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TRIS(3-t-BUTYL-5-METHYLPYRAZOLYL)HYDROBORATO DERIVATIVES OF COPPER AND THALLIUM: THE STRUCTURAL INFLUENCE OF A 5-METHYL SUBSTITUENT

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Abstract—The molecular structures of the tris(3-t-butyl-5-methylpyrazolyl)hydroborato derivatives of copper and thallium $\{[Tp^{Bu^t,Me}]Cu\}_2$, $[Tp^{Bu^t,Me}]CuCl$ and $Tl[Tp^{Bu^t,Me}]$, have been determined by X-ray diffraction. Comparison of these structures with those of $\{[Tp^{Bu^t}]Cu\}_2$, $[Tp^{Bu^t}]CuCl$ and $Tl[Tp^{Bu^t}]$ demonstrates the structural role that alkyl substitution at the remote 5-position of the pyrazolyl group may play in modifying the coordination environment about a metal centre.

In recent years, the tris(pyrazolyl)hydroborato ligand system $[Tp^{R,R'}]$†[1] has found widespread use in the study of copper chemistry. In this regard, some specific applications of tris(pyrazolyl)hydroborato ligation include: (*i*) the syntheses of the first stable copper carbonyl and nitrosyl derivatives, [Tp]Cu(CO)[2] and $[Tp^{Bu^t}]Cu(NO)$,[3,4] (*ii*) the syntheses of model complexes for biomimetic studies,[3,5–8] and (*iii*) the use of $[Tp^{Me_2}]Cu(\eta^2\text{-}C_2H_4)$ as a catalyst for carbene and nitrene transfer to form cyclopropanes, cyclopropenes and aziridines.[9] Here, we report the syntheses and structures of the copper complexes, $\{[Tp^{Bu^t,Me}]Cu\}_2$ and $[Tp^{Bu^t,Me}]CuCl$, and also the structure of the thallium derivative, $Tl[Tp^{Bu^t,Me}]$, in order to address the structural role that alkyl substitution at the remote 5-position of the pyrazolyl group may play in modifying the coordination environment about a metal centre.

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† The nomenclature adopted here for *tris*(pyrazolyl)hydroborato ligands is based on that described by Trofimenko.[1a] Thus, the *tris*(pyrazolyl)hydroborato ligands are represented by the abbreviation Tp, with the 3- and 5-alkyl substituents listed respectively as superscripts.

RESULTS AND DISCUSSION

The steric environment about a metal centre may be readily modified by appropriate substitution at the 3-position of the pyrazolyl group of the tris(pyrazolyl)hydroborato ligand, as illustrated by the increasing cone angles of the ligand across the series [Tp](184°) < $[Tp^{Me_2}]$(224°) < $[Tp^{Bu^t}]$(244°).[10] Indeed, the large bulk of the $[Tp^{Bu^t}]$ ligand is such that the formation of six-coordinate sandwich complexes $[Tp^{Bu^t}]_2M$ is effectively inhibited, whereas six-coordinate complexes of the type $[Tp]_2M$ are common.[1] Moreover, the steric demand of the $[Tp^{Bu^t}]$ ligand is presumably the principal factor that is responsible for the isolation of monomeric four-coordinate alkyl and hydride complexes of the type $[Tp^{Bu^t}]MX$, such as $[Tp^{Bu^t}]MR$ (M = Be,[11] Mg,[12] Zn[13] and Cd[14,15]) and $[Tp^{Bu^t}]MH$ (M = Be,[16] Zn[17] and Cd[18]). A further illustrative example of the structural changes that may be induced by alkyl substitution at the 3-position of the pyrazolyl group is provided by the series of copper(I) tris(pyrazolyl)hydroborato complexes $\{[Tp]Cu\}_2$,[6] $\{[Tp^{Me_2}]Cu\}_2$,[6] $\{[Tp^{Ph_2}]Cu\}_2$[19] and $\{[Tp^{Bu^t}]Cu\}_2$.[19] Although each complex is a dimer with bridging tris(pyrazolyl)hydroborato ligands, the structures differ in the manner in which the tris(pyrazolyl)hydroborato ligand bridges the two copper centres, as illustrated in Fig. 1. In $\{[Tp]Cu\}_2$ both tris(pyrazolyl)hydroborato ligands bridge the

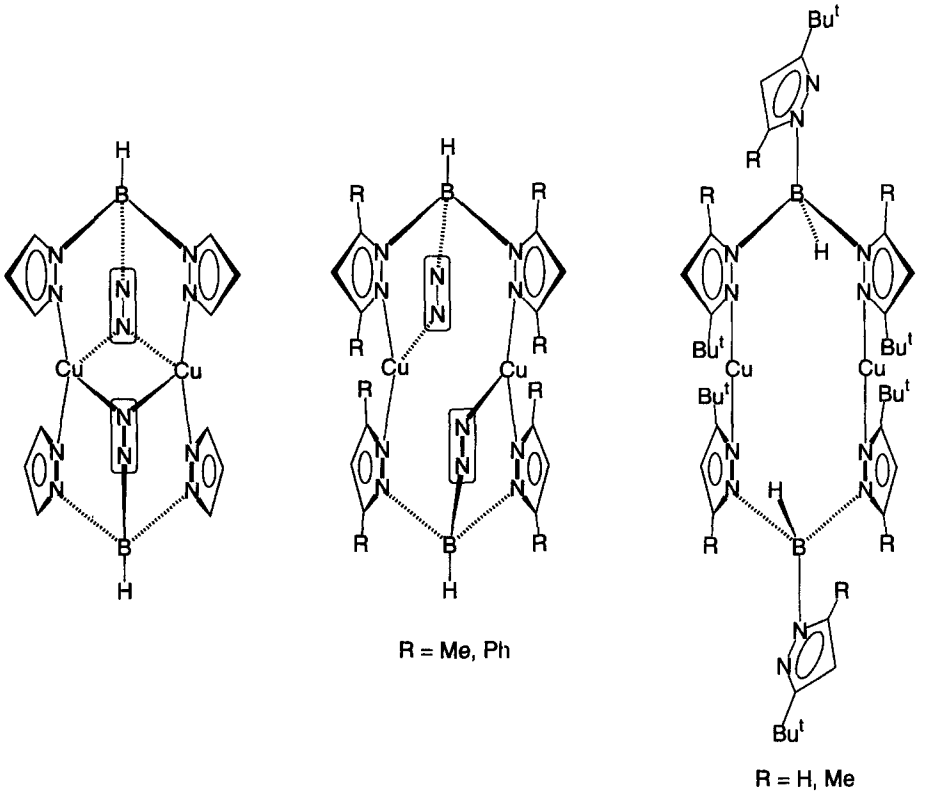

Fig. 1. Molecular structures of $\{[Tp^{RR'}]Cu\}_2$ dimers.

