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Crystal structure and further applications of the chiral derivatising agent η^2-ethene platinum-DIOP

Russell Fulwood [a], David Parker [a,*], George Ferguson [b] and Branko Kaltner [b]

[a] *Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE (UK)*
[b] *Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1 (Canada)*

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Abstract

The crystal structure of the zerovalent DIOP-platinum ethene complex has been determined. The complex has been used as a chiral derivatising agent for the analysis of the enantiomeric purity of cyclohexene derivatives, e.g. damascone, and certain chiral norbornenes.

Introduction

The enantiomerically pure zerovalent platinum and palladium ethene complexes of the chiral biphosphine 'DIOP' **1** and **2** have been investigated as chiral derivatising agents for the determination of the enantiomeric purity of chiral η^2-donors [1–3]. Displacement of the bound ethene may be effected with chiral alkynes, allenes and relatively strained or electron-poor alkenes. Thus chiral norbornene derivatives and enones quickly displace ethane, whereas simple unconjugated cyclohexane or cyclopentene derivatives fail to react. The resultant diastereoisomeric species are amenable to ^{31}P NMR spectroscopic analysis, and integration of anisochronous resonances permits a direct measurement of substrate enantiomeric purity.

The structure of the DIOP-palladium-ethene complex **2** has been reported previously [4]. In this paper the crystal structure of the platinum analogue (*R*)-**1** is described, together with some further examples of the use of **1** as a chiral derivatising agent.

Results and discussion

Large colourless crystals of **1** were obtained from dimethylsulphoxide solution and the structure of the complex was established by X-ray crystallography. A diagram of the molecule is shown in Fig. 1. The complex is isomorphous with the palladium analogue, **2** which was studied previously, [4]. The carbon–carbon bond length of the bound ethene in **1** is 1.402(9) Å, compared to 1.366(11) Å for **2**. These

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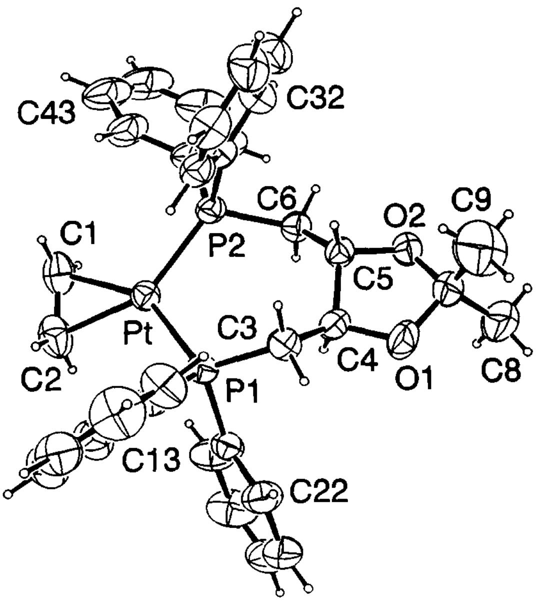


Fig. 1. A view of (*R*)-**1** showing the crystallographic numbering scheme. Ellipsoids are at the 50% level.

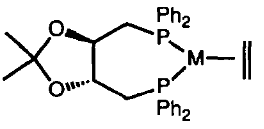
values may be compared to those of 1.337(2) Å for free ethene, 1.434(13) and 1.45(2) for the bis(triphenylphosphine) and seven-ring chelating biphosphine complexes **3** and **5** respectively, Table 1 [5,6]. The length of the carbon–carbon bond in ethene complexes is directly related to the π-donor ability of the d^{10} metal species. This π-donor ability has been correlated with the relative order of the promotion energy from the $(n-1)$ d^{10} state to the $(n-1)$ d^{9} np state. This increases in the order 1.72, 3.28 to 4.23 eV for nickel, platinum and palladium [7]. The strength of the metal–olefin bond in the Group 10 triad is dependent primarily on π-donation from

Table 1

Comparison of bond distances (Å) and angles (°) in metal (0) phosphine ethene complexes [a]

