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Supplementary Material

Table S1. Observed C-H(D) stretching frequencies (in cm^{-1}) for the ethyl groups of **1**, **1**-h_1, **2**, and **2**-h_1, and calculated scaled harmonic frequencies (in cm^{-1}) for **1**, **1**-h_1, **2a**, and **2a**-h_1.[a]

	$CH_3CH_2TiCl_3$			$CHD_2CD_2TiCl_3$			$CH_3CH_2TiCl_3$(diphosphine)			$CHD_2CD_2TiCl_3$(diphosphine)		
group	ν_{obs} (1)	ν_{calc} (1)	assignment/ local sym.	ν_{obs} (1)	ν_{calc} (1)	assignment/ conformer[b]	ν_{obs} (2)	ν_{calc} (2a)	assignment/ local sym.	ν_{obs} (2)	ν_{calc} (2a)	assignment/ conformer[b]
$C_\alpha H_2$	2933[c]	2929	$\nu_{as}CH_2$" (a")	2199sh	2192	$\nu_{as}CD_2$"(2)	3028[c]	3028	$\nu_{as}CH_2$" (a")	2275	2274	$\nu_{as}CD_2$"(1)
					2191	$\nu_{as}CD_2$"(1)					2273	$\nu_{as}CD_2$"(2)
	2878[c]	2879	ν_sCH_2" (a')	2105	2112	ν_sCD_2"(1)	2933	2960	ν_sCH_2" (a')	2172	2169	ν_sCD_2"(2)[e]
					2112	ν_sCD_2"(2)				2172	2173	ν_sCD_2"(1)
$C_\beta H_3$	2980[d]	2978	$\nu_{as}CH_3$ (a")	2953[c]	2953	ν^{is}CH"(2)	2970	2964	$\nu_{as}CH_2$" (a")	2933[c]	2933	ν^{is}CH"(2)
				2927[c]	2927	ν^{is}CH'(1)						
										2225	2225	$\nu_{as}CD_2$"(1)
	2963[d]	2956	$\nu_{as}CH_3$ (a')[e]	2235sh	2230	$\nu_{as}CD_2$"(1)	ol[f]	2899	ν_sCH_2" (a')	2172	2180	νCD"(2)[e]
				2216	2217	ν_{as}CD'D"(2)[e]				2100	2125	ν_sCD_2"(1)
	2878[d]	2898	ν_sCH_3 (a')[e]	2150	2147	ν_sCD_2"(1)	2615	2585	νCH' (a')	2585[c]	2585	ν^{is}CH'(1)
				2150	2139	ν_sCD'D"(2)[e]				1929	1907	νCD'(2)

[a] Scale factors - $EtTiCl_3$: methyl CH" 0.951, CH' 0.968; methylene 0.971. $EtTiCl_3$(dhpe): methyl CH" 0.930, CH' 0.917; methylene 0.953. The very small differences between the two CH" bonds in both the methyl and methylene groups have been ignored. Calculated νCD values have been multiplied by 1.011 to offset anharmonicity. [b] Refers to the conformer with the unique C_β-H bond in (1) or out of (2) the $TiC_\alpha C_\beta$ plane. [c] Frequency used for scaling the DFT force field. [d] Likely to be affected by Fermi Resonance. [e] These descriptions are approximate. [f] ol signifies overlay by features arising from the dmpe ligand.

Table S2. Comparison of GIAO chemical shifts (δ in ppm) calculated at the DFT level of theory for Me_2TiCl_2, $MeTiCl_3$ and $EtTiCl_3$ (**1**).

molecule	nucleus	δ (exp)[a]	δ (DFT)	nucleus	δ (exp)[a]	δ (DFT)
Me_2TiCl_2	CH_3	2.58	2.48	C	99.6	82.6
$MeTiCl_3$	CH_3	2.95	2.69	C	118.2	93.2
$EtTiCl_3$	CH_2	3.3	3.19	C_α	139.6	117.7
	CH_3	2.0	1.68	C_β	21.4	26.5

[a] This work: ^1H and ^{13}C chemical shifts determined at 243 K.

