Electronic Supplementary Information for DaltonTransactions

Synthesis, Structures and Reactivity of 2-Phosphorylmethyl-1H-pyrrolato Complexes of Titanium, Yttrium and Zinc

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Supporting Information

^{1}H and $^{1}H\{^{31}P\}$ NMR spectra of the PCH_2 region of complex **6a**;

NMR spectra of the reaction intermediates of **3a** with $Y[N(SiHMe_2)_2]_3(THF)_2$;

^{1}H NMR spectrum of **9b.**

^{13}C NMR chemical shifts of 2-phosphorylmethyl-1*H*-pyrroles and their complexes.

^{13}C NMR data of *tert*-butyl substituted pyrrole aldehydes.

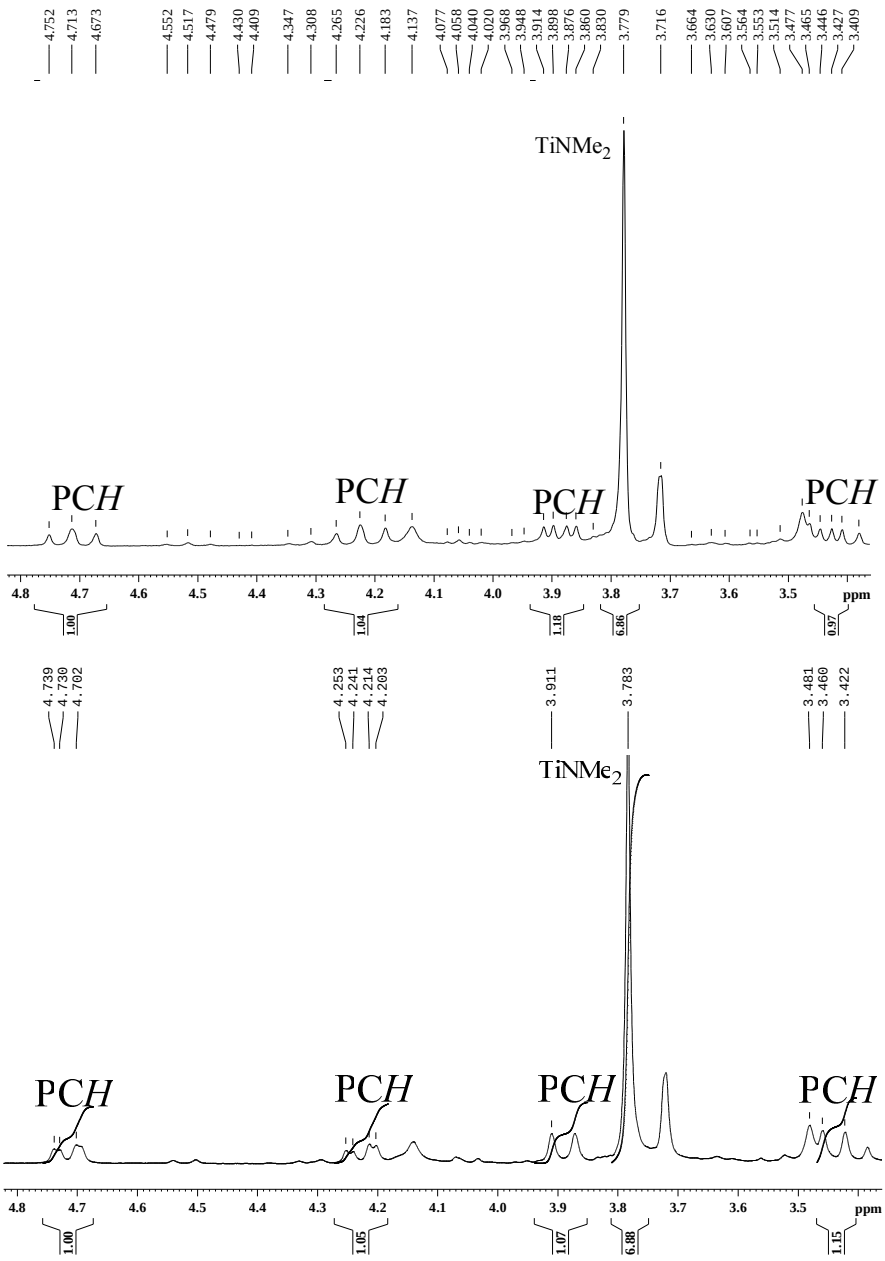


Figure S1. Top: ^{1}H NMR spectrum of complex **6a** in the region of the P-CH_2 signals, showing the coupling pattern of the diastereotopic hydrogen atoms. Bottom: The same region with ^{31}P decoupling.

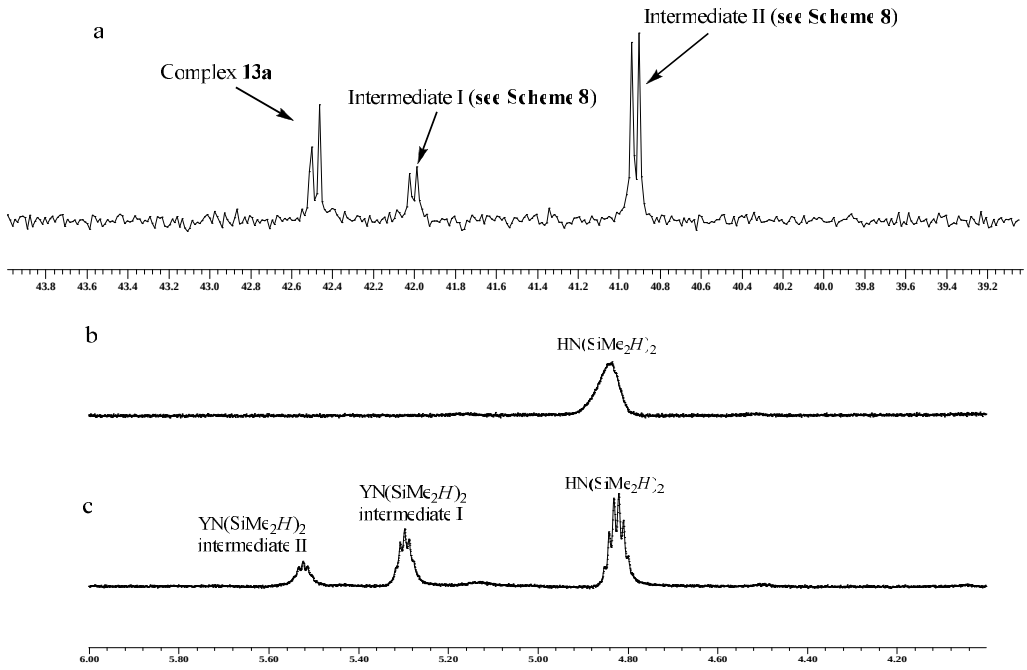


Figure S2**. (**a) $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **3a** with $Y[N(SiHMe_2)_2]_3(THF)_2$ after 3 min. (b) and (c) show sections of the ^{1}H NMR spectrum of the in-situ NMR experiment of the same reaction after the same time period.

