The Effect of a 3-Benzyl Group on the Coordination Chemistry of Homoscorpionate Ligands

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New homoscorpionate ligands containing a 3-benzyl substituent, hydrotris(3-benzyl-5-methylpyrazol-1-yl)borate, $Tp^{Bn,Me}$, and hydrotris(3-benzyl-4-phenylpyrazol-1-yl)borate, $Tp^{Bn,4Ph}$, have been synthesized, and the dynamic behavior of a number of metal complexes was studied by NMR. Structures of the complexes $Tl[Tp^{Bn,Me}]$, **1**, $Tl[Tp^{Bn,4Ph}]$, **2**, $Co[Tp^{Bn,Me}][Tp^{Np}]$, **3**, $Mo[Tp^{Bn,Me}](CO)_2NO$, **4**, $Co[Tp^{Bn,4Ph}][Tp]$, **5**, and $Mo[Tp^{Bn,Me}](CO)_2(\eta^3\text{-methallyl})$, **6**, were determined by X-ray crystallography. In the $Tp^{Bn,Me}$ ligand, the benzyl group is freely rotating and provides less steric hindrance to the coordinated metal than a neopentyl group, but steric hindrance is increased in the $Tp^{Bn,4Ph}$ ligand, where the rotation of the benzyl substituent is restricted by the 4-phenyl substituent.

Introduction

The first examples of "second generation" homoscorpionate ligands, which permit control of the pocket around the coordinated metal, were those containing a *tert*-butyl or a phenyl substituent in the 3-position, i.e., the ligands Tp^{tBu} and Tp^{Ph}.[1] Much research has been done with those ligands and with their analogues.[2] A later modification of the Tp^{tBu} ligand entailed the introduction of a methylene spacer between the pyrazolyl 3-carbon and the *tert*-butyl group, converting the latter to a neopentyl substituent and the ligand to Tp^{Np}.[3] On one hand, the Tp^{Np} ligand still permitted the facile formation of isolable tetrahedral $M[Tp^{Np}]X$ complexes, just as did Tp^{tBu}, but on the other hand, it also produced stable octahedral complexes of the type $M[Tp^{Np}]_2$, although they could be thermally rearranged to the isomeric species $M[Tp^{Np*}]_2$. This was impossible with the Tp^{tBu} ligand.

The variations in the size and geometry of 3-R substutuents have a pronounced effect on the coordination chemistry and on the catalytic effectiveness of specific Tp^R metal complexes. This has been conclusively demonstrated in several studies. In one of them, a series of Tp^R copper(I) complexes was used in achieving carbene transfer and activation of C—H bonds. Thus, in the cyclopropanation reaction by way of carbene transfer from ethyl diazoacetate to styrene and to other olefins, by far the most active ligand was Tp^{Ms} (Ms = mesityl).[4,5] On the other hand, in the rather similar cyclopropenation of acetylenes, the catalysts derived from Tp^{Ms} gave only mediocre results, but those based on Tp^{Cy} were superb performers.[6] For carbon—hydrogen bond activation via carbene insertion, the Tp^{Ms} ligand proved to be the best.[7] It was also found to be the most effective ligand in a study of olefin polymerization using $Ti[Tp^x]Cl_3$ plus MAO.[8]

We wanted to explore how the coordination chemistry of the Tp^{Ph} ligand will change with the introduction of a methylene spacer between the pyrazolyl 3-C and a phenyl group and also how the coordination chemistry of the new Tp^{Bn} ligand might be affected by introducing other substituents on the pyrazolyl ring. Two ligands of this type were synthesized: one with an additional 4-phenyl substituent ($Tp^{Bn,4Ph}$), the other with a 5-methyl substituent ($Tp^{Bn,Me}$). The former could be expected to exhibit restricted rotation of the benzyl group, while in the latter such rotation should be unimpeded. Selected aspects of the coordination chemistry of these two new ligands were studied and compared with those of other related Tp^x ligands.

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$Tp^{Bn,4Ph}$ X = H, Z = Ph

$Tp^{Bn,Me}$ X = Me, Z = H
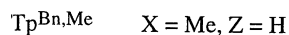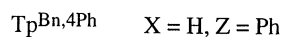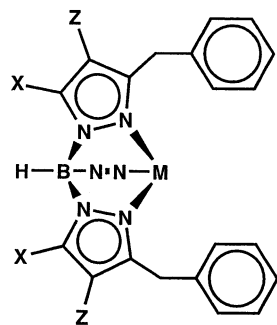
-(N-N)- is the third, hidden $pz^{Bn,X,Z}$ group

Experimental Section

All chemicals were commercial reagent grade and were used as received. 1-Phenyl-2,4-pentanedione was purchased from Eastman, and 1,3-diphenylacetone was purchased from Aldrich. The compound $Tl[Tp^{4Bo,4,6Me2}]$ was prepared according to literature.[9] Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls or as KBr pellets with a Perkin-Elmer 1625 FTIR infrared spectrophotometer, using 16 scans. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. The compounds were studied with typical conditions of 16K data points, a sweep width of 3000−4000 Hz, 90° pulse angles, and a recycle time of 4−5 s.

3-Benzyl-4-phenylpyrazole. The formylation of 300 g (1.4 mol) of 1,3-diphenylacetone with excess ethyl formate was done as described for the formylation of acetophenone.[1] The water extract of the sodium salt was treated with an equimolar amount of hydrazine hydrate and a slight excess of acetic acid, followed by extraction with methylene chloride. The yellow extract was stripped and distilled in vacuo, discarding all the fractions boiling up to 160 °C/1.5 Torr. The molten pot residue was poured into a 9:1 heptane/toluene mixture, which resulted in separation of a solid, which was filtered off, washed with hot hexane, and air-dried. The overall yield of 3-benzyl-4-phenylpyrazole was 86 g (26%). Mp 134−135 °C. ^1H NMR: 10.4−10.8 (broad hump, 1 H, NH), 7.52 (s, 1 H, H-5), 7.35 (m, 4 H, phenyl), 7.25 (m, 4 H, phenyl) 7.16 (m, 2 H, phenyl), and 4.14 (s, CH_2) ppm. ^{13}C NMR: 31.6, 120.4, 126.3, 126.5, 127.7, 128.48, 128.55, 128.63, 133.1, 134.6, 138.4, and 141.7 ppm. Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.1; H, 5.98; N, 12.0. Found: C, 81.9; H, 6.13; N, 11.8.

