Supporting Information

Mono, bis, and tris(phosphoramidate) titanium complexes: Synthesis, structure, and reactivity investigations

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Selected NMR Spectra

Bis(phosphoramidate) Complexes

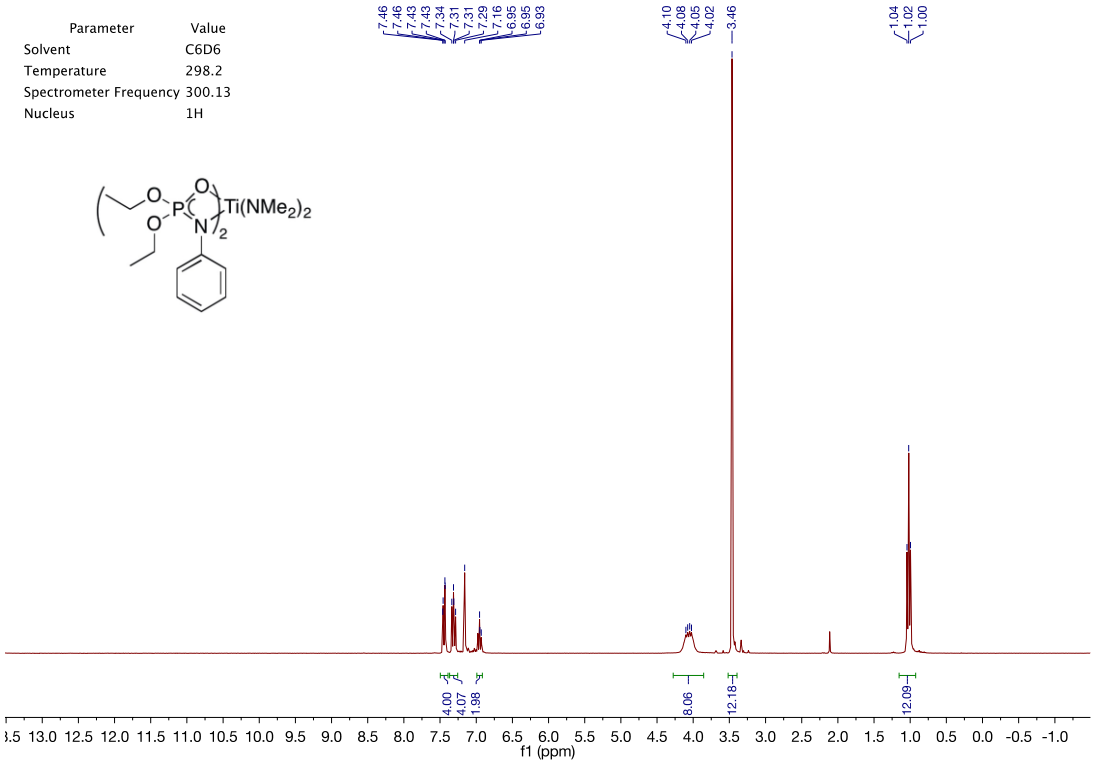


Figure 1 ^{1}H NMR spectrum of bis(phosphoramidate) complex **1**

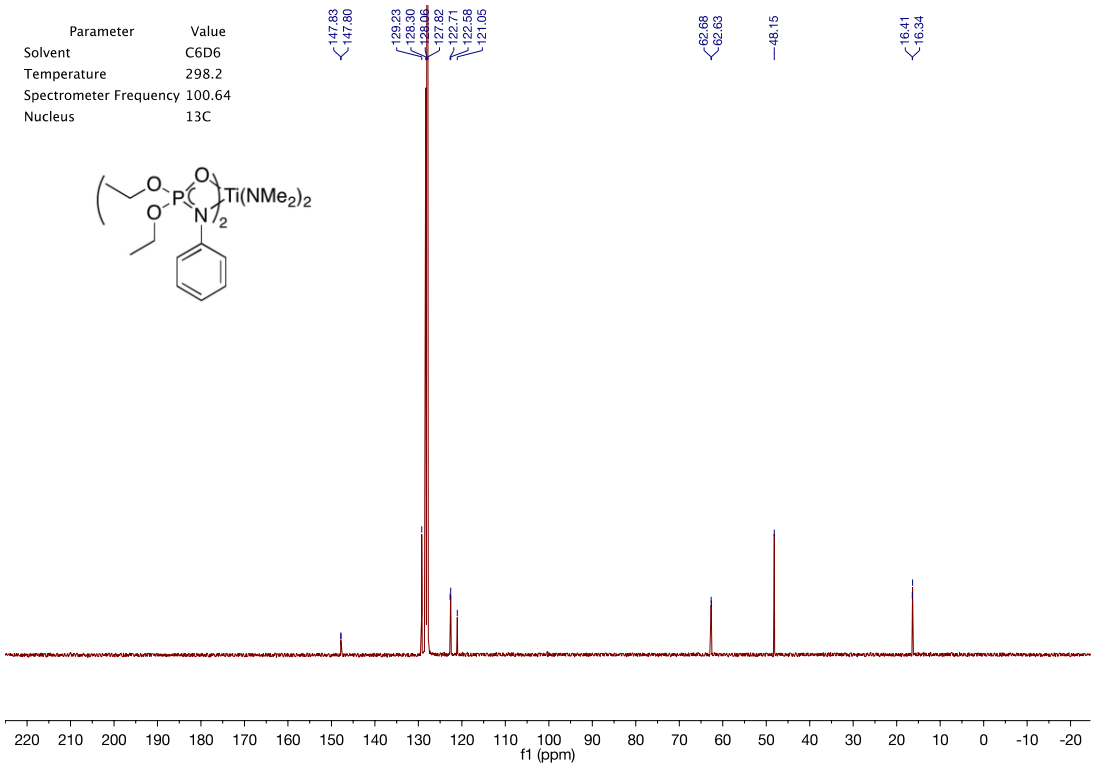


Figure 2 ^{13}C NMR spectrum of bis(phosphoramidate) complex **1**

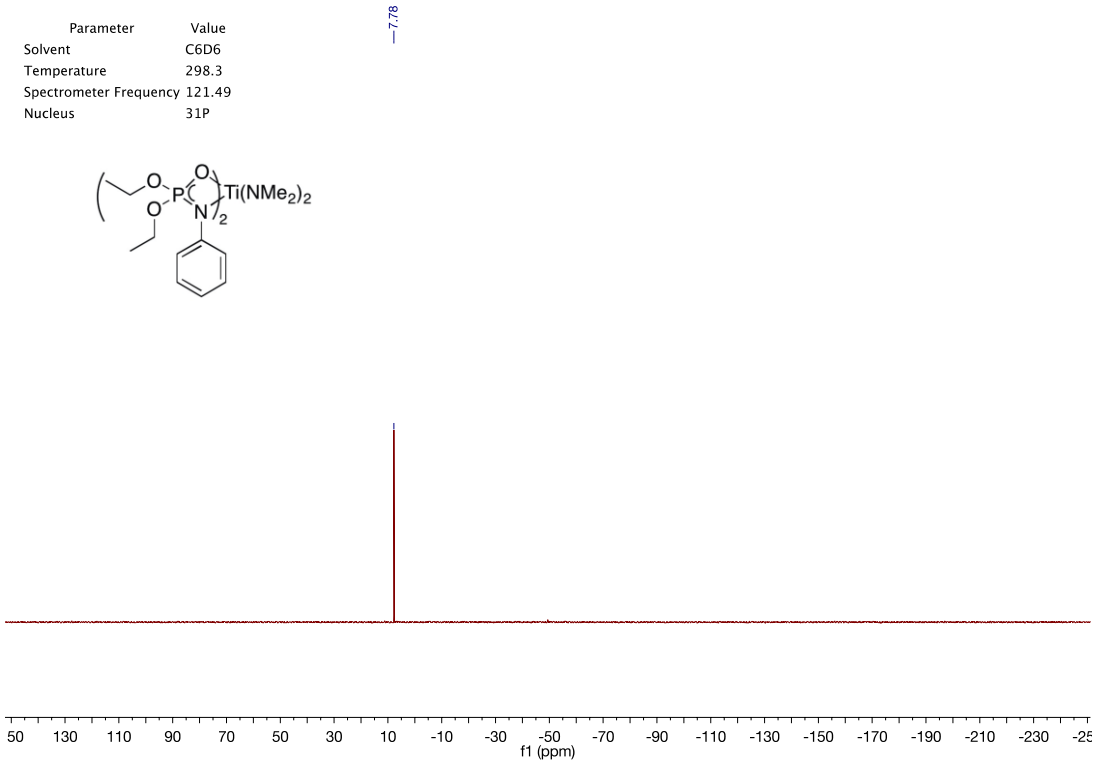


Figure 3 ^{31}P NMR spectrum of bis(phosphoramidate) complex **1**

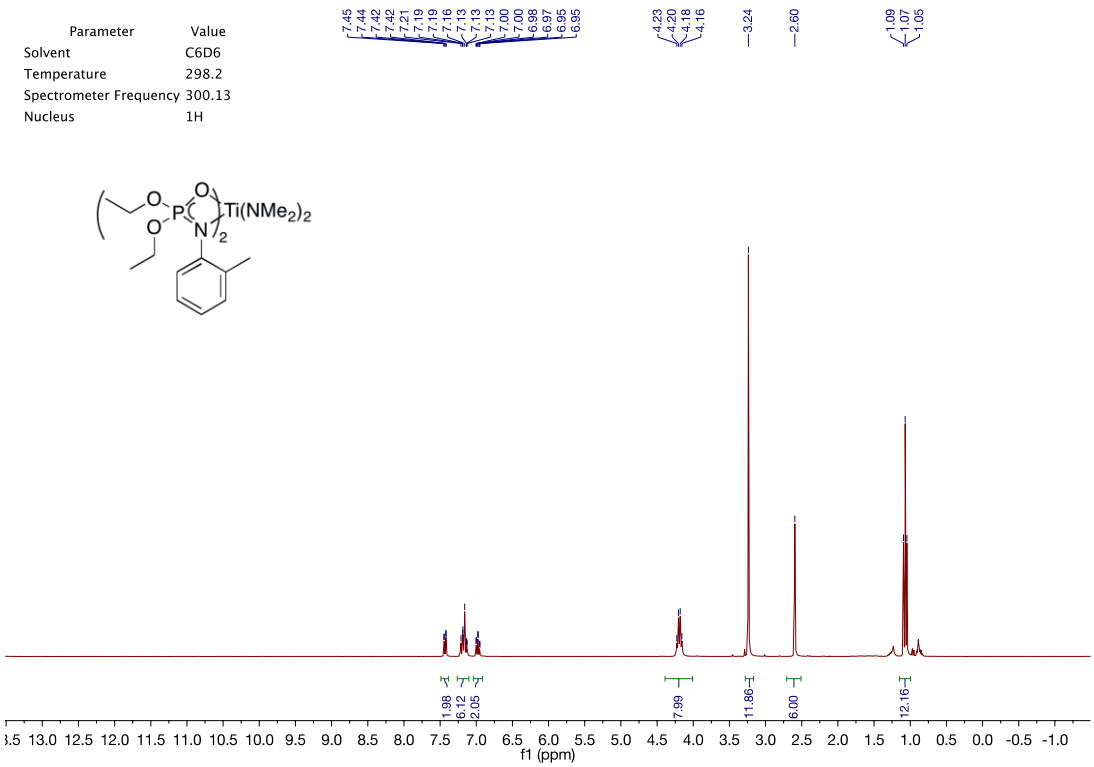


