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Journal of Organometallic Chemistry 560 (1998) 197–209

Journal of Organometallic Chemistry

Synthesis and diastereoselective functionalisation of tricarbonyl[(3a,7a)-octahydro-3-substituted-2-(η^6-phenyl) benzoxazole]chromium(0) complexes

Paul D. Woodgate *, Yogendra Singh, Clifton E.F. Rickard

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Received 12 December 1997

Abstract

Two novel tricarbonyl[(3a,7a)-octahydro-3-substituted-2-(η^6-phenyl)benzoxazole]chromium(0) complexes have been synthesised in excellent yield and characterised by X-ray crystallography. Treatment of complex **1** with butyllithium followed by electrophile quench (MeI, MeSSMe, Me_3SiCl, Me_3SnCl, Ph_2PCl, $PhCH_2Br$, PhCHO) gave 1,2-disubstituted (η^6-arene)$Cr(CO)_3$ complexes in excellent yield, by completely diastereoselective *ortho*-deprotonation. The structures of the products **5** and **10** have been established by X-ray crystallographic analyses.

Keywords: Carbonyl; Chromium; Crystal structure; Stereoselection

1. Introduction

(η^6-Arene)tricarbonylchromium(0) complexes are particularly useful for the asymmetric synthesis of a variety of organic molecules, as the transition metal imparts several useful properties to the associated aromatic ligand [1–7]. An approach to the aglycone of pseudopterosin G by Schmalz illustrates most of the advantageous properties to be gained upon complexation of an arene to this transition metal [8]. The planar chirality of unsymmetrically *ortho*-disubstituted complexes has stimulated much interest in the development of synthetic routes to such complexes in non-racemic form. Recently, attention has been focused on two approaches to their synthesis, both involving stereoselective *ortho*-deprotonation of an (η^6-arene)$Cr(CO)_3$ complex. These approaches utilise either a chiral non-racemic auxiliary to achieve diastereoselective *ortho*-deprotonation [2,7,9–16] or a chiral non-racemic lithium amide base to achieve enantioselective *ortho*-deprotonation [17–22]. The stereochemical outcome of these asymmetric deprotonation methodologies depends on the nature of the chiral auxiliary employed and on the substituents present in the free arene, respectively. In view of these observations, and of earlier work in our laboratory involving chiral acetal-mediated asymmetric functionalisation of (η^6-arene)$Cr(CO)_3$ complexes [16], we decided initially to investigate the effect of a simple chiral racemic oxazolidine auxiliary on the asymmetric *ortho*-deprotonation of the chromium complexes. We expected that an oxazolidine moiety would make a useful extension to this area since it should be capable of inducing regio- and stereoselective *ortho*-deprotonation, in addition to being a readily removable or replaceable group at a subsequent stage.

To our knowledge, there are no reported examples of chiral oxazolidine auxiliary mediated diastereoselective *ortho*-deprotonation of (η^6-arene)$Cr(CO)_3$ complexes. In this paper, we report the details of the diastereoselective metallation of tricarbonyl[(3a,7a)-octahydro-3-substituted-2-(η^6-phenyl)benzoxazole]chromium(0) com-

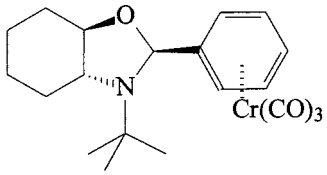
* Corresponding author.

0022-328X/98/$19.00
PII S0022-328X(98)00492-6

plexes and the subsequent reaction with several electrophiles. In addition, a synthetic approach to the octahydrobenzoxazole ring system is described.

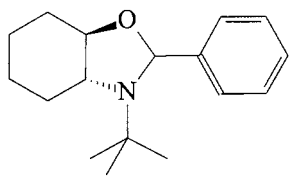
2. Results and discussion

Tricarbonyl[(3a,7a-*trans*)-octahydro-3-(*t*-butyl)-2-(η^6-phenyl)benzoxazole]chromium(0) (**1**)



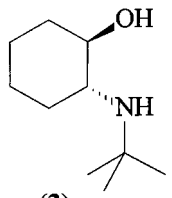
(**1**)

was the first substrate for our investigation, since it was envisaged that the steric congestion of a bulky group on nitrogen of the oxazolidine moiety would favour diastereoselective *ortho*-deprotonation. The free ligand, octahydrobenzoxazole (**2**),



(**2**)

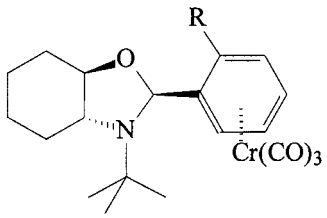
was obtained quantitatively by condensation of (dimethoxymethyl)benzene [24] with *trans*-2-(*t*-butylamino)cyclohexanol (**3**)



(**3**)

[25], itself prepared from 7-oxabicyclo[4.1.0]heptane [26]. Complex **1** was synthesised by heating a mixture of the octahydrobenzoxazole **2** and hexacarbonylchromium(0) in dibutyl ether/THF (4:1) under reflux [23]. It crystallised as yellow needles and showed two C≡O stretching absorptions in its IR spectrum (1968 and 1885 cm^{-1}). It analysed correctly for $C_{20}H_{25}CrNO_4$ and showed the molecular ion at m/z 395 in MS. The ^{1}H-NMR and ^{13}C-NMR spectra were consistent with the proposed structure. A single crystal X-ray structure analysis of **1** was undertaken in order to investigate the spatial arrangement of the ligands about the chromium moiety (Fig. 1, Tables 1–3) as an indicator of their potential to influence the diastereoselectivity of *ortho*- (or *meta*-) deprotonation.

In the event, treatment of complex **1** with butyllithium (1.2 molar equivalents), the base commonly employed for ring deprotonation of (η^6-arene)$Cr(CO)_3$ complexes under kinetic control [27], and subsequent reaction of the aryllithium with iodomethane gave the *ortho*-monomethylated complex **4** (98%).



(**4**, R = Me

5, R = SMe)

This compound showed the molecular ion at m/z 409 in MS, accurate mass measurement of which was correct for $C_{21}H_{27}CrNO_4$, and the ^{1}H-NMR and ^{13}C-NMR data were also in agreement with the proposed structure. ^{1}H-NMR and ^{13}C-NMR spectroscopic analyses of the crude product mixture showed no evidence of the other diastereoisomer. Furthermore, there was no trace of product(s) resulting from competitive abstraction of the benzylic proton, a problem that has been encountered in acetal (dioxolane) systems [9,16]. Potential benzylic deprotonation in the oxazolidine (**1**) is probably not favoured on steric grounds, since H(2) is oriented towards the bulky $Cr(CO)_3$ moiety (Fig. 1).

Deprotonation of the complex **1** as above, followed by quenching with dimethyl disulfide, resulted in the isolation of complex **5** (100%), again as a single diastereoisomer. Complex **5** crystallised as yellow needles, analysed correctly for $C_{21}H_{27}CrNO_4S$ and showed the molecular ion at m/z 441 in MS. The ^{1}H- and ^{13}C-NMR spectra were consistent with the proposed structure. A single crystal X-ray analysis of the product **5** established exclusive pro-*R* deprotonation-quenching of complex **1** (Fig. 2, Table 1 and Tables 4 and 5). This completely diastereoselective deprotonation reflects a combination of steric and chelation controls. The pro-*R* deprotonation is consistent with the

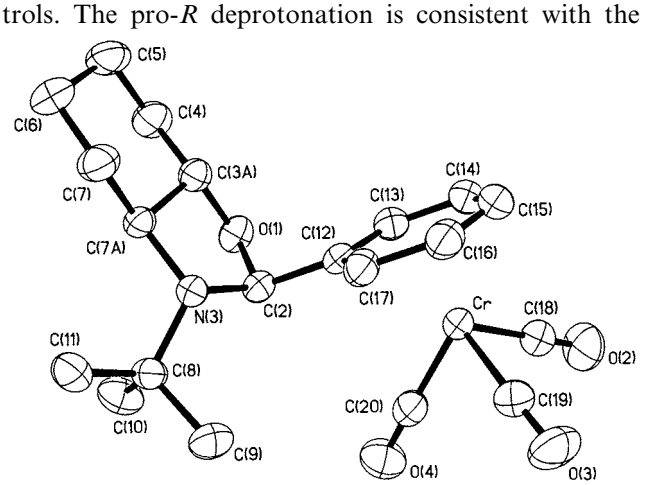


Fig. 1. The atomic arrangement in **1**.