two copper centres in an approximately symmetric manner, so that each Cu^I centre is a four-coordinate distorted tetrahedron. In contrast, the tris(pyrazolyl)hydroborato ligands in $\{[Tp^{Me_2}]Cu\}_2$ and $\{[Tp^{Ph_2}]Cu\}_2$ bridge the two copper centres in an asymmetric manner, so that the coordination number of copper is reduced to three, with a distorted trigonal planar arrangement. This trend is continued for the complex $\{[Tp^{Bu^t}]Cu\}_2$, giving rise to a structure in which one of the pyrazolyl groups of each ligand is not coordinated, and each copper centre is two-coordinate and linear. The separation between the two copper centres in $\{[Tp^{Bu^t}]Cu\}_2$ [3.284(8) Å][3,19] is also substantially greater than the separations in $\{[Tp]Cu\}_2$ [2.660(1) Å],[6] $\{[Tp^{Me_2}]Cu\}_2$ [2.506(1) Å][6] and $\{[Tp^{Ph_2}]Cu\}_2$ [2.544(2) Å.][19]

In addition to alkyl substitution at the 3-position of the pyrazolyl group, which serves to modify the environment about the metal centre, alkyl substitution at the 5-position is expected to provide a protective environment for the B—H moiety. Other than increasing the stability of the ligand system by protecting the B—H group, alkyl substitution at the remote 5-position would not necessarily be anticipated to exert a strong structural change at the metal centre.‡ However, recent work by Reger has demonstrated that remote substitution can indeed influence the coordination environment about a metal centre. For example, substitution at boron results in the complexes $[pzTp]_2Pb$ and $[Tp]_2Pb$ exhibiting different structures. Thus, as a result of intraligand interactions, the potentially tridentate tetrakis(pyrazolyl)borato ligand [pzTp] acts only as a bidentate ligand in the lead complex $[pzTp]_2Pb$, whereas the tris(pyrazolyl)hydroborato ligands in the analogue $[Tp]_2Pb$ are tridentate.[20] Related effects have also been observed in other systems.[21] Here we address the structural role that alkyl substitution at the remote 5-position may play in modifying the coordination environment about a metal centre by comparing the structures of $\{[Tp^{Bu^t,Me}]Cu\}_2$, $[Tp^{Bu^t,Me}]CuCl$ and $Tl[Tp^{Bu^t,Me}]$ with those of $\{[Tp^{Bu^t}]Cu\}_2$, $[Tp^{Bu^t}]CuCl$ and $Tl[Tp^{Bu^t}]$.

‡ It has, however, been suggested that non-bonded repulsions between 5-alkyl groups should lead to a tighter ligand "bite" (see ref. 23).

Structure of $\{[Tp^{Bu^t,Me}]Cu\}_2$

$\{[Tp^{Bu^t,Me}]Cu\}_2$ was synthesized by the reaction of $Tl[Tp^{Bu^t,Me}]$ with excess CuCl, followed by treatment with NH_3:

$$Tl[Tp^{Bu^t,Me}] \xrightarrow[(ii)\ NH_3]{(i)\ CuCl} [Tp^{Bu^t,Me}]Cu\}_2. \qquad (1)$$

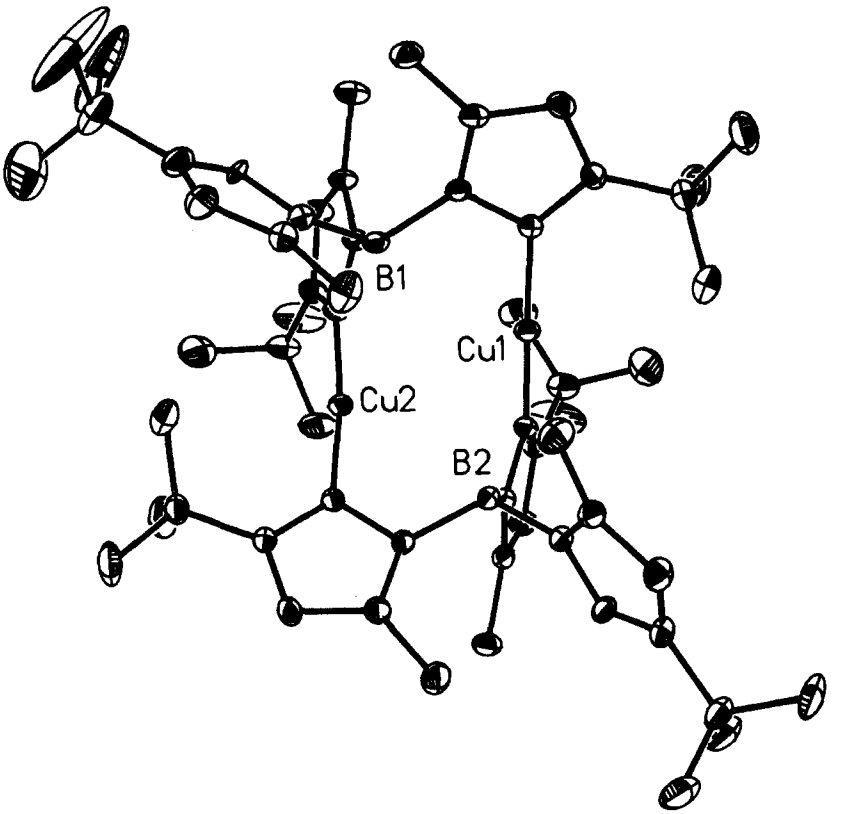

Fig. 2. View of $\{[Tp^{Bu^t,Me}]Cu\}_2$ illustrating the cyclic structure.

