JEOL MH-100 spectrometer. Proton-decoupled ^{31}P spectra were obtained on a JEOL C-60 spectrometer using a CAT program on a PDP8-I computer. Analyses and molecular weight measurements were performed by the Microanalytical Service in the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University, by Miss Brenda Stevenson and Dr. Joyce Fildes and associates.

Materials. AR grade solvents were used without further purification. $Pt(CH_3)_2(SP)$ (I) and $PtCl(CH_3)(SP)$ were prepared by reaction of SP with $Pt(CH_3)_2(COD)$ and $PtCl(CH_3)(COD)$, respectively.[17]

Preparation of $PtI(CH_3)(SP)$. A large excess (0.19 g) of sodium iodide was added to a solution of $PtCl(CH_3)(SP)$ (0.10 g) in acetone (30 ml), and the mixture was refluxed for 3 hr. After evaporation to dryness under reduced pressure, the residue was extracted with dichloromethane. The solution was filtered and, after addition of hexane, concentrated to give $PtI(CH_3)(SP)$ (II) as a pale yellow solid (87.5% yield). The complex was dried at room temperature under vacuum. *Anal.* Calcd for $C_{21}H_{20}IPPt$: C, 40.3; H, 3.2; I, 20.3; P, 5.0; mol wt 625. Found: C, 39.9; H, 3.4; I, 20.2; P, 5.3; mol wt (vpo, $CHCl_3$, 25°) 645. ^1H nmr spectrum (δ, $CDCl_3$, ppm downfield from TMS): *Pt*-CH_3 (doublet with satellites), 1.27, $|^2J_{Pt-CH_3}| = 74$ Hz, $|^3J_{P-Pt-CH_3}| = 4.5$ Hz; H_A (doublet with satellites), 5.42, $|J_{Pt-H_A}| = 43$ Hz; H_B (doublet of doublets, with satellites), 3.79, $|J_{Pt-H_B}| = 36$ Hz, $|J_{P-H_B}| = 1.5$ Hz; H_C (doublet of doublets, with satellites), 6.08, $|J_{Pt-H_C}| = 32$ Hz; $|J_{H_AH_B}| < 1$ Hz; $|J_{H_BH_C}| = 14$ Hz; $|J_{H_AH_C}| = 8.5$ Hz. ^{31}P nmr spectrum (CH_2Cl_2): singlet at 26.7 ppm downfield from external 85% H_3PO_4, with satellites, $|^1J_{Pt-P}| = 4018$ Hz.

Reaction of $Pt(CH_3)_2(SP)$ (I) with Iodine. Iodine (0.045 g, 0.177 mol) was added to $Pt(CH_3)_2(SP)$ (0.09 g, 0.175 mmol) dissolved in dichloromethane (5 ml) to give a bright orange solution. It was evaporated under reduced pressure and the resulting orange oil was recrystallized from dichloromethane–hexane to give a yellow solid, identified by its nmr spectrum as $PtI(CH_3)(SP)$ (II) (85% yield).

Reaction of $Pt(CH_3)_2(SP)$ (I) with Iodomethane. A solution of $Pt(CH_3)_2(SP)$ (I) (0.5 g, 0.97 mmol) in dichloromethane (20 ml) was treated with iodomethane (0.5 ml, 7.9 mmol). The solution was allowed to stand for 2 days and then evaporated under reduced pressure to give a colorless oil. The ^1H nmr spectrum of part of this oil in $CDCl_3$ showed a complex pattern in the region δ 0–2.5 ppm but no peak characteristic of III at δ 2.56 ppm.

The oil was dissolved in chloroform and allowed to stand for 1 week, and again the solution was evaporated under reduced pressure. The ^1H nmr spectrum of the residue showed that it consisted predominantly of a mixture of $[PtI(CH_3)_3]_4$ (approximately 20%), $PtI(CH_3)(SP)$ (II) (approximately 40%), and III (approximately 40%).

