Weakly-coordinating anions stabilise the unprecedented monovalent and divalent η-benzene nickel cations $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_6H_6)Ni(\eta\text{-}C_5H_5)]^{2+}$ and $[Ni(\eta\text{-}C_6H_6)_2]^{2+}$

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Received (in Cambridge, UK) 9th March 2000, Accepted 15th March 2000

Nickelocene in benzene reacts with the Brønsted acid H_2O–$B(C_6F_5)_3$ to give the salt $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_6H_6)Ni(\eta\text{-}C_5H_5)][B_3(\mu\text{-}O)_3(C_6F_5)_5]$ which is the first example of a triple-decker nickel sandwich with a bridging η-benzene ligand; the borate anion is also unprecedented; treatment of $Ni(\eta\text{-}C_5H_5)_2$ with Brookhart's acid $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ in benzene gives the paramagnetic bis(η-benzene)nickel derivative $\{[Ni(\eta\text{-}C_6H_6)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]_2{\cdot}Ni(\eta\text{-}C_5H_5)_2\}$ in which nickelocene is present as a molecule of crystallisation.

Large and very weakly coordinating anions $[BR_4]^-$ [R = 3,5-$(CF_3)_2C_6H_3$, C_6F_5] have recently attracted interest owing to their ability to stabilise highly electrophilic metal cations.[1] The strong Lewis acid $B(C_6F_5)_3$, is currently of interest as a methyl abstracting agent and activator of early transition metal Ziegler–Natta polymerisation systems.[2] Recently the mono-aquo adduct H_2O–$B(C_6F_5)_3$ was reported, and the solution behaviour as a Brønsted acid was described.[3,4]

Here, we report reaction between nickelocene and the Brønsted acids H_2O–$B(C_6F_5)_3$ or $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (Brookhart's acid) which give unexpected new chemistry.

Treatment of nickelocene with Brookhart's acid $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ in toluene gives green–blue crystals of the Ni(III) compound $[Ni(\eta\text{-}C_5H_5)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ **1**†. The nickelocenium cation has been isolated previously as the BF_4^- salt,[5] but no crystal structure was reported. The cation $[Ni(\eta\text{-}C_5Me_5)_2]^+$ has been structurally characterised as C_{60}^- and $[HTCNQF_4]^-$ salts.[6] The crystal structure of **1** has been determined and the ORTEP of $[Ni(\eta\text{-}C_5H_5)_2]^+$ (Fig. 1) shows eclipsed cyclopentadienyl rings as observed in $[Ni(\eta\text{-}C_5H_5)_2]$.[7] The average Ni–C distance of 2.075 Å is slightly shorter than in $[Ni(\eta\text{-}C_5H_5)_2]$ (2.178 Å). The magnetic moment of **1** at room temperature is 1.69 μ_B and corresponds to one unpaired electron, consistent[8] with the ground state configuration $\delta^4\sigma^2\pi^1$.

Treatment of nickelocene with H_2O–$B(C_6F_5)_3$ in CH_2Cl_2–benzene, gave brown crystals of the triple-decker sandwich compound $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_6H_6)Ni(\eta\text{-}C_5H_5)][B_3(\mu\text{-}O)_3(C_6F_5)_5]$ **2**. In contrast, the reaction between nickelocene and the Brønsted acid $HBF_4{\cdot}Et_2O$ gave the cation $[Cp_3Ni_2]^+$.[9] We envisage the cation $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_6H_6)Ni(\eta\text{-}C_5H_5)]^{2+}$ is formed by the addition of two intermediate $[Ni(\eta\text{-}C_5H_5)]^+$ fragments to a benzene molecule. Each nickel centre is formally equivalent to the 18-electron centres in $[Ni(\eta\text{-}C_5H_5)(\eta^3\text{-allyl})]$.[10] The crystal structure of **2** (Fig. 2) shows the rings are eclipsed with an average Ni–C_{Cp} distance of 2.121 Å, and the C–C–C angles lie between 106.6(5) and 109.2(4)°; the corresponding Ni–$C_{benzene}$ distance is 2.168 Å, with the C–C–C angles between 118.5(6) and 121.8(5)°. This compound is the first η-benzene–nickel(II) sandwich compound to be structurally characterised. The only other η-benzene–nickel compound is the Ni(0) phosphine compound, $[Ni(\eta\text{-}C_6H_6)(Bu^t_2PCH_2PBu^t_2)]$.[11] Nickel(II) compounds with one η-toluene or η-mesitylene ligand have been structurally characterised.[12]

The counter ion in **2** is a new dianion. The six-membered B_3O_3 ring is surrounded by five C_6F_5 groups, giving one neutral, three-coordinate boron, B(1), and two anionic tetrahedral boron centres, B(2) and B(3). There are only two non-solvent moieties present in the crystal structure, and to maintain electrostatic balance we assign a charge of −2 to the anion. The average B–O bond distance is 1.448 Å and the average B–O–B angle is 120.9°. The anion likely results from acidic decomposition and aryl group loss in H_2O–$B(C_6F_5)_3$.