The molecular structure was determined by X-ray diffraction and two views of the dimeric molecule are presented in Figs 2 and 3. A view highlighting the 12-membered ring of the dimer is shown in Fig. 4. Selected bond lengths and angles are listed in Table 1. Comparison with the structure of

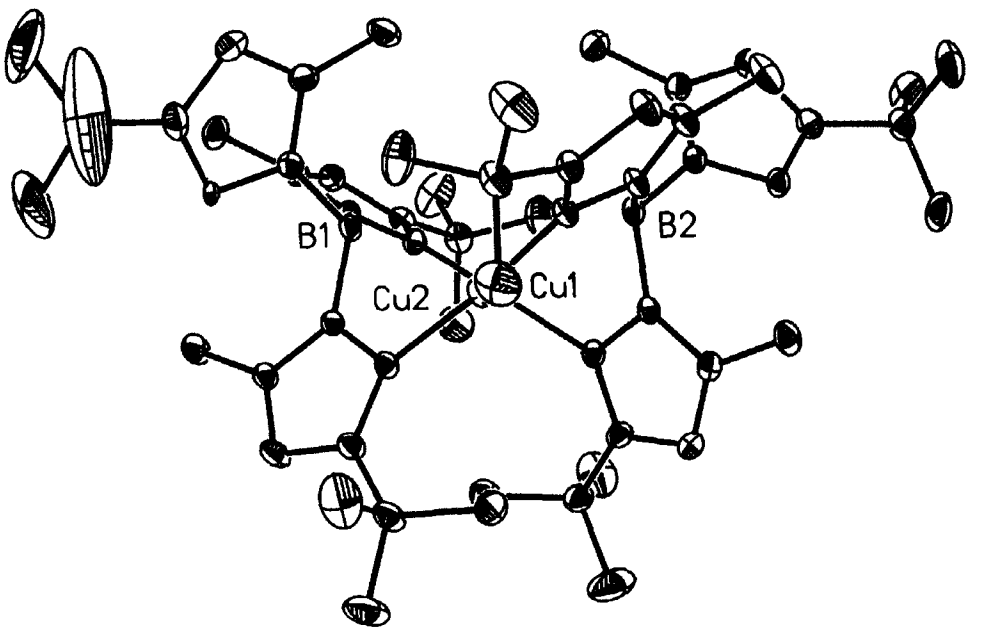

Fig. 3. View of $\{[Tp^{Bu^t,Me}]Cu\}_2$ along the Cu $\cdots$ Cu vector.

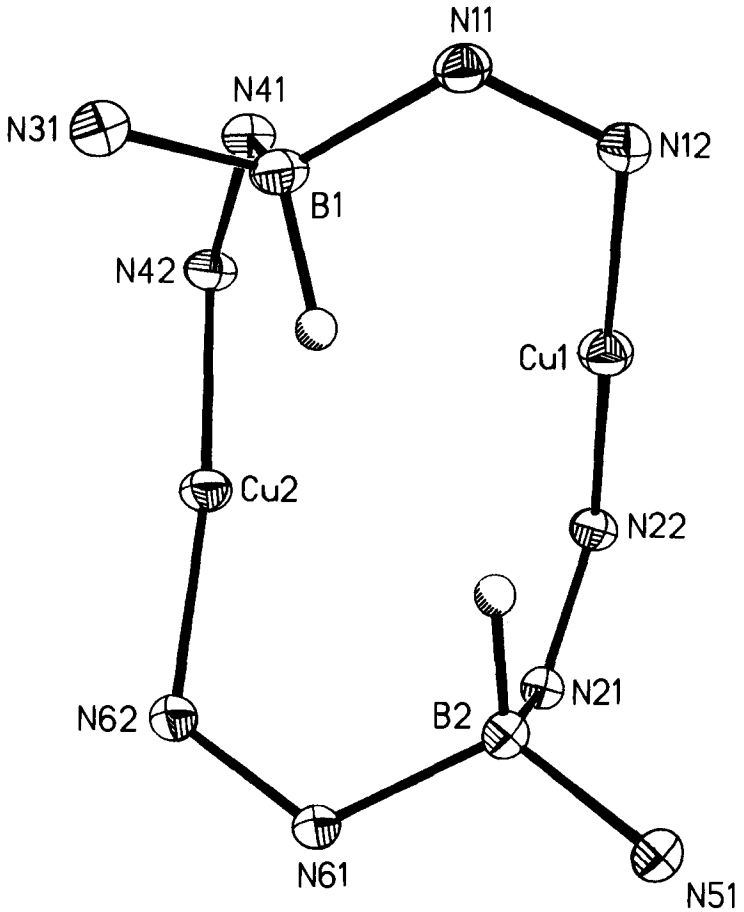

Fig. 4. View of $\{[Tp^{Bu^t,Me}]Cu\}_2$ highlighting the 12-membered ring.

$\{[Tp^{Bu^t}]Cu\}_2$[3,19] indicates that there is relatively little perturbation in the core geometry of the two structures. For example, the average Cu—N bond length [1.89(1) Å] in $\{[Tp^{Bu^t,Me}]Cu\}_2$ is very similar to that in $\{[Tp^{Bu^t}]Cu\}_2$ [1.87(1) Å]. Likewise, the Cu···Cu separations in $\{[Tp^{Bu^t,Me}]Cu\}_2$ and $\{[Tp^{Bu^t}]Cu\}_2$ are also very similar, 3.300(5) and 3.284(8) Å, respectively.

Although the incorporation of the 5-methyl substituent does not result in any significant change in the solid state structure of $\{[Tp^{Bu^t,Me}]Cu\}_2$ as far as the coordination environment about copper is concerned, it does influence the fluxional nature of the molecule in solution. Thus, Tolman has demonstrated that $\{[Tp^{Bu^t}]Cu\}_2$ is fluxional on the NMR time scale at room temperature, and a static structure indicating the presence of three equivalent sets of pyrazolyl groups (corresponding to the asymmetric dimeric structure adopted in the solid state) is only observed at −56°C. In contrast, the incorporation of the 5-methyl substituent results in the complex $\{[Tp^{Bu^t,Me}]Cu\}_2$ exhibiting a static ^1H NMR spectrum at room temperature, showing three sets of t-butyl-methylpyrazolyl groups (Fig. 5).

