Remote Rotamer Control: The Effect of a 4-*tert*-Butyl Group on the Coordination Chemistry of Tp^{R} Ligands

Arnold L. Rheingold,[a] Louise M. Liable-Sands,[a] James A. Golan,[a] and Swiatoslaw Trofimenko*[a]

Keywords: Scorpionates / Cobalt / Rotamer control / Borates / N ligands

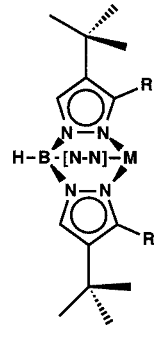
Three novel homoscorpionate ligands containing a *tert*-butyl group in the 4-position have been synthesized: hydrotris(4-*tert*-butylpyrazol-1-yl)borate (Tp^{4tBu}), hydrotris(4-*tert*-butyl-3-*p*-tolylpyrazol-1-yl)borate (Tp^{Tol,4tBu}), and hydrotris(4-*tert*-butyl-3-isopropylpyrazol-1-yl)borate (Tp^{iPr,4tBu}). The 4-*tert*-butyl group does not alter the coordination chemistry of the first two ligands, relative to their 4-H analogues, however, the coordination chemistry of the third ligand is dramatically changed, making it a "tetrahedral enforcer". The complexes Co[Tp^{4tBu}][Tp^{Np}] (**1**), Tl[Tp^{Tol,4tBu}] (**2**), Rh[Tp^{Tol,4tBu}](CO)$_2$ (**3**), Co[Tp^{iPr,4tBu}]Cl (**4**), Co[Tp^{iPr,4tBu}]N$_3$ (**5**) and Co[Tp^{iPr,4tBu}]NCS (**6**) have been structurally characterized.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Many of the reported highlights of homoscorpionate [hydrotris(pyrazol-1-yl)borate] coordination chemistry were associated with the use of Tp^{R} ligands containing a specific R substituent in the 3-position.[1] This defined and restricted the size and geometry of the hydrophobic pocket surrounding the coordinated metal atom. In addition to the size of the 3-substituent, it was also important to exert some control over the orientation of asymmetric substituents with regard to the pyrazolyl plane. These substituents included planar rings, such as a phenyl or substituted phenyl, or asymmetric aliphatic groups, such as isopropyl or cycloalkyl (cyclopropyl,[2] cyclobutyl,[3] cyclopentyl,[2] and cyclohexyl[4]), which could exist as different rotamers. In the case of phenyl, its coplanarity with the pyrazolyl ring was approached by means of an ethylene tether,[5] and achieved by means of an ethyne,[6] or methylene tether.[5] Conversely, approximate orthogonality of the phenyl ring to the pyrazolyl plane resulted from placing 2,6-dimethyl substituents on the phenyl group, as in Tp^{Ms},[7] or fusing two benzo rings in the 2,3- and 5,6-positions, as in Tp^{Ant}.[8] Since the last two methods of restricting the rotational freedom of the phenyl ring also altered its nature, by converting a phenyl into a mesityl or a 9-anthryl substituent, we sought to investigate the restriction of rotation of the 3-R group through "remote control", by placing a *tert*-butyl group in the 4-position of the Tp^{R} ligand.

To this end we have synthesized ligands of the general type Tp^{R,4tBu} with R = isopropyl or *p*-tolyl, and also the ligand Tp^{4tBu}, where R = H. Some aspects of their coordination chemistry were studied, and compared with the behavior of Tp^{x} analogues containing either H or Br in the 4-position. Although a number of homoscorpionate ligands have been described containing 4-substituents (halide, linear alkyl groups, phenyl), none possess the steric bulk of a *tert*-butyl group.[1]



-[N-N]- is the third, hidden, 3-R-4-(*tert*-butyl)pyrazolyl ring

R = H, isopropyl, *p*-tolyl

Results and Discussion

The new ligands Tp^{4tBu}, Tp^{Tol,4tBu}, and Tp^{iPr,4tBu} were synthesized by reaction of KBH$_4$ with an excess of the appropriate molten pyrazole. They were isolated, purified, and characterized as their respective Tl salts.[9]

The ligand with R = H (Tp^{4tBu}) was sterically unhindered around the 3-position, as in the parent ligand Tp. It was structurally characterized as part of the heteroleptic complex Co[Tp^{4tBu}][Tp^{Np}] (**1**) by NMR spectroscopy and by X-ray crystallography (Figure 1). The Co–N bonds of the Tp^{4tBu} ligand are shorter than those of Tp^{Np} (average

---

[a] Department of Chemistry and Biochemistry, University of Delaware,
Newark, DE 19716, USA

DOI: 10.1002/ejic.200300005 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

bond lengths 2.13 and 2.17 Å, respectively), consistent with the unsubstituted 3-position. In the structure of Co[Tp$^{4t\mathrm{Bu}}$][Tp$^{\mathrm{Np}}$], unidirectional sideways twisting of the neopentyl groups around the B−Co axis can be seen. This was also observed in other structurally characterized Tp$^{\mathrm{Np}}$ derivatives.[10] Furthermore, the paramagnetic NMR spectrum of **1** closely resembles that of the known analogue Co[Tp][Tp$^{\mathrm{Np}}$][11] with each proton type uniquely defined. However, the signal in the 40−50 ppm range assigned to the 4-H proton is absent, and a new signal for the *tert*-butyl group is prominent at $\delta = -6.1$ ppm. As expected, Tp$^{4t\mathrm{Bu}}$ forms stable octahedral M[Tp$^{4t\mathrm{Bu}}$]$_2$ complexes and labile tetrahedral M[Tp$^{4t\mathrm{Bu}}$]X complexes, which are unstable with respect to the octahedral species.