A chromatography column was prepared with a suspension of Florisil in *n*-pentane, and the mixture was introduced onto the column in solution in a small volume of dichloromethane. The column was then eluted with *n*-pentane–dichloromethane mixtures, the proportion of dichloromethane being gradually increased. Initial fractions contained $[PtI(CH_3)_3]_4$ (9:1 *n*-pentane–dichloromethane). Later fractions (1:2 *n*-pentane–dichloromethane) contained $PtI(CH_3)(SP)$ (II) and then, only partially separated from II, III. Samples rich in III were fractionally crystallized from chloroform–*n*-hexane, and the less soluble fractions were combined. Recrystallization from $CHCl_3$–hexane, followed by drying under vacuum, gave a chloroform solvate of III approximately 90% pure, with II present as an impurity. *Anal.* Calcd for $C_{22}H_{22}IPPt\cdot{}^1/_{10}CHCl_3$: C, 40.75; H, 3.4; Cl, 1.6; I, 19.5; P, 4.8. Found: C, 40.3; H, 3.8; Cl, 1.6; I, 19.8; P, 4.6. ^1H nmr spectrum (δ, $CDCl_3$, ppm downfield from TMS): *Pt*-CH_3 (doublet with satellites), 1.47, $|^2J_{Pt-CH_3}| = 72.5$ Hz, $|^3J_{P-Pt-CH_3}| = 4.5$ Hz; *C*-CH_3 (singlet with satellites), 2.56, $|J_{Pt-CH_3}| = 15.5$ Hz; H_A (singlet with satellites), 5.80, $|J_{Pt-H_A}| = 41$ Hz; H_B (singlet with satellites), 3.95, $|J_{Pt-H_B}| = 38.5$ Hz. ^{31}P nmr spectrum: singlet at 21.4 ppm downfield from H_3PO_4, with satellites, $|^1J_{Pt-P}| = 4108$ Hz.

When iodomethane (5 ml, 79 mmol) was added to a solution of $Pt(CH_3)_2(SP)$ (0.707 g, 1.4 mmol) in chloroform (20 ml) and the solution was allowed to stand 3 weeks, the major product was $[PtI(CH_3)_3]_4$ and no formation of III was detected. However, when iodomethane (0.014 ml, 0.22 mmol) was added to a solution of I (0.058 g, 0.11 mmol) in $CDCl_3$ (0.4 ml) in an nmr tube and the reaction was followed over several days by ^1H nmr, peaks corresponding to I were observed to decrease slowly, with a corresponding increase in peaks due to $[PtI(CH_3)_3]_4$, II, and III.

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Registry No. I, 39530-95-5; II, 52699-07-7; III, 52699-08-8; $PtCl(CH_3)(SP)$, 52730-54-8.

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Contribution No. 3266 from the Department of Chemistry,
University of California, Los Angeles, California 90024

