Hydrogenation by Cyanocobaltate. Part 5.[1] Pseudo-contact Shift by Ion Association between Organocyanocobaltates(III) and Tris(ethylenediamine)cobalt(II) Ion in the Catalytic System of Tricyano(ethylenediamine)cobaltate(II)

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The pseudo-contact shift observed with alkylpentacyanocobaltates(III) and tetracyano(η-methylallyl)cobaltates(III) has been explained by the formation of ion pairs such as $[Co(en)_3]^{2+},[Co(CN)_5R]^{3-}$ (en = ethylenediamine; R = $CH_2CH{:}CMe_2$, CH_2Ph, or $CH_2C_6H_4Me$-*o*, -*m*, or -*p*). The equilibrium constant for the reaction $[Co(en)_3]^{2+} + [Co(CN)_5R]^{3-} \rightleftharpoons [Co(en)_3]^{2+},[Co(CN)_5R]^{3-}$ has been estimated to be 0.67 ± 0.02 dm^3 mol^{-1} when R = $CH_2C_6H_4Me$-*o*. The observed pseudo-contact shifts are qualitatively explained by calculations on simple models of the ion pairs, in which $[Co(en)_3]^{2+}$ is located on the principal axis of the cyano-complexes at the opposite side of the organic ligands and the distance between the two cobalt atoms is *ca.* 5.5—6 Å. Steric configurations of the organic ligands are discussed.

IN the n.m.r. study of the hydrogenation of butadiene and isoprene catalysed by aminetricyanocobaltate(II) [amine = ethylenediamine (en), 2,2′-bipyridine (bipy), or 1,10-phenanthroline (phen)] we observed the pseudo-contact shift with the σ-alkenyl and η-methylallyl groups of the intermediate complexes in the en system, and the broadening without shift in the bipy and phen systems.[1] We proposed the formation of cyanide-bridged paramagnetic dimeric complexes such as $[R(NC)_4Co{-}CN{-}Co(CN)_3(en)]^{4-}$ to explain the behaviour, but further detailed studies revealed that the explanation was wrong. In this paper we report that the pseudo-contact shift is due to the formation of an ion pair between organocyanocobaltates(III) and tris(ethylenediamine)cobalt(II) ion, and describe the structures of the ion pairs as determined by the pseudo-contact-shift method.

EXPERIMENTAL

The solutions of the organocyanocobaltate(III) for the spectroscopic measurements were prepared as follows. (*a*) Cobalt(II) chloride, K[CN], and amine (ratio Co : CN : amine variable, [Co] = 0.2 mol dm^{-3}) were mixed in a hydrogen atmosphere at room temperature and in D_2O (en system) or D_2O–CD_3OD (1 : 1) (bipy and phen systems). After the hydrogen absorption, butadiene or isoprene was added. (*b*) To the solutions of complexes which were prepared at CN : Co = 6 : 1 as in (*a*) but in the absence of amine, a solution of $[Co(amine)_3]^{2+}$ was added (total cobalt concentration maintained constant). (*c*) Alkyl halides such as benzyl bromide, *o*-, *m*-, and *p*-methylbenzyl bromides, methyl iodide, *etc.* were added to the $[Co(CN)_5]^{3-}$ solution (CN : Co = 6 : 1), and then a solution of $[Co(en)_3]^{2+}$ or $[Ni(en)_3]^{2+}$ was added after the completion of the above reactions.

N.m.r. spectra were recorded on a Varian HR-220 spectrometer; $Na[O_2CC_2D_4SiMe_3]$ was used as internal reference. A JES-3BS-X spectrometer and Shimadzu MB-2B magnetic balance were used for measurements of e.s.r. spectra and magnetic susceptibility, respectively.

