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Mono- and bis-(iminophosphoranyl)methane titanium complexes

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The reaction of the bis(iminophosphoranyl)methanes, $CH_2(R_2P{=}NSiMe_3)_2$ (R = Ph **1**, Me **2** or Cy **3**) with two equivalents of Cp^*TiCl_3 ($Cp^* = C_5Me_5$) gave, *via* elimination of two moles of trimethylsilyl chloride, the air and moisture sensitive bimetallic titanium bis(iminophosphoranyl)methane complexes, $[(Cp^*TiCl_2)_2\{\mu\text{-}(N{=}PR_2)_2CH_2\text{-}\kappa N,N'\}]$ (R = Ph **7**, Me **8** or Cy **9**). The monometallated complexes, $[Cp^*TiCl_2\{(N{=}PR_2)CH_2(R_2P{=}NSiMe_3)\text{-}\kappa N\}]$ (R = Ph **4**, Me **5** or Cy **6**) were observed as intermediates in the reaction by ^{31}P NMR spectroscopy but attempts to isolate the pure monosubstituted products from reactions of the bis(silyliminophosphoranyl)methane and the titanium reagent conducted under equimolar stoichiometry were not successful; instead only mixtures of the mono- and di-substituted complexes were generated. Crystal structures of **7** and **8** revealed different molecular structures; in **7** the imidotitanium groups lie in a mutual *trans* orientation across the molecule whereas in **8** they lie on the same side of the molecule.

Introduction

Early transition metal complexes with multiply bonded first row main-group ligands have become the subject of intense interest because of their extensive applications in organic and polymer synthesis.[1–4] Interestingly, certain nitrogen (*e.g.* phosphoranimides[5]) and carbon (*e.g.* phosphorus ylide complexes[6]) and the recently discovered bis(phosphoranimido)methanediides[7–10] display short bonds to the metal center, suggestive of doubly bonded interactions similar to those of imide or carbene ligands as the result of extensive delocalization within the MXP (X = CR or N) unit. These phosphorus-substituted, multiply bonded, metal complexes are remarkably stable. Although Group 4 phosphinimide complexes are sparse, some titanium monophosphinimide[11–13] complexes and a few examples of zirconium and hafnium phosphinimide complexes[14–16] containing monophosphinimide ligands have recently been reported and the importance of these systems is just emerging.[11,12,17] The bis(iminophosphoranyl)alkane ligands with methylene or longer chain hydrocarbon backbones have provided only one structurally characterized example.[18] Herein we describe the synthesis and characterization including structural analysis of several mono- and di-substituted titanium complexes of bis(iminophosphoranyl)methane ligands. We chose the pentamethylcyclopentadiene titanium precursor because of the increased bulk offered by this substituent which might have favoured limited substitution products.

Bis(phosphines) are readily oxidized to bis(iminophosphoranyl)methanes by azides (the Staudinger reaction) and we used trimethylsilyl azide to provide the silylated imides. The present phosphoranimidotitanium complexes were synthesized from these silylated ligands through straightforward transmetallation reactions involving a simple stepwise elimination of trimethylsilyl chloride. In these reactions the backbone P–C–P of the ligand was unaffected in contrast to our recently described systems in which the methylene group of these same $CH_2(R_2P{=}NR)_2$ ligands is deprotonated in a direct reaction with certain early transition metal alkyl[9] or amido[8,10] precursors to form multiply bonded "pincer" bis(iminophosphoranyl)methanediide complexes which have characteristics of metal carbenes.[7,8,10,19]

Experimental

All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glove-box. Solvents were dried and distilled under argon prior to use. The $CH_2(Ph_2P{=}NSiMe_3)_2$ **1** ligand was prepared by the literature procedure;[20] in a similar fashion, the ligands **2** and **3** were prepared starting from trivalent bis(phosphino)methanes obtained commercially. The cyclopentadienyl titanium complex Cp^*TiCl_3 ($Cp^* = C_5Me_5$) was obtained from Strem Chemicals and used as supplied. NMR spectra were recorded on Bruker WH-200, 300 and 400 spectrometers. Shifts were determined with reference to the deuterium signal of the solvent employed. The ^1H and ^{13}C NMR chemical shifts are reported in ppm from external Me_4Si and the ^{31}P NMR spectra in ppm from external 85% H_3PO_4. Positive values reflect downfield shifts. Infrared spectra were recorded on a Nicolet 7199 infrared spectrometer.

