

# Synthesis of chiral multidentate tertiary arsines with As<sub>4</sub> or As<sub>6</sub> donor atoms

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Reaction of 1,1,1-tris(chloromethyl)ethane with *ca.* three equivalents of sodium or lithium (2-dimethylarsinophenyl)methylarsenide in thf gave several products including the tetra(tertiary arsine) ( $R_{As}^*$ ,  $R_{As}^*$ )-, ( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ )- and ( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ )-1-(chloromethyl)-1,1-bis{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane and the hexa(tertiary arsine) ( $R_{As}^*$ ,  $R_{As}^*$ ,  $R_{As}^*$ )-1,1,1-tris{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane. The latter is the first example of a chiral hexa(tertiary arsine). The products from the reaction have been separated by complexation to cobalt(III). The three diastereomers of the tetra(tertiary arsine) each bind to the metal centre in a completely stereoselective manner: the ( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ ) and ( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ ) forms of the ligand each form a single *trans* dichloro complex and the ( $R_{As}^*$ ,  $R_{As}^*$ ) diastereomer a *cis-a* complex. The structure of the latter has been confirmed by an X-ray analysis. Three other complexes have also been isolated from this reaction: *trans*-dichlorobis[1,2-phenylenebis(dimethylarsine)cobalt(III) chloride, a *cis-a* complex of the cyclic chiral tetra(tertiary arsine) ( $R_{As}^*$ ,  $S_{As}^*$ ,  $R_{As}^*$ )-5,6,7,8,9-pentahydro-6-{[(2-dimethylarsinophenyl)methylarsino]methyl}-1,4,6-trimethylbenzo[*b*]-[1,4]diarsacycloheptane and a cobalt(III) complex of the chiral hexa(tertiary arsine). The structures of the latter two complexes have been confirmed by X-ray analyses.

The first reported synthesis of a ligand containing more than two arsenic donor atoms was by Barclay and Nyholm in 1953 who prepared the tri(tertiary arsine) MeAs[(CH<sub>2</sub>)<sub>3</sub>AsMe<sub>2</sub>]<sub>2</sub> (Triars).<sup>1</sup> Since this time a range of multidentate ligands containing arsenic donor atoms have been reported including the tri(tertiary arsines) RAs[(CH<sub>2</sub>)<sub>3</sub>AsMe<sub>2</sub>]<sub>2</sub> [where R = Ph, Cl(CH<sub>2</sub>)<sub>2</sub> or CH<sub>2</sub>CHCH<sub>2</sub>], PhAs(C<sub>6</sub>H<sub>4</sub>AsPh<sub>2</sub>-2)<sub>2</sub>, MeAs(C<sub>6</sub>H<sub>4</sub>AsMe<sub>2</sub>-2)<sub>2</sub>, ClCH<sub>2</sub>C(CH<sub>2</sub>AsPh<sub>2</sub>)<sub>3</sub>, ClCH<sub>2</sub>C(CH<sub>2</sub>AsI<sub>2</sub>)<sub>3</sub> and MeC(CH<sub>2</sub>AsMe<sub>2</sub>)<sub>3</sub>, and the branched tetra(tertiary arsines) As[(CH<sub>2</sub>)<sub>3</sub>AsMe<sub>2</sub>]<sub>3</sub>, As(C<sub>6</sub>H<sub>4</sub>AsPh<sub>2</sub>-2)<sub>3</sub>, C(CH<sub>2</sub>AsMe<sub>2</sub>)<sub>4</sub> and As(C<sub>6</sub>H<sub>4</sub>AsMe<sub>2</sub>-2)<sub>3</sub>.<sup>2</sup> Several chiral, linear tetra(tertiary arsines) have also been synthesized including ( $R_{As}^*$ ,  $R_{As}^*$ )-C<sub>6</sub>H<sub>4</sub>[AsMe(C<sub>6</sub>H<sub>4</sub>AsMe<sub>2</sub>-2)]<sub>2</sub>-1,2 (Qars), ( $R_{As}^*$ ,  $R_{As}^*$ )-C<sub>6</sub>H<sub>4</sub>{AsMe[(CH<sub>2</sub>)<sub>3</sub>-AsMe<sub>2</sub>]}<sub>2</sub>-1,2 (Fars), and ( $R_{As}^*$ ,  $R_{As}^*$ )-C<sub>2</sub>H<sub>4</sub>{AsPh[(CH<sub>2</sub>)<sub>3</sub>-AsMe<sub>2</sub>]}<sub>2</sub>-1,2 (Tetars).<sup>3</sup> All three linear tetra(tertiary arsines) were isolated as a separable mixture of racemic and *meso* diastereomers. Bosnich *et al.* also successfully resolved the racemic form of Tetars.<sup>3</sup> Furthermore, several macrocyclic ligands have been prepared containing three, four or six arsenic donor atoms.<sup>4</sup> Only one example of a chelating hexa(tertiary arsine), *viz.* C<sub>6</sub>H<sub>4</sub>{As[(CH<sub>2</sub>)<sub>3</sub>AsMe<sub>2</sub>]}<sub>2</sub>-1,2, has been reported to date.<sup>5</sup>

In this paper we report on the synthesis of the tetra(tertiary arsine) ( $R_{As}^*$ ,  $R_{As}^*$ )-, ( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ )- and ( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ )-1-(chloromethyl)-1,1-bis{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane and the hexa(tertiary arsine) ( $R_{As}^*$ ,  $R_{As}^*$ ,  $R_{As}^*$ )- and ( $R_{As}^*$ ,  $R_{As}^*$ ,  $S_{As}^*$ )-1,1,1-tris{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane. The latter is the first example of a chiral hexa(tertiary arsine).

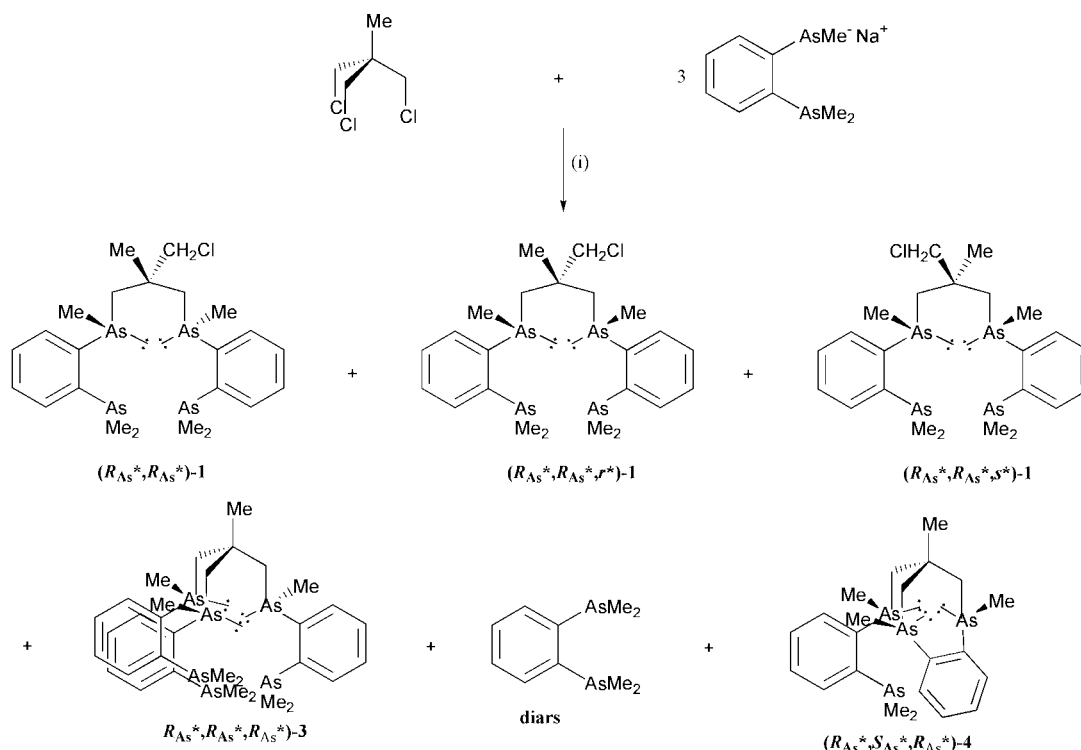
## Results and discussion

### Synthesis

Reaction of 1,1,1-tris(chloromethyl)ethane with *ca.* three equivalents of sodium (2-dimethylarsinophenyl)methylarsenide

