JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 16
1986

Preparation and Properties of Inclusion Compounds of Transition Metal Complexes of Cyclo-octa-1,5-diene and Norbornadiene with Cyclodextrins

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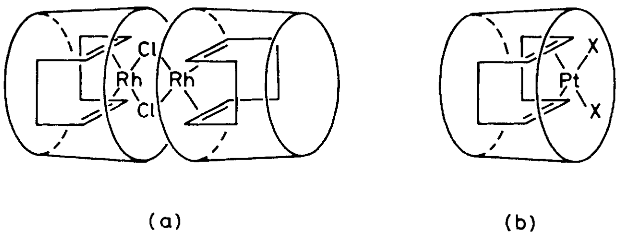
2 : 1 (cyclodextrin : guest) inclusion compounds were obtained in high yields by the treatment of β-cyclodextrin (β-CD) with $[(L)RhCl]_2$ (L = norbornadiene or cyclo-octa-1,5-diene, cod) and 1 : 1 inclusion compounds were obtained by the reaction of β-CD with $(cod)PtX_2$ (X = Cl, Br, or I) in high yields, while γ-CD formed 1 : 1 inclusion compounds with $(cod)PtX_2$ (X = Br or I); the formation of inclusion compounds is selective.

Recently inclusion compounds of transition metal complexes with crown ethers[1] and cryptands[2] have attracted much attention because of their unique structures and properties. However, there are few reports on the preparation of inclusion compounds of transition metal complexes with their natural counterparts, cyclodextrins (CD),† although they form inclusion compounds with a wide variety of compounds, ranging from purely nonpolar molecules to small ions. We previously reported the preparation and properties of inclusion compounds of ferrocene and its analogues with cyclodextrins as an example of cyclodextrin inclusion compounds of organometallic complexes.[3] These observations prompted us to examine the interaction of CD with alkene–metal complexes which are used as catalysts in a variety of organic syntheses. Now we have found that β- and γ-cyclodextrin form inclusion compounds with some alkene–transition metal complexes and that the formation of the inclusion compounds is selective. We report here the preparation and characterization of cyclodextrin inclusion compounds of neutral cyclo-octa-1,5-diene (cod) and norbornadiene (nbd) transition metal complexes.



(a) (b)

Figure 1. Proposed structures of (a) β-CD–$[(cod)RhCl]_2$ and (b) β-CD–$(cod)PtX_2$ (X = Cl, Br, and I).

Inclusion compounds of alkene–metal complexes with cyclodextrins were prepared by adding fine crystals of the complexes to a stirred saturated aqueous solution of the CD at 40 °C. The product which precipitated was washed with water to remove the remaining CD, and dried *in vacuo*. Non-included metal complexes were removed by washing the residue with tetrahydrofuran. During this process, the included guest was not liberated from the CD cavity. The product was recrystallized from water or aqueous ethanol.

Table 1 shows the results for the preparation of inclusion compounds of CD–alkene–metal complexes. β-CD formed 2:1 (CD:guest) inclusion compounds with di-μ-chloro-bis(cyclo-octa-1,5-diene)dirhodium, $[(cod)RhCl]_2$, and di-μ-chloro-bis(norbornadiene)dirhodium, $[(nbd)RhCl]_2$, in high yields. γ-CD formed 2:1 inclusion compounds with $[(cod)RhCl]_2$ in 29% yield, but it did not form inclusion compounds with $[(nbd)RhCl]_2$ which is smaller than $[(cod)RhCl]_2$. It is noteworthy that $[(nbd)RhCl]_2$ was specifically included in β-CD. β-CD also formed inclusion compounds with dihalogeno(cyclo-octa-1,5-diene)platinum complexes, $(cod)PtX_2$, (X = Cl, Br, or I), in high yields. γ-CD formed inclusion compounds with $(cod)PtI_2$ quantitatively, whereas it did not form inclusion compounds with $(cod)PtCl_2$, and with $(cod)PtBr_2$ gave the inclusion compounds in a low yield, indicating that γ-CD appears to discriminate the size of the guest compounds, especially the halogen part.

We could not obtain inclusion compounds of any neutral alkene–metal complexes tested with α-CD. Examination of Corey–Pauling–Koltun (C.P.K.) models shows that these alkene–metal complexes are a little too large to be fully included in the α-CD cavity.‡

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† After this manuscript had been submitted, the synthesis and the *X*-ray structure of an ionic complex, α-CD–$[Rh(cod)(NH_3)_2][PF_6]\cdot 6H_2O$ (D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 786) and related articles were published (D. R. Alston, T. H. Lilley, and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1985, 1600; D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *ibid.*, p. 1602).