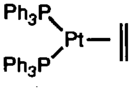
	1	**2**	**3**	**5**
Bond distances				
M–P(1)	2.261(4)	2.289(2)	2.265(4)	2.260(3)
M–P(2)	2.254(1)	2.289(2)	2.270(4)	2.257(3)
M–C(1)	2.109(5)	2.122(9)	2.116(8)	2.108(18)
M–C(2)	2.100(5)	2.119(8)	2.106(9)	2.122(17)
C(1)–C(2)	1.402(9)	1.366(11)	1.434(13)	1.45(2)
Bond angles				
P(1)–M–P(2)	105.25(4)	106.41(7)	111.60(7)	105.0(1)
C(1)–M–C(2)	38.9(3)	37.6(13)	39.70(35)	40.2(6)
P(1)–M–C(2)	108.8(2)	108.0(2)	103.88	107.8(4)
P(2)–M–C(1)	107.1(2)	108.1(2)	104.83	106.9(4)
Dihedral angle				
PMP–CPtC	4.9(4)	5.8(3)	1.6(3)	2.3(7)

[a] Other data from references 4–6.



1 M = Pt

2 M = Pd



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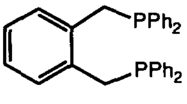

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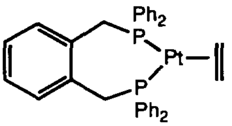

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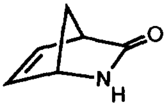

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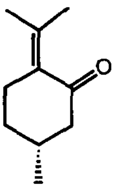

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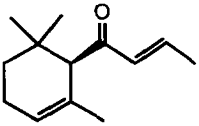

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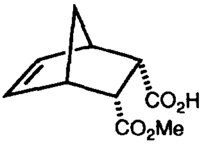

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the metal to the LUMO of the olefin ligand. Thus the metal with the greater electron availability may be expected to form the more stable alkene complex, as is observed. The coordination geometry about the platinum is trigonal and almost planar with a dihedral angle of 4.9(4)° between the PPtP and CPtC planes. Similarly small angles have been observed in the related structures of **2**, **3** and **5**, Table 1. The chelate bite angle (PPtP) in **1** is 105.25(4)° which is very similar to that in **2** and in the seven-ring chelate complex **5**. These three values are rather smaller than the PPtP angle in **3**, (111.60(7)°), and may reflect the slight steric compression caused by the presence of non-bonded interactions between the hydrogens of the coordinated ethene and the *ortho*-hydrogens of the P-phenyl rings. Such intramolecular H · · · H contacts are in range of 2.40 to 2.45 Å [6].

The bicyclic lactam **6** was recently prepared by Roberts [8], and it smoothly displaces the coordinated ethene ligand of **1** in tetrahydrofuran solution. Selective binding of platinum to the more open *exo*-face of 2-azabicyclo[2.2.1]hept-5-en-3-one, **6**, occurs, and two diastereoisomeric species may be observed by ^{31}P NMR spectroscopy (Fig. 2), corresponding to complexation of the (−)- and (+)-enantiomers.

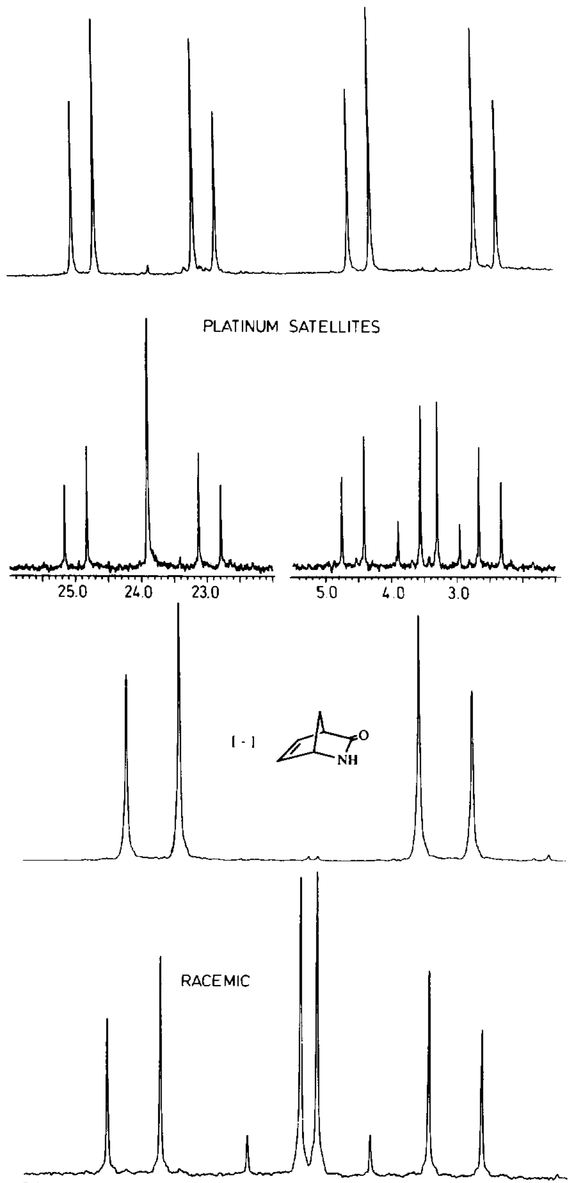
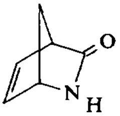
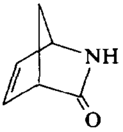
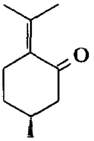
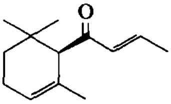
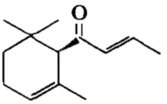
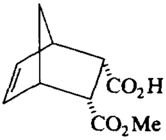