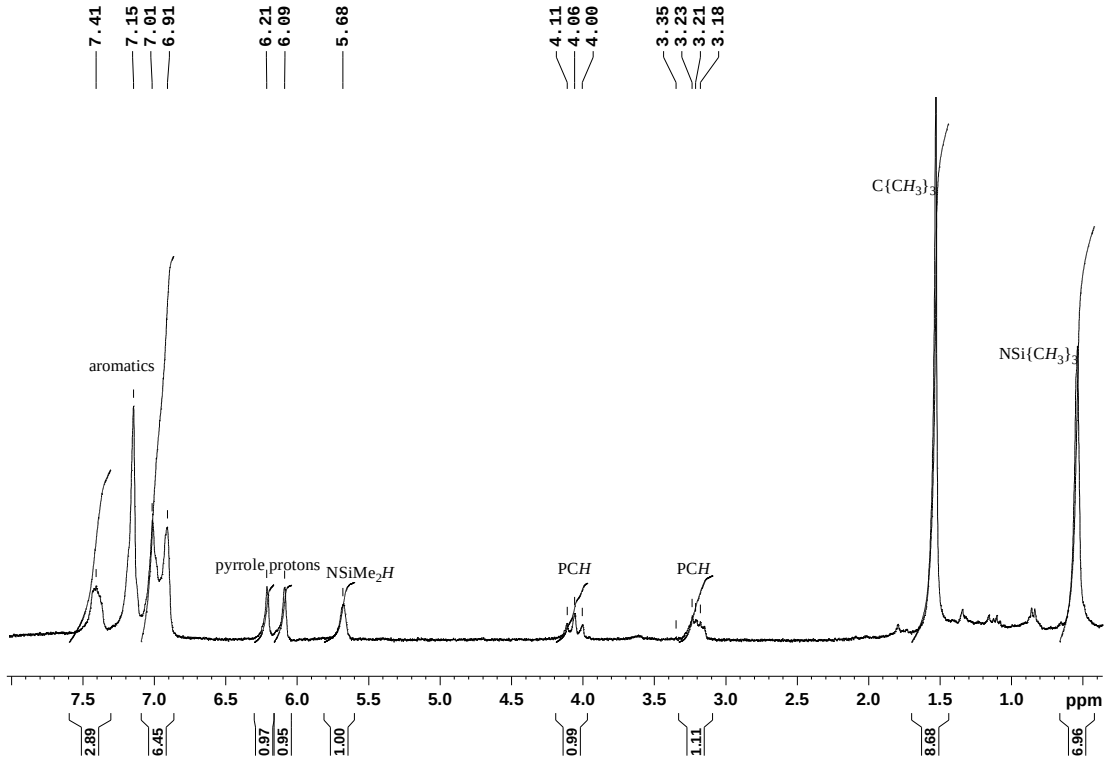
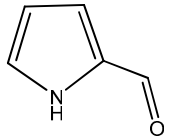
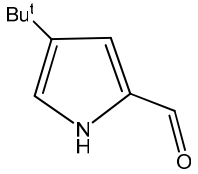
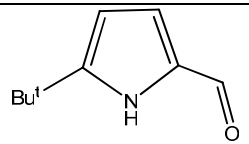


Figure S3. ^{1}H NMR spectrum of $Y[N(SiHMe_2)_2][NC_4H_3(5\text{-}Bu^t)\text{-}2\text{-}CH_2P(O)Ph_2]_2$ (**9b**).

^{13}C NMR chemical shifts of 2-phosphorylmethyl-1*H*-pyrroles and their complexes