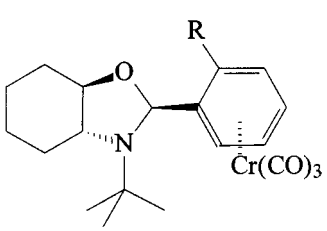
Table 1
Data collection and processing parameters

	1	5	10	11
Empirical formula	$C_{20}H_{25}CrNO_4$	$C_{21}H_{27}CrNO_4S$	$C_{27}H_{31}CrNO_5$	$C_{23}H_{23}CrNO_6S$
Formula weight	395.41	441.50	501.53	493.48
Temperature (K)	293	203	203	293
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	6.8889(1)	7.9777(1)	11.6324(2)	10.4106(2)
b (Å)	14.4452(1)	23.5464(1)	14.5640(5)	14.9451(2)
c (Å)	19.2171(3)	11.9112(1)	15.5413(2)	15.3039(1)
β (°)		106.514(4)	109.77(2)	108.532(5)
V (Å^3)	1912.32(4)	2144.06(3)	2477.79(8)	2257.63(5)
Z	4	4	4	4
$D_{calc.}$ (g cm^{-3})	1.373	1.368	1.344	1.452
Absorption coefficient (mm^{-1})	0.62	0.66	0.50	0.64
$F(000)$	832	928	1056	1024
Crystal size (mm)	$0.53\times0.22\times0.20$	$0.40\times0.28\times0.18$	$0.36\times0.31\times0.19$	$0.48\times0.38\times0.36$
Theta range for data collection (°)	3–56	3–56	3–52	4–56
Reflections observed $I>2\sigma(I)$	4056	4296	3909	4370
Independent reflections	4308 [R_{int} 0.0184]	4829 [R_{int} 0.0168]	4842 [R_{int} 0.0213]	5103 [R_{int} 0.0153]
A (min max)	0.734 0.886	0.779 0.891	0.841 0.911	0.749 0.803
Least-squares weights a,b	0.0408 0.40	0.0389 0.76	0.0342 1.82	0.0569 0.93
No. of variables in LS	235	257	310	298
Absolute structure parameter	0.00(2)			
Function minimised	$\Sigma w(F_O^2-F_C^2)^2$	$\Sigma w(F_O^2-F_C^2)^2$	$\Sigma w(F_O^2-F_C^2)^2$	$\Sigma w(F_O^2-F_C^2)^2$
R (observed data)	0.0251	0.0269	0.0437	0.366
wR_2 (all data)	0.0681	0.0746	0.1063	0.1093
Goodness of fit on F^2	0.937	1.031	1.116	1.009
Largest difference peak and hole (e Å^{-3})	+0.17 −0.21	+0.26 −0.39	+0.26 −0.34	+0.47 −0.41

$R=\Sigma||F_O|-|F_C||/\Sigma|F_O|$; $wR_2=\{\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}$; weight $=1.0/[\sigma^2(F_O^2)+a*P^2+b*P]$, $P=(F_O^2+2F_C^2)/3$

delivery of the base to the proximal *ortho*-arene hydrogen via co-ordination of the lithium counterion to the oxazolidine oxygen. The alternative pro-S deprotonation is not observed, presumably because chelation of the lithium cation to the oxazolidine nitrogen is precluded by the steric bulk of the N-*t*-butyl group. Simpkins has observed a similar effect of the *t*-butyl group during *ortho*-deprotonation of (η^6-*t*-butoxybenzene)tricabonylchromium(0) mediated by a chiral non-racemic base [22].

In order to expand the generality and demonstrate the efficiency of this deprotonation-electrophile quench sequence, the anion of **1** was reacted with a range of electrophiles. Introduction of silicon, phosphorus, tin and carbon substituents proceeded smoothly to give complexes **6**–**10** in excellent yields (Table 6). In all of these cases, ^{1}H-NMR and ^{13}C-NMR spectroscopic analyses of the crude product indicated completely regio- and diastereoselective substitution. This suggests that the diastereoselection is determined by the deprotonation step, and also demonstrates that the formation of carbon–carbon as well as carbon–heteroatom bonds is chemically feasible in this system. The stereochemistry at the newly created benzylic position of **10**

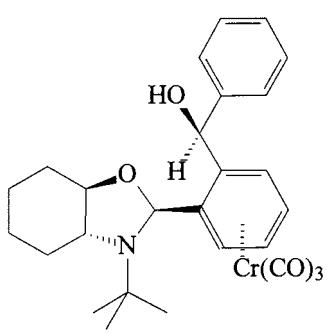


(**6**, R = SiMe3

7, R = PPh2

8, R = SnMe3

9, R = CH_2Ph)



(**10**)

was established as (*S**) by a single crystal X-ray crystallographic analysis (Fig. 3, Table 1 and Tables 7 and 8). This stereochemistry is consistent with the

Table 2
Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

	x	y	z	U_{eq}
Cr	4256(1)	8028(1)	1296(1)	32(1)
N(3)	459(2)	8078(1)	3157(1)	30(1)
O(1)	3515(2)	7566(1)	3550(1)	38(1)
O(2)	8184(2)	8279(1)	656(1)	66(1)
O(3)	2623(3)	8908(1)	6(1)	63(1)
O(4)	4813(3)	9925(1)	1908(1)	66(1)
C(2)	2561(2)	8041(1)	2991(1)	32(1)
C(3a)	2093(2)	6876(1)	3728(1)	35(1)
C(4)	2459(3)	6346(1)	4394(1)	48(1)
C(5)	733(4)	5676(1)	4478(1)	55(1)
C(6)	−1247(3)	6159(2)	4431(1)	56(1)
C(7)	−1482(3)	6760(1)	3770(1)	45(1)
C(7a)	231(2)	7431(1)	3754(1)	32(1)
C(8)	−299(2)	9044(1)	3279(1)	35(1)
C(9)	−153(3)	9585(1)	2594(1)	55(1)
C(10)	791(4)	9569(1)	3858(1)	53(1)
C(11)	−2446(3)	8979(1)	3474(1)	47(1)
C(12)	2965(2)	7516(1)	2308(1)	33(1)
C(13)	4797(3)	7098(1)	2210(1)	42(1)
C(14)	5208(3)	6620(1)	1585(1)	51(1)
C(15)	3796(3)	6535(1)	1062(1)	50(1)
C(16)	1983(3)	6962(1)	1154(1)	46(1)
C(17)	1541(3)	7442(1)	1783(1)	37(1)
C(18)	6672(3)	8178(1)	900(1)	43(1)
C(19)	3228(3)	8578(1)	510(1)	41(1)
C(20)	4579(3)	9192(1)	1679(1)	43(1)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

approach of the sterically less hindered *exo* face of the aryllithium complex to the *re*-face of the carbonyl group of benzaldehyde. Thus, two new carbon–carbon stereocentres have been created cleanly.

Table 3
Selected bond lengths (Å) for **1**

Cr–C(18)	1.8427(19)
Cr–C(19)	1.8475(19)
Cr–C(20)	1.8483(19)
Cr–C(14)	2.2092(19)
Cr–C(16)	2.2133(19)
Cr–C(15)	2.2259(18)
Cr–C(13)	2.2429(17)
Cr–C(17)	2.2563(17)
Cr–C(12)	2.2635(15)
N(3)–C(2)	1.4830(19)
N(3)–C(7a)	1.4886(19)
N(3)–C(8)	1.509(2)
O(1)–C(2)	1.4343(19)
O(1)–C(3a)	1.438(2)
C(2)–C(12)	1.541(2)
C(3a)–C(4)	1.513(2)
C(3a)–C(7a)	1.514(2)
C(4)–C(5)	1.542(3)
C(5)–C(6)	1.535(3)
C(6)–C(7)	1.548(3)
C(7)–C(7a)	1.527(2)

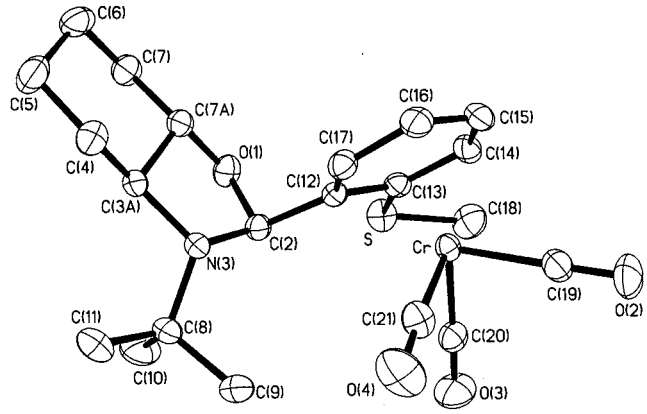


Fig. 2. The atomic arrangement in **5**.

In order to investigate whether an N-tosyl substituent (as opposed to N-*t*-butyl) would also allow *ortho*-deprotonation of the complexed arene, and potentially diastereoselectively at the pro-*S* site (cf. earlier) if chelation control via the sulfonyl oxygen could dominate, [(3a,7a-*cis*)-octahydro-2-(η^6-phenyl)-3-(*p*-toluenesulfonyl)benzoxazole]tricarbonylchromium(0) (**11**)

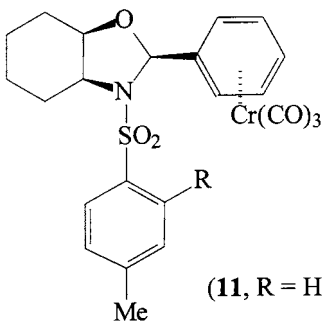
Table 4
Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**

	x	y	z	U_{eq}
Cr	1800(1)	5298(1)	2866(1)	19(1)
S	3997(1)	6620(1)	4198(1)	30(1)
N(3)	2088(1)	6454(1)	294(1)	23(1)
O(1)	2224(1)	7158(1)	1725(1)	28(1)
C(2)	2617(2)	6568(1)	1565(1)	23(1)
C(3a)	1084(2)	6963(1)	−247(1)	24(1)
C(4)	−614(2)	6893(1)	−1231(1)	32(1)
C(5)	−1350(2)	7496(1)	−1568(2)	40(1)
C(6)	−1565(2)	7841(1)	−526(2)	38(1)
C(7)	93(2)	7853(1)	515(1)	32(1)
C(7a)	656(2)	7243(1)	782(1)	24(1)
C(8)	3579(2)	6296(1)	−174(1)	31(1)
C(9)	4285(2)	5720(1)	343(2)	41(1)
C(10)	5065(2)	6734(1)	100(2)	50(1)
C(11)	2870(3)	6221(1)	−1502(2)	51(1)
C(12)	1617(2)	6209(1)	2231(1)	21(1)
C(13)	2136(2)	6215(1)	3487(1)	22(1)
C(14)	1137(2)	5914(1)	4097(1)	26(1)
C(15)	−393(2)	5622(1)	3471(1)	29(1)
C(16)	−934(2)	5622(1)	2244(1)	29(1)
C(17)	103(2)	5906(1)	1636(1)	25(1)
C(18)	4614(2)	6347(1)	5671(2)	42(1)
O(2)	1349(2)	4205(1)	4039(1)	45(1)
C(19)	1556(2)	4630(1)	3611(1)	29(1)
O(3)	5697(2)	5171(1)	3664(1)	47(1)
C(20)	4198(2)	5224(1)	3374(1)	27(1)
O(4)	2000(2)	4541(1)	893(1)	50(1)
C(21)	1879(2)	4845(1)	1629(1)	29(1)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 5
Selected bond lengths (Å) for **5**

