

B—N bond cleavage by cobalt(II) in acetato(3,5-diphenylpyrazole)-[tris(3,5-diphenylpyrazolyl)borato]-cobalt(II)

David J. Harding,^{a*} Harry Adams^b and Thawatchai Tuntulani^c

^aDepartment of Chemistry, School of Science, Walailak University, Thasala, Nakorn Si Thammarat 80160, Thailand, ^bDepartment of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, England, and ^cDepartment of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
Correspondence e-mail: h david@wu.ac.th

Received 23 March 2005

Accepted 4 May 2005

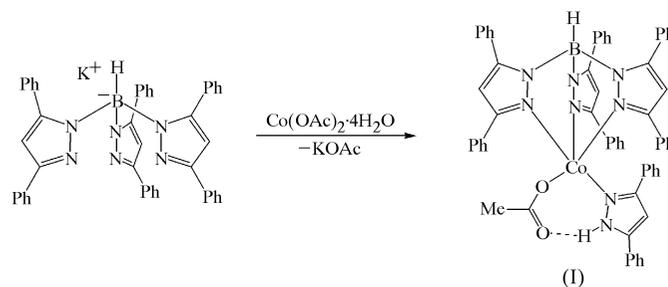
Online 20 May 2005

The reaction of cobalt(II) acetate with potassium tris(pyrazolyl)borate (KTP^{Ph2}) affords the title complex, [Co(Tp^{Ph2})(O₂CMe)(Hpz^{Ph2})] (Hpz^{Ph2} is 3,5-diphenylpyrazole) or [Co(C₄₅H₃₄BN₆)(C₂H₃O₂)(C₁₅H₁₂N₂)], as a result of cobalt-induced B—N bond cleavage of the tris(pyrazolyl)borate ligand. The cobalt complex exhibits a distorted CoN₄O coordination geometry with a κ^3 -coordinated Tp^{Ph2} ligand and monodentate acetate and pyrazole ligands. In addition, the non-coordinated acetate O atom is involved in a weak intramolecular hydrogen-bonding interaction with the pyrrole NH group.

Comment

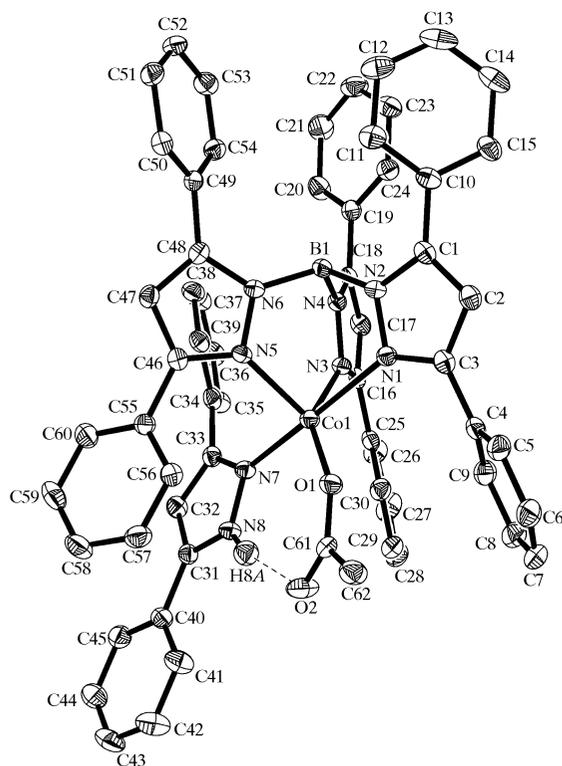
The tris(pyrazolyl)borate ligands, HB(pz)₃[−], first introduced by Trofimenko (1993), have found widespread use in coordination chemistry. Their popularity arises from their ease of preparation and the readiness with which their steric and electronic properties may be varied. The use of tris(pyrazolyl)borates of intermediate steric bulk, namely tris(3,5-diphenylpyrazolyl)borate (Tp^{Ph2}), is of particular interest to us as these compounds inhibit the formation of chemically inactive sandwich complexes, ML₂ [L = tris(pyrazolyl)borate], without enforcing tetrahedral geometry upon the metal. Tris(3,5-diphenylpyrazolyl)borate was first synthesized by Kitajima *et al.* (1992) and since then many complexes with Cu^I and Cu^{II} have appeared (Carrier *et al.*, 1993; Halcrow *et al.*, 1997; Chia *et al.*, 2000; Foster *et al.*, 2000). In contrast, Co^{II} (Ruman *et al.*, 2002) and Ni^{II} (Guo *et al.*, 1998) complexes remain poorly represented. Indeed, in the case of Co^{II}, the only reported complex, [Co(Tp^{Ph2})(NO₃)], was isolated as a by-product (Ruman *et al.*, 2002). The reaction of cobalt(II) acetate tetrahydrate with KTP^{Ph2} in a 1:1 molar ratio yields deep-purple crystals shown by X-ray analysis to be [Co-

