Inorg. Chem. **2004**, *43*, 4927–4934

Inorganic Chemistry
Article

# Cobalt Half-Sandwich, Sandwich, and Mixed Sandwich Complexes with Soft Tripodal Ligands

**Christopher A. Dodds,[†] Mario-Alexander Lehmann,[†] Jonathan F. Ojo,[‡] John Reglinski,[*,†] and Mark D. Spicer[*,†]**

*Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, U.K., and Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria*

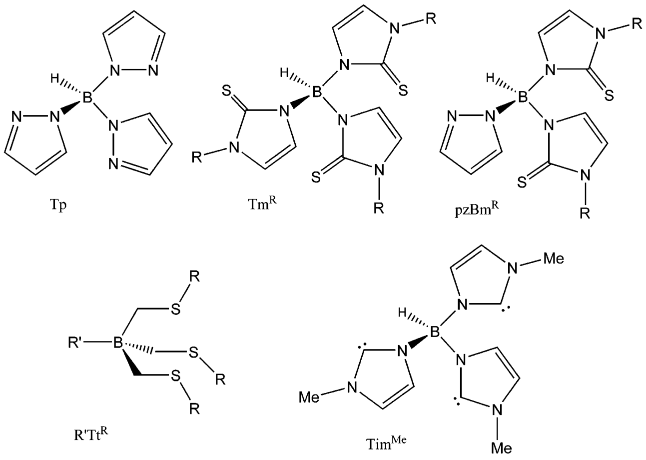
Received March 16, 2004

Reaction of sodium hydrotris(methimazolyl)borate ($NaTm^{Me}$) with cobalt halides leads to the formation of paramagnetic pseudotetrahedral $[Co(Tm^{Me})X]$ ($X = Cl$, Br, I), of which the bromide has been crystallographically characterized. Mass spectrometry reveals the presence of higher molecular weight fragments $[Co(Tm^{Me})_2]^+$ and $[Co_2(Tm^{Me})_2X]^+$ in solution. Aerial oxidation in donor solvents (e.g. MeCN) leads to formation of the $[Co(Tm^{Me})_2]^+$ cation, which has been crystallographically characterized as the $BF_4^-$, $ClO_4^-$, $Br^-$, and $I^-$, salts. Attempts to prepare the mixed sandwich complex, $[Co(Cp)(Tm^{Me})]^+$, resulted in ligand decomposition to yield $[Co(mtH)_3I]I$ (mtH = 1-methylimidazole-2-thione), but with the more electron donating methylcyclopentadienyl ($Cp^{Me}$) ligand, $[Co(Cp^{Me})(Tm^{Me})]I$ was isolated and characterized. Electrochemical measurements reveal that the cobalt(III) $Tm^{Me}$ complexes are consistently more difficult to reduce than their Tp and Cp congeners.

## Introduction

The reactivity of metal-based reagents and catalysts is modulated to a great extent by the nature of the ligands which complete their coordination sphere. Typically this reactivity is controlled by alteration of steric bulk and electron donor properties. Although the chemical literature is rich in studies which seek to design new ligand systems, many workers regularly return to the ubiquitous cyclopentadienide (Cp) and phosphine ligands as their basic chemical building blocks. While phosphines are readily altered, both sterically and electronically, such alteration for cyclopentadienyl ligands is much more difficult to achieve.[1] Consequently there has been significant interest in generating facially capping ligands that facilitate such tuning of the metal center. In 1966 Trofimenko[2] introduced the somewhat harder facially capping ligands, the polypyrazolylborate anions (Tp and pzTp; Chart 1), the metal complexes of which in many instances parallel those formed with Cp. More recently broadly analogous softer ligand systems such as the tetrakis{(methylthio)-methyl}borate anion (Tt)[3] and the hydrotris(methimazolyl)-borate anion ($Tm^{Me}$)[4] have appeared. Concurrent with the appearance of these soft tripodal ligands, Fehlhammer has reported the synthesis of a much harder ligand motif (cf.

**Chart 1**



---

[*] Authors to whom correspondence should be addressed. E-mail: j.reglinski@strath.ac.uk (J.R.); m.d.spicer@strath.ac.uk (M.D.S.). Tel: +44 141 548 2349 (J.R.); +44 141 548 2800 (M.D.S.). Fax: +44 141 552 0876 (J.R. and M.D.S.).

[†] University of Strathclyde.

[‡] Obafemi Awolowo University.

(1) Tolman, W. B. *Chem. Rev.* **1977**, *77*, 313.

(2) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842.

(3) Ge, P.; Haggerty, B. S.; Rheingold, A. L.; Riordan, C. G. *J. Am. Chem. Soc.* **1994**, *16*, 8406.

(4) Cassidy, I.; Garner, M.; Kennedy, A. R.; Reglinski. J.; Spicer, M. D. *J. Chem. Soc., Chem. Commun.* **1996**, 1975.

10.1021/ic0496525 CCC: $27.50

Tp) namely the tripodal N-heterocyclic carbene ligand, hydrotris(1-methyl-imidazol-2-ylidene)borate anion (Tim)[5] and its iron(III) and cobalt(III) complexes, $[M(Tim)_2]^+$. Thus, a great diversity of facially capping tripodal ligands is now available.

A systematic investigation of the chemistry of $Tm^{Me}$, a softer analogue of Cp and Tp, is ongoing in our laboratories. A consistent theme in these studies has been the parallels between the complexes of these three facially capping ligands (in particular their bonding and structures) in an attempt to decipher the trends and divergent reaction profiles of these popular ligand systems. Recent work on molybdenum and tungsten carbonyl complexes[6] has highlighted some aspects of the bonding in these species. Although $Tm^{Me}$ has been identified as a soft analogue of Cp (which is in turn softer than Tp), the effects of these ligands on the carbonyl stretching frequencies in $[W(L)(CO)_3I]$ and in $[Mo(L)(CO)_2(\eta^3\text{-}C_3H_5)]$ (L = Cp, Tp, $Tm^{Me}$) places them in the order Cp < Tp < Tm in terms of their donor ability to the metal center. Thus, the application of the terms "hard" and "soft" in these systems is apparently not particularly helpful. Rather, the trends would appear to relate to the bonding modes of the respective ligands. The $Tm^{Me}$ ligand may be considered a $\sigma$-donor, $\pi$-donor, which results in greater electron density at the metal center than for Tp ($\sigma$-donor only) and Cp ($\sigma$-donor, $\pi$-acceptor). This varying electron donor ability also modulates the structural characteristics of the allyl ligand in $[Mo(L)(CO)_2(\eta^3\text{-}C_3H_5)]$, with clear trends in both the Mo−C distances to and C−C distances within the allyl fragments being observed.