Preparations

(a) $[(Cp^*TiCl_2)_2\{\mu\text{-}(N{=}PPh_2)_2CH_2\text{-}\kappa N,N'\}]$ 7. Solid $CH_2(Ph_2P{=}NSiMe_3)_2$ **1** (0.483 g, 0.86 mmol) was added to a stirred toluene solution (15 mL) of the titanium complex Cp^*TiCl_3 (0.5 g, 1.73 mmol) which was then heated to 130 °C for 3 h. The solution was cooled to room temperature and the solvent evaporated to half of the original volume. The reaction vessel was again recharged with fresh toluene and the solution then heated to 130 °C for 12 h. The solution was cooled to room temperature and the solvent evaporated completely to yield a foamy pale orange solid. This solid residue was dissolved in 6 mL of a 1 : 1 mixture of diethyl ether and hexane and left to stand at −15 °C for 24 h. During this period orange-yellow crystals deposited, which were collected by filtration and dried. Yield (calculated for $\mathbf{7}\cdot Et_2O$): 0.65 g, 0.65 mmol, 76%. IR data (Nujol mull): 1588w, 1575w, 1481m, 1436s, 1309w, 1137s, 1103s, 1024m, 999m, 800s, 788s, 763m, 743s, 733s, 719m, 693s, 677m, 667w, 617w. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.93 (m, 8H, CH, *o*-H of Ph), 7.07 (m, 8H, CH, *m*-H of Ph), 6.95 (m, 4H, CH, *p*-H of Ph), 4.48 (t, $^2J_{PH} = 15.3$ Hz, 2H, CH_2, PCP), 3.25 (q, CH_2, Et_2O), 1.95 (s, 30H, CH_3, C_5Me_5), 1.10 (t, CH_3,

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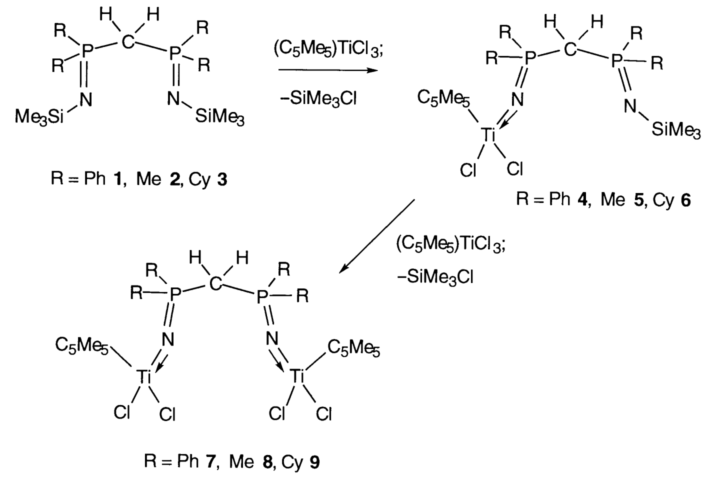

Scheme 1

Et_2O). ^{13}C-{^1H} NMR (100.6 MHz, C_6D_6, 298 K): δ 132.4 (t, $^2J_{PC}$ = 5.2, CH, *o*-C of Ph), 132.1 (s, CH, *p*-C of Ph), 130.6 (m, C, *i*-C of Ph), 128.9 (t, $^3J_{PC}$ = 6.5, *m*-C of Ph), 127.2 (s, C, C_5Me_5), 65.8 (s, CH_2, Et_2O), 32.7 (t, $^1J_{PC}$ = 55.0 Hz, CH_2, PCP), 15.5 (s, CH_3, Et_2O), 13.0 (s, CH_3, C_5Me_5). ^{31}P-{^1H}NMR (161.9 MHz, C_6D_6, 298 K): δ −4.0 (s). These crystals slowly lost their ether of solvation upon standing eventually to form an amorphous material which was then crushed and dried under vacuum to obtain consistent analytical data for the ether free product. Calc. for $C_{45}H_{52}Cl_4N_2P_2Ti_2$: C, 58.72; H, 5.69; N, 3.04. Found: C, 58.87; H, 5.79; N, 3.03%. The crystal structure analysis was carried out on a protected etherate complex.

