ELECTRONIC SUPPLEMENTARY DATA

Catalytic dechlorination of polychlorinated biphenyls (PCBs) using amine functionalised titanocenes

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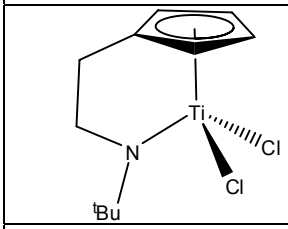
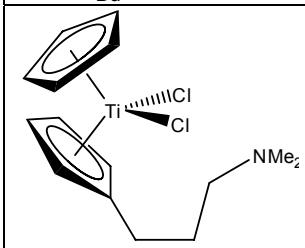
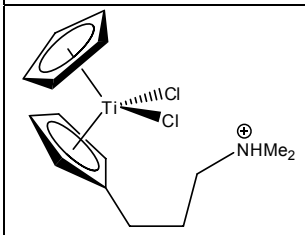
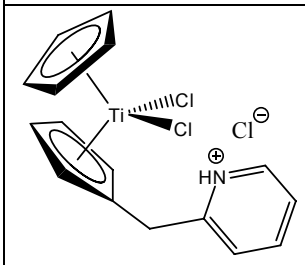
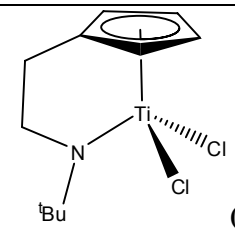
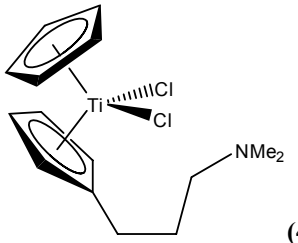
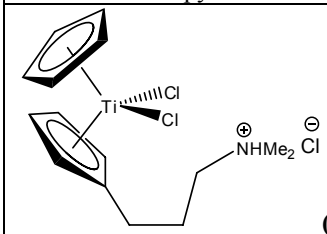
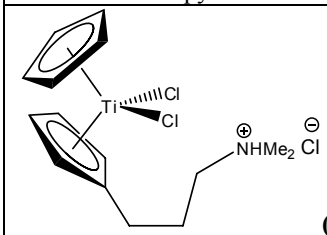
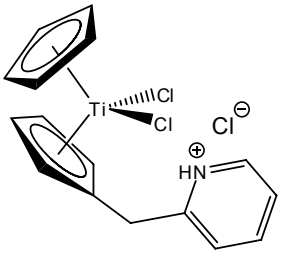
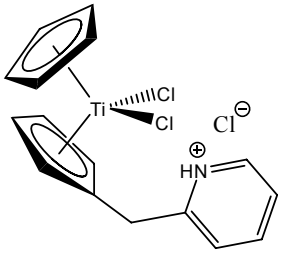
Contents

SUP 1 ^{11}B NMR data for diglyme solutions of various catalysts with one equivalent of BH_3·THF and Schwartz reactions of Cp_2TiCl_2 with different bases. Samples run at room temperature and data corrected relative to a PPN[BH_4] in $CHCl_3$ insert

Species	Chemical Shift (ppm)	J(^{11}B-^{1}H) (Hz)	Multiplicity
 ·BH_3 **(4)**	–6.43	103.4	q
 ·BH_3 **(5)**	–6.27	107.4	q
 ·BH_3 **(6)**	–7.17	106.0	q
 ·BH_3 **(7)**	–5.97	106.0	q
Pyridine·BH_3	–1.94	95.3	q
DMO·BH_3	–1.66	96.9	q
Diglyme with BH_3·THF	16.43	16.8	q

Sup 2 ^{11}B NMR data obtained from aliquots of various Schwartz reactions. Samples run in diglyme at room temperature and data corrected relative to a $PPN[BH_4]$ in $CHCl_3$ insert

Schwartz reaction	Time of aliquot (hours)	Data at given reaction time		
		Chemical shift (ppm)	J(^{11}B-^{1}H) (Hz)	Mulitplicity
 **(4.12)** with pyridine	0	-5.85	93.1	q
	1	-5.94	104.8	q
	24	Too broad		
 **(4.13)** with pyridine	0	-5.82	100.8	q
	1	6.22	104.8	q
	24	8.06, –18.90	Unknown	
 **(4.14)** with pyridine	0	–5.89	97.0	q
	1	–5.34, –3.34	Unknown	
	24	–9.25, –20.93	Unknown	
 **(4.14)** with DMO	0	–3.15	81.4	q
	1	–3.67	95.7	q
	24	–3.39	91.9	q
 with pyridine	0	–5.66	107.4	q
	1	–5.85	100.8	q
	24	Too broad		
 with DMO	0	–3.27	93.1	q
	1	–3.44	87.9	q
	24	–3.41	92.4	q

Sup 3: Crystal data and refinement details for (4)

