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Phosphine Complexes of Trivalent Early Transition Metals. X-ray Crystal Structure of the d^1–d^1 Dimer $[TiCl_3(dippe)]_2$ and Synthesis of the Alkyl $CrMeCl_2(dippe)(thf)$

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Treatment of $TiCl_3(thf)_3$ (thf = tetrahydrofuran) with the chelating phosphine 1,2-bis(diisopropylphosphino)ethane (dippe) gives two products: the purple dimer $[TiCl_3(dippe)]_2$ and the green monomer $TiCl_3(dippe)(thf)$. The two compounds may be readily interconverted by loss or addition of the thf ligand. The dimer is coupled antiferromagnetically, and its X-ray crystal structure reveals an octahedral geometry about each titanium(III) center and a Ti···Ti distance of 3.44 Å. The dippe ligands each chelate a titanium atom and are trans to the bridging chlorides; the dimer thus possesses approximate D_{2h} symmetry. Reactions of $MCl_3(thf)_3$, where M is vanadium or chromium, with dippe yield the monomeric thf adducts $MCl_3(dippe)(thf)$. The bromovanadium analogue $VBr_3(dippe)(thf)$ and the chromium acetonitrile adduct $CrCl_3(dippe)(MeCN)$ are also described. Addition of dippe to $CrMeCl_2(thf)_3$ gives the chromium(III) alkyl $CrMeCl_2(dippe)(thf)$ which has been shown to be a slow ethylene polymerization catalyst at room temperature. NMR and EPR studies of the dippe adducts are described. Crystal data for $[TiCl_3(dippe)]_2\cdot PhMe$: orthorhombic, space group *Pbcn*, with a = 15.586 (5) Å, b = 14.442 (4) Å, c = 21.639 (6) Å, V = 4871 (2) Å^3, Z = 4, R_F = 6.4%, R_{wF} = 6.6% for 196 variables and 1231 data with $I > 2.58\sigma(I)$.

Introduction

We have recently described the synthesis of coordinately unsaturated chromium(II) and iron(II) alkyls of stoichiometry $MR_2(dippe)$, where dippe is the bulky bidentate phosphine 1,2-bis(diisopropylphosphino)ethane.[1,2] These unusual 12- and 14-electron organometallic species are high spin (four unpaired electrons per metal center) and adopt square-planar (Cr) or tetrahedral (Fe) geometries that are rare for organometallic derivatives of these divalent metals. In addition, the $MR_2(dippe)$ alkyls readily react with small molecules such as CO and H_2 to give acyls[3] and hydrides;[4] in certain cases, hydrogenation in arene solvents leads to loss of alkane and formation of zerovalent π-arene complexes.[4] In general, the $MR_2(dippe)$ complexes provide an excellent opportunity to explore the chemistry of nonclassical (non-18-electron) organometallic species.

The $MR_2(dippe)$ alkyls are prepared from the corresponding halide complexes $MX_2(dippe)$.[5] We have been interested in comparing the structures and reactivities of these divalent molecules with corresponding trivalent derivatives of the early first-row transition metals. Suitable dippe adducts of the trivalent metal halides are therefore required to serve as starting materials. We now describe the coordination chemistry of dippe with the trichlorides of titanium, vanadium, and chromium. The synthesis of organometallic derivatives from these complexes has been explored briefly, and the preparation of a chromium(III) alkyl is detailed.

Results

The transformations observed in this study are summarized below. The spectroscopic properties and magnetic behavior of the new compounds are given in the Experimental Section and will be summarized in the Discussion.

Preparation of the Halo Complexes. Treatment of $TiCl_3(thf)_3$ with 1 equiv of dippe in diethyl ether yields two isolable products: a purple, ether-insoluble compound and a green, ether-soluble compound. Analytical data (Table I) lead to the stoichiometries $TiCl_3(dippe)$ (**1**) and $TiCl_3(dippe)(thf)$ (**2**) for the purple and green compounds, respectively. The green and purple compounds can be interconverted: an ether suspension of complex **1** turns green upon addition of excess thf, while **2** dissolves in toluene to give a purple solution. Furthermore, if the reaction of $TiCl_3(thf)_3$ with dippe is carried out in toluene, only the thf-free product, **1**, is isolated. The X-ray crystal structure of **1** is described in the Discussion.

$$\underset{\mathbf{1}}{\tfrac{1}{2}[TiCl_3(dippe)]_2} \underset{-thf}{\overset{+thf}{\rightleftharpoons}} \underset{\mathbf{2}}{TiCl_3(dippe)(thf)}$$

The reaction of $VCl_3(thf)_3$ with dippe in toluene yields orange prisms of the new complex $VCl_3(dippe)(thf)$ (**3**). We have found that crystallization from toluene is not consistently successful but that the same product may be obtained reproducibly as a bright yellow precipitate if the reaction is carried out in a 2:1 mixture of pentane and diethyl ether. The yellow precipitate is easier to isolate than the orange crystals from toluene, is analytically pure, and can be used in subsequent reactions. The bromide analogue $VBr_3(dippe)(thf)$ (**4**) can be obtained as a bright orange precipitate in a similar manner from $VBr_3(thf)_3$.