This behavior prompted us to return to the analysis of analogues of cyclopentadienyl complexes and, in particular, those of iron and cobalt. The chemistry of iron[7] with $Tm^{Me}$ was found to be dominated by the formation of $[Fe(Tm^{Me})_2]$, at face value a direct analogue of ferrocene. However, unlike ferrocene, it was found to be a high-spin iron(II) species (again consistent with a $\pi$-donor ligand) which decomposed under oxidizing conditions rather than forming a ferrocenium ion analogue. Subsequently, our attention has turned to cobalt. A series of cobalt(II) and cobalt(III) adducts with the anionic face-capping ligands Tp,[8] Cp,[9] $Tm^{Ph}$,[10] $pzBm^{Me}$,[10] Tt,[11] and Tim[5b] is well established, and thus, an extension to the soft face-capping ligand, $Tm^{Me}$, was considered desirable. The results of our studies are reported herein.

## Experimental Section

All chemicals were commercially obtained and used without further purification. Sodium[12] and thallium[13] hydrotris(methimazolyl)borate, $[CoCp(CO)I_2]$, and $[CoCp^{Me}(CO)I_2]$[14] were prepared by published methods. All NMR spectra were recorded on a Bruker AMX 400 spectrometer operating at 400.1 MHz for $^1H$, 100 MHz for $^{13}C$, and 94.94 MHz for $^{59}Co$. $^1H$ and $^{13}C$ spectra were referenced to internal solvent peaks and thus to TMS, while $^{59}Co$ spectra were referenced to external 1.0 M $K_3[Co(CN)_6]$ in $D_2O$. Magnetic measurements were determined at room temperature in the solid state using an MSB1 magnetic susceptibility balance. UV−visible spectra were recorded in solution (dichloromethane, acetonitrile, 300−850 nm) using a Perkin-Elmer Lambda 16 spectrometer and by solid-state reflectance using a Photonics CCD array UV−visible spectrometer (400−900 nm) and a Perkin-Elmer Lambda 19 spectrometer (900−2000 nm). Mass spectra were recorded at the EPRSC facilities at University of Wales, Swansea, U.K., using a Finnegan MAT95 or MAT900.

**Preparation of $[Co(Tm^{Me})Cl]$.** $CoCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol) was refluxed with $TlTm^{Me}$ (0.28 g, 0.5 mmol) in acetone (100 mL) for 3 h. The thallium chloride precipitate was removed by filtration and the solution reduced in volume. The product was precipitated as an olive green solid by addition of excess hexane, collected by filtration, washed twice with diethyl ether, and dried in vacuo. Yield: 0.92 g, 41%.

Anal. Found: C, 29.72; H, 3.83; N, 16.76. Calcd for $C_{12}H_{16}BClCoN_6S_3\cdot 0.75CH_2Cl_2$: C, 30.07; H, 3.46; N, 16.50. [Although the microanalysis can be scaled using lattice solvent as presented, the microanalysis data for the compounds obtained from these reactions show great variation. Mass spectrometry clearly shows trace amounts of the oxidized species $[Co(Tm^{Me})_2]^+$ (*m/e* 761.4) and appreciable amounts of the dimeric species $[(Co\{Tm^{Me}\})_2X]^+$ (X = Cl, *m/e* 855.4; X = Br, *m/e* = 900.8; X = I, *m/e* 947.4) are also present.] FTIR [$\nu$/cm$^{-1}$ (KBr disk)]: 2435 (B−H). MS (FAB; *m/e*): 410.0, $[M^+ - Cl]$; 761.4, $[Co(Tm^{Me})_2]^+$; 855.4, $[Co_2(Tm^{Me})_2Cl]^+$. $\mu_{eff}$ (298 K) = 4.19 $\mu_B$. UV−visible (solid state; $E_{max}$, cm$^{-1}$): 4250 (sh), 4580 (sh), 4890, 5730, 7250, 14 330, 15 432 (sh), 24 510, 32 470. UV−visible ($CH_2Cl_2$ solution, $5.2 \times 10^{-4}$ mol dm$^{-3}$, $E_{max}$/cm$^{-1}$ ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$)): 13 590 (568), 14 290 (713), 15 090 (491), 22 125 (sh, 268), 27 170 (2203).

**Preparation of $[Co(Tm^{Me})Br]$.** $TlTm^{Me}$ (1.00 g, 1.8 mmol) was suspended in acetone (50 mL) to which a solution of $CoBr_2$ (0.40 g, 1.8 mmol) in acetone (30 mL) was added. The mixture was refluxed while stirring for 3 h. The thallium bromide precipitate was removed by filtration and the solution reduced in volume. The product was precipitated by addition of excess diethyl ether. The solid was collected by filtration, and the resulting olive green solid was washed twice with ether and dried in vacuo. Yield: 0.63 g, 71%. Crystals suitable for X-ray analysis were obtained from acetone by slow solvent evaporation.

Anal. Found: C, 29.72; H, 3.61; N, 16.91. Calcd for $C_{12}H_{16}BBrCoN_6S_3$: C, 29.40; H, 3,29; N, 17.15. FTIR [$\nu$/cm$^{-1}$ (KBr disk)]: 2425 (B−H). MS (EI; *m/e*): 410.1, $[M^+ - Br]$; 490.9, $[M^+]$; 761.0, $[Co(Tm^{Me})_2]^+$; 900.8, $[Co_2(Tm^{Me})_2Br]^+$. $\mu_{eff}$ (298 K) = 4.91 $\mu_B$. UV−visible (solid state; $E_{max}$, cm$^{-1}$): 4150 (sh), 4590 (sh), 4830, 5710, 7460 (sh), 1330 (sh), 14 290, 15 150, 25 000, 35 710. UV−visible ($CH_2Cl_2$ solution, $1.0 \times 10^{-3}$ mol dm$^{-3}$, $E_{max}$/cm$^{-1}$

---

(5) (a) Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 310. (b) Fränkel, R.; Kernbach, U.; Bakola-Christianopoulou, M.; Plaia, U.; Suter, M.; Ponikwar, W.; Moinet, C.; Fehlhammer, W. P. *J. Organomet. Chem.* **2001**, *617−618*, 530.

