References

Bolhuis, F. van, Koster, B. P. & Migchelsen, T. (1967). *Acta Cryst.* **23**, 90–91.

Ejsmont, K. & Kubiak, R. (1997). *Acta Cryst.* **C53**, 1051–1054.

Ibers, J. A., Pace, L. J., Martinsen, J. & Hoffman, B. M. (1982). *Struct. Bonding (Berlin)*, **50**, 1–55.

Janczak, J. & Kubiak, R. (1999*a*). *Polyhedron*. In the press.

Janczak, J. & Kubiak, R. (1999*b*). *Inorg. Chim. Acta*. In the press.

Janczak, J. & Kubiak, R. (1999*c*). *Acta Cryst.* Submitted.

Janczak, J., Kubiak, R. & Hahn, F. (1999*a*). *Inorg. Chim. Acta*, **281**, 195–200.

Janczak, J., Kubiak, R. & Hahn, F. (1999*b*). *Inorg. Chim. Acta*. In the press.

Janczak, J., Kubiak, R. & Jezierski, A. (1999). *Inorg. Chem.* Submitted.

Karle, I. L. (1955). *J. Chem. Phys.* **23**, 1739.

Kubiak, R. & Janczak, J. (1993). *J. Alloys Compd*, **204**, L7–8.

Kubiak, R. & Janczak, J. (1997). *Proc. SPIE Int. Soc. Opt. Eng.* **3179**, 52–55.

Kubiak, R. & Razik, M. (1998). *Acta Cryst.* **C54**, 483–485.

Kuma (1997). *KM*-4 *Software*. Version KM4b8. Kuma Diffraction, Wrocław, Poland.

Marks, T. J. (1980). *Angew. Chem.* **102**, 886–908; *Angew. Chem. Int. Ed. Engl.* **29**, 857–879.

Millan, A., Bailey, P. M. & Maitlis, P. M. (1982). *J. Chem. Soc. Dalton Trans.* pp. 73–77.

Palmer, S. M., Stanton, J. L., Jaggi, N. K., Hoffman, B. M. & Ibers, J. A. (1985). *Inorg. Chem.* **24**, 2040–2046.

Ray, L. R., Gulliver, D. J., Levanson, W. & Webster, M. (1983). *Inorg. Chem.* **22**, 2362–2366.

Schweiger, K., Huckstadt, H. & Homborg, H. (1998). *Z. Anorg. Allg. Chem.* **624**, 167–168.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Tebbe, K. F. & Plewa, M. (1982). *Z. Anorg. Allg. Chem.* **489**, 111–125.

Acta Cryst. (1999). C55, 361-363

(η^6-Arylhimachalene)tricarbonylchromium(0)

Bahija Abouhamza,[a] Larbi El Firdoussi,[a] Smaïl Allaoud,[a] Abdellah Karim,[a] Alejandro F. Barrero[b] and Miguel Quirós[b]

[a]Laboratoire de Chimie de Coordination, Faculté des Sciences Semlalia, Marrakech, Morocco, and [b]Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain. E-mail: mquiros@goliat.ugr.es

(Received 6 July 1998; accepted 5 October 1998)

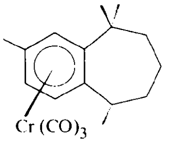
Abstract

The reaction of Cr(CO)$_6$ with arylhimachalene yields the title aryl organometallic compound, tricarbonyl[(1,2,3,4,4a,9a-η)-(7*S*)-3,5,5,9-tetramethyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene]chromium(0), $[\mathrm{Cr}(\mathrm{C}_{15}\mathrm{H}_{22})(\mathrm{CO})_3]$, with the hydrocarbon linked to a Cr(CO)$_3$ tripod group. The crystal structure of one of the stereoisomeric products, *i.e.* that with the tripod *anti* to the methyl group on the asymmetric carbon, is presented here.

Comment

Organic molecules complexed with tricarbonylchromium have attracted much attention in recent years (Solladie-Cavallo, 1989; Sardone *et al.*, 1996). In order to establish the stereochemistry of the final metal-free targets, it is essential to know the spatial structure of the complexes. In a previous work, we have shown that the formation of π-allylpalladium complexes of a natural sesquiterpenic series occurs with high regio- and stereoselectivity (Chiaroni *et al.*, 1993: El Firdoussi *et al.*, 1997).