Treatment of nickelocene with Brookhart's acid in benzene gives red–brown crystals of **3** and the crystal structure of **3** shows the presence of $Ni(\eta\text{-}C_5H_5)_2$, $Ni(\eta\text{-}C_6H_6)_2$ and two

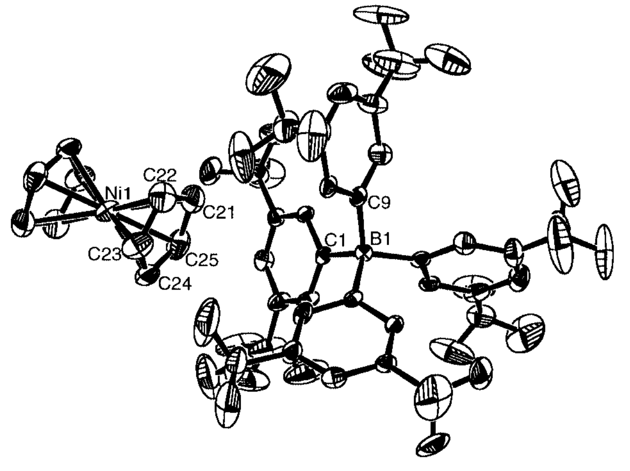


Fig. 1 Crystal structure of **1**. Selected bond lengths (Å) and angles (°): Cp_{cent}–Ni(1) 1.70, B(1)–C(1) 1.631(8), B(1)–C(9) 1.636(8); C(23)–C(22)–C(21) 109.3(8), C(22)–C(21)–C(25) 105.3(7), C(23)–C(24)–C(25) 106.6(7), C(22)–C(23)–C(24) 108.4(7), C(24)–C(25)–C(21) 109.1(7).

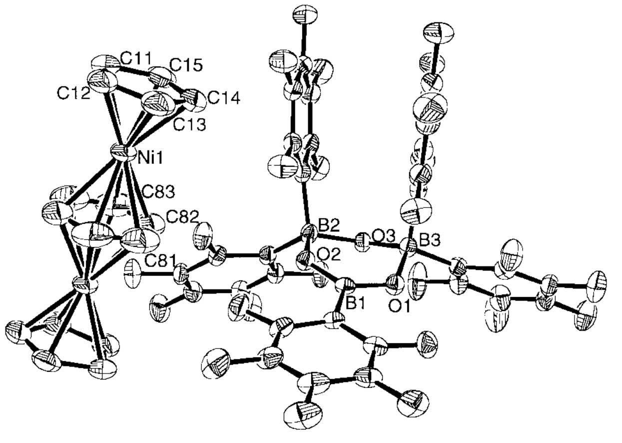
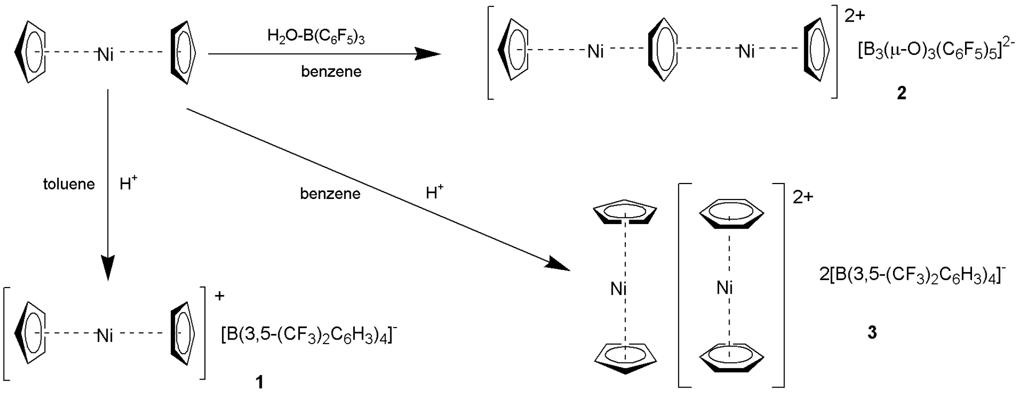


Fig. 2 Crystal structure of **2**. Selected bond lengths (Å) and angles (°): Cp_{cent}–Ni(1) 1.744, $benzene_{cent}$–Ni(1) 1.795, B(1)–O(1) 1.349(4), B(2)–O(2) 1.438(4), B(3)–O(3) 1.549(4); O(1)–B(1)–O(2) 123.8(3), O(2)–B(2)–O(3) 108.0(2), O(1)–B(3)–O(3) 107.6(2).

