$AlMe_3$ and $ZnMe_2$ adducts of an Imido Titanium Methyl Cation: Crystallographic, Spectroscopic and DFT studies

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Supporting Information

Figure S1: ^{1}H NMR spectrum of $[Ti(N^tBu)(Me_3[9]aneN_3)(\mu\text{-}Me)_2AlMe_2]^+$ (**7**$^+$) at room temperature.

Figures S2 – S4: ^{1}H NMR spectra of the cation $[Ti(\mu\text{-}N^tBu)(Me_3[9]aneN_3)(\mu\text{-}Me)_2ZnMe]^+$ (**8**$^+$) at different temperatures with and without added $ZnMe_2$

Supporting DFT information: Complete reference for Gaussian 03 (reference 81 in the main text); Cartesian coordinates for the molecules optimised at B3PW91 and electronic energies (a.u.).

Further discussion of the bridging methyl groups: (i) bridging methyl group geometries and (ii) electronic structures of the adducts: Ti···H-C interactions.

References for the Supporting Information.

Figure S1. ^{1}H NMR spectrum of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(μ-Me)$_2$AlMe$_2$]$^{+}$ (**7**$^{+}$) at 293 K.

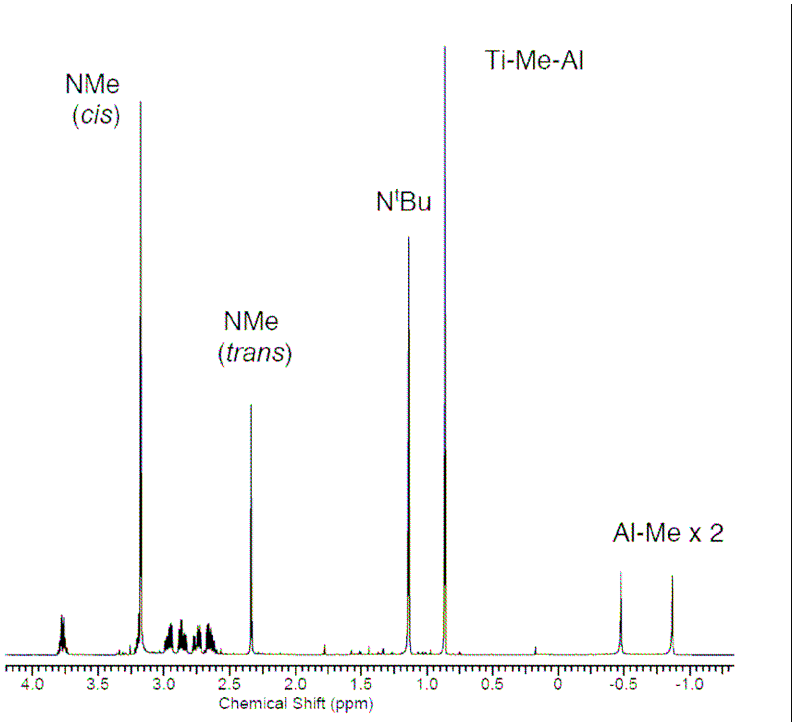


Figure S2. ^{1}H NMR spectra of the cation [Ti(μ-N^{t}Bu)(Me$_3$[9]aneN$_3$)(μ-Me)$_2$ZnMe]$^{+}$ (**8**$^{+}$) at 293 K and 233 K.