(b) [(Cp*TiCl$_2$)$_2${μ-(N=PMe$_2$)$_2$CH$_2$-κ*N*,*N*′}] 8. Solid $CH_2(Me_2P{=}NSiMe_3)_2$ **2** (0.215 g, 0.69 mmol) was added to a toluene solution (10 mL) of the titanium complex Cp*$TiCl_3$ (0.5 g, 1.73 mmol) and stirred at room temperature. After 15 h the solvent was evaporated under vacuum. The residue obtained therefrom was dissolved in 15 mL of a 5 : 1 mixture of toluene–THF and stirred for 24 h. The resultant solution was concentrated to one-third of the original volume to precipitate a yellowish orange solid which was isolated by filtration, washed with hexane and dried. Yield: 0.38 g, 0.57 mmol (82%). IR data (Nujol mull): 1398w, 1305m, 1295m, 1167s, 1023w, 945s, 920s, 871m, 847w, 798s, 753m. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 2.07 (s, 30H, CH_3, C_5Me_5), 1.91 (t, $^2J_{PH}$ = 14.0, 2H, CH_2, PCP), 1.31 (d, $^2J_{PH}$ = 12.4 Hz, 12H, CH_3, Me–P). ^{13}C-{^1H} NMR (100.6 MHz, C_6D_6, 298 K): δ 126.8 (s, C, C_5Me_5), 31.9 (t, $^1J_{PC}$ = 55.6, CH_2, PCP), 18.5 (d, $^1J_{PC}$ = 69.8 Hz, CH_3, Me-P), 13.1 (s, CH_3, C_5Me_5). ^{31}P-{^1H} NMR (161.9 MHz, C_6D_6, 298 K): δ 3.6 (s). Calc. for $C_{25}H_{44}Cl_4N_2P_2Ti_2$: C, 44.67; H, 6.60; N, 4.17. Found: C, 44.27; H, 6.59; N, 4.13%.

[(Cp*TiCl$_2$)$_2${μ-(N=PCy$_2$)$_2$CH$_2$}-κ*N*,*N*′}] 9. Solid $CH_2(Cy_2P{=}NSiMe_3)_2$ **3** (0.503 g, 0.86 mmol) was added to a stirred toluene solution (15 mL) of Cp*$TiCl_3$ (0.5 g, 1.73 mmol) and heated to 130 °C. After 15 h of reaction at reflux the solvent was evaporated to half of the original volume. The vessel was again recharged with fresh toluene and the solution again heated to 130 °C for 48 h. The solvent was then evaporated completely to produce a foamy pale yellow solid. This solid residue was mixed with hexane and a pale yellow precipitate obtained which was collected by filtration and dried under vacuum. Yield: 0.64 g, 0.68 mmol (79%). IR data (Nujol mull): 1272w, 1183w, 1170m, 1123s, 1108s, 1077m, 1042w, 1026w, 1000w, 918w, 889w, 855m, 827w, 803m, 767m, 732w, 696w. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 3.42 (t, $^2J_{PH}$ = 13.6 Hz, 2H, CH_2, PCP), 2.61 (m, 4H, CH, *i*-H of Cy), 2.29 (m, 4H, CH_2, Cy), 2.07 (m, 4H, CH_2, Cy), 1.72 (m, 8H, CH_2, Cy), 1.57 (m, 4H, CH_2, Cy), 1.41 (m, 8H, CH_2, Cy), 1.12 (m, 4H, CH_2, Cy). ^{13}C-{^1H} NMR (100.6 MHz, C_6D_6, 298 K): δ 126.4 (s, C, C_5Me_5), 39.1 (m, CH, *i*-C of Cy), 27.7 (s, CH_2, *m*-C of Cy), 27.3 (s, CH_2, *m*-C of Cy), 26.7 (t, $^2J_{PC}$ = 6.0, CH_2, *o*-C of Cy), 26.4 (t, $^2J_{PC}$ = 6.5 Hz, CH_2, *o*-C of Cy), 26.2 (s, CH_2, *p*-C of Cy), 18.9 (t, $^1J_{PC}$ = 42.5 Hz, CH_2, PCP), 13.0 (s, CH_3, C_5Me_5). ^{31}P-{^1H} NMR (161.9 MHz, C_6D_6, 298 K): δ 24.6 (s). Calc. for $C_{45}H_{76}Cl_4N_2P_2Ti_2$: C, 57.22; H, 8.11; N, 2.97. Found: C, 57.31; H, 8.10; N, 2.86%.

