cylinder, the apparatus was set up in a fume hood. Tygon tubing was employed and the THF was maintained at 0° during the diborane addition. After the system was thoroughly flushed with nitrogen, diborane was added without nitrogen until the first acetone trap, which contained ~200 ml of acetone, began to warm. At this point, depending on the rate of diborane addition, the solution contained 3–5 g of diborane/100 ml of the solution. Generally, after the first acetone trap began to warm, diborane addition was continued for an additional 10–20 min. The solution was most conveniently used when its concentration was between 4 and 6 g of diborane/100 ml of solution. The diborane–THF solution was then warmed to room temperature while the system was flushed with nitrogen. The fritted-disk bubbler was removed from the solution and it was replaced with a rubber septum. A known amount (~2 ml) was syringed into a 100-ml flask containing ~20 ml of water and which was connected to a 1-l. graduated cylinder filled with mineral oil. The hydrogen evolution was measured and the concentration of the solution was calculated as follows: grams of diborane per 100 ml of solution = (volume of H_2 (ml)/volume of diborane–THF solution used (ml))(0.0184), at 23° and 740 mm. *Caution! If the diborane–THF solution is permitted to become more concentrated than 8 g of diborane/100 ml of solution, the solution will be spontaneously flammable in air.* It is suggested that when the first acetone trap warms that the concentration be checked. If the concentration is too low, insert the fritted-disk bubbler, flush the system with nitrogen, and continue diborane addition. Diborane–THF solutions containing about 4 g of diborane/100 ml of solution cannot be stored for more than a few hours because at these high concentrations diborane reacts with THF to form *n*-butyl borate.

Preparation of 1,6-$B_8C_2H_{10}$.—This will be given as the general method. Into a 500-ml three-necked round-bottom flask equipped with a nitrogen inlet and a rubber septum were placed 5.0 g (4.42×10^{-2} mol) of $B_7C_2H_{13}$ and 75 ml of diethyl ether. After flushing the system with nitrogen, 0.90 g (2.25×10^{-2} mol) of 60% sodium hydride–mineral oil dispersion was slowly added as a solid. About 15 min after addition, the solution was cooled to 0° and 63 ml (2.5 g, 9.0×10^{-2} mol of diborane) of a 4.0 g of diborane/100 ml of the THF solution was added with a syringe over 5 min. The resulting slurry was stirred for 30 min. Into the slurry was then syringed 5.0 g of $B_7C_2H_{13}$ dissolved in 75 ml of diethyl ether followed by 63 ml of the above diborane–THF solution. The reaction mixture was stirred at 0° for 3 hr and then quickly filtered through a medium-fritted disk filter in air. The ether solvents were fractionated from the product under high vacuum using a vacuum-jacketed Vigreux column (1-in. diameter × 18 in.) which was topped with a sublimation apparatus. The cold finger of the sublimation apparatus was used to control the rate of evaporation of the solvents. After most of the solvent was evaporated, ~15 ml of *n*-pentane was condensed into the apparatus and the product was washed back into the flask. The resulting slurry was placed on a chromatography column packed with silica gel (2-in. diameter × 8 in.) and the product was eluted with *n*-pentane. The fraction containing the product was evaporated to dryness under high vacuum using the above Vigreux column–sublimation apparatus. The product was sublimed under high vacuum at room temperature to a −80° cold finger. The yield was 8.0 g or 74%, which was increased to 82% by washing the chromatography column with methylene chloride and isolating 1.0 g of unreacted $B_7C_2H_{13}$. *Caution! The $B_7C_2H_{13}$ recovered will often spontaneously inflame after being exposed to air for a few minutes.* It should be further purified before assuming that it is safe to store.

C-Monomethyl and C,C′-Dimethyl Derivatives of 1,6-$B_8C_2H_{10}$.—The C-monomethyl and C,C′-dimethyl derivatives of 1,6-$B_8C_2H_{10}$ were prepared by the procedure given for 1,6-$B_8C_2H_{10}$ and using $B_7C_2H_{12}(CH_3)$ and $B_7C_2H_{11}(CH_3)_2$, respectively, as starting materials. The procedure for the isolation of these two derivatives was somewhat different than for 1,6-$B_8C_2H_{10}$. After the chromatography step and evaporation of the pentane, the sublimation apparatus was replaced with an alembic distillation apparatus[6] and the product was distilled under high vacuum at room temperature and was collected at −80°. The yields of the crude C-monomethyl isomer mixture and of the C,C′-dimethyl derivatives were 86 and 85%, respectively, without recovery of unreacted starting carborane.