(6) Garner, M.; Lehmann, M.-A.; Reglinski, J.; Spicer, M. D. *Organometallics* **2001**, *20*, 5233.

(7) Garner, M.; Lewinski, K.; Pattek-Janczyk, A.; Reglinski, J.; Sieklucka, B.; Spicer, M. D.; Szaleniec, M. *Dalton Trans.* **2003**, 1181.

(8) (a) Fujihara, T.; Schönherr, T.; Kaizaki, S. *Inorg. Chim. Acta* **1996**, *249*, 135. (b) Hayashi, A.; Nakajima, K.; Nonoyama, M. *Polyhedron* **1997**, *16*, 4087.

(9) E.g.: In *Comprehensive Organometallic Chemistry II*; Atwood, J. D., Vol. Ed.; Pergamon Press: London, 1995; Vol. 8, p 88.

(10) Kimblin, C.; Churchill, D. G.; Bridgewater, B. M.; Girard, J. N.; Quarless, D. A.; Parkin, G. *Polyhedron* **2001**, *20*, 1891.

(11) Ohrenberg, C.; Ge, P.; Schebler, P.; Riordan, C. G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 749.

(12) Armstrong, D. R.; Cassidy, I. D.; Kennedy, A. R.; Reglinski, J.; Slavin, P. A.; Spicer, M. D. *J. Chem. Soc., Dalton Trans.* **1999**, 2119.

(13) Kennedy, A. R.; Reglinski, J.; Slavin, P. A.; Spicer, M. D. *J. Chem. Soc., Dalton Trans.* **2000**, 239.

(14) King, R. B. *Inorg. Chem.* **1966**, *5*, 82.

**Table 1.** Crystallographic Data

| | $[Co(Tm^{Me})Br]$ | $[Co(Tm^{Me})_2]BF_4\cdot 0.5H_2O\cdot 0.25THF$ | $[Co(mtH)_3I]I$ |
|---|---|---|---|
| empirical formula | $C_{12}H_{16}BBrCoN_6S_3$ | $C_{25}H_{35}B_3CoF_4N_{12}O_{0.75}S_6$ | $C_{12}H_{18}CoI_2N_6S_3$ |
| fw | 490.14 | 875.37 | 655.23 |
| $T$/K | 123 | 123 | 123 |
| cryst system | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/n$ (no. 14) | $C2/c$ (no. 15) | $Pc2_1n$ (no. 33) |
| $a$/Å | 12.0655(6) | 34.0403(7) | 11.302(5) |
| $b$/Å | 12.4897(7) | 12.8344(3) | 16.167(5) |
| $c$/Å | 12.7057(7) | 19.2489(5) | 11.902(5) |
| $\alpha$/deg | 90 | 90 | 90 |
| $\beta$/deg | 95.714(3) | 101.540(1) | 90 |
| $\gamma$/deg | 90 | 90 | 90 |
| $Z$ | 4 | 8 | 4 |
| $V$/Å$^3$ | 1905.2(2) | 8239.6(3) | 2174.7(15) |
| $\mu_{calc}$/mm$^{-1}$ | 3.334 | 1.411 | 3.924 |
| $F$(000) | 980 | 3472 | 1252 |
| cryst size/mm | 0.2 × 0.2 × 0.2 | 0.4 × 0.15 × 0.04 | 0.4 × 0.2 × 0.2 |
| radiatn | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ |
| no. rflcns measd | 13 621 | 17 044 | 4596 |
| no. unique reflcns | 4210 ($R_{int} = 0.0694$) | 9437 ($R_{int} = 0.0359$) | 2410 ($R_{int} = 0.0275$) |
| no. params | 221 | 495 | 222 |
| $R^a$ ($I > 2\sigma(I)$) | 0.0462 | 0.0559 | 0.0293 |
| $R_w{}^b$ (all reflcns) | 0.1066 | 0.1643 | 0.0747 |
| GOF | 1.023 | 1.038 | 1.061 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$)): 13 640 (371, sh), 14 220 (459, sh), 14 810 (522), 16 390 (sh, 325), 21 410 (sh, 214), 27 250 (2797).

**Preparation of $[Co(Tm^{Me})I]$.** A solution of $CoI_2$ (0.626 g, 2 mmol) in 100 mL of acetone was added to a suspension of $TlTm^{Me}$ (1.11 g, 2 mmol) in acetone (250 mL). The mixture was refluxed under continuous stirring for 4 h. The initially blue solution of the cobalt salt turned green. The filtered solution was treated with 500 mL of diethyl ether to precipitate a green solid. The solid was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.33 g, 31%.

Anal. Found: C, 30.15; H, 3.82; N, 13.80. Calcd for $C_{12}H_{16}BCoIN_6S_3\cdot Me_2CO$: C, 30.26; H, 3.72; N, 14.12. [See comments after analytical data for $[Co(Tm^{Me})Cl]$]. FTIR [$\nu$/cm$^{-1}$ (KBr disk)]: 2437 (B−H). MS (FAB; $m/e$): 410.0, [M$^+$ − I]; 761.4, $[Co(Tm^{Me})_2]^+$; 947.0, $[Co_2(Tm^{Me})_2I]^+$. $\mu_{eff}$ (298 K) = 4.35 $\mu_B$. UV−visible (solid state; $E_{max}$, cm$^{-1}$): 4530 (sh), 4860, 5480, 7350 (sh), 13 040, 13 700, 14 560 (sh), 25 190, 34 840. UV−visible ($CH_2Cl_2$ solution, 4.1 × 10$^{-4}$ mol dm$^{-3}$, $E_{max}$/cm$^{-1}$ ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$)): 13 190 (691), 13 760 (602), 14 560 (513), 21 600 (sh, 2030), 25 580 (5517).

**Preparation of $[Co(Tm^{Me})_2]BF_4$.** $TlTm^{Me}$ (0.175 g, 1.6 mmol) and $NaBF_4$ (0.18 g, 1.6 mmol) were added to a solution of $[Co(Tm^{Me})Br]$ (0.200 g, 0.4 mmol) in acetonitrile (250 mL). The solution was stirred for 4 days in a beaker covered with a watch glass. The solvent losses through evaporation were replaced regularly. The initially green solution slowly turned brown over this period. Toward the end of this period, molecular sieve was added to remove some of the water. The mixture was then filtered and the filtrate taken to dryness in vacuo. The resulting brown solid was redissolved in the minimum amount of dry dichloromethane, cooled, and filtered through Celite. A dark red crystalline product was obtained from dichloromethane solution by vapor diffusion with THF. Yield: 0.13 g, 38%.