(Tp^{Ph2})(O₂CMe)(Hpz^{Ph2})] (Hpz^{Ph2} is 3,5-diphenylpyrazole), (I). The high purity of the tris(pyrazolyl)borate reagent, *i.e.* KTP^{Ph2}, indicates that the source of Hpz^{Ph2} is not a ligand impurity but the result of metal-mediated B—N bond cleavage. Interestingly, the reaction between Co(O₂CMe)₂ and the related ligand KTP^{Ph} yields [Co(Tp^{Ph})(O₂CMe)] as the only product (Kremer-Aach *et al.*, 1997). However, reactions with Cu^{II} salts (X = Cl and O₂CMe) yield B—N-cleaved products, [Cu(Tp^{Ph})X(Hpz^{Ph})], apparently as a result of the increased Lewis acidity of Cu²⁺ compared with Co²⁺ (Halcrow *et al.*, 1997; Chia *et al.*, 2000). Thus, it appears that the subtle differences between Tp^{Ph2} and Tp^{Ph} result in the formation of B—N-cleaved products.



The results of X-ray analysis are supported by the FAB mass spectrum, which shows a strong peak at 787 corresponding to [Co(Tp^{Ph2})(O₂CMe)]⁺ and a weaker signal at 1008 suggesting the presence of [Co(Tp^{Ph2})(O₂CMe)(Hpz^{Ph2})]⁺. IR spectroscopy shows a strong B—H stretch at 2627 cm^{−1}, indicative of a κ^3 -coordinated Tp^{Ph2} ligand, while an N—H stretch at 3427 cm^{−1} confirms the presence of a bound pyrazole group. Moreover, the difference in the symmetric and asymmetric stretch of the acetate ligand [$\Delta\nu(\text{CO}_2) = 149 \text{ cm}^{-1}$] indicates that the ligand is monodentate (Kremer-Aach *et al.*, 1997). Finally, elemental analysis (see *Experimental*) of the bulk sample was consistent with the formulation [Co(Tp^{Ph2})(O₂CMe)(Hpz^{Ph2})], and thus the crystals were considered representative of the sample.

The complex crystallizes in the triclinic space group $P\bar{1}$, with no solvent molecules in the crystal structure. The cobalt ion is five-coordinate (Fig. 1) and adopts a coordination geometry intermediate between trigonal bipyramidal (tbp; with N1 and N7 as the axial atoms, and N5, N3 and O1 as the equatorial atoms) and square pyramidal (with N1, N7, N3 and O1 as the basal atoms, and N5 as the apical atom). Of particular note is the N3—Co1—O1 angle, which is nearly 30° greater than an ideal tbp equatorial angle, and the N3—Co1—N5 and O1—Co1—N5 angles, which are significantly contracted (Table 1). The highly distorted geometry around the metal atom is probably a result of the large steric bulk of the Tp^{Ph2} and pyrazole ligands. As expected, the Tp^{Ph2} ligand is κ^3 -coordinated, although in contrast to [Co(Tp^{Ph2})(η^2 -NO₃)], the Co—N_{pz} bonds are not all equivalent, with the Co—N1 bond approximately 0.2 Å longer than the Co—N3 and Co—N5 bonds (Ruman *et al.*, 2002). A similar observation has been noted in the structure of [Co(Tp^{Ph})(NCS)(THF)] (THF is


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level. The hydrogen-bonding interaction of H8A to O2 is shown by a dashed line. Other H atoms have been omitted for clarity.

tetrahydrofuran), where the Co–N_{pz} bonds are 2.054 (4), 2.079 (4) and 2.180 (4) Å (Calabrese *et al.*, 1986). The acetate ligand in (I) is bound in a monodentate fashion, with a weak intramolecular N–H···O hydrogen bond between the non-coordinated acetate O atom and the pyrrole NH group (Table 2). An almost identical interaction occurs in the structure of [Cu(Tp^{Ph})(O₂CMe)(Hpz^{Ph})], where the O···N distance is 2.612 (5) Å and the O···H–N angle is 149° (Chia *et al.*, 2000).

