Synthesis and Reactivity of bis(η-1,4-Di-*tert*-butylbuta-1,3-diene)cobalt; the X-Ray Crystal Structure of the Anionic Butadiene Sandwich Complex [K(18-crown-6)(thf)$_2$][Co(η-$C_4H_4Bu^t{}_2$)$_2$]

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Cocondensation of cobalt atoms with 1,4-di-*tert*-butylbuta-1,3-diene affords the stable, paramagnetic butadiene sandwich compound [Co(η-$C_4H_4Bu^t{}_2$)$_2$], which is a reactive source of Co^0 fragments; reduction of [Co(η-$C_4H_4Bu^t{}_2$)$_2$] with potassium affords the first crystallographically characterised homoleptic butadiene sandwich complex, [Co(η-$C_4H_4Bu^t{}_2$)$_2$]$^-$, in which the bonding is that of a genuine diene rather than a metallacyclopentene.

The strategy of using ligands with bulky substituents to impart stability to coordinatively and electronically unsaturated organometallics is well documented. We have recently described the use of the bulky arene 1,3,5-tri-*tert*-butylbenzene in the synthesis of the transition metal and lanthanide sandwich complexes [M(η-$C_6H_3Bu^t{}_3$)$_2$] (M = Zr, Hf, Y, La),[1,2] and the use of a bulky diene 1,4-di-*tert*-butylbuta-1,3-diene in the synthesis of early transition metal butadiene sandwich complexes [M(η-$C_4H_4Bu^t{}_2$)$_2$] (M = Ti, V).[3] The latter are rare examples of stable homoleptic butadiene complexes, the only other examples being [M(μ-C_4H_6)$_3$], M = Mo, W; the predominant products from the reactions of metal atoms with the parent butadiene are butadiene oligomers.

The cycloocta-1,5-diene (cod) complexes [M(cod)$_2$] (M = Fe, Co),[4,5] identified on the basis of their IR spectra and oxidative decomposition products, have been prepared by metal vapour synthesis but their extreme thermal instability precluded characterisation by conventional techniques. We describe here the synthesis, characterisation and reactions of the new complex [Co(η-$C_4H_4Bu^t{}_2$)$_2$], isolable as a crystalline material stable at room temperature.

Cocondensation of cobalt atoms with 1,4-di-*tert*-butylbuta-1,3-diene results in the formation of a dark-orange matrix. After extraction with dry hexane, filtration and removal of the excess of ligand, [Co(η-$C_4H_4Bu^t{}_2$)$_2$], **1**, may be sublimed under high vacuum (70–80 °C, 10^{-4} mbar) (1 bar = 10^5 Pa) as golden-yellow crystals (yield *ca.* 20%),†‡ see Scheme 1. Compound **1** is an air-sensitive material, highly soluble in hydrocarbon solvents and thermally stable up to 100 °C.

Compound **1** shows no features appropriate for a diamagnetic complex in the ^{1}H NMR spectrum in the region δ 15 to −5. While **1** shows only a weak, broad feature centred at g = 2.18 in the ESR spectrum in toluene solution at room temperature, an intense frozen solution spectrum at 90 K has axial symmetry, with $g_\parallel = 2.074$, $A(\text{Co})_\parallel = 18.8$ G and $g_\perp = 2.081$, $A(\text{Co})_\perp < 7$ G (hyperfine coupling of Co unresolved in $g_\perp$) (1 G = 10^{-4} T).

The variation of the solution magnetic moment of **1** with temperature has been determined by Evans' method.[6] **1** exhibits Curie–Weiss behaviour ($C = 0.363$, $\theta = -12.0$ K) with a temperature-independent moment of 1.75 μ_B, ($\mu_B \simeq 9.274 \times 10^{-24}$ J T^{-1}) close to the spin-only value of 1.73 μ_B. Such behaviour is consistent with a monomeric, 17-electron complex containing one unpaired electron in a non-degenerate highest occupied molecular orbital (HOMO), and militates decisively against a dinuclear 18-electron complex with a Co–Co bond.

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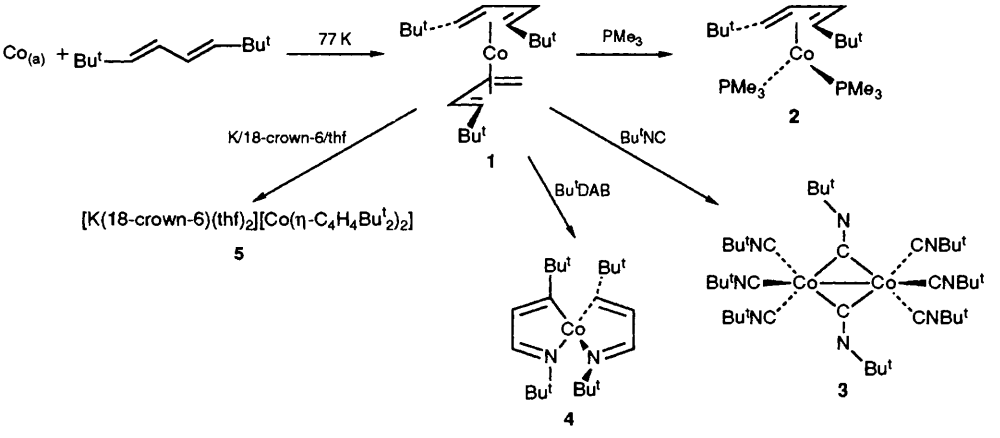
† Parent ions, with the appropriate isotope pattern, were observed in the mass spectra of **1–3**.

