distribution within the cluster, disparate μ_2-bridging Co—CO bond lengths are observed. The bridging carbonyl distances range from 1·862 (8) to 2·034 (8) Å and follow the trend observed in other phosphine-substituted clusters (Richmond & Kochi, 1986, 1987b). The cross section in Fig. 2 shows the asymmetric bridging carbonyls. It is readily seen that the shorter bridging Co—CO bonds are associated with the more highly substituted Co(1) atom consistent with the $d\pi \rightarrow \pi^*$ backbonding electronic effect. The terminal Co—CO, Co—P, C—C, and P—C distances and angles are unexceptional and deserve no further comment.

At this point we cannot say with certainty whether the initial dmpe ligand coordinates in a bridging or chelating fashion. Assuming a stepwise substitution process is operative, the intermediate monosubstituted phosphine cluster PhCCo$_3$(CO)$_8$(η^1-dmpe) with a free, dangling phosphine group is expected to react in an associative manifold to furnish either the bridged or the chelated cluster PhCCo$_3$(CO)$_7$(dmpe). The subtle entropic balance between these two pathways undoubtedly controls which cluster is initially produced. Infrared studies are planned in order to address the coordination mode of the first dmpe ligand.

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Structure of [HTMPP]₃W₂Cl₉ [HTMPP = Tris(2,4,6-trimethoxyphenyl)phosphonium]

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Abstract. Tris(2,4,6-trimethoxyphenyl)phosphonium nonachloroditungstate(III)–pyridine–tetrahydrofuran (1/2/1), $3C_{27}H_{34}O_9P^+.W_2Cl_9^{3-}.2C_5H_5N.C_4H_4O$ (1), $M_r = 2513\cdot7$, triclinic, $P\bar{1}$, $a = 16\cdot993$ (5), $b = 24\cdot746$ (9), $c = 14\cdot094$ (4) Å, $\alpha = 95\cdot170$ (2), $\beta = 111\cdot690$ (2), $\gamma = 87\cdot630$ (3)°, $V = 5484$ (3) Å^3, $Z = 2$, $D_x = 1\cdot522$ g cm^{-3}, λ(Mo $K\alpha) = 0\cdot71073$ Å, $\mu = 24\cdot7$ cm^{-1}, $F(000) = 2540$, $T = 295$ K, $R = 0\cdot057$ for 9260 unique reflections total with $F_o^2 > 3\sigma(F_o^2)$. The asymmetric unit is composed of one triply bonded confacial bioctahedral $[W_2Cl_9]^{3-}$ dimer with three crystallographically independent protonated phosphine counterions, HTMPP$^+$, and three interstitial solvent molecules (two pyridines and one tetrahydrofuran). The W—W distance is 2·4329 (6) Å, the average W—Cl bridging distance is 2·490 (6) Å, and the average W—Cl terminal distance is 2·414 (6) Å.

Introduction. One of the current interests in our laboratory is the reactivity of a new triphenylphosphine derivative, TMPP [TMPP = tris(2,4,6-trimethoxyphenyl)phosphine]. This unusually bulky and basic functionalized phosphine has already exhibited a diverse range of coordination modes from

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$3C_{27}H_{34}O_9P^+.W_2Cl_9^{3-}.2C_5H_5N.C_4H_4O$

Table 1. *Positional and equivalent isotropic thermal parameters (Å^2) and their e.s.d.'s for* [HTMPP]$_3$W$_2$Cl$_9$.2py.THF

