Electronic Supplemental Information

The roles of 4f and 5f orbitals in bonding: a magnetochemical, crystal field, density functional theory, and multi-reference wavefunction study

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Experimental Details

General. Work was performed using Schlenk techniques and an inert atmosphere glovebox. Solvents were freshly distilled from sodium/benzophenone ketyl. Cp"H, tBuNC, and CyNC were prepared as previously described. $Cp"_3U$ was previously reported.[1] $Cp"_3La$ and $Cp"_3Nd$ were previously prepared by different routes.[2] $Nd[N(SiMe_3)_2]_3$ and $La[N(SiMe_3)_2]_3$ were prepared as described by Bradley *et al.*[3] $U[N(SiMe_3)_2]_3$ was prepared as described by Andersen.[4]

$Cp"_3U$ (**4**). $U[N(SiMe_3)_2]_3$ [4] (1.00 g, 1.39 mmol) was dissolved in 50 mL of toluene, and Cp"H (1.4 mL, 1.2 g, 5.6 mmol) was added using a syringe. The solution was heated to reflux for 3 days. The toluene was removed slowly under reduced at 105 °C giving a dark oil. The flask was heated to 90 °C under dynamic vacuum. The greenish brown solid residue was dissolved in 50 mL of hexane. The solution was filtered, and the volume of the filtrate was reduced to ca. 3 mL. Cooling to –80 °C produced black, diamond shaped blocks (0.31 g, 25 %). MP: 232 – 235 °C. ^{1}H NMR, □□□ 20.78 (1 H, FWHH = 17 Hz), –4.78 (2 H, FWHH = 18 Hz), –9.35 (18 H, FWHH = 7 Hz) ppm. IR: 3075(w), 3050(w), 1315(w), 1245(s), 1205(w), 1195(w), 1070(m), 915(s), 830(s), 770(m), 750(s), 685(m), 635(m), 610(w), 480(m), 375(m), 350(w), 325(w), 290(m), 240(w) cm^{-1}. MS (M)+, m/z (calcd., found): 865 (100, 100), 866 (67, 76), 867 (42, 48), 869 (6, 19). Elemental analysis, calculated for $C_{33}H_{63}Si_6U$: C, 45.7; H, 7.33 %. Found: C, 45.5; H, 7.17 %.

$Cp"_3Nd$ (**1**). $Nd[N(SiMe_3)_2]_3$ [3] (2.00 g, 3.20 mmol) was dissolved in 50 mL of toluene, and Cp"H (2.53 mL, 2.15 g, 10.2 mmol) was added using a syringe. The solution was heated to 110 °C. After stirring for 5 days, the color had changed from blue to green. The toluene was slowly removed under vacuum at 100 °C giving oily, green blocks. The blocks were dissolved in 50 mL of hexane, and the solution was filtered. The volume of the solution was reduced to ca. 25 mL.

Cooling to –20 °C produced large light green, diamond shaped prisms (1.68 g, 68 %). MP: 191 – 196 °C. ^{1}H NMR, 33.70 (1 H, FWHH = 27 Hz), 15.15 (2 H, FWHH = 35 Hz), –7.53 (18 H, FWHH = 5 Hz) ppm. IR: 3050(w), 1320(w), 1245(s), 1209(w), 1201(w), 1079(s), 920(s), 833(s), 778(s), 751(s), 690(m), 641(m), 621(m) cm^{-1}. MS (M-CH_3)+, m/z (calcd., found): 754 (63, 63), 755(70, 70), 756(100, 100), 757(78, 79), 758(84, 84), 759(47, 46), 760(37, 36), 761(18, 18), 762(22, 21), 763(12, 11). Elemental analysis, calculated for $C_{33}H_{63}Si_6Nd$: 51.3; H, 8.22 %. Found: C, 50.3; H, 8.29 %. Note: most elemental analyses for complexes of the Cp" ligand are low in C, presumably due to the formation of SiC.