Figure 4 ^{1}H NMR spectrum of bis(phosphoramidate) complex **2**

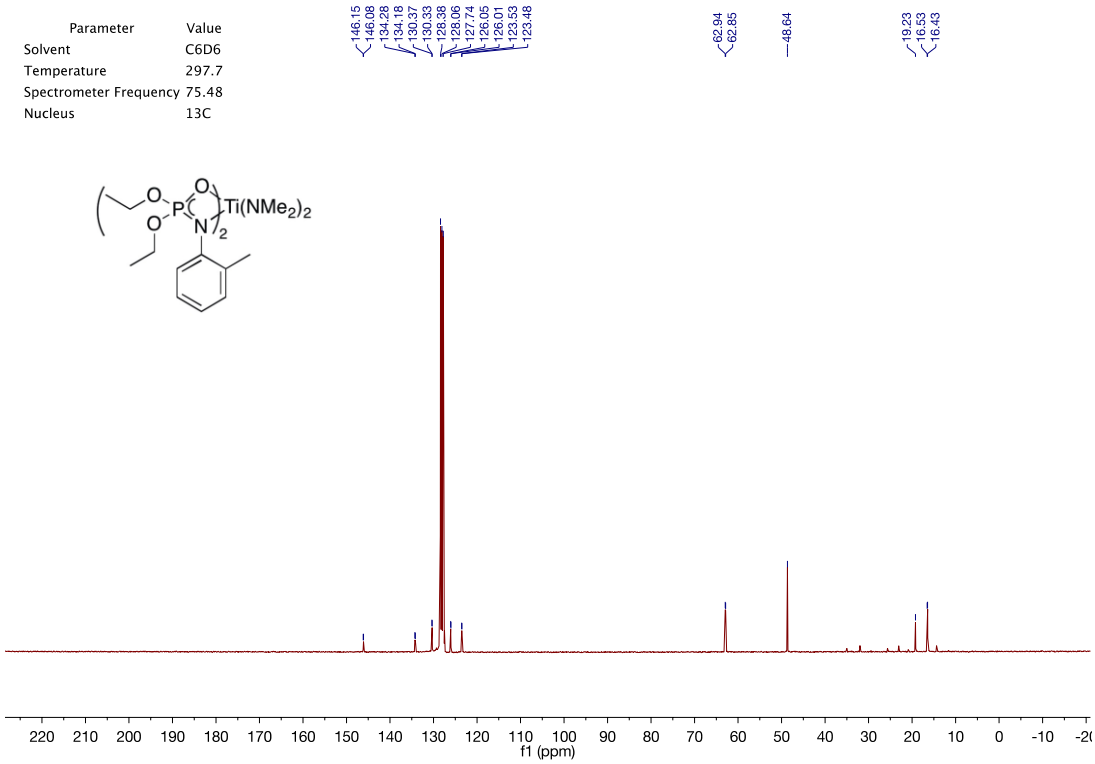


Figure 5 ^{13}C NMR spectrum of bis(phosphoramidate) complex **2**

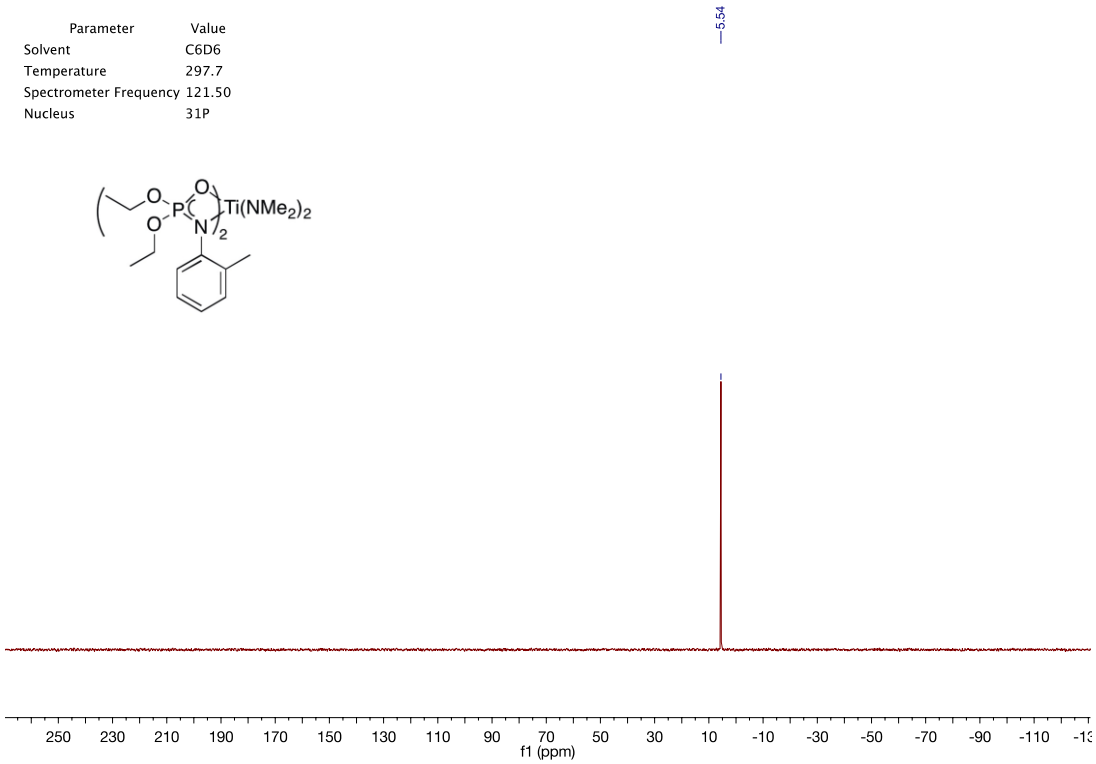


Figure 6 ^{31}P NMR spectrum of bis(phosphoramidate) complex **2**

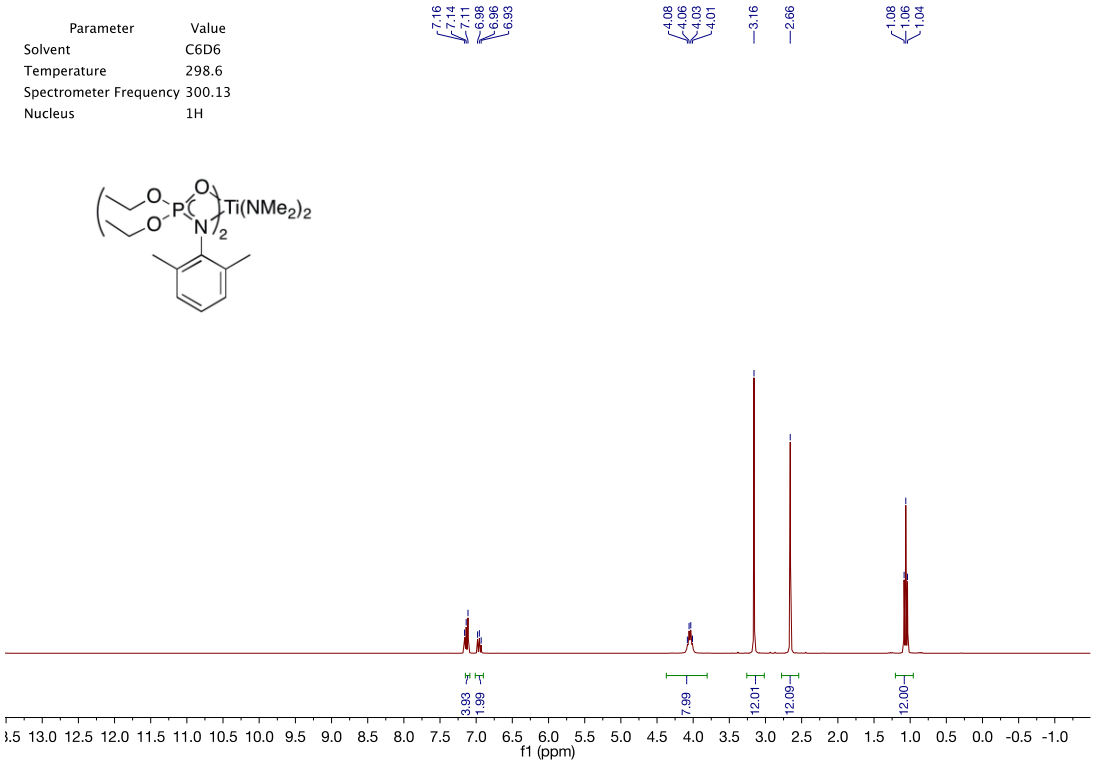


Figure 7 ^{1}H NMR spectrum of bis(phosphoramidate) complex **3**

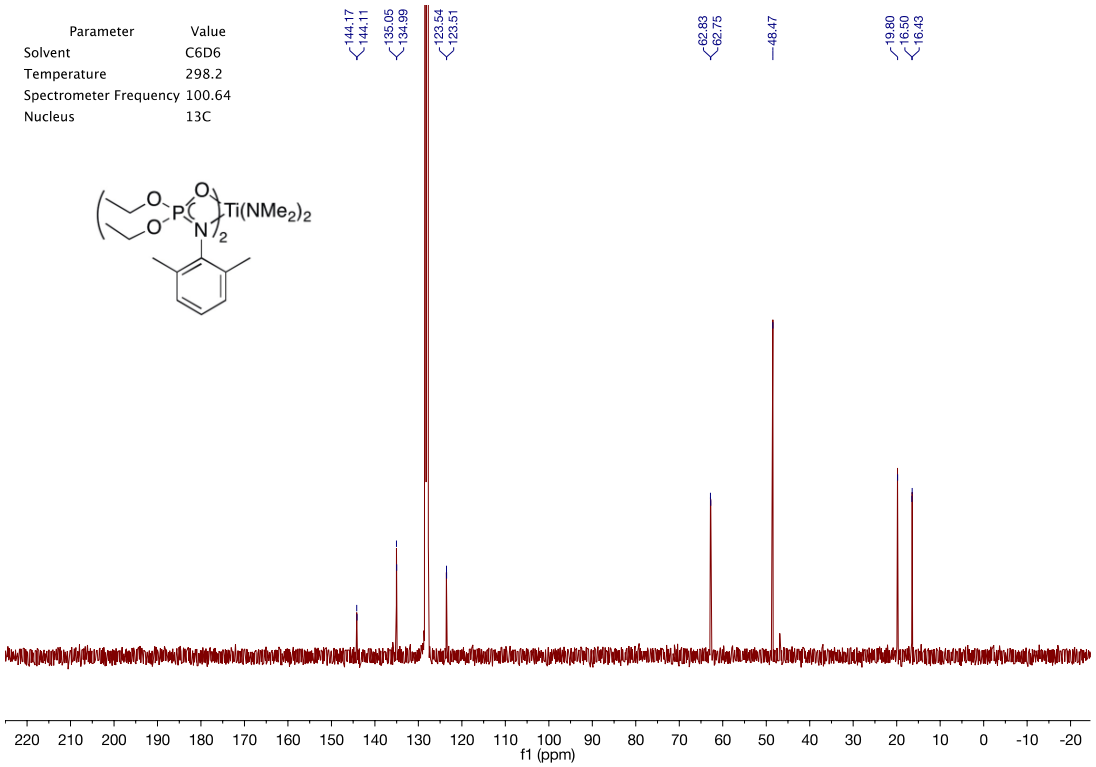


Figure 8 ^{13}C NMR spectrum of bis(phosphoramidate) complex **3**

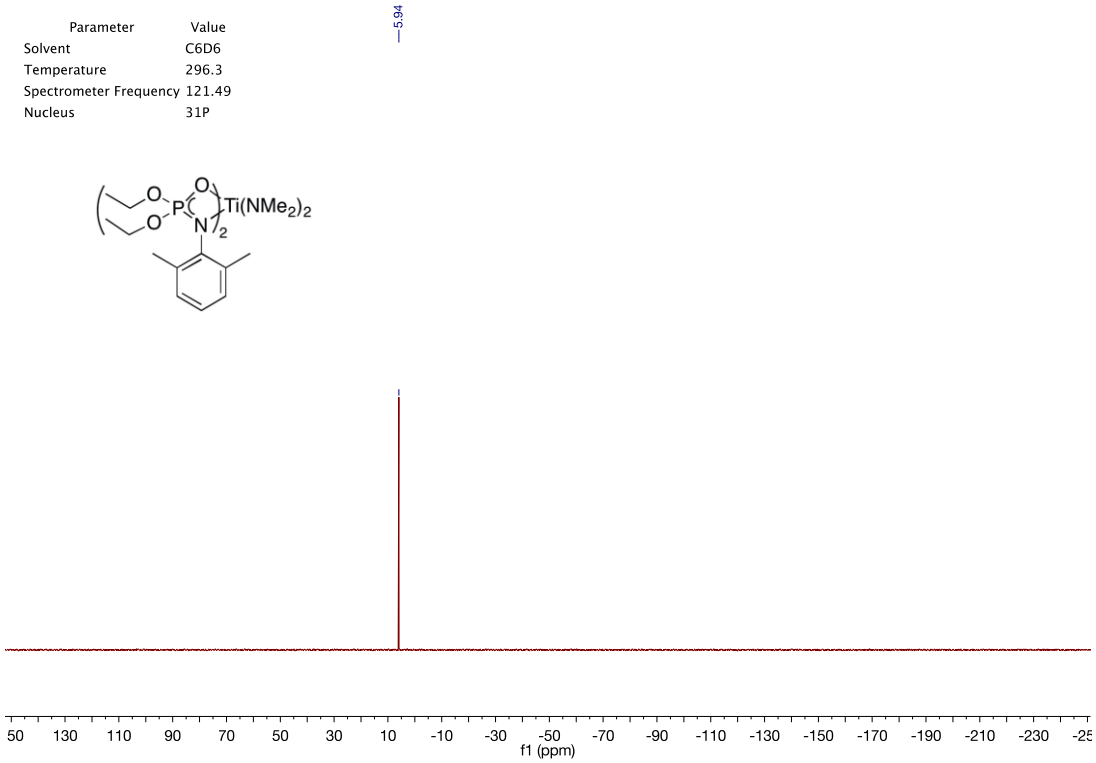


Figure 9 ^{31}P NMR spectrum of bis(phosphoramidate) complex **3**

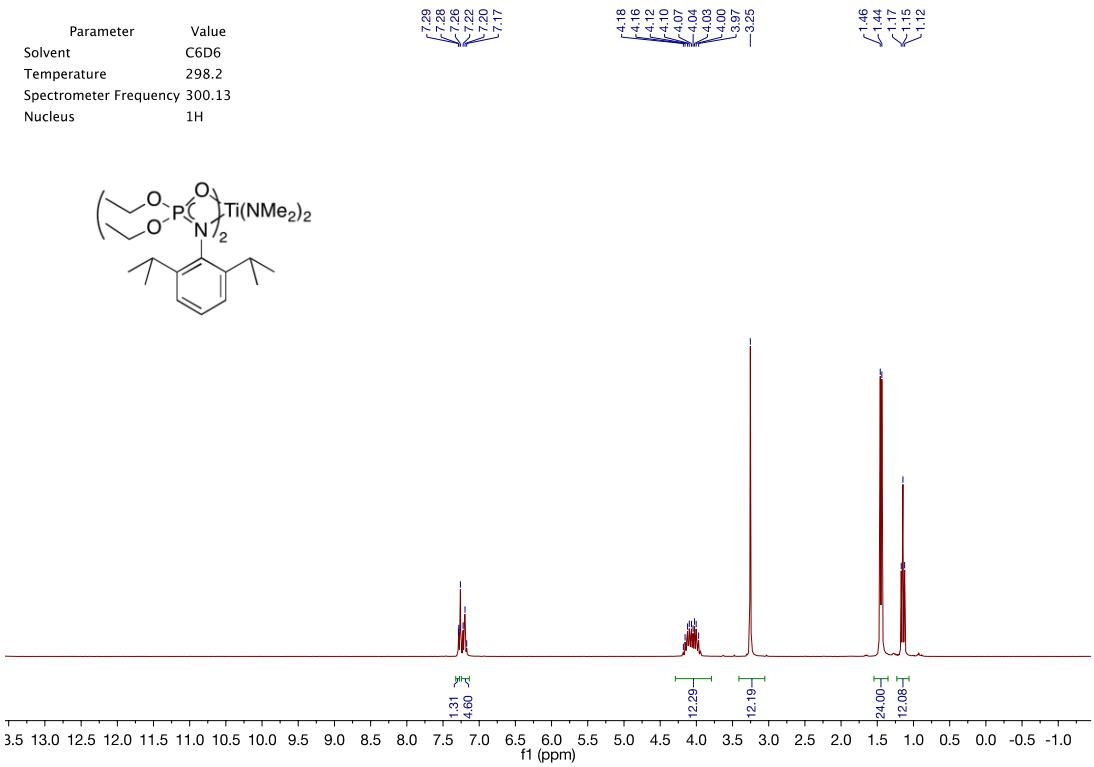