The reaction of arylhimachalene with hexacarbonylchromium(0) yields two stereoisomers of the corresponding organometallic compound, the existence of which has been established using high resolution NMR spectroscopy. The relative proportions are 60/40, respectively, for the *syn* and *anti* dispositions of the Cr(CO)$_3$ group with respect to the methyl group (C15) at the asymmetric carbon. Good quality single crystals could be obtained for the *anti* isomer, (I), the structure of which is presented here.



(I)

The molecular structure of this compound consists of a Cr atom in the zero oxidation state coordinated by three carbon monoxide molecules and the phenyl ring of arylhimachalene in a η^6 manner. The tricarbonyl–phenyl–chromium(0) residue is a well known motif in organometallic chemistry (see Bentele *et al.*, 1997) and it is even a textbook example for building molecular orbitals (Cotton, 1990), but we have not found a reference to any other compound in which the phenyl ring belongs to a natural product derivative. A view of the molecular structure of (I) is shown in Fig. 1.

The coordination sphere displays the expected linear Cr—C—O disposition, with the carbon monoxide molecules perpendicular to one another and the three C atoms defining a plane parallel to the phenyl ring. The Cr atom is 1.721 (2) Å above the average phenyl plane and is virtually exactly over the centroid of the ring, despite the different Cr—C distances shown in Table 1; such small differences among these distances have also been observed in analogous compounds (Oike *et al.*,

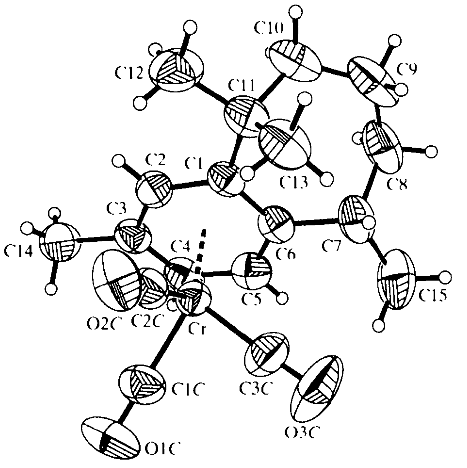


Fig. 1. View of the title compound, with the non-H atoms represented by 50% probability ellipsoids.

1987). The conformation around the Cr—X line (where X is the centroid of the phenyl ring) is neither exactly eclipsed nor staggered, the torsion angle C2—X—Cr—C2C being −18.7 (4)°. The $Cr(CO)_3$ tripod is located on the side of the organic molecule opposite the methyl group (C15) at the asymmetric carbon (C7), thereby defining the *anti* isomer.

The seven-membered ring is folded in such a way that atoms C8, C9 and C10 fall on the side of the phenyl ring opposite to the metal atom. In this way, the C12 and C15 methyl groups occupy equatorial positions and the C13 atom an axial position, which minimizes steric repulsions. A quite short H···H contact (1.90 Å) is present between the H atom at C7 and one of those of the C13 methyl group (H132), the staggered conformation of this methyl group being supported by ΔF maps and the refinement of the corresponding torsional parameter. Despite this, the staggered conformation is still the most stable because a short H···H contact, in this case with H92, would also be present in the eclipsed conformation.

Experimental

Arylhimachalene was obtained by heating a mixture of α-, β- and γ-himachalene at 533 K in the presence of a catalytic amount of Pd/C (5%). (η^6-Arylhimachalene)tricarbonylchromium was synthesized by the reaction of $Cr(CO)_6$ with arylhimachalene in $^n Bu_2O$/dioxane/THF. The products of this reaction were separated by SiO_2 chromatography, crystals of the title compound being obtained by evaporation of the corresponding fraction of the $^n Bu_2O$/dioxane/THF solution.

