Journal of Organometallic Chemistry, 424 (1992) 79–86
Elsevier Sequoia S.A., Lausanne
JOM 22283

The coordination of functionalised diphosphines to rhodium. Reactions with $[\{RhCl(CO)_2\}_2]$ to give binuclear complexes. Crystal structure of *cis*-$[\{RhCl(CO)\}_2\{\mu\text{-}(C_7H_4NS)_2PCH_2P(C_7H_4S)_2\}_2]\cdot 2C_4H_8O$

Mohammad F.M. Al-Dulaymmi, David L. Hughes and Raymond L. Richards

AFRC-IPSR Nitrogen Fixation Laboratory and School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9RQ (UK)

(Received August 1, 1991)

Abstract

Treatment of $[\{RhCl(CO)_2\}_2]$ with the functionalised diphosphines $(C_6H_4SMe\text{-}2)_2PCH_2P(C_6H_4\text{-}SMe\text{-}2)_2$ (mtppm) and $(C_7H_4NS)_2PCH_2P(C_7H_4NS)_2$ (dbtpm) gives the binuclear complexes $[ClRh(\mu\text{-}CO)(\mu\text{-mtppm})_2Rh(CO)]Cl$ (**A**) and *cis*-$[\{RhCl(CO)\}_2(\mu\text{-dbtpm})_2]$ (**B**) respectively. The structure of **B** has been confirmed by an X-ray structure determination which shows the essentially square-planar rhodium atoms to be ligated by a terminal chloride, a terminal carbonyl *trans* to the chloride, and a phosphorus from each of two bridging dbtpm ligands; the planes about the two Rh atoms are 13° from being eclipsed.

Introduction

We have recently described a series of functionalised diphosphines, prepared in order to explore the possibility of synthesising multinuclear complexes with mixed P–X (X = N, S, O, etc.) ligation [1]. We have shown that with ligands such as $(C_7H_4NS)_2PCH_2CH_2P(C_7H_4NS)_2$ (dbtpe) and $(C_6H_4SMe\text{-}2)_2PCH_2CH_2P\text{-}(C_6H_4SMe\text{-}2)_2$ (mtppe) mixed ligation does occur in binuclear complexes of rhodium *e.g.* P–N in $[\{RhCl(dbtpe)\}_2]^{2+}$ (**C**) [1]. In **C**, the $P\text{–}CH_2\text{–}CH_2\text{–}P$ linkage allows sufficient flexibility for P–P chelation at each rhodium, with additional P–N ligation between rhodiums. We were interested to see what effect reducing the P–P linkage to $P\text{–}CH_2\text{–}P$ would have, and we found that the dominant linkage is then P–P bridging between rhodiums to give binuclear complexes as described below.

Preparation and structure of binuclear complexes

Complexes were obtained by treatment of $[\{RhCl(CO)_2\}_2]$ with the diphosphines in tetrahydrofuran (THF). Reaction of mtppm proceeded as shown in reaction 1 to give the red-brown binuclear complex **A** which is a 1 : 1 electrolyte in CH_2Cl_2, and

