C(7)	0.7037 (5)	0.3696 (5)	0.0152 (4)	5.3 (3)
C(8)	0.8285 (5)	0.4823 (5)	0.0011 (4)	5.3 (4)
C(9)	0.7884 (5)	0.5628 (5)	0.0355 (4)	5.0 (3)
C(10)	0.7615 (6)	0.6310 (5)	0.1491 (4)	6.4 (4)

† Occupancy of 0.85.
‡ Occupancy of 0.15.

Table 2. *Geometric parameters* (Å, °)

Cu—N(1)	2.092 (5)	N(3)—C(6)	1.484 (9)
Cu—N(2)	2.015 (5)	N(4)—C(7)	1.499 (9)
Cu—N(3)	2.030 (5)	N(4)—C(8)	1.491 (9)
Cu—N(4)	2.025 (5)	N(5)—C(9)	1.471 (8)
Cu—N(5)	2.157 (5)	N(5)—C(10)	1.47 (1)
N(1)—C(1)	1.467 (9)	C(2)—C(3)	1.50 (1)
N(1)—C(2)	1.474 (9)	C(4)—C(5)	1.50 (1)
N(2)—C(3)	1.46 (1)	C(6)—C(7)	1.50 (1)
N(2)—C(4)	1.480 (9)	C(8)—C(9)	1.48 (1)
N(3)—C(5)	1.49 (1)		
N(1)—Cu—N(2)	84.4 (2)	Cu—N(3)—C(6)	106.6 (4)
N(1)—Cu—N(3)	140.2 (2)	C(5)—N(3)—C(6)	117.5 (6)
N(1)—Cu—N(4)	99.6 (2)	Cu—N(4)—C(7)	108.5 (4)
N(1)—Cu—N(5)	108.0 (2)	Cu—N(4)—C(8)	107.3 (4)
N(2)—Cu—N(3)	84.6 (2)	C(7)—N(4)—C(8)	111.9 (5)
N(2)—Cu—N(4)	167.8 (2)	Cu—N(5)—C(9)	103.8 (4)
N(2)—Cu—N(5)	104.9 (2)	Cu—N(5)—C(10)	117.9 (4)
N(3)—Cu—N(4)	85.1 (2)	C(9)—N(5)—C(10)	112.1 (5)
N(3)—Cu—N(5)	111.8 (2)	N(1)—C(2)—C(3)	108.7 (6)
N(4)—Cu—N(5)	84.9 (2)	N(2)—C(3)—C(2)	108.2 (6)
Cu—N(1)—C(1)	120.1 (5)	N(2)—C(4)—C(5)	108.8 (6)
Cu—N(1)—C(2)	106.7 (4)	N(3)—C(5)—C(4)	107.4 (6)
C(1)—N(1)—C(2)	111.4 (6)	N(3)—C(6)—C(7)	107.1 (6)
Cu—N(2)—C(3)	106.7 (4)	N(4)—C(7)—C(6)	110.2 (5)
Cu—N(2)—C(4)	109.7 (4)	N(4)—C(8)—C(9)	110.9 (5)
C(3)—N(2)—C(4)	114.5 (6)	N(5)—C(9)—C(8)	109.7 (5)
Cu—N(3)—C(5)	106.1 (4)		

The structure was solved for non-H atoms by direct and Fourier methods, and refinement was by full-matrix least squares [O(1′) refined isotropically]. H atoms were found by a difference Fourier method and theoretical calculation. The high value of $(\Delta/\sigma)_{max}$ results from the disordered perchlorate groups. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71180 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1026]

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Preparation of Chiral Tricarbonyl(η^6-arene)chromium(0) Complexes Derived from (*S*)-2-Indolinecarboxylic Acid

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Abstract

The title diastereomeric mixture of (*S*,*S*)- and (*R*,*S*)-tricarbonyl[methyl *N*-*tert*-butyldimethylsilyl-(*S*)-η^6-indolene-2-carboxylate]chromium(0) was prepared by first converting (*S*)-2-indolinecarboxylic acid to *N*-*tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester. The enantiomerically pure ester was subjected to complexation conditions using triammine(tricarbonyl)chromium and hexacarbonylchromium to yield a 1:1 diastereomeric mixture of the corresponding tricarbonyl(η^6-arene)chromium(0) complexes. Chromatographic separation of the two diastereomers which result from addition of the tricarbonyl fragment to either face of the arene portion of the ester was effected. The bonding distances for the two diastereomers are very similar, but they have significantly different molecular conformations. These differences appear to result primarily from differences in the steric interaction between the acid ester group and the tricarbonylchromium fragment.