‡ Satisfactory microanalyses have been obtained for **1–4**.



Scheme 1

While **1** is quite stable at room temperature, we have found it to be very reactive towards a variety of other ligands. In particular, $[\mathrm{Co}(\eta\text{-}\mathrm{C_4H_4Bu^t{}_2})_2]$ is a versatile source of $\mathrm{Co^0}$ in solution, reacting with phosphines, diazadienes and isonitriles leading to the replacement of either one or both diene ligands, forming the novel half-sandwich complex $[\mathrm{Co}(\eta\text{-}\mathrm{C_4H_4Bu^t{}_2})(\mathrm{PMe_3})_2]$, **2**, $[\mathrm{Co(Bu^tNCHCHNBu^t)_2}]$,[7] **3** and $[\mathrm{Co_2(CNBu^t)_8}]$,[8] **4**, respectively, see Scheme 1.‡§

As an electron-deficient complex, **1** is susceptible to reduction. Reaction with potassium in tetrahydrofuran (thf) in the presence of 18-crown-6 affords claret-red crystals of $[\mathrm{K(18\text{-}crown\text{-}6)(thf)_2}][\mathrm{Co}(\eta\text{-}\mathrm{C_4H_4Bu^t{}_2})_2]$, **5**, in quantitative yield, see Scheme 1. The single-crystal X-ray structure¶ of this 18-electron anion clearly demonstrates the pseudo-tetrahedral arrangement of C=C double bonds about the cobalt. The latter is in contrast to the structure of $[\mathrm{Co(cod)_2Li(thf)_2}]$ in which the geometry is described as trigonal bipyramidal by virtue of bridging coordination from the diene to the coordinatively unsaturated lithium counterion.[9] A tetrahedral distribution of Bu^t groups about the metal dictates considerable coordinative saturation, and is probably the source of the stability of these complexes and the electronically unsaturated titanium and vanadium analogues.[3] The lengthening of the C=C double bonds and shortening of the C–C single bonds upon complexation in **5** compared with values typical of free dienes is indicative of the synergic bonding present in this type of

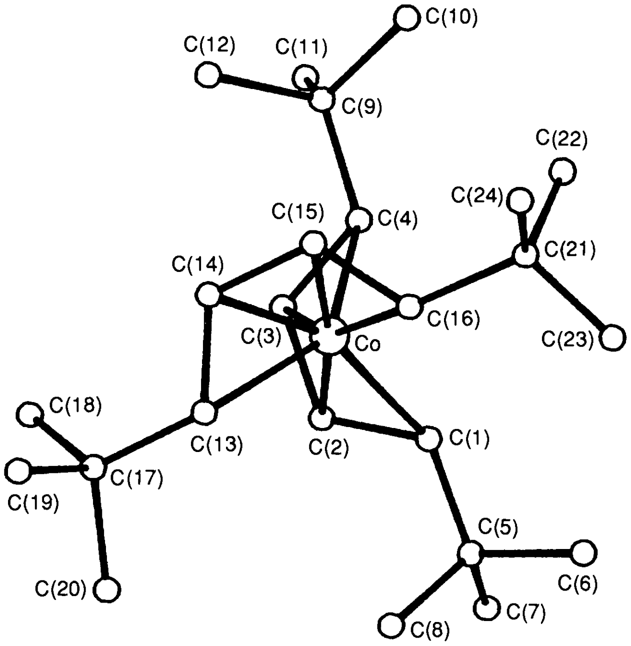


Fig. 1 Molecular structure of the anion of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co–C(1) 2.139(10), Co–C(2) 1.988 (11), Co–C(3) 2.018(9), Co–C(4) 2.168(10), C(1)–C(2) 1.399(14), C(2)–C(3) 1.42(2), C(3)–C(4) 1.411(14), Co–C(13) 2.168(10), Co–C(14) 2.022(10), Co–C(15) 1.988(11), Co–C(16) 2.132(10), C(13)–C(14) 1.42(2), C(14)–C(15) 1.416(15), C(15)–C(16) 1.41(2). Maximum deviation of Bu^t groups from plane defined by butadiene skeleton is 0.04(1) Å or 1.5(4)°.