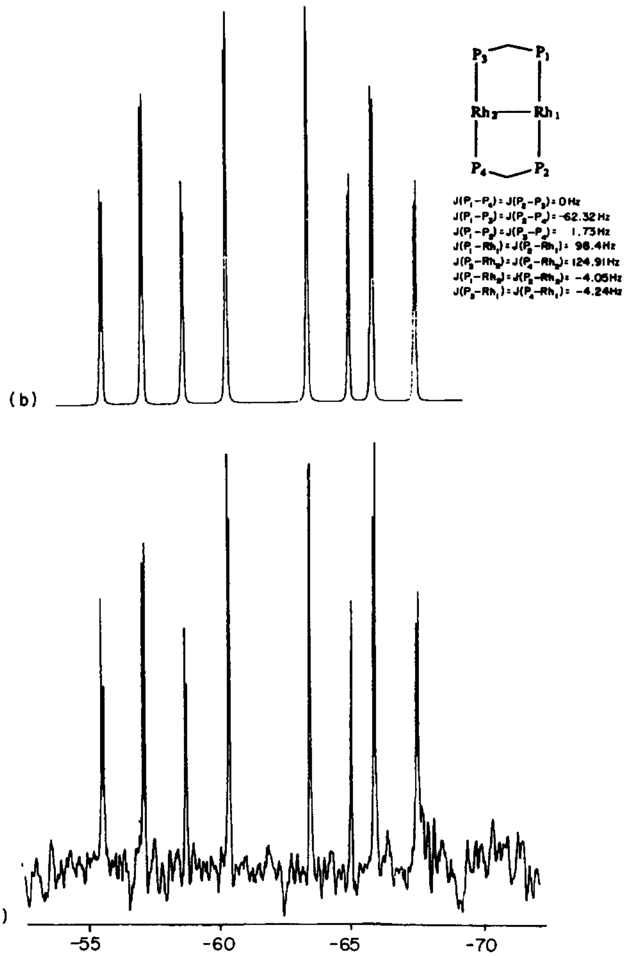


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2Cl(\mu\text{-}CO)(CO)(\mu\text{-}mtppm)_2]Cl$: (a) real spectrum; (b) simulated spectrum.

is formulated as shown in reaction (1) by analysis and on the following spectroscopic evidence.

A has two CO bands in its IR spectrum at 2000 and 1750 cm^{-1}, consistent with terminal and bridging carbonyls respectively [2].

Its $^{31}P\{^1H\}$ NMR spectrum at 90 MHz shows the splitting in Fig. 1, indicating an asymmetrical species which analyses as an AA′BB′XY system, where AA′BB′ = ^{31}P and XY = ^{103}Rh. The spectrum has been simulated very closely as shown using the parameters $J(P1\text{–}P4) = J(P2\text{–}P3) = 0$ Hz, $J(P1\text{–}P3) = J(P2\text{–}P4) = -62.32$ Hz, $J(P1\text{–}P2) = J(P3\text{–}P4) = 1.73$ Hz, $J(P1\text{–}Rh1) = J(P2\text{–}Rh1) = 98.4$ Hz, $J(P3\text{–}Rh2) = J(P4\text{–}Rh2) = 124.91$ Hz, $J(P1\text{–}Rh2) = J(P2\text{–}Rh2) = -4.05$ Hz, $J(P3\text{–}Rh1) = J(P4\text{–}Rh1) = -4.24$ Hz.

Reaction of dbtpm with $[\{RhCl(CO)_2\}_2]$ in THF gave a deep red solution from which red crystals of **B** were obtained. They are stable in the solid state, but gradually lose their brightness due to loss of solvent of crystallisation. The IR spectrum of **B** showed two CO bands at 1990 and 1980 cm^{-1}, consistent with two

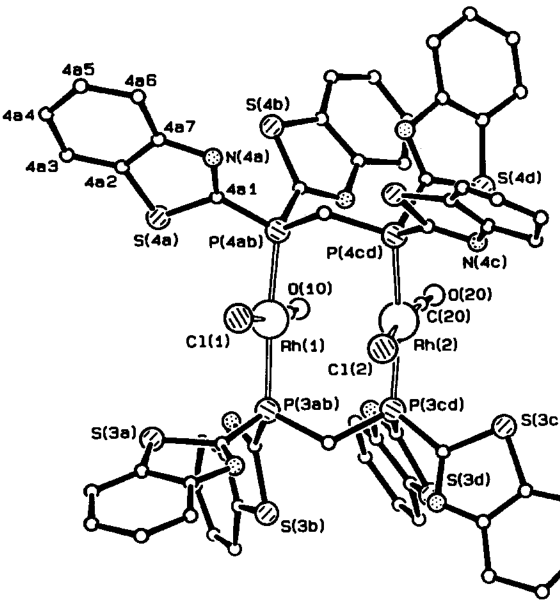
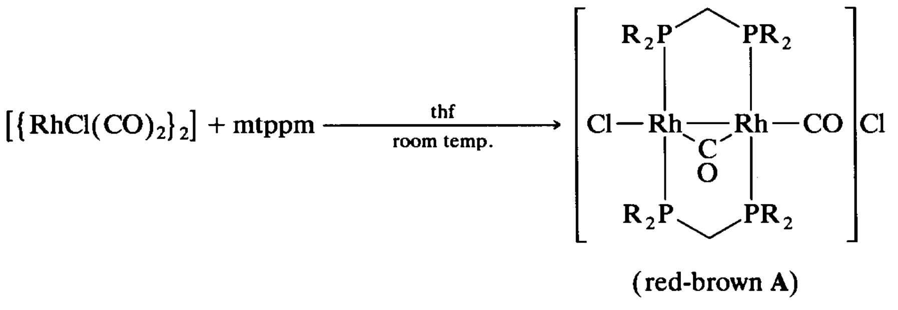
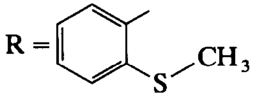