3-Benzyl-5-methylpyrazole. This pyrazole was obtained in 94% yield by the reaction of 1-phenyl-2,4-pentanedione with hydrazine hydrate. Mp 75−76 °C. ^1H NMR: 12.2 (s, 1 H, NH), 7.1−7.3 (m, 5-H, phenyl), 5.76 (s, 1 H, 4-H), 3.92 (s, 2 H, CH_2), 2.19 (s, 3 H, CH_3) ppm. ^{13}C NMR: 11.9, 33.6, 103.8, 126.2, 128.4, 128.6, 139.4, 143.4, 148.6 ppm. Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.7; H, 6.98; N, 16.3. Found: C, 76.6; H, 7.13; N, 16.1.

Tl[Tp^{Bn,Me}] (1). A mixture of 21 (120 mmol) g of 3-benzyl-5-methylpyrazole and 1.5 g (28 mmol) of KBH_4 was heated in an oil-bath up to 280 °C until 1.6 L of hydrogen was evolved and

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further evolution stopped. The melt was cooled, dissolved in THF, and converted to the Tl salt, as described for **2** (see below), which was obtained in 15 g (73%) yield. Mp 117−119 °C. IR: BH 2508 cm^{-1}. ^1H NMR: 7.1−7.3 (m, 5 H, phenyl), 5.74 (s, 1 H, H-4), 3.91 (s, 2 H, CH_2), 2.38 (s, 3 H, Me) ppm. ^{13}C NMR: 13.0, 34.2, 104.9, 126.2, 128.7, 140.3, 144.4, 150.8 ppm. Anal. Calcd for $C_{33}H_{34}BN_6Tl$: C, 54.3; H, 4.66; N, 11.5. Found: C, 54.4; H, 4.78; N, 11.2.

Co[Tp^{Bn,Me}]$_2$. A two-phase mixture containing $Tl[Tp^{Bn,Me}]$ in methylene chloride and aqueous $Co(ClO_4)_2$ was stirred vigorously for 3 h. The layers were separated, and the organic layer was passed through a short alumina column and evaporated. A yellow solid was obtained in 83% yield. Mp 330−332 °C. IR: BH 2527 cm^{-1}. NMR: 106 (1 H, BH), 48.2 (3 H, H-4), 42.2 (9 H, Me), 0.23 (3 H, *p*-H), −2.38 (6 H, *m*-H), −16.7 (6 H, *o*-H), −90.4 (6 H, CH_2) ppm. Anal. Calcd for $C_{66}H_{67}B_2CoN_{12}$: C, 71.5; H, 6.14; N, 15.2. Found: C, 71.8; H, 6.29; N, 14.9.

Co[Tp^{Bn,Me}][Tp^{Np}] (3). An equimolar mixture of $Tl[Tp^{Bn,Me}]$ and $Co[Tp^{Np}]Cl$ was stirred in methylene chloride until the blue color disappeared. The slurry was filtered, and the filtrate was passed through a short alumina column. Evaporation of the filtrate produced $Co[Tp^{Bn,Me}][Tp^{Np}]$ as a yellow solid in 74% yield. Mp 220−221 °C. IR: BH 2518 cm^{-1}. NMR: 105 (2 H, BH, BH′), 75.8 (3 H, H-5), 50.0 (3 H, H-5′), 48.4 (3 H, H-4), 42.4 (9 H, Me), 5.3 (3 H, *p*-H), −1.5 (6 H, *m*-H), −15.1 (6 H, *o*-H), −17.1 (27 H, *t*-Bu), −87.4 (6 H, CH_2), −95.2 (6 H, CH_2) ppm. Anal. Calcd for $C_{57}H_{74}B_2CoN_{12}$: C, 67.9; H, 7.35; N, 16.7. Found: C, 68.2; H, 7.46; N, 16.6.

Mo[Tp^{Bn,Me}](CO)$_2$NO and W[Tp^{Bn,Me}](CO)$_2$NO. These compounds were prepared by mixing 2.0 mmol quantities of $Tl[Tp^{Bn,Me}]$ and $Mo(CO)_6$ or $W(CO)_6$ in 40 mL of DMF. The mixture was stirred and heated until CO evolution stopped and a yellow solution was obtained. At this point, 2.3 mmol of *n*-butyl nitrite was added, and the solution was stirred until CO evolution ceased. It was then poured, after cooling, into 200 mL of chloroform in a 1 L Erlenmeyer flask, along with 700 mL of cold water. After vigorous stirring, the layers were separated, and the organic layer was chromatographed on alumina, collecting the yellow-orange band. Evaporation of the solvent produced the yellow-orange products, which were purified by recrystalization from toluene/heptane. Yields ranged from 64 to 82%.

Mo[Tp^{Bn,Me}](CO)$_2$NO. Mp 215−218 °C (dec). IR: BH 2537, CO 2009, 1916, NO 1652 cm^{-1}. NMR: 7.2−7.3 (m, 5 H, Ph), 5.62 (s, 2 H, H-4), 5.50 (s, 1 H, H-4), 4.34 (s, 4 H, CH_2), 4.14 (s, 2 H, CH_2), 2.34 (s, 6 H, Me), 2.28 (s, 6 H, Me) ppm. Anal. Calcd for $C_{35}H_{34}BMoN_7O_3$: C, 59.4; H, 4.81; N, 13.9. Found: C, 59.6; H, 5.00; N, 13.7.

W[Tp^{Bn,Me}](CO)$_2$NO. Mp 234−236 °C. IR: BH 2552, CO 1994, 1895, NO 1641 cm^{-1}. NMR: 7.2−7.3 (m, 5 H, Ph) 5.64 (s, 2 H, H-4), 5.50 (s, 1 H, H-4), 4.34 (s, 4 H, CH_2), 4.14 (s, 2 H, CH_2), 2.36 (s, 6 H, Me), 2.30 (s, 6 H, Me) ppm. Anal. Calcd for $C_{35}H_{34}BN_7O_3W$: C, 52.8; H, 4.28; N, 12.3. Found: C, 52.9; H, 4.35; N, 12.2.