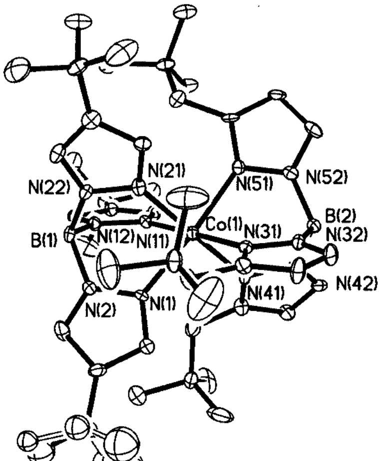


Figure 1. ORTEP plot of the structure of Co[Tp$^{4t\mathrm{Bu}}$][Tp$^{\mathrm{Np}}$] (**1**); selected bond lengths [Å] and angles [°]: Co−N(1) 2.128(6), Co−N(11) 2.129(7), Co−N(21) 2.131(7), Co−N(31) 2.163(7), Co−N(41) 2.164(7), Co−N(1) 2.175(7); N(1)−Co−N(11) 84.8(3), N(1)−Co−N(21) 84.6(3), N(21)−Co−N(11) 87.1(3), N(31)−Co−N(41) 86.9(3), N(31)−Co−N(51) 87.4(3), N(41)−Co−N(51) 87.7(3)

Reaction of Tl[Tp$^{4t\mathrm{Bu}}$] with [Pd(η^3-methallyl)Cl]$_2$ yielded the stable complex Pd[Tp$^{4t\mathrm{Bu}}$][η^3-methallyl]. The NMR spectrum of this compound shows only one type of 3-(*tert*-butyl)pyrazolyl group, which is consistent with the rapid exchange of the coordinated and uncoordinated pyrazolyl groups, as was observed earlier in similar Pd[Tp$^{\mathrm{x}}$][η^3-methallyl] complexes. In short, [Tp$^{4t\mathrm{Bu}}$] behaves similarly to the parent ligand Tp.

The ligand [Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$]$^-$ was synthesized by reaction of KBH$_4$ with molten 4-(*tert*-butyl)-3-(*p*-tolyl)pyrazole, and it was characterized as Tl[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$] (**2**) by NMR spectroscopy and X-ray crystallography (Figure 2). The twist angles of the tolyl group with respect to the pyrazolyl plane are 101, 102, and 121°, respectively. The deviation from orthogonality of the pyrazolyl and tolyl molecular planes is, on average, 18°. Unlike the closely related Tl[Tp$^{\mathrm{Tol}}$],[12] which forms a head-to-head dimer in the crystal, Tl[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$] is monomeric. The Tl−N distances are the same for both compounds (2.58 Å), and fall within the range for Tl[Tp$^{\mathrm{x}}$] compounds (2.50−2.73 Å).[13] However, in Tl[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$], the N−Tl−N angles are smaller than those in Tl[Tp$^{\mathrm{Tol}}$] (average angles 74° and approximately 77°, respectively). In other Tl[Tp$^{\mathrm{x}}$] compounds, such angles range from 65.3 to 79.4°.[13]

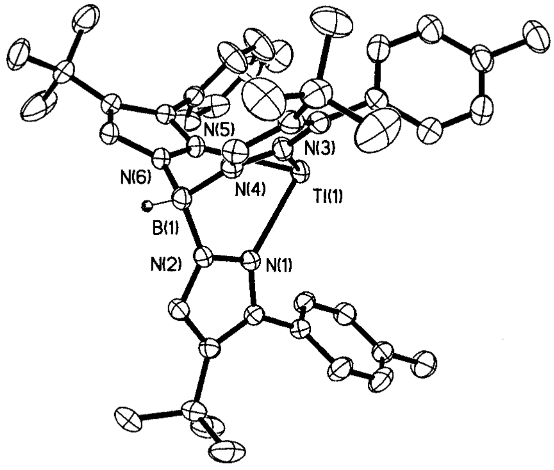


Figure 2. ORTEP plot of the structure of Tl[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$] (**2**); selected bond lengths [Å] and angles [°]: Tl−N(1) 2.580(2), Tl−N(3) 2.550(3), Tl−N(5) 2.560(2); N(1)−Tl−N(3) 73.55(8), N(5)−Tl−N(3) 74.15(8), N(1)−Tl−N(5) 73.58(8)

The reaction of Tl[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$] with anhydrous CoCl$_2$ in chloroform yielded the tetrahedral complex Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$]Cl, which could be used to synthesize mixed complexes. For instance, its reaction with Tl[Tp] proceeded easily, producing the heteroleptic species Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$][Tp]. The proton NMR spectrum of Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$][Tp] is in agreement with a structure that has not undergone any rearrangement. Assignment of the NMR resonances was aided by comparison with the related complex Co[Tp$^{\mathrm{Tol}}$][Tp], which was synthesized from Co[Tp$^{\mathrm{Tol}}$]Cl and Tl[Tp]. The *ortho*- and *meta*-protons of the tolyl substituent in both complexes appear as sharp resonances, rather than as two separate peaks or as broad resonances. This indicates a sufficient degree of oscillation of the tolyl group around the C-3 bond (despite the presence of the 4-*tert*-butyl substituent) to render them spectroscopically equivalent on the NMR timescale.

The complex Rh[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$](CO)$_2$ (**3**) was prepared by bubbling CO into a solution of the Rh[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$](COD) intermediate prepared in situ from **2** and the Rh(COD)Cl dimer. The IR spectrum of this compound contains two sets of carbonyl peaks: 2080, 2059, 2015, and 1980 cm^{-1}, with the BH stretching frequency at 2443 cm^{-1}. The presence of four CO peaks suggests that the compound contains both κ^3 and κ^2 species, which is not unusual for complexes of this general type.[14] The structure of **3** was determined by X-ray crystallography (Figure 3). The Rh center is five-coordinate, with one long (2.43 Å) and two short (2.12 and 2.13 Å) Rh−N bonds. This type of five-coordination leads to the lowest energy structure for Rh[Tp$^{\mathrm{x}}$](CO)$_2$ complexes, as has been predicted by Webster and Hall on the basis of density functional calculations for the various structures that a Rh[Tp$^{\mathrm{x}}$](CO)$_2$ species can adopt.[14] The deviation from orthogonality of the tolyl and pyrazolyl planes varied: 26 and 25° for the pyrazolyl arms containing the two short

Rh−N bonds, and 10° for the arm with the long axial Rh−N bond. The N−Rh−N angles average 83.4°.

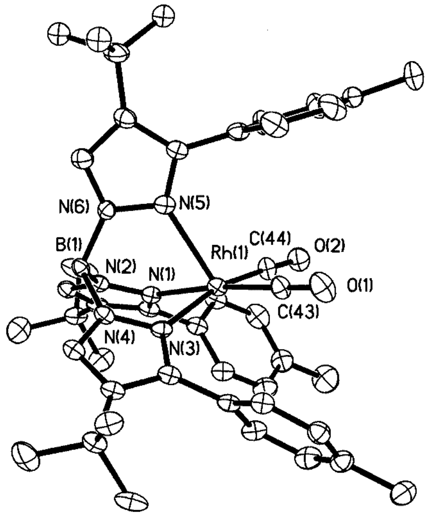


Figure 3. ORTEP plot of the structure of $Rh[Tp^{Tol,4tBu}](CO)_2$ (**3**); selected bond lengths [Å] and angles [°]: Rh−N(1) 2.116.4(4), Rh−N(3) 2.132.4(4), Rh−N(5) 2.426.4(4), Rh−C(44) 1.851(5), Rh−C(43) 1.856(5); N(1)−Rh−N(3) 85.05(13), N(1)−Rh−N(5) 84.02(13), N(5)−Rh−N(3) 81.34(13), C(43)−Rh−C(44) 85.4(2)

