Reaction of $[Mo(CO)_6]$ with $Ph_2P(CH_2)_6PPh_2$ (dpph): The Synthesis of $[Mo(CO)_3(dpphn)]$ [dpphn = $Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$] and *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ and the Crystal Structure of the Latter†

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The complex $[Mo(CO)_3(dpphn)]$ [dpphn = $Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$] was prepared from $[Mo(CO)_6]$ and $Ph_2P(CH_2)_6PPh_2$ (dpph) in refluxing decahydronaphthalene *via* a dehydrogenation process. The dpph bridged, bimetallic complex *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ was also prepared from the same starting materials, but in refluxing toluene. Crystals of the latter are triclinic, space group $P\bar{1}$, with $a = 11.989(2)$, $b = 13.304(4)$, $c = 16.011(5)$ Å, $\alpha = 109.59(2)$, $\beta = 88.32(2)$, $\gamma = 109.71(2)°$, $Z = 1$ and $R = 0.051$ for 3866 observed reflections. The compound has a *trans* bridged 18-membered ring structure. The *trans* geometry may be due to the steric effect of the diphenylphosphino groups during the thermolytic substitution reaction. The Mo–P bond lengths are similar, but the Mo–CO bond lengths are significantly different, with the bonds inside the 18-membered ring being shorter than those outside.

There are only a few reports concerning the reaction between $Ph_2P(CH_2)_6PPh_2$ (dpph) and Group 6B metal carbonyls. Dietsche[1] reported that treatment of $[Mo(CO)_6]$ with 0.5 molar equivalent dpph in refluxing $EtOCH_2CH_2OCH_2CH_2OH$ for 5–20 min gives the bridged dinuclear complex $[(OC)_5Mo\{Ph_2P(CH_2)_6PPh_2\}Mo(CO)_5]$. The same product and the chromium and tungsten homologues have also been synthesised by Hor[2] from $[M(CO)_6]$ (M = Cr, Mo or W) and dpph with Me_3NO as initiator in MeCN at room temperature.

In the present study $[Mo(CO)_3(dpphn)]$ [dpphn = $Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$] and *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ were prepared from a 1:1 molar ratio of $[Mo(CO)_6]$ and dpph in refluxing decahydronaphthalene or toluene *via* thermolytic decarbonylation. Dehydrogenation of dpph by rhodium and iridium complexes to form the corresponding dpphn complexes has been reported,[3,4] but not by $[Mo(CO)_6]$. In order to elucidate the detailed three-dimensional architecture of the unusual *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ and as part of a series of studies on bidentate phosphine derivatives of Group 6B metal carbonyls,[5,6] the crystal structure was investigated by X-ray diffraction.

Results and Discussion

The complex $[Mo(CO)_3(dpphn)]$ was synthesised from $[Mo(CO)_6]$ and dpphn previously and its crystal structure investigated.[7] In this work $[Mo(CO)_3(dpphn)]$ has been obtained *via* dehydrogenation of dpph by $[Mo(CO)_6]$ in refluxing decahydronaphthalene and characterized by IR spectroscopy, elemental analysis and X-ray structure determination. Dehydrogenation of dpph by $[M_2X_2(C_8H_{12})_2]$ (M = Rh, X = Cl or Br; M = Ir, X = Cl) in refluxing mesitylene to form the corresponding dpphn complexes, $[MX(dpphn)]$, has been reported and a mechanism for the dehydrogenation proposed.[3,4] Other phosphine ligands containing saturated hydrocarbon groups also undergo dehydrogenation: tri-*o*-tolylphosphine by $RhCl_3$,[8] 2,2′-bis(diphenylphosphino)bibenzyl by $[Rh_2Cl_2(C_8H_{12})_2]$,[9,10] and 1,6-bis(di-*tert*-butylphosphino)hexane by $RhCl_3{\cdot}3H_2O$.[11]

