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Experimental

General considerations. All reactions and manipulations of air and moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and glovebox techniques. Reagents were purchased from commercial suppliers and used as received, unless stated otherwise. Deuterated solvents were dried over Na/K alloy prior to use or degassed and stored over mol. sieves (4Å) (fluorobenzene- d_5). Other solvents were dried by percolation over columns of aluminum oxide (THF and toluene), R3-11 supported Cu based oxygen scavenger (THF, pentane and toluene) and mol. sieves (pentane and toluene), or by distillation from Na/K alloy (cyclohexane). Fluorobenzene, 1,2-difluorobenzene and α,α,α -trifluorotoluene were dried and stored over mol. sieves. The compounds Cp^*_2ScMe ,¹ Cp^*_2TiMe ,² Cp^*_2VMe ,³ $[\text{Cp}_2\text{Fe}][\text{BPh}_4]$,⁴ and $[\text{PhNMe}_2\text{H}][\text{BPh}_4]$ ⁵ were prepared according to literature procedures. ^1H and ^{19}F NMR spectra were recorded on a Varian Unity 500 or Varian Gemini 200 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances. IR spectra were recorded on a Mattson 4020 Galaxy FT-IR spectrophotometer. GC-MS spectra were recorded at 70 eV using a HP5973 mass-selective detector attached to a HP6890 GC equipped with a HP-5MS biphenyl/dimethylsiloxane (5/95) column. The elemental analyses were performed by the Microanalytical Department of the University of Groningen or by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr. In case of the analyses performed at the University of Groningen, each value is the average of two independent determinations. Some of these analyses show low, but reproducible carbon values. This is a common observation for organometallic complexes with a high carbon-content, and is associated with the formation of inert carbide species. In all cases V_2O_5 was added to the samples to reduce the formation of such species. The analysis performed under different conditions by Kolbe do not suffer from these low carbon values. The values reported in this case are single measurements.

$[\text{Cp}^*_2\text{Sc}][\text{BPh}_4]$ (1a). Toluene (5 mL) was added to a mixture of 507 mg (1.5 mmol) of Cp^*_2ScMe , and 627 mg (1.5 mmol) of $[\text{PhNMe}_2\text{H}][\text{BPh}_4]$. After 1 h, the solvent was evaporated, the resulting yellow solid was washed with pentane (3x5 mL), affording 631 mg (1.0 mmol, 67%) of $[\text{Cp}^*_2\text{Sc}][\text{BPh}_4]$. IR (KBr pellet) 3052(s), 2982(s), 2911(s), 2859(s), 2728(w), 1602(w), 1580(m), 1479(s), 1428(s), 1382(s), 1263(m), 1239(m), 1183(w), 1150(m), 1066(m), 1031(m), 884(w), 848(w), 802(w), 732(s), 703(s), 604(m), 432(m) cm^{-1} . Anal. Calcd for $\text{C}_{44}\text{H}_{50}\text{BSc}$: C, 83.39; H, 7.95. Found: C, 83.16; H, 7.95.⁶ The ^1H NMR spectrum of the solution after dissolution of the compound in $\text{THF}-d_8$ is identical to that of the bis-THF adduct **5a** described above. In a different experiment (without stirring of the reaction mixture), yellow crystals formed during the reaction, which were suitable for a single crystal X-ray analysis. Compound **1a** is slightly soluble in C_6D_6 , but insufficiently to record ^1H and ^{13}C NMR spectra.

$[\text{Cp}^*_2\text{Ti}][\text{BPh}_4]$ (1b). To a mixture of 0.75 g (2.2 mmol) of Cp^*_2TiMe and 0.95 g (2.2 mmol) of $[\text{PhNMe}_2\text{H}][\text{BPh}_4]$, 40 mL of toluene was added at $-30\text{ }^\circ\text{C}$. Gas evolution was observed as the solution was gradually warmed to RT. After 1h the toluene was removed at reduced pressure, and the crystalline solid was washed with pentane (3 x 20 mL). Drying the product in vacuum afforded 1.2 g (1.8 mmol, 86%) of $[\text{Cp}^*_2\text{Ti}][\text{BPh}_4]$ as red-brown crystals, suitable for single crystal X-ray diffraction. IR (KBr pellet) 3050 (s), 2997(s), 2982(s), 2908(s), 2860(s), 1599(w), 1580(m), 1478(s), 1426(s), 1381(s), 1306(w), 1265(m), 1181(w), 1147(m), 1066(m), 1029(s), 1019(s), 844(m), 733(s), 703(s), 624(w), 607(s), 525(w), 476(w), 464(w), 425(w) cm^{-1} . Anal. Calcd for $\text{C}_{44}\text{H}_{50}\text{BTi}$: C, 82.89; H, 7.90. Found: C, 79.62; H,

8.06.⁷ The ¹H NMR spectrum of the compound after dissolution in THF-*d*₈ was identical to that of the corresponding THF adduct **5b**.

[Cp*₂V][BPh₄] (1c). To a mixture of 201 mg (0.60 mmol) of Cp*₂VMe, and 242 mg (0.59 mmol) of [PhNMe₂H][BPh₄], 5 mL of toluene was added. After 1h, the toluene was evaporated at reduced pressure, and the product was washed with pentane (3 x 3 mL). Evaporation of the volatiles at reduced pressure yielded 263 mg (0.42 mmol; 71%) of [Cp*₂V][BPh₄] as a brown powder. IR (KBr pellet) 3134(m), 3051(s), 2998(s), 2982(s), 2965(s), 2907(m), 1601(w), 1579(m), 1478(s), 1456(m), 1427(s), 1382(m), 1308(m), 1264(m), 1181(w), 1146(m), 1126(w), 1067(m), 1030(m), 1019(m), 890(w), 846(m), 805(w), 765(w), 738(s), 706(s), 624(w), 607(m), 540(w), 478(w), 465(w). Recrystallization of the compound from 1,2-difluorobenzene/cyclohexane afforded reddish crystals that were used in an X-ray diffraction study. Crystals thus obtained were also submitted for analysis. Anal. Calcd for C₄₄H₅₀BV: C, 82.49; H 7.87. Found: C, 80.86; H, 7.86.⁷

[Cp*₂Ti][BPh₄] (1b) from Cp*₂TiH and [Cp₂Fe][BPh₄]. At -78°C, 50 mL of toluene was slowly added to a mixture of solid Cp*₂TiH (1.00 g, 3.14 mmol) and [Cp₂Fe][BPh₄] (1.54 g, 3.05 mmol). The reaction mixture was allowed to warm to room temperature while stirring, while gas evolution was observed. After 2 h the solvent was decanted from the brown precipitate, and the solid was rinsed repeatedly with pentane. After prolonged drying in vacuum (0.005 mm Hg), 1.48 g of brown powder was isolated (2.32 mmol, 76%). The IR spectrum of the compound is similar to the one reported above. Dissolution of the compound in THF-*d*₈ yielded a product identified by ¹H NMR spectroscopy as **5b**.

[Cp*₂V][BPh₄] (1c) from Cp*₂V and [Cp₂Fe][BPh₄]. Toluene (10 mL) was added at -60 °C to a mixture of 450 mg (1.4 mmol) of Cp*₂V and 677 mg (1.3 mmol) of [Cp₂Fe][BPh₄]. The reaction mixture was allowed to warm to room temperature and stirred for 1 h after which the mother liquid was decanted, and the solvent removed at reduced pressure. Washing with pentane (2 x 20 mL) resulted in 740 mg (1.2 mmol, 83%) of a brown solid. The IR spectrum of the compound is identical to that of **1c** as prepared from Cp*₂VMe (see above).