Table S3. Comparison of experimental and GIAO chemical shifts (δ in ppm) calculated at the DFT level of theory for $EtTiCl_3$(dmpe) (**2**).

nucleus	expt.[a] T=183 K / T=313 K	eclipsed	staggered
$TiCH_2CH_3$[b]	2.70[c] / 2.57	2.20[d]	1.98[e]
$TiCH_2$[b]	2.53 / 2.76	2.39	2.72
PCH_2[b]	2.29 / 2.24	2.13, 1.94	2.04, 1.83
PCH_2[b]	2.15	2.10, 1.68	1.96, 1.61
PCH_3[b]	1.68 / 1.66	1.56, 1.46	1.40, 1.43
PCH_3[b]	1.53	1.48, 1.50	1.53, 1.35

[a] ^1H chemical shifts from Ref 14 (determined at -90° C). [b] Average values. [c] The ^1H chemical shifts also show a temperature dependence: for decreasing temperature the $TiCH_2CH_3$ signal is shifted to lower frequency while the $TiCH_2$ signal is shifted to higher frequency. [d] Individual values are: $H_{agostic}$ 3.63, $H_{anagostic}$ 1.51/1.45. [e] Individual values are: 2.21, 1.80, 1.92.

Table S4. Optimised geometries of $EtTiCl_3$ (**1**) at different computational levels.[a]

parameter	GED	BPW91/I	BP86/III	BPW91/II
Ti-C	209.0(15)	2.052	2.059	2.028
C-C	152.6(11)	1.530	1.529	1.546
$C\text{-}H_\beta{}'$[b]	110.4(10)	1.103	1.107	1.107
$C\text{-}H_\beta{}''$[b]	110.4(10)	1.099	1.103	1.103
TiCl'[b]	219.5(3)	2.207	2.205	2.217
TiCl''[b]	219.5(3)	2.206	2.208	2.216
<CCH'[b]	109.0[c]	110.6	110.9	109.9
<CCH''[b]	109.0[c]	111.9	111.4	111.7
<TiCC	116.6(11)	117.2	111.5	114.4
<$CTiCl'$[b]	104.6(4)	105.3	106.1	104.6
<$CTiCl''$[b]	104.6(4)	105.6	104.9	105.4

[a] Bond distances in pm and angles in degrees. [b] Atom in the symmetry plane is denoted by (′); atom not in the symmetry plane is denoted by (″). [c] Assumed value.

Table S5. Optimised geometries of $EtVCl_3$ (**7**) at different computational levels.[a]

parameter	BPW91/II C_s	BPW91/I C_1	BPW91/I C_s	BP86/III C_1	BPW91/II C_s	BPW91/I C_1	BP86/III C_1
	eclipsed				staggered		
V-Cl	197.4	199.7	199.7	200.7	198.9	201.5	201.1
C-C	154.7	152.6	152.6	152.2	154.7	153.1	151.8
C_α-H	110.1	109.8[c]	109.8	110.0[c]	110.8	110.4[c]	110.9[d]
C-H_β'[b]	112.1	112.1	112.1	111.9	110.8	110.4	110.5
M-Cl"[b]	221.2	218.8[c]	218.8	219.9[c]	220.0	217.2[c]	217.7[c]
C-H_β"[b]	110.0	109.8[c]	109.8	109.9[c]	110.2	109.8[c]	110.0[c]
M-Cl'[b]	218.8	216.6	216.6	217.5	218.7	216.1	218.5
M···H_α	257.6	260.7[c]	260.7	110.7[c]	253.5	254.9[c]	248.4[c]
M···H_β[e]	232.8	224.2	224.3	226.5	307.3	314.3[c]	322.9[c]
<VCH	110.5	111.4[c]	111.4	110.7[c]	106.5	105.9[c]	101.7[d]
<CCH_β'[b]	114.3	114.1	114.1	113.4	108.8	109.6	110.5
<CCH_β"[b]	111.1	112.1[c]	112.1	111.7[c]	112.2	112.3[c]	111.5[c]
<MCC	93.5	91.1	91.1	91.8	108.2	111.2	116.6
<CMCl"[b]	99.1	98.6	98.5	97.9	101.2	102.3	105.8
<CMCl"[b]	112.0	112.6[c]	112.7	111.3[c]	108.6	107.9[c]	103.1[c]
τVCCH'[b]	0	0.003	0	-8.5	180	179.0	-173.5