Crystal identification	jh2
Chemical formula	$C_{11}H_{17}Cl_2NTi$
Formula weight	282.06
Temperature (K)	150.0(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/m$
a (Å)	7.3084(15)
b (Å)	10.576(2)
c (Å)	8.5363(17)
α (°)	90
β (°)	102.70(3)
γ (°)	90
Cell volume (Å^3)	643.7(2)
Z	2
Calculated density (g/cm^3)	1.455
Absorption coefficient (mm^{-1})	1.048
F_{000}	292
Crystal size (mm)	0.06 x 0.08 x 0.26
Description of crystal	Red prism
Absorption correction	None
θ range for data collection (°)	$6.0 \leq \theta \leq 27.5$
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 12$, $-11 \leq l \leq 11$
Reflections measured	2695
Unique reflections	1534
R_{int}	0.018
Reflections collected ($I > 3\sigma(I)$)	2695
Refinement method	Full-matrix least-squares on F^2 [SHELXL-97]
Parameters refined	89
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.074
R_1[a]	0.0393
wR_2[b]	0.0975
Residual electron density (min, max) (e Å^{-3})	-0.407, 0.346

[a] $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Sup 4: Bond lengths (Å) for (4)

Ti(1) - N(1)	1.899(3)	N(1) - C(5)	1.524(5)
Ti(1) - Cl(1)	2.2871(8)	C(1) - C(1)	1.402(5)
Ti(1) - Cl(1)	2.2871(8)	C(1) - C(2)	1.409(3)
Ti(1) - C(3)	2.334(3)	C(2) - C(3)	1.405(3)
Ti(1) - C(2)	2.340(2)	C(3) - C(2)	1.405(3)
Ti(1) - C(2)	2.340(2)	C(3) - C(4)	1.494(4)
Ti(1) - C(1)	2.360(2)	C(4) - C(5)	1.426(5)
Ti(1) C(1)	2.360(2)	C(4) - C(5)	1.426(5)
N(1) - C(6)	1.513(4)	C(6) - C(8)	1.516(6)
N(1) - C(5)	1.524(5)	C(6) - C(7)	1.520(4)

Note – H atoms have been excluded

Sup 5: Bond angles (°) for (4)

N(1) - Ti(1) - Cl(1)	108.35(5)	C(6) - N(1) - C(5)	111.2(3)
N(1) - Ti(1) - Cl(1)	108.35(5)	C(6) - N(1) - C(5)	111.2(3)
Cl(1) - Ti(1) - Cl(1)	105.25(4)	C(5) - N(1) - C(5)	32.0(3)
N(1) - Ti(1) - C(3)	75.47(11)	C(6) - N(1) - Ti(1)	124.0(2)
Cl(1) - Ti(1) - C(3)	125.55(3)	C(5) - N(1) - Ti(1)	122.4(2)
Cl(1) - Ti(1) - C(3)	125.55(3)	C(5) - N(1) - Ti(1)	122.4(2)
N(1) - Ti(1) - C(2)	95.31(9)	C(1) - C(1) - C(2)	107.82(14)
Cl(1) - Ti(1) - C(2)	143.80(7)	C(1) - C(1) - Ti(1)	72.73(6)
Cl(1) - Ti(1) - C(2)	92.19(7)	C(2) - C(1) - Ti(1)	71.79(13)
C(3) - Ti(1) - C(2)	34.99(7)	C(3) - C(2) - C(1)	108.5(2)
N(1) Ti(1) - C(2)	95.31(9)	C(3) - C(2) - Ti(1)	72.24(15)
Cl(1) - Ti(1) - C(2)	92.19(7)	C(1) - C(2) - Ti(1)	73.35(14)
Cl(1) - Ti(1) - C(2)	143.80(7)	C(2) - C(3) - C(2)	107.3(3)
C(3) - Ti(1) - C(2)	34.99(7)	C(2) - C(3) - C(4)	125.76(14)
C(2) - Ti(1) - C(2)	57.85(12)	C(2) - C(3) - C(4)	125.76(14)
N(1) - Ti(1) - C(1)	129.70(10)	C(2) - C(3) - Ti(1)	72.77(15)
Cl(1) - Ti(1) - C(1)	113.78(7)	C(2) - C(3) - Ti(1)	72.77(15)
Cl(1) - Ti(1) - C(1)	86.06(7)	C(4) - C(3) - Ti(1)	110.6(2)
C(3) - Ti(1) - C(1)	58.21(9)	C(5) - C(4) - C(5)	34.3(3)
C(2) - Ti(1) - C(1)	34.87(8)	C(5) - C(4) - C(3)	111.1(3)
C(2) - Ti(1) - C(1)	57.78(9)	C(5) - C(4) - C(3)	111.1(3)
N(1) - Ti(1) - C(1)	129.70(10)	C(4) - C(5) - N(1)	110.4(3)
Cl(1) - Ti(1) - C(1)	86.06(7)	N(1) - C(6) - C(8)	111.1(3)
Cl(1) - Ti(1) - C(1)	113.78(7)	N(1) - C(6) - C(7)	109.2(2)
C(3) - Ti(1) - C(1)	58.21(9)	C(8) - C(6) - C(7)	108.7(2)
C(2) - Ti(1) - C(1)	57.78(9)	N(1) - C(6) - C(7)	109.2(2)
C(2) - Ti(1) - C(1)	34.87(8)	C(8) - C(6) - C(7)	108.7(2)
C(1) - Ti(1) - C(1)	34.55(13)	C(7) - C(6) - C(7)	109.9(3)

Note – H atoms have been excluded