Synthesis and Properties of the Divalent 1,2-Bis(dimethylphosphino)ethane (dmpe) Complexes $MCl_2(dmpe)_2$ and $MMe_2(dmpe)_2$ (M = Ti, V, Cr, Mn, or Fe). *X*-Ray Crystal Structures of $MCl_2(dmpe)_2$ (M = Ti, V, or Cr), $MnBr_2(dmpe)_2$, $TiMe_{1.3}Cl_{0.7}(dmpe)_2$, and $CrMe_2(dmpe)_2$†

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The reaction of transition-metal dichlorides with 1,2-bis(dimethylphosphino)ethane (dmpe) leads to the brightly coloured, highly-crystalline octahedral complexes *trans*-$MCl_2(dmpe)_2$ (M = Ti, V, Cr, or Fe). Although the Mn analogue could not be prepared, both *trans*-$MnBr_2(dmpe)_2$ and *trans*-$MnI_2(dmpe)_2$ can be obtained from the respective dihalides. Alkylation of the $MX_2(dmpe)_2$ (X = halide) compounds with either LiMe or $MgMe_2$ leads to the dimethyl complexes *trans*-$MMe_2(dmpe)_2$ (M = V, Cr, or Mn); the titanium complex isolated under these conditions is a mixture of *trans*-TiMeCl(dmpe)$_2$ and *trans*-$TiMe_2(dmpe)_2$, while the iron species obtained is *cis*-$FeMe_2(dmpe)_2$. Magnetic susceptibility and e.s.r. measurements indicate a low-spin state for all the complexes except the manganese halide derivatives, and metal–ligand bond lengths observed in those complexes structurally characterised by *X*-ray crystallographic methods are consistent with the proposed ground-state configurations. There is a similarity between the electronic structures of the $MCl_2(dmpe)_2$ species and the metallocenes $M(\eta^5\text{-}C_5H_5)_2$, while the $MMe_2(dmpe)_2$ compounds resemble $M(\eta^5\text{-}C_5Me_5)_2$. Our studies indicate a progressive change in the nature of the M–Me groups upon lowering the electron count from 18 (Fe) to 14 (Ti). Thus, the titanium complex *trans*-$TiMe_{1.3}Cl_{0.7}(dmpe)_2$ appears to contain a distorted methyl group involving a Ti ··· H–C interaction due to donation of C–H bond electrons into an empty orbital on the metal.

We describe a series of 1,2-bis(dimethylphosphino)ethane (dmpe) complexes of divalent transition metals; part of this work has been published in preliminary notes.[1] The complexes have the stoicheiometry *trans*-$MX_2(dmpe)_2$ (M = Ti, V, Cr, Mn, or Fe; X = Me or halide). The geometric and electronic structures of these complexes are strongly dependent on the number of valence electrons; of particular interest is the apparent distortion of methyl groups bound to a 14-electron titanium centre.

Results and Discussion

Halide Complexes.—The syntheses of the dmpe adducts of divalent first-row transition elements are relatively straightforward, involving the interaction of a metal dichloride with dmpe in a suitable solvent. This method works extremely well for $FeCl_2$ in toluene to give the known[2] emerald green *trans*-$FeCl_2(dmpe)_2$ in high yield. However, dichlorides of earlier first-row transition metals prepared by high-temperature routes[3] react only sluggishly if at all with dmpe. Instead, solvates of the metal dichlorides prepared by low-temperature routes must be used; thus, the reactions of '$VCl_2(thf)_2$'[4] and $CrCl_2(thf)$[5] with dmpe in toluene readily lead to red-orange *trans*-$VCl_2(dmpe)_2$ and yellow-green *trans*-$CrCl_2(dmpe)_2$, respectively. Although no adducts of divalent titanium proved suitable as starting materials (see below), red-black *trans*-$TiCl_2(dmpe)_2$ can be prepared in high yield in a 'one-pot' reaction of $TiCl_4$, dmpe, and magnesium in tetrahydrofuran (thf). The *trans* stereochemistry for all these complexes has been established spectroscopically and crystallographically (see below). No evidence for the existence of the corresponding *cis* isomers has been obtained under the conditions we have employed.

All attempts to prepare *trans*-$MnCl_2(dmpe)_2$ were unsuccessful. For example, treatment of $MnCl_2$ or $MnCl_2(thf)_2$ in toluene, dichloromethane, chlorobenzene, thf, or neat dmpe did not produce any of the desired product, even after prolonged refluxing in these solvents. Instead, a colourless monoadduct, $MnCl_2(dmpe)$, forms that is insoluble in solvents with which it does not react; this species was not investigated further. Evidently, Mn–Cl bridging competes effectively with adduct formation with a second equivalent of dmpe. However, both $MnBr_2$ and MnI_2 react readily with dmpe in dichloromethane to give the colourless species *trans*-$MnBr_2(dmpe)_2$ and *trans*-$MnI_2(dmpe)_2$. It is well known that bromide and iodide are poorer bridging ligands than chloride, and this phenomenon undoubtedly is responsible for the observed behaviour.[6]

Some $MCl_2(dmpe)_2$ compounds of the second- and third-row transition elements that are closely related to the first-row species are known. The diamagnetic ruthenium and osmium complexes[7] are notable in that they led to the synthesis of the first alkyl–hydride compounds,[8] and to an early example of C–H bond activation.[9] More recently, the niobium,[10] tantalum,[11] molybdenum,[12] and tungsten[12] complexes have been reported. Whereas phosphine complexes of the second- and third-row elements are common,[13] those of the early first-row elements are not. Many iron(II) phosphine complexes exist,[13] but manganese(II) phosphine complexes are relatively rare. The only monomeric phosphine adduct of a manganese(II) halide is

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† Bis[1,2-bis(dimethylphosphino)ethane-*PP'*]dichloro-titanium(II), -vanadium(II), and -chromium(II); bis[1,2-bis(dimethylphosphino)ethane-*PP'*]dibromomanganese(II); bis[1,2-bis(dimethylphosphino)ethane-*PP'*]chloro(methyl)titanium(II) (Cl/Me = 0.7/1.3); and bis[1,2-bis(dimethylphosphino)ethane-*PP'*]dimethylchromium(II) respectively.

Supplementary data available (No. SUP 56125, 13 pp.): anisotropic thermal parameters, full lists of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Properties and analytical data for new *trans*-MX$_2$(dmpe)$_2$ compounds and *cis*-FeMe$_2$(dmpe)$_2$

Compound	Colour	M.p/°C	Analysis (%)[a] C	H	P	Cl
TiCl$_2$(dmpe)$_2$	Red-black	150[b]	34.4	7.60	29.5	17.0
			(34.4)	(7.70)	(29.6)	(16.9)
VCl$_2$(dmpe)$_2$	Red-orange	340	34.4	7.65	28.2	16.6
			(34.2)	(7.65)	(29.4)	(16.8)
CrCl$_2$(dmpe)$_2$	Yellow-green	270[b]	34.1	7.55	29.2	16.4[c]
			(34.1)	(7.60)	(29.3)	(16.8)
MnBr$_2$(dmpe)$_2$	Colourless	155—159	28.1	6.15	24.2	31.1[d]
			(28.0)	(6.25)	(24.1)	(31.0)
MnI$_2$(dmpe)$_2$	Colourless	210—215	23.6	5.30	19.9	41.8[e]
			(23.7)	(5.25)	(20.3)	(41.7)
TiMe$_{1.3}$Cl$_{0.7}$(dmpe)$_2$	Red-black	100[b]	39.7	9.00	31.6	7.7
			(39.2)	(8.85)	(31.1)	(7.9)
VMe$_2$(dmpe)$_2$	Dark yellow	145[b]	43.7	10.0	33.3	
			(44.1)	(10.0)	(32.5)	
CrMe$_2$(dmpe)$_2$	Red-orange	195[b]	44.0	10.2	32.9	
			(44.0)	(10.0)	(32.4)	
MnMe$_2$(dmpe)$_2$	Dark orange	84—88	43.2	9.90	31.8	
			(43.6)	(9.95)	(32.1)	
cis-FeMe$_2$(dmpe)$_2$	Orange	*f*	43.9	10.0	32.0	
			(43.6)	(9.90)	(32.1)	

[a] Calculated values in parentheses. [b] With decomposition. [c] Cr: 12.1 (12.3%). [d] Br analysis. [e] I analysis. [f] Decomposes at ~90 °C.