[a] Bond distances in pm and angles in degrees. [b] Atom in the symmetry plane is denoted by ('); atom not in the symmetry plane is denoted by ("). [c] Average value. [d] Average value: individual values are C_α-H = 111.2 and 100.5 pm; <VCH = 97.4 and 106.0°. [e] Shortest V···H_β distance.

Table S6. Salient structural parameters for the model systems $EtScCl_2$ (**4**) and $EtTiCl_2$ (**5**).[a]

parameter	$EtScCl_2$	$EtScCl_2$	$EtScCl_2$	$EtTiCl_2$	$EtTiCl_2$	$EtTiCl_2$
	ecl[b]	stag[b]	stag[b]/112°	ecl[b]	stag[b]	stag[b]/112°
ΔE_{rel}	0	0.95	2.85	0	0.985	0.99
N_{imag}	0	1	-	0	0	-
<MCC	86.5	83.5	112.0	85.6	107.5	112.0
M-C	213.7	212.9	214.8	206.5	206.9	207.1
C-C	152.6	154.2	154.0	152.1	154.1	154.0
C_β-H'[c]	114.8	110.2	110.4	115.2	110.4	110.4
C_β-H"[c]	109.8	111.4	110.3	109.7	110.2	110.1
M-Cl	232.3	232.3	231.9	223.2	223.1	223.1
<MCH	115.8	118.4	108.5	114.5	108.7	106.9
$<CCH_\beta$'[c]	114.4	114.7	112.4	113.3	111.1	111.1
$<CCH_\beta$"[c]	114.1	112.8	112.3	114.2	112.6	112.4
<ClMCl	128.7	128.1	129.1	126.7	127.9	128.0
<CMCl	115.4	115.4	114.9	114.0	115.2	115.4
$M\cdots H_\beta$[d]	216.2	253.7	326.4	207.5	311.0	320.9
$M\cdots C_\beta$	254.8	248.2	307.7	246.8	292.8	300.8

[a] Bond distances in pm, angles in degrees, and energies in kcal mol^{-1}. [b] The labels 'ecl' and 'stag' specify the ethyl group conformation. The value of 112° relates to the MCC angle. [c] Atom in the symmmetry plane is denoted by ('); atom out of the symmetry plane is denoted by ("). [d] Shortest M···Hβ distance.

Table S7. Gaussian basis sets employed for calculations.

atom	type	desig.	basis orbitals	contractions	ref
Sc, Ti, V	AE[a]	I	[14s11p6d]/(10s8p3d)	[51111111111/41111111/411]	38
Cl	AE	I	[13s10p1d]/(6s5p1d)	[631111/52111/1]	39
P	AE	I	[13s9p1d]/(6s5p1d)	[631111/42111/1]	39
C	6-311G(d)	I	[11s5p1d]/(4s3p1d)	[6311/311/1]	40
H	6-311G(d)	I	[5s]/(3s)	[311]	40
Sc, Ti, V	ECP	II	[8s5p5d]/(3s3p2d)	[341/311/41]	41b
Zr, Nb	ECP	II	[8s6p4d]/(3s3p2d)	[341/321/31]	41b
Cl, P	ECP	II	[3s3p]/(2s2p)	[21/21]	41a
C, O	AE	II	[10s5p]/(3s2p)	[721/41]	42
H	AE	II	[4s]/(2s)	[31]	42

[a] Ti: supplemented with two diffuse p orbitals (exponents 0.156 and 0.0611).