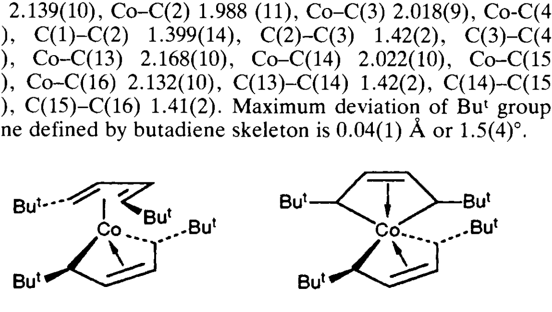


Fig. 2

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§ *ESR data* for **2** in toluene solution (298 K); weak, broad feature centred at $g = 2.12$. Intense pseudo-axial frozen solution spectrum (90 K), $g_\parallel = 2.003$, $A(\mathrm{Co})_\parallel = 47.6$ G, $g_\perp = 2.110$, $A(\mathrm{Co})_\perp < 10$ G (unresolved). ^{1}H NMR data for **2** in [^{2}H$_8$]toluene solution (298 K): δ −13.6 (s, br, fwhm 490 Hz, C*H*), δ 3.8 [s, br, fwhm 45 Hz, $\mathrm{C(C{\it H}_3)_3}$], δ 13.7 [s, br, fwhm 82 Hz, $\mathrm{P(C{\it H}_3)_3}$], δ 33.6 [s, br, fwhm 149 Hz, $\mathrm{P(C{\it H}_3)_3}$], δ 53.8 (s, br, fwhm 490 Hz, C*H*).

ESR data for **3** in toluene solution (298 K): weak isotropic octet centred at $g = 2.090$, $A(\mathrm{Co})_{\mathrm{iso}} = 62.2$ G. Intense frozen solution spectrum (94 K), $g_\perp = 1.947$, $A(\mathrm{Co})_\perp \approx 59$ G ($g_\perp$ and $g_\parallel$ overlap such that only seven of the eight cobalt hyperfine lines are resolved), $g_\parallel = 2.026$, $A(\mathrm{Co})_\parallel < 5$ G (unresolved). IR (Nujol) ν_{CN}/cm^{-1} 1460.

^{1}H NMR data for **4** in [^{2}H$_8$]toluene solution (298 K): δ 1.41 [$\mathrm{C(C{\it H}_3)_3}$]. M.p. 141 °C.

¶ *Crystal data* for **5**: $\mathrm{C_{42}H_{80}CoKO_8}$, $M = 811.1$, crystal size = *ca.* 0.4 × 0.4 × 0.3 mm, monoclinic space group $P2_1/c$, $a = 10.448(4)$, $b = 19.953(5)$, $c = 23.834(6)$ Å, $\beta = 93.33(2)°$, $V = 4967.4$ Å^3, $Z = 4$, $D_c = 1.09$ g cm^{-3}, $F(000) = 1768$, monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 4.7$ cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ–2θ scan mode. 5962 unique data were measured for $2 < \theta < 25°$, 2504 data with $|F^2| > 2\sigma(F^2)$, 464 variables, $R = 0.074$, $R_w = 0.088$ $\{w = [\sigma^2(F)]^{-1}, \Sigma w(|F_o| - |F_c|)^2$ minimised$\}$, $S = 2.3$, maximum and minimum peaks in final Fourier difference synthesis +0.67, −0.28 eÅ^{-3}. There was no crystal decay during data collection and no correction was made for absorption. The non-hydrogen atoms were located by direct methods and difference maps. Refinement was by full-matrix least-squares analysis with anisotropic thermal parameters on all non-hydrogen atoms except one disordered thf ligand in the cation, in which the C atoms were refined isotropically. Hydrogen atoms for the various ions were all held fixed at calculated positions with $U_{\mathrm{iso}} = 1.3\,U_{\mathrm{eq}}$ for the parent atom. 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.

complex. The cobalt-terminal carbon bond lengths are significantly longer than the cobalt-internal carbon bond lengths, with the Bu^t substituents lying in the plane of the butadiene skeleton. These features are typical of late transition metal butadiene complexes and suggest that the complex is best formulated as an L_2–diene complex of Co^{-1} **1** rather than an LX_2–metallacyclopentene complex of Co^I **A** or Co^{III} **B**.[10]

Compounds **1** and **5** therefore represent the first homoleptic butadiene complexes of cobalt, and **5** is the first crystallographically characterised butadiene sandwich complex. The facile syntheses of compounds **2**–**4** suggest **1** to be a versatile source of Co^0 in solution, and further study of the chemistry of these compounds in underway.

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References

1 F. G. N. Cloke, M. F. Lappert, G. A. Lawless and A. C. Swain, *J. Chem. Soc., Chem. Commun.*, 1987, 1667.

2 J. G. Brennan, F. G. N. Cloke, A. A. Sameh and A. Zalkin, *J. Chem. Soc., Chem. Commun.*, 1987, 1668.

3 F. G. N. Cloke and A. McCamley, *J. Chem. Soc., Chem. Commun.*, 1991, 1470, and references cited therein.

4 R. Mackenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 1974, 650.

5 P. L. Timms and T. W. Turney, *Adv. Organomet. Chem.*, 1977, **15**, 53.

6 J. L. Deutsch and S. M. Polling, *J. Chem. Educ.*, 1969, **46**, 167.

7 G. Van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 152.

8 W. E. Carroll, M. Green, A. M. R. Galas, M. Murray, T. W. Turney, A. J. Welch and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 80.

9 K. Jonas, R. Mynott, C. Krüger, J. C. Sekutowski and Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 767.

10 G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem.*, 1985, **24**, 1.