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Cobalt as a Probe for Zinc in Metalloenzyme Model Compounds? A Comparison of Spectroscopic Features and Coordination Geometry of Four- and Five-Coordinate Complexes. Crystal and Molecular Structures of [Co(η^3-Tp^{Ph})(η^2-Tp^{Ph})], [(η^3-Tp^{Ph})Zn(anthranilate)], and [(η^3-Tp^{Ph})M(η^2-acac)] (Tp^{Ph} = Hydrotris(3-phenylpyrazol-1-yl)borate, acac = Pentane-2,4-dionate, and M = Zn, Co)

Andreas Kremer-Aach, Wolfgang Kläui,* Ralf Bell, Angela Strerath,
Hartmut Wunderlich, and Dietrich Mootz

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf,
Universitätsstrasse 1, D-40225 Düsseldorf, Germany

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The reaction of cobalt(II) perchlorate with 1 equiv each of potassium hydroxide and potassium hydrotris(3-phenylpyrazolyl)borate (KTp^{Ph}) leads to the formation of the blood-red bis(ligand) complex [Co(η^3-Tp^{Ph})(η^2-Tp^{Ph})]. This compound crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.690(5)$ Å, $b = 34.243(15)$ Å, $c = 12.923(4)$ Å, $\beta = 96.17(3)°$, $Z = 4$, $V = 4703(3)$ Å^3, and $R = 0.040$. The molecular structure contains a square CoN$_5$ pyramid with an agostic BH···Co interaction of 2.17(2) Å. One Tp^{Ph} ligand acts tridentate; the other, bidentate. The reaction of KTp^{Ph} with zinc and cobalt halides yields a series of heteroleptic halogeno complexes [(Tp^{Ph})MX]. The zinc species are all tetrahedral, while in the case of cobalt(II) the UV−vis spectra indicate an equilibrium of tetra- and pentacoordinated species depending on the anion size and the donor properties of the solvent. Metathesis reactions with carboxylates yield mononuclear complexes [(Tp^{Ph})M(O$_2$CR)]; M = Zn(II), Co(II); RCO$_2$$^-$ = acetate, benzoate, 4-fluorobenzoate, and 4-nitrobenzoate. The infrared bands ν_{as}(CO$_2$) and ν_{sym}(CO$_2$) indicate monodentate carboxylate ligands in the zinc complexes in the solid state and in solution. The cobalt complexes [(Tp^{Ph})Co(carboxylate)] are dark blue in dichloromethane and in the solid state when grown from dichloromethane solution. Tetrahydrofuran solutions and crystals grown from tetrahydrofuran are pink, purple, or reddish violet. The 2-aminobenzoate (anthranilate) complexes [(Th^{Ph})M(anthranilate)], M = Zn(II), Co(II), have been prepared. [(η^3-Tp^{Ph})Zn(anthranilate)] crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.205(4)$ Å, $b = 15.643(3)$ Å, $c = 15.116(3)$ Å, $\beta = 98.86(2)°$, $Z = 4$, $V = 3085(1)$ Å^3, and $R = 0.034$. Anthranilate acts as a chelating oxygen ligand with Zn−O distances of 1.932(2) and 2.460(2) Å. The amino group is not involved in metal coordination. The reaction of the chloro complexes [(Tp^{Ph})MCl] with sodium or potassium acetylacetonate leads to isotypic zinc and cobalt complexes [(η^3-Tp^{Ph})M(η^2-acac)]. Both crystallize in the monoclinic space group $P2_1/c$, with $Z = 4$, the zinc compound with $a = 16.334(3)$ Å, $b = 11.545(2)$ Å, $c = 15.816(3)$ Å, $\beta = 94.77(1)°$, $V = 2972(1)$ Å^3, and $R = 0.039$ and the cobalt compound with $a = 16.358(7)$ Å, $b = 11.519(2)$ Å, $c = 15.847(6)$ Å, $\beta = 95.30(3)°$, $V = 2973(2)$ Å^3, and $R = 0.035$. The structures are best described as slightly distorted trigonal bipyramids with the two axial positions occupied by one of the acetylacetonate O and one of the tripodal N donor atoms. Ligand profiles of Tp^{Ph} and related ligands have been calculated to visualize the angular encumbrance of the ligands.

Introduction

In its complexes zinc commonly has coordination numbers 4, 5, or 6.[1] In zinc enzymes it seems important that the metal ion can adopt coordination numbers 4 and 5, but not easily coordination number 6.[2] In the absence of readily accessible X-ray structures the evidence for the metal environment comes mainly from spectroscopic studies. It is often possible to probe the metal environment in enzymes with cobalt in lieu of zinc since cobalt(II) has a similar tendency toward coordination numbers smaller than 6. To model situations where the steric requirements restrict the coordination numbers to 4 and possibly 5, ligands of the type tris(3-R-5-R′-pyrazol-1-yl)borate (abbreviated in the following as Tp$^{R,R'}$)[3] have been used. Complexes of the ligand Tp$^{t\text{-}Bu}$ with 3d transition metal ions are exclusively tetrahedral[4,5] whereas the smaller ligand Tp^{Me,Me} favors octahedral coordination geometry.[6] The intermediate steric demand of Tp^{Ph} allows the formation of complexes with

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(3) Abbreviation introduced by Trofimenko. See: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

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Table 1. Crystallographic Data for [Co(η^3-Tp^{Ph})(η^2-Tp^{Ph})] (**1**), [(η^3-Tp^{Ph})Zn(anthranilate)] (**5**) [(η^3-Tp^{Ph})Zn(η^2-acac)] (**7**), and [(η^3-Tp^{Ph})Co(η^2-acac)] (**8**)

	1	5	7	8
formula	$C_{54}H_{44}B_2N_{12}Co$	$C_{34}H_{28}BN_7O_2Zn$	$C_{32}H_{29}BN_6O_2Zn$	$C_{32}H_{29}BN_6O_2Co$
fw	941.6	642.8	605.8	599.4
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group; *Z*	$P2_1/n$; 4	$P2_1/n$; 4	$P2_1/c$; 4	$P2_1/c$; 4
a, Å	10.690(5)	13.205(4)	16.334(3)	16.358(7)
b, Å	34.243(15)	15.643(3)	11.545(2)	11.519(2)
c, Å	12.923(4)	15.116(3)	15.816(3)	15.847(6)
β, deg	96.17(3)	98.86(2)	94.77(1)	95.30(3)
V, Å^3	4703(3)	3085(1)	2972(1)	2973(2)
2θ range, deg	4−50	4−55	4−55	4−55
obs;^{a} all data	5344; 8291	3611; 7118	3761; 6805	4783; 6788
no. of refd variables	798	406	495	495
g in wt^b	0.059	0.043	0.048	0.054
ρ(calc), g cm^{-3}	1.330	1.384	1.354	1.339
μ(Mo Kα), mm^{-1}	0.417	0.840	0.866	0.617
T, K	293	293	293	293
R1;^{a} wR2^c	0.040; 0.095	0.034; 0.083	0.039; 0.083	0.035; 0.089
$\Delta\rho$, e Å^{-3}	−0.23; 0.28	−0.24; 0.25	−0.52; 0.25	−0.21; 0.39

[a] $|F_o| \geq 4\sigma_F$, $R1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b] g in $1/w = \sigma^2(F_o^2) + [g(1/3F_o^2 + 2/3F_c^2)]^2$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

coordination number 4, 5, or 6.[7] The bis(ligand) complexes [Mn(Tp^{Ph})$_2$] and [Fe(Tp^{Ph})$_2$] are octahedral[8] whereas we have found [Zn(Tp^{Ph})$_2$] to be tetrahedral with both ligands acting bidentate.[9] We were surprised to find the corresponding cobalt complex [Co(Tp^{Ph})$_2$] not isotypic. It does not show the deep blue color typical of tetrahedral cobalt(II) nor the low extinction coefficients of octahedral complexes. We have now determined its crystal structure. The different structures of [Zn(Tp^{Ph})$_2$] and [Co(Tp^{Ph})$_2$] have led us to compare the structures of a series of homologous zinc and cobalt complexes each containing the tripodal nitrogen ligand Tp^{Ph} and an additional bidentate oxygen ligand.

Experimental Section

General Procedures. All preparations were carried out under nitrogen using standard Schlenk techniques. Membrane filters (regenerated cellulose, 1.0 μm, Schleicher & Schuell) were used to filter off small particles. KTp^{Ph}, the halogeno complexes [(Tp^{Ph})ZnX] (X = Cl, Br, I, SCN), and [(Tp^{Ph})Co(SCN)THF] were obtained according to literature procedures.[7] Sodium acetylacetonate was prepared by adding sodium methylate to acetylacetone in methanol/THF (1:1). All other chemicals were reagent grade and used as recieved. Electronic spectra were recorded on a Perkin-Elmer Lambda-5 spectrophotometer. Absorbance maxima are given as λ_{max}/nm (ϵ/M^{-1} cm^{-1}). ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker AM 200 SY NMR spectrometer at 25 °C. Chemical shifts (δ, ppm) are downfield from internal TMS. IR spectra were recorded on a Bruker FT-IR spectrometer, Model IFS 66, and are reported in cm^{-1}. FAB-MS spectra were run on a VG-Analytical ZAB-HF spectrometer with a *m*-nitrobenzyl alcohol matrix; EI-MS were run on a Varian MAT 311 A spectrometer. Elemental analyses were performed with a Perkin-Elmer Analyser 2400 and Perkin-Elmer AAS 3100.

Preparation of Complexes. Bis[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [Co(Tp^{Ph})$_2$] (1). KTp^{Ph} (480 mg; 1.0 mmol) was stirred for 2 h with Co(ClO$_4$)$_2$·6H$_2$O (366 mg; 1.0 mmol) in 20 mL of THF. The solution was filtered through Celite and KOH (40 mg, 1 mmol) dissolved in MeOH (3 mL) was added dropwise. After being stirred for 2 h the solution was again filtered through Celite. The red filtrate was evaporated to dryness under reduced pressure, and the residue was dissolved in CH$_2$Cl$_2$/heptane (20 mL/10 mL). The solvent was slowly removed at 40 °C until crystallization began. Slow cooling to −30 °C yielded blood-red needles (405 mg, 86%). IR: 2467, 2176 (ν(BH)). MS/EI (*m/e*): 940 (M$^+$, 67%), 796 ([M − (3-Phpz)]$^+$, 51%), 652 ([M − 2(3-Phpz)]$^+$, 20%), 500 ([M − Tp^{Ph}]$^+$, 63%), 356 ([M − Tp^{Ph} − (3-Phpz)]$^+$, 100%). UV−vis (CH$_2$Cl$_2$): 449 (59), 510 (55), 549 (82). Anal. Calcd for $C_{54}H_{44}N_{12}B_2Co$: C, 68.88; H, 4.71; N, 17.85; Co 6.26. Found: C, 68.71; H, 4.80; N, 17.93; Co, 6.41. The analogous reaction of Co(ClO$_4$)$_2$·6H$_2$O with 2 equiv of KTp^{Ph} led to good yields of the product, but it was contaminated with 3-phenylpyrazole and cobalt hydroxide. The reaction of [(Tp^{Ph})CoCl] with equimolar amounts of KTp^{Ph} yields the product as well, but the reaction is rather sluggish.

(Chloro)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II)·tetrahydrofuran, [(Tp^{Ph})CoCl]·THF (2a·THF). KTp^{Ph} (480 mg; 1.0 mmol) was stirred for 2 h with anhydrous CoCl$_2$ (130 mg; 1.0 mmol) in 20 mL of THF. The solution was filtered through Celite and reduced to 3 mL. Slow diffusion of hexane into the THF solution yielded deep blue crystals. IR: 2468 (ν(BH)). MS/FAB (*m/e*): 536 ([M − THF]$^+$, 48%), 500 ([M − Cl − THF]$^+$, 100%), 392 ([M − THF − (3-Phpz)]$^+$, 94%), 356 ([M − THF − Cl − (3-Phpz)]$^+$, 82%). UV−vis (CH$_2$Cl$_2$): 543 (88), 595 (284), 628 (347), 667 (252). Anal. Calcd for $C_{27}H_{22}N_6BClCo{\cdot}C_4H_8O$: C, 61.26; H, 4.97; N, 13.83; Co 9.70. Found: C, 61.28; H, 4.98; N, 13.87; Co, 9.70.

