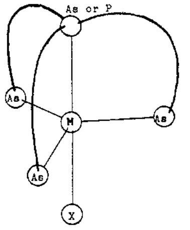
Although a number of five-coordinate rhodium(I) complexes have been reported in the past few years, a regular trigonal bipyramidal structure is not yet known. Rhodium compounds whose structures have been determined, *e.g.*, $RhCl[(C_6H_5)_2PCH_2CH_2CH{=}CH_2]_2$,[17] $RhH(CO)[(C_6H_5)_3P]_3$,[19] and $RhH[(C_6H_5)_3P]_4$,[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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[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]

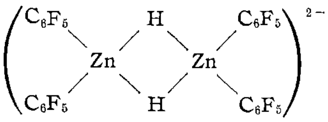
Received March 18, 1970

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°

	Mol wt		
Mole fraction solvent	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).

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Unlike previously characterized organozinc hydride complexes, which yield low-field ^1H nmr resonances,[2] the pentafluorophenyl derivatives cannot be readily studied by proton nmr since diethyl ether solutions give spectra which show peaks due to the solvent only. A similar situation was previously encountered for diethyl ether solutions of $NaHZn(C_6H_5)_2$. In that case it was possible to observe a signal at 4.33 ppm downfield from tetramethylsilane when the complex was studied in tetrahydrofuran.[2] Unfortunately, attempts to prepare $NaHZn(C_6F_5)_2$ in tetrahydrofuran were not successful.

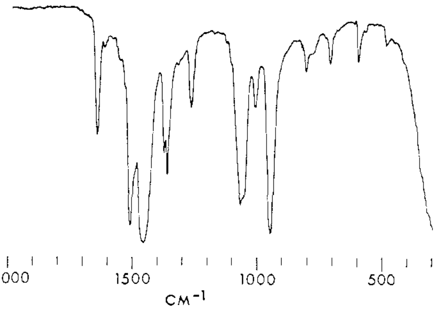

Figure 1.—Infrared spectrum for a Nujol mull of $Zn(C_6F_5)_2$. The two bands between 1400 and 1600 cm^{-1} are due to $Zn(C_6F_5)_2$, but the shoulder at 1375 cm^{-1} is a Nujol absorption.

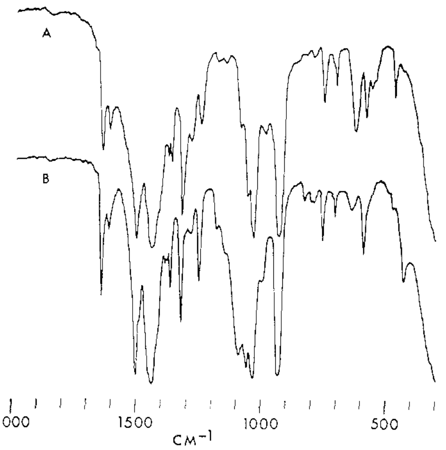

Figure 2.—Infrared spectra for Nujol mulls of (A) $NaHZn(C_6F_5)_2$ and (B) $NaDZn(C_6F_5)_2$.

Infrared studies of ether-free lithium and sodium salts of bis(pentafluorophenyl)zinc hydrides reveal zinc–hydrogen stretching and deformation frequencies. Comparison of Figure 1 with Figure 2A shows a broad underlying feature in the 1300–1700-cm^{-1} region for $NaHZn(C_6F_5)_2$. In the spectrum of the deuterium analog, this band is shifted to the 1000–1200-cm^{-1} region. These zinc–hydrogen stretching frequencies are *ca.* 50 cm^{-1} lower than those found for the analogous phenyl derivatives. These frequencies are much lower than the value of 1825 cm^{-1} reported for $[HZnN(CH_3)C_2H_4N(CH_3)_2]_2$,[4] which is known to contain terminal hydrogens bonded to Zn.[5] This large difference between the Zn–H frequencies indicates the presence of bridging hydrogens in the pentafluorophenyl complexes. A deformation frequency is observed at 625 cm^{-1} for $NaHZn(C_6F_5)_2$ and at 770 cm^{-1} for the lithium salt. The large influence of the cation indicates that the alkali metal is associated with the hydride in the solid state. Upon finding the deformation frequencies[6] for these pentafluorophenyl complexes, we reexamined the spectra of $LiHZn(C_6H_5)_2$ and $LiDZn(C_6H_5)_2$ where deformation frequencies were found at 788 and 552 cm^{-1}, respectively. As may be seen in Table II these frequencies are similar in the phenyl- and pentafluorophenylzinc hydride complexes.

