($t_{2g}^6e_g^2$) ground state, with intraconfigurational transitions to ^1E_g and $^1A_{1g}$ states. The $^3A_{2g} \rightarrow {}^1E_g$ transition is observed as a shoulder in $Ni(H_2O)_6^{2+}$ at 15,400 cm^{-1}; we observed this transition at 13,114 cm^{-1} for $Ni(en)_3^{2+}$ as a resolved peak at 77°K in $MgCl_2$–aqueous glass solution. The $^3A_{2g} \rightarrow {}^1A_{1g}$ transition has been assigned to some weak bands observed[7,8] at 4°K for $NiSiF_6 \cdot 6H_2O$ crystal in the region 24,330–24,450 cm^{-1}. At 80°K in $Ni(dipy)_3Br_2 \cdot 6H_2O$ crystal, this transition was assigned[9] to a shoulder at 20,960 cm^{-1}. For $Ni(en)_3^{2+}$ in $MgCl_2$–aqueous glass solution at 77°K we observed a series of extremely well-resolved peaks at 21,372, 21,623, and 21,817 cm^{-1} (Figure 1, bottom). These peaks must correspond to the 0, 0 and vibrational components of the $^3A_{2g} \rightarrow {}^1A_{1g}$ intraconfigurational transition. Five complexes of Ni(II) were studied in our work, with aniline, gly$^-$, en, dipy, and *o*-phen as ligands, showing a relative insensitivity of this transition to ligand field strength. The broad band centered on 25,000 cm^{-1} (Figure 1, bottom) probably corresponds to the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition.

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(7) R. Pappalardo, *Nuovo Cimento*, 6, 392 (1957).

(8) M. H. L. Pryce and G. Agnetta, *Phil. Mag.*, **10**, 477 (1964).

(9) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

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The Existence of the Nickel(IV) Dication Derived from Nickelocene and a Cationic Boron Hydride Analog

Sir:

The exceptional stabilities of the d^6 bis(cyclopentadienyl)metallocenes, iron(II) ferrocene, $(\pi\text{-}C_5H_5)_2Fe$, and the cobalt(III) cobalticinium ion, $(\pi\text{-}C_5H_5)_2Co^+$, have been attributed to the retention of the inert gas configuration about the metal atom. Although nickelocene can be oxidized to a formal nickel(III) ion, $(\pi\text{-}C_5H_5)_2Ni^+$, further oxidation to the "electronically stable" d^6 nickel(IV) species, $(\pi\text{-}C_5H_5)_2Ni^{2+}$, has not been previously observed.[1-3] Wilkinson, Pauson, and Cotton found that complete disruption of the molecule occurred during an attempted electrochemical oxidation in an ethanolic electrolyte solution.[1] At room temperature we have observed similar results using cyclic voltammetry in acetonitrile solution; however, upon cooling the electrolyte, two reversible redox couples for the nickelocene system could be obtained. The voltammogram at −40° is presented in Figure 1. The nickel(II)–(III) couple (reduction peak potential at −0.09 V *vs.* sce) has been investigated previously by polarography.[1] The appearance of a reversible nickel(III)–(IV) couple at +0.77 V shows that the formal d^6 nickel(IV) ion, $(\pi\text{-}C_5H_5)_2Ni^{2+}$, actually does exist. No attempt was made to isolate this strongly oxidizing species, inasmuch as it rapidly decomposed in the electrolyte solution at temperatures above 0°.

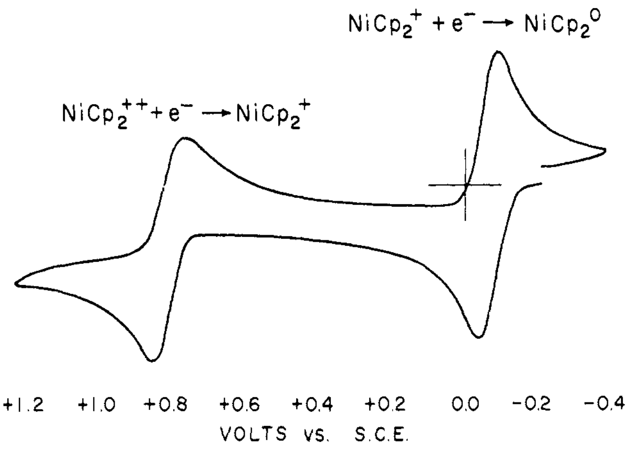

Figure 1. Cyclic voltammogram of the $(\pi\text{-}C_5H_5)_2Ni$ system; run in acetonitrile solution at −40°; anodic scan began at −0.2 V at 0.05 V/sec.