Cr–C(21)	1.8346(15)
Cr–C(19)	1.8423(15)
Cr–C(20)	1.8426(15)
Cr–C(15)	2.2097(14)
Cr–C(17)	2.2127(13)
Cr–C(16)	2.2282(14)
Cr–C(14)	2.2314(13)
Cr–C(12)	2.2662(13)
Cr–C(13)	2.2743(13)
S–C(13)	1.7640(14)
S–C(18)	1.7996(17)
N(3)–C(2)	1.4751(17)
N(3)–C(3a)	1.4824(17)
N(3)–C(8)	1.4982(17)
O(1)–C(7a)	1.4360(17)
O(1)–C(2)	1.4483(16)
C(2)–C(12)	1.5297(18)
C(3a)–C(7a)	1.5149(19)
C(3a)–C(4)	1.526(2)
C(4)–C(5)	1.545(2)
C(5)–C(6)	1.534(3)
C(6)–C(7)	1.533(2)
C(7)–C(7a)	1.5104(19)



(**11**, R = H
14, R = Me)

was synthesised. The octahydrobenzoxazole **12** was synthesised by heating a mixture (4:1) of (dimethoxymethyl)benzene and *cis*-2-(*p*-toluenesulfonylamino) cyclohexanol (**13**) in toluene under reflux; in turn **13** was easily prepared from cyclohexene by treatment with chloramine-T trihydrate and osmium tetraoxide [27]. Complex **11** was obtained by heating the N-tosylbenzoxazole (**12**) with hexacarbonylchromium(0) in dibutyl ether/THF (9:1) under reflux [23]. It showed two peaks in its IR spectrum, characteristic of metal

Table 6
Diastereoselective deprotonation/electrophile quench of **1**

Electrophile	Product	Yield (%)
Me_3SiCl	**6**	100
Ph_2PCl	**7**	100
Me_3SnCl	**8**	94[a]
$PhCH_2Br$	**9**	98
PhCHO	**10**	100

[a] Starting material **1** recovered.

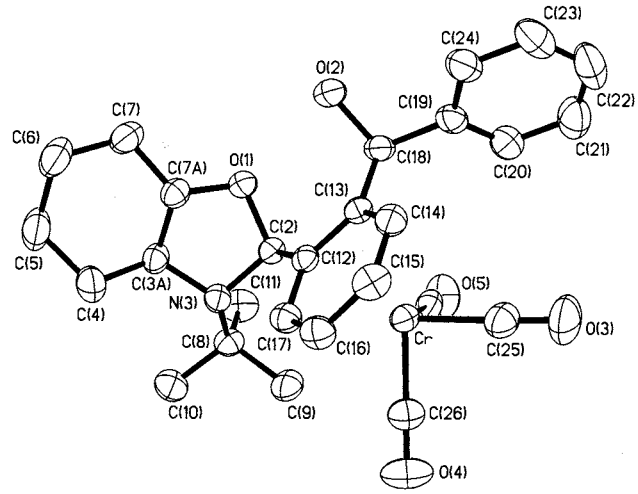
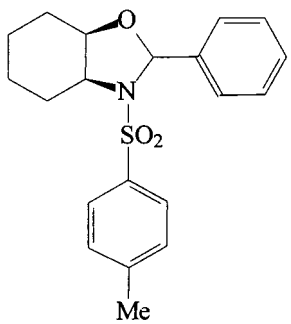
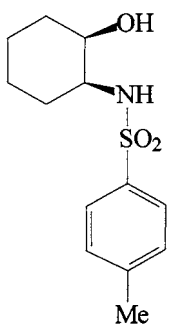


Fig. 3. The atomic arrangement in **10**.

C≡O absorptions (1970 and 1894 cm^{-1}) and showed the molecular ion at *m/z* 493 in MS, which had a correct accurate mass measurement for $C_{23}H_{23}CrNO_6S$. The ^{1}H-NMR and ^{13}C-NMR spectral data were also in agreement with the proposed structure. A single crystal X-ray diffraction analysis of **11** established that one of the sulfonyl oxygen atoms was oriented towards one of the *ortho* hydrogens in the complexed ring (Fig. 4, Table 1 and Tables 9 and 10). However, treatment of complex **11** with butyllithium (1 molar equivalent) and subsequent reaction with iodomethane (2 molar equiva-



(**12**)



(**13**)

lents) followed by D_2O afforded mainly the product of sulfonylarene *ortho*-deprotonation, tricarbonyl[(3a,7a-*cis*)-octahydro-2-(η^6-phenyl)-3-(2,4-dimethylsulfonylbenzene)benzoxazole]chromium(0) (**14**) (50%). Compound **14** showed two C≡O stretching absorptions in its IR spectrum (1976 and 1888 cm^{-1}), and the accurate mass measurement of its molecular ion was correct for $C_{24}H_{25}CrNO_6S$. The ^{1}H-NMR and ^{13}C-NMR spectra were consistent with the proposed structure. Also isolated from the reaction mixture were methyl *p*-toluenesulfinate (**15**) (7%) and tricarbonyl[(3a,7a-*cis*)-(3a,4,5,6,7,7a)-hexahydro-2-(η^6-phenyl)benzoxazole]chromium (0) (**16**) (8%), together with recovered but non-deuterated starting complex **11** (41%). The identity of **15** rests upon its ^{1}H-NMR data and MS that showed the molecular ion at *m*/*z* 170, correct accurate mass measurement for $C_8H_{10}O_2S$. The oxazoline **16** showed two peaks characteristic of metal C≡O absorptions in its IR spectrum (1976 and 1904 cm^{-1}). The accurate mass measurement of the molecular ion of **16** was correct for $C_{16}H_{15}CrNO_4$, and the ^{1}H-NMR data was in agreement

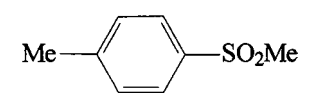
Table 7
Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **10**

	x	*y*	*z*	U_{eq}
Cr	3329(1)	6933(1)	3776(1)	31(1)
N(3)	6919(2)	7392(1)	5583(1)	32(1)
O(1)	6635(1)	8798(1)	4805(1)	36(1)
O(2)	5040(2)	9623(1)	3275(1)	48(1)
O(3)	626(2)	6985(2)	2797(2)	77(1)
O(4)	3074(2)	5273(2)	4833(2)	73(1)
O(5)	2888(2)	8095(2)	5218(1)	59(1)
C(2)	5987(2)	8031(2)	5019(2)	30(1)
C(3a)	8103(2)	7741(2)	5563(2)	36(1)
C(4)	9035(3)	7070(2)	5433(2)	54(1)
C(5)	10124(3)	7633(3)	5372(2)	65(1)
C(6)	9765(3)	8386(2)	4645(2)	59(1)
C(7a)	7718(2)	8367(2)	4740(2)	35(1)
C(7)	8729(2)	8997(2)	4718(2)	48(1)
C(8)	6848(2)	7189(2)	6514(2)	36(1)
C(9)	5639(2)	6697(2)	6384(2)	47(1)
C(10)	7873(3)	6523(2)	7000(2)	47(1)
C(11)	6948(3)	8051(2)	7099(2)	51(1)
C(12)	5173(2)	7580(2)	4118(2)	29(1)
C(13)	4286(2)	8097(2)	3407(2)	29(1)
C(14)	3599(2)	7630(2)	2604(2)	35(1)
C(15)	3736(2)	6678(2)	2489(2)	40(1)
C(16)	4569(2)	6178(2)	3185(2)	39(1)
C(17)	5293(2)	6631(2)	3990(2)	35(1)
C(18)	4110(2)	9134(2)	3495(2)	34(1)
C(19)	2875(2)	9474(2)	2871(2)	37(1)
C(20)	1910(2)	9556(2)	3196(2)	48(1)
C(21)	774(3)	9843(2)	2629(2)	60(1)
C(22)	591(3)	10044(2)	1725(2)	63(1)
C(23)	1542(3)	9968(2)	1392(2)	56(1)
C(24)	2686(3)	9691(2)	1961(2)	46(1)
C(25)	1669(3)	6948(2)	3169(2)	46(1)
C(26)	3168(2)	5906(2)	4418(2)	44(1)
C(27)	3050(2)	7636(2)	4660(2)	37(1)

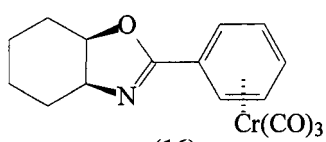
U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 8
Selected bond lengths (Å) for **10**

Cr–C(27)	1.830(3)
Cr–C(25)	1.841(3)
Cr–C(26)	1.843(3)
Cr–C(14)	2.198(2)
Cr–C(13)	2.206(2)
Cr–C(15)	2.236(2)
Cr–C(12)	2.235(2)
Cr–C(17)	2.238(2)
Cr–C(16)	2.242(2)
N(3)–C(2)	1.473(3)
N(3)–C(3a)	1.479(3)
N(3)–C(8)	1.506(3)
O(1)–C(7a)	1.441(3)
O(1)–C(2)	1.448(3)
O(2)–C(18)	1.430(3)
C(2)–C(12)	1.547(3)
C(3a)–C(7a)	1.509(3)
C(3a)–C(4)	1.523(4)
C(4)–C(5)	1.538(4)
C(5)–C(6)	1.528(4)
C(6)–C(7)	1.533(4)
C(7a)–C(7)	1.502(3)



(15)



(16)

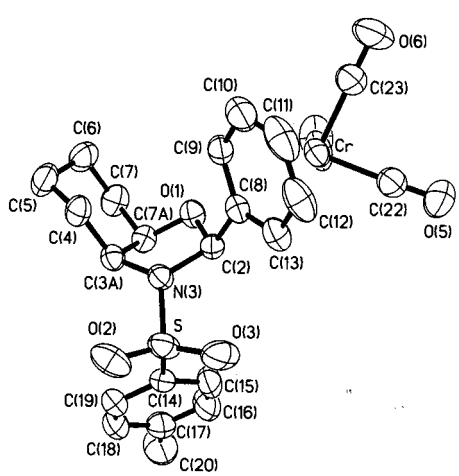


Fig. 4. The atomic arrangement in **11**.

