$(2,5\text{-}C_4H_2Bu^t{}_2N)_2Co$: the First Diazacobaltocene[1]

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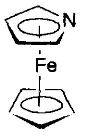
The synthesis of the 1,1′-diazacobaltocene **5** and its oxidation to the cobalticenium salt **7** is reported; **5** is characterised by X-ray structure analysis and cyclic voltammetry.

Although azaferrocene **1**[2,3] and azacymantrene **2**[3] have been mentioned as the first metal azacyclopentadienides[4] more than 25 years ago, stabilisation of the first 1,1′-diazametallocene **3**[5] has been reported only recently.[6] Apparently, both nucleophilic attack by the basic nitrogen atoms[7] in the diazametallocene structure and σ-rearrangement of the coordinated pyrrolide (pyr) ligand is prohibited by the steric demand of the *tert*-butyl substituents.

It seems remarkable that stabilisation of the diazametallocene structure by steric overcrowding is also affected with the



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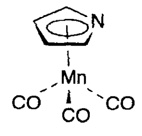

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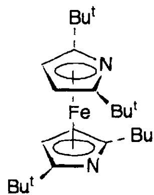

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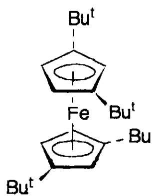

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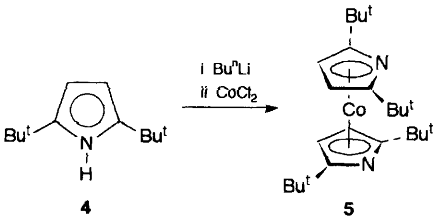

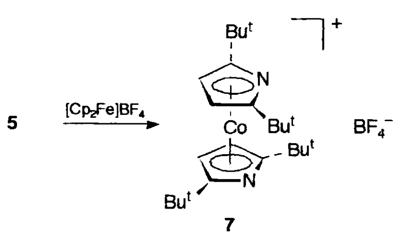

much more reactive cobaltocene system.[8] In fact, 2,2′,5,5′-tetra-*tert*-butyl-1,1′-diazacobaltocene **5** is obtained from $CoCl_2$ and lithiated 2,5-di-*tert*-butylpyrrole **4**[9] as a dark-violet solid in good yield.† The X-ray structure‡ reveals a geometry (C_2 symmetry) for the molecule (Fig. 1) very similar to that observed for the isotypic diazaferrocene **3**.[5] On comparison of the two metallocenes, the additional electron of **5** situated presumably in an antibonding molecular orbital causes a slight lengthening of the ligand to metal bond (pyr$_{centre}$–Co 1.758 Å) while the C–C and C–N distances between the ring atoms are decreased. The interplanar and torsion angles formed by the ring ligands (pyr–pyr′ 8.8 and N–pyr$_{centre}$–pyr′$_{centre}$–N′ 85.2°) show only minor deviations from those of the iron analogue **3**. Although a torsion angle P–Cp$_{centre}$–Cp′$_{centre}$–P′ of 90° has been calculated for 1,1′-diphosphaferrocene[10] the conformation observed in **3** and **5** seems to be a consequence from steric interactions between the bulky butyl substituents as is demonstrated by the analogous molecular structure of 1,1′,3,3′-tetra-*tert*-butylferrocene **6**.[11]