TABLE II

INFRARED ABSORPTION FREQUENCIES FOR Zn–H OR Zn–D MODES

Compound	Asym str, cm^{-1}	Asym def, cm^{-1}	ν_H/ν_D[a]
$NaHZn(C_6F_5)_2$	1300–1700	625	1.46
$NaDZn(C_6F_5)_2$	1000–1200	426	
$LiHZn(C_6F_5)_2$	. . .	770	1.47
$LiDZn(C_6F_5)_2$	. . .	523	
$LiHZn(C_6H_5)_2$	1250–1650	788	1.43
$LiDZn(C_6H_5)_2$	900–1200	552	

[a] Isotopic ratio for deformation frequencies.

In summary, $NaHZn(C_6F_5)_2$ has been characterized as a dimeric species in diethyl ether solution. The molecular weight data in conjunction with infrared spectra indicate that the compound contains double hydrogen bridges.

Experimental Section

Bis(pentafluorophenyl)zinc was prepared as a crystalline solid by the procedure of Noltes and Van den Hurk,[7] using standard Schlenk techniques. Lithium hydride (Matheson Coleman and Bell), sodium hydride (Fluka), lithium deuteride (Metal Hydrides, Inc.), and sodium deuteride (Fluka) were used as obtained. All solvents were distilled under nitrogen and stored over hydrides in glass containers equipped with Teflon-in-glass needle valves and O-ring joints. Vacuum-line and drybox techniques used for all preparations, manipulations, and analyses have been described previously.[2,8]

$NaHZn(C_6F_5)_2$ was prepared by stirring $Zn(C_6F_5)_2$ (0.7 g, 1.7 mmol), NaH (0.2 g, 9 mmol), and diethyl ether (3 ml) for 39 hr at 0°. Separation from excess NaH by filtration followed by solvent removal under high vacuum produced a finely divided white solid, which was shown to be free from coordinating ether by infrared spectra (Fluorolube mull). This compound is much more soluble than the analogous $NaHZn(C_6H_5)_2$, especially at 0°. *Anal.* Calcd for $NaHZn(C_6F_5)_2$: Na/Zn/H, 1/1/1. Found: Na/Zn/H, 1.00/1.00/1.03. $NaDZn(C_6F_5)_2$, $LiHZn(C_6F_5)_2$, and $LiDZn(C_6F_5)_2$ were prepared similarly, although longer reaction periods (60–90 hr) were necessary for the lithium salts, which formed oily residues upon solvent removal. *Anal.* Calcd for $LiHZn(C_6F_5)_2$: Zn/H, 1.00. Found: Zn/H, 1.12. The use of tetrahydrofuran as solvent resulted in incomplete reaction after 36 hr of stirring $Zn(C_6F_5)_2$ with NaH (Zn/H = 1.74).

Infrared spectra were obtained on Nujol or Fluorolube mulls between KBr plates using a Beckman IR 10. Molecular weight determinations were performed using vapor pressure depression techniques,[8] at 0 ± 0.01°. Depressions of 2–8 ± 0.05 mm were observed. Solute concentrations were varied by solvent removal.

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Proton nmr spectra were recorded on a Varian A-60. Attempts were made to obtain Raman spectra on an instrument employing a SPEX 1400-II double monochromator and Ar ion laser excitation. The samples decomposed in the laser beam even when cooled to −100°.