Moreover, there is no evidence for fluxionality of $\{[Tp^{Bu^t,Me}]Cu\}_2$ on the NMR time scale at temperatures up to 90°C! A possible origin for the

Table 1. Selected bond lengths (Å) and angles (°) for $\{[Tp^{Bu^t,Me}]Cu\}_2$

Cu(1)—N(12)	1.886(3)	Cu(1)—N(22)	1.881(3)
Cu(2)—N(42)	1.899(3)	Cu(2)—N(62)	1.885(3)
N(12)—Cu(1)—N(22)	178.2(2)	N(42)—Cu(2)—N(62)	173.0(2)

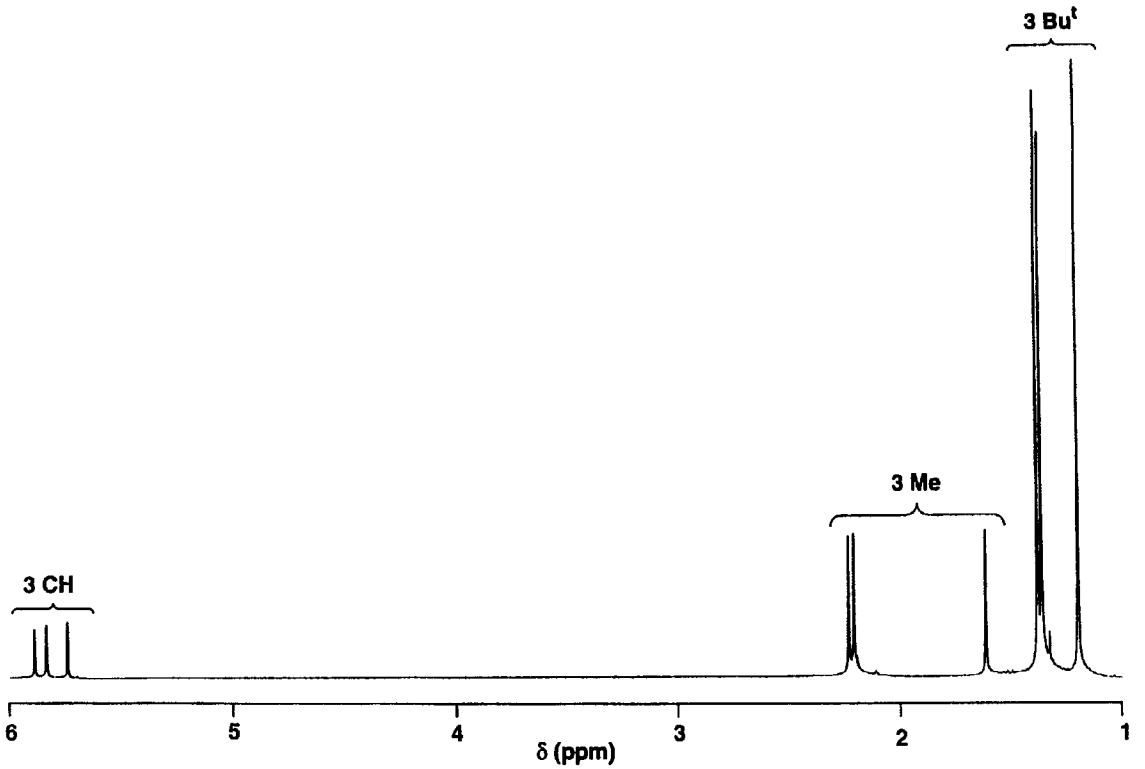

Fig. 5. 400 MHz ^{1}H NMR spectrum of $\{[Tp^{Bu^t,Me}]Cu\}_2$.

pronounced difference in fluxionality of the two derivatives $\{[Tp^{Bu^t}]Cu\}_2$ and $\{[Tp^{Bu^t,Me}]Cu\}_2$ may reside in the increased steric interactions between the 5-methyl substituents that would result in a transition state (or intermediate) in which all three pyrazolyl groups are coordinated to the dicopper moiety in a fashion analogous to the structure of $\{[Tp^{Me_2}]Cu\}_2$[6] (Fig. 1).

Structure of $[Tp^{Bu^t,Me}]CuCl$

Although the 5-methyl substituent does not significantly change the coordination environment about the copper centres in $\{[Tp^{Bu^t,Me}]Cu\}_2$, an interesting perturbation is observed at the two copper centres in $[Tp^{Bu^t}]CuCl$[22] and $[Tp^{Bu^t,Me}]CuCl$.

The complex $[Tp^{Bu^t,Me}]CuCl$ was synthesized by the reaction of $Tl[Tp^{Bu^t,Me}]$ with $CuCl_2$:

$$Tl[Tp^{Bu^t,Me}] + CuCl_2 \longrightarrow [Tp^{Bu^t,Me}]CuCl + TlCl. \quad (2)$$

The molecular structure was determined by X-ray diffraction, as shown in Fig. 6. Selected bond lengths and angles are listed in Table 2. For comparative purposes, two orthogonal views of the coordination geometry about copper in both complexes, $[Tp^{Bu^t,Me}]CuCl$ and $[Tp^{Bu^t}]CuCl$, are given in Fig. 7. As is apparent from Fig. 7, both complexes have coordination geometries that deviate from local C_{3v} symmetry, but do exhibit mirror symmetry which, in the case of $[Tp^{Bu^t,Me}]CuCl$, is crystallographically imposed. The most interesting feature of the structures of $[Tp^{Bu^t,Me}]CuCl$ and $[Tp^{Bu^t}]CuCl$ resides in the location of the chloride ligand. Even though the Cu—Cl bond lengths in $[Tp^{Bu^t,Me}]CuCl$ [2.168(1) Å] and $[Tp^{Bu^t}]CuCl$ [2.143(2) Å][22] are very similar,* the two complexes differ substantially in the position of the chloride ligands in their respective mirror planes. Thus, the Cl—Cu—N(32) bond angle of 113.2(1)° in $[Tp^{Bu^t}]CuCl$ expands considerably to 142.8(1)° for Cl—Cu—N(12) in $[Tp^{Bu^t,Me}]CuCl$. This change is accompanied by an increased separation of the pyrazolyl groups on either side of the mirror plane, from 92.0(1)° for N(12)—Cu—N(22) in $[Tp^{Bu^t}]CuCl$ to 102.9(1)° for N(22)—Cu—N(22′) in $[Tp^{Bu^t,Me}]CuCl$.

Structure of $Tl[Tp^{Bu^t,Me}]$

In addition to promoting a structural change at the copper centre of $[Tp^{Bu^t,Me}]CuCl$, the influence of

* For comparison, the Cu—Cl bond length in $[Tp^{Pr^i}]CuCl$ is also similar [2.125(6) Å]. See ref. 7(d).