RESULTS

Figure 1 shows the shifts of the reference peak in the solutions for hydrogenation of isoprene by aminecyanocobaltates [method (*a*)]. These shifts correlate with the concentration of the paramagnetic species in solution,[2] and it can be seen that the concentration of the paramagnetic species which participates in the paramagnetic shift is greater at the lower CN : Co ratio, and greater in the en than in the bipy and phen systems. The great difference in the reference shifts in these systems at CN : Co $\geqslant$ 3 : 1 is noteworthy and may relate to the fact that the formation of $[Co(CN)_3R(amine)]^-$ (R = $CH_2CH{:}CHMe$ or $CH_2CH{:}CMe_2$) is much greater in the bipy and phen than the en system.

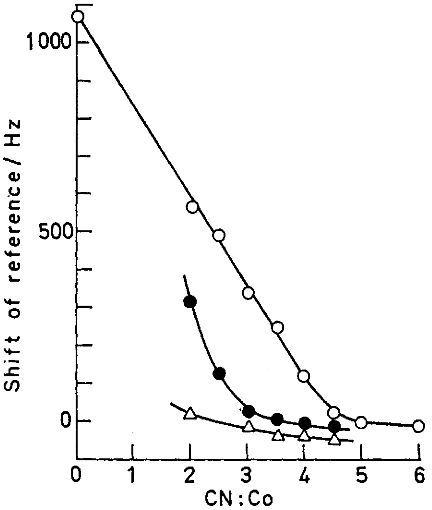

FIGURE 1 Shifts of the reference peak in solutions for hydrogenation of isoprene by aminecyanocobaltates(II) $[Co(CN)_m(amine)_n]^{(2-m)+}$; amine = en (○), bipy (●), and phen (△)

Proton signals of the organic ligands of $[Co(CN)_5(CH_2CH{:}CMe_2)]^{3-}$ (1) and $[Co(CN)_4(\eta\text{-}1\text{-}Me\text{-}C_3H_4)]^{2-}$ (2) prepared by method (*a*) shifted in proportion to the shifts of the reference peak. Figure 2 shows the result for the former complex.

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[1] Part 4, T. Funabiki, S. Kasaoka, K. Matsumoto, and K. Tarama, *J.C.S. Dalton*, 1974, 2043.

[2] J. A. Pople, W. G. Schneider, and J. J. Bernstein, ' High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, pp. 20 and 80.

The shifts with $[Co(CN)_3(CH_2CH{:}CMe_2)(en)]^-$ and $[Co(CN)_3(CH_2CH{:}CHMe)(en)]^-$ were very small ($<\frac{1}{7}$) in comparison with those with (1) and (2), respectively. In the bipy and phen systems, broadening without shift was observed with (1), (2), and $[Co(CN)_3R(amine)]^-$ ($R = CH_2CH{:}CMe_2$ or $CH_2CH{:}CHMe$) even at CN : Co = 3 : 1 where the shift of the reference was small. Addition of $[Co(amine)_3]^{2+}$ to the solution of (1) and (2) [method (*b*)] reproduced the results observed by method (*a*). Figure 2 shows an example of the en system. On the other hand, addition of a solution containing $[Co(CN)_5]^{3-}$ and $[Co(CN)_3(en)]^-$ in place of $[Co(en)_3]^{2+}$ did not cause shifts of the peaks of (1) and (2).

Shifts by addition of $[Co(en)_3]^{2+}$ were investigated with some other $[Co(CN)_5R]^{3-}$ and $[Co(CN)_4(\eta\text{-}R)]^{2-}$ complexes [method (*c*)]. In the cases of benzyl complexes, one *o*- and one *m*-proton were observed with benzyl and *p*-methylbenzyl complexes $\{[Co(CN)_5(CH_2Ph)]^{3-}$ (3) and $[Co(CN)_5(CH_2C_6H_4Me\text{-}p)]^{3-}$ (6), respectively}, and two *m*-protons with the *o*-methylbenzyl complex $[Co(CN)_5(CH_2C_6H_4Me\text{-}o)]^{3-}$ (4) and two *o*-protons with the *m*-methylbenzyl complex $[Co(CN)_5(CH_2C_6H_4Me\text{-}m)]^{3-}$ (5). Addition of a large excess of $[Co(en)_3]^{2+}$ to a solution of (4) gave shifts which approached maximum values (Figure 3). Complex (4) was most suitable for this experiment because the formation of $[Co(CN)_3(CH_2C_6H_4Me\text{-}o)(en)]^-$ was strongly suppressed, probably by the steric interaction between the *o*-methyl group and the en ligand. The shift of the methyl proton of the methyl complex was the same as those of the methylene protons of other σ complexes.