Crystal data

$[Cr(C_{15}H_{22})(CO)_3]$
$M_r = 338.36$
Orthorhombic
$P2_12_12_1$
$a = 9.3138 (8)$ Å
$b = 10.1641 (8)$ Å
$c = 18.0633 (15)$ Å
$V = 1710.0 (2)$ Å^3
$Z = 4$
$D_x = 1.314$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 12.6–15.9°$
$\mu = 0.678$ mm^{-1}
$T = 293 (2)$ K
Prism
0.30 × 0.25 × 0.20 mm
Yellow

Data collection

Stoe Stadi-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3481 measured reflections
3481 independent reflections
1797 reflections with $I > 2\sigma(I)$

$\theta_{max} = 32.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 27$
3 standard reflections
frequency: 60 min
intensity decay: 5.9%

Refinement

Refinement on F^2
$R(F) = 0.086$
$wR(F^2) = 0.116$
$S = 1.329$
3454 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 1.0P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.301$ e Å^{-3}
$\Delta\rho_{min} = -0.276$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.15 (5)

Table 1. *Selected geometric parameters (Å, °)*

Cr—C3C	1.819 (7)	Cr—C6	2.240 (5)
Cr—C2C	1.834 (7)	Cr—C3	2.245 (6)
Cr—C1C	1.841 (7)	Cr—C1	2.257 (5)
Cr—C2	2.187 (6)	C1C—O1C	1.155 (7)
Cr—C5	2.196 (6)	C2C—O2C	1.158 (7)
Cr—C4	2.220 (6)	C3C—O3C	1.161 (7)
C3C—Cr—C2C	88.1 (3)	O1C—C1C—Cr	179.2 (6)
C3C—Cr—C1C	89.3 (3)	O2C—C2C—Cr	179.3 (6)
C2C—Cr—C1C	88.7 (3)	O3C—C3C—Cr	177.3 (7)

Friedel pairs were not measured since the absolute configuration determination was not an important goal of this work. Nevertheless, the Flack parameter, even if not too properly behaved, seems to confirm the selected enantiomer, which agrees with the known configuration of the organic ligand. The displacement parameters of the H atoms were fixed at 1.2 times those of their parent atoms. The weighting scheme was chosen as a compromise between good $wR2$ and good goodness-of-fit values. Other schemes that yield better goodness-of-fit values lead to much worse $wR2$ values and higher s.u.'s. The value of $R1$ is somewhat high, this perhaps being due to the relatively high limit selected for θ. If reflections with $\theta > 25°$ are cut off, this value drops to 0.0532.

Data collection: *STADI4* (Stoe & Cie, 1996*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1067). Services for accessing these data are described at the back of the journal.

References

Bentele, H. J., Sünkel, K. & Beck, W. (1997). *Chem. Ber.* **130**, 1475–1477.

Chiaroni, A., Riche, C., El Firdoussi, L., Benharref, A. & Karim, A. (1993). *Acta Cryst.* C**49**, 365–368.

Cotton, F. A. (1990). *Chemical Applications of Group Theory*, 3rd ed., pp. 247–249. New York: Wiley Interscience.

El Firdoussi, L., Allaoud, S., Karim, A., Barrero, A. F., Quirós, M., Castanet, Y. & Mortreux, A. (1997). *Acta Cryst.* C**53**, 710–712.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Oike, H., Kai, Y., Miki, K., Tanaka, N. & Kasai, N. (1987). *Bull. Chem. Soc. Jpn*, **60**, 1993–1999.

Sardone, N., Seresini, P. & Zecchi, G. (1996). *Acta Cryst.* C**52**, 613–615.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Solladie-Cavallo, A. (1989). *Advances in Metalorganic Chemistry*, Vol. 1, pp. 99–133. London: JAI Press.

Stoe & Cie (1996*a*). *STADI4. Diffractometer Control Program*. Version 1.06. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1996*b*). *X-RED. Data Reduction Program*. Version 1.08. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1999). C55, 363-365

(*Z*)- and (*E*)-1-methylthio-1-triphenylstannyl-2-phenylethene

Clemens Bruhn,[a] Dirk Steinborn,[a] Tomáš Lébl[b] and Jaroslav Holeček[b]

[a]*Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle (Saale), Germany, and* [b]*Department of General and Inorganic Chemistry, University of Pardubice, Cs. legii 565, CZ-53210 Pardubice, Czech Republic. E-mail: bruhn@chemie.uni-halle.de*

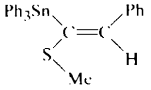
(Received 17 September 1998; accepted 19 November 1998)