The complex *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ was also prepared from the same starting materials, $[Mo(CO)_6]$ and dpph, but in refluxing toluene. Its IR spectrum in the carbonyl stretching region shows absorptions at 2018w, 1948w and 1874s cm^{-1} (KBr pellet) in accord with the CO stretching modes exhibited by *trans*-$ML_2(CO)_4$ species, *i.e.* A_{1g} (Raman active), B_{1g} (Raman active) and E_u (IR active).[12,13] The *trans* geometry may be due to the steric effect of the bulky diphenylphosphino groups exerted during the thermolytic substitution reaction. Since only the decarbonylation product is formed in refluxing toluene, dehydrogenation of dpph by $[Mo(CO)_6]$ must require more vigorous condition, *e.g.* refluxing decahydronaphthalene (b.p. = 188 °C).

Atomic positional parameters and selected bond lengths and angles of *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$ are listed in Tables 1 and 2, respectively. The molecular structure is shown in Fig. 1. The molecule consists of two Mo atoms, each bonded to four equatorial carbonyls and two P atoms from different tertiary phosphine termini of the two diphosphine ligands. The coordination around each metal is distorted octahedral with the bond angles of the three principal axes P(1)–Mo–P(2), C(1)–Mo–C(3) and C(2)–Mo–C(4) 173.26(7), 177.2(3) and 171.6(3)° respectively. The deviation of these angles from the ideal for octahedral geometry may be due to the orientation of the phenyl groups, especially phenyl rings A and C. Deviation for the former may be attributed to the molecule being more bulky inside the 18-membered ring. Because of the *trans* geometry and the presence of an inversion centre at the middle of the molecule, a *trans* bis(dpph) bridged rectangular 18-membered ring structure is formed with two P–Mo–P axes and two dpph groups as the four sides.

† *trans*-Bis[μ-1,6-bis(diphenylphosphino)hexane-κ*P*:κ*P*′]-bis(tetracarbonylmolybdenum).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Fractional atomic coordinates, with estimated standard deviations (e.s.d.s) in parentheses, for *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	0.025 29(6)	0.774 70(6)	0.232 50(4)	C(4C)	0.315 6(8)	0.524 0(6)	0.348 0(5)