By comparison, the related complex $Rh[Tp^{Br3}](CO)_2$ shows only two CO bands in its IR spectrum: $\tilde{\nu}$ = 2080 and 2012 cm^{-1}, each with a hint of a shoulder at higher frequency. This compound also has one long (2.53 Å) and two short (2.12 and 2.12 Å) Rh−N bonds.[15] The somewhat longer Rh−N bond might reflect the lower nucleophilicity of the tribromopyrazolyl arm, and would be consonant with the rather high frequency of the B−H stretch, which is at 2585 cm^{-1}. In other structurally characterized $Rh[Tp^x](CO)_2$ complexes, the axial Rh−N bonds are longer, ranging from 2.55 to 2.64 Å.[14] From all the above data we can conclude that while the *tert*-butyl group in the 4-position does not permit free rotation of the 3-aryl substituent, neither does it enforce orthogonality between the pyrazolyl and tolyl planes. The 4-*tert*-butyl group allows for sufficient oscillation of the tolyl group around the C-3 bond, so that the tolyl substituent can deviate considerably from orthogonality relative to the pyrazolyl plane (we have examples which deviate by up to 31°) in order to accommodate other ligands attached to the metal atom. Thus, the difference in steric hindrance between Tp^{Tol} and $Tp^{Tol,4tBu}$ becomes rather insignificant.

While the coordination behavior of $[Tp^{Tol,4tBu}]^-$ is still fairly similar to that of $[Tp^{Tol}]^-$, major spectroscopic differences and differences in chemical reactivity can be observed between $[Tp^{iPr,4tBu}]^-$ and its closest steric analogue, $[Tp^{iPr,4Br}]^-$. The ^1H NMR spectrum of $Tl[Tp^{iPr,4Br}]$ exhibits a sharp doublet and septuplet,[11] assigned to the isopropyl groups. However, in the ^1H NMR spectrum of $Tl[Tp^{iPr,4tBu}]$, the resonances assigned to the methyl groups appear as a small broad hump at δ = 1.4 ppm. The signal for the tertiary hydrogen atom is not visible, and can only be discerned through integration in the δ = 3.1−3.5 ppm range. The difference was even more dramatic in the ^{13}C NMR spectrum. In the spectrum of $Tl[Tp^{iPr,4Br}]$, the resonance assigned to the isopropyl methyl group is only slightly broadened. However, it is split into a doublet in the spectrum of $Tl[Tp^{iPr,4tBu}]$. The value of J = 218 Hz, is the largest known ^{13}C-^{205}Tl coupling observed in $Tl[Tp^x]$ complexes. It significantly exceeds those found in $Tl[Tp^{tBu,iPr}]$ (J = 167 Hz),[16] $Tl[Tp^{tBu}]$ (J = 171 Hz),[17] $Tl[Tp^{tBu,Tn}]$ (J = 183 Hz),[11] and $Tl[Tp^{tBu,Me}]$ (J = 197 Hz).[18]

In terms of their coordination chemistry, $[Tp^{iPr,4tBu}]$ forms different complexes from those of $[Tp^{iPr,4Br}]$,[19] and resembles those of $[Tp^{tBu}]$.[20] Thus, stable compounds of the type $M[Tp^{iPr,4tBu}]X$, where X = halide or pseudohalide, are readily prepared. They do not add solvent molecules, as was observed in the case of the $M[Tp^{iPr,4Br}]X$ analogues, which readily form five-coordinate complexes with small donor molecules, such as methanol or THF (although on air-drying, the solvent is gradually lost). Thus, one could regard $[Tp^{iPr,4tBu}]$ as a bona fide "tetrahedral enforcer", no less so than $[Tp^{tBu}]$. The complex $Co[Tp^{iPr,4tBu}]Cl$ (**4**) was structurally characterized (Figure 4).

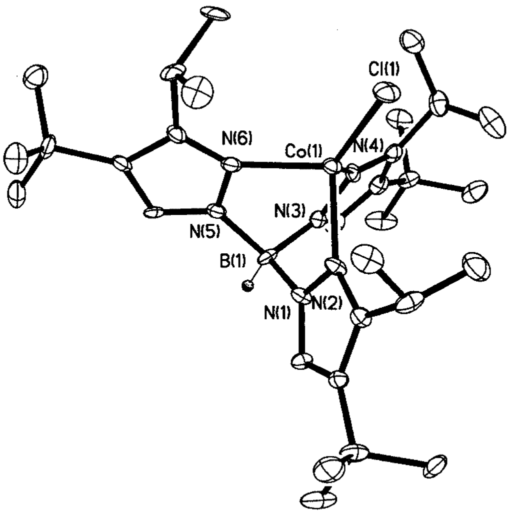


Figure 4. ORTEP plot of the structure of $Co[Tp^{iPr,4tBu}]Cl$ (**4**); selected bond lengths [Å] and angles [°]: Co−N(2) 2.040(3), Co−N(4) 2.024(6), Co−N(6) 2.058(7); N(2)−Co−N(4) 95.4(3), N(2)−Co−N(6) 94.2(3), N(4)−Co−N(6) 95.74(11)

Another distinguishing feature of $[Tp^{iPr,4tBu}]^-$, as compared with $[Tp^{iPr,4Br}]$, is the fact that while reaction of $Co[Tp^{iPr,4Br}]X$ with Tl[Tp] or Tl[Tp*] readily yields the heteroleptic complexes $Co[Tp^{iPr,4Br}][Tp]$ and $Co[Tp^{iPr,4Br}][Tp^*]$, respectively,[21] **4** does not undergo such reactions. For instance, stirring a solution of **4** with the least-hindered homoscorpionate ligand, Tl[Tp], for 26 h, did not produce the heteroleptic complex, but only a very small amount of $Co[Tp]_2$. This type of behavior was also observed for $Co[Tp^{tBu}]Cl$. Obviously, the 4-*tert*-butyl group does not permit rotation of the isopropyl substituent so as to direct the two methyl groups away from the coordinated metal atom and toward the 4-position of the pyrazolyl ring, which is a precondition for the formation of heteroleptic species