	x	y	z	B
W(1)	0·43451 (3)	0·23835 (2)	0·22730 (4)	3·30 (1)
W(2)	0·28072 (3)	0·23304 (2)	0·15889 (4)	3·64 (1)
Cl(1)	0·5190 (2)	0·2192 (2)	0·1232 (2)	5·00 (8)
Cl(2)	0·5085 (2)	0·3209 (1)	0·3091 (3)	5·15 (9)
Cl(3)	0·5289 (2)	0·1864 (1)	0·3628 (2)	4·41 (8)
Cl(4)	0·3515 (2)	0·2971 (2)	0·0893 (2)	5·14 (9)
Cl(5)	0·3659 (2)	0·1499 (1)	0·1495 (2)	4·29 (8)
Cl(6)	0·3552 (2)	0·2559 (1)	0·3451 (2)	4·00 (8)
Cl(7)	0·1974 (2)	0·2087 (2)	−0·0187 (3)	6·0 (1)
Cl(8)	0·1912 (2)	0·3107 (2)	0·1630 (3)	5·69 (9)
Cl(9)	0·2022 (2)	0·1736 (2)	0·2181 (3)	6·0 (1)
P(1)	0·9443 (2)	0·2905 (2)	0·4929 (2)	3·98 (8)
P(2)	0·3584 (2)	0·6075 (1)	0·1636 (2)	3·87 (8)
P(3)	0·7236 (2)	0·9507 (2)	0·3846 (3)	3·99 (8)
O(1)	0·8125 (6)	0·2090 (4)	0·3694 (7)	6·5 (3)
O(2)	0·9187 (7)	0·1688 (5)	0·1011 (8)	9·3 (4)
O(3)	1·0525 (5)	0·2986 (4)	0·3866 (6)	6·1 (2)
O(4)	0·7891 (5)	0·3274 (4)	0·3253 (7)	5·8 (3)
O(5)	0·8057 (8)	0·5152 (5)	0·4214 (9)	9·4 (4)
O(6)	1·0126 (6)	0·3866 (4)	0·6202 (7)	6·1 (3)
O(7)	0·7809 (5)	0·3025 (4)	0·5259 (7)	6·0 (3)
O(8)	0·8547 (7)	0·1810 (5)	0·7956 (7)	8·8 (3)
O(9)	1·0399 (6)	0·2107 (4)	0·6240 (7)	5·9 (3)
O(10)	0·4329 (6)	0·5003 (3)	0·2379 (6)	5·0 (2)
O(11)	0·6356 (6)	0·5651 (4)	0·5543 (7)	5·6 (3)
O(12)	0·4349 (5)	0·6862 (3)	0·3314 (6)	4·5 (2)
O(13)	0·4526 (6)	0·6273 (4)	0·0381 (6)	6·3 (3)
O(14)	0·3901 (7)	0·4706 (6)	−0·1896 (8)	9·6 (4)
O(15)	0·2295 (6)	0·6681 (4)	0·0252 (6)	6·2 (3)
O(16)	0·2805 (5)	0·5646 (4)	0·3025 (6)	5·8 (2)
O(17)	0·0142 (6)	0·6514 (5)	0·1685 (8)	7·7 (3)
O(18)	0·239 (1)	0·4502 (7)	0·063 (1)	14·5 (7)
O(19)	0·8475 (6)	0·8823 (4)	0·5179 (6)	5·6 (3)
O(20)	0·9302 (7)	0·9986 (4)	0·8208 (8)	7·1 (3)
O(21)	0·7337 (6)	1·0560 (4)	0·4951 (7)	5·7 (2)*
O(22)	0·6243 (5)	0·9019 (4)	0·4687 (7)	5·9 (2)
O(23)	0·3701 (6)	1·0036 (5)	0·3389 (8)	8·8 (3)
O(24)	0·6164 (5)	1·0396 (3)	0·2602 (6)	4·7 (2)
O(25)	0·6636 (5)	0·9011 (4)	0·1875 (7)	6·2 (3)
O(26)	0·8642 (7)	0·9725 (5)	0·0642 (8)	10·4 (3)
O(27)	0·8587 (6)	1·0292 (4)	0·3949 (7)	6·9 (3)