(Chloro)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [(Tp^{Ph})CoCl] (2a). KTp^{Ph} (480 mg; 1.0 mmol) was stirred for 2 h with anhydrous CoCl$_2$ (130 mg; 1.0 mmol) in 20 mL of THF. The solution was filtered through Celite and evaporated to dryness. The residue was redissolved in 40 mL of CH$_2$Cl$_2$ and filtered through a membrane. The filtrate was diluted with 20 mL of heptane and slowly evaporated until precipitation began. After the filtrate was allowed to stand at −30 °C for several days, blue crystals (365 mg, 68%) of **2a** were collected. IR: 2503 (ν(BH)). MS/FAB was identical with that of the THF adduct. UV−vis (CH$_2$Cl$_2$): 544 (62), 599 (386), 633 (597), 664 (512). Anal. Calcd for $C_{27}H_{22}N_6BClCo$: C, 60.54; H, 4.14; N, 15.69; Co 11.20. Found: C, 60.29; H, 4.11; N, 15.61; Co, 11.00.

(Bromo)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [(Tp^{Ph})CoBr] (2b). KTp^{Ph} (2.00 g; 4.16 mmol) was stirred for 2 h with CoBr$_2$ (438 mg; 4.40 mmol) in 50 mL of THF. The turbid solution was filtered through Celite and evaporated to dryness. The blue residue was dissolved in 40 mL of CH$_2$Cl$_2$. Addition of 20 mL of heptane, filtration through a membrane, and slow evaporation of the solvent yielded 1.03 g (88%) of deep blue crystals. IR: 2502 (ν(BH)). MS/EI (*m/e*): 581 (M$^+$, 39%), 500 ([M − Br]$^+$, 51%), 436 ([M − (3-Phpz)]$^+$, 34%), 355 ([M − Br − (3-Phpz)]$^+$, 100%). UV−vis (CH$_2$Cl$_2$): 565 (88), 610 (408), 646 (648). Anal. Calcd for $C_{27}H_{22}N_6BBrCo$: C, 55.90; H, 3.82; N, 14.49; Co 10.16. Found: C, 55.92; H, 3.63; N, 14.44; Co, 9.96.

[Hydrotris(3-phenylpyrazol-1-yl)borato](thiocyanato)cobalt(II), [(Tp^{Ph})CoSCN] (2c). KTp^{Ph} (2.00 g; 4.16 mmol) was stirred for 2 h with Co(SCN)$_2$ (770 mg; 4.40 mmol) in 50 mL of THF. After filtration, the solvent was evaporated in vacuo, and the oily residue was taken up in 10 mL of CH$_2$Cl$_2$ for chromatography on silica. The

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) of the Non-Hydrogen Atoms of [Co(η^3-Tp^{Ph})(η^2-Tp^{Ph})] (**1**) with Estimated Standard Deviations (Esd's) in Parentheses[a]

	x	*y*	*z*	*U*(eq)
Co	2206(1)	1400(1)	3774(1)	37(1)
B(1)	−463(4)	1595(1)	4360(3)	47(1)
B(2)	4044(3)	1187(1)	2576(3)	44(1)
N(11)	539(2)	1679(1)	5287(2)	50(1)
N(12)	1784(2)	1608(1)	5227(2)	44(1)
N(21)	−198(2)	1834(1)	3405(2)	46(1)
N(22)	837(2)	1761(1)	2908(2)	42(1)
N(31)	−427(2)	1159(1)	4077(2)	44(1)
N(32)	632(2)	987(1)	3770(2)	39(1)
N(41)	4341(2)	941(1)	3565(2)	39(1)
N(42)	3499(2)	952(1)	4288(2)	36(1)
N(51)	4405(2)	1614(1)	2785(2)	44(1)
N(52)	3628(2)	1820(1)	3358(2)	40(1)
N(61)	4642(2)	1015(1)	1672(2)	47(1)
N(62)	5925(2)	1009(1)	1694(2)	49(1)
C(11)	2378(3)	1664(1)	6192(3)	52(1)
C(12)	1496(4)	1767(1)	6855(3)	77(1)
C(13)	371(4)	1776(1)	6268(3)	72(1)
C(14)	3729(3)	1589(1)	6481(2)	50(1)
C(15)	4646(4)	1672(1)	5842(3)	63(1)
C(16)	5896(4)	1591(1)	6154(4)	76(1)
C(17)	6255(5)	1438(2)	7116(4)	84(1)
C(18)	5367(5)	1355(2)	7762(4)	88(2)
C(19)	4120(4)	1425(1)	7451(3)	72(1)
C(21)	776(3)	2014(1)	2101(3)	49(1)
C(22)	−301(4)	2244(1)	2103(3)	68(1)
C(23)	−878(4)	2124(1)	2917(3)	61(1)
C(24)	1687(3)	2027(1)	1316(2)	49(1)
C(25)	1972(4)	1702(1)	767(3)	65(1)
C(26)	2752(4)	1731(2)	−21(3)	77(1)
C(27)	3241(4)	2075(2)	−264(4)	84(1)
C(28)	2981(6)	2396(2)	274(4)	104(2)
C(29)	2193(5)	2377(1)	1065(3)	87(2)
C(31)	337(3)	604(1)	3642(2)	42(1)
C(32)	−891(3)	542(1)	3854(3)	57(1)
C(33)	−1334(3)	893(1)	4118(3)	57(1)
C(34)	1215(3)	301(1)	3355(2)	44(1)
C(35)	1131(4)	−72(1)	3764(3)	62(1)
C(36)	1913(4)	−369(1)	3509(3)	71(1)
C(37)	2796(4)	−301(1)	2858(3)	64(1)
C(38)	2906(3)	67(1)	2435(3)	56(1)
C(39)	2111(3)	362(1)	2683(3)	47(1)
C(41)	3902(3)	687(1)	5031(2)	41(1)
C(42)	5019(3)	520(1)	4775(3)	51(1)
C(43)	5252(3)	683(1)	3860(3)	49(1)
C(44)	3251(3)	587(1)	5946(2)	45(1)
C(45)	3825(4)	332(1)	6687(3)	58(1)
C(46)	3266(4)	225(1)	7556(3)	71(1)
C(47)	2122(4)	376(1)	7722(3)	73(1)
C(48)	1520(4)	626(1)	6997(3)	64(1)
C(49)	2065(3)	724(1)	6114(3)	52(1)
C(51)	4095(3)	2188(1)	3431(2)	46(1)
C(52)	5152(4)	2208(1)	2907(3)	65(1)
C(53)	5328(4)	1843(1)	2520(3)	61(1)
C(54)	3512(3)	2511(1)	3956(2)	46(1)
C(55)	2361(4)	2481(1)	4341(3)	63(1)
C(56)	1842(4)	2796(1)	4825(4)	71(1)
C(57)	2459(4)	3143(1)	4914(4)	72(1)
C(58)	3604(5)	3178(1)	4548(4)	82(1)
C(59)	4125(4)	2867(1)	4080(3)	68(1)
C(61)	6166(3)	809(1)	854(2)	46(1)
C(62)	5045(4)	689(1)	286(3)	61(1)
C(63)	4109(3)	822(1)	829(3)	57(1)
C(64)	7475(3)	751(1)	632(2)	50(1)
C(65)	8465(3)	921(1)	1245(3)	56(1)
C(66)	9683(4)	864(1)	1037(3)	67(1)
C(67)	9945(5)	640(2)	225(4)	100(2)
C(68)	8984(4)	464(2)	−372(3)	117(2)
C(69)	7759(4)	523(2)	−174(4)	102(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) of the Non-Hydrogen Atoms of [(η^3-Tp^{Ph})Zn(anthranilate)] (**5**) with Esd's in Parentheses[a]

	x	*y*	*z*	*U*(eq)
Zn	3403(1)	2675(1)	1943(1)	48(1)
B	1470(2)	2384(2)	2693(2)	63(1)
O(1)	4722(1)	2594(1)	1546(1)	57(1)
O(2)	4187(1)	3908(1)	1299(1)	67(1)
N(1)	5628(2)	5081(2)	1023(2)	102(1)
N(11)	2114(2)	1560(1)	2787(1)	60(1)
N(12)	3008(2)	1495(1)	2438(1)	53(1)
N(21)	2101(2)	3108(1)	3214(1)	55(1)
N(22)	3060(1)	3296(1)	3047(1)	51(1)
N(31)	1218(1)	2623(1)	1695(1)	56(1)
N(32)	1977(1)	2728(1)	1173(1)	49(1)
C(1)	4864(2)	3363(2)	1281(2)	51(1)
C(2)	5861(2)	3550(2)	978(1)	45(1)
C(3)	6495(2)	2872(2)	806(2)	58(1)
C(4)	7410(2)	3012(2)	509(2)	71(1)
C(5)	7712(2)	3832(2)	390(2)	77(1)
C(6)	7134(2)	4507(2)	554(2)	75(1)
C(7)	6185(2)	4386(2)	855(2)	58(1)
C(11)	1948(2)	818(2)	3188(2)	72(1)
C(12)	2718(2)	271(2)	3116(2)	74(1)
C(13)	3378(2)	701(2)	2632(2)	54(1)
C(14)	4294(2)	381(2)	2299(2)	56(1)
C(15)	4906(3)	−236(2)	2774(2)	80(1)
C(16)	5718(3)	−591(2)	2426(3)	99(1)
C(17)	5932(2)	−342(2)	1609(3)	92(1)
C(18)	5356(2)	278(2)	1148(2)	77(1)
C(19)	4528(2)	632(2)	1481(2)	62(1)
C(21)	1861(2)	3633(2)	3845(2)	64(1)
C(22)	2665(2)	4171(2)	4105(2)	61(1)
C(23)	3411(2)	3940(2)	3599(2)	49(1)
C(24)	4433(2)	4307(2)	3596(2)	50(1)
C(25)	4613(2)	5163(2)	3795(2)	66(1)
C(26)	5569(2)	5511(2)	3784(2)	78(1)
C(27)	6352(2)	5022(2)	3572(2)	78(1)
C(28)	6201(2)	4168(2)	3394(2)	72(1)
C(29)	5252(2)	3813(2)	3412(2)	59(1)
C(31)	313(2)	2709(2)	1181(2)	66(1)
C(32)	446(2)	2862(2)	323(2)	64(1)
C(33)	1503(2)	2856(1)	330(2)	50(1)
C(34)	2065(2)	2940(1)	−429(2)	48(1)
C(35)	1596(2)	3314(2)	−1215(2)	69(1)
C(36)	2073(3)	3358(2)	−1958(2)	89(1)
C(37)	3049(3)	3039(2)	−1923(2)	84(1)
C(38)	3528(2)	2667(2)	−1153(2)	70(1)
C(39)	3036(2)	2608(2)	−414(2)	56(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

blue band was collected and the solution reduced to 40 mL. After addition of 20 mL of heptane the solution was slowly concentrated under reduced pressure. Recrystallization from CH_2Cl_2/hexane afforded deep blue needles (1.65 g, 71%). IR: 2508 (ν(BH)), 2070 (ν(CN)). MS/EI (*m/e*): 558 (M^+, 54%), 500 ($[M - SCN]^+$, 100%), 354 ($[M - SCN - (3\text{-Phpz})]^+$, 44%). UV−vis ($CH_2Cl_2$): 535 (80), 595 (552), 628 (900). Anal. Calcd for $C_{28}H_{22}N_7BSCo$: C, 60.23; H, 3.97; N, 17.56; Co 10.56. Found: C, 60.32; H, 3.90; N, 17.73; Co, 11.04.