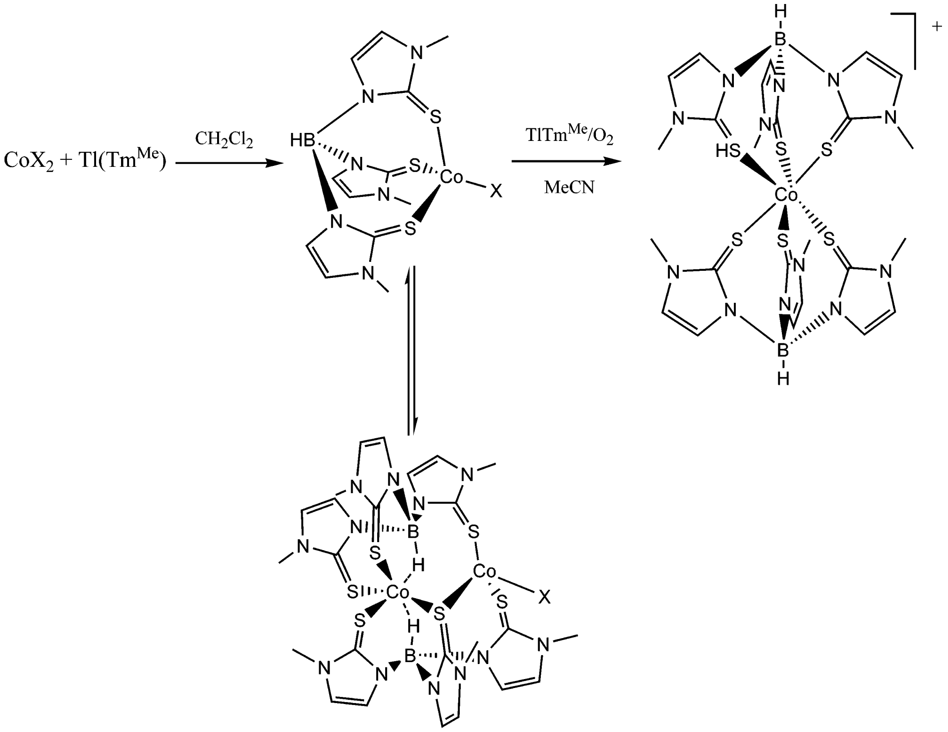
Analysis. Found: C, 31.67; H, 4.21; N, 18.44. Calcd for $C_{24}H_{32}B_3F_4CoN_{12}S_6\cdot 3H_2O$: C, 31.95; H, 4.24; N, 18.63. FTIR [$\nu$/cm$^{-1}$ (KBr disk)]: 2433 (B−H). $^1$H NMR (400 MHz, $CDCl_3$; $\delta$/ppm): 3.70 (s, 3H, $CH_3$); 6.96 (d, 1H, CH); 7.05 (d, 1H, CH). UV−visible (solution, $CH_2Cl_2$, 9.4 × 10$^{-5}$ mol dm$^{-3}$; $E_{max}$/cm$^{-1}$ ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$)): 21 010 (sh, 8940), 25 000 (15 580), 40 980 (sh, 15 180).

**Preparation of $[Co(Tm^{Me})(Cp^{Me})]I$.** $[Co(Cp^{Me})(CO)I_2]$ (0.31 g, 0.74 mmol) was placed in a Schlenk tube equipped with a stirring bar. To this was added dry THF (25 mL) and the resulting mixture cooled to −40 °C. $NaTm^{Me}$ (0.276 g, 0.74 mmol) was added and the mixture allowed to warm to room temperature with stirring. The green solid which formed was collected and washed with diethyl ether. A crystalline product was obtained from chloroform−diethyl ether by vapor diffusion. Yield: 0.32 g, 70%.

Anal. Found: C, 34.65; H, 3.55; N, 13.01. Calcd for $C_{18}H_{23}BCoIN_6S_3$: C, 35.08; H, 3.73; N, 13.66. FTIR [$\nu$/cm$^{-1}$ (KBr disk)]: 2469 (B−H). $^1$H NMR (400 MHz, acetone-$d_6$; $\delta$/ppm): 1.77 (s, 3H, $CH_3$ Cp); 3.89 (s, 3H, $CH_3$ Tm); 5.23−5.43 (m, 4H, CH); 7.04 (d, 1H, CH); 7.41 (d, 1H, CH). MS (FAB; $m/e$): 489.2, [M$^+$]; 410.1, [M$^+$ − Cp$^{Me}$]. UV−visible (solution, $CH_2Cl_2$, 4.2 × 10$^{-5}$ mol dm$^{-3}$; $E_{max}$/cm$^{-1}$ ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$)): 15 665 (2625), 26 040 (sh, 14 597), 29 070 (31 896).

**X-ray Crystallography.** Crystals were coated in mineral oil and mounted on glass fibers. Data were collected at 123 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K$\alpha$ radiation. The structures were solved by direct methods, and the remaining atoms located in difference electron density maps. Full-matrix least-squares refinement was based on $F^2$, with all non-hydrogen atoms refined anisotropically where possible. While hydrogen atoms were mostly observed in the difference maps, they were placed in calculated positions riding on the parent atoms. Crystals of $[Co(Tm^{Me})_2]BF_4\cdot 0.5H_2O\cdot 0.25THF$ lost solvent rapidly. As a result, the solvent molecule positions were partially occupied, and the solvent atoms were thus refined isotropically. The solution of the structure of $[Co(Cp^{Me})(Tm^{Me})]I$ was problematic. The crystals were obtained only with great difficulty and were far from ideal. The structure was initially solved in space group $C2/m$, in which the cobalt atom was apparently situated on a mirror plane, and thus the $Tm^{Me}$ ligand was disordered over two sites. The observed ligand geometry was significantly distorted from that normally expected. It would appear that this is an example of a "partial polar ambiguity", in which a polar structure is solved in a nonpolar space

**Scheme 1**



group to a false minimum.[15] This most commonly occurs, as in this case, when centrosymmetrically disposed heavy atoms dominate the phasing of the overall noncentrosymmetric structure. We have reprocessed the data in the polar space group *C*2, and while this was some improvement, we have been unable to fully resolve this problem and refine the structure to a satisfactory ("true") minimum. Nevertheless, the other experimental data (NMR, MS, and elemental analysis) associated with this compound all support the structure found by crystallography. We thus present a pictorial representation of the structure but have withheld the crystallographic and structural parameters in the knowledge that they may not be fully reliable.