P(1)	−0.174 79(17)	0.754 64(16)	0.178 73(12)	C(5C)	0.404 8(7)	0.612 2(7)	0.336 6(5)
P(2)	0.232 07(17)	0.794 51(16)	0.268 65(12)	C(6C)	0.379 1(6)	0.692 4(6)	0.311 9(5)
C(1)	−0.007 5(6)	0.611 0(6)	0.150 9(4)	C(1D)	0.323 7(6)	0.795 8(5)	0.175 4(4)
C(2)	0.090 1(7)	0.841 1(6)	0.137 0(5)	C(2D)	0.297 2(7)	0.699 7(6)	0.100 8(5)
C(3)	0.048 7(7)	0.932 2(6)	0.312 9(5)	C(3D)	0.359 3(8)	0.696 2(7)	0.026 5(5)
C(4)	−0.029 2(6)	0.732 6(6)	0.339 1(4)	C(4D)	0.450 7(8)	0.790 1(7)	0.027 3(5)
C(5)	−0.234 4(6)	0.865 4(6)	0.239 0(4)	C(5D)	0.481 0(8)	0.886 3(7)	0.099 5(6)
C(6)	−0.263 2(6)	0.866 6(6)	0.331 8(4)	C(6D)	0.416 8(8)	0.888 6(6)	0.173 4(5)
C(7)	−0.284 7(9)	0.970 6(7)	0.384 3(5)	O(1)	−0.026 6(5)	0.519 7(4)	0.105 6(3)
C(8)	0.318 4(6)	0.922 4(5)	0.358 6(4)	O(2)	0.128 1(5)	0.882 5(5)	0.085 7(4)
C(9)	0.276 9(7)	0.923 2(6)	0.450 4(4)	O(3)	0.057 7(5)	1.022 3(5)	0.362 0(4)
C(10)	0.320 9(10)	1.033 7(7)	0.516 0(5)	O(4)	−0.058 7(5)	0.711 7(5)	0.402 6(3)
C(1A)	−0.302 7(6)	0.627 4(5)	0.171 3(4)	C(1E)	0.864 6(11)	0.273 1(9)	0.236 2(7)
C(2A)	−0.409 3(6)	0.603 5(6)	0.124 3(4)	C(2E)	0.911 2(10)	0.206 2(9)	0.272 9(7)
C(3A)	−0.506 9(6)	0.510 5(6)	0.120 8(5)	C(3E)	0.931 0(10)	0.248 2(9)	0.361 9(7)
C(4A)	−0.500 2(7)	0.439 5(6)	0.164 1(5)	C(4E)	0.906 2(11)	0.336 8(9)	0.420 3(7)
C(5A)	−0.395 1(7)	0.462 4(6)	0.211 2(5)	C(5E)	0.868 6(11)	0.399 1(10)	0.380 4(8)
C(6A)	−0.296 9(6)	0.554 8(6)	0.214 2(5)	C(6E)	0.853 4(10)	0.366 0(9)	0.288 5(7)
C(1B)	−0.179 9(6)	0.753 9(5)	0.064 8(4)	C(7E)	0.846 0(14)	0.224 5(12)	0.146 6(10)
C(2B)	−0.172 1(7)	0.660 7(6)	−0.003 5(4)	C(1F)	0.361 5(10)	0.269 9(8)	0.402 9(7)
C(3B)	−0.166 7(7)	0.658 2(7)	−0.089 7(5)	C(2F)	0.306 1(9)	0.212 7(8)	0.315 9(6)
C(4B)	−0.168 2(8)	0.749 2(7)	−0.109 7(5)	C(3F)	0.376 4(10)	0.179 1(8)	0.253 3(7)
C(5B)	−0.171 3(8)	0.845 3(7)	−0.042 7(5)	C(4F)	0.490 8(11)	0.192 7(9)	0.266 3(7)
C(6B)	−0.178 4(8)	0.847 0(7)	0.044 0(5)	C(5F)	0.544 4(11)	0.240 3(9)	0.351 0(7)
C(1C)	0.262 0(6)	0.684 6(5)	0.299 5(4)	C(6F)	0.478 4(10)	0.284 5(9)	0.417 8(7)
C(2C)	0.173 0(7)	0.596 3(6)	0.312 1(5)	C(7F)	0.303 8(14)	0.315 0(12)	0.472 3(9)
C(3C)	0.200 5(7)	0.514 5(6)	0.336 8(5)				

