dimethylglyoximato)cobalt(III) at 55 °C (Figure 1) shows an imperfectly resolved four-proton doublet at δ 3.7 p.p.m. and a more clearly resolved one-proton methine quintet at δ 5.6 p.p.m.; the spectrum at —35 °C is that expected for a single (static) σ-bonded complex, the saturated methylene-proton resonance being obscured by the larger 12-proton singlet dimethylglyoximate resonance at δ 2.3 p.p.m. At the higher temperatures the residual hydroxyl resonance of the solvent is sufficiently broad as



(1a) R=H, L=OH₂ (2) (1b) (1)

(3a) R=Me,L =OH₂



(2)

$$[\mathrm{Co^{II}(Hdmg)_2(py)}] + [\mathrm{Co^{III}(Hchdd)_2(py)(CH_2R)}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Co^{III}(Hdmg)_2(py)(CH_2R)}] + [\mathrm{Co^{II}(Hchdd)_2(py)}] \quad (3)$$

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[1] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 1969, **3**, 109.

[2] C. J. Cooksey, D. Dodd, C. Gatford, M. D. Johnson, G. J. Lewis, and D. M. Titchmarsh, *J.C.S. Perkin II*, 1972, 655.

[3] D. Dodd and M. D. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 2279.

[4] M. Rosenblum, *Accounts Chem. Res.*, 1974, **7**, 122; also mentions the cycloaddition to allylbis(dimethylglyoximato)-pyridinecobalt(III) in a footnote.

[5] S. R. Su and A. Wojcicki, *Inorg. Chem.*, 1975, **14**, 89; *Inorg. Chim. Acta*, 1974, **8**, 55.

to be undetected, but as the temperature is decreased this singlet resonance moves downfield, becomes increasingly well resolved, and at -35 °C overlaps the olefinic methylene resonance at δ *ca.* 5.7 p.p.m. Similar temperature-dependent spectra of other allylcobaloximes have been described in a preliminary publication.[3]

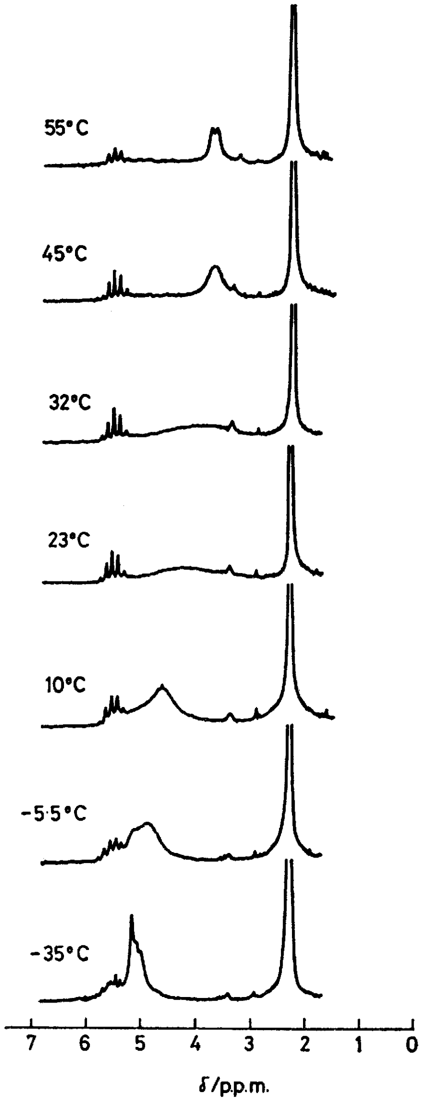

FIGURE 1 Temperature dependence of the ^{1}H n.m.r. spectrum (100 MHz) of 0.5 mol dm^{-3} allylaquabis(dimethylglyoximato)-cobalt(III) in CDCl$_3$–CD$_3$OD

This dynamic character could be the result of one or both of two processes: a unimolecular exchange *via* a transient η-allylcobaloxime (2) (or some related species in which the α- and γ-methylene groups may become equivalent) as in equation (1), or a bimolecular process involving a repeated displacement of cobaloxime(II) from the α-carbon by attack of cobaloxime(II) at the γ-carbon [equation (2)] in a manner related to that already observed for exchange in alkylcobaloximes [equation (3)].[6,*]

In our preliminary publication [3] we suggested that the dynamic character was solely a result of an intramolecular process involving reaction (1), because of the marked effect of more strongly co-ordinating ligands, such as pyridine, in reducing the proportion of the five-co-ordinate intermediate (2), and because the same temperature dependence was observed with 0.4 and 2×10^{-2} mol dm^{-3} solutions of allylaquabis(dioximato)cobalt(III). Only in the intramolecular mechanism is the same first-order rate coefficient (rate as measured by n.m.r. methods) demanded for such different concentrations of substrate. Moreover, as outlined below, the observed resolution of the four-proton methylene doublet at the highest temperatures would not be expected in a bimolecular exchange process promoted by the paramagnetic cobaloxime(II).

