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THE TRIS[3-(9-ANTHRYL)PYRAZOL-1-YL]HYDROBORATO LIGAND, $[Tp^{Ant}]$: COMPOSITIONAL DISORDER BETWEEN A VACANCY AND A CHAIN OF THREE ATOMS

RUNYU HAN and GERARD PARKIN*

Department of Chemistry, Columbia University, New York, NY 10027, U.S.A.

and

S. TROFIMENKO*

Du Pont Company, Experimental Station 302/216, Wilmington, DE 19880-0302, U.S.A.

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Abstract—A new tris(pyrazolyl)hydroborato ligand with anthryl substituents in the 3-position, tris[3-(9-anthryl)pyrazol-1-yl]hydroborate, $[Tp^{Ant}]$, has been synthesized by the reaction of KBH_4 with 3-(9-anthryl)pyrazole and characterized as the thallium derivative, $Tl[Tp^{Ant}]$. The thallium reagent was used to prepare the cobalt and molybdenum derivatives, $[Tp^{Ant}]CoNCS$ and $[Tp^{Ant}]Mo(CO)_2(\eta^3\text{-}CH_2C(Me)CH_2)$. The molecular structure of $[Tp^{Ant}]CoNCS$, contaminated with *ca* 6% $Tl[Tp^{Ant}]$, has been determined by X-ray diffraction, thereby providing an example of compositional disorder between a vacancy and a chain of three atoms.

Regiospecific space control around the metal centre in poly(pyrazolyl)borate complexes has involved placement of aliphatic, aromatic or heterocyclic substituents in the 3-position of the pyrazolyl ring.[1] For 3-aryl substituents, the variation of the interplanar angle between the pyrazolyl and 3-aryl groups may also serve to modify the steric environment about a metal centre. Indeed, recent studies have involved the synthesis of $[Tp^{Ms}]MX$ complexes (Ms = mesityl), in which the interaction between the *ortho* methyl groups of the mesityl substituents and the MX moiety promotes non-coplanarity of the two groups.[2] In this paper, we examine the use of a planar 9-anthryl substituent in the 3-position to provide a ligand system in which the aryl and pyrazolyl planes are strongly inhibited from adopting a coplanar orientation.

RESULTS AND DISCUSSION

A large series of tris(pyrazolyl)hydroborato ligands has been conveniently prepared by the reaction of KBH_4 with the appropriate pyrazole.[1] Since the steric environment created at a metal centre upon coordination of a tris(pyrazolyl)hydroborato ligand varies markedly with the nature of the substituent in the 3-position, we were interested in preparing a derivative which incorporated planar substituents that are restricted from coplanarity with the pyrazolyl groups. In this regard, we note that the simple phenyl substituent may lie almost coplanar with the pyrazolyl group, thereby allowing the formation of six-coordinate sandwich complexes such as $[Tp^{Ph}]_2M$ (M = Mn, Fe).[3] We considered that incorporation of the larger anthryl substituent would inhibit coplanarity with the pyrazolyl group due to steric interactions with the metal centre and its substituents, and would thereby stabilize half-sandwich complexes of the type $[Tp^{Ant}]MX$.

The requisite 3-(9-anthryl)pyrazole was prepared from 9-acetylanthracene, in a manner analogous to the synthesis of other 3-arylpyrazoles.[4,5] The tris[3-(9-anthryl)pyrazol-1-yl]hydroborato ligand $[Tp^{Ant}]$ was subsequently synthesized by the reaction of 3-

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*Authors to whom correspondence should be addressed.

(9-anthryl)pyrazole with KBH_4 in a melt, and was isolated as the thallium derivative $Tl[Tp^{Ant}]$ after addition of $TlNO_3$. The ^1H NMR spectrum of $Tl[Tp^{Ant}]$ is indicative of a dynamic structure in which the (1,8), (2,7), (3,6) and (4,5) sets of protons of each anthryl substituent are chemically equivalent.

