A Triplet Biradical Organocalcium Species derived from Partial Oxygen Quenching of a Substituted Cyclopentadienyl Calcium Compound

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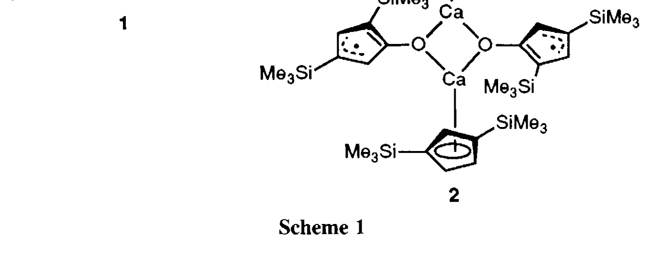
Reaction of $[Ca\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2]$ **1**, in toluene with oxygen yields the stable, rigid biradical $[Ca\{\eta\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}\{\mu\text{-}OC_5H_2\text{-}2,4\text{-}(SiMe_3)_2\}]_2$ **2**, characterised by an X-ray structure determination [Ca–O 2.298(3), 2.210(3) Å; Ca–centroid 2.374(–)°; Ca–O–Ca 105.4(1)°; O–Ca–centroid 149.4(–), 125.8(–)°] and EPR spectroscopy (resonance at g = 9.01, 4.21, 3.87 result from a super-exchange interaction between two unpaired electrons in the biradical).

Within the realm of Group 2 organometallic chemistry several metallocene compounds for the heavier elements have been prepared and structurally characterised[1–6] but little is known about their reactions.[1,6] Herein we report the reaction of $[Ca\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2]$ **1** with oxygen in toluene yielding a novel, stable, main-group biradical $[Ca\{\eta\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}\{\mu\text{-}OC_5H_2\text{-}2,4\text{-}(SiMe_3)_2\}]_2$ **3**, which has been structurally characterized and studied using EPR spectroscopy.

Colourless toluene solutions of **1** under an atmosphere of oxygen rapidly turn orange then dark brown after consumption of half an equivalent of oxygen. The orange solutions are EPR-active and yield orange crystals of **2**;† the brown solutions yield intractable oils. Compound **1** is coordinatively unsaturated and readily binds with the oxygen-centred molecules tetrahydrofuran (thf) and dimethoxyethane.[5] The primary process in the formation of **2** (Scheme 1) may involve



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Scheme 1

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† Repeated attempts to obtain an analytically pure sample of **2** were unsuccessful and the characterization rests on reproducible EPR data, and the crystal structure.