Mo[Tp^{Bn,Me}](CO)$_2$(η^3-methallyl) (6). An equimolar mixture of the crude $K[Tp^{Bn,Me}]$ ligand and $Mo(CO)_2(\eta^3$-methallyl)(MeCN)$_2$Cl was stirred in chloroform for 1 h and then chromatogtraphed on alumina, collecting the bright yellow band. This eluate was evaporated, and the residue was stirred with methanol and filtered. The product, which was obtained in 38% yield, was recrystallized by overlaying a chloroform solution with methanol. The melting point gradually decomposes from 182 °C. IR: BH 2544, CO 1931, 1837 cm^{-1}. NMR: 7.25−7.43 (two overlapping m, 11 H, phenyl), 7.13 (m, 4 H, phenyl), 5.75 (s, 2 H, H-4), 5.47 (s, 1 H, H-4), 4.81

(s, 2 H, methylene on the C2 axis), 4.73 (d, $J = 15.5$ Hz, 2 H, methylene), 4.47 (d, $J = 15.8$ Hz, 2 H, methylene), 3.48 (s, 2 H, *syn*-methallyl), 2.35 (s, 6 H, 5-Me), 1.98 (s, 3 H, 5-Me), 1.59 (s, 2 H, *anti*-methallyl), 1.33 (s, 3 H, methallyl Me) ppm. Anal. Calcd for $C_{39}H_{41}BMoN_6O_2$: C, 63.9; H, 5.60; N, 11.5. Found: C, 64.1; H, 5.77; N, 11.3.

When Tl[Tp^{Bn,Me}] was used instead of the K salt in this reaction, only trace amount of the desired material was obtained, and it could not be separated from dark brown byproducts.

Tl[Tp^{Bn,4Ph}] (2). A mixture of 78 g (330 mmol) of 3-benzyl-4-phenylpyrazole and 5.1 g (94 mmol) of KBH$_4$ was refluxed in 200 mL of 4-methylanisole, the hydrogen evolution being measured with a wet-test-meter. After about half the theoretical amount had evolved, 4-methylanisole was distilled out at atmospheric pressure, whereupon hydrogen evolution accelerated, and soon the theoretical 6.8 L was obtained. The cooled residue was dissolved in THF and stirred with an excess of aqueous TlNO$_3$. Tl[Tp^{Bn,4Ph}] was extracted with methylene chloride, and the extracts were passed through a bed of alumina and were evaporated, yielding a syrup. Stirring it with a mixture of methanol, acetone, and 2-propanol gave a white solid, obtained in 58 g (67%) yield. Mp 178−180 °C. IR: BH 2432 cm^{-1}. ^{1}H NMR: s 7.83 (1 H, H5), m 7.29 (4 H), m 7.16 (4 H), m 7.06 (2 H), s 4.08 (2 H, CH$_2$) ppm. ^{13}C NMR: 33.1, 120.9, 126.1, 126.6, 128.0, 128.6, 129.0, 129.3, 134.1, 135.4, 140.4, 149.0 ppm. Anal. Calcd for $C_{48}H_{40}BN_6Tl$: C, 63.0; H, 4.37; N, 9.18. Found: C, 62.6; H, 4.52; N, 8.96.

Co[Tp^{Bn,4Ph}]Cl. A mixture of 2 mmol of Tl[Tp^{Bn,4Ph}] and a large excess of anhydrous CoCl$_2$ was stirred in 50 mL of chloroform for 4 h. The blue solution was filtered, and the filtrate was passed through an alumina column. Evaporation of the blue eluate produced Co[Tp^{Bn,4Ph}]Cl in 67% yield. It was recrystallized from toluene/heptane. M.p. 164−166 °C. IR: BH 2507 cm^{-1}. NMR: 40.3 (3 H, H-4), 1−9 (36 H, phenyls and CH$_2$), −18.1 (1 H, BH) ppm. Anal. Calcd for $C_{48}H_{40}BClCoN_6$: C, 71.5; H, 4.96; N, 10.4. Found: C, 71.6; H, 5.12; N, 10.3.

Co[Tp^{Bn,4Ph}][Tp]. The Co[Tp^{Bn,4Ph}]Cl complex was prepared in situ by stirring the Tl salt with excess anhydrous CoCl$_2$ in methylene chloride for 6 h. The mixture was filtered, and the blue color was "titrated" by adding Tl[Tp] in small portions until the color changed to yellow. The mixture was filtered through Celite, and the filtrate was evaporated, yielding a peachy-yellow solid, which was recrystallized from octane. Mp 250−252 °C. IR: BH 2444 cm^{-1}. NMR: 113 (1 H, BH), 110 (1 H, BH′), 88 (3 H, H-5), 84 (3 H, H-5′), 41.8 (3 H, H-4), 4.0 (6 H, *m*-Ph), 3.3 (3 H, *p*-Ph), −2.2 (3 H, *p*-Bn), −4.2 (6 H, *o*-Ph), −20.6 (6 H, *m*-Bn), −93 (6 H, *o*-Bn), −99 (3 H, H-3). Anal. Calcd for $C_{57}H_{50}B_2CoN_{12}$: C, 69.6; H, 5.09; N, 17.1. Found: C, 69.7; H, 5.13; N, 17.0.

Co[Tp^{Bn,4Ph}][Tp*]. This peachy-yellow complex was prepared as above, using Tl[Tp*] instead of Tl[Tp]. Mp 239−241 °C. IR: BH 2518, 2448 cm^{-1}. NMR: 108 (2 H, BH and BH′), 83.0 (3 H, H-5), 48.1 (3 H, H-4), 44.8 (9H, 5-Me), 4.4 (6 H, *m*-Ph), 3.5 (3 H, *p*-Ph), −0.1 (6 H, *o*-Ph), −1.1 (3 H, *p*-Bn), −1.92 (6 H, *m*-Bn), −13.3 (6 H, *o*-Bn), −76.0 (9 H, 3-Me), −93.0 (6 H, CH$_2$) ppm. Anal. Calcd for $C_{63}H_{62}B_2CoN_{12}$: C, 70.9; H, 5.81; N, 15.7. Found: C, 71.0; H, 5.95; N, 15.5.