[Cp*₂Sc(FC₆H₅)₂][BPh₄] (2a) from [Cp*₂Sc][BPh₄]. [Cp*₂Sc][BPh₄] (25.9 mg, 41 μmol) was dissolved in 1 mL of fluorobenzene. Slow evaporation of the solvent at reduced pressure afforded 8.9 mg (9 μmol, 21%) of yellow crystals of [Cp*₂Sc(FC₆H₅)₂][BPh₄].2C₆H₅F. Anal. Calcd for C₅₆H₆₀BF₂Sc·2C₆H₅F: C, 79.85; H, 6.93. Found: C, 80.22; H, 7.86.⁶ The crystals were further characterized by X-ray diffraction. Dissolution of the compound in THF-*d*₈ results in the clean formation of the bis-THF adduct **5a**.

[Cp*₂Ti(FC₆H₅)][BPh₄] (2b). Fluorobenzene (40 mL) was added to a frozen mixture of 660 mg (1.98 mmol) of Cp*₂TiMe and 874 mg (1.98 mmol) of [PhNMe₂H][BPh₄]. The frozen mixture was allowed to warm to ambient temperature and the reaction mixture was stirred. The color darkened while gas evolution was observed. After 3h the solution was decanted and concentrated. Crystallization by slow diffusion of pentane into the fluorobenzene solution yielded 869 mg (1.04 mmol, 53%) of [Cp*₂Ti(FC₆H₅)][BPh₄](C₆H₅F). Anal. Calcd for C₅₀H₅₅BFTi·C₆H₅F: C, 81.06; H, 7.29; Ti: 5.77. Found: C, 80.36; H, 7.40; Ti, 5.62.⁷ IR (nujol/KBr) 441(w), 469(w), 484(w), 503(w), 520(w), 535(w), 611(s), 625(w), 688(m), 705(s), 732(s), 754(s), 773(w), 804(m), 842(m), 900(w), 990(m), 1018(m), 1063(m), 1106(m), 1155(m), 1181(w), 1213(m), 1262(m), 1304(w), 1307(w), 1378(s), 1529(w), 1578(m), 2672(w),

2726(w), 2855(s) cm^{-1} . Dissolution of the compound in d_8 -THF and analysis by ^1H NMR spectroscopy showed resonances corresponding to the THF adduct **5b** and free fluorobenzene.

[Cp*₂Ti(FC₆H₅)] [BPh₄] (2b) from [Cp*₂Ti] [BPh₄]. At -40°C, 20 mL of fluorobenzene was added to 0.40 g (0.63 mmol) of solid [Cp*₂Ti] [BPh₄]. The mixture turned green instantaneously. While stirring, the mixture was warmed to ambient temperature. The solution was filtered, and the fluorobenzene solvent was removed at reduced pressure. The resulting green solid was rinsed repeatedly with pentane. After prolonged drying in vacuum (to 0.005 mm Hg) this yielded 0.39 g (0.54 mmol, 85%) of [Cp*₂Ti(FC₆H₅)] [BPh₄]. The IR spectrum of the compound is similar to that described above. Crystals suitable for X-ray diffraction were obtained from fluorobenzene by slow diffusion of pentane into the solution, and were found to have the stoichiometry [Cp*₂Ti(FC₆H₅)] [BPh₄].C₆H₅F.

Reaction of [Cp*₂V] [BPh₄] with C₆H₅F. [Cp*₂V] [BPh₄] (96 mg, 0.15 mmol) was dissolved in fluorobenzene. After 12 h the solution was filtered and the solvent evaporated at reduced pressure. The brown, oily precipitate was washed with pentane affording 52 mg of a brown solid. The ^1H NMR spectrum of the compound in THF- d_8 is similar to that of **5c**; the ^{19}F NMR showed no signals for fluorobenzene.

[Cp*₂Sc(C₆H₄F₂)] [BPh₄] (3a). 1,2-Difluorobenzene (0.5 mL) was added to 24.8 mg (39 μmol) of [Cp*₂Sc] [BPh₄]. On top of the solution, 3 mL of cyclohexane was layered carefully. Slow mixing of the two layers resulted in the precipitation of 12.9 mg (17 μmol , 44%) of [Cp*₂Sc(F₂C₆H₄)] [BPh₄]. The ^1H NMR spectrum of the compound in THF- d_8 revealed signals for the THF adduct **5a** and 1,2-difluorobenzene. Anal. Calcd for C₅₀H₅₄BF₂Sc: C, 80.30; H, 7.28. Found: C, 80.03; H, 7.11.⁶ IR (KBr pellet) 3052(s), 3033(m), 2982(m), 2967(m), 2920(s), 2909(s), 2853(m), 1604(m), 1592(m), 1579(m), 1487(s), 1429(s), 1319(m), 1266(m), 1232(m), 1185(w), 1152(w), 1066(m), 1031(m), 883(w), 846(w), 747(s), 744(s), 704(s), 607(m), 450(m). Recrystallization of the compound from 1,2-difluorobenzene/cyclohexane afforded crystals suitable for a single-crystal X-ray diffraction study.

[Cp*₂Ti(F₂C₆H₄)] [BPh₄] (3b). [Cp*₂Ti] [BPh₄] (54.2 mg, 85 μmol) was dissolved in 0.5 mL of 1,2-difluorobenzene. The green solution was layered with 2.5 mL of cyclohexane. Slow diffusion of the cyclohexane into the 1,2-difluorobenzene solution afforded 58.6 mg (68 μmol , 80%) of blue-green crystals of [Cp*₂Ti(1,2-F₂C₆H₃)] [BPh₄].(C₆H₄F₂). The ^1H NMR spectrum of the compound in THF- d_8 was identical to that of the mono-THF adduct **5b** and showed resonances for 1,2-difluorobenzene. Anal. Calcd for C₅₀H₅₄BF₂Ti.C₆H₄F₂: C, 77.69; H, 6.75; Ti, 5.33. Found: C, 77.68; H, 6.85; Ti, 5.53.⁶ IR (KBr pellet) 3052(m), 3035(m), 3000(m), 2982(m), 2922(m), 2907(m), 2864(w), 2852(w), 1616(w), 1595(w), 1580(m), 1506(m), 1490(s), 1451(m), 1427(s), 1382(m), 1326(w), 1302(w), 1267(m), 1233(m), 1184(w), 1153(w), 1121(w), 1100(w), 1065(m), 1022(m), 824(m), 742(s), 733(s), 703(s), 624(w), 609(m), 563(w), 547(w), 450(m). In a separate experiment, 34 mg (55 μmol) of [Cp*₂Ti] [BPh₄] was dissolved in 0.5 mL of 1,2-difluorobenzene. From this solution, 40.2 mg (46 μmol , 84%) of blue-green crystals of [Cp*₂Ti(1,2-F₂C₆H₃)] [BPh₄].(C₆H₄F₂) were obtained after slow diffusion of cyclohexane into the solution. These crystals were used for an X-ray analysis.

[Cp*₂Sc][B(C₆F₅)₄] (1a'). Toluene (1 mL) was added to a mixture of 30.6 mg (93 μmol) of Cp*₂ScMe and 73.0 mg (91 μmol) of [PhNMe₂H][B(C₆F₅)₄]. The resulting solution was layered with cyclohexane resulting in a brownish, oily precipitate. Upon standing for one week, the compound crystallized to yield 55.3 mg (56 μmol; 62%) of [Cp*₂Sc][B(C₆F₅)₄] after decanting the toluene solvent and washing with pentane (2 x 2 mL). IR (KBr pellet) 2961(m), 2920(m), 2872(m), 1644(m), 1603(s), 1515(s), 1465(m), 1385(m), 1277(s), 1250(w), 1090(s), 1049(w), 1028(w), 980(s), 774(m), 757(m), 728(w), 684(m), 661(m), 608(w), 574(w), 461(m) cm⁻¹. Anal. Calcd for C₄₄H₃₀BF₂₀Sc: C, 53.19; H, 3.04. Found: C, 53.16; H, 3.32.⁷ The ¹H NMR spectrum of the complex in THF-*d*₈ is very similar to that of **5a**, with the exception of the resonances for the counterion.

