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A Novel Type of Optically Active Diketonate Ligand and Its Rhodium Complex[†]

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The growing interest in asymmetric synthesis and the rapidly increasing use of enantiomerically pure compounds as catalysts and auxiliaries require speedy and accurate methods for determination of enantiomeric excess. NMR spectroscopy is an attractive method for this, as it is in most cases fast and simple to perform. Recently, several groups reported the determination of enantiomeric excess of chiral phosphines or hydrocarbon compounds by coordination to a suitable optically active organometallic compound or metal complex.[2] One of the most common methods involves the use of chiral lanthanoid diketonate shift reagents, where it has been possible to determine the optical purity of alcohols, aldehydes, amines, carboxylic amides, etc.[3] Apart from this, chiral (diketonato)metal complexes have also found applications in catalysis, as was recently demonstrated by Togni et al.,[4] who employed the chiral Lewis acid bis[(1*R*)-3-(heptafluorobutyryl)camphorato]oxovanadium(IV) complex as catalyst in the so-called hetero-Diels–Alder reactions between an aldehyde and a diene of the Danishefsky type.[5] In most cases, they obtained good enantiomeric excesses.[4a] Chiral diketonate complexes have also found applications as stationary phases in the gas-chromatographic separation of enantiomers.[6] The enantiopure camphor-derived ligands mentioned above and their lanthanide complexes are commercially available.

We have sought a route to a completely different type of chiral diketonate ligand, starting from an optically active (diolefin)iron complex. The easily available ketone complex **1**, derived from the optically pure natural product (1*R*)-myrtenal, serves as a convenient starting material.[7] It had previously been shown that (dienone)tricarbonyliron complexes, similar to **1**, can be deprotonated to generate a stable enolate.[8] This is also possible for **1**, as treatment with the nonnucleophilic base lithium diisopropylamide (LDA) readily generates the enolate **2**, which on treatment with chlorotrimethylsilane ((TMS)Cl) almost quantitatively converts into the trimethylsilyl enol ether complex **3**[9] (Scheme 1). Similar silyl enol ether complexes with planar chirality have also been described by Franck-Neumann et al.[10]

On treatment of **2** with pivaloyl chloride, however, the reaction takes a completely different course, as we observed the formation of the β-dicarbonyl compound **4**, predominantly present in the enol form.[11] Complex **4** represents another example of a chiral β-dicarbonyl compound, possessing both central and planar chirality. In order to test whether **4** might also be suitable as a chiral chelating ligand, we treated **4** with $[(COD)RhCl]_2$ as follows: Sodium carbonate (0.75 g, 7 mmol) was added to **4** (0.30 g, 0.72 mmol, 2.0 equiv) in methylene chloride (20 mL). The mixture was stirred for 1 h at room temperature. Bis[(μ-chloro)(cycloocta-1,5-diene)rhodium][12] (0.18 g, 0.36 mmol) was added, the reaction mixture was stirred for 19 h at room temperature and then filtered over Celite, and the solvent was evaporated. The residue was repeatedly washed with small portions of hexane. After the solid was dried in vacuo, **5** was obtained as an orange solid (0.45 g, 99%). Spectroscopic as well as analytical data confirmed the formulation of **5** as a iron–rhodium bimetallic species,[13] with rhodium coordinated to the β-diketonate ligand.

We were able to grow single crystals of complex **5**[14] by slow evaporation from hexane. The molecular structure is shown in Figure 1.