(d) [Cp*TiCl$_2${(N=PR$_2$)CH$_2$(R$_2$P=NSiMe$_3$)-κ*N*}] (R = Ph 4, Me 5 or Cy 6). Solid ligand **1** (0.386 g), **2** (0.215 g) or **3** (0.403 g) (0.70 mmol) was added to a toluene (10 mL) solution containing an equimolar quantity of Cp*$TiCl_3$ (0.20 g, 0.70 mmol). The pale yellowish orange solutions obtained were stirred at room temperature for 12 h. In each case the ^{31}P NMR spectrum (Table 1) recorded after this time indicated the presence of both the monosubstituted (**4**–**6**) and disubstituted (**7**–**9**) complexes. Crystallization from these solutions gave only low yields of the dititaniated complexes.

X-Ray crystallography

The structures of **7**·OEt_2 and **8** were determined by single crystal X-ray analysis. Experimental details are listed in Table 2.

CCDC reference numbers 156268 and 156269.

See http://www.rsc.org/suppdata/dt/b0/b010112p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Treatment of the bis(iminophosphoranyl)methanes, $CH_2(R_2P{=}NSiMe_3)_2$ (R = Ph **1**,[20] Me = **2** or Cy = **3**), with two equivalents of Cp*$TiCl_3$ in toluene either at room temperature or under solvent reflux conditions gave a mixture of products (**4**–**9**) (Scheme 1). The pure disubstituted titanium products (**7**–**9**) were formed in a high yield only after removal of the trimethylsilyl chloride by-product from the reaction medium. In the case of the less bulky methyl ligand derivative **2** the reaction proceeded rapidly at room temperature, whereas the phenyl (**1**) and cyclohexyl (**3**) ligands required longer time at reflux temperature (≈120 °C) to ensure complete reaction. Attempts to isolate the pure monosubstituted complexes (**4**–**6**) from reactions conducted with equimolar ratios of ligand and Cp*$TiCl_3$ at room temperature were unsuccessful. The resultant product mixture invariably contained both the monosubstituted and disubstituted complexes (as deduced from their characteristic ^{31}P NMR spectra).

In all of these reactions, the highly acidic methylene protons on the P–C–P backbone were not affected. It is worth mentioning here however that the back-bone of the closely related ethane bridged bis(iminophosphoranyl)ethane ligand was spontaneously deprotonated by $TiCl_4$, a strong Lewis acid.[21]

Table 1 The ^{31}P-{^{1}H} NMR (161.9 MHz, C_6D_6, 298 K) spectroscopic data[a]

