ORGANOMETALLICS

Volume 17, Number 21, October 12, 1998

Communications

Diastereoselective Preparation of Chiral-at-Metal Organometallic Complexes Using a Chelating Sulfoxide−Carboxylate Ligand

Michael Otto, Jonathan Parr,* and Alexandra M. Z. Slawin

Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE12 3TU, U.K.

Received July 10, 1998

*Summary: Using the bidentate ligand (R)-2-[(R)-phenylsulfinyl]propionic acid (**1**), a range of new chiral-at-metal complexes of general formula [(L)M(S,O)Cl] have been prepared where L = Cp*, M = Rh^{III} (**2**), Ir^{III} (**3**), L = p-cymene, M = Ru^{II} (**4**), Os^{II} (**5**), and L = $C_6(CH_3)_6$, M = Ru^{II} (**6**) and S,O is the monoanion obtained from the K(t-BuO) deprotonation of **1**. Molecular structures for **2**−**6** are reported, confirming that these complexes are formed with excellent stereospecificity at the metal center in moderate (59%, **6**) to excellent (92%, **3**) isolated single-isomer yields.*

The chemical literature contains a wealth of reports on the use of chiral bidentate ligands in the preparation of complexes of transition metals which have applications in asymmetric catalysis.[1] The majority of these reports focus on the use of a small number of by now well-known ligands, usually diphosphines and phosphorus−nitrogen (P,N) ligands.[2] Although there are some tremendously powerful reagents developed from this basis, there are other approaches available which have received relatively little attention and which may prove as useful. With such an end in mind, we are interested in the preparation of chiral-at-metal complexes[3] with potential catalytic applications, especially examples where their resolution is facile.[4]

A practical approach to this resolution involves the use of chiral bidentate ligands with mixed donor sets, so that complexation to prochiral metal fragments gives diastereomeric products which can subsequently be resolved. The appearance of a publication detailing the highly efficient resolution of a chiral ruthenium compound using a monodentate chiral sulfoxide ligand[5] suggested to us the possibility of using chelating ligands comprising such donor groups in this way.

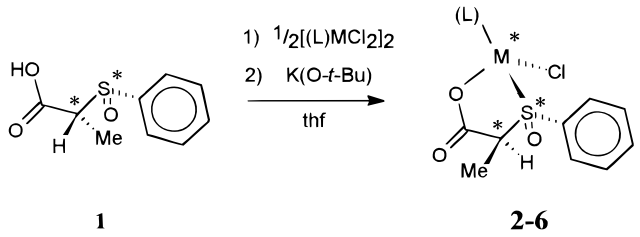
A search of the literature for a suitable ligand yielded the acid **1**, which was previously prepared by Seebach as part of an investigation into the methodology of chiral sulfoxide preparation.[6] When deprotonated, **1** presents a monobasic [S,O] donor set where the S(IV) can be thought of as a much softer donor than the carboxylate oxygen. As such, the monoanion of **1** is an excellent prospect for our purposes, since the complexes formed might also be expected to show an electronic asymmetry toward any substrate coordinated to the metal transoid

* To whom correspondence should be addressed.

(1) Kagan, H. B. In *Comprehensive Organometallic Chemistry*, 1st ed.; Abel, E., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 8, p 463.
(2) For leading references see: Takaya, H.; Ohta, T.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993. Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051.
(3) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.
(4) Grotjahn, D. B.; Joubran, C.; Hubbard, J. L. *Organometallics* **1996**, *15*, 1230. Alcock, N. W.; Brown, J. M.; Maddox, P. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1532. Parr, J.; Loza, M. L.; Slawin, A. M. Z. *Polyhedron* **1997**, *16*, 2321.
(5) Faller, J. W.; Ma, Y. *Organometallics* **1992**, *11*, 2726.
(6) Breitschuh, R.; Seebach, D. *Synthesis* **1992**, 1170.

S0276-7333(98)00588-3 CCC: $15.00
Publication on Web 09/24/1998

Scheme 1. Preparation of 2−6[a]



1 **2-6**

[a] Asterisks indicate stereogenic centers.

to the chelate,[7] thereby enhancing the likelihood of such compounds being useful reagents.