Figure 10 ^{1}H NMR spectrum of bis(phosphoramidate) complex **4**

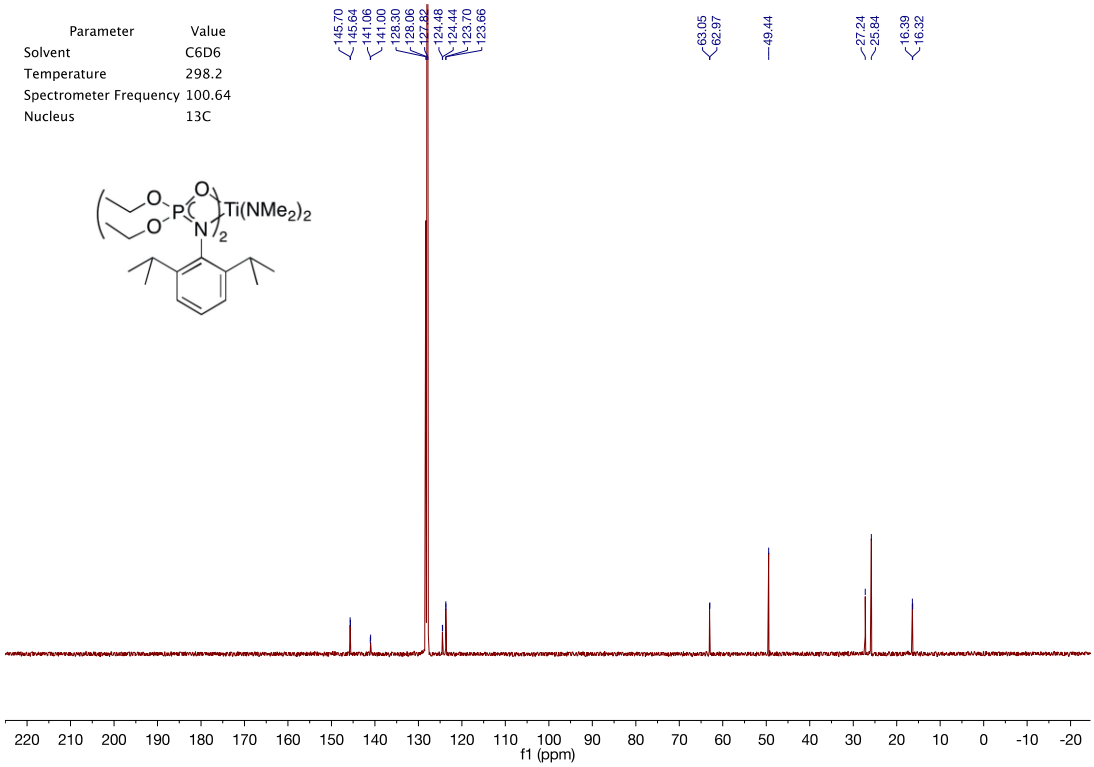


Figure 11 ^{13}C NMR spectrum of bis(phosphoramidate) complex **4**

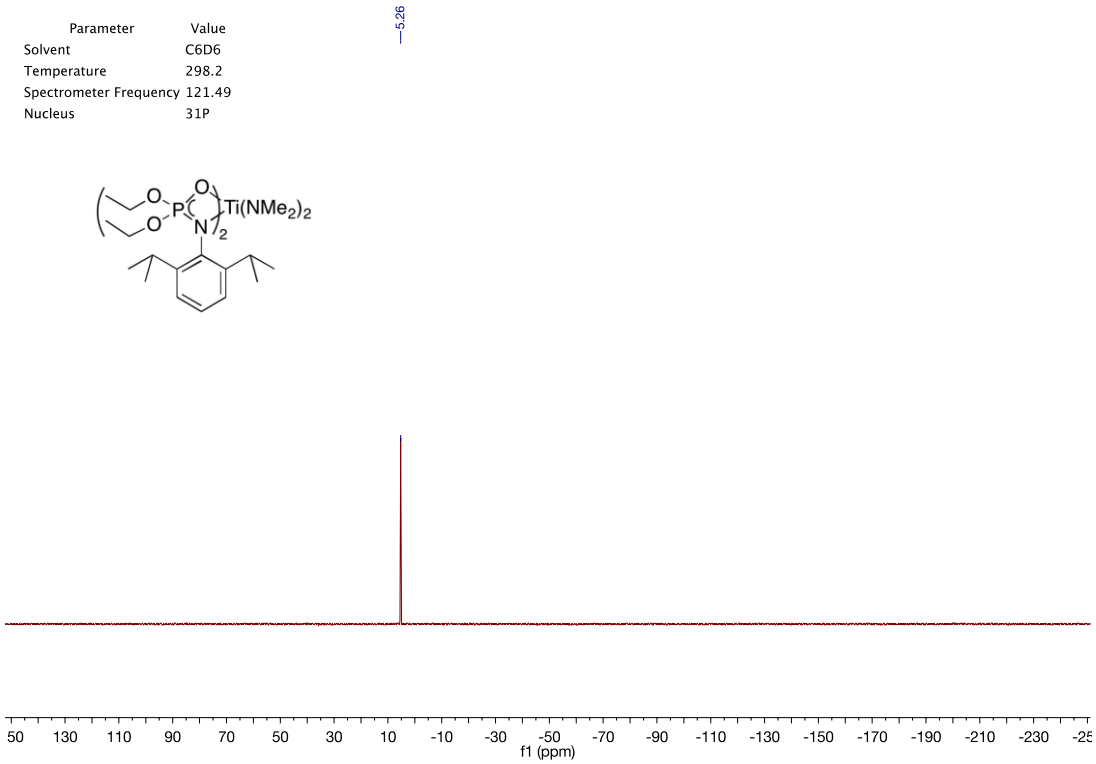


Figure 12 ^{31}P NMR spectrum of bis(phosphoramidate) complex **4**

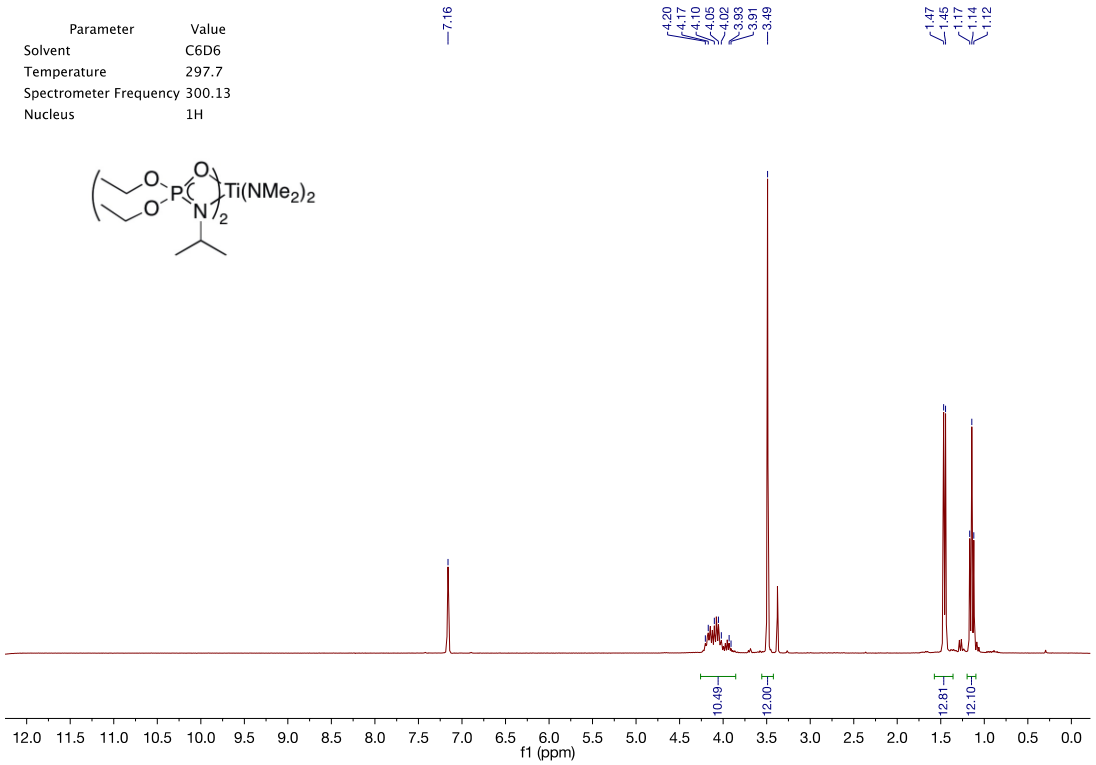


Figure 13 ^{1}H NMR spectrum of bis(phosphoramidate) complex **5**

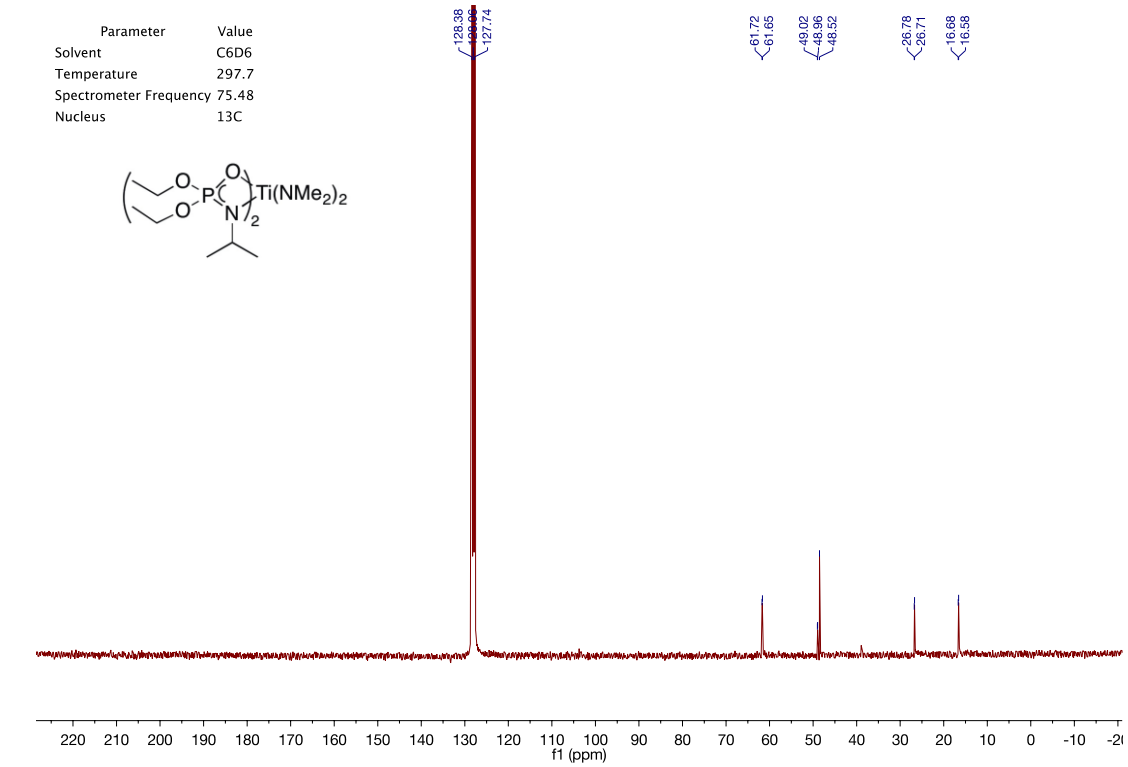


Figure 14 ^{13}C NMR spectrum of bis(phosphoramidate) complex **5**

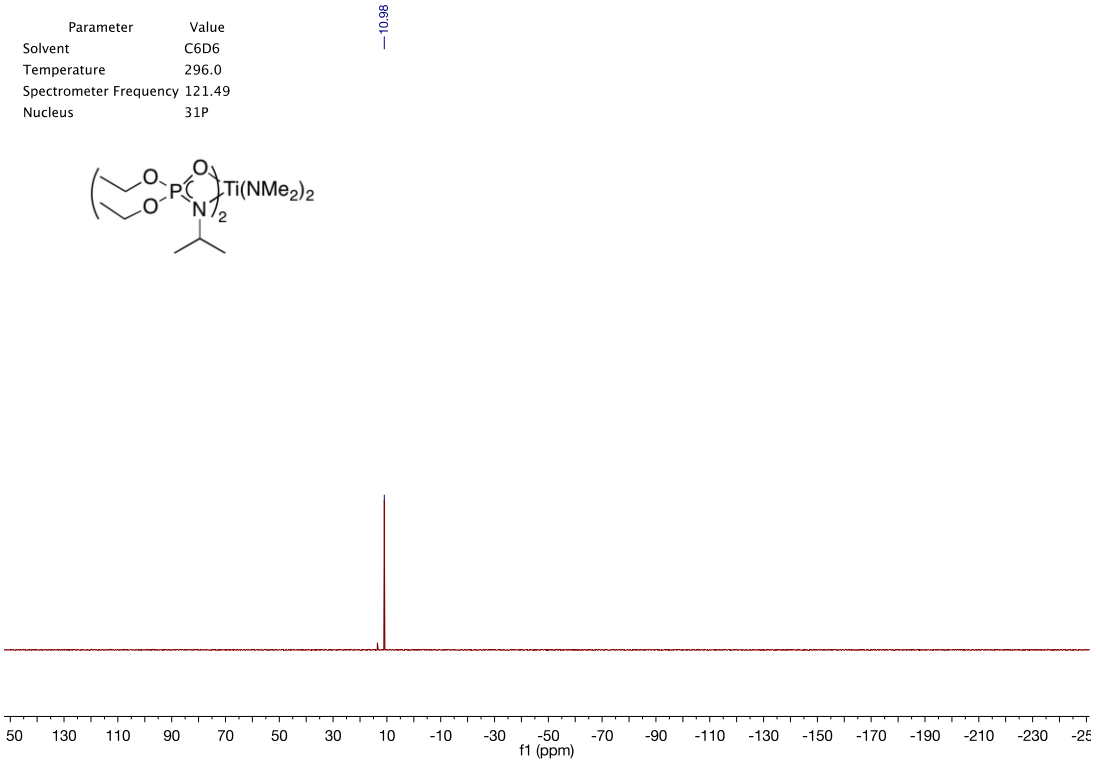


Figure 15 ^{31}P NMR spectrum of bis(phosphoramidate) complex **5**

