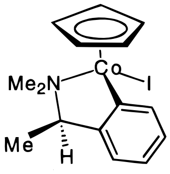
Organometallics **2000,** *19,* 2427 2427

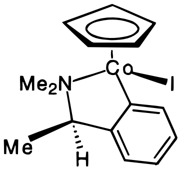
About the Configurational Stability of Optically Active Half-Sandwich Organometallic Compounds

Sir: This contribution is a response to the Note Added in Proof in the immediately preceding correspondence.[1]

We have recently been interested in half-sandwich organocobalt complexes in which anionic bidentate ligands are bound to a cobalt(III) center in order to evaluate their behavior in solution.[2] We have thus obtained various stable compounds, and with the optically active ligands (*R*)- and (*S*)-1-(dimethylamino)-1-phenylethane we obtained a mixture of diastereomers. For instance, compounds **1a**,**b** exist in solution as a 96:4 mixture of diastereomers, and as this ratio was unchanged with time (over 1 week), we concluded that this mixture was stable on the laboratory time scale.

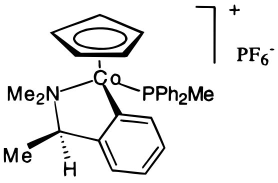


1a

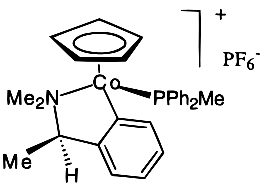


1b

This behavior is in marked contrast to that of another mixture of diastereomers **2a**,**b** (obtained by substitution of the iodide of **1a**,**b** by a PPh_2Me ligand) which appeared to be a 4:1 mixture of diastereoisomers (their formation was controlled kinetically) shortly after their synthesis.



2a

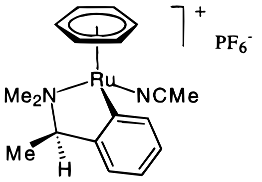


2b

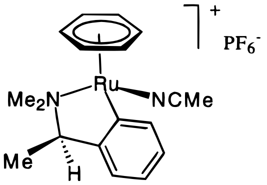
This composition then changed very slowly with time, and after ca. 1 week it consisted of 100% of the major isomer, the minor isomer having totally epimerized to the major one, **2a**. Since the composition of this mixture changed slowly with time, we concluded that the mixture **2a**,**b** was not stable on the laboratory time scale. Strictly speaking, however, the cobalt compounds **1a**,**b** to which Brunner and Zwack referred[1] are not configurationally stable at the metal center; hence, we have somehow misinterpreted the results depicted in our paper.[2]

Nevertheless, we became aware of the problem raised by Brunner and Zwack when we studied the behavior of ruthenium compounds related to those depicted above. Recently we reported the synthesis of compounds which were obtained via the cycloruthenation reaction of the optically active ligand (*R*)-1-(dimethylamino)-1-phenylethane.[3]

The resulting product was a 75:25 mixture of the diastereoisomers **3a**,**b** in CD_3CN, but we found that this composition was very much dependent upon the solvent used (70:30 in CD_3OD, 65:35 in CD_2Cl_2, and 63:37 in $CDCl_3$). We thus decided to investigate the structure of the solid via ^{13}C NMR spectroscopy, and we carried out a $^1H \rightarrow ^{13}C$ CP/MAS study of it. The resolution of the spectrum was good enough to allow us to conclude that the compound in the solid state was a single diastereoisomer; hence, the presence of both diastereomers in solution can only be explained by a fast epimerization of the diastereomer found in the solid state. Further results connected to this research theme and their relevance to the cobalt complexes[2] will be published in due time.[4]



3a



3b

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[1] Brunner, H.; Zwack, T. *Organometallics* **2000**, *19*, 2423.

[2] Meneghetti, M. R.; Grellier, M.; Pfeffer, M.; Dupont, J.; Fischer, J. *Organometallics* **1999**, *18*, 5560.

[3] Fernandez, S.; Pfeffer, M.; Ritleng, V.; Sirlin, C. *Organometallics* **1999**, *18*, 2390.

[4] Bertani, P.; Hirschinger, J.; Pfeffer, M.; Ritleng, V. To be submitted for publication.

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