	Compound	δ_A	δ_X	$^2J_{PP}$/Hz	$\Delta\delta$
1	$CH_2(Ph_2P{=}NSiMe_3)_2$		−5.2		
2	$CH_2(Me_2P{=}NSiMe_3)_2$		−2.1		
3	$CH_2(Cy_2P{=}NSiMe_3)_2$		14.6		
4	[Cp*$TiCl_2${(N=PPh_2)CH_2(Ph_2P=$NSiMe_3$)-κ*N*}]	−0.6(d)	−5.6(d)	14.1	4.6
5	[Cp*$TiCl_2${(N=PMe_2)CH_2(Me_2P=$NSiMe_3$)-κ*N*}]	5.7(d)	−1.5(bs)	15.0	7.8
6	[Cp*$TiCl_2${(N=PCy_2)CH_2(Cy_2P=$NSiMe_3$)-κ*N*}]	28.2(d)	13.2(d)	17.0	13.6
7	[(Cp*$TiCl_2$)$_2${μ-(N=PPh_2)$_2CH_2$-κ*N*,*N′*}]	−4.0(s)			1.2
8	[(Cp*$TiCl_2$)$_2${μ-(N=PMe_2)$_2CH_2$-κ*N*,*N′*}]	3.6(s)			5.7
9	[(Cp*$TiCl_2$)$_2${μ-(N=PCy_2)$_2CH_2$-κ*N*,*N′*}]	24.6(s)			10.0

[a] δ_A corresponds to the titaniated phoshoranimide moiety; δ_X to the silylated phosphinimine moiety; $\Delta\delta = \delta_A - \delta_L$, where δ_L corresponds to the parent silylated ligands.

Table 2 Crystallographic experimental details for **7**·OEt_2 and **8**

	7·OEt_2	**8**
Empirical formula	$C_{49}H_{62}Cl_4N_2OP_2Ti_2$	$C_{25}H_{44}Cl_4N_2P_2Ti_2$
Formula weight	994.55	672.16
Crystal system	Monoclinic	Triclinic
Space group	*I*2/*a* (a non-standard setting of *C*2/*c* [no. 15])	$P\bar{1}$ (no. 2)
a/Å	38.964(3)	8.2280(6)
b/Å	16.7659(13)	14.4238(11)
c/Å	15.6148(10)	29.3043(13)
α/°		77.264(5)
β/°	94.3748(17)	87.215(5)
γ/°		80.334(5)
V/Å^3	10171.0(13)	3343.8(4)
Z	8	4
μ(Mo-Kα)/mm^{-1}	0.623	8.032
T/°C	−80	−60
Total data collected	22438	9549
Independent reflections	9972	8832
$R1$ [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0508	0.0749
$wR2$ [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1335	0.2179

The complexes **7**–**9** are pale orange or yellow crystalline solids which are soluble in polar organic solvents. Analytical, infrared and multinuclear NMR spectroscopic data of **7**–**9** were consistent with the formation of disubstituted titanium bis(iminophosphoranyl)methane complexes. The IR spectra show intense $\nu_{P=N}$ absorptions at 1137 cm^{-1} for **7**, 1167 cm^{-1} for **8** and 1108 cm^{-1} for **9**. These absorptions occur at a lower energy relative to the parent compounds **1**–**3** (which absorb at approximately 1280 cm^{-1}), which is as expected given the elongation of the phosphorus–nitrogen bond in the complexes **7**–**9** revealed by X-ray crystallography results (*vide infra*). This elongation arises from electron delocalization within the multiply bonded metal–nitrogen–phosphorus moiety.

The ^{31}P NMR data are in Table 1. Complexes **7**–**9** show one sharp singlet indicating that the phosphorus centers are chemically equivalent and these are shifted downfield by a few ppm relative to the parent silylated ligand. The monosubstituted complexes **4**–**6** display an AX type pattern as expected for two chemically different phosphorus nuclei. In these latter cases the ^{31}P chemical shift values of the coordinated phosphoranimide moieties (δ_A) are shifted downfield relative to the values (δ_L) found for the parent silylated ligand. The chemical shift differences are expressed as $\Delta\delta$ values in Table 1. The value δ_X which lies closer to the "free" ligand value is assigned to the silylated phosphinimine moiety.