Mono(phosphoramidate) Complexes

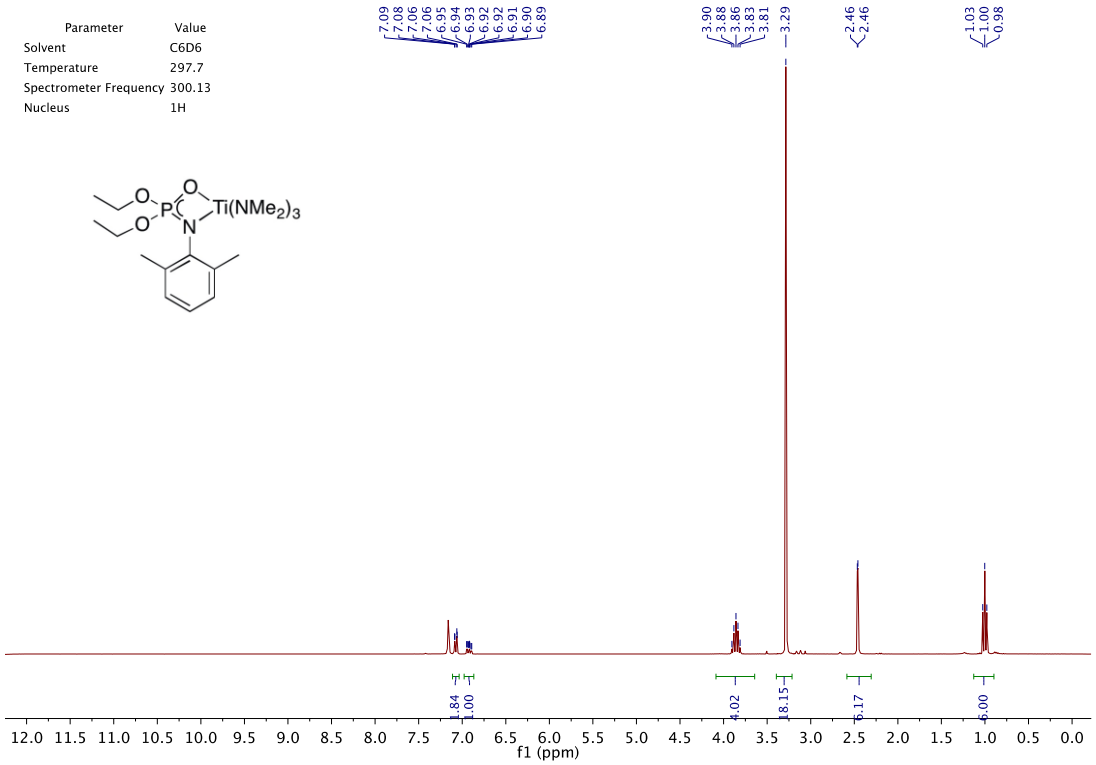


Figure 16 ^{1}H NMR spectrum of mono(phosphoramidate) complex **6**

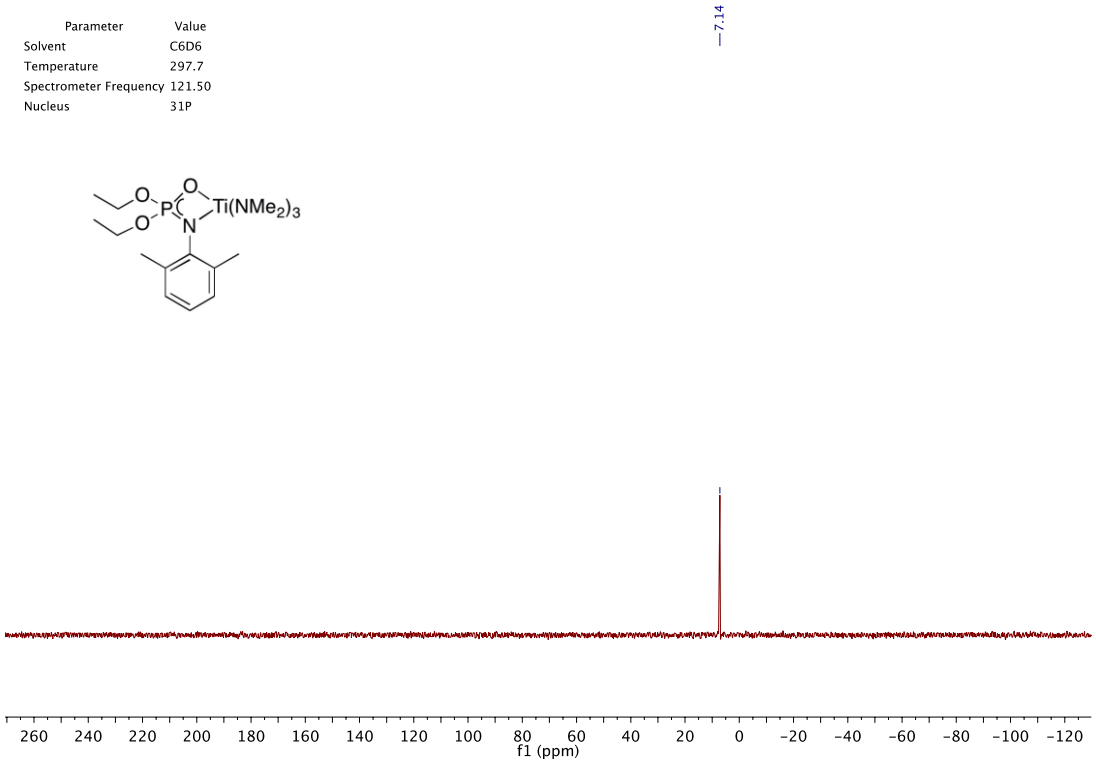


Figure 17 ^{13}C NMR spectrum of mono(phosphoramidate) complex **6**

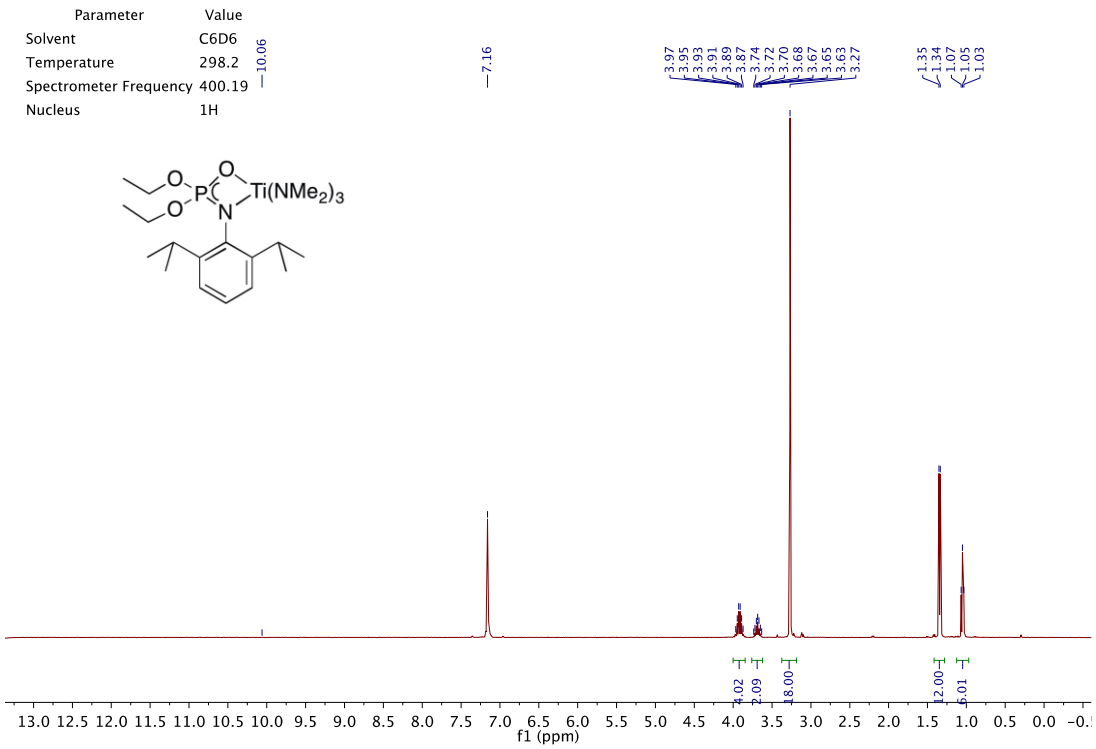


Figure 18 ^{1}H NMR spectrum of mono(phosphoramidate) complex **7**

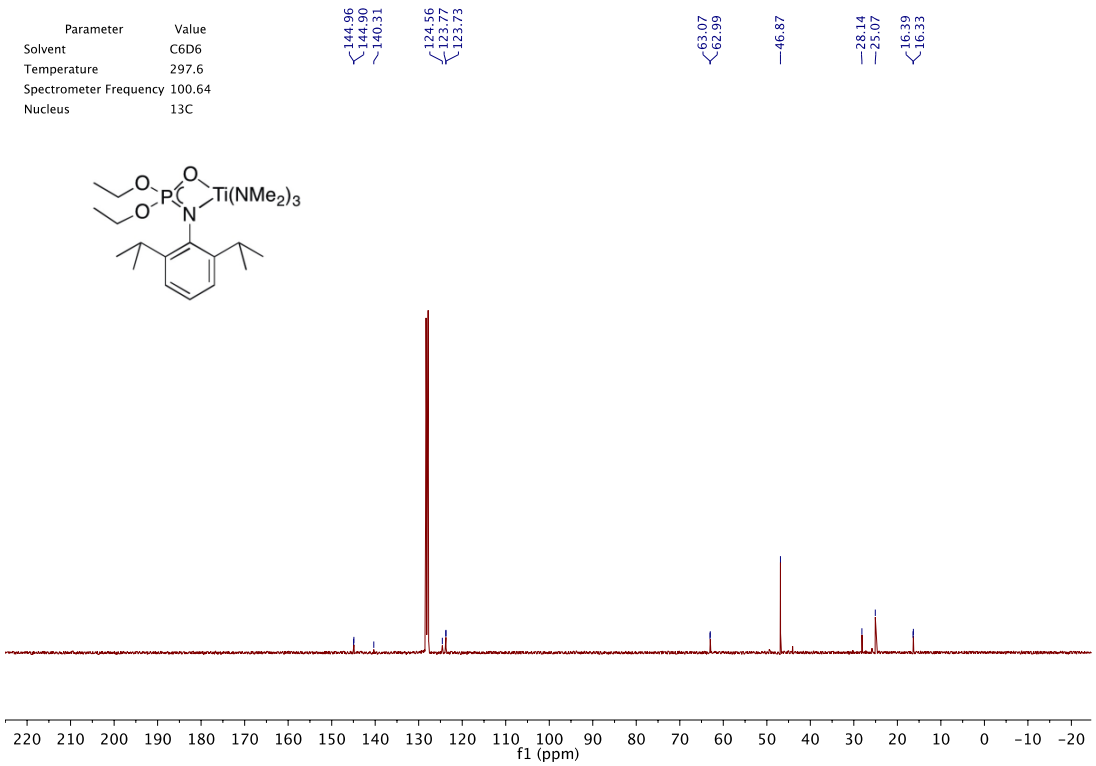
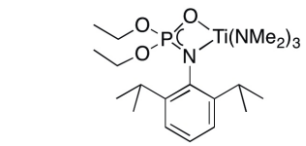


Figure 19 ^{13}C NMR spectrum of mono(phosphoramidate) complex **7**

Parameter	Value
Solvent	C6D6
Temperature	297.7
Spectrometer Frequency	121.49
Nucleus	31P