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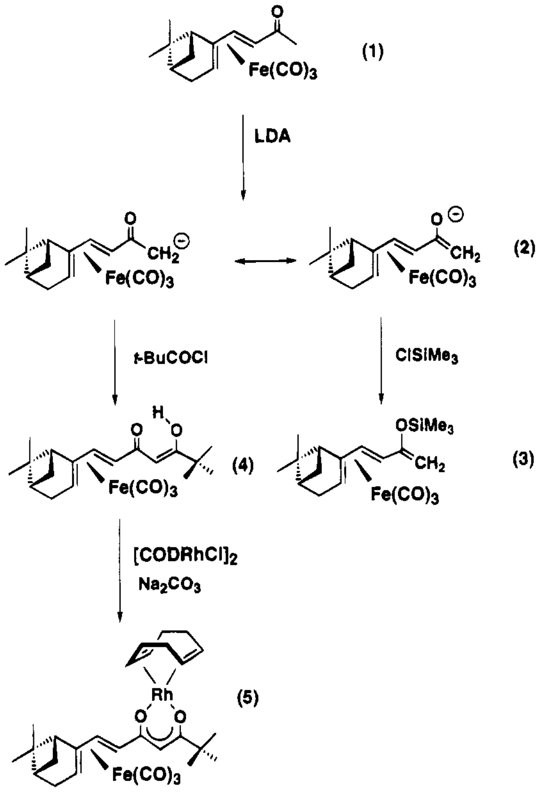
[†] Optically Active Transition Metal Complexes. 5. For part 4, see ref 1.
[‡] Corresponding author for crystallographic analysis.
(1) Englert, U.; Pfister, B.; Salzer, A. *Organometallics*, in press.
(2) (a) Albert, J.; Granell, J.; Muller, G.; Sainz, D.; Font-Bardia, M.; Solans, X. *Tetrahedron Asymmetry* **1995**, *6*, 325. (b) Wypchlo, K.; Duddeck, H. *Tetrahedron Asymmetry* **1994**, *5*, 27. (c) Cotton, F. A.; Favello, R. L.; Gerards, M.; Snatzke, G. *J. Am. Chem. Soc.* **1990**, *112*, 8979.
(3) Parker, D. *Chem. Rev.* **1991**, *91*, 1441 and the references cited therein.
(4) (a) Togni, A. *Organometallics* **1990**, *9*, 3106. (b) Togni, A.; Rist, G; Rihs, G.; Schweiger, A. *J. Am. Chem. Soc.* **1993**, *115*, 1908.
(5) Danishefsky, S. *Chemtracts: Org. Chem.* **1989**, *2*, 273 and references cited therein.
(6) Schurig, V. *Chromatographia* **1980**, *13*, 263.
(7) Salzer, A.; Schmalle, H.; Stauber, R.; Streiff, S. *J. Organomet. Chem.* **1991**, *408*, 403.
(8) Meier, E. Diploma Thesis, University of Zurich, 1991.
(9) IR (hexane): ν(CO) 2040, 1978, 1962 cm^{-1}; ν(C=C) 1635 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.38 (d, ^3J = 8.2 Hz, 1H, $\mathrm{C}H{=}$), 4.17, 3.96 (2d, ^2J = 1.2 Hz, 2H, 2 × $\mathrm{C}H{=}$), 2.60–2.51, 2.20–1.90 (2m, 5H, 3 × $\mathrm{C}H$, $\mathrm{C}H_2$), 1.64 (d, J = 7.3 Hz, 1H, $\mathrm{C}H$), 1.33–1.19 (m, 4H, $\mathrm{C}H$, $\mathrm{C}H_3$), 0.98 (d, ^3J = 8.2 Hz, 1H, $\mathrm{C}H{=}$), 0.87 (s, 3H, $\mathrm{C}H_3$), 0.16 (s, 9H, $\mathrm{Si}(\mathrm{C}H_3)_3$]. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 213.01, 156.62, 115.89, 89.51, 79.98, 54.09, 52.84, 47.48, 42.39, 40.06, 37.01, 29.72, 26.07, 22.06, −0.14.
(10) Franck-Neumann, M.; Abdali, A.; Colson, P.-J.; Sedrati, M. *Synlett* **1991**, 331.

0020-1669/95/1334-6231$09.00/0

Scheme 1



The two subunits of the bimetallic complex **5** are slightly tilted along the central bond C9−C10. The butadiene system C2/C3/C8/C9 coordinating the $Fe(CO)_3$ group and the diketonate O10/C10/C11/C12/O12 chelating the Rh(COD) moiety enclose a dihedral angle of 23.6(6)°. The Rh center is coordinated by the two oxygen atoms of the diketonate and the centers of gravity of the COD double bonds C20═C21 and C24═C25 in a very close to square planar geometry.