Comment

(*S*)-α,α-Diphenyl(indolin-2-yl)methanol, when converted to the corresponding oxazaborolidine using borane, has been shown to be effective as a catalyst for the enantioselective reduction of prochiral ketones using boranes (Martens, Dauelsberg, Behnen & Wallbaum, 1992). This observation was in accordance with pioneering work (Corey, Bakshi & Shibata, 1987) which established the general utility of chiral (*S*)-proline derived oxazaborolidines as extremely versatile enantioselective catalysts for the reduction of a variety of prochiral ketones using hydrides. The preparation and separation of both diastereomers (1-*S*,*S* and 1-*R*,*S*) of the tricarbonyl(η^6-arene)chromium(0) complexes of *N*-*tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester has been achieved. The structures represent synthetic precursors to both diastereomers of the tricarbonyl(η^6-arene)chromium(0) complexes of

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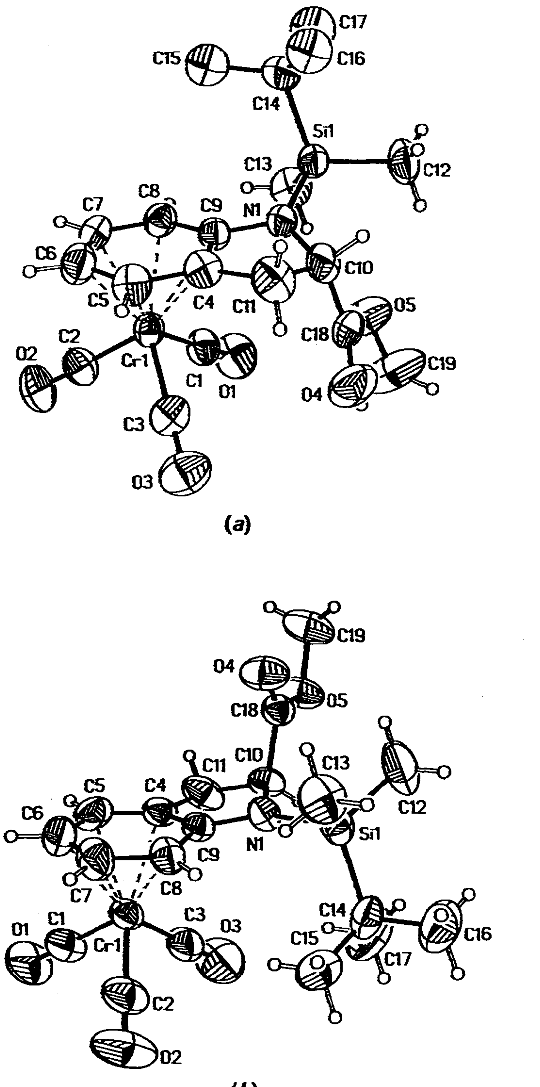
(*S*)-α,α-diphenyl(indolin-2-yl)methanol. Which, by virtue of their inbuilt axial chirality, will allow the effect of both the steric bulk and potential attractive interactions of the tricarbonylchromium group to be monitored with respect to the transition-state assembly involved in the oxazaborolidine-catalyzed enantioselective reduction of prochiral ketones using the derived oxazaborolidines. Such effects have been demonstrated previously, using systems derived from tricarbonyl(η^6-arene)chromium(0) complexes of norephedrines as catalysts for the enantioselective addition of dialkyl zincs to aldehydes (Heaton & Jones, 1992).



(*a*)

(*b*)

Fig. 1. Views showing the labeling of the non-H atoms. Thermal ellipsoids are shown at the 50% probability level for (*a*) 1-*S*,*S* and (*b*) 1-*R*,*S*.