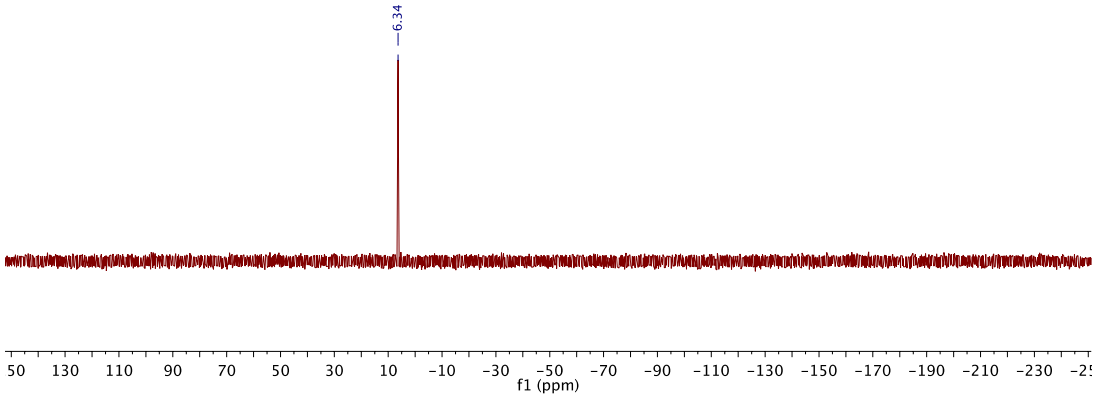


Figure 20 ^{31}P NMR spectrum of mono(phosphoramidate) complex **7**

Tris(phosphoramidate) Complexes

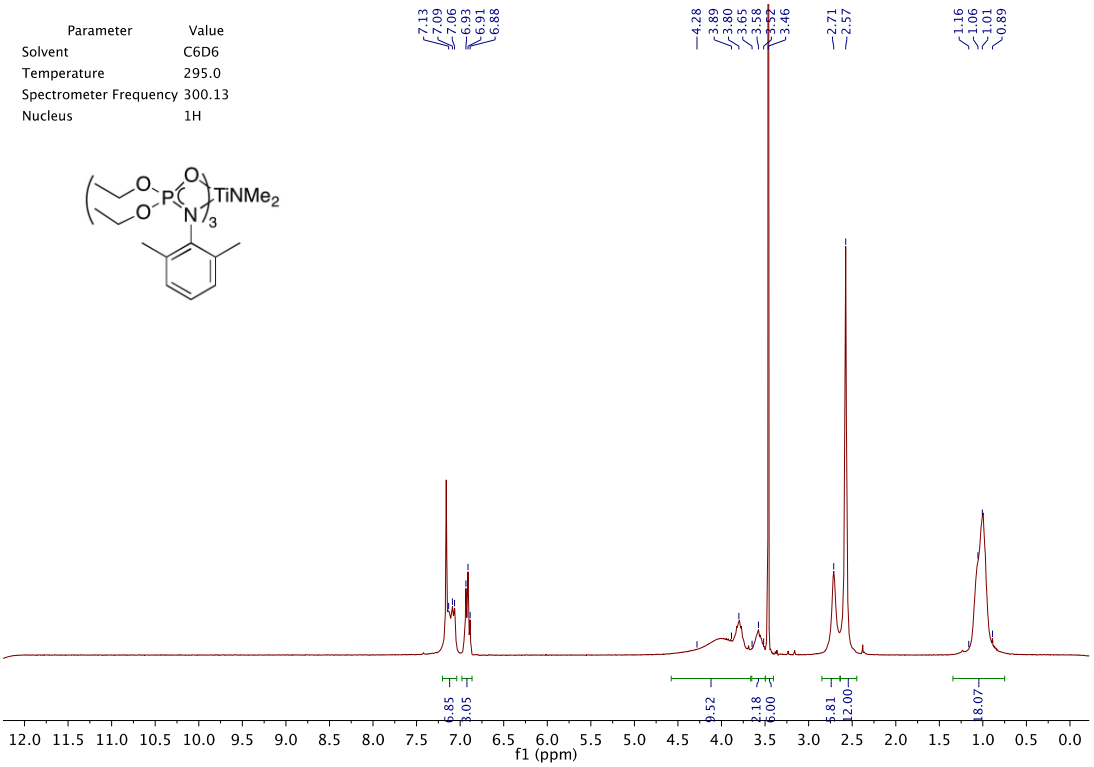


Figure 21 ^{1}H NMR spectrum of tris(phosphoramidate) complex **8**

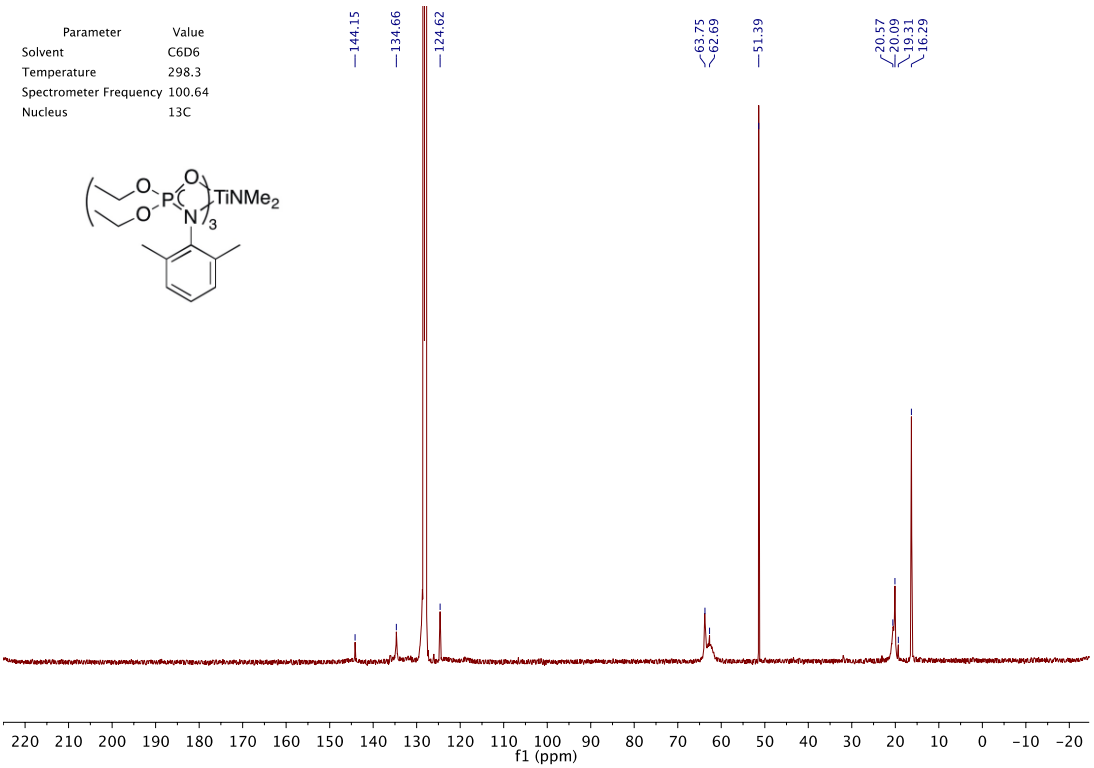


Figure 22 ^{13}C NMR spectrum of tris(phosphoramidate) complex **8**

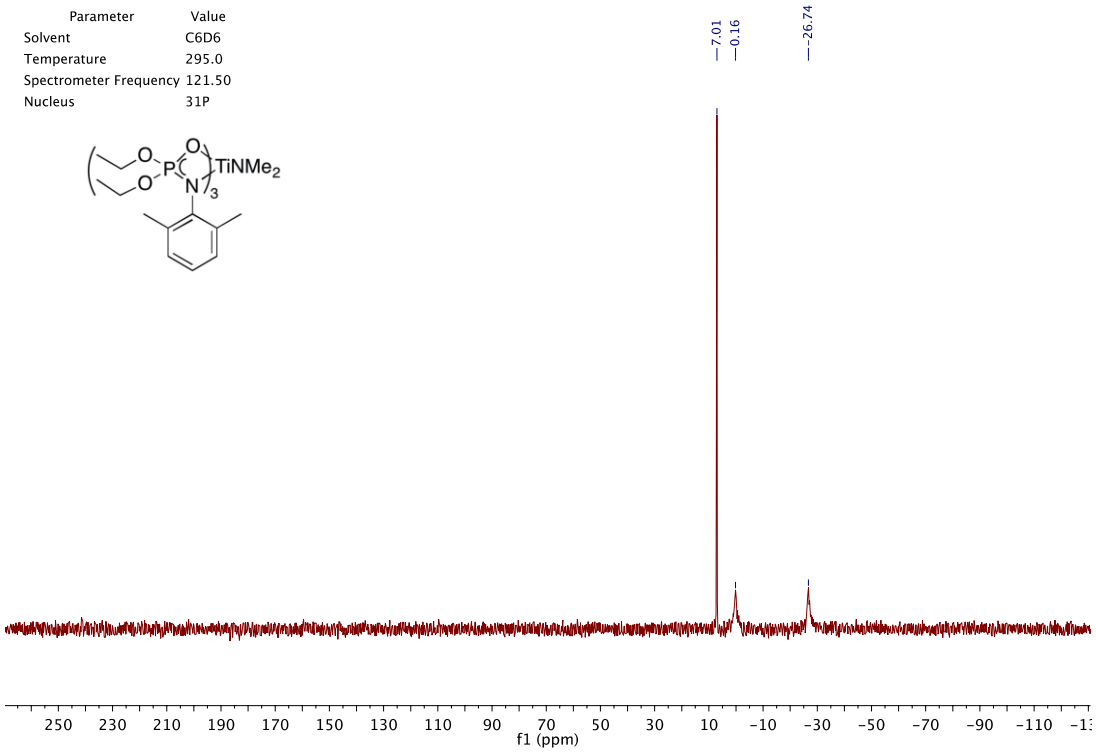


Figure 23 ^{31}P NMR spectrum of tris(phosphoramidate) complex **8**

Redistribution of Mono(phosphoramidate)s in Solution

Specifically, mono(phosphoramidate) complex **6**, was dissolved in C_6D_6. No bis(phosphoramidate) titanium species were observed by either ^{1}H and ^{31}P spectroscopy. After sitting for at room temperature for 1 hour, the same sample was again analyzed by ^{1}H and ^{31}P NMR spectroscopy. A significant amount of the bis(phosphoramidate) **3** was observed, as shown in the stacked plot below.

