Inorganica Chimica Acta, 112 (1986) 35–39

Preparation and X-ray Structure of $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppp)]BPh_4$ (pz = pyrazolate; dppp = 1,3-bisdiphenylphosphinopropane)*

L. A. ORO, D. CARMONA

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Cientìficas, 50009 Saragossa, Spain

J. REYES

Departamento de Química, Escuela Técnica Superior de Ingenieros Industriales, Universidad de Zaragoza, 50009 Saragossa, Spain

C. FOCES-FOCES and F. H. CANO

Departamento de Rayos-X, Instituto Rocasolano, Consejo Superior de Investigaciones Científicas, Serrano 119, 28006 Madrid, Spain

Received June 5, 1985

Abstract

The cationic complex $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppp)]BPh_4$ has been prepared by adding 1,3-bisdiphenylphosphinopropane (dppp) and $NaBPh_4$ to a methanol suspension of the neutral compound $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$. The structure of the complex was established by X-ray crystallography. It crystallizes in the space group $P\bar{1}$ with cell dimensions of a = 15.1870(6), b = 17.5060(8), c = 11.4897(3) Å, α = 97.793(3), β = 96.707(2), γ = 94.281(4). The two rhodium atoms are separated by 3.260(1) Å.

Introduction

In recent years several dinuclear rhodium complexes containing metal centres in oxidation states I [1–3] or III [4] joined to one other by a pair of bridging *exo*-bidentate pyrazolate ligands (pz) have been reported. We have also described some examples of triply-bridged homovalent rhodium compounds [5–7] and mixed valence rhodium(III)–rhodium(I) pyrazolate bridged dinuclear complexes [8]. We now describe the preparation of an unusual heterobridged mixed-valence complex bridged by one carbonyl group and two pyrazolate ligands.

Results and Discussion

We recently reported the synthesis of the heterovalent Rh(III)–Rh(I) complex $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ (pz = pyrazolate) [8]. This complex reacts with 1,3-bisdiphenylphosphinopropane (dppp) in methanol suspension and in the presence of $NaBPh_4$ to form an orange material. This material shows a single, strong carbonyl absorption at 1785 cm^{-1}, characteristic of a bridging carbonyl group, and is probably formed by ionization of the chlorine from the Rh(III) atom and coordination of the dppp ligand to the initially square-planar Rh(I) atom. Elemental analysis supports the $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppp)]BPh_4$ formulation, and conductivity measurements confirm the ionic formulation. In order to obtain an unambiguous characterization of this complex, an X-ray diffraction study was undertaken.

The structure of the cation is shown in Fig. 1. Table I collects selected parameters. The cation

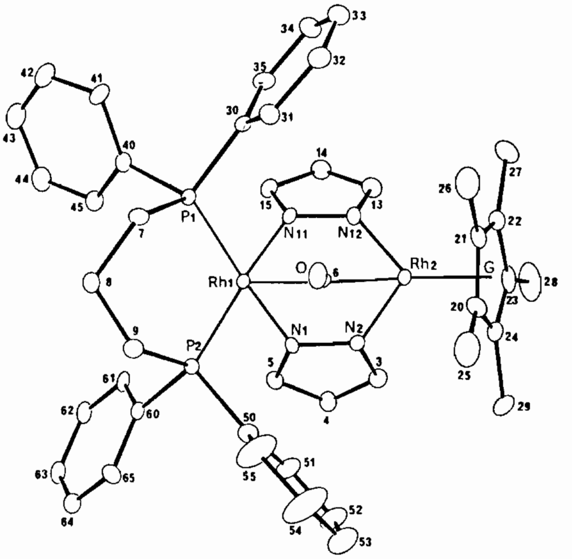

Fig. 1. An ORTEP view of the cation showing the numbering system.

---

*Dedicated To Professor Rafael Usón on the occasion of his 60th birthday.