However, the bimolecular mechanism can almost certainly intrude and may be dominant under some conditions, *i.e.* when the concentration of cobaloxime(II) is sufficiently high, either as adventitious impurity (allylcobaloximes are particularly prone to thermolysis or photolysis) [7] or when added. Thus, the ^{1}H n.m.r. spectrum of allyl- or 2-methylallyl-bis(cyclohexanedione dioximato)pyridinecobalt(III) [(4) and (5), respectively] is markedly dependent on the purity and age of the sample and the conditions of measurement. Freshly purified samples show a spectrum (CDCl$_3$) similar to that at the low-temperature limit of Figure 1 (except that the cyclohexanedione dioximate proton resonances do not obscure the saturated methylene-proton doublet), whereas older samples show spectra in which there is appreciable coalescence; even fresh samples show some coalescence within a few minutes at ambient temperature [Figure 2(*a*) (*i*)]. In the latter cases, when coalescence occurs, the pyridine α-proton resonances also show very marked broadening, but the β- and γ-pyridine proton resonances are relatively well resolved. The coalescence is removed and the spectra revert to the low-temperature limit when a *trace* amount of carbon tetrachloride or bromotrichloromethane is added to the solution [Figure 2(*a*) (*ii*)] but after a short time, during which 4,4,4-trichlorobutene (6) or 4,4,4-trichloro-2-methylbutene (7), together with [Co$^{\mathrm{III}}$(CCl$_3$)(Hchdd)$_2$(py)] (8) and [Co$^{\mathrm{III}}$X(Hchdd)$_2$(py)] (9; X = Br or Cl) are formed, the spectra again show increased coalescence [Figure 2(*a*) (*iii*)]. The sequence is repeated when further trace amounts of polyhalogenomethane are added, until formation of the trichlorobutene and halogenocobaloxime is complete.

This retardation in the presence of the polyhalogenomethane is ascribed to a sequence of reactions involving (*i*) a reaction between the low concentration of cobaloxime(II) and the polyhalogenomethane [equation (5)] to give the halogenocobaloxime (9) and trichloromethyl

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[*] Hdmg = Dimethylglyoximate(1−), Hchdd = cyclohexanedione dioximate (1−).

[6] D. Dodd, M. D. Johnson, and B. L. Lockman, *J. Amer. Chem. Soc.*, 1977, **99**, 3664.

[7] C. Bied-Charreton and A. Gaudemer, *J. Organometallic Chem.*, 1977, **124**, 299.

radicals, which can either (*ii*) react with the allylcobaloxime to give the observed trichlorobutene and regenerate cobaloxime(II) [equation (4), a reaction discussed in detail elsewhere[8]] or (*iii*) combine with cobaloxime (II)[9] to give the diamagnetic trichloromethylcobaloxime (8) [equation (6)]. The latter reaction would cause a decrease in the low concentration of cobaloxime(II) which is the catalyst for the process causing coalescence. Indeed, the addition of a trace amount of cobaloxime(II) to the fresh solution of the allylcobaloxime causes the expected increase in the extent of coalescence.

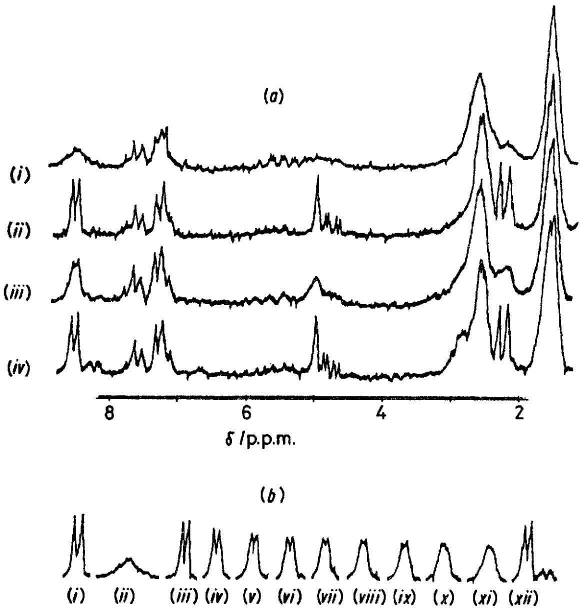

FIGURE 2 (*a*) Spectrum of allylbis(cyclohexanedione dioximato)-pyridinecobalt(III) (4) (50 mg cm^{-3}, in $CDCl_3$): (*i*) after 10 min; then (*ii*) after addition of $CBrCl_3$ (2 mg); then (*iii*) after a further 12 min; then (*iv*) after further addition of $CBrCl_3$. (*b*) Pyridine α-proton resonances of (4): (*i*) fresh solution; (*ii*) as in (*a*) (*i*); (*iii*) as in (*a*) (*ii*); (*iv*) after a further 5 min; (*v*)—(*xi*) at further 1-min intervals; (*xii*) after further addition of $CBrCl_3$

