evaporated, leaving a crystalline residue which was recrystallized from toluene and dried at 60°. The ^1H spectrum in toluene-d_8 included a hydride resonance identical with that of $[(C_6H_5)_2N_3Rh]_3$-C_8H_{12} while the ^{19}F spectrum (phenyl decoupled) of a fresh methylene chloride solution consisted of a temperature-independent singlet at −118.8 ppm (from F-11). On standing, additional resonances appeared at −118.4, −117.3, and −116.4 ppm. The analytical sample was again recrystallized from toluene and dried at 60° for 16 hr *in vacuo* (yield 0.71 g, 21%). *Anal.* Calcd for $C_{44}H_{42}F_6N_9Rh_3$: C, 47.20; H, 3.78; F, 10.18; N, 11.26; mol wt 1120. Found: C, 48.02; H, 3.25; F, 9.82; N, 11.33; mol wt 1190 (freezing point in benzene).

The observed aromatic:vinylic:methylene:hydridic proton nmr ratio was 25:3.3:8.7:5.5 compared with the calculated ratio of 24:4:8:6.

Registry No. I, 36126-19-9; I-F, 36126-20-2; II, 36118-98-6; II-F, 36118-99-7; III, 34840-63-6; IV, 36126-21-3; IV-F, 36126-22-4; V, 36118-96-4; V-F, 36118-97-5; VI, 36059-83-3; VI-F, 36059-84-4; VII, 36118-91-9; VIII, 36126-13-3; VIII-F, 36126-14-4; IX, 36126-15-5; X, 36126-16-6; XI, 36126-17-7; XI-F, 36085-75-3; XII, 12717-64-5; XII-F, 12717-61-2; XIII, 12717-59-8; $[(Ph_3P)_2RhN_3Ph_2]_2$, 12717-67-8; $Ph_2N_3Rh(C_8H_{12})NH_3$, 36118-95-3; $[Ni(N_3Ph_2)_2]_2$, 36126-18-8.

Contribution No. 2119 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Transition Metal and Carborane Derivatives Obtained from Octadecaborane(22)

RAYMOND L. SNEATH[1] and LEE J. TODD*

Received April 17, 1972

Reaction of *n*- or *i*-$B_{18}H_{20}^{2-}$ with a variety of phosphine- and carbonyl-substituted complexes of cobalt, rhodium, nickel, palladium, and platinum produced new metal-borane complexes of the general type $(B_{18}H_{20})M(\text{ligand})_n$. Cyclohexyl isocyanide reacts with *i*-$B_{18}H_{22}$ to form the carborane $B_{18}H_{20}CNH_2C_6H_{11}$. A nonpolar complex $B_{18}H_{20}(py)_2$ has been obtained by the reaction of pyridine with *n*-$B_{18}H_{22}$.

Introduction

Multigram quantities of a mixture of two isomeric $B_{18}H_{22}$ molecules can be conveniently prepared from $B_{10}H_{14}$ by the method of Pitochelli and Hawthorne.[2] Decaborane-14 is converted to $B_{10}H_{10}^{2-}$ which is oxidatively coupled with ferric chloride to form $B_{20}H_{18}^{2-}$. Controlled decomposition of the hydronium salt of $B_{20}H_{18}^{2-}$ yields the mixture of $B_{18}H_{22}$ isomers. The two isomers are separated by the column chromatographic procedure of Plesek and coworkers.[3] The structures of the two isomers have been determined by X-ray studies.[4,5] The $B_{18}H_{22}$ isomers are structurally related to decaborane and can be viewed as two decaborane molecules which are condensed together so that each half shares in common atoms B(6) and B(7) in the decaborane numbering system. These condensed-cage type boron hydrides are of particular interest because of the unique bonding which must be present at the juncture of the cage fragments. Employing reactions which had been successful earlier in decaborane(14) chemistry, we have been able to insert both metal and nonmetal elements into the B_{18} framework. The syntheses and characterizations of these new derivatives are the subject of this paper.

Experimental Section

Apparatus and Materials. The proton nmr spectra were obtained on a Varian HA-100 or HR-220 spectrometer. All boron (^{11}B) nmr spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer and were externally referenced to $BF_3\cdot(C_2H_5)_2O$. Boron spectral integrals were obtained with a Lasico plainimeter.

The infrared spectra for which no solvent is indicated were measured as KBr disks. Infrared spectra were obtained with a Perkin-Elmer 621 or 137 instrument. The absorptions are reported as strong (s), medium (m), or weak (w). Spectra in the visible or ultraviolet range were obtained on a Cary 14 instrument. Mass spectra were obtained on an Atlas CH-7 or AEI MS-9 instrument. Molecular weights were obtained in $CHCl_3$ with a Mechrolab 301-A osmometer.