Table 2. Magnetic susceptibility and *X*-band e.s.r. data for *trans*-MX$_2$(dmpe)$_2$

Compound	$\mu_{eff.}$/B.M.[a]	E.s.r. parameters[b]
TiCl$_2$(dmpe)$_2$	2.9 ± 0.1	Silent
VCl$_2$(dmpe)$_2$	3.7 ± 0.1	$D = 0.46, \lambda = 0.09$[c]
VMe$_2$(dmpe)$_2$	3.7 ± 0.1	$D = 0.85, \lambda = 0.08$
CrCl$_2$(dmpe)$_2$	2.8 ± 0.1	Silent
CrMe$_2$(dmpe)$_2$	2.8 ± 0.1	Silent
MnBr$_2$(dmpe)$_2$	5.9 ± 0.2	$D = 0.63, \lambda = 0.03, A(^{55}\text{Mn}) = 0.0079$
MnI$_2$(dmpe)$_2$	5.9 ± 0.2	$D = 0.85, \lambda = 0.03, A(^{55}\text{Mn}) = 0.0070$
MnMe$_2$(dmpe)$_2$	2.4 ± 0.2	$g_\perp = 2.037, g_\parallel = 2.056, A_\perp(^{55}\text{Mn}) = 0.0065,$ $A_\perp(^{31}\text{P}) = 0.0014$

[a] At 25 °C in toluene; B.M. = 0.927×10^{-23} A m^2. [b] At −196 °C in toluene glass; *D* and *A* in cm^{-1}. [c] At 25 °C: $g = 2.004$, $A(^{51}\text{V}) = 0.0079$, $A(^{31}\text{P}) = 0.0025$ cm^{-1}.

trans-MnCl$_2$(dmpb)$_2$ [dmpb = 1,2-bis(dimethylphosphino)benzene].[14] By contrast, a number of phosphine adducts of stoicheiometry MnX$_2$(PR$_3$) have been reported,[15] but these are polymeric; for instance, MnI$_2$(PMe$_2$Ph) has an infinite chain structure with alternating tetrahedral and octahedral sites.[16,*] However there are several organomanganese(II) phosphine species of stoicheiometries Mn$_2$R$_4$(PR'$_3$)$_2$,[17] MnR$_2$(PR'$_3$)$_2$,[18] and Mn(η^5-C$_5$H$_5$)$_2$(PR$_3$).[19] Apart from a few carbonyl species, only three types of phosphine adducts of chromium(II) have been reported: various CrCl$_2$(PR$_3$)$_2$ adducts that were only studied in solution,[14,20] the quadruply-bonded dimer Cr$_2$(CH$_2$SiMe$_3$)$_4$(PMe$_3$)$_2$,[21] and the square species *trans*-Cr[N(SiMe$_3$)$_2$]$_2$(PMe$_3$)$_2$.[22] Similarly, only three vanadium(II) phosphine complexes are known: the dimers V$_2$Cl$_4$(PEt$_3$)$_4$[23] and V$_2$(η^5-C$_5$H$_5$)$_2$Cl$_2$(PEt$_3$)$_2$,[24] and the 2,3,7,8,12,13,17,18-octaethylporphyrin (oep) complex V(oep)(PMe$_2$Ph)$_2$.[25] For titanium(II) the only phosphine complexes known are substituted analogues of Ti(η^5-C$_5$H$_5$)$_2$(CO)$_2$.[26] No well defined coordination complexes of titanium(II) exist, although a few poorly characterized adducts of TiCl$_2$ have been claimed.[27] It is possible that some of these are actually Ti^{III} species, given the dark blue colour and magnetic moments (*ca.* 1.1 B.M.) observed for many of them. For example, 'TiCl$_2$(MeCN)$_2$'[27] is possibly a Ti^{III} dimer with reductively coupled acetonitrile groups, such as those observed in some niobium and tantalum species.[28]

All the MX$_2$(dmpe)$_2$ (X = halide) complexes are monomeric and highly crystalline. They are soluble in toluene, thf, dichloromethane, and acetonitrile, sparingly soluble in diethyl ether, and essentially insoluble in light petroleum. Physical properties and microanalytical data are included in Table 1, magnetic susceptibility and e.s.r. data in Table 2, and ^{1}H n.m.r. data in Table 3. The compounds are air sensitive, especially in solution, however, all but the titanium complex may be handled briefly as solids in air.

Electronic Structures of Halide Complexes.—Magnetic susceptibility data obtained in toluene at room temperature indicate a low-spin configuration for all the MX$_2$(dmpe)$_2$ complexes except MnBr$_2$(dmpe)$_2$ and MnI$_2$(dmpe)$_2$ (Table 2). Thus, the number of unpaired electrons varies across the series: Ti (2), V (3), Cr (2), Mn (5), Fe (0). The magnetic moments are all near the spin-only values, suggesting orbitally non-degenerate ground states in each case. This is a reflection of the

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[*] *trans*-MnI$_3$(PMe$_3$)$_2$ is also known (B. Beagley, C. A. McAuliffe, K. Minter, and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1984, 658).

Table 3. ^1H N.m.r. data[a] for *trans*-$MX_2(dmpe)_2$ and *cis*-$FeMe_2(dmpe)_2$

Compound	PMe_2	PCH_2
$TiCl_2(dmpe)_2$	−3.1 (s, 50)	7.9 (s, 50)
$VCl_2(dmpe)_2$	−25.9 (s, 1 400)	−9.8 (s, 800)
$VMe_2(dmpe)_2$	−13.5 (s, 440)	11.7 (s, 500)
$CrCl_2(dmpe)_2$	−33.5 (s, 310)	−13.1 (s, 240)
$CrMe_2(dmpe)_2$	−28.6 (s, 310)	0.9 (s, 260)
$MnBr_2(dmpe)_2$	51.0 (s, 1 560)	26.0 (s, 1 330)
$MnI_2(dmpe)_2$	53.5 (s, 1 420)	29.5 (s, 1 500)
$MnMe_2(dmpe)_2$	−12.7 (s, 340)	−14.8 (s, 400)
$FeCl_2(dmpe)_2$	1.35 ('quin', 8.0)	1.96 ('quin', 15.0)
cis-$FeMe_2(dmpe)_2$[b]	0.87 (s, 6.0)	1.31 (m)
	0.94 (d, 4.4)	1.45 (m)
	1.01 ('t', 5.4)	
	1.20 ('t', 6.7)	

[a] Shifts in δ/p.p.m. in C_6D_6 at 25 °C. Value after singlet designation is full-width at half-maximum in Hz. Value after multiplet designation is separation between outer lines in Hz. Quotation marks indicate non-binomial multiplets. [b] Fe–Me: δ −0.64 ('q', 27.3 Hz).

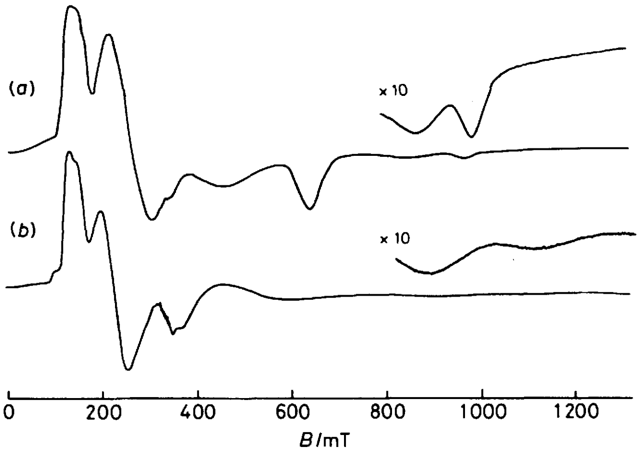

Figure 1. E.s.r. spectra of (*a*) *trans*-$VCl_2(dmpe)_2$ and (*b*) *trans*-$VMe_2(dmpe)_2$

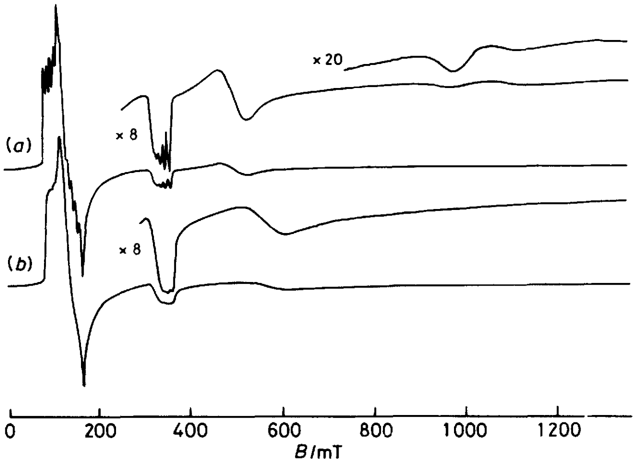

Figure 2. E.s.r. spectra of *trans*-$MnX_2(dmpe)_2$ [X = Br (*a*), or I (*b*)]

fact that the d_{xy}, d_{xz}, and d_{yz} orbitals of the pseudo-t_{2g} set are slightly split in energy, consistent with the D_{2h} point symmetry of the complexes.

