Electronic Supplementary Information for:

Homo and heteropolymetallic Group 4 molecular nitrides

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Table S1 Kinetic data for the dynamic NMR process observed for a solution of complex $[(\eta^5\text{-}C_5H_5)Cl_2Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**9**) in $CDCl_3$.

T (K)	k (s^{-1})	1/T (K^{-1})	lnk	ln(k/T)
233	2	0.00429	0.69315	–4.75789
243	7	0.00412	1.94591	–3.54715
253	23	0.00395	3.13549	–2.39790
263	75	0.00380	4.31749	–1.25467
268	122	0.00373	4.80402	–0.78697
273	190	0.00366	5.24702	–0.36245
280	355	0.00357	5.87212	0.23733
287	545	0.00348	6.30079	0.64130
294	875	0.00340	6.77422	1.09064
298	1110	0.00336	7.01212	1.31502
305	1525	0.00328	7.32975	1.60944
313	2230	0.00319	7.70976	1.96355

Figure S1 Arrhenius plot for the exchange in complex $[(\eta^5\text{-}C_5H_5)Cl_2Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**9**) in $CDCl_3$.

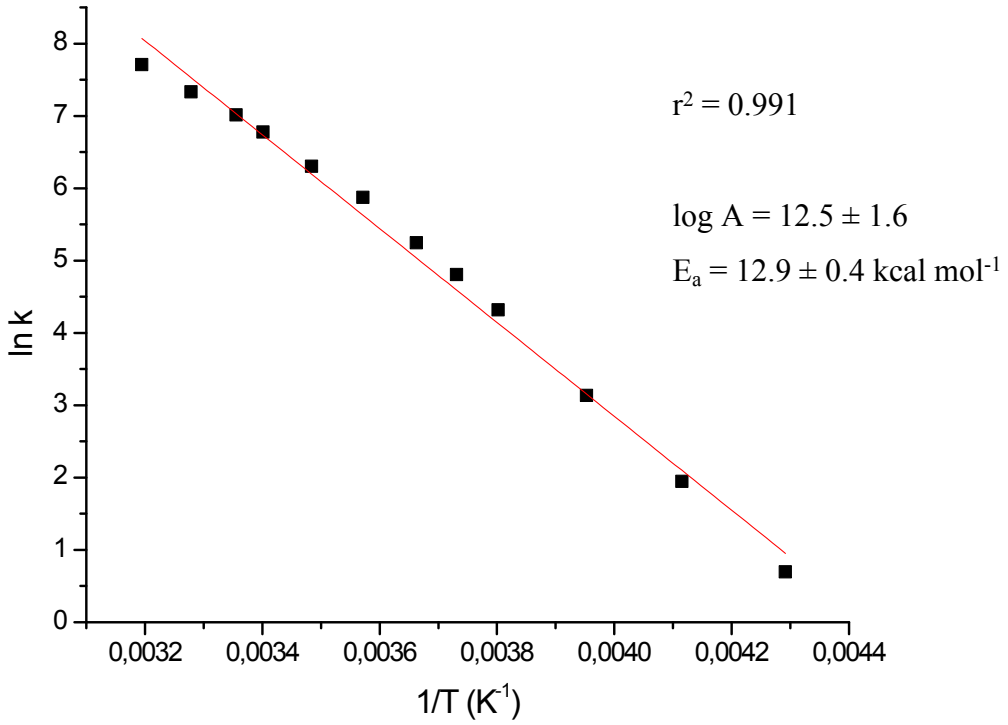
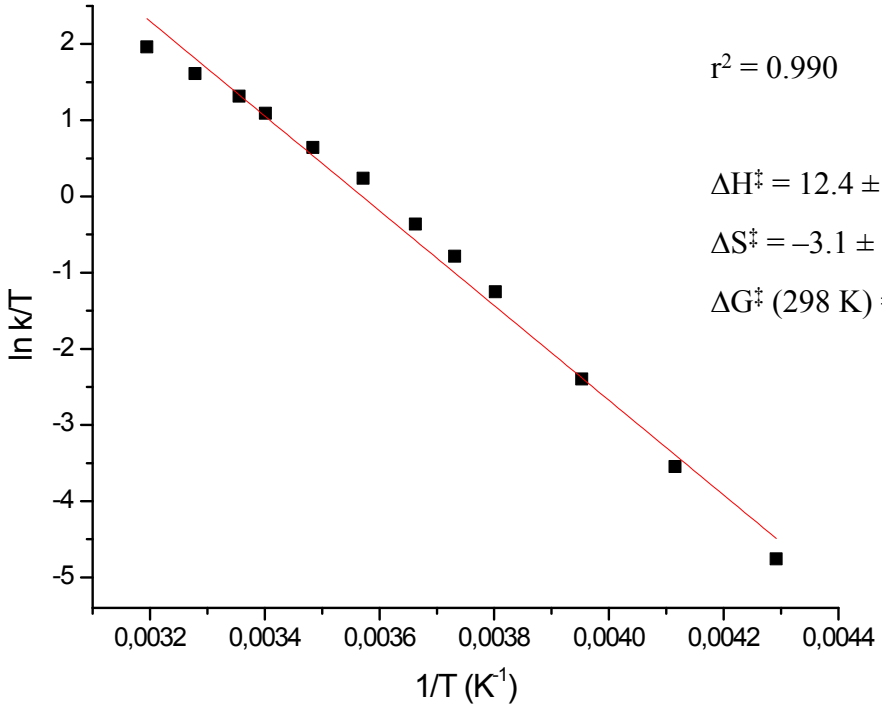


Figure S2 Eyring plot for the exchange in complex $[(\eta^5\text{-}C_5H_5)Cl_2Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**9**) in $CDCl_3$.