The $B_{18}H_{22}$ isomers and their salts were made by the method of Hawthorne[2] with the exception that their separation was accomplished by column chromatography using the method of Plesek.[3] $(PPh_3)_2NiCl_2$,[6] *trans*-$(PPh_3)_2Rh(CO)Cl$,[7] and $(Ph_2PCH_2CH_2PPh_2)$-MCl_2 (where M = Ni,[8] Pd,[9] or Pt[10]) were prepared by published methods. $Co_2(CO)_8$ was purchased from Strem Chemicals. Elemental analyses were performed either at the University of Illinois Microanalytical Laboratory or by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

***n*-$B_{18}H_{20}Ni[P(C_6H_5)_3]_2$.** To a stirred slurry of 0.1 g of sodium hydride in 10 ml of dry tetrahydrofuran (THF) was added in small portions 0.2 g (0.92 mmol) of *n*-$B_{18}H_{22}$. Gas evolution was noted and the solution turned bright yellow. The solution was stirred at room temperature for 3 hr and Schlenk filtered into a 25-ml dropping funnel. The solution of $Na_2[n\text{-}B_{18}H_{20}]$ was then added dropwise to a stirred THF solution of 0.6 g (0.92 mmol) of $(Ph_3P)_2NiCl_2$. After all of the $Na_2[n\text{-}B_{18}H_{20}]$ had been added, the solution was stirred at reflux for 12 hr. The solvent was removed under vacuum after adding a small amount of silica gel to the mixture. The products were chromatographed on a silica gel column. Benzene eluted a red fraction. The crude product was crystallized from methylene chloride–hexane to give 0.214 g (27% yield) of *n*-$B_{18}H_{20}Ni(PPh_3)_2$.

The infrared spectrum of the complex contained absorption maxima at 3050 (w), 2416 (w), 1541 (s), 1483 (m), 1439 (s), 1190 (w), 1158 (w), 1093 (s), 1010 (m), 997 (m), 920 (w), 737 (m), 685 (s), 518 (s), 501 (m) cm^{-1}. The proton nmr spectrum of this complex in $CDCl_3$ gave a broad, poorly resolved resonance centered at τ 2.52. The elemental analyses of this compound and the other new compounds reported in this paper are given

---

[1] NIH Predoctoral Fellow, 1968–1971.

[2] A. R. Pitochelli and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 84, 3218 (1962).

[3] J. Plesek, S. Hermanek, and F. Hanousek, *Collect. Czech. Chem. Commun.*, 33, 699 (1968).

[4] P. G. Simpson and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 48, 1490 (1962).

[5] P. G. Simpson, K. Folting, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 85, 1879 (1963).

[6] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, 83, 394 (1961).

[7] D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syn.*, 11, 99 (1969).

[8] G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

[9] M. J. Hudson, R. J. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 40 (1968).

[10] G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).

Table I. Analytical Data for the $B_{18}H_{22}$ Derivatives

	% C		% H		% N		% metal		% B	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
n-$B_{18}H_{20}Ni(PPh_3)_2$	54.32	54.07	6.27	6.26			7.36	7.33		
$(CH_3)_4N[n$-$B_{18}H_{20}Co(CO)_3]$	19.47	19.67	7.47	7.46	3.24	3.87	13.65	13.44		
$(CH_3)_4N[n$-$B_{18}H_{20}Rh(CO)PPh_3]$	40.40	40.02	6.92	6.91	2.07	2.30				
n-$B_{18}H_{20}Ni(diphos)$[a]	46.49	46.60	6.54	6.83			8.72	8.75		
n-$B_{18}H_{20}Pd(diphos)$	43.39	43.37	6.12	6.00			14.80	14.42		
i-$B_{18}H_{20}Ni(diphos)$	46.49	46.43	6.59	6.68			8.74	8.77	28.94	28.56
i-$B_{18}H_{20}Pt(diphos)$	38.57	38.58	5.95	5.61					23.93	23.70
i-$B_{18}H_{20}Pd(diphos)$	43.39	43.62	6.12	6.57						
n-$B_{18}H_{20}(C_5H_5N)_2$	32.20	32.25	8.11	8.01	7.51	7.50				
i-$B_{18}H_{20}CNH_2C_6H_{11}$	25.79	25.61	10.20	10.12	4.30	4.23				
$(i$-$B_{18}H_{18}CNH_2C_6H_{11})Ni(diphos)$	51.20	50.91	7.08	7.41	1.79	1.93	7.50	7.71		

[a] Diphos is the abbreviation for 1,2-bis(diphenylphosphino)ethane.

Table II. Electronic Spectra in Acetonitrile Solutions of $B_{18}H_{22}$ Derivatives

Compd	Maxima, mμ (ε)
n-$B_{18}H_{20}Ni(diphos)$	565 (1200)
	361 (15,400)
	276 (17,350)
n-$B_{18}H_{20}Ni(PPh_3)_2$	404 (1500)
	276 (18,600)
$(CH_3)_4N[n$-$B_{18}H_{20}Co(CO)_3]$[a]	384 (3000)
	336 (3600)
$(CH_3)_4N[n$-$B_{18}H_{20}Rh(CO)PPh_3]$	360 (3600)
	257 (15,200)
n-$B_{18}H_{20}Pd(diphos)$	377 (7000)
	325 (16,000)
i-$B_{18}H_{20}Pt(diphos)$	412 (5440)
	341 (6000)
	292 (22,300)
i-$B_{18}H_{20}Ni(diphos)$	408 (4540)
	341 (5250)
	291 (18,300)
i-$B_{18}H_{20}Pd(diphos)$	356 (18,100)
	266 (26,800)
$B_{18}H_{20}(C_5H_5N)_2$	403 (14,800)
	250 (17,700)
	402 Sh (3150)
$(i$-$B_{18}H_{18}CNH_2C_6H_{11})Ni(diphos)$	353 (7000)
	315 Sh (8000)
	260 (11,000)

[a] In acetone solution.

in Table I. The electronic spectral data for these complexes are given in Table II.