Bonding distances for the two diastereomers are virtually identical. Slight differences in bonding angles and significant differences in the molecular conformation of the disubstituted indolinyl group appear to arise from the increased steric interaction between the acid ester group and the tricarbonylchromium fragment upon complexation of the *S* face of the arene, resulting in rotation of the acid ester group to an orientation tangential to the steric bulk of the tricarbonylchromium fragment. In both complexes, the silyl fragment assumes an orientation which minimizes interaction of the *tert*-butyl group with the acid ester group. The indolinyl group in both complexes has an envelope comformation, in which the atoms are approximately coplanar [for 1-*S*,*S*: maximum deviation = 0.05 Å, mean deviation = 0.03 (2) Å; for 1-*R*,*S*: maximum deviation = 0.10 Å, mean deviation = 0.06 (3) Å] except for the C(10) atom, which is displaced toward the *S* face of the plane by 0.30 Å for 1-*S*,*S* and by 0.28 Å for 1-*R*,*S*. The larger deviations from planarity in the indolinyl group in the 1-*R*,*S* form appear to result from steric repulsion between the tricarbonylchromium fragment and the *tert*-butyl group of the silyl fragment.

The methyl C atoms of the *tert*-butyl group of the 1-*S*,*S* form are disordered over two sets of equivalent sites which are related by a 24° rotation about the Si—C bond; no such disorder was observed in the 1-*R*,*S* form. In spite of the fact that 1-*R*,*S* is the more ordered solid, 1-*S*,*S* appears to be the more stable crystalline form, as it has a higher melting point (411 *versus* 369 K), a lower average thermal motion (0.067 *versus* 0.071 Å^2) and smaller *V*/*Z* value (538 *versus* 541 Å^3). It is interesting to note that, although the two diastereomers have significantly different conformations and exhibit no obvious similarities in crystal packing, they crystallize in the same space group with nearly identical unit-cell dimensions.

Experimental

Enantiomer 1-*S*,*S*

Crystal data

$[Cr(C_{16}H_{25}NO_2Si)(CO)_3]$
$M_r = 427.49$
Orthorhombic
$P2_12_12_1$
$a = 10.327\ (4)$ Å
$b = 11.306\ (3)$ Å
$c = 18.427\ (6)$ Å
$V = 2152\ (1)$ Å^3
$Z = 4$
$D_x = 1.32$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 14$–$20°$
$\mu = 0.60$ mm^{-1}
$T = 294$ K
Parallelepiped
0.29 × 0.23 × 0.21 mm
Yellow

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.97, T_{max} = 1.00
1646 measured reflections
1646 independent reflections
1426 observed reflections [$I > 3\sigma(I)$]

θ_{max} = 22.5°
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 97 reflections intensity variation: ±1%

Refinement

Refinement on F
Final R = 0.0383
wR = 0.0485
S = 1.51
1426 reflections
243 parameters
$w = 1/(\sigma^2F + 0.0005\sigma F)$

$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Enantiomer 1-*R*,*S*

Crystal data

$[Cr(C_{16}H_{25}NO_2Si)(CO)_3]$
M_r = 427.49
Orthorhombic
$P2_12_12_1$
a = 10.183 (3) Å
b = 11.618 (4) Å
c = 18.290 (5) Å
V = 2164 (1) Å^3
Z = 4
D_x = 1.31 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 13–22°
μ = 0.60 mm^{-1}
T = 294 K
Parallelepiped
0.27 × 0.27 × 0.20 mm
Yellow

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.98, T_{max} = 1.00
1654 measured reflections
1654 independent reflections
1328 observed reflections [$I > 3\sigma(I)$]

θ_{max} = 22.5°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 97 reflections intensity variation: ±1%

Refinement

Refinement on F
Final R = 0.0289
wR = 0.0369
S = 1.09
1328 reflections
245 parameters
$w = 1/(\sigma^2F + 0.0005\sigma F)$

$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. Atoms C(15)–C(17) and C(15*A*)–C(17*A*) represent equivalent alternative sites for the disordered *tert*-butyl group.

