Transition Metal–Hydrogen–Alkali Metal Bonds: Syntheses and Structures of $W(PMe_3)_3H_5Na$(15-crown-5), $W(PMe_3)_3H_5K$(18-crown-6), and $[W(PMe_3)_3H_5Li]_4$

Judith A. Bandy,[b] Adam Berry,[a] Malcolm L. H. Green,[a] and Keith Prout[b]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, U.K.*

Treatment of $W(PMe_3)_3H_6$ with Bu^nLi, NaH, or KH gives $W(PMe_3)_3H_5M$, M = Li, Na, or K, or, with the appropriate crown ethers $W(PMe_3)_3H_5Na$(15-crown-5) and $W(PMe_3)_3H_5K$(18-crown-6): the crystal structures of the crown ether compounds of sodium and potassium and of $[W(PMe_3)_3H_5Li]_4$ have been determined.

High-energy transition metal compounds are associated with enhanced reactivity towards normally inert substrates. One strategy towards high-energy transition metal centres is to bond the metal to a more electropositive ligand atom. We have previously prepared the first or early examples of compounds containing bonds between Mo(or W)–Li,[1] Mo(or W)–Al,[2] and Mo–Mg,[3] by the alkane-elimination reaction (1) where M is a transition metal and M′ = Li, Mg, or Al.

$$\text{M–H} + \text{M}'\text{–R} \rightarrow \text{M–M}' + \text{RH} \qquad (1)$$

Here we describe new compounds containing M–M′ or M–H_n–M′ interactions, where M = W and M′ = Li, Na, or K. Treatment of $W(PMe_3)_3H_6$ (**1**) in tetrahydrofuran (thf) with NaH or KH gives yellow crystalline compounds which lose thf *in vacuo* giving powders of empirical stoicheiometry $W(PMe_3)_3H_5Na$ (**2**) and $W(PMe_3)_3H_5K$ (**3**) respectively.

It was not possible to obtain crystals of (**2**) and (**3**) suitable for crystal structure determinations. However, addition of 15-crown-5 to thf solutions of (**2**) gives $W(PMe_3)_3H_5Na$(15-crown-5), (**4**), and addition of 18-crown-6 to solutions of (**3**) gives $W(PMe_3)_3H_5K$(18-crown-6) (**5**), both of which yield excellent crystals.†

The structures of (**4**) and (**5**) are shown in Figures 1 and 2 respectively, with selected distances and angles. The crown ether ring in (**4**) is found to be disordered and only one orientation is shown (occupancies of the two contributing conformations refined to 0.505 and 0.495). It was possible to locate and refine isotropically the five hydrogens attached to tungsten in (**5**), yielding three hydrides towards potassium and two away. The dispositions of the phosphine ligands around tungsten in both complexes relative to the alkali metal are similar, suggesting that the hydrides of (**4**) may be located in similar positions to those of (**5**). In both (**4**) and (**5**) the crown ethers are found to co-ordinate to the alkali metals which are themselves pulled out of the best planes defined by the ether oxygens (into which they are able to fit[4]). The displacements of 1.10 Å for Na(1) in (**4**) and 0.76 Å for K(1) in (**5**) show that there are strong interactions with the transition metal centres. Similar displacements have been found for potassium in $(\eta\text{-}C_5H_5)_2Mo(\mu\text{-}H)K$(18-crown-6) (0.866 Å)[5] and in a number of other crown ether complexes of alkali metals with strong interactions between anion and cation.[6]

$W(PMe_3)_3H_6$
(**1**)

$[W(PMe_3)_3H_5M]_n$
n = 1, (**2**) M = Na
(**3**) M = K
n = 4, (**6**) M = Li

$W(PMe_3)_3H_5M(X)$
(**4**) M = Na, X = 15-crown-5
(**5**) M = K, X = 18-crown-6

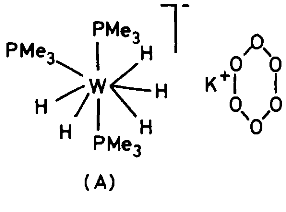
$W(PMe_3)_3H_5SnBu^n_3$
(**7**)

We can envisage two extreme types of interaction (A) and (B) between the two metal centres in (**5**) [and by inference in (**4**)]. Case (A) is purely ionic whereas in (B) the three bridging hydrides take part in two-electron three-centre bonding.