$$VX_3(thf)_3 + dippe \rightarrow \underset{\substack{\mathbf{3},\ X = Cl \\ \mathbf{4},\ X = Br}}{VX_3(dippe)(thf)} + 2thf$$

Interaction of $CrCl_3(thf)_3$ with dippe in pentane–diethyl ether yields the octahedral complex $CrCl_3(dippe)(thf)$ (**5**). Recrystallization of **5** from acetonitrile results in the isolation of the nitrile adduct $CrCl_3(dippe)(MeCN)$ (**6**). The IR spectrum of **6** shows bands at 2310 and 2276 cm^{-1} for coordinated acetonitrile.

$$CrCl_3(thf)_3 + dippe \rightarrow \underset{\mathbf{5}}{CrCl_3(dippe)(thf)} + 2thf$$

$$CrCl_3(dippe)(thf) + MeCN \rightarrow \underset{\mathbf{6}}{CrCl_3(dippe)(MeCN)} + thf$$

Preparation and Reactivity of $CrMeCl_2(dippe)(thf)$. Alkylation of $CrCl_3(dippe)(thf)$ with excess $AlMe_3$ gives a bright green solution that yields an impure green oil. If the reaction of $CrCl_3(thf)_3$ with $AlMe_3$ is carried out in the absence of dippe, however, $CrMeCl_2(thf)_3$ can be isolated as green crystals free of aluminum-containing impurities.[6] Addition of 1 equiv of dippe to this complex displaces two thf molecules, and the green chromium alkyl $CrMeCl_2(dippe)(thf)$ (**7**) may be isolated and purified by recrystallization from thf.

$$CrMeCl_2(thf)_3 + dippe \rightarrow \underset{\mathbf{7}}{CrMeCl_2(dippe)(thf)} + 2thf$$

Attempts to prepare trialkyl derivatives by alkylation of $CrCl_3(dippe)(thf)$ were unsuccessful. Treatment of $CrCl_3(dippe)(thf)$ with dialkylmagnesium reagents results in disproportionation to a mixture of the known chromium(II) alkyls $CrR_2(dippe)$[2] and the chromium(IV) species CrR_4[7,8] for R = CH_2CMe_3

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Table I. Physical and Microanalytical Data for the MX_3(dippe) Complexes

compd	color	mp, °C	anal. calcd, % C	anal. calcd, % H	anal. calcd, % X	anal. found, % C	anal. found, % H	anal. found, % X
$[TiCl_3(dippe)]_2\cdot PhMe$ (**1**)	purple	225 dec	45.4	7.84	23.0	43.6	8.14	23.1
$TiCl_3$(dippe)(thf) (**2**)	green	111 dec	44.2	8.19	21.8	44.0	8.32	22.0
VCl_3(dippe)(thf) (**3**)	yellow-orange	115 dec	44.0	8.20	21.6	43.2	8.16	22.4
VBr_3(dippe)(thf) (**4**)	orange	148 dec	34.6	6.45	38.3	33.4	6.42	38.2
$CrCl_3$(dippe)(thf) (**5**)	blue	>250	43.9	8.18	21.6	42.2	8.29	21.3
$CrCl_3$(dippe)(MeCN) (**6**)[a]	blue	>250	41.6	7.59	23.1	41.7	7.74	24.2
$CrMeCl_2$(dippe)(thf) (**7**)	green	80 dec	44.2	8.19	21.8	44.0	8.32	22.0

[a] N: calcd, 3.04; found, 3.22.

and CH_2SiMe_3. Alkylation with methyllithium yields a yellow, pyrophoric product that contains lithium but does not contain dippe. This product has been identified by IR as the known quadruply bonded chromium(II) dimer $Li_4Cr_2Me_8\cdot 4thf$.[9,10]

Reaction of $CrMeCl_2$(dippe)(thf) (**7**) with ethylene yields modest amounts of polyethylene under mild conditions (10 atm, 25 °C). The polymer contains a trace (0.14%) of chromium impurity, and its physical properties and ^{13}C NMR spectrum are consistent with the presence of branched polyethylene.[11] The branching might occur through a free-radical process or by formation of oligomeric olefins that can be incorporated into the polymer. The former is less likely because radical polymerization of ethylene usually requires temperatures and pressures much higher than the reaction conditions used. The synthetic precursor to **7**, $CrMeCl_2(thf)_3$, also can serve as an ethylene polymerization catalyst.[6]

Discussion

Titanium. Two complexes, $TiCl_3$(dippe) (**1**) and $TiCl_3$(dippe)(thf) (**2**), are obtained upon addition of dippe to $TiCl_3(thf)_3$, and there is an equilibrium between these two compounds in solution. Evidence supporting the formulation of **2** as a thf adduct is the presence of resonances due to free thf in the ^1H NMR spectrum of **2** dissolved in MeCN-d_3. Although **2** is undoubtedly octahedral, there are at least two possibilities for the structure of solvate-free **1**. Loss of thf from $TiCl_3$(dippe)(thf) could generate either a five-coordinate monomer, $TiCl_3$(dippe), or a six-coordinate halide-bridged dimer, $[TiCl_3(dippe)]_2$. Both five- and six-coordinate adducts of titanium trihalides have been reported;[12-16] for example, *trans*-$TiBr_3(NMe_3)_2$[15] and *mer*-$TiCl_3(py)_3$[16] adopt trigonal-bipyramidal and octahedral structures, respectively.