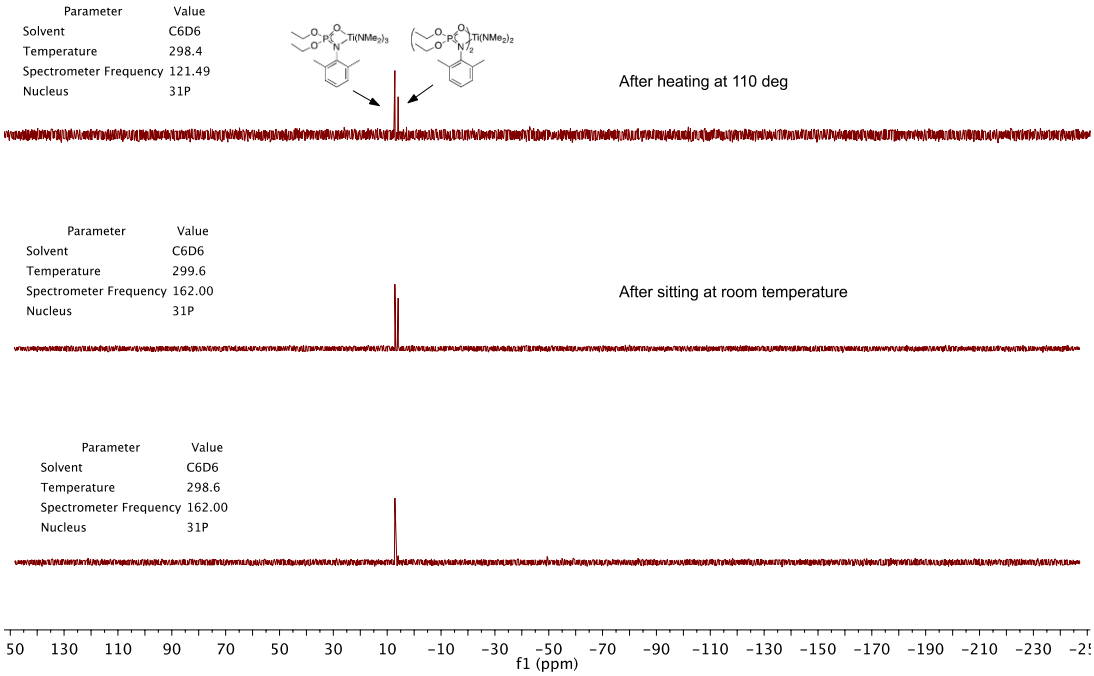


Figure 24 Redistribution of complex **6** to form **3** as observed by ^{31}P NMR spectroscopy

This solution phase behavior was also observed with bulkier mono(phosphoramidate) complex **7**, as shown below in both ^{31}P and ^{13}C NMR spectra.

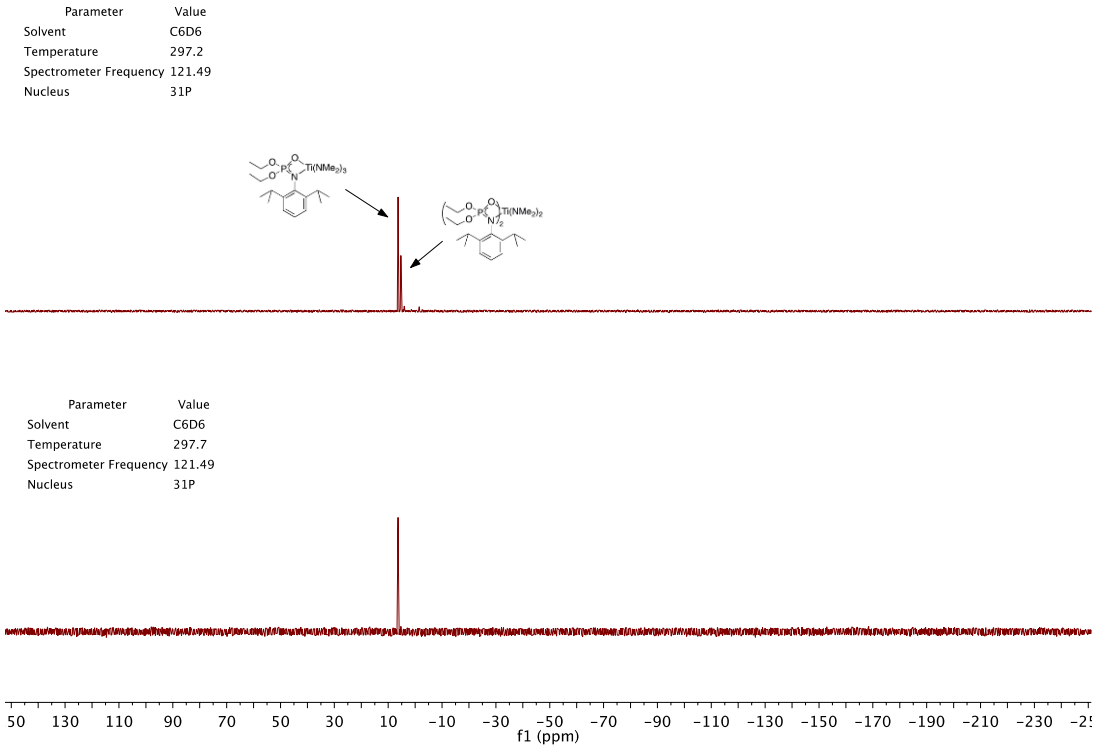


Figure 25 Redistribution of complex **7** to form **4** as observed by ^{31}P NMR spectroscopy

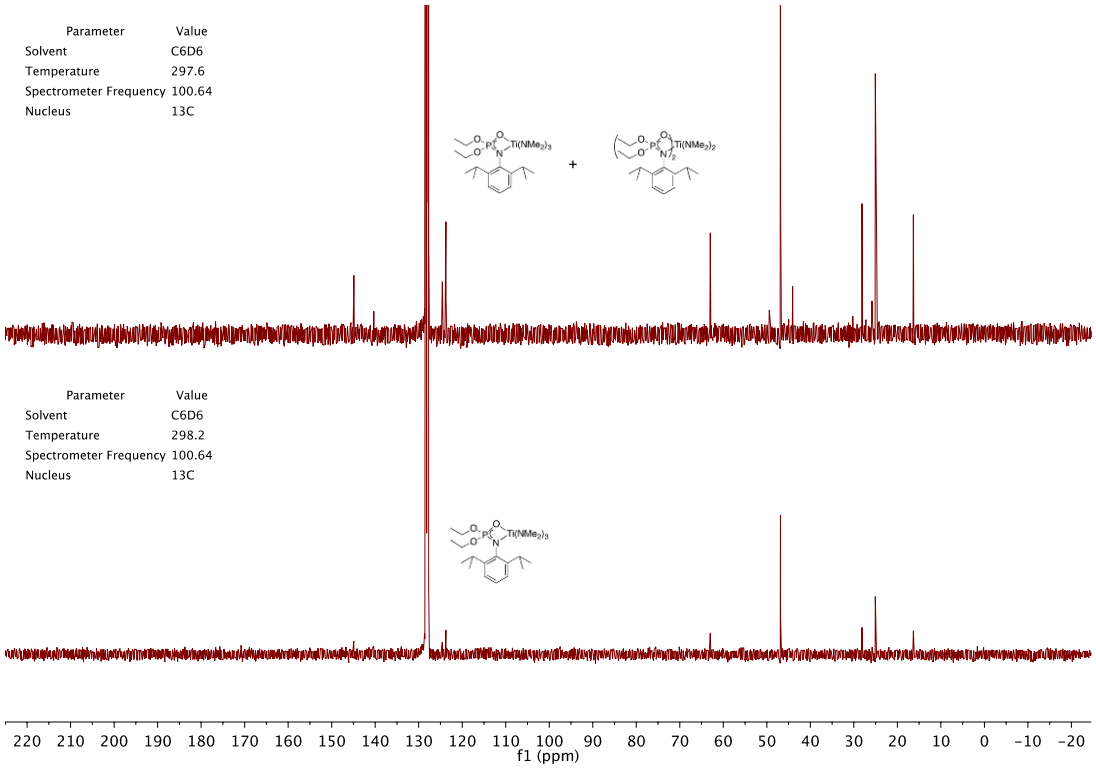


Figure 26 Redistribution of complex **7** to form **4** as observed by ^{13}C NMR spectroscopy

Variable Temperature NMR Spectroscopy

A mixture of mono- and bis(phosphoramidate)s in C_6D_6 was heated from room temperature to 75 °C. Analysis of the mixture by ^{31}P NMR spectroscopy (top) and ^{1}H NMR spectroscopy (bottom) reveals no change in the diagnostic signals in both spectra.