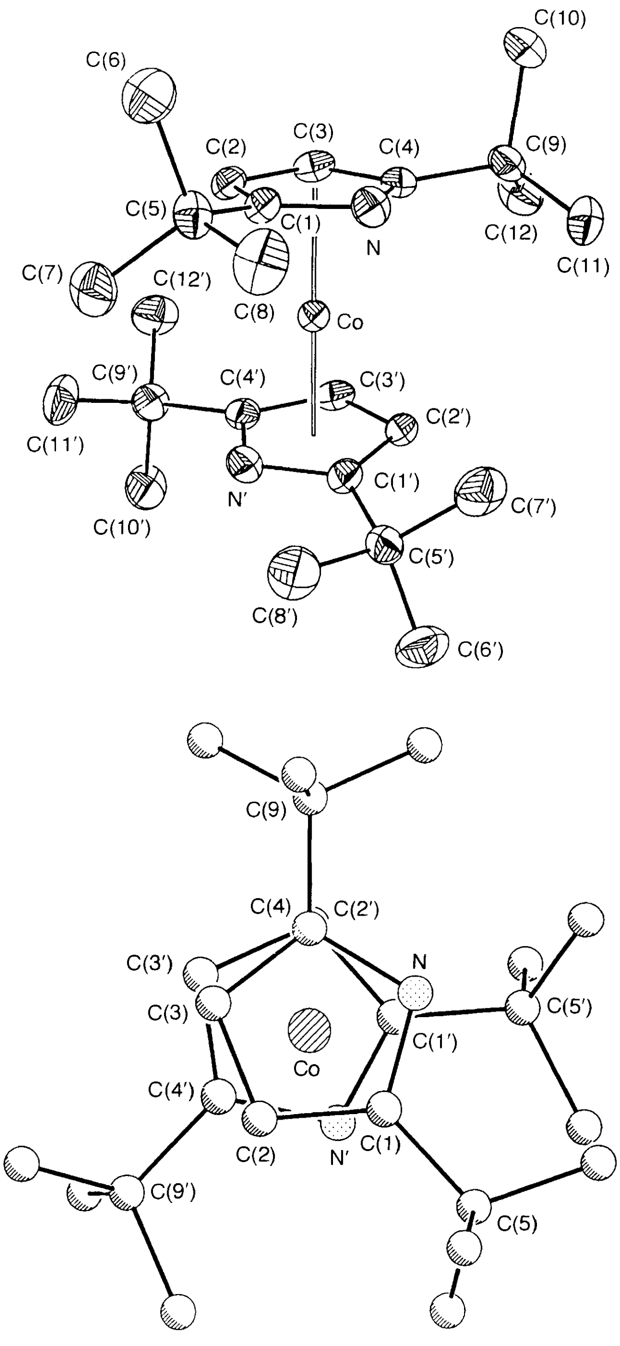

Fig. 1 Two views of the structure of $(2,5\text{-}C_4H_2Bu^t{}_2N)_2Co$ **5**. Selected bond lengths (Å) and angles (°): Co–N 2.176(3), Co–C(1) 2.158(3), Co–C(2) 2.090(4), Co–C(3) 2.109(3), Co–C(4) 2.105(3), N–C(1) 1.368(4), N–C(4) 1.418(4), C(1)–C(2) 1.437(5), C(2)–C(3) 1.414(5), C(3)–C(4) 1.402(5); N–Co–C(1′) 116.8(1), C(2)–Co–C(4′) 110.5(1), C(3)–Co–C(3′) 106.0(2), N–C(1)–C(2) 109.7(3), N–C(4)–C(3) 110.7(3), C(1)–N–C(4) 106.3(3), C(1)–C(2)–C(3) 107.3(3), C(2)–C(3)–C(4) 106.0(3).

In contrast with cobaltocene, **5** is fairly stable to air in the solid state. Although alkyl substituents are known to raise the reduction potentials of cobalticenium ions,[12] cyclic voltammetry of **5** (Fig. 2) shows its potential of the reversible one-electron oxidation to be shifted anodically compared to cobaltocene[13] by *ca.* 0.5 V.[14] A similar effect has been observed from the comparison of pyridine and benzene chromium complexes.[15] On the preparative scale, oxidation is

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† Stoichiometric amounts of $CoCl_2$ are added to 5.38 g (29.0 mmol) lithium 2,5-di-*tert*-butylpyrrolide (obtained from **4** and n-butyllithium) in 70 ml toluene and 10 ml tetrahydrofuran. The mixture is evaporated after 1 h and extracted with 40 ml n-pentane. Crystallisation from n-pentane at −78 °C gives 70% of **5** as dark-violet crystals, m.p. 113 °C (decomp.). MS (70 eV): m/z = 415 (54%, M^+), 400 (3, $[M^+ - Me]$), 343 (4, $[M^+ - Me, Bu]$), 179 (18, $C_4H_2Bu_2NH^+$), 164 (100, $[C_4H_2Bu_2NH^+ - Me]$) and further fragments.

‡ *Crystal data* for $(2,5\text{-}C_4H_2Bu^t{}_2N)_2Co$ **5**: tetragonal, space group $P\bar{4}2_1c$, $a = b = 8.653(1)$, $c = 31.162(6)$ Å, $U = 2333.11$ Å^3, $Z = 4$, $D_c = 1.169$ g cm^{-3}, $\mu = 0.73$ mm^{-1}, empirical absorption correction. The structure analysis is based on 2697 independent reflections (Mo-Kα, $2\theta_{max}$ 60°), 1841 of which were observed $[F_0 \geqslant 4\sigma(F_0)]$. The structure was solved using direct methods and refined using SHELXTL to $R = 0.037$, $R_w = 0.033$. 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.