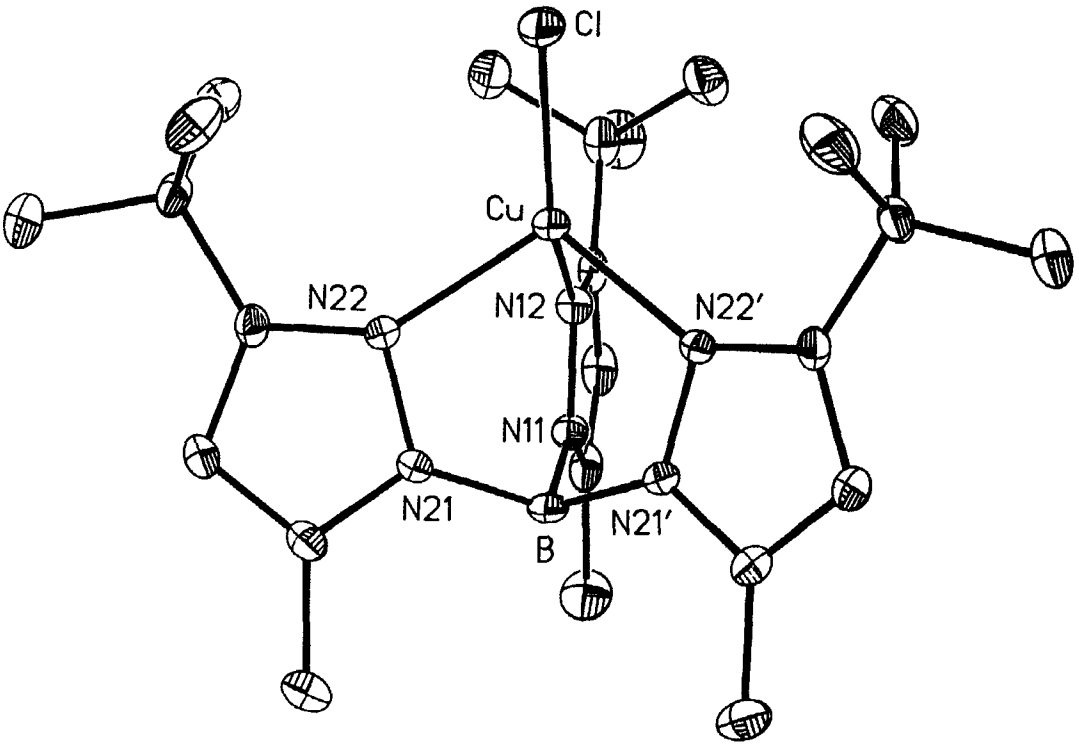

Fig. 6. Molecular structure of $[Tp^{Bu^t,Me}]CuCl$.

the 5-methyl substituent may also be noted, albeit to a lesser degree, on the environment about thallium in $Tl[Tp^{Bu^t,Me}]$.[23] The molecular structure of $Tl[Tp^{Bu^t,Me}]$ exhibits crystallographic three-fold symmetry in which each of the t-butyl substituents are oriented in such a manner as to maximize the distance between all the methyl groups and the thallium centres (see Figs 8 and 9). In contrast, $Tl[Tp^{Bu^t}]$[24] does not exhibit molecular three-fold symmetry and only possesses a mirror plane in which one of the t-butyl substituents is oriented such that the methyl group, which is co-planar with the pyrazolyl group, is directed towards thallium, so that there is a single close non-bonded interaction.

EXPERIMENTAL

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum and Schlenk techniques.[25] Solvents were purified and degassed by standard procedures. ^1H and ^{13}C NMR spectra were measured on Varian VXR 200, 300 and 400 spectrometers. IR spectra were recorded as KBr pellets on a Perkin–Elmer 1600 FTIR spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (CH_4) techniques.

Table 2. Selected bond lengths (Å) and angles (°) for $[Tp^{Bu^t,Me}]CuCl$

Cu—Cl	2.168(1)	Cu—N(12)	1.928(3)
Cu—N(22)	2.071(2)	Cu—N(22′)	2.071(2)
Cl—Cu—N(12)	142.8(1)	Cl—Cu—N(22)	111.6(1)
N(12)—Cu—N(22)	90.6(1)	Cl—Cu—N(22′)	111.6(1)
N(12)—Cu—N(22′)	90.6(1)	N(22)—Cu—N(22′)	102.9(1)

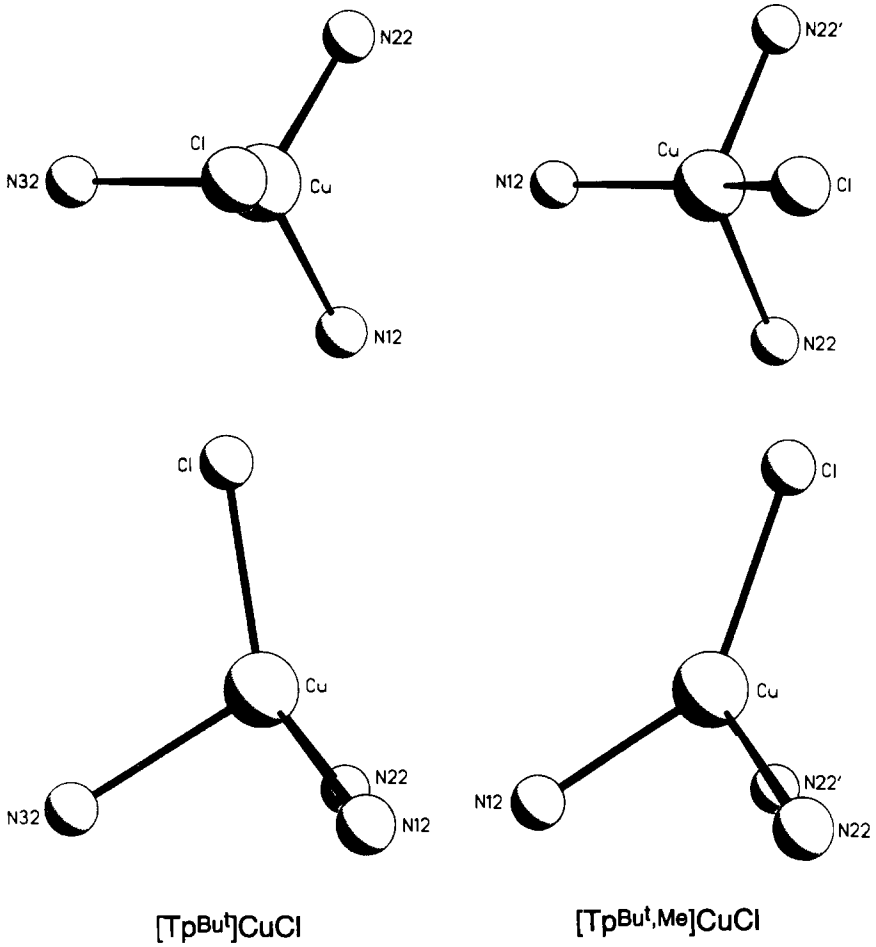

Fig. 7. Comparison of the molecular structures of [Tp$^{Bu^t}$]CuCl and [Tp$^{Bu^t,Me}$]CuCl.