(Acetato)[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), [(Tp^{Ph})Zn(OAc)] (3a). To a solution of [(Tp^{Ph})ZnCl] (1.08 g, 2.0 mmol) in THF (50 mL) was added silver acetate (235 mg, 2.01 mmol) in the absence of light, and the solution was stirred overnight. A white solid was filtered off through Celite, and the solvent was removed under reduced pressure. The residue was dissolved in 15 mL of CH_2Cl_2 and microfiltered. Colorless crystals were grown from CH_2Cl_2/hexane (820 mg, 72%). ^{1}H NMR ($CDCl_3$), δ: 1.61 (s, 3, CH_3CO); 6.47 (d, 3, $J = 2.3$ Hz, 4-*H* in Phpz); 7.3−7.5 (m, 9, C$H_{m,p}$ in Ph); 7.7−7.8 (m, 6, CH_o in Ph); 7.81 (d, 3, $J = 2.3$ Hz, 5-*H* in Phpz). ^{13}C NMR ($CDCl_3$), δ: 21.3 (*C*H_3CO); 104.2 (4-*C* in pz); 127.5, 128.1 (C_o, C_m in Ph); 128.4 (C_p in Ph); 131.6 (C_i in Ph); 137.4 (5-*C* in pz); 154.6 (3-*C* in pz); 178.9 (CH_3*C*O). IR: 2507 (ν(BH)), 1631, 1601 ($\nu_{as}(CO_2)$), 1365 (ν_{sym}(CO)). MS/FAB (*m/e*): 565 (M^+, 45%); 505 ($[M - (OAc)]^+$, 73%); 421 ($[M = (3\text{-Phpz})]^+$, 100%); 361 ($[M - (3\text{-Phpz}) - (OAc)]^+$, 92%).

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) of the Non-Hydrogen Atoms of [(η^3-Tp^{Ph})Zn(η^2-acac)] (**7**) with Esd's in Parentheses[a]

	x	*y*	*z*	*U*(eq)
Zn	2336(1)	1251(1)	2568(1)	37(1)
B	2986(2)	−619(3)	3844(2)	41(1)
O(1)	2477(1)	2838(2)	2205(1)	46(1)
O(2)	1317(1)	1100(2)	1736(1)	47(1)
N(11)	3511(1)	479(2)	4040(1)	40(1)
N(12)	3487(1)	1408(2)	3495(1)	36(1)
N(21)	2079(1)	−333(2)	3941(1)	38(1)
N(22)	1721(1)	628(2)	3560(1)	36(1)
N(31)	3095(1)	−1004(2)	2932(1)	40(1)
N(32)	2862(1)	−309(2)	2255(1)	37(1)
C(11)	4059(2)	2155(2)	3822(2)	39(1)
C(12)	4439(2)	1709(3)	4575(2)	52(1)
C(13)	4077(2)	662(3)	4686(2)	49(1)
C(14)	4291(2)	3214(2)	3380(2)	40(1)
C(15)	4540(2)	4192(3)	3847(2)	59(1)
C(16)	4808(2)	5169(3)	3443(3)	77(1)
C(17)	4846(2)	5182(3)	2590(3)	73(1)
C(18)	4607(2)	4224(3)	2120(3)	65(1)
C(19)	4326(2)	3237(3)	2516(2)	48(1)
C(21)	927(2)	607(2)	3733(2)	35(1)
C(22)	786(2)	−363(2)	4213(2)	45(1)
C(23)	1518(2)	−926(2)	4332(2)	46(1)
C(24)	345(2)	1531(2)	3456(2)	40(1)
C(25)	607(2)	2642(3)	3297(2)	51(1)
C(26)	52(3)	3514(3)	3069(3)	69(1)
C(27)	−770(2)	3279(4)	3006(3)	78(1)
C(28)	−1039(2)	2189(4)	3140(3)	87(1)
C(29)	−485(2)	1310(3)	3372(2)	63(1)
C(31)	3018(2)	−888(2)	1552(2)	42(1)
C(32)	3351(2)	−1977(3)	1786(2)	55(1)
C(33)	3393(2)	−2003(2)	2647(2)	51(1)
C(34)	2825(2)	−417(2)	700(2)	45(1)
C(35)	2830(2)	758(3)	528(2)	50(1)
C(36)	2619(2)	1168(4)	−276(2)	66(1)
C(37)	2416(3)	412(4)	−932(3)	79(1)
C(38)	2427(3)	−752(4)	−778(3)	87(1)
C(39)	2630(2)	−1163(3)	28(2)	69(1)
C(41)	2416(2)	4545(4)	1399(4)	74(1)
C(42)	2084(2)	3361(2)	1581(2)	45(1)
C(43)	1416(2)	2937(3)	1100(2)	48(1)
C(44)	1053(2)	1850(3)	1196(2)	47(1)
C(45)	290(3)	1528(5)	645(4)	88(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Anal. Calcd for $C_{29}H_{25}N_6BO_2Zn$: C, 61.57; H, 4.45; N, 14.85; Zn 11.56. Found: C, 61.43; H, 4.41; N, 14.77; Zn, 11.51.

(Benzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), [(Tp^{Ph})Zn(OBz)] (3b) was prepared from silver benzoate in the same manner as **3a**; yield 740 mg (59%) of colorless crystals. ^{1}H NMR (CDCl$_3$), δ: 6.51 (d, 3, J = 2.3 Hz, 4-H in Phpz); 7.2−7.3 (m, 9, C$H_{m,p}$ in Ph); 7.3−7.5 (m, 5, CH_{ar} in OBz); 7.7−7.8 (m, 6, CH_o in Ph); 7.85 (d, 3, J = 2.3 Hz, 5-H in Phpz). ^{13}C NMR (CDCl$_3$), δ: 21.3 (CH$_3$CO); 104.8 (4-C in pz); 127.9, 130.7 (C_o', C_m' in OBz); 128.1, 128.8 (C_o, C_m in Ph); 130.8 (C_p in Ph); 132.1 (C_i in Ph); 132.2 (C_p' in OBz); 134.5 (C_i' in OBz); 137.7 (5-C in pz); 155.4 (3-C in pz); 170.2 (CO in OBz). IR: 2499 (ν(BH)), 1614, 1572 (ν_{as}(CO$_2$)), 1366 (ν_{sym}(CO)). MS/EI (m/e): 625 (M$^+$, 39%); 505 ([M − (OBz)]$^+$, 9%); 483 ([M − (3-Phpz)]$^+$, 30%). Anal. Calcd for $C_{34}H_{27}N_6BO_2Zn$: C, 65.05; H, 4.33; N, 13.39; Zn 10.41. Found: C, 64.83; H, 4.24; N, 13.50; Zn, 10.53.

(Acetato)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [(Tp^{Ph})Co(OAc)] (4a) was prepared from [(Tp^{Ph})CoCl] in the same manner as **3a**; yield 960 mg (86%) of blue crystals from CH$_2$Cl$_2$. IR: 2470 (ν(BH)), 1541 br (ν_{as}(CO$_2$)), 1369 (ν_{sym}(CO$_2$)). MS/EI (m/e): 559 (M$^+$, 76%); 500 ([M − (OAc)]$^+$, 100%); 416 ([M − (3-Phpz)]$^+$, 32%); 355 ([M − (3-Phpz) − (OAc)]$^+$, 59%). Pink crystals from THF. IR: 2470 (ν(BH)), 1539 (ν_{as}(CO)$_2$), 1458 (ν_{sym}(CO$_2$)). UV−vis: (CH$_2$Cl$_2$) 510 (58), 580 (112), 756 (18); (THF) 514 (62). Anal. Calcd for $C_{29}H_{25}N_6BO_2Co\cdot C_4H_8O$: C, 62.77; H, 5.27; N, 13.31; Co 9.33. Found: C, 62.30; H, 5.20; N, 13.27; Co, 9.33.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) of the Non-Hydrogen Atoms of [(η^3-Tp^{Ph})Co(η^2-acac)] (**8**) with Esd's in Parentheses[a]

	x	*y*	*z*	*U*(eq)
Co	2337(1)	1248(1)	2587(1)	35(1)
B	2982(1)	−622(2)	3901(2)	42(1)
O(1)	2493(1)	2868(1)	2287(1)	46(1)
O(2)	1353(1)	1145(1)	1755(1)	44(1)
N(11)	3496(1)	484(1)	4078(1)	40(1)
N(12)	3463(1)	1391(1)	3518(1)	37(1)
N(21)	2072(1)	−337(1)	3980(1)	40(1)
N(22)	1722(1)	615(1)	3580(1)	38(1)
N(31)	3086(1)	−1037(1)	2998(1)	42(1)
N(32)	2858(1)	−335(1)	2321(1)	39(1)
C(11)	4045(1)	2143(2)	3822(1)	40(1)
C(12)	4438(1)	1716(2)	4578(2)	55(1)
C(13)	4077(1)	684(2)	4713(1)	51(1)
C(14)	4282(1)	3188(2)	3368(1)	41(1)
C(15)	4522(2)	4192(2)	3808(2)	58(1)
C(16)	4798(2)	5144(2)	3387(2)	76(1)
C(17)	4863(2)	5106(2)	2534(2)	74(1)
C(18)	4635(2)	4115(3)	2097(2)	61(1)
C(19)	4338(1)	3166(2)	2501(1)	46(1)
C(21)	928(1)	609(2)	3740(1)	37(1)
C(22)	775(1)	−355(2)	4230(1)	47(1)
C(23)	1501(1)	−923(2)	4366(1)	47(1)
C(24)	356(1)	1543(2)	3450(1)	41(1)
C(25)	629(2)	2658(2)	3309(2)	54(1)
C(26)	79(2)	3537(2)	3073(2)	72(1)
C(27)	−747(2)	3319(3)	2977(2)	83(1)
C(28)	−1024(2)	2220(3)	3109(2)	86(1)
C(29)	−477(1)	1338(2)	3350(2)	64(1)
C(31)	3014(1)	−927(2)	1621(1)	44(1)
C(32)	3337(2)	−2014(2)	1858(2)	56(1)
C(33)	3374(1)	−2046(2)	2716(2)	53(1)
C(34)	2832(1)	−438(2)	772(1)	47(1)
C(35)	2862(1)	737(2)	607(2)	54(1)
C(36)	2661(2)	1170(3)	−197(2)	68(1)
C(37)	2433(2)	417(3)	−858(2)	83(1)
C(38)	2420(2)	−743(3)	−710(2)	92(1)
C(39)	2613(2)	−1177(3)	96(2)	73(1)
C(41)	2443(2)	4613(3)	1515(3)	74(1)
C(42)	2118(1)	3413(2)	1659(1)	44(1)
C(43)	1460(1)	2995(2)	1139(1)	49(1)
C(44)	1098(1)	1906(2)	1214(1)	47(1)
C(45)	344(3)	1582(4)	642(3)	85(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(Benzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II),[(Tp^{Ph})Co(OBz)] (4b) was prepared from [(Tp^{Ph})CoCl] and silver benzoate in the same manner as **3a**; yield 1130 mg (91%) of blue crystals from CH$_2$Cl$_2$. IR: 2456 (ν(BH)), 1604, 1594 (ν_{as}(CO$_2$)), 1369 (ν_{sym}(CO$_2$)). MS/EI (m/e): 620 (M$^+$, 43%); 499 ([M − (OBz)]$^+$, 10%); 478 ([M − (3-Phpz)]$^+$, 26%); 355 ([M − (3-Phpz) − (OBz)]$^+$, 31%). Pink crystals from THF. IR: 2456 (ν(BH)), 1594 (ν_{as}(CO$_2$)), 1429 (ν_{sym}(CO$_2$)). UV−vis: (CH$_2$Cl$_2$) 514 (62), 582 (148), 768 (16); (THF) 515 (68). Anal. Calcd for $C_{34}H_{27}N_6BO_2Co$: C, 65.72; H, 4.38; N, 13.52; Co 9.48. Found: C, 65.72; H, 4.30; N, 13.60; Co, 9.22.

