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Note

Three-Center, Two-Electron M$\cdots$H–B Bonds in Complexes of Ni, Co, and Fe and the Dihydrobis(3-*tert*-butylpyrazolyl)borate Ligand

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Introduction

Since the introduction of the poly(pyrazolyl)borate anions as ligands in the field of inorganic chemistry, a vast amount of work has been done, resulting in the synthesis of a large variety of coordination and organometallic compounds.[1] These molecules constitute a very versatile ligand family, due to the facility with which their electronic and steric characteristics may be altered by the introduction of different substituents at the pyrazolyl rings or, to a lesser extent, at the boron atom. Even though the tris(pyrazolyl)borates, Tp′, have been employed most widely,[2] currently the analogous bis(pyrazolyl)borates are receiving increasing attention. Despite their structural simplicity, these ligands are able to adopt different coordination modes. For the bis(pyrazolyl)borates, the more common bonding form is the bidentate[1] κ^2N,N', but monodentate κ^1N binding has been ascertained[3,4] and examples of the still rare, nonclassical κ^3N,N',H and κ^2N,H coordination are also known.[5,6] In this paper we report the formation of nickel, cobalt, and iron complexes of composition $M[Bp^{R,R'}]_2$ (R = *t*-Bu; R′ = H, Me) in which the metal center adopts a distorted octahedral structure consisting of a MN_4 square planar arrangement and two strong *trans*-M$\cdots$H–B interactions. We additionally report the structural characterization by X-ray methods of the known compound[7,8] $Ni[Tp^{tBu}](Cl)$ that results from the unexpected, metal-induced rearrangement of Bp^{tBu} into Tp^{tBu}.

Experimental Section

General Procedures. Microanalyses were by the Microanalytical Service of the University of Seville. Infrared spectra were obtained from Perkin-Elmer spectrometers, models 577 and 684. The NMR instruments were Bruker AMX-500, Bruker DRX-400, and Bruker AMX-300 spectrometers. All manipulations were performed under dry, oxygen-free nitrogen by following conventional Schlenk techniques. The compounds $TlBp^{tBu}$ [7] and $TlBp^{tBu,Me}$ [9] were obtained by published procedures, as well as the alkyl derivatives $Ni(CH_2R)X(PMe_3)_2$ (R = $SiMe_3$,[10] CMe_2Ph,[10] CN,[11] CO_2Et[11]). μ_{eff}

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for complexes **2**−**4** were determined by following Evans' method, using a 10% solution of cyclohexane in CD_2Cl_2 as the solvent. For each compound, measurements were conducted in triplicate giving similar μ_{eff} values of which the respective averages are reported.

Reaction of Alkyl Complexes of Composition $Ni(CH_2R)Cl(PMe_3)_2$ with $Tl[Bp^{tBu}]$. Formation of $Ni[Tp^{tBu}]Cl$ (1). All nickel alkyls investigated reacted similarly. A typical procedure is as follows: To a solution of $Ni(CH_2CN)Cl(PMe_3)_2$ (0.33 g, 1.12 mmol) in THF (20 mL) was added a solution of $Tl[Bp^{tBu}]$ (0.52 g, ca. 1.12 mmol) in THF (10 mL). After 1.5 h of stirring at room temperature, the solvent was removed and the resulting solid was extracted with a mixture of Et_2O/petroleum ether (20:20 mL). After centrifugation the solution was concentrated and cooled to −20 °C. Purple crystals (0.1 g) of the compound $Ni[Tp^{tBu}]Cl$ (**1**) were isolated. Yield 20%. IR (Nujol): 2520 (B−H) cm^{-1}.