$(CH_3)_4N[n$-$B_{18}H_{20}Co(CO)_3]$. Four hundred milligrams (1.85 mmol) of n-$B_{18}H_{22}$ was converted to n-$B_{18}H_{20}{}^{2-}$ by the procedure described in the previous synthesis. The tetrahydrofuran solution of $Na_2(n$-$B_{18}H_{20})$ was placed in a dropping funnel and then added slowly to a stirred solution of 0.6 g (1.75 mmol) of $Co_2(CO)_8$ in 50 ml of dry THF. The solution was stirred at room temperature for 3 hr. The solvent was removed under vacuum giving a red-brown oil. This was dissolved in a minimum amount of acetone and water was added. Tetramethylammonium chloride precipitated a red-brown solid. The precipitate was collected by filtration and dissolved in acetone and a small amount of silica gel was added. The acetone was then removed under vacuum and the compound was chromatographed on a silica gel column. Methylene chloride eluted a red-orange compound. The compound was crystallized from methylene chloride–hexane giving 0.125 g (20% yield) of $(CH_3)_4N[n$-$B_{18}H_{20}Co(CO)_3]$.

The infrared spectrum of the complex contains absorption maxima at 2916 (w), 2846 (w), 2521 (s), 2075 (s), 2035 (s), 2020 (s), 1478 (m), 1076 (w), 1047 (w), 1018 (w), 990 (w), 941 (m), 914 (w), 843 (w), 764 (w), 664 (w), 539 (m), and 493 (m) cm^{-1}.

n-$B_{18}H_{20}Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$. One hundred milligrams (0.46 mmol) of n-$B_{18}H_{22}$ was converted to $Na_2(n$-$B_{18}H_{20})$ by the procedure described previously in this section. The THF solution of $Na_2(n$-$B_{18}H_{20})$ was added slowly to 0.345 g (0.665 mmol) of $Cl_2Ni(Ph_2PCH_2CH_2PPh_2)$ dissolved in 50 ml of dry THF. The solution was then stirred at reflux for 4 hr. The mixture was filtered and a small amount of silica gel was added to the filtrate. The THF was removed under vacuum and the crude product was chromatographed on a silica gel column. Benzene eluted a dark purple compound which was crystallized from methylene chloride–hexane giving 0.2 g (32% yield) of dark purple $(n$-$B_{18}H_{20})Ni(Ph_2PCH_2CH_2PPh_2)$.

The infrared spectrum of this complex contained absorption maxima at 3054 (w), 2533 (s), 1485 (m), 1433 (s), 1187 (w), 1160 (w), 1097 (m), 993 (m), 910 (w), 809 (w), 734 (m), 689 (s), 522 (s), 514 (m) cm^{-1}. The proton nmr spectrum in $CDCl_3$ solution exhibits a broad, poorly resolved resonance centered at τ 2.66. The complex was too insoluble to observe the methylene proton resonance.

n-$B_{18}H_{20}Pd[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$. One hundred milligrams (0.46 mmol) of n-$B_{18}H_{22}$ was treated in 10 ml of dry THF with excess sodium amalgam. The mixture was stirred at room temperature for 12 hr. The solution was then removed from the reaction flask with a syringe and added dropwise to 0.265 g (0.46 mmol) of $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ in 10 ml of dry THF. The solution was refluxed for 12 hr. The solvent was then removed under vacuum and the compound was chromatographed on a silica gel column. Benzene eluted a red-orange fraction. After evaporation of the eluate to a small volume, it was spotted on four 8-in. × 8-in. silica gel tlc plates. Benzene eluted a bright yellow band. The yellow band was scraped from the plate and the compound was washed off of the silica gel with methylene chloride. The compound was then crystallized from CH_2Cl_2–hexane giving 0.08 g (11% yield) of bright yellow crystals of $(n$-$B_{18}H_{20})Pd(diphos)$.

The infrared spectrum of this complex contained absorption maxima at 3050 (w), 2533 (s), 1483 (m), 1430 (s), 1187 (w), 1160 (w), 1101 (s), 1045 (w), 1022 (w), 993 (m), 906 (w), 809 (w), 727 (s), 697 (s), 684 (s), 668 (m), and 518 (s) cm^{-1}.

$(CH_3)_4N[(n$-$B_{18}H_{20})Rh(CO)P(C_6H_5)_3]$. Two hundred and fifty milligrams (1.12 mmol) of $[(CH_3)_4N]_2[n$-$B_{18}H_{20}]$[13] was stirred at room temperature with 400 mg (1.72 mmol) of $RhCl(CO)(PPh_3)_2$ in 50 ml of acetonitrile for 6 hr. During this period of time, the initial yellow solution had turned dark red. The solvent was then removed under vacuum and the solid was chromatographed on a silica gel column. Methylene chloride eluted a red solid. The solid was crystallized from CH_2Cl_2–hexane to give 50 mg (12% yield) of $(CH_3)_4N[(n$-$B_{18}H_{20})Rh(CO)PPh_3]$. This compound decomposed at 140° without melting.

The infrared spectrum of this complex contained absorption maxima at 3345 (w), 2538 (s), 1976 (s), 1480 (m), 1432 (m), 1181 (w), 1156 (w), 1089 (m), 1043 (m), 1011 (m), 993 (m), 739 (m), and 495 (s) cm^{-1}.