Fig. 2. Structure of the Rh complex **B** in *cis*-[{RhCl(CO)}$_2$(μ-dbtpm)$_2$]·2thf. The atom labelling in each of the benzothiazoyl groups follows the same pattern.

carbonyls in a *cis*-arrangement as is seen for *cis*-[{RhCl(CO)}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$] (**D**) which has bands at 1994 and 1972 cm^{-1} [3]. The ^{31}P[^{1}H] NMR spectrum of **B** shows the phosphorus atoms to be equivalent. Thus the structure appears to be analogous to **D**; this was confirmed by X-ray crystallography as described below.



(1)



*The molecular structure of cis-[{RhCl(CO)}$_2$(μ-dbtpm)$_2$] · 2thf (**B**)*

The structure of **B**, determined by X-ray diffraction methods, is shown in Fig. 2. The molecule has a conventional binuclear structure with two approximately linear and parallel Cl–Rh–CO moieties bridged by two (dbtpm) ligands. The two rhodium atoms are 3.238(3) Å apart, which is consistent with no formal metal–metal bond and is in fact significantly longer than the non-bonded Rh–Rh separations of 3.152(8) and 3.155(4) Å observed in [Rh$_2$(CO)$_2$(μ-Cl)(μ-dppm)$_2$][BF$_4$] [4] and

[$Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2$] [5], respectively. In our structure, each rhodium has a square-planar coordination, with chlorine, carbonyl and two mutually *trans* phosphorus atoms forming the square. The two planes are rotated *ca.* 13° from the

Table 1

Final atomic coordinates (fractional × 10^4) for the complex **B**. Esds are in parentheses

