Monocyclopentadienyl Yttrium Chemistry: Incorporation of Alkoxides as Supporting Ligands and Synthesis of $[Y(C_5Me_5)(OC_6H_3Bu^t{}_2)(\mu\text{-}H)]_2$

Colin J. Schaverien,*[a] John H. G. Frijns,[a] Hero J. Heeres,[b] J. R. van den Hende,[b] Jan H. Teuben[b] and Anthony L. Spek[c]

[a] *Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Postbus 3003, 1003 AA Amsterdam, The Netherlands*
[b] *Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*
[c] *Laboratory for Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Reaction of the crystallographically characterised $[Y(C_5Me_5)(OC_6H_3Bu^t{}_2)_2]$ **2** with $LiCH(SiMe_3)_2$ affords the mixed alkyl–alkoxide species $[Y(C_5Me_5)\{CH(SiMe_3)_2\}(OC_6H_3Bu^t{}_2)]$ **3** which, on subsequent hydrogenation, gives the hydride bridged dimer $[\{Y(C_5Me_5)(OC_6H_3Bu^t{}_2)(\mu\text{-}H)\}_2]$ **4**; ^{89}Y NMR spectra of these, and related complexes, allows C_5Me_5, $OC_6H_3Bu^t{}_2$ and $CH(SiMe_3)_2$ group contributions to be determined.

The recent growth in organolanthanide chemistry has primarily focused on complexes stabilised by the bis(pentamethylcyclopentadienyl) ligand system. Dimeric complexes, $[\{Ln(C_5Me_5)_2H\}_2]$, have been shown[1] to be extremely active for ethylene polymerization. Replacement of the pentamethylcyclopentadienyl ligands by hard, electronegative ancillary ligands such as alkoxides would be expected[2] to further suppress β-hydrogen elimination and chain termination steps owing to the relative thermodynamic instability of the resultant hydride and to the additional electropositivity of the proximate lanthanide, or related metal, centre. To study the influence of such ligands, a pathway to alkoxide ligand incorporation in yttrium chemistry has been developed, which also allows a direct probe by ^{89}Y NMR spectroscopy.

Reaction of $[Y(OC_6H_3Bu^t{}_2)_3]$ **1**[3] with KC_5Me_5 (toluene, 100 °C, 16 h) resulted in the formation of $[Y(C_5Me_5)(OC_6H_3Bu^t{}_2)_2]$ **2**[†] in 70–80% isolated yield. The X-ray structure of **2**[‡] (Fig. 1) is isostructural with its cerium congener.[4,5]

$$\underset{\mathbf{2}}{[Y(C_5Me_5)(OC_6H_3Bu^t{}_2)_2]} + LiCH(SiMe_3)_2 \rightarrow \underset{\mathbf{3}}{[Y(C_5Me_5)CH(SiMe_3)_2(OC_6H_3Bu^t{}_2)]}$$

Scheme 1

$$\underset{\mathbf{3}}{[Y(C_5Me_5)CH(SiMe_3)_2(OC_6H_3Bu^t{}_2)]} + H_2 \rightarrow \underset{\mathbf{4}}{[\{Y(C_5Me_5)(OC_6H_3Bu^t{}_2)(\mu\text{-}H)\}_2]}$$