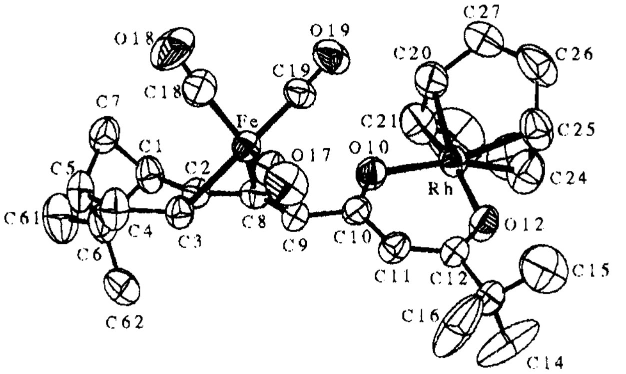


Figure 1. PLATON[14d] plot of the bimetallic compound **5** with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Fe−C2 2.132(8); Fe−C3 2.176(7); Fe−C8 2.065(7); Fe−C9 2.117(7); Rh−O10 2.049(5); Rh−O12 2.055(6); Rh−C20 2.103(9); Rh−C21 2.09(1); Rh−C24 2.09(1); Rh−C25 2.096(9); O10−Rh−O12 90.3(2); C20−Rh−C25 82.2(4); C21−Rh−C24 83.2(5).

We are currently investigating whether this novel type of optically active diketonate can also act as a ligand toward other metals, such as lanthanoids, and whether such complexes might find new applications as chiral shift reagents or in homogeneous catalysis.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant SFB 380) and the Fonds der chemischen Industrie for financial support.

Supporting Information Available: Tables of atomic positional parameters, general anisotropic displacement parameters, and complete bond distances and angles for **5** (10 pages). Ordering information is given on any current masthead page.

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(11) Preparation of **4**: Diisopropylamine (0.39 g, 3.89 mmol, 0.60 mL, 1.1 equiv) in ether (20 mL) was cooled to −78 °C. *n*-Butyllithium (3 mL of a 1.32 M solution in hexane, 3.90 mmol, 1.1 equiv) was added dropwise, and the reaction mixture was stirred for 0.75 h. The ketone complex **1** (1.17 g, 3.54 mmol) in ether (20 mL) was added dropwise. After another hour of stirring at −78 °C, pivaloyl chloride (0.43 g, 3.54 mmol, 0.45 mL) was added dropwise, and the mixture was stirred at −78 °C for 2.25 h. The mixture was allowed to reach to room temperature, and the solvent was evaporated. The residue was dissolved in hexane (50 mL), and the solution was filtered over Celite. The solvent was evaporated, and the crude product was purified by chromatography [SiO_2, eluant hexane/ether (10:1)]. After evaporation of the solvent, **4** was obtained as a viscous, orange-red oil (0.77 g, 52%). EI-MS [*m/z* (relative intensity)]: $M^+ - C_4H_9$ 357 (0.54), $M^+ - 3CO$ 330 (1.25), $M^+ - C_4H_9 - CO$ 329 (0.79), $M^+ - C_4H_9 - 2CO$ 301 (2.13), $M^+ - Fe(CO)_3$ 274 (2.03), 217.0 [5.23%, $M^+ - C_4H_9 - Fe(CO)_3$], Fe 57 (100). IR (hexane): ν(CO) 2053, 1994, 1974 cm^{-1}; ν(C═C) 1601 cm^{-1}. ^1H-NMR (300 MHz, C_6D_6): δ 5.80 (d, $^3J = 7.7$ Hz, 1H, C*H*═), 5.62 (s, 1H, C*H*), 2.30−1.60 (3m, 5H, 3 × C*H*, CH_2), 1.44 (br d, 1H, C*H*═), 1.24 (d, $^2J = 10.1$ Hz, 1H, C*H*), 1.12 (s, 3H, CH_3), 1.10 [s, 9H, C(CH_3)$_3$], 0.72 (s, 3H, CH_3), 0.42 (d, $^3J = 7.7$ Hz, 1H, C*H*═). ^{13}C-NMR (75 MHz, C_6D_6): δ 211.71, 196.56, 194.06, 119.71, 95.43, 81.47, 54.94, 48.73, 47.45, 42.51, 39.92, 38.45, 36.86, 29.89, 27.55, 26.01, 21.99.

