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Note

cis- and *trans*-Bis(1-phenyl-2,3,4,5-tetramethylphosphole)tetracarbonylmolybdenum(0), [Mo(CO)$_4$(tmpPh)$_2$]. Syntheses and structures

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Abstract

1-Phenyl-2,3,4,5-tetramethylphosphole reacts with [Mo(CO)$_6$] to give the mono- and bis(phosphole) complexes [Mo(CO)$_5$L] and *cis*- and *trans*-[Mo(CO)$_4$L$_2$], where L = C$_4$Me$_4$PPh (tmpPh). The new complexes have been characterised by spectroscopic methods, supplemented by single-crystal X-ray analyses in the case of the bis(phosphole) isomers. The isomeric bis-tmpPh complexes show little evidence of the overcrowding which is thought to lengthen bonds and distort the metal coordination in the corresponding bis-PPh$_3$ and bis-PCy$_3$ isomers. The structural basis for the greater stability of the *trans* isomers is briefly considered: the *cis* → *trans* isomerisation typically involves little change in the mean Mo–CO distance, whereas there is a marked shortening of the Mo–P bonds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Carbonyl; Isomerisation; Phosphole; *trans*-Influence

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1. Introduction

We have recently shown that the reactivity of dimolybdenum thiolate complexes is changed when C$_5$H$_5$ is replaced by C$_5$Me$_5$ [1]. Indeed, it is generally true that the reactivity of such systems can be fine-tuned by judicious choice of ligands: for example, six-electron donor groups with widely differing steric and electronic properties can replace the cyclopentadienyl ligand with which they are isolobal [2]. In particular, the Me$_4$C$_4$P tetramethylphospholyl ring is almost the same size as C$_5$Me$_5$ but is a weaker electron-donor than C$_5$H$_5$ [3]. Accordingly, we tried to make η^5-phospholyl analogues of the known η^5-cyclopentadienyl thiolato-bridged dimolybdenum complexes containing the {Cp$_2$Mo$_2$(μ-SMe)$_3$} nucleus [4] by reacting 1-phenyl-2,3,4,5-tetramethylphosphole with [Mo(CO)$_6$]. However, even at high temperature in refluxing diglyme, treatment of the phosphole with hexacarbonylmolybdenum(0) did not give rise to P–Ph bond cleavage, a reaction which has been successfully used with other metals to generate η^5-phospholyl complexes [5]. Instead, mono- and bis(phosphole) complexes [Mo(CO)$_5$L] (**1**), and *cis*- and *trans*-[Mo(CO)$_4$L$_2$] (**2**) and (**3**) [L = C$_4$Me$_4$PPh (tmpPh)] were formed.

The isomerisation of *cis*-[Mo(CO)$_4$L$_2$] phosphine complexes, such as **2**, to the thermodynamically more stable *trans* form has been much studied and attempts have been made, notably by Cotton and co-workers, to relate the reactivities of the *cis* complexes to their solid state structures [6]. The *trans*-isomers formed as products of these reactions have only recently attracted similar interest: structural comparisons of *cis*- and

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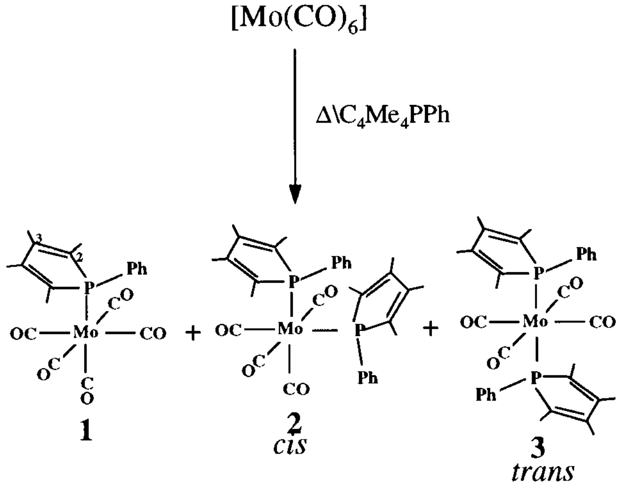
trans-[Mo(CO)$_4$L$_2$] isomers have so far been limited to the bis(tricyclohexylphosphine) (L = PCy$_3$) complexes, which are particularly crowded [7], and to the bis-PPh$_3$ complexes [8]. In the latter example the *trans*-isomer was co-crystallised with 1,4-bis(diphenylphosphino)-2,5-difluorobenzene, while it has been suggested that the *cis*-(PPh$_3$)$_2$ complex exhibits structural distortions not found in other *cis*-[Mo(CO)$_4$L$_2$] species [6,8b]. We therefore now report the crystal structures of the isomers **2** and **3**. These are also of interest since phospholes, L, and [Mo(CO)$_6$] are known to undergo photochemical reactions to give [Mo(CO)$_4$L$_2$] complexes in which the phosphole ligands have undergone Diels–Alder dimerisation, a reaction they do not show in the absence of [Mo(CO)$_6$] [9].