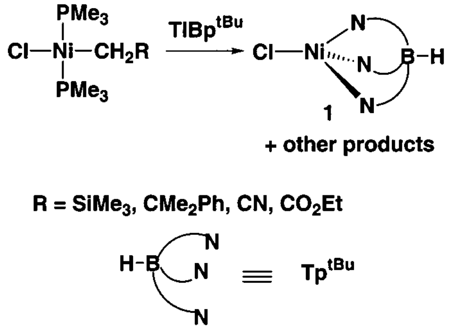
$Ni[Bp^{tBu}]_2$ (2). A solution of $Tl[Bp^{tBu}]$ (0.92 g, ca. 2 mmol) in THF (20 mL) was added to a suspension of $NiCl_2(py)_4$ (0.45 g, 1 mmol) in THF (20 mL). The reaction mixture was stirred for 2 h. The solvent was removed under vacuum and the residue extracted with a mixture of Et_2O/petroleum ether (20:5 mL). After centrifugation, the solution was concentrated and cooled to −20 °C. A blue crystalline solid (0.35 g) was isolated. Yield: 61%. Anal. Calcd for $NiC_{28}H_{48}N_8B_2$: C, 58.3; H, 8.3; N, 19.4. Found: C, 58.0; H, 8.6; N, 19.1. IR (Nujol): 2480 (B−H), 2050 (B−H−M) cm^{-1}. $\mu_{eff} = 2.9\ \mu_B$. By a similar procedure but with employment of $Tl[Bp^{tBu,Me}]$, the corresponding compound $Ni[Bp^{tBu,Me}]_2$ (**3**) was obtained. Yield: 55%. Anal. Calcd for $NiC_{30}H_{52}N_8B_2$: C, 60.7; H, 8.9; N, 17.7. Found: C, 61.0; H, 9.1; N, 17.9. IR (Nujol): 2470 (B−H), 2045 (B−H−M) cm^{-1}. $\mu_{eff} = 2.8\ \mu_B$.

$Co[Bp^{tBu}]_2$ (4) and $Fe[Bp^{tBu}]_2$ (5). A solution of $CoCl_2{\cdot}6H_2O$ (0.108 g, 0.46 mmol) in THF (20 mL) was added to a solution of $Tl[Bp^{tBu}]$ (0.40 g, 0.91 mmol) in THF (20 mL). A cloudy suspension was obtained. The reaction mixture was stirred for 2 h. The solvent was removed under vacuum and the residue extracted with a mixture of Et_2O/petroleum ether (30:10 mL). The solution was concentrated and left at −20 °C. A purple crystalline solid was obtained (0.15 g). Yield: 57%. Anal. Calcd for $CoC_{28}H_{48}N_8B_2$: C, 58.3; H, 8.3; N, 19.4. Found: C, 58.3; H, 8.1; N, 19.7. IR (Nujol): 2470 (B−H), 2080 (B−H−M) cm^{-1}. $\mu_{eff} = 3.7\ \mu_B$. Starting from $FeCl_2{\cdot}4H_2O$, the same procedure was used for the preparation of $Fe[Bp^{tBu}]_2$ (**5**), which was isolated as a pale blue crystalline solid from Et_2O/petroleum ether solutions. Yields of pure material were always low (ca. 20%) due probably to the high instability of this complex, which decomposes to become a yellow material in the presence of traces of air, especially in solution. Anal. Calcd for $FeC_{28}H_{48}N_8B_2$: C, 58.6; H. 8.4; N, 19.5. Found: C, 58.4; H, 8.3; N, 19.9. IR (Nujol): 2460 (B−H), 2080 (B−H−M) cm^{-1}.

Results and Discussion

Some years ago, we reported the first examples of complexes of monodentate coordination of a Tp′ ligand.[3a,b] In addition, we described related aryl derivatives with a κ^1N-Bp^{tBu} group that were obtained by reacting $Ni(Ar)Br(PMe_3)_2$ with $Tl[Bp^{tBu}]$. With the purpose of extending the latter studies to the resembling Ni−alkyls, we have carried out the reactions of *trans*-$Ni(CH_2R)Cl(PMe_3)_2$ (R = $SiMe_3$, CMe_2Ph, CN, CO_2Et) and $Tl[Bp^{tBu}]$. However, in contrast with these results, and despite the similar reaction conditions utilized, orange solutions are generated which give, invariably, low yields (ca. 20%) of purple crystals of the same compound, **1**, regardless of the Ni−alkyl starting material (Scheme 1).