(4-Nitrobenzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), [(Tp^{Ph})Zn(OBz-4-NO$_2$)] (3c). [Tp^{Ph}ZnCl] (1.08 g, 2.0 mmol) and 4-nitrobenzoic acid (0.35 g, 2.1 mmol) were dissolved in THF (50 mL). KO-t-Bu in 2 mL of methanol was added, and the solution was stirred for 2 h at room temperature. A white precipitate was filtered off, and the solvent was removed in vacuo. The residue was dissolved in CH$_2$Cl$_2$/heptane, the solution slowly evaporated, and the crude product recrystallized from CH$_2$Cl$_2$/hexane; yield 0.83 g (55%) of colorless crystals. ^{1}H NMR (CDCl$_3$), δ: 5.33 (s, 2, CH_2Cl$_2$); 6.52 (d, 3, J = 2.3 Hz, 4-H in Phpz); 7.2−7.3 (m, 9, C$H_{m,p}$ in Ph); 7.7−7.8 (m, 6, CH_o in Ph); 7.82 (d, 2, J = 8.9 Hz, CH_o in Ar); 7.87 (d, 3, J = 2.3 Hz, 5-H in Phpz); 8.20 (d, 2, J = 8.9 Hz, CH_m in Ar). ^{13}C NMR (CDCl$_3$), δ: 105.1 (4-C in pz); 123.5 (C_m' in Ar); 128.3, 129.0 (C_o, C_m in Ph); 129.3 (C_p in Ph); 131.5 (C_i in Ph); 132.3 (C_o' in Ar); 138.0 (5-C in pz); 140.6 (C_i' in Ar); 150.1 (C_p' in Ar); 155.5 (3-C in pz); 171.3 (CO in Ar). IR: 2480 (ν(BH)), 1650, 1596 (ν_{as}(CO$_2$)), 1366 (ν_{sym}(CO$_2$)). MS/EI (m/e): 670 (M$^+$, 100%); 527 ([M − (3-Phpz)]$^+$, 96%); 504 ([M − (OBz-

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for $[Co(\eta^3\text{-}Tp^{Ph})(\eta^2\text{-}Tp^{Ph})]$ (**1**)

Co−N(12)	2.103(2)	N(11)−N(12)	1.364(3)
Co−N(22)	2.138(2)	N(21)−N(22)	1.361(3)
Co−N(32)	2.199(2)	N(31)−N(32)	1.372(3)
Co−N(42)	2.124(2)	N(41)−N(42)	1.366(3)
Co−N(52)	2.201(2)	N(51)−N(52)	1.367(3)
Co−H(2)	2.17(2)	N(61)−N(62)	1.369(3)
N(11)−B(1)	1.546(4)	N(41)−B(2)	1.536(4)
N(21)−B(1)	1.531(4)	N(51)−B(2)	1.528(4)
N(31)−B(1)	1.538(4)	N(61)−B(2)	1.510(4)

N(12)−Co−N(22)	94.1(1)	Co−N(12)−N(11)	114.5(2)
N(12)−Co−N(32)	89.0(1)	Co−N(22)−N(21)	113.8(2)
N(12)−Co−N(42)	99.2(1)	Co−N(32)−N(31)	112.1(2)
N(12)−Co−N(52)	102.5(1)	Co−N(42)−N(41)	105.1(2)
N(22)−Co−N(32)	83.7(1)	Co−N(52)−N(51)	105.7(2)
N(22)−Co−N(42)	165.4(1)	N(11)−B(1)−N(21)	110.6(2)
N(22)−Co−N(52)	86.9(1)	N(11)−B(1)−N(31)	109.4(2)
N(32)−Co−N(42)	90.4(1)	N(21)−B(1)−N(31)	108.4(2)
N(32)−Co−N(52)	165.7(1)	N(41)−B(2)−N(51)	110.6(2)
N(42)−Co−N(52)	96.0(1)	N(41)−B(2)−N(61)	111.2(3)
N(12)−Co−H(2)	170(1)	N(51)−B(2)−N(61)	113.0(3)
N(22)−Co−H(2)	94(1)	N(12)−N(11)−B(1)	121.4(2)
N(32)−Co−H(2)	97(1)	N(22)−N(21)−B(1)	120.9(2)
N(42)−Co−H(2)	73(1)	N(32)−N(31)−B(1)	122.0(2)
N(52)−Co−H(2)	73(1)	N(42)−N(41)−B(2)	117.5(2)
		N(52)−N(51)−B(2)	115.6(2)
		N(62)−N(61)−B(2)	119.8(2)

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for $[(\eta^3\text{-}Tp^{Ph})Zn(anthranilate)]$ (**5**)

Zn−N(12)	2.087(2)	N(11)−N(12)	1.369(2)
Zn−N(22)	2.042(2)	N(21)−N(22)	1.361(2)
Zn−N(32)	2.057(2)	N(31)−N(32)	1.377(2)
Zn−O(1)	1.932(2)	B−N(11)	1.539(4)
Zn−O(2)	2.460(2)	B−N(21)	1.547(4)
C(1)−O(1)	1.291(3)	B−N(31)	1.540(4)
C(1)−O(2)	1.239(3)		

N(12)−Zn−N(22)	88.9(1)	O(1)−Zn−O(2)	58.3(1)
N(12)−Zn−N(32)	98.2(1)	Zn−O(1)−C(1)	102.4(1)
N(22)−Zn−N(32)	91.6(1)	Zn−O(2)−C(1)	79.5(2)
N(12)−Zn−O(1)	109.9(1)	N(11)−B−N(21)	108.7(2)
N(22)−Zn−O(1)	127.6(1)	N(11)−B−N(31)	109.1(2)
N(32)−Zn−O(1)	128.1(1)	N(21)−B−N(31)	109.9(2)
N(12)−Zn−O(2)	168.2(1)	O(1)−C(1)−O(2)	119.8(2)
N(22)−Zn−O(2)	96.3(1)	O(1)−C(1)−C(2)	117.1(2)
N(32)−Zn−O(2)	98.5(1)	O(2)−C(1)−C(2)	123.2(2)
Zn−N(12)−N(11)	110.6(1)	N(12)−N(11)−B	121.5(2)
Zn−N(22)−N(21)	112.3(2)	N(22)−N(21)−B	120.4(2)
Zn−N(32)−N(31)	110.8(1)	N(32)−N(31)−B	121.5(2)

4-NO$_2$)]$^+$, 16%); 361 ([M − (3-Phpz) - (OBz-4-NO$_2$)]$^+$, 96%). Anal. Calcd for $C_{34}H_{26}N_7BO_4Zn{\cdot}CH_2Cl_2$: C, 55.48; H, 3.72; N, 12.94; Zn 9.72. Found: C, 55.66; H, 3.64; N, 12.94; Zn, 9.51.

(4-Fluorobenzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), [(Tp^{Ph})Zn(OBz-4-F)] (3d) was prepared from 4-fluorobenzoic acid in the same way as **3c**; yield 0.45 g (35%) of colorless crystals. ^{1}H NMR (CDCl$_3$), δ: 6.51 (d, 3, J = 2.3 Hz, 4-*H* in Phpz); 7.00, 7.25, 7.44 (m, 4, C*H* in Ar); 7.2−7.3 (m, 9, C$H_{m,p}$ in Ph); 7.7−7.8 (m, 6, CH_o in Ph); 7.85 (d, 3, J = 2.3 Hz, 5-*H* in Phpz). ^{13}C NMR (CDCl$_3$), δ: 105.0 (4-*C* in pz); 114.9 (d, $^2J_{FC}$ = 22 Hz, C_m' in Ar); 128.3, 128.9 (C_o, C_m in Ph); 129.1 (C_p in Ph); 130.8 (d, $^4J_{FC}$ = 3 Hz, C_i' in Ar); 132.3 (C_i in Ph); 133.0 (d, $^3J_{FC}$ = 9 Hz, C_o' in Ar); 137.9 (5-*C* in pz); 155.5 (3-*C* in pz); 165.4 (d, $^1J_{FC}$ = 250 Hz, C_p' in Ar); 173.1 (*C*O in Ar). IR: 2495 (ν(BH)), 1620, 1603 (ν_{as}(CO$_2$)), 1365 (ν_{sym}(CO$_2$)). MS/EI (*m/e*): 643 (M$^+$, 33%); 504 ([M − (OBz-4-NO$_2$)]$^+$, 33%). Anal. Calcd for $C_{34}H_{26}N_6BFO_2Zn$: C, 63.23; H, 4.06; N, 13.01; Zn 10.12. Found: C, 63.05; H, 4.11; N, 13.19; Zn, 9.81.

(4-Nitrobenzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [(Tp^{Ph})Co(OBz-4-NO$_2$)] (4c) was prepared from [(Tp^{Ph})CoCl] in the same way as **3c**; yield 0.30 g (23%) of blue needles. IR: 2494 (ν(BH)), 1565 (ν_{as}(CO$_2$)), 1368 (ν_{sym}(CO$_2$)). MS/EI (*m/e*): 665 (M$^+$, 51%); 522 ([M − (3-Phpz)]$^+$, 42%); 498 ([M − (OBz-4-NO$_2$)]$^+$, 25%); 355 ([M − (3-Phpz) − (OBz-4-NO$_2$)]$^-$, 100%). UV−vis: (CH$_2$Cl$_2$) 517 (70), 586 (198), 767 (15); (THF) 525 (70), 596 (28), 622 (22), 669 (6). Anal. Calcd for $C_{34}H_{26}N_7BO_4Co$: C, 61.28; H, 3.93; N, 14.71; Co 8.84. Found: C, 61.40; H, 3.85; N, 14.80; Co 8.69.

(4-Fluorobenzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [(Tp^{Ph})Co(OBz-4-F)] (4d) was prepared from [(Tp^{Ph})CoCl] and 4-fluorobenzoic acid in the same way as **3c**; yield 1.10 g (86%) of blue crystals. IR: 2490 (ν(BH)), 1604, 1554 (ν_{as}(CO$_2$)), 1389 (ν_{sym}(CO$_2$)). MS/EI (*m/e*): 639 (M$^+$, 62%); 498 ([M − (OBz-4-F)]$^+$, 27%); 355 ([M − (3-Phpz) − (OBz-4-F)]$^+$, 84%). UV−vis (CH$_2$Cl$_2$) 514 (70), 586 (164), 758 (16); (THF) 516 (70), 592 (32), 622 (26), 665 (8). Anal. Calcd for $C_{34}H_{26}N_6BFO_2Co$: C, 63.87; H, 4.10; N, 13.14; Co 9.22. Found: C, 63.67; H, 4.06; N, 13.28; Co 9.13.

(2-Aminobenzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), [(Tp^{Ph})Zn(anthranilate)] (5). Through a solution of anthranilic acid (0.70 g; 5.1 mmol) in 50 mL of CH$_2$Cl$_2$ was bubbled gaseous HCl for 0.5 h. The resulting voluminous precipitate was filtered off, dried, and dissolved in 30 mL of methanol. The solution was stirred in the dark for 2 d with Ag$_2$O (1.16 g; 5 mmol). The solvent was evaporated and to the residue was added a solution of [(Tp^{Ph})ZnCl] (2.71 g; 5.0 mmol) in 50 mL of CH$_2$Cl$_2$. After overnight stirring, the precipitate was filtered off. Addition of 20 mL of hexane to the filtrate led to the colorless microcrystalline product (1.71 g; 53%). ^{1}H-NMR (CDCl$_3$), δ: 6.45 (d, J = 2.3 Hz, 3, 4-*H* in pz), 6.5 − 6.6 (m, 4, C*H*-in Ar), 7.2−7.4 (m, 9, C$H_{m,p}$ in Ph), 7.4 (s, 2, NH_2), 7.6 −7.8 (m, 6, CH_o in Ph), 7.80 (d, J = 2.3 Hz, 3, 5-*H* in pz). ^{13}C-NMR (CDCl$_3$), δ: 104.9 (4-*C* in pz), 116.1 (H*C*CNH$_2$), 116.4 (O$_2$CCH*C*H), 128.2, 128.9 ($C_{o,m}$ in Ph), 129.1 (C_p in Ph), 129.1 (*C*CO$_2$), 132.3 (C_i in Ph), 133.1 (H*C*CCO$_2$), 133.7 (H*C*CHCNH$_2$), 137.8 (5-*C* in pz), 150.6 (*C*NH$_2$), 155.5 (3-*C* in pz), 168.3 (R*C*O$_2$). IR: 2480 (ν(BH)), 1619, 1578, 1538 (ν_{as}(CO$_2$)), 1365 (ν_{sym}(CO$_2$)). MS/EI (*m/e*): 641 (M$^+$, 9%), 504 ([M − OBz-2-NH$_2$]$^+$, 23%), 496 ([M − (3-Phpz)]$^+$, 18%), 361 ([M − (OBz-2-NH$_2$) - (3-Phpz)]$^+$, 19%). Anal. Calcd for $C_{34}H_{28}N_7BO_2Zn$: C, 63.53; H, 4.39; N, 15.25; Zn, 10.17; B, 1.68. Found: C, 63.53; H, 4.23; N, 15.40; Zn, 10.21; B, 1.82.