Table 9
Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **11**

	x	y	z	U_{eq}
Cr	2152(1)	8176(1)	884(1)	42(1)
S	−2663(1)	6183(1)	507(1)	51(1)
N(3)	−1034(1)	5991(1)	984(1)	38(1)
O(1)	777(1)	6348(1)	2260(1)	42(1)
O(2)	−3192(2)	5427(1)	−66(1)	71(1)
O(3)	−2757(2)	7065(1)	121(1)	76(1)
O(4)	3123(14)	8235(9)	2933(10)	86(3)
O(4′)	2661(13)	8419(9)	2920(10)	76(2)
O(5)	1438(2)	10127(1)	763(2)	78(1)
O(6)	4925(2)	8805(2)	1008(2)	97(1)
C(2)	−103(2)	6736(1)	1449(1)	37(1)
C(3a)	−625(2)	5173(1)	1551(1)	40(1)
C(4)	284(2)	4577(1)	1190(1)	48(1)
C(5)	1072(3)	3916(2)	1920(2)	61(1)
C(6)	1940(2)	4423(2)	2755(2)	62(1)
C(7)	1086(2)	4986(1)	3176(1)	54(1)
C(7a)	88(2)	5586(1)	2492(1)	41(1)
C(8)	685(2)	7061(1)	831(1)	39(1)
C(9)	1959(2)	6695(1)	884(2)	50(1)
C(10)	2585(3)	6947(2)	227(2)	68(1)
C(11)	1943(3)	7567(2)	−471(2)	73(1)
C(12)	716(3)	7938(2)	−504(2)	66(1)
C(13)	71(2)	7692(1)	143(1)	50(1)
C(14)	−3399(2)	6200(1)	1401(2)	47(1)
C(15)	−3269(3)	6956(2)	1951(2)	72(1)
C(16)	−3783(3)	6955(2)	2672(2)	79(1)
C(17)	−4444(2)	6211(2)	2868(2)	63(1)
C(18)	−4582(2)	5470(2)	2305(2)	59(1)
C(19)	−4067(2)	5453(1)	1575(2)	51(1)
C(20)	−4994(4)	6225(2)	3665(2)	93(1)
C(21)	2582(3)	8266(2)	2138(2)	65(1)
C(22)	1680(2)	9374(2)	809(2)	52(1)
C(23)	3872(2)	8559(2)	976(2)	59(1)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

with the proposed structure. Compounds **15** and **16** arise from benzylic deprotonation-elimination followed by methylation of the expelled sulfinate anion. ^{1}H-NMR and ^{13}C-NMR analyses of the crude product mixture showed no evidence for products resulting from deprotonation of the (η^6-arene)Cr(CO)$_3$ moiety of **11**. This outcome was not unexpected in view of the strong electron-withdrawing and co-ordinating properties of the sulfonyl moiety. An efficient *ortho*-lithiation of uncomplexed sulfonyl-substituted arenes has been reported [28].

In summary, a number of 1,2-disubstituted (η^6-arene)Cr(CO)$_3$ complexes have been synthesised in excellent yield by a completely diastereoselective *ortho*-deprotonation/electrophile quench sequence mediated by (3a,7a-*trans*)-octahydro-3-(*t*-butyl)benzoxazole.

2.1. X-ray crystal structures for **1**, **5**, **10** and **11**

Data were collected on a Siemens SMART diffractometer with a CCD area detector and graphite monochromated Mo–K$_\alpha$ radiation. The data collection for each crystal covered a nominal hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal and covered 0.3° in ω. The crystal-to-detector distance was 5.0 cm. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing duplicate reflections; no evidence of decay was found. Unit cell parameters were obtained by least-squares fit to all data with $I > 10\sigma(I)$. The data were corrected for Lorentz and polarisation effects and empirical absorpton corrections applied [29]. Equivalent reflections were averaged to give the unique data set. Details of crystal data and data collection parameters are given in Table 1.

2.2. Structure solution and refinement

The structures were solved by direct methods using SHELXS [30] and refined by full-matrix least-squares on F^2 using SHELXL [31]. Atomic scattering factors were for neutral atoms. All non-hydrogen atoms were allowed to refine anisotropically. For **11**, one of the carbonyl oxygen atoms shows evidence of disorder and has been treated as two half atoms. Hydrogen atoms

Table 10
Selected bond lengths (Å) for **11**

Cr–C(21)	1.831(2)
Cr–C(23)	1.842(2)
Cr–C(22)	1.851(2)
Cr–C(12)	2.204(2)
Cr–C(10)	2.208(2)
Cr–C(11)	2.212(2)
Cr–C(9)	2.223(2)
Cr–C(13)	2.223(2)
Cr–C(8)	2.2442(17)
S–O(2)	1.4284(18)
S–O(3)	1.4348(17)
S–N(3)	1.6441(15)
S–C(14)	1.768(2)
N(3)–C(3a)	1.483(2)
N(3)–C(2)	1.498(2)
O(1)–C(2)	1.412(2)
O(1)–C(7a)	1.449(2)
C(2)–C(8)	1.516(2)
C(3a)–C(7a)	1.525(2)
C(3a)–C(4)	1.526(3)
C(4)–C(5)	1.521(3)
C(5)–C(6)	1.513(3)
C(6)–C(7)	1.510(3)
C(7)–C(7a)	1.513(3)

were placed geometrically and refined with a riding model (including free rotation for methyl groups) with U_{iso} 20% (50% for methyl groups) greater than the carrier atom. Refinement details are given in Table 1. Final atomic co-ordinates and important bond distances are given in Tables 2–5 and Tables 7–10. Lists of hydrogen co-ordinates, full bond lengths and angles and anisotropic thermal parameters can be obtained from the authors (CEFR).

The crystal structure determinations established the stereochemistries and the absolute stereochemistry for **10**. The figures show the observed geometry of each compound and give the numbering scheme. Each compound has the arene–$Cr(CO)_3$ piano stool arrangement with the carbonyl groups staggered with respect to the arene ring. The Cr–CO distances are all comparable (average 1.841 Å), as are the distances between the chromium and the mean plane of the arene ring (average 1.725 Å).

3. Experimental

Melting points were determined on a Reichert microscopic hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 Fourier-transform spectrometer as films on sodium chloride plates, unless otherwise stated. NMR spectra were recorded in deuteriochloroform on a Bruker AM 400 spectrometer, and MS spectra were recorded on a VG 7070 spectrometer operating at a nominal accelerating voltage of 70 eV. Flash column chromatography was performed on Kieselgel S (150–230 mesh) under positive nitrogen pressure. All reactions were performed under an atmosphere of dry nitrogen and the operations involving tricarbonylchromium(0) complexes were protected from light. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use, and toluene and benzene were distilled from sodium. Dichloromethane, methanol, dibutyl ether, iodomethane, dimethyl disulfide, chlorotrimethylsilane and chlorodiphenylphosphine were distilled from calcium hydride. Pre-distilled solvents were used in recrystallization and purification of compounds by chromatographic techniques. All other reagents were used as-obtained from commercial sources. The concentration of butyllithium was determined by titration against 1,3-diphenylpropan-2-one tosylhydrazone.

3.1. Trans-2-(t-butylamino)cyclohexanol (3)

A mixture of 7-oxabicyclo[4.1.0]heptane (2 g, 20 mmol), *t*-butylamine (6 g, 8.5 ml, 82 mmol) and water (10 ml) was refluxed for 45 h under nitrogen. The reaction mixture was cooled and extracted with dichloromethane (3×25 ml). The combined organic layer was washed with brine (15 ml), dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give the title compound as a pale yellow solid. Recrystallization from hexanes/ethyl acetate gave colourless crystals (2.1 g, 60%), m.p. 48–50°C ([25]: 47–48.5°C) (Found: M^+, 171.1627; $C_{10}H_{21}NO$. Calc.: M, 171.1623). ν_{max} ($CDCl_3$) 3453, 3422, 2934, 2860, 1479, 1463, 1450, 1391, 1362, 1277, 1226, 1125, 1102, 1080, 1044 cm^{-1}. δ_H 0.95–1.05 (m, 1H), 1.11 (s, 9H, NC(CH_3)$_3$), 1.23–1.32 (m, 3H), 1.65–1.74 (m, 2H), 1.96–2.02 (m, 1H), 2.04–2.09 (m, 1H), 2.23 (ddd, *J* 3.8, 9.2, 11.2 Hz, 1H, H-2), 2.93 (ddd, *J* 4.2, 9.2, 9.8 Hz, 1H, H-1). δ_C 24.45 (C-4), 25.82 (C-5), 30.58 (=NC**Me**$_3$), 32.68 (C-3), 34.83 (C-6), 50.68 (=N**C**Me$_3$), 58.12 (C-2), 74.24 (C-1).