By analogy with the homolytic displacement of cobaloxime(II) from allylcobaloximes by halogenomethyl radicals[8] [*e.g.* equation (4)], we propose that the catalysis involves the homolytic cobalt-for-cobalt S_H2' displacement reaction of equations (2) and (7). This can influence the ^1H n.m.r. spectrum in two ways: an exchange-induced broadening of the aliphatic and olefinic proton resonances with concurrent broadening of the α-, rather than the β- and γ-, pyridine proton resonances, which is indicative of the paramagnetic interaction of the co-ordinated pyridine with the cobaloxime(II) to which it is attached for a small proportion of the time at ambient temperature. Such broadening is not a result of exchange between co-ordinated pyridine and free ligand because of the small chemical-shift difference between the α-protons of these species.

We have therefore demonstrated that cobalt-for-cobalt exchange does take place with allylcobaloximes and cobaloxime(II) reagents by observing the formation of $[Co^{III}(CH_2CH=CH_2)(Hdmg)_2(py)]$ (1) from the reaction of (4) and $[Co^{II}(Hdmg)_2(py)]$ (10) in methanol at 0 °C [equation (7)]. Even using 4.5×10^{-3} mol dm^{-3} solutions of reagents, equilibration is complete within 5 min, the observed rate of exchange (R 1.5×10^{-4} mol^2 dm^{-6} s^{-2})[6] being equivalent to a second-order rate coefficient k_2 of 7 dm^3 mol^{-1} s^{-1}. Although this reaction does not distinguish between cobalt-for-cobalt exchange by attack at the α- or the γ-carbon of the allyl group, the measured rate coefficient is of the correct order of magnitude to account for the dynamic character at higher temperatures if it is assumed that a substantial part involves S_H2' attack at the γ-carbon.

The corresponding exchange through an S_E2' displacement of cobaloxime(III) by cobaloxime(III) impurities is most unlikely because of the virtual absence of the necessary reactive five-co-ordinate cobaloxime(III) species. Indeed, the addition of the chlorocobaloxime (9a) and a trace amount of thallium(I) nitrate to the solution of allylcobaloxime causes a decrease in the extent of coalescence, and the S_E2 exchange of cobaloxime(III) with *alkyl*cobaloxime(III) species is many orders of magnitude slower than the S_H2 reaction.[6]

Similar, but less obvious, dynamic equilibria are almost certainly involved with unsymmetrically substituted allylcobaloximes in solution, for which one isomer dominates.[2] Such exchanges were alluded to in an earlier paper on allylcobaloximes,[2] but their full significance, particularly with regard to cobaloxime(II) exchange,[6] was not appreciated at that time.

Character of Propadienyl- and Prop-2-ynyl-cobaloximes. — Aquabis(dimethylglyoximato)propadienylcobalt(III) (11; L = OH_2) shows no dynamic characteristics and no tendency to transform into the isomeric prop-2-ynylcobaloxime (12). However, the complex previously believed[2] to be bis(dimethylglyoximato)prop-2-ynyl-(pyridine)cobalt(III) does not have the simple formula as in (12), but is probably a bimetallic complex (13).

$[Co(CH=C=CH_2)(Hdmg)_2L]$ (11) $[Co(CH_2C\equiv CH)(Hdmg)_2L]$ (12)

$[(py)(Hdmg)_2Co(C\equiv CCH_2)Co(Hdmg)_2(py)]$ (13)

The earlier observation[2] that the ^1H n.m.r. spectrum of (13) shows two equivalent dimethylglyoximate methyl-proton resonances separated by 0.11 p.p.m. was not explained. However, the ^{13}C n.m.r. spectrum clearly shows that there are two distinct sets of dimethylglyoximate ligands *and* two sets of pyridine ligands, a broad α-carbon resonance characteristic of carbon bound to cobalt, and a weak resonance which we ascribe to the central carbon. The solution i.r. spectrum clearly shows a C≡C stretch at 2 135 cm^{-1} ($CHCl_3$ or $CDCl_3$) which confirms the presence of the prop-2-ynyl ligand; similarly, the observation that the propadienylcobaloxime is formed in solution during some reactions of complex (13)

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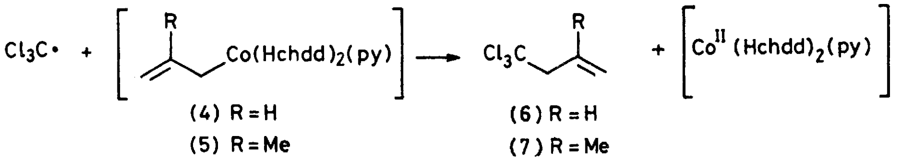
[8] A. Bury, C. J. Cooksey, T. Funabiki, B. D. Gupta, and M. D. Johnson, *J.C.S. Perkin II*, in the press.
[9] E. D. McKenzie, unpublished work.

confirms the presence of the three-carbon unit. Unfortunately, the slight instability of the complex ensures that elemental analysis cannot establish the composition with certainty.