Co[Tp^{Bn,4Ph}][Tp^{4Bo,4,6Me2}]. This bright yellow complex was prepared as above, using Tl[Tp^{4Bo,4,6Me2}]. Mp 290−292 °C. IR: BH 2453, 2460 cm^{-1}. NMR: 114 (1 H, BH′), 111 (1 H, BH), 84.8 (3 H, H-5), 49.9 (3 H, H-4), 14.1 (9 H, Bo-6 M3), 11.2 (3 H, Bo-5H), 4.1 (6 H, *o*-Ph), 3.2 (3 H, *p*-Ph), −0.2 (6 H, *m*-Ph), −2.4 (3 H, *p*-Bn), −4.1 (6 H, *m*-Bn), −19.3 (6 H, *o*-Bn), −93.5 (6 H, CH$_2$), −97.0 (3 H, Bo-3H) ppm. Anal. Calcd for $C_{75}H_{68}B_2CoN_{12}$: C, 74.0; H, 8.22; N, 13.8. Found: C, 74.1; H, 8.32; N, 13.7.

Table 1. CO and NO Frequencies in Tp^{x}Mo(CO)$_2$NO Complexes (in cm^{-1})

Tp^x ligand	CO	CO	NO	ref
Tp	2025	1933	1666	12
pzTp	2024	1927	1685	12
Tp*	2016	1925	1673	12
Tp^{i}Pr	2005	1920	1650	13
Tp^{i}Pr,4Br	2025	1920	1670	13
Tp^{i}Pr,Me	1990	1900	1650	14
Tp^{Et2}	2014	1924	1670	15
Tp^{i}Bu	2000	1908	1655	1
pz^{0}Tp^{t}Bu	2030	1926	1670	1
Tp^{Ph}	2000	1910	1660	1
pz^{o}Tp^{Ph}	2020	1945	1670	1
Tp^{An}	2010	1910	1660	10
Tp$^{Ph−4−Cl}$	2011	1920	1664	16
Tp$^{\alpha Nt}$	2014	1924	1666	16
Tp^{Tn}	2014	1924	1661	16
Tp^{CF3,Tn}	2033	1947	1697	16
Tp^{Me3}	2013	1920	1654	11
Tp*^{Et}	2013	1920	1654	11
Tp*^{Bu}	2013	1820^a	1655	11
Tp*^{Am}	2013	1919	1655	11
Tp*^{Bn}	2014	1921	1655	17
Tp^{Bn,Me}	2009	1916	1655	b
Tp^{Bn,4Ph}	2010	1922	1665	b
Tp^{Br3}	2025	1936	1688	18

^{a} Abbreviations for the homoscropionate ligands are used according to ref 2. ^{b} This work.

Mo[Tp^{Bn,4Ph}](CO)$_2$NO and W[Tp^{Bn,4Ph}](CO)$_2$NO. These complexes were synthesized the same way as their M[Tp^{Bn,Me}](CO)$_2$NO analogues and were obtained in 70−80% yield.

Mo[Tp^{Bn,4Ph}](CO)$_2$NO. Mp 214−217, dec around 260 °C. IR: BH 2481, CO 2010, 1922, NO 1665 cm^{-1}. NMR: 8.06 (s, 2 H, H-5), 7.90 (s, 1 H, H-5), 7.2−7.3 (m, 24 H, Ph), 7.14 (d, 4 H, *o*-H), 6.90 (d, 2 H, *o*-H), 4.55 (s, 2 H, CH$_2$), 4.50 (s, 2 H, CH$_2$), 4.26 (s, 2 H, CH$_2$) ppm. Anal. Calcd for $C_{50}H_{40}BMoN_7O_3$: C, 67.2; H, 4.48; N, 11.0. Found: C, 67.5; H, 4.59; N, 10.7.

W[Tp^{Bn,4Ph}](CO)$_2$NO. Mp 277−279 °C. IR: BH 2480, CO 1995, 1900, NO 1651 cm^{-1}. NMR: 7.95 (s, 2 H, H-5), 7.89 (s, 1 H, H-5), 7.2−7.3 (m, 24 H, Ph), 7.12 (d, 4 H, *o*-H), 6.85 (d, 2 H, *o*-H), 4.57 (s, 2 H, CH$_2$), 4.52 (s, 2 H, CH$_2$), 4.33 (s, 2 H, CH$_2$) ppm. Anal. Calcd for $C_{50}H_{40}BN_7O_3W$: C, 61.2; H, 4.08; N, 10.0. Found: C, 61.3; H, 4.13; N, 10.1.

X-ray Crystal Structure Determinations. Diffraction intensity data were collected with Siemens P4/CCD (**1**, **2**, **3**, **4**, **6**) and Bruker Smart Apex CCD (**5**) diffractometers. Crystal data collections and refinement parameters are given in Table 1[10−18]. The space goups for structures **3**, **4**, and **6** were chosen based on the systematic absences in the diffraction data and for **1**, **2**, and **5** based on intensity statistics. The structures were solved using the direct methods,

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Table 2. Summary of X-ray Diffraction Data