The proton nmr spectrum of this compound in acetone-d_6 exhibited a broad complex resonance centered at τ 2.60 (15 H) and a sharp singlet at τ 6.64 (12 H).

i-$B_{18}H_{20}Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$. To 0.5 g of sodium hydride in 10 ml of dry THF was added 0.5 g (2.23 mmol) of i-$B_{18}H_{22}$. Gas evolution was noted and the solution turned bright yellow. The solution was stirred at room temperature for 4 hr. The solution was Schlenk filtered, placed in a dropping funnel, and added slowly to 1.3 g (2.46 mmol) of $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ dissolved in 50 ml of dry THF. The solution was stirred at room temperature for 4 hr. The solvent was removed under vacuum and the residue was chromatographed on an alumina column. Methylene chloride eluted a red compound. The compound was crystallized from CH_2Cl_2–hexane giving 0.175 g (26 % yield) of $(i$-$B_{18}H_{20})Ni(Ph_2PCH_2CH_2PPh_2)$. The infrared spectrum of the compound exhibited absorption maxima at 3054 (w), 2548 (s), 1480 (m), 1439 (s), 1185 (w), 1156 (w), 1095 (m), 995 (m), 924 (w), 872 (w), 805 (w), 739 (m), 687 (s), 647 (w), and 510 (m) cm^{-1}.

i-$B_{18}H_{20}Pd[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$. Three hundred and fifty milligrams (0.94 mmol) of $[(CH_3)_4N]_2$-i-$B_{18}H_{20}$ was added to 0.510 g (0.94 mmol) of $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ in dry benzene. The reaction was stirred at reflux for 18 hr. The solvent was removed under vacuum and the yellow product was chromatographed on a silica gel column. Toluene eluted a yellow compound which was crystallized from CH_2Cl_2–hexane to give 0.90 g (12.5% yield) of $(i$-$B_{18}H_{20})Pd(Ph_2PCH_2CH_2PPh_2)$.

The infrared spectrum of the compound exhibited absorption maxima at 3050 (w), 2933 (w), 2546 (s), 1459 (s), 1405 (w), 1100 (m), 995 (m), 974 (w), 905 (w), 872 (m), 808 (m), 743 (m), 697 (m), 689 (s), 518 (s), and 480 (m) cm^{-1}.

i-$B_{18}H_{20}Pt[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$. Two hundred and fifty milligrams (1.16 mmol) of i-$B_{18}H_{22}$ was treated with NaH in dry THF. The yellow solution containing i-$B_{18}H_{20}{}^{2-}$ ion was added dropwise to 0.150 g (1.13 mmol) of $(Ph_2PCH_2CH_2PPh_2)$-$PtCl_2$ in 50 ml of THF. The solution was stirred at room temperature for 5 hr. The solvent was removed under vacuum and the orange compound chromatographed on an alumina column. A 1:1 mixture of methylene chloride and chloroform eluted a bright yellow compound which was crystallized from CH_2Cl_2–hexane to give 0.15 g (18.6% yield) of $(i$-$B_{18}H_{20})Pt(Ph_2PCH_2CH_2PPh_2)$. The infrared spectrum of this compound contained absorption maxima at 3041 (w), 2916 (w), 2510 (s), 991 (m), 950 (w), 872 (m), 814 (m), 735 (s), 683 (s), 668 (s), and 514 (s) cm^{-1}.

$B_{18}H_{20}(NC_5H_5)_2$. A benzene solution of n-$B_{18}H_{22}$ (0.5 g, 2.3 mmol) was brought to reflux and a benzene solution of 0.632 g (8 mmol) of pyridine was added slowly to the refluxing solution. The initial colorless solution turned red-orange. After addition of the pyridine, the solution was refluxed for 48 hr. The solvent was removed under vacuum and the compound was spotted onto three 8-in. × 8-in. silica gel tlc plates. Benzene eluted a bright orange band. The band was removed from the plate and the orange compound eluted from the silica gel with CH_2Cl_2. The compound was crystallized from CH_2Cl_2–hexane to give 100 mg (12% yield) of orange crystals of $B_{18}H_{20}(NC_5H_5)_2$.

The infrared spectrum of this compound (KBr disk) exhibited absorption maxima at 2520 (s), 1624 (w), 1487 (m), 1458 (s), 1209 (w), 1172 (w), 1078 (w), 989 (m), 766 (m), and 671 (m) cm^{-1}. The proton nmr spectrum in acetone-d_6 exhibited resonances at τ 2.21 (doublet, 2 H), 2.69 (triplet, 1 H) and 3.11 (quartet, 2 H).

i-$B_{18}H_{20}CNH_2C_6H_{11}$. One-half gram (2.31 mmol) of i-$B_{18}H_{22}$ was dissolved in 20 ml of dry benzene and placed in a dropping funnel. Into another dropping funnel was placed 0.44 g (4 mmol) of cyclohexyl isocyanide in 20 ml of dry benzene. Both solutions were added slowly to 200 ml of dry benzene in a 500-ml flask at room temperature with rapid stirring. The solution was stirred at room temperature for 12 hr. The temperature of the reaction was then raised to 50° and maintained there for 72 hr. The benzene was removed under vacuum and the yellow solids dried on a vacuum line. The solids were soxhlet extracted with hexane for 18 hr. The solids from the extraction cup were dissolved in CH_2Cl_2. A small amount of silica gel was added and the solvent was removed under vacuum. The crude product was chromatographed on a silica gel column and benzene eluted a yellow compound. The yellow solids were then chromatographed on a neutral alumina column with CH_2-Cl_2 which eluted a pale yellow solid. The solid was crystallized from CH_2Cl_2–hexane to give 0.230 g (31% yield) of pale yellow $B_{18}H_{20}CN$-$H_2C_6H_{11}$, mp 216–219°.