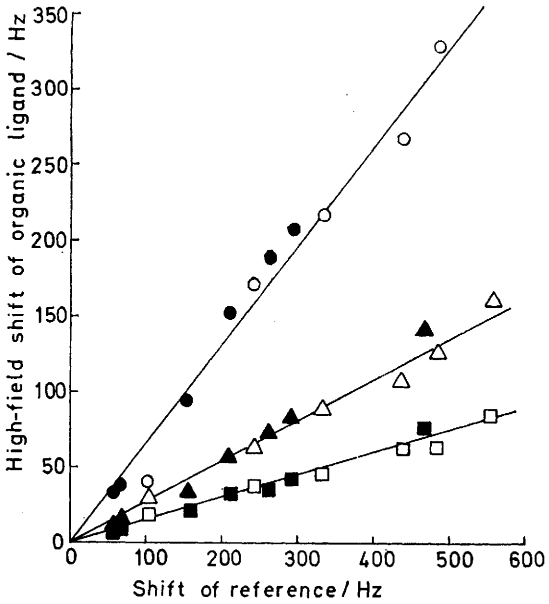

FIGURE 2 Shifts of the proton signals in $[Co(CN)_5(CH_2CH{:}CMe_2)]^{3-}$. Method (A) (○) CH_2; (△), (□) CH_3; Method (B): (●), CH_2; (▲), (■) CH_3

Addition of a $[Ni(en)_3]^{2+}$ solution resulted only in peak broadening without shift. Addition of $[Co(en)_3]^{2+}$ to a solution of $[Co(Hdmg)_2(CH_2Ph)(H_2O)]$ [Hdmg = dimethylglyoximato(1—)] did not cause a shift of the benzyl protons.

The magnetic susceptibility was measured of a solution of Co : CN : en = 1 : 3 : 1 prepared in a nitrogen atmosphere, and a $\mu_{eff.}$ value of 2.68 B.M. for the cobalt was obtained.* Referring to $\mu_{eff.}$ 1.72 B.M. for $[Co(CN)_5]^{3-}$,[3] and 4.56 B.M. for $[Co(en)_3]^{2+}$,[4] and assuming a $\mu_{eff.}$ 1.72 B.M. for $[Co(CN)_3(en)]^-$ and that the solution contains only these three species, the proportion of $[Co(en)_3]^{2+}$ in the solution was estimated to be 34%. Measurement of the e.s.r. spectrum of the above solution at 77 K showed the broad resonance of $[Co(en)_3]^{2+}$ ($\bar{g}$ 4.4) in addition to the hyperfine spectra of $[Co(CN)_5]^{3-}$ and probably $[Co(CN)_3(en)]^-$.[1] When the solution was treated with hydrogen and isoprene, the hyperfine structure disappeared and the peak of $[Co(en)_3]^{2+}$ remained without change in intensity. By comparing the intensity of the resonance of $[Co(en)_3]^{2+}$ in the e.s.r. spectrum and the shift of the reference peak in the n.m.r. spectrum with those of a pure solution of $[Co(en)_3]^{2+}$ of the same total cobalt concentration, the proportion of $[Co(en)_3]^{2+}$ estimated by the two methods were 32 and 31%, respectively.