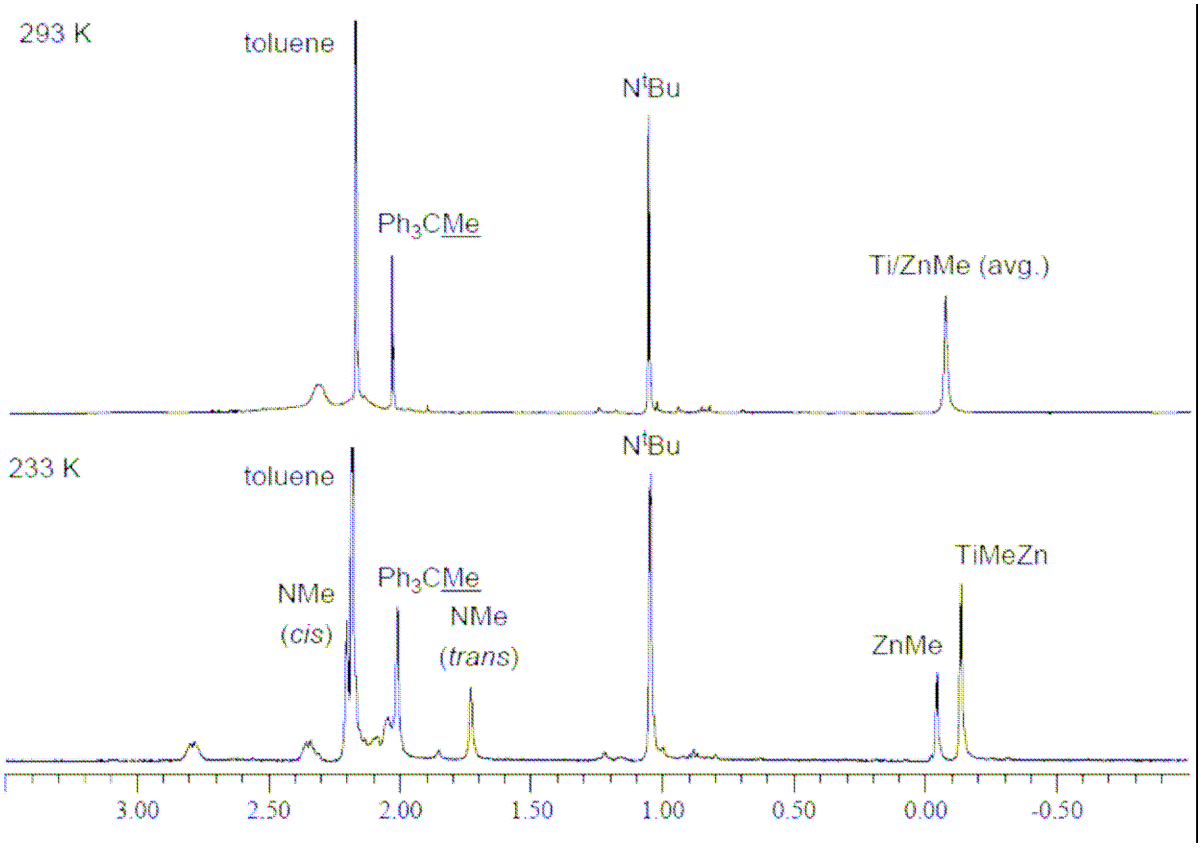


Figure S3. ^{1}H NMR spectra of the cation [Ti(μ-N^{t}Bu)(Me$_3$[9]aneN$_3$)(μ-Me)$_2$ZnMe]$^{+}$ (**8**$^{+}$) and *ca.* 1 equiv. added ZnMe$_2$ (as a toluene solution) at 293 K and 233 K.

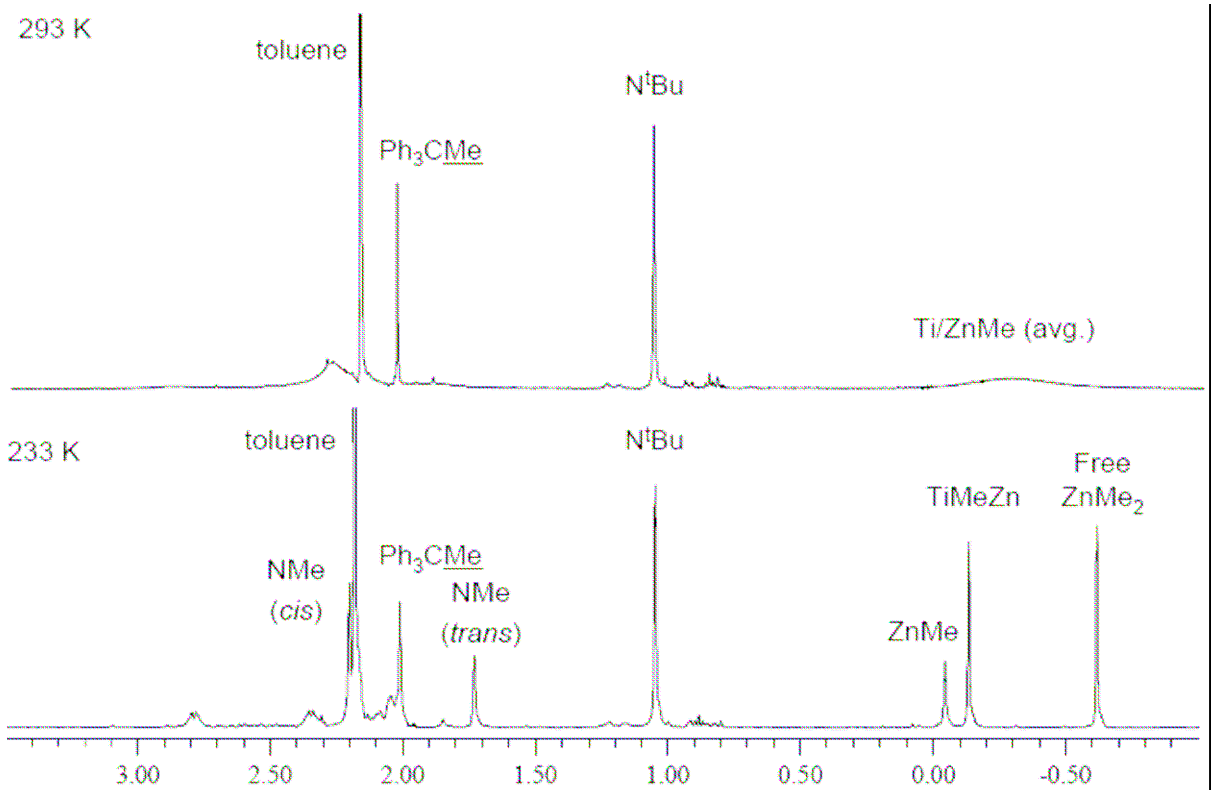
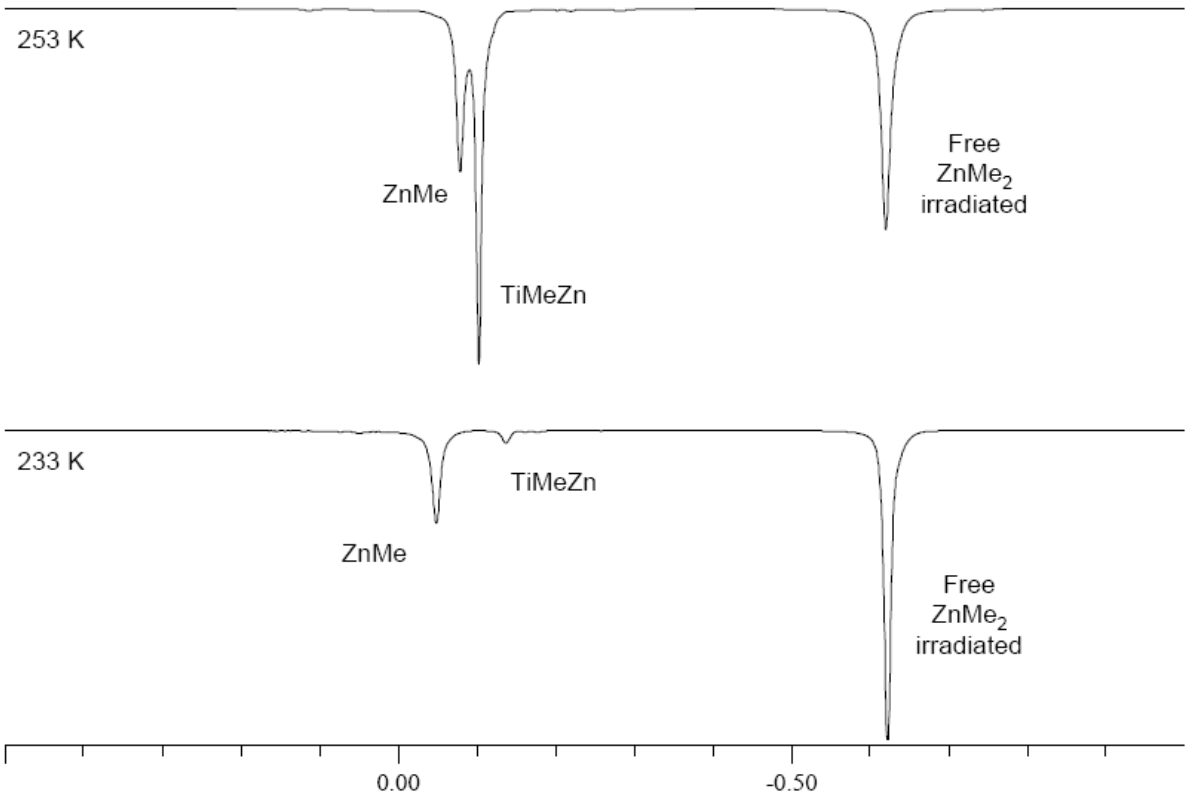