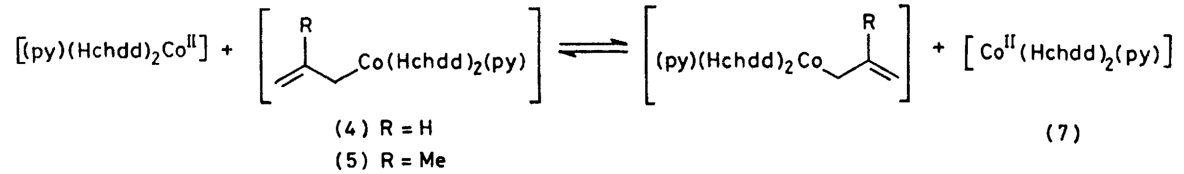
(4)

$$[\mathrm{Co^{II}(Hchdd)_2(py)}] + \mathrm{CCl_3X} \longrightarrow [\mathrm{CoX(Hchdd)_2(py)}] + \mathrm{Cl_3C}\cdot \qquad (5)$$

(9a) X = Cl
(X = Cl or Br) (9b) X = Br

$$\mathrm{Cl_3C}\cdot + [\mathrm{Co^{II}(Hchdd)_2(py)}] \longrightarrow [\mathrm{Co(CCl_3)(Hchdd)_2(py)}] \qquad (6)$$

(8)



(7)

Reactions of Propadienyl- and Allyl-cobaloximes with Tetracyanoethylene.—The reaction of cinnamylbis(dimethylglyoximato)pyridinecobalt(III) (14; L = py) with tetracyanoethylene in methylene chloride is typical of those of many other allylcobaloximes, giving a variety of products of different colours. The only organocobaloxime that could be isolated was *trans*-bis(dimethylglyoximato)pyridine(3,3,4,4-tetracyano-2-phenylcyclopentyl)cobalt(III) (15; L = py). The variation of the yield of this product from (14; L = OH_2) as

TABLE 1

Hydrogen-1 n.m.r. spectra [a] and analysis of allyl- and propadienyl-cobaloximes [CoR(oximato)$_2$L]

R	L	Oximate	Analysis (%) [b] C	H	N	^{1}H N.m.r. H^1	H^2	H^3	H^4	Oximate	Other	Comments
CH$_2$CH=CH$_2$	OH$_2$ [c]	Hdmg	37.0 (37.9)	5.9 (6.1)	15.8 (16.1)	3.72 [d]	5.60 [e]	3.72 [d]		2.26 [f]		10% CD$_3$OD
	OH$_2$ [c]	Hchdd	44.7 (45.0)	6.1 (6.3)	13.9 (14.0)	3.85 [d]	5.63 [e]	3.85 [d]		2.8, 1.8 [g]		50% CD$_3$OD
	py	Hdmg				2.23 [d]	5.57	4.89		2.13 [f]		+0.33 mol dm^{-3} py
	[N$_3$]$^-$ [h]	Hdmg				*i*	5.51	4.80		2.16		0.33 mol dm^{-3}
	py	Hchdd	51.3 (52.1)	6.2 (6.1)	15.3 (15.2)	2.42	5.58	5.00		2.7, 1.6 [g]		+trace CBrCl$_3$
CH$_2$CMe=CH$_2$	OH$_2$ [c]	Hdmg				3.66		3.66		2.27 [f]	1.71 [f] (Me)	+10% CD$_3$OD
	py [j]	Hdmg	47.6 (48.2)	6.0 (6.2)	16.7 (16.5)	3.57				2.22 [f]	1.73 [f] (Me)	
CH$_2$CH=CHMe	OH$_2$	Hdmg	40.7 (39.8)	6.5 (6.4)	15.4 (15.5)	*ca.* 2.40 [k]	5.0	5.0	1.00 [d]	2.24		+10% CD$_3$OD
	imidazole·0.5H$_2$O	Hdmg	42.7 (42.8)	6.1 (6.2)	20.2 (20.0)	2.30 [k]	5.35	5.35	1.21 [d]	2.13	7.58, 7.00 (imidazole)	
	NH$_2$Ph·H$_2$O	Hdmg	47.4 (47.5)	6.5 (6.6)	15.4 (15.5)	2.35 [k]	5.31	5.31	1.08 [d]	1.99		
CH$_2$CH=CHPh	OH$_2$	Hdmg	47.9 (48.1)	5.8 (5.9)	13.2 (13.2)	2.54 [l]	5.99	6.57 [m]		2.17		10% CD$_3$OD
	imidazole·H$_2$O [n]	Hdmg	48.3 (48.8)	5.4 (5.9)	17.1 (17.0)							
CH=C=CH$_2$	OH$_2$	Hdmg	38.1 (38.2)	5.6 (5.5)	16.2 (16.2)	4.72		4.36		2.31		50% CD$_3$OD