The structure solution and refinement used the program SHELX-97[16] and the graphical interface WinGX.[17] A summary of the crystallographic parameters is given in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 238056−238058. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ U.K. (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk; www http://www.ccdc.cam.ac.uk).

## Results and Discussion

Treatment of cobalt(II) halides with the hydrotris(methimazolyl)borate anion ($Tm^{Me}$) at a variety of molar ratios in noncoordinating solvents (e.g. $CH_2Cl_2$ or acetone) quickly leads only to the formation of complexes with the empirical formula $[Co(Tm^{Me})X]$ (X = Cl, Br, and I, Scheme 1). Of the three species prepared, the bromide was successfully structurally characterized, revealing a pseudotetrahedral motif around the cobalt (Figure 1).

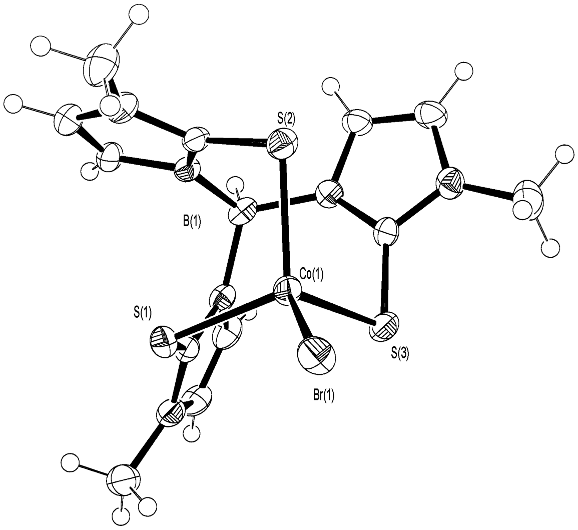


**Figure 1.** X-ray crystal structure of $[Co(Tm^{Me})Br]$.

As expected, there is close structural homology between this compound and the previously reported $Tm^{Me}$ adduct of zinc[4,18] and the tetrakis{(methylthio)methyl}borate (Tt) adduct of cobalt(II)[11] (Table 2). The metal−sulfur distances for the two cobalt complexes are in agreement with those found for the analogous $[Zn(Tm^{Me})Br]$ complex once the small extension to the bond distances is included to compensate for the slightly larger cation. The influence of the eight-membered rings generated by $Tm^{Me}$ is evident in these comparisons. In adopting a classic facially capping arrangement, the $Tm^{Me}$ ligand requires to tilt the methimazole rings at an angle (37.9°(av)) to the main HB···Co axis to accommodate the larger ring size. This added flexibility at

---

[15] Kuchta, M. C.; Parkin, G. *New J. Chem.* **1998**, 523 and references therein.

[16] Sheldrick, G. M. *SHELXL-97*, *Programs for Crystal Structure Analysis*, release 97-2; Institüt für Anorganische Chemie, der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[17] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

[18] Cassidy, I.; Garner, M.; Kennedy, A. R.; Potts, G. B. S.; Reglinski, J. R.; Slavin, P. A.; Spicer, M. D. *Eur. J. Inorg. Chem.* **2002**, 1235.

**Table 2.** Comparison of M−S Bond Distances and ∠S−M−S Angles for Tetrahedral Soft Tripodal Complexes of Cobalt(II) and Zinc(II)

| $[Co(Tm^{Me})Br]$ | $[Zn(Tm^{Me})Br]$ | $[Co(PhTt)Cl]$ |
|---|---|---|
| | $d$(M−S)/Å | |
| 2.319 | 2.355 | 2.320 |
| 2.328 | | 2.321 |
| 2.328 | | 2.3256 |
| | ∠S−M−S/deg | |
| 109.9 | 105.35 | 99.1 |
| 105.4 | | 98.4 |
| 107.9 | | 100.5 |

the methimazolyl units forces the bite angle of $Tm^{Me}$ to somewhat larger values (∠S−M−S ∼ 108°) than found for the analogous Tt complex (∠S−M−S ∼ 99°), thus facilitating the formation of a more regular tetrahedral environment for the cobalt cation. This contrasts starkly with Parkin's $[Co(Tm^{Ph})_2]$,[10] which adopts a highly distorted pseudooctahedral geometry, in which each ligand coordinates through two thione sulfur atoms and additionally via the B−H moiety. It is not clear why the alternative geometry is adopted in this case. While, on the surface, it might appear that steric effects are the cause, on further inspection this seems unlikely. In particular, steric effects would favor a 1:1 complex, $[Co(Tm^{Ph})X]$, analogous to our complex. It seems more likely that this is electronic in nature, the electron-withdrawing phenyl group lessening the electron-donating ability of the thione.

The full characterization of the $[Co(Tm^{Me})X]$ species (X = Cl, I) was problematic. This was particularly reflected in widely differing values in the microanalysis and by a tendency to slowly oxidize in solution. Indeed, mass spectrometry clearly shows evidence for the presence of two species with higher molecular weights in solution. A species with $m/e = 761.4$ was seen in the spectra of all three compounds, indicative of the oxidized species $[Co^{III}(Tm^{Me})_2]^+$ (Scheme 1). However, more intriguing is the presence of a second, heavier molecular ion, consistent with a dimeric complex of formula $[Co_2(Tm^{Me})_2X]^+$ (X = Cl, Br, I; see Figure 1). Rabinovich has observed a similar species using $Tm^{tBu}$ as ligand and has been successful in crystallographically characterizing the $PF_6^-$ salt.[19] In his complex both $Tm^{tBu}$ ligands bridge between the two metal centers, but the cobalt atoms have nonidentical coordination spheres; one cobalt has an $S_4H_2$ donor set, while the other has an $S_3Br$ donor set.