3.2. (3a,7a-Trans)-octahydro-3-(t-butyl)-2-phenylbenzoxazole (2)

A mixture of *trans*-(*t*-butylamino)cyclohexanol (**3**) (1.5 g, 8.8 mmol), (dimethoxymethyl)benzene (5.5 g, 36.2 mmol) and PPTS (70 mg, 0.28 mmol) was dissolved in dry toluene (65 ml) and heated to reflux under an atmosphere of nitrogen for 100 h, with a small Soxhlet apparatus containing 4 Å molecular sieves placed between the reaction flask and the reflux condenser. The reaction mixture was cooled, diluted with diethyl ether (35 ml), stirred with saturated sodium hydrogencarbonate (0.5 ml), dried over anhydrous sodium carbonate, and filtered. The solvent was removed under reduced pressure and the yellow oil obtained was distilled (Kugelrohr, 135°C/0.4 mmHg) to afford the title compound (100%) as a colourless oil (Found: M^+, 259.1941; $C_{17}H_{25}NO$. Calc.: M, 259.1936). ν_{max} (neat) 2968, 2938, 2868, 1450, 1393, 1358, 1254, 1225, 1199, 1167, 1124, 1067, 1006, 985, 920, 908, 854, 735, 701 cm^{-1}. δ_H 1.08 (s, 9H, NC(CH_3)$_3$), 1.15 (ddd, *J* 3.9, 3.9, 13 Hz, 1H), 1.28 (ddd, *J* 3.7, 3.7, 13 Hz, 1H), 1.34–1.41 (m, 1H), 1.48 (dddd, *J* 3.8, 11.9, 11.9, 11.9 Hz, 1H), 1.65–1.71 (m, 2H), 1.93–1.96 (m, 1H), 2.14–2.18 (m, 1H), 2.53 (ddd, *J* 2.9, 10, 11 Hz, 1H, H-3a), 3.22 (ddd, *J* 3.5, 10, 11.2 Hz, 1H, H-7a), 5.58 (s, 1H, H-2), 7.22 (t, *J* 7.2 Hz, 1H), 7.30 (dd, *J* 7.2, 7.2 Hz, 2H), 7.65 (dd, *J* 1, 7.2 Hz, 2H). δ_C 23.64 (C-5), 24.51 (C-6), 27.55 (=NC**Me**$_3$), 29.62 (C-4), 33.25 (C-7), 53.94 (=N**C**Me$_3$), 64.09 (C-3a), 79.25 (C-7a), 91.00 (C-2), 127.30 (C-4′), 127.47 (C-2′, 3′, 5′, 6′), 143.71 (C-1′). *m*/*z* 259 (M^+, 5%), 244 (M-Me, 54), 202 (M-C_4H_9, 6), 182 (M-C_6H_5, 22), 138 ($C_9H_{16}N$, 100), 126 ($C_7H_{12}NO$, 24), 105 (C_6H_5CO, 10), 91 ($C_6H_5CH_2$, 16), 81 (C_5H_5O, 27), 77 (C_6H_5, 10), 58 (C_3H_8N, 31), 57 (C_4H_9, 17), 41 (C_3H_5, 23).

3.3. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-phenyl)benzoxazole]chromium(0) (**1**)

A mixture of (3a,7a-*trans*)-octahydro-3-(*t*-butyl)-2-phenylbenzoxazole (1 g, 3.86 mmol) and hexacarbonylchromium(0) (1.4 g, 6.36 mmol) was dissolved in dibutyl ether (32 ml) and THF (8 ml) and the solution was purged with dry nitrogen for 1 min. The solution was then heated under reflux, with a continuous flow of nitrogen, for 46 h. The yellow solution was cooled, diluted with diethyl ether (20 ml), filtered through Celite, and the solvent was evaporated under vacuum. Column chromatography of the yellow residue on silica gel with hexanes containing increasing quantities of diethyl ether gave the title complex (1.51 g, 3.82 mmol, 99%). Recrystallization from hexanes/diethyl ether gave yellow needles, m.p. 148–149°C. (Found: C, 60.85; H, 6.35; N, 3.54: $C_{20}H_{25}CrNO_4$. Calc.: C, 60.75; H, 6.4; N, 3.5%). (Found: M^+, 395.1191. $C_{20}H_{25}CrNO_4$. Calc.: M, 395.1189). ν_{max} ($CDCl_3$) 2972, 2943, 2872, 1968, 1885, 1449, 1414, 1396, 1361, 1328, 1254, 1214, 1180, 1116, 1063, 1008 cm^{-1}. δ_H 1.14 (s, 9H, NC(CH_3)$_3$), 1.18–1.32 (m, 3H), 1.53 (dddd, *J* 3.8, 11.7, 11.7, 11.7 Hz, 1H), 1.69–1.80 (m, 2H), 2.04–2.10 (m, 2H), 2.46 (ddd, *J* 2.9, 10, 11 Hz, 1H, H-3a), 3.24 (ddd, *J* 3.4, 10, 11.2 Hz, 1H, H-7a), 5.22 (ddd, *J* 1, 6.3, 6.3 Hz, 1H), 5.25 (ddd, *J* 1, 6.3, 6.3 Hz, 1H), 5.36 (s, 1H, H-2), 5.41 (dddd, *J* 1, 1, 6.3, 6.3 Hz, 1H, H-4′), 5.83 (ddd, *J* 1, 1, 6.3 Hz, 1H, H-2), 5.99 (ddd, *J* 1, 1, 6.3 Hz, 1H, H-6). δ_C 23.90 (C-5), 24.70 (C-6), 27.70 (=NC**Me**$_3$), 29.59 (C-4), 33.48 (C-7), 54.61 (=N**C**Me$_3$), 64.32 (C-3a), 79.94 (C-7a), 89.06 (d), 89.48 (d), 90.20 (C-2), 94.60 (C-2), 95.24 (d), 95.79 (d), 113.30 (C-1′), 233.01 ($Cr(CO)_3$). *m*/*z* 395 (M^+, 15%), 339 (M-2CO, 9), 311 (M-3CO, 31), 254 (M-3CO–C_4H_9, 100), 229 (M-3CO–C_6H_{10}, 12), 213 ($C_6H_5Cr(CO)_3$, 12), 155 (C_6H_5CrCN, 13), 129 (C_6H_5Cr, 6), 81 (C_5H_5O, 6), 58 (C_3H_8N, 6), 57 (C_4H_9, 6), 52 (Cr, 45), 41 (C_3H_5, 9).

3.4. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-2′-methylphenyl)benzoxazole]chromium(0) (**4**)

Complex **1** (137 mg, 0.35 mmol) was dissolved in dry THF (10 ml) and cooled to −78°C for 35 min. Butyllithium (2.47 mol l^{-1} in hexanes, 0.17 ml, 0.42 mmol) was added. The reaction mixture was stirred at −78°C for 2.5 h and iodomethane (0.06 ml, 0.96 mmol) was then added. After stirring at −78°C for 3.5 h, the reaction mixture was allowed to warm to room temperature over 45 min. Saturated aqueous sodium hydrogencarbonate (three drops) was added, the solution was dried over anhydrous sodium carbonate, diluted with diethyl ether (25 ml), and filtered through Celite. Evaporation of the solvent and recrystallization of the residue from hexanes/diethyl ether afforded the title complex (139 mg, 98%) as yellow crystals, m.p. 196–197°C (Found: M^+, 409.1339; $C_{21}H_{27}CrNO_4$. Calc.: M, 409.1345). ν_{max} ($CDCl_3$) 2969, 2940, 2868, 1964, 1878, 1473, 1456, 1422, 1394, 1381, 1360, 1327, 1253, 1213, 1194, 1116, 1064, 1038, 1009 cm^{-1}. δ_H 1.68 (s, 9H, NC(CH_3)$_3$), 1.21–1.40 (m, 3H), 1.52 (dddd, *J* 4, 11.7, 11.7, 11.7 Hz, 1H), 1.70–1.81 (m, 2H), 1.97–2.01 (m, 1H), 2.09–2.13 (m, 1H), 2.31 (s, 3H, CH_3), 2.48 (ddd, *J* 2.7, 10, 10 Hz, 1H, H-3a), 3.06 (ddd, *J* 3.3, 10, 11.3 Hz, 1H, H-7a), 5.02 (dd, *J* 1, 6 Hz, 1H, H-3′), 5.17 (ddd, *J* 1, 6, 6 Hz, 1H), 5.46 (ddd, *J* 1, 6, 6 Hz, 1H), 5.50 (s, 1H, H-2), 6.25 (dd, *J* 1, 6 Hz, 1H, H-6′). δ_C 19.40 (**Me**), 23.96 (C-5), 24.80 (C-6), 27.81 (=NC**Me**$_3$), 29.86 (C-4), 33.45 (C-7), 54.79 (=N**C**Me$_3$), 64.84 (C-3a), 79.52 (C-7a), 87.75, 88.55, 92.19 (C-2), 95.71, 95.76, 110.15 (C-2′), 110.98 (C-1′), 233.47 ($Cr(\mathbf{C}O)_3$). *m*/*z* 409 (M^+, 22%), 353 (M-2CO, 3), 325 (M-CO, 34), 268 (M-3CO–C_4H_9, 100), 243 (M-3CO–C_6H_{10}, 15), 227 ($MeC_6H_4Cr(CO)_3$, 16), 169 (MeC_6H_4CrCN, 13), 57 (C_4H_9, 9), 52 (Cr, 48), 41 (C_3H_5, 10).