The complexes **2**−**6** were all prepared by the same route, outlined in Scheme 1. The preparation of **2** is given as an example, along with the analytical data for all complexes prepared.[8] The products **2**−**6** are expected to have three chiral centers, two on the ligand and a third on the pseudotetrahedral metal formed on complexation. Initial predictions led to the expectation of a mixture of isomers *R*,*S*,*R* and *S*,*S*,*R*, with the descriptors referring to the metal, the S(IV), and C(2), respectively. (The descriptor of the S(IV) changes on complexation, as the lowest priority position in the free ligand becomes the highest priority in the complex.) However, the products isolated were exclusively *R*,*S*,*S* in high yield. This encompasses two unexpected results: first, the selectivity in the formation of the chiral metal, and second, the inversion of the chirality at C(2). If we take the selectivity at the metal first, it seems likely that this preference is a consequence of the steric constraint imposed by the phenyl substituent on the S(IV). The two possible configurations *R* and *S* at the metal give rise to quite different dispositions of this sterically demanding group relative to the polyhapto ligand, so that in the *S* isomer this phenyl would be brought very close to the ring ligand, whereas in the *R* isomer these groups are oriented away from each other. The molecular structure of **2** is shown in Figure 1 and is isostructural with **3**. The molecular structures of **5**, isostructural with **4**, and **6** are given in Figures 2 and 3, respectively.[9] Selected bond length and angle data are presented in Table 1.

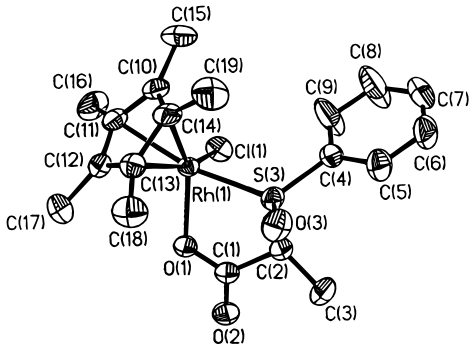


Figure 1. Molecular structure of **2**, shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

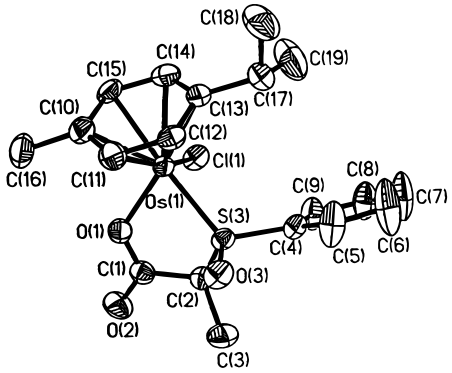


Figure 2. Molecular structure of **5**, shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The chirality at C(2) in the starting material was established by crystallography and by comparison of spectroscopic and polarimetric data with those in the original report of Seebach. It is evident that there is an epimerization that takes place during the reaction, but the origin of the stereoselectivity is not clear. The free acid itself is isomerized rapidly in thf solution in the presence of K(*t*-BuO), but under these conditions there is no diastereoselectivity and a 50:50 mixture of *R*,*S* and *R*,*R* is obtained. Since there is a selectivity in this isomerization during these complexations, we conclude that the chiral complex formed on initial association of the ligand with the metal directs the sense of the reprotonation at C(2). Seemingly, then, this preparative route gives simultaneous selectivity in the chirality both at the metal and at C(2).

The ^{1}H NMR spectra of the crude reaction products **2**−**6** indicate the presence of small amounts (ca. 1−5%)

(7) See for example: Faller, J. W.; Nguyen, J. T.; Ellis, W.; Mazzieri, M. R. *Organometallics* **1993**, *12*, 1434. Faller, J. W.; Murray, H. H.; Chao, K. H. *Organometallics* **1984**, *3*, 1231.

