Electronic Supplementary Material (ESI) for Dalton Transactions.

Homo- and heteroleptic alkoxycarbene f-element complexes and their reactivity towards acidic N-H and C-H bonds

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Supplementary Information

Crystallographic data were collected on an Oxford Diffraction Xcalibur diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

Table S1. Experimental details for the crystal structure refinements

Crystal parameters	**1-Y**	**1-Sc**	**1-Ce**	**2-Y**
Empirical formula	$C_{20}H_{27}N_{2O}Y$	$C_{20}H_{27}N_2OSc$	$C_{24}H_{35}CeN_2O_2$	$C_{25}H_{39}N_4O_2Y$
Molecular weight [g/mol]	400.34	356.39	523.66	516.51
Temperature [K]	173(2)	170(2)	173(2)	173(2)
Wavelength Mo-K_α [Å]	0.71073	0.71073	0.71073	0.71073
Crystal size [mm]	0.35 × 0.20 × 0.20	0.77 × 0.37 × 0.23	0.70 × 0.49 × 0.40	0.35 × 0.25 × 0.20
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
space group	$Pna2_1$	$Pna2_1$	P2(1)/c	P-1
a (Å)	16.6328(7)	16.7257(3)	10.3917(11)	10.0822(11)
b (Å)	8.2556(3)	8.10390(10)	16.4222(4)	16.768(2)
c (Å)	14.5112(6)	13.9844(3)	15.567(3)	17.2137(15)
α (°)	90	90	90	109.721(9)
β (°)	90	90	108.53(2)	90.413(8)
γ (°)	90	90	90	91.683(9)
Cell volume [Å^3]	1992.59(14)	1895.49(6)	2518.8(6)	2737.7(5)
Z	4	4	4	4
Density $\rho_{calc.}$ [g cm^{-3}]	1.335	1.249	1.381	1.253
Absorption coefficient μ [mm^{-1}]	2.935	0.396	1.827	2.156
F (000)	832	760	1068	1088
θ range for data collection [°]	3.09 - 30.30	2.91 - 27.48	3.79 - 29.95	3.15 - 29.74
Index ranges	-21≤*h*≤22, -11≤*k*≤11, -18≤*l*≤20	-21≤*h*≤21, -10≤ *k* ≤10, -18≤*l*≤18	-13≤*h*≤13, -21≤ *k* ≤21, -19≤*l*≤18	-13≤*h*≤13, -22≤*k*≤23, -22≤*l*≤19
Reflections collected	22991	17354	17031	25848
Reflections unique	5331 [R_{int} = 0.0674]	4341 [R_{int} = 0.0301]	5502 [R_{int} = 0.0199]	13239 [R_{int} = 0.0382]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/Restraints/Parameters	5331/1/221	4341/1/221	5502/0/272	13239/46/602
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Goodness-of-fit on F^2 (*GOF*)	1.028	1.045	1.071	1.040
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0477, wR_2 = 0.0753	R_1 = 0.0295, wR_2 = 0.06588	R_1 = 0.0326, wR_2 = 0.0753	R_1 = 0.0480, wR_2 = 0.0778
R indices (all data)	R_1 = 0.0897, wR_2 = 0.0859	R_1 = 0.0349, wR_2 = 0.0686	R_1 = 0.0408, wR_2 = 0.0823	R_1 = 0.0854, wR_2 = 0.0888
Largest difference peak and hole (e Å^{-3})	0.502 and -0.387	0.192 and -0.178	1.897 and -1.119	0.487 and -0.509

Table S1 (continued).