[generated *in situ* from ( $\pm$ )-1-(dimethylarsino)-2-(methylarsino)benzene, ( $\pm$ )-**2**,<sup>6</sup> and sodium] in thf at  $-20 \pm 5^\circ\text{C}$  produced a number of products that were most conveniently separated by complexation to cobalt(III) (Scheme 1). Isolated complexes include *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl<sup>7,8</sup> and three diastereomeric complexes of the tetra(tertiary arsine) 1-(chloromethyl)-1,1-bis{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane, **1**, *viz.* *cis-a*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $R_{As}^*$ )-**1**}]Cl, *trans*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ )-**1**}]Cl and *trans*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ )-**1**}]Cl. Two further compounds have also been isolated: a cobalt(III) complex of the chiral hexa(tertiary arsine) ( $R_{As}^*$ ,  $R_{As}^*$ ,  $R_{As}^*$ )-1,1,1-tris{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane, ( $R_{As}^*$ ,  $R_{As}^*$ ,  $R_{As}^*$ )-**3**, and a *cis-a* complex of the cyclic chiral tetra(tertiary arsine) ( $R_{As}^*$ ,  $S_{As}^*$ ,  $R_{As}^*$ )-5,6,7,8,9-pentahydro-6-{[(2-dimethylarsinophenyl)methylarsino]methyl}-1,4,6-trimethylbenzo[*b*][1,4]diarsacycloheptane, ( $R_{As}^*$ ,  $S_{As}^*$ ,  $R_{As}^*$ )-**4**, *viz.* [Co{( $R_{As}^*$ ,  $R_{As}^*$ ,  $R_{As}^*$ )-**3**}]Cl<sub>3</sub> and *cis-a*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $S_{As}^*$ ,  $R_{As}^*$ )-**4**}]Cl. All of the complexes were separated via a combination of fractional crystallisation techniques and ion exchange chromatography.

Clearly incomplete substitution of the three chloro groups in 1,1,1-tris(chloromethyl)ethane was apparent under these reaction conditions resulting in the formation of the tetra(tertiary arsine) **1**. The quadridentate ligand exists in three diastereomeric forms: a racemic form, ( $R_{As}^*$ ,  $R_{As}^*$ )-**1**, containing two chirotopic<sup>9</sup> arsenic stereocentres, and two *meso* diastereomers each containing three stereogenic atoms, two chirotopic arsenic stereocentres and a pseudo asymmetric carbon centre or more correctly achirotopic<sup>9</sup> carbon stereocentre, *viz.* ( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ )- and ( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ )-**1**. Furthermore, they each bind to cobalt(III) in a completely stereoselective manner: the ( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ ) and ( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ ) forms of the ligand each form a single *trans* dichloro complex, *trans*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $S_{As}^*$ ,  $r^*$ )-**1**}]Cl and *trans*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $S_{As}^*$ ,  $s^*$ )-**1**}]Cl and the ( $R_{As}^*$ ,  $R_{As}^*$ ) diastereomer a *cis-a* complex, *cis-a*-[CoCl<sub>2</sub>{( $R_{As}^*$ ,  $R_{As}^*$ )-**1**}]Cl.



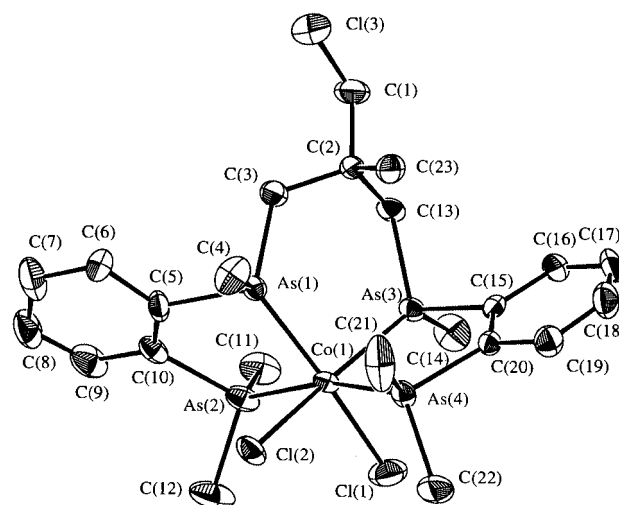
**Scheme 1** Only one enantiomer of each chiral compound is shown. (i) thf,  $-78\text{ }^{\circ}\text{C}$ .

The isolation of a cobalt(III) complex containing the chelating hexa(tertiary arsine) ( $R_{As^*}, R_{As^*}, R_{As^*}$ )-**3** provides clear-cut evidence that complete substitution of the three chloro groups in 1,1,1-tris(chloromethyl)ethane should be possible under the appropriate conditions. Indeed, when the reaction was carried out in the presence of *ca.* five equivalents of sodium (2-dimethylarsinophenyl)methylarsenide in thf no evidence was found for the presence of the disubstituted compounds ( $R_{As^*}, S_{As^*}, R_{As^*}$ )-, ( $R_{As^*}, S_{As^*}, S_{As^*}$ )- and ( $R_{As^*}, R_{As^*}$ )-**1**. The  $^1\text{H}$  NMR spectrum of the crude product from the reaction contained no resonances that could be attributed to the chloromethyl group and the mass spectrum was devoid of a peak corresponding to the molecular ion of **1**. The latter did, however, contain a peak at  $m/z$  867 corresponding to the  $[M^+ - 15]$  ion of **3**. The products from the reaction were again separated by complexation to cobalt(III) and included *trans*- $[\text{CoCl}_2(\text{diars})_2]\text{Cl}$ ,  $[\text{Co}\{(R_{As^*}, R_{As^*}, R_{As^*})\text{-3}\}]\text{Cl}_3$  and *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, S_{As^*}, R_{As^*})\text{-4}\}]\text{Cl}$ . The hexadentate ligand exists in two racemic diastereomeric forms, both of which contain three chirotopic arsenic stereocentres, *viz.* ( $R_{As^*}, R_{As^*}, R_{As^*}$ )- and ( $R_{As^*}, R_{As^*}, S_{As^*}$ )-**3**. Only the former is a chelating agent. Several compounds have been isolated by ion exchange chromatography that appear to be isomeric, dinuclear cobalt(III) complexes of ( $R_{As^*}, R_{As^*}, S_{As^*}$ )-**3**. None of these, however, has been structurally authenticated, to date.<sup>†</sup>

### Crystal structure determinations

The structures of the complexes *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, R_{As^*})\text{-1}\}]\text{PF}_6$ ,  $[\text{Co}\{(R_{As^*}, R_{As^*}, R_{As^*})\text{-3}\}]\text{PF}_6$  and *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, S_{As^*}, R_{As^*})\text{-4}\}]\text{PF}_6$  were determined by single crystal X-ray analyses. The three hexafluorophosphate salts were prepared by

<sup>†</sup> Based on the amount of  $[\text{Co}\{(R_{As^*}, R_{As^*}, R_{As^*})\text{-3}\}]\text{Cl}_3$  isolated from the two reactions, *ca.* 20–30% of the crude product from these reactions would be expected to consist of cobalt(III) complexes containing ( $R_{As^*}, R_{As^*}, S_{As^*}$ )-**3**. Several complexes have been isolated that are believed to be isomeric dinuclear cobalt(III) complexes containing the non-chelating ( $R_{As^*}, R_{As^*}, S_{As^*}$ ) diastereomer of the hexa(tertiary arsine), however, none of these has unambiguously been identified, to date. The possibility of dinuclear cobalt(III) complexes containing non-chelating diastereomers of diarsacycloheptane **4** also being present has further hampered the identification process.