3.5. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-2′-trimethylsilylphenyl)benzoxazole]chromium(0) (**6**)

Complex **1** (200 mg, 0.51 mmol) was dissolved in dry THF (20 ml) and cooled to −78°C for 45 min. Butyllithium (2.47 mol l^{-1} in hexanes, 0.26 ml, 0.64 mmol) was added and the reaction mixture was stirred at −78°C for 2.5 h. Chlorotrimethylsilane (0.2 ml, 1.6 mmol) was then added. After stirring for 2.5 h at −78°C, the reaction mixture was allowed to warm to r.t. over 45 min. The solvent was evaporated to dryness under reduced pressure and the residue was taken up in diethyl ether (40 ml) and filtered through Celite. Evaporation of the diethyl ether and recrystallization of the residue from hexanes gave the title complex (235 mg, 100%) as a yellow solid, m.p. 155–156°C. (Found: C, 59.0; H, 7.2; N, 3.0: $C_{23}H_{33}CrNO_4Si$. Calc.: C, 59.1; H, 7.1; N, 3.0%). (Found: M^+, 467.1580; $C_{23}H_{33}CrNO_4Si$. Calc.: M, 467.1584). ν_{max} ($CDCl_3$) 2973, 2944, 2869, 1961, 1878, 1510, 1458, 1408, 1361, 1320, 1249, 1224, 1175, 1116, 1094, 1064, 1036, 1008, 980, 945, 845 cm^{-1}. δ_H 0.36 (s, 9H, Si(CH_3)$_3$), 1.13 (s, 9H, NC(CH_3)$_3$), 1.14–1.32 (m, 3H), 1.53 (dddd, *J* 3.8, 11.7, 11.7, 11.7 Hz, 1H), 1.66–1.78 (m, 2H), 1.96–2.07 (m, 2H), 2.46 (ddd, *J* 2.8, 10, 10 Hz, 1H, H-3a), 2.96 (ddd, *J* 3.5, 10, 11.4 Hz, 1H, H-7a), 5.29–5.34 (m, 2H), 5.45 (s, 1H, H-21), 5.48 (ddd, *J* 1.7, 6, 6 Hz, 1H), 6.16 (dd, *J* 1, 6 Hz, 1H, H-6′). δ_C 0.39 (–Si**Me**$_3$), 24.03 (C-5), 24.87 (C-6), 27.82 (=NC**Me**$_3$), 30.01 (C-4), 33.58 (C-7), 54.71 (=NCMe$_3$), 64.99 (C-3a), 79.60 (C-7a), 89.03, 91.90,

93.94, 94.54, 98.58, 101.46 (C-2′), 119.28 (C-1′), 233.48 ($Cr(\mathbf{C}O)_3$). *m/z* 467 (M^+, 51%), 452 (M-Me, 2), 411 (M-2CO, 2), 383 (M-3CO, 62), 367 ($C_{19}H_{29}CrNOSi$, M-3CO–Me–H, 72), 351 ($C_{18}H_{25}CrNOSi$, M-3CO–2-Me–2H, 44), 326 (M-3CO–C_4H_9, 72), 311 ($C_{15}H_{21}CrNOSi$, M-3CO–C_4H_9–Me, 100), 286 ($Me_3SiC_6H_4Cr(CO)_3$, 29), 252 (M-3CO–C_4H_9–Me_3Si–H, 48), 244 (M-3CO–C_4H_9–C_6H_{10}, 15), 229 ($Me_3SiC_6H_4COCr$, 20), 73 ($SiMe_3$, 15), 57 (C_4H_9, 18), 52 (Cr, 77).

3.6. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-2′-methylthiophenyl)benzoxazole]chromium(0) (**5**)

The general procedure was the same as described for the preparation of **6**. Complex **1** (215 mg, 0.54 mmol) was treated with butyllithium (2.47 mol l^{-1} in hexanes, 0.28 ml, 0.69 mmol) and dimethyl disulfide (0.3 ml, 3.3 mmol) to give the title complex in 100% yield. Recrystallization from hexanes/diethyl ether afforded yellow needles, m.p. 178.4–179.5°C. (Found: C, 57.1; H, 6.1; N, 3.2: $C_{21}H_{27}CrNO_4S$. Calc.: C, 57.1; H, 6.2; N, 3.2%). (Found: M^+, 441.1068; $C_{21}H_{27}CrNO_4S$. Calc.: M, 441.1066). ν_{max} ($CDCl_3$) 2972, 2943, 2875, 1968, 1890, 1479, 1459, 1445, 1411, 1392, 1362, 1319, 1227, 1212, 1169, 1115, 1062, 1038, 1009, 970 cm^{-1}. δ_H 1.11–1.17 (m, 1H), 1.18 (s, 9H, $NC(C\mathbf{H}_3)_3$), 1.26–1.41 (m, 2H), 1.54 (dddd, *J* 3.8, 11.7, 11.7, 11.7 Hz, 1H), 1.70–1.81 (m, 2H), 2.00–2.04 (m, 1H), 2.10–2.14 (m, 1H), 2.41 (s, 3H, $SC\mathbf{H}_3$), 2.51 (ddd, *J* 2.9, 10, 10 Hz, 1H, H-3a), 3.07 (ddd, *J* 3.5, 10, 11.3 Hz, 1H, H-7a), 5.09 (dd, *J* 1, 6 Hz, 1H, H-3′), 5.13 (ddd, *J* 1, 6, 6 Hz, 1H), 5.49 (ddd, *J* 1, 6, 6 Hz, 1H), 5.69 (s, 1H, H-2), 6.31 (dd, *J* 1, 6 Hz, 1H, H-6′). δ_C 16.38 (–S**Me**), 24.00 (C-5), 24.83 (C-6), 27.86 (=NC**Me**$_3$), 29.91 (C-4), 33.63 (C-7), 54.95 (=N**C**Me_3), 64.89 (C-3a), 79.66 (C-7a), 86.21, 86.42, 88.94 (C-2), 94.72, 95.05, 112.49 (C-1′), 116.53 (C-2′), 232.88 ($Cr(\mathbf{C}O)_3$). *m/z* 441 (M^+, 11%), 385 (M-2CO, 23), 357 (M-3CO, 60), 300 (M-3CO–C_4H_9, 100), 285 (M-3CO–C_4H_9–Me, 39), 275 (M-3CO–C_6H_{10}, 6), 259 ($MeSC_6H_4Cr(CO)_3$, 10), 253 (M-3CO–C_4H_9–SMe, 24), 213 ($C_6H_5Cr(CO)_3$, 14), 201 ($MeSC_6H_4CrCN$, 8), 58 (C_3H_8N, 17), 57 (C_4H_9, 19), 52 (Cr, 63), 41 (C_3H_5, 25).

3.7. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-2′-diphenylphosphinophenyl)benzoxazole]-chromium(0) (**7**)

The general procedure was the same as described for the preparation of **6**. Complex **1** (260 mg, 0.66 mmol) was treated with butyllithium (2.47 mol l^{-1} in hexanes, 0.34 ml, 0.84 mmol) and chlorodiphenylphosphine (0.48 ml, 2.67 mmol) to give the title complex in 100% yield. Recrystallization from hexanes/diethyl ether afforded yellow crystals, m.p. 231°C (Found: M^+, 579.1615. $C_{32}H_{34}CrNO_4P$. Calc.: M, 579.1630). ν_{max} ($CDCl_3$) 2966, 2943, 2872, 1967, 1879, 1475, 1434, 1411, 1399, 1358, 1318, 1224, 1213, 1172, 1114, 1061, 1038, 1009, 986, 699 cm^{-1}. δ_H 0.58–0.63 (m, 1H), 0.86–1.06 (m, 2H), 1.09–1.24 (m, 11H), 1.49–1.60 (m, 2H), 2.00–2.03 (m, 1H), 2.36 (ddd, *J* 2.7, 10, 10 Hz, 1H, H-3a), 2.64 (ddd, *J* 3.5, 10, 10 Hz, 1H, H-7a), 4.72 (ddd, *J* 1, 1, 6 Hz, 1H, H-3′), 5.20 (ddd, *J* 1, 6, 6 Hz, 1H, H-5′), 5.49 (dddd, *J* 1, 1, 6, 6 Hz, 1H, H-4′), 5.94 (d, *J* 2 Hz, 1H, H-2), 6.20 (ddd, *J* 1, 2.7, 6 Hz, 1H, H-6′), 7.29–7.35 (m, 10H). δ_C 23.89 (C-5), 24.81 (C-6), 28.05 (=NC**Me**$_3$), 28.85 (C-4), 33.71 (C-7), 54.66 (=N**C**Me_3), 64.73 (C-3a), 79.92 (C-7a), 89.43 (d, *J* 7 Hz), 92.18 (C-2), 92.48, 94.34 (d, *J* 5 Hz), 97.97 (d, *J* 3 Hz), 104.06 (d, *J* 30 Hz, C-2′), 119.22 (d, *J* 20 Hz, C-1′), 128.15 (d, *J* 7 Hz, 2 × ArH *m*), 128.38 (d, *J* 5 Hz, 2 × ArH *m*), 129.23 (2 × ArH *p*), 132.68 (d, *J* 19 Hz, 2 × ArH *o*), 134.80 (d, *J* 20 Hz, 2 × ArH *o*), 136.00 (d, *J* 14 Hz, 2 × ArH *ipso*), 232.60 ($Cr(\mathbf{C}O)_3$). *m/z* 579 (M^+, 5%), 495 (M-3CO, 85), 438 (M-3CO–C_4H_9, 100), 397 ($Ph_2PC_6H_4Cr(CO)_3$, 5), 386 (M-3CO–C_4H_9–Cr, 11), 313 ($Ph_2PC_6H_4Cr$, 6), 261 ($Ph_2PC_6H_4$, 4), 252 (M-3CO–PPh_2–C_4H_9–H, 5), 212 ($C_6H_4Cr(CO)_3$, 9), 52 (Cr, 72).