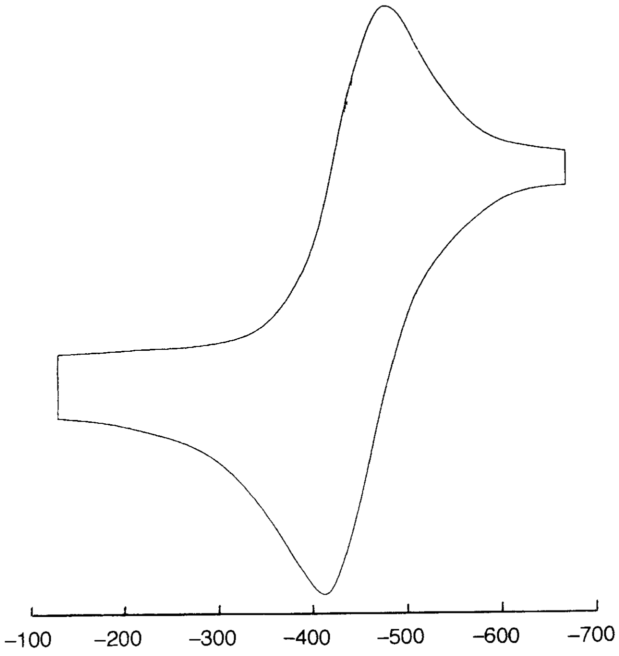

Fig. 2 Cyclic voltammetry of $(2,5\text{-}C_4H_2Bu^t{}_2N)_2Co$ **5** (10^{-4} mol dm^{-3} in MeCN) *vs.* Ag–AgCl–3 mol dm^{-3} KCl with 10^{-1} mol dm^{-3} $[(n\text{-}C_4H_9)_4N]BF_4$; 80 mV s^{-1}; ($E_{ox}$: −407 mV, E_{red}: −470 mV, $E_{\frac{1}{2}}$ −439 mV, i_{ox}/i_{red}: 0.96)

best achieved by use of ferricenium salts.§ The stable diamagnetic tetrafluoroborate salt **7** is isoelectronic with the iron compound **3** and shows as well the characteristic upfield coordination shift of the ring carbon atoms (**4**: δ 101.5 and 139.7).

Owing to the relevance of cobaltocene in organometallic synthesis,[16] reduction of **5** should provide a useful route to azacyclopentadienyl cobalt species.

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References

1 For Part 12 of the series: Heterocycles as Ligands, see N. Kuhn, M. Schulten, R. Boese and D. Bläser, *Chem. Ber.*, in the press.
2 R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 796.
3 K. K. Joshi, P. L. Pauson, A. R. Qazi and W. H. Stubbs, *J. Organomet. Chem.*, 1964, **1**, 471.
4 For a recent review on azacyclopentadienyl metal compounds, see N. Kuhn, *J. Chim. Soc. Belges*, 1990, **99**, 707.
5 N. Kuhn, K. Jendral, R. Boese and D. Bläser, *Chem. Ber.*, 1991, **124**, 89.
6 Stabilisation of the diazaferrocene structure is favoured by blocking the nitrogen atoms with Lewis acidic fragments, see N. Kuhn, E.-M. Horn, R. Boese and N. Augart, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1368; 1989, **28**, 342; N. Kuhn and E.-M. Horn, *Inorg. Chim. Acta*, 1990, **170**, 155; N. Kuhn, E.-M. Horn, R. Boese and D. Bläser, *Chem. Ber.*, 1989, **122**, 2275; N. Kuhn, A. Kuhn and E.-M. Lampe, *Chem. Ber.*, 1991, **124**, 997.
7 For the basicity of azacyclopentadienyl ligands in azaferrocenes, see N. Kuhn, M. Schulten, E. Zauder, N. Augart and R. Boese, *Chem. Ber.*, 1989, **122**, 1891.
8 There are only a few examples for azacyclopentadienyl cobalt compounds; N. Kuhn, H. Brüggemann, M. Winter and V. M. de Bellis, *J. Organomet. Chem.*, 1987, **320**, 391; K. J. Chase and R. M. Grimes, *Organometallics*, 1989, **8**, 2492.
9 R. Ramaaseul and A. Rassat, *Chem. Commun.*, 1965, 453.
10 N. M. Kostic and R. F. Fenske, *Organometallics*, 1983, **2**, 1008.
11 Z. L. Kaluski, A. I. Gusev, A. E. Kalinin and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1972, **13**, 950; R. Boese and M. Antipin, unpublished results.
12 See, *e.g.* N. El Murr and E. Laviron, *Can. J. Chem.*, 1976, **54**, 3350; U. Koelle and F. Khouzami, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 640.
13 U. Koelle, *J. Organomet. Chem.*, 1978, **152**, 225.
14 Unfortunately, the potential of the known oxidation of $(1,3\text{-}C_5H_3Bu^t{}_2)_2Co$ has not been reported, J. Okuda, *J. Organomet. Chem.*, 1990, **385**, C39.
15 C. Elschenbroich, J. Koch, J. Kroker, M. Wünsch, W. Massa, G. Baum and G. Stork, *Chem. Ber.*, 1988, **121**, 1983.
16 For a review, see K. Jonas, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 292.

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§ Stoichiometric amounts of ferricenium tetrafluoroborate are added to a solution of 0.64 g (1.55 mmol) **5** in 4 ml dichloromethane. After 30 min the cobalticenium salt is precipitated by addition of 40 ml of diethyl ether. Recrystallisation from dichloromethane–diethyl ether gives 72% of **7** as yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, Bu^t), 6.32 (s, 4H, azacyclopentadienyl H); ^{13}C NMR ($CDCl_3$): δ 30.02 (Me), 33.23 (quaternary C) 82.21 (C-3,4), 137.58 (C-2,5).