Monohapto Co-ordination of Poly(*tert*-butylpyrazolyl)borate Ligands in Nickel and Palladium Complexes

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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 co-ordination 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 ascribed[4] 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 co-ordination 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 $\cdots$ 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*-$[Ni(C_6H_4X\text{-}p)Br(PMe_3)_2]$ (X = H, Me or OMe)[7] with the thallium salt[2a] of the $HB(3\text{-}Bu^tC_3H_2N_2)_3$ 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 observed over a period of 5–10 min, but longer exposures to CO effect reduction to $[Ni(CO)_2(PMe_3)_2]$. However, the aroyls **2a**–**2c** can be obtained in good yields starting from *trans*-$[Ni\{C(O)C_6H_4X\text{-}p\}Br(PMe_3)_2]$[7] [equation (2)]. Compounds **2a**–**2c** slowly lose CO in solution but are sufficiently stable for full spectroscopic characterization.

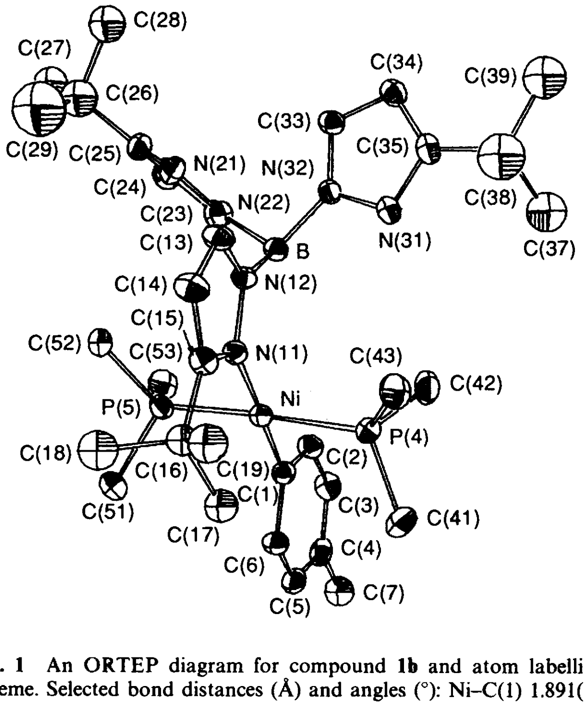

Fig. 1 An ORTEP diagram for compound **1b** and atom labelling scheme. Selected bond distances (Å) and angles (°): Ni–C(1) 1.891(8), Ni–N(11) 1.947(6), Ni–P(4) 2.207(2), Ni–P(5) 2.214(2); C(1)–Ni–P(4) 86.8, C(1)–Ni–P(5) 86.1, N(11)–Ni–P(4) 93.6, N(11)–Ni–P(5) 93.5; average deviation of 0.02 Å from the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

$$\textit{trans}\text{-}[Ni(C_6H_4X\text{-}p)Br(PMe_3)_2] \xrightarrow[-TlBr]{Tl[HB(3\text{-}Bu^tC_3H_2N_2)_3],\ -20\ ^\circ C}$$

$$\textit{trans}\text{-}[Ni(C_6H_4X\text{-}p)\{HB(3\text{-}Bu^tC_3H_2N_2)_3\}(PMe_3)_2] \quad (1)$$

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

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 cm^3) was added $Tl[HB(3\text{-}Bu^tC_3H_2N_2)_3]$ (0.3 g, *ca.* 0.5 mmol) dissolved in thf (10 cm^3). 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 cm^3), 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.

$$\textit{trans}\text{-}[\mathrm{Ni\{C(O)C_6H_4X\text{-}}\textit{p}\mathrm{\}Br(PMe_3)_2]} \xrightarrow[-\mathrm{TlBr}]{\mathrm{Tl[HB(3\text{-}Bu^tC_3H_2N_2)_3]},\ -20\ ^{\circ}\mathrm{C}}$$

$$\textit{trans}\text{-}[\mathrm{Ni\{C(O)C_6H_4X\text{-}}\textit{p}\mathrm{\}\{HB(3\text{-}Bu^tC_3H_2N_2)_3\}(PMe_3)_2]} \quad (2)$$

$$(\mathrm{X = H}\ \mathbf{2a},\ \mathrm{Me}\ \mathbf{2b},\ \mathrm{OMe}\ \mathbf{2c})$$

mutually *trans* PMe_3 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 $^{13}C-\{^1H\}$ 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 ORTEP[12] perspective view of the molecules of compound **1b** which contain a slightly distorted square-planar 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(3-*tert*-butylpyrazolyl)borate ligand, yields analogous complexes of formulation $[Ni(C_6H_4X\text{-}p)\{H_2B(3\text{-}Bu^tC_3H_2N_2)_2\}(PMe_3)_2]$ in which only one pyrazolyl ring is bonded to the metal. Similarly, the interaction of $[PdPh(Br)(PMe_3)_2]$[13] with $Tl[HB(3\text{-}Bu^tC_2H_2N_2)_3]$ gives colourless crystals of $[PdPh\{HB(3\text{-}Bu^tC_3H_2N_2)_3\}(PMe_3)_2]$, 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 co-ordination 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*-$[NiPh(Br)(PMe_3)_2]$ with Na(cp), $K[HB(pz)_3]$ or $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ takes place with loss of one of the PMe_3 ligands and formation of phenyl complexes of composition[14] $[NiPhL(PMe_3)]$ [L = cp, $HB(pz)_3$ or $HB(3,5\text{-}Me_2C_3HN_2)_3$].

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* *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, $\beta = 102.43(3)°$, $U = 4018(2)$ Å^3, $Z = 4$, $D_c = 1.13$ g cm^{-3}, $F(000) = 1472$, λ(Mo-Kα) = 0.710 96 Å (graphite monochromator), $\mu = 5.90$ cm^{-1}, 295 K, Kappa diffractometer, ω–2θ 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 $[I \geqslant 2\sigma(I)]$ 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 correction[10] 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^t 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.