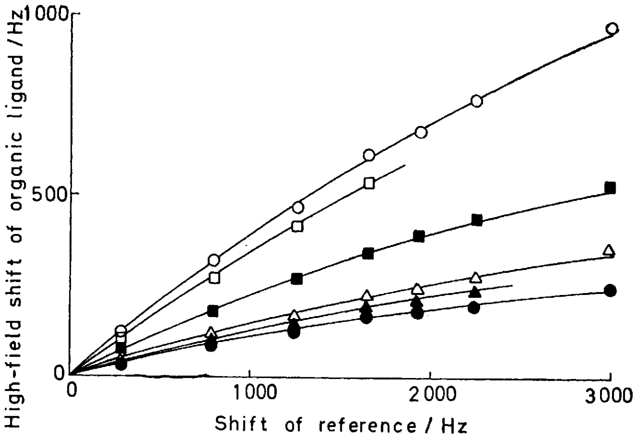

FIGURE 3 Shifts of the proton signals of $[Co(CN)_5(CH_2C_6H_4Me\text{-}o)]^{3-}$: (○) α-$CH_2$; (□) *o*-H; (■) *o*-$CH_3$; (△) *m*-H; (▲) *m*-H′; (●) *p*-H

In the bipy and phen systems, solutions at Co : CN : amine = 1 : 3 : 1, which were treated with hydrogen and isoprene and observed at 77 K after removal of precipitates, did not show the e.s.r. peaks corresponding to the $[Co(amine)_3]^{2+}$ species, but the hyperfine spectra, which corresponded most probably to $[Co(CN)_3(amine)]^-$, were observed ($g_\perp$ 2.14, $g_\parallel$ 1.99, $a_\perp$ 77.3 G, $a_\parallel$ 37.8 G when amine = bipy). Peaks of $[Co(amine)_3]^{2+}$ were observed only at the lower CN : Co ratio.

DISCUSSION

There seem to be three probable mechanisms to explain the pseudo-contact shift observed with Co^{III}–R complexes: (*i*) formation of Co^{II}–R by inner-sphere and (*ii*) outer-sphere electron transfer from cobalt(II) species; (*iii*) ion-pair formation between Co^{III}–R and cobalt(II) species. Although we proposed mechanism (*i*) for the paramagnetic complex $[Co(CN)_3(en)]^-$, the present

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 G = 10^{-4} T.

[3] A. W. Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.

[4] S. Datta, *Phil. Mag.*, 1934, **17**, 585.

results clearly indicate that $[Co(en)_3]^{2+}$ is the paramagnetic species which is responsible for the pseudo-contact shift since: (*a*) the addition of the solution containing $[Co(CN)_5]^{3-}$ and $[Co(CN)_3(en)]^-$ to the solution of (1) and (2) did not bring about a shift; (*b*) the addition of $[Co(en)_3]^{2+}$ [method (*b*)] reproduced the results observed by method (*a*); and (*c*) the estimation of the concentration of $[Co(en)_3]^{2+}$ by three different methods gave good agreement. It seems unreasonable to propose mechanism (*i*) for the co-ordinatively saturated complex $[Co(en)_3]^{2+}$. As for mechanism (*ii*), it is said that reaction is rapid when the electronic and geometrical configurations do not change after reaction {*e.g.* $[Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-}$},[5] but slow when they do.[6] The reaction $[Co(en)_3]^{2+} + [Co(CN)_5R]^{3-} \rightleftharpoons [Co(en)_3]^{3+} + [Co(CN)_5R]^{4-}$ is in the latter category, but the single n.m.r. peaks rather than the independent Co^{III}–R and Co^{II}–R peaks indicate that the reaction is rapid. So mechanism (*ii*) is improbable in the present case.

In the reports of the pseudo-contact shift in paramagnetic complexes,[7,8] the formation of an ion pair between cations and ionic complexes has been studied, *e.g.* $[NBu_4]^+,[MI_3(PPh_3)]^-$ ($M = Co^{II}$ or Ni^{II})[9] and $[NBu_4]^+,[Fe(CN)_6]^{3-}$.[10] But no study has been reported, to our knowledge, of the pseudo-contact shift on formation of an ion pair between an anionic organometallic complex and a cationic complex. The following experimental results support ion-pair formation between $[Co(CN)_5R]^{3-}$ or $[Co(CN)_4R]^{2-}$ and $[Co(en)_3]^{2+}$. (*i*) The shifts of $[Co(CN)_3R(en)]^-$ species were much smaller than those of $[Co(CN)_5R]^{3-}$. (*ii*) A shift was not observed with benzylcobaloxime. These two results are consistent with the formation of an ion pair being dependent on the product of the charges of the two ions. (*iii*) Broadening without shift was observed by the addition of $[Ni(en)_3]^{2+}$ to $[Co(CN)_5R]^{3-}$. Since in the case of Ni^{II} the pseudo-contact shift is negligible, the dipolar broadening indicates an interaction between two ions. (*iv*) The shift pattern for each complex indicates that the contribution of the contact shift is negligible even though the paramagnetic species is Co^{II}.

