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Several four-co-ordinate nickel and palladium aryl and aroyl complexes containing the bulky bis- or tris-(3-tert-butylpyrazolyl)borate ligands have been prepared, in which the poly(pyrazolyl)borate group adopts monohapto co-ordination, both in solution and in the solid state.

The poly(pyrazolyl)borate anions have emerged as a prominent class of ligands in co-ordination chemistry.^{1,2} Of these ligands, the tris(pyrazolyl)borates, $HB(pz)_3^-$ (pz = unsubstituted or substituted pyrazolyl fragment), are of particular significance since they are usually considered as sterically and electronically similar to the ubiquitous cyclopentadienyl anions, cp (cp = unsubstituted or substituted cyclopentadienyl group). Both types of ligands may undergo hapticity changes. Several coordination modes have been ascertained ³ for cp of which η^1 , η^3 and η^5 are of the greatest interest due to their possible interconversion. In the case of $HB(pz)_3^-$ hapticity changes seem to be, in some instances, of crucial importance. For example, the thermodynamic preference of vinyl-hydride isomer over the corresponding olefinic formulation in an iridium system has been ascribed⁴ to a change in the co-ordination mode of the $HB(pz_2)_3^-$ ligand from η^2 to η^3 . However, and despite the plethora of compounds of these ligands, only the η^2 and η^3 coordination models^{1,5} have been unequivocally established although complexes containing η^2 -tris- or -bis-(pyrazolyl)borate ligands in which there is a strong M-N bond and a weaker M ... N interaction are known.⁶ Here we describe the use of the bulky tris(3-tert-butylpyrazolyl)borate ligand to prepare a series of four-co-ordinate organometallic complexes of nickel in which the nature of the metal centre and of the coligands provides a sterically demanding environment that forces η^1 -co-ordination of the borate group.

The reaction of the arylnickel derivatives trans-[Ni(C₆H₄Xp)Br(PMe₃)₂] (X = H, Me or OMe)⁷ with the thallium salt ^{2a} of the HB(3-Bu'C₃H₂N₂)₃ anion proceeds smoothly at low temperatures † as depicted in equation (1). Compounds 1a-1c can be isolated as yellow-to-orange crystalline materials. No reaction with carbon monoxide [20 °C, 1 atm (101 325 Pa)] is

P(4)C(18) C(2 C(19) C(51) C(41) C(17 C(6 C(7) ťÐ Fig. 1 An ORTEP diagram for compound 1b and atom labelling

scheme. Selected bond distances (Å) and angles (°): Ni-C(1) 1.891(8), Ni-N(11) 1.947(6), Ni-P(4) 2.207(2), Ni-P(5) 2.214(2); C(1)-Ni-P(4) 86.8, C(1)-Ni-P(5) 86.1, N(11)-Ni-P(4) 93.6, N(11)-Ni-P(5) 93.5; average deviation of 0.02 Å from the mean co-ordination plane

trans-[Ni(C₆H₄X-p)Br(PMe₃)₂] $\xrightarrow{\text{TI[HB(3-Bu'C_3H_2N_2)_3], -20 °C}}$

 $trans-[Ni(C_6H_4X-p){HB(3-Bu'C_3H_2N_2)_3}(PMe_3)_2]$ (1)

(X = H 1a, Me 1b, OMe 1c)

observed over a period of 5-10 min, but longer exposures to CO effect reduction to [Ni(CO)₂(PMe₃)₂]. However, the aroyls **2a-2c** can be obtained in good yields starting from *trans*- $[Ni{C(O)C_6H_4X-p}Br(PMe_3)_2]^7$ [equation (2)]. Compounds 2a-2c slowly lose CO in solution but are sufficiently stable for full spectroscopic characterization.

NMR studies of complexes 1 and 2 show the presence of two



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[†] Typical preparation: to a cold (-20 °C) solution of [NiPh(Br)- $(PMe_3)_2$ ⁷ (0.19 g, ca. 0.5 mmol) in tetrahydrofuran (thf) (20 cm³) was added Tl[HB(3-Bu'C₃H₂N₂)₃] (0.3 g, ca. 0.5 mmol) dissolved in thf (10 cm³). Formation of a whitish precipitate (TlBr) was immediately observed. The suspension was allowed to warm to room temperature and then stirred for 3 h, after which the solvent was removed in vacuo. The residue was extracted with light petroleum (b.p. 40-60 °C) (20 cm³), the suspension centrifuged and the resulting solution concentrated under vacuum and cooled at -20 °C overnight. Yellow needles (0.21 g, 63%) of the desired product, 1a, were collected. The aroyls 2a-2c can be prepared similarly but work-up of the corresponding reactions should be effected at 0 °C. Satisfactory analytical data for all new compounds have been obtained.

