Synthesis of Optically Active η^6-Benzene–Ruthenium Complexes

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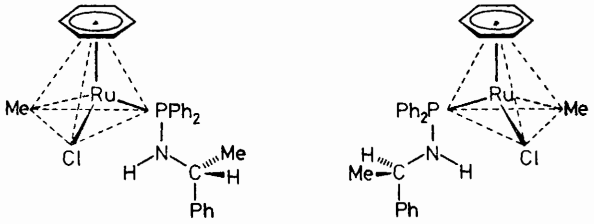
Summary The first examples of optically active arene–ruthenium complexes (+)-(**1**) and (−)-(**1**), prepared by the stepwise reaction of benzene(dichloro)ruthenium dimer with dimethylmercury and (*R*)-(+)-$Ph_2PNHCH(Me)Ph$ and separated by chromatography, have stable configurations even in solution at 60 °C.

THE importance of chirality as a probe to follow the stereochemical course of reactions of organometallic complexes has been emphasized in recent years.[1] Although the number and variety of organometallic complexes which contain an asymmetric metal atom are rapidly increasing, there is, as yet, no report of the resolution of a chiral organometallic arene–ruthenium complex. A recent communication described the preparation but not resolution of chiral η^6-arene–ruthenium compounds.[2] Moreover, there is only one reported example of a resolved arene complex which contains chromium as the asymmetric metal atom.[3] We now report the first examples, (+)-(**1**) and (−)-(**1**), of optically active Ru complexes, which differ only in the configuration at the asymmetric Ru atom.



(1)

(+)-(**1**): $[\alpha]^{25}_{578}$ + 645°, $[\alpha]^{25}_{546}$ + 970°, $[\alpha]^{25}_{436}$ −1080°; (−)-(**1**): $[\alpha]^{25}_{578}$ −565°, $[\alpha]^{25}_{546}$ −840°, $[\alpha]^{25}_{436}$ + 765° (1 mg ml^{-1}, C_6H_6).

A convenient synthesis of $[\eta^6\text{-}C_6H_6RuCl(Me)(PR_3)]$,[4,5] where R = Ph, has been described and involves the alkylation of $[(\eta^6\text{-}C_6H_6RuCl_2)_2]$ by dimethylmercury in acetonitrile followed by addition of a tertiary phosphine.[4] By employing the optically active phosphine (*R*)-(+)-$Ph_2PNHCH(Me)$-Ph[6] a pair of diastereoisomers is obtained which can be separated by dry-column chromatographic techniques[7] using alumina and ether–acetonitrile (15:1).

The more soluble isomer (−)-(**1**) (16% yield) as isolated from the first band during chromatography contained a small amount of the isomer (+)-(**1**) (*ca.* 10%). Pure (−)-(**1**) could be obtained by repeating the chromatographic step. Recrystallization from either benzene–hexane at 5 °C or acetonitrile at −30 °C yielded yellow needles of (−)-(**1**), m.p. 143—145 °C. The less soluble isomer (+)-(**1**) (19% yield) was obtained optically pure from the second band of the chromatogram as a yellow solid. Recrystallization from acetonitrile at −30 °C afforded orange prisms, m.p. 175—177 °C.

Both diastereoisomers (+)-(**1**) and (−)-(**1**) gave satisfactory elemental analyses. Their mass spectra showed the molecular ion. The c.d. spectra of (+)-(**1**) and (−)-(**1**) are depicted in the Figure. Compounds (+)-(**1**) and (−)-(**1**) differ in their ^{1}H n.m.r. spectra ($CDCl_3$, Me_4Si): (+)-(**1**), τ 8·70 [d, J(Me–P) 6·2 Hz, Ru–Me], 8·99 [d, J(Me–CH) 7·2 Hz, C–Me], 6·00 (m, C–H), 4·93 [d, J(C_6H_6–P) 0·9 Hz, η^6–C_6H_6], and 2·68 (m, Ph); (−)-(**1**), τ 9·17 [d, J(Me–P) 6·3 Hz, Ru–Me], 8·97 [d, J(Me–CH) 7·2 Hz, C–Me], 6·00 (m, C–H), 4·87 [d, J(C_6H_6–P) 0·9 Hz, η^6–C_6H_6], and 2·76 (m, Ph). The difference in the Ru–Me resonances and, to some extent, in the η^6–C_6H_6 resonances is sufficiently large to allow their use as a gauge of optical purity as well as a monitor of epimerization reactions.

Both isomers have stable configurations at room temperature in the solid state as well as in benzene, toluene, or chloroform solutions when kept oxygen-free. Moreover, no epimerization can be observed upon heating these solutions up to 60 °C for at least 18 h. Therefore, the utility of (+)-(**1**) and (−)-(**1**) in investigations of the stereochemistry of reactions at Ru–ligand bonds is evident.

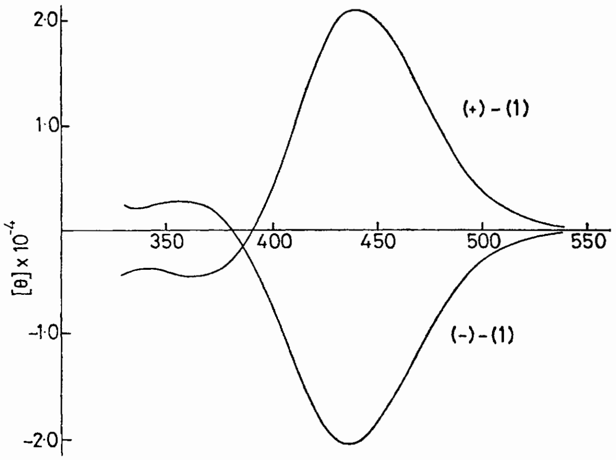


FIGURE. C.d. spectra of (+)-(**1**) and (−)-(**1**) in *ca.* 0·002 M C_6H_6 solution at 20 °C.

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