Atom	*x*	*y*	*z*	SOF [a]
Rh(1)	1832(1)	1210(1)	1122(1)	
Cl(1)	1569(5)	2033(5)	1749(3)	
C(10)	1903(15)	533(14)	604(10)	
O(10)	1934(11)	98(12)	285(9)	
Rh(2)	2729(1)	2315(1)	519(1)	
Cl(2)	2959(6)	3145(5)	1257(4)	
C(20)	2673(19)	1681(18)	−93(13)	
O(20)	2659(13)	1344(13)	−433(8)	
C(3a1)	3162	1010	2507	0.6
S(3a)	2627(7)	411(7)	2802(5)	0.6
C(3a2)	2963	938	3392	0.6
C(3a3)	2894	781	3909	0.6
C(3a4)	3310	1210	4373	0.6
C(3a5)	3795	1795	4320	0.6
C(3a6)	3865	1951	3803	0.6
C(3a7)	3449	1522	3339	0.6
N(3a)	3535	1550	2820	0.6
C(3b1)	3453(16)	−8(15)	1786(11)	
S(3b)	4450(5)	−256(6)	2138(4)	
C(3b2)	4176(18)	−1207(18)	1909(12)	
C(3b3)	4739(22)	−1771(20)	2048(15)	
C(3b4)	4416(24)	−2378(24)	1845(16)	
C(3b5)	3625(25)	−2523(26)	1519(17)	
C(3b6)	3077(22)	−1855(20)	1394(15)	
C(3b7)	3397(17)	−1150(16)	1607(12)	
N(3b)	2978(15)	−545(13)	1547(10)	
P(3ab)	3050(5)	913(5)	1782(3)	
C(3)	3893(16)	1539(16)	1802(11)	
P(3cd)	3892(5)	1779(5)	1086(3)	
C(3c1)	4784(16)	2345(16)	1257(11)	
S(3c)	4863(7)	3007(8)	807(6)	
C(3c2)	5863(20)	3193(20)	1241(14)	
C(3c3)	6355(35)	3722(35)	1125(25)	
C(3c4)	7064(29)	3736(27)	1539(19)	
C(3c5)	7314(29)	3395(26)	2028(19)	
C(3c6)	6751(23)	2835(22)	2110(17)	
C(3c7)	5994(19)	2794(18)	1689(13)	
N(3c)	5420(11)	2333(14)	1730(10)	
C(3d1)	4247(16)	936(15)	877(11)	
S(3d)	5320(5)	768(6)	1026(5)	
C(3d2)	5055(16)	−64(16)	739(11)	
C(3d3)	5606(24)	−637(21)	710(15)	
C(3d4)	5292(23)	−1286(22)	470(15)	
C(3d5)	4426(22)	−1389(22)	315(15)	
C(3d6)	3877(22)	−884(19)	329(14)	
C(3d7)	4221(17)	−211(16)	587(12)	
N(3d)	3781(15)	369(12)	650(11)	

eclipsing position and show *cis* arrangements of the pairs of chloride and carbonyl ligands.

The molecules are separated by normal van der Waals distances. The THF solvent molecules occupy some of the gaps between these complex molecules;

Table 1 (continued)

Atom	*x*	*y*	*z*	SOF [a]
C(4a1)	−201(16)	1616(16)	716(11)	
S(4a)	−315(6)	805(5)	1031(5)	
C(4a2)	−1270(17)	1088(16)	1022(12)	
C(4a3)	−1803(19)	746(20)	1226(14)	
C(4a4)	−2510(21)	1108(19)	1213(14)	
C(4a5)	−2662(21)	1798(19)	997(14)	
C(4a6)	−2134(22)	2170(23)	776(15)	
C(4a7)	−1407(16)	1794(16)	799(11)	
N(4a)	−784(15)	2088(14)	620(12)	
C(4b1)	274(17)	1350(16)	−201(11)	
S(4b)	−752(5)	1179(6)	−561(4)	
C(4b2)	−503(19)	988(18)	−1136(13)	
C(4b3)	−979(20)	769(17)	−1664(13)	
C(4b4)	−678(20)	649(19)	−2078(14)	
C(4b5)	125(18)	725(17)	−1966(13)	
C(4b6)	677(18)	975(15)	−1466(11)	
C(4b7)	319(17)	1098(16)	−1046(12)	
N(4b)	750(14)	1304(12)	−508(10)	
P(4ab)	682(4)	1702(4)	507(3)	
C(4)	753(16)	2686(15)	400(12)	
P(4cd)	1529(5)	2930(5)	100(3)	
C(4c1)	1611(17)	3958(14)	197(12)	
S(4c)	937(9)	4415(8)	410(7)	
C(4c2)	1380(22)	5273(20)	354(16)	
C(4c3)	1271(23)	6014(19)	472(21)	
C(4c4)	1666(40)	6440(23)	466(30)	
C(4c5)	2221(45)	6485(27)	267(19)	
C(4c6)	2502(33)	5677(25)	142(20)	
C(4c7)	2001(28)	5090(20)	175(15)	
N(4c)	2165(23)	4354(15)	73(14)	
C(4d1)	992(16)	2931(15)	−649(11)	
S(4d)	1506(5)	2838(5)	−1113(3)	
C(4d2)	587(18)	2871(18)	−1664(13)	
C(4d3)	471(24)	2896(22)	−2218(16)	
C(4d4)	−277(26)	2981(24)	−2547(20)	
C(4d5)	−904(27)	2985(23)	−2383(18)	
C(4d6)	−788(21)	3021(19)	−1821(14)	
C(4d7)	0(18)	3015(17)	−1442(12)	
N(4d)	175(14)	2964(12)	−874(9)	
C(3x1)	3259	971	2537	0.4
S(3x)	2486(11)	771(10)	2814(7)	0.4
C(3x2)	3205	866	3462	0.4
C(3x3)	3099	796	3977	0.4
C(3x4)	3755	915	4468	0.4
C(3x5)	4515	1105	4444	0.4
C(3x6)	4621	1176	3928	0.4
C(3x7)	3965	1056	3437	0.4
N(3x)	3967	1113	2898	0.4

