Formation and Isomerisation of Olefin π-Complexes of Cyanocobaltate(I) with Diethyl Maleate and Fumarate

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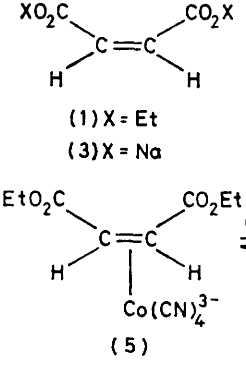
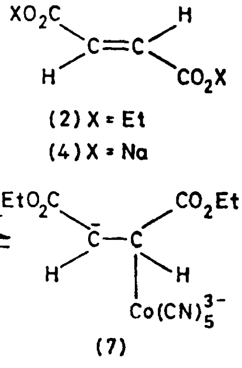
Summary ^{13}C and ^{1}H n.m.r. evidence has been obtained for the formation of olefin π-complexes of $[Co(CN)_4]^{3-}$ with diethyl maleate (**1**) and fumarate (**2**) and disodium maleate (**3**) and fumarate (**4**); the complex of (**1**) isomerises to that of (**2**) probably *via* a σ-complex of the carbanion (**7**).

OLEFIN π-complexes of many kinds of transition metals are known, but little has been reported on cobalt complexes, despite the fact that in the chemistry of vitamin B_{12} and related complexes olefin π-complexes have been proposed as important intermediates.[1] Schrauzer *et al.*[2] have reported the formation of rather stable cobaloxime(I)–olefin π-complexes and their rearrangement to σ-complexes. Silverman and Dolphin[3] have proposed the intermediate formation of unstable and undetectable cobaloxime(III)- and cobalamin(III)–olefin π-complexes and their rearrangement to σ-complexes. Previously,[4] we described the intermediate formation of cyanocobaltate(I)–*cis*- and -*trans*-cinnamonitrile π-complexes in the cyanation of bromostyrenes by $[Co(CN)_5]^{3-}$ in alkaline solution. I report here clear n.m.r. evidence for the direct formation of π-complexes with maleates and fumarates on addition of these substrates to alkaline solutions of cyanocobaltate at CN : Co < 5 : 1. Jackman *et al.*[5] have reported that maleate anion isomerises at CN : Co = 6 : 1 to fumarate anion *via* a half-hydrogenated σ-complex which may be detected by n.m.r. spectroscopy. I also report here that the π-complex of (**1**) isomerises to that of (**2**) without formation of a half-hydrogenated σ-complex.



(**1**) X = Et
(**3**) X = Na



(**2**) X = Et
(**4**) X = Na

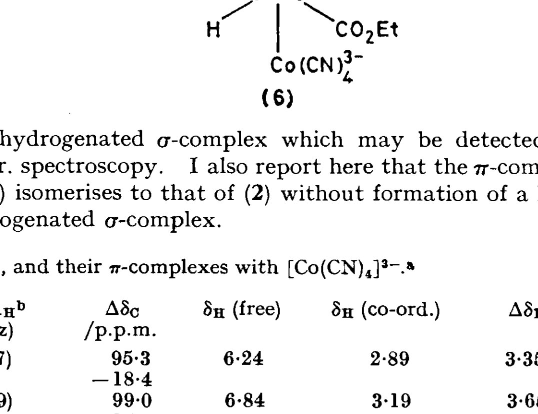


TABLE. ^{13}C and ^{1}H n.m.r. data for maleates, fumarates, and their π-complexes with $[Co(CN)_4]^{3-}$.[a]

Olefin		δ_C (free) /p.p.m.	($^{1}J_{C-H}$[b] /Hz)	δ_C(co-ord.) /p.p.m.	($^{1}J_{C-H}$[b] /Hz)	$\Delta\delta_C$ /p.p.m.	δ_H (free)	δ_H (co-ord.)	$\Delta\delta_H$
(1)	–CH=	129·8	(166)	34·5	(157)	95·3	6·24	2·89	3·35
	–CO_2–	165·2		183·6		−18·4			
(2)	–CH=	133·7	(169)	34·7	(159)	99·0	6·84	3·19	3·65
	–CO_2–	164·9		179·9		−15·0			
(3)	–CH=	131·3	(160)	41·5	(152)	81·8	6·00	3·06	2·94
	–CO_2–	176·2		—[c]					
(4)	–CH=	136·1	(162)	42·5	(153)	93·6	6·50	3·08	2·42
	–CO_2–	175·5		—[c]					

[a] Measured on JEOL FX-100 and Varian HR-220 spectrometers. [b] Doublet. [c] Not observed.

D_2O (1·2 cm^3) was added under a hydrogen atmosphere at 30 °C to a mixture of $CoCl_2$, KCN, and KOH ([Co] = 0·4 mol dm^{-3}, CN:Co:OH = 4·5:1:2). The mixture was stirred for 20 min; addition of (**1**) or (**2**) (0·4 mol dm^{-3}) then caused an immediate colour change from pale yellow to dark red. As shown in the Table, large up-field shifts of the olefinic carbon and proton resonances and downfield shifts of the carboxy carbon resonances were observed in the ^{13}C and ^{1}H n.m.r. spectra. These shifts and J_{C-H} values are characteristic of olefin π-complexes of transition metals.[6] The formation of $[Co(CN)_5]^{4-}$ from $[Co(CN)_5H]^{3-}$ in alkaline solution,[7] and the dissociation of the CN ligand to form $[Co(CN)_4]^{3-}$,[8] have been reported. Although the ^{13}CN peaks are too small and indistinct for one to be able to distinguish, at the moment, whether the Co^{I} species for the π-complex formation is $[Co(CN)_5]^{4-}$ or $[Co(CN)_4]^{3-}$, I prefer the latter on the basis of the 18-electron rule and because π-complexes are formed at CN:Co$<$5:1; accordingly, I propose structures (**5**) and (**6**) for these complexes.

Compounds (**1**) and (**2**) are hydrolysed in alkaline solution, and their unco-ordinated anions were observed by n.m.r. spectroscopy. When the disodium salt (**3**) or (**4**) was added in place of (**1**) or (**2**), however, yellow solutions were obtained, and the n.m.r. spectra indicated that π-complexes were formed with these olefins (Table). A large portion of (**3**) or (**4**) remained free, which indicated that these π-complexes are less stable than those of (**1**) and (**2**), a reflection of the fact that olefin π-complexes are stabilised by electron-accepting substituents. The hydrolysis of (**1**) and (**2**) occurred only in an initial stage (probably before co-ordination) and co-ordinated (**1**) and (**2**) were hardly hydrolysed at all. This must be because electron transfer from Co^{I} to olefins makes the olefins electron-rich enough to inhibit the hydrolysis.

It is interesting to note that deuterium was not incorporated in these π-complexes, and that the peak of (**5**) at δ 2·89 shifted to δ 3·19 without decrease in the intensity. This indicates that (**5**) isomerises to (**6**) without incorporation of deuterium, *i.e.*, not *via* a half-hydrogenated σ-complex. This isomerisation was slow at 30 °C but more rapid at elevated temperatures, and was faster at CN:Co = 4·95 than at 4·5. I propose that the isomerisation proceeds *via* a σ-complex such as (**7**), in which an electron may be delocalised over the carboxy-group. An analogous carbanion intermediate has been proposed in the formation of σ-styrylcobaloxime(III) from halogenostyrenes and cobaloxime(I).[9] This is a new type of isomerisation of an olefin π-complex and suggests that similar processes may occur in the reactions of cobalamins and cobaloximes.

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