Elemental analyses were measured using a Perkin–Elmer 2400 CHN Elemental Analyser. Tl[Tp$^{Bu^t,Me}$] was prepared by the literature method.[23]

Synthesis of {[Tp$^{Bu^t,Me}$]Cu}$_2$

A solution of Tl[Tp$^{Bu^t,Me}$] (0.80 g, 1.27 mmol) in THF (30 cm^3) was added dropwise to a suspension of excess CuCl (0.63 g, 6.38 mmol) in THF (10 cm^3), resulting in the immediate formation of a tan precipitate. The mixture was stirred for 30 min at room temperature and filtered. The solvent was removed from the dark yellow filtrate under reduced pressure giving a tan solid, which was dissolved in benzene (30 cm^3) and treated with NH_3 (1 atm). The addition of NH_3 resulted in the immediate deposition of a tan precipitate. The mixture was filtered after stirring for 2 h at room temperature. The solvent was removed from the colourless filtrate *in vacuo* and the product was recrystallized from pentane (20 cm^3) at −78°C. The crystals of {[Tp$^{Bu^t,Me}$]Cu}$_2$ were isolated by filtration and dried *in vacuo* (0.22 g, 20%). Found for {[Tp$^{Bu^t,Me}$]Cu}$_2$: C, 59.9; H, 8.3; N, 17.9. Calc.: C, 59.2; H, 8.3; N, 17.3%. ^{1}H NMR (C_6D_6): δ 1.20, 1.36, 1.38 (each 18H, s, 3 sets of pairs of Bu^t groups), 1.61, 2.20, 2.23 (each 6H, s, 3 sets of pairs of Me groups), 5.72, 5.81, 5.89 (each 2H, s, 3 sets of pairs of CH groups) (BH groups not observed). ^{13}C NMR (C_6D_6): δ 31.09, 31.13, 31.41 [each 6C, q, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$, 3 sets of pairs of C(CH_3)$_3$ groups], 10.61. 12.18, 12.36 (each 2C, $^1J_{C-H} = 126$, 3 sets of pairs of Me groups), 102.20 (2C, d, $^1J_{C-H} = 165$, pair of *C*H groups), 104.20 (2C, d, $^1J_{C-H} = 170$, pair of *C*H groups), 105.02 (2C, d, $^1J_{C-H} = 172$, pair of *C*H groups), 142.80, 146.42, 147.58 (each 2C, s, 3 sets of pairs of C groups), 161.47, 161.74, 163.30 (each 2C, s, 3 sets of pairs of C groups) [*C*(CH_3)$_3$ resonances were not located]. IR data: 2365 [ν(B—H)]. Mass spectrum: $m/z = 974$ (M^+).

Synthesis of [Tp$^{Bu^t,Me}$]CuCl

A solution of Tl[Tp$^{Bu^t,Me}$] (0.35 g, 0.56 mmol) in benzene (20 cm^3) was added dropwise to a yellow–

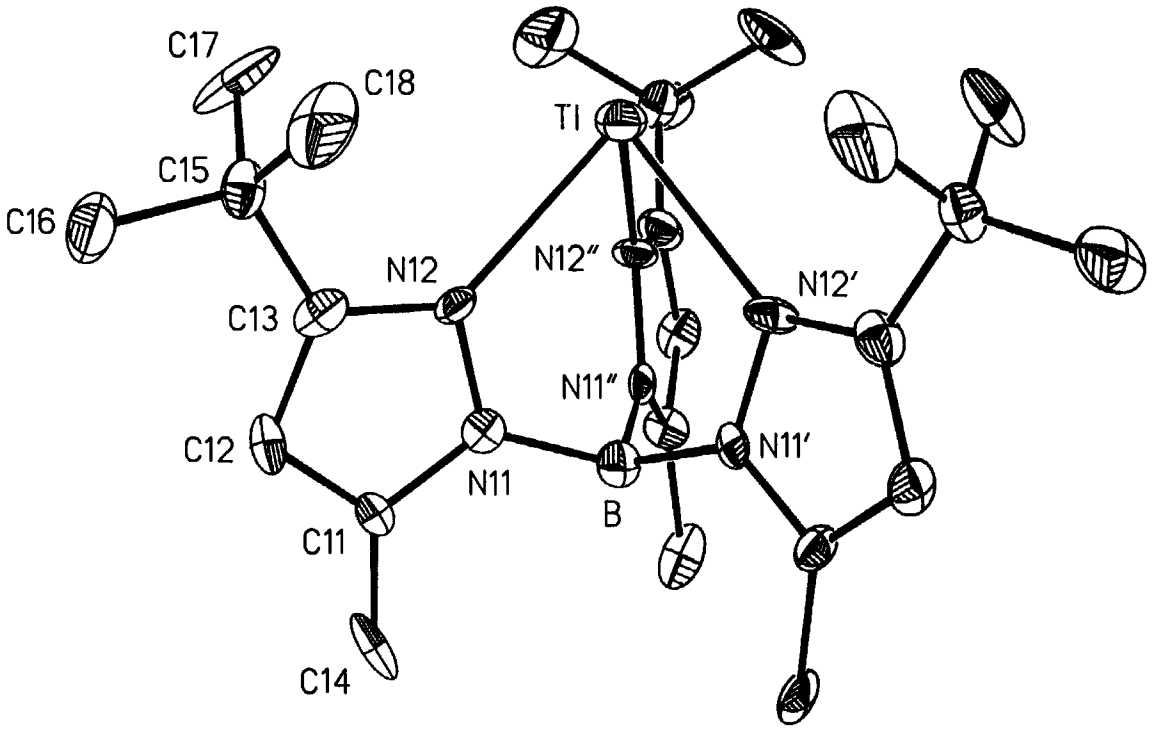

Fig. 8. Molecular structure of Tl[Tp$^{Bu^t,Me}$]. Selected bond lengths (Å) and angles (°): Tl—N(12) 2.50(2), N(12)—Tl—N(12′) = 77.9(7).