0020-1693/86/$3.50

TABLE I. Selected Bond Distances (Å), Bond Angles and Torsion Angles (°)

Rh(1)–P(1)	2.264(2)	Rh(2)–G[a]	1.835(4)
Rh(1)–P(2)	2.289(2)	Rh(1)–Rh(2)	3.260(1)
Rh(1)–N(1)	2.092(6)	Rh(2)–N(2)	2.071(6)
Rh(1)–N(11)	2.086(6)	Rh(2)–N(12)	2.109(6)
Rh(1)–C(6)	2.060(7)	Rh(2)–C(6)	2.032(8)
Rh(2)–C(20)	2.196(7)	C(20)–C(21)	1.426(14)
Rh(2)–C(21)	2.184(8)	C(21)–C(22)	1.424(14)
Rh(2)–C(22)	2.207(9)	C(22)–C(23)	1.405(14)
Rh(2)–C(23)	2.209(10)	C(23)–C(24)	1.406(15)
Rh(2)–C(24)	2.187(10)	C(24)–C(20)	1.438(14)
C(6)–O	1.185(9)		
P(1)–Rh(1)–P(2)	95.8(1)	G–Rh(2)–N(2)	129.5(2)
P(1)–Rh(1)–N(11)	90.0(2)	G–Rh(2)–N(12)	130.6(2)
P(1)–Rh(1)–N(1)	172.0(2)	G–Rh(2)–C(6)	122.4(2)
P(1)–Rh(1)–C(6)	93.3(2)	N(12)–Rh(2)–N(2)	81.7(2)
P(2)–Rh(1)–N(11)	173.4(2)	N(12)–Rh(2)–C(6)	89.9(3)
P(2)–Rh(1)–N(1)	91.2(2)	N(2)–Rh(2)–C(6)	89.0(3)
P(2)–Rh(1)–C(6)	92.1(2)	Rh(1)–C(6)–Rh(2)	106.7(3)
N(1)–Rh(1)–N(11)	82.7(2)	Rh(1)–C(6)–O	120.1(6)
N(1)–Rh(1)–C(6)	90.2(3)	Rh(2)–C(6)–O	134.1(6)
N(11)–Rh(1)–C(6)	90.5(3)		
Rh(1)–P(1)–C(7)	116.4(3)	Rh(1)–P(2)–C(9)	118.9(3)
Rh(1)–P(1)–C(30)	114.2(3)	Rh(1)–P(2)–C(50)	115.8(3)
Rh(1)–P(1)–C(40)	115.0(3)	Rh(1)–P(2)–C(60)	110.9(2)
C(7)–P(1)–C(30)	104.2(3)	C(9)–P(2)–C(50)	103.4(4)
C(7)–P(1)–C(40)	99.5(4)	C(9)–P(2)–C(60)	102.5(4)
C(30)–P(1)–C(40)	105.7(4)	C(50)–P(2)–C(60)	103.5(4)
Rh(1)–N(1)–C(5)	136.1(5)	Rh(2)–N(2)–C(3)	131.6(6)
Rh(1)–N(1)–N(2)	114.8(4)	Rh(2)–N(2)–N(1)	119.8(5)
Rh(1)–N(11)–C(15)	133.3(5)	Rh(2)–N(12)–C(13)	131.3(6)
Rh(1)–N(11)–N(12)	116.2(4)	Rh(2)–N(12)–N(11)	117.9(4)
Rh(1)–P(1)–C(7)–C(8)	−48.3(6)	Rh(1)–N(1)–N(2)–Rh(2)	−2.1(6)
P(1)–C(7)–C(8)–C(9)	83.4(7)	N(1)–N(2)–Rh(2)–N(12)	−61.5(5)
C(7)–C(8)–C(9)–P(2)	−74.7(7)	N(2)–Rh(2)–N(12)–N(11)	63.6(5)
C(8)–C(9)–P(2)–Rh(1)	35.1(7)	Rh(2)–N(12)–N(11)–Rh(1)	−1.5(6)
C(9)–P(2)–Rh(1)–P(1)	−7.6(3)	N(12)–N(11)–Rh(1)–P(1)	−63.0(5)
P(2)–Rh(1)–P(1)–C(7)	13.1(5)	N(11)–Rh(1)–N(1)–N(2)	65.4(5)
C(30)–P(1)–C(7)–C(8)	−175.1(5)	C(50)–P(2)–C(9)–C(8)	165.1(6)
C(40)–P(1)–C(7)–C(8)	76.0(6)	C(60)–P(2)–C(9)–C(8)	−87.6(6)
Rh(1)–P(1)–C(30)–C(31)	−97.8(7)	Rh(1)–P(2)–C(50)–C(55)	118.5(10)
Rh(1)–P(1)–C(40)–C(41)	−158.8(6)	Rh(1)–P(2)–C(60)–C(65)	167.0(6)
N(2)–Rh(2)–G–C(20)	−88.3(6)	G–Rh(2)–N(2)–N(1)	161.5(4)
N(12)–Rh(2)–G–C(20)	154.4(6)	G–Rh(2)–N(2)–N(11)	−160.2(4)
C(6)–Rh(2)–G–C(20)	31.6(7)	G–Rh(2)–N(2)–O	4.9(10)
N(2)–Rh(2)–G–C(21)	−160.1(5)		