(8) A solution of (*R*,*R*)-**1** (77 mg, 0.38 mmol) and $[Cp^*RhCl_2]_2$ (120 mg, 0.38 mmol) in thf (10 mL) was stirred for 30 h before the addition of K(O-*t*-Bu) (42.5 mg, 0.38 mmol). The reaction mixture was stirred for a further 2 h, giving a clear orange solution. The solvent was removed in vacuo, the solid residue extracted with CH_2Cl_2 (2 mL), and this extract filtered through Celite. The slow diffusion of hexane vapor into this solution at room temperature gave crystals of **2** in 82% yield (160 mg). Mp: 180 °C. ^{1}H NMR: δ 1.27 (d, 3H, C(3)H_3), 1.70 (s, 15H, Cp*), 4.18 (q, 1H, C(2)*H*), 7.55−8.33 (m, 5H, C_6H_5). Anal. Calcd for $C_{19}H_{24}O_3SClRh$: C, 48.47; H, 5.14. Found: C, 48.21; H, 5.0. **3** was prepared analogously in 92% yield. Mp: 175−176 °C. ^{1}H NMR: δ 1.32 (d, 3H, C(3)H_3), 1.70 (s, 15H, Cp*), 4.15 (q, 1H, C(2)*H*), 7.54−8.29 (m, 5H, C_6H_5). Anal. Calcd for $C_{19}H_{24}O_3SClIr$: C, 40.74; H, 4.32. Found: C, 40.36; H, 4.25. **4** was obtained in 79% yield. Mp: 173−174 °C. ^{1}H NMR: δ 1.13 (d, 6H, C(CH_3)$_2$), 1.20 (d, 3H, C(3)H_3), 2.18 (s, 3H, C(16)H_3), 2.80 (hept, 1H, C(17)*H*), 3.91 (q, 1H, C(2)*H*), 5.40−5.72 (m, 4H, C_6H_4), 7.52−8.27 (m, 5H, C_6H_5). Anal. Calcd for $C_{19}H_{22}O_3SClRu$: C, 48.87; H, 4.75. Found: C, 48.58; H, 4.61. **5** was obtained in 72% yield. Mp: 177−178 °C. ^{1}H NMR: δ 1.02 (d, 6H, C(CH_3)$_2$), 1.28 (d, 3H, C(3)H_3), 2.28 (s, 3H, C(16)H_3), 2.76 (hept, 1H, C(17)*H*), 4.05 (q, 1H, C(2)*H*), 5.55−5.89 (m, 4H, C_6H_4), 7.51−8.25 (m, 5H, C_6H_5). Anal. Calcd for $C_{19}H_{22}O_3SClOs$: C, 41.04; H, 3.99. Found: C, 40.85; H, 4.06. **6** was obtained in 59% yield. Mp: 194−196 °C. ^{1}H NMR: δ 1.19 (d, 3H, C(3)H_3), 2.07 (s, 18H, C$_6$(CH_3)$_6$), 3.94 (q, 1H, C(2)*H*), 7.52−8.28 (m, 5H, C_6H_5). Anal. Calcd for $C_{27}H_{27}O_3SClRu$: C, 50.86; H, 5.49. Found: C, 50.92; H, 5.31. All ^{1}H NMR spectra were recorded at 250 MHz in $CDCl_3$ and referenced to external TMS.

(9) Structural data were collected using a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation. Crystal data for **2**: $C_{19}H_{24}O_3SClRh$, 470.80, orthorhombic, space group $P2_12_12_1$, a = 9.51350(10) Å, b = 14.3246(2) Å, c = 14.7892(2) Å, V = 2015.43(4) Å^3, Z = 4, D_c = 1.552 g/cm^3, μ = 1.098 mm^{-1}, R (R_w) = 0.022 (0.054) for 4689 observed reflections. **3**: $C_{19}H_{24}O_3SClIr$, 560.09, orthorhombic, space group $P2_12_12_1$, a = 9.4732(3) Å, b = 14.3708(4) Å, c = 14.8939(4) Å, V = 2027.62(10) Å^3, Z = 4, D_c = 1.835 g/cm^3, μ = 6.834 mm^{-1}, R (R_w) = 0.027 (0.053) for 4738 observed reflections. **4**: $C_{19}H_{23}O_3SClRu$, 467.95, monoclinic, space group $P2_1$, a = 8.5373(5) Å, b = 11.8656(7) Å, c = 9.7966(6) Å, β = 95.1950(10)°, V = 988.32(10) Å^3, Z = 2, D_c = 1.572 g/cm^3, μ = 1.048 mm^{-1}, R (R_w) = 0.031 (0.050) for 3587 observed reflections. **5**: $C_{19}H_{23}O_3SClOs$, 557.08, monoclinic, space group $P2_1$, a = 8.5531(2) Å, b = 11.8841(2) Å, c = 9.76410(10) Å, β = 95.4060(10)°, V = 988.07(3) Å^3, Z = 2, D_c = 1.872 g/cm^3, μ = 6.708 mm^{-1}, R (R_w) = 0.031 (0.077) for 4112 observed reflections. **6**: $C_{21}H_{27}O_3SClRh$, 496.01, orthorhombic, space group $P2_12_12_1$, a = 8.52870(10) Å, b = 15.1311(7) Å, c = 16.6571(3) Å, V = 2149.58(5) Å^3, Z = 4, D_c = 1.533 g/cm^3, μ = 0.969 mm^{-1}, R (R_w) = 0.030 (0.066) for 4956 observed reflections.