Fig. 2. ^{31}P NMR spectrum (298 K, 162 MHz, C_6D_6) of DIOP-Pt-**6**. The lower spectra are for an enriched sample of (−)-**6** (98.6 (±0.2)%) compared to racemate. The upper spectra show the high and low frequency platinum satellites.

The non-equivalence of the platinum–phosphorus coupling constants accounts for the different appearance of the high and low frequency platinum satellites (upper spectra in Fig. 2), Table 2. A sample of the (−)-**6** was analysed by integration of the separate resonances giving a value of 98.6 (±0.2%) for the enantiomeric purity. The tetrasubstituted alkene pulegone, **7**, also displaces ethene from **1**, and again face-

Table 2

^{31}P NMR data and enantiomeric purity of chiral alkenes **6–9** [a]

Alkene	$\delta(P_a)$ (ppm)	$\delta(P_b)$ (ppm)	$J(P_aP_b)$ (Hz)	$J(PtP_a)$ (Hz)	$J(PtP_b)$ (Hz)	e.e. (%)
[−] 	14.77	12.73	55	3301	3313	98.6 [0.2]
[+] 	13.80	13.51	55	3595	3094	[b]
{*R*} 	14.36	11.14	60	3381	3419	> 98
{*R*} 	14.17 [12.55]	11.68 [10.55]	65 [60]	3523 [3815]	3571 [3835]	> 99.7
{*S*} 	12.82 [12.79]	12.30 [10.44]	63 [62]	3668 [3493]	3854 [3728]	> 99.7
	15.06	13.58	71	3472	3443	[c]

[a] values in parentheses refer to constitutionally isomeric species related by binding of the *si* [or *re*] face of the enone. Spectra were recorded at 298 K and in C_6D_6. [b] Not analysed: data from racemate. [c] Enantiomeric purity could not be determined as no shift non-equivalence was observed.

selective complexation occurs, presumably through binding of the less-hindered *si* face of the exocyclic double bond.

The enone damascone, **8**, is a chiral molecule of considerable interest in the perfume industry: the *S*-enantiomer in particular possesses a powerful fragrance [9]. Samples of both enantiomers [(*R*)-(+)-damascone $[\alpha]_D^{20} = +490°$ (*c* 4.0, $CHCl_3$), (*S*)-(−)-damascone, $[\alpha]_D^{20} = -487°$ (*c* 4, $CHCl_3$)] were analysed separately by ^{31}P NMR using **1** as a chiral derivatising agent. The binding of the *si* and *re* faces of the enone double bond occurred non-selectively and two constitutional isomers were observed in each case (Table 2). No signal due to the diastereoisomeric complex could be discerned and an enantiomeric purity of at least 99.7% may be stated for each enantiomer, in accord with the optical rotation measurements, [9]. Finally, the norbornene derivative **9** [10] was examined. Again ethene displacement occurred readily, but in this case the ^{31}P NMR signals (at 101 MHz) of the diastereoisomeric complexes were isochronous and so the enantiomeric purity could not be determined. This behaviour contrasts with that of the isomeric *trans*-2,3-dicarboxybicyclo[2.2.1]hept-5-ene substrates, which are amenable to analysis [4].