(2-Aminobenzoato)[hydrotris(3-phenylpyrazol-1-yl)borato]cobalt(II), [(Tp^{Ph})Co(anthranilate)] (6). A mixture of equimolar amounts of sodium anthranilate (318 mg; 2.0 mmol) and anthranilic acid (275 mg; 2.0 mmol) dissolved in 5 mL of methanol was added in the dark to a suspension of silver acetate (670 mg; 4.01 mmol) in 30 mL of THF. After 24 h of stirring, [Tp^{Ph}CoBr] (2.30 g; 3.96 mmol) in 70 mL of THF was added. After 2 h the suspension was brought to dryness, and the solid residue was extracted with 50 mL of CH$_2$Cl$_2$. To the filtered solution was added 20 mL of heptane. The solvent was distilled off in vacuo until precipitation began. Slow cooling to −30 °C afforded 1.95 g (77%) of a pink powder, soluble with a blue color in CH$_2$Cl$_2$, toluene, and benzene and with a pink-red color in THF and MeCN. IR: 2472 (ν(BH)), 1617, 1588, 1577 (ν_{as} (CO$_2$)), 1405 (ν_{sym}(CO$_2$)). MS/EI (*m/e*): 636 (M$^+$, 51%), 500 ([M − OBz-2-NH$_2$]$^+$, 9%), 491 ([M − (3-Phpz)]$^+$, 100%), 354 ([M − (OBz-2-NH$_2$) − (3-Phpz)]$^+$, 23%), 348 ([M − 2(3-Phpz)]$^+$, 72%). UV−vis: (CH$_2$Cl$_2$) 504 (49), 584 (70), 755 (10); (THF) 513 (28). Anal. Calcd for $C_{34}H_{28}N_7BO_2Co{\cdot}C_4H_8O$: C, 64.42; H, 5.12; N, 13.84; Co, 8.83. Found: C, 64.16; H, 5.06; N, 13.62; Co 8.52.

[Hydrotris(3-phenylpyrazol-1-yl)borato](pentane-2,4-dionato)zinc(II), [(Tp^{Ph})Zn(acac)] (7). To a solution of [(Tp^{Ph})ZnCl] (1.07 g, 2.0 mmol) and acetylacetone (0.22 mL, 2.1 mmol) in THF (70 mL) was added solid KO-*t*-Bu. After overnight stirring, the solvent was evaporated in vacuo, and the colorless residue was dissolved in 40 mL of CH$_2$Cl$_2$. After microfiltration, 20 mL of heptane was added, and the volume was reduced at 40 °C until crystallization began. Slow cooling to 0 °C led to 850 mg (70%) of colorless crystals. ^{1}H NMR (CDCl$_3$), δ: 1.17 (s, 6, C*H*$_3$CO); 5.00 (s, 1, COC*H*CO); 6.44 (d, 3, J = 2.3 Hz, 4-*H* in Phpz); 7.3−7.7 (m, 15, C*H* in Ph); 7.80 (d, 3, J = 2.3 Hz, 5-*H* in Phpz). ^{13}C NMR (CDCl$_3$), δ: 27.7 (*C*H$_3$CO); 100.4 (CO*C*HCO); 104.9 (4-*C* in pz); 128.2 (C_p in Ph); 128.5, 128.7 (C_o, C_m in Ph); 133.8 (C_i in Ph); 137.1 (5-*C* in pz); 154.7 (3-*C* in pz); 192.8 (CH$_3$*C*O). IR: 2451 (ν(BH)), 1600 (ν(CO$_2$)). MS/FAB (*m/e*): 605 (M$^+$, 27%); 505 ([M − (acac)]$^+$, 27%); 461 ([M − (3-Phpz)]$^+$, 100); 361 ([M − (3-Phpz) − (acac)]$^+$, 35%). Anal. Calcd for $C_{32}H_{29}N_6BO_2Zn$: C, 63.44; H, 4.83; N, 13.87; Zn 10.79. Found: C, 63.36; H, 4.86; N, 13.79; Zn, 10.48.

[Hydrotris(3-phenylpyrazol-1-yl)borato](pentane-2,4-dionato)cobalt(II), [(Tp^{Ph})Co(acac)] (8). KTp^{Ph} (480 mg; 1.0 mmol) was stirred for 2 h with CoCl$_2$ (202 mg; 1.0 mmol) in 20 mL of THF. After

Table 8. Selected Interatomic Distances (Å) and Angles (deg) for [(η^3-Tp^{Ph})M(η^2-acac)], M = Zn (**7**) and Co (**8**)

	7	**8**
M−N(12)	2.293(2)	2.257(2)
M−N(22)	2.062(2)	2.078(2)
M−N(32)	2.073(2)	2.072(2)
M−O(1)	1.940(2)	1.948(1)
M−O(2)	2.041(2)	1.987(2)
N(11)−N(12)	1.375(3)	1.369(3)
N(21)−N(22)	1.369(3)	1.365(3)
N(31)−N(32)	1.367(3)	1.367(3)
O(1)−C(42)	1.282(3)	1.284(3)
O(2)−C(44)	1.266(3)	1.270(2)
C(42)−C(43)	1.368(4)	1.380(3)
C(43)−C(44)	1.402(4)	1.397(3)
N(12)−M−N(22)	88.1(1)	87.3(1)
N(12)−M−N(32)	83.5(1)	82.6(1)
N(22)−M−N(32)	96.7(1)	94.7(1)
N(12)−M−O(1)	90.2(1)	88.4(1)
N(22)−M−O(1)	129.3(1)	127.2(1)
N(32)−M−O(1)	133.5(1)	136.7(1)
N(12)−M−O(2)	179.5(1)	179.0(1)
N(22)−M−O(2)	92.2(1)	93.6(1)
N(32)−M−O(2)	96.0(1)	97.8(1)
O(1)−M−O(2)	90.0(1)	90.7(1)
M−O(1)−C(42)	127.5(2)	126.4(1)
M−O(2)−C(44)	126.2(2)	127.0(1)
O(1)−C(42)−C(41)	114.1(3)	114.6(2)
O(1)−C(42)−C(43)	125.8(3)	125.7(2)
O(2)−C(44)−C(43)	124.2(3)	124.3(4)
O(2)−C(44)−C(45)	116.1(3)	115.7(2)
C(42)−C(43)−C(44)	125.8(3)	125.1(2)
M−N(12)−N(11)	108.6(1)	110.4(1)
M−N(22)−N(21)	113.6(2)	114.9(1)
M−N(32)−N(31)	114.6(2)	116.6(1)
N(12)−N(11)−B	121.8(2)	121.7(2)
N(22)−N(21)−B	120.6(2)	120.1(2)
N(32)−N(31)−B	121.3(2)	120.2(2)
N(11)−B−N(21)	109.1(2)	109.0(2)
N(11)−B−N(31)	108.7(2)	108.8(2)
N(21)−B−N(31)	110.1(2)	109.5(2)

removal of the insoluble salts, sodium acetylacetonate (134 mg, 1.1 mmol) was added. The color changed overnight from deep blue to purple-red. The solvent was evaporated in vacuo, and the residue was taken up in 20 mL of CH_2Cl_2. After filtration, the volume was reduced to 5 mL and chromatographed on silica. The reddish-brown band was eluted, and after addition of 20 mL of heptane, the solvent was evaporated until precipitation started. Slow cooling to −30 °C led to blood-red crystals (370 mg, 62%). IR: 2466 (ν(BH)), 1587 (ν (CO_2)). MS/FAB (*m/e*): 599 (M^+, 15%), 500 ($[M - (acac)]^+$, 15%), 456 ($[M - (3\text{-Phpz})]^+$, 100%), 356 ($[M - (3\text{-Phpz}) - (acac)]^+$, 20%). UV−vis ($CH_2Cl_2$): 440 (79), 530 (41), 551 (45), 672 (14). Anal. Calcd for $C_{32}H_{29}N_6BO_2Co$: C, 64.13; H, 4.88; N, 14.02; Co 9.83. Found: C, 64.12; H, 4.82; N, 14.00; Co, 9.77.

Determination of Crystal Structures. The X-ray data for **1**, **5**, **7**, and **8** were measured at room temperature on a SYNTEX/SIEMENS P2$_1$/P3 four-circle diffractometer with graphite-monochromated Mo Kα radiation. A correction for absorption was not applied. The structures were solved from the Patterson function and all non-hydrogen atoms refined with anisotropic displacement parameters. The hydrogen atoms in **1**, **7**, and **8** were directly located and refined isotropically, whereas those in **5** were generated and added in a riding mode. Crystallographic data are summarized in Table 1. Positional and equivalent isotropic displacement parameters of the non-hydrogen atoms are given in Tables 2−5, with selected interatomic distances and angles given in Tables 6−8. For simplicity, quotations from these tables in the subsequent text are made with reduced accuracy and without standard deviations. All calculations were performed with the program systems SHELXTL PLUS[10a] and SHELXL-93.[10b]

Results

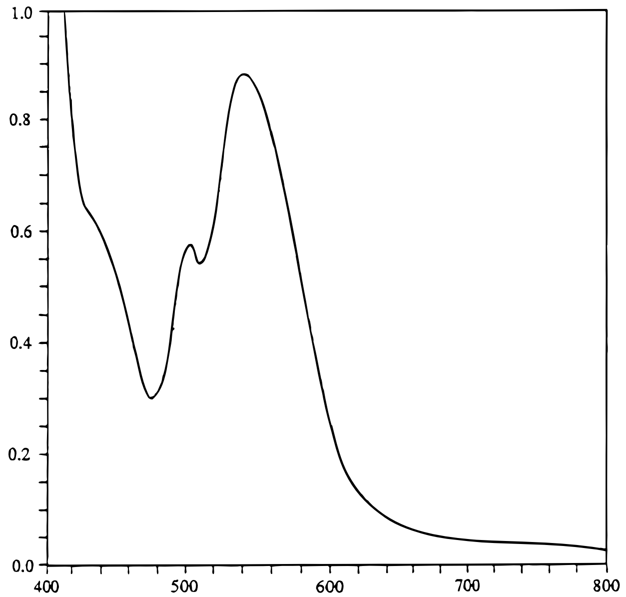

Figure 1. UV−vis spectrum ($\epsilon \times 10^{-2}$ vs. λ/nm) of [Co(η^3-Tp^{Ph})(η^2-Tp^{Ph})] (**1**) in tetrahydrofuran or dichloromethane solution.

In a recent publication we have reported on the tris(pyrazolyl)borate complex [Zn(Tp^{Ph})$_2$].[9] Its unexpected structure with the two tripodal ligands Tp^{Ph} acting bidentate induced us to try the synthesis of the corresponding cobalt compound. The seemingly straightforward reaction of cobalt chloride or perchlorate with the potassium salt KTp^{Ph} leads to a mixture of products from which it is difficult to isolate crystals of the desired compound. Blood-red crystals of [Co(Tp^{Ph})$_2$] (**1**) are accessible, however, from the labile hydroxo complex [(Tp^{Ph})Co(OH)] (eq 1). The

$$\mathrm{KTp^{Ph} + Co(ClO_4)_2{\cdot}6H_2O + KOH \rightarrow [(Tp^{Ph})Co(OH)] + 2KClO_4 + 6H_2O}$$

$$\mathrm{2[(Tp^{Ph})Co(OH)] \rightarrow [Co(Tp^{Ph})_2] + Co(OH)_2} \qquad (1)$$

UV-vis spectra in tetrahydrofuran and dichloromethane are identical with $\epsilon = 82\ M^{-1}\ cm^{-1}$ at $\lambda_{max} = 550$ nm (see Figure 1). The low extinction indicates that the cobalt ion in **1** is not tetrahedrally coordinated.[11]

The crystal structure shows the cobalt ion in **1** to be pentacoordinated (Figure 2). The 5-fold coordination results from one ligand being tris-chelating and the other bidentate. The metal−nitrogen distances (2.10−2.20 Å) (Table 6) are longer than those in the nonisotypic zinc compound [Zn(Tp^{Ph})$_2$] (2.01 and 2.02 Å).[9] The coordination polyhedron in **1** can be described as square pyramidal or—including the BH···Co interaction of 2.17 Å—as octahedral. A comparison of the deviations of the angles from those of a regular octahedron and square pyramid is given in Table 9.[12] The average deviations are 8.2° (O_h) and 7.6° (C_{4v}).