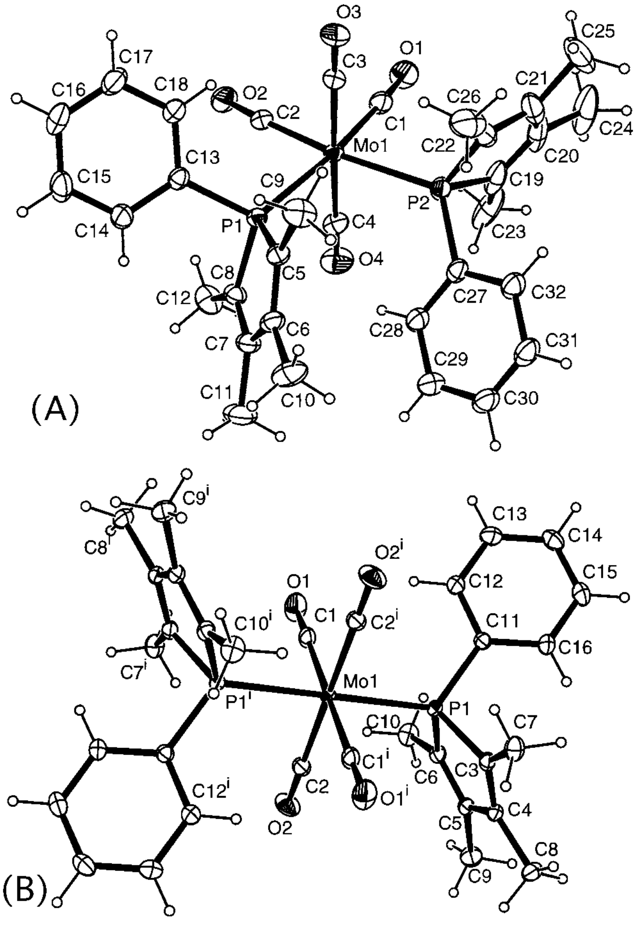


Fig. 1. Molecular drawings of (A) **2** and (B) **3** showing the atom numbering and 20% probability ellipsoids for non-hydrogen atoms. Symmetry code: (*i*) $-x$, $-y$, $-z$.

2. Results and discussion

The complexes **1**–**3** were obtained as products of the reaction of [Mo(CO)$_6$] with tmpPh. The respective IR spectra show the expected set of ν(CO) bands for octahedral [Mo(CO)$_5$L] and *cis*- and *trans*-[Mo(CO)$_4$L$_2$] species. Likewise, the ^{31}P, ^{1}H and ^{13}C NMR spectra accord with the presence of one tmpPh ligand in **1** and with two equivalent tmpPh ligands which are *cis* in **2** and *trans* in **3**. The ^{13}C spectra of **2** and **3** are complicated because of the strong coupling between the two phosphorus atoms: pseudo triplets are observed instead of doublets of doublets; in the case of **2** an isotope effect, for which there is a precedent [5a], could explain the abnormal resonance pattern for the carbon atoms linked to the phosphorus atoms: six such resonances, suggesting the superposition of two doublets of doublets, were observed. Mass spectroscopy confirmed the mononuclear nature of the complexes and indicated unambiguously the presence of five carbonyl ligands in **1** and four in **2** and **3**. These conclusions are confirmed for **2** and **3** by the results of diffraction analyses (Fig. 1). Molecules of **3** lie on crystallographic inversion centres.