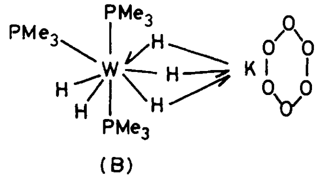
Clearly, the bonding in (**4**) and (**5**) will lie between the extremes represented by (A) and (B). The metal–metal distances of 3.215(6), W–Na in (**4**), and 3.660(1) Å, W–K in (**5**), are comparable with the sums of their covalent radii (1.54, Na and 1.96 Å, K derived spectroscopically;[7] W, 1.6 Å approximately from W–W single bonds). However, the mean potassium–bridging hydride distance of 2.78 Å is also close to the value of 2.854 Å[8] observed in potassium hydride.

Treatment of $W(PMe_3)_3H_6$ (**1**) with n-butyl-lithium in pentane gives the highly water- and oxygen-sensitive tetramer $[W(PMe_3)_3H_5Li]_4$, (**6**), which is a yellow crystalline solid soluble in Et_2O. The crystal structure of (**6**) has been determined.†

The molecular structure is shown in Figure 3; five of the trimethyl phosphine groups were found to be rotationally



(A)



(B)

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† *Crystal data:* (**4**) $W(PMe_3)_3H_5Na$(15-crown-5), $C_{19}H_{52}NaO_5P_3W$, M = 660.4, monoclinic, space group $P2_1/n$, a = 11.943(2), b = 15.273(8), c = 16.878(3) Å, β = 90.04(2)°, U = 3078.5 $Å^3$, D_c = 1.43 Mg m^{-3}, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 41.78 cm^{-1}, $F(000)$ = 1344, R = 5.75%, R_w = 8.46% for 3884 reflections $I > 3\sigma(I)$, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å. (**5**) $W(PMe_3)_3H_5K$(18-crown-6), $C_{21}H_{56}KO_6P_3W$, M = 720.6, monoclinic, space group $P2_1/n$, a = 10.362(3), b = 16.168(4), c = 20.480(4) Å, β = 98.66(2)°, U = 3391.9 $Å^3$, D_c = 1.41 Mg m^{-3}, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 38.89 cm^{-1}, $F(000)$ = 1472, R = 2.33%, R_w = 2.51% for 3966 reflections $I > 3\sigma(I)$, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å. (**6**) $[W(PMe_3)_3H_5Li]_4$, $C_{36}H_{128}Li_4P_{12}W_4$, M = 1696.3, triclinic, space group $P\bar{1}$, a = 14.472(2), b = 14.561(4), c = 10.813(4) Å, α = 104.40(3), β = 114.64(2), γ = 102.55(2)°, U = 1867.8 $Å^3$, D_c = 1.51 Mg m^{-3}, Z = 1 (molecular symmetry $\bar{1}$), $\mu(\text{Mo-}K_\alpha)$ = 67.77 cm^{-1}, $F(000)$ = 832, R = 3.59%, R_w = 4.63% for 5598 reflections $I > 3\sigma(I)$, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å. The air-sensitive crystals were mounted under argon in capillaries. Data collection used an Enraf–Nonius CAD4 diffractometer in the ω–2θ mode out to θ = 25° (**4**), 26° (**5**), 26° (**6**). Structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. Disorder was resolved for the 15-crown-5 ring of (**4**) and trimethylphosphine groups of (**6**). No hydrogens were located for (**6**) but those for (**4**) and (**5**), apart from hydrides, were included in calculated positions riding on the attached carbon atom. The 5 hydrides of (**5**) were located and refined. Crystallographic calculations used the Oxford CRYSTALS package[10] on the VAX 11/750 of the Chemical Crystallography Laboratory, Oxford University. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