**Fig. 1** Molecular structure of the cation *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, R_{As^*})\text{-1}\}]^+$ .

treatment of the appropriate chloride salts with aqueous ammonium hexafluorophosphate. In each case suitable crystals for X-ray analysis were obtained by recrystallisation of the respective hexafluorophosphate salt from acetone–2-propanol, to give dark purple needles of *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, R_{As^*})\text{-1}\}]\text{PF}_6$  and bright yellow prisms of  $[\text{Co}\{(R_{As^*}, R_{As^*}, R_{As^*})\text{-3}\}]\text{PF}_6 \cdot \text{CH}_3\text{COCH}_3 \cdot 0.3\text{H}_2\text{O}$ , or *n*-butanol–acetone to give large red-brown needles of *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, S_{As^*}, R_{As^*})\text{-4}\}]\text{PF}_6 \cdot \frac{1}{3}n\text{-C}_4\text{H}_9\text{OH} \cdot \frac{1}{3}\text{H}_2\text{O}$ . The stereochemistries of the three cations *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, R_{As^*})\text{-1}\}]^+$ ,  $[\text{Co}\{(R_{As^*}, R_{As^*}, R_{As^*})\text{-3}\}]^{3+}$  and *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, S_{As^*}, R_{As^*})\text{-4}\}]^+$  are shown in Figs. 1, 2 and 3, respectively. All three complexes are racemic with both  $\Delta$  and  $\Lambda$  forms of the cations being present in the respective unit cells. Only the  $\Lambda$  form is shown for the cations *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, R_{As^*})\text{-1}\}]^+$  and *cis-a*- $[\text{CoCl}_2\{(R_{As^*}, S_{As^*}, R_{As^*})\text{-4}\}]^+$  and the  $\Delta$  configuration for the cation  $[\text{Co}\{(R_{As^*}, R_{As^*}, R_{As^*})\text{-3}\}]^{3+}$ . Selected bond lengths and angles for the three cations are given in Table 1. The Co–As bond lengths do not vary appreciably (2.30–2.36 Å) and are similar to those previously reported

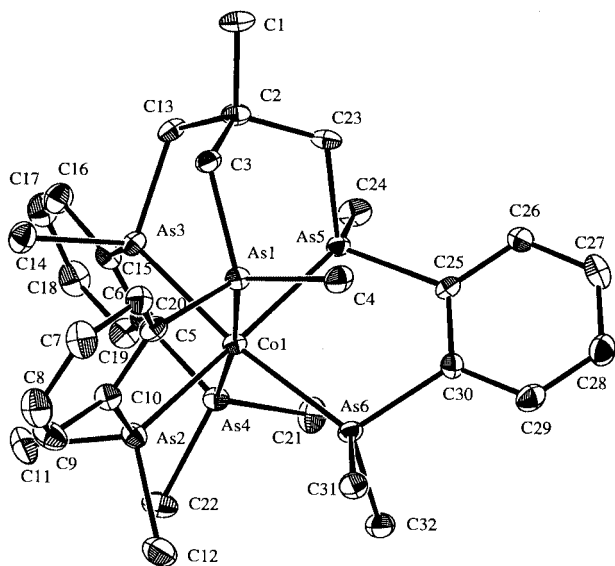


Fig. 2 Molecular structure of the cation  $[\text{Co}\{(R_{\text{As}}^*, R_{\text{As}}^*, R_{\text{As}}^*)\text{-3}\}]^{3+}$ .

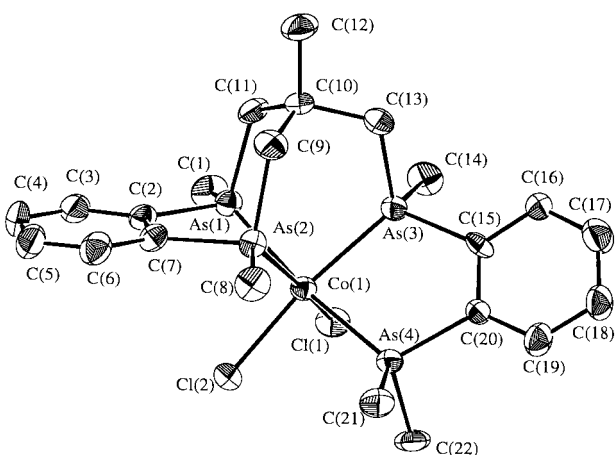


Fig. 3 Molecular structure of the cation  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, R_{\text{As}}^*)\text{-4}\}]^+$ .

for related cobalt(III) complexes containing tertiary arsine ligands.<sup>7,8</sup>

It is clear from the structural data for the cation  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, R_{\text{As}}^*)\text{-1}\}]^+$  that only two of the chloro groups in 1,1,1-tris(chloromethyl)ethane have been substituted by the (2-dimethylarsinophenyl)methylarsenide ion. Furthermore, both stereogenic arsenic atoms of the quadridentate ligand have the same relative configurations. Complete substitution of the chloro groups in 1,1,1-tris(chloromethyl)ethane by the (2-dimethylarsinophenyl)methylarsenide ion is confirmed from the structural data for the cation  $[\text{Co}\{(R_{\text{As}}^*, R_{\text{As}}^*, R_{\text{As}}^*)\text{-3}\}]^{3+}$ . The data reveal a  $C_3$  symmetric cation containing a chelating hexa(tertiary arsine) with three stereogenic arsenic atoms that have the same relative configurations. The structural data for the cation  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, R_{\text{As}}^*)\text{-4}\}]^+$  are similarly consistent with complete substitution of the chloro groups in 1,1,1-tris(chloromethyl)ethane, however, the ligand only contains a single (2-dimethylarsinophenyl)methylarsino moiety. The other two chloro groups have been replaced by a single 1,2-phenylenebis(methylarsino) moiety forming a diarsacycloheptane ring. The resultant quadridentate ligand has three stereogenic arsenic atoms, two of which are members of the diarsacycloheptane ring and have opposite relative configurations.