The phosphole ligands in **2** and **3** are virtually identical. The C=C–C=C butadiene unit within each ring is almost perfectly planar and displays bond lengths [C=C 1.335(5)–1.361(7), C–C 1.459(8)–1.484(4) Å] consistent with little or no delocalisation. The endocyclic P–C bonds [1.804(3)–1.816(3) Å] are very slightly shorter than the P–C(Ph) bonds [1.833(2)–1.837(2) Å]. The rings are slightly folded, by 9.0(2)° in **3** and by 5.0(2 and 6.4(2)° in **2**, into shallow envelopes with the P atom at the flap. The PC$_3$ units are pyramidal, with symmetrical Ph–P–C angles [101.6(1)–104.7(1)°] which are rather more obtuse than the endocyclic C–P–C angles [91.7(1)–92.9(2)°]. Similar structural features in free and W(CO)$_5$-complexed 2,5-di(2-pyridyl)phospholes have been interpreted in terms of a lack of conjugation between the P atom and the dienic portion of the phosphole ring [10]. We note that the C16–C11–P1–C3 and –C6 angles in **3** [21.0(3) and −74.9(2)°] agree to within 3° with corresponding angles for the two phosphole ligands in **2**. The similar conformations

Table 1
Selected structural data (Å and °) for isomeric *cis* and *trans*-[$Mo(CO)_4L_2$] complexes [a]

	Mo–P		Δ(Mo–P)	Mo–CO			Δ(*cis*)	Δ(Mo–CO)	P–Mo–P	Ref.
Isomer	*cis*	*trans*		*cis*		*trans*	*cis*		*cis*	
				trans to P	*trans* to CO	*trans* to CO				
L = tmpPh	2.550(1) 2.537(1)	2.480(1)	−0.064	1.981(2) 1.982(2)	2.031(2) 2.033(2)	2.025(3) 2.024(3)	−0.051	0.018	101.7(1)	This work
L = PPh_3	2.576(2) 2.577(2)	2.500(1)	−0.076	1.972(8) 1.973(9)	2.059(9) 2.022(9)	2.016(5) 2.005(5)	−0.067	0.004	104.6(1)	[8]
L = PCy_3	2.649(4) 2.659(4)	2.544(1)	−0.111	1.97(2) 1.97(2)	2.01(2) 2.02(2)	2.020(4) 2.028(3)	−0.05	0.03	105.1	[7]
CSD [b]	2.532	2.491	−0.041	1.980(2)	2.026(3)	2.020(3)	−0.046	0.017		

[a] Δ(Mo–P) and Δ(Mo–CO) are the increases in the *mean* Mo–P and Mo–CO bond lengths on going from the *cis* to the *trans* isomer. Δ(*cis*) is the difference between the mean lengths of the Mo–CO bonds *trans* to P and *trans* to CO in *cis* complexes.

[b] Database means: a search of the Cambridge Structural Database for [$Mo(CO)_4L_2$] structures (L = tertiary phosphine) yielded 87 hits for *cis* complexes and six for *trans* complexes. Three atypical *cis* structures (NEGNIW, POGMIW, TOGNAE) were excluded from the mean calculations.

of the phospholes in **2** and **3** and the absence of specific intramolecular contacts between the phosphole ligands of **2** suggest that steric crowding is not particularly significant in either molecule. Moreover, it is apparent from Fig. 1(A) that the structure of **2** is not conducive to reaction between the coordinated phosphole rings which are not close to one another, lending weight to the suggestion that a seven-coordinate $M(CO)_5L_2$ species rather than **2** may be involved in the Diels–Alder phosphole dimerisation reaction [9b].

