

to the merocyanines), it is anticipated that recognition of alkali-metal cations in the neighborhood of the spiropyran unit is essential. Indeed, the absorption spectra of **3**⁹ and **4**¹⁰ were not at all affected by the alkali-metal iodides, and **5**,¹⁰ the corresponding acyclic analogue of **1a**, showed much less Li⁺ selectivity than **1a**. Furthermore, little change in the spectrum of **3** occurred even in the presence of 1 equiv of *N*-acetylmonoaza-18-crown-6 (**6b**) and the alkali-metal iodides.¹¹ These results substantiate the interpretation previously described.

In conclusion, the present work demonstrates that recognition of lithium cations causes a spiropyran to isomerize to a merocyanine, of which structural details have been obtained for the first time.¹² This result illustrates the concept of a new type of artificial receptor in which guest recognition induces a change in the molecular structure, which in turn causes development of a spectral signal.

Supplementary Material Available: Preparations and physical and spectral data for **1**, **4**, **5**, and **8** (5 pages). Ordering information is given on any current masthead page.

(9) Berman, E.; Fox, R. E.; Thomson, F. D. *J. Am. Chem. Soc.* **1959**, *81*, 5605–5608.

(10) Spiropyran **4** and **5** were prepared from the corresponding chloroacetamides by a manner similar to that described for **1**.

(11) On the basis of picrate extractions, it was found that alkali-metal cation complexing abilities of model compounds **6** decreased in the order Na⁺ > Li⁺ > K⁺ for **6b** and K⁺ > Li⁺ > Na⁺ for **6c**. CPK molecular models showed, however, that the radius of the cavity of spiropyran **1** was smaller than that of the corresponding model compounds **6**.

(12) Toppet et al. reported an NMR study on merocyanines and suggested their trans structure, but details were not given: Toppet, S.; Quintens, W.; Smets, G. *Tetrahedron* **1975**, *31*, 1957–1958.

Application of Tetrakis(trifluoroacetato)dirhodium(II) to Determination of Chirality: The First Structural Characterization of an Axial Bisolefin Complex of a Dimetal Core

F. Albert Cotton* and Larry R. Falvello

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University College Station, Texas 77843

Michael Gerards and Günther Snatzke*

Fakultät für Chemie, Lehrstuhl für Strukturchemie Ruhr-Universität Bochum, 4630 Bochum, Germany

Received July 20, 1990

It was recognized several years ago¹ that M₂(O₂CR)₄ molecules could serve as chromophores capable of manifesting the chirality of organic molecules with donor functionalities as readily observable CD effects in the visible region of the spectrum. For this purpose Mo₂(O₂CCH₃)₄ was first employed.^{1,2} Other studies have provided a great deal of information about the assignment of the spectrum³ and the response of the Mo₂⁴⁺ chromophore to chiral surroundings.⁴ Nevertheless, Mo₂(O₂CCH₃)₄ and related Mo₂⁴⁺ species are not entirely satisfactory because of their low acceptor strength in the axial position, so that they form optically active complexes only by ligand-exchange reactions with bidentate ligands such as carboxylic acids, diols, aminoles, and others. The search for a more effective compound then turned to the Rh₂(O₂CR)₄ molecules, which are stable, easily prepared and handled,⁵ and