Table 1 (continued)

Atom	*x*	*y*	*z*	SOF [a]
THF solvent molecules				
C(50)	1186(16)	−435(16)	3471(8)	
C(51)	662	172	3525	
C(52)	−138	−148	3504	
C(53)	−42	−963	3521	
C(54)	804	−1133	3546	
C(60)	5681(39)	899(44)	3684(29)	0.25
C(61)	5430	818	4187	0.25
C(62)	5330	11	4274	0.25
C(63)	5378	−378	3763	0.25
C(64)	5764	144	3470	0.25
C(70)	3282(76)	4855(69)	2582(43)	0.25
C(71)	2442	5101	2250	0.25
C(72)	1862	4568	2367	0.25
C(73)	2340	3886	2592	0.25
C(74)	3217	4092	2786	0.25
C(75)	2666(31)	4757(36)	2780(21)	0.5
C(76)	2282	4266	3088	0.5
C(77)	2461	3489	2983	0.5
C(78)	3142	3522	2758	0.5
C(79)	3055	4267	2478	0.5

[a] SOF = Site occupancy factor, if different from 1.0.

Table 2

Selected bond dimensions in **B**. Lengths are in ångstrøms, angles in degrees. Esds are in parentheses

In the coordination spheres of the rhodium atoms			
Rh(1) ··· Rh(2)	3.238(3)		
Rh(1)–Cl(1)	2.347(9)	Rh(2)–Cl(2)	2.337(10)
Rh(1)–C(10)	1.838(25)	Rh(2)–C(20)	1.92(3)
Rh(1)–P(3ab)	2.282(8)	Rh(2)–P(3cd)	2.210(8)
Rh(1)–P(4ab)	2.267(8)	Rh(2)–P(4cd)	2.292(8)
Rh(2)–Rh(1)–Cl(1)	99.7(2)	Rh(1)–Rh(2)–Cl(2)	89.7(2)
Rh(2)–Rh(1)–C(10)	84.9(8)	Rh(1)–Rh(2)–C(20)	96.8(10)
Rh(2)–Rh(1)–P(3ab)	90.9(2)	Rh(1)–Rh(2)–P(3cd)	84.6(2)
Rh(2)–Rh(1)–P(4ab)	83.4(2)	Rh(1)–Rh(2)–P(4cd)	90.6(2)
Cl(1)–Rh(1)–C(10)	172.8(8)	Cl(2)–Rh(2)–C(20)	172.4(10)
Cl(1)–Rh(1)–P(3ab)	89.9(3)	Cl(2)–Rh(2)–P(3cd)	83.8(3)
Cl(1)–Rh(1)–P(4ab)	83.5(3)	Cl(2)–Rh(2)–P(4cd)	86.5(3)
C(10)–Rh(1)–P(3ab)	95.6(8)	C(20)–Rh(2)–P(3cd)	92.8(10)
C(10)–Rh(1)–P(4ab)	91.6(8)	C(20)–Rh(2)–P(4cd)	97.4(10)
P(3ab)–Rh(1)–P(4ab)	170.4(3)	P(3cd)–Rh(2)–P(4cd)	169.2(3)
In the carbonyl ligands			
C(10)–O(10)	1.15(3)	C(20)–O(20)	1.06(4)
Rh(1)–C(10)–O(10)	178.3(23)	Rh(2)–C(20)–O(20)	177.9(29)
Torsion angles about the Rh ··· Rh vector			
Cl(1)–Rh(1)–Rh(2)–Cl(2)	17.6(3)		
C(10)–Rh(1)–Rh(2)–C(20)	8.1(13)		
P(3ab)–Rh(1)–Rh(2)–P(3cd)	11.5(3)		
P(4ab)–Rh(1)–Rh(2)–P(4cd)	13.3(3)		