Cp"$_3$La (**7**). La[N($SiMe_3$)$_2$]$_3$ [3] (0.62 g, 1.0 mmol) was dissolved in 30 mL of toluene, and Cp"H (0.90 mL, 0.74 g, 3.5 mmol) was added using a syringe. The solution was heated to reflux. After three days, the toluene was removed under reduced pressure at 100 °C giving an oily white solid. The solid residue was dissolved in 50 mL of hexane, and the solution was filtered. The volume of the filtrate was reduced to ca. 10 mL. Cooling to –80 °C produced colorless, diamond shaped prisms (0.44 g, 57 %). MP: 155 – 160 °C. ^{1}H NMR, 6.86 (m, 3 H), 0.33 (s, 18 H) ppm. IR: 3074(w), 3051(m), 1319(s), 1246(s), 1210(s), 1203(m), 1078(s), 1041(m), 920(s), 832(s), 774(s), 752(s), 689(s), 640(s), 621(s) cm^{-1}. MS: (M-H)+, m/z (calcd., found): 765(100, 100), 766(87, 68), 767(54, 42), 768(27, 17). Elemental analysis, calculated for $C_{33}H_{63}Si_6La$: C, 51.7; H, 8.28 %. Found: C, 51.0; H, 8.30 %.

Cp"$_3$U•*t*BuNC (**5**). Cp"$_3$U (0.50 g, 0.58 mmol) was dissolved in 50 mL hexane, and *t*BuNC (0.07 mL, 0.05 g, 0.6 mmol) was added using a syringe. The color of the solution immediately changed from deep green to dark purple. After stirring for one hour, the solvent was removed under reduced pressure. The purple solid residue was dissolved in 100 mL of hexane, and the solution

was filtered. The volume of the filtrate was reduced to ca. 40 mL, and the solution was heated to redissolve the solid. Cooling to –20 °C produced purple blocks (0.20 g, 36 %). MP: 230 – 232 °C. ^{1}H NMR, □□□□0.44 (2H, FWHH =15 Hz), –2.55 (18 H, FWHH = 12 Hz), 8.85 (1H, FWHH = 10 Hz), –11.25 (3 H, FWHH = 22 Hz) ppm. IR: 3060(w), 2140(s), 1315(w), 1245(s), 1070(s), 925(s), 830(s), 815(w), 775(w), 750(m), 680(w), 630(m), 610(w), 480(w), 365(w), 290(w) cm^{-1}. MS not done because of Cp"$_3$Nd•*t*BuNC result. Elemental analysis, calculated for $C_{36}H_{72}NSi_6U$: C, 48.10; H, 7.64; N, 1.48 %. Found: C, 46.8; H, 7.63; N, 1.38 %.

Cp"$_3$Nd•*t*BuNC (**2**). Cp"$_3$Nd (0.50 g, 0.65 mmol) was dissolved in 30 mL hexane, and *t*BuNC (0.08 mL, 0.06 g, 0.7 mmol) was added using a syringe. The initially bright green solution immediately turned pale blue. After 1 minute, a blue solid precipitated. The volatile components were removed under reduced pressure. The light blue solid residue was dissolved in 50 mL of hexane, and the solution was filtered. The volume of the filtrate was reduced to ca. 30 mL, and the solution was heated to dissolve the solid. Cooling to –20 °C produced light blue blocks (0.47 g, 85 %). MP: 222 –223 °C. ^{1}H NMR, □ = 9.73 (1 H, FWHH = 150 Hz), 8.89(2 H,□□ FWHH = 100 Hz), –1.93 (18 H,□ FWHH = 18 Hz), –7.21 (3 H,□ FWHH = 35 Hz) ppm. IR: 3059(m), 2178(s), 1318(w), 1247(s), 1207(m), 1077(s), 923(m), 835(s), 779(m), 754(s), 687(m), 638(m), 622(m) cm^{-1}. MS: only Cp"$_3$Nd observed. Elemental analysis, calculated for $C_{38}H_{72}NNdSi_6$: C, 53.3; H, 8.48; N, 1.64 %. Found: C, 52.5; H, 8.78; N, 1.57 %.