C-Monophenyl Derivative of 1,6-$B_8C_2H_{10}$.—The C-monophenyl derivative was prepared by the procedure given for 1,6-$B_8C_2H_{10}$ and using $B_7C_2H_{12}(C_6H_5)$ as starting material. The isolation of the product did not require use of the Vigreux column. The product was sublimed under high vacuum at 50° to a −80° cold finger. The yield of 1-(C_6H_5)-1,6-$B_8C_2H_{10}$ was 81%, without recovery of unreacted starting carborane.

Further Purification of 1,6-$B_8C_2H_{10}$ and Its C-Substituted Derivatives.—Because of very small amounts of air and thermally unstable impurities in the products isolated as described above, the 1,6-$B_8C_2H_{10}$ carborane and its C-substituted derivatives, with the exception of the C-phenyl derivative, should be passed under high vacuum through a column (1-in. diameter × 18 in.) heated at 300° and collected with a sublimation or alembic distillation apparatus. This purification step is necessary if the 1,6 isomer will be thermally rearranged to the 1,10 isomer in a sealed glass tube as described elsewhere.[1,2]

Acknowledgment.—We wish to thank the Office of Naval Research for support of this work.

[6] M. F. Hawthorne, *et al.*, *Inorg. Syn.*, **10**, 103 (1967).

CONTRIBUTION NO. 1833 FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation and Characterization of Chlorotri(3-butenyl)phosphinorhodium(I)

BY PETER W. CLARK AND GEORGE E. HARTWELL

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Several transition metal complexes containing bidentate ligands in which one donor is a group V or VI atom and the other an olefin have been prepared, and a few reactions involving the olefin have been reported.[1,2] During an investigation of hydrogenation and hydroformylation mechanisms using ligands of the type $R_mP[(CH_2)_n\text{—}CH\text{=}CH_2]_{3-m}$, where $m = 0, 1,$ or 2 and $n = 0, 1, 2,$ or 3 with various platinum metals, we have prepared and characterized the novel trigonal bipyramidal compound $RhClP(CH_2CH_2CH\text{=}CH_2)_3$ which contains a tetradentate phosphine with three equivalent rhodium–olefin π bonds.

Experimental Section

Phosphorus trichloride (Matheson Coleman and Bell) and 4-bromo-1-butene (Pierce Chemical Co.) were used without further purification. The rhodium complexes $[Rh(CO)_2Cl]_2$ and $[Rh(C_2H_4)_2Cl]_2$ were prepared by the literature methods.[3,4] All solvents were dried before use.

The infrared spectra were recorded on a Perkin-Elmer 137 and a Perkin-Elmer 621 spectrometer and Raman spectra on a Cary 81 spectrometer using the He–Ne laser excitation at 6328 Å. Proton magnetic resonance spectra and the decoupled proton magnetic resonance spectra were obtained with a Varian HA100 spectrometer. The molecular weight was measured using a

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[1] R. Jones, *Chem. Rev.*, **68**, 785 (1968).

[2] R. S. Nyholm, *Suom. Kemistilehti B*, **42**, 165 (1969).

[3] J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211 (1966).

[4] R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

Mechrolab Model 301-A vapor pressure osmometer. Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany. All preparations were carried out under nitrogen.

Preparation of $P(CH_2CH_2CH{=}CH_2)_3$.—This ligand was prepared by a Grignard reaction carried out under an atmosphere of nitrogen in dry diethyl ether. The Grignard was prepared by the slow addition of 4-bromo-1-butene (66.0 g, 0.489 mol) in 150 ml of ether to magnesium turnings (13.2 g, 0.544 g-atom) in 300 ml of refluxing ether. When the formation of the Grignard was complete, phosphorus trichloride (18.7 g, 0.136 mol) in 250 ml of ether was added dropwise to the solution while maintaining the temperature at 0°. Upon completion, the excess Grignard was hydrolyzed with 50 g of ammonium chloride in 250 ml of water. The organic layer was removed, dried (Na_2SO_4), and distilled. The air-sensitive ligand was collected between 65 and 75° at 1 mm pressure; yield 18 ml (54%).