Experimental

KTp^{Ph2} was prepared according to the literature method of Kitajima *et al.* (1992). Co(O₂CMe)₂·4H₂O (82 mg, 0.33 mmol) was dissolved in a tetrahydrofuran–methanol (5:1 ml) solution. KTp^{Ph2} was then dissolved in tetrahydrofuran (5 ml) and added dropwise to the metal solution, resulting in a colour change from orange to red–brown. The solution was stirred for 4 h and then reduced to dryness *in vacuo*. The solid was washed with ethanol (3 × 5 ml) and then with diethyl ether (5 ml). The solid was redissolved in dichloromethane (2 ml) and then filtered through celite, yielding a deep-pink–purple solution that was layered with hexanes (10 ml). After 2 d, deep-purple crystals were collected and washed with hexane and ether to give [Co–(Tp^{Ph2})(O₂CMe)(Hpz^{Ph2})] (yield 131 mg, 44%). Analysis calculated for C₆₂H₄₉BCoN₈O₂ (*M_r* = 1007.83): C 73.89, H 4.90, N 11.12%; found: C 73.85, H 5.16, N 11.06%. MS/FAB (*m/e*): 1008, 787. IR (KBr, cm⁻¹): 3427 (νNH), 2627 (νBH), 1558 [ν(CO₂)_{as}], 1409 [ν(CO₂)_{sym}].

Crystal data

[Co(C₄₅H₃₄BN₆)(C₂H₃O₂)–
(C₁₅H₁₂N₂)]
M_r = 1007.83
Triclinic, *P* $\bar{1}$
a = 13.5669 (12) Å
b = 14.0474 (12) Å
c = 15.4195 (14) Å
 α = 84.568 (2)°
 β = 66.500 (1)°
 γ = 67.199 (1)°
V = 2478.1 (4) Å³

Z = 2
D_x = 1.351 Mg m⁻³
Mo K α radiation
Cell parameters from 7380
reflections
 θ = 4.4–53.1°
 μ = 0.40 mm⁻¹
T = 150 (2) K
Block, purple
0.39 × 0.21 × 0.21 mm

Data collection

Bruker SMART 1000
diffractometer
 ω scans
Absorption correction: multi-scan
(SADABS; Bruker 1997)
T_{min} = 0.859, *T_{max}* = 0.920
28 606 measured reflections

11 119 independent reflections
7921 reflections with *I* > 2σ(*I*)
R_{int} = 0.041
 θ_{max} = 27.6°
h = –17 → 17
k = –18 → 18
l = –20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.044
wR(*F*²) = 0.105
S = 1.03
11 119 reflections
669 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.4199P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 0.36 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Co1–O1	1.9712 (14)	Co1–N7	2.1443 (16)
Co1–N3	2.0305 (16)	Co1–N1	2.2896 (16)
Co1–N5	2.0347 (16)		
O1–Co1–N3	147.09 (6)	N5–Co1–N7	94.55 (6)
O1–Co1–N5	109.95 (6)	O1–Co1–N1	82.87 (6)
N3–Co1–N5	96.58 (6)	N3–Co1–N1	79.34 (6)
O1–Co1–N7	103.17 (6)	N5–Co1–N1	87.00 (6)
N3–Co1–N7	93.45 (6)	N7–Co1–N1	172.76 (6)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N8–H8A···O2	0.88	1.78	2.637 (2)	163

H atoms were positioned geometrically and refined using a riding model (including torsional freedom for methyl groups), with C–H distances of 0.95–0.98 Å, and with *U*_{iso}(H) values constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge the Thailand Research Fund (MRG4680139) for supporting this work and Walailak University for a collaborative research grant (both to DJH). The authors also thank Professor M. D. Ward of the University of Sheffield for the use of laboratory facilities during the course of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1208). Services for accessing these data are described at the back of the journal.

References

- Bruker (1997). *SMART, SAINT, SHELXTL* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Calabrese, J. C., Trofimenko, S. & Thompson, J. S. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1122–1123.
- Carrier, S. M., Ruggiero, C. E., Houser, R. P. & Tolman, W. B. (1993). *Inorg. Chem.* **32**, 4889–4899.
- Chia, L. M. L., Radojevic, S., Scowen, I. J., McPartlin, M. & Halcrow, M. A. (2000). *J. Chem. Soc. Dalton Trans.* pp. 133–140.
- Foster, C. L., Liu, X., Kilner, C. A., Thornton-Pett, M. & Halcrow, M. A. (2000). *J. Chem. Soc. Dalton Trans.* pp. 4563–4568.
- Guo, S., Ding, E., Yin, Y. & Yu, K. (1998). *Polyhedron*, **17**, 3841–3849.
- Halcrow, M. A., Davies, J. E. & Raithby, P. R. (1997). *Polyhedron*, **16**, 1535–1541.
- Kitajima, N., Fujisawa, K., Fujimoto, C., Moro-oka, Y., Hashimoto, S., Kitagawa, T., Toriumi, K., Tatsumi, K. & Nakamura, A. (1992). *J. Am. Chem. Soc.* **114**, 1277–1291.
- Kremer-Aach, A., Kläui, W., Bell, R., Strerath, A., Wunderlich, H. & Mootz, D. (1997). *Inorg. Chem.* **36**, 1552–1563.
- Ruman, T., Ciunik, Z., Mazurek, J. & Wolowiec, S. (2002). *Eur. J. Inorg. Chem.* pp. 754–760.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.