	x	y	z	U_{eq}
Enantiomer 1-*S*,*S*				
Cr(1)	0.0228 (1)	0.1104 (1)	0.7063 (1)	0.042 (1)
Si(1)	−0.3379 (2)	−0.0664 (2)	0.5799 (1)	0.048 (1)
O(1)	0.1010 (5)	−0.0656 (5)	0.5944 (3)	0.080 (2)
O(2)	0.2394 (5)	0.0396 (5)	0.8032 (3)	0.076 (2)
O(3)	0.1948 (6)	0.2876 (5)	0.6339 (3)	0.084 (2)
O(4)	−0.0345 (6)	0.2278 (5)	0.4904 (3)	0.089 (2)
O(5)	−0.1008 (6)	0.0427 (5)	0.4781 (3)	0.082 (2)
N(1)	−0.2433 (5)	0.0599 (5)	0.6022 (2)	0.045 (2)
C(1)	0.0729 (6)	0.0032 (6)	0.6375 (3)	0.052 (2)
C(2)	0.1556 (6)	0.0666 (6)	0.7648 (4)	0.053 (2)
C(3)	0.1271 (7)	0.2201 (6)	0.6628 (4)	0.055 (2)
C(4)	−0.1606 (6)	0.2057 (6)	0.6753 (3)	0.050 (2)
C(5)	−0.1116 (6)	0.2506 (6)	0.7416 (3)	0.055 (2)
C(6)	−0.0910 (7)	0.1758 (6)	0.7992 (4)	0.061 (2)
C(7)	−0.1122 (6)	0.0540 (6)	0.7904 (3)	0.054 (2)
C(8)	−0.1575 (6)	0.0065 (5)	0.7257 (3)	0.046 (2)
C(9)	−0.1894 (5)	0.0852 (5)	0.6686 (3)	0.041 (2)
C(10)	−0.2226 (6)	0.1657 (6)	0.5552 (3)	0.055 (2)
C(11)	−0.2023 (7)	0.2673 (6)	0.6075 (4)	0.064 (3)
C(12)	−0.3966 (8)	−0.0419 (8)	0.4860 (3)	0.079 (3)
C(13)	−0.2343 (8)	−0.2015 (7)	0.5839 (4)	0.073 (3)
C(14)	−0.4837 (7)	−0.0773 (7)	0.6428 (4)	0.072 (3)
C(15)	−0.4552 (17)	−0.0838 (17)	0.7232 (9)	0.078 (5)
C(16)	−0.5664 (19)	0.0407 (18)	0.6290 (11)	0.081 (5)
C(17)	−0.564 (2)	−0.1921 (19)	0.6171 (12)	0.091 (7)
C(15*A*)	−0.4437 (17)	−0.1456 (16)	0.7175 (10)	0.075 (5)
C(16*A*)	−0.537 (2)	0.048 (2)	0.6599 (12)	0.0100 (7)
C(17*A*)	−0.592 (2)	−0.1508 (19)	0.6046 (12)	0.087 (6)
C(18)	−0.1077 (7)	0.1510 (6)	0.5054 (3)	0.056 (2)
C(19)	−0.0003 (11)	0.0228 (8)	0.4257 (5)	0.0125 (5)
Enantiomer 1-*R*,*S*				
Cr(1)	0.1283 (1)	0.3997 (1)	0.7156 (1)	0.047 (1)
Si(1)	0.4921 (1)	0.3991 (2)	0.8806 (1)	0.052 (1)
O(1)	−0.1441 (4)	0.3841 (5)	0.6568 (3)	0.098 (2)
O(2)	0.1487 (5)	0.6440 (4)	0.6663 (4)	0.110 (2)
O(3)	0.0131 (5)	0.4650 (5)	0.8585 (3)	0.109 (2)
O(4)	0.4679 (4)	0.0908 (4)	0.8578 (2)	0.072 (2)
O(5)	0.3390 (4)	0.0625 (3)	0.9545 (2)	0.064 (1)
N(1)	0.3619 (4)	0.3172 (3)	0.8434 (2)	0.044 (1)
C(1)	−0.0389 (6)	0.3912 (6)	0.6791 (3)	0.065 (2)
C(2)	0.1411 (7)	0.5507 (6)	0.6857 (4)	0.071 (2)
C(3)	0.0595 (6)	0.4417 (5)	0.8022 (3)	0.065 (2)
C(4)	0.2049 (5)	0.2383 (4)	0.7662 (3)	0.050 (2)
C(5)	0.1505 (6)	0.2131 (5)	0.6986 (4)	0.067 (2)
C(6)	0.1975 (7)	0.2731 (6)	0.6373 (3)	0.073 (3)
C(7)	0.2927 (6)	0.3572 (6)	0.6448 (3)	0.066 (2)
C(8)	0.3496 (5)	0.3809 (5)	0.7130 (3)	0.049 (2)
C(9)	0.3124 (5)	0.3155 (4)	0.7730 (3)	0.040 (2)
C(10)	0.2943 (5)	0.2258 (4)	0.8860 (3)	0.045 (2)
C(11)	0.1744 (6)	0.1902 (5)	0.8407 (3)	0.066 (2)
C(12)	0.5494 (8)	0.3205 (6)	0.9631 (4)	0.100 (3)
C(13)	0.6299 (5)	0.4092 (6)	0.8143 (3)	0.078 (2)
C(14)	0.4302 (6)	0.5457 (5)	0.9082 (3)	0.062 (2)
C(15)	0.3956 (8)	0.6189 (5)	0.8417 (3)	0.088 (3)
C(16)	0.5369 (8)	0.6083 (7)	0.9520 (4)	0.098 (3)
C(17)	0.3070 (8)	0.5343 (7)	0.9576 (4)	0.101 (3)
C(18)	0.3803 (5)	0.1206 (4)	0.8964 (3)	0.048 (2)
C(19)	0.4006 (7)	−0.0473 (5)	0.9678 (4)	0.088 (3)