$r^2 = 0.990$

$\Delta H^{\ddagger} = 12.4 \pm 0.4$ kcal mol^{-1}

$\Delta S^{\ddagger} = -3.1 \pm 1.4$ cal mol^{-1} K^{-1}

$\Delta G^{\ddagger}$ (298 K) = 13.3 kcal mol^{-1}

Table S2 Selected lengths (Å) and angles (º) for **13**.

Molecule 1			
Zr(1)–N(12)	2.194(3)	Zr(1)–N(13)	2.203(3)
Zr(1)–N(23)	2.447(3)	Mg(1)–N(23)	2.131(4)
Zr(1)–Cl(1)	2.607(1)	Zr(1)–Cl(2)	2.620(1)
Mg(1)–Cl(1)	2.512(2)	Mg(1)–Cl(2)	2.469(2)
Ti(1)–N(12)	1.957(3)	Ti(1)–N(13)	1.940(3)
Ti(2)–N(12)	1.972(4)	Ti(2)–N(23)	1.908(3)
Ti(3)–N(13)	1.969(3)	Ti(3)–N(23)	1.906(3)
Ti(1)–N(1)	1.915(4)	Ti(2)–N(1)	1.931(3)
Ti(3)–N(1)	1.939(3)	Ti(1)···Ti(2)	2.834(1)
Ti(1)···Ti(3)	2.831(1)	Ti(2)···Ti(3)	2.780(1)
Zr(1)···Ti(1)	3.074(1)	Zr(1)···Ti(2)	3.114(1)
Zr(1)···Ti(3)	3.127(1)	Zr(1)···Mg(1)	3.259(2)
N(12)–Zr(1)–N(13)	77.7(1)	N(12)–Zr(1)–N(23)	76.4(1)
N(13)–Zr(1)–N(23)	75.9(1)	Cl(1)–Zr(1)–Cl(2)	82.4(1)
Cl(1)–Zr(1)–Cm(1)	101.8(1)	Cl(2)–Zr(1)–Cm(1)	100.0(1)
N(12)–Zr(1)–Cl(1)	151.1(1)	N(12)–Zr(1)–Cl(2)	95.5(1)
N(12)–Zr(1)–Cm(1)	107.0(1)	N(13)–Zr(1)–Cl(1)	89.8(1)
N(13)–Zr(1)–Cl(2)	150.0(1)	N(13)–Zr(1)–Cm(1)	110.0(1)
N(23)–Zr(1)–Cl(1)	75.3(1)	N(23)–Zr(1)–Cl(2)	74.1(1)
N(23)–Zr(1)–Cm(1)	173.6(1)	Cl(1)–Mg(1)–Cl(2)	87.5(1)
Cl(1)–Mg(1)–Cm(2)	118.6(1)	Cl(2)–Mg(1)–Cm(2)	118.1(1)
N(23)–Mg(1)–Cl(1)	83.0(1)	N(23)–Mg(1)–Cl(2)	82.9(1)
N(23)–Mg(1)–Cm(2)	148.6(1)	N(12)–Ti(1)–N(13)	90.1(1)
N(12)–Ti(2)–N(23)	95.7(1)	N(13)–Ti(3)–N(23)	95.4(1)
N(12)–Ti(1)–N(1)	86.8(2)	N(13)–Ti(1)–N(1)	87.1(1)
N(12)–Ti(2)–N(1)	85.9(2)	N(23)–Ti(2)–N(1)	87.3(1)
N(13)–Ti(3)–N(1)	85.6(1)	N(23)–Ti(3)–N(1)	87.1(1)
Zr(1)–Cl(1)–Mg(1)	79.1(1)	Zr(1)–Cl(2)–Mg(1)	79.6(1)
Zr(1)–N(23)–Mg(1)	90.5(1)	Ti(2)–N(23)–Mg(1)	136.3(2)
Ti(3)–N(23)–Mg(1)	130.1(2)	Zr(1)–N(23)–Ti(2)	90.4(1)
Zr(1)–N(23)–Ti(3)	91.0(1)	Ti(2)–N(23)–Ti(3)	93.6(2)
Zr(1)–N(12)–Ti(1)	95.4(1)	Zr(1)–N(12)–Ti(2)	96.6(1)
Ti(1)–N(12)–Ti(2)	92.4(1)	Zr(1)–N(13)–Ti(1)	95.6(1)
Zr(1)–N(13)–Ti(3)	96.9(1)	Ti(1)–N(13)–Ti(3)	92.8(1)
Ti(1)–N(1)–Ti(2)	95.0(2)	Ti(1)–N(1)–Ti(3)	94.6(2)
Ti(2)–N(1)–Ti(3)	91.9(1)		