Figure S4. Partial ^{1}H NMR difference spectra of the cation [Ti(μ-N^{t}Bu)(Me$_3$[9]aneN$_3$)(μ-Me)$_2$ZnMe]$^+$ (**8**$^+$) and *ca.* 1 equiv. added ZnMe$_2$ (as a toluene solution) at 253 K and 233 K with low energy irradiation of the ZnMe$_2$ resonance.



SUPPORTING DFT INFORMATION

Complete reference for Gaussian 03:

Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

Cartesian coordinates for the molecules optimized at B3PW91 and electronic energies (au)

$AlMe_3$: E = -362.105531900

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C,2.2572680107,2.9119868654,1.3217713888
H,2.9282952434,2.0612826919,1.4714350318
H,2.8589205993,3.826315256,1.3412383111
H,1.5556531807,2.9502134556,2.1609792594
C,-0.644082001,-3.2462202894,0.1008131516
H,-1.2901674926,-4.124521887,-0.0406634596
H,0.1610699593,-3.2916560079,-0.6363438618
H,-0.204865397,-3.2956662528,1.0984149653
C,-1.4272307185,1.2025384448,-2.7007689593
H,-0.7049593738,1.9942955103,-2.4957682205
H,-0.9664199005,0.4702723148,-3.3668661968
H,-2.3009327377,1.6293142236,-3.2115894553
C,-1.4552486312,1.3742177956,2.5988776024
H,-0.6313154509,0.9664657109,3.1873672826
H,-1.141691505,2.3340990522,2.1871955756
H,-2.3122891025,1.5234129949,3.2692849602

13 : E = -792.006740541

Ti,0.0315184767,0.0365325951,-0.6493827518
C,1.9375811221,-1.125050624,-1.5243177582
C,1.5087130442,-0.1972023989,-2.4939024843
C,1.6595898213,1.1070659179,-1.9505107308
C,2.2300089905,0.9734497167,-0.6596530288
C,2.3745547126,-0.4009269263,-0.381443954
C,-1.9037809714,1.2898226553,-1.3206238261
C,-1.3676374638,0.6519600935,-2.4557370247
C,-1.4753485809,-0.7538336293,-2.2602057658
C,-2.1130693514,-0.9675556528,-1.015584799
C,-2.3441144646,0.2884618839,-0.4149198826
H,1.4365563102,2.0384943354,-2.45559203
H,1.1400385493,-0.4373755661,-3.4817685266
H,2.5057482814,1.7864222225,-0.0030962642
H,2.7899057021,-0.8262207209,0.5221385994
H,1.9428880055,-2.2020340733,-1.6363821035
H,-2.367787757,-1.9296985263,-0.5935838344
H,-1.181151929,-1.5216130468,-2.9641047564
H,-2.8220883553,0.4595296498,0.5408938142
H,-1.9668185394,2.3590859766,-1.165616003
H,-0.9671153485,1.1461713014,-3.3304377816
C,-0.0390432911,1.669705571,0.9262236344