A Nickel(IV) Complex of the $B_8CH_9{}^{3-}$ Ligand

Chris G. Salentine, Richard R. Rietz, and M. Frederick Hawthorne*

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The first reported monocarbon carborane compounds of Ni(IV) were anionic bis complexes of the carbollide ion, $B_{10}CH_{11}{}^{3-}$, and some of its substituted derivatives.[1] We have recently reported neutral η-cyclopentadienylnickel(IV) complexes of the carbollide ligand[2] and also neutral bimetallic monocarbon complexes of the $B_7CH_8{}^{5-}$ ion containing formal $(\eta\text{-}C_5H_5Co)^{2+}$ and $(\eta\text{-}C_5H_5Ni)^{3+}$ units.[3] We now report a novel nickel(IV) complex of the $(\eta\text{-}1\text{-}B_8CH_9)^{3-}$ ligand, η-cyclopentadienyl-η-nonahydro-1-carba-*nido*-nonaboratonickel(IV),[4] constituting the first *closo*-metallocarborane in which a metal is unambiguously bound to a B_4 face.[5] This also constitutes the first existence of a "B_8C" fragment, as there are no known monocarbon carboranes or carborane anions containing eight boron atoms. The ligand is the third in a series of $B_nCH_{n+1}{}^{3-}$ carborane anions ($n = 7$ and 10 are known[1,2,6]), and the η-cyclopentadienyl complex is the second homolog in a series of neutral $C_5H_5Ni^{IV}B_nCH_{n+1}$ complexes.[2] These compounds are of particular interest since they obey the proposed[7] $2n + 14$ electron rule for closo n-vertex polyhedral heteroboranes and are thus, as neutral complexes, predicted to be stable species which will undergo polyhedral rearrangements (as found for $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})^2$) and a variety of other reactions characteristic of the $B_nC_2H_{n+2}$ carboranes and cobaltacarboranes.[7b]

Results and Discussion

In a recent paper[2] on the synthesis of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}$

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(4) We have used IUPAC rule 7.2, *Pure Appl. Chem.*, 30, 683 (1972); *i.e.*, the ligand is numbered in ascending planes from the vertex opposite the open face with the heteroatom (carbon) receiving the lowest possible number (here, 1).

(5) This has been proposed[3] for the related complex $(C_5H_5)_2Co^{III}Ni^{IV}B_7CH_8$ but the spectroscopic data do not uniquely define the structure; there have also been reports of *closo*-metallocarboranes containing B_2C_2 bonding faces [see W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 4565 (1973); R. N. Grimes, *et al.*, *ibid.*, 96, 3090 (1974)] and a *nido*-metallocarborane containing a B_4 face [see V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95, 5078 (1973)].

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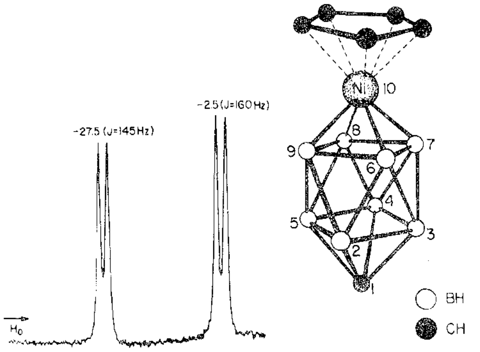

Figure 1. Proposed structure and 80.5-MHz ^{11}B nmr spectrum (CH_2Cl_2 solution) of I.

$B_{10}CH_{11}$) we reported a minor product of the reaction as $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_8CH_9)$, I. We obtained a small yield of the latter compound from $B_{10}H_{12}C[N(CH_3)_3]$[1d] as outlined below

$$B_{10}H_{12}C[N(CH_3)_3] \xrightarrow{3Na} Na_3B_{10}CH_{11} + N(CH_3)_3 + {}^1/_2H_2$$

$$Na_3B_{10}CH_{11} + NaC_5H_5 + NiBr_2\cdot 2C_2H_4(OCH_3)_2 \dashrightarrow \xrightarrow{O_2}$$
$$\underset{8\text{-}16\%}{C_5H_5NiB_{10}CH_{11}} + \underset{<<1\%}{C_5H_5NiB_8CH_9}$$

The bright yellow complex I was difficult to purify (see Experimental Section) and could be obtained in only very small quantities.