For reaction (1), equations (2) and (3) may be written where δ, δ_o, and δ_p denote the chemical shift of the protons observed, of $[Co(CN)_5R]^{3-}$, and of $[Co(en)_3]^{2+}$, $[Co(CN)_5]^{3-}$, respectively. Figure 4 shows an example of a linear correlation between $(\delta - \delta_o)^{-1}$ and $[Co(en)_3{}^{2+}]^{-1}$ for the *o*-methylbenzyl complex (4). Values of K(dm^3 mol^{-1}) and $\delta_p - \delta_o$ (p.p.m.) obtained for each proton are: α-CH$_2$ (0.66, 16.1), *o*-CH$_3$ (0.65, 14.1), *o*-H (0.66, 9.3), *m*-H (0.67, 5.9), *m*-H′ (0.65, 5.2), and *p*-H (0.69, 4.2). Figure 4 and $K = 0.67 \pm 0.02$ dm^3 mol^{-1} support mechanism (*iii*) and equation (1).

$$[Co(en)_3]^{2+} + [Co(CN)_5R]^{3-} \overset{K}{\rightleftharpoons} [Co(en)_3]^{2+}, [Co(CN)_5R]^{3-} \quad (1)$$

$$\delta = \frac{[Co(CN)_5R^{3-}]\delta_o + [Co(en)_3{}^{2+}, Co(CN)_5R^{3-}]\delta_p}{[Co\text{–}R]_T} \quad (2)$$

$$\delta - \delta_o = \frac{K[Co(en)_3{}^{2+}]}{1 + K[Co(en)_3{}^{2+}]}(\delta_p - \delta_o) \quad (3)$$

Since the relative pseudo-contact shifts can be described solely in terms of molecular geometry,[7,8] $3\cos^2(\theta_i - 1)/r_i{}^3$ (for θ_i and r_i see Figure 5) was computed on a FACOM 230-75 for each proton to determine the most probable distance between the cobalt atoms and the configurations of the organic ligands. The models we propose for the ion pairs are illustrated in Figure 5. Although structural parameters of some transition-metal η-methylallyl and σ-alkyl complexes have been determined by *X*-ray analysis, data for crystals are not necessarily applicable to the structures in solution, and the position of hydrogen has not been determined. Calculations were carried out on simple models, assuming for the η-methylallyl complex a planar methylallyl group perpendicular to the Co–CN(axial) axis and equal distances between the cobalt atom and the three allyl carbon atoms, and for the σ-alkyl complex a regular

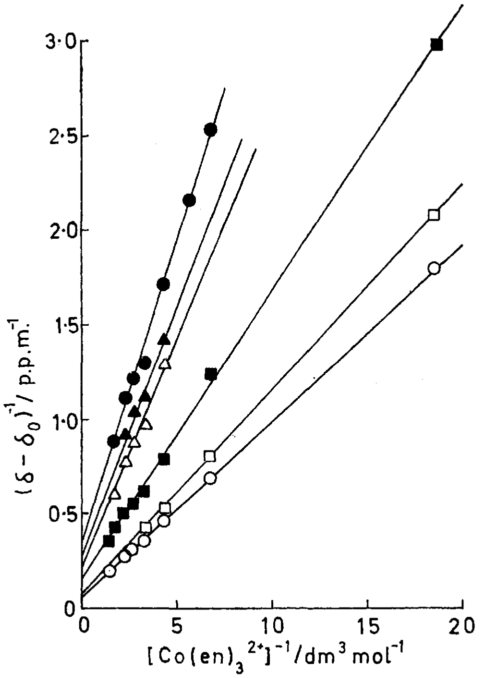

FIGURE 4 Relation between $[Co(en)_3{}^{2+}]^{-1}$ and $(\delta - \delta_o)^{-1}$ for $[Co(CN)_5(CH_2C_6H_4Me\text{-}o)]^{3-}$: (○) α-CH$_2$; (□) *o*-H; (■) *o*-CH$_3$; (△) *m*-H; (▲) *m*-H′; (●) *p*-H. The concentration of $[Co(en)_3]^{2+}$ was determined from the shift of the reference peak