Preparation of $RhClP(CH_2CH_2CH{=}CH_2)_3$.—$P(CH_2CH_2CH{=}CH_2)_3$ (0.50 ml, 2.04 mmol) in 5 ml of benzene was added dropwise over a period of 10 min to a gently refluxing solution of $[Rh(CO)_2Cl]_2$ (0.40 g, 1.03 mmol) in 20 ml of benzene under nitrogen. The solution rapidly turned pale yellow, and after about 15 min of additional refluxing, white crystals of the compound $RhClP(CH_2CH_2CH{=}CH_2)_3$ appeared. The solution was refluxed for another hour, cooled, and filtered. The crystals were washed with small portions of benzene, then ether, and then dried under vacuum to yield 0.53 g (77%) of the product, mp 155° uncorrected. The compound was also prepared from $[Rh(C_2H_4)_2Cl]_2$ under the same conditions, but only in a 32% yield. *Anal.* Calcd for $RhClP(CH_2CH_2CH{=}CH_2)_3$: mol wt 334.6; C, 43.1; H, 6.30; P, 9.25; Cl, 10.59. Found: mol wt 363 (in chloroform); C, 42.88; H, 6.41; P, 9.11; Cl, 10.38.

Discussion

Although a few rhodium(I) ethylene complexes have been isolated, longer chain monoolefin complexes are reported only in solution.[5] Spectral studies on $RhCl(C_2H_4)[(C_6H_5)_3P]_2$ and the related propylene complex indicate the formation constant for the proplyene complex is at least 2000 times smaller than that for ethylene.[6] Wilkinson relates this large difference in formation constants to the inability of $RhCl(C_2H_4)[(C_6H_5)_3P]_2$ to activate hydrogen, while catalytic hydrogenation is easily accomplished at 1 atm for other monoolefins in the presence of $RhCl[(C_6H_5)_3P]_3$. One method of studying these weaker metal–olefin interactions is to take advantage of the chelate effect with the C=C double bond as a part of a tertiary substituted group V molecule. Upon formation of a σ bond between the group V atom and a metal, the olefinic group may also be in a suitable orientation for bonding, particularly if the resulting ring contains 5.5 or 6.5 members (the metal–olefin interaction is considered as centered on the C=C double bond). Using such ligands we have begun a program to study these weaker rhodium–olefin interactions and their relation to the mechanisms of hydrogenation and hydroformylation.

The potentially tetradentate ligand $P(CH_2CH_2CH{=}CH_2)_3$ results in a pale yellow solution of $RhClP(CH_2CH_2CH{=}CH_2)_3$ upon addition to $[Rh(C_2H_4)_2Cl]_2$ or $[Rh(CO)_2Cl]_2$ in refluxing benzene. Air stable, off white crystals of the complex were collected upon cooling the solution. Molecular weight determinations in chloroform indicate a monomeric species, and the complex is nonconducting in chloroform. Conductance measurements in methanol, however, are consistent with a 1:1 electrolyte.

In striking contrast to the complexes of bidentate olefinic ligands,[7] this complex in deuteriochloroform at room temperature shows no sign of free olefin in its proton magnetic resonance spectrum (Figure 1). The spectrum is relatively simple and shows the expected upfield shifts of the olefinic protons upon formation of a metal–olefin bond (Table I), and a decrease in the magnitude of the coupling constants compared with the free ligand. The assigned rhodium–proton coupling

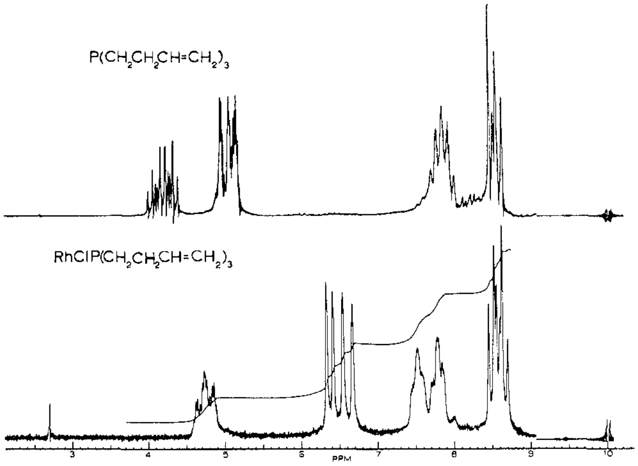
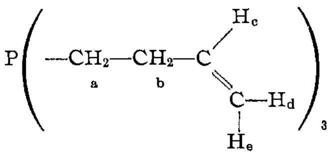


Figure 1.—The 100-MHz pmr spectra in $CDCl_3$.