The much more stable bis(dicarbollyl)nickel(IV) analog, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Ni$,[4,5] exhibited redox properties similar to the nickelocene system, *i.e.*, two reversible one-electron couples by cyclic voltammetry. The reduction peak potentials are given in Table I.

Table I. Reduction Peak Potentials of the π-Cyclopentadienyl, π-(3)-1,2-Dicarbollylnickel Complexes[a]

Compounds	$M^{IV} + e^- \rightarrow M^{III}$	$M^{III} + e^- \rightarrow M^{II}$
$(C_5H_5)_2Ni$[b]	Dication $\xrightarrow{+0.77}$ cation	Cation $\xrightarrow{-0.09}$ neutral
$(C_5H_5)Ni(B_9C_2H_{11})$	Cation $\xrightarrow{+0.46}$ neutral	Neutral $\xrightarrow{-0.52}$ anion
$Ni(B_9C_2H_{11})_2$	Neutral $\xrightarrow{+0.18}$ anion	Anion $\xrightarrow{-0.56}$ dianion

[a] Obtained by cyclic voltammetry in acetonitrile solution at room temperature; 0.1 *N* tetraethylammonium perchlorate supporting electrolyte; measured in volts *vs.* sce. [b] Run at −40°.

Intermediate in stability to the bis-ligand systems above is the mixed sandwich species, $(\pi\text{-}C_5H_5)Ni[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ (**1**). This newly discovered formal nickel(III) complex was prepared in low yield from the reaction of a 5:1 mixture of sodium cyclopentadienide and disodium (3)-1,2-dicarbollide[5] with $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$[6] in tetrahydrofuran. The initially formed nickel(II) complex was air-oxidized in water to the neutral nickel(III) derivative. **1** is brown-green [$\lambda_{max}^{CHCl_3}$ (ε) 327 (22,200) and 434 mμ (2600)] and paramagnetic (μ_{eff} = 1.99 BM in $CHCl_3$ solution) as expected for a d^7 configuration. *Anal.* Calcd for

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(1) G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, **76**, 1970 (1954).

(2) J. C. Goan, E. Berg, and H. E. Podall, *J. Org. Chem.*, **29**, 975 (1964). These authors postulate a $(C_5H_5)_2Ni \cdot 2p$-chloroanil adduct as $(C_5H_5)_2Ni^{2+}$ with a *p*-chloroanil dianion.

(3) Oxidation or reduction steps in these types of metal complexes cannot be attributed exclusively to the metal atom, inasmuch as electrons are removed from (or added to) *molecular* orbitals; however, for convenience, we have assigned fixed formal charges for the ligands and denoted redox steps of the complexes by changes in the formal oxidation states of the metal atoms.

(4) L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **89**, 470 (1967).

(5) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

(6) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 71.

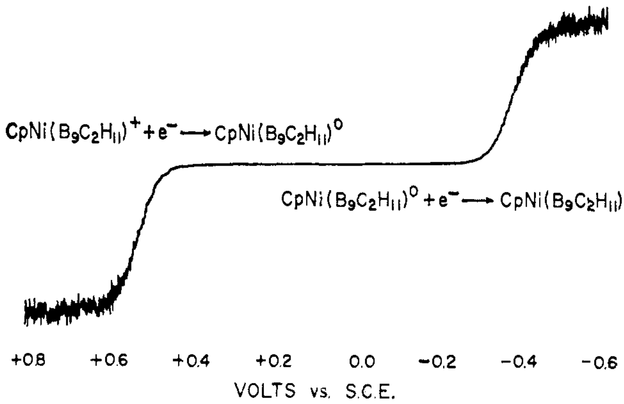

Figure 2. Rotating platinum polarogram of $(\pi\text{-}C_5H_5)Ni[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ run in acetonitrile solution at room temperature.