The 80.5-MHz ^{11}B nmr spectrum, shown in Figure 1, consists of two doublets of equal area at −2.5 (160) and −27.5 (145) [chemical shift, ppm relative to $F_3B\cdot O(C_2H_5)_2$ (coupling constant, Hz)]. The 100-MHz ^1H nmr spectrum, obtained in CS_2, consists of a sharp singlet at τ 4.18 and a broad resonance at τ 2.05 of relative areas 5:1, respectively. The sharp singlet was assigned to the cyclopentadienyl protons and the broad singlet to carborane C–H. The latter resonance is shifted downfield with respect to the three known isomers of $B_8C_2H_{10}$;[8] however, we have previously observed low-field apical carborane C–H resonances in various metallocarboranes.[3,9]

The mass spectrum of I exhibits a cutoff at *m/e* 234 corresponding to the $^{12}C_6{}^1H_{14}{}^{11}B_8{}^{60}Ni^+$ ion. At 12 eV, with loss of hydrogen minimized, relative peak intensities in the parent envelope agree within 10% with those calculated from a computer simulation of the expected statistical distribution. Due to the limited availability of pure I, we obtained a high-resolution mass spectrum to confirm the empirical formula: calcd for $^{12}C_6{}^1H_{14}{}^{11}B_8{}^{64}Ni^+$, 238.1120; found, 238.1122.

Cyclic voltammetry[10] shows a reversible reduction with $E_{p/2} = -0.93$ V (*vs.* sce), presumed to be $Ni^{IV} + e^- \rightarrow Ni^{III}$ by comparison with reduction potentials of the three isomers of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}B_{10}CH_{11})$.[2] The infrared spectrum of I is presented in the Experimental Section.

We propose that I has the gross geometry of a bicapped Archimedean antiprism (Figure 1). It may be noted that this is the only reasonable structure compatible with the ^{11}B nmr data; *i.e.*, each doublet is assigned to a ring of four boron atoms.

If terminal BH and CH bonds are excluded from the polyhedral system of the $B_8CH_9{}^{3-}$ anion, 22 electrons remain for polyhedral bonding. A molecular orbital scheme, analogous to that for $B_{10}H_{10}{}^{2-}$ ion,[11] would place six electrons in the square pyramid in the apical region of the $B_8CH_9{}^{3-}$ ion, ten electrons between the two four-membered rings of boron atoms, and six electrons in four approximately sp^3 orbitals directed toward the vacant apex position associated with the open face. The four atomic orbitals present in the open square face may be used with the idealized C_{4v} symmetry of the ligand to generate a strongly bonding A_1 orbital, two degenerate and nonbonding E orbitals, and one strongly antibonding orbital of B_1 symmetry. Conceptually, the six electrons would occupy the A_1 and the two E orbitals which are of appropriate symmetry to combine with the empty formal Ni(IV) A_1 and E atomic orbitals. Here we see a close parallel to the cyclobutadiene dianion in terms of bonding to transition metals as was first recognized for the similar relationship of the cyclopentadienide and dicarbollide ions.[12]

In addition to the bonding exhibited by I, this is the first example of an eight-boron monocarbon carborane fragment. We presume the $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_8CH_9)$ observed in the synthesis of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$ arose through a degradation of the latter compound.[6]

Experimental Section

Physical Measurements. The 80.5-MHz ^{11}B nmr spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. The 100-MHz ^1H nmr spectra were measured with a Varian HA-100 spectrometer. The electrochemical apparatus for cyclic voltammetry has been described previously.[2] Infrared spectra were determined using a Perkin-Elmer Model 421 sodium chloride spectrophotometer. Mass spectra were obtained using an Associated Electrical Industries Model MS-9 spectrometer.

Materials. The Ni(II) reagent, $NiBr_2\cdot 2C_2H_4(OCH_3)_2$, and the $B_{10}H_{12}C[N(CH_3)_3]$ were prepared as previously described.[1d,2] Silica gel, 60–200 mesh, was obtained from Baker Chemical Co. Dicyclopentadiene (Aldrich) was converted to C_5H_6 immediately prior to use. Tetrahydrofuran (THF) was freshly distilled from $LiAlH_4$ and collected under nitrogen. THF solutions of NaC_5H_5 were prepared as previously described.[2] Hexane and dichloromethane were distilled over $CaSO_4$.

