Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Synthesis and Structural Characterisation of an Yttrium-Alkyl-Alkylidene

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Synthesis and Spectroscopy

All manipulations were carried out under anaerobic and anhydrous conditions. Toluene (30 ml) was added to a pre-cooled (–78 °C) mixture of $[Y(CH_2SiMe_3)_3(THF)_2]$ (1.72 g, 3.48 mmol) and $H_2C(PPh_2NSiMe_3)_2$ (1.85 g, 3.48 mmol) and the mixture was allowed to slowly warm to room temperature with stirring over 18 hours. Volatiles were removed *in vacuo* and the resulting pale yellow solid was recrystallised from hexane/toluene (5:2 ml) to afford **1** as colourless crystals. Yield: 1.21 g, 43%. Anal. Calcd for $C_{39}H_{57}N_2OP_2Si_3Y$: C, 58.19; H, 7.14; N, 3.48. Found: C, 58.07; H, 7.09; N, 3.51. ^{1}H NMR (d_6-benzene, 298 K): δ –0.18 (d, $^2J_{YH}$ = 2.88 Hz, 2H, CH_2Si), 0.16 (s, 18H, NSi(CH_3)$_3$), 0.65 (s, 9H, CH$_2$Si(CH_3)$_3$), 1.43 (m, 4H, OCH$_2$CH_2), 3.93 (m, 4H, OCH_2CH$_2$), 7.12 (m, br, 16H, *o*- and *m*-Ar-C*H*) and 7.81 (m, br, 4H, *p*-Ar-C*H*). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ 3.78 (NSi(*C*H$_3$)$_3$), 4.86 (CH$_2$Si(*C*H$_3$)$_3$), 24.92 (OCH$_2$*C*H$_2$), 33.17 (d, $^1J_{YC}$ = 43.90 Hz, *C*H$_2$Si), 60.08 (td, $^1J_{PC}$ = 131.86 Hz, $^1J_{YC}$ = 4.88 Hz, Y*C*P$_2$), 69.86 (O*C*H$_2$CH$_2$), 129.14 (Ar-*C*), 131.36 (Ar-*C*) and 139.32 (t, $^1J_{PC}$ = 50.34 Hz, *i*-Ar-*C*). One Ar-*C* resonance was obscured by the C_6D_6 solvent resonance. ^{31}P{^{1}H} NMR (d_6-benzene, 298 K): δ 7.30 (d, $^2J_{YP}$ = 11.53 Hz, N*P*C).

DFT Calculations

The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2006.01.[1, 2] The restricted relativistic geometry optimization DFT calculations for **1** employed a

Slater type orbital (STO) triple-ζ-plus one polarization function basis set from the ZORA/TZP database of the ADF suite for all atoms. Frozen core basis sets were used for C (1s), N (1s), O (1s), Si (2p), P (2p) and Y (4p). Scalar relativistic (SR) approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects. The local density approximation (LDA) with the correlation potential due to Vosko *et al* was used in all of the DFT calculations.[3] Gradient corrections were performed using the functionals of Becke[4] and Perdew[5] (BP). Natural Bond Orbital analyses were performed using NBO v5[6] using the results of DFT calculations in which all electron basis sets were used as follows: ZORA/DZ for all H atoms and the C atoms pendant to the Si atoms, and ZORA/TZP for all other atoms. We chose this approach because of memory storage limitations in NBO v5. The Kohn-Sham orbitals were visualized in MOLEKEL.[7]

References

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[4] A. D. Becke, *Phys. Rev. A*, 1988**, 38**, 3098.