Structural data for **2** and **3** are compared with corresponding values for the isomeric PPh_3 and PCy_3 complexes and with database mean values in Table 1. In the *cis* complexes Δ(*cis*), the mean difference in length between Mo–CO bonds *trans* to P and those *trans* to CO, is virtually constant and is negative, indicating that CO has a greater *trans* influence than the P-donor ligands. However, Δ(Mo–CO), the increase in mean Mo–CO bond length on *cis*→*trans* isomerisation, is small, except for the PCy_3 complexes where the mean Mo-CO distance may be significantly greater in the *trans* isomer. By contrast, the negative Δ(Mo–P) values indicate that on average the Mo–P bonds shrink when the configuration at the metal atom changes from *cis* to *trans*. This may be partly ascribed to *trans* influence (CO > phosphine), but the steric bulk of the phosphine may also be a factor since $|\Delta(\text{Mo–P})|$ increases along the series tmpPh < PPh_3 < PCy_3, as indeed do the Mo–P distances themselves in the *cis* and *trans* series of complexes. Whatever the explanation, the structural results indicate that Mo–P bonds are shorter and stronger in the *trans* isomer while the average length of the Mo–CO is little different in the two isomers; they are therefore consistent with the *trans* isomer having the greater thermodynamic stability. The P–Mo–P angles in the *cis* complexes also show some dependence on the steric bulk of L though Cotton [8b] has emphasised the difficulties of assessing steric effects in these complexes through ‘crude arguments based on purely geometric criteria’. As an illustration of this it is worth noting that the mean molecular volume for the *trans*-tmpPh complex is 22 $Å^3$ less than for the *cis*-isomer; for the PCy_3 complexes there is a slightly greater decrease of 32 $Å^3$ in molecular volume on going from the *cis* to the *trans* isomer. This contributes relatively little, 1–2 J mol^{-1} in free energy, to the stabilisation of the *trans* isomer but it is unexpected given that the *cis* isomer is normally considered to be more overcrowded than its *trans* counterpart.

The structures of **2** and **3** display bond lengths which are close to the average values for $Mo(CO)_4L_2$ complexes. When L is the bulky PPh_3 ligand, or the even more demanding PCy_3 species, more distortion of the Mo coordination and longer Mo–P bonds are observed, especially in the *cis* series.

3. Experimental

Reactions were performed under nitrogen using standard Schlenk techniques and solvents were deoxygenated and dried by standard methods. A mixture of [$Mo(CO)_6$] (2 g, 7.6 mmol) and C_4Me_4PPh (1.65 g, 7.6 mmol) was stirred under reflux in THF or diglyme for 2 h. The colorless solution became yellow-orange during this time. The solvent was removed under vacuum. Recrystallisation from dichloromethane and pentane gave separately **1**, **2** and **3** as colorless crystals; yield 25% **1**, 20% **2**, 10% **3**. Compound **3** has low solubility in dichloromethane and pentane and **2** has low solubility in pentane.

3.1. Analysis of **1**

Found C, 50.7; H, 3.9; P, 7.5; $C_{19}H_{17}PMoO_5$ requires: C, 50.4; H, 3.8; P, 6.9%. NMR ($CDCl_3$): ^1H δ: 7.40, 7.37 (5H, m, C_6H_5), 2.00 (6H, s, $2 \times C_3CH_3$), 1.97 (d, $J_{PH} = 12.0$Hz, 6H, $2 \times C_2CH_3$). $^{13}C\{^1H\}$ δ: 209.5 (d, $J_{PC} = 19.5$ Hz, CO_{trans}), 205.7 (d, $J_{PC} = 8.6$ Hz, CO_{cis}), 143.7 (d, $J_{PC} = 14.6$ Hz, C_3), 136.5 (d, $J_{PC} = 39.9$ Hz, C_2), 132.1 (d, $J_{PC} = 12.5$ Hz, C_{ortho}),130.5 (d, $J_{PC} = 2.0$ Hz, C_{para}), 129.4 (d, $J_{PC} = 31.3$ Hz, C_{ipso}), 128.9 (d, $J_{PC} = 9.8$ Hz, C_{meta}), 13.5 (d, $J_{PC} = 8.6$ Hz, C_3CH_3), 11.8 (d, $J_{PC} = 17.5$ Hz, C_2CH_3). ^{31}P δ: 51.7.IR (CH_2Cl_2, cm^{-1}), (ν_{CO}): 2070(s), 1935(s). MS (m/z):452 $[M]^+$, 424 $[M-CO]^+$, 396 $[M-2CO]^+$, 368 $[M-3CO]^+$, 340 $[M-4CO]^+$, 312 $[M-5CO]^+$.