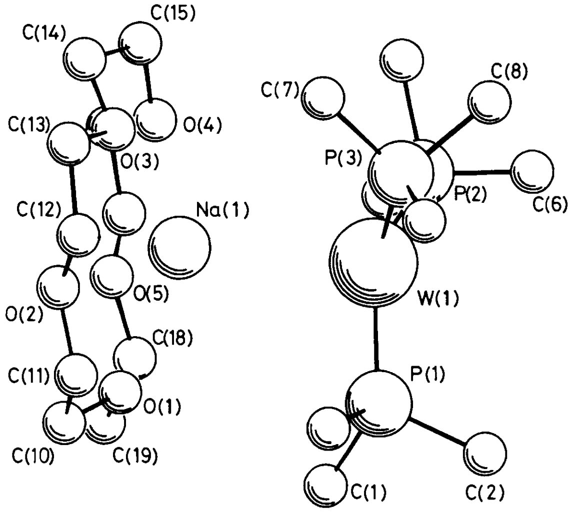

Figure 1: Molecular structure of (**4**). Selected distances (Å) and angles (°) [O(1)—(5) refer to one orientation of the disordered 15-crown-5 molecule and O(11)—(15) to the other]: W(1)–Na(1) 3.215(6), W(1)–P(1) 2.415(4), W(1)–P(2) 2.392(4), W(1)–P(3) 2.392(4), Na(1)–O(1) 2.48(2), Na(1)–O(2) 2.66(4), Na(1)–O(3) 2.46(3), Na(1)–O(4) 2.50(3), Na(1)–O(5) 2.52(3), Na(1)–O(11) 2.46(2), Na(1)–O(12) 2.70(4), Na(1)–O(13) 2.60(3), Na(1)–O(14) 2.46(4), Na(1)–O(15) 2.58(4), Na(1)–oxygen plane 1.10; P(1)–W(1)–P(2) 145.6(1), P(1)–W(1)–P(3) 103.1(2), P(2)–W(1)–P(3) 99.8(2).

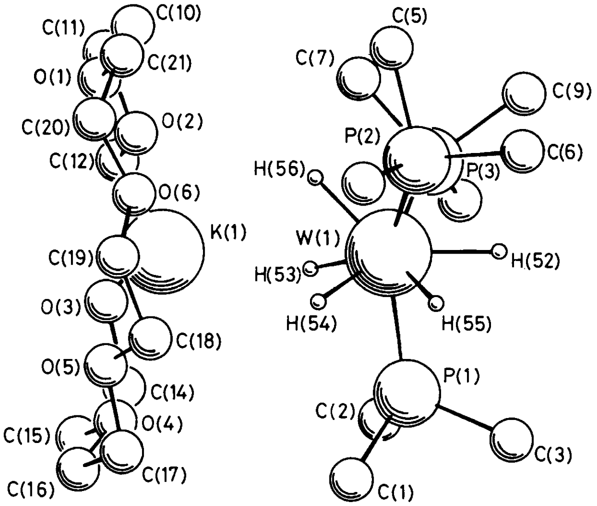

Figure 2. Molecular structure of (**5**). Selected distances (Å) and angles (°): W(1)–K(1) 3.660(1), W(1)–P(1) 2.406(1), W(1)–P(2) 2.394(1), W(1)–P(3) 2.389(2), mean W–H(bridging) 1.75, mean W–H(terminal) 1.75, mean K–H(bridging) 2.78, K(1)–O(1) 2.949(5), K(1)–O(2) 2.812(5), K(1)–O(3) 2.935(4), K(1)–O(4) 2.872(4), K(1)–O(5) 2.907(4), K(1)–O(6) 2.820(4), K(1)–oxygen plane 0.764; P(1)–W(1)–P(2) 146.54(5), P(1)–W(1)–P(3) 104.01(5), P(2)–W(1)–P(3) 97.32(6).

disordered and only one orientation for each group is given. The discrete tetrameric M_4Li_4 ring is reminiscent of that found for the compounds $[M(\eta\text{-}C_5H_5)_2HLi]_4$,[1] M = Mo, W, though in (**6**) the W–Li bonds are found to alternate in length around the essentially planar ring suggesting the presence of bridging hydrides which could not be located by *X*-ray methods. Again the arrangement of the phosphines around tungsten is similar to that observed for (**5**) and it is reasonable to suggest that some of the missing hydrides may be bridging the W(1)–Li(1) and W(2)–Li(2) bonds. There is no evidence for any C–Li interactions.

