Hydrogenation by Cyanocobaltate. Part IV.[1] Hydrogenation of Conjugated Dienes by 2,2′-Bipyridinetricyano-, Tricyano(ethylenediamine)-, and Tricyano(1,10-phenanthroline)-cobaltate(II) Complexes

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Hydrogenation of butadiene and isoprene catalysed by aminetricyanocobaltate(II) ions [amine = ethylenediamine (en), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen)] has been studied. The effect of the CN : Co ratio on the selectivity and the optical, e.s.r., and n.m.r. spectra suggests that the active species is $[Co(CN)_3(am)]^-$. Intermediate complexes have been detected by n.m.r. spectroscopy, and a high-field shift by the 'ring current' observed with the bipy and phen complexes indicated that the am ligands co-ordinate to the cobalt atom in the *cis*-configuration with respect to an alkenyl ligand. Pseudo-contact shifts have been observed with the intermediate complexes in the en system, and broadening without shift in the bipy and phen systems. These behaviours are explained in terms of the formation of cyanide-bridged paramagnetic dimeric complexes. Catalytic activity is controlled by the lability of the Co–H bond of hydrido-complexes $[Co(CN)_3(am)H]^-$ rather than the stability of the intermediate complexes.

In an attempt to increase the catalytic activity of pentacyanocobaltate(II) ion to hydrogenation, it has been found that substitution of amine groups for cyanide results in even more active catalysts. Piringer and his co-workers [2] studied the hydrogenation of buta-1,3-diene in the presence of ethylenediamine (en) and similar amines (am). *trans*-But-2-ene was the major product at CN : Co < 5 : 1 (am = en), while but-1-ene formation was predominant at CN : Co = 2 : 1 [am = 2,2′-bipyridine (bipy)]. Dimeric complexes, $[(NC)_4Co(\mu\text{-en})Co(CN)_4]^{4-}$ and $[(NC)_4Co(\mu\text{-en})(\mu\text{-}H_2)Co(CN)_4]^{4-}$, were proposed as the active species for the former reaction, and the presence of monomeric species was presumed for the latter on steric grounds.[2,3] Schwab and Mandre [4] proposed that the complexes $[\{Co(CN)_2(bipy)\}_2]$ and $[\{Co(CN)_2(bipy)\}_2H_2]$ were more highly active than pentacyanocobaltate(II) ion. Substitution by 1,10-phenanthroline (phen) was thought to lead to formation of the co-ordinatively saturated complex $[Co(CN)_2(phen)_2]$ which was inactive. Wymore [5] suggested the complexes $[Co(CN)_3(bipy)]^-$ and $[Co(CN)_3(bipy)H]^-$ as active species. Intermediate species present in these systems were believed to be similar to those in the $[Co(CN)_5]^{3-}$ system, but there was no firm evidence. In connection with studies on the hydrogenation of conjugated dienes by pentacyanocobaltate(II) ion, we now report on hydrogenation by aminetricyanocobaltate(II) ions.

EXPERIMENTAL

Reactions were carried out in the vessel described previously.[6] Water or water–methanol was used as solvent. Optical spectra were recorded on Hitachi EPS-3T and Union RA-1300 spectrophotometers, the latter for rapid scans. E.s.r. spectra were measured on a JES-3BS-X instrument at 77 K in glycerol–methanol. N.m.r. spectra were measured on a Varian HR-220 spectrometer at room temperature in D_2O or D_2O–CD_3OD.

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[1] Part III, T. Funabiki, M. Mohri, and K. Tarama, *J.C.S. Dalton*, 1973, 1813.

[2] A. Farcas, U. Luca, and O. Piringer, *Proc. 11th Internat. Conf. Co-ordination Chem.*, Haifa and Jerusalem, 1968, Elsevier, Amsterdam (1968), p. 29.

[3] O. Piringer and A. Farcas, *Z. phys. Chem.* (*Frankfurt*), 1965, **46**, 190; 1966, **49**, 321.

[4] G. M. Schwab and G. Mandre, *J. Catalysis*, 1968, **12**, 103.

[5] C. E. Wymore, *Chem. Eng. News*, 1968, 52.

[6] T. Funabiki, M. Matsumoto, and K. Tarama, *Bull. Chem. Soc. Japan*, 1972, **45**, 2723.

RESULTS

Hydrogenation of Conjugated Dienes.—Tables 1 and 2 show results of the hydrogenation of butadiene and isoprene in the presence of en, bipy, and phen at various CN : Co ratios. Both phen and bipy were more effective in the formation of terminal olefins at low CN : Co ratios than en. Although the en and bipy solutions were almost homogeneous, solutions of phen were heterogeneous {[Co] = 0·2M in water–methanol (1 : 1)}.* Increase in the alcohol content to dissolve the phen complex resulted in formation of a violet precipitate of, probably, the ion $[\mathrm{Co_2(CN)_{10}}]^{6-}$ at CN : Co = *ca.* 5 : 1. The composition of the products of reaction was dependent on the reaction time, suggesting the formation of rather stable intermediates.[6] The catalytic activity of solutions of various Co : CN : am ratios was investigated by measuring the initial rate of hydrogenation of *trans*-1-phenylbuta-1,3-diene, and the order of activity in water–methanol (1 : 1) was: Co : 3CN : bipy (4·6) > Co : 3CN : phen (3·7) > Co : 3CN : en (1·3) > Co : 5CN (1·2) > Co : 6CN (1·0), where numbers in parentheses indicate relative initial rates. The rate of reaction of the en system became very small after *ca.* 20 min (to *ca.* one tenth the initial rate). This deactivation was not observed in water, where the relative initial rate was 0·4. Increasing am content decreased the catalytic activity. The products formed were similar in the three am systems (Co : CN : am = 1 : 3 : 1), *i.e.* *trans*-Ph·CH:CH·CH$_2$·Me : *trans*-Ph·CH$_2$·CH:CH·Me : *cis*-Ph·CH$_2$·CH:CH·Me = 87 : 10 : 3. This composition, and the ratio of *cis*-Ph·CH$_2$·CH:CH·Me : *trans*-Ph·CH$_2$CH:CH·Me (0·20—0·28 : 1), indicated the presence of both σ- and η-allyl intermediates in solution.[1] The effect of the Co : CN : am ratio on the product composition was not so remarkable, but paralleled that found in the cases of butadiene and isoprene.

