Journal of Organometallic Chemistry, 443 (1993) C39–C40

JOM 23144PC

Preliminary Communication

Synthesis and X-ray structure of a highly-hindered *N*-functionalized alkyl-cobalt(II) complex *trans*-$[\overline{\text{Co}\{[\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}}\text{-2}\}_2]$

Wing-Por Leung, Hung-Kay Lee, Zong-Yuan Zhou and Thomas C.W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T. (Hong Kong)

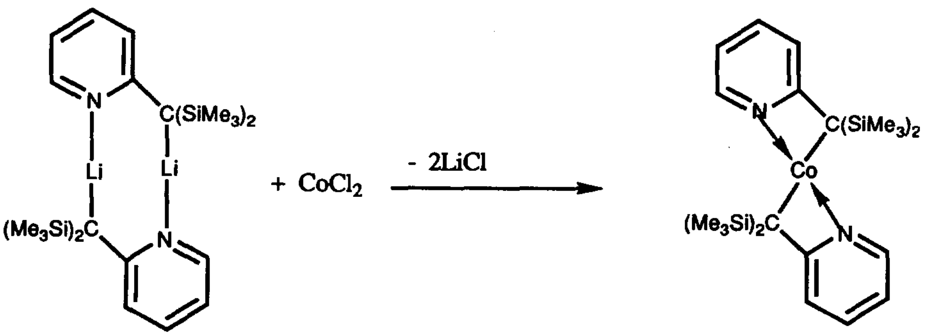
(Received July 13, 1992)

Abstract

The thermally-stable cobalt(II) dialkyl compound CoR_2 [R = $C(SiMe_3)_2C_5H_4N$-2] (**1**) has been prepared by reaction of $[\{LiR\}_2]$ with cobalt(II) chloride in ether. An X-ray structural study has revealed a centrosymmetric molecular skeleton (for two nearly identical independent molecules) in which a pair of sterically-hindered, functionalized pyridine ligands R^- are *trans*-chelated to the central planar four-coordinate cobalt(II) atom, with mean Co–C_α and Co–N distances of 2.094(6) Å and 1.919(4) Å respectively, and a C_α–Co–N angle of 69.6(2)°.

A new cobalt(II) dialkyl, CoR_2 [R = $C(SiMe_3)_2C_5H_4N$-2] (**1**), of remarkable thermal stability has been obtained from the reaction of $[(LiR)_2]$ [1] with $CoCl_2$ in ether (Scheme 1). Compound **1** was isolated in good yield (81%) as a deep-red crystals (m.p. 116–118°C) and characterized by microanalysis, mass spectrometry {*m/z* 531 [M^+]} and X-ray crystal structural study [15 *]. It can be sublimed at *ca.* 160°C under vacuum (ca. 10^{-2} mmHg). This high thermal stability of **1** contrasts with the low stability of $Co(mesityl)_2$ which decomposes easily at room temperature [2]. In addition, cobalt(II) dibutyl and dibutenyl have been observed as intermediates which decompose readily to alkanes or their coupled products [3]. The versatility of R^- in the preparation of metal alkyls has been demontrated previously in the synthesis of a variety of compounds. For example, compounds such as dimeric $(MR)_2$ (M = Li [1], Cu [4], Ag [5]) and monomeric MR_2 (M = Mg, Zn, Cd, Hg [6] and Sn [7]), M(R)X [M = Sn, X = Cl, $N(SiMe_3)_2$] [7], $M(R)Cl_2$ (M = As, Sb, Bi) [8], AlR_2Cl, and $[AlR_2][AlCl_4]$ [9] have been prepared and structurally characterized. To our knowledge compound **1** is the first well-characterized neutral dialkyl compound of cobalt(II) since only the preparation of the pentacoordinate cobalt(II) dimethyltris(trimethylphosphine) complex $[CoMe_2(PMe_3)_3]$ has been reported [10].

In the solid state compound **1** contains two independent molecules of nearly the same structure (Fig. 1), each being located at a crystallographic inversion centre. The central cobalt(II) atom is planar four-coordinate, being surrounded by a pair of ligands R^- in a *trans*-chelating fashion with mean Co–C_α and Co–N bond distances of 2.094(6) and 1.919(4) Å, respectively. This Co–C_α distance is significantly longer than the corresponding bond distances of 1.931(5) Å in



Scheme 1.

Correspondence to: Dr. W.-P. Leung.

* References numbers with asterisks indicate notes in the list of references.