Cp"$_3$La•*t*BuNC (**8**). Cp"$_3$La (0.50 g, 0.65 mmol) was dissolved in 50 mL of hexane, and *t*BuNC (0.08 mL, 0.06 g, 0.7 mmol) was added using a syringe. After 15 minutes, white solid precipitated from the colorless solution. After stirring for one hour, the hexane was removed under reduced pressure. The white solid residue was dissolved in 100 mL of hexane, and the

solution was filtered. The volume of the filtrate was reduced to ca. 50 mL, and heated to redissolve all of the product. Cooling to –80 °C produced colorless blocks (0.34 g, 61 %). MP: 222 –223 °C. ^{1}H NMR, □ = 6.83 (1 H, s), 6.63(2 H, s), 1.07 (3 H, s), 0.45 (18 H, s) ppm. IR: 3056(m), 2178(s), 1317(m), 1247(s), 1206(m), 1076(s), 1061(w), 922(s), 830(s), 774(s), 754(s), 687(m), 638(s), 622(m) cm^{-1}. Elemental analysis, calculated for $C_{38}H_{72}LaNSi_6$: C, 53.7; H, 8.53; N, 1.65 %. Found: C, 52.6; H, 8.64; N, 1.69 %.

Cp"$_3$U•CyCN (**6**). Cp"$_3$U (0.50 g, 0.58 mmol) was dissolved in 30 mL of hexane, and cyclohexyl isocyanide (0.08 mL, 0.07 g, 0.6 mmol) was added using a syringe. The color of the solution immediately changed from dark green to dark purple. After stirring for one hour, the hexane was removed under reduced pressure. The resulting dark purple solid residue was dried under vacuum for 3 hours then dissolved in 70 mL of hexane, and the solution was filtered. The volume of the filtrate was reduced to ca. 40 mL. Cooling to –20 °C produced purple blocks (0.36 g, 64 %). MP: 190 – 191 °C. ^{1}H NMR, □ = 0.87 (2 H, FWHH = 18 Hz), –2.64 (56H, FWHH = 10 Hz), –4.75 (3H, FWHH = 31 Hz), –5.71 (2H, FWHH =30 Hz), –6.21 (2H, □□ FWHH = 27 Hz), –7.76 (6H, FWHH =70 Hz), –9.44 (2H, FWHH =27 Hz), –10.16 (2 H, FWHH = 20 Hz), –53.32 (1H, FWHH = 36 Hz) ppm; assignment of the cyclohexyl resonances was based upon the integrated areas and chemical shifts of the resonances. IR: 3062(m), 2153(s), 1318(m), 1243(s), 1207(m), 1076(s), 1055(w), 922(s), 834(s), 779(s), 749(s), 687(m), 638(s), 618(m) cm^{-1}. Elemental analysis, calculated for $C_{40}H_{74}NSi_6U$: C, 49.2; H, 7.65; N, 1.44 %. Found: C, 48.7; N, 7.87; N, 1.35 %.

Cp"$_3$Nd•CyCN (**3**). Cp"$_3$Nd (0.50 g, 0.65 mmol) was dissolved in 30 mL of hexane, and cyclohexyl isocyanide (0.09 mL, 0.08 g, 0.7 mmol) was added using a syringe. The initially green solution immediately turned pale blue. After stirring for one hour, the solvent was removed under

reduced pressure, and the blue solid residue was dissolved in 100 mL of hexane. The solution was filtered, and the volume of the filtrate was reduced to ca 50 mL. Cooling to –20 °C produced light blue blocks (0.50 g, 88 %). MP: 186 – 189 °C. ^{1}H NMR: □ = 9.93 (3 H, FWHH = 66 Hz), 8.64 (6 H, FWHH = 100 Hz), –1.81 (56 H, FWHH = 11 Hz), –3.78 (4 H,□□ FWHH = 70 Hz), –7.24 (2 H,□ FWHH = 28 Hz), –8.26(2 H,□□ FWHH = 35 Hz,), –13.94(1 H, FWHH = 45 Hz) ppm; assignment of the cyclohexyl resonances was based upon integrated areas and chemical shifts of the resonances. IR: 3107(w), 3085(w), 3061(m), 2723(w), 2183(s), 1319(m), 1248(s), 1211(m), 1077(s), 1057(m), 1039(w), 1018(w), 963(w), 924(s), 894(w), 835(s), 780(s), 750(s), 686(m), 640(s), 621(s) cm^{-1}. Elemental analysis, calculated for $C_{40}H_{74}NNdSi_6$: C, 54.5; H, 8.46; N, 1.59 %. Found: C, 52.7; H, 8.59; N, 1.51 %.