TABLE 1

Hydrogenation of butadiene in the presence of amines [a]

				Product/mol % [b]		
am	Co :	CN :	amine	But-1-ene	*trans*-but-2-ene	*cis*-but-2-ene
en	1	5	1—3	39	57	4
	1	4—2	1—3	12	85	3
bipy	1	5	1·1	38	42	20
	1	4	1·1	16	80	4
	1	3	1·1	42	54	4
	1	2	2	74	24	2
phen	1	5	1·1	36	45	19
	1	4	1·1	14	80	6
	1	3	1·1	16	78	6
	1	3	1·1	45	50	5 [c]

[a] [Co] = 0·2M, in water–methanol (1 : 1) at 20 °C. [b] Composition after 2 h. [c] Water–methanol (2 : 3).

TABLE 2

Hydrogenation of isoprene in the presence of amines [a]

				Product/mol % [b]		
am	Co :	CN :	amine	3-Methylbut-1-ene	2-Methylbut-1-ene	2-Methylbut-2-ene
	1	6	0	14	59	27 [c]
	1	4	0	2	5	93 [c]
en	1	5	1	2	74	24
	1	4	1	3	35	62
	1	3	1	5	34	61
	1	2	2	7	55	38
bipy	1	4	1	2	66	32
	1	3	1	4	83	13
phen	1	4	1	3	73	24
	1	3	1	4	83	13

[a] [Co] = 0·2M, in water–methanol (1 : 1), at 20 °C, and isoprene : Co = 2 : 1. Isoprene was added after preliminary dihydrogen absorption. [b] Composition after 1 h. [c] In water.

Optical and E.S.R. Spectra.—Wymore noted that the characteristic band of the ion $[\mathrm{Co(CN)_5}]^{3-}$ at 968 nm shifted to 1 000 nm at CN : Co = 3 : 1 in the presence of bipy.[5] Similar shifts were observed with en to 1 050 nm and with phen to 1 160 nm. The peak at 650 nm, previously believed to correspond to the complex $[\mathrm{Co(CN)_2(bipy)_2}]$, was also observed at low CN : Co ratios with the three amines. In the u.v. region, Piringer and his co-workers [7] noted a new band at 258 nm in addition to the band of $[\mathrm{Co(CN)_5}]^{3-}$ at 278 nm in the presence of en. Figure 1 shows spectra recorded in the present study on the rapid-scan spectrophotometer. It clearly demonstrates that $[\mathrm{Co(CN)_5}]^{3-}$ is initially formed and that cyanide ligands in the ion are exchanged with en to give $[\mathrm{Co(CN)_3(en)}]^{-}$. The equilibrium concentrations of the two complexes were dependent on the concentrations of cyanide ion and en. Both u.v. peaks diminished in an atmosphere of dihydrogen. In the cases of bipy and phen, the amines showed strong bands in this region obstructing observation of spectral changes. Figure 2 shows the effect of the CN : Co ratio on spectra of the bipy system. A similar effect was also observed in the phen system, but was very small.

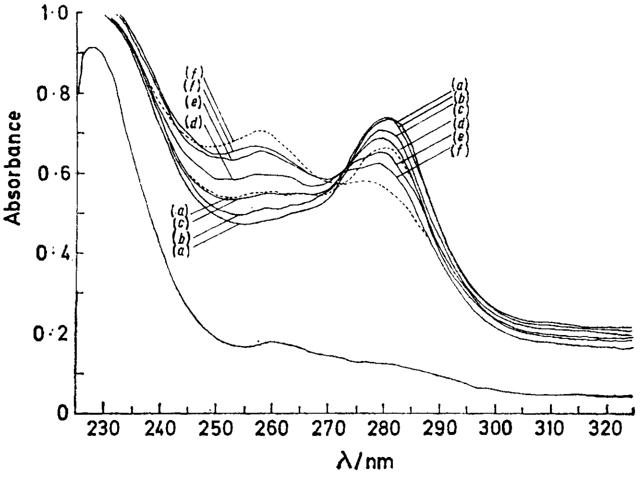

FIGURE 1 Rapid-scan u.v. spectra of cyanocobaltate(II) solution in the presence of en in a 2 mm cell, [Co] = 1·25 × 10^{-3}M, at 20 °C and 1 ms scan speed: (——), Co : CN : en = 1 : 3 : 1; (— — —), Co : CN : en = 1 : 3 : 2; (*a*), 1; (*b*) 3; (*c*), 5; (*d*), 10; (*e*), 20; and (*f*), 40 ms after mixing

Figure 3 shows e.s.r. spectra of glycerol–methanol solutions in the presence of excess of en at various CN : Co ratios. The spectrum at CN : Co = 5 : 1 coincided with that of pentacyanocobaltate(II).[8] At CN : Co < 5 : 1, an additional band appeared at *g* = *ca.* 2·28, suggesting formation of a new complex. In the absence of en the spectra

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* 1M = 1 mol dm^{-3}.

[7] R. Ripan, A. Farcas, and O. Piringer, *Z. anorg. Chem.*, 1966, **346**, 211.

[8] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 2256; J. P. Maher, *J. Chem. Soc.* (*A*), 1968, 2818; M. E. Kimball, D. W. Pratt, and W. C. Kaska, *Inorg. Chem.*, 1968, **7**, 2006; Fun-Dow Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 3760; M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 2069.

were independent of the CN : Co ratio, except for the intensity.

N.M.R. Spectra.—As demonstrated previously,[9] n.m.r. spectra of the reaction solution offered direct information on the formation and structure of the intermediate complexes.