(12) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(13) Anal. Calcd (found) for $C_{29}H_{37}FeO_5Rh$: C, 55.79 (55.92); H, 5.97 (6.31). SIMS-MS [*m/z* (relative intensity)]: $M^+ - H$ 623 (3.83), $M^+ - 2CO$ 568.0 (31.2), $M^+ - 3CO$ 540 (10.9), $M^+ - H - Fe(CO)_3$ 483 (9.2), $C_{21}H_{26}FeO_5 - 2CO$ 358 (98.9), $C_{21}H_{26}FeO_5 - 2CO$ 330 (100), $C_8H_{12}Rh$ 210 (14.9), Rh 103 (13.4). IR (hexane): ν(CO) 2046, 1986, 1968 cm^{-1}; ν(C═O) 1557, 1527 cm^{-1}. ^1H-NMR (300 MHz, C_6D_6): δ 5.71 (m, 2H, C*H*, C*H*═), 4.54−4.22 [m, 4H, 4 × C*H*═(COD)], 2.50−1.60 (m, 13H, 3 × C*H*, 1 × CH_2, 4 × CH_2(COD)], 1.36 [br d, 1H, C*H*═), 1.31 [d, $^2J = 10.4$ Hz, 1H, C*H*), 1.14 [s, 12H, CH_3, C(CH_3)$_3$], 0.73 (s, 3H, CH_3), 0.69 (d, $^3J = 8.1$ Hz, 1H, C*H*═). ^{13}C-NMR (75 MHz, C_6D_6): δ 212.45, 194.86, 184.64, 118.27, 95.40, 82.91, 76.74 [d, ^1J(Rh,C) = 14.7 Hz], 76.56 [d, ^1J(Rh,C) = 15.0 Hz], 76.38 [d, ^1J(Rh,C) = 14.0 Hz], 76.31 [d, ^1J(Rh,C) = 14.4 Hz], 54.07, 52.08, 47.41, 42.51, 40.66, 39.81, 36.94, 30.68 [d, ^2J(Rh,C) = 5.2 Hz], 30.59 [d, ^2J(Rh,C) = 16.4 Hz], 29.81, 28.68, 25.92, 21.96.

(14) (a) Structure determination of **5**: $C_{29}H_{37}FeO_5Rh$, fw 624.37, transparent orange parallelepiped with approximate dimensions 0.50 × 0.45 × 0.40 mm, Enraf-Nonius CAD-4 diffractometer, graphite monochromator, Mo Kα radiation ($\lambda = 0.7107$ Å), $T = 258$ K. Crystal data: monoclinic, space group $P2_1$ (No. 4), $a = 10.339(9)$ Å, $b = 12.554(9)$ Å, $c = 11.289(6)$ Å, $\beta = 104.08(6)°$, $V = 1421(2)$ Å^3, $Z = 2$, $d_{calc} = 1.461$ g cm^{-3}, μ(Mo Kα) = 11.17 cm^{-1}, $F_{000} = 644$. Data collection: 4354 reflections on the $h,\pm k,\pm l$ hemisphere with the ω scan type, 4073 independent data, empirical absorption correction (DIFABS,[14b] min corr 0.730, max corr 1.142, av corr 0.960). Structure solution (SDP[14c]) was by Patterson and Fourier difference methods. Convergence results: 3524 independent observations with $I > 2\sigma(I)$, 324 variables, $R = 0.052$, $R_w = 0.061$ ($w^{-1} = \sigma_{F_o}{}^2$), GOF = 1.215; hydrogen atoms in riding geometry (C−H = 0.98 Å, $B_{iso}(H) = 1.3[B_{eq}(C)]$). (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. (c) B. A. Frenz, and Enraf-Nonius SDP, Version 5.0, 1988. (d) Spek, A. L. PLATON-94. University of Utrecht, The Netherlands, 1994.