O(28)	0·399 (1)	0·884 (1)	0·133 (2)	22·3 (9)*
C(1)	0·9347 (7)	0·2521 (5)	0·3766 (9)	4·0 (3)*
C(2)	0·8700 (8)	0·2147 (6)	0·321 (1)	5·3 (3)*
C(3)	0·8647 (9)	0·1848 (6)	0·227 (1)	6·0 (4)*
C(4)	0·9304 (9)	0·1993 (6)	0·195 (1)	5·5 (3)*
C(5)	0·9923 (8)	0·2347 (6)	0·240 (1)	4·8 (3)*
C(6)	0·9939 (8)	0·2625 (5)	0·3313 (9)	4·3 (3)*
C(7)	0·735 (1)	0·1753 (8)	0·313 (1)	8·2 (5)*
C(8)	0·987 (1)	0·1804 (9)	0·054 (1)	10·0 (6)*
C(9)	1·123 (1)	0·3057 (8)	0·351 (1)	8·3 (5)*
C(10)	0·9022 (7)	0·3589 (5)	0·4722 (9)	3·8 (3)*
C(11)	0·8275 (8)	0·3700 (5)	0·3877 (9)	4·4 (3)*
C(12)	0·7955 (9)	0·4229 (6)	0·372 (1)	5·9 (4)*
C(13)	0·8414 (9)	0·4615 (6)	0·443 (1)	6·2 (4)*
C(14)	0·9161 (9)	0·4561 (6)	0·529 (1)	5·5 (3)*
C(15)	0·9442 (8)	0·4015 (6)	0·540 (1)	5·1 (3)*
C(16)	0·705 (1)	0·3339 (7)	0·245 (1)	6·8 (4)*
C(17)	0·837 (1)	0·5597 (8)	0·490 (1)	9·4 (6)*
C(18)	1·059 (1)	0·4268 (8)	0·701 (1)	7·9 (5)*
C(19)	0·9116 (7)	0·2569 (5)	0·5790 (9)	4·1 (3)*
C(20)	0·8327 (8)	0·2680 (6)	0·588 (1)	4·7 (3)*
C(21)	0·8098 (9)	0·2427 (6)	0·662 (1)	5·3 (3)*
C(22)	0·8672 (8)	0·2081 (6)	0·720 (1)	5·2 (3)*
C(23)	0·9457 (9)	0·1945 (6)	0·714 (1)	6·2 (4)*
C(24)	0·9661 (8)	0·2205 (6)	0·639 (1)	5·2 (3)*
C(25)	0·6937 (9)	0·3073 (7)	0·519 (1)	6·4 (4)*
C(26)	0·769 (1)	0·1931 (8)	0·807 (1)	8·4 (5)*
C(27)	1·1025 (9)	0·1728 (7)	0·689 (1)	6·5 (4)*
C(28)	0·4386 (7)	0·5934 (5)	0·2840 (8)	3·5 (3)*
C(29)	0·4714 (8)	0·5410 (5)	0·3106 (9)	4·2 (3)*
C(30)	0·5378 (7)	0·5329 (5)	0·4008 (9)	4·1 (3)*
C(31)	0·5711 (8)	0·5772 (5)	0·4680 (9)	4·4 (3)*
C(32)	0·5396 (7)	0·6310 (5)	0·4496 (9)	4·0 (3)*
C(33)	0·4717 (7)	0·6366 (5)	0·3554 (9)	3·7 (3)*
C(34)	0·4617 (8)	0·4446 (6)	0·262 (1)	5·2 (3)*
C(35)	0·6809 (9)	0·6087 (6)	0·628 (1)	5·7 (4)*
C(36)	0·4681 (8)	0·7345 (6)	0·400 (1)	4·8 (3)*
C(37)	0·3621 (7)	0·5643 (5)	0·0581 (9)	3·9 (3)*
C(38)	0·4126 (8)	0·5806 (6)	0·0036 (9)	4·6 (3)*
C(39)	0·4207 (9)	0·5480 (5)	−0·078 (1)	6·5 (4)*
C(40)	0·3771 (9)	0·5004 (6)	−0·106 (1)	6·1 (4)*
C(41)	0·3242 (9)	0·4803 (6)	−0·062 (1)	5·6 (3)*