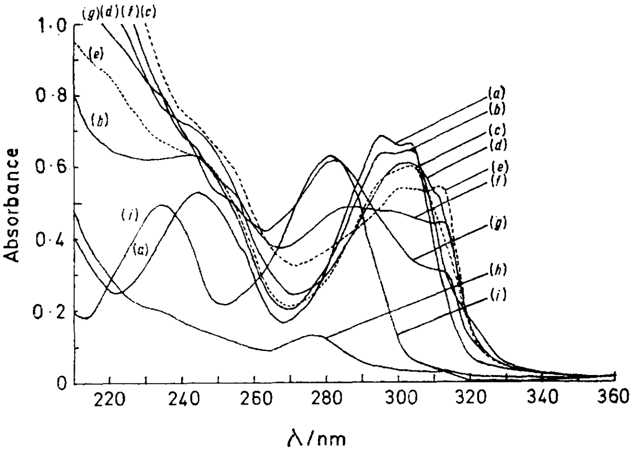

FIGURE 2 U.v. spectra of cyanocobaltate(II) solution in the presence of bipy in a 10 mm cell, $[\mathrm{Co}] = 5 \times 10^{-5}$M in water–methanol. Co : CN : bipy = 1 : 0 : 1 (*a*), 1 : 1 : 1 (*b*), 1 : 2 : 1 (*c*), 1 : 3 : 1 (*d*), 1 : 4 : 1 (*e*), 1 : 5 : 1 (*f*), 1 : 6 : 1 (*g*), 1 : 5 : 0 (*h*), and 0 : 0 : 1 (*i*)

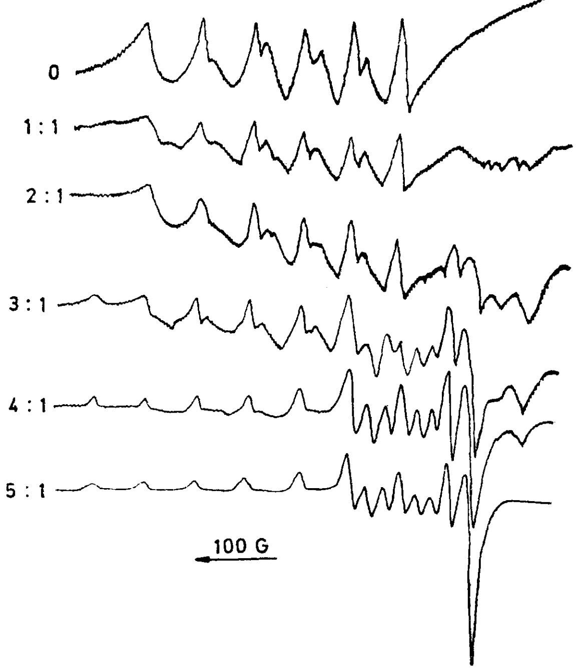

FIGURE 3 E.s.r. spectra of cyanocobaltate(II) solution in the presence of en

Figure 4 shows spectra of the en system (en : Co ≃ 2 : 1) in the hydrogenation of butadiene. At CN : Co = 4 : 1, the spectrum indicated formation of $[\{1\text{—}3\text{-}\eta\text{-}syn\text{-}(1\text{-methylallyl})\}\mathrm{Co(CN)_4}]^{2-}$ but not of a σ-but-2-enyl complex. At CN : Co = 3·5 : 1, a small peak, assigned to the ion $[\mathrm{(MeCH{:}CH{\cdot}CH_2)Co(CN)_3(en)}]^-$, was observed and its relative intensity increased at CN : Co = 3 : 1. Methyl protons of the *cis*- and *trans*-isomers of the σ-complex could be distinguished. Assignment of the methylene protons was not definite on account of overlap with the en protons. It is noteworthy that the solution at low CN : Co ratio contained paramagnetic species and the peaks of the η-methylallyl complex shifted to high magnetic field depending on the amount of paramagnetic species present, while those of the σ-complex hardly shifted. The shift was diminished on passage of air through the solution. Some shift data are

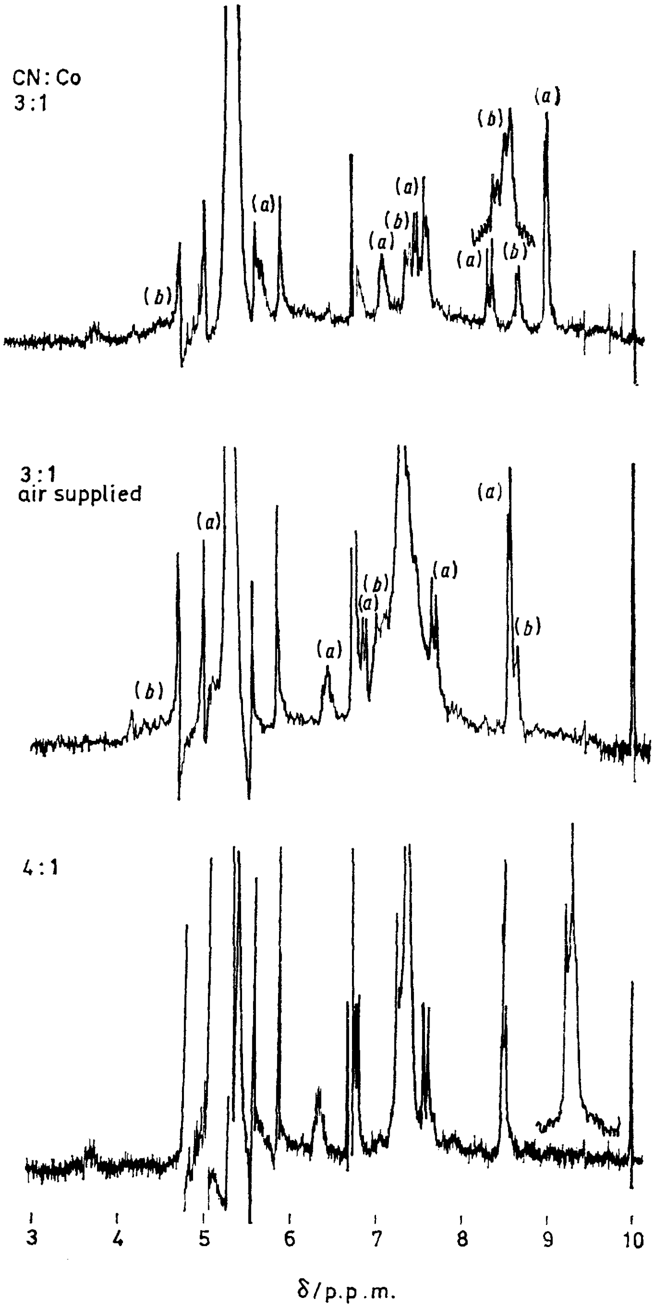

FIGURE 4 N.m.r. spectra of reaction solutions in the hydrogenation of butadiene in the presence of en in D_2O–CD_3OD, at 220 MHz and room temperature: (*a*), $[(\eta\text{-1-methylallyl})\mathrm{Co(CN)_4}]^{2-}$; (*b*), [(*trans*- and *cis*-MeCH:CH·CH)$\mathrm{Co(CN)_3(en)}$]$^-$