$(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_8CH_9)$, I. In a nitrogen-flushed 500-ml, three-necked flask equipped with a mechanical stirrer, N_2 inlet, and condenser was placed 6.0 g (31.4 mmol) of $B_{10}H_{12}C[N(CH_3)_3]$ followed by 200 ml of THF. To this was added 2.9 g (126 mmol) of sodium metal cut into small pieces. With stirring, the mixture was brought to reflux and heated 30 hr. Excess sodium was removed and the solution containing the insoluble complex $Na_3B_{10}CH_{11}\cdot 2THF$ was cooled to 0°. To this was added a THF solution of 100 mmol of NaC_5H_5, followed by a THF slurry of 35 g (88 mmol) of $NiBr_2\cdot 2C_2H_4(OCH_3)_2$. The mixture was stirred 1 hr at 0°; then the ice bath was removed and O_2 was bubbled through for $^1/_2$ hr. The mixture was filtered through Celite and added to 30 g of silica gel. The solvent was removed on a rotary evaporator, and the resulting solid was put on a 4 × 30 cm silica gel chromatography column and eluted with hexane.

The complex I eluted rapidly as a yellow band; the solvent was evaporated leaving *ca.* 30 mg of an orange-yellow oil. Two components were identified by high-pressure liquid chromatography on an instrument described previously.[13] Attempted sublimation and thick-layer paper chromatography (CHROMAR Sheet from Mallinckrodt) resulted in very little separation. Thus the two components were separated by the high-pressure technique on a small analytical column.[13] The first compound to elute in hexane was a colorless,

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unidentified oil followed closely by the yellow complex I. Evaporation of the solvent, followed by slow sublimation at room temperature under high vacuum to a cold finger cooled to 10°, yielded *ca.* 5 mg of pure, crystalline I, mp 133–135° (open capillary). Infrared spectrum (CS_2 solution): 2585 (vs), 2535 (vs), 2290 (w), 2125 (m), 1730 (w), 1445 (s), 1265 (w), 1100 (m), 1010 (m), 915 (m), 845 (w), 825 (vs), 755 (m), 705 (m) cm^{-1}.

Continued elution of the silica gel column with CH_2Cl_2–hexane mixtures resulted in the isolation of the following species as previously reported:[2] $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$, $[Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})_2]^{2-}$, and $B_9CH_{10}^-$.

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Registry No. I, 52540-76-8; $B_{10}H_{12}C[N(CH_3)_3]$, 12373-48-7.

Contribution from the Research School of Chemistry,
Australian National University, Canberra, 2600, Australia

Correcting an Error. Effect of Perchlorate Ion on Hg^{2+}-Promoted Hydrolysis of Cobalt(III)-Coordinated Glycine Esters

D. A. Buckingham* and M. Wein

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The recent report[1] that high concentrations of ClO_4^- change the mechanism of hydrolysis of glycine ethyl ester in *cis*-$[Co(en)_2X(glyOEt)]^{2+}$ ions (X = Cl, Br) following removal of X with Hg^{2+} came as a surprise to us since similar experiments in our hands on the same[2] and related[3] compounds had failed to suggest any change in mechanism on varying the electrolyte. Normally, removal of halide as HgX^+ results in the exclusive entry of the carbonyl oxygen into the coordination sphere to form a chelated glycine ester intermediate.[2-4] This intermediate subsequently hydrolyzes by an acid-independent pathway (pH ≤3) with acyl-oxygen bond rupture[5] and without opening of the chelate ring. This is represented by Scheme I. The recent publication[1] claims that at high ClO_4^- concentrations (≥4 *M*) a significant amount of the aquo monodentate ester complex $[Co(en)_2(H_2O)(glyOEt)]^{3+}$ is formed and that this compound is relatively inert and only slowly ($t_{1/2}$ = 23 min) reverts to the chelated ester intermediate by loss of bound water. (See Scheme II.) This claim is contrary to our experience with closely related aquo-β-alanine isopropyl ester[6] and *cis*-aquoglycineamide[7] complexes, and since it was largely based on rather unconvincing pmr results, it seemed important to repeat the experiments. This note reports our results.