Table S1: Comparison of the crystal field parameters of **1** with other studies

	Cp''_3Nd (**1**)	$(C_5Me_4H)_3Nd$[5]	$(C_5H_4t\text{-}Bu)_3Nd$[6]	$(C_5H_4SiMe_3)_3Nd$[6]	$(C_5Me_5)_3Nd$[7]	Tp_3Nd[8]
F^2	71714	69800	69254	69478	70067	71714
F^4	35286	51172	51662	51496	51314	52182
F^6	52182	35380	34800	35003	35582	35286
ζ	881	878	879	877	880	881
B_0^2	–3184	–3037	–2733	–2831	–2858	–512
B_0^4	1597	1028	1256	1172	971	–969
B_0^6	973	1096	911	926	1043	153
B_6^6	–2665	–2307	–2521	–2504	–1906	828

Table S2: Occupation of the micro states and the related orbitals for **1** and **4**

Cp''_3Nd (**1**)					Cp''_3U (**4**)				
energy levels, cm^{-1}	**state**	**orbital**	**spin up**	**spin down**	**energy levels, cm^{-1}**	**state**	**orbital**	**spin up**	**spin down**
–745	$\|\pm1\rangle$	f_{xz^2} f_{yz^2}	0.991	0.991	– 2078	$\|+3\rangle$	$f_{x(x^2-3y^2)}$	0.5[a]	0.5[a]
			0.991	0.991	–1308	$\|\pm2\rangle$	f_{xyz} $f_{zx^2-y^2}$	1	1
–313	$\|0\rangle$	f_{z^3}	0.995	0.995				1	1
–241	$\|\pm2\rangle$	f_{xyz}, $f_{z(x^2-y^2)}$	0.983	0.983	–92	$\|\pm1\rangle$	f_{xz^2} f_{yz^2}	1	1
			0.983	0.983				1	1
233	$\|+3\rangle$	$f_{x(x^2-3y^2)}$	0.500[a]	0.500[a]	1135	$\|\pm0\rangle$	f_{z^3}	1	1
2113	$\|-3\rangle$	$f_{y(3x^2-y^2)}$	0.501[a]	0.494[a]	3746	$\|-3\rangle$	$f_{y(3x^2-y^2)}$	0.5[a]	0.5[a]

a) CONDON returns the orbital occupancies as $|\ m_J\ >$, which are complex numbers. The f-orbitals are real (i.e. $f_{x(x^2-3y^2)} = 2^{-1/2}\ (|+3> + i|-3>)$). Consequently, the states labeled "|+3>" and "|–3>" are actually mixtures of |+3> and |–3>.

Table S3: Occupation of the micro states and the related orbitals of **2** and **3**

Cp″$_3$Nd•*t*BuNC (**2**)					Cp″$_3$Nd•CyNC (**3**)				
energy levels, cm^{-1}	**state**	**orbital**	**spin up**	**spin down**	**energy levels, cm^{-1}**	**State**	**orbital**	**spin up**	**spin down**
–500	$\|\pm1\rangle$	f_{xz^2} f_{yz^2}	0.908	0.908	–765	$\|\pm1\rangle$	f_{xz^2} f_{yz^2}	0.908	0.908
			0.580	0.327				0.580	0.327
–77	$\|+3\rangle$	$f_{x(x^2-3y^2)}$	0.491[a]	0.493[a]	–407	$\|0\rangle$	f_{z^3}	0.984	0.984
–52	$\|\pm2\rangle$	f_{xyz} $f_{zx^2-y^2}$	0.889	0.889	–21	$\|\pm2\rangle$	f_{xyz} $f_{z(x^2-y^2)}$	0.889	0.889
			0.908	0.908				0.908	0.908
60.9	$\|0\rangle$	f_{z^3}	0.981	0.981	300	$\|+3\rangle$	$f_{x(x^2-3y^2)}$	0.491[a]	0.493[a]
1127	$\|-3\rangle$	$f_{y(3x^2-y^2)}$	0.501[a]	0.499[a]	1677	$\|-3\rangle$	$f_{y(3x^2-y^2)}$	0.501[a]	0.499[a]

a) CONDON returns the orbital occupancies as $|\ m_J\ >$, which are complex numbers. The f-orbitals are real (i.e. $f_{x(x^2-3y^2)} = 2^{-1/2}$ (|+3> + i|–3>)). Consequently, the states labeled "|+3>" and "|–3>" are actually mixtures of |+3> and |–3>.