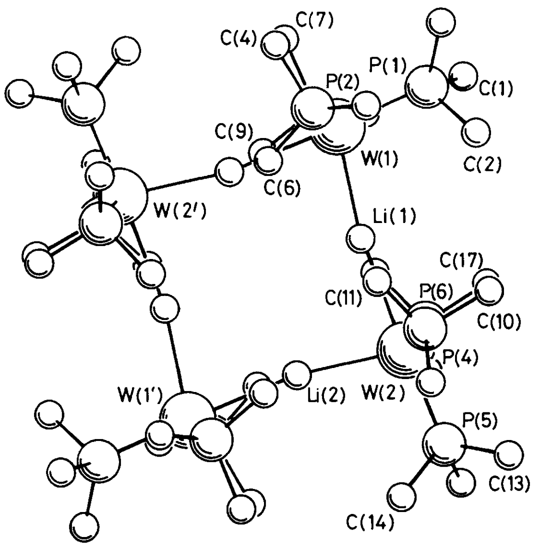

Figure 3. Molecular structure of (**6**). Selected distances (Å) and angles (°), centrosymmetrically related atoms denoted by primes: W(1)–Li(1) 2.77(1), W(1)–Li(2′) 2.92(2), W(2)–Li(1) 2.93(1), W(2)–Li(2) 2.79(2), W(1)–P(1) 2.412(3), W(1)–P(2) 2.421(3), W(1)–P(3) 2.435(2), W(2)–P(4) 2.412(2), W(2)–P(5) 2.425(3), W(2)–P(6) 2.432(2); Li(2′)–W(1)–Li(1) 79.9(4), W(1)–Li(1)–W(2) 169.7(6), Li(1)–W(2)–Li(2) 80.1(4), W(2)–Li(2)–W(1′) 170.3(6), P(1)–W(1)–P(2) 97.2(1), P(1)–W(1)–P(3) 100.8(1), P(2)–W(1)–P(3) 144.6(1), P(4)–W(2)–P(5) 96.19(9), P(4)–W(2)–P(6) 143.19(9), P(5)–W(2)–P(6) 100.6(1).

Compounds (**2**)—(**6**) give very similar ^{1}H and ^{31}P n.m.r. spectra in [$^2H_8$]thf solution.‡ The $^{31}P\{^1H\}$ spectra show singlets at about −25 p.p.m. which split to binomial sextets in the $^{31}P\{^1H\text{-Me}\}$ spectra. In all the ^{1}H n.m.r. spectra, resonances assignable to 5 hydrides show interesting temperature dependence, as shown in Figure 4 for (**6**). This behaviour is consistent with a solution structure analogous to the solid state structure of (**5**) in which there are three bridging