compound	1	2	3	4	5	6
form	$C_{33}H_{34}BN_6Tl$	$C_{48}H_{40}BN_6Tl$	$C_{57}H_{74}B_2CoN_{12}$	$C_{35}H_{34}BMoN_7O_3$	$C_{57}H_{50}B_2CoN_{12}\cdot0.25(C_7H_8)$	$C_{39}H_{41}BMoN_6O_2$
fw	729.84	916.04	1007.83	707.44	1006.67	732.53
space group	P-1	P-1	$Fdd2$	$P2_1/c$	P-1	$P2_1/c$
a, Å	9.1568(10)	11.726(2)	39.719(5)	10.5901(11)	10.4113 (8)	9.5893(9)
b, Å	10.2567(12)	18.278(3)	46.895(7)	21.912(2)	11.7946(9)	10.2418(10)
c, Å	16.93.43(19)	20.322(7)	12.5159(18)	14.7632(15)·	45.028(3)	37.997(3)
α, deg	74.781(3)	107.213(16)			97.254(1)	
β, deg	88.472(2)	91.78(3)		90.233(2)	92.009(2)	94.997(2)
γ, deg	82.112(2)	100.238(14)			105.460(1)	
V, Å	1520.1(3)	4078.2(16)	23312(2)	3425.7(6)	5273.0(7)	3706.8(6)
Z,Z'	2,1	4,2	16,1	4,1	42	4,1
cryst color, habit	colorless, block	colorless, blade	colorless, block	orange, block	yellow, block	yellow, cubic
D(calc), g cm^{-3}	1.595	1.495	1.149	1.372	1.268	1.313
μ(Mo Kα), cm^{-1}	5.345	4.002	3.40	4.28	3.80	3.95
temp, K	173(2)	295	218(2)	218(2)	150(1)	218(2)
diffractometer	Siemens P4/CCD	Siemens P4/CCD	Siemens P4/CCD	Siemens P4/CCD	Bruker Smart Apex CCD	Siemens P4/CCD
radiation				Mo Kα ($\lambda = 0.71073$ Å)		
$R(F)$, %^{a}	3.39	5.33	8.11	6.36	6.63	4.72
$R(wF^2)$, %^{b}	8.68	11.91	19.50	15.76	14.61	11.95

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R(\omega F^2) = \{\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]\}^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o, 0)]/3$.

completed by subsequent Fourier syntheses, and refined by full matrix least-squares procedures on reflection intensities (F^2). SADABS absorption corrections were applied to all data (Sheldrick, G. M. (1998), SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, USA).

In all structures, non-hydrogen atoms were refined with anisotropic displacement coefficients. In the **1**, **3**, **4**, and **5** structures, the hydrogen atoms were treated as idealized contributions. In **2** and **6**, the positions of the H atoms at boron as well as the H atoms in the methallyl group in **6** were found on the F-map and refined. In the structures of **3**, **4**, and **6**, one of the phenyl rings was disordered over two positions, with occupation multiplicity $m =$ 0.51/0.49 (**3**), 0.39/0.61 (**4**), and 0.48/0.52 (**6**). Although for **3** there are no residual density peaks greater than 1.0 electron/Å^3, a treatment of **3** by SQUEEZE program indicated the existence in the crystal structure of a free space, which could be partially occupied by solvent molecules. In the **5** structure, there was a disordered solvate toluene molecule. The program SQUEEZE was used to treat it.[19] Correction of the X-ray data for **5** by SQUEEZE (56 electrons/cell) was close to the required value (50 electrons/cell).

All software and sources scattering factors are contained in the SHLXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison WI).

Results and Discussion

The two new ligands were prepared by the reaction of the appropriate pyrazole with KBH$_4$: K[Tp^{Bn,Me}] was synthesized in the neat melt, K[Tp^{Bn,4Ph}] was synthesized in refluxing 4-methylanisole, and both were characterized as their Tl salts. In neither of the two Tl salts was there any evidence for ^{13}C$-^{205}$Tl coupling, in contrast to Tl[Tp^{Np}], where such coupling was observed.[3] The structures of Tl[Tp^{Bn,Me}], **1** (Figure 1), and Tl[Tp^{Bn,4Ph}], **2** (Figure 2), were determined by X-ray crystallography. The average Tl—N bond distances were 2.59 Å for **1** (2.58, 2.59, 2.60 Å) and distinctly longer, 2.64 Å, for **2** (2.63, 2.58, 2.72 Å), also showing a wider spread of the Tl—N bond distances. These values are well
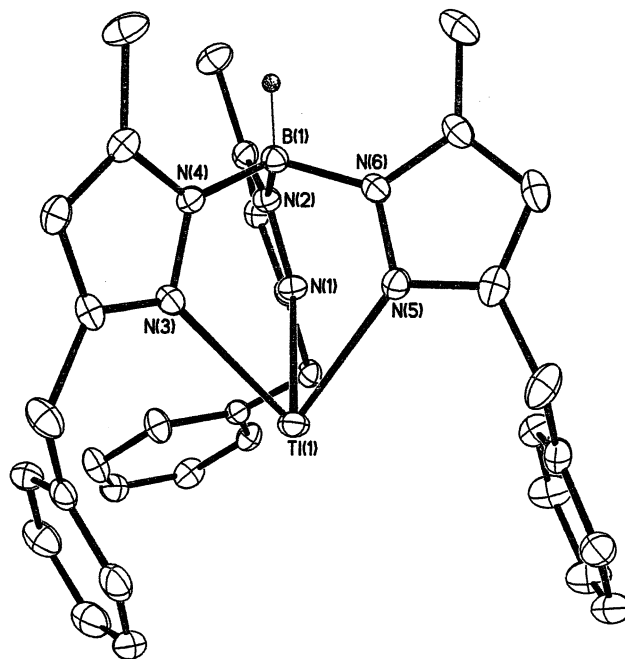
(19) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

Figure 1. ORTEP plot of the structure of Tl[Tp^{BnMe}], **1**, selected bond lengths (Å) and angles (deg): Tl—N(1), 2.588(3); Tl—N(3), 2.598(4); Tl—N(5), 2.580(4); N(1)—Tl-N(3), 77.1(1); N(1)—Tl—N(5), 73.4(1); N(5)—Tl—N(3), 72.4(1).

within the range of Tl—N bond distances found in a variety of Tl[Tp^x] species.[20,21]

It turned out that the coordination chemistry of the ligands Tp^{Bn,Me} and Tp^{Bn,4Ph} was indeed defined not only by the 3-benzyl group but also by the other substituents. We took Tp^{Bn,Me} to be equivalent to an otherwise unsubstituted "Tp^{Bn}", since the 5-methyl group was too distant from the 3-benzyl to have any effect on its rotation. On the other hand, Tp^{Bn,4Ph} represented a "Tp^{Bn}" ligand with restricted rotation of the benzyl group, due to the 4-Ph, to a degree that was to be determined.

(20) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107.
(21) Craven, E.; Mutlu, E.; Lundberg, D.; Temizdemir, S.; Dechert, S.; Brombacher, H.; Janiak, C. *Polyhedron* **2002**, *21*, 553.