Scheme 2

[†] *Selected NMR data* for **2**: ^1H NMR (C_6D_6, 25 °C): δ 7.25 (d, 2H, H_m), 6.85 (t, 1H, H_p), 1.86 (s, 15H, C_5Me_5) and 1.53 (s, 36H, CMe_3). For **3** ^1H NMR (C_6D_6, 25 °C): δ 7.25 (d, 2H, H_m), 6.85 (t, 1H, H_p), 1.91 (s, 15H, C_5Me_5), 1.48 (s, 18H, CMe_3), 0.26 (s, 18H, $SiMe_3$) and −0.39 [d, 1H, $C\mathit{H}(SiMe_3)_2$]; ^{13}C NMR (C_7D_8, −80 °C): δ 158.0 (s, C_{ipso}), 134.7 (s, C_o), 124.7 (d, C_m), 118.7 (s, C_5Me_5), 116.4 (d, C_p), 33.8 (s, $\mathit{C}Me_3$), 32.0 (d, $^1J_{YC}$ 33 Hz), 30.9 (q, $C\mathit{Me}_3$), 10.4 (q, $C_5\mathit{Me}_5$) and 2.7 (q, $SiMe_3$); ^{29}Si NMR (C_7D_8, −80 °C): δ −12.2 ($w_{\frac{1}{2}}$ 12 Hz). For **4** ^1H NMR (C_6D_6, 25 °C): δ 7.29 (d, 4H, H_m), 6.86 (t, 2H, H_p), 5.64 (t, 2H, J_{YH} 35 Hz, YH), 2.02 (s, 30H, C_5Me_5), 1.57 (s, 36H, CMe_3). Satisfactory elemental analyses (C, H, Y) were obtained.

[‡] *Crystal data* for **2**: $C_{38}H_{57}YO_2$, M = 634.77, orthorhombic, space group *Pbnn*, a = 12.114(1), b = 17.254(1), c = 33.306(2) Å, U = 6961.5(8) Å^3, $F(000)$ = 2720 electrons, Mo–Kα (Zr-filtered) radiation, T = 100 K, Z = 8, D_c = 1.211 g cm^{-3}, μ(Mo-Kα) = 17.1 cm^{-1}. A redundant set of 6531 reflections (5871 unique) were collected on an Enraf-Nonius CAD 4 diffractometer. The structure was solved by Patterson methods (SHELXS-86). Full matrix least-squares refinement for 3279 reflections considered observed [$I \geqslant 2.5\,\sigma(I)$] collected in the range $1.2° \leqslant 2\theta \leqslant 50.8°$ and with 423 parameters converged at R = 0.048, R_w = 0.042 {weights $w = [\sigma_c{}^2(F_o)]^{-1}$, where $\sigma_c{}^2(F_o)$ is the variance in F_o due to counting statistics}. All hydrogen atoms were placed at calculated positions and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