[a] 0.66 mol dm^{-3} in CDCl$_3$; fresh solutions. [b] Calculated values are given in parentheses. [c] At 50 °C near high-temperature limit. [d] Doublet. [e] Quintuplet, *J* 11.2 ± 0.3 Hz. [f] Singlet. [g] Two broad multiplets. [h] [AsPh$_4$]$^+$ as counter ion. [i] Obscured. [j] Spectrum deteriorated. Dynamic system, high-temperature limit quoted. [k] Doublet partially obscured. [l] Doublet, *J* 8 Hz. [m] Doublet, *J* 15 Hz. [n] Only slightly soluble.

a function of the concentrations of added ligand and reagent is shown in Table 2. The best yield was obtained using (14; L = imidazole) without added pyridine and the crystal structure of the product [9] (15; L = imidazole) (Figure 3) has been described in a preliminary communication.[10] Minor products which may have contained the cinnamyl moiety bonded indirectly to the cobalt were unstable.

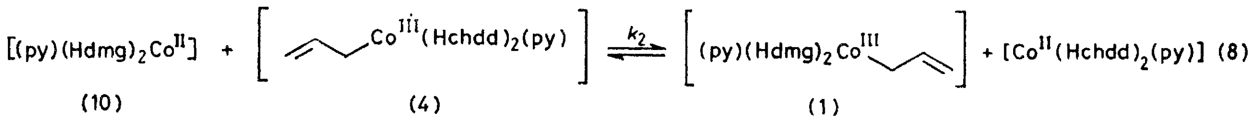
TABLE 2

Reaction of cinnamylaquabis(dimethylglyoximato)-cobalt(III) with $C_2(CN)_4$

[complex]	[pyridine]	$[C_2(CN)_4]$ [a]	Yield of (15; L = py)
	mol dm^{-3}		
0.08	0	0.08	10 [b]
0.08	0.08	0.08	25 [c]
0.08	0.16	0.08	15
0.40	0.80	0.40	15
0.08	0.32	0.08	5
0.40	2.40	0.08	0
0.08	0.08	0.16	50
0.08	0.08	0.24	50
0.08	0.12	0.24	55
0.08	0	0.16	60 [d]

[a] Added last. [b] 1 mol of pyridine was added before work-up. [c] Same product starting from (14; L = py) without added pyridine. [d] (14; L = imidazole) as reagent, (15; L = imidazole) as product.

Similar cyclopentylcobaloximes (Table 3) were also obtained from the reactions of allyl- and but-2-enyl-cobaloximes, (18) and (17) respectively. In the case of (18; L = imidazole) the yield of cyclic product was almost quantitative, but no cyclic product could be obtained from bis(dimethylglyoximato)(2-methylallyl)-pyridinecobalt(III) (19) and $C_2(CN)_4$. Complex (11; L = py) also reacts with $C_2(CN)_4$ and with hexafluoroacetone * to give the cyclic products (23) and (25), respectively, and in the reaction of the bimetallic cobaloxime (13) with $C_2(CN)_4$ the propadienyl proton resonances are evident prior to the formation of the cyclic product (23).



Mechanism of the Cycloaddition Reactions.—The similarity of the cycloaddition reactions of the allyl- and

$$[Fe(CHR'CH{=}CHR)(\eta\text{-}C_5H_5)(CO)_2] \quad (26)$$

$$[Fe(CH{=}C{=}CH_2)(\eta\text{-}C_5H_5)(CO)_2] \quad (27)$$

$$[Co\{O_2CH(C_6H_4Me\text{-}m)Me\}(Hdmg)_2(py)] \quad (28)$$

propadienyl-cobaloximes with those of the corresponding allyl- [11] and propadienyl-iron [12] complexes (26) and (27), which have been extensively investigated,[4] indicates that the mechanisms are probably identical, involving zwitterionic intermediates such as (16), (22), and (24),