Compound	^{13}C NMR chemical shift (δ), C-P coupling constants in parenthesis (Hz)										
	Phenyl or cyclohexyl carbons				Pyrrole carbons					Alkyl carbons	
	C-P	*ortho*	*meta*	*para*	C^2	C^3	C^4	C^5	CH_2P	CMe_3	CMe_3
2a	131.93 (99.3)	128.38(11.7)	131.22 (9.3)	131.01 (2.5)	124.18 (8.2)	115.10 (6.6)	121.60 (3.0)	110.42 (3.0)	30.42 (69.0)	N/A	N/A
2b	132.01 (98.8)	128.50 (11.5)	131.33 (9.3)	131.75 (2.7)	123.60 (7.1)	11140 (6.6)	107.79 (2.7)	144.73 (3.3)	31.75 (69.7)	30.62	27.77
2c	132.38 (99.0)	128.40 (11.5)	131.38 (9.3)	131.88 (2.7)	123.86 (8.2)	114.54 (6.6)	136.80 (3.3)	115.81 (3.3)	30.72 (68.6)	30.77	27.93
2d	23.58 (57.1)	26.81 (2.7), 26.65 (2.7)	25.76 (2.8), 25.52 (3.0)	26.03	125.78 (7.1)	114.70 (5.5)	121.32 (2.7)	110.71 (2.2)	36.24 (64.2)	N/A	N/A
2e	23.80 (57.6)	26.85 (3.0), 26.70 (3.0)	25.75 (2.3), 25.46 (3.0)	26.04	125.70 (7.2)	114.70 (5.5)	137.02 (2.7)	115.31 (2.7)	36.28 (64.2)	30.79	28.01
3a	131.97 (99.3)	128.58 (11.8)	130.83 (9.4)	131.96 (2.6)	121.03 (9.4)	108.20 (7.5)	118.23	107.86	29.73 (69.3)	N/A	N/A
3b	132.15 (98.8)	130.93 (12.1)	131.24 (9.3)	131.99 (2.7)	119.21 (9.3)	107.58 (7.7)	102.03 (1.1)	142.65 (3.3)	30.08 (69.2)	30.46	31.34
3c	132.11 (99.4)	128.54 (11.5)	130.51 (9.3)	131.70 (2.7)	120.80 (9.3)	113.02 (7.7)	135.54 (3.3)	106.93 (1.1)	30.45 (69.2)	31.67	30.42
3d	22.45 (57.8)	26.66 (2.0), 26.50 (2.4)	25.66 (2.6), 25.07 (3.4)	25.87	122.87 (8.8)	107.08 (7.1)	117.72	107.80	36.56 (63.7)	N/A	N/A
3e	23.29 (57.3)	27.22 (4.0), 26.55 (4.6)	25.60 (2.6), 24.97 (3.3)	25.89	122.90 (7.7)	105.75 (6.8)	135.61	112.64	35.72 (62.9)	31.79	30.48
4a	129.82 (102.4)	128.41 (12.5)	131.45 (11.2)	132.21 (3.9)	122.74 (7.9)	109.18 (7.7)	131.81	107.65	30.39 (64.8)	N/A	N/A
5c	132.16-131.41				121.49 (9.2)	106.44 (6.5)	132.51	125.79	31.61 (65.8)	33.00	31.05
5d	27.07-25.08				124.55 (9.2), 123.19 (10.2)	106.69-106.00	131.94 (1.0), 131.46 (1.0)	106.69-106.00	35.37 (56.5), 34.59 (64.09)	N/A	N/A
6c	132.84-127.63				123.90 (7.3), 123.73 (7.3)	105.30 (7.7), 104.21 (8.2)	under 132.84-127.63	127.23 (1.6), 125.69 (1.3)	31.12 (84.3)	32.37, 31.90	31.81, 30.36
7b	130.42 (60.6), 129.29 (54.5)	128.52 (12.1)	131.71 (10.3), 131.45 (10.3)	132.83 (2.4), 132.08 (2.4)	124.12 (11.3)	109.94 (8.0)	104.32	151.58 (2.5)	32.65 (86.0)	32.55	32.93
8a	Under 132.08-129.07	128.92 (11.8)	Under 132.08-129.07		119.47 (5.1)	109.72 (7.5)	135.55	108.32	29.64 (67.1)	N/A	N/A
9b	Under 132.43-131.89	128.55 (12.1)	Under 132.43-131.89		122.52 (9.9)	110.41 (8.8)	104.36	153.24	29.97 (66.9)	33.04	33.56

^{13}C NMR data of tert-butyl substituted pyrrole aldehydes

Compound	^{13}C NMR chemical shift (δ)				
	CHO	C^2	C^3	C^4	C^5
	179.59	132.84	132.84, 127.23 or 122.10	132.84, 127.23 or 122.10	132.84, 127.23 or 122.10
	179.20	132.48?	122.52 or 118.63	138.58?	122.52 or 118.63
	178.43	131.62?	122.83 or 107.21	122.83 or 107.21	152.08?

Notes:
It was not possible to distinguish between H carrying ring carbons. ? indicates that unequivocal assignments of chemical shift for carbons other than those carrying Bu^t groups was not possible using 2D ^{1}H/^{13}C correlation experiments.