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[6] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' Wiley–Interscience, New York, 1958.

[7] G. N. La Mar, W. D. Horrocks, jun., and R. H. Holm, ' NMR of Paramagnetic Molecules. Principles and Applications,' Academic Press, New York, 1973.

[8] G. A. Webb, *Ann. Rep. N.M.R. Spectroscopy*, 1975, **6A**, 1.

[9] G. N. La Mar, *J. Chem. Phys.*, 1965, **43**, 235.

[10] D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, 1965, **9**, 1281.

tetrahedral angle for the α-carbon atom which is located on the principal axis. Of course, examples of failure of these assumptions are known with each type of complexes,[11–15] *e.g.* 119.7° for the Co–C_α–C_β angle in $K_3[Co(CN)_5(C_2F_4H)]$.[16]

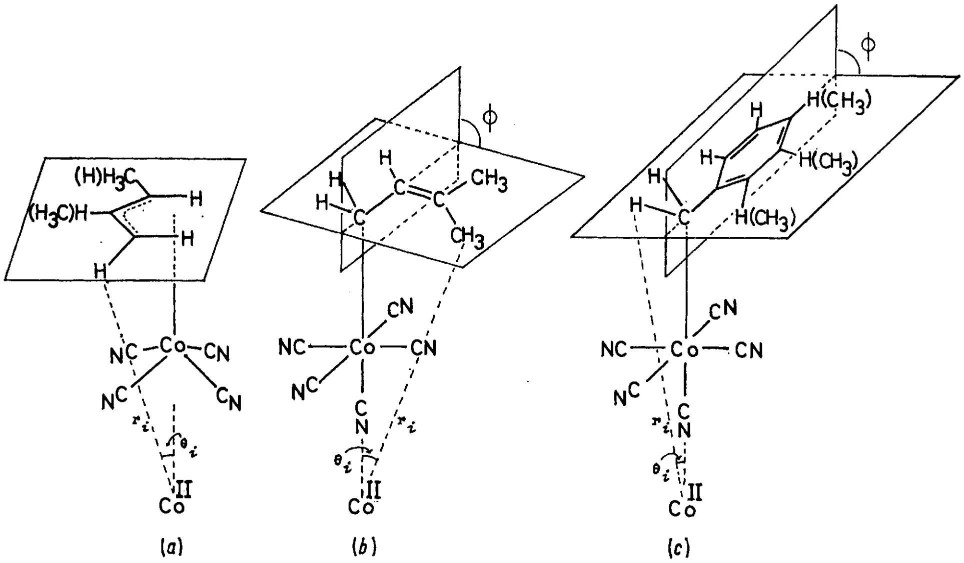

FIGURE 5 Models of ion pairs

In the case of the η-methylallyl complex, similar shifts of the 1- and 2-methyl protons and equal shifts of the 1- and 3-*anti*-protons (greater than that of the *syn*) support the model. As shown in Table 1, the observed and calculated values nearly agree when R (the distance between the allyl plane and the Co^{II}) was *ca.* 7.5 Å.