The thallium complex $Tl[Tp^{Ant}]$ has been used as a reagent for the synthesis of some other derivatives. For example, the cobalt derivative $[Tp^{Ant}]CoNCS$ was prepared by the reaction of $Tl[Tp^{Ant}]$ with $Co(NCS)_2$ in toluene [eq. (1)] and the molybdenum complex $[Tp^{Ant}]Mo(CO)_2\{\eta^3\text{-}CH_2C(Me)CH_2\}$ was prepared by the reaction of $Tl[Tp^{Ant}]$ with $(MeCN)_2Mo(CO)_2(Cl)\{\eta^3\text{-}CH_2C(Me)CH_2\}$ [eq. (2)].

$$Co(NCS)_2 + Tl[Tp^{Ant}] \longrightarrow [Tp^{Ant}]CoNCS + TlNCS \quad (1)$$

$$(MeCN)_2Mo(CO)_2(Cl)\{\eta^3\text{-}CH_2C(Me)CH_2\} + Tl[Tp^{Ant}] \longrightarrow [Tp^{Ant}]Mo(CO)_2\{\eta^3\text{-}CH_2C(Me)CH_2\} + TlCl + 2\,MeCN. \quad (2)$$

The structure of the $[Tp^{Ant}]$ ligand has been established by single crystal X-ray diffraction studies on the cobalt complex $[Tp^{Ant}]CoNCS$. However, the cobalt complex was obtained as a green solid–solution with the thallium derivative, due to the ability of the two complexes to co-crystallize.* As a consequence of the co-crystallization, the crystallographic "site" occupied by the CoNCS moiety was necessarily disordered with a thallium atom. Refinement of site occupancies indicated that the composition of the crystal was approximately $[Tp^{Ant}](CoNCS)_{0.94}Tl_{0.06}$. Although co-crystallization is common,[6] $[Tp^{Ant}](CoNCS)_{0.94}Tl_{0.06}$ provides an interesting example in which a crystallographic site is disordered between a vacancy and a chain of three atoms. The ability of $[Tp^{Ant}]CoNCS$ and $[Tp^{Ant}]Tl$, which differ substantially in the number of atoms at the disordered site, to co-crystallize is presumably due to the fact that the disordered site is enclosed within the pocket that is provided by the tris(pyrazolyl)hydroborato ligand.

ORTEP drawings for the two molecules are shown in Figs 1–3, and selected bond lengths and angles are listed in Table 1. However, since it is well established that co-crystallization may result in the incorrect determination of bond lengths,[6] the values listed in Table 1 should be interpreted with care.

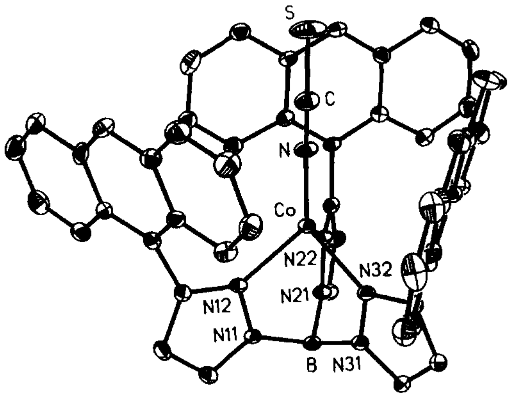

Fig. 1. Molecular structure of the $[Tp^{Ant}]CoNCS$ moiety in $[Tp^{Ant}](CoNCS)_{0.94}Tl_{0.06}$.

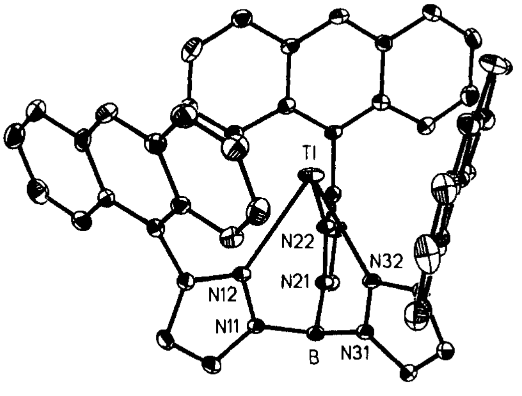

Fig. 2. Molecular structure of the $[Tp^{Ant}]Tl$ moiety in $[Tp^{Ant}](CoNCS)_{0.94}Tl_{0.06}$.