Experimental

All manipulations were carried out under argon by standard Schlenk techniques. Complex **1** was prepared as described previously [1] and crystals suitable for analysis were obtained from dimethylsulphoxide solution. The derivatisation of **1** with chiral η^2-donors followed the methods outlined earlier [1].

Table 3

Final atomic parameters ($\times 10^4$, $\times 10^5$ for Pt, P1 and P2) and equivalent isotropic thermal parameters B_{iso} (Å^2)

	x	y	z	B_{iso} [a]
Pt	11720(1)	25000	23296(1)	2.950(8)
P1	15593(10)	7467(10)	32113(8)	3.05(4)
P2	−9080(11)	30380(10)	22221(9)	3.03(4)
O1	−773(4)	98(4)	4880(3)	5.9(2)
O2	−2073(3)	1759(3)	4530(3)	4.1(1)
C1	1856(6)	3792(5)	1503(5)	5.1(3)
C2	2869(5)	2959(6)	1961(5)	5.3(3)
C3	195(4)	53(4)	3550(4)	3.5(2)
C4	−290(4)	864(4)	4242(3)	3.4(2)
C5	−1497(4)	1651(4)	3733(4)	3.1(2)
C6	−1297(5)	2931(4)	3422(4)	3.2(2)
C7	−1920(5)	641(5)	5026(4)	4.5(2)
C8	−1673(7)	841(8)	6143(5)	7.6(4)
C9	−3132(10)	−149(8)	4506(8)	9.1(6)
C11	2090(5)	−439(4)	2517(3)	3.7(2)
C12	1338(5)	−1425(5)	2070(5)	5.1(3)
C13	1833(8)	−2271(6)	1549(5)	6.7(4)
C14	3042(7)	−2124(6)	1451(4)	6.1(3)
C15	3797(6)	−1154(7)	1875(5)	6.1(3)
C16	3336(6)	−301(6)	2405(5)	5.1(3)
C21	2880(4)	699(4)	4454(3)	3.4(2)
C22	3186(6)	−366(6)	5024(5)	5.1(3)
C23	4168(6)	−354(7)	5998(5)	6.5(3)
C24	4838(6)	682(8)	6379(5)	6.3(3)
C25	4558(7)	1703(6)	5821(5)	6.6(3)
C26	3592(6)	1718(5)	4858(4)	5.1(2)
C31	−2303(4)	2191(3)	1351(3)	3.2(2)
C32	−3612(4)	2542(9)	1181(3)	4.4(2)
C33	−4640(5)	1836(6)	590(5)	5.8(3)
C34	−4403(6)	786(6)	156(5)	5.5(3)
C35	−3121(6)	429(4)	302(4)	4.7(3)
C36	−2070(5)	1132(4)	895(4)	3.8(2)
C41	−1378(4)	4593(4)	1814(4)	3.7(2)
C42	−1305(6)	4943(5)	872(5)	5.5(3)
C43	−1577(7)	6105(7)	528(6)	7.1(4)
C44	−1932(7)	6947(6)	1120(7)	7.5(4)
C45	−2021(7)	6623(5)	2043(7)	7.1(4)
C46	−1760(6)	5434(5)	2386(5)	5.4(3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 4. Bond distances (Å) and angles (°) in complex **1**.