### NMR Spectra

The  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra of the complexes  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, R_{\text{As}}^*)\text{-1}\}]\text{Cl}$ ,  $[\text{Co}\{(R_{\text{As}}^*, R_{\text{As}}^*, R_{\text{As}}^*)\text{-3}\}]\text{Cl}_3$  and

Table 1 Selected non-hydrogen interatomic distances (Å) and interatomic angles ( $^\circ$ ) for  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, R_{\text{As}}^*)\text{-1}\}]\text{PF}_6$ , A; of  $[\text{Co}\{(R_{\text{As}}^*, R_{\text{As}}^*, R_{\text{As}}^*)\text{-3}\}]\text{PF}_6 \cdot \text{CH}_3\text{COCH}_3 \cdot 0.3\text{H}_2\text{O}$ , B; and  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, R_{\text{As}}^*)\text{-4}\}]\text{PF}_6 \cdot \frac{1}{3}n\text{-C}_4\text{H}_9\text{OH} \cdot \frac{1}{3}\text{H}_2\text{O}$ , C

|                      | A         | B         | C        |
|----------------------|-----------|-----------|----------|
| Co–As(1)             | 2.299(2)  | 2.332(2)  | 2.319(2) |
| Co–As(2)             | 2.343(2)  | 2.362(2)  | 2.345(2) |
| Co–As(3)             | 2.303(2)  | 2.342(2)  | 2.328(3) |
| Co–As(4)             | 2.321(2)  | 2.364(2)  | 2.364(2) |
| Co–As(5)             | —         | 2.355(2)  | —        |
| Co–As(6)             | —         | 2.360(2)  | —        |
| Co–Cl(1)             | 2.275(4)  | —         | 2.253(4) |
| Co–Cl(2)             | 2.289(3)  | —         | 2.249(4) |
| As(1)–Co–Cl(1)/As(5) | 169.5(1)  | 85.25(5)  | 92.2(1)  |
| As(2)–Co–Cl(1)/As(5) | 84.8(1)   | 171.77(7) | 168.6(1) |
| As(3)–Co–Cl(1)/As(5) | 86.1(1)   | 86.36(6)  | 88.4(1)  |
| As(4)–Co–Cl(1)/As(5) | 87.5(1)   | 95.43(6)  | 91.7(1)  |
| As(1)–Co–Cl(2)/As(6) | 86.7(1)   | 92.94(6)  | 101.7(1) |
| As(2)–Co–Cl(2)/As(6) | 86.24(8)  | 92.93(6)  | 85.4(1)  |
| As(3)–Co–Cl(2)/As(6) | 169.8(1)  | 172.34(7) | 170.7(1) |
| As(4)–Co–Cl(2)/As(6) | 83.30(8)  | 94.64(6)  | 86.0(1)  |
| Cl(1)–Co–Cl(2)       | 96.7(1)   | —         | 92.9(1)  |
| As(5)–Co–As(6)       | —         | 86.00(5)  | —        |
| As(1)–Co–As(2)       | 85.44(6)  | 86.67(5)  | 77.12(6) |
| As(1)–Co–As(3)       | 92.32(5)  | 85.91(5)  | 87.51(7) |
| As(1)–Co–As(4)       | 102.86(6) | 172.42(7) | 171.1(1) |
| As(2)–Co–As(3)       | 103.82(6) | 94.56(6)  | 95.09(8) |
| As(2)–Co–As(4)       | 166.21(7) | 92.78(6)  | 99.35(9) |
| As(3)–Co–As(4)       | 87.02(5)  | 86.59(5)  | 84.67(8) |

$\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, R_{\text{As}}^*)\text{-4}\}]\text{Cl}$  in  $\text{CD}_3\text{OD}$  can be rationalised in terms of the solid state structures of their respective hexafluorophosphate analogues. Six singlet methyl resonances were observed in the  $^1\text{H}$  NMR spectrum of  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, R_{\text{As}}^*)\text{-1}\}]\text{Cl}$ . The signals associated with two of the seven methyl groups in the complex were coincident ( $\delta$  2.07) and have been assigned to a methyl group on each of the two dimethylarsino moieties. The structural data suggest the protons attached to C(12) and C(22) reside in similar chemical environments. The most upfield singlet resonance at  $\delta$  0.63 is assigned to the CMe group due to shielding by the adjacent phenylene moiety. Four doublets and an AB quartet were also observed for the diastereotopic protons of the two  $\text{AsCH}_2$  groups and the chloromethyl group, respectively. The  $^1\text{H}$  NMR spectrum of  $[\text{Co}\{(R_{\text{As}}^*, R_{\text{As}}^*, R_{\text{As}}^*)\text{-3}\}]\text{Cl}_3$  similarly contained three singlet methyl resonances for the nine  $\text{AsMe}$  groups in keeping with the  $C_3$  symmetry of the cation. A pair of doublets was also observed for the diastereotopic protons of the three equivalent  $\text{AsCH}_2$  groups as well as a singlet CMe resonance. Individual singlet and doublet resonances were similarly observed in the  $^1\text{H}$  NMR spectrum of  $\text{cis-}a\text{-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, R_{\text{As}}^*)\text{-4}\}]\text{Cl}$  for the six methyl groups and the diastereotopic protons of the three  $\text{AsCH}_2$  moieties, respectively, consistent with the  $C_1$  symmetry of the cation. Furthermore, the respective  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra contained the appropriate number of carbon resonances in accordance with the structural data for the three complexes. In the case of the complex  $[\text{Co}\{(R_{\text{As}}^*, R_{\text{As}}^*, R_{\text{As}}^*)\text{-3}\}]\text{Cl}_3$  the assignments were confirmed by the recording of a  $^1\text{H}$ -coupled  $^{13}\text{C}$  NMR spectrum. Selected NMR data are given in Tables 2 and 3.

The stereochemistry of the cobalt(III) complexes containing  $(R_{\text{As}}^*, S_{\text{As}}^*, r^*)$ - and  $(R_{\text{As}}^*, S_{\text{As}}^*, s^*)$ -1 was assigned on the basis of NMR evidence. The  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra of the complexes  $\text{trans-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, r^*)\text{-1}\}]\text{Cl}$  and  $\text{trans-}[\text{CoCl}_2\{(R_{\text{As}}^*, S_{\text{As}}^*, s^*)\text{-1}\}]\text{Cl}$  in  $\text{CD}_3\text{OD}$  each contained three singlet  $\text{AsMe}$  resonances consistent with the proposed  $C_s$  symmetry of the two cations. The signals for the  $\text{AsMe}$  groups were coincident in the respective spectra of the two complexes. Singlet resonances were also observed for the CMe and  $\text{CH}_2\text{Cl}$  groups and doublets for the diastereotopic protons of the equivalent

**Table 2** Selected  $^1\text{H}$  NMR data for cobalt(III) complexes in  $\text{CD}_3\text{OD}$ 

| Compound  | $\delta(\text{AsMe})$             | $\delta(\text{CMe})$ | $\delta(\text{AsCH}_2)$                  | $\delta(\text{CH}_2\text{Cl})$ |
|---|-----------------------------------|----------------------|--|--------------------------------|
| <i>cis-a</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-1}]Cl                                       | 1.80s, 1.87s, 2.07s, 2.11s, 2.15s | 0.63s                | 1.77d, 2.06d, 2.25d, 2.30d               | 3.21, 3.27 ABq                 |
| <i>trans</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>S</i> <sub>As</sub> <sup>*</sup> , <i>r</i> <sup>*</sup> )-1}]Cl               | 1.81s, 1.88s, 2.07s               | 1.48s                | 2.40d, 3.11d                             | 4.02s                          |
| <i>trans</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>S</i> <sub>As</sub> <sup>*</sup> , <i>s</i> <sup>*</sup> )-1}]Cl               | 1.81s, 1.88s, 2.07s               | 1.66s                | 2.51d, 2.89d                             | 3.74s                          |
| [Co{( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-3}]Cl <sub>3</sub>                  | 1.80s, 2.15s, 2.44s               | 1.66s                | 2.53d, 3.09d                             | —                              |
| <i>cis-a</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>S</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-4}]Cl | 1.67s, 1.79s, 1.92s, 2.12s, 2.36s | 1.28s                | 1.49d, 1.56d, 2.17d, 2.22d, 2.26d, 2.36d | —                              |