Experimental Section

Table I. Spectrophotometric Rate Data[a]

$[Hg(ClO_4)_2]$, *M*	$[NaClO_4]$, *M*	k_{obsd}, min^{-1}	Comments
(a) Following Removal of Bromide from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$			
0.4	0.8	0.53	Total OD change = 0.085
0.4	0.8	0.58	
0.4	3.4	0.17	
0.4	3.4	0.17	
0.4	3.4	0.17	
0.4	3.4	0.16	Total OD change = 0.089
(b) $[Co(en)_2(glyOEt)](ClO_4)_3$			
0.4	0	0.55	
0.4	0	0.26	D_2O–$DClO_4$ solvent
0.4	0.8	0.42	Total OD change = 0.084
0.4	0.8	0.47	
0.4	3.4	0.18	
0.2	3.4	0.18	
0.4	3.4	0.18	
0.4	3.6	0.060	D_2O–$DClO_4$ solvent

[a] At 32°, 487 nm, [Co] = 0.018 or 0.009 *M*, $[HClO_4]$ = 0.2 *M*; 0.1-OD slide wire.

Table II. Pmr Rate Data in D_2O[a]

$[DClO_4]$, *M*	$[Hg(ClO_4)_2]$, *M*	$[NaClO_4]$, *M*	k_{obsd}, min^{-1}
(a) Following Removal of Bromide from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$			
0.1	0.3	0.8	0.30
0.1	0.4	3.6	0.07
0.2	0.3	3.8	0.07
(b) $[Co(en)_2(glyOEt)](ClO_4)_3$			
0.2	0.4	0	0.28
0.2	0.4	3.6	0.055
0.2	0.4	3.6	0.066,[b] 0.060[c]
0.1	0.3	3.8	0.066

[a] At 32° and [Co] ≈ 0.1–0.2 *M*. [b] CH_3 of ethanol. [c] CH_3 of ethyl ester.

The $[Co(en)_2X(glyOEt)]Br_2$ (X = Cl, Br) compounds were prepared by standard procedures;[2] $[Co(en)_2(glyOEt)](ClO_4)_3$ was prepared using dry acetone instead of methanol as in a previously reported method.[8] All other reagents were Analar grade. $Hg(ClO_4)_2$ solutions in H_2O or D_2O were made up as required using HgO and concentrated $HClO_4$ or $DClO_4$. Kinetic data were collected on a Gilford 2400 spectrophotometer (487 nm) and on a Jeol Model JNH 4H-100 spectrometer, at 32°. Chromatographic analyses used Dowex 50W-X2 ion-exchange resin and 1 *M* $NaClO_4$ as eluent.

Results and Discussion

To avoid interference from removal of halide we chose *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ and a relatively high concentration of Hg^{2+} (0.2–0.4 *M*). Under these conditions loss of bromide is very fast ($t_{1/2}$ < 5 sec) and this allows the subsequent fate of the immediate reaction product(s) to be studied quantitatively. Two experiments with *cis*-$[Co(en)_2Cl(glyOEt)](ClO_4)_2$ established that following removal of chloride (0.8 *M* Hg^{2+}) this compound behaved in a manner identical with that of the bromo complex.

Rate data for the reaction following removal of bromide are given in Table I (spectrophotometric, 487 nm) and Table II (pmr). The pmr data were obtained by following the growth of the CH_3 resonance of ethanol or the decay of the ester CH_3 signal, Figure 1. All data were collected at 32°, the nmr probe temperature. Also given are rate data for hydrolysis of the chelated ester using separately prepared $[Co(en)_2(glyOEt)](ClO_4)_3$. The method used in making this complex ensures the absence of coordinated water and its purity was verified by its pmr spectrum (acetone-d_6) and by

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