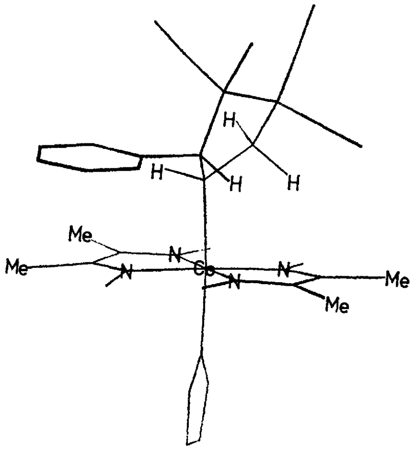


FIGURE 3 View of *trans*-bis(dimethylglyoximato)imidazole-(3,3,4,4-tetracyano-2-phenylcyclopentyl)cobalt(III) showing the *trans*-1,2 configuration, the parallel planes of the dioximate ligands and the phenyl group, and the non-linearity of the axial ligand–metal–axial ligand bonds

which ring-close to give the observed products. The unstable organocobaloximes are probably formed either as a result of an alternative breakdown of the intermediates in which the cobaloxime moiety migrates to the anionic centre to give an effective insertion product, or as a result of competing electron-transfer processes.

The main difference between the allylcobaloxime and allyliron systems is the lability of the sixth axial ligand in the former case. Thus, although some cycloaddition takes place with (14; L = OH_2), the presence of a more strongly co-ordinating axial ligand such as pyridine or preferably imidazole improves the yield, despite the fact that these ligands react with tetracyanoethylene. Yields are therefore maximised by adding a small excess of both axial ligand and $C_2(CN)_4$ to allow for the competing processes.

The *trans* stereochemistry of the product (15; L = imidazole), determined by *X*-ray analysis, is also in accord with the cycloaddition reactions of allyliron complexes, and implies that the conversion of (14) into (16) involves a *trans-antarafacial* migration of the cobaloxime moiety. Such a σ–π migration and the subsequent π–σ migration in the formation of (15) from (16) have adequate precedent in organocobaloxime chemistry in, for example, the acid-catalysed reactions of β-acetoxy-

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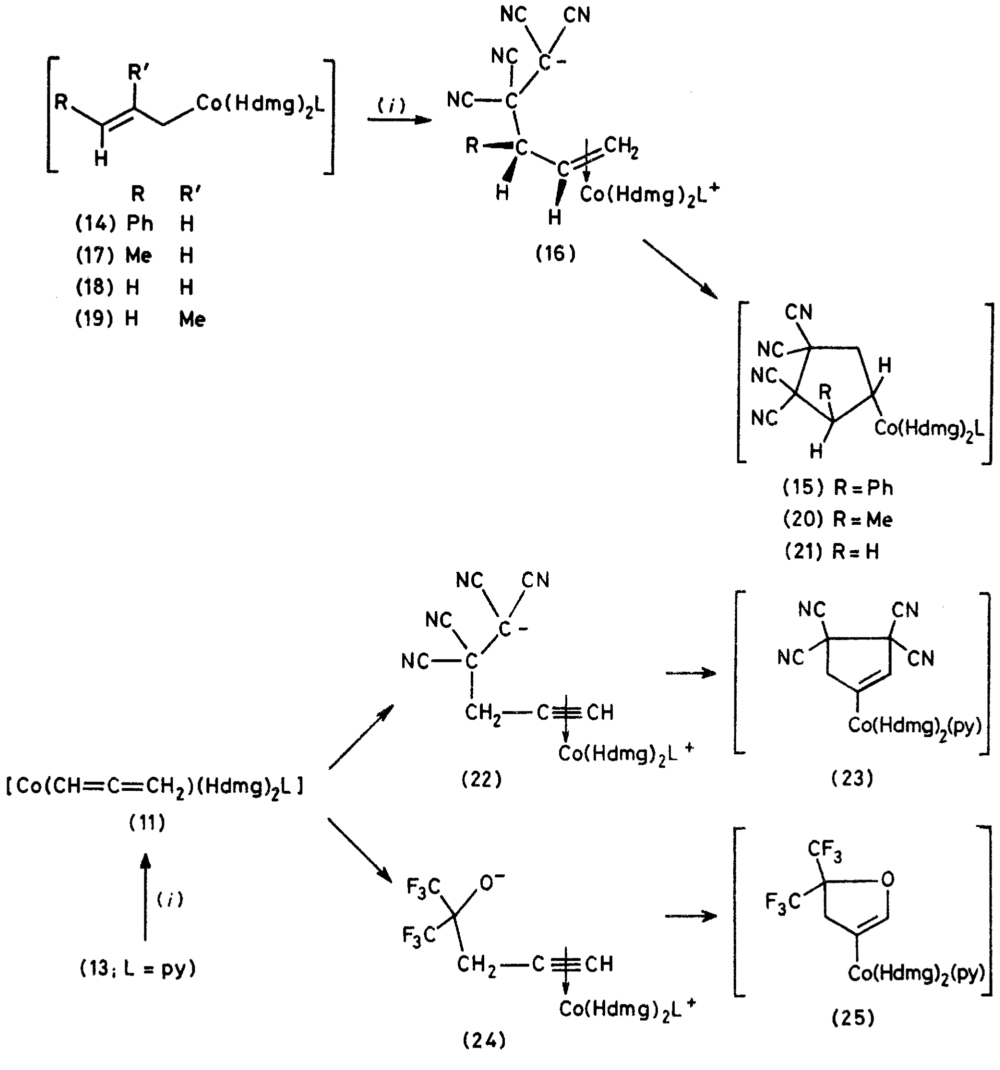
* D. W. Lichtenberg and A. Wojcicki (*Inorg. Chem.*, 1975, **14**, 1295) formulate corresponding products from propadienyliron complexes as 2,3-dihydrofuryliron complexes. Our mechanism suggests that the 4,5-dihydrofurylmetal complexes are formed.