The infrared spectrum of this compound (KBr disk) exhibited absorption maxima at 3295 (m), 2825 (m), 2558 (s), 1626 (s), 1464 (w), 1451 (m), 1389 (w), 1368 (w), 1151 (w), 1062 (w), 945 (m), 935 (m), and 728 (m) cm^{-1}. The proton nmr spectrum in acetone-d_6 exhibited resonances at τ 0.68 (2 H), 6.19 (1 H), 8.15 (3 H), 8.35 (3 H) and 8.62 (4 H).

$[i$-$B_{18}H_{18}CNH_2C_6H_{11}]Ni(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. Two hundred and fifty milligrams (0.76 mmol) of i-$B_{18}H_{20}CNH_2C_6H_{11}$ was stirred with excess NaH in dry THF for 12 hr after gas evolution stopped. The yellow solution was removed with a syringe and added dropwise to 0.405 g (0.76 mmol) of $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ dissolved in 50 ml of dry THF. The solution was stirred for an additional 8 hr. The solvent was then removed under vacuum and the solids were chromatographed on a silica gel column. Benzene eluted a brown compound. After the brown compound had been eluted, a dark red compound was eluted with a 3:1 mixture of benzene–CH_2-Cl_2. The red complex was then chromatographed on an alumina column and CH_2Cl_2 eluted a red fraction. The red compound was crystallized from CH_2Cl_2–hexane to give 0.1 g (16.6% yield) of $(i$-$B_{18}H_{18}CNH_2C_6H_{11})Ni(Ph_2PCH_2CH_2PPh_2)$.

The infrared spectrum of this compound as a KBr pellet exhibited absorption maxima at 3275 (w), 3046 (w), 2925 (m), 2846 (w), 2500 (s), 1595 (s), 1483 (m), 1433 (m), 1251 (m), 1187 (m), 1091 (m), 1055 (w), 1014 (m), 993 (w), 735 (m), 689 (m), and 516 (s) cm^{-1}.

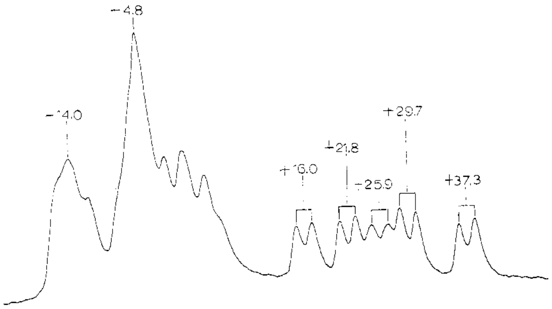

Figure 1. The 70.6-MHz ^{11}B nmr spectrum of $(CH_3)_4N[(B_{18}H_{20})$-$Co(CO)_3]$ in acetone solution referenced to $BF_3{\cdot}O(C_2H_5)_2$.

Results and Discussion

Transition Metal Complexes of the $B_{18}H_{22}$ Isomers. The reaction of $Na_2(n$-$B_{18}H_{20})$ and $(Ph_3P)_2NiCl_2$ in a 1:1 mole ratio in tetrahydrofuran solution produced red $(n$-$B_{18}H_{20})$-$Ni(PPh_3)_2$ in 27% yield. The infrared spectrum of the complex exhibited a strong absorption at 2541 cm^{-1} (terminal B-H stretch), a broad, weak band at 1900 cm^{-1} (a B-H-B bridge frequency), and absorptions at 1483, 1439, 1093, 737, and 685 cm^{-1} which could be attributed to the triphenylphosphine ligand. The elemental analyses of this complex and the others reported in this paper are given in Table I. The proton nmr spectrum of the complex in $CDCl_3$ solution exhibited a poorly resolved multiplet centered at τ 2.52 which is in the region expected for phenyl protons. Reaction of $Na_2(n$-$B_{18}H_{20})$ with $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ under the same conditions described above produced purple $(Ph_2PCH_2CH_2PPh_2)Ni(n$-$B_{18}H_{20})$ in 32% yield. An attempted osmometric molecular weight measurement was hampered by the low solubility of the complex. A rough value of 776 was obtained in chloroform solution (calcd for $C_{26}H_{44}B_{18}NiP_2$: 672). Due to the limited solubility, the ^{11}B nmr spectra of the neutral complexes described in this article could not be obtained. A slightly different procedure was used to obtain a palladium complex in this series. Reaction of n-$B_{18}H_{22}$ with sodium amalgam in tetrahydrofuran and subsequent reaction of the product solution with $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ afforded yellow $(n$-$B_{18}H_{20})Pd$-$(Ph_2PCH_2CH_2PPh_2)$ in 11% yield.

When $Na_2(n$-$B_{18}H_{20})$ was treated with nearly an equimolar amount of $Co_2(CO)_8$ in refluxing THF, the red anionic complex $(n$-$B_{18}H_{20})Co(CO)_3{}^-$ was obtained in 20% yield as the tetramethylammonium salt. The infrared spectrum of this salt contained a strong absorption at 2521 cm^{-1} (terminal B-H stretch) and sharp absorptions at 2075, 2035, and 2020 cm^{-1} attributed to carbonyl stretching vibrations. The 70.6-MHz ^{11}B nmr spectrum of this complex is presented in Figure 1. While this spectrum is too complex for complete interpretation, some interesting points are apparent. The 70.6-MHz ^{11}B nmr spectra of n-$B_{18}H_{22}$ and n-$B_{18}H_{20}{}^{2-}$ contain three and two doublets each of area 2 at high field, respectively. In the ^{11}B nmr spectrum of the cobalt complex there are five doublets, each of area 1 in the +16.0- to +37.3-ppm region. This suggests that the metal atom is bonded to one of the open faces of the n-$B_{18}H_{20}{}^{2-}$ ion, destroying the symmetry of the uncomplexed boron hydride. Stirring an acetonitrile solution of $[(CH_3)_4N]_2[(n$-$B_{18}H_{20})$