© 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

M[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$][Tp^{x}]. On the contrary, it locks the isopropyl substituent, so that it straddles the pyrazolyl plane with both methyl groups forking towards the coordinated metal atom. Such rotameric disposition of the isopropyl methyl groups has been established only for a few structurally characterized tetrahedral compounds of the type M[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]X.[19,22] However, the rotameric disposition of a 3-isopropyl group with the two methyl groups directed away from the coordinated metal atom is ubiquitous in all heteroleptic complexes M[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$][L],[21,23] as well as in other homoscorpionate complexes containing a 3-*i*Pr substituent, such as those of Tp$^{i\mathrm{Pr},\mathrm{Me}}$,[24] and of Tp$^{i\mathrm{Pr}2}$.[25]

Despite the failure to form the heteroleptic complex Co[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$][Tp] by reaction of Co[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$]Cl with [Tp]$^{-}$, displacement of the chloride ion by other simple monodentate ions is feasible, as was demonstrated by the heterogeneous reaction of **4** with solid NaN$_3$ in ethyl acetate, which resulted in the formation of Co[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$]N$_3$ (**5**) as the only product, in good yield. Its structure, as well as that of the related complex Co[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$]NCS (**6**), which was prepared by the heterogeneous reaction of Tl[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$] and Co(NCS)$_2$, was determined by X-ray crystallography (Figures 5 and 6, respectively).

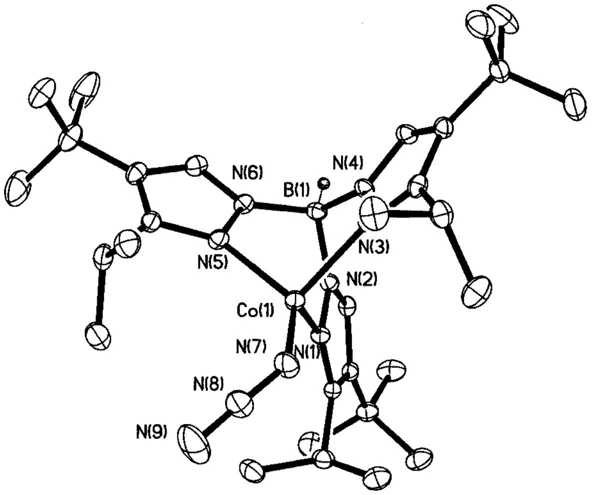


Figure 5. ORTEP plot of the structure of Co[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$]N$_3$ (**5**); selected bond lengths [Å] and angles [°]: Co−N(1) 2.011(2), Co−N(3) 2.044(2), Co−N(5) 2.032(2), Co−N(7) 1.911(2); N(1)−Co−N(3) 96.38(9), N(1)−Co−N(5) 93.82(9), N(5)−Co−N(3) 94.84(9), N(1)−Co−N(7) 121.61(10), N(3)−Co−N(7) 117.81(10), N(5)−Co−N(7) 125.47(10)

If one compares the Co−N bond lengths and N−Co−N angles in three related and structurally characterized complexes, Co[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]NCS, Co[Tp*t*Bu]NCS, and **6**, we see that **6** has the longest Co−N bond (average bond length 2.029 Å), Co[Tp$^{t\mathrm{Bu}}$]NCS has the shortest (2.019 Å), and Co[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]NCS has a bond length of intermediate value (2.024 Å). Compound **6** also has the widest average N−Co−N angle (95.7°), followed by Co[Tp$^{t\mathrm{Bu}}$]NCS (95.4°) and Co[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]NCS (95.2°).

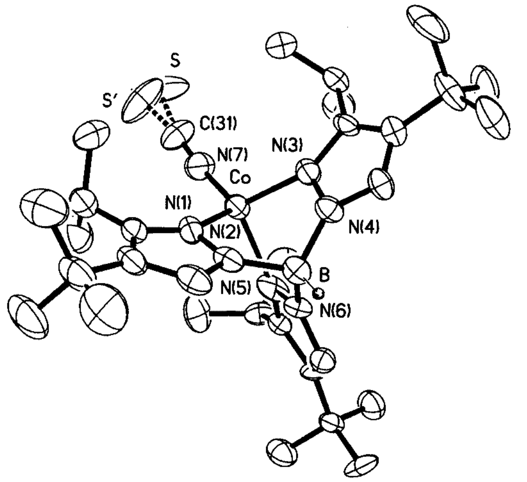


Figure 6. ORTEP plot of the structure of Co[Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$]NCS (**6**); selected bond lengths [Å] and angles [°]: Co−N(1) 1.984(8), Co−N(3) 2.021(7), Co−N(5) 2.081(9), Co−N(7) 1.898(10); N(1)−Co−N(3) 97.0(3), N(1)−Co−N(5) 94.4(3), N(5)−Co−N(3) 95.6(3)

Comparing the average Co−N bond lengths and N−Co−N angles of complex **4** with those of Co[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]Cl and Co[Tp$^{t\mathrm{Bu}}$]Cl, we find that the above-mentioned bond lengths and angles in **4** are closer to those of Co[Tp$^{t\mathrm{Bu}}$]C, than to those of Co[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]Cl. In **4**, the two values are 2.033(5) Å and 95.1°, in Co[Tp$^{t\mathrm{Bu}}$]Cl they are 2.038 Å and 95.1°,[26] while in Co[Tp$^{i\mathrm{Pr},4\mathrm{Br}}$]Cl they are 2.039(6) Å and 94.4°, respectively.[22] In the related complex **5**, these values are 2.029 Å and 95.0°, respectively.

Conclusion

We have prepared several Tp^{x} ligands of the general type [Tp$^{\mathrm{R},4t\mathrm{Bu}}$]$^{-}$ where R = H, isopropyl, or *p*-tolyl, and found that the presence of the 4-*tert*-butyl group strongly blocks the rotational freedom of a 3-isopropyl group. Therefore, the 3-isopropyl group behaves like a 3-*tert*-butyl group (a "tetrahedral enforcer") with a fixed rotameric conformation in which the two methyl groups are forked towards the coordinated metal atom. This significantly changes the coordination chemistry of [Tp$^{i\mathrm{Pr},4t\mathrm{Bu}}$]$^{-}$, relative to all other Tp^{x} ligands containing 3-isopropyl substituents. On the other hand, the effect of a 4-*tert*-butyl group on the 3-*p*-tolyl substituent in [Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$] is less pronounced, since the 4-*tert*-butyl substituent still permits substantial latitude for oscillation, if not free rotation, of the 3-tolyl group. Thus, the formation of the heteroleptic complex Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$][Tp] was as easy as that of Co[Tp$^{\mathrm{Tol}}$][Tp]. When 3-R = H, [Tp$^{4t\mathrm{Bu}}$]$^{-}$ behaves like the parent ligand [Tp]$^{-}$, except that the melting points of its derivatives are higher, and its NMR spectrum is simpler.