C,0.0162260114,-1.7661922637,0.7276294359
H,0.9076203563,-2.1858866096,1.2063731632
H,0.0300127873,-2.1903133836,-0.293486198
H,-0.8677230289,-2.2156790907,1.1946421261
H,0.7978632509,2.0371894901,1.5313630736
H,-0.9718540069,2.0272580224,1.3766481149
H,0.0448632458,2.232330824,-0.0206849173
Zn,-0.0781828645,-0.127668298,2.1090619526
C,-0.1820860534,-0.2324394805,4.0414554808
H,-1.0840029119,-0.7716932871,4.3467770394
H,0.6836631059,-0.768465447,4.4422107928
H,-0.2080994238,0.7652406019,4.4878118719

7q : E = -956.679021168

Ti	0.07995	0.43326	-0.00546
Al	2.73521	-0.48781	-0.00136
N	0.48657	2.05938	0.00782
N	-0.90743	-1.75893	-0.06977
N	-1.74406	0.57432	-1.36193
N	-1.7001	0.45801	1.42383
C	1.46969	-0.20733	-1.69706
C	1.43654	-0.29538	1.67685
C	4.15711	0.87071	0.0513
C	3.17102	-2.41663	-0.04563
C	0.88963	3.42944	0.0097
C	-1.47782	-1.90863	-1.42309
C	-2.36857	-0.7158	-1.76689
C	-2.66055	1.48365	-0.63274
C	-2.94493	0.93632	0.76094
C	-1.84357	-0.86861	2.06814
C	-1.89519	-1.97702	1.01585
H	1.28935	-1.19431	-2.13334
H	2.3853	0.17976	-2.16922
H	0.73705	0.50426	-2.118
H	1.12609	-1.27842	2.04389
H	2.38013	-0.06189	2.19398
H	0.79529	0.48913	2.11671
H	4.82174	0.72543	0.91238
H	4.79808	0.81833	-0.83793
H	3.76788	-2.66548	-0.93205
H	3.78041	-2.70127	0.82126
H	2.3041	-3.09133	-0.0537
H	-2.05785	-2.836	-1.53087
H	-0.64445	-1.96857	-2.12696
H	-2.58519	-0.7201	-2.83983
H	-3.33549	-0.80627	-1.26343
H	-3.60547	1.62593	-1.17438
H	-2.15629	2.45021	-0.56276
H	-3.64924	0.10131	0.70864
H	-3.43287	1.70873	1.36371
H	-2.73983	-0.9151	2.70098
H	-0.97844	-1.00642	2.72049
H	-2.895	-2.02851	0.57331
H	-1.73637	-2.94303	1.50656
H	-0.14005	-2.41887	0.03031
H	-1.43769	1.0693	-2.19615
H	-1.44454	1.13462	2.13919
H	1.52676	3.65106	-0.85644
H	0.02625	4.10882	-0.02695
H	1.46437	3.66849	0.91392
H	3.77439	1.89614	0.11063

8q : E = -901.544128528

Ti,-0.0728749474,0.0263169019,0.0313424591
Zn,0.3939941245,-0.1751313915,2.5608407413
N,1.5017863486,0.0666987507,0.7577047676
N,-1.9770107532,-0.1040544177,-1.3930973454
N,0.4739389634,-1.3282642579,-1.7630985068
N,0.2866229745,1.4600443806,-1.7196398969
C,-1.0822558108,-1.4466558752,1.3338333627
C,-0.9889688052,1.6675155904,1.1029416544
C,2.9065117716,0.1870744411,1.0623084132
C,-1.9968840455,-1.4608122355,-1.9757278192
C,-0.6498762263,-1.7706021524,-2.6275612072
C,1.5282462322,-0.5664102674,-2.4697955124
C,1.0249267146,0.8261901769,-2.8430458227
C,-1.0016453078,2.0690325822,-2.1160659743
C,-2.0318928419,0.9798959043,-2.4058216103
H,-2.151007746,-1.2298310596,1.224966353
H,-0.9981894537,-1.9005648499,2.3335919943
H,-0.8177074218,-2.2869456834,0.6683997444
H,-2.0476029322,1.7573242825,0.8221957201
H,-0.9965190082,1.6876397312,2.2048071352
H,-0.4754563347,2.5993111331,0.8225589055
H,-2.8018635091,-1.5870111417,-2.7129451356
H,-2.1924526964,-2.1642533585,-1.1614239763
H,-0.5823197744,-2.8420207468,-2.8424465928
H,-0.568932119,-1.2624957824,-3.5930318377
H,1.8742786732,-1.0874014888,-3.3730308097
H,2.3751679717,-0.4886793084,-1.7836988718
H,0.3575862602,0.769995964,-3.708274727
H,1.8718311023,1.4460648433,-3.1549843638
H,-0.8923237413,2.7196804663,-2.9942954843
H,-1.3350208505,2.6907203049,-1.2826244137
H,-1.8534098027,0.5421567817,-3.3925886616
H,-3.030266513,1.4272782416,-2.4519771615
H,-2.7715988255,-0.0116403791,-0.7660378039
H,0.9156027131,-2.1416522463,-1.3408639832
H,0.8694494663,2.1821446164,-1.3034342626
H,3.2952537457,-0.6989703123,1.5805955175
H,3.4931648328,0.3085266997,0.141161725
H,3.1107340979,1.0595710107,1.696062543
C,0.742334804,-0.0504110497,4.4635347343
H,1.3270603074,0.8441385443,4.6962596362
H,-0.1951140916,-0.0035917538,5.0256980282
H,1.3027391153,-0.9243984835,4.8099200027