The pentacoordinated cobalt complex **1** is not inert. It reacts with CoX$_2$ in dichloromethane to give deep blue tetrahedral complexes (eq 2). The complexes **2a−c** can also be prepared

$$\mathrm{[Co(Tp^{Ph})_2] + CoX_2 \rightarrow \underset{\textbf{2a−c}}{2[(Tp^{Ph})CoX]}} \qquad (2)$$

$$\mathrm{X = Cl, Br, NCS}$$

from KTp^{Ph} and anhydrous cobalt salts in dichloromethane. Trofimenko et al. have determined the crystal structure of a red

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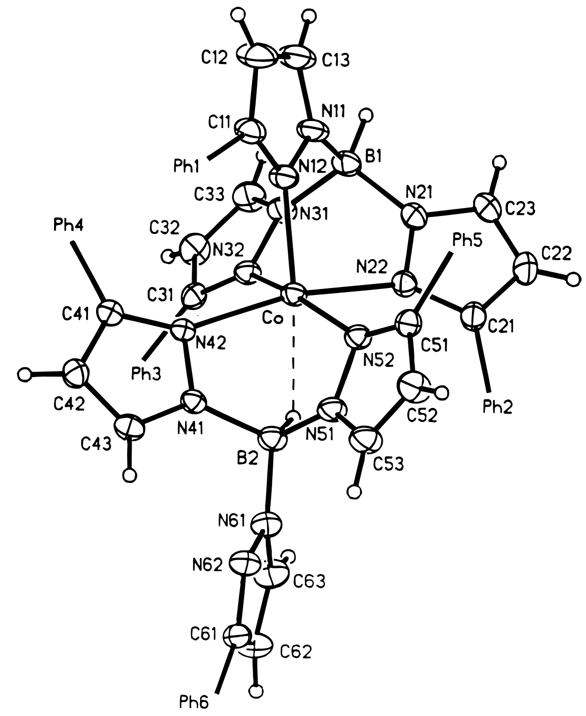

Figure 2. Molecular structure of [Co(η^3-Tp$^{\mathrm{Ph}}$)(η^2-Tp$^{\mathrm{Ph}}$)] (**1**) including labeling. For clarity, the phenyl rings have been replaced by Ph(1)–Ph(6). Ellipsoids of 25% probability are shown.[10a]

Table 9. Deviation of the Observed Angles (deg) in **1** from Regular Octahedral and Square Pyramidal Coordination[12]

angle	measd	octahedron	Δ(o)	square pyramid	Δ(sqp)
N(12)–Co–H(2)	170	180	10.0		
N(22)–Co–N(42)	165.4	180	14.6	151.9	13.5
N(32)–Co–N(52)	165.7	180	14.3	151.9	13.8
N(22)–Co–N(32)	83.6	90	6.4	86.6	3.0
N(22)–Co–N(52)	86.9	90	3.1	86.6	0.3
N(32)–Co–N(42)	90.4	90	0.4	86.6	3.8
N(42)–Co–N(52)	96.0	90	6.0	86.6	9.4
N(12)–Co–N(22)	94.1	90	4.1	104.1	10.0
N(12)–Co–N(32)	89.0	90	1.0	104.1	15.1
N(12)–Co–N(42)	99.2	90	9.2	104.1	4.9
N(12)–Co–N(52)	102.5	90	12.5	104.1	1.6
N(22)–Co–H(2)	94	90	6		
N(32)–Co–H(2)	97	90	7		
N(42)–Co–H(2)	73	90	17		
N(52)–Co–H(2)	73	90	17		

tetrahydrofuran adduct of [(Tp$^{\mathrm{Ph}}$)CoNCS] (**2c**).[7a] This five-coordinate cobalt complex loses the tetrahydrofuran ligand and turns deep blue when dissolved in dichloromethane. Both the chloro complex **2a** and the bromo complex **2b** have different extinction coefficients in tetrahydrofuran and dichloromethane solutions as well, but the effect is much less pronounced. [(Tp$^{\mathrm{Ph}}$)CoCl(THF)], a tetrahydrofuran adduct of **2a**, can be isolated. It is a blue compound. Without X-ray structures it seems difficult to assess the role of tetrahydrofuran in this case. It is interesting to note the contrasting behavior of the analogous zinc complexes [(Tp$^{\mathrm{Ph}}$)ZnX], X = Cl, Br, NCS. None of them forms adducts with tetrahydrofuran.

This suggested to study systematically the coordination behavior of zinc and cobalt complexes [(Tp$^{\mathrm{Ph}}$)M(OOCR)] with potentially bidentate carboxylate ligands. We have prepared the carboxylate complexes from the halide complexes [(Tp$^{\mathrm{Ph}}$)MX] and the corresponding silver carboxylate or the carboxylic acid in the presence of potassium *tert*-butyl alcoholate (eq 3). In Table 10 are given in the carboxylate stretching vibrations $\nu_{\mathrm{as}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ of the complexes **3a–d, 4a–d** in solution and in the solid state. The difference $\Delta\nu(\mathrm{CO_2}) = \nu_{\mathrm{as}}(\mathrm{CO_2}) - \nu_{\mathrm{sym}}(\mathrm{CO_2})$ is a useful probe for the coordination mode.[13] The large values $\Delta\nu(\mathrm{CO_2})$ of **3a–d** indicate that in all the zinc complexes the carboxylate ligands are η^1-bonded or intermediate between monodentate and bidentate.[14] This agrees well with the infrared data and the Zn–O distances of [(Tp$^{\mathrm{Ph}}$)Zn(hydrogenmalonate)], $\Delta\nu(\mathrm{CO_2})$ = 198 cm^{-1}, Zn–O 1.88 and 2.90 Å, and the data from [(Tp$^{\mathrm{Ph}}$)Zn(phenylacetate)], $\Delta\nu(\mathrm{CO_2})$ = 229 cm^{-1}, Zn–O 1.94 and 2.44 Å.[15] Neither **3a–d** nor the zinc complexes characterized in Darensbourg's laboratory change their coordination mode when dissolved in tetrahydrofuran. The cobalt carboxylate complexes **4a–d,** however, behave markedly different. They show different $\Delta\nu(\mathrm{CO_2})$ values and different colors in the solid state and in solution. Dichloromethane solutions of [(Tp$^{\mathrm{Ph}}$)Co(acetate)] (**4a**) and [(Tp$^{\mathrm{Ph}}$)Co(benzoate)] (**4b**), and crystals grown from dichloromethane are dark blue. Tetrahydrofuran solutions and crystals grown from tetrahydrofuran are pink, purple, or red-violet. The electronic spectra of **4b** in dichloromethane and tetrahydrofuran solution are depicted in Figure 3. The blue shift of the absorption and the decrease in the extinction coefficient (ϵ < 70 M^{-1} cm^{-1}) upon dissolution in tetrahydrofuran is accompanied by a decrease in $\Delta\nu(\mathrm{CO_2})$. Both indicate a transition toward coordination numbers larger than four brought about by tetrahydrofuran and/or bidentate carboxylate coordination. We cannot exclude an equilibrium mixture of several species. Pink crystals of **4a** contain 1 mol of tetrahydrofuran; the crystals of **4b** are stable in the presence of mother liquor only. When dry, they degrade and turn blue. We have not been able to grow single crystals of these pink cobalt complexes. In an attempt to see whether varying the electronic properties of benzoate can change the hapticity we have prepared **3,4c** and **3,4d**, the *p*-nitro- and *p*-fluoro-substituted analogs of **3,4b**. As judged from their infrared and UV–vis spectra they behave like the unsubstituted zinc and cobalt benzoate complexes **3,4b**.

$$[(\mathrm{Tp}^{\mathrm{Ph}})\mathrm{MX}] + \mathrm{RCOOM'} \rightarrow \underset{\mathbf{3a-d,\ 4a-d}}{[(\mathrm{Tp}^{\mathrm{Ph}})\mathrm{M(OOCR)}]} + \mathrm{M'X} \qquad (3)$$

X = Cl, Br; M′ = K, Ag; M = Zn (**3**), Co (**4**);
R = Me (**a**), Ph (**b**), *p*-NO$_2$Ph (**c**), *p*-F-Ph (**d**)

In a further attempt to stabilize coordination number 5 we tried to introduce 2-aminobenzoate (anthranilate), a potential chelating N,O-ligand. The possible binding modes of anthranilate are depicted in Figure 4. The synthesis of [(Tp$^{\mathrm{Ph}}$)Co(anthranilate)] (**6**), is difficult. It is hampered by the fact that insoluble polymeric [Co(anthranilate)$_2$]$_x$ has a high tendency to form. It was not possible to prepare [(Tp$^{\mathrm{Ph}}$)M(anthranilate)], M = Zn (**5**) or Co (**6**) from [(Tp$^{\mathrm{Ph}}$)MCl] and anthranilic acid or from [(Tp$^{\mathrm{Ph}}$)CoCl] and sodium anthranilate. The cobalt complex **6** could however be prepared in good yield as a red microcrystalline solid from an in situ prepared suspension of silver anthranilate in an acetic acid/sodium acetate buffer solution and [(Tp$^{\mathrm{Ph}}$)CoBr] in tetrahydrofuran/methanol. It is a a labile compound that dissolves with pink-red color in tetrahydrofuran and dismutates in solution within a few hours

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Table 10. Carboxylate Stretching Vibrations (cm^{-1}) $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ for the Complexes **3a–d** and **4a–d** in Solution and in the Solid State

complex	color	solvent[a]	Matrix	$\nu_{as}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu(CO_2)$
$[(Tp^{Ph})Zn(OAc)]$ (**3a**)	colorless	THF/CH_2Cl_2	KBr	1601	1365	236
		THF	solution	1605	1365	240
		CH_2Cl_2	solution	1602	1367	235
$[(Tp^{Ph})Zn(OBz)]$ (**3b**)	colorless	THF/CH_2Cl_2	KBr	1613/1572	1365	248/207
		THF	solution	1624/1616	1365	259/251
		CH_2Cl_2	solution	1623/1616	1366	257/250
$[(Tp^{Ph})Zn(OBz\text{-}4\text{-}NO_2)]$ (**3c**)	colorless	THF/CH_2Cl_2	KBr	1650/1596	1366	284/230
		THF	solution			
		CH_2Cl_2	solution			
$[(Tp^{Ph})Zn(OBz\text{-}4\text{-}F)]$ (**3d**)	colorless	THF/CH_2Cl_2	KBr	1620/1603	1365	255/238
		THF	solution			
		CH_2Cl_2	solution			
$[(Tp^{Ph})Co(OAc)]$ (**4a**)	pink	THF	KBr	1539	1458	81
	blue	CH_2Cl_2	KBr	1541 br	1369	172
	purple	THF	solution	1539	covered	
	blue	CH_2Cl_2	solution	1559	1369	190
$[(Tp^{Ph})Co(OBz)]$ (**4b**)	pink	THF	KBr	1594	1429	165
	blue	CH_2Cl_2	KBr	1594	1369	225
	violet	THF	solution	1594/1526	1424	170/102
	blue	CH_2Cl_2	solution	1603/1595	1369	234/226
$[(Tp^{Ph})Co(OBz\text{-}4\text{-}NO_2)]$ (**4c**)	blue	CH_2Cl_2	KBr	1565	1368	197
$[(Tp^{Ph})Co(OBz\text{-}4\text{-}F)]$ (**4d**)	blue	CH_2Cl_2	KBr	1604/1554	1389	215/165

[a] Crystallized from and dissolved in, respectively.

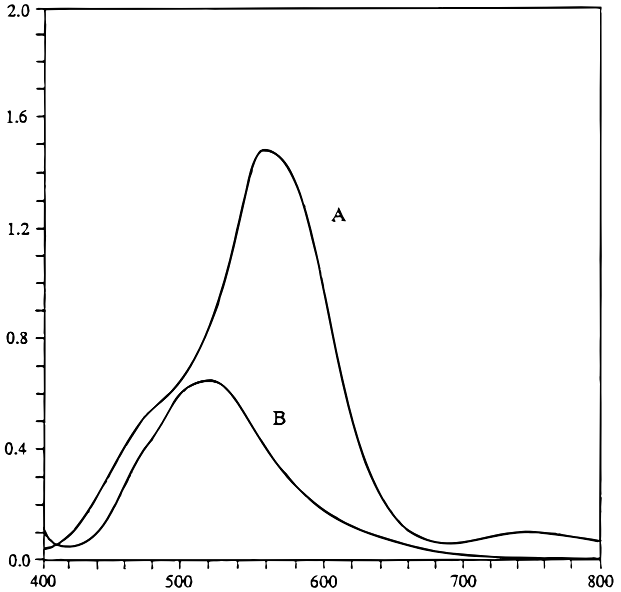

Figure 3. UV–vis spectra ($\epsilon \times 10^{-2}$ vs. λ/nm) of $[(Tp^{Ph})Co(benzoate)]$ (**4b**) in dichloromethane (A) and tetrahydrofuran (B) solution.