Experimental Section

General: All chemicals were commercial reagent grade and were used as received. 4-(*tert*-Butyl)-3-isopropylpyrazole and 4-*tert*-butyl-3-(*p*-tolyl)pyrazole were prepared according to a literature procedure,[27] as was Co[Tp$^{\mathrm{Np}}$]Cl.[10] [Pd(η^{3}-methallyl)Cl]$_2$ was purchased from Strem. 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. ^{1}H NMR spectra were obtained with a Nicolet NT360WB spectrometer. The compounds were studied under typical conditions, with 16 K data points, a sweep width of 3000−4000 Hz, 90° pulse angles, and a recycle time of 4−5 s. ^{13}C NMR: pulse width, 9.00 µs; acq. time 819.20 ns; recycle time 1.0 s; number of acq. 8192; frequency 75.43 MHz; spec. width 20000 H_3.

4-*tert*-Butylpyrazole: A mixture of pyrazole (136 g, 2 mol) and *tert*-butyl chloride (279 g, 3 mol) was heated for 6 h at 220 °C in an autoclave. After cooling, the autoclave contents were stirred in a mixture of alkaline ice water, and the products were extracted with chloroform. The extracts were filtered through alumina, stripped, and distilled under atmospheric pressure. The fraction boiling in the 176−196 °C range was obtained in 28 g yield. It was (by NMR) 40% pyrazole and 60% 1,4-di(*tert*-butyl)pyrazole. The residue obtained was almost pure 4-*tert*-butylpyrazole (90 g, 36%, by NMR spectroscopy), contaminated only by a small amount of 1,4-bis(*tert*-butyl)pyrazole. The product was purified by recrystallization the 176−196 °C range was obtained in 28 g yield. It was (by NMR) δ = 11.2 (s, broad, 1 H, NH), 7.44 (s, 2 H, H-3,5), 1.27 (s, 9 H, *t*Bu) ppm. The literature reports 4-*tert*-butylpyrazole to be a yellowish oil.[28]

K[Tp$^{4t\mathrm{Bu}}$]: A mixture of 4-*tert*-butylpyrazole [50 g, 0.40 mol, contaminated with traces of the innocuous 1,4-bis(*tert*-butyl)pyrazole] and KBH_4 (5.4 g, 0.10 mol) was stirred and heated gradually without any solvent. Hydrogen began to evolve at 140 °C, and evolution of the theoretical 7.5 L was completed at 220 °C. Excess 4-*tert*-butylpyrazole, and traces of 1,4-bis(*tert*-butyl)pyrazole, were removed by distillation under vacuum. The molten product was cooled, transferred to a 500-mL Erlenmeyer flask, and boiled with 300 mL of octane. The slurry was cooled, the solid was filtered off, and washed with hexane, producing the crude potassium salt in a 90% (38 g) yield. IR: $\tilde{\nu}$ = 2390 (BH, broad) cm^{-1}.

Tl[Tp$^{4t\mathrm{Bu}}$]: All of the above crude K[Tp$^{4t\mathrm{Bu}}$] was converted into Tl[Tp$^{4t\mathrm{Bu}}$] by dissolving it in a minimum amount of THF, and stirring the resulting solution with an excess of aqueous $TlNO_3$ solution for 1 h. Thereafter, 1 L of water was added, along with 500 mL of chloroform. The organic layer was separated, and passed through a layer of alumina. Evaporation of the solvent gave the crude product in an 86% (45 g) yield. The product was purified by recrystallization from undecane. The fine needles sintered from 280 °C, and melted and decomposed at 282−283 °C. IR: $\tilde{\nu}$ = 2450 (BH, broad) cm^{-1}. NMR: δ = 7.54 (s, 3 H, 5-H), 7.42 (s, 3 H, 3-H), 1.24 (s, 27 H, *t*Bu) ppm; BH (1 H) was detected by integration in the δ = 3.4−5.4 ppm range. ^{13}C NMR: δ = 29.6 (*C*Me$_3$), 32.3 (C*Me$_3$*), 131.4 (C-4), 132.3 (C-5), 136.4 (C-3) ppm. $C_{21}H_{37}BN_6Tl$ (588.76): calcd. C 43.1, H 5.81, N 14.4; found C 43.0, H 6.10, N 14.2.

Pd[Tp$^{4t\mathrm{Bu}}$][η^{3}-methallyl]: A mixture of Tl[Tp$^{4t\mathrm{Bu}}$] (1.2 g, 2 mmol) and the Pd(η^{3}-methallyl)Cl dimer (0.76 g, 2 mmol) was stirred in 30 mL of chloroform for 1 h. The slurry was filtered, and the filtrate concentrated to give a white solid, which was recrystallized from toluene/heptane. M.p. 154−156 °C (dec.). IR: $\tilde{\nu}$ = 2462 (BH) cm^{-1}. ^{1}H NMR: δ = 7.39 (s, 3 H, 3-H), 7.35 (s, 3 H, 5-H), 3.66 (s, 2 H, *syn*), 2 87 (2 H, *anti*), 2.09 (s, 3 H, Me), 1.21 (s, 27 H, *t*Bu) ppm. $C_{25}H_{41}BN_6Pd$ (542.88): calcd. C 55.4, H 7.56, N 15.5; found 55.6, H 7.72, N 15.3.

Co[Tp$^{4t\mathrm{Bu}}$][Tp$^{\mathrm{Np}}$] (1): A mixture of Tl[Tp$^{4t\mathrm{Bu}}$] (1.2 g, 2 mmol) and Co[Tp$^{\mathrm{Np}}$]Cl (1.1 g, 2 mmol) was stirred in 150 mL of dichloromethane. Within 10 min, the blue color changed to a pale yellow. The slurry was filtered through Celite, yielding a bright yellow solution, which on evaporation yielded **1** (1.3 g, 74%) as a pale yellow solid. It was recrystallized from undecane. M.p. 295−296 °C (with darkening and dec.). IR: $\tilde{\nu}$ = 2442 (BH, Tp$^{\mathrm{Np}}$) and 2449 (BH, Tp$^{4t\mathrm{Bu}}$) cm^{-1}. ^{1}H NMR: δ = 115.6 and 113 (1 H each, BH, BH′) 93.2 and 82.2 (3 H each, 5-H and 5′-H), 44.7 (3 H, 4-H), −6.26 (27 H, 4-*t*Bu), −21.3 (27 H, neopentyl *t*Bu), −100.7 (3 H, 3-H), −103.7 (6 H, CH_2) ppm. $C_{45}H_{74}B_2CoN_{12}$ (863.72): calcd. C 62.6, H 8.57, N 19.5; found C 62.7, H 8.69, N 19.2.