‡ According to the report by Stoddart *et al.* $[Rh(cod)(NH_3)_2][PF_6]\cdot 6H_2O$ is positioned almost exactly over the centre of the torus in α-CD. One of the two ethylene groups is inserted: D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 786.

Table 1. Preparation of CD–alkene–metal complexes.

		Product	
CD	Guest	Yield, %	CD : Guest
α	$[(\mathrm{cod})\mathrm{RhCl}]_2$	0	—
β		90[a]	2 : 1
γ		29	2 : 1
α	$[(\mathrm{nbd})\mathrm{RhCl}]_2$	0	—
β		100	2 : 1
γ		0	—
α	$(\mathrm{cod})\mathrm{PtCl}_2$	0	—
β		99	1 : 1
γ		0	—
α	$(\mathrm{cod})\mathrm{PtBr}_2$	0	—
β		100	1 : 1
γ		14	1 : 1
α	$(\mathrm{cod})\mathrm{PtI}_2$	0	—
β		90	1 : 1
γ		100	1 : 1

[a] U.v. (H_2O) $\lambda_{\max.}$ (log ε) 305 (3.57), 345 (3.44), and 396 nm (3.65); ^{1}H n.m.r. (360 MHz, D_2O) δ 3.50 (H-2), 3.56 (H-4), 3.78 (H-5), 3.86 (H-6), 3.98 (H-3), and 5.00 (H-1); c.d. (H_2O) $\lambda_{\max.}$ ([θ]), 313 (+6000) and 405 nm (−6000).

The inclusion compounds were characterized by elemental analysis and their i.r., u.v., and ^{1}H n.m.r. spectra. The ^{1}H n.m.r. spectrum of the β-CD–$[(\mathrm{cod})\mathrm{RhCl}]_2$ inclusion complex in D_2O showed two sets of resonances for apparently two different CD species. One of them is superimposable with that of free β-CD and the other, which could represent complexed CD, showed large shifts of the signals for H-1, H-2, and H-5 of β-CD to lower frequency and of that for H-3 to higher frequency (footnote in Table 1). This implies that exchange between free and complexed CD is slow on the n.m.r. time-scale. Stoicheiometries were determined by elemental analysis, including atomic absorption analysis of the metal contents, and from their ^{1}H n.m.r. spectra. All the inclusion compounds obtained in this work were stoicheiometric 1 : 1 or 2 : 1 (host to guest) complexes depending on the size of the guest compounds.

The inclusion compounds were thermally stable. β-CD–$[(\mathrm{cod})\mathrm{RhCl}]_2$, for example, did not liberate the guest when heated at 200 °C *in vacuo*. Under these conditions the alkene complex sublimes. Thermogravimetric analyses showed that the inclusion compound was stable up to 280 °C and decomposed at around the m.p. (decomp. point) of β-CD.

Absorption and c.d. spectra of the inclusion compounds were measured in ethylene glycol and in aqueous solution. A large induced Cotton effect was observed in the case of the β-CD–$[(\mathrm{cod})\mathrm{RhCl}]_2$ inclusion compound (footnote in Table 1), while a very weak induced Cotton effect was observed with the γ-CD inclusion compound, indicating that the guest compound was fixed well in the β-cyclodextrin ring.

According to C.P.K. molecular models, cyclo-octa-1,5-diene- and norbornadiene-metal complexes appear to fit well into the β-CD cavity as shown in Figure 1, whereas $[(\mathrm{nbd})\mathrm{RhCl}]_2$ and $(\mathrm{cod})\mathrm{PtCl}_2$ are too small to fit in the γ-CD cavity. $[(\mathrm{cod})\mathrm{RhCl}]_2$ and $(\mathrm{cod})\mathrm{PtX}_2$ (X = Br or I) are large enough to fit in the γ-CD cavity. The proposed structures for the β-CD–$[(\mathrm{cod})\mathrm{RhCl}]_2$ and β-CD–$(\mathrm{cod})\mathrm{PtX}_2$ complexes are shown in Figure 1.

Received, 25th November 1985;§ Com. 1664

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§ Received in revised form 25th April 1986.