[a] G being the centroid of the five-membered ring.

consists of two rhodium centres bridged by a carbonyl and two pyrazolate groups. The two phosphorus atoms of a dppp ligand and a η^5-bonded C_5Me_5 ring complete the coordination spheres of the Rh(1) and Rh(2) atoms respectively. Rh(1) is five-coordinated, having a distorted tetragonal pyramid geometry with the carbonyl ligand at the apex. The coordination geometry of the Rh(2) is that loosely referred to as a 'three-legged piano stool'. The Rh–N distances are comparable to those found in other dinuclear pyrazolate rhodium complexes [2, 4–8]. From the available data, there is no simple correlation between the Rh–N distances and the oxidation state of the metal centres. An interesting feature of this structure is the existence of the carbonyl ligand bridging the two metal centres, which are not bonded to each other (Rh–Rh separation is 3.260(1) Å). The C(6)–O length has a value comparable to those found for this group in some rhodium complexes [9, 10], and the angles around C(6) have values similar to those in dinuclear Pd [11] and Pt [12] complexes in which a CO group bridges two non-bonded metals. The Rh(1)–C(6)–Rh(2) angle and the Rh–C(6) distances are greater than the corresponding ones for transition metal–metal bonded carbonyl complexes [13]. Although the environment is asymmetric (Rh(1)–C(6)–O < Rh(2)–C(6)–O), the geometry involving C(6) is planar, the angles around adding 359.9(9)°. All these facts, together with the low ν(CO) absorption frequency observed (1785 cm^{-1}), have led to the classification of this type of CO group as ketonic carbonyl and to the suggestion that, in some cases, these compounds should be considered as dimetallated ketones [9, 10, 12, 14–18]. The geometry of the *cis*-pyrazolate bridging ligands seems to be able to stabilize this unusual species [15], whereas for *exo*-bidentate P- or As-donor ligands a *trans*-disposition is required (e.g. dppm or dpam) [9, 10, 12, 14–18].

Further studies are now under way investigating the extension of this interesting preparative reaction to other related systems, in order to obtain further information on the ability of the *cis*-Rh(μ-pz)$_2$Rh framework to stabilize this type of carbonyl coordination.

Experimental

Reactions were carried out in air. The solvents were dried by standard methods and distilled before use. C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Conductivities were measured at 20 °C in *ca.* 5×10^{-4} M acetone solutions using a Philips 9501/01 conductimeter. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets.

Preparation of the Complex [(C_5Me_5)Rh(μ-pz)$_2$(μ-CO)Rh(dppp)]BPh$_4$

NaBPh$_4$ (80.5 mg; 0.24 mmol) and dppp (80.9 mg; 0.20 mmol) in methanol were added successively to a suspension of complex [(C_5Me_5)ClRh(μ-pz)$_2$Rh(CO)$_2$] (111.0 mg; 0.20 mmol) in methanol. The solid dissolved and immediately the slow precipitation of an orange material was observed. The mixture was stirred for 4 days; then the resulting solid was recovered by filtration. The complex was washed with MeOH and Et$_2$O and air-dried. Yield: 48%. *Anal.* Found: C, 66.1; H, 5.5; N, 4.5. $C_{68}H_{67}N_4BOP_2Rh_2$ requires: C, 65.1; H, 5.5; N, 4.3%. Λ_M = 82 Ω^{-1} cm^2 mol^{-1}.