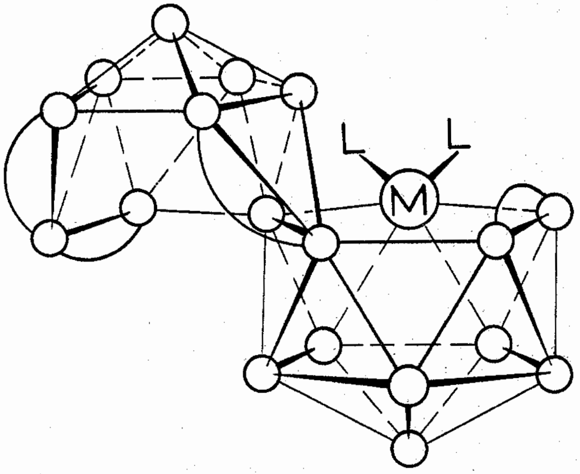

Figure 2. The proposed structure of $(n\text{-}B_{18}H_{20})Ni(PPh_3)_2$ (M = Ni; L = PPh_3).

and $(PPh_3)_2Rh(CO)Cl$ at room temperature for 6 hr gave a 12% yield of red $(CH_3)_4N[(n\text{-}B_{18}H_{20})Rh(CO)PPh_3]$. The infrared spectrum of this complex contained a strong absorption at 2538 cm^{-1} (B–H stretch) and a sharp band at 1976 cm^{-1} (C≡O stretch). The proton nmr spectrum exhibited a multiplet at τ 2.6 of area 15 and a singlet at τ 6.64 of area 12 which are attributed to the protons of the phenyl groups and the protons of the tetramethylammonium ion, respectively. The ^{11}B nmr spectrum of the rhodium complex is very similar to the spectrum of $(CH_3)_4N[(n\text{-}B_{18}H_{20})Co(CO)_3]$ suggesting the same mode of bonding of the $n\text{-}B_{18}H_{20}{}^{2-}$ ligand in the cobalt and rhodium complexes. The reaction of $B_{10}H_{12}{}^{2-}$ with $(Ph_3P)_2Rh(CO)Cl$ was reported to give the yellow complex $(CH_3)_4N[(B_{10}H_{12})Rh(CO)(PPh_3)_2]$.[11] The fact that the corresponding rhodium complex of $n\text{-}B_{18}H_{20}{}^{2-}$ has one less triphenylphosphine ligand may be due to steric crowding about the metal atom by the $n\text{-}B_{18}H_{20}{}^{2-}$ ligand which aids in irreversible dissociation of one of the triphenylphosphine ligands. Alternatively the $B_{10}H_{12}{}^{2-}$ and $n\text{-}B_{18}H_{20}{}^{2-}$ ligands may coordinate with the metal in different ways. A more definitive structural study will be needed to solve this problem.

Metal complexes of $i\text{-}B_{18}H_{20}{}^{2-}$ can be synthesized with equal facility and in comparable yields to the complexes of $n\text{-}B_{18}H_{20}{}^{2-}$. Employing the procedures described above, reaction of $i\text{-}B_{18}H_{20}{}^{2-}$ with the corresponding $(Ph_2PCH_2CH_2PPh_2)MCl_2$ produced $(i\text{-}B_{18}H_{20})M(Ph_2PCH_2CH_2PPh_2)$ where (M = Ni, Pd, Pt). The X-ray study of $[(CH_3)_4N]_2Ni(B_{10}H_{12})_2$ has been reported.[12] We propose that the modes of bonding of the $B_{18}H_{20}{}^{2-}$ and $B_{10}H_{12}{}^{2-}$ ligands to transition metals are similar as illustrated in Figure 2.

Reaction of $B_{18}H_{22}$ with Lewis Bases. The reaction of $B_{10}H_{14}$ with Lewis Bases to form $B_{10}H_{12}$(Lewis base)$_2$ is a general reaction for a large variety of Lewis bases. With triethylamine, *n*- and $i\text{-}B_{18}H_{22}$ are deprotonated to give triethylammonium salts of *n*- and $i\text{-}B_{18}H_{21}{}^-$.[13] Acetonitrile was not observed to react with the $B_{18}H_{22}$ hydrides even under reflux conditions.[13] We observed that reaction of $n\text{-}B_{18}H_{22}$ with pyridine produced a 12% yield of orange $B_{18}H_{20}(C_5H_5N)_2$. This composition was confirmed by elemental analysis and the mass spectrum which cut off at *m/e* 376 corresponding to the parent ion $^{11}B_{18}{}^{1}H_{30}{}^{14}N_2{}^{12}C_{10}{}^+$. The high-resolution mass spectrum of this compound contained a peak at *m/e* 375.4141 (calcd for $^{11}B_{17}{}^{10}B_1{}^{12}C_{10}{}^{1}H_{30}{}^{14}N_2$: 375.4162). The 70.6-MHz ^{11}B nmr spectrum of $B_{18}H_{20}(C_5H_5N)_2$ is given in Figure 3. The large number of boron resonances of unit area in this spectrum suggest that the molecule is unsymmetrically substituted with the pyridine ligands or the system has rearranged. A light yellow crystalline product soluble in very polar solvents is also formed in this reaction. The ^{11}B nmr spectrum of this compound suggests that it is not $n\text{-}B_{18}H_{21}{}^-$ or $n\text{-}B_{18}H_{20}{}^{2-}$. Further study of this material is in progress.