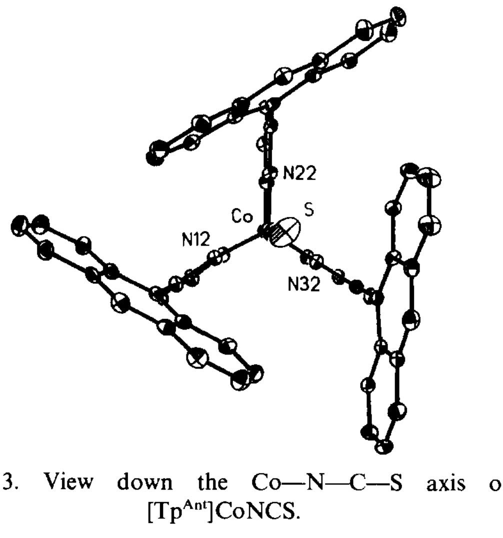

Fig. 3. View down the Co—N—C—S axis of $[Tp^{Ant}]CoNCS$.

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*Co-crystallization of $[Tp^{Ant}]CoNCS$ with $Tl[Tp^{Ant}]$ may be the reason for the green appearance of $[Tp^{Ant}]CoNCS$, compared with the blue colour of other four-coordinate $[Tp^{x}]CoNCS$ derivatives. See ref. 1.

Table 1. Selected bond lengths (Å) and angles (°) for $[\mathrm{Tp}^{\mathrm{Ant}}](\mathrm{CoNCS})_{0.94}\mathrm{Tl}_{0.06}$

$[\mathrm{Tp}^{\mathrm{Ant}}]$CoNCS			
Co—N	1.887(4)	Co—N(12)	2.033(3)
Co—N(22)	2.017(3)	Co—N(32)	2.039(3)
N—C	1.136(6)	C—S	1.618(4)
N—Co—N(12)	125.4(1)	N—Co—N(22)	125.8(1)
N—Co—N(32)	121.2(1)	N(12)—Co—N(22)	92.0(1)
N(12)—Co—N(32)	91.8(1)	N(22)—Co—N(32)	90.9(1)
Co—N—C	178.0(4)	N—C—S	179.8(3)
$\mathrm{Tl}[\mathrm{Tp}^{\mathrm{Ant}}]$			
Tl—N(12)	2.694(4)	Tl—N(22)	2.703(4)
Tl—N(32)	2.634(4)		
N(12)—Tl—N(22)	65.3(1)	N(12)—Tl—N(32)	66.6(1)
N(22)—Tl—N(32)	65.6(1)		

Nevertheless, the average Co—N [2.03(1) Å] and Tl—N [2.68(3) Å] bond lengths in $[\mathrm{Tp}^{\mathrm{Ant}}](\mathrm{CoNCS})_{0.94}\mathrm{Tl}_{0.06}$ are within reason since the values are similar to the respective values in the derivatives $[\mathrm{Tp}^{\mathrm{Bu^t}}]$CoNCS [2.02(1) Å]* and $\mathrm{Tl}[\mathrm{Tp}^{\mathrm{Bu^t}}]$ [2.59(1) Å].[7]† The axial view of $[\mathrm{Tp}^{\mathrm{Ant}}]$CoNCS, shown in Fig. 3, illustrates that the anthryl groups are prevented from lying coplanar with the pyrazolyl groups, and exhibit interplanar angles of *ca* 41°, 65° and 81°.‡ The $[\mathrm{Tp}^{\mathrm{Ant}}]$ ligand therefore offers potential in providing an environment that is less sterically demanding than that created by the $[\mathrm{Tp}^{\mathrm{Bu^t}}]$ ligand, but is sufficient to inhibit the formation of sandwich complexes of the type $[\mathrm{Tp}^{\mathrm{Ant}}]_2\mathrm{M}$ due to the non-coplanarity of the anthryl and pyrazolyl groups.

EXPERIMENTAL

All chemicals were reagent grade and used as received, with the exception of $(\mathrm{MeCN})_2\mathrm{Mo}(\mathrm{CO})_2\mathrm{Cl}\{\eta^3\text{-}\mathrm{CH_2C(Me)CH_2}\}$, which was prepared by the literature method.[9] Elemental analyses were carried out by Microanalysis, Inc. of Wilmington, Delaware. IR spectra were obtained as Nujol mulls with a Perkin–Elmer 1625 FTIR spectrophotometer using 16 scans. ^{1}H NMR spectra were obtained with a Nicolet NT360WB spectrometer using typical conditions of 16K data points, a sweep width of 3000–4000 Hz, 90° pulses and a recycle time of 4–5 s.