Table 2. *Geometric parameters* (Å, °)

	1-*S*,*S*	1-*R*,*S*
Cr(1)—C(1)	1.829 (7)	1.831 (6)
Cr(1)—C(2)	1.814 (7)	1.842 (7)
Cr(1)—C(3)	1.828 (7)	1.798 (6)
Cr(1)—C(4)	2.253 (7)	2.231 (5)

Cr(1)—C(5)	2.204 (7)	2.203 (6)
Cr(1)—C(6)	2.203 (7)	2.172 (7)
Cr(1)—C(7)	2.179 (7)	2.175 (6)
Cr(1)—C(8)	2.231 (6)	2.265 (5)
Cr(1)—C(9)	2.316 (6)	2.361 (5)
Si(1)—N(1)	1.778 (5)	1.768 (4)
Si(1)—C(12)	1.854 (7)	1.858 (7)
Si(1)—C(13)	1.866 (8)	1.858 (6)
Si(1)—C(14)	1.903 (7)	1.885 (6)
O(1)—C(1)	1.150 (9)	1.149 (8)
O(2)—C(2)	1.158 (8)	1.143 (8)
O(3)—C(3)	1.164 (9)	1.165 (8)
O(4)—C(18)	1.184 (9)	1.189 (7)
O(5)—C(18)	1.325 (9)	1.326 (6)
O(5)—C(19)	1.44 (1)	1.442 (7)
N(1)—C(9)	1.375 (7)	1.382 (6)
N(1)—C(10)	1.492 (8)	1.486 (6)
C(4)—C(5)	1.416 (9)	1.386 (9)
C(4)—C(9)	1.400 (9)	1.422 (7)
C(4)—C(11)	1.49 (1)	1.506 (8)
C(5)—C(6)	1.374 (9)	1.404 (9)
C(6)—C(7)	1.40 (1)	1.384 (9)
C(7)—C(8)	1.388 (8)	1.403 (8)
C(8)—C(9)	1.417 (8)	1.388 (7)
C(10)—C(11)	1.51 (1)	1.533 (8)
C(10)—C(18)	1.509 (9)	1.516 (7)
C(14)—C(15)	1.51 (2)	1.525 (9)
C(14)—C(16)	1.60 (2)	1.53 (1)
C(14)—C(17)	1.61 (2)	1.55 (1)
C(14)—C(15*A*)	1.63 (2)	
C(14)—C(16*A*)	1.55 (2)	
C(14)—C(17*A*)	1.56 (2)	
C(1)—Cr(1)—C(2)	90.9 (3)	90.5 (3)
C(1)—Cr(1)—C(3)	88.8 (3)	88.5 (3)
C(2)—Cr(1)—C(3)	90.0 (3)	91.8 (3)
N(1)—Si(1)—C(12)	106.0 (3)	106.5 (3)
N(1)—Si(1)—C(13)	109.5 (3)	110.4 (2)
N(1)—Si(1)—C(14)	110.2 (3)	109.8 (2)
C(12)—Si(1)—C(13)	110.3 (4)	108.9 (3)
C(12)—Si(1)—C(14)	108.6 (3)	109.4 (3)
C(13)—Si(1)—C(14)	112.1 (4)	111.7 (3)
C(18)—O(5)—C(19)	116.1 (6)	116.6 (4)
Si(1)—N(1)—C(9)	126.5 (4)	129.7 (3)
Si(1)—N(1)—C(10)	126.1 (4)	122.0 (3)
C(9)—N(1)—C(10)	107.0 (5)	108.1 (4)
Cr(1)—C(1)—O(1)	178.1 (6)	178.8 (6)
Cr(1)—C(2)—O(2)	178.8 (6)	179.1 (6)
Cr(1)—C(3)—O(3)	178.3 (6)	177.5 (6)
C(5)—C(4)—C(9)	120.0 (6)	121.4 (5)
C(5)—C(4)—C(11)	131.1 (6)	130.3 (5)
C(9)—C(4)—C(11)	108.6 (5)	108.2 (4)
C(4)—C(5)—C(6)	120.1 (6)	118.1 (5)
C(5)—C(6)—C(7)	119.3 (6)	120.7 (6)
C(6)—C(7)—C(8)	122.2 (6)	121.1 (5)
C(7)—C(8)—C(9)	118.2 (6)	118.9 (5)
N(1)—C(9)—C(4)	111.5 (5)	111.8 (4)
N(1)—C(9)—C(8)	128.6 (5)	129.0 (4)
C(4)—C(9)—C(8)	119.8 (5)	119.0 (4)
N(1)—C(10)—C(11)	105.0 (5)	106.1 (4)
N(1)—C(10)—C(18)	112.2 (5)	112.0 (4)
C(11)—C(10)—C(18)	111.2 (6)	108.1 (4)
C(4)—C(11)—C(10)	102.7 (5)	103.0 (4)
Si(1)—C(14)—C(15)	116.4 (8)	111.5 (4)
Si(1)—C(14)—C(16)	105.8 (8)	109.4 (5)
Si(1)—C(14)—C(17)	106.3 (9)	110.4 (4)
C(15)—C(14)—C(16)	107 (1)	108.4 (5)
C(15)—C(14)—C(17)	110 (1)	109.0 (5)
C(16)—C(14)—C(17)	110 (1)	108.0 (5)
Si(1)—C(14)—C(15*A*)	110.1 (7)	
Si(1)—C(14)—C(16*A*)	110.1 (9)	
Si(1)—C(14)—C(17*A*)	109.0 (9)	
C(15*A*)—C(14)—C(16*A*)	110 (1)	
C(15*A*)—C(14)—C(17*A*)	108 (1)	
C(16*A*)—C(14)—C(17*A*)	109 (1)	
O(4)—C(18)—O(5)	123.7 (7)	124.4 (5)
O(4)—C(18)—C(10)	124.3 (6)	126.4 (5)
O(5)—C(18)—C(10)	112.0 (6)	109.1 (4)