Table S4: Occupation of the micro states and the related orbitals of **5** and **6**

Cp″$_3$U•*t*BuNC (**5**)					Cp″$_3$U•CyNC (**6**)				
energy levels, cm^{-1}	**State**	**orbital**	**spin up**	**spin down**	**energy levels, cm^{-1}**	**State**	**orbital**	**spin up**	**spin down**
–1745	|±1>	f_{xz^2} f_{yz^2}	0.723	0.723	–1220	|±1>	f_{xz^2} f_{yz^2}	0.892	0.892
			0.723	0.723				0.892	0.892
–508	|±2>	f_{xyz} $f_{zx^2-y^2}$	0.723	0.723	–853	|+3>	$f_{x(x^2-3y^2)}$	0.762[a]	0.762[a]
			0.723	0.723					
-75	|+3>	$f_{x(x^2-3y^2)}$	0.604[a]	0.604[a]	167	|±2>	f_{xyz} $f_{zx^2-y^2}$	0.882	0.882
								0.882	0.882
1857	|–3>	$f_{y(3x^2-y^2)}$	1.000[a]	1.000[a]	864	|–3>	$f_{y(3x^2-y^2)}$	0.501[a]	0.499[a]
2729	|0>	f_{z^3}	0.605	0. 605	2100	|0>	f_{z^3}	0.761	0.761

a) CONDON returns the orbital occupancies as $|m_J>$, which are complex numbers. The f-orbitals are real (i.e. $f_{x(x^2-3y^2)} = 2^{-1/2}$ (|+3> + i|–3>)). Consequently, the states labeled "|+3>" and "|–3>" are actually mixtures of |+3> and |–3>.

Table S5: Properties of Cp_3Nd•tBuNC (2') calculated in the gas phase and in solution

	PBE0-SR Gas	PBE0-SR Hexane
M−C (Å)	2.603	2.599
C≡N (Å)	1.165	1.163
N−C (tBu) (Å)	1.439	1.441
Angle (CNC)	178.7	179.2
Ligand binding energy (kcal mol^{-1})	-16.37	-15.66