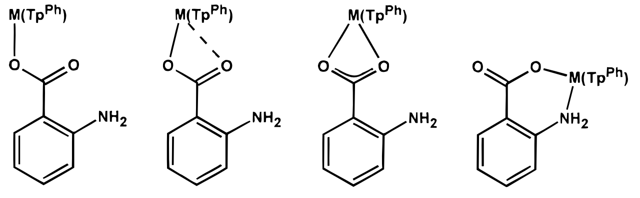

Figure 4. Binding modes of anthranilate.

to give the insoluble polymeric cobalt anthranilate (eq 4). We

$$2[(Tp^{Ph})Co(anthranilate)] \underset{\mathbf{6}}{} \rightarrow [Co(anthranilate)_2]_x + \underset{\mathbf{1}}{[Co(Tp^{Ph})_2]} \quad (4)$$

have not been successful in growing single crystals of the red cobalt complex **6**. The off-white zinc complex **5** is accessible similarly. It is less prone to dismutation. We have been able to grow single crystals of **5** from toluene/heptane and have determined the X-ray structure. The molecular structure of **5** is shown in Figure 5. Anthranilate is not an N,O-chelating ligand. It acts as oxygen ligand intermediate between monodentate and bidentate with Zn-O bond distances of 1.93 and 2.46 Å (Table 7). The amino group is not involved in the bonding to the metal. Instead there is an intramolecular NH···O hydrogen bond (distance N···O 2.72 Å) to the carboxylate oxygen atom that is weakly coordinating to zinc. The infrared spectra of **5** in the solid state and in tetrahydrofuran and dichloromethane solution are nearly identical, with $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ of 1620 and 1365 cm^{-1}, respectively. These carboxylate stretching vibrations and the Zn–O bond distances of **5** agree well with the values of the carboxylate complex $[(Tp^{Ph})Zn(phenylacetate)]$ reported by Darensbourg et al. (see above).[15]

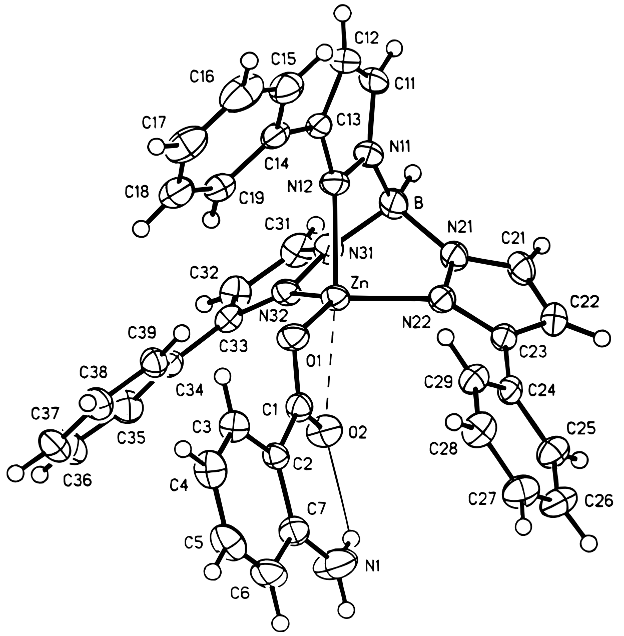

Figure 5. Molecular structure of $[(\eta^3\text{-}Tp^{Ph})Zn(anthranilate)]$ (**5**). For further details see Figure 2.

Although we have no crystal structure of the cobalt anthranilate complex **6**, the mass spectrum shows it to be a monomeric compound and the infrared spectra indicate that the zinc complex **5** and the cobalt complex **6** have very similar solid state

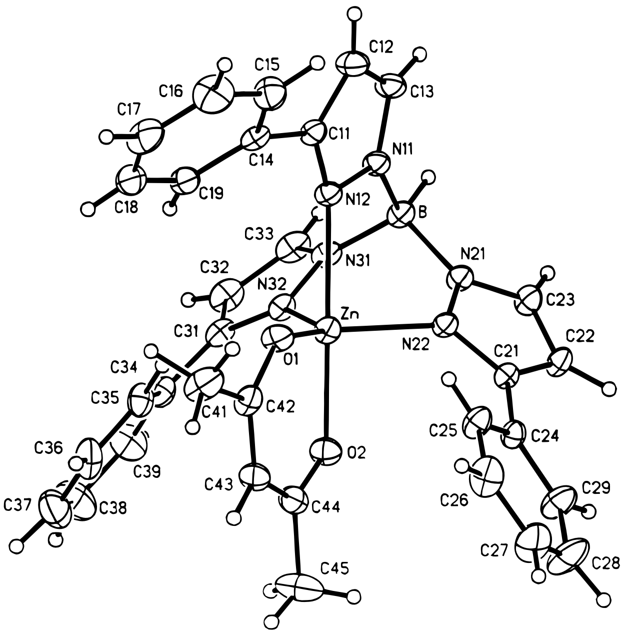

Figure 6. Molecular structure of $[(\eta^3\text{-Tp}^{Ph})Zn(\eta^2\text{-acac})]$ (**7**). For further details see Figure 2.

structures. The amino group again is not coordinating and $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ are 1617 and 1405 cm^{-1}. The solution behavior of **6** is complex. Its UV−vis spectrum in dichloromethane shows the same band pattern as that of the carboxylate complexes described above, but the extinction of the absorption maximum is unusually low ($\epsilon = 70\ M^{-1}\ cm^{-1}$ at $\lambda_{max} = 584$ nm). A shoulder at 500 nm coincides with the absorption maximum in the spectrum measured in tetrahydrofuran ($\epsilon = 49\ M^{-1}\ cm^{-1}$ at $\lambda_{max} = 504$ nm). The obvious interpretation of the spectrum is an equilibrium of tetra- and pentacoordinated cobalt in solution. This is supported by the observation that the blue solutions of the cobalt anthranilate complex **6** in dichloromethane, carbon tetrachloride, or toluene reversibly turn red when cooled below −30 °C.

Our results with the zinc and cobalt carboxylate complexes **3a**−**d**, **4a**−**d**, **5**, and **6** indicated that it should be possible to force pentacoordination with a bidentate oxygen ligand even in zinc complexes of the tripodal nitrogen ligand Tp^{Ph}. Acetylacetonate (acac) is a ligand that forms highly stable chelates with 3d transition metals. We have prepared the zinc and cobalt acetylacetonate complexes $[(Tp^{Ph})M(acac)]$, M = Zn (**7**) and Co (**8**), from the chloro complexes $[(Tp^{Ph})MCl]$ and sodium or potassium acetylacetonate. Complex **8** has a blood-red color in dichloromethane and in tetrahydrofuran solution as well as in the solid state. Single crystals of **7** and **8** were grown from dichloromethane/heptane solutions at −30 °C. The two compounds are isotypic. The molecular structure of **7** is shown in Figure 6. The metal coordination polyhedron is a nearly regular trigonal bipyramid with the axial positions occupied by one of the acac O and one of the tripodal N donor atoms (O−M−N 179° for **7** and **8**). The axial bond lengths M−O (2.04 and 1.99 Å) and M−N (2.29 and 2.26 Å) are significantly longer than the corresponding equatorial ones (1.94 and 1.95 Å and 2.06−2.08 Å). The six-membered acac chelate ring is planar within 0.04 Å with five nearly identical angles around 126° and O−M−O close to 90°. The solid state structure of the cobalt complex **8** is retained in solution. The UV−vis spectra in dichloromethane and tetrahydrofuran are identical with $\lambda_{max} = 440$ nm, $\epsilon = 79\ M^{-1}\ cm^{-1}$.

Discussion

The molecular structures of $[Co(Tp^{Ph})_2]$ (**1**) and $[Zn(Tp^{Ph})_2]$[9] show that the ligand Tp^{Ph} forms zinc and cobalt complexes with drastically different coordination spheres. In the tetrahedral zinc complex both ligands act bidentate with one pyrazole ring turned away from the metal. In the cobalt complex **1** only one ligand has this conformation (see Figure 7). With the second ligand acting tridentate, the metal takes up a square pyramidal geometry. The intermediate steric requirements of Tp^{Ph} obviously are ideally suited to study the small but important structural preferences of cobalt and zinc ions in a ligand sphere of nitrogen donors. This contrasts with the behavior of the less bulky ligand $Tp^{Me,Me}$ that allows coordination number six in all bis(ligand) complexes $[M(Tp^{Me,Me})_2]$ and of the more bulky ligand $Tp^{t\text{-}Bu}$ that does not form bis(ligand) complexes, but nearly always forces coordination number four. A second ligand of intermediate steric encumbrance, viz. $Tp^{i\text{-}Pr}$, forms bisligand metal complexes.[16] However, it has been reported to isomerize from [HB(3-isopropylpyrazol-1-yl)$_3$] to [HB(3-isopropylpyrazol-1-yl)$_2$(5-isopropylpyrazol-1-yl)] during complex formation. Thereby it reduces its steric bulk to such an extent that octahedral coordination becomes possible. For that reason it seems less well suited to study the subtle differences between zinc and cobalt coordination chemistry.

We have calculated the cone angles of different ligands $Tp^{R,R'}$ to quantify their steric requirements. It looks as if the cone angle concept is not very helpful in assessing the steric bulk of these flexible tridentate ligands. In particular it has very little predictive power for the question whether a ligand $Tp^{R,R'}$ allows formation of bis(ligand) complexes $[M(Tp^{R,R'})_2]$. Alternatives to the cone angle concept of Tolman[17] are the solid cone angle Ω proposed by Immirzi and Musco[18] and the ligand profile of Ferguson et al.[19,20] These methods have been introduced to better describe the steric requirements of bulky and flexible phosphine ligands that can adopt unsymmetrical conformations. The diagrams that Ferguson and Oliver[21] have used to display the ligand profiles are an informative way of visualizing the spatial arrangement of monodentate ligands in complexes. We have found that the ligand profile concept can be applied successfully as well to tris-chelating ligands like the tripyrazolylborates $Tp^{R,R'}$.[22] In Figure 8 are shown the ligand profiles of Tp^{Ph}, $Tp^{t\text{-}Bu,Me}$, and $Tp^{t\text{-}Bu}$ using the linear graphic representation of Ferguson (left) and the circular diagram of Oliver[21] (right). The ligand profile not only gives some measure of the bulkiness of a ligand but also provides information about the gaps between the substituents in the ligand. Profiles a and b, e.g., of two similar *tert*-butyl-substituted Tp ligands seem to illustrate the effect of different conformations of the substituents. A comparison of the profiles of Tp^{Ph} in $[(Tp^{Ph})ZnCl]$ (c) and in $[(Tp^{Ph})Co(acac)]$ (d) shows how the Tp^{Ph} ligand minimizes the steric interaction with the acac ligand by changing the gaps

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(16) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(18) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *25*, L41−L42.

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(20) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* **1978**, *17*, 2965−2589.

(21) Smith, J. D.; Oliver, J. *Inorg. Chem.* **1978**, *17*, 2585−2589.

(22) To standardize the ligand profiles in a manner similar to the instructions Tolman has given for the determination of cone angles, we have taken the atomic coordinates from the actual crystal structure, but have set the position of the metal center so that the metal−ligand distance, i.e. the three metal−nitrogen bond lengths, is 2.10 Å This procedure should of course be modified for ligand profile calculations of tripodal $Tp^{R,R'}$ ligands that do not act trischelating. Nearly always it is the peripheral hydrogen atoms that define the ligand profile. For that reason we have always included hydrogen positions and the hydrogen van der Waals radius in our calculations.

(23) Parkin, G. Private communication.

(24) Alsfasser, R.; Trofimenko, S.; Looney, A.; Parkin, G.; Vahrenkamp, H. *Inorg. Chem.* **1991**, *30*, 4098.