Table 1 *(cont.)*

	x	y	z	B
C(42)	0·3182 (8)	0·5135 (6)	0·025 (1)	5·0 (3)*
C(43)	0·502 (1)	0·6488 (7)	−0·018 (1)	6·5 (4)*
C(44)	0·348 (1)	0·4215 (8)	−0·225 (1)	9·2 (5)*
C(45)	0·1758 (9)	0·7023 (7)	−0·054 (1)	6·4 (4)*
C(46)	0·2534 (7)	0·6175 (5)	0·1651 (9)	3·8 (3)*
C(47)	0·2258 (8)	0·5975 (5)	0·2369 (9)	4·2 (3)*
C(48)	0·1444 (8)	0·6088 (6)	0·237 (1)	5·1 (3)*
C(49)	0·0921 (8)	0·6424 (6)	0·163 (1)	5·2 (3)*
C(50)	0·1165 (9)	0·6647 (6)	0·090 (1)	5·6 (3)*
C(51)	0·1978 (8)	0·6506 (6)	0·0927 (9)	4·6 (3)*
C(52)	0·257 (1)	0·5449 (7)	0·381 (1)	7·0 (4)*
C(53)	−0·044 (1)	0·6866 (7)	0·098 (1)	7·7 (5)*
C(54)	0·2716 (6)	0·5035 (4)	0·0784 (7)	2·0 (2)*
C(55)	0·7914 (8)	0·9703 (5)	0·5120 (9)	4·2 (3)*
C(56)	0·8447 (8)	0·9303 (5)	0·5700 (9)	4·2 (3)*
C(57)	0·8906 (8)	0·9415 (6)	0·6751 (9)	4·5 (3)*
C(58)	0·8826 (8)	0·9915 (6)	0·717 (1)	5·0 (3)*
C(59)	0·8324 (8)	1·0345 (6)	0·662 (1)	5·0 (3)*
C(60)	0·7872 (8)	1·0202 (5)	0·5605 (9)	4·2 (3)*
C(61)	0·8903 (9)	0·8367 (6)	0·574 (1)	6·1 (4)*
C(62)	0·926 (1)	1·0508 (9)	0·874 (2)	11·0 (6)*
C(63)	0·711 (1)	1·1063 (7)	0·541 (1)	6·9 (4)*
C(64)	0·6181 (7)	0·9713 (5)	0·3631 (9)	3·9 (3)*
C(65)	0·5750 (8)	0·9412 (6)	0·4103 (9)	4·6 (3)*
C(66)	0·4916 (9)	0·9527 (6)	0·403 (1)	5·6 (3)*
C(67)	0·4510 (9)	0·9949 (6)	0·342 (1)	5·4 (3)*
C(68)	0·4883 (8)	1·0255 (6)	0·2914 (9)	4·6 (3)*
C(69)	0·5724 (7)	1·0128 (5)	0·3020 (9)	3·9 (3)*
C(70)	0·583 (1)	0·8670 (8)	0·512 (1)	8·3 (5)*
C(71)	0·319 (1)	1·0432 (8)	0·273 (1)	8·8 (5)*
C(72)	0·5720 (8)	1·0766 (6)	0·186 (1)	5·2 (3)*
C(73)	0·7641 (7)	0·9640 (5)	0·2896 (9)	3·8 (3)*
C(74)	0·7297 (8)	0·9327 (6)	0·196 (1)	5·0 (3)*
C(75)	0·7620 (8)	0·9327 (6)	0·119 (1)	5·2 (3)*
C(76)	0·829 (1)	0·9665 (7)	0·137 (1)	6·5 (4)*
C(77)	0·8646 (9)	1·0022 (6)	0·226 (1)	6·1 (4)*
C(78)	0·8314 (8)	0·9987 (6)	0·305 (1)	5·0 (3)*
C(79)	0·618 (1)	0·8701 (7)	0·089 (1)	7·5 (4)*
C(80)	0·843 (1)	0·9317 (7)	−0·023 (1)	7·5 (4)*
C(81)	0·936 (1)	1·0620 (7)	0·419 (1)	7·5 (4)*
C(82)	0·060 (1)	0·443 (1)	0·187 (2)	12·7 (8)*
C(83)	−0·003 (1)	0·4513 (9)	0·091 (2)	10·8 (6)*
C(84)	0·917 (1)	0·4527 (9)	0·077 (2)	10·1 (6)*
C(85)	−0·108 (1)	0·4392 (9)	0·147 (2)	10·0 (6)*
C(86)	−0·055 (1)	0·4255 (9)	0·242 (2)	10·2 (6)*
C(87)	0·701 (2)	0·733 (1)	0·376 (2)	17 (1)*
C(88)	0·657 (2)	0·761 (1)	0·288 (2)	18 (1)*
C(89)	0·669 (1)	0·742 (1)	0·196 (2)	12·8 (8)*
C(90)	0·736 (2)	0·713 (1)	0·198 (2)	13·8 (8)*
C(91)	0·786 (1)	0·693 (1)	0·288 (2)	12·4 (7)*
C(92)	0·680 (2)	0·124 (1)	0·984 (2)	18 (1)*
C(93)	0·337 (1)	0·820 (1)	0·004 (2)	12·2 (7)*
C(94)	0·396 (2)	0·781 (1)	0·085 (2)	15 (1)*
C(95)	0·436 (2)	0·829 (1)	0·173 (2)	14·7 (9)*
N(1)	0·029 (1)	0·4299 (8)	0·260 (1)	12·7 (6)*
N(2)	0·770 (1)	0·6978 (8)	0·372 (1)	13·4 (6)*