[10] D. Dodd, M. D. Johnson, I. P. Steeples, and E. D. McKenzie, *J. Amer. Chem. Soc.*, 1976, **98**, 6399.

[11] A. Cutler, D. Entholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *J. Amer. Chem. Soc.*, 1976, **98**, 3495.

[12] S. Raghu and M. Rosenblum, *J. Amer. Chem. Soc.*, 1973, **95**, 3060.

ethyl-[13] and formylmethyl-cobaloximes,[14,15] and attack of electrophiles at the γ-carbon of allylmetal complexes is a common process.



(i) $C_2(CN)_4$

Character of Substituted Cyclopentylcobaloximes and Related Asymmetric Cobaloximes.—Bis(dimethylglyoximato)organocobalt(III) complexes in which either the organic ligand or the axial base is asymmetric have two diastereotopic pairs of methyl groups which may be manifested as two different methyl resonances in the ^{1}H n.m.r. spectrum.[16] Usually, the difference is slight, but in the case of (15; R = Ph) the difference in chemical shift is particularly large due to the close proximity of the phenyl group which, as the crystal structure shows, lies close to and almost parallel with the equatorial ligand plane (Figure 3). A similar large difference is observed in the spectrum of bis(dimethylglyoximato)-[1-(*m*-tolyl)ethyldioxo]pyridinecobalt(III) (28) which also has the tolyl group close to and parallel with the equatorial ligand plane.[17] In each case, the difference in chemical shift ($\Delta\delta$) is temperature dependent (Figure 4), but in the chosen solvents the temperature could not be obtained where rotation about the carbon–cobalt bond was restricted sufficiently to give four sets of methyl resonances.

EXPERIMENTAL

Materials.—Allyl- and propadienyl-aquacobaloximes were prepared by the reaction of the appropriate allyl or prop-2-ynyl halide with a two-fold excess of aquabis(cyclohexanedione dioximato)cobalt(II) or aquabis(dimethylglyoximato)-cobalt(II) in methanol under anaerobic conditions in the

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presence of a three-fold excess of aqueous methanolic sodium hydroxide at −20 °C. After warming to room temperature the solutions were evaporated until crystals of the aqua-complex were formed. These were filtered off under nitrogen, washed with iced water, and dried *in vacuo*. The corresponding allyl- and propadienyl-bis(dioximato)-(ligand)cobalt(III) complexes were prepared by addition of the appropriate ligand to a solution of the aqua-complex in methanol. The new complexes prepared are shown in Table 1. Tetracyanoethylene was recrystallised from methylene chloride.

TABLE 3

Products $[CoR'(Hdmg)_2L]$ of reaction of tetracyanoethylene with allylbis(dimethylglyoximato)-(ligand)cobalt(III), $[CoR(Hdmg)_2L]$