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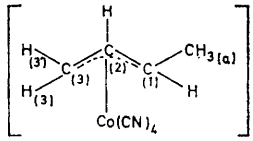
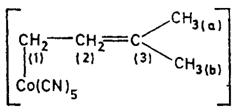
[9] T. Funabiki and K. Tarama, *Chem. Comm.*, 1971, 1177.

TABLE 3

Shifts (Hz) in peaks of the complexes to high field of spectra in the absence of paramagnetic species

Complex	H_1	H_2	H_3	H_3'	H_a
	170	164	162	158	100
	114	*	113	114	69
	52	*	44	50	23
	34	*	20	29	7
	25	*	12	21	1
	H_1	H_2	H_a	H_b	
	124	*	25	37	
	35	26	3	7	
	23	19	3	3	
	17	17	2	2	

* Overlap with solvent protons.

given in Table 3. Shifts of the protons on the η-allyl carbon atoms were similar and greater than that of the methyl proton. In contrast to the systems with bipy and phen and without amines, the peak of the methyl proton of the η-methylallyl complex was not a symmetric doublet.

In the hydrogenation of isoprene in the presence of en, peaks of the two σ-3-methylbut-2-enyl complexes were observed at CN : Co < 5 : 1 (Figure 5). One of the complexes was $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_5]^{3-}$, which was observed at CN : Co > 5 : 1,[6] and peaks of an η-allyl complex were not observed. The other complex was assigned to $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_3(en)]^-$. The formation of this complex was remarkable in comparison with that of $[(MeCH{:}CH{\cdot}CH_2)Co(CN)_3(en)]^-$ in the hydrogenation of butadiene as shown by the absence of $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_5]^{3-}$ at CN : Co = 3 : 1. Peaks of the latter complex shifted

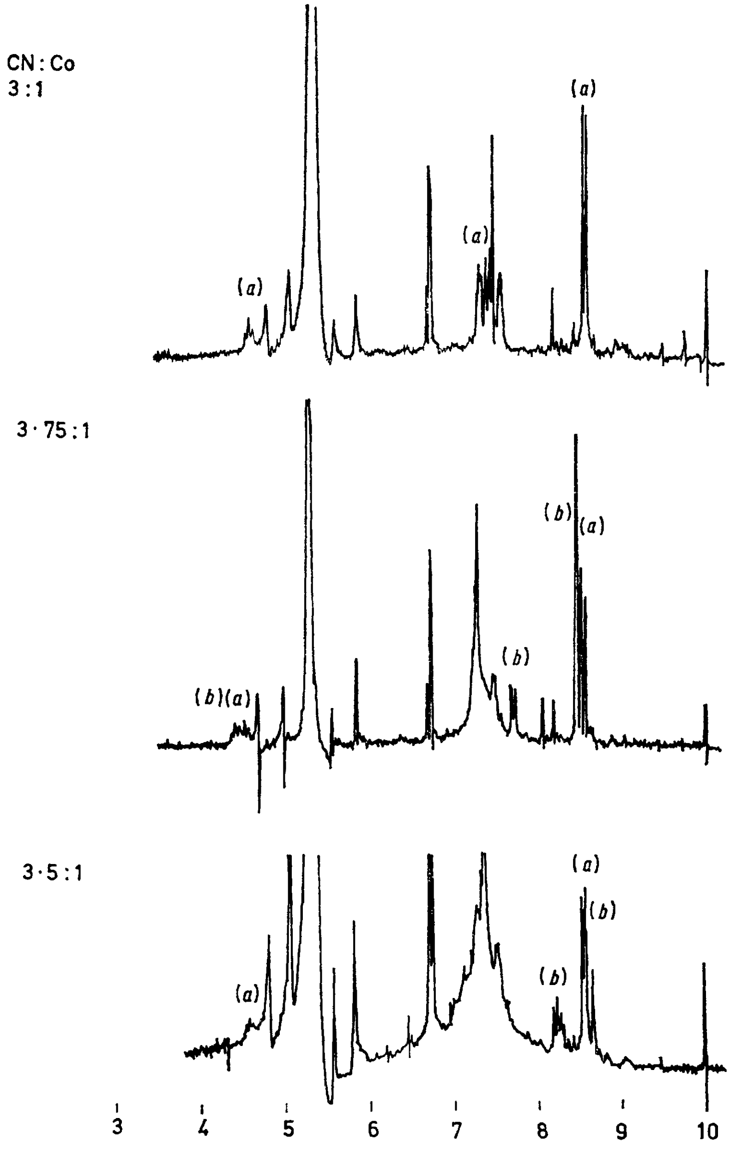


FIGURE 5 N.m.r. spectra of reaction solutions in the hydrogenation of isoprene in the presence of en in D_2O–CD_3OD, at 220 MHz and room temperature: (*a*), $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_3(en)]^-$; (*b*), $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_5]^{3-}$. The spectrum at CN : Co = 3·5 : 1 is that after 1 h. The initial spectrum was similar to that at CN : Co = 3·75 : 1

characteristically to high field in the presence of the paramagnetic species, while those of $[(\mathrm{Me_2C{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(en)}]^-$ hardly shifted. The shift of the methylene protons was much greater than that of the methyl and was similar to that of the olefinic proton at least when the shift was small.