3.2. Analysis of **2**

Found: C, 59.7; H, 5.4; P, 10.0; $C_{32}H_{34}P_2MoO_4$ requires: C, 60.0; H, 5.3; P, 9.7%. NMR ($CDCl_3$): ^1H δ: 7.30 (10H, m, C_6H_5), 1.86 (12H, s, $4 \times C_3CH_3$), 1.83 (d, $J_{PH} = 11.1$Hz, 12H, $4 \times C_2CH_3$). $^{13}C\{^1H\}$ δ: 214.0 (m, CO_{trans}), 210.5 (*ps* t, $J_{PC} = 9.2$ Hz, CO_{cis}), 142.9 (m, C_3), 136.3 (m, C_2), 132.4 (m, C_{ipso}),132.0 (*ps* t, $J_{PC} = 5.8$ Hz, C_{ortho}), 128.7 (s, C_{para}), 128.4 (*ps* t, $J_{PC} = 4.5$ Hz, C_{meta}), 13.9 (*ps* t, $J_{PC} = 4.0$ Hz, C_3CH_3), 12.2 (*ps* t, $J_{PC} = 8.7$ Hz, C_2CH_3). ^{31}P δ: 52.3. IR (CH_2Cl_2, cm^{-1}), (ν_{CO}): 2010(s), 1905(sh), 1890(s), 1870(sh). MS (m/z):640 $[M]^+$, 618 $[M-CO]^+$, 584 $[M-2CO]^+$, 556 $[M-3CO]^+$, 528 $[M-4CO]^+$.

3.3. Analysis of **3**

Found: C, 59.1; H, 5.4%; $C_{32}H_{34}P_2MoO_4$ requires: C, 60.0; H, 5.3%. NMR ($CDCl_3$): ^1H δ: 7.50, 7.37 (10H, m, C_6H_5), 1.99 (12H, s, $4 \times C_3CH_3$), 1.98 (d, $J_{PH} = 10.4$Hz, 12H, $4 \times C_2CH_3$). $^{13}C\{^1H\}$ δ: 210.9 (*ps* t, $J_{PC} = 8.5$ Hz, CO), 141.2 (*ps* t, $J_{PC} = 7.4$ Hz, C_3), 138.9 (dd, $J_{PC} = 19.0$Hz, C_2), 132.4 (dd, partially obscured by C_{ortho} signal, $J_{PC} = 14.1$ Hz, C_{ipso}), 132.1 (*ps* t, $J_{PC} = 6.5$ Hz, C_{ortho}), 129.5 (s, C_{para}), 128.4 (*ps* t, $J_{PC} = 4.7$ Hz, C_{meta}), 13.4 (*ps* t, $J_{PC} = 4.3$ Hz, C_3CH_3), 12.0 (*ps* t, $J_{PC} = 8.7$ Hz, C_2CH_3). ^{31}P δ: 64.5. IR (CH_2Cl_2, cm^{-1}), (ν_{CO}): 1880(s). MS (m/z):640 $[M]^+$, 618 $[M-CO]^+$, 584 $[M-2CO]^+$, 556 $[M-3CO]^+$, 528 $[M-4CO]^+$.

Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison.

3.4. X-ray analyses of **2** and **3**

Measurements were made on an Enraf-Nonius CAD4 diffractometer with Mo–K_α radiation, $\lambda = 0.71073$ Å, using standard procedures [11].