9q : E = -1444.27944004

Ti,0,0.0424551359,0.0262638282,-0.9249185517
Zn,0,-0.2585994543,0.0767741917,1.8238026487
N,0,1.7228746181,0.0064131428,-0.9268171525
N,0,-2.4336664948,-0.0408836086,-1.4810330798
N,0,-0.2338601099,-1.4203450082,-2.7982404381
N,0,-0.3207538335,1.5063341574,-2.7580951977
C,0,-0.3097942767,-1.6635163987,0.5670381393
C,0,-0.2933649404,1.7687672666,0.5144953051
C,0,1.5898096316,0.0557871066,3.0200735207
C,0,-2.048730456,0.1236532693,3.0536807672
C,0,3.1743292606,0.0073267432,-0.8759700604
C,0,-2.6167288147,-1.4046157226,-2.0188165305
C,0,-1.6507097049,-1.7303574156,-3.1463550736
C,0,0.4200355594,-0.6257651875,-3.8660987828
C,0,-0.1963420042,0.7503898248,-4.0402972058
C,0,-1.686359338,2.0684418708,-2.6066373069
C,0,-2.7590019638,0.9950610335,-2.4963454959
H,0,-1.3198824539,-2.0787557501,0.6406549285
H,0,0.2965771887,-2.1531925669,1.3403295358
H,0,0.1610907393,-2.0763408861,-0.339236109

H,0,-1.3027940973,2.1769951673,0.4106311583
H,0,0.1596385087,2.2790893112,1.3769253726
H,0,0.3476473634,2.156339137,-0.2919623884
H,0,1.9920167912,0.2257315317,2.0142298692
H,0,-2.5121770109,0.7663500677,2.297165
H,0,-2.57770163,-0.835258064,3.0453469347
H,0,-3.648070176,-1.5562629329,-2.3771276576
H,0,-2.4642088139,-2.1026186307,-1.1906513068
H,0,-1.7519821078,-2.7925000404,-3.395169022
H,0,-1.9256852532,-1.1915582481,-4.0565732764
H,0,0.3738928912,-1.1615576617,-4.8273865027
H,0,1.470486866,-0.5278275536,-3.5881690256
H,0,-1.1797836326,0.6777810051,-4.5104856507
H,0,0.4227639794,1.3144830085,-4.7463960109
H,0,-1.9264374211,2.7335729346,-3.4506366544
H,0,-1.6804633068,2.6874906305,-1.7051228106
H,0,-2.9243946429,0.5192974836,-3.4668373607
H,0,-3.7096300408,1.4836402144,-2.2511103979
H,0,2.068710676,-0.8636931962,3.3752419086
C,0,-3.3198732482,0.1242050229,-0.3152182104
H,0,-3.0416922385,-0.5803729752,0.4687345191
H,0,-3.2238120518,1.1359035649,0.0825091322
H,0,-4.3723039873,-0.0441260332,-0.5868277917
C,0,0.5219898237,-2.6868266162,-2.6542689466
H,0,1.5283914162,-2.4736931525,-2.2915992274
H,0,0.0217781097,-3.3416152506,-1.9376533988
H,0,0.5853399485,-3.2140674926,-3.6159430492
C,0,0.6472084058,2.6281821433,-2.7846514541
H,0,0.5670868477,3.2246589977,-1.8742189988
H,0,1.6604100193,2.2321717945,-2.852084039
H,0,0.4525659744,3.2867191808,-3.6419454494
C,0,3.7675841289,-0.0922925336,-2.2928148316
H,0,4.8605778446,-0.0591187837,-2.2453117981
H,0,3.4908453591,-1.0344331631,-2.777417668
H,0,3.4409345737,0.7401203229,-2.9247977242
C,0,3.656870756,-1.2001681095,-0.0532472313
H,0,4.7505012664,-1.213422485,-0.0044372503
H,0,3.271724081,-1.1624116747,0.9679432644
H,0,3.328340086,-2.1397315884,-0.509170881
C,0,3.6557625011,1.3172123284,-0.2267988374
H,0,3.2624514113,1.4254923246,0.7871112078
H,0,4.7488697096,1.3345703969,-0.1692592942
H,0,3.3342590945,2.1841093487,-0.8126323147
Zn,0,-0.1785536137,-0.1449323455,4.2600788806
C,0,-0.1116200295,-0.325179385,6.1960135527
H,0,-0.2792338999,0.6544457261,6.6580012629
H,0,-0.8794583285,-1.0073307777,6.5736104766
H,0,0.8668363516,-0.690019212,6.5217940381
H,0,-2.3263944173,0.6183029648,3.9947668375
H,0,1.9743964588,0.8871211692,3.6235430405