**Table 3** Selected  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR data for cobalt(III) complexes in  $\text{CD}_3\text{OD}$ 

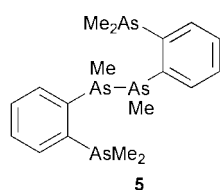
| Compound  | $\delta(\text{AsMe})$                  | $\delta(\text{CMe})$ | $\delta(\text{AsCH}_2)$ | $\delta(\text{CMe})$ | $\delta(\text{CH}_2\text{Cl})$ |
|---|--|----------------------|-------------------------|----------------------|--------------------------------|
| <i>cis-a</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-1}]Cl                                       | 11.39s, 11.50s, 12.18s, 13.18s, 13.93s | 24.90s               | 36.28s, 37.40s          | 40.33s               | 56.06s                         |
| <i>trans</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>S</i> <sub>As</sub> <sup>*</sup> , <i>r</i> <sup>*</sup> )-1}]Cl               | 10.13s, 11.27s, 12.52s                 | 31.95s               | 28.59s                  | 42.84s               | 53.78s                         |
| <i>trans</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>S</i> <sub>As</sub> <sup>*</sup> , <i>s</i> <sup>*</sup> )-1}]Cl               | 10.13s, 11.27s, 12.52s                 | 25.84s               | 28.59s                  | 42.24s               | 58.77s                         |
| [Co{( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-3}]Cl <sub>3</sub>                  | 19.05s, 20.40s, 21.79s                 | 34.93s               | 38.97s                  | 37.68s               | —                              |
| [Co{( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-3}]Cl <sub>3</sub> <sup>a</sup>     | 19.05q, 20.40q, 21.79q                 | 34.93q               | 38.97t                  | 37.68s               | —                              |
| <i>cis-a</i> -[CoCl <sub>2</sub> {( <i>R</i> <sub>As</sub> <sup>*</sup> , <i>S</i> <sub>As</sub> <sup>*</sup> , <i>R</i> <sub>As</sub> <sup>*</sup> )-4}]Cl | 3.10s, 5.22s, 11.89s, 12.36s, 15.90s   | 33.35s               | 34.74s, 36.39s, 37.56s  | 40.84s               | —                              |

<sup>a</sup> Selected  $^{13}\text{C}$  NMR data, *i.e.*  $^1\text{H}$  coupled.

AsCH<sub>2</sub> moieties in the  $^1\text{H}$  NMR spectra of the complexes. It is noteworthy that the singlet CMe resonance for *trans*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *r*<sup>\*</sup>)-1}]Cl is upfield of that recorded for *trans*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *s*<sup>\*</sup>)-1}]Cl and *vice versa* for the singlet CH<sub>2</sub>Cl resonances. Molecular models suggest that the CMe group in *trans*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *r*<sup>\*</sup>)-1}]Cl is shielded by a neighbouring 1,2-phenylene group, the same moiety shielding the CH<sub>2</sub>Cl group in the diastereomeric complex *trans*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *s*<sup>\*</sup>)-1}]Cl.

#### Analysis of the reaction between 1,1,1-tris(chloromethyl)ethane and the (2-dimethylarsinophenyl)methylarsenide ion

The reaction of 1,1,1-tris(chloromethyl)ethane with sodium (2-dimethylarsinophenyl)methylarsenide proceeds smoothly to form the disubstituted tetra(tertiary arsine) **1**, however, substitution of the third chloro group in the substrate is clearly more difficult as evidenced by the requirement of a twofold excess of the arsenide reagent to effect complete substitution. Indeed, no significant change in the degree of substitution was observed when the reaction was performed with three equivalents of the arsenide reagent at elevated temperatures or using the more reactive lithium (2-dimethylarsinophenyl)methylarsenide [generated *in situ* from ( $\pm$ )-**2** and lithium or *n*-butyllithium in thf]. A competing reaction is the formation of 1,2-bis(2-dimethylarsinophenyl)-1,2-dimethyldiarsane, **5**. Metal assisted methylation of the latter has previously been postulated to account for the formation of *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl in reactions involving the (2-dimethylarsinophenyl)methylarsenide ion.<sup>8</sup> Here the formation of diarsane **5** from sodium (2-dimethylarsinophenyl)methylarsenide was invoked to occur *via* reduction of the chloro group in ( $\pm$ )-(2-aminophenyl)(2-chlorophenyl)methylphosphine to give ( $\pm$ )-(2-aminophenyl)methylphenylphosphine. No evidence for the reduction of a chloro group in **1** has been found in the present work. Such an occurrence would have led to the isolation of a dichlorocobalt(III) complex containing the tetra(tertiary arsine) 2,2-bis{[(2-dimethylarsinophenyl)methylarsino]methyl}propane. The formation of **5**, however, also takes place in solutions of sodium (2-dimethylarsinophenyl)methylarsenide in thf. For example, when such a solution was stirred over a period of *ca.* one week at ambient temperature,



**5**

it slowly decolourised. The rate of the reaction was greatly enhanced by the addition of a catalytic amount of a free radical initiator such as azobis(isobutyronitrile), AIBN. The  $^1\text{H}$  NMR spectrum and the mass spectrum of the crude product were consistent with **5** being the primary product. Reaction of the crude product with hexaaquacobalt(II) chloride in acidified methanol followed by oxidation in air gave *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl as the sole product. The formation of the related tetramethyldiarsane, (AsMe<sub>2</sub>)<sub>2</sub>, in reactions involving thf solutions of sodium dimethylarsenide is well known, *e.g.* in the preparation of diars from C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>-1,2 and sodium dimethylarsenide.<sup>10</sup>

The conversion of (2-dimethylarsinophenyl)methylarsenide ion to diars may also be linked to the formation of the cyclic chiral tetra(tertiary arsine) (*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *R*<sub>As</sub><sup>\*</sup>)-**4**. The precursor to the latter is presumably disubstituted tetra(tertiary arsine) **1**. The mechanism of the reaction is not known but it is not inconceivable that quaternisation of a terminal dimethylarsino group in **1** by the chloromethyl moiety could take place to give an intermediate arsonium salt that is subsequently reduced by sodium (2-dimethylarsinophenyl)methylarsenide to give diars and (*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *R*<sub>As</sub><sup>\*</sup>)-**4**.

## Experimental

### Procedures and materials

Reactions involving air-sensitive reagents were performed under argon using Schlenk techniques. Solvents were dried and purified by distillation under argon. The NMR spectra were recorded on a Varian Gemini II spectrometer operating at 300 ( $^1\text{H}$ ) or 75 MHz ( $^{13}\text{C}$ - $\{^1\text{H}\}$ ). Chemical shifts are reported as  $\delta$  values relative to Me<sub>4</sub>Si. Elemental analyses were performed by staff within the Research School of Chemistry.

The compounds 1,1,1-tris(chloromethyl)ethane<sup>11</sup> and ( $\pm$ )-1-(dimethylarsino)-2-(methylarsino)benzene, ( $\pm$ )-**2**,<sup>6</sup> were prepared by literature procedures.