The EPR spectrum of **1** as a frozen glass in toluene/CH_2Cl_2 shows a two-component pattern characteristic of an axially symmetric system with $g_{\parallel} = 1.893$ and $g_{\perp} = 1.945$ (line widths ~70 G). The low-field component is a poorly resolved triplet due to phosphorus hyperfine coupling; the coupling constant, ~0.0019 cm^{-1}, is slightly lower than the values reported for other titanium(III) phosphine complexes.[13,17,18] The room-temperature solution spectrum consists of a broad signal at $g_{iso} = 1.956$ (line width ~300 G). The marked broadening of the spectrum at room temperature indicates that magnetic exchange is occurring and suggests that **1** may in fact be a dimer. Consistent with this hypothesis, the ^1H NMR spectrum of **1** consists of relatively sharp (fwhm 40 Hz) resonances for the dippe ligand that are shifted

Table II. Crystallographic Data for $[TiCl_3(dippe)]_2\cdot PhMe$ (**1**)

$C_{35}H_{72}Cl_6P_4Ti_2$
space group: *Pbcn*
$T = 25$ °C
$a = 15.586$ (5) Å
$b = 14.442$ (4) Å
$c = 21.639$ (6) Å
$V = 4871$ (2) Å^3
$Z = 4$
mol wt = 925.27
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.262$ g cm^{-3}
$\mu_{calcd} = 8.09$ cm^{-1}
transm coeff: 0.744-0.851
$R_F = 0.064$
$R_{wF} = 0.066$

Table III. Atomic Coordinates for $[TiCl_3(dippe)]_2\cdot PhMe$ (**1**)

	x/a	*y/b*	*z/c*
Ti	0.9059 (2)	0.0540 (1)	0.5206 (1)
Cl1	1.0425 (2)	0.0235 (2)	0.5737 (2)
Cl2	0.9468 (2)	0.2001 (2)	0.4887 (2)
Cl3	0.8423 (2)	−0.0793 (2)	0.5582 (2)
P1	0.7539 (3)	0.0971 (3)	0.4745 (2)
P2	0.8325 (3)	0.1368 (3)	0.6167 (2)
C1	0.7005 (10)	0.1646 (14)	0.5341 (8)
C2	0.7222 (10)	0.1600 (15)	0.5908 (8)
C3	0.7574 (10)	0.1821 (10)	0.4097 (7)
C4	0.8002 (10)	0.1456 (12)	0.3538 (7)
C5	0.6689 (10)	0.2214 (10)	0.3948 (8)
C6	0.6775 (10)	0.0066 (12)	0.4515 (8)
C7	0.7145 (10)	−0.0614 (10)	0.4097 (8)
C8	0.6160 (12)	−0.0224 (15)	0.4932 (11)
C9	0.8738 (12)	0.2516 (12)	0.6378 (8)
C10	0.9620 (11)	0.2495 (13)	0.6579 (9)
C11	0.8194 (13)	0.3114 (12)	0.6760 (9)
C12	0.8149 (12)	0.0629 (12)	0.6851 (7)
C13	0.8923 (11)	0.0217 (12)	0.7134 (7)
C14	0.7480 (12)	0.0933 (13)	0.7279 (7)
C15A	0.0012 (21)	0.3991 (13)	0.2164 (11)
C16A	−0.0041	0.3358	0.1679
C17A	−0.0083	0.2411	0.1803
C18A	−0.0073	0.2098	0.2413
C19A	−0.0020	0.2731	0.2898
C20A	0.0023	0.3677	0.2774
C21A	0.0059	0.5023	0.2031
C15B	0.0081 (28)	0.2784 (19)	0.2891 (15)
C16B	0.0076	0.3077	0.2276
C17B	0.0016	0.4018	0.2139
C18B	−0.0039	0.4666	0.2615
C19B	−0.0034	0.4373	0.3229
C20B	0.0026	0.3432	0.3367
C21B	0.0147	0.1752	0.3021

Table IV. Selected Bond Distances (Å) and Angles (deg) in $[TiCl_3(dippe)]_2\cdot PhMe$ (**1**)