7q' : E = -956.693364412

Ti,-0.2209750862,0.3819488532,0.3596889622
Al,1.3803098324,-1.0230093304,2.0545935426
N,1.4789676301,0.5160015434,0.7641370188
N,-2.3268478496,0.3590153522,-0.727861263
N,-0.1399686993,-1.2442605188,-1.2590538538
N,0.0584032291,1.4849860631,-1.5930646275
C,-0.79488577,-1.1951620903,1.8661601858
C,-0.894073545,2.1414964377,1.3124989189
C,2.133522517,-2.6928482232,1.3104235904
C,1.8311248648,-0.4275504176,3.87100605
C,2.7848547527,1.1373216545,0.7427155251
C,-2.6139117048,-1.0414034346,-1.1001044198
C,-1.4347865655,-1.6287693104,-1.8752941547
C,0.8801120104,-0.7748787521,-2.2220227016
C,0.5209809776,0.6237960425,-2.7146904064
C,-1.1805108046,2.2412019388,-1.8884230066
C,-2.3844591171,1.3033166925,-1.8727525752
H,-0.6059079897,-1.5498170573,2.8925947011
H,-1.1813674525,-2.070027117,1.3333253853
H,-1.6369583648,-0.5033846345,2.0475257499
H,3.2274401096,-2.6800080023,1.399013969
H,1.7965510095,-3.5615619412,1.8902094963
H,1.6539452243,-1.2208213794,4.6080002651
H,2.8926637314,-0.1646390165,3.9561572517
H,1.2570967462,0.4492047681,4.1925013225
H,-3.5317879427,-1.134692554,-1.696767076
H,-2.7745789123,-1.5996650401,-0.1736570849
H,-1.5354806813,-2.7176129917,-1.9308641696
H,-1.446646372,-1.2710801576,-2.9090218691
H,0.9826760978,-1.4569598533,-3.0768731307
H,1.832975774,-0.7550447887,-1.6882672585
H,-0.2777133448,0.572154243,-3.4605862292
H,1.3822104445,1.0707469004,-3.2211998636
H,-1.1192408656,2.7516892042,-2.8588644724
H,-1.2848731602,3.0027792931,-1.1138775975
H,-2.4249496639,0.7216838443,-2.7987547287
H,-3.3047753281,1.8958030191,-1.8490204376
H,-3.0009176584,0.6545303988,-0.0268322249
H,0.2504676788,-2.0391936033,-0.7559538086
H,0.7897983708,2.1539087064,-1.3638078399
H,3.5898161628,0.4140145178,0.5537926742
H,2.8414616828,1.901885715,-0.044111105
H,2.9996923048,1.6360886503,1.6956643539
H,1.9205900293,-2.9175149047,0.256636995
H,-0.7421308649,1.9386528102,2.383739248
H,-0.2696188653,3.0169476291,1.0928758775
H,-1.944699691,2.42885956,1.1773454254

7Q' : E = -1192.45402253

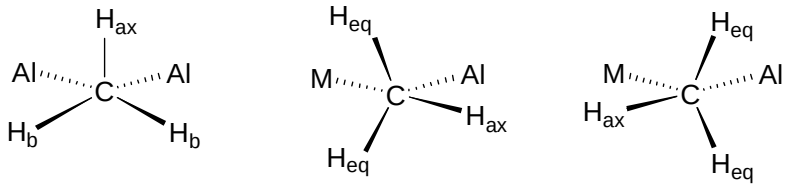
Ti	0.12904	-0.18784	-0.39876
Al	-2.2803	-1.46724	-0.13984
N	-1.48571	0.41615	-0.02607
N	2.59434	-1.02866	-0.61543
N	1.13582	-0.2299	1.75714
N	1.5522	1.71559	-0.33931
C	-0.32402	-2.37461	-0.44164
C	0.04846	0.03674	-2.49191
C	-2.92298	-2.23769	1.56606
C	-3.25649	-1.8338	-1.81867
C	-2.57457	1.42653	0.07994
C	2.86022	-1.70591	0.66842
C	2.48837	-0.84803	1.86882
C	1.18209	1.21338	2.08758
C	1.97217	2.01284	1.06492
C	2.72519	1.40423	-1.1985
C	3.47695	0.15459	-0.78052
H	-1.07278	-3.17911	-0.5025
H	0.33112	-2.70063	0.37195
H	0.20589	-2.47419	-1.39553
H	-3.98269	-2.50304	1.465
H	-2.39678	-3.16766	1.81787
H	-2.88629	-2.74752	-2.30221
H	-4.32471	-1.99985	-1.63329
H	-3.1819	-1.03608	-2.56638
H	3.92038	-1.99492	0.75636
H	2.2869	-2.6369	0.67632