**Reaction of 1,1,1-tris(chloromethyl)ethane with *ca.* three equivalents of sodium (2-dimethylarsinophenyl)methylarsenide. Isolation of [OC-6-33-(*R*<sub>As</sub><sup>\*</sup>, *R*<sub>As</sub><sup>\*</sup>)-], [OC-6-22-(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *r*<sup>\*</sup>)-] and [OC-6-22-(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *s*<sup>\*</sup>)-]dichloro[1-(chloromethyl)-1,1-bis{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane-As, As', As'', As''']cobalt(III) chloride, *cis-a*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *R*<sub>As</sub><sup>\*</sup>)-1}]Cl, *trans*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *r*<sup>\*</sup>)-1}]Cl and *trans*-[CoCl<sub>2</sub>{(*R*<sub>As</sub><sup>\*</sup>, *S*<sub>As</sub><sup>\*</sup>, *s*<sup>\*</sup>)-1}]Cl**

Sodium foil (0.30 g, 0.013 mol) was added to a stirred solution of compound ( $\pm$ )-**2** (3.52 g, 0.0129 mol) in thf (70 cm<sup>3</sup>) at 0 °C.

The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting deep red solution was added dropwise over a period of 2 h to a solution of 1,1,1-tris(chloromethyl)ethane (0.75 g, 4.28 mmol) dissolved in thf (25 cm<sup>3</sup>) at -78 °C. After the addition was complete, the reaction mixture was stirred at -25 ± 5 °C for 15 days and then at room temperature for 30 days. The resulting pale yellow solution was refluxed for 3 h. Water (5 cm<sup>3</sup>) was added dropwise to the colourless solution and the solvent removed. Dichloromethane (50 cm<sup>3</sup>) and water (50 cm<sup>3</sup>) were added, the organic layer was separated off and the aqueous layer extracted with more dichloromethane (2 × 50 cm<sup>3</sup>). The combined organic extracts were dried (MgSO<sub>4</sub>), filtered and the solvent removed to give a clear, pale yellow oil (3.86 g). The yellow oil was subsequently taken up in hot methanol (80 cm<sup>3</sup>). Hexa-aquacobalt(II) chloride (1.25 g, 5.25 mmol) in methanol (75 cm<sup>3</sup>) was added followed by hydrochloric acid (10 mol dm<sup>-3</sup>, 5 cm<sup>3</sup>) and air was drawn through the solution for 3 h. The solvent was removed and the dark green residue dissolved in water (100 cm<sup>3</sup>) by heating the mixture at reflux for 4 h. The solution was reduced in volume by ca. 50% and left to stand overnight. Dark green crystals were deposited from the solution (1.65 g). The mother liquor was taken to dryness to give a purple-brown microcrystalline material (1.90 g).

A sample of the dark green crystalline material (0.5 g) was dissolved in the minimum volume of methanol and loaded onto an ion-exchange column [250 × 25 mm, Dowex 50W-X8, cation exchange resin]. The column was eluted with HCl-methanol (0.5 mol dm<sup>-3</sup>, elution rate ca. 2 cm<sup>3</sup> min<sup>-1</sup>). The first fraction collected contained exclusively *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl [where diars = 1,2-phenylenebis(dimethylarsine)] (0.14 g). Data for this complex were identical to those previously reported.<sup>7,8</sup> Two further fractions were collected containing a mixture of the diastereomeric complexes *trans*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, r<sup>\*</sup>)-1}]Cl, *trans*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, s<sup>\*</sup>)-1}]Cl and *cis-α*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]Cl (0.34 g). These were combined and separated on a second ion-exchange column [250 × 25 mm, Dowex 50W-X8, cation exchange resin]. The column was eluted with HCl-methanol (0.25 mol dm<sup>-3</sup>, elution rate ca. 2 cm<sup>3</sup> min<sup>-1</sup>). The first fraction collected contained exclusively *trans*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, r<sup>\*</sup>)-1}]Cl (0.048 g, overall yield 3%) (Found: C, 33.9; H, 4.5; Cl, 16.1. Calc. for C<sub>23</sub>H<sub>35</sub>As<sub>4</sub>Cl<sub>4</sub>Co·H<sub>2</sub>O: C, 33.3; H, 4.5; Cl, 17.1%). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 1.48 (s, 3 H, CMe); 1.81 (s, 6 H, 2 AsMe); 1.88 (s, 6 H, 2 AsMe); 2.07 (s, 6 H, 2 AsMe); 2.40 (d, 2 H, <sup>2</sup>J<sub>HH</sub> 13.3, 2 CHH); 3.11 (d, 2 H, <sup>2</sup>J<sub>HH</sub> 13.3 Hz, 2 CHH); 4.02 (s, 2 H, CH<sub>2</sub>Cl) and 7.80–8.25 (m, 8 H, aromatics). <sup>13</sup>C-<sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 10.13 (s, 1 C, AsMe); 11.27 (s, 1 C, AsMe); 12.52 (s, 1 C, AsMe); 28.59 (s, 2 C, AsCH<sub>2</sub>); 31.95 (s, 1 C, CMe); 42.84 (s, 1 C, CMe); 53.78 (s, 1 C, CH<sub>2</sub>Cl); 132.15, 133.39, 133.62, 133.68, 139.62 and 140.04 (s, 12 C, aromatics). The second fraction contained exclusively *trans*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, s<sup>\*</sup>)-1}]Cl (0.108 g, overall yield 7%). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 1.66 (s, 3 H, CMe); 1.81 (s, 6 H, 2 AsMe); 1.88 (s, 6 H, 2 AsMe); 2.07 (s, 6 H, 2 AsMe); 2.51 (d, 2 H, <sup>2</sup>J<sub>HH</sub> 12.7, 2 CHH); 2.89 (d, 2 H, <sup>2</sup>J<sub>HH</sub> 12.7 Hz, 2 CHH); 3.74 (s, 2 H, CH<sub>2</sub>Cl) and 7.80–8.25 (m, 8 H, aromatics). <sup>13</sup>C-<sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 10.13 (s, 1 C, AsMe); 11.27 (s, 1 C, AsMe); 12.52 (s, 1 C, AsMe); 25.84 (s, 1 C, CMe); 28.59 (s, 2 C, AsCH<sub>2</sub>); 42.24 (s, 1 C, CMe); 58.77 (s, 1 C, CH<sub>2</sub>Cl); 132.15, 133.39, 133.62, 133.68, 139.62 and 140.04 (s, 12 C, aromatics). A third fraction contained *cis-α*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]Cl (0.080 g). Further quantities of the latter were isolated from the purple-brown residue described above.

The purple-brown microcrystalline material (1.90 g) was dissolved in water (100 cm<sup>3</sup>) and the solution extracted with dichloromethane (3 × 50 cm<sup>3</sup>). The combined organic extracts were dried (MgSO<sub>4</sub>), filtered and the solvent removed to give a red-brown residue containing *cis-α*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]Cl and *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl (0.68 g). These were combined and separated on an ion-exchange column [150 × 15 mm, Dowex 50W-X8, cation exchange resin]. The column was eluted with