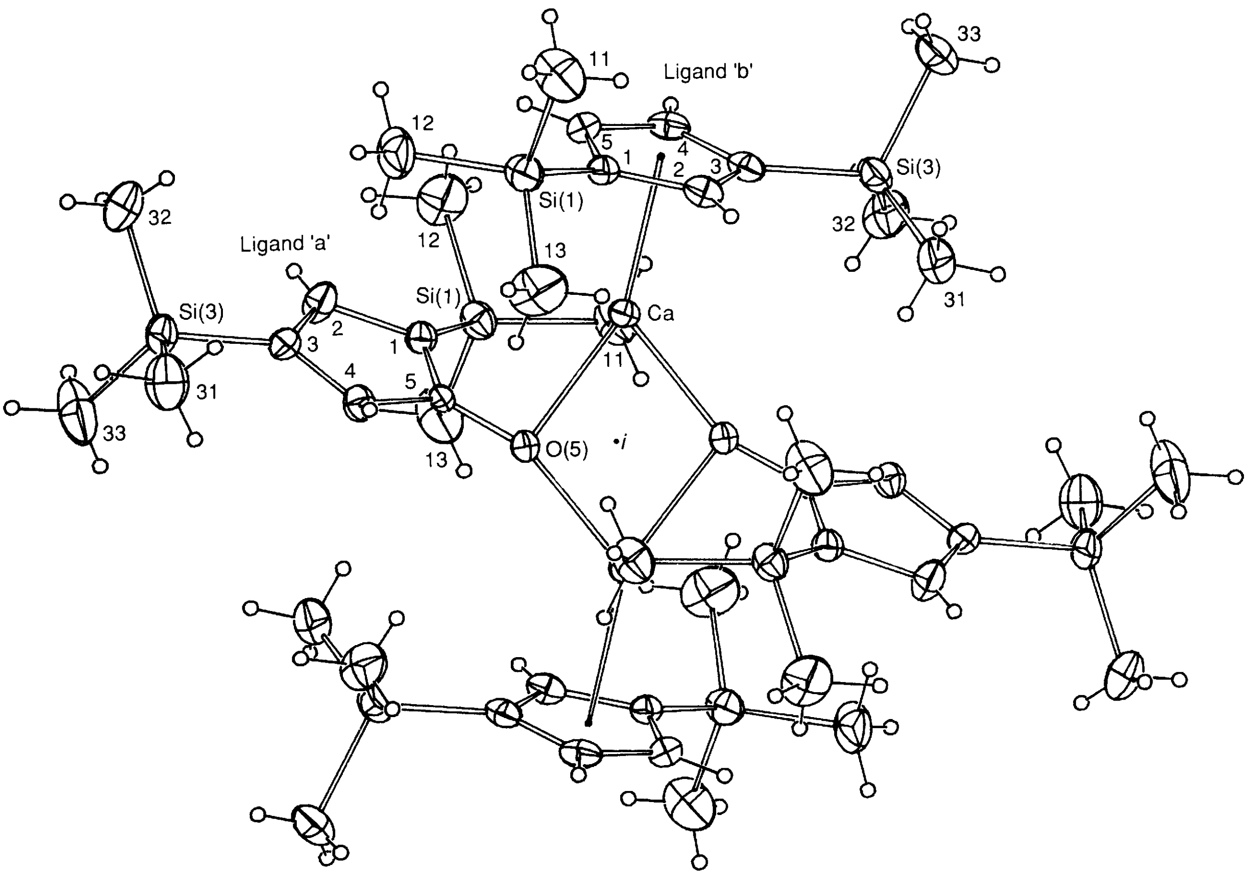

Fig. 1 Projection of the crystallographically centrosymmetric molecules of [Ca{η-C_5H_3-1,3-$(SiMe_3)_2$}{μ-OC_5H_2-2,4-$(SiMe_3)_2$}$]_2$ **2**, showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii of 0.1 Å for hydrogen atoms. Selected bond distances (Å) and angles (°): Ca–O(a5, a5′) 2.298(3), 2.210(3); Ca–C(b1,2,3,4,5) 2.651(5), 2.622(6), 2.670(5), 2.670(5), 2.670(5); Ca–Centroid 2.374(–), Ca···Ca′ 3.585(2); O(a5)···O(a5′) 2.734(5); C(a1)–C(a2) 1.502(9); C(a2)–C(a3) 1.426(8); C(a3)–C(a4) 1.393(10); C(a4)–C(a5) 1.479(6); C(a1)–C(a5) 1.370(8); O(a5)–C(a5) 1.334(7); O(a5)–Ca–O(a5′) 74.6(1); Ca–O(a5)–Ca′ 105.4(1); Ca, Ca′–O(a5)–C(a5) 96.2(2), 156.9(3); O(a5)–Ca–Centroid 149.4(–); O(a5′)–Ca–Centroid 125.8(–).

complexation of dioxygen to two calcium centres, along the lines established for transition metal species. A reaction pathway involving complexation of dioxygen to one metal centre followed by migratory insertion yielding intermediate {$(Me_3Si)_2C_5H_3$}OOCa{$C_5H_3(SiMe_3)_2$} species, similar to those in organomagnesium–oxygen reactions,[7] is unlikely since this would result in diamagnetic products.