[Cp*₂Ti][B(C₆F₅)₄] (1b') from Cp*₂TiMe and [(C_nH_{2n+2})₂NMeH][B(C₆F₅)₄] (n = 16-18). Cyclohexane (0.5 mL) and 32.6 mg (98 μmol) of Cp*₂TiMe in another 0.5 mL of cyclohexane was layered on top of 1.04 g of a 10.8 weight% ISOPARTM solution (94 μmol) of [(C_nH_{2n+2})₂NMeH][B(C₆F₅)₄] (n = 16-18). The two layers mixed slowly, resulting in a brown, oily precipitate. Overnight greenish-brown crystals precipitated, that were suitable for X-ray analysis. Washing of the crystals with pentane (2 mL) resulted in 75 mg (75 μmol, 77%) of [Cp*₂Ti][B(C₆F₅)₄]. The ¹H and ¹⁹F NMR spectrum of the compound in THF-*d*₈ is similar to that of **5b'**. Anal. Calcd for C₄₄H₃₀BF₂₀Ti: C, 52.99; H, 3.03. Found: C, 50.75; H, 3.35.⁷

[Cp*₂Ti][B(C₆F₅)₄] (1b') from Cp*₂TiMe and [PhNMe₂H][B(C₆F₅)₄]. To a mixture that was frozen in liquid nitrogen of 122 mg (0.37 mmol) of Cp*₂TiMe and 320 mg (0.35 mmol) of [PhNMe₂H][B(C₆F₅)₄], 10 mL of fluorobenzene was added. The reaction mixture was stirred for 1 h, resulting in a green solution. The solvent was removed in vacuum and the resulting green oil was washed 5 times with 10 mL of pentane. After drying in vacuum, this afforded 0.30 g (0.3 mmol, 86%) of [Cp*₂Ti][B(C₆F₅)₄]. The ¹H and ¹⁹F NMR spectra of the compound in THF-*d*₈ show resonances for the THF adduct **5b'** and for a diamagnetic impurity with a resonance at 2.05 ppm (17% assuming the impurity involves a [Cp*₂M] fragment). Hence, no satisfactory elemental analysis could be obtained

[Cp*₂Ti(FC₆H₅)][B(C₆F₅)₄] (2b'). To a mixture of 33.0 mg (99 μmol) of Cp*₂TiMe and 75.6 mg (94 μmol) of [PhNMe₂H][B(C₆F₅)₄] 1 mL of fluorobenzene was added. Slow diffusion of 3 mL of cyclohexane into the fluorobenzene resulted in 79.3 mg (80 μmol; 80%) of green crystals. The compound was recrystallized from fluorobenzene/cyclohexane to afford crystals that were suitable for a single-crystal X-ray analysis. Crystals thus obtained were also submitted for elemental analysis. The IR (KBr pellet) 2981(w), 2926(m), 2858(m), 1643(m), 1597(w), 1514(s), 1464(s), 1384(m), 1276(m), 1222(w), 1163(w), 1092(s), 1021(w), 979(s), 774(m), 756(m), 726(w), 684(m), 661(m), 610(w), 574(w), 531(w), 475(w) cm⁻¹. Anal. Calcd for C₅₀H₃₅BF₂₁Ti: C, 54.92; H, 3.23. Found: C, 53.84; H, 3.34.⁷ The ¹H and ¹⁹F NMR spectrum of the compound in THF-*d*₈ showed resonances for **5b'** and fluorobenzene.

[Cp*₂V][B(C₆F₅)₄] (1c'). Fluorobenzene (1.5 mL) was added to a mixture of 55.0 mg (0.16 mmol) of Cp*₂VMe and 125.7 mg (0.16 mmol) of [PhNMe₂H][B(C₆F₅)₄]. The resulting solution was layered with cyclohexane (3 mL), which afforded 140.2 mg (0.14 mmol; 89%) of red crystals after slow diffusion of the two solvents, removal of the supernatant, and washing with pentane (2x1 mL). IR (KBr pellet) 2981(w), 2924(w), 2867(w), 1644(m), 1603(s), 1515(s), 1463(m), 1385(m), 1278(s), 1085(w), 1023(w),

980(s), 775(m), 757(m), 726(w), 684(m), 661(m), 604(w), 574(w) cm^{-1} . Anal. Calcd for $\text{C}_{44}\text{H}_{30}\text{BF}_{20}\text{V}$: C, 52.83; H, 3.02. Found: C, 52.14; H, 3.04.⁷

[Cp*₂Sc(THF)₂][BPh₄] (5a). THF (1 mL) was added to a mixture of Cp*₂ScMe (61.3 mg, 0.19 mmol) and [PhNMe₂H][BPh₄] (76.1 mg, 0.17 mmol). Pentane (3 mL) was carefully layered on top of the resulting yellow reaction mixture affording 85.2 mg (0.11 mmol, 65%) of yellow crystals of [Cp*₂Sc(THF)₂][BPh₄] after slow mixing of the two solvents by diffusion. ¹H NMR (THF-*d*₈, 200MHz, RT) δ 7.29 (m, 8H, BPh₄), 6.87 (t, 7.3 Hz, 8H, BPh₄), 6.72 (t, 7.3 Hz, 4H, BPh₄), 3.58 (t, 6.1 Hz, THF), 1.93 (s, 15H, Cp*), 1.77 (t, 6.1 Hz, THF). IR (KBr pellet) 3048(s), 3033(s), 2979(s), 2951(s), 2937(s), 2908(s), 2868(s), 2857(s), 1603(w), 1579(m), 1478(s), 1438(w), 1426(s), 1380(m), 1341(w), 1316(w), 1297(w), 1266(w), 1251(w), 1180(w), 1169(w), 1143(m), 1065(m), 1031(w), 1006(s), 971(w), 915(w), 838(s), 821(s), 733(s), 705(s), 672(w), 625(w), 606(m), 478(w), 464(w), 450(w) cm^{-1} . Anal. Calcd. for $\text{C}_{52}\text{H}_{66}\text{BO}_2\text{Sc}$: C, 80.28; H, 8.55; Sc, 5.66. Found: C, 79.98; H, 8.61; Sc, 5.70. Recrystallization from THF-*d*₈/pentane afforded yellow crystals suitable for an X-ray diffraction study.