X-ray Analysis

Table II presents the main characteristics of the X-ray analysis. The final atomic coordinates for the non-hydrogen atoms are listed in Table III. Thermal parameters, hydrogen parameters and structural factors can be obtained from the authors on request.

TABLE II. Crystal Analysis at Room temperature

Crystal Data	
Formula	$C_{68}H_{67}N_4BOP_2Rh_2$
Crystal habit	Transparent, orange, prismatic
Crystal dimensions (mm)	0.10 × 0.27 × 0.43
Symmetry	Triclinic
Space group	$P\bar{1}$
Unit cell determination:	
least-squares fit to θ(Cu) < 45°	100 reflexions
Unit cell	
a (Å)	15.1870(6)
b (Å)	17.5060(8)
c (Å)	11.4897(3)
α (°)	97.793(3)
β (°)	96.707(2)
γ (°)	94.281(4)
V (Å^3)	2993.0(2)
Z	2
D (g cm^{-3})	1.370
M	1234.87
F(000)	1272
μ (cm^{-1})	54.16
Experimental data	
Technique and stability	Cu Kα. Four-circle PW1100 Philips diffractometer. Graphite oriented monochromator. No decay (inside capillar)
Collection mode: ($w/2\theta$), 1.5° scan width, 1° × 1° det. apertures	θ < 55° (1 min/reflection)
Total independent data	7508
Observed data ($I > 3\sigma(I)$)	6393
Solution and refinement	X-Ray 76 System [19]. Vax 11/750. Patterson and Dirdif [20]. Least-squares on Fobs only
Final shift/error	0.08
Parameters:	
number of variables	971
degrees of freedom	5422
ratio of freedom	6.6
Weighting scheme	Empirical as to give no trends in $\langle w\Delta F^2\rangle$ *vs.* $\langle \lvert F_o \rvert \rangle$ or $\langle \sin\theta/\lambda \rangle$
Maximum thermal factors (Å^2)	U_{11} (C55) = 0.21(2)
Final ΔF peak	2.0 eÅ^{-3} near the Rh atoms
Final R, R_w	0.067, 0.075
Atomic factors	International Tables for X-ray Crystallography [21]

TABLE III. Final Atomic Coordinates and Thermal Parameters as: $U_{\mathrm{eq}} = \frac{1}{3}\Sigma(U_{ij}a_i{}^*a_j{}^*a_ia_j\cos(a_i,a_j)) \times 10^4$