TABLE 1

Pseudo-contact shifts relative to 1- and 3-*anti*-protons[a] in the η-methylallyl group in the ion pair $[Co(en)_3]^{2+}$, $[Co(CN)_4(\eta\text{-}MeC_3H_4)]^{2-}$

		Shift		
	R[b]/Å	3-*syn*-H	1-*syn*-CH_3	2-CH_3
Obs.		0.84[c,d]	0.68[c]	0.66[d]
Calc.[e]	6.5	0.82	0.55	
	7.0	0.84	0.60	
	7.5	0.86	0.64	
	8.0	0.88	0.67	
	8.5	0.89	0.70	

[a] Observed shifts of 1- and 3-*anti*-H were equal. [b] Distance between Co^{II} and the allyl plane. [c] 1-Methylallyl complex. [d] 2-Methylallyl complex. [e] Structural parameters used for calculation: C–H(allyl) 1.07, C–C(allyl) 1.36, C–CH_3 1.54, and C–H(CH_3) 1.09 Å; C–C–C 120°.

In the case of the 3,3-dimethylallyl complex (**1**) the $C_\beta{:}C_\gamma(CH_3)_2$ group can rotate about the C_α–C_β bond. In our model [Figure 5(*b*)] the shift of one methyl group was affected greatly by varying the rotation angle but that of another only slightly. Although the agreement of the calculated and observed values is rather poor, the results in Table 2 suggest the configuration in which the $C_\beta{:}C_\gamma(CH_3)_2$ plane is approximately parallel to the plane including the Co–CN(axial) axis.

TABLE 2

Pseudo-contact shifts of two methyl protons relative to the α-methylene proton in the ion pair $[Co(en)_3]^{2+}$, $[Co(CN)_5(CH_2CH{:}CMe_2)]^{3-}$

		ϕ[a]/°			
	R[b]/Å	90	60	30	0
Obs.		0.42 : 0.23			
Calc.[c]	7.0[d]	0.69 : 0.38	0.52 : 0.37	0.45 : 0.36	0.43 : 0.36
	7.5[d]	0.72 : 0.41	0.55 : 0.40	0.47 : 0.39	0.45 : 0.39
	8.0[d]	0.75 : 0.44	0.57 : 0.43	0.49 : 0.42	0.47 : 0.41
	5.5[e]	0.47 : 0.20	1.08 : 0.20	4.19 : 0.18	7.08 : 0.17
	6.0[e]	0.54 : 0.31	1.17 : 0.32	3.57 : 0.32	5.97 : 0.31
	6.5[e]	0.59 : 0.40	1.23 : 0.43	3.17 : 0.45	5.08 : 0.45

[a] Rotation angle of the $C_\beta{:}C_\gamma(CH_3)_2$ group about the C_α–C_β bond [see Figure 5(*b*)]. [b] Distance between Co^{II} and C_α. [c] Structural parameters used for calculation: C–H 1.09, C_α–C_β 1.52, C_γ–CH_3 1.54, and C_β–C_γ 1.34 Å; Co–C_α–C_β and Co–C_α–H 109.46, C_α–$C_\beta{:}C_\gamma$ 123, and $C_\beta{:}C_\gamma$–CH_3 111.5°. [d] Co^{II} located at the side of the axial cyanide ligand. [e] Co^{II} located at the side of the organic ligand.

Results for the benzyl complexes are shown in Table 3. As seen from the proton signals of the *o*- and *m*-hydrogens, the phenyl ring must be perpendicular to the plane of

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[13] H. Dietrich and R. Utlech, *Naturwiss.*, 1973, **50**, 613.

[14] R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 22.

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[16] R. Mason and D. R. Russell, *Chem. Comm.*, 1965, 182.

Co–C_α–C_β(phenyl) in the benzyl and *p*-methylbenzyl complexes, but rotates about the C_α–C_β(phenyl) bond in the *o*- and *m*-methylbenzyl complexes so that the *o*- or *m*-*methyl group* moves away from the cyanide ligands. This was qualitatively reproduced by calculation, although the agreement between the calculated and observed values was not satisfactory especially with the *m*- and *p*-methyl protons.