[Cp*₂Ti(THF)][BPh₄] (5b). THF (2 mL) was added to a mixture of 52.4 mg (0.16 mmol) of Cp*₂TiMe and 68.4 mg (0.15 mmol) of [PhNMe₂H][BPh₄]. When no further gas evolution was observed (after 15 minutes), cyclohexane (3 ml) was layered carefully on top of the green reaction mixture. Diffusion of the two layers resulted in 57.3 mg (0.07 mmol, 47%) of [Cp*₂Ti(THF)][BPh₄]. THF as green crystals, that were isolated after decanting the supernatant and drying at reduced pressure. ¹H NMR (THF-*d*₈, 200MHz, RT): δ 11.70 (br, $\Delta\nu_{1/2}$ = 402 Hz, Cp*), 7.6-6.6 (BPh₄). IR (KBr pellet) 3052(s), 3032(s), 2995(s), 2981(s), 2906(s), 2861(s), 1592(w), 1580(m), 1478(s), 1426(s), 1380(s), 1338(m), 1265(m), 1244(w), 1183(w), 1145(w), 1126(w), 1104(w), 1094(w), 1066(w), 1030(m), 1014(m), 916(w), 847(m), 803(w), 743(s), 732(s), 704(s), 625(w), 606(m), 484(w), 463(w), 442(m) cm^{-1} . Anal. Calcd. for $\text{C}_{52}\text{H}_{66}\text{BO}_2\text{Ti}$: C, 79.89; H, 8.51; Ti, 6.13. Found: C, 79.94; H, 8.43; Ti, 6.33.

Reaction of Cp*₂TiMe with [PhNMe₂H][BPh₄] in THF (Toepler pump experiment). A flask containing a mixture of 14.2 mg (42.6 μmol) of Cp*₂TiMe and 21.5 mg (48.7 μmol) of [PhNMe₂H][BPh₄] was attached to a vacuum line, and evacuated. THF (1 mL) was condensed onto the mixture at -196 °C and the vessel was warmed to RT. The reaction mixture turned green and gas evolution was observed. The amount of gas was determined by transferring the volatiles in a series of freeze-thaw cycles through a cold-trap (cooled with a liquid nitrogen/ethanol mixture) into a calibrated volume. A total amount of 35 μmol (0.81 equivalents) of methane was formed (identified by GC analysis). The organometallic product was isolated by evaporation of the volatiles and washing with pentane, and identified as [Cp*₂Ti(THF)][BPh₄] by ¹H NMR spectroscopy.

[Cp*₂V(THF)][BPh₄] (5c). THF (1 mL) was added to a mixture of 58.2 mg (0.17 mmol) of Cp*₂VMe, and 70.2 mg (0.16 mmol) of [PhNMe₂H][BPh₄]. The resulting green solution was carefully layered with 3 mL of cyclohexane, affording 94.4 mg (83%) of green crystals of [Cp*₂V(THF)][BPh₄]. ¹H NMR (THF-*d*₈, 200 MHz, RT): δ 7.7-6.5 (*PhB*). IR (KBr pellet) 3052(s), 3030(m), 2994(s), 2980(s), 2907(s), 2857(m), 1579(m), 1478(s), 1450(w), 1426(s), 1380(m), 1362(w), 1340(w), 1264(m), 1182(w), 1144(m), 1066(m), 1019(s), 918(w), 863(s), 743(s), 731(s), 703(s), 642(w), 606(m), 483(w), 462(w), 434(w), 413(w) cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{58}\text{BOV}$: C, 80.89; H, 8.20; V, 7.15. Found: C, 80.76; H, 8.26; V, 7.10.

[Cp*₂Ti(THF)][BPh₄] (5b) from Cp*₂TiH and [Cp₂Fe][BPh₄]. A mixture of solid Cp*₂TiH (1.87 g, 5.86 mmol) and [Cp₂Fe][BPh₄] (2.28 g, 4.51 mmol) was cooled to -40 °C after which 60 mL of THF was gradually added while stirring. Evolution of molecular hydrogen was observed (identified by GC). The mixture was warmed to ambient temperature and stirred overnight. The solvent was pumped off from the resulting green solution, and the residue was rinsed twice with 25 mL of pentane to remove ferrocene and residual Cp*₂TiH. Drying at reduced pressure yielded 2.48 g (3.49 mmol, 77%) of [Cp*₂Ti(THF)][B(C₆H₅)₄]. The compound was spectroscopically (¹H NMR and IR) identical to the material obtained above in the reaction of Cp*₂TiMe with [PhNMe₂H][BPh₄] in THF. Crystals suitable for X-ray diffraction were obtained by slow solvent evaporation from a solution of [Cp*₂Ti(THF)][BPh₄] in neat THF. Crystals thus obtained were found to have the stoichiometry [Cp*₂Ti(THF)][BPh₄].THF.

Reaction of Cp*₂TiH with [Cp₂Fe][BPh₄] in THF (Toepler pump experiment). A vessel charged with a mixture of solid Cp*₂TiH (1.455 g, 4.56 mmol) and [Cp₂Fe][BPh₄] (2.18 g, 4.32 mmol) was connected to a vacuum line attached to a Toepler pump. The evacuated mixture was frozen in liquid nitrogen and 30 mL of THF was condensed into the vessel. The vessel was closed and the mixture was allowed to warm to ambient temperature after which it was stirred for 2 h. The amount of gas released was determined by pumping the gas through a cold-trap (cooled with liquid nitrogen) into a calibrated volume using a Toepler pump, in a series of freeze-thaw cycles. A total of 2.09 mmol of gas (identified as H₂ by GC analysis) was collected, 0.48 equivalents of H₂ as calculated on [Cp₂Fe][BPh₄]. The organometallic product was worked up as described above, and identified as [Cp*₂Ti(THF)][BPh₄] using ¹H NMR spectroscopy.

[Cp*₂V(THF)][BPh₄] (5c) from Cp*₂V and [Cp₂Fe][BPh₄]. THF (20 mL) was added to a cooled mixture (-40 °C) of 270 mg (0.84 mmol) of Cp*₂V and 437 mg (0.86 mmol) of [Cp₂Fe][BPh₄]. After 12 h the solution was decanted, and the brown precipitate was dried at reduced pressure. The compound was recrystallized from THF/pentane, yielding 304 mg (51%) of [Cp*₂V(THF)][BPh₄]. The compound was spectroscopically (¹H NMR and IR) identical to the material obtained above in the reaction of Cp*₂VMe with [PhNMe₂H][BPh₄] in THF.

Generation of [Cp*₂Ti(THF)][B(C₆F₅)₄] (5b'). To a mixture of 5.6 mg (16.8 μmol) of Cp*₂TiMe and 16.2 mg (17.6 μmol) of [PhNMe₂H][B(C₆F₅)₄], 0.5 mL of THF-d₈ was added. ¹H NMR (THF-d₈, 200 MHz, RT): δ 11.7 (br, Δv_{1/2} = 286 Hz, Cp*), 7.24 (br, m-PhNMe₂), 6.87 (br, o-PhNMe₂), 6.80 (br, p-PhNMe₂), 3.00 (s, PhNMe₂); ¹⁹F NMR (THF-d₈, 200 MHz, RT): δ -133.79 (br, o-F), -165.89 (t, 19.81 Hz, p-F), -169.35 (br. t, m-F).

Complete reference 38a : Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Hättig, C.; Horn, H.; Huber, C.; Huniar, U.; Kattannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Treutler, O.; Tsereteli, K.; Unterreiner, B.; Von Arnim, M.; Weigend, F.; Weis, P.; Weiss H. Turbomole Version 5, january 2002. Theoretical Chemistry Group, University of Karlsruhe.