The molecular projection of **2** and selected structural parameters are given in Fig. 1.‡ The metal centres are three-coordinate, treating each of the symmetrically bound pentahapto ligands as occupying one coordination site. Metal–carbon distances, mean 2.65_7 Å, are marginally shorter than in the thf adduct of **1**, mean 2.68_2 Å,[5] and the only other monocyclopentadienyl structure available for comparison, [Ca(η-C_5Me_5)(μ-I)$(thf)_2]_2$, mean 2.67 Å.[3] Within the [Ca_2(μ-O_2)] core there is some asymmetry with Ca–O distances 2.298(3) and 2.210(3) Å. These are only 5 and 0.5% longer than the Ca–O distance for the neutral oxygen donor in the thf adduct of **1**. Noteworthy features of the O-centred ligand include the C–O distance and the variation of the C–C distance within the ring. The C–O distance, 1.334(7) Å, and adjacent C–C distance for the carbon bearing a trimethylsilyl group, 1.370(8) Å, compare with those in metal enolates, *e.g.* 1.330(6) and 1.342(6) Å, in [{LiOC(Bu^t)CH_2}$_6$],[8] and it is tempting to assign this part as a metal enolate arguing that the slightly long C–C distance is a consequence of the polarizing influence of silicon. The connecting distances to the outer carbons, 1.503(9) and 1.479(6) Å, are close to acceptable single bonds based on sp^2 carbon centres and these outer carbons can therefore be considered as a separate delocalised system, possibly that of an allyl radical. Associated C–C distances, 1.426(8) and 1.383(10) Å, mean 1.40_5 Å, are only marginally longer than those in the allyl anions, *viz*. 1.38 Å in allyl$^-$, and 1.385 Å in 1,3-diphenylallyl$^-$.[9] Unfortunately, the exchange-coupled EPR spectrum does not provide a distance between the unpaired electrons and consequently the technique cannot distinguish between an allyl radical and an allyl anion.

Two unpaired electrons, each situated on an oxygenated cyclopentadienyl ring, potentially interact through a super-exchange (antiferromagnetic or ferromagnetic) pathway involving the overlap of the π(O-cyclopentadienyl)–p(O)–p(O)–π(O-cyclopentadienyl) orbitals or through space (dipole–dipole interaction). The distance between the unpaired electrons is roughly 7.5 Å indicating that at least the two unpaired electrons should be dipole–dipole coupled. EPR spectra of radical species containing a single unpaired electron can be readily distinguished from those of a biradical in which the electrons are exchange- or dipole–dipole-coupled.[10]

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‡ *Crystal structure determination* (T = 295 K; CAD4 diffractometer, crystals mounted in capillaries): $C_{44}H_{82}Ca_2O_2Si_8$, M = 948.0, monoclinic, space group $P2_1/c$, a = 12.354(6), b = 20.51(1), c = 13.97(1) Å, β = 123.28°, U = 2958(6) Å^3, $F(000)$ = 1028; Z = 2, D_c = 1.06 g cm^{-3}, μ(Mo-Kα) = 3.4 cm^{-1}, no absorption correction, specimen 0.52 × 0.40 × 0.35 mm, 3628 unique reflections, 2487 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 45°; R = 0.042, R_w = 0.034. Hydrogen atoms were refined in x, y, z, U_{iso}. 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.