H	2.54119	-1.4663	2.77223
H	3.23036	-0.05884	2.01318
H	1.61374	1.37159	3.08836
H	0.14908	1.56707	2.11906
H	3.04333	1.82305	1.16835
H	1.84051	3.07889	1.27806
H	3.42283	2.25592	-1.20029
H	2.3471	1.29012	-2.21636
H	4.0293	0.33103	0.14655
H	4.24497	-0.04523	-1.53747
H	-2.84846	-1.58677	2.44394
H	-0.72439	-0.66357	-2.83464
H	-0.28727	1.02853	-2.81051
H	0.97464	-0.20943	-3.02389
C	0.91633	2.92567	-0.91321
H	0.5949	2.72771	-1.93568
H	0.04787	3.20776	-0.32142
H	1.62647	3.76348	-0.92259
C	2.84743	-1.97856	-1.7158
H	2.2148	-2.8613	-1.6082
H	2.62363	-1.50786	-2.67461
H	3.89606	-2.30872	-1.72274
C	0.20865	-0.89554	2.7009
H	-0.79552	-0.49216	2.57076
H	0.1731	-1.967	2.49831
H	0.5347	-0.74439	3.73909
C	-3.94052	0.79685	0.41601
H	-4.69919	1.58421	0.46097
H	-4.27318	0.0949	-0.35706
H	-3.93469	0.2922	1.38603
C	-2.70552	2.15831	-1.26359
H	-3.49943	2.91007	-1.20697
H	-1.77925	2.66533	-1.54032
H	-2.95904	1.45513	-2.06118
C	-2.24887	2.41152	1.21256
H	-3.04082	3.16257	1.29507
H	-2.18451	1.8919	2.17405
H	-1.311	2.94533	1.04044

FURTHER DISCUSSION OF THE BRIDGING METHYL GROUPS.

(i) Bridging methyl group geometries. Homo-[1-14] and hetero-bimetallic[8,9,15-31] complexes with a pentacoordinate bridging methyl group, and the nature of metal-hydrogen (agostic type) interactions in general,[32-34] are topics of continuing importance in organometallic chemistry. Limiting geometries relevant to this work are illustrated in Fig. S5, with specific emphasis on trialkyl aluminum systems. Al_2Me_6 itelf has been shown through neutron diffraction[3] (supported by DFT[35]) to possess bridging methyl groups with distorted square base pyramidal (SBP) type geometries. In contrast, rare earth tetraalkyl aluminates $(L)M(\mu\text{-}CH_2R)_2Al(CH_2R)_2$ almost invariably possess structures with distorted trigonal bipyramidal structures of the type TBP-1. [15,24-31,36,37] The rare earth metal M and one methyl hydrogen (H_{ax}) occupy the formal axial positions while the Al and two other hydrogen atoms (H_{eq}) occupy the equatorial sites, the latter making *two* $Ln\cdots H_{eq}$ close contacts. This has been confirmed by neutron diffraction for $Nd(AlMe_4)_3$.[15] The close approach of the two H_{eq} atoms to the rare earth metal has led to the concept of "polyagostic bonding".[26,27,33] These neutral rare earth systems have been proposed as structural models for cationic transition metal AlR_3 adducts.[38]

Figure S5. Limiting SBP and TBP geometries for pentacoordinate methyl groups.



SBP **TBP-1** **TBP-2**

Several rare earth metallocene adducts $Cp^R{}_2M(\mu\text{-}CH_2R)_2Al(CH_2R)_2$ (Cp^R = Cp or substituted cyclopentadienyl; M = Group 3 or lanthanide; R = H or Me) have been structurally characterized (these are neutral analogues of $\mathbf{7}^+$ and **12**). In most cases, the H atoms for the $\mu\text{-}CH_2R$ groups were either not located or their positions were rendered unreliable by disorder. For compounds with $\mu\text{-}CH_2Me$ groups, the orientation of the methyl substituents clearly suggest trigonal bipyramidal geometries for the bridging carbon atoms, with *two* C-H bonds oriented toward the rare earth metal (mode TBP-1). However, for neutral *ansa*-scandocene complexes $Cp^R{}_2Sc(\mu\text{-}Me)_2AlMe_2$ the

geometries at the bridging carbons differed. The resultant structures could be classified as distorted square base pyramidal (SBP) or distorted trigonal bipyramidal (TBP-2). In each case only *one* H_{eq} is oriented toward the Sc.

In the case of the cationic titanocene system **12**, the geometry at each bridging carbon is best considered as distorted trigonal bipyramidal (TBP-2 in Fig. S5) with the axial sites occupied by Al and the single μ-H atom closest to Ti (Ti···H_{ax} = 2.29 Å). This H_{ax} lies 0.09 Å out of the metallocene equatorial plane containing the Ti and two μ-C atoms. Defining the mid-point of the two bridging carbons as "μ-C_{mid}", the torsion angles Ti–(μ-C_{mid})–C–H for the bridging methyls are 5.2 (H atom closest to Ti), 115.0 and 124.9 °, consistent with distorted TBP-2 type geometries attributed to these carbon atoms. The orientations of the μ-methyl groups in **12** are approximately intermediate between the two situations found in the isoelectronic scandocenes $Cp^R_2Sc(\mu\text{-}Me)_2AlMe_2$. The TBP-2 type coordination for **12** persists in the $ZnMe_2$ adduct $[Cp_2Ti(\mu\text{-}Me)_2ZnMe]^+$ (**13**, Fig. 3). One μ-methyl C-H bond points toward the metal (Ti···H = 2.29 Å) and lies almost exactly in the Ti(μ-$C)_2$Zn plane (Ti–(μ-C_{mid})–C–H torsion angle avg. 2.6 ° *vs*. 120.4 and 118.6 ° for the other C-H bonds which are oriented toward the ZnMe group).