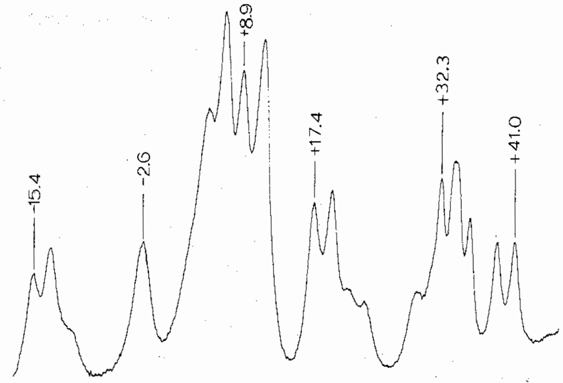

Figure 3. The 70.6-MHz ^{11}B nmr spectrum of $B_{18}H_{20}(py)_2$ in acetone solution referenced to $BF_3 \cdot O(C_2H_5)_2$.

Decaborane-14 reacts with the Lewis base alkyl isocyanide in an unusual manner to produce a one-carbon carborane with the general formula, $B_{10}H_{12}CNH_2R$.[14] Reaction of $i\text{-}B_{18}H_{22}$ with 1 equiv of cyclohexyl isocyanide produced pale yellow $B_{18}H_{20}CNH_2C_6H_{11}$, mp 216–219°, in 31% yield. The infrared spectrum of this compound contained absorptions at 3295 cm^{-1} (N-H stretch) and 1626 cm^{-1} (NH_2 deformation). Proton exchange of the new carborane in $D_2O\text{-}CH_3OD$ resulted in a decrease in intensity of the 3295- and 1626-cm^{-1} bands and the appearance of a new peak at 2410 cm^{-1} (N-D stretch). The proton nmr spectrum of $B_{18}H_{20}CNH_2C_6H_{11}$ in acetone-d_6 solution exhibited complex resonances in the range of τ 6.19–8.62 attributed to the cyclohexyl protons and a broad singlet at τ 0.68 (NH_2 group). When the carborane was deuterated (*vide supra*), the low-field resonance was no longer observed. The mass spectrum of this compound cut off at *m/e* 329 corresponding to the parent ion $^{11}B_{18}{}^{1}H_{33}{}^{14}N_1{}^{12}C_7{}^+$. The high-resolution mass spectrum of this compound contained a peak measured at 329.4272 (calcd for $^{11}B_{18}{}^{1}H_{33}{}^{14}N_1{}^{12}C_7$: 329.4278). The 70.6-MHz ^{11}B nmr spectrum of $B_{18}H_{20}CNH_2C_6H_{11}$ is given in Figure 4. The available spectral data lead us to suggest that the reaction of cyclohexyl isonitrile with $i\text{-}B_{18}H_{22}$ results in insertion of the isonitrile carbon atom into the boron hydride cage to form a one-carbon carborane. We propose the structure presented in Figure 5 for $B_{18}H_{20}CNH_2C_6H_{11}$.

Treatment of $B_{18}H_{20}CNH_2C_6H_{11}$ with sodium hydride in tetrahydrofuran solution resulted in vigorous hydrogen evolution. The solution containing the deprotonated carborane was added to a THF solution of $(Ph_2PCH_2CH_2PPh_2)NiCl_2$. After purification, dark red needle crystals of $(B_{18}H_{18}CNH_2C_6H_{11})Ni(Ph_2PCH_2CH_2PPh_2)$ were obtained in 16% yield. This complex had limited solubility in dimethyl sulfoxide-d_6 and exhibited weak resonances at τ 2.75 and 6.5–9.0 corre-

---

[11] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1, 2072 (1968).

[12] L. J. Guggenberger, *J. Amer. Chem. Soc.*, 94, 114 (1972).

[13] F. P. Olsen, R. C. Vasavada, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 90, 3946 (1968).

[14] D. E. Hyatt, D. A. Owen, and L. J. Todd, *Inorg. Chem.*, 5, 1749 (1966).

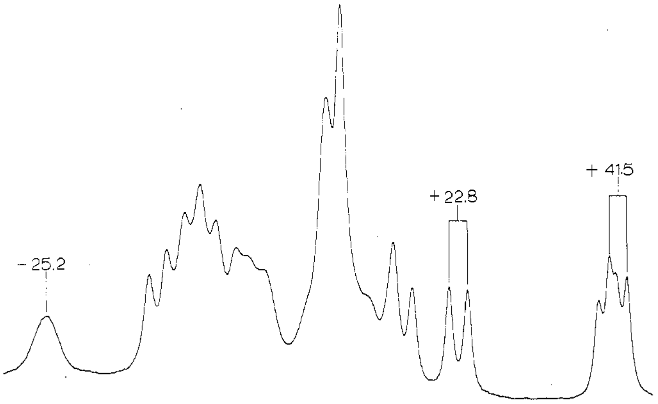

Figure 4. The 70.6-MHz ^{11}B nmr spectrum of $B_{18}H_{20}CNH_2C_6H_{11}$ in acetone solution referenced to $BF_3 \cdot O(C_2H_5)_2$.

sponding to the phenyl and cyclohexyl protons, respectively. We propose that the $CNH_2C_6H_{11}$ group is inserted into one and the $Ni(Ph_2PCH_2CH_2PPh_2)$ group is inserted into the other open face of the B_{18} framework. This gives the most sterically favorable bonding arrangement if framework rearrangements do not occur.