In the ^{1}H NMR spectra the methylene proton resonances are observed as triplets due to the coupling of two equivalent phosphorus atoms; the signals are shifted downfield from the corresponding "free" ligand values. These signals are observed as positive triplets in the ^{13}C-{^{1}H} APT (Attached Proton Test) NMR spectra clearly indicating that these carbon atoms carry two protons, but in these cases the chemical shift values are slightly shifted upfield from the corresponding methylene carbon signal of the "free" ligands.

Table 3 Selected metrical parameters (bond lengths in Å, angles in °) for **7** and **8**

	7	**8a**[a]	**8b**[a]
Ti(1)–Cp* centroid$_{ave}$	2.055	2.056	2.052
Ti(1)–Cl(1)	2.2990(1)	2.306(2)	2.275(3)
Ti(1)–Cl(2)	2.291(1)	2.296(2)	2.251(4)
Ti(1)–N(1)	1.790(3)	1.769(5)	1.755(6)
Ti(1)–N(2)	1.806(3)	1.796(5)	1.791(6)
P(1)–N(1)	1.580(3)	1.578(5)	1.574(6)
P(2)–N(2)	1.584(3)	1.571(5)	1.576(5)
P(1)–C(1)	1.831(3)	1.800(7)	1.796(7)
P(2)–C(1)	1.816(4)	1.805(7)	1.807(7)
P–C$_{average}$[b]	1.806(4)	1.786(8)	1.787(8)
Ti(1)–N(1)–P(1)	158.4(2)	160.5(4)	172.8(5)
Ti(2)–N(2)–P(2)	160.0(2)	156.9(4)	154.9(3)
N(1)–P(1)–C(1)	109.3(2)	113.2(3)	111.7(3)
N(2)–P(2)–C(1)	112.7(2)	112.0(3)	111.1(3)
P(1)–C(1)–P(2)	122.1(2)	119.6(4)	120.3(4)

[a] **8a** and **8b** are two independent molecules of **8** which are present in each asymmetric unit. [b] The average of all the P–C bond lengths pertaining to the phenyl or methyl substituents.

The molecular structures of [(Cp*$TiCl_2$)$_2${μ-(N=PPh_2)$_2CH_2$-κ*N*,*N′*}] **7** and [(Cp*$TiCl_2$)$_2${μ-(N=PMe_2)$_2CH_2$-κ*N*,*N′*}] **8** are shown in Fig. 1(a) and 1(b)[22] respectively. The pertinent bond distances and angles are listed in Table 3. In each case the bis(phosphoranimide) ligand is subtended by two Cp*$TiCl_2$ units. The main difference demonstrated by the two complexes is the, perhaps surprising, completely different orientation of the phosphoranimide units with respect to the P–C–P frame.

Table 4 Selected structural data for cyclopentadienyltitanium phosphinimide complexes

Compound		Ti–N/Å	N–P/Å	Ti–N–P/°	Ref.
$CpTiMe(NPBu^t_3)(\mu\text{-}Me)B(C_6F_5)_3$		1.765(3)	1.612(4)	176.0(2)	12
$Cp^*TiCl_2\{NP(NMe_2)_2(2,4\text{-}Me_2PN_2C_2)\}$		1.781(6)	1.669(6)	161.3(5)	13(*a*)
$CpTiCl_2(NPMe_3)$		1.746(3)	1.568(3)	170.7(2)	13(*b*)
$Cp^*TiCl_2\{NPPh_2(NHSiMe_3)\}$		1.781(3)	1.581(3)	165.2(2)	13(*c*)
$CpTiCl_2\{NPPh_2(NSMe_2O)\}$		1.764(2)	1.595(2)	158.7(1)	13(*d*)
$CpTiCl_2(NPPh_3)$		1.78(1)	1.56(1)	174.7(9)	13(*e*)
$Cp^*TiF_2(NPPh_3)$		1.809(6)	1.567(6)	152.7(4)	18
$[(Cp^*TiCl_2)_2\{\mu\text{-}(NPPh_2)_2CH_2\text{-}\kappa N,N'\}]$	**7**	1.790(3)	1.580(3)	158.4(2)	This work
		1.806(3)	1.584(3)	160.0(2)	
$[(Cp^*TiCl_2)_2\{\mu\text{-}(NPMe_2)_2CH_2\text{-}\kappa N,N'\}]$	**8a**	1.769(5)	1.578(5)	160.5(4)	This work
		1.796(5)	1.571(5)	156.9(4)	
	8b	1.755(6)	1.574(6)	172.8(5)	
		1.791(5)	1.576(5)	154.9(3)	