Scheme 1



The IR spectrum of this complex shows no absorptions attributable to the original alkyl and PMe_3 ligands and only one B−H stretching at ca. 2520 cm^{-1}. This is in the range expected for κ^3-Tp^{tBu}.[7,8] Moreover, the simplicity of the IR spectrum in this region contrasts with the multiplicity of the bands anticipated for an $M[Bp^{R,R'}]$ compound. Oftentimes, the IR spectra of these derivatives exhibit more than two ν(B−H) absorptions (e.g. six in the wavenumber interval 2410−2178 cm^{-1},[7] in the case of $Tp[Bp^{tBu}]$; see also ref 13). Analytical and other spectroscopic data are entirely consistent with formulation of **1** as $Ni[Tp^{tBu}]Cl$,[7,8] thereby confirming the unexpected conversion of the Bp^{tBu} ligand into Tp^{tBu} (Scheme 1). Degradation of $Tp^{R,R'}$ ligands by Lewis- or Brönsted-acid-induced cleavage of B−N bonds is a well-known feature of their metal chemistry;[14,15] hence, it appears logical it applies also to $M[Bp^{R,R'}]$ fragments. It is, nevertheless, remarkable that a Tp^{tBu} ligand can be formed under such mild reaction conditions (20 °C, 1.5 h), in contrast with the high temperatures needed for the synthesis of $K[Tp^{tBu}]$ from $K[Bp^{tBu}]$ and 3(5)-*tert*-butylpyrazole (ca. 150 °C, 12 h [7]).

To rule out the adventitious presence of $Tl[Tp^{tBu}]$ in the $Tl[Bp^{tBu}]$ reagent used, the latter was carefully recrystallized several times. To ascertain unequivocally the structure of the reaction product,[7,8] an X-ray crystallographic study was undertaken. Again, to avoid confusion, the unit cells of 10 different crystals obtained from separate crops were analyzed, yielding identical cell parameters. Figure 1 shows an ORTEP view of the structure of **1**, confirming the presence of the Tp^{tBu} ligand and its tridentate N,N′,N″ coordination. The

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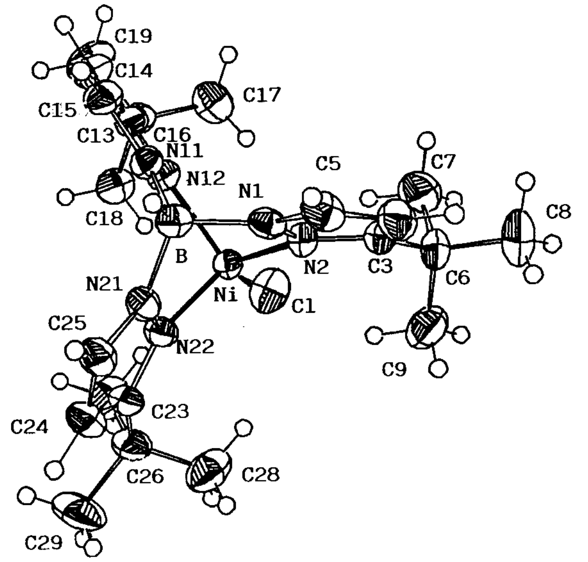

Figure 1. ORTEP representation of the molecular structure of compound **1**.

Table 1. Crystal and Structure Refinement Data for Complexes **1** and **2**

param	**1**	**2**
chem formula	$C_{21}H_{34}BN_6ClNi$	$C_{28}H_{48}B_2N_8Ni$
fw	831.39	577.1
space group	*Pn*	$P2_1/c$
a, Å	9.707(3)	9.275(2)
b, Å	15.241(3)	17.678(2)
c, Å	8.515(3)	10.290(1)
β, deg	100.66(3)	105.85(1)
Z	2	2
V, Å	1238.0(7)	1623.6(4)
ρ_{calcd}, g cm^{-3}	1.28	1.428
T, °C	21	21
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
μ, cm^{-1}	9.13	6.27
data collcd	(−13, 0, 0) to (13, 21, 12)	(−11, 0, 0) to (11, 22, 13)
unique data	3604	3723
unique data $I \geq 2\sigma(I)$	2468	2699
R(int), %	3.8	2.2
std rflcns	3/153	3/147
R	3.3	3.5
R_w	3.4	4.8

structural parameters (Table 1) are very similar to those found previously for other M[Tp^{tBu}]X derivatives[7,8] (M = Fe, Co; X = Cl, NCS) and merit no further discussion.