Crystallographic Data

In a glovebox, suitable crystals were mounted on top of a glass fiber. The crystals were aligned in a cold nitrogen stream on a Enraf-Nonius⁸ CAD-4F (**1b** and **3b**) or a Bruker⁹ SMART APEX CCD (all others) diffractometer. The unit cells were determined as listed in Table 1, Table 2 and Table 3. The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.¹⁰

The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. In case of **1a**, **1c**, **2a**, **2b**, **4b** and [Cp*₂TiF(THF)][BPh₄] subsequent difference Fourier synthesis resulted in the location of all hydrogen atoms, which coordinates and isotropic displacement parameters were refined. In **1b**, subsequent difference Fourier synthesis resulted in location most but not all hydrogen atoms due to a disordered, cocrystallized THF molecule. A disorder model with the same conformation and bond restraints was used in the refinement, yielding a site occupancy ratio of 85:15 for the disordered solvent molecule. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their appropriate hybridization at the C-atoms. The methyl groups were refined as rigid, rotating groups. Two common isotropic thermal parameters for the H-atoms were refined; one for the aromatic and one for the methyl hydrogen atoms. In **2c** and **2c'**, some atoms showed unrealistic displacement parameters, suggesting some degree of disorder, which is in line with the weak scattering power of the crystals investigated. In the neighborhood of the V atoms in **2c** and **2c'**, residual density was found. The electron densities of the dislocated V positions have been described by two site occupancy factors with separately refined displacement parameters. The site occupancy factors of the major fractions of the disordered V positions refined to values of 0.8363(3) and 0.830(7) for **2c** and 0.890(3) for **2c'**. The hydrogen atoms in **2c** were generated by geometrical considerations, which coordinates and isotropic displacement parameters were refined. Some hydrogen atoms did not behave well in the refinement, and were ultimately set to riding mode. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using sp² or sp³ hybridization at the C-atom as appropriate, with $U_{\text{iso}} = c \times U_{\text{equiv}}$ of their parent atom, where $c = 1.2$ for the non-methyl hydrogen atoms and $c = 1.5$ for the methyl hydrogen atoms, and where values U_{equiv} are related to the atoms to which the hydrogen atoms are bonded. The hydrogen atoms in **2c'** were found by a difference Fourier synthesis except for the hydrogen atoms attached to C(16) and C(19), which were included riding on their carrier atoms with their positions calculated using sp³ hybridization. These methyl groups were refined as rigid groups, which were allowed to rotate freely. In **3a**, the hydrogen atoms were generated by geometrical consideration, similar as in **2c**, without further complications. A disordered fluorobenzene solvent molecule complicated refinement of **3b**. The site occupancy factor of the major fraction refined to a value of 0.656(5). A subsequent difference Fourier synthesis showed the positions of most hydrogen atoms. These were treated similar as in **2c**. This is also true for the hydrogen atoms in **4a**. Refinement of the structure of **4a** was frustrated by a disorder problem in one tetraphenylborate anion: the carbon atoms showed unrealistic displacement parameters when allowed to vary anisotropically, suggesting dynamic disorder (dynamic means that the smeared electron density is due to fluctuations of the atomic positions within each unit cell). This is in line with the weak scattering power of the crystals investigated. It was not possible to satisfactorily describe the smeared electron density by different site occupancy factors.

Some atoms of the Cp*-ligand in **5a'** showed unrealistic displacement parameters when allowed to vary anisotropically, suggesting dynamic disorder. The hydrogen atoms were again included as in **3a**, except for those of the bridging methyl group. In case of the latter, the hydrogen atoms were fixed at a C-H bond length of 1.0 Å and refined as such. A similar disorder in the Cp*-ligands was found in complex **2a'** and **2b'**. These structures were refined as described for **5a'**. The hydrogen atoms in **3b'** were obtained similar as in **2c**. Refinement was frustrated by a twin/fragmented problem: although the $wR2$ value did not decrease substantial while switching to anisotropic refinement, no unrealistic displacement parameters were obtained.

In all crystal structure determinations, final refinement on F^2 was carried out by full-matrix least-squares techniques. Convergence was reached at $wR(F^2)$ and $R(F)$ values as listed in Table 1, Table 2 and Table 3 for reflections with $F_o \geq 4.0 \sigma(F_o)$. Except for **2c** and **3b'**, the final difference Fourier map was essentially featureless: no significant peaks having chemical meaning above the general background were observed. In **2c** few peaks of max. $1.76(6) \text{ e}/\text{\AA}^3$ were observed, but neglected being residual peaks of the minor fraction of the disordered Cp*-ligand; in **3b'**, the final difference Fourier map showed features within the range -0.8 to $2.5(1) \text{ e}/\text{\AA}^3$.

In each analysis, the positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h [w(|F_o|^2 - k|F_c|^2)|^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2F_c^2] / 3$. F_o and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined. Crystal data, data collection, and refinement parameters are summarized in Table 1, Table 2 and Table 3.

Table 1. Summary of crystallographic data for **5a-c** and **1a-c**.

	5a(d₁₆)	5b	5c	1a	1b	1c
Molecular formula	C ₅₂ H ₅₀ BD ₁₆ O ₂ Sc	C ₅₂ H ₅₄ BO ₂ Ti	C ₄₈ H ₅₈ BOV	C ₄₄ H ₅₀ BSc	C ₄₄ H ₅₀ BTi	C ₄₄ H ₅₀ BV
FW	794.85	781.79	712.74	634.65	637.56	640.63
Diffractionmeter	SMART APEX CCD	CAD-4F	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD
Temp (K)	90	130	100	100(1)	100(1)	100(1)
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	P2 ₁ /c	P2 ₁ /c	P-1	P-1	P-1	P-1
a (Å)	10.4868(5)	17.995(2)	10.3736(6)	11.8975(8)	13.3636(7)	13.3504(7)
b (Å)	21.575(1)	13.483(1)	11.7889(7)	12.4108(8)	15.0600(7)	15.1039(8)
c (Å)	18.957(1)	18.008(2)	16.450(1)	12.7617(8)	17.7873(9)	17.7288(9)
α (deg)			92.277(1)	97.330(1)	97.131(1)	96.341(1)
β (deg)	95.806(1)	90.060(8)	103.375(1)	102.134(1)	90.604(1)	90.936(1)
γ (deg)			92.858(1)	104.130(1)	91.970(1)	92.728(1)
V (Å ³)	4267.1(4)	4369.2(8)	1952.0(2)	1754.4(2)	3549.6(3)	3548.2(3)
Z	4	4	2	2	4	4
Dcalc (g/cm ³)	1.237	1.188	1.213	1.201	1.193	1.199
F(000)	1680	1684	764	680	1364	1368
μ (Mo K α), cm ⁻¹	2.13	2.35	2.9	2.4	2.71	3.09
θ range (deg.)	2.17, 29.81	1.13, 26.0	2.58, 29.65	2.61, 27.52	2.29, 25.03	2.30, 26.37
$wR(F^2)$	0.1295	0.1322	0.1021	0.1193	0.1265	0.1640
reflections	11341	7140	9852	7509	12451	14173
parameters	769	546	692	615	1229	1183
R(F)	0.0557	0.0535	0.0373	0.0477	0.0532	0.0583
for $F_o > 4.0 \sigma(F_o)$						
Goof	1.015	1.025	1.053	1.022	0.986	1.035
Weighting (a,b)	0.0542, 0.1137	0.0537, 4.1137	0.0596, 0.4981	0.0532, 0.5410	0.0562, 0.0	0.0880, 1.9333

Table 2. Summary of crystallographic data for **2a,b** and **3a,b**.