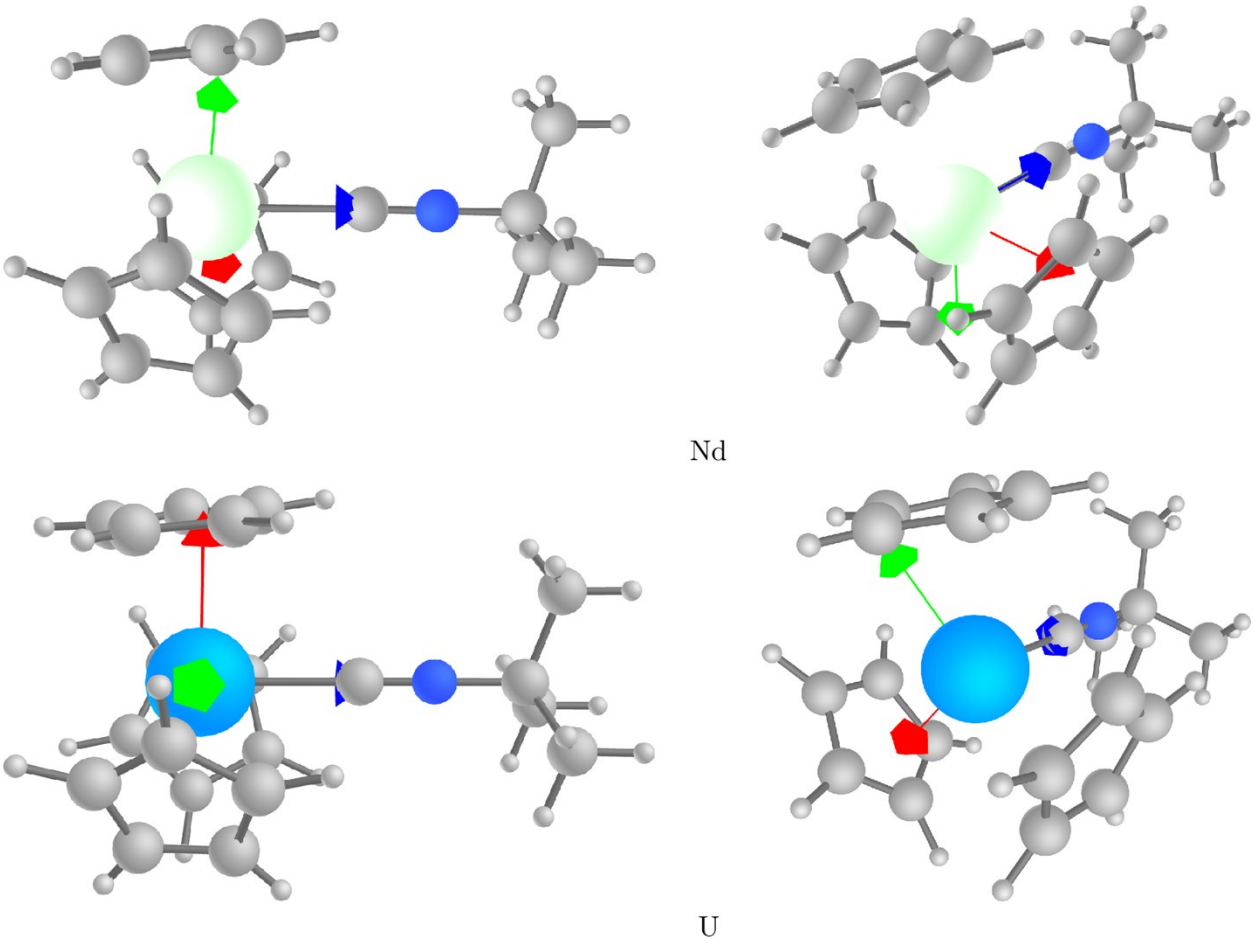

Figure S1: Top - Main magnetic axes of complex **2'**. Bottom – Main magnetic axes of complex **5'**.

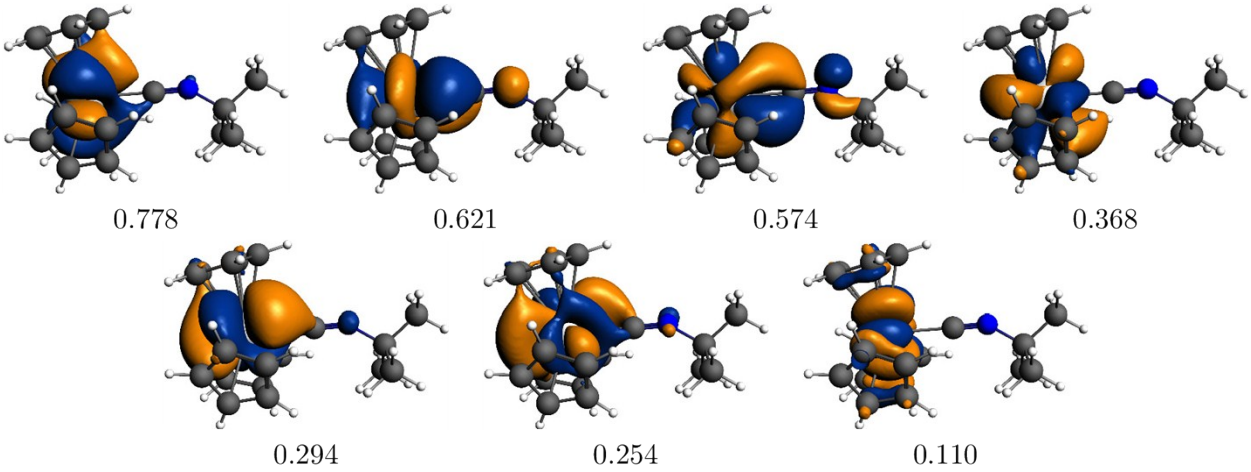

Figure S2: Natural orbitals (NOs) of $(C_5H_5)_3U\bullet{}^tBuNC$ (**5'**) with a bent CNC moiety, and corresponding occupations. Isosurfaces at ±0.03 atomic units

References

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