Ti-Cl1	2.459 (4)	P1-C3	1.87 (2)
Ti-Cl1′	2.462 (4)	P1-C6	1.84 (2)
Ti-Cl2	2.310 (4)	P2-C2	1.84 (2)
Ti-Cl3	2.313 (4)	P2-C9	1.84 (2)
Ti-P1	2.645 (5)	P2-C12	1.85 (2)
Ti-P2	2.658 (5)	C1-C2	1.27 (2)
P1-C1	1.82 (2)	Ti···Ti	3.438 (2)
Cl2-Ti-Cl3	169.6 (2)	Cl2-Ti-P2	86.6 (1)
Cl1-Ti-P1	173.6 (2)	Cl2-Ti-P1	85.4 (1)
Cl1′-Ti-P2	173.4 (2)	Cl3-Ti-Cl1	86.6 (1)
P1-Ti-P2	78.6 (2)	Cl2-Ti-Cl1	93.7 (1)
Ti-Cl1-Ti′	88.6 (1)	Cl2-Ti-Cl1′	94.5 (1)
Cl1-Ti-Cl1′	91.4 (1)	P2-Ti-Cl1	95.0 (1)

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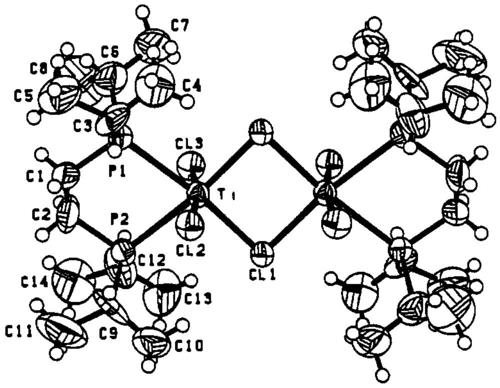

Figure 1. Molecular structure of $[TiCl_3(dippe)]_2$.

less than 1 ppm from their diamagnetic positions. In addition, an upper limit of 1.0 μ_B per titanium center was determined for the magnetic moment of **1** in solution at room temperature by Evans' method. Antiferromagnetic coupling has been observed previously in other titanium(III) dimers such as $[(C_5H_4Me)_2TiX]_2$ (X = Cl, Br) and $[Cp_2Ti]_2[BiIm]$ (BiIm = biimidazolate).[19-22] These observations suggest that **1** adopts a dimeric structure in solution, although the presence of small amounts of monomeric species cannot be ruled out.

In order to confirm the molecular structure of **1**, it has been examined crystallographically. Crystal data are given in Table II, atomic coordinates are presented in Table III, and selected bond distances and angles are collected in Table IV. A perspective view of the molecule is shown in Figure 1. The crystallographic results show that **1** is indeed a chloride-bridged dimer, $[TiCl_3(dippe)]_2$, in the solid state. The dimer possesses a crystallographically imposed inversion center, but overall the molecule closely approaches ideal D_{2h} symmetry. The dimer is composed of two edge-sharing octahedra with each titanium center residing in a slightly distorted octahedral environment. The unit cell also contains one disordered toluene molecule per dimer unit, and upon close examination of the infrared spectrum, bands at 1606 and 1596 cm^{-1} are present that may be attributed to this lattice toluene.

In the dimer, the phosphine ligands are trans to the two bridging chlorides and cis to the two terminal chloride ligands on each metal center. The Ti_2Cl_2 core is planar as required by symmetry and nearly square: the $Ti-Cl_b$ and $Ti-Cl_b'$ distances of 2.459 (4) and 2.462 (4) Å are essentially equal, and the $Cl_b-Ti-Cl_b'$ and $Ti-Cl_b-Ti'$ angles of 91.4 and 88.6° are very close to 90°. Although the Ti···Ti contact of 3.438 (2) Å is rather long and indicates that little metal–metal bonding is present, this distance is substantially shorter than the Ti···Ti contacts in other chloride-bridged Ti^{III} dimers. For example, in $[Cp_2TiCl]_2$ the titanium centers are 3.93 Å apart.[19] In this particular case, the Cp ligands evidently prevent the metals from more closely approaching each other.

In **1**, the two terminal chloride ligands on each titanium center are trans to one another and are bent toward the phosphine ligands with a $Cl_t-Ti-Cl_t$ angle of 169.6 (2)°. This distortion undoubtedly occurs to minimize steric repulsions between the two sets of terminal chlorides; if the terminal chlorides on the adjacent titanium centers were not bent away from each other, they would be substantially closer together than the 3.6-Å sum of their van der Waals radii.[23] The bending of the $Cl_t-Ti-Cl_t$ angles increase the Cl···Cl contact distance between the terminal chloride ligands on the adjacent titanium centers from the Ti···Ti distance of 3.44 Å to an acceptable 3.86 Å. For comparison, the Cl···Cl distance between the two bridging chlorides is only 3.52 Å.

The $Ti-Cl_t$ distances of ca. 2.31 Å are somewhat shorter than might be expected: related distances in other titanium(III) compounds such as $TiCl_3(thf)_3$[24] and $[TiCl_2(thf)_4]^+$[25] range from 2.35 to 2.40 Å. In **1**, the long Ti–P and $Ti-Cl_b$ bonds in the equatorial plane may allow the axial terminal chlorides to bond more strongly to the metal than usual.