	2a	2b	3a	3b
Molecular formula	C ₆₈ H ₇₀ BF ₄ Sc	C ₅₆ H ₆₀ BF ₂ Ti	C ₅₀ H ₃₄ BF ₂ Sc	C ₅₆ H ₅₈ BF ₄ Ti
FW	1019.01	829.79	748.74	865.75
Diffractionmeter	SMART APEX CCD	CAD-4F	SMART APEX CCD	SMART APEX CCD
Temp (K)	100(1)	130	100(1)	100(1)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c	P-1
a (Å)	10.004(5)	11.992(1)	19.286(1)	12.1741(6)
b (Å)	30.858(2)	13.649(2)	21.404(1)	13.8252(7)
c (Å)	18.220(1)	14.883(1)	20.393(1)	14.7794(7)
α (deg)		90.95(1)		91.177(1)
β (deg)	103.678(1)	109.499(8)	90.399(1)	109.854(1)
γ (deg)		90.865(9)		93.221(1)
V (Å ³)	5465.1(5)	2295.5(4)	8418.0(7)	2333.9(2)
Z	4	2	8	2
Dcalc (g/cm ³)	1.238	1.200	1.181	1.232
F(000)	2160	882	3180	914
μ(Mo Kα), cm ⁻¹	1.9	2.3	2.16	2.36
θ range (deg.)	2.24, 26.26	1.45, 27.0	2.21, 26.89	2.36, 28.28
wR(F ²)	0.1388	0.1407	0.2118	0.1676
reflections	11105	9284	16555	11292
parameters	947	561	993	791
R(F)	0.0551	0.0536	0.0707	0.0603
for Fo > 4.0 σ(Fo)				
Goof	1.016	1.115	1.030	1.021
Weighting (a,b)	0.0628, 1.6264	0.0459, 3.1280	0.1102, 1.500	0.0834, 1.1200

Table 3. Summary of crystallographic data for **4a'**, **1a'-c'** and **2b'**.

	4a'	1a'	1b'	1c'	2b'
Molecular formula	C ₆₅ H ₆₃ BF ₂₀ Sc ₂	C ₄₄ H ₃₀ BF ₂₀ Sc	C ₄₄ H ₃₀ BF ₂₀ Ti	C ₄₄ H ₃₀ BF ₂₀ V	C ₅₀ H ₅₅ BF ₂₁ Ti
FW	1324.91	994.46	997.37	100.43	1093.47
Diffractionmeter	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD
Temp (K)	100(1)	100(1)	100(1)	100(1)	100(1)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	P2 ₁ /c	P2 ₁	P2 ₁	P-1	P-1
a (Å)	15.8365(7)	9.951(1)	9.9750(8)	11.1664(7)	10.574(1)
b (Å)	19.0317(9)	17.027(2)	17.053(1)	12.8945(8)	15.127(2)
c (Å)	19.9246(9)	12.025(1)	12.0218(9)	15.671(1)	15.421(2)
α (deg)				98.400(1)	70.485(2)
β (deg)	91.706(1)	93.335(2)	93.967(1)	109.737(1)	84.384(2)
γ (deg)				102.362(1)	78.187(2)
V (Å ³)	6002.5(5)	2034.0(4)	2040.1(3)	2015.2(2)	2274.5(5)
Z	4	2	2	2	2
Dcalc (g/cm ³)	1.466	1.624	1.624	1.649	1.596
F(000)	2720	1000	1002	1004	1102
μ(Mo Kα), cm ⁻¹	3.29	3.07	3.35	3.73	3.12
θ range (deg.)	2.31, 19.06	2.39, 22.30	2.37, 22.61	2.84, 29.67	2.32, 27.12
wR(F ²)	0.2265	0.1799	0.2780	0.1084	0.3137
reflections	8909	7053	7044	10110	9045
parameters	825	589	607	703	668
R(F)	0.0806	0.0645	0.0941	0.0394	0.1016
for Fo > 4.0 σ(Fo)					
Goof	1.018	1.037	1.040	1.021	1.085
Weighting (a,b)	0.0958, 13.578	0.0967, 0.7590	0.1956, 0.0	0.0599, 0.9970	0.0899, 30.7755
Flack's par. (x)		0.03(5)	-0.05(7)		

Computational Data

Calculations were performed using the Turbomole program^{11a,b}, coupled to a PQS Baker optimizer.¹² Geometries were fully optimized at the bp86¹³/RIDFT¹⁴ level using the Turbomole SV(P) basisset^{11c,d} on all atoms (small-core pseudopotential^{11c,e} on Sc, Ti and V). The energies are relative to the base-free metallocene cations and do not include zero-point energies or thermal corrections, and the anions have been omitted.

Table 4. RIDFT/bp86 results for $[\text{Cp}_2\text{ML}_n]^+$ and $[\text{Cp}^*_2\text{ML}_n]^+$ systems (M = Sc, Ti, V; L = C₆H₅F, 1,2-C₆H₄F₂, THF). Energies (kcal/mol) are for the reaction $\text{Cp}'_2\text{M} + 2 \text{L} \rightarrow \text{Cp}'_2\text{ML}_n + (2-n) \text{L}$. Distances in Å; angles in °.

Cp'	M	L	n	constraint	E _{rel}	M-X (calcd)	C-F (calcd)	M-F-C (calcd)	M-X (X-ray)	C-F (X-ray)	M-F-C (X-ray)
Cp	Sc	C ₆ H ₅ F	1		-21.68	2.22	1.42	142.15			
		C ₆ H ₅ F	2		-33.79	2.27, 2.28	1.41, 1.41	163.79, 158.55			
		C ₆ H ₄ F ₂	1		-28.35	2.37, 2.37	1.39, 1.39				
		THF	1		-36.50	2.20					
		THF	2		-42.73	2.27, 2.28					
		THF	2		-19.85	2.18	1.42	142.22			
	Ti	C ₆ H ₅ F	1		-28.14	2.32, 2.32	1.40, 1.40	155.99, 151.44			
		C ₆ H ₅ F	2		-26.53	2.34, 2.34	1.38, 1.38				
		C ₆ H ₄ F ₂	1		-35.14	2.15					
		THF	1		-51.17	2.29, 2.27			2.19 - 2.24		
		THF	2		-18.10	2.22	1.41	139.66			
		THF	2		-19.90	2.25, 3.26	1.41, 1.37	142.67, 149.63			
Cp*	Sc	C ₆ H ₅ F	1		-18.92	2.26, 3.00	1.39, 1.35				
		C ₆ H ₅ F	1		-35.12	2.12					
		THF	1		-24.61	2.18, 2.22					
		THF	2								
	Ti	C ₆ H ₅ F	1		-14.44	2.29	1.41	165.71			
		C ₆ H ₅ F	2		-20.54	2.39, 2.40	1.40, 1.40	168.88, 167.54	2.27, 2.29	1.41, 1.41	172.21, 165.27
		C ₆ H ₅ F	2	Sc-F = 2.28	-19.03	2.28, 2.28	1.41, 1.41	160.85, 175.56			
		C ₆ H ₄ F ₂	1		-17.17	2.45, 2.45	1.38, 1.38		2.33, 2.33	1.39, 1.40	
		C ₆ H ₄ F ₂	1	Sc-F = 2.33	-18.46	2.33, 2.33	1.38, 1.38				
		THF	1		-23.05	2.29					
		THF	2		-27.83	2.38, 2.36			2.30, 2.27		
		THF	2	Sc-O = 2.28	-27.59	2.28, 2.28					
	V	Cp*(C-H)	0		0.00		1.12, 1.13		2.16 - 2.27	0.99 - 1.11	
		Cp*(C-H)	2	Ti-H = 2.18	2.42	2.18, 2.18	1.16, 1.16				
		C ₆ H ₅ F	1		-11.58	2.27	1.41	164.61	2.15	1.40	168.8
		C ₆ H ₅ F	1	Ti-F = 2.15	-9.45	2.15	1.42	159.52			
		C ₆ H ₅ F	2		-13.94	2.47, 2.51	1.39, 1.39	165.40, 164.73			
		C ₆ H ₄ F ₂	1		-15.37	2.40, 2.40	1.38, 1.38		2.33, 2.09	1.38, 1.39	
		C ₆ H ₄ F ₂	1	Ti-F = 2.31	-14.83	2.31, 2.31	1.38, 1.38				
		THF	1		-19.19	2.25			2.12		
		THF	1	Ti-O = 2.12	-18.29	2.12					
		THF	2		-15.73	2.37, 2.48					
	V	Cp*(C-H)	0		0.28				2.06, 2.11	1.05, 1.06	
		Cp*(C-H)	1		0.00	2.10	1.16				
		Cp*(C-H)	1	V-H = 2.09	0.02	2.09	1.16				
		C ₆ H ₅ F	1		-6.55	2.33	1.40	163.28	1.83	1.36	167.3
		C ₆ H ₅ F	2		-9.28	2.37, 4.00	1.40, 1.37	165.24, 152.76			
		C ₆ H ₄ F ₂	1		-6.44	2.39, 3.19	1.38, 1.35				
		THF	1		-13.79	2.23			2.12		
		THF	1	V-O = 2.15	-13.21	2.15					
		THF	2								