X-Band e.s.r. spectra were recorded for all the $MX_2(dmpe)_2$ compounds as frozen toluene solutions at −196 °C. Not unexpectedly, the $S = 1$ species $TiCl_2(dmpe)_2$* and $CrCl_2(dmpe)_2$ are e.s.r. silent, while the $S = \frac{3}{2}$, $VCl_2(dmpe)_2$, and the $S = \frac{5}{2}$, $MnX_2(dmpe)_2$, complexes are e.s.r. active. The spectrum of $VCl_2(dmpe)_2$ at −196 °C comprises two broad low-field features at *ca.* 140 and 240 mT, and several weaker features out to *ca.* 1 000 mT (Figure 1); no hyperfine structure due to ^{51}V ($I = \frac{7}{2}$) or ^{31}P ($I = \frac{1}{2}$) was evident. By contrast, an isotropic spectrum at room temperature shows an approximately 40-line pattern at $g = 2.004$, yielding $A(^{51}V) = 0.0079$ cm^{-1} and $A(^{31}P) = 0.0025$ cm^{-1}. The spectra of the $MnX_2(dmpe)_2$ complexes at −196 °C also show low-field features at *ca.* 100 and 140 mT, with weaker transitions to higher field (Figure 2). Hyperfine coupling due to ^{55}Mn ($I = \frac{5}{2}$) is evident in the low-field region, the essentially isotropic coupling of *ca.* 0.0075 cm^{-1} being slightly better resolved in the bromo-complex.

Analysis of the e.s.r. spectra may be performed using the spin Hamiltonian given in equation (1) where *D* is a zero-field

$$\mathcal{H} = \beta B\cdot g\cdot S + D[S_z^2 - \tfrac{1}{3}S(S+1) + \lambda(S_x^2 - S_y^2)] + S\cdot A\cdot I \quad (1)$$

splitting parameter, and λ is a symmetry parameter that can vary from zero for axial symmetry to one-third for maximum possible rhombic symmetry.[29] In both the d^3 and d^5 cases, *g* was assumed to be isotropic and equal to 2.00, as usual.[30] Matching of observed resonances to calculated transitions was accomplished using the *D*–*B* plot method for $S = \frac{3}{2}$ or $S = \frac{5}{2}$.[30]

The Hamiltonian parameters derived from the spectra are included in Table 2. The complexes $VCl_2(dmpe)_2$ and $MnX_2(dmpe)_2$ have λ parameters indicative of near-axial symmetry ($\lambda < 0.1$). This is consistent with a *trans* stereochemistry, with the axial symmetry being broken slightly due to the two-fold rather than four-fold geometry of the equatorial ligand set. The higher zero-field splitting parameter, *D*, observed for $MnI_2(dmpe)_2$ *vs.* $MnBr_2(dmpe)_2$ is indicative of increased covalency (better σ and π overlap) in the Mn–I bond.[31]

Interestingly, the e.s.r. spectrum of *trans*-$MnBr_2(dmpe)_2$ is identical to that of manganocene in a $Mg(\eta^5\text{-}C_5H_5)_2$ matrix.[32] Indeed, there is an electronic similarity between all the metallocenes[33] and the $MX_2(dmpe)_2$ complexes, in that the latter are near-axially symmetric species whose magnetic moments and zero-field splittings closely parallel the metallocenes. It is particularly notable that the anomalous high-spin nature of manganocene is mirrored by the anomalous high-spin nature of the $MnX_2(dmpe)_2$ compounds among their first-row analogues.

As noted above, with the exception of $FeCl_2(dmpe)_2$, all the complexes are paramagnetic. However, ^1H n.m.r. spectra can be observed; these have two broad singlets, one for the PMe_2 groups and one for the PCH_2 groups of the dmpe ligands. While the precise chemical shifts and linewidths of these resonances vary from complex to complex, the single environments observed are consistent with a *trans* geometry in every case.

It is of interest to determine whether the electronic analogy between the $MX_2(dmpe)_2$ complexes and the metallocenes is reflected in a correlation of their ^1H n.m.r. spectra. The ^1H n.m.r. resonances of the metallocenes are known to show a progressive upfield trend in chemical shift along the series: V (δ

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* A weak resonance near $g = 2$ is observed, but this feature is most consistent with an $S = \frac{1}{2}$ species probably arising from trace oxidation to titanium(III). We thank Professor L. Belford for assistance on this point.

Table 4. Molecular geometry parameters [distances (Å) and angles (°)] for the complexes $MCl_2(dmpe)_2$ (M = Ti, V, or Cr) and $MnBr_2(dmpe)_2$

	$TiCl_2(dmpe)_2$	$VCl_2(dmpe)_2$	$CrCl_2(dmpe)_2$	$MnBr_2(dmpe)_2$
M–Cl	2.446(4)	2.446(4), 2.434(4)	2.351(3), 2.345(3)	2.666(3)
M–P	2.586(5)	2.495(5), 2.501(5) 2.499(5), 2.500(5)	2.371(3), 2.365(3) 2.371(7), 2.368(3)	2.655(4)
P–C(CH_2)	1.84(2)	1.81(1)—1.84(1)	1.835(7)—1.872(7)	1.90(5)
P–C(Me)	1.82(2)—1.87(2)	1.79(1)—1.82(1)	1.804(7)—1.855(7)	1.76(5)—1.95(5)
C(CH_2)–C(CH_2)	1.53(4)	1.26(1),* 1.54(1)	1.41(1), 1.52(1)	1.55(5)
P–M–P	77.8(2)	81.6(2), 81.3(2)	82.7(1), 82.9(1)	78.8(1)
M–P–C(CH_2)	103.6(5)	105.2(4)—107.0(4)	106.9(2)—109.4(2)	102(1)
M–P–C(Me)	118(1)—122(1)	118.2(4)—122.8(4)	118.6(2)—123.1(2)	118(3)—123(1)

* Artificially low value due to thermal motion.

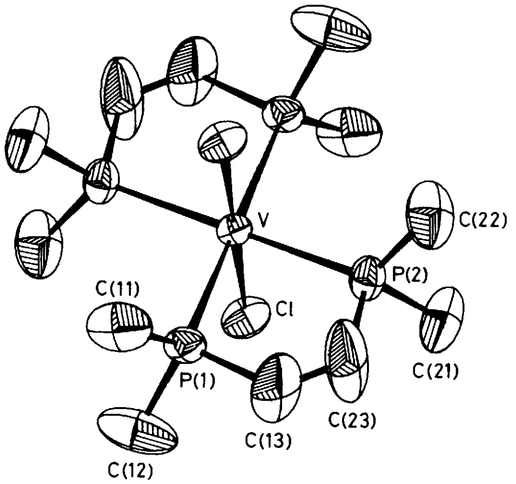


Figure 3. Structure of *trans*-$VCl_2(dmpe)_2$

+308), Cr (+314), Mn (+26), Co (−54), Ni (−255).[34] A similar trend was observed in the trivalent compounds $M(acac)_3$ [acac = acetylacetonate(1−)] from titanium to iron.[35] In both cases, it was demonstrated that the pseudo-contact contribution to the chemical shift was negligible, and that the contact shift term was responsible for this variation with the metal. The contact shifts in turn depended on the amount and nature of charge transfer between the metal *d* orbitals (which steadily decrease in energy with increasing nuclear charge) and the ligand π system (either cyclopentadienyl or acac).[35,36]

The pseudo-contact term is proportional, *inter alia*, to the degree of *g*-anisotropy ($g_\parallel - g_\perp$) and the inverse cube of the metal–proton distance.[36] For $VCl_2(dmpe)_2$ and the $MnX_2(dmpe)_2$ complexes, *g* is essentially isotropic and the metal–proton distances are rather long at *ca.* 3—4 Å. In these cases, at least, the pseudo-contact contribution will be small, and it is reasonable to suggest that this will generally be true for all the $MX_2(dmpe)_2$ compounds. Accordingly, the contact term is expected to dominate as it does in the $M(\eta^5\text{-}C_5H_5)_2$ and $M(acac)_3$ series. Nevertheless, while an upfield trend is observed from $TiCl_2(dmpe)_2$ through $CrCl_2(dmpe)_2$, the dmpe resonances in $MnX_2(dmpe)_2$ complexes are shifted well *downfield*. This is evidently not a halide effect, since $MnBr_2(dmpe)_2$ and $MnI_2(dmpe)_2$ have nearly identical shifts. Instead, we propose that the population of the e_g orbitals in these high-spin complexes is responsible for this anomaly. In contrast to cyclopentadienyl and acac groups, the dmpe ligands do not have a delocalized π system, and thus transmission of spin density on to the ligand must largely occur *via* σ orbitals. The population of the metal e_g orbitals (which have σ symmetry with respect to the ligands) would therefore be expected to have a comparatively large effect on the ligand spin density. Evidently, this effect is opposite in sign relative to that of electrons in the pseudo-t_{2g} set, so that the ^1H n.m.r. resonances in the $MnX_2(dmpe)_2$ complexes are shifted far downfield.