Figure 2. ORTEP plot of the structure of Tl[Tp^{Bn,4Ph}], **2**, selected bond lengths [Å] and angles (deg): Tl–N(1), 2.632(8); Tl–N(3), 2.583(7); Ti–N(5), 2.712(8); N(1)–Tl–N(3), 71.2(2); N(1)–Tl–N(5), 73.6(2); N(5)–Tl–N(3), 78.3(2).

The Tp^{Bn,Me} ligand readily formed the homoleptic complex Co[Tp^{Bn,Me}]$_2$, which was yellow, as is typical of octahedral Co[Tp^x]$_2$ complexes. Its ^{1}H NMR spectrum consisted of seven well-separated sharp resonances ranging from +106 to −90 ppm, thus confirming the overall symmetry of the molecule as D_{3d}, and being proof that the ligand Tp^{Bn,Me} was not rearranged to Tp$^{(Bn,Me)*}$. Furthermore, the fact that the benzyl methylene resonance was at −90 ppm, instead of around −70 ppm as is found typically in octahedral Co(II) complexes containing a 3-Me group, implied a structure in solution in which the methylene protons were in closer proximity to the cobalt atom than the average distance of hydrogens of a freely rotating 3-methyl group.[22]

At the same time, attempts to isolate a stable Co[Tp^{Bn,Me}]Cl complex were unsuccessful. Although the typical reaction of Tl[Tp^{Bn,Me}] with excess CoCl$_2$ in chloroform did yield a blue solution characteristic of Co[Tp^{Bn,Me}]Cl, upon concentration and evaporation of the solvent, the color changed to yellow, and only the octahedral bis-complex, Co[Tp^{Bn,Me}]$_2$, was isolated. Thus, the formation of octahedral heteroleptic complexes of the type Co[Tp^{Bn,Me}][Tp^x] by the reaction of Co[Tp^{Bn,Me}]Cl with Tl[Tp^x] was not readily possible. However, such complexes could be prepared by the reverse reaction. For instance, the octahedral heteroleptic complex Co[Tp^{Bn,Me}][Tp^{Np}], **3**, was readily synthesized by the reaction of Co[Tp^{Np}]Cl with Tl[Tp^{Bn,Me}]. It exhibited a clean and sharp NMR spectrum in the 105 to −99.5 range, consistent with the expected structure. The fact that the methylene resonances were slightly broadened implied some degree of dynamic behavior, while their separation of 8 ppm suggested that one of the ligands had its CH$_2$ group closer to the cobalt than the other, exhibiting, therefore, the larger chemical shift, and we assumed that it would be the benzyl group, which is less sterically restrictive than a neopentyl group.[22]

Since **3** offered the opportunity to compare the spatial demand of the Tp^{Bn,Me} and Tp^{Np} ligands bonded to the same
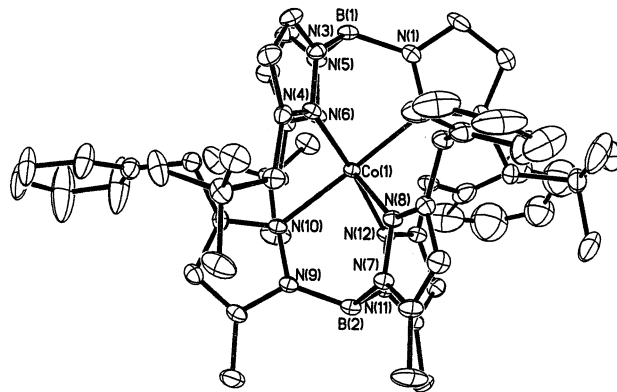
(22) The sensitivity of the chemical shifts of protons in octahedral Tp-derived Co(II) complexes to their position with respect to the cobalt is such that a 5° angular variation at a constant distance of 3 Å results in an 11 ppm change of the chemical shift, while a 0.1 Å distance change at a constant angle of 110° produces a 13 ppm shift. (a) Lamar, G. N.; Jesson, J. P.; Meakin, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1286. (b) Domaille, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5392.

Figure 3. ORTEP plot of the structure of Co[Tp^{BnMe}][Tp^{Np}], **3**, selected bond lengths (Å) and angles (deg): Co–N(2), 2.161(3); Co–N(4), 2.163(4); Co–N(6), 2.216(3); Co–N(8), 2.173(3); Co–N(10), 2.142(3); Co–N(12), 2.150(4); N(4)–Co–N(2), 88.21(13); N(4)–Co–N(6), 89.04(13); N(6)–Co–N(2), 84.97(13); N(8)–Co–N(10), 90.27(13); N(8)–Co–N(12), 87.06(13); N(10)–Co–N(12), 84.95(13).

cobalt atom, its structure was determined by X-ray crystallography (Figure 3). Ignoring the 3-substituents, the two Tp ligands were arranged symmetrically around the cobalt core. The average Co–N distance in Tp^{Np} was 2.180 Å, and thus the longest observed for this ligand. In other heteroleptic Co[Tp^{Np}][Tp^x] complexes, the average Co–N distances ranged from 2.137 to 2.175 Å.[23] By comparison, the Co–N distances in heteroleptic octahedral complexes of Tp^{Ph}, Tp^{Ph,4Me}, and Tp^{Ph,4Et} were all 2.223 Å.[23] The average Co–N distance in Tp^{Bn,Me} was 2.155 Å, matching that of the rather unhindered ligand Tp^{Tn} in its homoleptic complex Co[Tp^{Tn}]$_2$.[24] These results point to lesser steric hindrance of a 3-benzyl substituent, as compared with neopentyl, and are consonant with the apparent lack of thermal rearrangement of the Tp^{Bn,Me} ligand in the Co[Tp^{Bn,Me}]$_2$ complex. The bite angles of the two ligands, as expressed by the N–Co–N angles, were essentially identical: 87.38(13)° for Tp^{Np} and 87.43(13)° for Tp^{Bn,Me}. The phenyl groups were arranged roughly parallel to the equatorial plane of the molecule.