Table 2 Selected bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$

Mo–P(1)	2.4703(21)	P(2)–C(1D)	1.829(7)
Mo–P(2)	2.4680(21)	C(1)–O(1)	1.134(8)
Mo–C(1)	2.037(7)	C(2)–O(2)	1.139(9)
Mo–C(2)	2.024(7)	C(3)–O(3)	1.163(9)
Mo–C(3)	1.986(8)	C(4)–O(4)	1.156(8)
Mo–C(4)	1.995(7)	C(5)–C(6)	1.512(9)
P(1)–C(5)	1.826(7)	C(6)–C(7)	1.461(10)
P(1)–C(1A)	1.833(7)	C(7)–C(10)	1.656(11)
P(1)–C(1B)	1.824(7)	C(8)–C(9)	1.536(10)
P(2)–C(8)	1.815(7)	C(9)–C(10)	1.420(10)
P(2)–C(1C)	1.833(7)		
P(1)–Mo–P(2)	173.26(7)	Mo–P(2)–C(1D)	113.38(23)
P(1)–Mo–C(1)	87.63(20)	C(8)–P(2)–C(1C)	101.2(3)
P(1)–Mo–C(2)	87.64(22)	C(8)–P(2)–C(1D)	103.5(3)
P(1)–Mo–C(3)	89.98(22)	C(1C)–P(2)–C(1D)	99.7(3)
P(1)–Mo–C(4)	94.37(21)	Mo–C(1)–O(1)	179.5(6)
P(2)–Mo–C(1)	90.15(21)	Mo–C(2)–O(2)	177.4(7)
P(2)–Mo–C(2)	86.17(22)	Mo–C(3)–O(3)	176.7(7)
P(2)–Mo–C(3)	92.40(22)	Mo–C(4)–O(4)	177.7(6)
P(2)–Mo–C(4)	92.13(21)	P(1)–C(5)–C(6)	113.5(5)
C(1)–Mo–C(2)	94.0(3)	C(5)–C(6)–C(7)	111.5(6)
C(1)–Mo–C(3)	177.2(3)	C(6)–C(7)–C(10)	110.0(6)
C(1)–Mo–C(4)	94.2(3)	P(2)–C(8)–C(9)	112.8(5)
C(2)–Mo–C(3)	87.5(3)	C(8)–C(9)–C(10)	112.1(6)
C(2)–Mo–C(4)	171.6(3)	C(7)–C(10)–C(9)	110.8(6)
C(3)–Mo–C(4)	84.4(3)	P(1)–C(1A)–C(2A)	120.5(5)
Mo–P(1)–C(5)	117.48(23)	P(1)–C(1A)–C(6A)	121.2(5)
Mo–P(1)–C(1A)	120.14(23)	P(1)–C(1B)–C(2B)	118.8(5)
Mo–P(1)–C(1B)	111.75(23)	P(1)–C(1B)–C(6B)	123.1(5)
C(5)–P(1)–C(1A)	100.2(3)	P(2)–C(1C)–C(2C)	122.2(5)
C(5)–P(1)–C(1B)	103.2(3)	P(2)–C(1C)–C(6C)	119.0(5)
C(1A)–P(1)–C(1B)	101.5(3)	P(2)–C(1D)–C(2D)	119.3(5)
Mo–P(2)–C(8)	116.49(23)	P(2)–C(1D)–C(6D)	124.1(5)
Mo–P(2)–C(1C)	120.02(23)		

The two Mo–P lengths for each metal are almost equal [2.470(2) and 2.468(2) Å] which is expected since the environments about the two P atoms are similar. However the Mo–CO bond lengths are significantly different with the bonds inside the 18-membered ring being shorter than those outside [2.037(7), 2.024(7); 1.986(8), 1.995(7) Å]. This may also be attributed to the greater steric hindrance among carbonyl groups C(1)–O(1) and C(2)–O(2) and phenyl groups A–D. The shortest bond length for Mo–C(3) [1.986(8) Å] and the smaller bond angles for C(2)–Mo–C(3) and C(3)–Mo–C(4) [87.5(3) and 84.4(3) Å] reflect the least hindrance between C(3)–O(3) and the two phosphine groups attached to the same Mo atom.

The range of the P–C bond lengths [1.815(7)–1.833(7) Å] and of the C–C bond lengths in the phenyl groups of the phosphines [1.351(12)–1.409(10) Å] is reasonable and there are no intermolecular contacts of structural significance. Atoms C(7) and C(10) are somewhat disordered, which was not resolved during the least-squares refinement. There are four toluene molecules per unit cell in the lattice, with the phenyl rings being almost parallel to the rectangular complexes. The single crystal collapsed if removed from the mother-liquor for a short period of time.

Experimental

All reactions were performed under dry oxygen-free N_2 in freshly distilled decahydronaphthalene or toluene. Infrared spectra were taken in potassium bromide pellets and recorded on a JASCO model 700 spectrophotometer, NMR spectra on C_6D_6 solutions on a Bruker 300 MHz spectrophotometer. Microanalyses were performed by the National Science Council, Taipei. Chemicals were purchased from Aldrich Chemical Company, except solvents which were from Merck.

Synthesis of $[Mo(CO)_3(dpphn)]$.—A mixture of $[Mo(CO)_6]$ (0.0792 g, 0.3 mmol) and $Ph_2P(CH_2)_6PPh_2$ (0.1362 g, 0.3 mmol) in decahydronaphthalene (15 cm^3) was refluxed with stirring for 80 min during which it gradually became yellowish brown. After cooling to −15 °C, the yellow precipitate was filtered off and recrystallized from CH_2Cl_2–MeOH, yield 0.13 g (72%) (Found: C, 63.60; H, 4.40. Calc. for $C_{33}H_{30}MoO_3P_2$: C, 62.65; H, 4.80%); ν_{max} at 1975s, 1871s and 1817 cm^{-1} (CO).