When bipy replaced en (bipy : Co = 1·1 : 1), the complex decreasing CN : Co. In contrast to the en system, the shift of the peaks of the η-methylallyl complex, which depends on the presence of paramagnetic species, was not observed. Alternatively the peaks of both complexes became broad at low CN : Co ratios. Peaks of co-ordinated and unco-ordinated bipy were observed at lower CN : Co ratios.

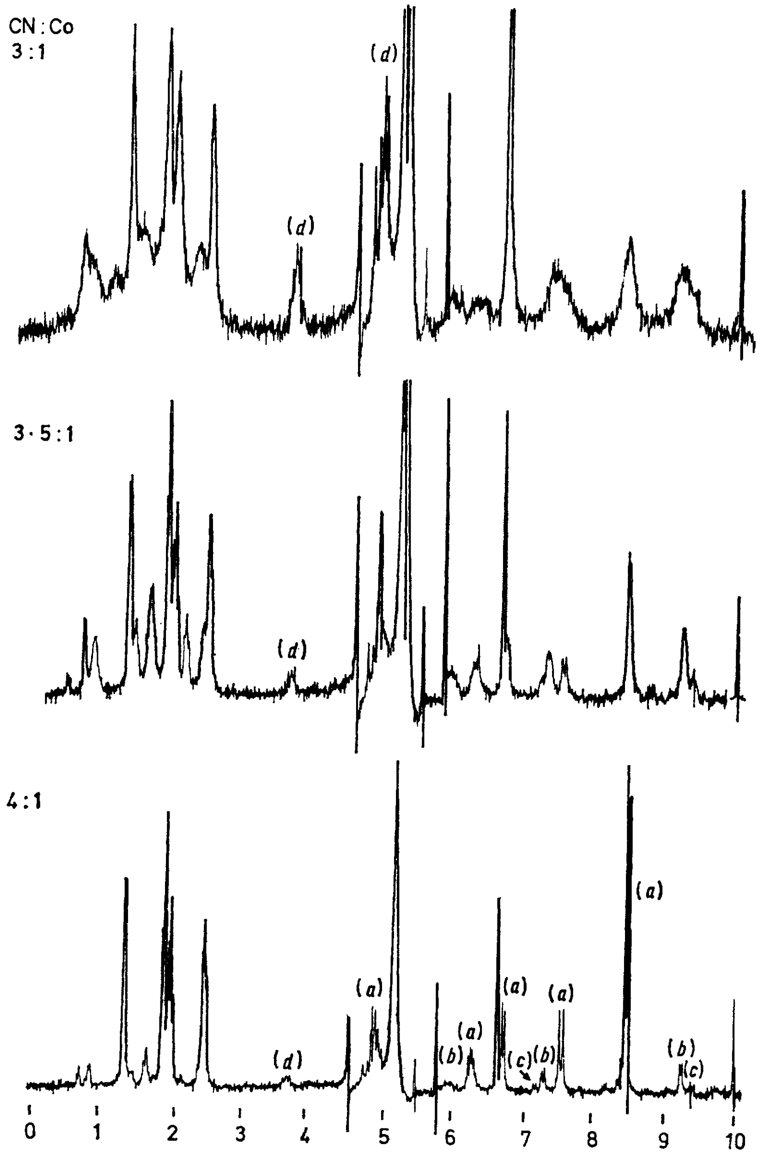


FIGURE 6 N.m.r. spectra of reaction solutions in the hydrogenation of butadiene in the presence of bipy in D_2O–CD_3OD, at 220 MHz and at room temperature: (*a*), $[(\eta\text{-1-methylallyl})\mathrm{Co(CN)_4}]^{2-}$; (*b*), $[(\textit{trans}\text{-}\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^-$; (*c*), $[(\textit{cis}\text{-}\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^-$; (*d*), butadiene

$[(\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^-$ was observed, even at CN : Co = 4·5 : 1, in the hydrogenation of butadiene. As shown in Figure 6, the peaks of the methyl and olefinic protons of the σ-complex shifted greatly to high field, and that of the methylene protons to low field, in comparison with those of $[(\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_5}]^{3-}$. The relative intensity of the peaks of $[(\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^-$ to those of $[(\eta\text{-1-methylallyl})\mathrm{Co(CN)_4}]^{2-}$ increased with Similar effects were observed in the hydrogenation of isoprene over the two σ-$\mathrm{Me_2C{:}CH{\cdot}CH_2}$ complexes of $[\mathrm{Co(CN)_5}]^{3-}$ and $[\mathrm{Co(CN)_3(bipy)}]^-$ (Figure 7). In addition, small peaks of $[(\mathrm{MeCH{:}CMe{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^-$ were detected.

In the presence of phen (phen : Co = 1·1 : 1), the results were similar to those of the bipy system, but the shift with co-ordinated phen was much greater than that with bipy. The solution after hydrogenation of butadiene at CN : Co =

4 : 1 in D_2O–CD_3OD (1 : 1) was heterogeneous, and complexes in the filtered solution were $[(\eta\text{-1-methylallyl})\mathrm{Co(CN)_4}]^{2-}$ and $[(\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_5}]^{3-}$. Additional CD_3OD increased the homogeneity of the product solution and the complex $[(\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(phen)}]^{-}$ was formed in place of $[(\mathrm{MeCH{:}CH{\cdot}CH_2})\mathrm{Co(CN)_5}]^{3-}$. This is consistent with the result in Table 1, and must be due to low solubility of phen and its complex in D_2O–CD_3OD (1 : 1), forming precipitates of, probably, $[\mathrm{Co(CN)_2(phen)_2}]$.