The complexes Mo[Tp^{Bn,Me}](CO)$_2$NO, **4**, and W[Tp^{Bn,Me}]-(CO)$_2$NO were also prepared by the reaction of Tl[Tp^{Bn,Me}] with the appropriate M(CO)$_6$, followed by the in situ reaction of the resulting [Mo[Tp^{Bn,Me}](CO)$_3$]$^-$ anion with butyl nitrite. The CO and NO stretches of the Mo complex fell within the range of analogous complexes, as shown in Table 1, which lists all the reported and some unreported Mo[Tp^x]-(CO)$_2$NO compounds. The structure of **4** (Figure 4) showed the phenyls to be turned away from the Mo atom and essentially parallel with the plane of the three coordinating nitrogen atoms. There was also disorder of the CO and NO ligands, the average Mo–C/N distance being 1.926(4) Å. An almost identical structure was found for W[Tp^{Bn,Me}](CO)$_2$-NO.[16] The CO/NO disorder was also found in the first such structure determined, Mo[Tp](CO)$_2$NO,[25] as well as in Mo[Tp^{An}](CO)$_2$NO[10] and Mo[Tp^{*Bn}](CO)$_2$NO.[11] However,

(23) Rheingold, A. L.; Yap, G. P. A.; Zakharov, L. N.; Trofimenko, S. *Eur. J. Inorg. Chem.* **2002**, 2335.

(24) Calabrese, J. C.; Domaille, P. J.; Trofimenko, S.; Long, G. J. *Inorg. Chem.* **1991**, *30*, 2795.

(25) Holt, E. M.; Holt, S. L.; Cavalito, F.; Watson, K. J. *Acta Chem. Scand.* **1976**, *A30*, 225−228.
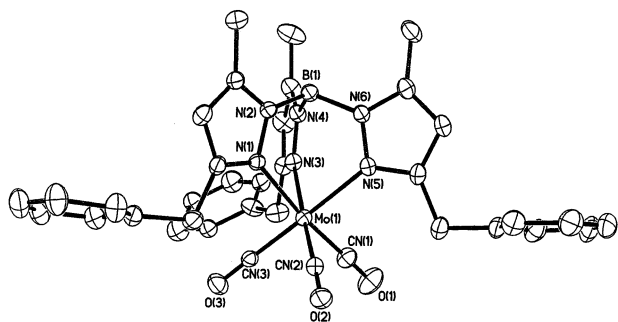
Figure 4. ORTEP plot of the structure of Mo[Tp^{BnMe}](CO)$_2$NO, **4**, selected bond lengths (Å) and angles (deg): Mo—N(1), 2.213(3); Mo—N(3), 2.219(3); Mo—N(5), 2.219(3); N(1)—Mo—N(3), 82.69.12); N(1)—Mo—N(5), 83.17(12); N(3)—Mo—N(5), 83.90(12).

Figure 5. ORTEP plot of the structure of Co[Tp^{Bn,4Ph}][Tp], **5**, selected bond lengths (Å) and angles (deg): Co—N(2), 2.137(2); Co—N(4), 2.112(3); Co—N(6), 2.145(3); Co—N(8), 2.186(2); Co—N(10), 2.195(2); Co—N(12), 2.167(2); N(4)—Co—N(2), 86.06(9); N(4)—Co—N(6), 84.72(10); N(6)—Co—N(2), 86.65(9).

in the closely related binuclear complex, Mo$_2$[Tp—Tp][(CO)$_2$NO]$_2$, there was apparently no disorder, with the Mo—C (carbonyl) distances being reported as 2.05(2) Å and Mo—N (nitrosyl) 1.81(3) Å.[26]

The average N—Mo distance in Mo[Tp^{Bn,Me}](CO)$_2$NO was 2.218(3), as compared with 2.213(4) Å in Mo[Tp](CO)$_2$NO, 2.216(13) Å in Mo$_2$[Tp—Tp][(CO)$_2$NO]$_2$, and 2.220(4) Å in Mo[Tp*^{Bu}](CO)$_2$NO. In the latter structure, the Mo—C (carbonyl) distances were 1.881(5) and 1.943(5) Å, while the Mo—N (nitrosyl) distance was 1.902(4) Å. In Mo[Tp*^{Bn}]-(CO)$_2$NO the average N—Mo distance was 2.225(3) Å, and the average disordered Mo—C/N distance was 1.912(4) Å.

The fact that the NMR spectra of Mo[Tp^{Bn,Me}](CO)$_2$NO and W[Tp^{Bn,Me}](CO)$_2$NO showed the 4-H, CH$_2$, and Me protons in 2:1 patterns indicated the absence of rotation of the M(CO)$_2$NO moiety around the B—Co axis on the NMR time scale and the presence of a $C2$ symmetry plane in the molecule. Similar 2:1 patterns have been found previously in related Mo[Tp^x](CO)$_2$NO complexes. At the same time, the fact that the methylene protons appeared as singlets was indicative of rotation of the benzyl groups around the C3—CH$_2$ bond. While the methylene resonances should have been in a 1:1:1 pattern of two protons each, corresponding to the two identical protons straddling the symmetry plane and the inner and outer methylene protons on either side of the symmetry plane, their appearance as two singlets in 2:1 ratio was most likely due to a coincidental overlap of two resonances.

In contrast to the Tp^{Bn,Me} ligand, which did not yield a stable Co[Tp^{Bn,Me}]Cl species, there was no problem in obtaining the stable Co[Tp^{Bn,4Ph}]Cl complex as a blue solid. It served as starting material for the preparation of several heteroleptic octahedral complexes by its reaction with an appropriate Tl[Tp^x] salt. This reaction could also be carried out in situ, titrating the "as prepared" blue solution of Co[Tp^{Bn,4Ph}]Cl, without its isolation, by adding Tl[Tp^x] in small portions until the disappearance of the blue color is reached. In this fashion, complexes such as Co[Tp^{Bn,4Ph}][Tp], **5**, Co[Tp^{Bn,4Ph}][Tp*], and Co[Tp^{Bn,4Ph}][Tp^{4Bo,4,6Me2}] were synthesized. In each case, the ^{1}H NMR spectrum was very clean and sharp, confirming that the complex was octahedral