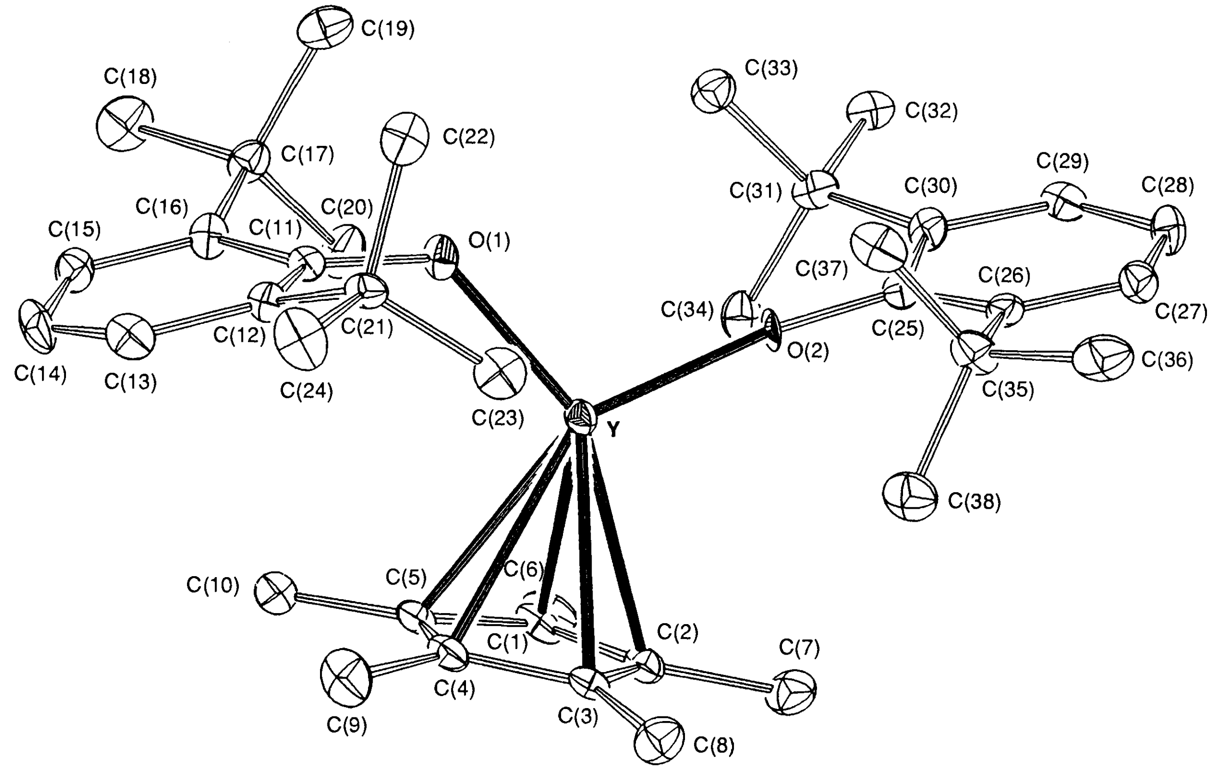

Fig. 1 Thermal ellipsoid plot for **2** drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Y–O(1) 2.096(4); Y–O(2) 2.059(3); O(1)–C(11) 1.351(6); O(2)–C(25) 1.356(6); Y–Cent 2.363(3); Y–O(1)–C(11) 128.6(3); Y–O(2)–C(25) 168.0(3); O(1)–Y–O(2) 107.0(1); Cent–Y–O(2) 125.8(1); Cent–Y–O(1) 125.6(1) (Cent = Centroid of C_5Me_5 ring).

Compound **2** reacts cleanly§ with $LiCH(SiMe_3)_2$ in hexane, with loss of $LiOC_6H_3Bu^t{}_2$, to give the mixed alkyl–alkoxide complex $[Y(C_5Me_5)\{CH(SiMe_3)_2\}(OC_6H_3Bu^t{}_2)]$ **3**.† In addition to the expected spectroscopic parameters for **3**,† its ^{29}Si NMR spectrum (C_7D_8, −80 °C) displayed a sharp singlet at δ −12.2 ($w_{\frac{1}{2}}$ = 12 Hz), no coupling to ^{89}Y being observed.[6]

In contrast to the facile hydrogenation observed for the bis(pentamethylcyclopentadienyl) series $[Ln(C_5Me_5)_2CH(SiMe_3)_2]$,[7] hydrogenation of **3** is conveniently performed and much cleaner if carried out under 10 bar of H_2 in a small stirred autoclave in hexane, yielding $[\{Y(C_5Me_5)(OC_6H_3Bu^t{}_2)(\mu\text{-}H)\}_2]$ **4**. The reaction is readily monitored in a high-pressure, sapphire 10 mm NMR tube[8] (20 bar H_2, 25 °C, C_6D_{12}). No intermediates were observed.

The hydride **4**† displays a diagnostic triplet in the ^1H NMR spectrum at δ 5.64 (J_{YH} 35.2 Hz), clearly indicating that the hydrides bridge two yttrium atoms. The coupling is similar to that found for other yttrium hydride species.[9] Only one isomer is observed, although NMR spectroscopy cannot distinguish between mutually *cis*- or *trans*-alkoxide–C_5Me_5 ligands. However, subsequent reactivity studies indicate *cis*-coordination. Low-temperature ^1H NMR (−90 °C, C_7D_8) studies on **4** provide no evidence for an asymmetric $Y(\mu\text{-}H)Y(H)$ dimer, analogous to that seen[10] for $[\{(C_5Me_5)_2YH\}_2]$.