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Optimized Geometry for 1

Y	0.00000	0.00000	0.00000
O	2.42010	0.00000	0.00000
C	2.92110	1.36580	0.00000
C	3.88870	1.46260	-1.16200
C	3.54670	0.24470	-2.00070
C	3.20510	-0.75630	-0.93580
C	-0.12540	1.81960	-1.53340
C	-1.57120	4.58240	-1.56640
C	1.47810	4.42420	-1.59330
C	-0.08630	3.73490	0.89930
H	4.10970	-1.13810	-0.42480
H	2.59940	-1.60990	-1.27730
H	2.65150	0.43910	-2.61890
H	4.36580	-0.08390	-2.65730
H	3.76900	2.41060	-1.70970
H	4.93020	1.40050	-0.80660
H	2.04490	2.02820	-0.13790
H	3.38260	1.56430	0.97950
H	-1.63080	4.60860	-2.66790
H	-2.50210	4.12450	-1.18740
H	-1.53410	5.62090	-1.19300
H	2.38820	3.93500	-1.20100
H	1.53260	4.40060	-2.69580
H	1.51170	5.48020	-1.27280
H	-0.10150	4.79350	1.21490
H	-0.97710	3.24190	1.33310
H	0.80380	3.26630	1.35930
H	-1.16270	1.58150	-1.86060
H	0.51960	1.70350	-2.43060
Si	-0.09220	3.58310	-0.97770
N	-0.78540	0.27940	2.13690
N	-0.44810	-2.02840	-0.97560
P	-2.34470	0.00330	1.69680
P	-2.06710	-1.87720	-0.71290
C	-2.34660	-0.43420	0.08130
C	1.66710	-4.05900	-1.08100
C	1.08620	-2.19380	-3.48970
C	-0.75420	-4.46750	-2.77670
C	-2.69010	-3.34750	0.13240
C	-1.81690	-4.34600	0.54330
C	-2.29060	-5.44420	1.24370
C	-3.64130	-5.54520	1.54010
C	-4.51640	-4.54190	1.14530
C	-4.04380	-3.44450	0.44640
C	-2.84390	-1.91160	-2.35300
C	-3.74140	-2.88770	-2.76870
C	-4.22590	-2.88240	-4.06920
C	-3.81360	-1.90700	-4.96260
C	-2.91920	-0.92600	-4.55110

C	-2.43960	-0.92760	-3.25370
C	-3.28380	1.53900	1.90850
C	-3.70210	1.97350	3.16220
C	-4.33920	3.19550	3.29990
C	-4.56000	3.99220	2.18480
C	-4.15050	3.55950	0.93170
C	-3.51780	2.33400	0.79350
C	-3.16230	-1.14120	2.83440
C	-4.54370	-1.08780	3.00930
C	-5.18150	-2.01950	3.81130
C	-4.44690	-3.01820	4.43530
C	-3.07400	-3.08760	4.24810
C	-2.43380	-2.15260	3.45030
C	1.81660	1.11150	3.12660
C	0.00230	-0.48230	4.92750
C	-0.60160	2.41890	4.29560
Si	0.34020	-3.13900	-2.05280
Si	0.01760	0.81230	3.57610
H	1.18980	-4.85400	-0.48020
H	2.38230	-4.55410	-1.76140
H	2.23920	-3.42600	-0.38140
H	1.67420	-2.85770	-4.14720
H	0.25420	-1.77510	-4.08580
H	1.73130	-1.34960	-3.18980
H	-1.45810	-4.06770	-3.52750
H	-0.11150	-5.21950	-3.27030
H	-1.34390	-4.98400	-1.99820
H	-4.72480	-2.63860	0.14640
H	-5.58000	-4.61160	1.39440
H	-4.01790	-6.41210	2.09280
H	-1.59830	-6.22990	1.56250
H	-0.75010	-4.23910	0.31300
H	-1.73040	-0.15540	-2.92430
H	-2.59370	-0.15020	-5.25130
H	-4.19230	-1.90800	-5.98960
H	-4.92860	-3.65800	-4.38890
H	-4.05190	-3.67390	-2.07050
H	-3.20120	1.94680	-0.18550
H	-4.33070	4.18460	0.05080
H	-5.06390	4.95800	2.29380
H	-4.66860	3.53140	4.28840
H	-3.54000	1.33530	4.03930
H	-1.34810	-2.18960	3.30510
H	-2.49300	-3.87730	4.73480
H	-4.95000	-3.75080	5.07520
H	-6.26500	-1.96210	3.95500
H	-5.11910	-0.29490	2.51720
H	2.27190	0.27190	2.56970
H	1.91820	2.03290	2.52640
H	2.40220	1.25900	4.05110
H	-1.02230	-0.73130	5.25330

H	0.48740	-1.41770	4.59920
H	0.55750	-0.10140	5.80320
H	-1.61540	2.34220	4.72150
H	0.08400	2.73740	5.10160
H	-0.62040	3.20850	3.52370