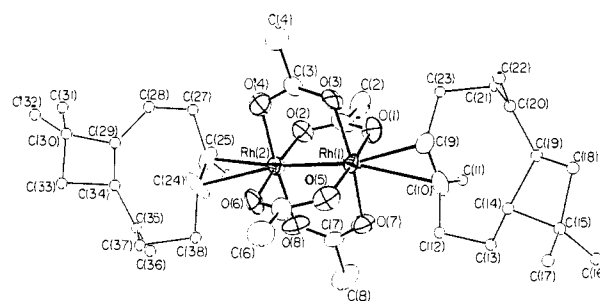


Figure 1. Molecular structure and atom-naming scheme for Rh₂(CF₃COO)₄(-)-*trans*-caryophyllene)₂, with atoms of the core represented by their 50% probability ellipsoids. Selected distances (in Å) and angles (in degrees): Rh(1)–Rh(2), 2.461 (1); ⟨Rh–O⟩_{av}, 2.052 [4]; Rh(1)–C(9), 2.46 (1); Rh(1)–C(10), 2.63 (1); Rh(2)–C(24), 2.46 (1); Rh(2)–C(25), 2.62 (1); ⟨Rh–Rh–O⟩_{av}, 87.2 [3]; Rh(2)–Rh(1)–C(9), 165.2 (3); Rh(2)–Rh(1)–C(10), 163.1 (3); Rh(1)–Rh(2)–C(24), 162.5 (3); Rh(1)–Rh(2)–C(25), 166.4 (3).

which also have well-understood electronic spectra.⁶

Recently it was shown⁷ that Rh₂(O₂CCF₃)₄ is broadly useful because of its (already well-established⁵) ability to bond many types of axial ligands. From spectral observations it even appeared capable of binding unfunctionalized olefins,^{7–9} presumably by direct attachment of C=C bonds at one or both of the axial positions. There has never before been structural evidence for the binding of *any* olefin to *any* M₂(O₂CR)₄ species.¹⁰ Moreover, in order to make the most intelligent interpretation of the induced CD effects for Rh₂(O₂CCF₃)₄/olefin systems, it is necessary to know the spatial relationship of the olefin molecule or molecules to the Rh₂(O₂CCF₃)₄ molecule. For these two reasons we have determined for the first time the structure of a M₂(O₂CR)₄(olefin)_n-type compound, namely, Rh₂(O₂CCF₃)₄(-)-*trans*-caryophyllene)₂.

The molecular structure is shown in Figure 1. The compound crystallizes in chiral space group *P*2₁2₁2₁ (No. 19), and the structure determination proceeded normally.¹¹ The caryophyllene molecules are bound through the endo double bonds and the binding appears to be strong though unsymmetrical. The Rh–C distances are longer to the more hindered carbon atoms (ca. 2.63 Å). The shorter Rh–C distances (both 2.46 (1) Å) are indicative of genuine bonding. The strength of the axial interaction is evidenced indirectly by the length of the Rh–Rh bond, 2.461 (1) Å, which is one of the longest known among all Rh₂(O₂CR)₄L₂ molecules.¹²

(5) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; John Wiley & Sons: New York, 1982. (b) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73. (c) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109.

(6) Trexler, J. W., Jr.; Schreiner, A. F.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 3265, and references cited therein.

(7) Gerards, M.; Snatzke, G. *Tetrahedron: Asymmetry* **1990**, *1*, 221.

(8) Schurig, V.; Bear, J. L.; Zlatkis, A. *Chromatographia* **1972**, *5*, 301; Mikes, F.; Schurig, V.; Gil-Av, E. *J. Chromatogr.* **1973**, *83*, 91; *Inorg. Chem.* **1986**, *25*, 945.

(9) Doyle, M. P.; Colman, M. R.; Chinn, M. S. *Inorg. Chem.* **1984**, *23*, 3684. Doyle, M. P.; Mahapatro, S. N.; Caughey, A. C.; Chinn, M. S.; Colman, M. R.; Harn, N. K.; Redwine, A. E. *Inorg. Chem.* **1987**, *26*, 3070.

(10) Axial interaction of benzene molecules with the metal dπ orbitals of Cr₂(O₂CCPh)₄ has previously been reported: Cotton, F. A.; Feng, X.; Kibala, P. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 2807.

(11) (a) Single crystals were obtained from hexane solutions of dirhodium tetra(trifluoroacetate) and excess of (-)-*trans*-caryophyllene by slow evaporation under argon. Rh₂F₁₂O₈C₃₈H₄₈, fw 1066.6, crystallizes in the orthorhombic system, space group *P*2₁2₁2₁, with *a* = 8.652 (1), *b* = 16.523 (3), *c* = 31.240 (7) Å; *V* = 4466 (1) Å³; *Z* = 4. The structure was solved by direct methods and refined (full matrix least squares) to residuals of *R* = 0.0456, *R*_w = 0.0579, quality of fit = 1.093, with 3069 observations (*F*_o² > 3σ(*F*_o²)) and 541 variables. The absolute configuration was established at the 99% confidence level^{11b} and is in agreement with the previously established configuration of (-)-*trans*-caryophyllene.^{11c} (b) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502. Program HamSig by L. M. Daniels. (c) Barton, D. H. R.; Nickon, A. *J. Chem. Soc.* **1954**, 4665. (d) Full details of the crystal structure analysis will be reported elsewhere.