trans-[Ni{C(O)C₆H₄X-p}Br(PMe₃)₂] $\xrightarrow{\text{TI[HB(3-Bu'C_3H_2N_2)_3], -20 °C}}_{\text{TID}}$ $trans-[Ni{C(O)C_6H_4X-p}{HB(3-Bu'C_3H_2N_2)_3}(PMe_3)_2]$ (2)

(X = H 2a, Me 2b, OMe 2c)

mutually trans PMe₃ groups and also demonstrate the existence of a high barrier to rotation of the aryl ring,⁸ in particular for 1a-1c. In addition, two distinct sets of pyrazolyl resonances (for both the CH and CBu^t groups) are observed in the ¹H and ¹³C-¹H} NMR spectra, indicating the presence of two types of pyrazolyl rings in a 1:2 ratio. This fact, coupled with the strong tendency of Ni^{II} to form four-co-ordinate square-planar structures in complexes of this type, suggests that the borate ligand in 1 and 2 is behaving as a monohapto, one-electron donor, and this has been confirmed by an X-ray study* carried out with compound 1b.

Fig. 1 shows an ORTEP¹² perspective view of the molecules of compound 1b which contain a slightly distorted squareplanar nickel centre. As expected for compounds of this type, the phenyl ring is perpendicular to the co-ordination plane, while the two phosphine ligands occupy mutually trans positions, with a P(4)-Ni-P(5) angle of 172.7°. The borate moiety is η^1 co-ordinated to nickel [Ni-N(11) 1.947(6) Å], with two of the pyrazolyl groups oriented away from the metal centre.

The reaction of the same arylnickel complexes with the bis(3tert-butylpyrazolyl)borate ligand, yields analogous complexes of formulation $[Ni(C_6H_4X-p){H_2B(3-Bu'C_3H_2N_2)_2}(PMe_3)_2]$ in which only one pyrazolyl ring is bonded to the metal. Similarly, the interaction of [PdPh(Br)(PMe₃)₂]¹³ with Tl[HB- $(3-Bu'C_2H_2N_2)_3$ gives colourless crystals of [PdPh{HB(3- $Bu^{t}C_{3}H_{2}N_{2}$ (PMe₃)₂], also containing a monohapto borate ligand.

The present observation of η^1 co-ordination for the bis- and tris-(pyrazolyl)borate ligands in these metal complexes allows an extension of the hapticity numbers encountered for poly-(pyrazolyl)borate groups from the well established η^3 and η^2 to the newly discovered η^1 and demonstrates that this kind of coordination can be adopted under appropriate circumstances. This may have important implications in our understanding of the solution behaviour of these compounds and hence in the design of catalytic systems based on complexes of these ligands. In the present case, adoption of the η^1 co-ordination mode seems to be largely steric in origin. It should be noted that the reaction of trans-[NiPh(Br)(PMe₃)₂] with Na(cp), K[HB(pz)₃] or K[HB(3,5-Me₂C₃HN₂)₃] takes place with loss of one of

* Crystal data. $C_{34}H_{59}BN_6NiP_2$, M = 683.34, monoclinic, space group $P2_1/n$, a = 12.626(4), b = 24.298(3), c = 13.413(3) Å, $\beta = 102.43(3)^\circ$ U = 4018(2) Å³, Z = 4, $D_c = 1.13$ g cm⁻³, F(000) = 1472, λ (Mo- $K\alpha$ = 0.710 96 Å (graphite monochromator), μ = 5.90 cm⁻¹, 295 K, Kappa diffractometer, ω -2 θ scan technique. The cell dimensions were refined by least squares, fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects; 7360 reflections measured, 3169 $[I \ge 2\sigma(I)]$ used in the refinement. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and P were taken from ref. 9. The structure was solved by Patterson and Fourier methods. An empirical absorption correction¹⁰ was applied at the end of the isotropic refinement. From the values of the thermal parameters there exists some non-resolvable disorder in the C atoms of the Bu' groups owing to their thermal motions. No trend in ΔF versus F or $(\sin \theta)/\lambda$ was observed. Final mixed refinement was undertaken with fixed isotropic factors and coordinates for H atoms. Final R 0.062 and R' 0.066 (unit weights). A final difference synthesis had no electron density greater than 0.40 e Å⁻³. Most of the calculations were carried out with the X-RAY 80 system.¹¹ Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx-xxv.