Atom	x/a	y/b	z/c	U_{eq}
Rh1	0.25826(3)	0.11240(3)	0.31139(4)	266(2)
Rh2	0.14700(3)	0.25243(3)	0.22923(5)	312(2)
C30	0.16344(50)	0.13547(45)	0.57042(64)	382(26)
C31	0.18398(58)	0.20457(50)	0.64763(74)	495(30)
C32	0.11491(79)	0.24302(61)	0.69519(82)	652(40)
C33	0.02932(73)	0.21306(72)	0.66751(93)	692(44)
C34	0.00789(61)	0.14494(69)	0.59239(93)	648(39)
C35	0.07498(60)	0.10593(57)	0.54354(77)	552(33)
C40	0.23077(51)	−0.01441(45)	0.51280(67)	405(26)
C41	0.19546(62)	−0.03777(51)	0.61143(72)	519(31)
C42	0.19345(73)	−0.11394(59)	0.62799(90)	652(38)
C43	0.22487(76)	−0.16856(57)	0.55012(106)	710(41)
C44	0.25696(72)	−0.14622(53)	0.44966(95)	648(37)
C45	0.25864(60)	−0.06959(45)	0.43137(73)	472(30)
P1	0.24979(12)	0.08767(10)	0.49834(15)	296(6)
C7	0.35055(48)	0.11387(47)	0.60412(60)	383(25)
C8	0.43397(51)	0.08558(49)	0.55752(67)	429(27)
C9	0.47310(50)	0.14034(48)	0.48214(68)	423(27)
P2	0.41008(12)	0.13532(10)	0.33336(16)	301(6)
C50	0.45346(56)	0.22324(46)	0.28144(73)	449(29)
C51	0.43508(78)	0.23267(65)	0.16508(99)	743(43)
C52	0.46606(95)	0.29887(88)	0.12443(132)	953(59)
C53	0.51627(127)	0.35693(79)	0.19942(168)	1128(74)
C54	0.53141(184)	0.34891(92)	0.31312(170)	1691(115
C55	0.50415(138)	0.28234(79)	0.35557(117)	1256(73)
C60	0.45975(49)	0.05777(42)	0.24593(63)	356(25)
C61	0.40903(51)	−0.01119(44)	0.20120(62)	377(26)
C62	0.44719(60)	−0.07068(49)	0.13736(71)	488(30)
C63	0.53551(64)	−0.06109(51)	0.11870(72)	511(32)
C64	0.58437(59)	0.00748(55)	0.16266(77)	523(32)
C65	0.54781(55)	0.06690(50)	0.22677(76)	487(30)
O	0.28293(38)	0.26432(31)	0.44157(51)	477(19)
C6	0.24264(50)	0.22826(42)	0.35443(74)	391(27)
N1	0.24971(40)	0.12501(34)	0.13203(51)	348(20)
N2	0.20460(42)	0.18477(36)	0.10194(52)	380(22)
C3	0.19286(60)	0.17770(52)	−0.01873(70)	490(30)
C4	0.23162(63)	0.11420(51)	−0.06431(67)	506(31)
C5	0.26638(56)	0.08257(46)	0.03258(67)	427(27)
N11	0.12068(40)	0.08775(32)	0.27076(50)	336(20)
N12	0.07486(39)	0.14560(35)	0.23505(54)	364(21)
C13	−0.00383(52)	0.11463(53)	0.18010(78)	506(32)
C14	−0.01203(58)	0.03764(52)	0.18245(86)	558(33)
C15	0.06851(55)	0.02278(44)	0.24055(69)	423(27)
C20	0.18388(57)	0.37769(41)	0.27140(94)	542(34)
C21	0.11291(62)	0.35675(45)	0.33521(75)	496(31)
C22	0.03775(60)	0.32741(48)	0.25077(83)	523(32)
C23	0.06190(68)	0.32817(54)	0.13650(84)	593(36)
C24	0.15142(73)	0.35821(49)	0.14744(90)	601(38)
C25	0.27157(95)	0.41685(60)	0.32254(157)	1048(62)
C26	0.11442(106)	0.37195(69)	0.46665(91)	912(53)
C27	−0.05262(75)	0.30366(73)	0.28155(144)	938(56)
C28	−0.00145(109)	0.30395(84)	0.02086(114)	1075(59)
C29	0.20551(108)	0.37431(65)	0.04992(135)	1053(63)
B	0.72319(64)	0.36191(54)	−0.10871(92)	469(33)
C70	0.62470(59)	0.34632(46)	−0.18878(77)	491(29)
C71	0.59556(78)	0.39254(63)	−0.27538(100)	741(42)
C72	0.50987(89)	0.38315(69)	−0.33532(102)	787(46)

(continued on facing page)