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‡ *N.m.r. data* (*J* in Hz). Compound (**2**), [$^2H_8$]thf; ^{1}H (room temp.): δ 1.44(27H, virtually coupled triplet, J'_{PH} 5.6, 3PMe$_3$), −5.3(2H, br s, 2W–H), and −6.1(3H, br s, 3W–H). ^{1}H (200 K): δ −4.3(1H, br m, W–H), −5.8(1H, br m, W–H), and −6.1(3H, br q, 3W–H). $^{31}P\{^1H\}$ [room temp., relative to (MeO)$_3$PO(external)]: −24.9 p.p.m. [s, *J*(P–W) 171.4]. $^{31}P\{^1H\text{-Me}\}$ (room temp.): −24.9 p.p.m. [sex, *J*(P–H) 26]. Compound (**3**), [$^2H_8$]thf; ^{1}H (185 K): δ 1.50(27H, br s, 3PMe$_3$), −4.74(1H, br m, W–H), −5.51[3H, br q, *J*(P–H) 21.7, 3W–H], and −5.74(1H, br m, W–H). $^{31}P\{^1H\}$ [room temp., relative to (MeO)$_3$PO (external)]: −25.61 p.p.m. [s, *J*(P–W) 167.8]. $^{31}P\{^1H\text{-Me}\}$ (room temp.): −25.61 p.p.m. [sex, *J*(P–H) 26]. Compound (**4**), [$^2H_8$]thf; ^{1}H (room temp.): δ 3.71(20H, br s, 15-crown-5), 1.48(27H, virtually coupled triplet, J'_{PH} 5.6, 3PMe$_3$), −5.14(2H, br q, J_{HP} 35.2, 2W–H), and −5.94(3H, br q, J_{HP} 20.7, 3W–H). Compound (**5**), [$^2H_8$]thf; ^{1}H (203 K): δ 3.82(24H, s, 18-crown-6), 1.62(27H, s, 3PMe$_3$), −4.32(1H, br m, W–H), −5.20(3H, br q, J_{HP} 23, 3W–H), and −6.21(1H, br m, W–H). Compound (**6**), [$^2H_8$]thf; ^{1}H (138 K): δ 1.46(27H, br s, 3PMe$_3$), −4.62(1H, br t, W–H), −6.00(3H, br m, W–H), and −7.10(1H, br s, W–H). ^{1}H (323 K): δ 1.52(27H, virtually coupled triplet, J'_{PH} 5.5, 3PMe$_3$), −5.60 (5H, v br s, 5W–H). $^{31}P\{^1H\}$ [room temp., relative to (MeO)$_3$PO (external)]: −24.03 p.p.m. [s, *J*(P–W) 175.2]. Compound (**7**), C_6D_6; ^{1}H (room temp.): δ 1.83(6H, m, 3–CH$_2$–), 1.56(6H, m, 3–CH$_2$–), 1.41(27H, virtually coupled triplet, J'_{PH} 3.6, 3PMe$_3$), 1.05(15H, m, 3–CH$_2$– and 3–CH$_3$), and −3.84[5H, q, *J*(P–H) 34.11, 5W–H]. $^{31}P\{^1H\}$ [room temp., relative to (MeO)$_3$PO (external)]: −31.54 p.p.m. [s, $J(^{31}P\text{–}^{183}W)$ 106.23, $J(^{31}P\text{–}^{117}Sn)$ 154.73, $J(^{31}P\text{–}^{119}Sn)$ 161.54]. $^{31}P\{^1H\text{-Me}\}$ (room temp.): −31.54 p.p.m. [sex, *J*(P–H) 26.62]. ^{119}Sn [light petroleum (b.p. 40—60 °C)]: 49.0 p.p.m. [q, *J*(Sn–W) 116, *J*(Sn–P) 162].