some THF sites are partially occupied, with occupancy depending for example on the orientation arrangement of the disordered benzothiazoyl groups of S(3a)/S(3x) (see Experimental and Table 1). The poor resolution in these regions and in some of the other benzothiazoyl groups does not allow a more critical analysis of the molecular dimensions and geometry of the complex.

Atomic coordinates and selected molecular dimensions are listed in Tables 1 and 2.

Experimental

All manipulations were carried out under pure dinitrogen by standard vacuum, Schlenk, and glove-box techniques. Solvents were dried and distilled under dinitrogen before use. NMR spectra were measured using a Bruker WP80 instrument and IR spectra (Nujol mulls) using Perkin–Elmer 598 or 883 spectrometers. Conductivities were obtained using a conductivity bridge (Portland Electronics). Microanalyses were by Mr. C.J. Macdonald of the Nitrogen Fixation Laboratory or Ms. K. Plowman of the University of Sussex. $[\{RhCl(CO)_2\}_2]$ was prepared by a published procedure [6].

Reaction of mtppm with $[\{RhCl(CO)_2\}_2]$. A mixture of $[\{RhCl(CO)_2\}_2]$ (0.11 g, 0.28 mmol) and mtppm (0.33 g, 0.58 mmol) in THF (25 ml) was stirred at room temperature for 24 h. The red-brown solid which separated was filtered off, washed with THF (10 ml) then ether (2 × 10 ml) and dried under vacuum. The product was identified as $[ClRh(\mu\text{-}CO)(\mu\text{-}mtppm)_2Rh(CO)]Cl$ (A) (Yield 0.2 g, 49%). Anal. Found: C, 48.9; H, 4.1. Calc. for $C_{60}H_{60}Cl_2O_2P_4Rh_2S_8$: C, 49.0; H, 4.1. IR ($cm^{-1}$) 2000, 1750.

Reaction of dbtpm with $[\{RhCl(CO)_2\}_2]$. A mixture of $[\{RhCl(CO)_2\}_2]$ (0.12 g, 0.31 mmol) and dbtpm (0.38 g, 0.62 mmol) in THF (25 ml), was stirred at room temperature. A clear red solution was obtained. This was stirred for 24 h, then filtered from the small amount of solid. Hexane was added slowly with stirring at 40° until the solid began to separate, then the solution was filtered and the filtrate kept at room temperature for 3 days. The red crystals which precipitated were filtered off and dried under vacuum (the crystals were used without drying for the the X-ray study. The product was identified as *cis*-$[\{RhCl(CO)\}_2(\mu\text{-}dbtpm)_2] \cdot 2thf$, (yield 0.35 g, 66.6%). Anal. Found: C, 48.2; H, 3.2; N, 6.5. Calc. for $C_{60}H_{36}Cl_2N_8O_2P_4Rh_2S_8 \cdot 2C_4H_8O$: C, 48.0; H, 3.1: N, 6.6. IR (cm^{-1}) 1990, 1980.

Crystal structure analysis of cis-$[\{RhCl(CO)\}_2(\mu\text{-}dbtpm)_2] \cdot 2thf$. Crystal data: $C_{60}H_{36}Cl_2N_8O_2P_4Rh_2S_8 \cdot 2C_4H_8O$, $M = 1702.3$, monoclinic, space group $P2_1/c$, $a = 17.469(5)$, $b = 18.156(7)$, $c = 25.517(7)$ Å, $\beta = 109.99(3)$, $U = 7605.1$ Å^3, $Z = 4$, $D_c = 1.487$ g cm^{-3}, $F(000) = 3440$, $\mu(\text{Mo-}K_\alpha) = 8.4$ cm^{-1}, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.71069$ Å.