TABLE III. *(continued)*

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C73	0.44910(82)	0.32873(69)	−0.31342(94)	765(43)
C74	0.47206(74)	0.28364(59)	−0.22748(99)	721(40)
C75	0.55905(60)	0.29296(50)	−0.16893(83)	547(32)
C80	0.79936(61)	0.39036(46)	−0.18832(84)	530(32)
C81	0.79580(84)	0.36344(62)	−0.30831(104)	780(45)
C82	0.86331(122)	0.38554(84)	−0.37491(140)	1086(67)
C83	0.93547(105)	0.43450(83)	−0.32129(164)	1026(67)
C84	0.94232(75)	0.46133(66)	−0.20325(139)	828(52)
C85	0.87584(63)	0.44073(54)	−0.13824(96)	616(36)
C90	0.74690(55)	0.27997(49)	−0.06291(81)	516(31)
C91	0.79356(76)	0.22635(54)	−0.12386(103)	727(40)
C92	0.80789(83)	0.15392(65)	−0.08044(152)	918(55)
C93	0.77921(87)	0.13715(67)	0.02153(137)	820(50)
C94	0.73347(81)	0.18911(71)	0.07999(118)	815(47)
C95	0.71773(65)	0.25851(54)	0.04216(94)	629(37)
C100	0.71773(59)	0.42764(47)	0.00599(81)	511(31)
C101	0.64857(59)	0.47684(50)	0.01295(87)	560(33)
C102	0.64503(74)	0.53270(58)	0.11097(105)	689(41)
C103	0.70981(90)	0.54156(66)	0.20672(108)	810(47)
C104	0.78005(87)	0.49289(70)	0.20211(104)	824(46)
C105	0.78287(67)	0.43834(57)	0.10582(90)	630(36)

Acknowledgement

This work was supported by the Comisión Asesora de Investigación Científica y Técnica, Grant 1790/82.

References

1 S. Trofimenko, *Inorg. Chem., 10,* 1372 (1971).

2 (a) R. Usón, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem., 205,* 247 (1981); (b) R. Usón, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem., 224,* 69 (1982).

3 (a) G. Minghetti, G. Banditelli and F. Bonati, *Inorg. Chem., 18,* 658 (1979); (b) G. Banditelli, A. L. Bandini, F. Bonati and G. Minghetti, *J. Organomet. Chem., 218,* 229 (1981).

4 L. A. Oro, D. Carmona, M. P. Lamata, C. Foces-Foces and F. H. Cano, *Inorg.Chim. Acta, 97,* 19 (1985).

5 L. A. Oro, D. Carmona, P. L. Pérez, M. Esteban, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.,* 973 (1985).

6 L. A. Oro, M. T. Pinillos, A. Tiripicchio and M. Tiripicchio-Camellini, *Inorg. Chim. Acta,.99,* L13 (1985).

7 L. A. Oro, D. Carmona, M. P. Lamata, M. C. Apreda, C. Foces-Foces, F. H. Cano and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.,* 1823 (1984).

8 L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.,* in press.

9 M. Cowie and T. G. Southern, *Inorg. Chem., 21,* 246 (1982).

10 J. T. Mague, *Inorg. Chem., 22,* 45 (1983).

11 M. L. Kullberg and C. P. Kubiak, *Organometallics, 3,* 632 (1984).

12 M. P. Brown, A. N. Keith, L. Manojlovic-Muir, K. W. Muir,.R. J. Puddephatt and K. R. Seddon, *Inorg.Chim. Acta, 34,* L223 (1979).

13 R. Colton and M. J. McCormick, *Coord. Chem. Rev., 32,* 1 (1980).

14 S. D. Robinson, *Inorg. Chim. Acta, 27,* L108 (1978).

15 J. Powell, A. Kuksis, S. C. Nyburg and W. W. Ng, *Inorg. Chim. Acta, 64,* L211 (1982).

16 P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 889 (1983).

17 B. R. Sutherland and M. Cowie, *Inorg. Chem., 23,* 1290 (1984), and refs. therein.

18 J. A. E. Gibson and M. Cowie, *Organometallics, 3,* 984 (1984), and refs. therein.

19 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, 'The X-ray System' (Technical report TR-446) Computer Science Center, Univ. Maryland, 1976.

20 P. T. Beurskens, W. Q. Bosman, H.-M. Doesburg, R. O. Gould, T. E. M. Van den Hark, P. A. J. Prick, J. H. Noordijk, G. Beurskens, V. Parthasarathi, H. J. Bruins Slot and R. C. Haltiwanger, 'Dirdif System', Crystallographic Laboratory Toernooiveld, Nijmegen, The Netherlands, 1983.

21 'International Tables for X-Ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.