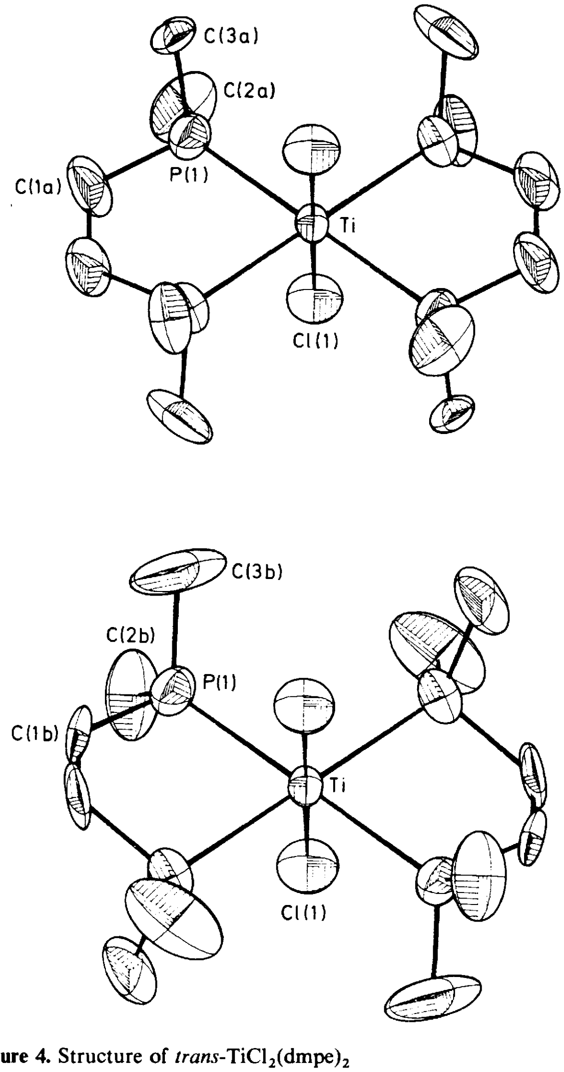


Figure 4. Structure of *trans*-$TiCl_2(dmpe)_2$

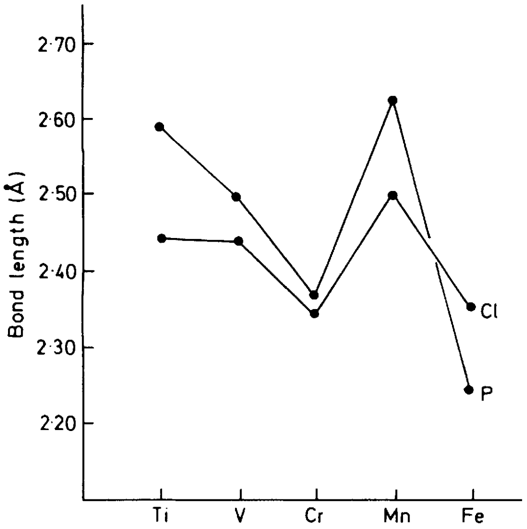


Figure 5. Variations in M–Cl and M–P distances in $MCl_2(dmpe)_2$

Molecular Structures of the Halide Complexes.—The structures of $VCl_2(dmpe)_2$ and $TiCl_2(dmpe)_2$, as representatives of the whole group, are shown in Figures 3 and 4. All compounds have the *trans* dihalide geometry which has been previously confirmed[37] for *trans*-$FeCl_2(dmpe)_2$. Selected bond lengths and angles are given in Table 4; variations in M–Cl and M–P distances are also plotted in Figure 5. In the $TiCl_2(dmpe)_2$ and $MnBr_2(dmpe)_2$ molecules, and to a slight extent in one of the two crystallographically independent molecules in each of the V and Cr structures, the geometry of the dmpe ligands is affected by disorder (see Experimental section). The dearth of related M^{II} structures does not allow any detailed general discussion of these structures, although of course they lend themselves to internal comparison. Nevertheless, a few structures of some relevance have been previously described, and it is useful first to mention these. Thus we find the V–Cl bond length here to be slightly shorter than the equivalent bond (2.462 Å) in $VCl_2(py)_4$ (py = pyridine),[38] whilst the Mn–Br bond length compares well with the Mn–Cl bond in $MnCl_2(dmpb)_2$, 2.502(1) Å,[14] when allowance is made for the difference in Br and Cl atomic radii. These data are consistent with a slight strengthening of the V–Cl bonds when the equatorial ligands change from a σ-only (or potentially π donating) pyridine to π-acceptor phosphines. The Ti–P bond in $TiCl_2(dmpe)_2$ is some 0.04 Å longer than those in $Ti(\eta^5\text{-}C_5H_4Me)_2(dmpe)_2$,[26c] possibly a reflection of differing steric factors coupled with a greater formal electron count on the metal in the C_5H_4Me complex allowing some π-electron drift to the phosphorus atoms. The V–P bond in $VCl_2(dmpe)_2$ is just slightly shorter (0.02 Å) than that in $V(oep)(PMe_2Ph)_2$,[25] which again may be a reflection of steric factor differences, as is also the fact that the Mn–P distance in $MnBr_2(dmpe)_2$ is 0.03 Å longer than in the dmpb structure mentioned above.[14]

Clearly, the most significant features to arise from analyses are the variations in M–Cl and M–P bond lengths within the series.

Most notable is the fact that the Ti–Cl and V–Cl bond lengths are essentially equal within experimental error, whilst the Ti–P and V–P lengths show a decrease of *ca.* 0.09 Å, as would be expected. A similar decrease occurs for the M–Cl bonds on going from V^{II} to Cr^{II}, but the difference between the V–P and Cr–P bond lengths is 0.13 Å. We view these differences to be consistent with a gradual decrease in M^{II} radius across the series coupled with an additional decrease in Cr–P bond length due to the possibility of Cr–P π bonding, and an increase in the strength (coupled with a decrease in length) of the Ti–Cl bond due to the avidity of the electron-poor Ti^{II} centre for extra electron density.

Finally, the increase in both M–Cl and M–P lengths on reaching manganese is consistent with the high-spin d^5 configuration and a large Mn^{2+} radius.

Methyl Complexes.—The $MX_2(dmpe)_2$ complexes can be alkylated with either methyl-lithium or dimethylmagnesium to give the dimethyl species $MMe_2(dmpe)_2$ for vanadium, chromium, manganese, and iron; all these species are various shades of orange. The stereochemistries of the complexes are *trans* except in the case of iron, where *cis*-$FeMe_2(dmpe)_2$ is the main product (see below). All these complexes are air- and moisture-sensitive, and are soluble in hydrocarbons and ethers.

Many attempts were made to isolate the titanium analogue, $TiMe_2(dmpe)_2$, without success. Stoicheiometric alkylation of $TiCl_2(dmpe)_2$ with LiMe or with $MgMe_2$ under a variety of conditions led only to the isolation of a red-black material of stoicheiometry *trans*-$TiMe_{1.3}Cl_{0.7}(dmpe)_2$. We therefore consider that the crystals isolated were a mixture of $TiMeCl(dmpe)_2$ and $TiMe_2(dmpe)_2$ (see below). With excess LiMe, an insoluble orange precipitate is formed that is thermally unstable at room temperature.

These methyl complexes include the first examples of titanium(II) and vanadium(II) alkyls although the benzyl, $Li_2V(CH_2Ph)_4$, has been claimed.[39] The only other chromium(II) alkyls known are quadruply-bonded dimers,[21,40] while for manganese(II) there are the binary alkyls $[MnR_2]_n$[41] and the $Mn_2R_4(PR'_3)_2$ and $MnR_2(PR'_3)_2$ species alluded to earlier.[17,18] Only for iron(II) are alkyl derivatives common, for example, *cis*-$FeMe_2(PMe_3)_4$[42] is known, and *trans*-$FeMe_2(dmpe)_2$ has been prepared[43] *via* a synthetic route different from the one described above that can give the *cis* isomer. The *trans*-$MMe_2(dmpe)_2$ complexes provide an opportunity to investigate the structures of a series of organometallic species as a function of electron count, from 14-electron '$TiMeCl(dmpe)_2$' to 18 in $FeMe_2(dmpe)_2$.