* Atoms refined isotropically. The equivalent isotropic displacement parameter is defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

monodentate (Dunbar & Haefner, 1990), chelating tridentate (Dunbar, Haefner & Pence, 1989) to a combination chelating–bridging mode (Chen & Dunbar, 1990). In the pursuit of further evidence of this ligand's versatility, we have discovered another feature of its chemistry. Protonation of the phosphine enables it to act as a large cation to balance the charge of a variety of anions. In this structure, three protonated TMPP molecules serve as cations in a salt of the known binuclear transition metal anion $[W_2Cl_9]^{3-}$ (Laudise & Young, 1960).

Experimental. WCl$_4$ (0·04 g, 1·23 mmol), TMPP (1·4 g, 2·63 mmol), and 0·2 M Na/Hg amalgam

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with e.s.d.'s for* [HTMPP]₃W₂Cl₉.2py.THF

W(1)—W(2)	2·4329 (6)	W(2)—Cl(4)	2·496 (3)
W(1)—Cl(1)	2·412 (3)	W(2)—Cl(5)	2·489 (3)
W(1)—Cl(2)	2·409 (3)	W(2)—Cl(6)	2·479 (3)
W(1)—Cl(3)	2·425 (3)	W(2)—Cl(7)	2·411 (3)
W(1)—Cl(4)	2·489 (3)	W(2)—Cl(8)	2·410 (3)
W(1)—Cl(5)	2·488 (3)	W(2)—Cl(9)	2·419 (3)
W(1)—Cl(6)	2·498 (2)		

W(2)—W(1)—Cl(1)	123·00 (8)	W(1)—W(2)—Cl(8)	122·47 (8)
W(2)—W(1)—Cl(2)	122·42 (7)	W(1)—W(2)—Cl(9)	123·57 (8)
W(2)—W(1)—Cl(3)	125·26 (7)	Cl(4)—W(2)—Cl(5)	99·06 (9)
W(2)—W(1)—Cl(4)	60·93 (7)	Cl(4)—W(2)—Cl(6)	100·0 (1)
W(2)—W(1)—Cl(5)	60·76 (6)	Cl(4)—W(2)—Cl(7)	84·5 (1)
W(2)—W(1)—Cl(6)	60·35 (6)	Cl(4)—W(2)—Cl(8)	82·9 (1)
Cl(1)—W(1)—Cl(2)	93·6 (1)	Cl(4)—W(2)—Cl(9)	175·8 (1)
Cl(1)—W(1)—Cl(3)	92·26 (9)	Cl(5)—W(2)—Cl(6)	95·63 (9)
Cl(1)—W(1)—Cl(4)	84·0 (1)	Cl(5)—W(2)—Cl(7)	86·1 (1)
Cl(1)—W(1)—Cl(5)	85·5 (1)	Cl(5)—W(2)—Cl(8)	176·8 (1)
Cl(1)—W(1)—Cl(6)	176·14 (9)	Cl(5)—W(2)—Cl(9)	83·9 (1)
Cl(2)—W(1)—Cl(3)	91·3 (1)	Cl(6)—W(2)—Cl(7)	174·8 (1)
Cl(2)—W(1)—Cl(4)	84·0 (1)	Cl(6)—W(2)—Cl(8)	86·43 (9)
Cl(2)—W(1)—Cl(5)	176·4 (1)	Cl(6)—W(2)—Cl(9)	82·6 (1)
Cl(2)—W(1)—Cl(6)	85·5 (1)	Cl(7)—W(2)—Cl(8)	91·6 (1)
Cl(3)—W(1)—Cl(4)	173·8 (1)	Cl(7)—W(2)—Cl(9)	92·7 (1)
Cl(3)—W(1)—Cl(5)	85·34 (9)	Cl(8)—W(2)—Cl(9)	94·0 (1)
Cl(3)—W(1)—Cl(6)	83·99 (9)	W(1)—Cl(4)—W(2)	58·43 (6)
Cl(4)—W(1)—Cl(6)	99·68 (9)	W(1)—Cl(6)—W(2)	58·53 (6)