Despite previous unsuccessful attempts[7] to synthesize Ni[Bp^{tBu}]$_2$, we have succeeded in obtaining moderate yields (ca. 60%) of this material, **2**, according to Scheme 2. Several Ni[Bp$^{R,R'}$]$_2$ compounds have been described in the literature.[7,16] They are orange in color and diamagnetic and, therefore, have a square planar structure. Contrarily, **2** is pale blue and its ^{1}H NMR spectrum displays abnormal chemical shifts and line widths, suggestive of its paramagnetic nature. Accordingly, application of Evans' method[12] gives μ_{eff} = 2.9 μ_B, in agreement with the value expected for an octahedral Ni(II) complex.[17]

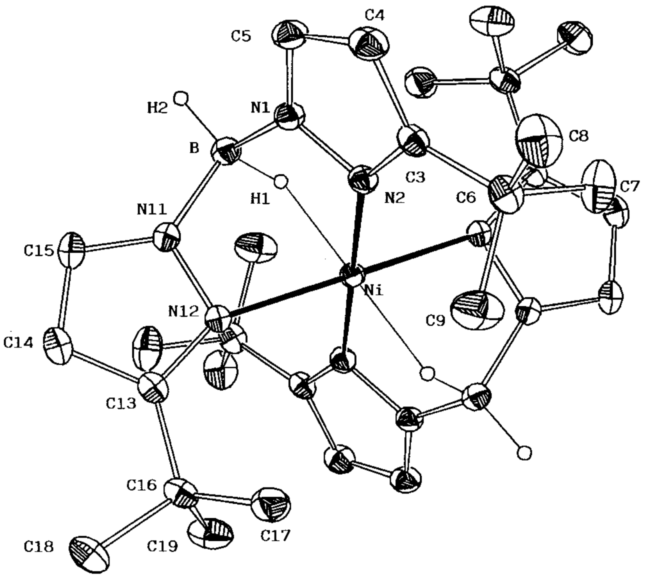

Figure 2. ORTEP representation of the molecular structure of compound **2**.

Scheme 2

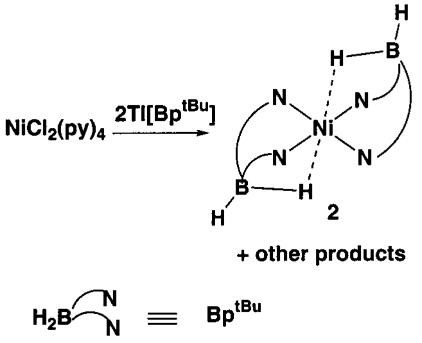

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **2**

Ni−N(2)	2.113(3)	N(2)−Ni−N(12)	86.6(1)
Ni−N(12)	2.120(3)	N(2)−Ni−H(1)	82(1)
Ni−H(1)	1.86(5)	N(12)−Ni−H(1)	82(1)
Ni−B	2.535(4)	Ni−H(1)−B	107(3)

The molecular structure of **2** (Figure 2, Tables 1 and 2) is, in fact, remarkably different from those exhibited by all other structurally characterized Ni[Bp$^{R,R'}$]$_2$ compounds. The nickel atom lies on a center of symmetry, and it is surrounded by a square planar arrangement of *t*-Bu-pyrazolyl nitrogen atoms, complemented by two *trans*-Ni···H−B interactions to make an overall tetragonally distorted, octahedral coordination. The Ni−H distances (1.86(5) Å) are shorter than in $[Ni(NCBH_3)_2(tren)](BPh_4)_2$ (2.1 Å[18]), and in accord with expectations, the B−H1 bond (1.26(5) Å) appears slightly longer than the uncoordinated B−H2 bond (1.15(5) Å). Additional support for the Ni···H−B interaction is provided by the observation of ν(B−H) absorptions of very different energy, at 2480 and 2050 cm^{-1}, the latter being assigned to the Ni···H−B linkages. An analogous compound, **3**, with composition Ni[Bp^{tBu,Me}]$_2$, can be isolated as a pale blue crystalline material from the analogous reaction of NiCl$_2$-

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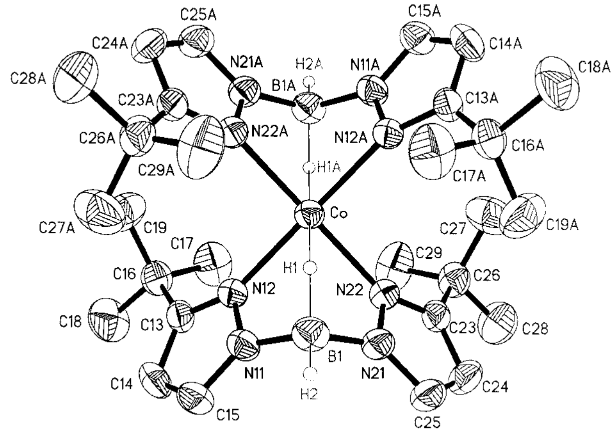

Figure 3. ORTEP representation of the molecular structure of compound **4**.