Tl[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$] (2): A mixture of 4-(*tert*-butyl)-3-tolylpyrazole (8.9 g, 42 mmol) and KBH_4 (0.56 g, 10 mmol) was heated in a test tube until the borohydride could not be seen anymore, and the initially vigorous evolution of hydrogen ceased. The product was cooled, dissolved in DMF, and stirred with excess aqueous $TlNO_3$. The product was extracted with dichloromethane, the extracts were washed three times with water, and were passed through a bed of alumina. Concentration of the filtrate gave **2** as a fibrous white solid, which was washed with methanol to remove unchanged 4-(*tert*-butyl)-3-tolylpyrazole. **2** was obtained in a 70% (6.5 g) yield. It was recrystallized from octane. M.p. 222−224 °C. IR: $\tilde{\nu}$ = 2435, 2472 sh (BH) cm^{-1}. ^{1}H NMR: δ = 7.53 (s, 1 H, 5-H), 7.23 (d, 2 H, tolyl A_2B_2), 7.11 (d, 2 H, tolyl A_2B_2), 2.34 (s, 3 H, Me) 1.63 (s, 9 H, *t*Bu) ppm. $C_{42}H_{52}BN_6Tl$ (856.11): calcd. C 59.0, H 6.08, N 9.82; found C 59.2, H 6.17, N 9.67.

Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$]Cl: A sample of **2** (1.7 g, 2.0 mmol) was stirred in 50 mL of chloroform with excess anhydrous $CoCl_2$. After 6 h, the slurry was filtered, and the filtrate was concentrated, yielding Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$]Cl (1.2 g, 82%), which was purified by recrystallization from a toluene/octane mixture; m.p. dec. > 280 °C. IR: $\tilde{\nu}$ = 2466 (BH) cm^{-1}. $C_{42}H_{52}BClCoN_6$ (746.11): calcd. C 67.6, H 6.97, N 11.3; found C 67.9, H 7.18, N 11.1.

Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$]NCS: This complex was prepared as above; however, $Co(NCS)_2$ was used instead of $CoCl_2$. It was obtained in a 78% yield. M.p. gradual dec. > 240 °C. IR: $\tilde{\nu}$ = 2476 (BH), 2068 (NCS) cm^{-1}. $C_{43}H_{52}BCoN_7S$ (768.75): calcd. C 67.2, H 6.77, N 12.8; found C 67.6, H 6.89, N 12.6.

Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$][Tp]: A mixture of Co[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$]Cl (0.75 g, 1.0 mmol) and Tl[Tp] (0.42 g, 1.0 mmol) was stirred in 50 mL of chloroform for 6 h. The slurry was filtered, and the filtrate was chromatographed on alumina. On concentration of the yellow-orange eluent, yellowish-orange crystals (0.51 g, 68%) were obtained. M.p. gradual dec. > 270 °C. IR: $\tilde{\nu}$ = 2452 (BH) cm^{-1}. NMR: δ = 114 (1 H, BH), 112 (1 H, BH′), 90.1 (3 H, 5-H), 80.9 (3 H, 5′-H), −3.15 (27 H, *t*Bu), −5.9 (9 H, Me), −9.2 (6 H, *m*-H), −49.1 (6 H, *o*-H), −103.4 (3 H, 3-H H) ppm. $C_{51}H_{62}B_2CoN_{12}$ (923.63): calcd. C 66.3, H 6.72, N 18.2; found C66.5, H 6.79, N 17.9.

Co[Tp$^{\mathrm{Tol}}$][Tp]: This complex was prepared as above from Co[Tp$^{\mathrm{Tol}}$]Cl (0.58 g, 1 mmol) and Tl[Tp] (0.42 g, 1 mmol), in an 82% (0.62 g) yield. M.p. sintered from 265 °C, gradual dec. > 275 °C. IR: $\tilde{\nu}$ = 2470 (BH) cm^{-1}. NMR: δ = 113 (1 H, BH), 112 (1 H, BH′), 89.4 (3 H, 5-H), 77.3 (3 H, 5′-H), 44.2 (3 H, 4-H), 41.8 (3 H, 4′-H), −1.88 (9 H, Me), −2.18 (6 H, *m*-H), −55.4 (6 H, *o*-H), −99.1 (3 H, 3-H) ppm. $C_{39}H_{38}B_2CoN_{12}$ (755.36): calcd. C 62.0, H 5.03, N 22.3; found C 62.1, H 5.15, N 22.1.

Rh[Tp$^{\mathrm{Tol},4t\mathrm{Bu}}$](CO)$_2$ (3): A mixture of **2** (0.86 g, 1 mmol) and the RhCl(COD) dimer (0.30 g, 1 mmol) was stirred in chloroform at room temperature for 2 h. The slurry, containing precipitated TlCl was stirred further with a stream of CO bubbling in for 1 h, and was then filtered through a pad of Celite. The filtrate was concentrated and the product, obtained in a 68% (0.55 g) yield, was recrystallized from toluene/heptane. M.p. 233−235 °C (dec.). IR: $\tilde{\nu}$ = 2443 (BH); 2028, 2059, 2015, 1980 (CO) cm^{-1}. ^{1}H NMR: slightly broadened resonances at δ = 7.6 (1 H, 5-H), 7.3 and 7.2 (2 H each, tolyl A_2B_2 pattern), 2.4 (3 H, Me), 1.2 (9 H, *t*Bu) ppm. $C_{44}H_{52}BN_6O_2Rh$ (810.66): calcd. C 65.2, H 6.42, N 10.4; found C 65.5, H 6.57, N 10.2.

Tl[Tp^{iPr,4tBu}]: A mixture of 4-(*tert*-butyl)-3-isopropylpyrazole (24 g, 130 mmol) and KBH_4 (2.0 g, 36 mmol) was heated to 220 °C, until the theoretical amount of hydrogen evolved. Excess 4-(*tert*-butyl)-3-isopropylpyrazole was sublimed out at 220 °C/1.5 Torr. The unsublimed crude K[Tp^{iPr,4tBu}] had $\tilde{\nu}$ = 2460 (BH) cm^{-1}, and it was converted into Tl[Tp^{iPr,4tBu}] as described for **2**. M.p. 222−224 °C. IR: $\tilde{\nu}$ = 2432 (BH) cm^{-1}. ^{1}H NMR: δ = 7.29 (s, 3 H, 5-H), 3.1−3.5 (very broad, 1 H, tertiary CH), 1.37 (broad hump, 18 H, isopropyl Me) and 1.26 (sharp s, 27 H, *t*Bu) ppm. ^{13}C NMR: δ = 26.1 (somewhat broad d, *J* = 218 Hz, CH*Me₂*), 27.5 (s, *C*HMe$_2$), 30.1 (sharp s, *C*Me$_3$), 31.7 (sharp s, C*Me₃*) 125.8 (broad s, C-5), 133.3 (very sharp s, C-4), 156.9 (broad s, C-3) ppm. $C_{30}H_{52}BN_6Tl$ (711.98): calcd. C 50.6, H 7.31, N 11.8; found 50.9, H 7.46, N 11.6%.