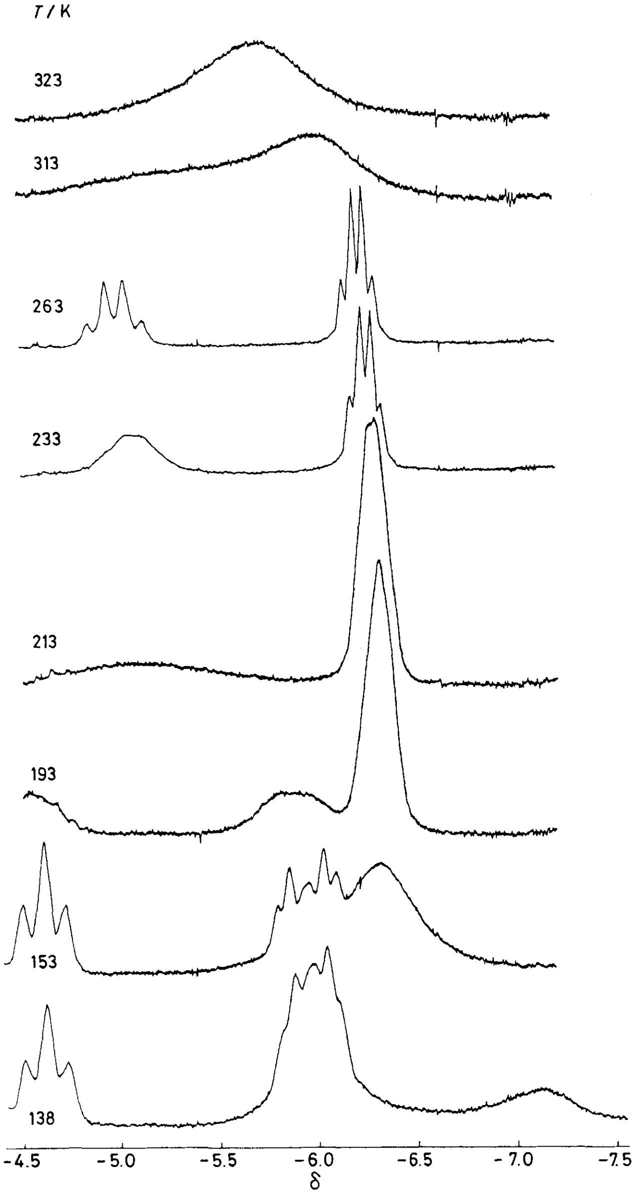

Figure 4. Partial variable temperature ^1H n.m.r. of $[W(PMe_3)_3H_5Li]_4$ (**6**) in $[^2H_8]$thf; only the hydride resonances are shown.

and two terminal hydrides. Above room temperature these become equivalent and, as the solution is cooled below 213 K, they split further until at 138 K four resonances are observed in the ratio 1 : 1 : 2 : 1.

The disposition of the hydrides in these compounds cannot be fully established without neutron diffraction studies and attempts to prepare suitable crystals are in hand.

Compounds (**2**), (**4**), and (**5**) in thf react with $SnBu^{n}{}_{3}Cl$ giving $W(PMe_3)_3H_5SnBu^{n}{}_{3}$ (**7**)‡ as white crystals (m.p. 27 °C) in *ca.* 50% yield.

In a recent paper[9] Caulton has reported the compounds $[K][OsH_3(PMe_2Ph)_3]$ and $[K][ReH_6(PMePh_2)_2]$ from treatment of $OsH_4(PMe_2Ph)_3$ and $ReH_7(PMePh_2)_2$ with KH. These compounds are clearly related to the ones described here but the crystal structures were not determined.

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References

1 F. W. S. Benfield, R. A. Forder, M. L. H. Green, G. A. Moser, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1973, 759; R. A. Forder and K. Prout, *Acta Crystallogr., Sect. B,* 1974, **30**, 2318.
2 R. A. Forder, M. L. H. Green, R. E. Mackenzie, J. S. Poland, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1973, 426; R. A. Forder and K. Prout, *Acta Crystallogr., Sect. B,* 1974, **30**, 2312.
3 M. L. H. Green, G. A. Moser, I. Packer, F. Petit, R. A. Forder, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1974, 839; K. Prout and R. A. Forder, *Acta Crystallogr., Sect. B,* 1975, **31**, 852; S. G. Davies, M. L. H. Green, K. Prout, A. Coda, and V. Tazzoli, *J. Chem. Soc., Chem. Commun.*, 1977, 135.
4 C. J. Pedersen, *J. Am. Chem. Soc.*, 1970, 92, 386.
5 J. A. Bandy, A. Berry, M. L. H. Green, R. N. Perutz, K. Prout, and J-N. Verpeaux, *J. Chem. Soc., Chem. Commun.*, 1984, 729.
6 C. Cambillau, G. Bram, U. Corset, and C. Riche, *Can. J. Chem.*, 1982, **60**, 2554; C. Cambillau, G. Bram, J. Corset, C. Riche, and C. Pascard-Billy, *Tetrahedron*, 1978, **34**, 2675; O. Nagano, *Acta Crystallogr., Sect. B,* 1979, **35**, 465.
7 G. Herzberg, 'Spectra of Diatomic Molecules,' Van Nostrand, Princeton, 1950, p. 546.
8 S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.*, 1958, **80**, 4782.
9 J. W. Bruno, J. C. Huffman, M. A. Green, and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 8310.
10 D. J. Watkin, J. R. Carruthers, and P. W. Betteridge, 1985, Crystals User Guide, Chemical Crystallography Laboratory, University of Oxford.