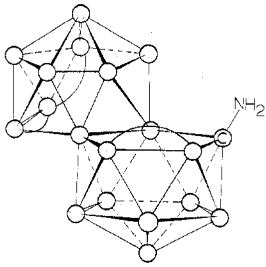

Figure 5. Proposed structure of *i*-$B_{18}H_{20}CNH_2C_6H_{11}$ (R = C_6H_{11}).

Registry No. *n*-$B_{18}H_{20}Ni(PPh_3)_2$, 36182-42-0; $(CH_3)_4N$[*n*-$B_{18}H_{20}Co(CO)_3$], 36182-41-9; $(CH_3)_4N$[*n*-$B_{18}H_{20}Rh(CO)PPh_3$], 36465-07-3; *n*-$B_{18}H_{20}$Ni(diphos), 36182-40-8; *n*-$B_{18}H_{20}$Pd(diphos), 36182-39-5; *i*-$B_{18}H_{20}$Ni(diphos), 36182-45-3; *i*-$B_{18}H_{20}$Pt(diphos), 36182-44-2; *i*-$B_{18}H_{20}$Pd(diphos), 36182-43-1; *n*-$B_{18}H_{20}(C_5H_5N)_2$, 12745-16-3; *i*-$B_{18}H_{20}CNH_2C_6H_{11}$, 12745-15-2; (*i*-$B_{18}H_{18}CNH_2C_6H_{11}$)Ni-(diphos), 12745-17-4.

Acknowledgments. The authors thank Mr. Ron Garber for some of the ^{11}B nmr measurements. This work was generously supported by the Office of Naval Research.

Contribution from the Naval Research Laboratory, Washington, D. C. 20390, and the John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Mass Spectral Studies of Some Manganese Carbonyls

F. E. SAALFELD,*[1a] M. V. McDOWELL,[1a] J. J. DeCORPO,[1a,b] A. D. BERRY,[1c] and A. G. MacDIARMID[1c]

Received April 17, 1972

Mass spectral studies have been carried out on a series of manganese carbonyls: $HMn(CO)_5$, $(CH_3)_3SiMn(CO)_5$, and $(CH_3)_3SiMn(CO)_x(PF_3)_{5-x}$ where x = 2-5. These studies include measurement of the fragmentation patterns and calculation of heats of formation of the compounds and some of their positive ions from appearance potential measurements. The heats of formation of the compounds are as follows (kcal/mol): $HMn(CO)_5$, -237; $(CH_3)_3SiMn(CO)_5$, -423; $(CH_3)_3SiMn(CO)_4(PF_3)$, -638; $(CH_3)_3SiMn(CO)_3(PF_3)_3$, -823; $(CH_3)_3SiMn(CO)_2(PF_3)_3$, -1023; $(CH_3)_3SiMn(CO)(PF_3)_4$, -1223.

Introduction

A large number of mass spectral studies of substituted metal carbonyl compounds have been reported in the literature in recent years.[2-20] Substituent effects, such as the σ-donor and π-acceptor properties, have been correlated with observed changes in the ionization potentials of the substituted metal carbonyls.[9-15] Svec and his coworkers[9,18] and Bidinosti and his students[19] have shown that the average ionic bond energies and average neutral bond energies are related. The findings of this report, summarizing the results of a mass spectral study of the compounds $HMn(CO)_5$, $(CH_3)_3SiMn(CO)_5$, and

---

(1) (a) Naval Research Laboratory. (b) NRC-NRL Resident Research Associate 1970-1972. (c) University of Pennsylvania.

(2) (a) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. J. MacDiarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968); (b) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *Inorg. Chem.*, **7**, 1465 (1968).

(3) F. E. Saalfeld, M. V. McDowell, A. P. Hagen, and A. G. MacDiarmid, *Inorg. Chem.*, **7**, 1665 (1968).

(4) A. G. MacDiarmid, *et al.*, *Pure Appl. Chem.*, **19**, 431 (1969).

(5) A. D. Berry and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **5**, 601 (1969).

(6) A. D. Berry, E. R. Carey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

(7) A. D. Berry, *et al.*, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

(8) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **92**, 2324 (1970).

(9) G. A. Junk, H. J. Svec, and R. J. Angelici, *J. Amer. Chem. Soc.*, **90**, 5758 (1968).

(10) H. J. Svec and G. A. Junk, *Inorg. Chem.*, **7**, 1688 (1968).

(11) W. Hieber and G. Wagner, *Z. Naturforsch. B*, **13**, 339 (1958).

(12) G. A. Junk and H. J. Svec, *J. Chem. Soc. A*, 3171 (1970).

(13) S. Pignataro and F. P. Lossing, *J. Organometal. Chem.*, **11**, 571 (1968).

(14) G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, *J. Organometal. Chem.*, **14**, 165 (1968).

(15) A. Foffani, S. Pignataro, J. Distefano, and G. Innorta, *J. Organometal. Chem.*, **7**, 473 (1967).

(16) D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **48**, 593 (1970).

(17) G. Distefano, A. Foffani, G. Innorta, and S. Pignataro, presented at the International Conference on Mass Spectrometry, Brussels, Aug 31-Sept 4, 1970.

(18) G. A. Junk and H. J. Svec, *Z. Naturforsch. B*, **23**, 1 (1968).

(19) D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

(20) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, "Recent Developments in Mass Spectroscopy," K. Ogata and T. Hayakawa, Ed., University Park Press, Baltimore, Md., 1970, p 1073.