(*S*)-Indoline-2-carboxylic acid methyl ester (Martens, Dauelsberg, Behnen & Wallbaum, 1992) was converted to *N-tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester using the standard protocol (Corey, Cho, Rucker & Hua, 1981). The silyl ester (0.295 g, 1.01 mmol) was dissolved in a mixture of tetrahydrofuran (2.5 ml) and di-*n*-butyl ether (25 ml). Triammine(tricarbonyl)chromium (0.567 g, 3.03 mmol) and hexacarbonylchromium (0.667 g, 3.03 mmol) were added, and the solution heated to reflux for 3.5 h. The mixture was cooled, filtered through silica gel (10 g) and then concentrated *in vacuo* to yield, as a yellow solid, a 1:1 mixture of the *S*,*S* and *R*,*S* diastereomers of tricarbonyl(η^6-arene)chromium(0) *N-tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester (0.42 g, 98%). The diastereomers were separated by silica-gel chromatography (Still, Kahn & Mitra, 1978) using 70% hexanes, 30% ethyl acetate as eluent, yielding (*S*)-tricarbonyl(η^6-arene)chromium(0) *N-tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester (m.p. 411 K; R_f = 0.62, 3:7 EtOAc:hexanes) and (*R*)-tricarbonyl(η^6- arene)chromium(0) *N-tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester (m.p. 369 K; R_f = 0.60, 3:7 EtOAc:hexanes), both as yellow crystals from ethanol.