Preparation of 3-(9-*anthryl*)*pyrazole*

A solution of 9-acetylanthracene (104 g, 0.47 mol) in ethyl formate (300 cm^3, a large excess) was added in a single portion to a stirred slurry of anhydrous sodium methoxide (27 g, 0.5 mol) in toluene (800 cm^3). A clear solution was obtained, which became a slurry within a minute. The solid was isolated by filtration after 1 h at room temperature, dissolved in methanol (800 cm^3), and treated sequentially with hydrazine hydrate (40 cm^3) and then acetic acid (50 cm^3). Water (2 dm^3) was added, and the amber resin was extracted with dichloromethane (800 cm^3). The extracts were filtered through alumina and the volatile components were removed *in vacuo*. The residue was recrystallized from toluene giving 3-(9-anthryl)pyrazole in two crops of 37 g and 24 g (total yield 61 g, 53%). Found: C, 83.5; H, 4.9; N, 11.3; Calc. for $\mathrm{C_{17}H_{12}N_2}$: C, 83.6; H, 4.9; N, 11.5%. M.p. 188–190°C. ^{1}H NMR ($\mathrm{CDCl_3}$, see below diagram for assignments): δ 8.48 (s, 1H, $\mathrm{H_g}$), 8.00 (dd, $J = 8$ and 1 Hz, 2H, $\mathrm{H_f}$), 7.77 (dd, $J = 9$ and 1 Hz, 2H, $\mathrm{H_c}$), 7.64 (d, $J = 1$ Hz, 1H, $\mathrm{H_a}$), 7.40 (m, 4H, $\mathrm{H_{d,e}}$), 6.53 (d, $J = 1$ Hz, 1H, $\mathrm{H_b}$) ($\mathrm{H_h}$ was observed by integration to be a broad resonance in the range

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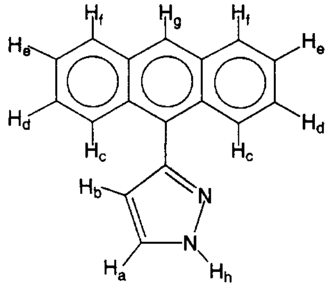
*Additional bond lengths in $[\mathrm{Tp}^{\mathrm{Bu^t}}]$CoNCS include: d(Co—NCS) = 1.911(3) Å, d(N—C) = 1.162(4) Å and d(C—S) = 1.605(4) Å.[4]

†The structures of $\mathrm{Tl}[\mathrm{Tp}^{p\text{-}\mathrm{Tol}}]$ [$d(\mathrm{Tl—N_{av}})$ = 2.58(1) Å][8a] and $\mathrm{Tl}[\mathrm{Tp}^{\mathrm{Ar_2}}]$ [Ar = p-$\mathrm{C_6H_4Bu^t}$; $d(\mathrm{Tl—N_{av}})$ = 2.61(5) Å][8b] have also been reported.

‡It is interesting to compare these interplanar angles with those of $\mathrm{Tl}[\mathrm{Tp}^{p\text{-}\mathrm{Tol}}]$, for which two independent molecules are present in the asymmetric unit, each residing on a crystallographic three-fold axis.[8a] Thus, whereas for one of the molecules of $\mathrm{Tl}[\mathrm{Tp}^{p\text{-}\mathrm{Tol}}]$ the p-tolyl group is almost coplanar with the pyrazolyl group with an interplanar angle of 1.8(9)°, the other molecule exhibits an interplanar angle of 29.6(7)°. It should, however, be recognized that comparison of the structures of $[\mathrm{Tp}^{\mathrm{Ant}}]$CoNCS and $\mathrm{Tl}[\mathrm{Tp}^{p\text{-}\mathrm{Tol}}]$ should not be over-interpreted in view of the presence of an axial substituent in $[\mathrm{Tp}^{\mathrm{Ant}}]$CoNCS.