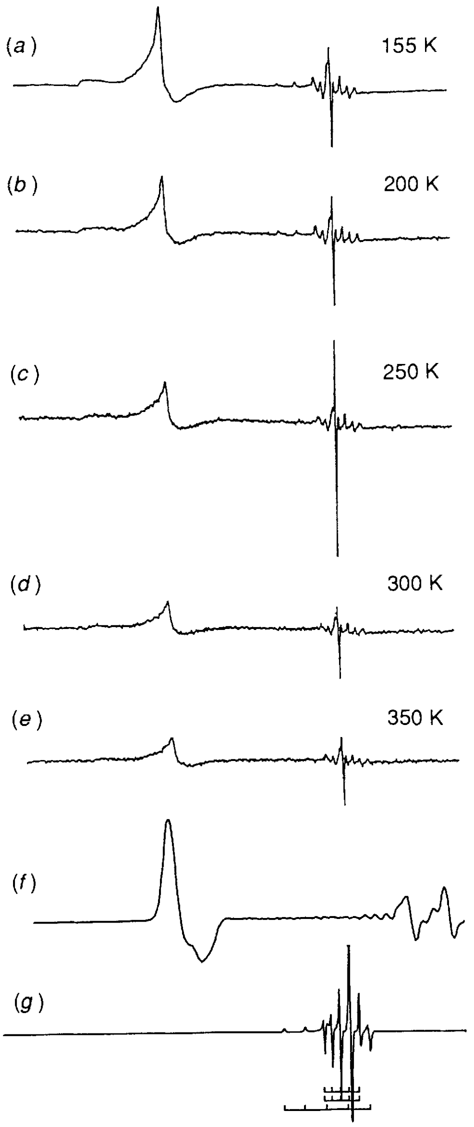

Fig. 2 Variable temperature EPR spectra (*a*–*e*) of a toluene solution of Ca$\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2$ **1**, after treatment with less than half an equivalent of oxygen, ν = 9.2592 GHz; (*f*) Computer simulation (program EXCHANGE[10]) of the g = 4.21 and 3.87 resonances assuming an axially symmetric exchange interaction. (*g*) Computer simulation (program EPR50FIT[15]) of the *g ca.* 2 resonances assuming a single unpaired electron is coupled to four magnetically equivalent protons (I = 2).

Variable temperature (155–355 K) EPR spectra [Fig. 2(*a*–*e*)] of the foregoing orange solutions contain three components; the first consists of an orthorhombic signal with resonances with effective g values of 9.01, 4.21 and 3.87. These resonances cannot be attributed to adventitious high spin iron(III) species in an orthorhombic environment as at room temperature the g anisotropy would be averaged out yielding resonances at *g ca.* 4.3 and 3.5, which is clearly not observed. In addition, the extremely short spin–lattice relaxation time usually prohibits the observation of high-spin ferric EPR signals at temperatures above 100 K. A reasonable computer simulation (using the Fortran program EXCHANGE[10]) of the g = 4.21 and 3.87 resonances can be obtained [Fig. 2(*f*)] assuming the unpaired electrons are exchange-coupled and the biradical exhibits axial symmetry (D = 0.479 cm^{-1}, E = 0.34 cm^{-1}, $g_{\parallel}$ = 2.5. $g_{\perp}$ = 1.5). The lack of resonance at g = 9.01 and the appearance of resonances around *g ca.* 1.5 is presumably a consequence of the lower (monoclinic) symmetry found in the molecule. Determination of the exchange coupling constant and whether the unpaired electrons are ferro- or antiferro-magnetically coupled would require variable temperature measurements between 4 and 150 K. Spin quenching of the unpaired electrons in the biradical by intermolecular association is presumably blocked by the large steric hindrance associated with the trimethylsilyl groups, particularly those on the 4-positions of the oxygenated rings. Overall, the present findings further highlight the potential of bulky ligands, in the present case a cyclopentadienyl[11] and an 'enolate' (see structural commentary), in imparting kinetic stability to unusual bonding configurations.

The second and third components consist of a singlet at g = 2.004 and the weak resonances flanking the singlet [Fig. 2(*a*–*e*)]. Attempts at simulating (using the Fortran program DISSIM[10]) the latter signal, assuming the two unpaired electrons were dipole–dipole coupled and each electron was coupled to magnetically equivalent protons (I = 1), were unsuccessful. In contrast, computer simulation (using the Fortran program EPR50FIT[12]) [Fig. 2(*g*)] based on the EPR-active species containing a single unpaired electron coupled to four magnetically equivalent protons yields the following parameters: $g_{\parallel}$ = 2.119. $g_{\perp}$ = 1.987, $A_{\parallel}$ = 188.3 × 10^{-4} cm^{-1}, $A_{\perp}$ = 79.1 × 10^{-4} cm^{-1}). Thus the second and third components are most likely by-products of the reaction. Treatment of the analogous strontium compound, Sr$\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2$,[5b] in toluene with oxygen gave an orange solution containing paramagnetic species, but only singlet species, with g_{av} close to the free-electron value (2.0089).

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