Molecule 2			
Zr(2)–N(56)	2.151(3)	Zr(2)–N(57)	2.494(3)
Zr(2)–N(67)	2.232(3)	Mg(2)–N(57)	2.094(4)
Zr(2)–Cl(3)	2.615(1)	Zr(2)–Cl(4)	2.606(1)
Mg(2)–Cl(3)	2.474(2)	Mg(2)–Cl(4)	2.521(2)
Ti(5)–N(56)	1.955(4)	Ti(5)–N(57)	1.918(3)
Ti(6)–N(56)	1.904(4)	Ti(6)–N(67)	1.994(3)
Ti(7)–N(57)	1.906(4)	Ti(7)–N(67)	1.996(3)
Ti(5)–N(2)	1.950(3)	Ti(6)–N(2)	1.912(3)

Ti(7)–N(2)	1.919(3)	Ti(5)···Ti(6)	2.809(1)
Ti(5)···Ti(7)	2.786(1)	Ti(6)···Ti(7)	2.853(1)
Zr(2)···Ti(5)	3.097(1)	Zr(2)···Ti(6)	3.063(1)
Zr(2)···Ti(7)	3.182(1)	Zr(2)···Mg(2)	3.281(2)
N(56)–Zr(2)–N(57)	76.4(1)	N(56)–Zr(2)–N(67)	77.9(1)
N(57)–Zr(2)–N(67)	75.1(1)	Cl(3)–Zr(2)–Cl(4)	81.4(1)
Cl(3)–Zr(2)–Cm(3)	101.3(1)	Cl(4)–Zr(2)–Cm(3)	103.2(1)
N(56)–Zr(2)–Cl(3)	150.2(1)	N(56)–Zr(2)–Cl(4)	93.7(1)
N(56)–Zr(2)–Cm(3)	108.4(1)	N(57)–Zr(2)–Cl(3)	74.0(1)
N(57)–Zr(2)–Cl(4)	74.1(1)	N(57)–Zr(2)–Cm(3)	174.8(1)
N(67)–Zr(2)–Cl(3)	91.3(1)	N(67)–Zr(2)–Cl(4)	149.1(1)
N(67)–Zr(2)–Cm(3)	107.7(1)	Cl(3)–Mg(2)–Cl(4)	86.0(1)
Cl(3)–Mg(2)–Cm(4)	118.3(1)	Cl(4)–Mg(2)–Cm(4)	119.7(1)
N(57)–Mg(2)–Cl(3)	84.3(1)	N(57)–Mg(2)–Cl(4)	82.9(1)
N(57)–Mg(2)–Cm(4)	147.3(1)	N(56)–Ti(5)–N(57)	96.3(2)
N(56)–Ti(6)–N(67)	89.9(1)	N(57)–Ti(7)–N(67)	95.4(1)
N(56)–Ti(5)–N(2)	85.3(2)	N(57)–Ti(5)–N(2)	86.5(2)
N(56)–Ti(6)–N(2)	87.8(2)	N(67)–Ti(6)–N(2)	86.4(1)
N(57)–Ti(7)–N(2)	87.8(2)	N(67)–Ti(7)–N(2)	86.1(1)
Zr(2)–Cl(3)–Mg(2)	80.3(1)	Zr(2)–Cl(4)–Mg(2)	79.6(1)
Zr(2)–N(57)–Mg(2)	90.9(1)	Ti(5)–N(57)–Mg(2)	133.3(2)
Ti(7)–N(57)–Mg(2)	133.2(2)	Zr(2)–N(57)–Ti(5)	88.2(1)
Zr(2)–N(57)–Ti(7)	91.7(1)	Ti(5)–N(57)–Ti(7)	93.5(2)
Zr(2)–N(56)–Ti(5)	97.8(2)	Zr(2)–N(56)–Ti(6)	98.0(2)
Ti(5)–N(56)–Ti(6)	93.4(2)	Zr(2)–N(67)–Ti(6)	92.7(1)
Zr(2)–N(67)–Ti(7)	97.5(1)	Ti(6)–N(67)–Ti(7)	91.3(1)
Ti(5)–N(2)–Ti(6)	93.3(2)	Ti(5)–N(2)–Ti(7)	92.1(1)
Ti(6)–N(2)–Ti(7)	96.3(2)		

Cm(1) = centroid of the C(41)–C(45) ring; Cm(2) = centroid of the C(46)–C(50) ring; Cm(3) = centroid of the C(81)–C(85) ring; Cm(4) = centroid of the C(86)–C(90) ring.

Figure S3 View along the a axe of the crystal lattice of **15**. Benzene molecules of crystallization are omitted for clarity.