The red, almost rectangular plate crystals lose solvent rapidly, so were sealed in capillary tubes. After photographic examination, one was mounted on an Enraf–Nonius CAD4 diffractometer (with monochromated radiation) for measurement of accurate cell dimensions (from the settings of 25 centred reflections having θ *ca.* 10.5°) and diffraction intensities (to $\theta_{max} = 20°$, at which level there were few observed reflections). During processing of the data, corrections were made for Lorentz-polarisation effects, absorption (from Ψ-scan measurements), and for negative intensities (by Bayesian statistics). 7043 independent reflections were read into the SHELX program [7], where the structure was determined by the heavy atom method. During the refinement process, poor dimensions and high thermal parameters in one benzothiazole group indicated disorder of the group in two orientations; the two systems were included as rigid groups with dimensions taken from the mean values of three of the best-behaving benzothiazole groups in the molecule. Final molecular dimensions and thermal parameters suggest that there is considerable thermal motion or possibly further disorder in some of the other benzothiazole groups.

Two molecules of the solvent, THF, are spread over four sites in the asymmetric unit. These molecules, with site occupancies of 0.25–1.0, were each refined as rigid, planar groups, and the resolution of these molecules is not wholly satisfactory.

The final cycles of refinement were by block-diagonal least-squares methods [8], concluding at $R = 0.135$ and $R_w = 0.141$ [7] for 4564 reflections (those having $I \geqslant \sigma_I$) weighted equally. For the 2523 reflections with $I \geqslant 2\sigma_I$, a structure factor calculation on the final atomic parameters gave $R = 0.077$, $R_w = 0.090$, with equal weights. Hydrogen atoms were included in idealised positions for six of the benzothiazole groups and in the methylene bridges. The C-atoms of another benzothiazole group were refined anisotropically to try to take account of the considerable vibration or disorder in that group. All other C-atoms were refined isotropically, and all heavier atoms (except the N atoms in the disordered benzothiazole group) were allowed anisotropic thermal parameters.

In the final difference map, all the major peaks (0.5–0.8 e $Å^{-3}$) are in the region of the THF molecules.

Scattering factors for neutral atoms were from ref. 9. Computer programs used have been noted above and in Table 4 of reference [10], and were run on the AFRC's VAX 11/750 computer at IHR-Glasshouse Crops Research Institute (Littlehampton).

Lists of H-atom coordinates, thermal parameters, complete bond lengths and angles, and structure factors are available from the authors.

Acknowledgments

We thank Dr. A.G. Avent for NMR measurements and the Iraqi Government for financial support to M.F.M. A.-D.

References

1 M.F.M. Al-Dulaymmi, P.B. Hitchcock and R.L. Richards, J. Organomet. Chem., 338 (1988) C31.
2 M. Cowie and S.K. Dwight, Inorg. Chem., 19 (1980) 2500.
3 M. Cowie, S.K. Dwight and A.R. Sanger, Inorg. Chem. Acta., 31 (1978) L407.
4 M. Cowie and S.K. Dwight, Inorg. Chem., 18 (1978) 2700.
5 C.P. Kubiak and R.J. Eisenberg, J. Am. Chem. Soc., 99 (1977) 6129.
6 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.
7 G.M. Sheldrick, SHELX-76, Program for crystal structure determination, University of Cambridge, 1976.
8 J.D. Owen, BLOKLS, Program for block-diagonal least-squares refinement, Rothamsted Experimental Station, Harpenden, Herts, 1982.
9 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974, pp. 99 and 149.
10 S.N. Anderson, R.L. Richards and D.L. Hughes, J. Chem. Soc., Dalton Trans., (1986) 245.