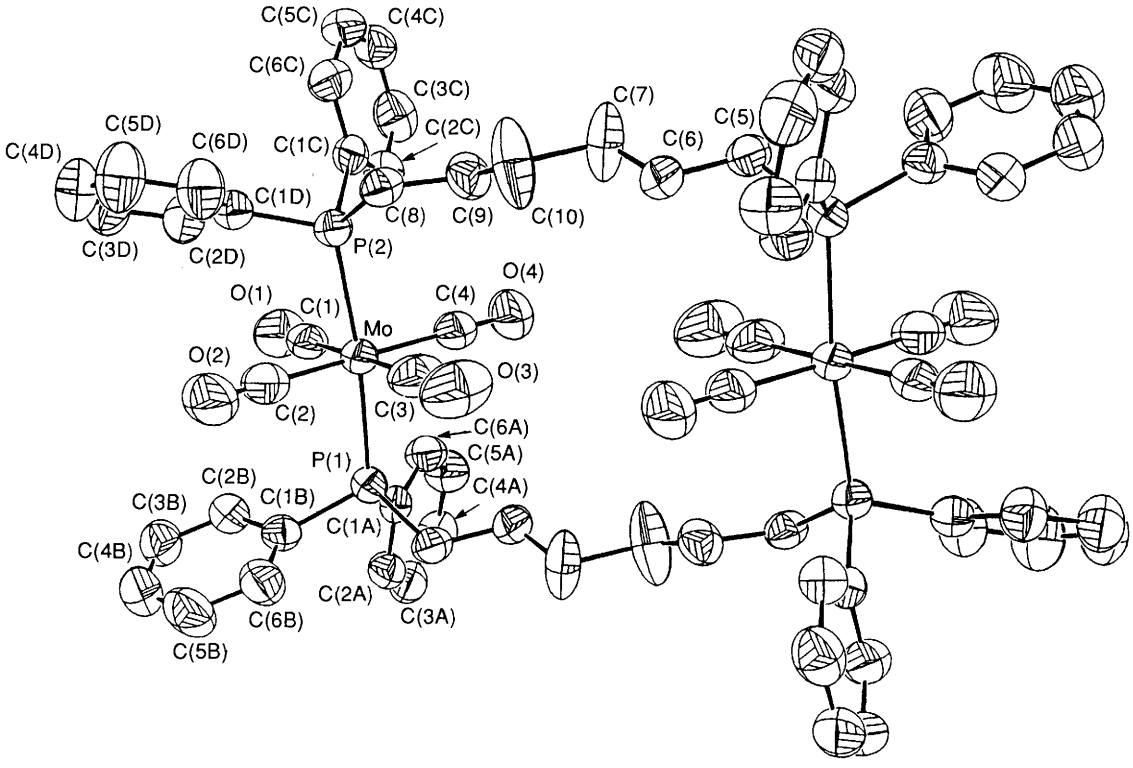

Fig. 1 Molecular structure of *trans*-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$

Synthesis of trans-$[Mo_2(CO)_8(\mu\text{-dpph})_2]$.—A solution of $[Mo(CO)_6]$ (0.1320 g, 0.50 mmol) and $Ph_2P(CH_2)_6PPh_2$ (0.2273 g, 0.50 mmol) in toluene (10 cm^3) was refluxed with stirring for 4 h. The clear solution gradually became yellowish brown. After reduction of the volume and cooling to −15 °C, the yellow solid formed was filtered off and recrystallized from toluene, yield 0.18 g (55%) (Found: C, 61.95; H, 4.55. $C_{68}H_{64}Mo_2O_8P_4$ requires C, 61.65; H, 4.85%); ν_{max} at 2018w, 1948w and 1874s cm^{-1} (CO); $\delta_H(C_6D_6)$ 0.63–2.48 (24 H, m, 12-CH_2) and 6.98–7.64 (40 H, m, 8-C_6H_5).