Compound **4** is soluble in alkane solvents. It is stable in solution at 25 °C without an H_2 atmosphere, and displays no tendency to disproportionate to, *e.g.* **2**. It polymerizes ethylene, albeit slowly. Addition of an excess of tetrahydrofuran (thf; 10 equiv.) to **4** does not result in monomer formation.[11]

The hydride is presumably constrained to bridge two yttrium centres because of yttrium's additional electrophilicity induced by the hard, electronegative alkoxide ligands, thus strengthening Y–R relative to Y–H, although the hydride may derive additional stabilization by bridging the electropositive yttrium centres.[2] Similar trends are common in organo-boron and -aluminium main group chemistry. Alkoxide π-donation is likely to be a secondary effect and may not be especially significant in comparing the relative effects on the metal of C_5Me_5 and alkoxide ligands (*vide infra*).[2a,2c,12]

To gain understanding into the effect of the ancillary ligands on the shielding at the metal centre, the ^{89}Y NMR spectra of compounds **1**, **2**, **3**, $[Y(C_5Me_5)_2CH(SiMe_3)_2]$, $[Y\{CH(SiMe_3)_2\}_3]$, and $[Y(C_5Me_5)_2(OC_6H_3Bu^t{}_2)]$ were determined¶ (Table 1). Almost all previous ^{89}Y NMR studies have been confined to aqueous systems.[13]

---

§ Although the mono(pentamethylcyclopentadienyl) complexes $[Ln(C_5Me_5)(OC_6H_3Bu^t{}_2)_2]$ (Ln = Y, La, Ce) are known, clean and selective monoalkylation is possible only for Ln = Y. In addition the tendency for disproportionation in the preparation of $[Y(C_5Me_5)(OC_6H_3Bu^t{}_2)_2]$ is much less than for its cerium or lanthanum counterparts (H. H. Heeres and J. H. Teuben, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 226). Unlike $[Ln(C_5Me_5)\{CH(SiMe_3)_2\}_2]$ (Ln = La,[6] Ce[5]), the putative $[Y(C_5Me_5)\{CH(SiMe_3)_2\}_2]$ cannot be prepared by reaction of **2** with $MCH(SiMe_3)_2$ (M = Li or K). No reaction occurs between **3** and $LiCH(SiMe_3)_2$, indicating that the remaining alkoxide is not susceptible to nucleophilic displacement. $[La(C_5Me_5)CH(SiMe_3)_2(OC_6H_3Bu^t{}_2)]$ could not be prepared, either by reaction of $[La(C_5Me_5)\{CH(SiMe_3)_2\}_2]$ with $HOC_6H_3Bu^t{}_2$ (1 equiv.), or by reaction of $[La(C_5Me_5)(OC_6H_3Bu^t{}_2)_2]$ with $LiCH(SiMe_3)_2$ (1 equiv.). These differences are presumably due to the size of the metal.

¶ ^{89}Y NMR spectra were measured on a Varian VXR-300 at a transmitter frequency of 14.697 MHz using 10 mm tubes with a microcell insert. The yttrium compound (200–250 mg) was dissolved in C_6D_6 (*ca.* 0.8 ml) giving solutions of *ca.* 0.3–0.4 mol dm^{-3}. Because of the negative nuclear Overhauser effect of ^{89}Y the decoupler was not used. Relaxation delays were typically 50 s. Shifts are with respect to 2 mol dm^{-3} YCl_3 in D_2O. 200–1000 transients were accumulated. Negative shifts imply a more shielded environment than the reference and so resonance occurs at higher field.

Table 1 ^{89}Y NMR data

Compound	^{89}Y NMR chemical shift[a]
$[Y\{CH(SiMe_3)_2\}_3]$	895.0[b]
1	168.4
$[Y(C_5Me_5)_2CH(SiMe_3)_2]$	78.9
2	21.0
YCl_3	0.0
$[Y(C_5Me_5)_2(OC_6H_3Bu^t_2)]$	−129.3
3	N.s.[c]

[a] Peak widths at half maximum ($w_{\frac{1}{2}}$) 2–10 Hz. [b] in $C_6D_5CD_3$. [c] No signal observable.