(13 ml, 2·60 mmol) were stirred in toluene at 273 K for 30 h. The solution was filtered to yield a green solid which was dissolved in a 1:1 mixture of acetonitrile and THF, filtered, and evaporated to a residue. Crystals of X-ray quality were grown by slow diffusion of hexane into a solution of the product in pyridine.

An irregularly shaped green-yellow crystal of approximate dimensions 0·40 × 0·35 × 0·30 mm was mounted in a capillary which was then sealed and examined on a Nicolet *P*3 diffractometer using graphite-monochromated Mo *Kα* radiation. 20 orientation reflections were used in the range $4 < 2\theta < 29°$ to refine the unit-cell parameters. Data of one hemisphere $(\pm h, \pm k, +l)$ were collected by ω scans for 2θ from 4–47° $[(\sin\theta)/\lambda = 0·561 \text{ Å}^{-1}]$ for 16 975 reflections. Periodically monitored check reflections indicated no significant decay over the period of data collection. Three azimuthal scans were collected and used to correct for absorption with the maximum and minimum transmission factors equal to 0·998 and 0·870, respectively.

The two W atoms were located from a Patterson map; the remainder of the atoms were located by subsequent difference Fourier maps and refined on *F* by employing the Enraf–Nonius (1979) *Structure Determination Package*. H atoms were not located and thus were omitted from the model. The W, Cl, P, as well as the methoxy group O atoms were refined anisotropically using the default scattering factors from *SDP*. 9260 total unique data with $F_o^2 > 3\sigma(F_o^2)$ were used to refine 757 parameters to residuals of *R* = 0·057 and *wR* = 0·067, $w = 4F_o^2/\sigma^2(F_o^2)$. The quality of fit was 1·633, and after the final cycle, the largest parameter shift/e.s.d. was 0·58. After a final

difference map, the largest positive peak was 1·354 e Å⁻³, and the largest negative peak was 0·943 e Å⁻³.
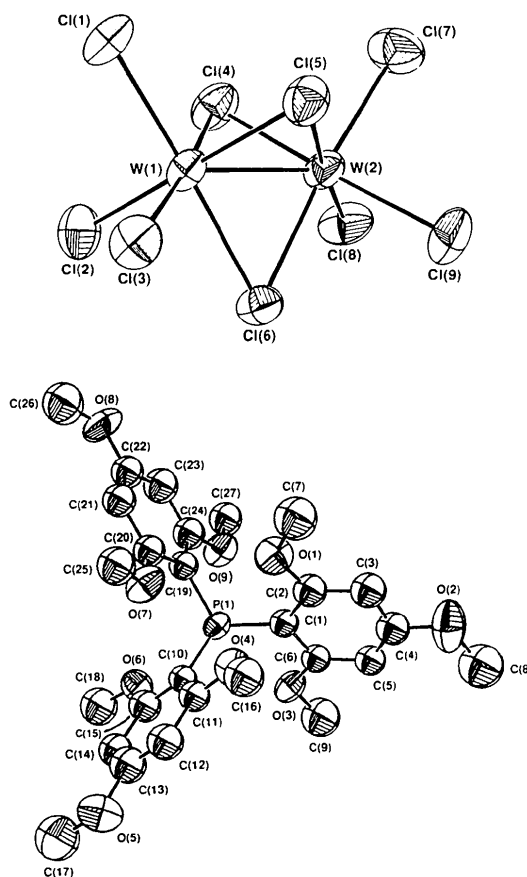