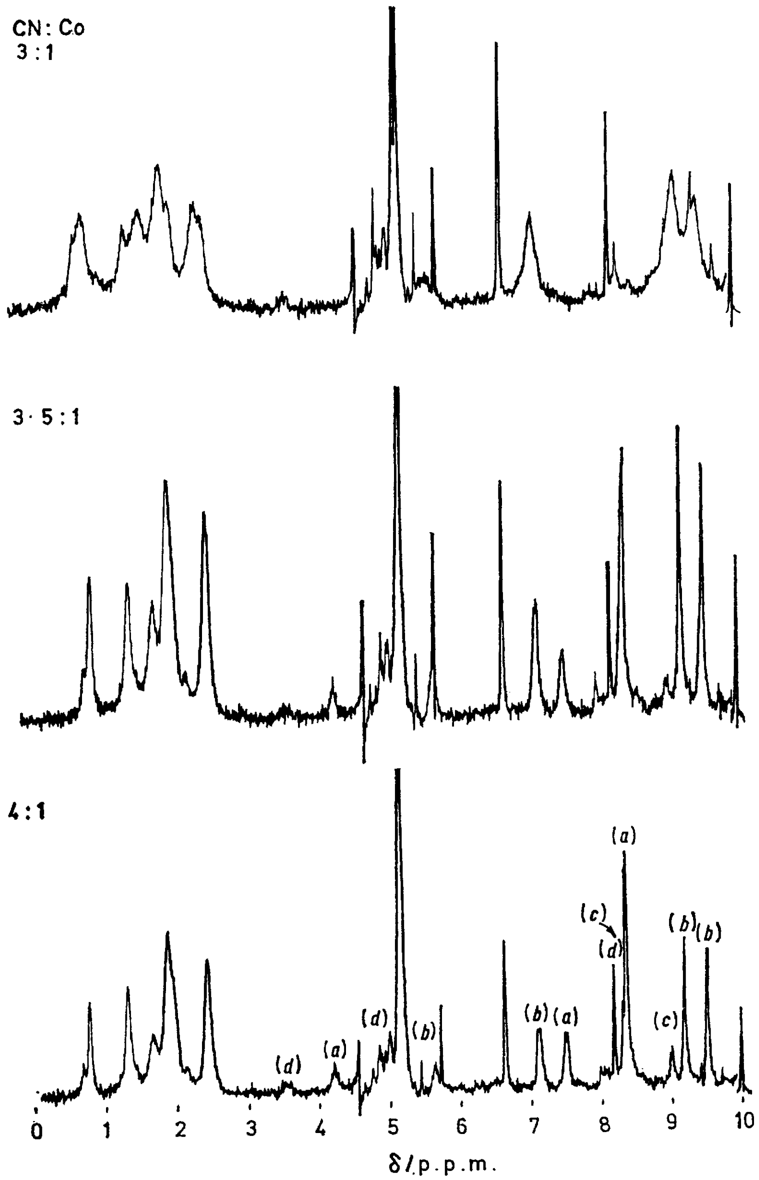


FIGURE 7 N.m.r. spectra of reaction solutions in the hydrogenation of isoprene in the presence of bipy in D_2O–CD_3OD, at 220 MHz and at room temperature: (*a*), $[(\mathrm{Me_2C{:}CH{\cdot}CH_2})\mathrm{Co(CN)_5}]^{3-}$; (*b*) $[(\mathrm{Me_2C{:}CH{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^{-}$; (*c*) $[(\mathrm{MeCH{:}CMe{\cdot}CH_2})\mathrm{Co(CN)_3(bipy)}]^{-}$; (*d*), isoprene

Chemical-shift data are summarised in Table 4.

DISCUSSION

Substitution of amines for cyanide groups in pentacyanocobaltate(II) ion is represented by equation (1), where am = en, bipy, and phen. The formation of complexes $[\mathrm{Co(CN)_2(am)_2}]$ was suggested by growth of the

$$[\mathrm{Co(CN)_5}]^{3-} + n(\mathrm{am}) \rightleftharpoons [\mathrm{Co(CN)}_m(\mathrm{am})_n]^{2-m} + 2n\mathrm{CN}^- \quad (1)$$

650 nm band at low CN : Co ratios, that of $[\mathrm{Co(am)_3}]^{2+}$ being indicated by the optical (Figure 2) and isotropic e.s.r. spectra (Figure 3). The complex $[\mathrm{Co(CN)_4(am)}]^{2-}$ is similar to $[(\eta\text{-allyl})\mathrm{Co(CN)_4}]^{2-}$, but may be much less stable; $[\mathrm{Co(CN)_2(am)}]$ is four-co-ordinate and similar to $[\mathrm{Co(CN)_2(MeCN)_2}]$ (ref. 10), but no evidence suggesting the formation of this complex has been obtained. These four- and six-co-ordinate complexes are probably inactive in the catalytic reaction. The complex $[\mathrm{Co(CN)(am)_2}]^{+}$ is analogous to cobaloximes and vitamin B_{12r}, but

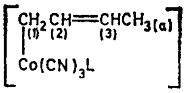
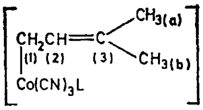
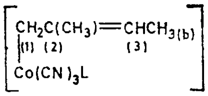
[10] D. A. White, A. J. Solodar, and M. M. Baizer, *Inorg. Chem.*, 1972, **11**, 2160.

must be much less stable as the two am ligands are not bonded to each other. As amines were observed to have an effect on the selectivity and formation of the σ-complexes with mixed ligands at CN : Co ratios between 3 and 5 : 1, $[Co(CN)(am)_2]^+$ is a less-probable active species. The most-probable active complex $[Co(CN)_3(am)]^-$ has a similar structure to $[Co(CN)_5]^{3-}$. E.s.r. spectra in Figure 3 showed the formation of a new complex at CN : Co < 5 : 1. The *g* value of the complex was similar to that of the cyano(methyl cyano) complex observed at CN : Co = 3 : 1 in methyl cyanide ($g_\perp$ *ca.* 2·28, $g_\parallel$ 2·00).[10] Although White *et al.* proposed the formation of the tetrahedral complex $[Co(CN)_3(MeCN)]^-$, based on the optical spectra, a square-pyramidal complex, $[Co(CN)_3(am)]^-$, seems to be more probable with bidentate ligands. As the band at 258 nm in the en system was very small at CN : Co = 4 : 1, $[(NC)_4Co(\mu\text{-en})Co(CN)_4]^{4-}$ is less probable as a stable complex in solution.