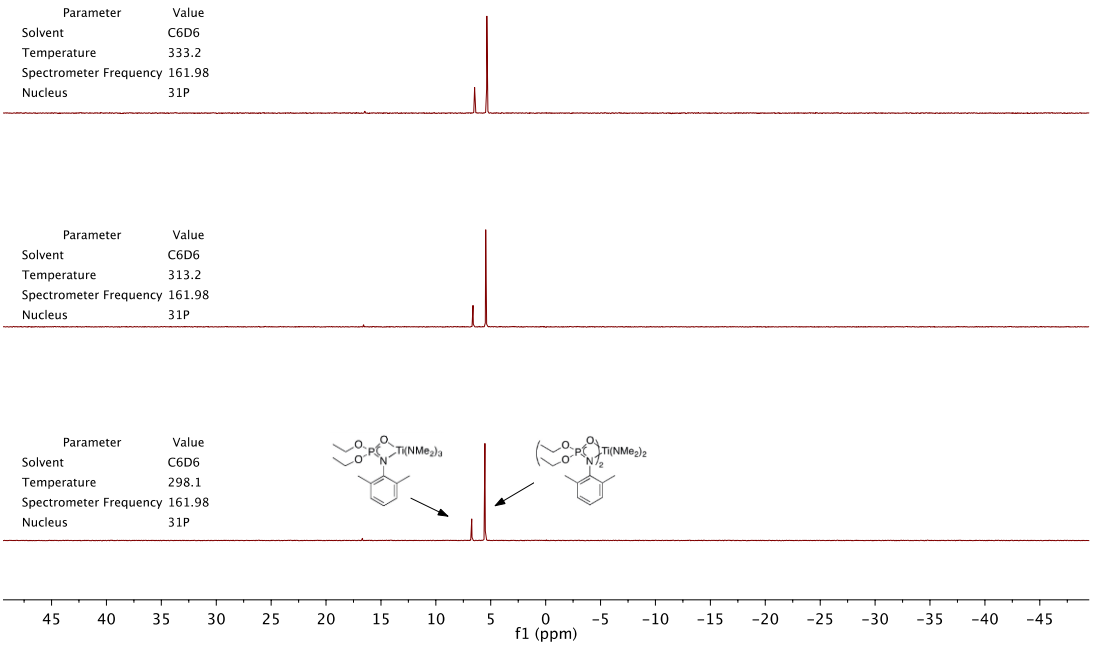


Figure 27 No change in the relative ratio of **3** and **6** was observed after heating to 75 °C and cooling

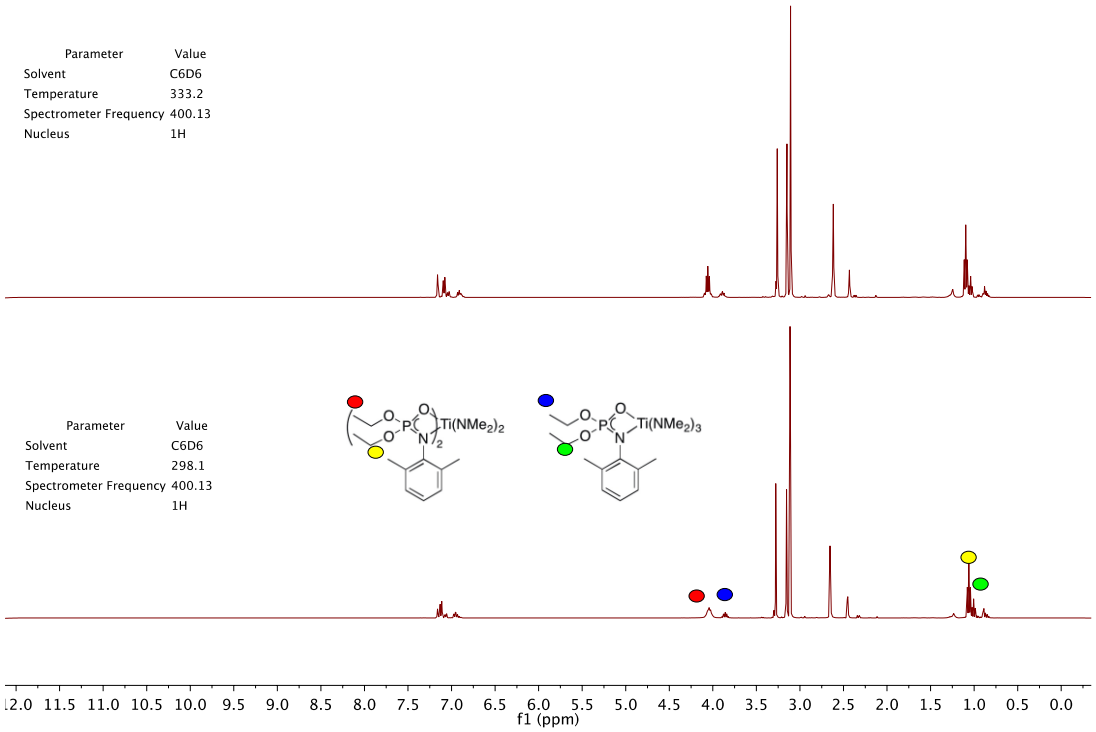


Figure 28 ^{1}H NMR spectra of a mixture of **3** and **6** at 298 K (bottom) and 333 K (top). No significant change was observed

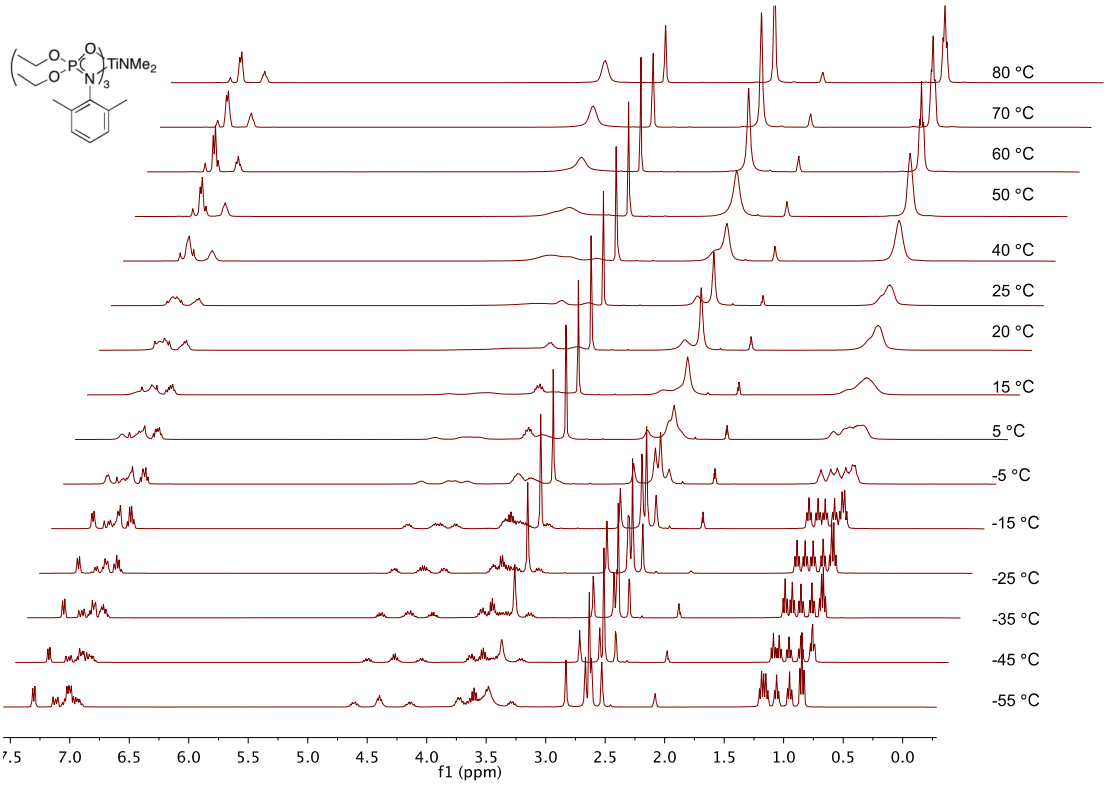


Figure 29 Variable temperature ^{1}H NMR spectra of complex tris(phosphoramidate) complex **8** (tol-d_8, 400 MHz)

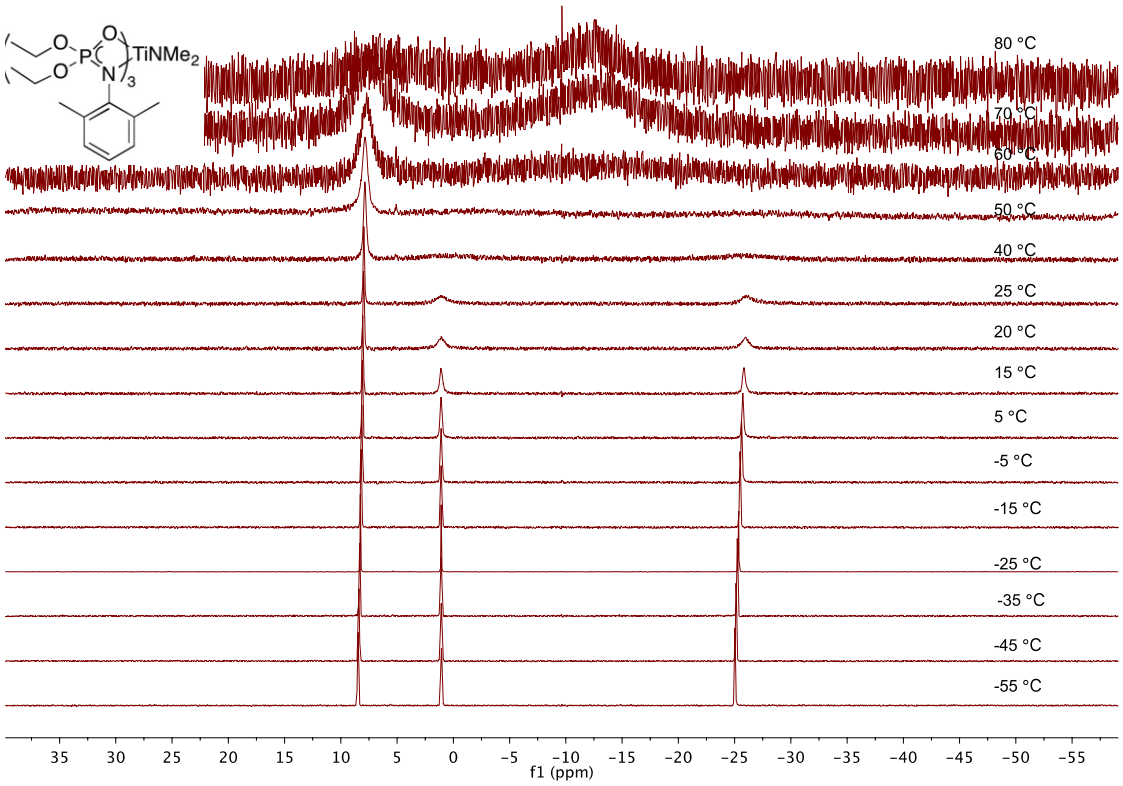


Figure 30 Variable temperature ^{31}P NMR spectra of tris(phosphoramidate) complex 8 (tol-d8, 400 MHz)