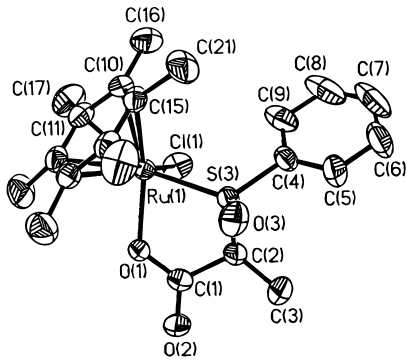


Figure 3. Molecular structure of **6**, shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) for 2−6

	2	**3**	**4**	**5**	**6**
M−S	2.3205(5)	2.2854(11)	2.2931(7)	2.2938(13)	2.3082(7)
M−Cl	2.4244(6)	2.422(12)	2.3996(8)	2.404(2)	2.4164(7)
M−O	2.096(2)	2.102(3)	2.087(2)	2.091(4)	2.104(2)
S−O	1.482(2)	1.479(4)	1.478(2)	1.468(4)	1.478(2)
$M-C_{av}$ (arene)[a]	2.165	2.177	2.221	2.201	2.222

	2	**3**	**4**	**5**	**6**
O−M−S	78.24	78.92	77.60	77.82	77.98
M−S−C(2)	99.91	100.89	100.57	101.2	99.82
S−M−Cl	94.15	94.07	89.58	89.19	90.59
O−M−Cl	87.64	84.85	86.20	85.05	86.14
O−M−S	78.24	78.92	77.60	77.82	77.98

[a] Calculated as the arithmetic mean.

of compounds which are sufficiently similar to the principal products to indicate that they are one of the other possible isomers which could be formed. They are formed in such small quantities that so far they resist identification, and although we are currently pursuing possible alternative routes to the isomers of **2**−**6**, we cannot identify these minor products with confidence.

The complexes prepared are of interest to us because of their potential application in catalysis, especially for asymmetric hetero Diels−Alder reactions. Chiral sulfoxides have a developed role in stereoselective synthesis in their own right,[10] but to our knowledge, only one report has appeared detailing the use of a chelating ligand comprising a chiral sulfoxide as a donor in homogeneous catalysis, and in this instance the catalyst species was not identified.[11] To ascertain whether the metals would be stereochemically rigid on dehalogenation to form Lewis acid species, **2** was treated with 1 equiv of $AgSbF_6$ in thf solution. The solution was filtered to remove AgCl and then equilibrated for 2 h before the addition of 1 equiv of PPh_3. The ^{31}P NMR of the resulting solution revealed a single peak (+34.63 ppm, $^1J\{^{103}Rh-^{31}P\} = 149.6$ Hz), indicating that no racemization had occurred, although this observation does not preclude the possibility that the complex has undergone an inversion.

We have demonstrated that it is possible to prepare a range of single-isomer chiral-at-metal compounds in high yield and high selectivity in a one-pot reaction using an economically cheap chiral sulfoxide ligand. The application of these complexes in homogeneous catalysis is currently under investigation in our laboratory.

Acknowledgment. We thank Johnson-Matthey plc for the generous loan of precious metal salts, Dr. Steve Aucott for the generous gift of $[(C_6(CH_3)_6)RuCl_2]_2$, and Dr. Pravat Bhattacharyya for helpful discussions.

Supporting Information Available: Listings giving complete crystallographic data and additional views of **2**−**6** (33 pages). Ordering information is given on any current masthead page.

OM9805887

(10) Mikolajczyk, M.; Drabowicz, J.; Kielbasinski, J. *Chiral Sulfur Reagents: Applications in Asymmetric and Stereoselective Synthesis*; CRC Press: Boca Raton, FL, 1997.

(11) Allen, J. V.; Bower, J. F.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1994**, *5*, 1895.