^a second molecule of THF dissociates

Table 5. Representations of HOMO's of the $[\text{Cp}_2\text{Sc}(\text{L})]$ cations

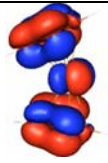
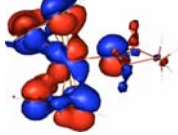
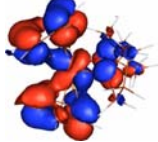
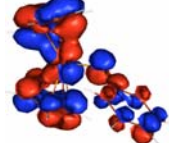
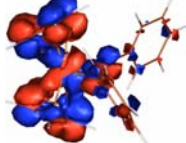
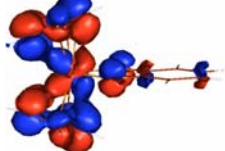
	HOMO
$[\text{Cp}_2\text{Sc}]$	
$[\text{Cp}_2\text{Sc}(\text{THF})]$	
$[\text{Cp}_2\text{Sc}(\text{THF})_2]$	
$[\text{Cp}_2\text{Sc}(\text{FC}_6\text{H}_5)]$	
$[\text{Cp}_2\text{Sc}(\text{FC}_6\text{H}_5)_2]$	
$[\text{Cp}_2\text{Sc}(\text{F}_2\text{C}_6\text{H}_4)]$	

Table 6. Representations of SOMO's and spin density representations of the $[\text{Cp}_2\text{Ti}(\text{L})]$ cations

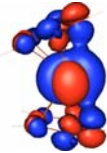
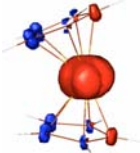
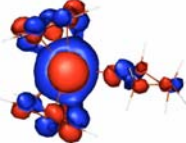
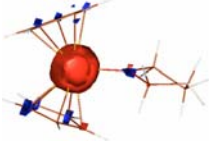
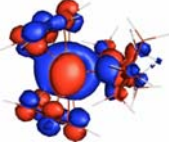
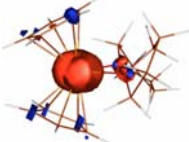
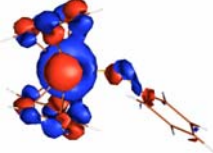
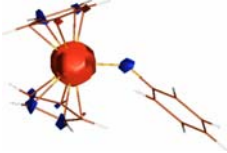
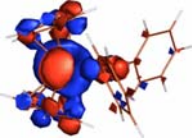

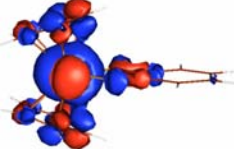
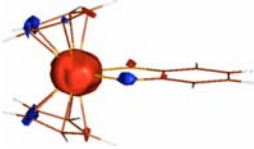
	SOMO	Spin density
$[\text{Cp}_2\text{Ti}]$		
$[\text{Cp}_2\text{Ti}(\text{THF})]$		
$[\text{Cp}_2\text{Ti}(\text{THF})_2]$		
$[\text{Cp}_2\text{Ti}(\text{FC}_6\text{H}_5)]$		
$[\text{Cp}_2\text{Ti}(\text{FC}_6\text{H}_5)_2]$		
$[\text{Cp}_2\text{Ti}(\text{F}_2\text{C}_6\text{H}_4)]$		

Table 7. Representations of SOMO's and spin density representations of the $[\text{Cp}_2\text{V}(\text{L})]$ cations

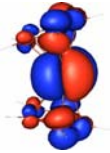
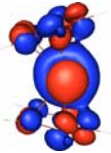
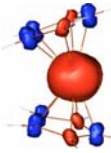
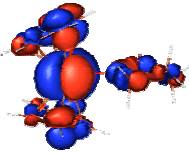
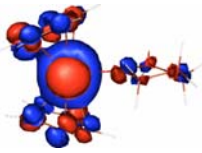
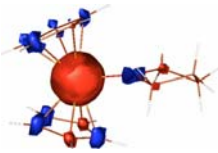
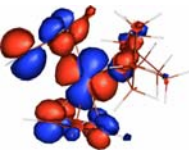
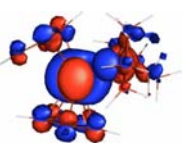
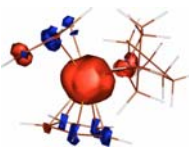
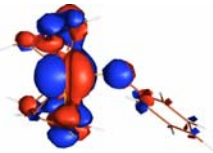
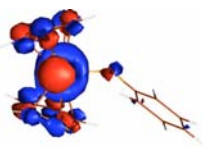
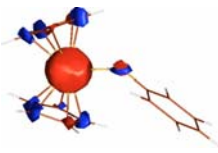
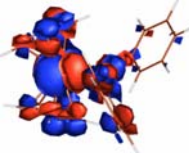
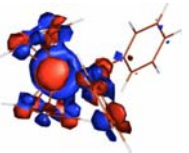
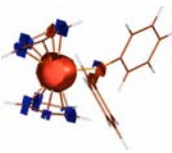
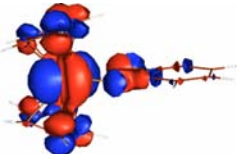
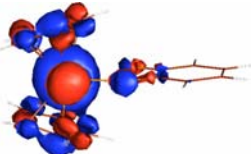
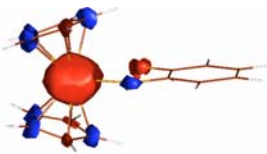
	SOMO (high)	SOMO (low)	Spin density
$[\text{Cp}_2\text{V}]$			
$[\text{Cp}_2\text{V}(\text{THF})]$			
$[\text{Cp}_2\text{V}(\text{THF})_2]$			
$[\text{Cp}_2\text{V}(\text{FC}_6\text{H}_5)]$			
$[\text{Cp}_2\text{V}(\text{FC}_6\text{H}_5)_2]$			
$[\text{Cp}_2\text{V}(\text{F}_2\text{C}_6\text{H}_4)]$			

Table 8. Representations of SOMO's of the $[\text{Cp}^*_2\text{Sc}(\text{L})]$ cations