TABLE I



$$P\left(-\underset{a}{CH_2}-\underset{b}{CH_2}-\overset{H_c}{C}{=}\underset{H_e}{C}-H_d\right)_3$$

Chemical Shift,[a,b] Ppm

Proton	Free ligand	Complex
a	8.52	8.55
b	7.82	7.61
c	4.15	4.71
d	5.06	6.36
e	4.98	6.60

Spin–Spin Coupling Constants[b]

	Free ligand	Complex
J_{bc}	6.0	3.0
J_{bd}	~1.3[c]	<0.5[c]
J_{be}	1.8	<0.5[c]
J_{cd}	10.0	9.0
J_{ce}	17.0	12.5
J_{de}	1.8	<0.5[c]
J_{Rh-c}	...	2.0
J_{Rh-d}	...	~1.5[c]
J_{Rh-e}	...	~1.5[c]

[a] Relative to TMS, τ = 10.0 ppm. [b] Assignments confirmed by homonuclear decoupling. [c] Not fully resolved.

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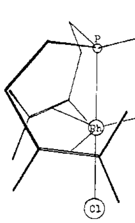
(5) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, p 394.

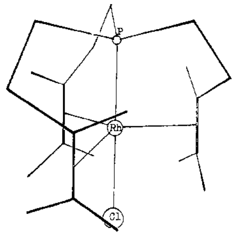
(6) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(7) For example, although the related ligand $(C_6H_5)_2PCH_2CH_2CH{=}CH_2$ functions as a bidentate ligand in rhodium(I) complexes in the solid state, infrared and nuclear magnetic resonance spectral studies in solution indicate equilibria containing nonbonded olefinic groups: unpublished observations.

constants are of the same order as previously observed for ethylene complexes.[8] The simplicity of the spectrum requires the three butene chains to be magnetically equivalent, and structures I and II can be drawn, each an optical isomer with a threefold axis of symmetry.



I



II

The infrared spectrum of the complex in bromoform is in agreement with the spectrum in the solid state (KBr disk, Figure 2) showing no absorption due to free olefin ($\nu(C{=}C)$ = 1639 cm^{-1}). The single strong absorption at 1502 cm^{-1}, due to a C—H bending mode[9] (previously assigned to the carbon–carbon stretch), is consistent with a single type of metal–olefin interaction in the complex. In addition the sequence of absorptions at 791, 810, 860, and 871 cm^{-1}, assigned as olefin C–H out of plane deformations, is consistent with the formation of the rhodium–olefin bonds.

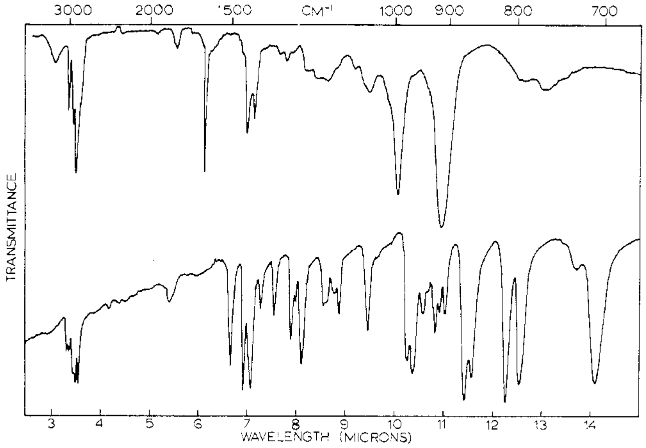
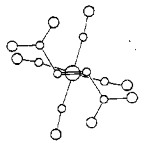


Figure 2.—Infrared spectra of $P(CH_2CH_2CH{=}CH_2)_3$ (top, neat film) and $RhClP(CH_2CH_2CH{=}CH_2)_3$ (bottom, KBr disk).