Bond distances			
Pt–P(1)	2.261(1)	C(12)–C(13)	1.390(8)
Pt–P(2)	2.254(1)	C(13)–C(14)	1.350(11)
Pt–C(1)	2.109(5)	C(14)–C(15)	1.356(10)
Pt–C(2)	2.109(5)	C(15)–C(16)	1.384(8)
P(1)–C(3)	1.839(4)	C(21)–C(22)	1.398(7)
P(1)–C(11)	1.827(5)	C(21)–C(26)	1.374(7)
P(1)–C(21)	1.823(4)	C(22)–C(23)	1.404(9)
P(2)–C(6)	1.843(5)	C(23)–C(24)	1.364(12)
P(2)–C(31)	1.831(4)	C(24)–C(25)	1.347(11)
P(2)–C(41)	1.834(4)	C(25)–C(26)	1.386(8)
O(1)–C(4)	1.437(5)	C(31)–C(32)	1.392(6)
O(1)–C(7)	1.437(6)	C(31)–C(36)	1.395(6)
O(2)–C(5)	1.433(5)	C(32)–C(33)	1.375(9)
O(2)–C(7)	1.401(6)	C(33)–C(34)	1.372(9)
C(1)–C(2)	1.402(9)	C(34)–C(35)	1.373(9)
C(3)–C(4)	1.525(6)	C(35)–C(36)	1.388(7)
C(4)–C(5)	1.521(6)	C(41)–C(42)	1.384(7)
C(5)–C(6)	1.521(6)	C(41)–C(46)	1.371(8)
C(7)–C(8)	1.494(9)	C(42)–C(43)	1.373(9)
C(7)–C(9)	1.530(10)	C(43)–C(44)	1.376(14)
C(11)–C(12)	1.377(7)	C(44)–C(45)	1.358(13)
C(11)–C(16)	1.396(7)	C(45)–C(46)	1.399(8)
Bond angles			
P(1)–Pt–P(2)	105.25(4)	O(2)–C(7)–C(9)	109.7(5)
P(1)–Pt–C(1)	147.5(2)	C(8)–C(7)–C(9)	113.7(6)
P(1)–Pt–C(2)	108.8(2)	P(1)–C(11)–C(12)	125.0(4)
P(2)–Pt–C(1)	107.1(2)	P(1)–C(11)–C(16)	116.9(4)
P(2)–Pt–C(2)	145.9(2)	C(12)–C(11)–C(16)	118.2(5)
C(1)–Pt–C(2)	38.9(3)	C(11)–C(12)–C(13)	120.3(5)
Pt–P(1)–C(3)	118.7(1)	C(12)–C(13)–C(14)	120.7(6)
Pt–P(1)–C(11)	111.8(2)	C(13)–(14)–C(15)	120.1(5)
Pt–P(1)–C(21)	118.6(2)	C(14–C(15)–C(16)	120.6(6)
C(3)–P(1)–C(11)	104.0(2)	C(11)–C(16)–C(15)	120.1(6)
C(3)–P(1)–C(21)	100.2(2)	P(1)–C(21)–C(22)	121.2(4)
C(11)–P(1)–C(21)	101.3(2)	P(1)–C(21)–C(26)	120.5(4)
Pt–P(2)–C(6)	115.8(2)	C(22)–C(21)–C(26)	118.3(5)
Pt–P(2)–C(31)	118.3(1)	C(21)–C(22)–C(23)	119.5(6)
Pt–P(2)–C(41)	115.6(2)	C(22)–C(23)–C(24)	120.4(6)
C(6)–P(2)–C(31)	100.5(2)	C(23)–C(24)–C(25)	120.1(5)
C(6)–P(2)–C(41)	102.5(2)	C(24)–C(25)–C(26)	120.8(6)
C(31)–P(2)–C(41)	101.7(2)	C(21)–C(26)–C(25)	120.9(5)
C(4)–O(1)–C(7)	109.5(3)	P(2)–C(31)–C(32)	121.1(4)
C(5)–O(2)–C(7)	107.0(3)	P(2)–C(31)–C(36)	120.1(3)
Pt–C(1)–C(2)	70.2(3)	C(32)–C(31)–C(36)	118.7(5)
Pt–C(2)–C(10	70.9(3)	C(31)–C(32)–C(33)	119.8(7)
P(1)–C(3)–C(4)	112.0(3)	C(32)–C(33)–C(34)	121.2(6)
O(1)–C(4)–C(3)	107.5(4)	C(33)–C(34)–C(35)	120.0(5)
O(1)–C(4)–C(5)	101.7(3)	C(34)–C(35)–C(36)	119.6(5)
C(3)–C(4)–C(5)	117.5(4)	C(31)–C(36)–C(35)	120.7(4)
O(2)–C(5)–C(4)	101.9(3)	P(2)–C(41)–C(42)	117.3(4)
O(2)–C(5)–C(6)	106.0(4)	P(2)–C(41)–C(46)	124.5(4)
C(4)–C(5)–C(6)	119.4(4)	C(42)–C(41)–C(46)	118.2(5)
P(2)–C(6)–C(5)	114.2(3)	C(41)–C(42)–C(43)	121.2(7)
O(1)–C(7)–O(2)	105.6(4)	C(42)–C(43)–C(44)	120.1(7)
O(1)–C(7)–C(8)	110.0(5)	C(43)–C(44)–C(45)	119.8(5)
O(1)–C(7)–C(9)	108.6(6)	C(44)–C(45)–C(46)	120.0(7)
O(2)–C(7)–C(8)	109.0(5)	C(41)–C(46)–C(45)	120.7(6)