Co[Tp^{iPr,4tBu}]Cl (4): This complex was prepared by stirring Tl[Tp^{iPr,4tBu}] (2.8 g, 4 mmol) in dichloromethane with a large excess of anhydrous $CoCl_2$. After 3 h, the blue slurry was filtered, the filtrate was chromatographed on alumina, and the deep blue eluent was concentrated. The crude product, obtained in a 73% (1.8 g) yield, was recrystallized from octane, producing deep blue needles, which did not melt up to 304 °C. IR: $\tilde{\nu}$ = 2502 (BH) cm^{-1}. NMR: δ = 34.6 (3 H, 5-H), 23.9 (3 H, C*H*Me$_2$), 10.7 (18 H, CH*Me₂*), 4.3 (27 H, *t*Bu) and −21.4 (1 H, BH) ppm. $C_{30}H_{52}BClCoN_6$ (601.98): calcd. C 59.8, H 8.63, N 14.0; found C 60.0, H 8.78, N 13.7.

Co[Tp^{iPr,4tBu}]N$_3$(5): This compound was obtained when **4** (0.6 g, 1 mmol) was stirred overnight in ethyl acetate with a large excess of solid NaN_3. The slurry was filtered through Celite, and the solution was concentrated, producing dark blue **5** in an 83% (0.50 g) yield. It melted at 272−274 °C, and on further heating fumes could be seen and the blue product turned purple. IR: $\tilde{\nu}$ = 2493 (BH), 2081 (N_3) cm^{-1}. NMR: δ = 42.2 (3 H, 5-H), 22.4 (3 H, C*H*Me$_2$), 9.03 (18 H, CH*Me₂*), 3.60 (27 H, *t*Bu), −9.2 (1 H, BH) ppm. $C_{30}H_{52}BCoN_9$ (609.12): calcd. C 59.2, H 8.55, N 20.7; found C 59.5, H 8.67, N 20.4.

Co[Tp$^{iPr,4-tBu}$]NCS (6): This compound was prepared as in the case of **4**, instead, Tl[Tp^{iPr,4tBu}] (1.4 g, 2 mmol) and a large excess of Co(NCS)$_2$ was used. It was obtained in a 65% (0.81 g) yield, as a deep blue solid. M.p. 269−271 °C. IR: $\tilde{\nu}$ = 2490 (BH), 2054 (NCS) cm^{-1}. NMR: δ = 41.3 (3 H, 5-H), 26.2 (3 H, C*H*Me$_2$), 9.18 (18 H, CH*Me₂*), 3.53 (27 H, *t*Bu), −6.15 (1 H, BH) ppm. $C_{31}H_{52}BCoN_7S$ (625.06): calcd. C 59.6, H 8.33, N 15.7; found C 59.7, H 8.41, N 15.5.

Attempts to Prepare the Heteroleptic Complex Co[Tp^{iPr,4tBu}][Tp]: Stirring equimolar amounts of Co[Tp^{iPr,4tBu}]Cl and TpTl in dichloromethane for 26 h showed no signs of a reaction. The greenish-blue solution was chromatographed, yielding two fractions: a minor yellow, and a dominant blue one. The material from the yellow fraction was identified as Co[Tp]$_2$ by its characteristic IR spectrum, while the blue fraction was unchanged Co[Tp^{iPr,4tBu}]Cl. A similar result was obtained when Co[Tp^{tBu}]Cl was stirred with Tl[Tp].

X-ray Crystal Structure Determinations: Diffraction intensity data were collected with Siemens P4 (**6**), Siemens P4/CCD (**1**), and

Table 1. Crystal data for compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{45}H_{74}B_2CoN_{12}$	$C_{42}H_{52}BN_6Tl$	$C_{44}H_{52}BN_6O_2Rh$	$C_{30}H_{52}BClCoN_6$	$C_{30}H_{52}BCoN_9$	$C_{31}H_{52}BCoN_7S$
Solvent		C_8H_{18}		$C_7H_8 + C_8H_{10}$	$CH_3CN + CH_2Cl_2$	
Formula mass	863.71	970.3	810.64	800.26	734.53	624.6
Space group	*Pbca*	$P2_1/c$	$C2/c$	$Pna2_1$	$P2_1/n$	$P\bar{1}$
	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
a [Å]	11.807(5)	11.5083(9)	40.119(3)	19.4457(18)	19.1519(10)	12.493(3)
b [Å]	19.605(7)	13.7222(11)	11.3128(9)	9.2549(9)	18.0914(9)	12.940(4)
c [Å]	43.493(6)	31.405(3)	18.5842(15)	26.369(2)	22.5068(2)	16.688(4)
α [°]	90.00	90.00	90.00	90.00	90.00	84.17(2)
β [°]	90.00	92.837(2)	98.078(2)	90.00	94.3820(10)	83.93(2)
γ [°]	90.00	90.00	90.00	90.00	90.00	67.92(2)
V [Å^3]	10068(11)	4953.4(7)	8350.9(12)	4745.6(8)	7775.5(7)	2480.3(11)
Z, *Z'*	8, 1	4, 1	8, 1	4, 1	8, 1	2, 1
Crystal color	yellow	colorless	yellow	blue	blue	blue
Habit	plates	blocks	blocks	blocks	blocks	thin plates
Size [mm]	0.25 × 0.40 × 0.50	0.30 × 0.36 × 0.38	0.10 × 0.10 × 0.15	0.10 × 0.25 × 0.45	0.10 × 0.30 × 0.30	0.12 × 0.28 × 0.32
Temperature [K]	173	218	100	150	150	298
D(calcd.) [g·cm^{-3}]	1.140	1.301	1.290	1.120	1.147	0.836
μ (Mo-K_α) [cm^{-1}][a]	3.83	32.98	4.52	4.53	5.43	4.09
Absorption corr.	SADABS	SADABS	SADABS	SADABS	SADABS	psi scans
*T*max	0.9103	0.4378	0.9562	0.9561	0.9410	0.9525
*T*min	0.8315	0.3671	0.9353	0.8222	0.8368	0.8802
R_1 (*F*) [%][b]	12.21	3.32	6.59	6.42	5.11	10.69
wR_2 (*F*) [%][c]	27.19	8.01	15.08	16.85	9.08	26.46
Instrumentation	CCD K1	Apex	Apex	Apex	Apex	P3/4
Solution method	direct methods	direct methods	Patterson	direct methods	direct methods	direct methods

[a] Mo-K_α: λ = 0.71073 [Å] using Bruker-Siemens CCD K1, Bruker-Nonius Apex CCD, and Siemens P3/4 instruments. [b] $R = \|F_o| - |F_c\|/|F_o|$. [c] $R(\omega F^2) = \{[\omega(F_o^2 - F_c^2)^2]/[\omega(F_o^2)^2]\}^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o^2)]/3$.