The P–Ti–P angle in **1** of 78.6° is normal and reflects the chelating nature of the dippe ligand. Titanium–phosphorus bond lengths in structurally characterized phosphine complexes of titanium[18,26-37] (including all oxidation states) range from 2.51 Å in $TiMe_2(dmpe)_2$[28] to 2.67 Å in $(C_7H_7)TiEt(dmpe)$.[34] Accordingly, the Ti–P distances of **1** of 2.645 and 2.658 Å are among the longest reported. The steric bulk of the dippe ligand is undoubtedly responsible for the long Ti–P distances in this six-coordinate complex. The relatively weak Ti–P bonding is consistent with the small phosphorus hyperfine coupling constants observed in the EPR spectrum of **1**. No other phosphine adducts of $TiCl_3$ have been crystallographically characterized.

Chemically related zirconium dimers $[ZrCl_3(PR_3)_2]_2$, where $PR_3 = P(n\text{-}Bu)_3$, PEt_3, PMe_2Ph, and $^1/_2$ dppe, are known and well characterized.[38,39] The zirconium analogues exhibit the same repulsion between the terminal chloride ligands as was seen in **1**: as the Zr–Zr distance decreases, the $Cl_t-Zr-Cl_t$ angle becomes smaller and deviates more from 180° as expected on steric grounds. Unlike **1**, the zirconium complexes have short M–M distances of 3.1 Å and are diamagnetic. These facts have resulted in the $[ZrCl_3(PR_3)_2]_2$ complexes being formulated with a Zr–Zr single bond. Presumably, the smaller size of titanium vs that of zirconium prevents the titanium d orbitals from interacting sufficiently in **1** to form a strong metal–metal bond. Interestingly, no hafnium(III) coordination complexes have been reported previously in the literature.[40]

Vanadium. Both $VCl_3(dippe)(thf)$ (**3**) and $VBr_3(dippe)(thf)$ (**4**) are readily obtained by the addition of dippe to $VX_3(thf)_3$; both are undoubtedly octahedral. It is interesting to note that a complex similar to **3** has been reported for the bidentate phosphine 1,2-bis(dimethylphosphino)ethane, dmpe. Addition of dmpe to $VCl_3(thf)_3$ gives $VCl_3(dmpe)(thf)$,[41] which is green in

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contrast to the orange color of $\mathrm{VCl_3}$(dippe)(thf). It is possible that the two complexes are structurally isomeric (*fac* vs *mer*).

Both **3** and **4** show resonances for free thf in their ^{1}H NMR spectra in MeCN-d_3, and this observation demonstrates that the thf ligands are labile. The magnetic moment of $\mathrm{VCl_3}$(dippe)(thf) (**3**) in tetrahydrofuran of 2.7 μ_B is close to the normal spin-only value for two unpaired electrons. Interestingly, the magnetic moment of **3** in benzene is only 1.5 μ_B, which suggests that in noncoordinating solvents **3** loses thf to give a chloride-bridged dimer analogous to **1**. In contrast, the bromide derivative $\mathrm{VBr_3}$(dippe)(thf) (**4**) shows a normal magnetic moment for $\mathrm{V^{III}}$ of $\mu_{eff} = 2.6$ μ_B in both benzene and thf. Evidently, the poorer bridging ability of bromide makes the formation of a bromide-bridged dimer from **4** less favorable than the formation of a chloride-bridged dimer from **3**.

The coordination chemistry of vanadium(III) resembles that of titanium(III) in that both five- and six-coordinate adducts have been reported previously. Among the phosphine adducts are several trigonal-bipyramidal complexes of stoichiometry $\mathrm{VX_3(PR_3)_2}$.[42-44] In comparison with our results for vanadium(III), the heavier group 5 metals niobium and tantalum are known to form dimeric complexes of stoichiometry $\mathrm{[MCl_3(PR_3)_2]_2}$ for both unidentate and bidentate phosphine ligands.[45,46] Like the zirconium(III) dimers discussed above, the niobium and tantalum dimers are diamagnetic and have metal–metal bonds. Monomeric phosphine adducts of tantalum(III) are also known.[47]

Chromium. Three chromium(III) dippe complexes have been isolated: the halo complexes $\mathrm{CrCl_3}$(dippe)(thf) (**5**) and $\mathrm{CrCl_3}$(dippe)(MeCN) (**6**) and the alkyl derivative $\mathrm{CrMeCl_2}$(dippe)(thf) (**7**). The magnetic moment of **5** in benzene is 3.8 μ_B, which is close to the spin-only value for $\mathrm{Cr^{III}}$. The kinetic stability of this d^3 complex toward loss of thf in noncoordinating solvents contrasts with the behavior of the titanium and vanadium analogues **2** and **3**, which lose thf readily upon dissolution in aromatic hydrocarbons. For **7**, the presence of coordinated thf can be verified by the appearance of free thf in the ^{1}H NMR spectrum upon hydrolysis of the complex in $\mathrm{C_6D_6}$. The magnetic moment of **7** is 3.7 μ_B; this is consistent with $\mathrm{Cr^{III}}$. Here again a monomeric octahedral structure is most likely adopted by this d^3 complex.[48]