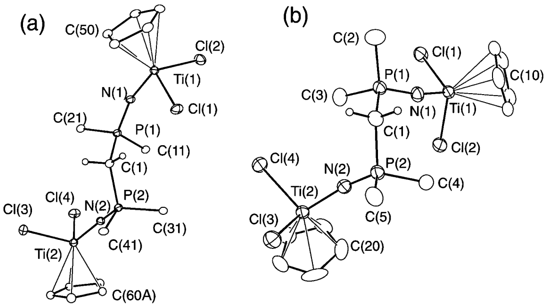

Fig. 1 Perspective ORTEP[22] plots of (a) $[(Cp^*TiCl_2)_2\{\mu\text{-}(N{=}PPh_2)_2CH_2\text{-}\kappa N,N'\}]$ **7** and (b) $[(Cp^*TiCl_2)_2\{\mu\text{-}(N{=}PMe_2)_2CH_2\}\text{-}\kappa N,N'\}]$ **8** showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at 20% probability level. The methylene hydrogen atoms are shown with arbitrarily small thermal parameters. All the other hydrogen atoms, the methyl carbons of the Cp* groups and all of the phenyl carbon (with the exception of the *ipso* carbon) atoms have been omitted for clarity.

The complex containing the phenyl substituents on phosphorus has a staggered type conformation, whereas the methyl phosphorus derivative shows the titanium–imine units to be eclipsed. The torsion angle of the N(1)–P(1)···P(2)–N(2) atoms in the case of **7** is 179.5° and the corresponding values in complex **8** are 106.1 and 110.2° for the two independent molecules present in one asymmetric unit. Thus the titanium phosphoranimide units are more widely separated in **7** than in **8**. The difference can be attributed to the difference in steric crowding about the phosphorus centers originating from substituents on the phosphorus atoms.

The titanium–nitrogen bond distances (see Table 3) in both cases are considerably shorter than titanium–amide bond lengths[23] and are closer to the distances found in normal metal imide complexes[24] and also phosphorus based substituted imide complexes.[25,26] This suggests a somewhat enhanced Ti–N bond interaction probably arising from delocalization of the N=P electron density into the Ti–N–P unit which increases the bond order of the latter and decreases the bond order of the former. This appears as P=N bond distances which are elongated compared to the parent bis(iminophosphoranyl)methane ligand systems {P–N 1.536(2) Å in **1**,[27] 1.546(2) Å in **3**[28]}. The Ti–N–P angles also widen substantially relative to typical angles seen generally for phosphinimido ligands as a result of this effect. This widening is especially pronounced in the case of **8** (where one of the two independent molecules shows an angle of 173°) although it is notable that the two molecules of **8** in the unit cell have very different angles about the nitrogen suggesting that an inter-molecular packing effect is also operative. Similar values of the Ti–N–P angles have been observed for titanium complexes containing terminal phosphinimide ligands;[11–13] examples with cyclopentadienyl substituents are listed in Table 4. The data show that the Ti–N bond distances vary between 1.716(3) and 1.873(4) Å, and the Ti–N–P angle is more linear when the metal center is less crowded. The P–C bond distances and the P–C–P bond angles are virtually unchanged relative to the values observed for the related "free" ligand systems.

Conclusion

Herein is described a series of monometallated and dimetallated phosphoranimide titanium complexes of bis(iminophosphoranyl)methane ligand systems. The crystal structures show a notable difference in the orientation of the phosphoranimidotitanium moieties depending on the substituents at the phosphorus centers. Current studies are exploring the chemical scope of these species.

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