Crystal data for complex 1

$C_{33}H_{36}PtO_2P_2$, *M* 721.68; monoclinic, $a = 10.666(2)$, $b = 11.105(3)$, $c = 13.818(3)$ Å, $\beta = 109.45(2)°$, $V = 1543.3(6)$ Å^3, $D_c = 1.553$ gcm^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 47.2$ cm^{-1}, $F(000) = 715.85$. Space group $P2_1$. Crystal dimensions 0.49 × 0.36 × 0.33 mm.

Data collection and processing

Intensity data were collected with a CAD4 diffractometer by the $\omega/2\theta$-scan method with $\omega = 0.6 + 0.35 \tan\theta$, to a maximum $2\theta = 53.8°$. Cell data were determined by a least squares analysis of the setting angles of 25 reflections with $20 < 2\gamma < 38°$. The range of indices was h −13 to 12, k −14 to 14, l −17 to 17. 6492 Unique reflections were collected. Data were corrected for absorption Lorentz and polarisation effects and during refinement for secondary extinction. The 5901 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement.

Structure analysis and refinement

The structure was solved by the heavy-atom method and refined by full-matrix, least-squares calculations. All non-hydrogen atoms were allowed anisotropic motion, with hydrogen atoms positioned geometrically (C–H 0.95 Å) and included (as riding atoms) in the structure factor calculations with an overall B_{iso} of 5 Å^2. The final cycle of refinement included 343 variable parameters and converged to $R = 0.021$, $R_w = 0.026$. The absolute configuration was established unequivocally by refinement of a $\delta f''$ multiplier. All calculations were performed on a PC 386 system with the NRCVAX suite of programs [11].

Final atom coordinates are shown in Table 3, and bond lengths and angles in Table 4. Lists of thermal parameters and structure factors are available from the authors.

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References

1 D. Parker and R.J. Taylor, Tetrahedron, 44 (1988) 2241.
2 D. Parker and R.J. Taylor, J. Chem. Soc., Chem. Commun., (1987) 1781.
3 K.V. Baker, J.M. Brown, N.A. Cooley, G.D. Hughes and R.J. Taylor, J. Organomet. Chem., 370 (1989) 397.
4 M. Hodgson, D. Parker, R.J. Taylor and G. Ferguson, J. Chem. Soc., Chem. Commun., (1987) 1309; idem., Organometallics, 7 (1988) 1761.
5 C.D. Cook and G.S. Jauhal, J. Am. Chem. Soc., 90 (1968) 1464; P.T. Cheng, C.D. Cook, S.C. Nyburg and K.Y. Wan, Inorg. Chem., 10 (1971) 2210.
6 M. Camalli, F. Caruso, S. Chaloupka, E.M. Leber, H. Rimmi and L.M. Venanzi, Helv. Chim. Acta., 73 (1990) 2263.
7 C.A. Tolman, W.C. Seidel and D.H. Gerlach, J. Am. Chem. Soc., 94 (1972) 2669.
8 S.J.C. Taylor, A.G. Sutherland, C. Lee, R. Wilson, S. Thomas, S.M. Roberts and C. Evans, J. Chem. Soc., Chem. Commun., (1990) 1120.
9 C. Fehr and J. Galindo, J. Am. Chem. Soc., 110 (1988) 6909.
10 R.A. Aitken and J.A. Gopal, Tetrahedron Asymm., 1 (1990) 517.
11 E.J. Gabe, Y. Le Page, J. P. Charland, F.L. Lee and P.S. White, J. Appl. Crystallogr., 22 (1989) 384.