An unsupported transition metal – lanthanide bond; synthesis and crystal structure of an Nd-Fe amido N-heterocyclic carbene complex

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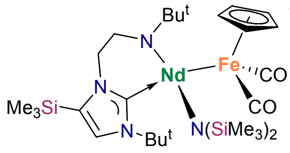

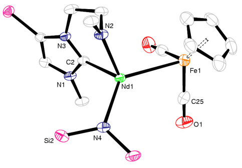

Experimental

General details

All manipulations of air-sensitive materials were carried out under a dry, oxygen free argon or dinitrogen atmosphere, using standard Schlenk techniques (rotary pump for vacuum 10^{-4} mbar) or in a glove box (Mbraun Unilab or Saffron) under dry dinitrogen. All NMR spectra were recorded on a Bruker DPX 300 spectrometer, operating frequency 300 MHz (^{1}H), 75 MHz (^{13}C), variable temperature unit set to 300 K unless otherwise stated. Chemical shifts are reported in parts per million, and referenced to residual solvent proton resonances calibrated against external TMS. IR spectra were recorded in the range 400-4000 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer as nujol mulls between NaCl discs. Mass spectra were run by Mr. A. Hollingworth on a VG Autospec instrument. Elemental analyses were determined by Dr. S. Boyer at London Metropolitan University.

All solvents used were either degassed and purified by passage through activated alumina towers prior to use, or were freshly distilled from the appropriate drying reagent under dinitrogen, and thoroughly degassed prior to use.. NMR spectroscopic grade benzene-d_6 was dried over potassium metal, thoroughly degassed by the freeze-thaw method and transferred under reduced pressure before use. The synthesis of $[Nd(L')(N'')(\mu\text{-}I)]_2$[2] and KFp, $K[FeCp(CO)_2]$[3] have been previously described.

Synthesis of $[Nd(L')(N'')\{FeCp(CO)_2\}]$ 1

A Schlenk was charged with $[Nd(L')(N'')(\mu\text{-}I)]_2$ (1.35 g, 1.86 mmol), $K[FeCp(CO)_2]$ (0.33g g, 1.86 mmol) and the mixture cooled (-78 °C). To this was added 30 ml thf, upon which the mixture became an orange-brown turbid suspension. The mixture was allowed to warm to room temperature over 16 hours, with stirring. Filtration by cannula, followed by removal

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of volatiles afforded **1** as an orange solid in 96 % yield (1.32 g). Recrystallisation of a solution of **1** in diethyl ether at -30 °C afforded yellow crystals of **1** suitable for a single crystal X-ray structural determination.

^{1}H NMR (C_6D_6, 298 K); δ 70.15 (s, 2H, CH_2), 20.12 (br s, 2H, CH_2), 4.74 (s, 9H, Bu^t), 1.12 (s, 5H, Cp), -1.91 (s, 9H, $SiMe_3$), -4.26 (br s, 27H, N{$SiMe_3$}$_2$ and Bu^t), -5.75 (s, 1H, CH).

MS (ES): m/z 627 ($[M-2(SiMe_3)_2-2H]^+$, 8 %), 555 ($[M-N(SiMe_3)_2-2CO-2H]^+$, 7 %), 146 ($[N(SiMe_3)_2-CH_2]^+$, 100 %).

Magnetic moment (Evans' method, C_6D_6, 298 K): 3.41 B.M.

FTIR (*v*, cm^{-1}): 1916 (s), 1845 (s), 1584 (w), 1252 (m), 1200 (m), 979 (s), 871 (m), 841 (s), 633 (m).

Analysis for **1**, calculated (found) for $C_{29}H_{55}N_4O_2Si_3FeNd$ (fw 776.11): C 44.88 (44.87); H 7.14 (7.10); N 7.22 (7.32).

X-ray Crystallography

Crystal data for compound **1** are given in Table 1. The structure was solved by direct methods and refined by least-squares methods on F^2 values, with anisotropic displacement parameters for non-H atoms, and with constrained riding hydrogen geometries. *U*(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL, and WinGX for structure solution, refinement, and molecular graphics.[1] CCDC 689392 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic data centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound	**1**
Crystal data	
Chemical formula	$C_{29}H_{55}FeN_4NdO_2Si_3$
M_r	776.13
Cell setting, space group	Triclinic, *P*-1
Temperature (K)	150 (2)
a, *b*, *c* (Å)	11.1340 (9), 11.7943 (9), 15.6599 (12)
α, β, γ (°)	94.396 (2), 107.987 (2), 100.847 (2)
V (Å^3)	1900.9 (3)
Z	2
D_x (Mg m^{-3})	1.356
Radiation type	Mo *K*α
μ (mm^{-1})	1.86
Crystal form, colour	Block, yellow
Crystal size (mm)	0.36 × 0.23 × 0.14
Data collection	
Diffractometer	Bruker SMART APEX CCD diffractometer
Data collection method	ω rotation with narrow frames
Absorption correction	Multi-scan (based on symmetry-related

	measurements)
$T_{\min}$	0.555
$T_{\max}$	0.781
No. of measured, independent and observed reflections	13589, 6642, 6078
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.024
$\theta_{\max}$ (°)	25.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.085, 1.10
No. of relections	6642 reflections
No. of parameters	376
H-atom treatment	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 1.766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.41, –1.02