Many phosphine adducts of $\mathrm{Cr^{III}}$ are known. Unidentate phosphines reportedly form complexes of the stoichiometries $\mathrm{CrX_3P_3}$, $\mathrm{CrX_3P_2}$, and $\mathrm{CrX_3P}$, and these species have been assigned monomeric, dimeric, and polymeric structures, respectively.[49-51] Bidentate phosphine complexes of $\mathrm{CrCl_3}$ very similar to **5** and **6** have also been reported and include $\mathrm{CrCl_3(dppe)(H_2O)}$, which is prepared from $\mathrm{CrCl_3}$ in wet dichloromethane.[52] Many chromium(III) complexes with bidentate ligands have the stoichiometry $\mathrm{CrCl_3(PP)_{1.5}}$ and are usually best formulated as $\mathrm{[CrCl_2(PP)_2][CrCl_4(PP)]}$ salts.[52] Tridentate phosphines have also been employed to prepare stable octahedral coordination complexes of chromium(III).[53-57] A few Lewis base adducts of $\mathrm{Cr^{III}}$ triaryls such as $\mathrm{CrPh_3(thf)_3}$ have been reported,[58-61] and $\mathrm{Cr^{III}}$ trialkyls have been synthesized successfully by using tripod phosphines such as trimpsi, $\mathrm{Me_3CSi(CH_2PMe_2)_3}$.[54,62]

We are currently investigating the synthesis and characterization of trivalent alkyls of Ti, Zr, Hf, and V analogous to $\mathrm{CrMeCl_2}$(dippe)(thf) that may serve as olefin polymerization catalysts. Few such species are known, but investigations of their chemistry may be facilitated by taking advantage of the unique steric and electronic properties of the dippe ligand.

Experimental Section

All operations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium (toluene), sodium/benzophenone (pentane, diethyl ether, tetrahydrofuran), or calcium hydride (acetonitrile). The complexes $\mathrm{TiCl_3(thf)_3}$,[63] $\mathrm{VCl_3(thf)_3}$,[63] $\mathrm{VBr_3(thf)_3}$,[64] $\mathrm{CrCl_3(thf)_3}$,[65] and $\mathrm{CrMeCl_2(thf)_3}$[6] were prepared via literature routes.

Microanalyses were performed by Josef Nemeth and Tom McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded as Nujol mulls on a Perkin-Elmer 599B spectrometer using CsI plates. The ^{1}H NMR data were recorded on a General Electric QE-300 spectrometer at 300 MHz. The NMR data were obtained from $\mathrm{C_6D_6}$ solutions (δ 7.15), and chemical shifts are reported in δ units (positive shifts to high frequency) and are uncorrected for the paramagnetic shift of the solvent. The X-band EPR experiments were performed on a Varian E-9 spectrometer with frozen toluene/dichloromethane solutions at −196 °C. Magnetic moments were determined by a modification of Evans' method.[66] Melting points were determined on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

Hexachlorobis[1,2-bis(diisopropylphosphino)ethane]dititanium(III)–Toluene (1). To a suspension of $\mathrm{TiCl_3(thf)_3}$ (1.19 g, 3.2 mmol) in toluene (40 mL) was added dippe (0.9 mL, 3.2 mmol). The solution immediately turned purple. After being stirred for 1 h, the solution was filtered and concentrated to ca. 20 mL. Cooling to −20 °C resulted in the formation of purple crystals, yield 0.89 g (60%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ 1.60 (s, fwhm 40 Hz, $\mathrm{CH}Me_2$), 1.42 (s, fwhm 40 Hz, $\mathrm{CH}Me_2$), ca. 1.9 (s, $\mathrm{P}CH_2$ + $CH\mathrm{Me_2}$). IR (CsI, $\mathrm{cm^{-1}}$): 2715 w, 1606 w, 1596 sh, 1416 s, 1296 w, 1249 s, 1164 s, 1115 w, 1094 w, 1081 w, 1056 s, 1031 s, 966 w, 929 s, 888 s, 861 s, 822 m, 741 s, 733 s, 696 s, 680 s, 657 ms, 646 sh, 613 m, 521 m, 474 s, 446 w, 381 s, 325 s, 295 s, 220 s.