Although the X-ray crystal structure of the bromide complex $[Co(Tm^{Me})Br]$ had been successfully determined, microanalyses of the bulk materials were variable and mass spectra indicated the presence of a dimeric complex and rearrangement products in solution (Scheme 1). The UV−visible reflectance spectrum of the crystalline $[Co(Tm^{Me})Br]$ used to obtain the structure (Figure 1) was recorded. This displayed absorption bands consistent with a pseudotetrahedral $d^7$ ion. A similar band profile was observed for the powders obtained from the respective chloride and iodide adducts indicating that the crystallographically characterized structure is representative of the bulk structures of the other two species prepared. Similarly the magnetic moments ($\mu_{eff}$) calculated are consistent with this analysis. Significantly, the band structure observed in the reflectance spectra is also maintained in the solution spectra, thus confirming that the major species in solution is also $[Co(Tm^{Me})X]$.

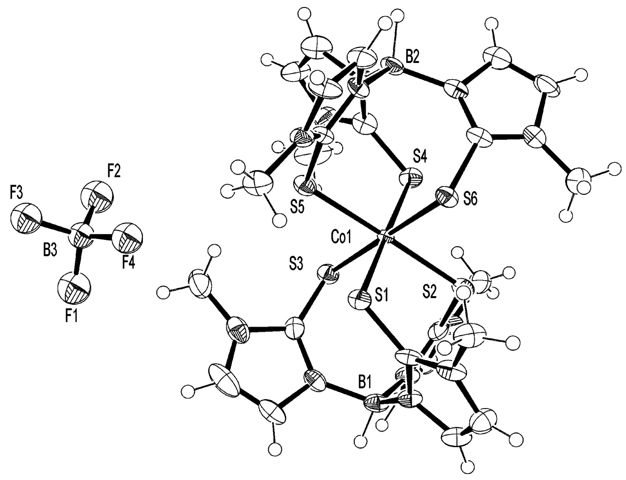


**Figure 2.** X-ray crystal structure of $[Co(Tm^{Me})_2]BF_4$.

Recrystallization of $[Co(Tm^{Me})Br]$ from donor solvents (e.g. acetonitrile) under aerobic conditions led to the formation of the red $[Co(Tm^{Me})_2]Br$ in poor yield (Scheme 1). The introduction of a second 1 equiv of $NaTm^{Me}$ into the reaction mixture and the addition of a suitable counteranion ($[BF_4]^-$, $[PF_6]^-$) during product isolation increased the yield substantially. $^1H$ NMR confirmed the low-spin, diamagnetic nature of the complex and showed the usual singlet arising from the *N*-methyl group and two doublets corresponding to the ring protons. The $^{59}Co$ NMR showed a single resonance at $\delta$ +8654 ppm, a little to high frequency of the normal range for cobalt ligated by six sulfur donors ($\delta$ +6500 to +7200 ppm in tris(dithiocarbamate)[20] and thioether[21] complexes). The line width (140 Hz) is remarkably narrow given the deviation from pure octahedral symmetry. The electronic spectrum was also consistent with an $S_6$ donor set. The lowest energy bands are at 21 010 and 25 000 $cm^{-1}$, which most likely arises from the splitting of the $^1A_{1g}-^1T_{1g}$ band observed in pure $O_h$ symmetry by the lower symmetry local environment at the metal. The energies of these bands are similar to the value of 19 530 $cm^{-1}$ in the $CoS_6$ complex, $[Co(L^1)\{MeS(CH_2)_2SMe\}]^{3+}$ ($L^1$ = 1,4,7,11-tetrathiacyclotetradecane).[21]

The $[Co(Tm^{Me})_2]^+$ complex can be considered as directly analogous to the cobaltacenium cation, with two face-capping ligands sandwiching the metal cation (Figure 2). It would seem that this cation is particularly stable, as a variety of salts ($Cl^-$, $Br^-$, $I^-$, $BF_4^-$, and $ClO_4^-$) have been crystallized from a range of different reactions and characterized by X-ray diffraction. [In this paper the X-ray crystal structure of [Co-

---

(19) (a) Rabinovich, D. Personal communication. (b) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, Advance Article, published on the web 7th Apr 2004.

(20) Bond, A. M.; Colton, R.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1985**, *24*, 1298.

(21) Jenkinson, J. J.; Levason, W.; Perry, R. J.; Spicer, M. D. *J. Chem. Soc., Dalton Trans.* **1989**, 453.

**Table 3.** Co−S Bond Distances and ∠S−Co−S Angles for $S_6$-Donor Complexes of Cobalt(III)

| $[Co(Tm^{Me})_2]^+$ | $[Co(ttcn)_2]^{3+}$ [a] | $[Co(Et_2dtc)_3]$ [b] |
|---|---|---|
| | $d$(Co−S)/Å | |
| 2.298 | 2.258 | 2.260 |
| 2.303 | 2.253 | 2.258 |
| 2.327 | 2.249 | 2.255 |
| | intra ∠S−Co−S/deg | |
| 95.0 | 91.0 | 77.8 |
| 97.1 | 90.8 | 75.9 (×2) |
| 94.9 | 90.6 | |
| 179.8 | 180 | 166.2 |
| 84.9 | 89.4 | 96.3−96.4 |
| 85.3 | 89.2 | |
| 82.7 | 89.0 | |

[a] Reference 22. [b] Reference 23.

$(Tm^{Me})_2]BF_4$ is reported. The data for this cation with other counteranions have been deposited at the Cambridge Crystallographic Data Centre and may be accessed free of charge as described in the Experimental Section quoting the following deposition numbers: 238059 ($Br^-$); 238060 ($I^-$); 238061 ($ClO_4^-$).]

The environment around the cobalt center (Table 3) is similar to that observed in other metal complexes, $[M(Tm^{Me})_2]^{n+}$. The ∠S−M−S angles are all close to 90°, with the values for the intraligand (bite) angles being slightly larger than the interligand angles. The six cobalt(III) to sulfur distances all similar to one another (2.298−2.327 Å) and as expected are slightly smaller than those found in the parent $[Co(Tm^{Me})Br]$ complex, principally due to the smaller diameter of the Co(III) ion. It is informative to note that the geometric preference of the smaller $d^6$ cation for octahedral coordination geometry is readily accommodated by this ligand system. Rather than hinder the formation of octahedral geometry, the Tm ligand reduces the twist of the methimazolyl rings relative to the HB−Co axis (33.3°(av) vs 37.9° in the tetrahedral $[Co(Tm^{Me})Br]$) such that it can interlock the pendant methyl groups. It is also notable that interligand S−Co−S angles are found to be smaller than 90°.