DOI: 10.1039/b001190h



Scheme 1

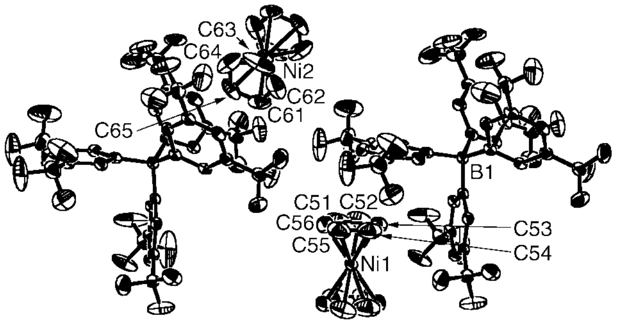


Fig. 3 Crystal structure of **3**. Selected bond lengths (Å) and angles (°): benzene$_{\mathrm{cent}}$–Ni(1) 1.713, Cp$_{\mathrm{cent}}$–Ni(2) 1.710, C(51)–C(52)–C(53) 124.2(15), C(56)–C(55)–C(54) 113.8(9), C(52)–C(51)–C(56) 126.2(16), C(63)–C(62)–C(61) 109.7(7), C(61)–C(65)–C(64) 107.0(7).

$[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ anions. The room temperature magnetic moment of **3** is 4.26 μ_B, corresponding to four unpaired electrons. These data are consistent with the presence in the crystal of neutral Ni(η-$C_5H_5)_2$ and dicationic [Ni(η-$C_6H_6)_2]^{2+}$; therefore we formulate this compound as {[Ni(η-$C_6H_6)_2$][B(3,5-$(CF_3)_2C_6H_3)_4]_2$·Ni(η-$C_5H_5)_2$}, and the nickelocene is present as a molecule of crystallisation (Fig. 3). The average Ni–C distance in the dication [Ni(η-$C_6H_6)_2]^{2+}$ is 2.079 Å and the C–C–C angles are between 113.8(9) and 126.2(16)°. Bis(η-hexamethylbenzene)nickel(II) has been reported,[13] but not structurally characterised.

The new and often surprising reactions are summarised in Scheme 1.

J. L. P. thanks the Spanish Goverment for financial support. L. H. D thanks St. John's College Oxford for a Junior Research Fellowship.

Notes and references

† *Crystal data*: **1**: $C_{42}H_{22}BF_{24}Ni$, M_w = 1052.12, monoclinic, space group *C*2/*c*, a = 15.792(3), b = 12.679(3), c = 21.434(4) Å, β = 91.52(3), U = 4290.1(15) Å^3, Z = 4, μ(Mo-Kα) = 0.588 mm^{-1}. T = 150 K, 2802 independent reflections were collected (R_{int} = 0.0000); R = 0.0948 and R_w = 0.1973. The fluorine atoms of the CF_3 groups were found to be disordered and modelled as occupying staggerred positions (F121–F123 s.o.f. 84%; F151–F153 s.o.f. 87% and F41–F43 s.o.f. 84%).

_**2**·CH_2Cl_2: $C_{47}H_{18}B_3Cl_2F_{25}Ni_2O_3$, M_w = 1326.37, triclinic, space group *P*1, a = 11.873(7), b = 13.526(8), c = 16.304(8) Å, α = 73.658(6), β = 75.969(6), γ = 71.607(6)°, U = 2350.0(5) Å^3, Z = 2, μ(Mo-Kα) = 1.06 mm^{-1}. T = 150 K; 8130 independent reflections were collected (R_{int} = 0.03); R = 0.0462 and R_w = 0.0572.

3: $C_{43}H_{23}BF_{24}Ni$, M_w = 1065.13, triclinic, space group $P\bar{1}$, a = 12.889(5), b = 13.191(6), c = 14.420(4) Å, α = 86.902(6), β = 90.131(6), γ = 61.171(6)°, U = 2143.55(14) Å^3, Z = 2, μ(Mo-Kα) = 0.590 mm^{-1}. T = 150 K; 7199 independent reflections were collected (R_{int} = 0.0000); R = 0.0797 and R_w = 0.2037. The fluorine atoms of the CF_3 groups have been modelled as disordered over two staggerred positions (F171–F173 s.o.f 49%, F341–F343 s.o.f 72% and F472–F473 s.o.f 74%).

CCDC 182/1576. See http://www.rsc.org/suppdata/cc/b0/b001190h/ for crystallographic files in .cif format.

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