The Raman spectrum of the complex has all peaks coincidental with the infrared spectrum, as expected for a molecule of C_3 symmetry. There is, however, a striking difference in the intensity of many peaks. The most intense peak in the Raman spectrum is at 417 cm^{-1} (corresponding to an absorption of medium intensity in the infrared) and is assigned as the symmetric ν(Rh–CC) stretching mode. Bands in the 400-cm^{-1} region of platinum(II)–olefin complexes have been assigned to this mode[9] and a related rhodium(I) complex, $[Rh(C_2H_4)Cl]_2$, has a corresponding absorption at 399 cm^{-1}.[10]

Several peaks are noted in the 1200–1300-cm^{-1} region of the Raman spectrum; a single peak at 1236 cm^{-1} (third in decreasing intensity) may be assigned as the $\nu(C{=}C)$, consistent with the recent normal-coordinate analyses of platinum–olefin complexes.[9]

Recent nmr studies of platinum[11] and rhodium[8] complexes indicate that the barrier to free rotation of a coordinated olefin about the metal–olefin axis is 10–15 kcal/mol. The most favorable orientations for the olefin are those that allow maximum overlap between the filled metal d orbitals and the antibonding orbitals on the carbon atoms. An olefin in the equatorial plane of a trigonal bipyramid can accept electron density from the $d_{x^2-y^2}$ or d_{xy} orbitals and if normal to the plane from the d_{xz} or d_{yz} orbitals of the metal. When this latter set of orbitals is also involved in bonding to the apical atoms, the planar configuration for the olefin appears more favorable for back-bonding. The molecular structures of several trigonal-bipyramidal iron tetracarbonyl monoolefin compounds have been determined[12–16] and in each case the olefin occupies an equatorial position with the axis of the carbon–carbon double bond within the equatorial plane or, due to steric interactions, inclined to the plane. For example, the crystal of (−)-(fumaric acid)$Fe(CO)_4$ contains three crystallographically distinct molecules, one with the olefin in plane and the other two with the olefin tilted 17° out of plane (III).[16]



III

Molecular models of $RhClP(CH_2CH_2CH{=}CH_2)_3$ can be constructed with either configuration for the carbon–carbon double bond (I and II). Neither seems preferred upon consideration of nonbonding interactions alone, but we favor structure I with all three carbon–carbon double bonds contained in the equatorial plane, or inclined to this plane in agreement with the structures of the monoolefin iron tetracarbonyl complexes and the configuration of one of the ligands in the complex $RhCl[(C_6H_5)_2PCH_2CH_2CH{=}CH_2]_2$ which was shown to exist as a distorted trigonal bipyramid.[17] *trans,trans, trans*-Cyclododeca-1,5,9-trienenickel(0) has a similar arrangement of three olefinic bonds about a metal in a trigonal plane.[18]

The complex $RhClP(CH_2CH_2CH{=}CH_2)_3$ thus contains three stable $5^1/_2$-membered rings on a trigonal bipyramid and exhibits unusual stability to dissociation of these rhodium–olefin bonds in solution, a consequence of the chelate effect for a tetradentate ligand.

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(8) R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 2519 (1969).

(9) J. Hiraishi, D. Finseth, and F. A. Miller, *Spectrochim. Acta*, **25A**, 1657 (1969).

(10) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(11) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

(12) A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

(13) D. Bright and O. S. Mills, *Chem. Commun.*, 211 (1966).

(14) P. Corradini, C. Pedone, and A. Sirigu, *ibid.*, 341 (1966).

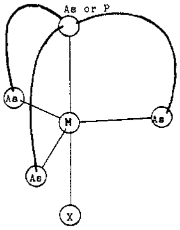
(15) M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **7**, 222 (1968).

(16) C. Pedone and A. Sirigu, *Inorg. Chem.*, **7**, 2614 (1968).

(17) P. W. Clark, G. E. Hartwell, R. R. Ryan, and R. O. Schaeffer, to be submitted for publication.

(18) B. Bogdanović, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966).

Although a number of five-coordinate rhodium(I) complexes have been reported in the past few years, a regular trigonal bipyramidal structure is not yet known. Rhodium compounds whose structures have been determined, *e.g.*, $RhCl[(C_6H_5)_2PCH_2CH_2CH{=}CH_2]_2$,[17] $RhH(CO)[(C_6H_5)_3P]_3$,[19] and $RhH[(C_6H_5)_3P]_4$,[20] show varying degrees of distortion from the regular geometry. The solid-state structure (IV) of two compounds with tetradentate ligands related to $P(CH_2CH_2CH{=}CH_2)_3$ but containing four group V atoms have been reported, $[PtI(QAS)][B(C_6H_5)_4]$[21] and $[Ni(CN)(TAP)]ClO_4$[22] (where QAS is tris(*o*-diphenylarsinophenyl)arsine and TAP is tris(3-dimethylarsinopropyl)phosphine). Each has a threefold axis but deviates from the trigonal bipyramidal structure by having the metal slightly out of the trigonal plane, toward the iodide ligand in the platinum compound but toward the apical phosphorus atom in the nickel compound. There is, therefore, no compelling reason to believe that all six olefinic carbons and the rhodium atoms will be strictly coplanar in $RhClP(CH_2CH_2CH{=}CH_2)_3$.[23]



IV

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors thank Mr. P. W. Koeneman for obtaining the Raman spectra.