HCl-methanol (0.25 mol dm<sup>-3</sup>, elution rate ca. 2 cm<sup>3</sup> min<sup>-1</sup>). The first fraction collected contained exclusively *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl (0.22 g). The second contained exclusively *cis-α*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]Cl (0.42 g, overall yield 14%) (Found: C, 32.7; H, 4.4; Cl, 16.0. Calc. for C<sub>23</sub>H<sub>35</sub>As<sub>4</sub>Cl<sub>4</sub>Co·2H<sub>2</sub>O: C, 32.6; H, 4.6; Cl, 16.7%). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 0.63 (s, 3 H, CMe); 1.77 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 16.2, AsCHH); 1.80 (s, 3 H, AsMe); 1.87 (s, 3 H, AsMe); 2.06 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 13.3, AsCHH); 2.07 (s, 6 H, 2 AsMe); 2.11 (s, 3 H, AsMe); 2.15 (s, 3 H, AsMe); 2.25 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 16.2, AsCHH); 2.30 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 13.3, AsCHH); 3.21, 3.27 (ABq, 2 H, <sup>2</sup>J<sub>HH</sub> 11.0 Hz, CH<sub>2</sub>Cl) and 7.70–8.25 (m, 8 H, aromatics). <sup>13</sup>C-<sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 11.39 (s, 1 C, AsMe); 11.50 (s, 2 C, AsMe); 12.18 (s, 1 C, AsMe); 13.18 (s, 1 C, AsMe); 13.93 (s, 1 C, AsMe); 24.90 (s, 1 C, CMe); 36.28 (s, 1 C, AsCH<sub>2</sub>); 37.40 (s, 1 C, AsCH<sub>2</sub>); 40.33 (s, 1 C, CMe); 56.06 (s, 1 C, CH<sub>2</sub>Cl); 131.14, 132.43, 133.37, 133.45, 133.63, 133.68, 139.32, 139.48, 142.03 and 142.25 (s, 12 C, aromatics).

The aqueous layer was taken to dryness to give a brown residue containing a mixture of cobalt(III) complexes of diars, the cyclic chiral tetra(tertiary arsine), (R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4, and the chiral hexa(tertiary arsine), (R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)- and (R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>)-3 (1.20 g). These were separated on an ion-exchange column [400 × 25 mm, Dowex 50W-X8, cation exchange resin]. The column was eluted with HCl-methanol (0.25 mol dm<sup>-3</sup>, elution rate ca. 2 cm<sup>3</sup> min<sup>-1</sup>). The first fraction collected contained exclusively *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl (0.22 g, overall yield 19%). A second fraction contained exclusively *cis-α*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4}]Cl (0.16 g, 3%). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 1.28 (s, 3 H, CMe); 1.49 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 16.2, AsCHH); 1.56 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 11.5, AsCHH); 1.67 (s, 3 H, AsMe); 1.79 (s, 3 H, AsMe); 1.92 (s, 3 H, AsMe); 2.12 (s, 3 H, AsMe); 2.17 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 11.5, AsCHH); 2.22 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 16.2, AsCHH); 2.26 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 11.5, AsCHH); 2.36 (s, 3 H, AsMe); 2.36 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 11.5 Hz, AsCHH) and 7.70–8.25 (m, 8 H, aromatics). <sup>13</sup>C-<sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 3.10 (s, 1 C, AsMe); 5.22 (s, 1 C, AsMe); 11.89 (s, 1 C, AsMe); 12.36 (s, 1 C, AsMe); 15.90 (s, 1 C, AsMe); 33.35 (s, 1 C, CMe); 34.74 (s, 1 C, AsCH<sub>2</sub>); 36.39 (s, 1 C, AsCH<sub>2</sub>); 37.56 (s, 1 C, AsCH<sub>2</sub>); 40.84 (s, 1 C, CMe); 129.07, 130.26, 131.52, 131.75, 131.98, 132.04, 133.62, 133.73, 140.35, 141.16, 141.95 and 146.27 (s, 12 C, aromatics). The column was then eluted with HCl-methanol (2.5 mol dm<sup>-3</sup>, elution rate ca. 2 cm<sup>3</sup> min<sup>-1</sup>). Five fractions were collected that are believed to contain diastereomeric, dinuclear cobalt(III) complexes of (R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>)-3 (0.50 g). The final fraction was eluted with HCl-methanol (3 mol dm<sup>-3</sup>, elution rate ca. 2 cm<sup>3</sup> min<sup>-1</sup>) and contained exclusively [Co{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-3}]Cl<sub>3</sub> (0.32 g, 7%). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 1.66 (s, 3 H, CMe); 1.80 (s, 9 H, 3 AsMe); 2.15 (s, 9 H, 3 AsMe); 2.44 (s, 9 H, 3 AsMe); 2.53 (d, 3 H, <sup>2</sup>J<sub>HH</sub> 13.2, 3 CHH); 3.09 (d, 3 H, <sup>2</sup>J<sub>HH</sub> 13.2, 3 CHH) and 7.98–8.33 (m, 12 H, aromatics). <sup>13</sup>C-<sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 19.05 (s, 3 C, 3 AsMe); 20.40 (s, 3 C, AsMe); 21.79 (s, 3 C, AsMe); 34.93 (s, 1 C, CMe); 37.68 (s, 1 C, CMe); 38.97 (s, 3 C, AsCH<sub>2</sub>); 132.56, 133.23, 135.67, 136.01, 136.09 and 139.63 (s, 12 C, aromatics). <sup>13</sup>C NMR (CD<sub>3</sub>OD): δ 19.05 (q, 3 C, <sup>1</sup>J<sub>CH</sub> 82, 3 AsMe); 20.40 (q, 3 C, <sup>1</sup>J<sub>CH</sub> 82, AsMe); 21.79 (q, 3 C, <sup>1</sup>J<sub>CH</sub> 82, AsMe); 34.93 (q, 1 C, <sup>1</sup>J<sub>CH</sub> 77, CMe); 37.68 (s, 1 C, CMe) and 38.97 (t, 3 C, <sup>1</sup>J<sub>CH</sub> 80 Hz, AsCH<sub>2</sub>).

#### Reaction of 1,1,1-tris(chloromethyl)ethane with ca. five equivalents of sodium (2-dimethylarsinophenyl)methylarsenide

Sodium foil (0.55 g, 0.0239 mol) was added to a stirred solution of compound (±)-2 (4.80 g, 0.0176 mol) in thf (250 cm<sup>3</sup>). The reaction mixture was stirred overnight and the resulting deep red solution added dropwise over a period of 2 h to a solution of 1,1,1-tris(chloromethyl)ethane (0.62 g, 3.53 mmol) dissolved in thf (70 cm<sup>3</sup>) at -78 °C. After the addition was complete, the reaction mixture was stirred at -25 ± 5 °C for 10 days. The solvent was removed by distillation and a solution of ammonium chloride (10 g) in water (150 cm<sup>3</sup>) added to the

colourless solution. Dichloromethane (100 cm<sup>3</sup>) was added, the organic layer separated off and the aqueous layer extracted with more dichloromethane (2 × 80 cm<sup>3</sup>). The combined organic extracts were dried (MgSO<sub>4</sub>), filtered and the solvent was removed to give a clear, pale yellow oil (4.23 g). The yellow oil (1.42 g) was subsequently taken up in hot methanol (80 cm<sup>3</sup>) and added to a solution of hexaaquacobalt(II) chloride (0.60 g, 2.54 mmol) in methanol (20 cm<sup>3</sup>) containing hydrochloric acid (10 mol dm<sup>-3</sup>, 3 cm<sup>3</sup>). Air was drawn through the solution for 4 h. The solvent was removed and the residue dried *in vacuo* (1.56 g). The mixture of cobalt(III) complexes (0.62 g) was dissolved in the minimum volume of methanol and loaded onto an ion-exchange column [350 × 25 mm, Dowex 50W, cation exchange resin]. The column was eluted with HCl–methanol (0.5 mol dm<sup>-3</sup>, elution rate *ca.* 2 cm<sup>3</sup> min<sup>-1</sup>). The first compound eluted from the column was *trans*-[CoCl<sub>2</sub>(diars)<sub>2</sub>]Cl [0.20 g, *ca.* 21% overall based on (±)-2]. The second complex eluted from the column was *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4}]Cl (0.058 g, *ca.* 15% overall based on 1,1,1-tris(chloromethyl)ethane]. Unchanged hexaaquacobalt(II) chloride (0.05 g) was also eluted. Several further fractions were collected over a 10 day period with HCl–methanol (3 mol dm<sup>-3</sup>, elution rate *ca.* 2 cm<sup>3</sup> min<sup>-1</sup>). Six fractions are believed to contain diastereomeric, dinuclear cobalt(III) complexes of (R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>)-3 (0.22 g). The final fraction contained exclusively [Co{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-3}]Cl<sub>3</sub> (0.06 g, 10%).