9–10.5 ppm). The ^{13}C NMR spectrum of 3-(9-anthryl)pyrazole has been reported elsewhere.[10]



Preparation of K[Tp^{Ant}] *and* Tl[Tp^{Ant}]

A mixture of 3-(9-anthryl)pyrazole (85 g, 0.35 mol) and KBH_4 (2.7 g, 0.05 mol) was heated and melted with stirring until 3.75 dm^3 of hydrogen (three equivalents), as measured with a wet-test meter, was evolved. The cooled melt was dissolved in THF (400 cm^3) and added dropwise to boiling toluene (250 cm^3), so that the THF was removed by distillation. Upon cooling, 3-(9-anthryl)pyrazole (26.2 g; 31% of the original amount, 54% of the excess) was recovered as off-yellow crystals. The solvent was removed from the filtrate *in vacuo*, and the residue was stirred with a mixture of ether (500 cm^3) and dichloromethane (100 cm^3). The mixture was filtered, and the solid was washed with ether giving crude K[Tp^{Ant}] as a white solid (33 g, 85%). The thallium derivative was prepared by dissolving crude K[Tp^{Ant}] (8 g) in THF (300 cm^3) and stirring with an aqueous solution of $TlNO_3$ (0.3 M, 60 cm^3). Water (500 cm^3) was added and the product was extracted into dichloromethane and filtered through alumina. The solvent was removed *in vacuo*, giving crude Tl[Tp^{Ant}] as an off-yellow solid (7.8 g, *ca* 80%). The yellow colour was removed by washing with a small amount of acetone, and recrystallization from toluene afforded Tl[Tp^{Ant}] as a white solid.* Found: C, 65.0; H, 3.7; N, 8.9. Calc. for $C_{51}H_{34}BN_6Tl$: C, 64.8; H, 3.6; N, 8.9%. M.p. 299–303°C. IR (cm^{-1}): 2450 [ν(B—H)]. ^{1}H NMR ($CDCl_3$, see above diagram for assignments): δ 8.27 (s, 3H, H_g), 8.16 (d, $J = 1$ Hz, 3H, H_a), 7.78 (d, $J = 8$ Hz, 6H, H_f), 7.68 (broad d, $J = 8$ Hz, 6H, H_c), 7.09 (dt, $J_d = 1$, $J_t = 8$ Hz, 6H, H_e), 6.55 (m, 9H, H_b, H_d).

Preparation of [Tp^{Ant}]Mo(CO)$_2$(η^3-CH$_2$C(Me)CH$_2$)

A mixture of $(MeCN)_2Mo(CO)_2Cl(\eta^3\text{-}CH_2C(Me)CH_2)$ (0.7 g, 2 mmol) and Tl[Tp^{Ant}] (1.9 g, 2 mmol) in dichloromethane (40 cm^3) was stirred at room temperature for 30 min. The TlCl which was deposited was removed by filtration, and the filtrate was purified by chromatography on alumina. The solvent was removed from the filtrate *in vacuo*, and the residue was recrystallized from toluene giving pale yellow crystals of [Tp^{Ant}]Mo(CO)$_2$(η^3-CH$_2$C(Me)CH$_2$) (1.6 g, 84%). Found: C, 72.4; H, 4.3; N, 9.2. Calc. for $C_{57}H_{41}BN_6O_2Mo$: C, 72.2; H, 4.3; N, 8.9%. M.p. 248–251°C. IR (cm^{-1}): 2490 [ν(B—H)], 1944 [ν(C=O)], 1864 [ν(C=O)]. ^{1}H NMR ($CDCl_3$): δ 8.56 (s, 1H), 8.44 (s, 2H), 8.13 (d, $J = 1$ Hz, 2H), 7.9–8.1 (m, 6H), 7.74 (d, $J = 8$ Hz, 4H), 7.3–7.5 (m, 11H), 7.04 (t, $J = 8$ Hz, 2H), 6.60 (d, $J = 1$ Hz, 1H), 6.47 (d, $J = 1$ Hz, 2H), 1.92 (s, 2H), 1.15 (s, 3H), −0.96 (s, 2H).

Preparation of [Tp^{Ant}]CoNCS

A mixture of Tl[Tp^{Ant}] (4.7 g, 5.0 mmol) and anhydrous $Co(NCS)_2$ (5 g, large excess) was stirred and refluxed overnight in toluene (250 cm^3). The mixture was filtered, and upon cooling the filtrate deposited a green solid which was recrystallized from toluene (2.6 g, 67%). IR (cm^{-1}): 2510 [ν(B—H)], 2080 [ν(NCS)]. Found: C, 72.2; H, 3.9; N, 11.1. Calc. for $C_{52}H_{34}BN_7CoS$: C, 72.7; H, 4.0; N, 11.4. Calc. for [Tp^{Ant}](CoNCS)$_{0.94}$Tl$_{0.06}$: C, 72.3; H, 4.0; N, 11.3%.