$C_5H_5NiB_9C_2H_{11}$: C, 32.82; H, 6.29; B, 37.98; Ni, 22.91. Found: C, 31.18; H, 6.19; B, 36.73; Ni, 21.44. High-resolution mass spectroscopy verified the formulation: Calcd for $^{60}Ni^{11}B_9{}^{12}C_7{}^{1}H_{16}$, 259.144; found, 259.142. The mixed ligand compound is electrochemically similar to the two analogous nickel systems discussed above; cyclic voltammetry gave two reversible redox couples (Table I). The polarogram (rotating platinum electrode) of **1** at room temperature in acetonitrile is shown in Figure 2. Here again the presence of a formal d^6 Ni(IV) species, which must be the cation $(\pi\text{-}C_5H_5)Ni[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]^+$, is demonstrated. The high reduction potential of the Ni(IV) complex, $E_{1/2} = +0.55$ V, indicates that the species is strongly oxidizing, and attempts to isolate it, chemically and electrochemically, have as yet been unsuccessful. The cation decomposed slowly in acetonitrile at room temperature, though much more slowly than its less stable bis(cyclopentadienyl)nickel(IV) analog.

Although several cationic boron hydride derivatives containing one boron atom[7] have been synthesized, with few exceptions, all the higher boron hydrides, polyhedral boranes, carboranes, etc., have been exclusively anionic or electrically neutral species.[8] However, electrochemistry has shown here that the driving force of a metal to attain its inert gas configuration apparently overcomes this charge precedence established by the electron-deficient boron hydrides.

The lowering of the Ni(IV) reduction potentials with successive dicarbollide ion substitution for cyclopentadienide ion is seen in Table I. This effect appears to be due to the higher formal negative charge of the dicarbollide ligand (−2, compared to −1 for cyclopentadienide), resulting in a less highly charged, hence more stable, formal Ni(IV) complex. A similar correlation regarding the lower +2 oxidation state cannot be made; the presence of one dicarbollide ligand makes the Ni(II) species obtained from **1** very strongly reducing compared to nickelocene, while the presence of two dicarbollide ion ligands does not appreciably alter the potential of this oxidation state.

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[7] N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

[8] For two exceptions, see W. R. Hertler, W. K. Knoth, and E. L. Muetterties, *Inorg. Chem.*, **4**, 288 (1965), regarding the protonated amino complex, $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2]^+$, and E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, p 110, concerning the $B_{10}H_7[S(CH_3)_2]_3{}^+$ cation.

[9] U. S. Public Health Service Predoctoral Fellow.

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Determination of Specific Surface Areas of Powders by Means of Dyes

Sir:

Van den Hul and Lyklema report[1] measurements of specific surface of samples of silver iodide by several methods. The values from dye adsorption differ considerably from those obtained by nitrogen adsorption. They used two cationic dyes: methylene blue (MB) and diethyl-2,2′-cyanine (DEC). They assumed flatwise adsorption of both dyes and a projected molecular area of 108 Å^2 for MB.

Investigations here[2] have shown that the best results with adsorption of cationic dyes are given if (a) the molecular area is that of the smallest enclosing rectangle rather than the actual projected area, and (b) account is taken of the fact that the dyes are adsorbed as ionic micelles from water. Thus for MB, 120 Å^2 is the best molecular area, and since this dye is adsorbed as a dimer, the specific surface thus calculated must be divided by two.

If the results given by Van den Hul and Lyklema are recalculated in this way, they are found to be in much better agreement with their nitrogen results, as shown in Table I. The lower results quoted by Van den Hul and Lyklema for DEC, compared with nitrogen data, are readily accounted for by the fact that they used ethanolic solution. This solvent would disaggregate the dye and interfere with its adsorption.

Table I

	Specific surface, m^2/g		
		Methylene blue	
Sample	N_2	Quoted[1]	Recalcd
A1	0.45	0.87	0.48
A2	0.38	0.61	0.34
B2	0.52	0.98	0.54
B3	0.30	0.65	0.36
C1	0.97	2.18	1.21
C2	1.99	2.14	1.19

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[1] H. J. Van den Hul and J. Lyklema, *J. Am. Chem. Soc.*, **90**, 3010 (1968).

[2] C. H. Giles, I. A. Easton, R. B. McKay, C. C. Patel, N. B. Shah, and D. Smith, *Trans. Faraday Soc.*, **62**, 1963 (1966).

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