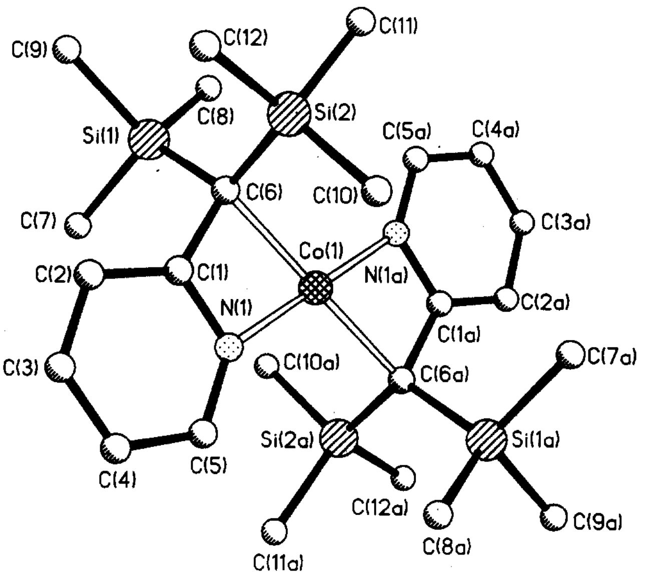


Fig. 1. Molecular structure of *trans*-[$\overline{\mathrm{Co}\{\mathrm{C(SiMe_3)_2C_5H_4N}}$-2}$_2$] (1) and the atom numbering scheme for each of the two nearly identical molecules in the asymmetric unit.

[Co(C_6F_5)$_2$(η^6-$C_6H_5CH_3$)] [11] and 1.994(3) Å in *trans*-[Co(mesityl)$_2$(PPhEt$_2$)$_2$] [12], presumably as a consequence of the greater steric demand of ligand R^- in compound **1**. Two SiMe$_3$ groups, one from each of the ligands R^-, are located in the vicinity of the idealized fifth and sixth octahedral sites on both sides of the coordination plane. Effective shielding of the cobalt(II) atom from potential reactants thus accounts for the remarkable stability of compound **1**. The C_α–Co–N bond angle of 69.6(2)° in **1** is relatively larger than the corresponding angles of 67.3(2)° and 59.0(2)° in the Mg [6] and Sn [7] analogues respectively, since both Main-Group metals adopt a tetrahedral coordination geometry.

The magnetic moment of 3.11 μ_B for the paramagnetic compound **1** in benzene, as measured by Evan's NMR method [13], is marginally higher than the values in the range of 2.1–2.9 μ_B reported for several d^7 square planar spin-paired bivalent cobalt complexes [14]. These high values are common for cobalt(II) complexes with one unpaired electron owing a large orbital contribution to the magnetic moment.

Acknowledgments

This work is supported by Hong Kong Research Grants Council Earmarked Grant A/C No. 221600010.

References and notes

1 D. Colgan, R. I. Papasergio, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, (1984) 1708.

2 M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, *83* (1961) 825.

3 D. B. Denney and W. R. Davis, *J. Organomet. Chem.*, *24* (1970) 537.

4 R. I. Papasergio, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, (1983) 1419.

5 R. I. Papasergio, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, (1984) 612.

6 M. J. Henderson, R. I. Papasergio, C. L. Raston, A. H. White and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, (1986) 672.

7 L. M. Engelhardt, B. S. Jolly, M. F. Lappert, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, (1988) 336.

8 C. Jones, L. M. Engelhardt, P. C. Junk, D. S. Hutchings, W. C. Patalinghug, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun:*, (1991) 1560.

9 L. M. Engelhardt, U. Kynast, C. L. Raston and A. H. White, *Angew. Chem., Int. Ed. Engl.*, *26* (1987) 681.

10 H. F. Klein and H. N. Karsch, *Chem. Ber.*, *109* (1976) 1453.

11 B. B. Anderson, C. L. Behrens, L. J. Radonovich and K. J. Klabunde, *J. Am. Chem. Soc.*, *98* (1976) 5390.

12 L. Falvello and M. Gerloch, *Acta Crystallogr., Sect. B*, *35* (1979) 2547.

13 D. F. Evans, *J. Chem. Soc.*, (1959) 2003.

14 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, (1959) 338.

15 Crystal data for **1**, $C_{24}H_{44}N_2Si_4Co$, M = 531.99, triclinic, space group $P\bar{1}$ (No. 2), a = 8.519(2), b = 11.906(6), c = 16.212(6) Å, α = 70.12(3), β = 80.74(3), γ = 82.96(3)°, V = 1522(1) Å^3, Z = 2, D_c = 1.161 g cm^{-3}. Monochromatized Mo Kα radiation, λ = 0.71073 Å, μ = 7.30 cm^{-1}. Data were collected using a crystal of dimensions *ca.* 0.26×0.24×0.34 mm, sealed in a capillary under dinitrogen, on a Nicolet R3m/V diffractometer. A total of 4850 unique reflections were measured for $2\theta_{max}$ = 50°, $+h \pm k \pm l$, and 3356 'observed' reflections with $|F_o| \geq 6\sigma(|F_o|)$ were used in the structure solution and refinement. The structure was solved by the Patterson method using the computer program SHELXTL-PLUS on a DEC MicroVAX II computer and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. The asymmetric unit comprises two 'half molecules' with both independent cobalt atoms occupying $\bar{1}$ sites. The weighting scheme $w = [\sigma^2(F_o) + 0.0003|F_o|^2]^{-1}$ was used, and the final residues were R = 0.064, wR = 0.066. The atomic coordinates, bond lengths and angles, temperature factors, and H atom parameters have been deposited at the Cambridge Crystallographic Data Centre.