Crystallography.—Crystal data. $C_{68}H_{64}O_8P_4Mo_2{\cdot}4C_7H_8$ **2**, crystal prepared from a toluene solution by evaporation, M = 1602.9, triclinic, space group $P\bar{1}$, a = 11.989(2), b = 13.304(4), c = 16.011(5) Å, α = 109.59(2), β = 88.32(2), γ = 109.71(2)°, U = 2255(1) $Å^3$, D_m = 1.20(3), Z = 1, D_c = 1.18 g cm^{-3}, $F(000)$ = 880, μ(Mo-Kα) = 3.9 cm^{-1}, crystal dimensions 0.25 × 0.30 × 0.40 mm.

Data collection and processing. CAD-4 diffractometer. Unit cell: 25 reflections, 2θ range 18.74–24.12°. The θ–2θ mode was employed with scan width = 0.60 + 0.35 tan θ, Mo-Kα radiation. Three standard reflections were monitored every 2 h: variation on I was ≤5%. Of 6227 reflections measured ($1.0 \leqslant \theta \leqslant 44.9°$; h, k, l −12 to 12, 0–14, −17 to 16, respectively), 5884 were unique, giving 3866 observed [$I \geqslant 2.0\sigma(I)$]. An absorption correction was made according to experimental ψ scans (maximum, minimum transmission factors = 0.999, 0.970).

Structure analysis and refinement. The structure was solved by the heavy-atom method. The positions of hydrogen atoms of the phenyl groups were calculated after isotropic refinement; the others were found from Fourier difference maps. None was refined in the least-squares cycle. Maximum shift/e.s.d. = 0.22. Peaks in final ΔF map were 0.520 to −0.400 e $Å^{-3}$. Secondary extinction coefficient 0.62(7) (length in μm). The weighting scheme $w = 1/\sigma^2(F_o)$, was employed with $\sigma(F_o)$ from counting statistics. The last least-squares cycle was calculated with 103 atoms, 427 parameters and 3866 reflections. The quantity minimized was $\Sigma w(KF_o - F_c)^2$, final R, R' and S' being 0.051, 0.041 and 2.51. Atomic scattering factors were taken from ref. 14. The computer programs used were the NRCC SDP VAX package [15] and ORTEP.[16]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 W. H. Dietsche, *Tetrahedron Lett.*, 1966, 6187.
2 T. S. A. Hor, *Inorg. Chim. Acta*, 1989, **158**, 5.
3 P. W. Clark, *J. Organomet. Chem.*, 1976, **110**, C13.
4 P. W. Clark, *J. Organomet. Chem.*, 1977, **137**, 235.
5 C.-H. Ueng and G.-Y. Hwang, *Acta Crystallogr., Sect. C*, 1991, in the press.
6 C.-H. Ueng and L.-C. Leu, *Acta Crystallogr., Sect. C*, 1991, in the press.
7 G. R. Clark, C. M. Cochrane and P. W. Clark, *J. Organomet. Chem.*, 1982, **236**, 197.
8 M. A. Bennett and P. A. Longstaff, *J. Am. Chem. Soc.*, 1969, **91**, 6266.
9 M. A. Bennett, P. W. Clark, G. B. Robertson and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 1972, 1011.
10 M. A. Bennett and P. W. Clark, *J. Organomet. Chem.*, 1976, **110**, 367.
11 R. Mason, G. Scollary, B. Moyle, K. T. Hardcastle, B. L. Shaw and C. J. Moulton, *J. Organomet. Chem.*, 1976, **113**, C49.
12 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432.
13 F. C. Bradley, E. H. Wong, E. J. Gabe and F. L. Lee, *Inorg. Chim. Acta*, 1986, **120**, L21.
14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
15 E. J. Gabe and F. L. Lee, *Acta Crystallogr., Sect. A*, 1981, **37**, S339.
16 Structure Determination Package, Enraf-Nonius, Delft, 1979.

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