3.5. Crystal data

$C_{32}H_{34}MoO_4P_2$, $M = 640.47$. Compound **2**: monoclinic, $a = 9.9097(4)$, $b = 21.3320(17)$, $c = 14.9143(9)$ Å, $\beta = 99.012(4)°$, $V = 3113.9(3)$ Å^3, $T = 293$ K, space group $P2_1/n$, Z = 4, μ(Mo–K_α) 0.557 mm^{-1}, 11 522 reflections ($\theta < 30°$) measured, 9019 unique ($R_{int} = 0.010$) used in refining 352 parameters. R_1(all data) = 0.0497, wR_2(all data) = 0.100, $|\Delta\rho| < 0.54$ e A^{-3}. Compound **3**: triclinic, $a = 8.8904(5)$, $b = 9.0712(5)$, $c = 11.2077(6)$ Å, $\alpha = 103.372(4)$, $\beta = 103.947(4)$, $\gamma = 112.398(4)°$, $V = 756.63(7)$ Å^3, $T = 293$ K, space group $P\bar{1}$, $Z = 1$, μ(Mo–K_α) 0.573 mm^{-1}, 3937 reflections ($\theta < 27°$) measured, 3291 unique ($R_{int} = 0.017$) used in refining 178 parameters. R_1(all data) = 0.040, wR_2(all data) = 0.077, $|\Delta\rho| < 0.35$ e A^{-3}.

All non-hydrogen atoms were refined with anisotropic displacement tensors. H-atom positions were determined from stereochemical considerations (phenyl H) or difference maps (methyl H) and subsequently rode on parent C atoms [12]. The carbon atoms of the P2 phosphole ring in **3** show very anisotropic displacement tensors ($U_{max} = 0.61$ Å^2) which may indicate disorder.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149038 for compound **2** and CCDC no. 149037 for compound **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] P. Schollhammer, F.Y. Pétillon, R. Pichon, S. Poder-Guillou, J. Talarmin, K.W. Muir, Lj. Manojlovic-Muir, Organometallics 14 (1995) 2277.

[2] J.F. Reglinski, M. Garner, I.D. Cassidy, P.A. Slavin, M.D. Spicer, D.R. Armstrong, J. Chem.Soc. Dalton Trans. (1999) 2119.

[3] P. Gradoz, D. Baudry, M. Ephritikhine, M. Lance, M Nierlich, J. Vigner, J.Organomet. Chem. 466 (1994) 107.

[4] F.Y. Pétillon, P. Schollhammer, J. Talarmin, K.W. Muir, Coord. Chem. Rev. 178–180 (1998) 203.

[5] (a) F. Nief, F. Mathey, L. Ricard, F. Robert, Organometallics **7** (1988) 921. (b) B. Deschamps, R. Ricard and F. Mathey, Organometallics 18 (1999) 5688. (c) A. Dupuis, M. Gouygou, J.C. Daran, G.G.A. Balavoine, Bull. Soc. Chim. Fr. 134 (1997) 357.

[6] (a) D.J. Darensbourg , M.A. Murphy, J. Am. Chem. Soc. 100 (1978) 463. (b) D.J. Darensbourg, Inorg. Chem. 21 (1979) 14. (c) F.A. Cotton, D.J. Darensbourg, S. Klein, B.W.S. Kolthammer, Inorg. Chem. 21 (1982) 2661 and references therein.

[7] (a) E.C. Alyea, G. Ferguson, S. Kannan, Acta Crystallogr. Sect. C 52 (1996) 765. (b) M. Watson, S. Woodward, G. Conole, M. Kessler, G. Sykara, Polyhedron 13 (1994) 2455.

[8] (a) G. Hogarth, T. Norman, Inorg. Chim. Acta. 254 (1997) 167. (b) F.A. Cotton, D.J. Darensbourg, S. Klein, B.W.S. Kolthammer, Inorg. Chem. 21 (1982) 294.

[9] (a) C.C. Santini, J. Fischer, F. Mathey, A. Mitschler, J. Am. Chem. Soc. 102 (1980) 5809. (b) S. Affandi, J.H. Nelson, J. Fischer, Inorg. Chem. 28 (1989) 4536.

[10] C. Hay, D. Le Vilain, V. Deborde, L. Toupet, R. Reau, J. Chem. Soc. Chem. Commun. (1999) 345.

[11] P. Schollhammer, F.Y. Pétillon, J. Talarmin, K.W. Muir, J. Organomet. Chem. 560 (1998) 245.

[12] Programs used: (a) G.M. Sheldrick, SHELX-97-Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998. (b) L.J. Farrugia, WinGX-A Windows Program for Crystal Structure Analysis, J. Appl. Crystallogr. 32 (1999) 837.