Crystal parameters	4	5	6	7
Empirical formula	$C_{40}H_{68}N_8O_4Th \cdot C_7H_8$	$C_{24}H_{32}N_3OY$	$C_{28}H_{34}N_3OY$	$C_{30}H_{51}N_6O_3Sc \cdot C_4H_5N$
Molecular weight [g/mol]	1049.20	467.43	517.49	655.82
Temperature [K]	173(2)	173(2)	173(2)	170(2)
Wavelength Mo-K_α [Å]	0.71073	0.71073	0.71073	0.71073
Crystal size [mm]	0.27 × 0.27 × 0.05	0.94 × 0.43 × 0.32	0.91 × 0.38 × 0.30	0.78 × 0.64 × 0.46
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	P-1	C 2/c	P2(1)/c	P-1
a (Å)	12.3655(4)	17.5456(5)	9.0723(11)	10.3280(3)
b (Å)	13.2013(5)	15.6123(5)	15.3819(8)	11.0932(3)
c (Å)	15.6014(5)	16.8818(5)	20.696(2)	17.6674(5)
α (°)	101.035(3)	90	90	74.577(3)
β (°)	90.494(2)	92.453(3)	103.351(11)	89.538(2)
γ (°)	95.738(3)	90	90	75.363(2)
Cell volume [Å^3]	2486.16(15)	4620.1(2)	2810.1(5)	1884.15(9)
Z	2	8	4	2
Density $\rho_{calc.}$ [g cm^{-3}]	1.401	1.344	1.223	1.156
Absorption coefficient μ [mm^{-1}]	3.079	2.543	2.097	0.236
F (000)	810	1952	1080	1.156
θ range for data collection [°]	2.9 - 27.5	3.02 - 27.06	3.00 - 27.00	3.49 - 29.24
Index ranges	-16≤*h*≤16, -17≤*k*≤17, -20≤*l*≤20	-21≤*h*≤22, -19≤ *k* ≤19, -21≤*l*≤21	-11≤*h*≤11, -19≤*k*≤19, -26≤*l*≤26	-13≤*h*≤13, -14≤ *k* ≤14, -22≤*l*≤22
Reflections collected	45682	15469	19195	34913
Reflections unique	11383 [R_{int} = 0.067]	5055 [R_{int} = 0.0316]	6156 [R_{int} = 0.0419]	7093 [R_{int} = 0.0310]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/Restraints/Parameters	11383/0/558	5055/0/266	6156/0/302	7093/0/418
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Goodness-of-fit on F^2 (*GOF*)	1.035	1.026	1.053	1.026
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0445, wR_2 = 0.1071	R_1 = 0.0318, wR_2 = 0.0716	R_1 = 0.0458, wR_2 = 0.1109	R_1 = 0.0383, wR_2 = 0.0900
R indices (all data)	R_1 = 0.0557, wR_2 = 0.1122	R_1 = 0.0513, wR_2 = 0.0777	R_1 = 0.0774, wR_2 = 0.1192	R_1 = 0.0511, wR_2 = 0.0973
Largest difference peak and hole (e Å^{-3})	3.882 and -2.568	0.334 and -0.357	0.578 and -0.482	0.238 and -0.334

Table S1 (continued).

Crystal parameters	8a	9	10
Empirical formula	$C_{25}H_{33}CeN_2O \cdot C_6H_6$	$C_{30}H_{46}N_4O_2Y \cdot C_5H_5$	$C_{35}H_{41}N_2O_2Y$
Molecular weight [g/mol]	595.76	648.70	610.61
Temperature [K]	173(2)	173(2)	173(2)
Wavelength Mo-K_α [Å]	0.71073	0.71073	0.71073
Crystal size [mm]	0.98 × 0.68 × 0.32	0.64 × 0.42 × 0.17	0.74 × 0.19 × 0.16
Crystal system	Triclinic	Tetragonal	Orthorhombic
space group	P-1	I4(1)/acd	P2(1)2(1)2(1)
a (Å)	11.2916(4)	17.618(5)	11.0941(8)
b (Å)	12.0218(4)	17.618(5)	13.9218(9)
c (Å)	12.7949(6)	47.904(5)	27.1465(13)
α (°)	108.824(4)	90	90
β (°)	95.048(3)	90	90
γ (°)	95.048(3)	90	90
Cell volume [Å^3]	1420.72(11)	14869(9)	4192.8(5)
Z	2	16	4
Density $\rho_{calc.}$ [g cm^{-3}]	1.393	1.159	0.967
Absorption coefficient μ [mm^{-1}]	1.626	1.601	1.415
F (000)	610	5504	1280
θ range for data collection [°]	3.06 – 29.65	3.27 – 25.70	3.00 – 26.05
Index ranges	-15≤*h*≤24, -15≤*k*≤16, -17≤*l*≤17	-12≤*h*≤18, -21≤*k*≤21, -58≤*l*≤58	-13≤*h*≤13, -10≤ *k* ≤17, -30≤*l*≤33
Reflections collected	20187	22420	14685
Reflections unique	7135 [R_{int} = 0.0156]	3529 [R_{int} = 0.0677]	7699 [R_{int} = 0.062]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/Restraints/Parameters	7135/556/443	3529/182/202	7699/0/366
Absorption correction	Multi-Scan	Multi-Scan	Analytical
Goodness-of-fit on F^2 (*GOF*)	1.075	1.055	1.008
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0200, wR_2 = 0.0536	R_1 = 0.0580, wR_2 = 0.1411	R_1 = 0.0738 wR_2 = 0.1515
R indices (all data)	R_1 = 0.0221, wR_2 = 0.0552	R_1 = 0.1093, wR_2 = 0.1624	R_1 = 0.1257, wR_2 = 0.1688
Largest difference peak and hole (e Å^{-3})	0.714 and -0.600	0.762 and -0.468	0.827 and -0.546