Fig. 1. *ORTEP* (Johnson, 1976) drawings of the two types of ions contained in the asymmetric unit of (1). Atoms are represented by their thermal ellipsoids drawn at the 50% probability level.
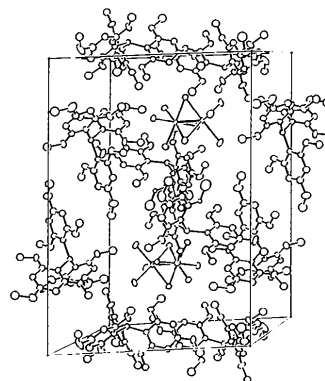

Fig. 2. Packing diagram (*ORTEP*; Johnson, 1976) for (1). The *b* axis is vertical, the *a* axis is horizontal, and the *c* axis is normal to the page.

Discussion. The refined atomic coordinates and equivalent isotropic displacement parameters are given in Table 1* with selected bond distances and angles in Table 2. The molecular structures of the two types of ions present in the asymmetric unit are presented in Fig. 1. The three-dimensional packing diagram is shown in Fig. 2

The binuclear tungsten molecule exhibits the expected confacial bioctahedral geometry with three bridging chlorides and three terminal chlorides per metal atom which are staggered with respect to the bridging atoms. The phosphonium cations adopt the characteristic triarylphosphine propeller arrangement of the aromatic rings.

The $[W_2Cl_9]^{3-}$ dimeric unit has been synthesized previously in the form of the Cs^+ (Lewis, Nyholm & Smith, 1969) and n-Bu_4N^+ (Ziegler & Risen, 1972) salts, and has been structurally characterized with a K^+ counterion (Watson & Waser, 1958). The earlier value of 2·409 Å for the W—W bond distance in the potassium salt does not differ significantly from the value of 2·4329 (6) Å for the corresponding distance in the present structure with a large phosphonium cation. The rigidity of the M—M bond in the tungsten system is in direct contrast to the extreme flexibility of the dimetal unit in the molybdenum analogue. Single-crystal studies of $Mo_2Cl_9^{3-}$ with various counterions have given values from 2·610 (2)

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* Full lists of bond lengths and· angles, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53229 (93 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

to 2·815 (3) Å for the Mo—Mo bond separation (Subbotin & Aslanov, 1986a; Saillant, Jackson, Streib, Folting & Wentworth, 1971; Stranger, Smith & Grey, 1989; Subbotin & Aslanov, 1986b). The present study demonstrates the increased tendency for the third-row transition elements to form strong metal–metal interactions.

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Bis(N-piperidyldithiocarbamato)copper(III) Hexafluorophosphate: an Unexpected Product from the Disproportionation of 1,12-Bis(N-piperidyl)-2,5,8,11-tetrathiadodeca-1,12-dithionato-Cu^I.PF$_6$

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Abstract. $[Cu(C_6H_{10}NS_2)_2]^+.PF_6^-$, $M_r = 529·1$, monoclinic, $P2_1/c$, $a = 7·816$ (2), $b = 18·428$ (2), $c = 13·883$ (2) Å, $\beta = 94·94$ (2)°, $V = 1992$ Å^3, $Z = 4$, $D_x = 1·764$ g cm^{-3}, $\lambda(Mo~K\alpha) = 0·71069$ Å, $\mu = 16·34$ cm^{-1}, $F(000) = 1072$, $T = 297$ (1) K, final $R = 0·039$ for 2508 observed reflections. The crystal contains two crystallographically independent bis(N-piperidyldithiocarbamato)copper(III) cations, each of which has its Cu atom at a centre of symmetry. Cations stack with a Cu$\cdots$Cu separation of only

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