Table 1. Crystal data for complex **1**

DFT Calculations

The calculations were performed using Gaussian 03 Revision D01[1] using the EPSRC National Service for Computational Chemistry Software. URL: http://www.nsccs.ac.uk resource under project Chem 481. The calculations employed the B3PW91 functional.[2,3] It has been shown[4-6] that large core relativistic effective core potentials (RECPs) optimized by the Stuttgart-Dresden group[7-9] are well adapted to the calculation of geometries of lanthanide complexes, as 4f electrons do not participate in a lanthanide-ligand bond. Thus, a basis set adapted to the RECP augmented by a polarization f function was used for Nd. The Stuttgart-Dresden basis set (SDD)[10-11] and ECP was employed for all other atoms. The model geometry **1** was optimized without any constraints and the energy minima for **1** and the $\{Nd\}^+$ and $[FeCp(CO)_2]^-$ fragments of **1** were verified by analytical frequency calculations. Calculations of the Nd-Fe interaction energy included corrections for thermal and zero point energies, the preparation energy for each of the $\{Nd\}^+$ and $[FeCp(CO)_2]^-$ fragments and for basis set superposition errors (BSSEs), which were calculated using the counter-poise correction.[12] Natural Bond Orbital analyses were performed using NBO v5.[13] The HOMO was visualized in MOLEKEL.[14]

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Optimized Geometry for 1

Energy = -438.748302650 a.u.

H	0.01540	-0.10640	-0.24000
H	-0.03590	0.10370	1.51790
H	1.53110	-0.07590	0.69500
C	0.48810	-0.40770	0.70190
H	-1.58920	-2.14390	0.02850

H	0.55010	-2.31710	-1.26990
H	-1.57890	-1.95440	1.78850
C	0.41280	-1.94490	0.84960
C	-1.05510	-2.41880	0.94520
H	2.11490	-2.24670	-0.47830
C	1.08640	-2.60470	-0.35920
H	-0.14020	-1.21860	3.49220
H	-0.02470	-0.01610	5.93930
H	-1.10800	-3.50680	1.06300
N	1.12300	-2.33230	2.11580
H	1.05610	-3.70070	-0.30430
H	2.01120	-4.35530	-3.31420
C	0.71320	-1.86310	3.36680
H	3.15790	-0.13500	6.16410
H	1.92880	-5.68180	-4.48720
C	-0.08100	-0.97330	6.47210
H	0.67930	-5.53500	-3.23280
C	1.75100	-5.41350	-3.43650
C	2.24770	-3.12330	2.23260
H	-0.98140	-1.50440	6.14010
H	-0.20060	-0.75130	7.54020
C	1.57410	-2.35000	4.31640
C	3.01930	-1.03420	6.77630
H	-0.78230	-5.83990	-0.68810
H	2.88400	-0.71850	7.81920
N	2.51100	-3.11870	3.58690
H	3.94240	-1.62340	6.72640
Si	1.48980	-2.01980	6.19450
H	5.03370	-3.12090	2.81910
H	3.88790	-3.28330	5.13260
Nd	3.71640	-4.52630	0.54130
H	4.93060	-5.14770	-2.46480
C	-0.50810	-6.89300	-0.54480
C	3.60970	-3.86330	4.24470
H	-0.50660	-7.37570	-1.53060
H	0.58260	-5.30190	2.08270
H	4.85420	-6.40810	-3.69690
Si	2.79320	-6.52310	-2.27530
C	4.86360	-4.06960	3.36000
H	-1.29100	-7.37140	0.06000
C	4.64570	-6.19170	-2.64040
N	2.48280	-6.17450	-0.55040
H	5.72000	-4.16330	4.04690
H	3.22860	-4.83630	4.57080
C	0.99850	-6.31570	2.08770
Si	1.19910	-7.04690	0.32270
N	4.80710	-5.20540	2.41560
C	1.35000	-3.66580	7.15110
H	2.73610	-8.47770	-3.83760
H	5.28680	-6.84520	-2.03370
H	1.94950	-6.29440	2.63660
H	1.41980	-8.63490	-2.66340
H	0.47660	-4.23820	6.81620
H	1.23500	-3.46810	8.22480
C	2.47200	-8.34600	-2.77890
H	0.30690	-6.95650	2.65220
H	2.23860	-4.29450	7.02020
H	7.21280	-5.56340	3.88820
H	3.08720	-9.03560	-2.18830

H	7.45690	-5.88700	2.15770
C	5.46690	-6.46310	2.86470
C	6.99420	-6.26790	3.07520
H	5.76630	-7.17820	0.81840
H	5.00070	-6.33610	5.01460
C	1.53010	-8.91910	0.58640
H	1.57360	-9.46760	-0.36040
H	4.20820	-7.65680	1.53100
H	3.78270	-7.21230	4.05100
H	0.72050	-9.35200	1.19110
C	5.27200	-7.50490	1.74380
C	4.85700	-7.02930	4.17520
H	2.47390	-9.08670	1.11940
H	7.47330	-7.22150	3.33530
H	5.70830	-8.47060	2.02900
H	5.33820	-7.97800	4.44880
O	4.11360	-0.56970	0.92950
O	3.65590	-2.29400	-2.86430
H	7.69290	-1.37800	-2.31470
C	4.68650	-1.40040	0.28450
C	4.42450	-2.40740	-1.95420
H	7.77960	-0.94770	0.35710
C	7.50380	-2.10860	-1.54190
Fe	5.57740	-2.49120	-0.69110
C	7.54810	-1.88360	-0.13140
C	7.12240	-3.48210	-1.75290
H	7.00170	-3.96020	-2.71410
C	7.21000	-3.12010	0.53590
H	7.18340	-3.27830	1.60320
C	6.95180	-4.11520	-0.46770
H	6.77550	-5.16770	-0.29380

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