Trichloro(tetrahydrofuran)[1,2-bis(diisopropylphosphino)ethane]titanium(III) (2). To a suspension of $\mathrm{TiCl_3(thf)_3}$ (1.75 g, 4.4 mmol) in diethyl ether (40 mL) was added dippe (1.3 mL, 4.4 mmol). The solution turned green, and a purple solid (**1**) precipitated. After being stirred for 5 h, the green solution was filtered, concentrated to ca. 20 mL, and cooled to −20 °C to give clusters of green-blue crystals, yield 0.3 g (14%). The ^{1}H NMR resonances for **2** could not be observed due to facile loss of thf to generate **1**. IR (CsI, $\mathrm{cm^{-1}}$): 2722 w, 1417 m, 1343 w, 1294 m, 1259 m, 1245 m, 1162 m, 1116 m, 1055 m, 1014 s, 966 w, 927 m, 885 m, 859 s, 818 m, 722 m, 676 s, 655 m, 612 m, 513 w, 469 m, 441 w, 359 s, 314 s, 274 w.

Trichloro(tetrahydrofuran)[1,2-bis(diisopropylphosphino)ethane]vanadium(III) (3). To a suspension of $\mathrm{VCl_3(thf)_3}$ (3.15 g, 7.9 mmol) in tetrahydrofuran (30 mL) was added dippe (2.3 mL, 7.9 mmol). The solution immediately turned orange-brown. After being stirred for 5 h, the solution was filtered and concentrated to ca. 20 mL. Cooling to −20 °C resulted in the formation of orange crystals, yield 2.20 g (57%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ 3.60 (s, fwhm 25 Hz, $I_{rel} = 12$), 1.47 (s, fwhm 30 Hz, $I_{rel} = 6$), 1.38 (s, fwhm 30 Hz, $I_{rel} = 6$), 0.90 (s, fwhm 20 Hz, $I_{rel} = 12$), −16.8 (s, fwhm 60 Hz, $I_{rel} = 4$), −24.5 (s, fwhm 100 Hz, $I_{rel} = 4$). IR (CsI, $\mathrm{cm^{-1}}$): 2700 w, 1412 m, 1339 w, 1291 w, 1246 m, 1161

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w, 1108 w, 1089 w, 1062 m, 1049 m, 1040 m, 1020 s, 961 w, 925 m, 867 s, 854 s, 821 m, 723 w, 693 m, 678 s, 651 m, 520 w, 470 w, 366 s, 339 s, 299 m, 272 m.

Tribromo(tetrahydrofuran)[1,2-bis(diisopropylphosphino)ethane]vanadium(III) (4). To a suspension of $VBr_3(thf)_3$ (1.01 g, 2.0 mmol) in a mixture of pentane (30 mL) and diethyl ether (15 mL) was added dippe (0.6 mL, 2.0 mmol). After the mixture had been stirred for 18 h, a bright orange precipitate had formed. The solid was isolated by filtration, washed with pentane (10 mL), and dried in vacuo; yield 0.91 g (73%). ^1H NMR (CD_2Cl_2, 25 °C): δ 4.08 (s, fwhm 15 Hz, $I_{rel} = 12$), 1.48 (s, fwhm 20 Hz, $I_{rel} = 6$), 1.37 (s, fwhm 20 Hz, $I_{rel} = 6$), 1.00 (s, fwhm 12 Hz, $I_{rel} = 12$), −16.6 (s, fwhm 60 Hz, $I_{rel} = 4$), −21.2 (s, fwhm 60 Hz, $I_{rel} = 4$). IR (CsI, cm^{-1}): 2715 w, 1417 m, 1343 m, 1295 m, 1266 m, 1249 m, 1164 m, 1117 w, 1094 w, 1068 m, 1033 m, 1017 s, 990 m, 969 w, 932 m, 886 m, 861 s, 822 m, 724 m, 691 m, 676 s, 652 m, 634 w, 614 m, 598 w, 519 w, 4776 m, 452 w, 295 s, 271 s.

Trichloro(tetrahydrofuran)[1,2-bis(diisopropylphosphino)ethane]chromium(III) (5). To a suspension of $CrCl_3(thf)_3$ (1.29 g, 3.4 mmol) in a mixture of pentane (30 mL) and diethyl ether (15 mL) was added dippe (1 mL, 3.5 mmol). After being stirred for 2 h, the solution had turned blue and a blue solid formed. The solid was isolated by filtration, washed with pentane (20 mL), and dried in vacuo; yield 1.32 g (79%). ^1H NMR (CD_2Cl_2, 25 °C): δ 5.9 (s, fwhm 900 Hz, 2 $CHMe_2$), 3.67 (s, fwhm 80 Hz, α-CH_2), 1.90 (s, fwhm 80 Hz, β-CH_2), −3.8 (s, fwhm 600 Hz, $CHMe_2$), −6.0 (s, fwhm 500 Hz, $CHMe_2$). IR (CsI, cm^{-1}): 2719 w, 1413 s, 1340 w, 1293 w, 1255 s, 1164 m, 1110 w, 1091 w, 1065 s, 1044 m, 1017 s, 962 w, 929 s, 886 sh, 856 vs, 821 s, 730 m, 699 s, 683 s, 656 s, 610 w, 593 w, 519 m, 468 w, 446 w, 361 s, 320 s, 266 m.