A comparison with other structurally characterized $CoS_6$ systems (Table 3) including the analogous complexes with trithiacyclononane (ttcn)[22] and diethyldithiocarbamate ($Et_2dtc$)[23] ligands indicates that cobalt sulfur distances are typical for the $CoS_6$ environment but at the higher end of the range. Considerable variation is again seen in the ∠S−M−S angles. The bite angles of the $Tm^{Me}$ ligands are greater than 90° indicative of highly flexible donor groups.

Curiously, although the structure of $[Co^{III}(Tm^{Me})_2]^+$ indicates that there is no steric barrier to the formation of $[Co^{II}(Tm^{Me})_2]$, we have been unable to obtain such a species. Attempts at direct preparation using a range of ligand transfer agents and a variety of metal precursors and reaction conditions were all unsuccessful. Furthermore, neither chemical nor electrochemical reduction of the $Co^{III}$ analogue gave any indication of such a species. This contrasts with Tp, which readily forms a stable $Co^{II}$ sandwich compound, $[Co(Tp)_2]$,[8] and Cp which forms cobaltacene, which is readily oxidized. Given that $Tm^{Me}$ places greater electron density at the metal center than Cp,[6] $[Co(Tm^{Me})_2]$ should oxidize even more readily than cobaltacene, which may explain our inability to observe this complex.

The synthetic protocol adopted for the preparation of the $[Co(Tm^{Me})_2]^+$ cation suggested that it should be possible to introduce an alternative facial ligand (e.g. Cp) into the coordination sphere of the cobalt center during the oxidation step. This would lead to the formation of mixed sandwich species, e.g. $[Co(Tm^{Me})(Cp)]^+$. A previous, sketchy report[24] of the formation of $[Co(Tp)(Cp)]^+$ gave hope that such species should be attainable. However, on repetition of the reaction, with replacement of $NaTm^{Me}$ with 1 equiv of NaCp in the second step, the $[Co(Tm^{Me})_2]^+$ cation was isolated once more. This suggested that reaction is driven not by the additional ligand but by a species already present. A likely candidate is the dimeric species $[\{CoTm^{Me}\}_2X]^+$ (Scheme 1),[19] which it is thought may facilitate $O_2$ oxidation of the metal center (possibly by coordinating molecular oxygen) and also providing the second $Tm^{Me}$ ligand. It is curious that the oxidation process is accelerated in the presence of donor solvents (e.g. $CH_3CN$), although this acceleration may result either from perturbation of the solution equilibrium to favor the dimer or by stabilization of the metal fragment which would be necessarily ejected from the dimer to form the $[Co(Tm^{Me})_2]^+$ cation.

O'Hare et al.[25] have recently prepared [Co(Cp)(Tp)]I by an alternative route, commencing from $CpCo(CO)I_2$. With employment of this route using $NaTm^{Me}$ in place of NaTp a green material was isolated. This analyzed poorly for the desired mixed sandwich product, the presence of $[Co(Cp)(Tm^{Me})]^+$ was not confirmed by mass spectrometry, and furthermore, the sample was paramagnetic. After many attempts to crystallize the material a small number of green crystals were obtained. Crystallographic analysis revealed these to be iodotris(methimazole)cobalt(II) iodide (Figure 3).

It appears that the $Tm^{Me}$ anion is oxidized in the presence of the $Co^{III}$ precursor, presumably via the B−H moiety. This results in fission of the B−N bonds thus releasing the three methimazoles, which coordinate to the metal. Unconfined by the apical boron, they are free to adopt their preferred orientation and distance from the metal center. The ∠S−M−S angles move to values expected for a tetrahedral geometry (108.52−110.55°). The M−S distances (2.331−2.336 Å) are now marginally larger than found in [Co(Tm)-Br] (Table 2) most probably due to the loss of the partial charge on the donors. Of some surprise is the orientation of the methimazoles, which invert with respect to the parent complexes, internalizing the metal center. It is tempting to invoke a weak $\pi$-interaction between the coordinated iodide and the methimazole rings, but with an average I to ring centroid distance of 3.947 Å, this seems unlikely. The uncoordinated iodide ion is located on the Co−I bond axis,

---

[22] Kuppers, H.-J.; Neves, A.; Pomp, C.; Venture, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1985**, *25*, 2400.

[23] Healy, P. C.; Connor, J. W.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 1083.

[24] O'Sullivan, D. J.; Lalor, F. J. *J. Organomet. Chem.* **1973**, *57*, C58.

[25] Brunker, T. J.; Barlow, S.; O'Hare, D. *Chem. Commun.* **2001**, 2052.

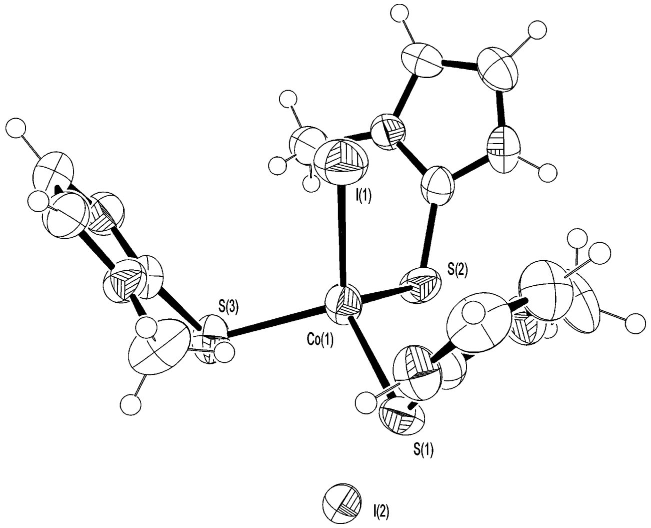


**Figure 3.** X-ray crystal structure of [Co(mtH)$_3$I]I.

at a distance of 4.11 Å from the cobalt. Inspection of the Cambridge Crystallographic Database revealed no analogous structurally characterized species.

Despite the structure determined from the crystals, there was evidence (including a parent ion in the mass spectrum) that the desired species was present to some extent in the bulk materials but that it was not stable for extended periods. It was believed that the CpCo fragment was too strongly oxidizing for the complex to be stable. Therefore, by an increase of the electron density at the cobalt center, it was envisaged that the oxidizing potential would be reduced rendering the oxidative ligand decomposition less favorable. Thus, Cp was replaced by the methyl analogue ($C_5H_4Me^-$, Cp$^{Me}$). Reaction of [Co(Cp$^{Me}$)(CO)I$_2$] with NaTm$^{Me}$ resulted in the successful isolation and characterization of the green, air-stable cation [Co(Cp$^{Me}$)(Tm$^{Me}$)]$^+$ (Figure 4) as the iodide salt.