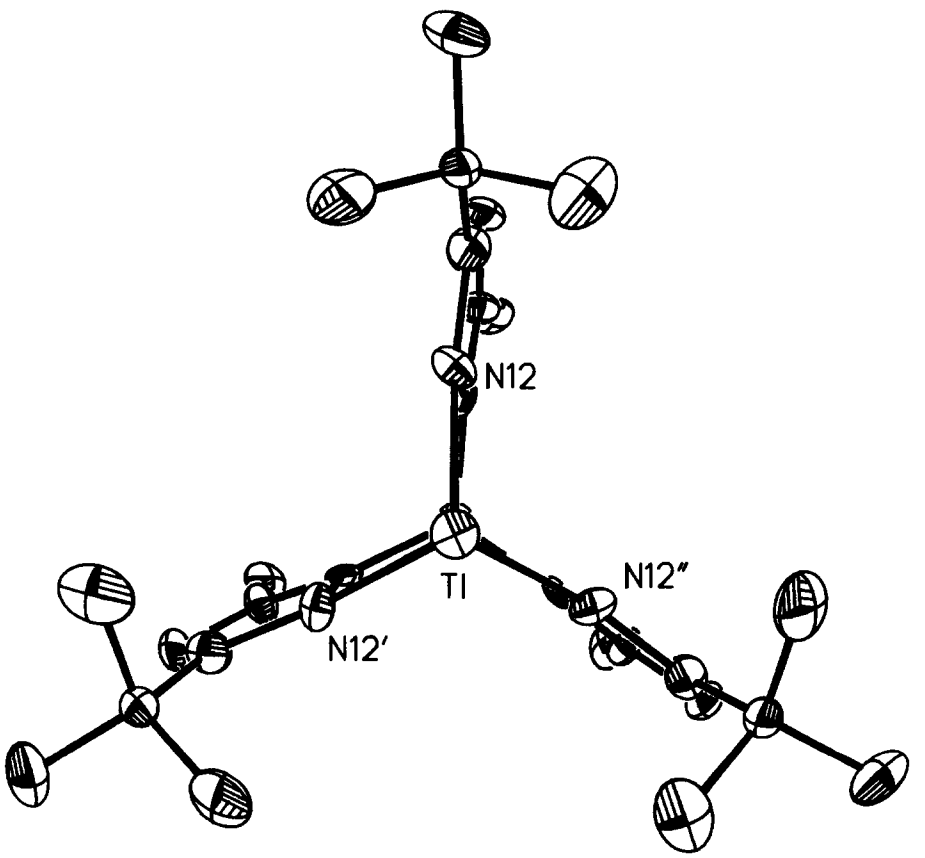

Fig. 9. View of Tl[Tp$^{Bu^t,Me}$] along the Tl···B vector.

brown suspension of $CuCl_2$ (0.11 g, 0.84 mmol) in benzene (10 cm^3), resulting in the immediate formation of a red–brown precipitate. The mixture was stirred for 30 min at room temperature and filtered. The solvent was removed from the dark red–brown filtrate giving an olive green microcrystalline solid. Recrystallization of the olive green microcrystalline solid from Et_2O (20 cm^3) at −78°C gave $[Tp^{Bu^t,Me}]CuCl$ as large red crystals (note: the colour of the product varies as a function of crystal size). The crystals of $[Tp^{Bu^t,Me}]CuCl$ were isolated by filtration and dried *in vacuo* (0.12 g, 42%). Found for $[Tp^{Bu^t,Me}]CuCl$: C, 55.2; H, 7.9; N, 16.6. Calc.: C, 55.2; H, 7.7; N, 16.1%. ^1H NMR (C_6D_6): δ 3.5 (broad, Me groups), 4.5 (broad, Bu^t groups) (CH and BH groups not observed). IR data: 2558 [ν(B—H)]. Mass spectrum m/z = 521 ($M^+ + 1$)

X-ray structure determination of $\{[Tp^{Bu^t,Me}]Cu\}_2$

Crystal data, data collection and refinement parameters for $\{[Tp^{Bu^t,Me}]Cu\}_2$ are summarized in Table 3. A single crystal of $\{[Tp^{Bu^t,Me}]Cu\}_2$ was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centred reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite monochromated Mo-K_α X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects (based on ψ-scans). The structure was solved using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[26] Systematic absences were consistent with the space groups $P1$ (No. 1) or $P\bar{1}$ (No. 2), but the structure was successfully solved with the choice $P\bar{1}$ (No. 2). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions [dC—H = 0.96 Å; U_{iso}(H) = 1.2U_{iso}(C)]. Block-diagonal least-squares refinement converged to R = 0.0399 (R_w = 0.0553).

X-ray structure determination of $[Tp^{Bu^t,Me}]CuCl$

Crystal data, data collection and refinement parameters for $[Tp^{Bu^t,Me}]CuCl$ are summarized in Table 3, and the general procedure is as described for $\{[Tp^{Bu^t,Me}]Cu\}_2$. Systematic absences were consistent with the space groups $P2_1$ (No. 4) or $P2_1/m$ (No. 11), but the structure was successfully solved with the choice $P2_1/m$ (No. 11). Most of the hydrogen

Table 3. Crystal and intensity collection data

	$\{[Tp^{Bu^t,Me}]Cu\}_2 \cdot 0.5(C_6H_6)$	$[Tp^{Bu^t,Me}]CuCl$	$Tl[Tp^{Bu^t,Me}]$
Formula	$C_{51}H_{83}N_{12}B_2Cu_2$	$C_{24}H_{40}N_6BCuCl$	$C_{24}H_{40}N_6BTl$
Formula weight	1013.0	522.4	627.8
Lattice	triclinic	monoclinic	cubic
Cell constants			
a (Å)	13.440(3)	9.103(2)	22.590(2)
b (Å)	14.040(3)	17.135(4)	22.590(2)
c (Å)	17.783(3)	9.702(1)	22.590(2)
α (°)	105.36(2)	90.0	90.0
β (°)	107.79(2)	112.17(1)	90.0
γ (°)	103.18(2)	90.0	90.0
V (Å^3)	2901(1)	1401(1)	11527(3)
Z	1	2	16
Radiation (λ, Å)	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)
Space group	$P\bar{1}$ (No. 2)	$P2_1/m$ (No. 11)	$I\bar{4}3d$ (No. 220)
ρ (calc.)/(g cm^{-3})	1.16	1.23	1.45
μ (Mo-K$_\alpha$)/(cm^{-1})	7.8	9.0	56.7
2θ range/(°)	3–45	3–55	3–55
No. of data [$F > 6\sigma(F)$]	5505	2120	477
No. of parameters	613	170	98
Goodness of fit	1.344	1.133	1.080
R	0.0399	0.0395	0.0422
R_w	0.0553	0.0489	0.0482

atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions [dC—H = 0.96 Å; U_{iso}(H) = 1.2U_{iso}(C)]. Block-diagonal least-squares refinement converged to $R = 0.0395$ ($R_w = 0.0489$).