Selected IR Spectra

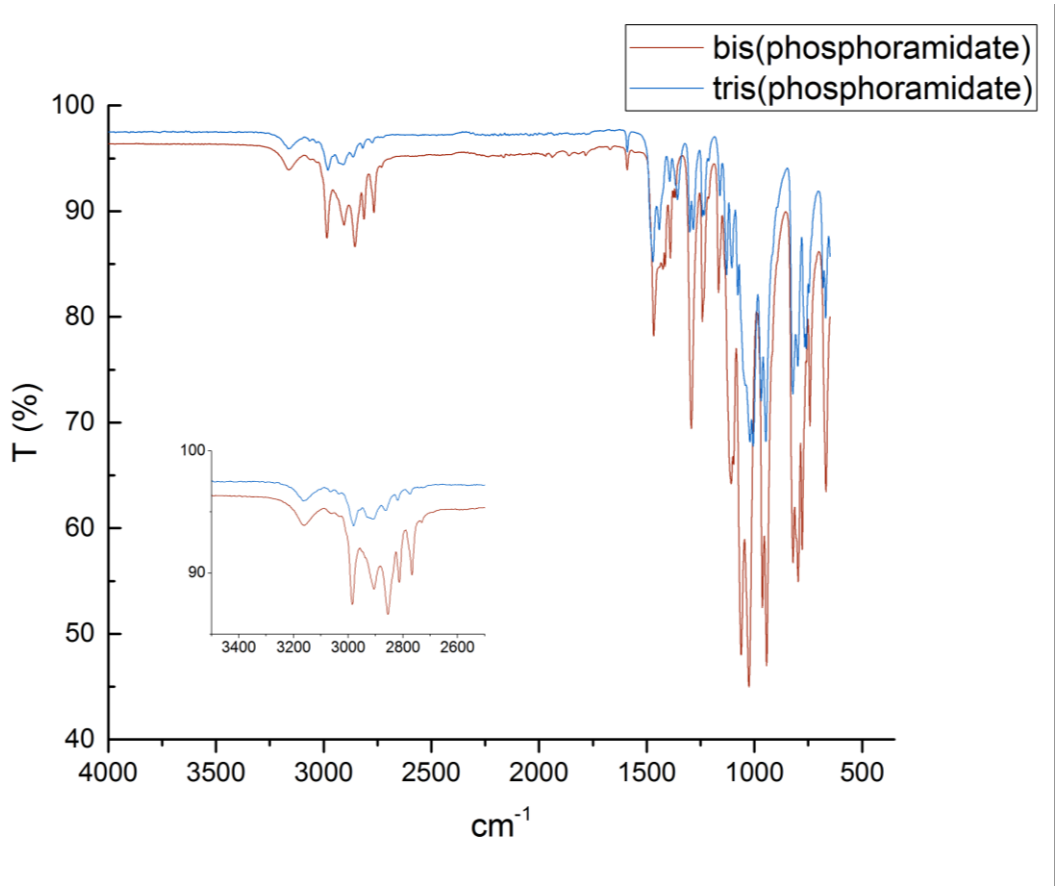


Figure 31 ATR IR spectra of bis(phosphoramidate **3** and mono(phosphoramidate) **6**

Accessing Mono(phosphoramidate)s *via* Ligand Redistribution

Specifically, bis(phosphoramidate) complex **3** (0.40g, 0.6 mmol) was dissolved in C_6D_6 (~1 mL) (top). To this solution was added $Ti(NMe_2)_4$ (10 eq, 6 mmol, 1.5 mL), Analysis of the mixture by ^1H NMR spectroscopy showed no evidence of the formation of mono(phosphoramidate) species **6** was observed (bottom). Furthermore, no change was observed when analyzing the ^{31}P NMR spectroscopy and no change was observed with upon heating the mixture to 65 °C.

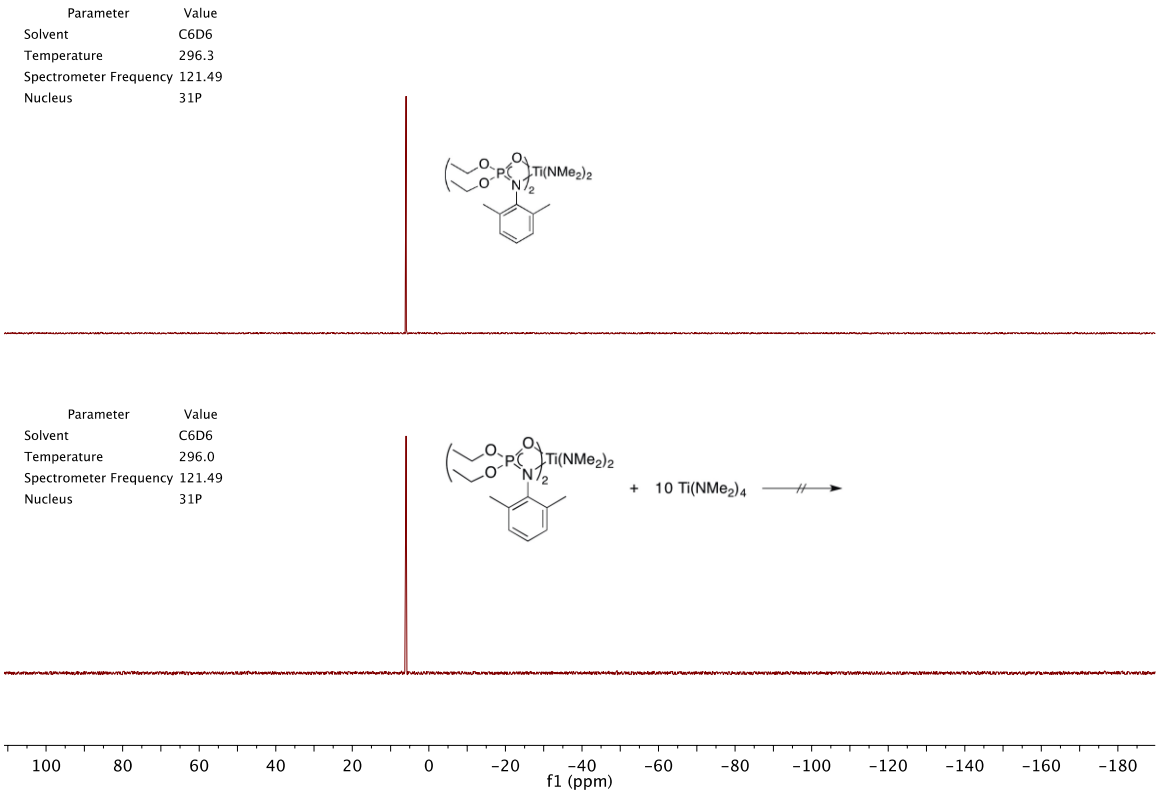


Figure 32 ^{1}H NMR spectrum of complex **1** (top) and compound **1** with an excess of $Ti(NMe_2)_4$ (bottom).

Selected bond lengths and angles for complexes

Complex 1

Bond Lengths /Å		Bond Angles /°	
Ti-O1	2.1838(16)	O1-Ti-N1	67.84(6)
Ti-N1	2.1603(19)		
		O1-P1-N1	101.78(9)
Ti-O2	2.1924(15)		
Ti-N2	2.1304(19)	O1-P1-O3	113.80(10)
		O1-P1-O4	114.81(10)
Ti-N3	1.9036(19)	O3-P1-O4	96.90(9)
Ti-N4	1.900(2)		
		O2-Ti-N2	67.84(6)
P1-O1	1.5026(16)		
P1-N1	1.609(2)	O2-P2-N2	101.78(9)
P1-O3	1.5684(18)		
		N1-Ti-N2	153.87(7)
P2-O2	1.5026(16)	N1-Ti-N3	94.72(8)
P2-N2	1.6058(19)	N1-Ti-N4	102.27(9)
P2-O5	1.5800(18)		
		N2-Ti-N3	102.41(8)
		N2-Ti-N4	94.72(8)

Complex 2

Bond Lengths /Å		Bond Angles /°	
Ti-O1	2.208(2)	O1-Ti-N1	67.61(9)
Ti-N1	2.120(3)		
		O1-P1-N1	102.22(13)
Ti-O2	2.226(2)		
Ti-N2	2.009(3)	O1-P1-O3	112.96(12)
		O1-P1-O4	114.58(12)
Ti-N3	1.911(3)	O3-P1-O4	100.00(12)
Ti-N4	1.908(3)		
		O2-Ti-N2	67.80(8)
P1-O1	1.509(2)		
P1-N1	1.586(3)	O2-P2-N2	102.00(13)
P1-O3	1.584(2)		
		N1-Ti-N2	151.56(9)
P2-O2	1.513(2)	N1-Ti-N3	94.27(11)
P2-N2	1.594(3)	N1-Ti-N4	105.44(11)

P2-O5	1.577(2)		
		N2-Ti-N3	104.78(11)
		N2-Ti-N4	93.80(11)
		N3-Ti-N4	95.28(11)

Complex 3

Bond Lengths /Å		Bond Angles /°	
Ti-O1	2.150(15)	O1-Ti-N1	67.0(4)
Ti-N1	2.16(3)		
		O1-P1-N1	100.9(11)
Ti-O2	2.29(4)		
Ti-N2	2.12(6)	O1-P1-O3	112.6(7)
		O1-P1-O4	114.9(7)
Ti-N3	1.82(2)	O3-P1-O4	100.7(6)
Ti-N4	2.06(3)		
		O2-Ti-N2	68.4(8)
P1-O1	1.508(8)		
P1-N1	1.577(12)	O2-P2-N2	108.0(3)
P1-O3	1.576(9)		
		N1-Ti-N2	149.9(5)
P2-O2	1.498(14)	N1-Ti-N3	109.5(12)
P2-N2	1.575(16)	N1-Ti-N4	89.7(5)
P2-O5	1.578(13)		
		N2-Ti-N3	96.6(5)
		N2-Ti-N4	101.0(2)
		N3-Ti-N4	98.5(5)

Complex 4

Bond Lengths /Å		Bond Angles /°	
Ti-O1	2.2533(16)	O1-Ti-N1	66.19(6)
Ti-N1	2.156(2)		
		O1-P1-N1	102.97(10)
Ti-O2	2.1929(15)		
Ti-N2	2.1038(19)	O1-P1-O3	111.92(9)
		O1-P1-O4	115.54(9)
Ti-N3	1.915(2)	O3-P1-O4	100.11(9)
Ti-N4	1.898(2)		
		O2-Ti-N2	68.26(7)

P1-O1	1.5018(17)		
P1-N1	1.5763(19)	O2-P2-N2	102.97(10)
P1-O3	1.5850(17)		
		N1-Ti-N2	147.86(7)
P2-O2	1.5018(17)	N1-Ti-N3	104.73(8)
P2-N2	1.5953(19)	N1-Ti-N4	95.27(8)
P2-O5	1.5715(16)		
		N2-Ti-N3	93.72(8)
		N2-Ti-N4	109.02(8)
		N3-Ti-N4	95.74(9)

Complex 6

Bond Lengths /Å		Bond Angles /°	
Ti-O1	2.223(6)	O1-Ti-N1	67.3(3)
Ti-N1	2.107(7)		
		O1-P1-N1	102.3(4)
Ti-N2	1.922(8)	O1-P1-O2	114.9(4)
Ti-N3	1.893(7)	O1-P1-O3	113.2(3)
Ti-N4	1.931(8)	O2-P1-O3	100.0(4)
P1-O1	1.514(6)	N1-Ti-N4	93.5(3)
P1-O2	1.570(7)	N2-Ti-N3	113.5(3)
P1-O3	1.567(6)	N2-Ti-N4	96.7(3)
P1-N1	1.570(8)	N3-Ti-N4	95.6(3)

Complex 8

Bond Lengths /Å		Bond Angles /°	
Ti-O1	2.2022(18)	O1-Ti-N1	68.66(8)
Ti-N1	2.068(2)		
		O1-P1-N1	101.98(10)
Ti-O2	2.0492(19)		
Ti-N2	2.151(2)	O1-P1-O4	111.44(11)
		O1-P1-O5	115.81(11)
Ti-O3	1.8909(19)	O4-P1-O5	101.54(10)
O3-P3	1.532(2)		
P3-N3	1.529(2)	O2-Ti-N2	69.20(8)
P3-O8	1.5896(19)		
		O2-P2-N2	100.59(11)
Ti-N4	1.889(2)		
		N1-Ti-N2	152.56(9)

P1-O1	1.5021(19)	N1-Ti-O3	101.58(9)
P1-N1	1.599(2)	N1-Ti-N4	94.14(9)
P1-O4	1.578(2)		
		N2-Ti-O3	91.37(8)
P2-O2	1.5237(19)	N2-Ti-N4	108.56(9)
P2-N2	1.579(2)		
P2-O5	1.5765(19)	O3-Ti-N4	96.38(9)
		O3-P3-N3	111.78(12)
		O3-P3-O8	102.40(11)
		O3-P3-O9	107.55(11)

References

(1) Garcia, P.; Lau, Y. Y.; Perry, M. R.; Schafer, L. L. *Angew. Chem. Int. Ed.* **2013**, 52, 9144-8.
(2) (a) Naktode, K.; Kottalanka, R. K.; Panda, T. K. *New J. Chem.* **2012**, 36, 2280-2285; (b) Gusev, O. V.; Ustynyuk, N. A.; Peganova, T. A.; Gonchar, A. V.; Petrovskii, P. V.; Pyssenko, K. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2009**, 184, 322-331.