X-ray structure determination of [Tp^{Ant}](CoNCS)$_{0.94}$Tl$_{0.06}$

Crystal data, data collection and refinement parameters are summarized in Table 2. A single crystal of [Tp^{Ant}](CoNCS)$_{0.94}$Tl$_{0.06}$ grown from a solution in CH_2Cl_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 ($\lambda = 0.71073$ Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects. The structure was solved using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[11] Systematic absences were consistent uniquely with the space

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*From this filtrate, a small amount of solid was obtained which appeared, on the basis of ^{1}H NMR spectroscopy, to be a mixture of Tl[Tp^{Ant}] and its isomer, Tl[HB(3-anthrylpz)$_2$(5-anthrylpz)].

Table 2. Crystal and intensity collection data for $[\mathrm{Tp}^{\mathrm{Ant}}](\mathrm{CoNCS})_{0.94}\mathrm{Tl}_{0.06}$

Formula	$C_{51.94}H_{34}N_{6.94}BS_{0.94}Co_{0.94}Tl_{0.06}$
Crystal colour	Green
Lattice	Orthorhombic
Cell constants	$a = 13.994(2)$ Å $b = 15.531(3)$ Å $c = 18.967(4)$ Å $V = 4122(2)$ Å^3
Z	4
$F(000)$	1778
λ	Mo-K_α (0.71073 Å, graphite monochromator)
Space group	$P2_12_12_1$ (No. 19)
2θ range	3–52°
Number of reflections with $F > 6\sigma(F)$	4372
Number of parameters varied	574
Goodness of fit	1.135
R	0.0378
R_w	0.0489

group $P2_12_12_1$ (No. 19). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were refined in calculated positions [d(C—H) = 0.96 Å; $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{iso}}(\mathrm{C})$]. Block-diagonal least-squares refinement converged to $R = 0.0378$ ($R_w = 0.0489$). Selected bond distances and angles are listed in Table 1.

CONCLUSION

In summary, the new tris(pyrazolyl)hydroborato ligand $[\mathrm{Tp}^{\mathrm{Ant}}]$, with 9-anthryl substituents in the 3-positions, has been prepared by the reaction of KBH_4 with 3-(9-anthryl)pyrazole. X-ray diffraction studies on $[\mathrm{Tp}^{\mathrm{Ant}}](\mathrm{CoNCS})_{0.94}\mathrm{Tl}_{0.06}$ confirm that the anthryl and pyrazolyl groups exhibit a high degree of non-coplanarity, and that the pocket that is created by such a ligand is capable of stabilizing crystallographic disorder between a vacancy and a chain of three atoms.

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REFERENCES

1. S. Trofimenko, *Chem. Rev.* 1993, **93**, 943.
2. A. L. Rheingold, C. B. White and S. Trofimenko, *Inorg. Chem.* 1993, **32**, 3471.
3. D. M. Eichhorn and W. H. Armstrong, *Inorg. Chem.* 1990, **29**, 3607.
4. S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.* 1987, **26**, 1507.
5. S. Trofimenko, J. C. Calabrese, J. K. Kochi, S. Wolowiec, F. B. Hulsbergen and J. Reedijk, *Inorg. Chem.* 1992, **31**, 3943.
6. (a) G. Parkin, *Accts Chem. Res.* 1992, **25**, 455; (b) G. Parkin, *Chem. Rev.* 1993, **93**, 887.
7. A. H. Cowley, R. L. Geerts, C. M. Nunn and S. Trofimenko, *J. Organomet. Chem.* 1989, **365**, 19.
8. (a) G. Ferguson, M. C. Jennings, F. J. Lalor and C. Shanahan, *Acta. Cryst.* 1991, C**47**, 2079; (b) E. Libertini, K. Yoon and G. Parkin, *Polyhedron* 1993, **12**, 2539.
9. R. G. Hayter, *J. Organomet. Chem.* 1968, **13**, P1.
10. C. Lopez, R. M. Claramunt, S. Trofimenko and J. Elguero, *Can. J. Chem.* 1993, **71**, 678.
11. G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, Göttingen, Germany (1981).