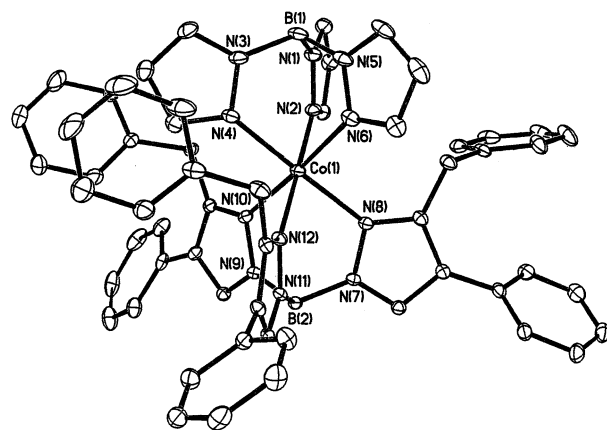and that the ligand Tp^{Bn,4Ph} was not rearranged. The assignments of similar peaks (such as the pyrazolyl 4 and 4′ protons) were done on the basis of the expected greater positive or negative chemical shift of the proton closer to the cobalt ion, as these shifts were quite sensitive to their distance from Co.[13] When the complex Co[Tp^{Bn,4Ph}][Tp] was dissolved in boiling octane, the solution was wine-red, but upon crystallization, the color reverted to the original yellow, implying the presence of a five-coordinate species in solution and involving detachment of one of the Tp^{Bn,4Ph} arms.

The structure of **5** was determined by X-ray crystallography (Figure 5). The crystal contains one molecule of toluene per four molecules of the complex. The cobalt is in an octahedral environment, although the phenyl and benzyl groups of the unrearranged Tp^{Bn,4Ph} ligand are not symmetrically disposed with respect to the C3 axis. As expected, the Co—N distances are substantially shorter for the parent Tp ligand than for Tp^{Bn,4Ph}, the average values being 2.131 Å for the former and 2.183 Å for the latter. Also, the bite of the ligand, as expressed by the average N— Co—N is somewhat tighter for the parent Tp than for Tp^{Bn,4Ph}, being 85.8° versus 86.9°. The NMR spectrum of **5** was sharp and consistent with overall dynamic C_{3v} symmetry, as each type of proton was represented only once, whereas, had the structure found in the crystal been present in solution, a more complicated spectrum would have been anticipated.

The M[Tp^{Bn,4Ph}](CO)$_2$NO complexes for M = Mo and W were also synthesized. Their NMR spectra, like those of their Tp^{Bn,Me} counterparts, showed the presence of a symmetry plane by having their 5-H and benzyl ortho-protons protons in a 2:1 pattern. However, in contrast to their Tp^{Bn,Me} counterparts, the benzyl methylene protons were in a 1:1:1 pattern of 2 protons each. This was consistent with the absence of rotation of the benzyl group around the C3—CH$_2$ bond, this structural rigidity finding its expression in increased steric hindrance of this ligand, and, consequently, a different coordinative behavior as compared with Tp^{Bn,Me}.

The rotation of the benzyl group in the Tp^{Bn,Me} ligand depends also on other ligands around the metal. In the complex Mo[Tp^{Bn,Me}](CO)$_2$(η^3-methallyl), **6**, the methylene

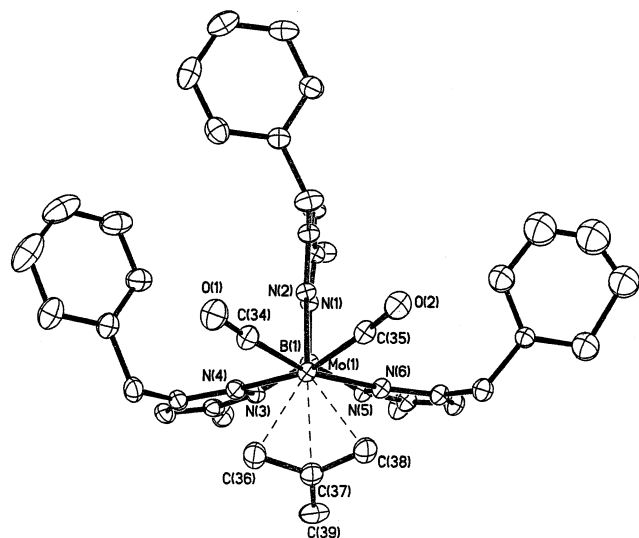(26) Harden, N. C.; Jeffery, J. C.; McCleverty, J. A.; Rees, L. H.; Ward, M. D. *New J. Chem.* **1998**, 661.

Figure 6. ORTEP plot of the structure of Mo[Tp^{Bn,Me}](CO)$_2$(η^3-methallyl), **6**, selected bond lengths (Å) and angles (deg): Mo−N(2), 2.219(2); Mo−N(4), 2.306(2); Mo−N(6), 2.319(2); N(4)−Mo−N(2), 75.10(8); N(4)−Mo−N(6), 92.98(8); N(6)−Mo−N(2), 76.34(8).

protons appeared as three well-separated resonances. One of these, a singlet, corresponded to the two identical methylene hydrogens next to the η^3-methallyl group, and the other two signals belonged to the "inner" and "outer" protons of the other benzyl methylenes. Since each methylene proton in those CH$_2$ links was different from the other, they exhibited coupling and appeared as doublets.

The structure of **6** (Figure 6) showed the benzyl substituents pointing their phenyl rings away from the metal and being approximately parallel with the equatorial plane of the molecule. The methyl group of the methallyl ligand was also pointing away from Mo. The average Mo−N bond length was 2.281 Å, significantly longer than in **4** (2.218 Å). The necessity to accommodate the methallyl ligand widened the N(4)−Mo−N(6) angle to 93.0°, while the average for the other two N−Mo−N angles was 75.7°.

Conclusion

The two novel ligands, Tp^{Bn,Me} and Tp^{Bn,4Ph}, each containing a 3-benzyl substituent have been synthesized. We showed that a 3-benzyl substituent is capable of rotation and renders the Tp ligand less hindered than a 3-neopentyl substituent, provided the 4-position is unsubstituted. A Tp^{Bn} ligand behaves, essentially, like Tp^{Me}, in being incapable of forming stable M[Tp^{Bn,Me}]X complexes. The presence of a 4-Ph substituent, however, prevents rotation of the benzyl group, and the inflexible Tp^{Bn,4Ph} ligand is capable of forming stable M[Tp^{Bn,4Ph}]X complexes, as well as a variety of heteroleptic complexes, M[Tp^{Bn,4Ph}][L], via replacement of the halide X.