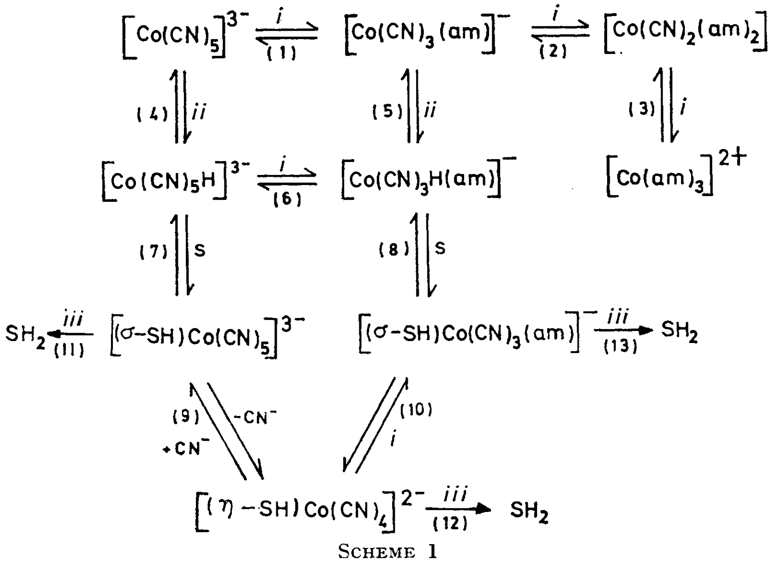
Thus, the results of the hydrogenations of conjugated dienes are reasonably explained by Scheme 1. The ligand-exchange reactions (1)—(3) were shown to occur by the optical and e.s.r. spectra (Figures 1—3). As the solutions contained two active species, the rate and amount of hydrogen absorption by $[Co(CN)_3(am)]^-$ was not determined, but $[Co(CN)_3H(am)]^-$ is probably less stable than $[Co(CN)_5H]^{3-}$ as indicated by the decreasing amount of hydrogen absorption with the CN : Co ratio.

TABLE 4

Chemical shifts (δ/p.p.m.) and coupling constants (Hz) of various cyanocobaltate(II) complexes *

		Chemical shift					Coupling constant		
Complex	L	H_1	H_2	H_3	H_a	H_b	$J(H_1-H_2)$	$J(H_3-H_a)$	$J(H_3-H_b)$
	$(CN)_2$	7·62 (t) 7·56 (c)	4·06	4·55	8·40 (t) 8·36 (c)		8·6 9·4	6·5 7·0	
	en	7·31 (t)	4·12	4·44	8·63 (t) 8·57 (c)		6 6		
	bipy	7·29 (t) 7·17 (c)		5·94	9·24 (t) 9·41 (c)		6·0	8·4	
	phen	7·29		6·53	9·76		6	8	
	$(CN)_2$	7·65	4·36		8·45	8·45	9·5		
	en	7·43	4·61		8·59	8·55	9·5		
	bipy	7·15	5·65		9·20	9·52	9·0		
	phen	7·15	5·80		9·71	10·14			
	bipy		8·30			9·00			7
	phen		8·10			9·03			

* Observed in D_2O–CD_3OD at room temperature; t and c denote *trans* and *cis*.



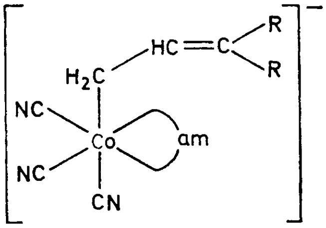
SCHEME 1

am = en, bipy, or phen; S = Conjugated diene; (*i*), $-CN^-$ + amine; (*ii*), H_2; (*iii*), $[Co(CN)_5H]^{3-}$ or $[Co(CN)_3(am)H]^-$

At CN : Co > 5 : 1, reactions (4), (7), and (11) are predominant irrespective of the presence of amine, and products are formed from a σ-SH complex. At CN : Co < 5 : 1, reaction (9) occurs and products are formed from a η-SH complex in the absence of amine. But in the presence of amine a σ-SH complex is formed even at CN : Co < 5 : 1 by reactions (8) and (10), and products are formed from the σ-SH and η-SH complexes. Thus, the selectivity of reaction depends on equilibrium

(10). Selective formation of *trans*-but-2-ene in the en system in the hydrogenation of butadiene indicates that the complex $[(\sigma\text{-SH})Co(CN)_3(en)]^-$ is much less stable than $[(\eta\text{-SH})Co(CN)_4]^{2-}$. In the bipy and phen systems, formation of but-1-ene at low CN : Co ratios indicates that the stability of the σ-SH complexes is comparable with that of the η-SH complexes. This was confirmed by the n.m.r. studies.

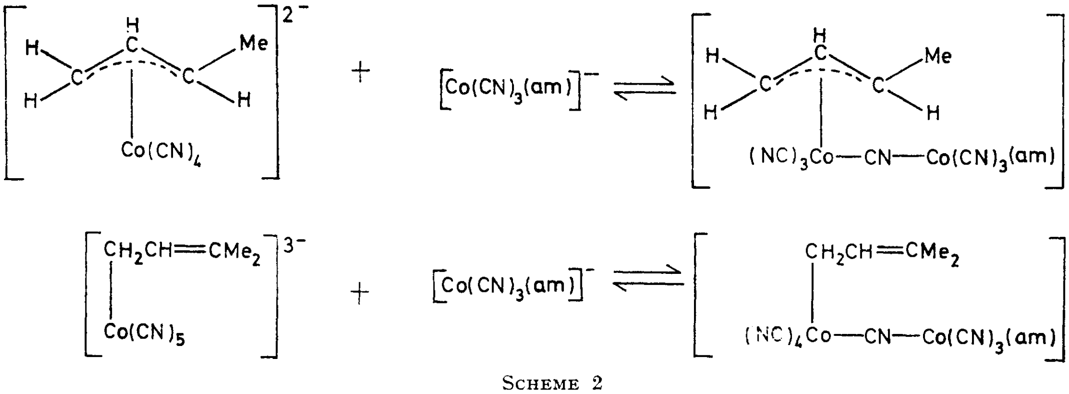
In the n.m.r. spectra of the intermediate complexes, the high-field shift of the methyl and olefinic protons of $[(\sigma\text{-SH})Co(CN)_3(bipy)]^-$ and $[(\sigma\text{-SH})Co(CN)_3(phen)]^-$ is ascribed to the 'ring current' because it is not observed with $[(\sigma\text{-SH})Co(CN)_3(en)]^-$, and suggests the structure (A) in which the amine co-ordinates to cobalt in the *cis*-configuration with respect to the alkenyl ligand. The *cis*-methyl proton signal appears at lower field than the *trans* in the complexes $[(\sigma\text{-SH})Co(CN)_5]^{3-}$ and $[(\sigma\text{-SH})Co(CN)_3(en)]^-$, but shifts to higher field under the influence of the 'ring current'. The methylene protons are not affected by the 'ring current,' and the shift to low field in $[(\sigma\text{-SH})Co(CN)_3(am)]^-$ in comparison with $[(\sigma\text{-SH})Co(CN)_5]^{3-}$ may be ascribed to the decrease in net charge density on substitution of a neutral am ligand for anionic cyanides.