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[19] S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

[20] R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

[21] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961).

[22] D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3424 (1967).

[23] Following submission of this article for publication, the solid state structure of $RhClP(CH_2CH_2CH{=}CH_2)_3$ was determined by M. M. Orrico, J. C. Huffman, and W. E. Streib, to be submitted for publication. The structure of the racemic compound agrees with structure I. The olefinic bonds are inclined to the equatorial plane of a trigonal bipyramid and the rhodium atom is slightly out of this plane toward the chloride ligand.

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Preparation and Characterization of Alkali Metal Hydride Complexes of Bis(pentafluorophenyl)zinc. Evidence for a Double Hydride Bridge

BY GREGORY J. KUBAS AND D. F. SHRIVER[1]

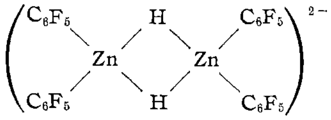
Received March 18, 1970

The following mobile equilibrium exists between dialkylzinc hydride complexes in dimethoxyethane[2]

$$R_2Zn + MHZnR_2 = MR_2Zn\text{-}H\text{-}ZnR_2$$

where R = CH_3 or C_2H_5; M = Li or Na. The 1:1 complex $MHZnR_2$ is monomeric in tetrahydrofuran solution while the 1:2 complex $MR_2ZnHZnR_2$ appears to exist as a singly hydride bridged species.[2] By contrast, diphenylzinc forms only 1:1 complexes with LiH or NaH, but these complexes are too insoluble for easy characterization in solution.[2] Therefore, their degree of aggregation is unknown.

The present study of pentafluorophenylzinc hydride complexes was initiated with the thought that the relatively high Lewis acidity of $Zn(C_6F_5)_2$ would promote the formation of strong zinc hydride bonds. Two unexpected results were the greater solubility of the pentafluorophenylzinc hydride complexes than their phenyl counterparts and the observation of Zn–H stretch and deformation frequencies. Molecular weight measurements in diethyl ether and infrared spectra indicate that these complexes may involve a double hydrogen bridge



Results and Discussion

Molecular weight measurements were facilitated by the high solubility of $NaHZn(C_6F_5)_2$ in diethyl ether at 0°. From the dimeric nature of the compound, illustrated by the data in Table I, it is tempting to postulate a double hydrogen bridge structure such as that illustrated above. As expected for ether solution the sodium ions are ion paired with the anion.

The number of ether molecules coordinated to each sodium ion can be roughly determined by correcting the molecular weights for various degrees of solvent coordination.[2] It may be seen in Table I that a solvation number in the range of 1–2 will yield the most consistent set of molecular weights. This result agrees with a model involving tight (inner-sphere) ion pairing between Na^+ and the anion. Presumably, the alkali metal ions are associated with the hydride bridge atoms in a structure analogous to that of $[NaHBe(C_2H_5)_2]_2 \cdot 2(C_2H_5)_2O$.[3]

TABLE I
MOLECULAR WEIGHT DETERMINATION OF $NaHZn(C_6F_5)_2$ IN DIETHYL ETHER AT 0°

Mole fraction solvent	Mol wt		
	Obsd	Cor[a]	Cor[b]
0.9555	757	897	1108
0.9659	789	897	1052
0.9727	795	883	996
0.9827	808	863	929
0.9859	818	865	917
0.9892	828	863	902

[a] Corrected for solvent coordination, assuming two molecules of diethyl ether coordinating to each sodium ion. [b] Corrected for solvent coordination, assuming four molecules of diethyl ether coordinating to each sodium ion. The calculated molecular weight for $[NaHZn(C_6F_5)_2]_2$ is 844.

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[1] Alfred P. Sloan Research Fellow 1967–1969, addressee for correspondence.

[2] G. J. Kubas and D. F. Shriver, *J. Amer. Chem. Soc.*, **92**, 1949 (1970).

[3] G. W. Adamson and H. M. M. Shearer, *Chem. Commun.*, 240 (1965).