Trichloro(acetonitrile)[1,2-bis(diisopropylphosphino)ethane]chromium(III) (6). Dark blue crystals of $CrCl_3(dippe)(CH_3CN)$ may be obtained by cooling saturated acetonitrile solutions of **5** to −20 °C. IR (CsI, cm^{-1}): 2713 w, 2310 m (CH_3CN), 2276 s (CH_3CN), 1418 m, 1301 w, 1252 m, 1163 m, 1112 w, 1091 w, 1062 s, 1036 m, 970 w, 951 w, 946 w, 886 m, 873 w, 821 s, 723 w, 700 s, 686 s, 655 m, 641 w, 616 w, 524 m, 481 w, 420 w, 359 s, 321 s.

Methyldichloro(tetrahydrofuran)[1,2-bis(diisopropylphosphino)ethane]chromium(III) (7). To a yellow-green solution of $CrMeCl_2(thf)_3$ (0.62 g, 1.8 mmol) in tetrahydrofuran (30 mL) was added dippe (0.5 mL, 1.8 mmol). The solution immediately turned dark green. After being stirred for 1 h, the solution was filtered and concentrated to ca. 5 mL. Cooling to −20 °C resulted in the formation of bright green crystals, yield 0.51 g (60%). The ^1H NMR spectrum of **7** in CD_2Cl_2 consisted of thf resonances plus broad, poorly defined peaks between δ +5 and −5. IR (cm^{-1}): 2689 w, 1388 m, 1270 w, 1225 m, 1138 m, 1090 w, 1080 w, 1069 m, 1041 s, 1030 w, 1002 s, 940 w, 905 m, 860 s, 848 s, 835 s, 800 m, 701 w, 672 m, 658 s, 634 m, 500 w, 460 m, 322 s.

Reaction of $CrMeCl_2(dippe)(thf)$ with Ethylene. A solution of $CrMeCl_2(dippe)(thf)$ (0.05 g, 0.11 mmol) in toluene (20 mL) was pressurized to 10 atm with ethylene. The reaction exhibited a slight exotherm, and after ~1 h, solid began to form. After it was stirred for 24 h, the solution had turned pale blue and a mass of polymer had formed. Some toluene was removed via cannula, and the rest was removed in vacuo. The sticky solid was washed repeatedly with absolute ethanol to yield a white powder. Additional polymer could be precipitated by adding ethanol to the toluene solution: mp 95–100 °C. Anal. Calcd: C, 85.56; H, 14.37. Found: C, 85.41; H, 14.23; Cr, 0.14. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): major peak (95%) at δ 29.9 (CH_2 backbone); smaller resonances (~5%) at δ 22.8, 29.0, 29.2, 29.5, 29.7, 29.8, 32.0, 33.9, 114.0, 126.8, 127.1.

Crystallographic Studies.[67] Single crystals of $[TiCl_3(dippe)]_2 \cdot PhMe$, grown from toluene, were sealed in thin-walled glass capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable prismatic crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures, followed by least-squares refinement with 15 reflections, yielded the cell dimensions given in Table II.

Data were collected in one octant of reciprocal space ($+h,+k,+l$), and data in the range $3.0 \leq 2\theta \leq 15.0°$ were collected in four additional octants ($-h,\pm k,\pm l$). Systematic absences for $0kl$ where $k \neq 2n$, $h0l$ where $l \neq 2n$, and $hk0$ where $h + k \neq 2n$ were consistent only with space group *Pbcn*. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Crystal decay corrections were applied with no significant change, and absorption corrections were applied (SHELX). Ten questionable reflections were deleted. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by using direct methods (SHELXS) and weighted and unweighted difference Fourier methods. The positions of the titanium, chlorine, and phosphorus atoms were deduced from an *E* map, and subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The toluene solvate molecule was disordered about the 2-fold axis in two antiparallel orientations (generating four different positions) and was constrained to ideal geometry. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.22/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, all non-hydrogen atoms (except the carbon atoms of the toluene solvate molecule) were independently refined with anisotropic thermal coefficients, and a group isotropic thermal parameter was varied for the hydrogen atoms, which were fixed in "idealized" positions with C–H = 0.95 Å. A group isotropic thermal parameter was also varied for the carbon atoms of the toluene solvate molecule. Successful convergence was indicated by the maximum shift/error of 0.056 in the last cycle. Final refinement parameters are given in Table II. The final difference Fourier map had no significant features. There were no apparent systematic errors among the final observed and calculated structure factors. Although the final thermal parameters were large and the uncorrected C–C bond lengths were shorter than expected, attempts to identify a discrete disorder model for the dippe ligand were unsuccessful.

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Supplementary Material Available: Tables S1–S4, giving full crystallographic details, calculated hydrogen atom positions, anisotropic thermal parameters, and complete bond distances and angles for $[TiCl_3(dippe)]_2$ (7 pages); a table of final observed and calculated structure factors for $[TiCl_3(dippe)]_2$ (5 pages). Ordering information is given on any current masthead page.

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(67) For details of the data collection and refinement procedure, see ref 10.