(12) The great majority have Rh–Rh distances between 2.37 and 2.45 Å. Only for Rh₂(O₂CCF₃)₄L₂ with L = P(OPh)₃ and P(Ph)₃ have distances of 2.47 and 2.49 Å been found. Cf. ref. 5a, p 314.

(1) Snatzke, G.; Wagner, U.; Wolff, H. P. *Tetrahedron* **1981**, *37*, 349.

(2) (a) Frelek, J.; Perkowska, A.; Snatzke, G.; Tima, M.; Wagner, U.; Wolff, H. P. *Spectrosc. Int. J.* **1983**, *2*, 274. (b) Lipták, A.; Frelek, J.; Snatzke, G.; Vlahov, I. *Carbohydr. Res.* **1987**, *164*, 149.

(3) Cotton, F. A.; Zhong, B. *J. Am. Chem. Soc.* **1990**, *112*, 2256, and earlier references cited therein.

(4) (a) Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Manojlovic-Muir, L.; Muir, K. W.; Peacock, R. D. *Inorg. Chem.* **1986**, *25*, 2511. (b) Chen, J.-D.; Cotton, F. A. *Inorg. Chem.*, in press.

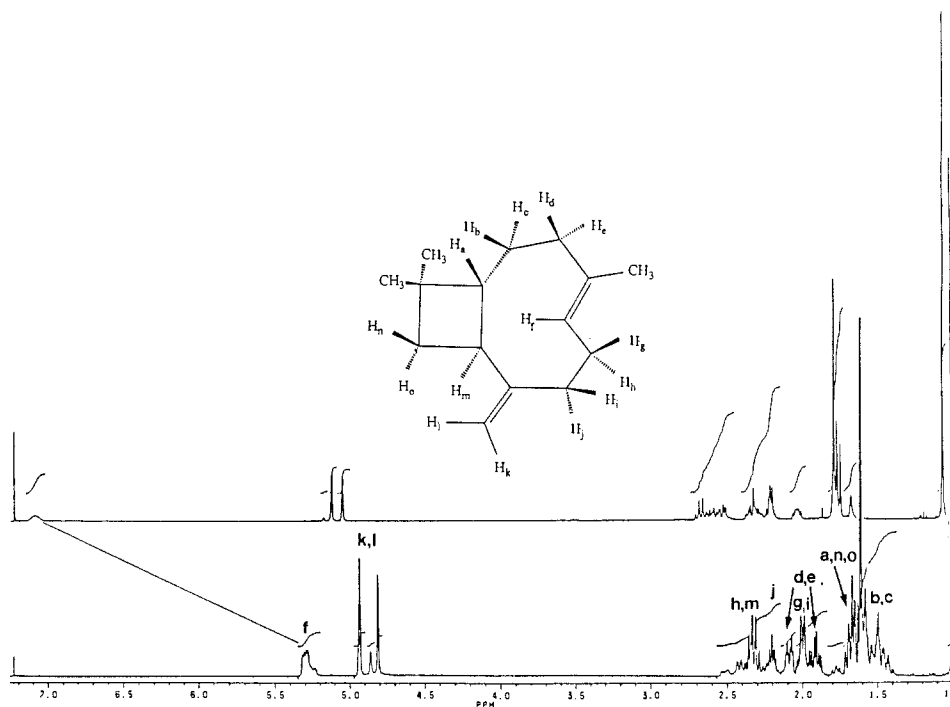


Figure 2. ^1H NMR spectra of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(-)\text{-trans-caryophyllene}_2$ (top) and of pure ligand (bottom) in CDCl_3 . The assignments of hydrogen atoms were made by different COSY experiments.