(py)$_4$ and Tl[Bp^{tBu,Me}]. This exhibits IR bands at 2470 and 2045 cm^{-1}, associated with the B$-$H stretches, and an effective magnetic moment in solution of 2.8 μ_B. All these data clearly point to a pseudooctahedral structure for **3** similar to that of **2**.

The structure of the nickel compounds **2** and **3** is very similar to that found by Parkin and co-workers[13] for the cobalt derivative Co[Bp^{tBu,iPr}]$_2$. As noted,[13] the adoption of the square planar distribution by the MN$_4$ coordination moiety of M[Bp^{tBu,R}]$_2$ compounds could be a way to minimize interligand steric interactions of the *t*-Bu substituents. Nonetheless, the short M$\cdots$H distances of 1.95 and 1.86 Å found in Co[Bp^{tBu,iPr}]$_2$ and in Ni[Bp^{tBu}]$_2$ (**2**), respectively, suggest that the M$\cdots$H$-$B interactions are not just sterically promoted but have instead a bonding contribution to the stability of the molecules. To establish the generality of this coordination geometry, we have extended our studies to the cobalt and iron complexes M[Bp^{tBu}]$_2$ (M = Co (**4**), Fe (**5**)).

Using the corresponding MCl$_2$$\cdot$$nH_2$O salts as starting materials in the reactions with Tl[Bp^{tBu}], the desired Co(II) and Fe(II) complexes **4** and **5** can be respectively obtained. For iron, low yields (ca. 20%) are consistently found. Additionally, it is worth remarking that pure FeCl$_2$$\cdot$4H$_2$O should be employed, since the use of partially oxidized salts diminishes the yield further and may even make the procedure unreliable. Compounds **4** and **5** are pink-purple and pale-blue crystalline solids, respectively. Both are paramagnetic; the cobalt derivative **4** has a solution magnetic moment μ_{eff} = 3.7 μ_B, whereas for the iron complex **5** its instability in solution has prevented accurate measurement of μ_{eff}.

Table 3. Unit Cell Parameters and Other Selected Crystallographic Data for Complexes **2**, **4**, and **5**

param	**2**	**4**	**5**
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
cryst system	monoclinic	monoclinic	monoclinic
a, Å	9.275(2)	9.3130(1)	9.342(1)
b, Å	17.678(2)	17.726(2)	17.761(3)
c, Å	10.290(1)	10.3193(11)	10.328(2)
β, deg	105.85(1)	105.864(2)	105.54(1)
Z	2	2	2
V, Å^3	1623.6(4)	1638.6(3)	1651.1(6)

The two compounds form monoclinic crystals in the space group $P2_1$/c, isostructural with those of the nickel analogue **2**. Because of its relationship, only the structure of **4** has been solved (see Supporting Information), and it is shown in Figure 3 as an ORTEP perspective view. Table 3 contains the unit cell parameters and other crystallographic data for **2**, **4**, and **5**, leaving no doubt about the similar coordination environment of the metal in the three M[Bp^{tBu}]$_2$ compounds.

In summary, the synthetic and structural studies on the complexes M[Bp^{tBu}]$_2$ (M = Fe, Co, Ni) repoted in this paper demonstrate that the most favorable coordination environment consists of a square planar MN$_4$ arrangement, complemented by two *trans*-M$\cdots$H$-$B interactions. These features are very similar to those reported for Co[Bp^{tBu,iPr}]$_2$[13] (which contains also a 3-*tert*-butylpyrazolyl substituent) but differ markedly from the characteristic ones of other M[Bp$^{R,R'}$]$_2$ derivatives of these metals since usually square planar (M = Ni) or tetrahedral (M = Fe, Co) structures are normally encountered for these compounds.

Acknowledgment. The DGESIC (Proyecto PB97-0733) and the Junta de Andalucía are thanked for financial support.

Supporting Information Available: Experimental details from X-ray crystallography and tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles for compounds **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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