3.8. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-2′-trimethylstannylphenyl)benzoxazole]chromium(0) (**8**)

The general procedure was the same as described for the preparation of **6**. Complex **1** (200 mg, 0.51 mmol) was treated with butyllithium (2.47 mol l^{-1} in hexanes, 0.27 ml, 0.67 mmol) and chlorotrimethylstannane (200 mg, 1.0 mmol, dissolved in THF (2 ml). Column chromatography of the crude product on silica gel with hexanes containing increasing quantities of diethyl ether gave the title complex (265 mg, 0.48 mmol, 94%). Recrystallization from hexanes afforded yellow needles, m.p. 138–139 °C (Found: M^+, 557.0849/559.0854; $C_{23}H_{33}CrNO_4Sn$. Calc.: M, 557.0831/559.0837). ν_{max} ($CDCl_3$) 2972, 2946, 2872, 1961, 1878, 1475, 1458, 1448, 1397, 1381, 1361, 1320, 1256, 1213, 1177, 1115, 1060, 1038, 1009, 978, 942, 864, 830, 772 cm^{-1}. δ_H 0.34 (s, 9H, $Sn(C\mathbf{H}_3)_3$), 1.13 (s, 9H, $NC(C\mathbf{H}_3)_3$), 1.13–1.33 (m, 3H), 1.52 (dddd, *J* 3.8, 11.6, 11.6, 11.6 Hz, 1H), 1.65–1.69 (m, 1H), 1.74–1.78 (m, 1H), 1.97–2.07 (m, 2H), 2.46 (ddd, *J* 2.8, 10, 10 Hz, 1H, H-3a), 2.96 (ddd, *J* 3.5, 10, 11.4 Hz, 1H, H-7a), 5.24 (dd, *J* 1.2, 6 Hz, 1H, H-3′), 5.31 (s, 1H, H-2), 5.33 (ddd, *J* 1.2, 6, 6 Hz, 1H), 5.42 (ddd, *J* 1.2, 6, 6 Hz, 1H), 6.14 (dd, *J* 1.2, 6 Hz, 1H,

H-6′). δ_C −7.05 (–Sn**Me**$_3$), 24.03 (C-5), 24.84 (C-6), 27.80 (=NC**Me**$_3$), 30.01 (C-4), 33.66 (C-7), 54.73 (=N**C**Me$_3$), 64.99 (C-3a), 79.95 (C-7a), 89.70, 91.71, 94.99, 95.67, 99.57, 102.83 (C-2′), 119.83 (C-1′), 233.80 (Cr(**C**O)$_3$). *m/z* 559 (M^+, 22%), 544 (M-Me, 6), 503 (M-2CO, 2), 475 (M-3CO, 29), 459 (M-Me–CO–C_4H_9, 28), 418 (M-3CO–C_4H_9, 70), 310 (M-3CO–Me_3Sn, 29), 252 ($C_{13}H_{14}CrNO$, M-3CO–C_4H_9–Me_3Sn–H, 100), 57 (C_4H_9, 24), 52 (Cr, 71).

3.9. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-2′-benzylphenyl)benzoxazole]chromium(0) (9)

Complex **1** (235 mg, 0.6 mmol) was dissolved in dry THF (20 ml) and cooled to −78°C for 45 min. Butyllithium (2.47 mol l^{-1} in hexanes, 0.32 ml, 0.79 mmol) was added and the reaction mixture was stirred for 2.5 h at −78°C. Benzyl bromide (0.3 ml, 2.52 mmol) was then added. After stirring at −78°C for 2.5 h, the reaction mixture was allowed to warm to r.t. over 45 min. Saturated aqueous sodium hydrogencarbonate (five drops) was added, the solution was dried over anhydrous sodium carbonate, diluted with diethyl ether (35 ml), and filtered through Celite. Evaporation of the solvent and recrystallization of the residue from hexanes gave the title complex (283 mg, 0.58 mmol, 98%) as a yellow solid, m.p. 164.7–166 °C (Found: M^+, 485.1653; $C_{27}H_{31}CrNO_4$. Calc.: M, 485.1658). ν_{max} ($CDCl_3$) 2972, 2943, 2872, 1964, 1894, 1496, 1456, 1397, 1362, 1327, 1213, 1179, 1115, 1063, 1034, 1007 cm^{-1}. δ_H 1.20 (s, 9H, NC(C**H**$_3$)$_3$), 1.22–1.38 (m, 3H), 1.49 (dddd, *J* 4, 11.7, 11.7, 11.7 Hz, 1H), 1.70–1.80 (m, 2H), 1.87–1.92 (m, 1H), 2.10–2.14 (m, 1H), 2.50 (ddd, *J* 2.5, 10, 10 Hz, 1H, H-3a), 3.10 (ddd, *J* 3.3, 10, 11.4 Hz, 1H, H-7a), 3.85 (d, *J* 16 Hz, 1H), 4.30 (d, *J* 16 Hz, 1H), 4.69 (dd, *J* 1, 6 Hz, 1H, H-3′), 5.22 (ddd, *J* 1, 6, 6 Hz, 1H), 5.36 (ddd, *J* 1, 6, 6 Hz, 1H), 5.67 (s, 1H, H-2), 6.29 (dd, *J* 1, 6 Hz, 1H, H-6′), 7.23–7.28 (m, 3H), 7.30–7.35 (m, 2H). δ_C 24.02 (C-5), 24.89 (C-6), 27.94 (=NC**Me**$_3$), 29.82 (C-4), 33.54 (C-7), 37.10 (Ph**C**H$_2$), 54.89 (=N**C**Me$_3$), 64.87 (C-3a), 79.81 (C-7a), 88.55, 88.83, 92.20 (C-2), 95.16, 95.30, 111.10 (C-2′), 113.29 (C-1′), 126.74, 128.50, 129.69, 137.86, 233.43 (Cr(CO)3). *m/z* 485 (M^+, 16%), 401 (M-3CO, 100), 386 (M-3CO–Me, 8), 344 (M-3CO–C_4H_9, 94), 303 ($C_6H_5CH_2C_6H_4Cr(CO)_3$, 13), 254 (M-3CO–C_4H_9–C_6H_5CH, 9), 245 ($C_6H_5CH_2C_6H_4CrCN$, 20), 219 ($C_6H_5CH_2C_6H_4Cr$, 20), 57 (C_4H_9, 11), 52 (Cr, 61).

3.10. Tricarbonyl[(3a,7a-trans)-octahydro-3-(t-butyl)-2-(η^6-(2′-phenylmethanol)phenyl)benzoxazole]chromium(0) (10)

The general procedure was the same as described for the preparation of **9**. Complex **1** (245 mg, 0.62 mmol) was treated with butyllithium (2.47 mol l^{-1} in hexanes, 0.35 ml, 0.86 mmol) and benzaldehyde (0.20 ml, 1.96 mmol) to give the title complex in 100% yield. Recrystallization from hexanes/dichloromethane afforded yellow crystals, m.p. 197–198°C. (Found: C, 64.45; H, 6.1; N, 2.65: $C_{27}H_{31}CrNO_5$. Calc.: C, 64.7; H, 6.2; N, 2.8%). (Found: M^+, 501.1601. $C_{27}H_{31}CrNO_5$. Calc: M, 501.1607). ν_{max} ($CDCl_3$) 3430, 2927, 2855, 1958, 1887, 1884, 1479, 1456, 1420, 1364, 1320, 1293, 1257, 1228, 1200, 1166, 1118, 1030, 1018 cm^{-1}. δ_H 1.18–1.23 (m, 1H), 1.23 (s, 9H, NC(C**H**$_3$)$_3$), 1.29–1.42 (m, 2H), 1.63 (dddd, *J* 4, 11.7, 11.7, 11.7 Hz, 2H), 1.72–1.84 (m, 2H), 2.02–2.06 (m, 1H), 2.13–2.17 (m, 1H), 2.58 (ddd, *J* 2.6, 10, 10 Hz, 1H, H-3a), 3.28 (ddd, *J* 3.4, 10, 11.2 Hz, 1H, H-7a), 4.62 (dd, *J* 1, 6 Hz, 1H, H-3′), 5.24 (ddd, *J* 1, 6, 6 Hz, 1H), 5.36 (ddd, *J* 1, 6, 6 Hz, 1H), 5.54 (d, *J* 2.4 Hz, 1H), 5.98 (d, *J* 2.4 Hz, 1H), 6.00 (s, 1H, H-2), 6.17 (dd, *J* 1, 6 Hz, 1H, H-6′), 7.34 (dt, *J* 1, 7 Hz, 1H), 7.42 (ddd, *J* 1, 7, 7 Hz, 2H), 7.66 (dd, *J* 1, 7 Hz, 2H). δ_C 23.84 (C-5), 24.72 (C-6), 27.92 (=NC**Me**$_3$), 29.68 (C-4), 33.41 (C-7), 55.13 (=N**C**Me$_3$), 64.32 (C-3a), 70.64 (Ph**C**H(OH)–), 79.95 (C-7a), 88.88, 91.15, 92.27, 93.75, 93.95, 111.30 (C-2′), 114.00 (C-1′, 127.31, 128.04, 128.08, 138.24, 232.64 (Cr(**C**O)$_3$). *m/z* 501 (M^+, 18%), 445 (M-2CO, 4), 417 (M-3CO, 46), 399 (M-3CO–H_2O, 4), 360 (M-3CO–C_4H_9, 68), 342 (M-3CO–C_4H_9–H_2O, 43), 319 ($C_6H_5CH(OH)C_6H_4Cr(CO)_3$, 9), 254 (M-3CO–$C_4H_9$–$C_6H_5CO$, 44), 245 ($C_6H_5CH_2C_6H_4CrCN$, 100), 105 ($C_6H_5CO$, 6), 57 ($C_4H_9$, 17), 52 (Cr, 67).