Electronic Structures of the Methyl Complexes.—The magnetic moments of the $MMe_2(dmpe)_2$ compounds indicate low-spin configurations across the series, including the complex $MnMe_2(dmpe)_2$. The low-spin nature of the latter is most apparent in its orange colour, compared with the colourless halides $MnBr_2(dmpe)_2$ and $MnI_2(dmpe)_2$. While the moment of $MnMe_2(dmpe)_2$ is somewhat higher than the spin-only value, this is evidently due to traces of high-spin products formed by hydrolysis rather than an electronic degeneracy (see e.s.r. data below). The observed ground states of the methyl complexes are consistent with the higher ligand-field strengths of alkyls *vs.* halides, making the e_g orbitals prohibitively high in energy. Whereas the $MX_2(dmpe)_2$ species resemble the metallocenes electronically, the $MMe_2(dmpe)_2$ species resemble $M(\eta^5\text{-}C_5Me_5)_2$,[33] which exclusively adopt low-spin configurations.

As was observed for the halide complexes, only $VMe_2(dmpe)_2$ and $MnMe_2(dmpe)_2$ give *X*-band e.s.r. spectra. The spectrum of $VMe_2(dmpe)_2$ at −196 °C is similar to its chloride analogue (Figure 1) and the Hamiltonian parameters deduced indicate, as expected, a larger zero-field splitting in the methyl complex. The frozen-solution spectrum of $MnMe_2(dmpe)_2$ in contrast is very different from its halide analogues, comprising a complex pattern near $g = 2$ (Figure 6). The sextet of binomial quintets evident is due to ^{55}Mn and ^{31}P hyperfine structure, respectively, and the spectrum is rather similar to that observed for the $S = \frac{1}{2}$ manganese metallacycle $Mn[o\text{-}(CH_2)_2C_6H_4](dmpe)_2$.[18] The small degree of g-anisotropy in $MnMe_2(dmpe)_2$ is not

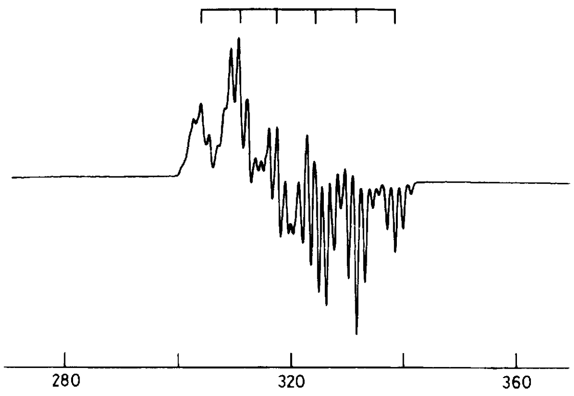


Figure 6. E.s.r. spectrum of *trans*-$MnMe_2(dmpe)_2$

Table 5. Molecular geometry parameters [distances (Å) and angles (°)] for $CrMe_2(dmpe)_2$ and '$TiMe_{1.3}Cl_{0.7}(dmpe)_2$'

	$CrMe_2(dmpe)_2$	$TiMe_{1.3}Cl_{0.7}(dmpe)_2$
M–C	2.168(4)	2.351(1)
M–P	2.342(1), 2.349(1)	2.520(1), 2.529(1)
P–C(CH_2)	1.846(9), 1.857(4)	1.859(3), 1.847(3)
P–C(Me)	1.822(4)—1.829(4)	1.820(3)—1.847(3)
C(CH_2)–C(CH_2)	1.514(6)	1.522(5)
P–M–P	82.7(1)	78.7(1)
M–P–C(CH_2)	108.8(2), 109.8(2)	110.0(2), 108.6(2)
M–P–C(Me)	119.2(2)—123.1(2)	117.7(2)—122.7(2)

consistent with an orbitally degenerate ground state such as that observed in $Mn(\eta^5-C_5Me_5)_2$.[32]

For the most part, the ^1H n.m.r. spectra of the paramagnetic methyl complexes resemble their respective halide analogues. However, the ^1H n.m.r. resonances of $MnMe_2(dmpe)_2$ are well upfield of those of $MnBr_2(dmpe)_2$ and $MnI_2(dmpe)_2$, and this is a further consequence of the differing spin states in these complexes. In no case was a resonance observed due to the metal-bound methyl groups; for $CrMe_2(dmpe)_2$ the search extended from δ +300 to −300 p.p.m. Evidently these protons experience very large contact shifts due to their proximity to the paramagnetic centre.

The ^1H n.m.r. spectrum of diamagnetic $FeMe_2(dmpe)_2$ confirms the *cis* geometry, with four different dmpe methyl environments discernible. The metal-bound methyl groups appear at δ − 0.64 as a second-order pattern that approximates to a binomial quartet. In the $^{13}C-\{^1H\}$ n.m.r. spectrum, the Fe–Me groups resemble a quintet at δ − 1.3, while the $^{31}P-\{^1H\}$ n.m.r. spectrum is a deceptively simple AA′BB′ pattern consisting of two 1:2:1 triplets.

The i.r. spectra of the methyl complexes contain absorptions not present in their halide precursors, and these additional features may be assigned to various modes involving the metal-bound methyl groups: ν(CH) at *ca.* 2 800, δ(CH) at *ca.* 1 100, ν(MC) at *ca.* 600, and δ(MC) at *ca.* 400 cm^{-1}.

The C–H stretching frequency exhibits a remarkable variation with the metal: Ti (2 750), V (2 758), Cr (2 785), Mn (2 800), Fe(>2 800 cm^{-1}). The ν(CH) absorption in the iron complex evidently is obscured by the C–H modes above 2 800 cm^{-1} due to the dmpe ligands, and such a location is typical of methyl groups bound to transition metals. However, the frequency steadily decreases as the number of valence electrons decreases, until ν(CH) for '$TiMeCl(dmpe)_2$' has an anomalously low energy. Absorptions in this region have previously been observed for some alkyl groups that bridge two transition metals,[17,41] and for some distorted alkylidene species with unusually small M–C–H angles.[44] In both cases, significant M···HC contacts[45] are responsible for the appearance of low-frequency bands in the i.r.

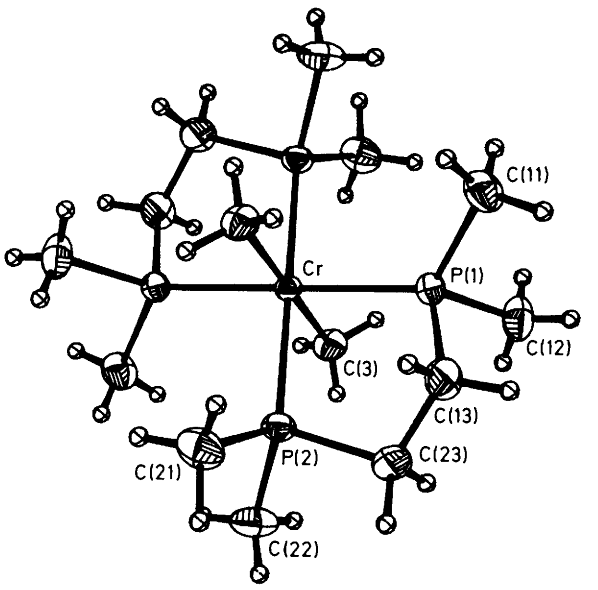
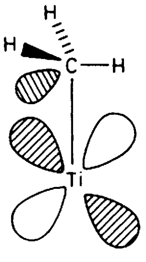


Figure 7. Structure of *trans*-$CrMe_2(dmpe)_2$

Structures of the Methyl Complexes.—The structure of the chromium dimethyl complex is given in Figure 7. The titanium complex, which must be considered a mixture of $TiMe_2(dmpe)_2$ and $TiMeCl(dmpe)_2$ (see Experimental section) is isostructural with the metal atoms lying on centres of symmetry. Selected bond lengths and angles are given in Table 5. Since it proved impossible to separate out Cl and methyl C sites in the Ti complex, it is possible that the Ti–C and Ti–Cl distances are rather similar. Bearing in mind the difference in M^{II} radii suggested by the variations in bond lengths in the dihalides, this is not impossible. Thus, if the Ti–Cl bonds in the dihalide are indeed shortened by additional electron drift to the metal, we might expect a monochloride to show this effect to a greater extent, giving a Ti–Cl bond perhaps as short as 2.40 Å. Additionally, on the basis of a Cr^{II}–C distance of 2.17 Å, we might expect a Ti^{II}–C distance of 2.17 + (2 × 0.08) = 2.33 Å (*ca.* 0.08 Å for each gap between metals). These two effects could therefore bring the Ti–Cl and Ti–C distances very close.