© 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Bruker Smart Apex CCD (**2**−**5**) diffractometers. Crystal data collections and refinement parameters are given in Table 1. The space groups for structures **1**−**5** were chosen based on systematic absences in the diffraction, and for **6**, based on intensity statistics. Structure **3** was solved using a Patterson function and the other structures were solved by direct methods, 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 [G. M. Sheldrick, *SADABS* (2.01), Bruker/Siemens Area Detector Adsorption Correction Program, Bruker AXS, Madison Wisconsin, USA, **1998**]. In all the structures, non-hydrogen atoms were refined with anisotropic displacement coefficients and the hydrogen atoms were treated as idealized contributions. In structure **1**, carbon atoms C5−C7 of the *tert*-butyl group were disordered over two positions with 50:50 occupation. Similar disorder was found for one of the *tert*-butyl groups in structure **3**, where the disorder atoms had occupation of 47:53. In structures **2** and **4**, the solvent molecules were quite disordered and were left as isotropic in the refinement. The solvent molecules (dichloromethane and acetonitrile) in structure **5** were quite disordered and were treated using the program SQUEEZE.[29] Correction of the X-ray data for **5** by SQUEEZE (249 electrons/cell) was close to the required value of (256 electrons/cell) for the mixed solvent. Structure **6** diffracted rather poorly, and the S atom was found to be disordered over two positions with 50:50 occupation. All other software and sources, scattering factors are contained in the SHELXTL (5.10) program package (G. M. Sheldrick, Bruker AXS, Madison, WI). CCDC-198497 (**1**), -198498 (**2**), -198499 (**3**), -198500 (**4**), -198501 (**5**), and -198502 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

---

[1] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**.

[2] A. L. Rheingold, G. P. A. Yap, L. M. Liable-Sands, I. A. Guzei, S. Trofimenko, *Inorg. Chem.* **1997**, *36*, 6261−6265.

[3] A. L. Rheingold, G. P. A. Yap, L. N. Zakharov, S. Trofimenko, *Eur. J. Inorg. Chem.* **2002**, 2335−2343.

[4] S. Trofimenko, A. L. Rheingold, L. M. Liable-Sands, *Inorg. Chem.* **2002**, 1889−1896.

[5] A. L. Rheingold, R. L. Ostrander, B. S. Haggerty, S. Trofimenko, *Inorg. Chem.* **1994**, *33*, 3666−3676.

[6] A. L. Rheingold, B. S. Haggerty, S. Trofimenko, *J. Chem. Soc., Chem. Commun.* **1994**, 1973−1974.

[7] A. L. Rheingold, C. B. White, S. Trofimenko, *Inorg. Chem.* **1993**, *32*, 3471−3477.

[8] R. Han, G. Parkin, S. Trofimenko, *Polyhedron* **1995**, 387−391.

[9] C. Janiak, *Main Group Metal Chem.* **1998**, *21*, 33−49.

[10] J. C. Calabrese, S. Trofimenko, *Inorg. Chem.* **1992**, *31*, 4810−4814.

[11] S. Trofimenko, unpublished results.

[12] G. Ferguson, M. C. Jennings, F. J. Lalor, C. Shanahan, *Acta Crystallogr., Sect. C* **1991**, *47*, 2079−2082.

[13] C. Janiak, *Coord. Chem. Rev.* **1997**, *167*, 107−216.

[14] C. E. Webster, M. B. Hall, *Inorg. Chim. Acta* **2002**, *330*, 268−282.

[15] A. L. Rheingold, L. M. Liable-Sands, C. L. Incarvito, S. Trofimenko, *J. Chem. Soc., J. Chem. Soc., Dalton Trans.* **2002**, 2297−2301.

[16] C. López, D. Sanz, R. Claramunt, S. Trofimenko, J. Elguero, *J. Organomet. Chem.* **1995**, *503*, 265−276.

[17] A. H. Cowley, R. L. Geerts, C. M. Nunn, S. Trofimenko, *J. Organomet. Chem.* **1989**, *365*, 19−22.

[18] S. Trofimenko, J. C. Calabrese, J. K. Kochi, S. Wolowiec, F. B. Hulsbergen, J. Reedijk, *Inorg. Chem.* **1992**, *31*, 3943−3950.

[19] S. Trofimenko, J. C. Calabrese, P. J. Domaille, J. S. Thompson, *Inorg. Chem.* **1989**, *28*, 1091−1101.

[20] S. Trofimenko, J. C. Calabrese, J. S. Thompson, *Inorg. Chem.* **1987**, *26*, 1507−1514.

[21] J. C. Calabrese, P. J. Domaille, J. S. Thompson, S. Trofimenko, *Inorg. Chem.* **1990**, *29*, 4429−4437.

[22] M. D. Olson, S. J. Rettig, A. Storr, S. Trofimenko, *Acta Crystallogr., Sect. C* **1991**, *47*, 1543−1544.

[23] M. D. Olson, S. J. Rettig, A. Storr, S. Trofimenko, *Acta Crystallogr., Sect. C* **1991**, *47*, 1544−1546.

[24] M. Cano, J. V. Heras, S. Trofimenko, A. Monge, E. Gutierrez, C. J. Jones, J. A. McCleverty, *J. Chem. Soc., Dalton Trans.* **1990**, 3577−3582.

[25] See ref.[1], pp. 137−140, also: M. Akita, S. Hikichi, *Bull. Chem. Soc., Jpn.* **2002**, *75*, 1657−1679.

[26] I. B. Gorrell, G. Parkin, *Inorg. Chem.* **1990**, *29*, 2452−2456.

[27] S. Trofimenko, A. L. Rheingold, L. M. Liable-Sands, R. M. Claramunt, C. López, M. D. Santa Maria, J. Elguero, *New. J. Chem.* **2001**, *25*, 819−823.

[28] C. Cativiela, J. I. G. Laureiro, J. Elguero, *Gazz. Chim. Ital.* **1986**, *116*, 119−125.

[29] P. Van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194−201.

Received January 8, 2003