**Preparation of [OC-6-33-(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)]dichloro-[1-(chloromethyl)-1,1-bis{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane-As, As', As'', As''']cobalt(III) hexafluorophosphate, *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]PF<sub>6</sub>**

The chloride salt *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]Cl (0.150 g, 0.0185 mmol) was dissolved in methanol (50 cm<sup>3</sup>) and a solution of ammonium hexafluorophosphate (0.20 g, 1.23 mmol) in water (5 cm<sup>3</sup>) added dropwise. More water (10 cm<sup>3</sup>) was added to give a dark purple precipitate that was subsequently collected, washed with water (5 cm<sup>3</sup>), methanol–water (1 : 1, 3 × 5 cm<sup>3</sup>) and diethyl ether (2 × 5 cm<sup>3</sup>), and dried *in vacuo* (0.138 g, 81%). The complex was recrystallised from acetone–2-propanol to give dark purple needles of *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]PF<sub>6</sub> (Found: C, 30.2; H, 3.8. Calc. for C<sub>23</sub>H<sub>35</sub>As<sub>4</sub>CoF<sub>18</sub>P<sub>3</sub>: C, 30.0; H, 3.9%).

**Preparation of [OC-6-22-(R\*, R\*, R\*)-(±)-[1,1,1-Tris{[(2-dimethylarsinophenyl)methylarsino]methyl}ethane-As, As', As'', As''', As''', As''', As''']cobalt(III) hexafluorophosphate, [Co{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-3}]PF<sub>6</sub>]**

A solution of ammonium hexafluorophosphate (0.025 g, 0.153 mmol) in water (5 cm<sup>3</sup>) was slowly added to a solution of [Co{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-3}]Cl<sub>3</sub> (0.050 g, 0.0477 mmol) in methanol (20 cm<sup>3</sup>) and the mixture stirred overnight. The resulting yellow precipitate was collected, washed with methanol–water (1 : 1, 3 × 5 cm<sup>3</sup>), methanol–diethyl ether (1 : 1, 3 × 2 cm<sup>3</sup>) and diethyl ether (5 cm<sup>3</sup>), and finally dried *in vacuo* (0.060 g, 91%). The complex was recrystallised from acetone–2-propanol to give bright yellow prisms of [Co{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-3}]PF<sub>6</sub> (Found: C, 30.1; H, 3.9. Calc. for C<sub>32</sub>H<sub>48</sub>As<sub>6</sub>CoF<sub>18</sub>P<sub>3</sub>·CH<sub>3</sub>COCH<sub>3</sub>: C, 29.3; H, 3.8%).

**Preparation of [OC-6-45-(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)]dichloro(5,6,7,8,9-pentahydro-6-{[(2-dimethylarsinophenyl)methylarsino]methyl}-1,4,6-trimethylbenzo[*b*][1,4]diarsacycloheptane-As, As', As'', As''')cobalt(III) hexafluorophosphate, *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4}]PF<sub>6</sub>**

The chloride salt *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4}]Cl (0.28 g,

0.368 mmol) was dissolved in hot methanol (20 cm<sup>3</sup>) and a solution of ammonium hexafluorophosphate (0.06 g, 0.368 mmol) in water (2 cm<sup>3</sup>) added dropwise. More water (5 cm<sup>3</sup>) was added to give a dark red precipitate that was subsequently collected, washed with cold water (2 × 5 cm<sup>3</sup>) and methanol–water (1 : 1, 5 cm<sup>3</sup>), and finally dried *in vacuo* (0.20 g, 62%). The complex was recrystallised from acetone–1-butanol to give large red-brown needles of *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4}]PF<sub>6</sub> (Found: C, 30.2; H, 3.8. Calc. for C<sub>22</sub>H<sub>32</sub>As<sub>4</sub>Cl<sub>2</sub>CoF<sub>6</sub>P: C, 30.3; H, 3.7%).

**X-Ray crystallography**

**Crystal data for *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-1}]PF<sub>6</sub>, A.** C<sub>23</sub>H<sub>35</sub>As<sub>4</sub>Cl<sub>3</sub>CoF<sub>6</sub>P, *M* = 921.47, monoclinic, space group *P*2<sub>1</sub> (no. 4), *a* = 9.284(3), *b* = 13.369(5), *c* = 13.437(4) Å, β = 106.44(3)°, *U* = 1599.6(9) Å<sup>3</sup>, *T* = 296 K, *Z* = 2, μ(Mo-Kα) = 49.94 cm<sup>-1</sup>, 5047 reflections measured, 4874 unique (*R*<sub>int</sub> = 0.079), 3848 with *I* > 3σ(*I*) which were used in all calculations. The final *R* and *R*' values were 0.0527 and 0.0584.

**Crystal data for [Co{(R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-3}]PF<sub>6</sub>·CH<sub>3</sub>COCH<sub>3</sub>·0.3H<sub>2</sub>O, B.** C<sub>35</sub>H<sub>54.6</sub>As<sub>6</sub>CoF<sub>18</sub>O<sub>1.3</sub>P<sub>3</sub>, *M* = 1439.75, orthorhombic, space group *Pbca* (no. 61), *a* = 13.080(3), *b* = 24.057(4), *c* = 31.300(4) Å, *U* = 9849(3) Å<sup>3</sup>, *T* = 193 K, *Z* = 8, μ(Cu-Kα) = 90.47 cm<sup>-1</sup>, 8059 reflections measured, 7312 with *I* > 2σ(*I*) which were used in all calculations. The final *R* and *R*' values were 0.047 and 0.054.

**Crystal data for *cis-a*-[CoCl<sub>2</sub>{(R<sub>As</sub><sup>\*</sup>, S<sub>As</sub><sup>\*</sup>, R<sub>As</sub><sup>\*</sup>)-4}]PF<sub>6</sub>·<sup>1</sup>/<sub>3</sub>n-C<sub>4</sub>H<sub>9</sub>OH·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O, C.** C<sub>23.33</sub>H<sub>36</sub>As<sub>4</sub>Cl<sub>2</sub>CoF<sub>6</sub>O<sub>0.66</sub>P, *M* = 901.70, trigonal, space group *R*3̄ (no. 146), *a* = 21.231(2), *b* = 21.231(2), *c* = 18.627(3) Å, *U* = 7272(2) Å<sup>3</sup>, *T* = 296 K, *Z* = 9, μ(Cu-Kα) = 111.7 cm<sup>-1</sup>, 7345 reflections measured, 2406 unique (*R*<sub>int</sub> = 0.048), 2104 with *I* > 2σ(*I*) which were used in all calculations. The final *R* and *R*' values were 0.041 and 0.042.

CCDC reference number 186/2161.

See <http://www.rsc.org/suppdata/dt/b0/b003981k/> for crystallographic files in .cif format.

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