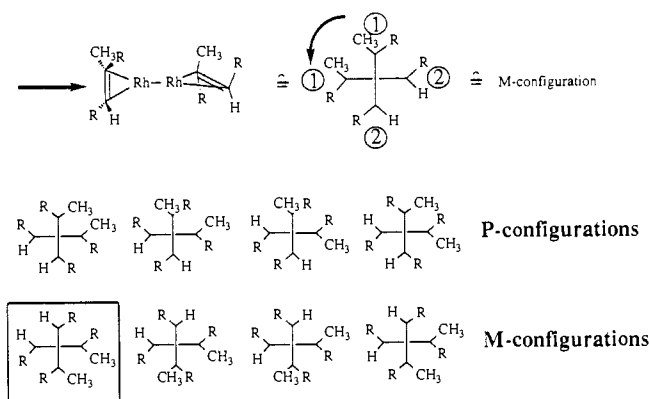


Figure 3. The eight possible isomers of dimetallic clusters with two chiral olefins of given absolute configuration. The two olefins are axially bound perpendicular to each other as in allenes. The framed isomer corresponds to the structure given in Figure 1.

The different distances between the metal and the two carbon atoms of the double bond (e.g., $\text{Rh}(1)\text{-C}(9)$, $\text{C}(10)$) are also reflected in the ^{13}C NMR spectrum of CDCl_3 solutions of the caryophyllene complex. The signals of these two carbon atoms were shifted in different directions and with different magnitudes. The signal of $\text{C}(10)$ was deshielded by 10 ppm from 135.37 (free ligand) to 145.31 ppm (in the complex); that of $\text{C}(9)$ was shielded ~ 5 ppm from 124.30 to 119.07 ppm. The same effects were observed for the complexes with 1-menthene and 3-carene. The ^1H NMR spectrum of the caryophyllene complex is given in Figure 2 and shows an enormous low-field shift for the signal of the olefin proton H_f , which is connected to $\text{C}(9)$ or $\text{C}(24)$, respectively.

Even knowing the absolute configuration of $(-)\text{-trans-caryophyllene}$,¹¹ we must still consider eight possible isomers of the complex because of the axis of chirality (allene type). They are summarized in Figure 3. Our complex has the configuration marked by a frame in Figure 3.

Previous spectroscopic studies⁷⁻⁹ of the binding of olefins to $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ in solution or the gas phase have either not indicated the stoichiometry or have explicitly favored 1:1 stoichiometry. The present characterization of a 1:2 complex suggests that more needs to be learned about these

systems both in solution and in the crystalline state.

Acknowledgment. We thank the National Science Foundation, the HOECHST AG, and the Fonds der Chemie for support and Dean John P. Fackler, Jr., for the use of his X-ray diffractometer. M.G. thanks the Heinrich Hertz Stiftung and the Gesellschaft der Freunde der RUB for providing grants.

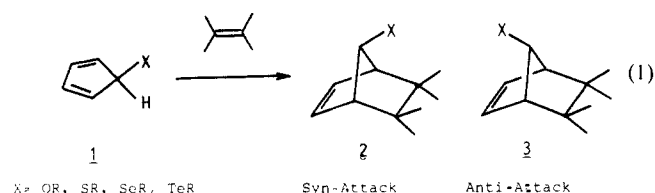
Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, and full listings of bond distances and angles (13 pages). Ordering information is given on any current masthead page.

Application of the Orbital Mixing Rule to Heteroatom-Dependent π -Facial Stereoselectivity in the Diels-Alder Reaction of 5-Substituted 1,3-Cyclopentadienes¹

Masaru Ishida, Yasufumi Beniya, Satoshi Inagaki,* and Shinzi Kato

Department of Chemistry, Faculty of Engineering
Gifu University, Yanagido, Gifu 501-11, Japan
Received July 5, 1990

The orbital mixing rule² gave an unprecedented insight into the π -facial stereoselectivity in the Diels-Alder reactions of 5-substituted cyclopentadienes (eq 1), while some other theories were



developed.³⁻⁶ These theories are in agreement with the selec-

(1) Presented at the 59th Annual Meeting of Chemical Society of Japan, Yokohama, April 1990.

(2) (a) Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509. (b) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.