(25) Yoon, K.; Parkin, G. *Inorg. Chem.* **1992**, *31*, 1656.

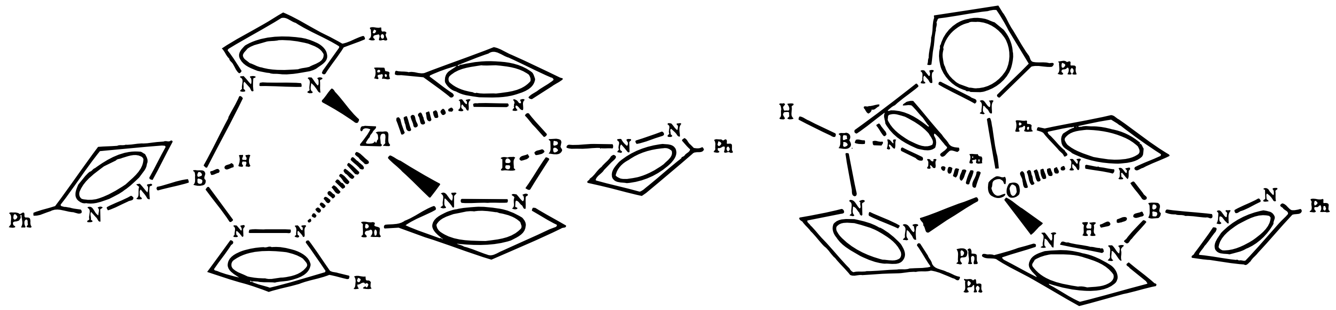

Figure 7. Schematic drawings of the molecular structures of [Zn(η^2-Tp^{Ph})$_2$] and [Co(η^3-Tp^{Ph})(η^2-Tp^{Ph})].

between the phenyl moieties—altering the "depth of tooth of the conic cog-wheel".[20] Ligand profiles clearly help to get a feeling for the intermeshing ability of bulky ligands in crowded complexes. It would be worthwhile to develop this concept further. The ligand profiles display the angular encumbrance of a ligand, but they do not give the distance of the metal center from the atoms defining the profile. Having this additional information in the diagram would certainly help in getting a better understanding of the reactivity of crowded metal complexes.

The X-ray structure of [Co(Tp^{Ph})$_2$] (**1**) reveals a BH···Co distance of 2.17 Å. A similar geometry has been observed in heteroleptic complexes of Tp^{Ph}.[26] Calabrese et al. have described this as an *agostic* BH···Co interaction. The importance of this interaction from an energy point of view is difficult to judge. From the characteristic UV−vis spectrum (see Figure 1) it seems obvious, however, that the chromophore is a CoN_5 square pyramid, not a CoN_5H octahedron; i.e., the *agostic* BH···Co interaction does not lead to an important perturbation of the cobalt valence shell.

The different preference of cobalt and zinc for coordination number 5 or 4, well documented in the structures of [M(Tp^{Ph})$_2$], is less pronounced but still visible in the complexes of the type [(Tp^{Ph})MX] and [(Tp^{Ph})M(carboxylate)]. The main evidence comes from the solvent dependence of the cobalt UV−vis spectra and the solvent independence of the IR spectra of the zinc carboxylate complexes. In the absence of a complete series of crystal structure determinations the role of THF in these complexes in solution and in the THF adducts in the solid state is still puzzling. What we would need is a correlation to the UV−vis spectra, i.e. the color change from blue to red, with the change of the carboxylate coordination from monodentate to bidentate. The anthranilate complex [(Tp^{Ph})Zn(anthranilate)] (**5**) is the only compound of the type [(Tp^{Ph})M(carboxylate)] we have a structure of, and to our knowledge, it is the first structurally characterized metal anthranilate complex in tripyrazolylborate chemistry. It is worth pointing out that anthranilate is an important ligand in zinc enzyme chemistry since it acts as carbonic anhydrase inhibitor.

With acetylacetonate as additional oxygen chelate ligand the situation is straightforward. Its strong chelate effect leads to isotypic complexes [(Tp^{Ph})M(acac)], M = Zn (**7**), Co (**8**), with trigonal bipyramidal metal coordination. As mentioned above we have no evidence that the structures in solution are significantly different from the solid state structures.

The ligand field stabilization of high-spin d^7 gives cobalt(II) a higher tendency to adopt pentacoordination in Tp^{Ph} complexes. Much of this seems compensated for by the steric bulk of the tripodal ligand Tp^{Ph}. Our results show that all in all only a very slight susceptibility remains to add donor solvent molecules. With the data presented here and the information from the literature on Tp^{Ph}Co complexes it is not possible to quantify this in any way. The ligand field stabilization of d^8 gives nickel(II) an even higher tendency for pentacoordination in related tris(pyrazolyl)borate complexes through either incorporation of donor solvents or formation of bridged dimers.[27] Especially worth mentioning in this respect is the elegant work of Parkin and Vahrenkamp on Tp$^{t\text{-Bu}}$ and Tp$^{t\text{-Bu,Me}}$ metal complexes as structural and functional models for carbonic anhydrase.[5,24,28,29] Parkin has shown that in the series of complexes [(Tp$^{t\text{-Bu}}$)M(NO$_3$)], M = Zn, Co, Ni, and Cu, the nitrate ligand is unidentate in the zinc complex and perfectly bidentate in the nickel and copper complexes. In the cobalt derivative it is intermediate between unidentate and symmetric bidentate.[5a,30] The correlation between the observed coordination mode of the nitrate ligands and the activity of metal-substituted carbonic anhydrase (Zn $>$Co $\gg$Ni, Cu) is striking.[31] Nitrate and bicarbonate are isoelectronic ligands,[32] and it might well be that a corresponding increase in bidentate character of bicarbonate in zinc-, cobalt-, and nickel-substituted carbonic anhydrase makes it increasingly difficult to catalyze the hydration of carbon dioxide.

Concluding Remarks

Zinc is a biologically important metal ion that is known to occur in over 200 proteins. It plays a vital role in enzymes like polymerases, ligases, transferases, or hydrolases. The structural details of metalloenzymes have become clear through a series of crystal structure determinations, but mechanistic details of the catalytic processes in metalloenzymes are still unknown in many cases. The "colorless" zinc in enzymes is especially difficult to study. An often used approach to probe

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(26) Calabrese, J. C.; Domaille, P. J.; Thompson, J. S.; Trofimenko, S. *Inorg. Chem.* **1990**, *29*, 4429.

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(30) It is interesting to note in this context that nitrate is intermediate between unidentate and symmetric bidentate in the less crowded zinc complex [(Tp^{Ph})Zn(NO$_3$)]. See: Alsfasser, R.; Powell, A. K.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 898.

(31) See also: Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496.

(32) For an ab initio comparison of the bonding modes of nitrate and bicarbonate see: Kumar, P. N. V. P.; Marynick, D. S. *Inorg. Chem.* **1993**, *32*, 1857.

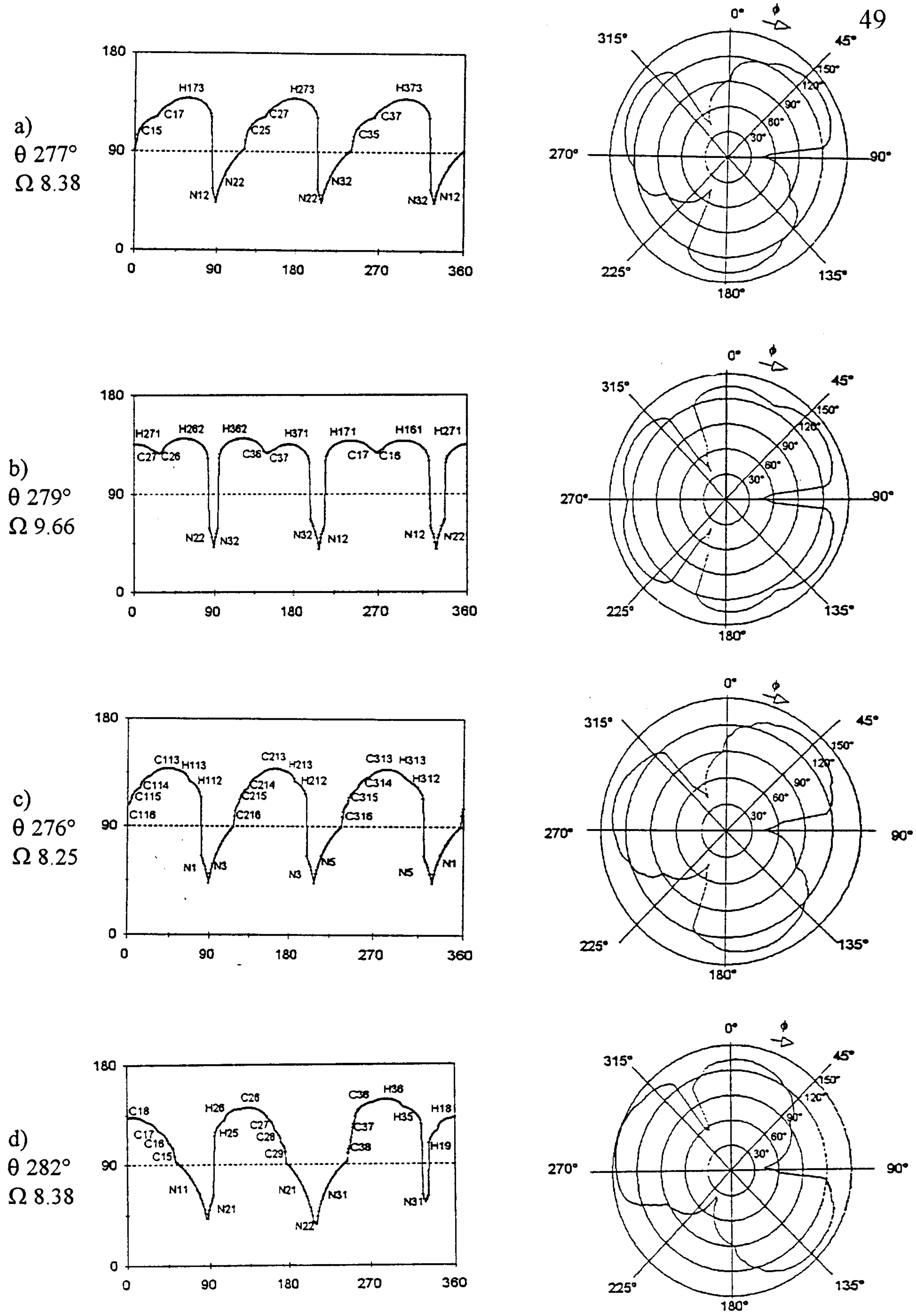

Figure 8. Ligand profiles, cone angles θ and solid cone angles Ω of $\mathrm{Tp}^{t\text{-Bu,Me}}$ in $[(\mathrm{Tp}^{t\text{-Bu,Me}})\mathrm{ZnOH}]$[23,24] (a) of $\mathrm{Tp}^{t\text{-Bu}}$ in $[(\mathrm{Tp}^{t\text{-Bu}})\mathrm{ZnCN}]$[23,25] (b), and of $\mathrm{Tp}^{\mathrm{Ph}}$ in $[(\mathrm{Tp}^{\mathrm{Ph}})\mathrm{ZnCl}]$[9] (c) and $[(\mathrm{Tp}^{\mathrm{Ph}})\mathrm{Co(acac)}]$ (**8**) (d).

the metal sites in zinc proteins is the so-called isomorphous substitution. Because of the similar ionic radius and the similar coordination chemistry, cobalt(II) has become *the substitute* for the native zinc. The detailed spectroscopy of the active sites in zinc enzymes made possible by this substitution and kinetic analyses that have been carried out with them have revealed in surprising detail the dynamics of active sites. Often a significant part of the zinc enzyme catalytic activity is retained after cobalt substitution—the hydrolase activity of cobalt carboxypeptidase is even higher than that of the zinc enzyme. It is generally accepted therefore that the results from cobalt enzymes are transferable to the native zinc enzymes. The structural differences of the cobalt and zinc model compounds that we have presented here shows on the one hand that it can be quite misleading to take cobalt as a probe for zinc in biological systems. On the other hand we can now investigate to what extent the different tendencies of the two metals to increase the coordination number from 4 to 5 determines their activity in enzyme model reactions.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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