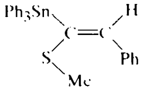
Abstract

The structures of the title compounds, (*Z*)-$Ph_3Sn—C(SMe)=CHPh$, (I), and (*E*)-$Ph_3Sn—C(SMe)=CHPh$, (II) {both $[Sn(C_6H_5)_3(C_9H_9S)]$, (1-methylthio-2-phenylethenyl)triphenyltin}, were determined by single-crystal X-ray diffraction at room temperature. Both structures consist of discrete molecules in which the Sn atom is tetrahedrally coordinated by three phenyl groups and one 1-methylthio-2-phenylethenyl group. The planar ethenyl skeleton forms angles of 58.9 (2) and 34.0 (3)° with the 2-phenyl substituent in (I) and (II), respectively, excluding π interactions between them. In *Z*-isomer (I), the methyl substituent on sulfur lies in the plane of the ethenyl group [torsion angle C—S—C=C 3.0 (5)°], but this is not the case in *E*-isomer (II), which reveals a torsion angle C—S—C=C of 156.1 (8)°.

Comment

The hydrometallation of non-symmetrically substituted alkynes can afford four possible isomeric ethenyl metal complexes. Especially in the case of alkynes $R'C\equiv CYR_n$ with Lewis basic heteroatom groups (YR_n = NR_2, PR_2, OR, SR; R/R' = alkyl, aryl, H), it might be difficult to predict the regio- and/or stereoselectivity. In the case of the hydrostannylation of $PhC\equiv CSPh$ by Ph_3SnH, both the non-catalysed and the Pd-catalysed reactions are quite selective and yield one major isomer at about 90–95% in each case. Because the assignment of the isomers by means of NMR spectroscopy (^1H, ^{13}C and ^{119}Sn) is not straightforward, the structures of both isomers were determined by single-crystal X-ray diffraction. The non-catalysed reaction gave (*Z*)-$Ph_3Sn—C(SMe)=CHPh$, (I), and the Pd-catalysed reaction (*E*)-$Ph_3Sn—C(SMe)=CHPh$, (II).


(I)


(II)

The molecular structures and numbering schemes are shown in Fig. 1. Both complexes consist of discrete molecules in which the Sn atoms are tetrahedrally coordinated by three phenyl ligands and one 1-methylthio-2-phenylethenyl ligand [C—Sn—C: 106.3 (1)–112.7 (1)° in (I) and 105.6 (3)–110.0 (3)° in (II)]. The three $Sn—C_{Ph}$ bond lengths are similar [(I): 2.131 (4)–2.143 (4), mean value 2.135 Å; (II): 2.135 (8)–2.162 (8), mean value 2.146 Å]. In the case of isomer (I), the $Sn—C_{ethenyl}$ bond seems to be slightly longer [(I): 2.173 (4); (II): 2.148 (7) Å]. There are no significant differences in the Sn—C bond lengths in $Ph_3Sn—CH=CH_2$ [$Sn—C_{Ph}$ 2.11 (3)–2.17 (4) and $Sn—C_{ethenyl}$ 2.07 (3)–2.15 (3) Å; Theobald & Trimaille, 1984] and (*Z*)-$Ph_3Sn—C(CMe_2OH)=CHMe$ [$Sn—C_{Ph}$ 2.118 (3)–2.129 (3) and $Sn—C_{ethenyl}$ 2.125 (3) Å; Willem *et al.*, 1994].

The ethenyl skeleton (C1–C3, Sn, S) is nearly planar [maximum deviation: 0.064 (3) Å for C2 in (I), and 0.027 (6) Å for C1 in (II)]. As in *trans*-$[Pt\{(E)\text{-}C(SMe)=CHPh\}Cl(PPh_3)_2]$ (Steinborn *et al.*, 1998), in *Z*-isomer (I), the methyl substituent on sulfur (C9) also lies in this plane [deviation 0.011 (8) Å; torsion angle C9—S—C1=C2 3.0 (5)°]; this is not the case in *E*-isomer (II) [deviation 0.73 (2) Å; torsion angle C9—S—C1=C2 156.1 (8)°]. Without obvious reason, the angles at the ethenyl C1 and C2 atoms exhibit