The structure of the chromium complex is very well defined, with all hydrogen atoms experimentally located and freely refined. The most significant feature is the indication that the CH_3 group bonds almost symmetrically, and that there is no Cr···H interaction. The Cr–C distance is similar to the terminal Cr–C bond length in the quadruply-bonded dimer $[Cr^{II}(CH_2SiMe_3)_2(PMe_3)]_2$ [21] although the Cr–P bonds in the monomer are *ca.* 0.1 Å shorter than those in the dimer. They are also slightly shorter than those in the chromium dihalide.

Although the disorder problem complicated the final definition of the structure of the chloromethyltitanium complex, it is worth commenting that at the end of the refinement, peaks were present in the neighbourhood of the C/Cl axial site, which could be refined as hydrogen atoms with the relevant occupancy factor (0.65). Moreover, the three positions corresponded to a slightly tilted CH_3 group, although with the rather large uncertainties attached to the positioning of these atoms we are not able to claim any confidence in the *X*-ray results.



(I)

The i.r. data leave little doubt that there is a significant perturbation in the C–H bond force constants. This in turn is a reflection of a change in the electron density, and may be due to a Ti••• H–C interaction such as that recently observed in $TiMeCl_3(dmpe)$.[46] This interaction would involve donation of C–H bonding electrons into an empty metal *d* orbital of π symmetry, as in (I).

Accordingly, the relevant *d* orbital must be one of the pseudo-t_{2g} set, and of all the $MX_2(dmpe)_2$ complexes discussed, only the d^2 titanium species possess a completely empty t_{2g} orbital. It has been suggested previously that a low-lying *vacant* orbital of proper symmetry is necessary to induce M ••• HC interactions, and that half-filled orbitals will not, despite a low electron count.[18]

We have no crystallographic data on d^3, $VMe_2(dmpe)_2$, but the above argument suggests that little distortion of the V–C–H angles should occur, much as was observed for d^4, $CrMe_2(dmpe)_2$. The peculiar i.r. stretching frequencies in these latter two complexes probably are a result only of the electropositive nature of the metal centres, which would polarize the M–C bond and concomitantly alter the C–H bond density. A vibrational study of the labelled complexes $M(CD_3)_2(dmpe)_2$ would test this hypothesis.

Experimental

Microanalyses were by Pascher (Bonn). Spectrometers: n.m.r., Perkin-Elmer R32 (^1H, 90 MHz), JEOL FX-90Q (^1H), Bruker WM 250 (^1H, ^{13}C, ^{31}P), positive chemical shifts downfield of $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P); e.s.r., Varian E-12 (*X*-band); i.r., Perkin-Elmer 683 (Nujol mulls, data in cm^{-1}). Magnetic moments were determined in toluene by a modification of Evans' method.[47] Melting points are uncorrected, and were determined in closed capillaries under argon.

All operations were carried out in vacuum or under purified argon using standard techniques. Solvents were distilled from sodium (toluene) or sodium–benzophenone [light petroleum (b.p. 40—60 °C), diethyl ether, or thf] under nitrogen immediately before use.

1,2-Bis(dimethylphosphino)ethane was prepared *via* a literature route.[48] Dimethylmagnesium and methyl-lithium were prepared from methyl chloride in diethyl ether and used as stock solutions. Anhydrous $MnCl_2$ was prepared by action of $SOCl_2$ on the hydrate followed by evacuation at 200 °C, $MnBr_2$ was obtained by heating the hydrate under vacuum to constant weight, while MnI_2 was prepared from manganese metal and iodine in diethyl ether. Both $TiCl_4$ and anhydrous $FeCl_2$ were obtained commercially and used without purification.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichlorotitanium*(II).—To a suspension of magnesium turnings (0.30 g, 12.3 mmol) in dmpe (3.0 cm^3, 20.0 mmol) and thf (150 cm^3) was added $TiCl_4$ (1.0 cm^3, 9.1 mmol). An exothermic reaction occurred immediately, and the initially yellow solution changed colour over 1 h through orange-red, dark yellow, green, blue, green, dark yellow, and finally dark orange. After stirring for a further 12 h, the solvent was removed, and the residue extracted with diethyl ether (3 × 100 cm^3). The combined extracts were filtered, treated with dioxane (1 cm^3), and filtered again. Concentration of the solution to *ca.* 200 cm^3 and cooling to −20 °C gave red-black needles of the complex. Two additional crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 2.65 g (70%). I.r.: 2 810w, 1 421s, 1 300s, 1 283s, 1 138m, 1 089w, 995m, 945vs, 928s, 892s, 865m, 834m, 792m, 733s, 700s, 640m, 441w, 320s [ν(TiCl)].

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichlorovanadium*(II).—To a suspension of '$VCl_2(thf)_2$'[4] (3.37 g, 12.7 mmol) in toluene (75 cm^3) was added dmpe (3.8 cm^3, 25.3 mmol). The solution slowly developed a red-purple colour, and was stirred for 24 h. The solution was filtered, concentrated to *ca.* 50 cm^3, and cooled to −20 °C to give bright red-orange prisms of the complex. Two further crops of crystals may be obtained from the supernatant. Yield: 3.05 g (57%). I.r.: 2 810w, 1 420s, 1 298s, 1 280s, 1 240w, 1 132m, 1 126m, 1 083m, 990m, 950vs, 925s, 888s, 863m, 841m, 832m, 791w, 735s, 700s, 640s, 627w, 439m, 312s [ν(VCl)].

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichlorochromium*(II).—To a suspension of $CrCl_2(thf)$[5] (5.57 g, 28.6 mmol) in toluene (150 cm^3) was added dmpe (8.5 cm^3, 56.7 mmol). The solution rapidly developed a brilliant apple green colour, and became noticeably warm. After 2 h, the solution was filtered, concentrated to *ca.* 100 cm^3, and cooled to −20 °C. The large yellow-green prisms were collected, and further crops may be obtained by concentration and cooling of the supernatant. Yield: 10.2 g (85%). I.r.: 2 810w, 1 420vs, 1 294s, 1 280s, 1 260w, 1 228w, 1 138m, 1 072m, 986m, 940vs, 923(sh), 890s, 861m, 840(sh), 833m, 783m, 731s, 700s, 632s, 452m, 375m, 338m [ν(CrCl)].

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dibromomanganese*(II).—To a suspension of $MnBr_2$ (2.66 g, 12.4 mmol) in dichloromethane (80 cm^3) was added dmpe (4.0 cm^3, 24.0 mmol). After 24 h, the $MnBr_2$ had dissolved, giving a pale yellow solution. The solution was filtered, concentrated to *ca.* 40 cm^3, and cooled to −20 °C. The large colourless prisms which form become opaque upon isolation. Further crops of crystals may be obtained from the supernatant. Recrystallization from toluene–dichloromethane (2:1) gives colourless prisms that remain transparent upon isolation. Yield: 6.38 g (77%). I.r.: 2 815w, 1 420s, 1 300s, 1 281s, 1 147s, 1 096m, 999m, 950vs, 895m, 870m, 834m, 803w, 735s, 704s, 642m, 633w, 434w.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*di-iodomanganese*(II).—To a suspension of MnI_2 (1.64 g, 5.31 mmol) in dichloromethane (50 cm^3) was added dmpe (1.7 cm^3, 11.3 mmol). The MnI_2 rapidly dissolved to give a pale orange solution. After 30 min, the solution was filtered, concentrated to *ca.* 30 cm^3, and cooled to −20 °C. Colourless prisms of the complex formed which became opaque upon isolation. The complex may be recrystallized from toluene to give transparent plates. Yield: 2.6 g (80%). I.r.: 2 810w, 1 420s, 1 415s, 1 300m, 1 283m, 1 138m, 1 093m, 994m, 955vs, 944vs, 932(sh), 887m, 866m, 842w, 829m, 802w, 736s, 701s, 642m, 632w, 628w.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichloroiron*(II).—To a suspension of $FeCl_2$ (1.06 g, 8.35 mmol) in toluene (100 cm^3) was added dmpe (2.75 cm^3, 16.5 mmol). The solution immediately developed a bright green colour, and was stirred for 4 h. The solution was filtered, concentrated to *ca.* 60 cm^3, and cooled to −20 °C. Emerald green crystals of the complex were obtained, and several further crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 3.21 g (90%). N.m.r. ^{13}C-{^{1}H} (C_6D_6, 25 °C): δ 30.3 [PCH_2, 'quin', 'J(PC)' = 12.3] and 13.0 [P*Me*$_2$, 'quin', 'J(PC)' = 5.2]; ^{31}P-{^{1}H} (C_6D_6, 25 °C): δ 59.4 [s, J(Fe–P) = 33.6 Hz].

'trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(*methyl*)-*titanium*(II)'.—To a solution of $TiCl_2(dmpe)_2$ (1.25 g, 2.96 mmol) in diethyl ether (50 cm^3) was added LiMe (5.3 cm^3 of a 1.1 mol dm^{-3} solution in diethyl ether, 5.83 mmol). A slight darkening of the solution occurred, and stirring was continued for 4 h. The solvent was removed, and the residue extracted with light petroleum (50 cm^3). The extract was filtered, concentrated to *ca.* 15 cm^3, and cooled to −20 °C to give red-black prisms of the complex. A second crop of crystals was obtained from the supernatant. Yield: 0.32 g (27%). I.r.: 2 810w, 2 750w [ν(CH)], 1 420s, 1 291s, 1 275s, 1 242w, 1 111m, 1 096m [δ(CH)], 1 075m, 985m, 940vs, 908(sh), 882s, 860w, 827m, 800w, 778s, 724s, 689s, 616s, 448w, 428m, 355m [ν(Ti–Cl)].

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dimethylvanadium*(II).—To a suspension of $VCl_2(dmpe)_2$ (0.46 g, 1.09 mmol) in diethyl ether (50 cm^3) was added LiMe (2.0 cm^3 of a 1.1 mol dm^{-3} solution in diethyl ether, 2.20 mmol). The solution slowly turned dark orange and after 1 h the solvent was removed. The residue was extracted with light petroleum (50 cm^3), the filtered extract concentrated to *ca.* 15 cm^3 and cooled to −20 °C to give dark yellow needles of the complex. Yield: 0.20 g (48%). I.r.: 2 758m [ν(CH)], 1 420s, 1 290s, 1 275s, 1 125m, 1 100m [δ(CH)], 1 074m, 983m, 940vs, 878s, 851m, 822s, 786w, 720s, 690s, 632s, 544m, 435m, 412s.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dimethylchromium*(II).—To a suspension of $CrCl_2(dmpe)_2$ (2.59 g, 6.12 mmol) in diethyl ether (70 cm^3) was added LiMe (12.0 cm^3 of a 1.1 mol dm^{-3} solution in diethyl ether, 13.2 mmol). The solution immediately turned orange, and after stirring for 4 h, the solvent was removed. The residue was extracted with light petroleum (130 cm^3) and the filtered extract concentrated to *ca.* 50 cm^3 and cooled to −20 °C. Bright red-orange prisms of the complex were isolated, and two further crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 2.0 g (85%). I.r.: 2 785m [ν(CH)], 1 420s, 1 290s, 1 276s, 1 220w, 1 110m, 1 065m, 987w, 930vs, 920(sh), 882s, 855w, 828m, 780m, 719s, 690s, 622s, 609(sh), 453m, 445m, 385m.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dimethylmanganese*(II).—(*a*) *From* $MnCl_2$. To a suspension of $MnCl_2$ (0.54 g, 4.29 mmol) and dmpe (1.4 cm^3, 9.33 mmol) in diethyl ether (50 cm^3) at −78 °C was added $MgMe_2$ (6.8 cm^3 of a 0.62 mol dm^{-3} solution in diethyl ether, 4.22 mmol). On warming to room temperature, the solution turned orange, and stirring was continued for a further 3 h. The solvent was removed, the residue extracted with light petroleum (50 cm^3), and the filtered extract concentrated to *ca.* 20 cm^3 and cooled to −20 °C. Dark orange prisms of the complex were isolated, and a further crop of crystals were obtained from the supernatant. Yield: 1.3 g (77%). I.r.: 2 810w, 2 800m [ν(CH)], 1 420s, 1 290s, 1 276s, 1 260w, 1 225m, 1 116m, 1 063m, 990w, 930vs, 883s, 852w, 829s, 787s, 711s, 687s, 634s, 462m, 450w, 406s.

(*b*) *From* $MnBr_2(dmpe)_2$. To a suspension of $MnBr_2(dmpe)_2$ (0.82 g, 1.59 mmol) in diethyl ether (50 cm^3) was added $MgMe_2$ (2.5 cm^3 of a 0.62 mol dm^{-3} solution in diethyl ether, 1.55 mmol). The solution turned orange and was stirred for 12 h. The solvent was removed, and the residue treated as above. Yield: 0.40 g (66%).

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dimethyliron*(II).—To a suspension of $FeCl_2(dmpe)_2$ (0.52 g, 1.22 mmol) in diethyl ether (50 cm^3) was added $MgMe_2$ (2.0 cm^3 of a 0.62 mol dm^{-3} solution in diethyl ether, 1.24 mmol). The solution initially turned red and subsequently bright yellow. After stirring for 2 h, the solvent was removed immediately and the residue extracted with light petroleum (50 cm^3). The filtered solution was concentrated to *ca.* 5 cm^3, and cooled to −20 °C to give orange prisms. Yield: 0.31 g (68%). If the initial solution is allowed to stand, isomerisation occurs and rapid work-up is required to avoid formation of substantial amounts of *trans* isomer (*ca.*

Table 6. Crystal data, details of intensity measurement, and structure refinement for $MCl_2(dmpe)_2$ [M = Ti (**A**), V (**B**), or Cr (**C**)], $MnBr_2(dmpe)_2$ (**D**), '$TiMe_{1.3}Cl_{0.7}$ $(dmpe)_2$' (**E**), and $CrMe_2(dmpe)_2$ (**F**)

Complex	(**A**)	(**B**)	(**C**)	(**D**)	(**E**)	(**F**)
M	419.09	422.13	432.19	515.03	392.55	382.35
Crystal system	Tetragonal	Monoclinic	Monoclinic	Tetragonal	Triclinic	Triclinic
a/Å	13.826(2)	13.242(2)	13.086(2)	14.014(2)	7.480(2)	7.524(1)
b/Å	13.826(2)	12.605(6)	12.440(3)	14.014(2)	9.039(1)	8.751(1)
c/Å	12.089(2)	13.255(5)	13.227(2)	12.220(7)	9.104(1)	9.132(1)
α/°	90	90	90	90	104.37(1)	103.91(1)
β/°	90	93.06(2)	92.82(1)	90	105.29(1)	106.18(1)
γ/°	90	90	90	90	100.61(1)	102.35(1)
U/Å^3	2 310.7	2 209.1	2 150.7	2 400.2	554.3	534.5
Space group	$P4_2/ncm$	$P2_1/a$	$P2_1/a$	$P4_2/ncm$	$P\bar{1}$	$P\bar{1}$
D_c/g cm^{-3}	1.204	1.269	1.306	1.424	1.176	1.187
Z	4	4	4	4	1	1
μ/cm^{-1}	4.82	9.00	9.94	40.21	7.73	7.59
$\theta_{min.}$, $\theta_{max.}$/°	2.0, 25.0	1.5, 25.0	1.5, 30.0	1.5, 25.0	1.5, 25.0	1.5, 28.0
Total unique data	1 084	3 883	6 786	1 134	2 415	2 574
Total observed $F_0 > 3\sigma(F_0)$	681	2 089	3 469	720	2 026	2 055
No. of parameters	74	248	310	74	164	164
Weight factor, g	0.000 25	0.0003	0.0005	Unit weights	0.0001	0.0004
Final R	0.064	0.059	0.055	0.072	0.031	0.030
Final R'	0.060	0.050	0.056	0.072	0.033	0.031
Treatment of H atoms	*a*	*b*	*a*	*a*	*c*	*c*

[a] Hydrogen atoms not included. [b] Hydrogen atoms inserted in idealised positions using AFIX facility in SHELX. [c] All hydrogens located and experimentally refined with isotropic thermal parameters.