3.11. (3a,7a-cis)-Octahydro-2-phenyl-3-(p-toluenesulfonyl)benzoxazole (12)

A mixture of *cis*-2-(*p*-toluenesulfonylamino)-cyclohexanol (**13**) (100 mg, 0.37 mmol), (dimethoxymethyl)benzene (226 mg, 1.48 mmol) and pyridinium *p*-toluenesulfonate (0.02 mmol) in dry toluene (35 ml) was refluxed under a nitrogen atmosphere for 48 h, with a small Soxhlet apparatus containing 4 Å molecular sieves placed between the reaction flask and the reflux condenser. The solvent was evaporated under reduced pressure and the oily residue was taken up in diethyl ether (20 ml), and stirred with saturated $NaHCO_3$ (five drops). The mixture was dried over anhydrous sodium carbonate, filtered and the volatiles removed under vacuum to give the title compound, as a pale brown solid (100%). Recrystallization from hexanes/diethyl ether afforded a white solid, m.p. 157.3–158.5°C (Found: M^+, 357.1377; $C_{20}H_{23}NO_3S$. Calc.: M, 357.1399). ν_{max} ($CDCl_3$) 2972, 2943, 2872, 1988, 1885, 1449, 1414, 1396, 1361, 1328, 1254, 1214, 1180, 1116, 1063, 1008 cm^{-1}. δ_H 1.23–1.26 (m, 1H), 1.37–1.76 (m, 5H), 2.00–2.11 (m, 2H), 2.38 (m, 3H),

3.50–3.55 (m, 1H, H-3a), 3.89 (ddd, *J* 4.6, 6.5, 11 Hz, 1H, H-7a), 6.01 (s, 1H, H-2), 7.34 (d, *J* 8 Hz, 2H), 7.39–7.47 (m, 3H), 7.74 (dd, *J* 2, 8 Hz, 2H), 7.80 (d, *J* 8 Hz, 2H). δ_C 19.41 (t), 21.10 (q), 22.90 (t), 26.92 (t), 29.48 (t), 57.69 (C-3a), 75.53 (C-7a), 90.75 (C-2), 126.90 (d), 127.32 (d), 127.82 (d), 128.38 (d), 129.56 (d), 135.02 (s), 138.46 (s), 143.64 (s). *m*/*z* 357 (M^+, 6%), 280 (M-C_6H_5, 46), 252 (M-C_6H_5CO, 2), 202 (M-$MeC_6H_4SO_2$, 98), 155 ($MeC_6H_4SO_2$, 19), 105 (C_6H_5CO, 22), 91 (MeC_6H_4, 100), 81 (C_5H_5O, 15), 77 (C_6H_5, 16).

*3.12. Tricarbonyl[(3a,7a-cis)-octahydro-2-(η^6-phenyl)-3-(p-toluenesulfonyl)benzoxazole]-chromium(0) (**11**)*

A mixture of (3a,7a-*cis*)-octahydro-2-phenyl-3-(*p*-toluenesulfonyl)benzoxazole (**12**) (0.8 g, 2.24 mmol) and hexacarbonylchromium(0) (0) (0.54 g, 2.45 mmol) was dissolved in dibutyl ether (36 ml) and THF (4 ml), and the solution was purged with dry nitrogen for 1 min. The solution was then heated under reflux, with a continuous flow of nitrogen, for 45 h. The resulting yellow solution was cooled, diluted with diethyl ether (20 ml) and filtered through Celite. Evaporation of the solvent and column chromatography of the yellow residue on silica with hexanes containing increasing quantities of dichloromethane gave the title complex (100%). Recrystallization from hexanes/diethyl ether afforded yellow crystals, m.p. 152–153.7°C (Found: M^+, 493.0651. $C_{23}H_{23}CrNO_6S$. Calc.: M, 493.0651). ν_{max} ($CDCl_3$) 3094, 2941, 2872, 1970, 1894, 1598, 1495, 1450, 1428, 1351, 1307, 1286, 1204, 1166, 1115, 1090, 1043, 1021, 989, 965, 873, 816 cm^{-1}. δ_H 1.09–1.18 (m, 1H), 1.33–1.61 (m, 4H), 1.68–1.72 (m, 1H), 1.92–1.99 (m, 1H), 2.07–2.11 (m, 1H), 2.46 (s, 3H), 3.26–3.28 (m, 1H, H-3a), 3.68 (ddd, *J* 4.6, 6.5, 11 Hz, 1H, H-7a), 5.30–5.38 (m, 3H), 5.58 (s, 1H, H-2), 5.73 (d, *J* 6 Hz, 1H), 5.95 (d, *J* 6 Hz, 1H), 7.37 (d, *J* 8 Hz, 2H), 7.76 (d, *J* 8 Hz, 2H). δ_C 19.79 (t), 21.61 (q), 23.31 (t), 27.10 (t), 29.93 (t), 58.20 (C-3a), 76.02 (C-7a), 88.70 (d), 90.80 (C-2), 90.88 (d), 91.20 (d), 93.12 (d), 93.81 (d), 108.41 (s), 127.79 (d), 130.24 (d), 134.65 (s), 144.64 (s), 232.45 (Cr(**C**O)$_3$). *m*/*z* 493 (M^+, 2%), 437 (M-2CO, 3), 409 (M-3CO, 29), 357 (M-3CO–Cr, 4), 327 (M-3CO–C_6H_{10}, 10), 280 (M-3CO–C_6H_5Cr, 42), 252 (M-3CO–C_6H_5 CrCO, 3), 202 (M-3CO–Cr–$MeC_6H_4SO_2$, 82), 171 (M-3CO–C_6H_{10}–$MeC_6H_4SO_2H$, 26), 155 ($MeC_6H_4SO_2$, 18), 105 (C_6H_5CO, 28), 91 (MeC_6H_4, 100), 81 (C_5H_5O, 15), 77 (C_6H_5, 17), 52 (Cr, 28).

*3.13. Deprotonation–iodomethane quenching of complex **11***

Complex **11** (160 mg, 0.32 mmol) was dissolved in dry THF (10 ml) and cooled to −78°C for 45 min. Butyllithium (1.94 mol l^{-1} in hexanes, 0.17 ml, 0.33 mmol) was added. The reaction mixture was stirred at −78°C for 1.5 h and iodomethane (0.04 ml, 0.64 mmol) was then added. After stirring for 2 h at −78°C, the reaction mixture was allowed to warm to r.t. over 45 min. D_2O (five drops) was added and the mixture was stirred for 25 min, then dried over anhydrous sodium carbonate, diluted with diethyl ether (25 ml) and filtered through Celite. Evaporation of the solvent and chromatography of the yellow residue on silica gel with hexanes containing increasing quantities of dichloromethane gave, in increasing order of polarity, tricarbonyl[(3a,7a-*cis*)-octahydro-2-(η^6-phenyl)-3-(2,4-dimethylsulfonylbenzene)benzoxazole]chromium(0) (**14**) (81 mg, 0.16 mmol, 50%), the starting complex (**11**) (67 mg, 0.14 mmol, 41%), methyl *p*-toluenesulfinate (**15**) (4 mg, 0.02 mmol, 7%), and tricarbonyl[(3a,7a-*cis*)-(3a,4,5,6,7,7a)-hexahydro-2-(η^6-phenyl)benzoxazole]chromium(0) (**16**) (9 mg, 0.03 mmol, 8%).

*3.13.1. Compound **14***

Found: M^+, 507.0797; $C_{24}H_{25}CrNO_6S$. Calc.: M, 507.0808). ν_{max} ($CDCl_3$) 2939, 2866, 1976, 1888, 1602, 1568, 1450, 1432, 1342, 1310, 1204, 1172, 1157, 1141, 1114, 1057, 973, 814 cm^{-1}. δ_H 1.07–1.66 (m, 6H), 2.22–2.32 (m, 2H), 2.37 (s, 3H), 2.41 (s, 3H), 3.64 (ddd, *J* 4.6, 6.5, 11 Hz, 1H), 4.01–4.10 (m, 1H), 5.20–5.34 (m, 3H), 5.69 (d, *J* 6 Hz, 2H), 5.85 (s, 1H, H-2), 7.06 (s, 1H), 7.13 (d, *J* 8 Hz, 1H), 7.89 (d, *J* 8 Hz, 1H). δ_C 19.96 (t), 20.30 (q), 21.35 (q), 23.35 (t), 27.13 (t), 29.26 (t), 57.78 (C-3a), 77.04 (C-7a), 88.08 (d), 90.31 (C-2), 90.65 (d × 2), 92.91 (d), 93.89 (d), 107.58 (s), 127.05 (d), 130.47 (d), 133.29 (s), 133.52 (d), 138.60 (s), 144.73 (s), 232.22 (Cr(**C**O)$_3$). *m*/*z* 507 (M^+, 4%), 479 (M-CO, 2), 451 (M-2CO, 9), 423 (M-3CO, 100), 341 (M-3CO–C_6H_{10}, 33), 294 (M-3CO–C_6H_5Cr, 16), 202 (M-3CO–Cr–$Me_2C_6H_3SO_2$, 47), 171 (M-3CO–C_6H_{10}–$Me_2C_6H_3SO_2H$, 66), 105 ($Me_2C_6H_3$, 37), 91 (MeC_6H_4, 18), 77 (C_6H_5, 13), 52 (Cr, 49).

*3.13.2. Compound **15***

Found: M^+, 170.0406; $C_8H_{10}O_2S$. Calc.: M, 170.0402). δ_H 2.46 (s, 3H), 3.03 (s, 3H), 7.37 (d, *J* 8 Hz, 2H), 7.83 (d, *J* 8 Hz, 2H). *m*/*z* 170 (M^+, 36%), 155 (M-Me, 38), 91 (MeC_6H_4, 100).

*3.13.3. Compound **16***

Found: M^+, 337.0390; $C_{16}H_{15}CrNO_4$. Calc.: M, 337.0406). ν_{max} ($CDCl_3$) 2943, 2864, 1976, 1904, 1638, 1450, 1349, 1156 cm^{-1}. δ_H 1.43–1.60 (m, 5H), 1.80–1.88 (m, 1H), 2.15–2.37 (m, 2H), 4.05–4.15 (m, 1H), 4.60–4.73 (m, 1H), 5.30–5.39 (m, 2H), 5.42 (d, *J* 6 Hz, 1H), 6.00 (d, *J* 6 Hz, 1H), 6.09 (d, *J* 6 Hz, 1H). *m*/*z* 337 (M^+, 6%), 281 (M-2CO, 6), 253 (M-3CO, 100), 201 (M-3CO–Cr, 4), 171 (M-3CO–C_6H_{10}, 12), 155 (C_6H_5 CrCN, 16), 81 (C_5H_5O, 6), 52 (Cr, 53).

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