(A) R=H or Me

Formation of the complex $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_5]^{3-}$ at CN : Co < 5 : 1 in the hydrogenation of isoprene is due to its poor reactivity and to the instability of the η-SH complexes for steric reasons.[6] The above system results in formation of the complex $[(\sigma\text{-SH})Co(CN)_3(am)]^-$, whereas hydrogenation of butadiene yields stable $[(\eta\text{-}1\text{-methylallyl})Co(CN)_4]^{2-}$; $[(MeCH{:}CMe{\cdot}CH_2)Co(CN)_3(am)]^-$ was detected when am = bipy or phen. The latter type of complex was proposed as an intermediate in formation of 2-methylbut-1-ene,[6] but the pentacyanocobaltate(II) analogue was not detected. These results may suggest that the aminetricyano-complexes are not less stable than the pentacyano-complexes. The relative proportion of the former to the latter indicates that stability of the former increases in the order am = en < bipy < phen.

The high-field shift of the peaks of the complexes $[(\eta\text{-}1\text{-methylallyl})Co(CN)_4]^{2-}$ and $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_5]^{3-}$ in the en system is well explained by the pseudo-contact shift, and suggests the presence of paramagnetic intermediates. As seen in Table 3, the relative shift of the methyl protons to that of methylene in the complex $[(Me_2C{:}CH{\cdot}CH_2)Co(CN)_5]^{3-}$ is very small in comparison with the relative shift of the methyl to η-allyl protons in $[(\eta\text{-}1\text{-methylallyl})Co(CN)_4]^{2-}$. This indicates that structures and configurations of these two complexes are retained in the paramagnetic intermediates. As the two complexes are diamagnetic, an electron is transferred from paramagnetic species to them. The most probable mechanism is that involving inner-sphere electron transfer from Co^{II} species, such as $[Co(CN)_3(en)]^-$, through a bridging cyanide ligand (Scheme 2). Although in the case of en shifts were observed and peaks were sharp, in the cases of bipy and phen shifts were hardly observed and peaks became broad. Shift and/or broadening are dependent on relaxation times of the electron spins and delocalisation of spin density in the ligand π-electron system. In the present case, only en is without an extended π-electron system, and this may contribute to the remarkably different results of the en systems from those of bipy and phen. Thus, the two typical results may be explained by Scheme 2, in which the paramagnetic intermediates are cyanide-bridged dimeric complexes. Monomeric Co^{II} species such as $[(\eta\text{-}1\text{-methylallyl})Co(CN)_4]^{3-}$ are common to the three amine systems and are less-probable intermediates. This is supported by the fact that formation of a monomeric Co^{II} species from a cyanide-bridged species is a slow step in the analogous electron-transfer reaction.[11]



SCHEME 2

Little shift of the ^{1}H n.m.r. lines of the complex $[(\sigma\text{-SH})Co(CN)_3(en)]^-$ indicates that bridged species are hardly formed in the en system. This is reasonable be-

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[11] J. P. Birk and J. Halpern, *J. Amer. Chem. Soc.*, 1968, **90**, 305.

cause absence of back donation of electrons from cobalt to en increases the electron density on the cobalt atom and the cyanide ligands. In the cases of bipy and phen, peaks of the σ-complexes became broad, suggesting formation of bridged species. Recently, a mechanism was proposed involving nucleophilic attack of a cobalt(II) species on a carbon atom attached to cobalt(III) in a system of cobalt(III)–Schiff-base complexes,[12] but the mechanism seems not to be applicable here.

Discussion of the relative activity of the amine tricyanocobaltate(II) complexes is complicated, because the solutions contained more than one active complex, and the complexes showed poor solubility as observed in the phen system. However, the bipy and phen systems were more active than pentacyanocobaltate(II). As shown in the n.m.r. studies, this enhancement of activity cannot be ascribed to stability of the intermediate complexes, but rather to lability of the Co–H bond in the hydrido-complexes. Provided the Co–H bond is labilised by weaker π-acceptors,[5] the catalytic activity of $[Co(CN)_3L]$ complexes increases in the order $L = (CN)_2 <$ phen $<$ bipy $<$ en. The results of the present study were consistent with this order, except for en. This may have been due to too low concentrations of the unstable complex $[Co(CN)_3(en)H]^-$. The asymmetric doublet of the methyl protons of the complex $[(\eta$-1-methylallyl)Co$(CN)_4]^{2-}$ in the en system in D_2O–CD_3OD is explained by overlap with the singlet methyl proton signal, indicating deuteriation of the proton and the Me group on the C_1 atom. This is probable when H–D exchange between Co–H and D_2O or CD_3OD is very rapid. This has been demonstrated previously,[13] and suggests a labile Co–H bond. A symmetric doublet was observed in the present study when the complex was prepared in water–methanol.

[4/262 *Received*, 11*th February*, 1974]

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[12] A. Van Den Bergen and B. O. West, *J. Organometallic Chem.*, 1974, **64**, 125.

[13] O. Piringer and A. Farcas, *Nature*, 1965, **206**, 1040.