Table 7. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

(*a*) $TiCl_2(dmpe)_2$

Atom	*x*	*y*	*z*
Ti(1)	5 000	5 000	5 000
Cl(1)	4 377(1)	4 377(1)	6 754(2)
P(1)	4 948(1)	3 288(1)	4 142(2)
C(1a)	3 743(12)	2 960(12)	3 612(18)
C(1b)	3 885(11)	3 342(9)	3 174(13)
C(2a)	5 238(15)	2 227(13)	5 069(20)
C(2b)	4 689(15)	2 183(14)	4 982(19)
C(3a)	5 741(12)	3 008(14)	2 982(13)
C(3b)	6 020(20)	2 890(19)	3 325(23)

(*b*) $MnBr_2(dmpe)_2$

Atom	*x*	*y*	*z*
Mn(1)	5 000	5 000	5 000
Br(1)	4 342(1)	4 342(1)	6 902(2)
P(1)	4 955(3)	3 256(3)	4 154(3)
C(1a)	3 754(24)	3 009(23)	3 627(36)
C(1b)	3 933(23)	3 369(20)	3 158(26)
C(2a)	5 152(35)	2 200(31)	4 988(47)
C(2b)	4 691(33)	2 148(32)	4 938(45)
C(3a)	5 704(34)	2 962(36)	3 046(43)
C(3b)	5 876(51)	2 843(47)	3 038(66)

(*c*) $TiMe_{1.3}Cl_{0.7}(dmpe)_2$

Atom	*x*	*y*	*z*
Ti	0	0	0
P(1)	2 544(1)	2 163(1)	2 334(1)
P(2)	1 041(1)	1 949(1)	−1 367(1)
C(11)	4 623(5)	1 787(4)	3 621(4)
C(12)	1 747(5)	3 406(4)	3 797(3)
C(13)	3 771(4)	3 668(3)	1 599(3)
C(23)	2 355(5)	3 882(3)	174(3)
C(21)	−690(5)	2 558(4)	−2 770(4)
C(22)	2 766(6)	1 626(5)	−2 416(5)
Cl	2 310(2)	−1 366(2)	−390(2)

(*d*) $CrMe_2(dmpe)_2$

Atom	*x*	*y*	*z*
Cr(1)	0	0	10 000
P(1)	961(1)	1 837(1)	8 679(1)
P(2)	2 393(1)	2 055(1)	12 271(1)
C(11)	−760(5)	2 443(4)	7 250(4)
C(12)	2 646(5)	1 513(4)	7 617(4)
C(13)	2 354(4)	3 882(3)	10 189(3)
C(21)	1 658(5)	3 296(4)	13 768(3)
C(22)	4 445(4)	1 663(4)	13 597(4)
C(23)	3 727(4)	3 674(3)	11 642(3)
C(3)	−2 109(4)	1 266(3)	10 336(3)

(*e*) $VCl_2(dmpe)_2$

Atom	*x*	*y*	*z*
V(1)	0	0	0
Cl(1)	611(1)	1 417(1)	1 137(1)
P(1)	17(1)	−1 270(1)	1 451(1)
C(11)	185(7)	−2 674(6)	1 233(6)
C(12)	807(8)	−1 045(7)	2 575(6)
C(13)	−1 232(7)	−1 186(9)	1 930(8)
P(2)	−1 764(1)	291(1)	516(2)
C(21)	−2 132(6)	1 545(6)	1 017(7)
C(22)	−2 831(6)	−24(7)	−335(8)
C(23)	−1 936(7)	−615(9)	1 557(8)
V(2)	5 000	5 000	0
Cl(2)	5 568(2)	3 497(1)	1 035(1)
P(3)	5 093(2)	3 833(2)	−1 518(1)
C(31)	5 161(6)	4 419(6)	−2 757(5)
C(32)	6 051(7)	2 798(6)	−1 538(6)
C(33)	3 908(6)	3 102(6)	−1 643(6)
P(4)	3 215(1)	4 348(2)	−107(1)
C(41)	2 138(6)	5 221(8)	−8(7)
C(42)	2 886(6)	3 261(6)	707(5)
C(43)	3 012(6)	3 818(7)	−1 393(5)

(*f*) $CrCl_2(dmpe)_2$

Atom	*x*	*y*	*z*
Cr(1)	0	0	0
Cl(1)	1 106(1)	1 392(1)	556(1)
P(1)	−1 397(1)	−1 216(1)	−22(1)
C(11)	−2 532(7)	968(10)	−823(12)
C(12)	−1 184(5)	2 639(4)	−168(8)
C(13)	−2 025(6)	1 089(7)	1 182(6)
P(2)	−443(1)	−267(1)	1 694(1)
C(21)	−974(6)	−1 551(5)	2 058(4)
C(22)	533(7)	−29(7)	2740(5)
C(23)	−1 401(6)	755(7)	1 993(5)
Cr(2)	0	5 000	5 000
Cl(2)	1 014(1)	3 540(1)	5 553(1)
P(3)	−1 466(1)	3 895(1)	5 115(1)
C(31)	−2 713(4)	4 534(6)	5 208(6)
C(32)	−1 527(7)	2 866(8)	6 104(9)
C(33)	−1 681(4)	3 140(6)	3 915(5)
P(4)	−85(1)	4 385(1)	3 304(1)
C(41)	726(4)	3 261(5)	2 968(5)
C(42)	40(7)	5 257(6)	2 221(5)
C(43)	−1 388(4)	3 818(5)	3 050(4)

20% after 2 h). I.r.: 2 810w, 1 420s, 1 290s, 1 272s, 1 226w, 1 188w, 1 152m, 1 115w, 1 062m, 986w, 930vs, 902w, 882s, 830s, 786m, 708s, 696s, 680s, 635s, 462m, 408m [δ(FeC)], 360m [δ(FeC)]. N.m.r: $^{13}C-\{^1H\}$ (C_6D_6, 25 °C), δ 34.7 [P*C*H_2, 'quin', '*J*(PC)' = 12.0], 28.4 [P*C*H_2, 'quin', '*J*(PC)' = 10.0], 22.1 [P*Me*$_2$, 't', '*J*(PC)' = 5.8], 18.9 [P*Me*$_2$, d, '*J*(PC)' = 3.4], 16.1 [P*Me*$_2$, 't', '*J*(PC)' = 7.7], 9.0 [P*Me*$_2$, 't', '*J*(PC)' = 10.9], and −1.3 [Fe-*Me*, 'quin', '*J*(PC)' = 23.5 Hz]; $^{31}P-\{^1H\}$ (C_6D_6, 25 °C) (AA′BB′ pattern), δ_A = 77.1, δ_B = 61.9, '*J*(AB)' = 27.1 Hz.

X-Ray Crystallographic Studies.—Crystals of all compounds were sealed under argon in thin-walled glass capillaries. Orientation matrices and associated cell dimension and intensity data were obtained following previously described procedures,[49] using an Enraf-Nonius CAD4 diffractometer and graphite monochromatised Mo-K_α radiation [λ(Mo-K_α) = 0.710 69 Å] at ambient temperature (295 K). The structures were solved *via* standard heavy-atom methods and refined by using full-matrix least squares,[50] with scattering factors based on parameters given in ref. 51; details are given in Table 6. The refinements were mostly straightforward, except for disorder problems in the case of the 'chloro–methyl' of titanium, and the tetragonal structures of $TiCl_2(dmpe)_2$ and $MnBr_2(dmpe)_2$.

The 'chloro-methyl' titanium complex crystallises in the triclinic space group $P\bar{1}$ with the metal atom sited on a centre of symmetry. The chlorine and methyl groups are thus disordered. At no time during the refinement of this structure were any indications given that the chlorine and carbon positions were separated, and in fact the refinement proceeded quite smoothly with the mixed site represented by a single atom. However, when this site was represented by a chlorine atom with an occupancy of 0.676, corresponding to an electron count of 11.5 ($\frac{1}{2}$Cl + $\frac{1}{2}$C), the thermal parameter was much higher than those of the phosphorus atoms. Equivalence between thermal parameters was achieved when the site was represented by a chlorine with an occupancy of 0.58, which corresponds to disorder of a system with the constitution $TiMe_{1.3}Cl_{0.7}$. This actually corresponds to the results of the elemental analysis for the bulk sample from which the crystal was chosen, and shows that the sample must be a mixture of $TiMe_2(dmpe)_2$ and $TiMeCl(dmpe)_2$ [or possibly $TiCl_2(dmpe)_2$]. It is probable therefore that the dimethyltitanium complex does exist. In the final stages of the refinement, peaks were present in the difference electron-density map near the axial site, which could be refined successfully as fractional (0.65) hydrogen atoms, and which suggested a 'tilted' methyl group. However, in view of the disorder present here, we cannot be confident that these particular results are completely reliable, and have not included these atoms in the final refinement.

In the case of the tetragonal $TiCl_2(dmpe)_2$ and $MnBr_2(dmpe)_2$ structures, the dmpe groups show disorder. The phosphorus atoms could each be represented by a single position, with fairly uniform anisotropic thermal parameters, but the methyl and methylene carbons were each disordered over two sites (labelled a and b in all tables and diagrams) and even then, the thermal motion was markedly anisotropic.

A small amount of disorder/high thermal motion also occurred for one of the two crystallographically independent molecules in $VCl_2(dmpe)_2$ and $CrCl_2(dmpe)_2$, leading to artificially low C–C distances between some of the dmpe methylene carbons.

Final atomic positional parameters are given in Table 7.

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