X-ray structure determination of Tl[Tp$^{Bu^t,Me}$]

Crystal data, data collection and refinement parameters are summarized in Table 3, and the general procedure is as described for {[Tp$^{Bu^t,Me}$]Cu}$_2$. Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects (based on ψ-scans). Systematic absences were consistent uniquely with the space group $I\bar{4}\,3d$ (No. 220). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions [dC—H = 0.96 Å; U_{iso}(H) = 1.2U_{iso}(C)]. Block-diagonal least-squares refinement converged to $R = 0.0422$ ($R_w = 0.0482$). Inversion of configuration indicted the correct absolute structure.

CONCLUSION

In summary, alkyl substitution at the remote 5-position of the pyrazolyl group in [Tp$^{R,R'}$]MX complexes may play a role in modifying the coordination environment about a metal centre. A possible explanation for the observed structural changes is that the bite of the ligand may be modified by increased repulsion between the 5-methyl substituents and the B—H group.[23] The presence of the 5-methyl substituents may also be manifested by changes in fluxionality. Thus, {[Tp$^{Bu^t}$]Cu}$_2$ is fluxional on the NMR time scale at temperatures greater than −56°C, whereas {[Tp$^{Bu^t,Me}$]Cu}$_2$ still exhibits a static ^{1}H NMR spectrum at 90°C.

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REFERENCES

1. (a) S. Trofimenko, *Chem. Rev.* 1993, **93**, 943; (b) S. Trofimenko, *Prog. Inorg. Chem.* 1986, **34**, 115; (c) K. Niedenzu and S. Trofimenko, *Top. Curr. Chem.* 1986, **131**, 1.
2. (a) M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Dalton Trans.* 1973, 2433; (b) M. R. Churchill, B. G. DeBoer, F. J. Rotella, O. M. Abu Salah and M. I. Bruce, *Inorg. Chem.* 1975, **14**, 2051.
3. S. M. Carrier, C. E. Ruggiero and W. B. Tolman, *J. Am. Chem. Soc.* 1992, **114**, 4407.
4. C. E. Ruggiero, S. M. Carrier, W. E. Antholine, J. W. Whitaker, C. J. Cramer and W. B. Tolman, *J. Am. Chem. Soc.* 1993, **115**, 11285.
5. C. R. Ruggiero, S. M. Carrier and W. B. Tolman, *Angew. Chem., Int. Edn. Engl.* 1994, **33**, 895.
6. C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.* 1976, **98**, 711.
7. (a) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.* 1992, **114**, 1277; (b) N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Am. Chem. Soc.* 1991, **113**, 6554; (c) J. Perkinson, S. Brodie, K. Yoon, K. Mosny, P. J. Carroll, T. V. Morgan and S. J. N. Burgmayer, *Inorg. Chem.* 1991, **30**, 719; (d) N. Kitajima, K. Fujisawa and Y. Moro-oka, *J. Am. Chem. Soc.* 1990, **112**, 3210; (e) N. Kitajima, T. Koda, Y. Iwata and Y. Moro-oka, *J. Am. Chem. Soc.* 1990, **112**, 8833; (f) N. Kitajima, K. Fujisawa and Y. Moro-oka, *Inorg. Chem.* 1990, **29**, 357; (g) N. Kitajima, K. Fujisawa, C. Fujimoto and Y. Moro-oka, *Chem. Lett.* 1989, 421; (h) N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.* 1988, 151; (i) N. Kitajima, S. Hikichi, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.* 1993, **115**, 5496.
8. W. B. Tolman, *Inorg. Chem.* 1991, **30**, 4877.
9. P. J. Pérez, M. Brookhart and J. L. Templeton, *Organometallics* 1993, **12**, 261.
10. S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.* 1987, **26**, 1507.
11. R. Han and G. Parkin, *Inorg. Chem.* 1993, **32**, 4968.
12. (a) R. Han and G. Parkin, *Organometallics* 1991, **10**, 1010; (b) R. Han and G. Parkin, *J. Am. Chem. Soc.* 1992, **114**, 748.
13. I. B. Gorrell, A. Looney and G. Parkin, *J. Chem. Soc., Chem. Commun.* 1990, 220.
14. A. Looney, A. Saleh. Y. Zhang and G. Parkin, *Inorg. Chem.* 1994, **33**, 1158.
15. [Tp^{Me_2}]CdR complexes have also been prepared. See D. L. Reger and S. S. Mason, *Organometallics* 1993, **12**, 2600.
16. R. Han and G. Parkin, *Inorg. Chem.* 1992, **31**, 983.
17. R. Han, I. B. Gorrell, A. Looney and G. Parkin, *J. Chem. Soc., Chem Commun.* 1991, 717.
18. (a) D. L. Reger, S. S. Mason and A. L. Rheingold, *J. Am. Chem. Soc.* 1993, **115**, 10406; (b) D. L. Reger, S. S. Mason and A. L. Rheingold, *J. Am. Chem. Soc.* 1994, **116**, 2233.
19. S. M. Carrier, C. E. Ruggiero, R. P. Houser and W. B. Tolman, *Inorg. Chem.* 1993. **32**, 4889.
20. D. L. Reger, M. F. Huff, A. L. Rheingold and B. S. Haggerty, *J. Am. Chem. Soc.* 1992, **114**, 579.

21. (a) A. H. Cowley, R. L. Geersts, C. M. Nunn and C. J. Carrano, *J. Organomet. Chem.* 1988, **341**, C27; (b) D. L. Reger, S. J. Knox, M. F. Huff, A. L. Rheingold and B. S. Haggerty, *Inorg. Chem.* 1991, **30**, 1754; (c) Y. Sohrin, H. Kokusen, S. Kihara, M. Matsui, Y. Kushi and M. Shiro, *J. Am. Chem. Soc.* 1993, **115**, 4128.
22. R. Han, A. Looney, K. McNeill, G. Parkin, A. L. Rheingold and B. S. Haggerty, *J. Inorg. Biochem.* 1993, **49**, 105.
23. S. Trofimenko, J. C. Calabrese, J. K. Kochi, S. Wolowiec, F. B. Hulsbergen and J. Reedijk, *Inorg. Chem.* 1992, **31**, 3943.
24. A. H. Cowley, R. L. Geerts, C. M. Nunn and S. Trofimenko, *J. Organomet. Chem.* 1989, **365**, 19.
25. (a) J. P. McNally, V. S. Leong and N. J. Cooper, *ACS Symp. Ser.* 1987, **357**, 6; (b) B. J. Burger and J. E. Bercaw, *ACS Symp. Ser.* 1987, **357**, 79.
26. G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, Göttingen, Germany (1981).