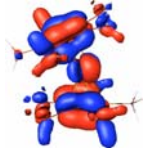
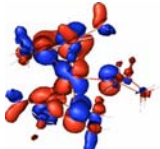
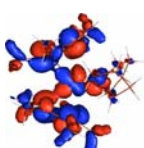
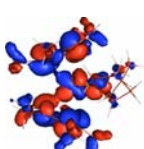
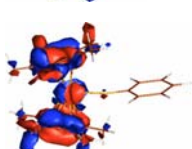
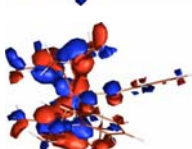
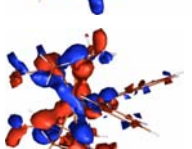
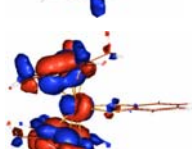
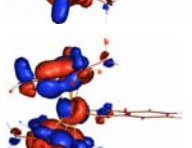
	HOMO
$[\text{Cp}^*_2\text{Sc}]$	
$[\text{Cp}^*_2\text{Sc}(\text{THF})]$	
$[\text{Cp}^*_2\text{Sc}(\text{THF})_2]$	
$[\text{Cp}^*_2\text{Sc}(\text{THF})_2]$ Sc-O: 2.28 Å	
$[\text{Cp}^*_2\text{Sc}(\text{FC}_6\text{H}_5)]$	
$[\text{Cp}^*_2\text{Sc}(\text{FC}_6\text{H}_5)_2]$	
$[\text{Cp}^*_2\text{Sc}(\text{FC}_6\text{H}_5)_2]$ Sc-F: 2.28 Å	
$[\text{Cp}^*_2\text{Sc}(\text{F}_2\text{C}_6\text{H}_4)]$	
$[\text{Cp}^*_2\text{Sc}(\text{F}_2\text{C}_6\text{H}_4)]$ Sc-F: 2.33 Å	

Table 9. Representations of SOMO's and spin density representations of the $[\text{Cp}^*_2\text{Ti}(\text{L})]$ cations

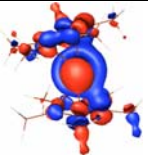
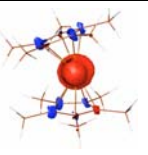
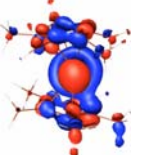

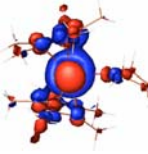

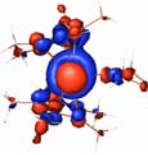
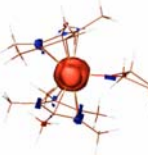
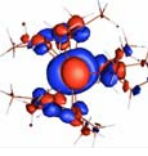

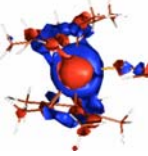
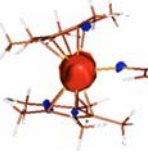
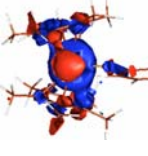
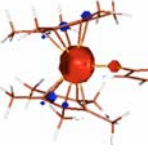
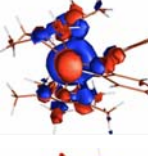
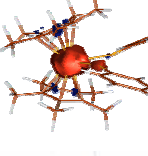
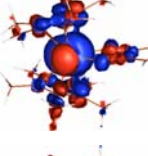
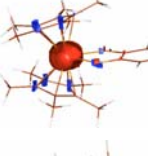
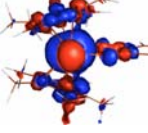
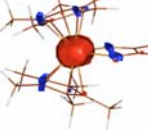

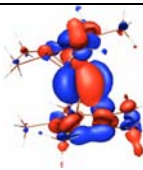
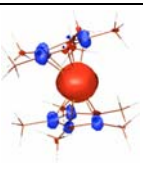


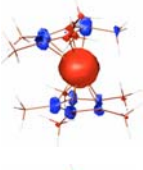
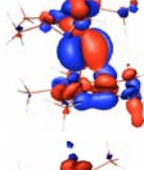
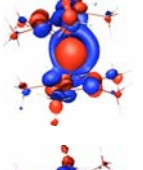
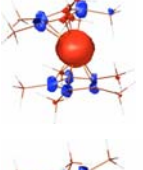
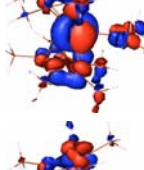
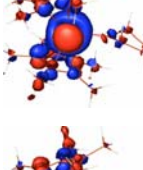
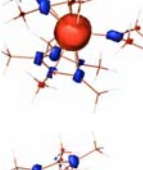
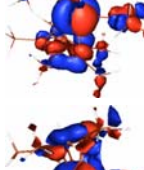
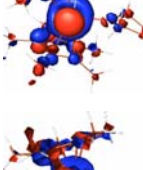
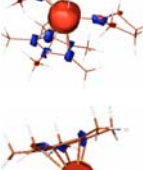


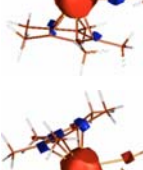
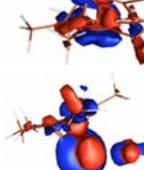
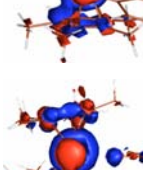




	SOMO	Spin density
$[\text{Cp}^*_2\text{Ti}]$		
$[\text{Cp}^*_2\text{Ti}]$ Ti-H: 2.18 Å		
$[\text{Cp}^*_2\text{Ti}(\text{THF})]$		
$[\text{Cp}^*_2\text{Ti}(\text{THF})]$ Ti-O: 2.12 Å		
$[\text{Cp}^*_2\text{Ti}(\text{THF})_2]$		
$[\text{Cp}^*_2\text{Ti}(\text{FC}_6\text{H}_5)]$		
$[\text{Cp}^*_2\text{Ti}(\text{FC}_6\text{H}_5)]$ Ti-F: 2.15 Å		
$[\text{Cp}^*_2\text{Ti}(\text{FC}_6\text{H}_5)_2]$		
$[\text{Cp}^*_2\text{Ti}(\text{F}_2\text{C}_6\text{H}_4)]$		
$[\text{Cp}^*_2\text{Ti}(\text{F}_2\text{C}_6\text{H}_4)]$ Ti-F: 2.33 Å		

Table 10. Representations of SOMO's and spin density representations of the $[\text{Cp}^*_2\text{V}(\text{L})]$ cations

	SOMO (high)	SOMO (low)	Spin density
$[\text{Cp}^*_2\text{V}]$			
$[\text{Cp}^*_2\text{V}]$			
$[\text{Cp}^*_2\text{V}]$ V-H: 2.09 Å			
$[\text{Cp}^*_2\text{V}(\text{THF})]$			
$[\text{Cp}^*_2\text{V}(\text{THF})]$ V-O: 2.15 Å			
$[\text{Cp}^*_2\text{V}(\text{FC}_6\text{H}_5)]$			
$[\text{Cp}^*_2\text{V}(\text{FC}_6\text{H}_5)_2]$			
$[\text{Cp}^*_2\text{V}(\text{F}_2\text{C}_6\text{H}_4)]$			

1 Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Noltemeyer, M.; Santarsiero, B. C.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

2 Luinstra, G. A.; Ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. *Organometallics* 1991, *10*, 3227.

3 Curtis, C. J.; Smart, C.; Robbins, J. L. *Organometallics* **1985**, *4*, 1283.

4 Calderazzo, F.; Pampaloni, G.; Rocchi, L.; Englert, U. *Organometallics* **1994**, *13*, 2592.

5 Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evevns, G. G. *Organometallics* **1992**, *11*, 362.

6 Measured at the Microanalytical department of H. Kolbe (Mülheim an der Ruhr).

7 Measured at the Microanalytical department of the University of Groningen

8 Enraf-Nonius CAD4/PC version 1.5c **1995**, Enraf-Nonius Delft, Scientific Instruments Division, Delft, The Netherlands.

9 *SMART*, *SAINT*, *SADABS*, *XPREP* and *SHELXL/NT*. *Smart Apex Software Reference Manuals* **2000**, Bruker AXS Inc., Madison, Wisconsin, USA.

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