As the Co–C_α, Co–CN, and C≡N bond lengths are *ca.* 2.0, 1.9, and 1.2 Å, respectively, the $Co^{III}\cdots Co^{II}$ and $Co^{II}\cdots NC$ distances in the σ complexes are *ca.* 5.5 and 2.5 Å, respectively, if we assume $R = 7.5$ Å (the distance between the Co^{II} and C_α). It seems reasonable to assume that the cation approaches the electron-rich nitrogen atom of the cyanide ligand, but it is also possible that the cation approaches from the side of the organic ligand. Computation on this alternative model gave the same results for the η-methylallyl complexes (Table 1) and better results to explain the small shifts of the *m*- and *p*-methyl protons of complexes (5) and (6) (Table 3). However, if we regard as significant the fact that the shifts of the *o*-proton of (4) and the *m*-proton of (5) were greater than those of complex (3), computation on this alternative model gave the opposite trend. In addition, the steric interaction between the alkyl group and the en ligands may interfere with the approach of $[Co(en)_3]^{2+}$ to the anion within the calculated distance. Hence, we prefer the first model.

TABLE 3

Pseudo-contact shifts of phenyl and methyl protons relative to the α-methylene proton in the ion pair $[Co(en)_3]^{2+}$, $[Co(CN)_5R]^{3-}$

	Complex R [a]/Å	ϕ [b]/°	Proton							
			o-H	*o*-H′	*m*-H	*m*-H′	*p*-H	*o*-CH_3	*m*-CH_3	*p*-CH_3
Obs.	(3; R = CH_2Ph)		0.81		0.33		0.22			
	(4; R = $CH_2C_6H_4Me$-*o*)		0.87		0.36	0.32	0.26	0.57		
	(5; R = $CH_2C_6H_4Me$-*m*)		0.86	0.74	0.42		0.24		0.11	
	(6; R = $CH_2C_6H_4Me$-*p*)		0.82		0.31					0.02
Calc.[c]	7.0 [d]	90	0.69		0.33		0.26	0.66	0.26	0.18
		80	0.76	0.64	0.34	0.32	0.26	0.59	0.25	0.18
	7.5 [d]	90	0.72		0.37		0.28	0.69	0.29	0.21
		80	0.79	0.66	0.38	0.35	0.28	0.62	0.27	0.21
	8.0 [d]	90	0.74		0.40		0.31	0.72	0.32	0.24
		80	0.81	0.68	0.42	0.38	0.31	0.65	0.31	0.24
	6.5 [e]	90	0.68		0.29		0.15	0.56	0.14	0.01
		80	0.60	0.81	0.27	0.31	0.15	0.68	0.13	0.01
	7.0 [e]	90	0.73		0.36		0.22	0.63	0.21	0.07
		80	0.64	0.85	0.38	0.40	0.22	0.74	0.21	0.07
	7.5 [e]	90	0.76		0.41		0.30	0.64	0.28	0.14
		80	0.68	0.88	0.40	0.48	0.30	0.79	0.30	0.14

[a] Distance between Co^{II} and C_α. [b] Rotation angle of phenyl ring about C_α–C_β (phenyl) bond [see Figure 5(*c*)]. [c] Structural parameters used for calculation: C–H(α-CH_2, CH_3) 1.11, C–H(phenyl) 1.08, C_α–C_β(phenyl) 1.51, and C=C(phenyl) 1.39 Å; Co–C_α–C_β (phenyl) and Co–C_α–H 109.46°. [d] Co^{II} located at the side of the axial cyanide ligand. [e] Co^{II} located at the side of the organic ligand.

It is seen that calculations based on the simple models account qualitatively for the observed shifts. Precise agreement is not expected since some factors of possible importance were not included in the models: shielding of protons from the paramagnetic dipoles by solvent molecules, the cobalt atom, and the cyanide ligands; motions including tumbling of $[Co(en)_3]^{2+}$ and $[Co(CN)_5R]^{3-}$; motions of two ions along the principal axis, *etc.*

In the bipy and phen systems we observed only broadening of the peaks but no shift. Ready ligand exchange between the cyanide and amine ligands lowers the concentration of $[Co(bipy)_3]^{2+}$ or $[Co(phen)_3]^{2+}$ which is essential to produce shifts. Broadening of the peak may be due to the ligand exchange, but attempts to confirm this by observing the temperature dependence of the n.m.r. peaks were not successful because of the instability of the complexes.

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