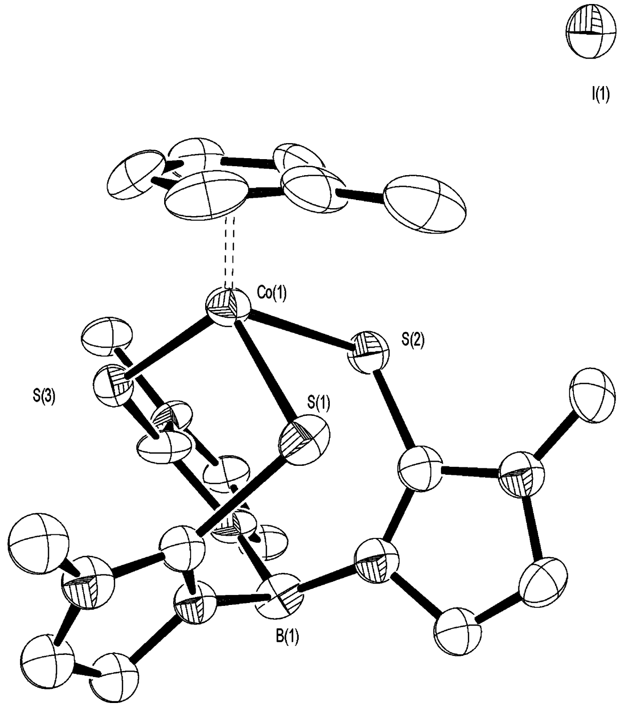


**Figure 4.** X-ray crystal structure of [Co(Cp$^{Me}$)(Tm$^{Me}$)]I.

The X-ray crystal structure determination for this complex was problematic (vide supra) resulting in the Tm$^{Me}$ ligand being unsymmetrically disposed about the cobalt center. This is clearly at variance with previous observations of the complexation of this ligand. In [Co(Tm$^{Me}$)$_2$]$^+$ and in the only other structurally characterized mixed sandwich compound involving the Tm$^{Me}$ ligand, [Ru(*p*-cymene)(Tm$^{Me}$)]$^+$,[26] the ligand geometry and disposition is symmetrical, as would be expected. Despite the problems with the metrical parameters, we are confident of the connectivity observed. Spectroscopic and analytical data for this compound are consistent with the observed structure. FAB mass spectrometry reveals the parent ion at $m/e = 489.2$ amu and fragmentation with loss of Cp$^{Me}$. The $^1$H NMR spectrum shows resonances for methylcyclopentadiene and Tm$^{Me}$ in a 1:1 ratio, but we have been unable to locate $^{59}$Co NMR resonances either for [Co(Tm$^{Me}$)(Cp$^{Me}$)]$^+$ or for [Co(Tp)(Cp)]$^+$. Presumably the symmetry in these species is sufficiently low for quadrupole broadening to render the resonances unobservable. Electrochemical reduction in CH$_2$Cl$_2$ showed an irreversible wave at −670 mV vs Ag/AgCl for [Co(Tm$^{Me}$)(Cp$^{Me}$)]$^+$, some 200 mV more negative than for [Co(Tp)(Cp)]$^+$,[27] reflecting the greater electron donor ability of the Tm$^{Me}$ ligand compared to Tp. Interestingly, for [Co(Tm$^{Me}$)$_2$]$^+$, no reduction was observed within the limits of solvent stability, suggesting that it is even less readily reduced than the pentamethylcobaltacenium cation (−1970 mV).[27] An irreversible oxidation was observed at +1.12 V (vs Ag/AgCl), which may arise either from oxidative ligand decomposition or from the Co$^{III}$/Co$^{IV}$ couple. It is our experience that ligand decomposition usually occurs at lower voltages (ca. +0.5 V) and believe this to be a metal-based oxidation.

## Concluding Remarks

Our study again reveals a considerable degree of structural homology between the cobalt complexes of Cp, Tp, and Tm$^{Me}$ but also highlights the electronic differences between the ligands. It is observed that Co$^{II}$ has a marked propensity for formation of a half-sandwich complex with the Tm$^{Me}$ ligand. By contrast, the sandwich compound [Co(Tp)$_2$] is formed with Co$^{II}$ halides in the presence of the Tp anion. Only in the case of very bulky Tp ligands (e.g. with $^t$Bu groups in the 3 position) is the tetrahedral geometry enforced.[28] While Cp tends to the sandwich compound (cobaltacene), examples with the more strongly electron donating Cp* do show some tendency to form half-sandwich motifs in [Co(Cp*)(py)Cl][29] and [Co(Cp*)($\mu$-Cl)]$_2$,[30] where coordination expansion is also observed. It would appear that

---

(26) Bailey, P. J.; Lorono-Gonzales, D. J.; McCormack, C.; Parsons, S.; Price, M. *Inorg. Chim. Acta* **2003**, *354*, 61.

(27) Brunker, T. J.; Cowley, A. R.; O'Hare, D. *Organometallics* **2002**, *21*, 3123.

(28) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

(29) Raabe, E.; Koelle, U. *J. Organomet. Chem.* **1985**, *279*, C29.

(30) Koelle, U.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 132.

the structures obtained in these systems are driven by the electron donor capacity of the ligands, and this assertion is supported by the electrochemical data. The reduction potentials of $[Co(L)_2]^+$ follow the expected pattern, with ease of reduction in the order

$$Tp_2 > TpCp > TpCp^* > Cp_2 > Cp^*_2 > Tm^{Me}{}_2$$

In particular, this is consistent with our inability to observe the species $[Co^{II}(Tm^{Me})_2]$ and explains the propensity to form the tetrahedral $[Co(Tm^{Me})X]$ species with cobalt(II).

**Acknowledgment.** We acknowledge the EPSRC Mass Spectrometry Service at the University of Wales, Swansea, U.K., and thank the EPSRC for funding (C.A.D). We also thank Michelle K. Taylor for undertaking the electrochemical measurements.

**Supporting Information Available:** X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0496525