From these ^{89}Y NMR chemical shifts (in C_6D_6), group contributions can be calculated. These are C_5Me_5, −91 to −110 ppm (calculated from the alkoxide and alkyl contributions); Cl, 0 ppm; $OC_6H_3Bu^t_2$, +56 ppm; $CH(SiMe_3)_2$, +298 ppm. These figures display good additivity and internal consistency. Correlation of these group contributions with the electrophilicity of yttrium are in good agreement with the observed[2c] effects of such ancillary ligands. Electronegativity differences in $Sc(C_5Me_5)_2R$ species have been discussed.[14]||

Further research examines the reactivity of **4** with alkenes, and attempts to ascertain whether polymerisation occurs at a dimeric centre.

We thank J. A. van Doorn (KSLA) for a helpful discussion.

Received, 12th December 1990; Com. 0/05591C

References

1 G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8111.

2 (*a*) J. W. Bruno, H. A. Stecher, L. R. Morss, D. C. Sonnenberger and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 7275; (*b*) S. P. Nolan, D. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1989, **111**, 7844; (*c*) Z. Lin and T. J. Marks, *J. Am. Chem. Soc.*, 1987, **109**, 7979.

3 P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499; P. B. Hitchcock, M. F. Lappert and R. G. Smith, *Inorg. Chim. Acta.*, 1987, **139**, 183.

4 H. J. Heeres, A. Meetsma and J. H. Teuben, *J. Chem. Soc., Chem. Commun.*, 1988, 962.

5 H. J. Heeres, A. Meetsma, J. H. Teuben and R. D. Rogers, *Organometallics*, 1989, **8**, 2637.

6 H. van der Heijden, C. J. Schaverien and A. G. Orpen, *Organometallics*, 1989, **8**, 255.

7 G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8091; K. H. den Haan, J. L. de Boer, J. H. Teuben, A. L. Spek, B. Kojic-Prodic, G. R. Hays and R. Huis, *Organometallics*, 1986, **5**, 1726; H. J. Heeres, J. Renkema, M. Booij, A. Meetsma and J. H. Teuben, *Organometallics*, 1988, **7**, 2495.

8 C. Roe, *J. Magn. Reson.*, 1985, **63**, 388.

9 K. H. den Haan, and J. H. Teuben, *J. Chem. Soc., Chem. Commun.*, 1986, 682; W. J. Evans, M. S. Solberger, S. I. Khan and R. Bau, *J. Am. Chem. Soc.*, 1988, **110**, 439; W. J. Evans, J. H. Meadows, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1984, **106**, 1291.

10 See ref. 12 in P. L. Watson and D. C. Roe, *J. Am. Chem. Soc.*, 1982, **104**, 6471; K. H. den Haan, Y. Wielstra and J. H. Teuben, *Organometallics*, 1987, **6**, 2053.

11 W. J. Evans, D. K. Drummond, T. P. Hanusa and R. J. Doedens, *Organometallics*, 1987, **6**, 2279.

12 P. J. Fagan, J. M. Manriquez, E. A. Maatta, E. A. Seyam and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6650.

13 R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, New York, 1978, p. 199. The exception is: W. J. Evans, J. H. Meadows, A. G. Kostka and G. L. Closs, *Organometallics*, 1985, **4**, 324.

14 J. A. Labinger and J. E. Bercaw, *Organometallics*, 1988, **7**, 926.

|| A Y–(C_5Me_5) bond is expected to be very polar, the electron affinities of the cyclopentadienyl radical and Cl$^{\bullet}$ being comparable. Two electronegative C_5Me_5 ligands bond primarily *via* the Y 4s orbital, hence Y–OAr or Y–R will bond essentially *via* the Y 3d orbitals.