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the PMe₃ ligands and formation of phenyl complexes of composition ¹⁴ [NiPhL(PMe₃)] [L = cp, HB(pz)₃ or HB(3,5- $Me_2C_3HN_2)_3].$

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References

- 1 S. Trofimenko, Prog. Inorg. Chem., 1986, 34, 115; A. Shaver, in Comprehensive Coordination Chemistry, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 245
- 2 (a) S. Trofimenko, J. C. Calabrese and J. S. Thompson, Inorg. Chem., 1987, 26, 1507; (b) C. E. Davies, I. M. Gardiner, J. C. Green, M. L. H. Green and N. J. Hazel, J. Chem. Soc., Dalton Trans., 1985, 669; (c) M. D. Curtis, K.-B. Shiu and W. M. Butler, J. Am. Chem. Soc., 1986, 108, 1550.
- 3 J. M. O'Connor and C. P. Casey, Chem. Rev., 1987, 87, 307; L. M. Hansen and D. S. Marynick, Organometallics, 1989, 8, 2173; M. S. Lawless and D. S. Marynick, Organometallics, 1991, 10, 543; W. D. Jones, V. L. Kuykendall and A. D. Selmeczy, Organometallics, 1991, 10, 1577; G. K. Anderson, R. J. Cross, S. Fallis and M. Rocamora, Organometallics, 1987, 6, 1440; A. A. Danopoulos, G. Wilkinson and D. J. Williams, J. Chem. Soc., Chem. Commun., 1991, 181; P. E. Bloyce, A. J. Rest and I. Whitwell, J. Chem. Soc., Dalton Trans., 1990, 813.
- 4 C. K. Ghosh, J. K. Hoyano, R. Krentz and W. A. G. Graham, J. Am. Chem. Soc., 1989, 111, 5480.
- 5 R. Alsfasser, S. Trofimenko, A. Looney, G. Parkin and H. Vahrenkamp, *Inorg. Chem.*, 1991, **30**, 4098; R. Han and G. Parkin, Organometallics, 1991, 10, 1010; R. Han, I. B. Gorrell, A. G. Looney and G. Parkin, J. Chem. Soc., Chem. Commun., 1991, 717; R. A. Kresinski, L. Isam, T. A. Hamor, C. J. Jones and J. A. McCleverty, J. Chem. Soc., Dalton Trans., 1991, 1835; S. G. Feng, L. Luan, P. White, M. S. Brookhart, J. L. Templeton and C. G. Young, Inorg. Chem., 1991, 30, 2582; J. C. Calabrese, P. J. Domaille, S. Trofimenko and G. J. Long, *Inorg. Chem.*, 1991, **30**, 2795; W. Jones and E. T. Hessell, *Inorg. Chem.*, 1991, **30**, 778; I. B. Gorrell and G. Parkin, *Inorg. Chem.*, 1990, **29**, 2452; L. Luan, P. S. White, M. Brookhart and J. L. Templeton, J. Am. Chem. Soc., 1990, 112, 8190; S. G. Feng, P. S. White and J. L. Templeton, J. Am. Chem. Soc., 1990, 112, 8192; M. Cano, J. V. Heras, S. Trofimenko, A. Monge, E. Gutiérrez, C. J. Jones and J. A. McCleverty, J. Chem. Soc., Dalton Trans., 1990, 3577; J. C. Calabrese, P. J. Domaille, J. S. Thompson and S. Trofimenko, Inorg. Chem., 1990, 29, 4429; R. Han and G. Parkin, J. Am. Chem. Soc., 1990, 112, 3662; E. Kime-Hunt, K. Spartalian, M. DeRusha, C. M.
- Nunn and C. J. Carrano, *Inorg. Chem.*, 1989, **28**, 4392. 6 M. I. Bruce, J. D. Walsh, B. W. Skelton and A. H. White, *J. Chem.* Soc., Dalton Trans., 1981, 956; A. J. Canty, B. W. Skelton and A. H. White, Aust. J. Chem., 1987, 40, 1609.
- 7 E. Carmona, M. Paneque and M. L. Poveda, Polyhedron, 1989, 8, 285.
- 8 J. S. Merola, Organometallics, 1989, 8, 2975; C. K. Ghosh and W. A. G. Graham, J. Am. Chem. Soc., 1987, 109, 4726; E. J. Probitts, D. R. Saunders, M. H. Stone and R. L. Mawby, J. Chem. Soc., Dalton Trans., 1986, 1167; M. Oki, Methods in Stereochemical Analysis, ed., A. P. Marchand, VCH, Deerfield Beach, FL, 1985, vol. 4, ch. 2
- 9 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4, pp. 72–98.
- 10 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 1983, **39**, 158. 11 J. M. Stewart, X-RAY 80 System, Computer Science Center, University of Maryland, College Park, MD, 1985. 12 C. K. Johnson, ORTEP II, Oak Ridge National Laboratory, TN,
- 1971.
- 13 L. Huang, F. Ozawa and A. Yamamoto, Organometallics, 1991, 9, 2611.
- 14 S. A. Hudson, M. C. Nicasio, M. Paneque and E. Carmona, unpublished work.

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