R	L	Product R′	Analysis (%) [a] C	H	N	Yield (%)	¹H N.m.r. (δ/p.p.m.) H¹	H²	H⁵	Hdmg	Other
Allyl	py	$CHCH_2C(CN)_2C(CN)_2CH_2$	49.2 (49.2)	4.5 (4.5)	23.3 (23.5)	95	*b*	*b*	*b*	2.19	8.52 (α-py)
But-2-enyl	py	$CHCH(Me)C(CN)_2C(CN)_2CH_2$ [c]	49.3 (50.1)	4.7 (4.7)	23.2 (22.9)	53	*b*	*b*	*b*	2.27	8.57 (α-py), 1.39 (Me) [d]
	imidazole	$CHCH(Me)C(CN)_2C(CN)_2CH_2$ [c]	46.5 (46.7)	4.8 (4.7)	26.2 (25.9)	65	*b*	*b*	*b*	2.22	7.50, 6.92,[e] 1.35 (Me) [d]
Cinnamyl	py	$CHCH(Ph)C(CN)_2C(CN)_2CH_2$ [c]	54.7 (54.8)	4.6 (4.6)	20.6 (20.6)	*f*	3.49 [g]	*b*	*b*	2.10, 1.87	8.42 (α-py), 7.46 (Ph)
	imidazole	$CHCH(Ph)C(CN)_2C(CN)_2CH_2$ [h]	51.8 (51.8)	4.4 (4.5)	23.0 (23.3)	60	3.50 [g]	*b*	*b*	2.05, 1.87	7.37,[e] 7.34 (Ph)
	4Me-py	$CHCH(Ph)C(CN)_2C(CN)_2CH_2$	54.9 (55.5)	4.8 (4.8)	19.8 (20.1)		3.52 [i]	*b*	*b*	2.11, 1.86	8.15 (α-py), 7.05 (β-py), 7.35 (Ph)
Propadienyl	py	$C{=}CHC(CN)_2C(CN)_2CH_2$	48.9 (49.3)	4.4 (4.5)	23.0 (23.3)	46		5.57 [j]	3.32 [j]	2.17	8.64 (α-py)
	py	$C{=}CHOC(CF_3)_2CH_2$	38.1 (39.8)	4.0 (3.8)	11.2 (12.2)	65			5.03 [j]	2.20	3.56 (H³)

[a] Calculated values are given in parentheses. [b] Obscured by Hdmg resonance. [c] Assumed to be the *trans* isomer. [d] Doublet, *J* 6 Hz. [e] Imidazole. [f] See Table 2. [g] *J* 10.1 Hz. [h] Crystal structure shows *trans* isomer. [i] *J* 9.5 Hz. [j] Triplet, *J* 1.5 Hz.

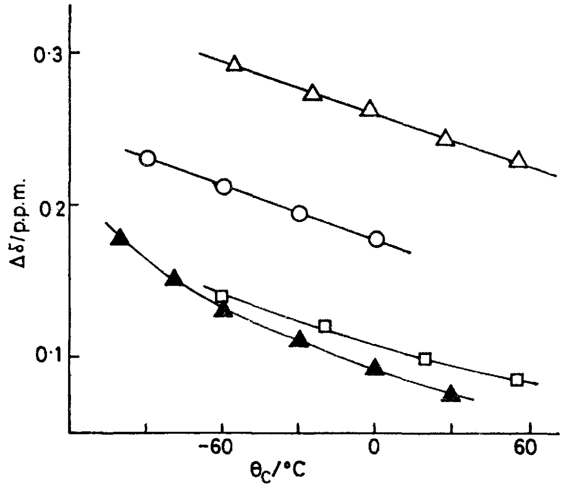

FIGURE 4 Temperature dependence of the chemical-shift differences between diastereotopic dimethylglyoximate methyl-proton resonances of (△) complex (15; L = py), (○) (15; L = imidazole), and (□) (28), all in $CDCl_3$, and (▲) (28) in CS_2

Temperature-dependent Spectra. Temperature-dependent ¹H n.m.r. spectra were recorded using a Varian HA 100 instrument for solutions of $\geqslant 0.1$ mol dm^{-3} under nitrogen in $CDCl_3$ containing sufficient CD_3OD for homogeneity, and using a Bruker FT 90 MHz instrument for more dilute solutions. Carbon-13 n.m.r. spectra were obtained on a Varian CFT20 instrument and ¹H spectra of allyl(pyridine)-cobaloximes on a Varian T60 instrument.

Cobalt-for-cobalt exchange reactions were studied by the method described elsewhere for alkyl(pyridine)cobaloximes.[6]

Reactions with Tetracyanoethylene.—The organocobaloxime (final concentration 0.08—0.4 mol dm^{-3}) in methylene chloride containing pyridine (final concentration 0—2.4 mol dm^{-3}) was treated with tetracyanoethylene (final concentration 0.08—2.4 mol dm^{-3}) at room temperature or below. After 1 h the solution was chromatographed on alumina or silica gel and the organocobalt products were eluted with methylene chloride–acetone mixtures. The influence of reagent concentrations on product yield is shown in Table 2 and the yields and characteristics of the organic products in Table 3.

Reactions with Hexafluoroacetone.—Bis(dimethylglyoximato)propadienyl(pyridine)cobalt(III) (0.4 g, 1 mmol) and hexafluoroacetone (2 g, 8 mmol) in dry methylene chloride (5 cm³) were sealed in a glass tube at −78 °C. The tube was allowed to stand at room temperature overnight and the contents were worked-up as for the products of reaction with $C_2(CN)_4$ (Table 3), yield 65%.

[8/172 *Received*, 1*st February*, 1978]