For **7Q** (and **7q**) the arrangement at each bridging methyl group is identical to that observed in the experimental structure $\mathbf{7}^+$ and in Al_2Me_6. Thus the μ-Me groups are probably better described as having distorted square base pyramidal geometries (SBP) with the H atoms labelled H(1) and H(4) in Fig. 2 occupying the axial positions. Note that in **7Q** and **7q** the C-H bonds of the bridging methyls are mutually eclipsed, whereas for Al_2Me_6 they are staggered.[3] The axial H atoms lie 0.99 Å above the Ti(μ-$C)_2$ plane of **7Q** whereas the basal H atoms lie on average 0.53 Å below this plane. The Ti–(μ-C_{mid})–C–H torsion angles for the bridging methyls are 98.1 ° (axial H), 25.1 ° (basal H closest to Ti) and 138.2 °. These are comparable to the corresponding Al–(μ-C_{mid})–C–H values of 96.4 (axial H), 27.4 (basal H closest to Al) and 140.4 °. Therefore in **7Q** and $\mathbf{7}^+$ the C-H bonds closest to titanium (Ti···H = 2.21 Å (**7Q**), 2.17(3) Å ($\mathbf{7}^+$)) are oriented more toward the imido ligand, whereas in **12** the corresponding H atoms lie approximately in the metallocene equatorial

plane. These features can be traced to specific differences between the energies and shapes of the $[Ti(N^tBu)(Me_3[9]aneN_3)]^{2+}$ and $[Cp_2Ti]^{2+}$ frontier orbitals as discussed further below.

The non-planar and asymmetrically bound $Ti(\mu\text{-}Me)_2Zn$ moiety in **8Q** is associated with differing geometries at the bridging methyl carbons, neither of which corresponds to the TBP-2 situation found in **13**. The methyl group that is slightly further from Ti (Ti-C = 2.224 Å) and closer to Zn (C(2)) has an approximate SBP geometry and a single closest Ti···H-C distance of 2.39 Å. The other carbon (C(1)) with a shorter Ti-C and longer C-Zn distance has an approximately TBP-1 geometry (equatorial Zn and axial Al). Thus *two* C-H bonds of this methyl are oriented toward Ti, but at a much longer distances (Ti···H = 2.62, 2.72 Å) than that for the other methyl group (Ti···H = 2.39 Å).

Despite the various μ-C geometries and C-H bond orientations, the differences in calculated apical and basal/equatorial C-H distances for **12**, **13**, **7Q**, **7q** and **8Q** are small (maximum variation *ca*. 0.01 Å). Nonetheless, the trends are as expected for formally square base pyramidal (shorter C-H_{ax}) and/or trigonal bipyramidal (longer C-H_{ax}) geometries.[39] We note that neither the neutron diffraction study of $Nd(AlMe_4)_3$ nor that of Al_2Me_6 found an experimentally significant difference in the various C-H distances of the bridging methyl groups (experimental $\Delta_{C\text{-}H}$ = 0.01(1) – 0.015(4) Å).[3,15] The calculations for **12**, **13**, **7Q**, **7q** and **8Q** are therefore fully consistent with these studies.

(ii) Electronic structures of the adducts: Ti···H-C interactions. As indicated in Fig. 4 (main text), the LUMO for $[Cp_2Ti]^{2+}$ is a d_{y^2} type orbital lying at low energy[40] and is not involved in the principal $Ti(\mu\text{-}Me)_2MMe_n$ (M = Al or Zn) bonding pattern (Fig. 4). This leaves it as a low-lying acceptor orbital perfectly suited to receive electron density through donation from the C-H_{ax} bonds of the bridging methyl groups. These agostic interactions therefore have to occur in the equatorial (yz) plane to achieve optimal overlap. This is the situation found in **12** and **13** (Fig. 3, main text) and results in approximate TBP-2 geometries for the bridging methyls. For $Ti(N^tBu)(Me_3[9]aneN_3)^{2+}$, the LUMO and LUMO+1 are involved in the $Ti(\mu\text{-}Me)_2Al$ bonding of **7Q**, leaving the LUMO+2 unused. However, this orbital is at considerably higher energy, and does

not have the proper orientation to receive density from a C-H bond of the bridging methyls. The only possible interaction for a bridging C-H bond in **7Q** (and hence $\mathbf{7}^+$) is with the σ^*(Ti-N) MO of the equatorial N atoms *trans* to the μ-carbon atoms. As the latter lies slightly above the Ti(μ-Me)$_2$Al best-fit plane, the optimum overlap is obtained when the C-H bond points below the plane, toward the imido ligand. This requires an adjustment of the bridging methyl group and an approximate SBP geometry, as observed experimentally for $\mathbf{7}^+$.

This analysis is supported by NBO (Natural Bond Orbital) 2nd order perturbation energetic contributions. These show a σ(C-H) → d_{y^2} interaction of 119.7 kJ mol^{-1} in **12**, but only a σ(C-H) → σ^*(Ti-N) interaction of 48.1 kJ mol^{-1} in **7Q**. Although the absolute values of these energies should not be considered by themselves, they clearly indicate a stronger Ti···H-(μ-C) agostic interaction in **12** than in **7Q**. We note in this context that the monoalkyl cation [Cp$_2$TiMe]$^+$ possesses a weak α-agostic interaction whereas [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me]$^+$ ($\mathbf{4}^+$) does not, again because of the shapes and energies of the metal fragment frontier orbitals.[1]

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