Structure solution was by direct methods. Structure refinement was by full-matrix least squares. The refinement of 1-*S*,*S* included positional parameters for the non-H atoms, anisotropic thermal parameters for the full-occupancy atoms and isotropic thermal parameters for the half-occupancy C atoms used to model the disordered *tert*-butyl group. H atoms bonded to the ordered C atoms were included in the structure-factor calculation at optimized positions (C—H = 0.96 Å) with a group isotropic thermal parameter [$U_{\rm iso}$ = 0.091 (6) Å^2]; those bonded to the half-occupancy atoms were not located. For 1-*R*,*S*, the refinement included positional and anisotropic thermal parameters for all the non-H atoms. H atoms were included as for 1-*S*,*S* [$U_{\rm iso}$ = 0.109 (5) Å^2]. Although the complexes were prepared with enantiomerically pure starting materials of known conformation, refinement of the alternative model was carried out in each case. For 1-*S*,*S*, the incorrect enantiomer yielded final residuals of R = 0.043, wR = 0.055 and S = 1.72. For 1-*R*,*S*, refinement of both enantiomers was carried out using two inequivalent octants (h, k, $\pm l$) of data; the model corresponding to the correct conformation gave residuals of R = 0.030, wR = 0.038 and S = 1.09, while the alternative model gave R = 0.037, wR = 0.046 and S = 1.28. H atoms were included in idealized positions using a riding model with a refined group isotropic thermal parameter for ordered atoms only. Computer programs: *SHELXTL* (Sheldrick, 1985). Corrections for Lorentz and polarization, real and imaginary anomalous dispersion: Cromer (1974).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data for both structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71211 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1037]

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Tetraphenylphosphonium Salts of 2-Telluro-5-methylthiophene and its Mercury(II) Metal Complex

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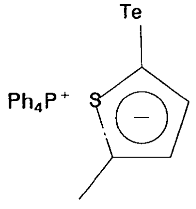
Abstract

Structures of the tetraphenylphosphonium salts of 2-telluro-5-methylthiophene and its mercury(II) metal complex, 2-tris(5-methyl-2-thienyltelluro)mercury(II) have been determined. Both compounds have ionic structures, with no close contacts between ions. The metal complex consists of three 2-telluro-5-methylthiophene ligands bound through the tellurium atoms in a trigonal-planar arrangement about the mercury(II) metal center. Addition of the methyl substituent to the thiophene ring avoids the rotational disorder which can occur upon complexation of the parent ion, 2-tellurothiophene.

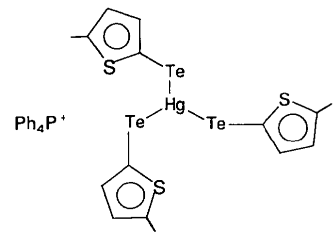
Comment

The complexation chemistry of organothiolate ligands has received considerable attention (Blower & Dilworth, 1987), in part because of their rich structural diversity (Lee, Craig, Ma, Scudder, Bailey & Dance, 1988; Pulla Rao, Dorfman & Holm, 1986; Christou, Hagen & Holm, 1982; Money, Huffman & Christou, 1988). The chemistry of organoselenium and organotellurium compounds, on the other hand, is much less developed (Gysling, 1986). The anion, 2-tellurothiophene, one of the few stable organotellurides (Engman & Cava, 1982), has been used to prepare one of only two known homoleptic metal organotelluride complexes, a tetrameric silver cluster, $Ag_4(TeC_4H_3S)_6^{2-}$ (Zhao, Adcock, Pennington & Kolis, 1990). We were interested in expanding the coordination chemistry of this ion; however, to avoid the formation of disordered complexes as a result of rotation of the thiophene ring about the C—Te bond, as was observed in the silver complex, we have modified the ligand by addition of a methyl substituent at the 5 position.

A solution (2.0 mmol) of the 2-telluro-5-methylthiophene ligand was prepared by dissolving methylthiophene (0.20 ml) in THF (10 ml) at 195 K, followed by addition of *n*-butyllithium (1.6 ml, 3.6 mmol). The solution was allowed to return to room temperature, at which time powdered elemental Te (2.0 mmol) was added. Tetraphenylphosphonium 2-telluro-5-methylthiophene (I) was formed by addition of a stoichiometric amount of tetraphenylphosphonium bromide to the above mixture; the resulting yellow solution was filtered, layered with diethyl ether and stored at 277 K overnight to generate yellow crystals in good yield. The metal complex, tris(2-telluro-5-methylthiophene)mercury(II) was formed by addition of $HgCl_2$ (0.5 mmol) in CH_3CN (10 ml) to a solution of (I) as described above, followed by filtration and layering with diethyl ether to form red crystals of the tetraphenylphosphonium salt (II).



(I)



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