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Preparation and Properties of Some Rare Earth and Americium Chelates

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Received December 19, 1969

Our continuing interest in methods for the separation of actinide elements has been directed to the volatile chelates of the lanthanides.[1–6] The assumption that trivalent lanthanides and actinides have similar properties was justified by the finding, reported herein, that americium chelates are volatile. 2,2,6,6-Tetramethyl-3,5-heptanedione (Hthd) was used to prepare the compound ^{243}Am(thd)$_3$ by the method of Eisentraut and Sievers[1] and 1,1,1,5,5,5-heptafluoro-2,4-pentanedione (Hhfa) was used to prepare Cs^{243}Am(hfa)$_4$ by a modification of the method of Lippard.[2] (See Table I.) Likewise a number of these chelates of the lanthanide elements were prepared for a direct comparison of properties. Elemental analyses were made for at least one representative of each crystal structure type. Identification of other members of isomorphous series were made by X-ray diffraction.

TABLE I
ANALYTICAL DATA FOR RARE EARTH AND AMERICIUM CHELATES CsM(hfa)$_4 \cdot n$H$_2$O

		% compn												
		C		H		H$_2$O		Cs		M^{3+}		Equiv wt[c]		
M	*n*	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C
Am	0	19.9	17.3	0.33	0.50			10.9	11.6	19.9	20.2			193–194
La[a]	1	21.5	21.7	0.54	0.39	1.61	1.50	11.9	11.2	12.4	11.9	1118	1121	186–187
Ce[b]	1					1.61	1.20					1119	1135	180–182
Pr[b]	1					1.60	1.62					1120	1126	188–189
Nd	0	21.6	21.6	0.36	0.38	0	0.07					1105	1103	191–192
Nd	1	21.3	21.5	0.53	0.43	1.6	2.2					1123	1143	189–191
Sm[b]	0											1111	1108	206–208
Eu	0	21.6	21.3	0.36	0.33	0	0.2	11.9	12.1			1113	1108	208–211
Tb[b]	0											1120	1135	216–220
Tm[b]	0											1130	1151	262–265

[a] Per cent F: found, 39.9; calcd, 40.8. [b] Identity established with X-ray powder diagram. [c] Titration in glacial acetic acid with perchloric acid.

All of the compounds except Nd(thd)$_3 \cdot$DMF and Am(thd)$_3$ were obtained as single crystals suitable for X-ray diffraction study. With these specimens the crystallographic data presented in Table II were obtained. Three of the structure types represented there have been the subject of crystal structure determinations. CsEu(hfa)$_4$ (and anhydrous CsAm(hfa)$_4$) was shown[7] to be composed of chains of Eu(hfa)$_4^-$ and Cs$^+$ ions. Between the chains there are only F···F contacts, which suggests the reason for its volatility. For Pr(thd)$_3$, which is isomorphous with the Nd(thd)$_3$ and Am(thd)$_3$ compounds listed here, a structure analysis by Erasmus and Boeyens[8] has revealed the presence of Pr$_2$(thd)$_6$ dimers packed together in a molecular crystal. We have carried out a refinement of this structure using X-ray diffractometer data from Nd(thd)$_3$ crystals, providing some additional details of thermal motion.[9] The crystal structure of CsLa(hfa)$_4 \cdot$H$_2$O is under investigation by Sands and coworkers.[10]

All of the CsLn(hfa)$_4$ compounds sublimed under vacuum in the temperature range 135–150° with little decomposition. The monohydrate of the lanthanum compound sublimed with little loss of water, as indicated by X-ray powder patterns and Karl Fischer analyses. There was an apparent loss of water on subliming CsNd(hfa)$_4 \cdot$H$_2$O with differences in the X-ray powder patterns occurring. Water analyses on the sublimate indicated 0.7% water, less than half that required by the monohydrate (1.59%). Both Nd(thd)$_3 \cdot$DMF and Nd(thd)$_3 \cdot$2DMF lost all of their DMF on heating *in vacuo* and reverted to Nd(thd)$_3$.

The compound Cs$_2$La(hfa)$_5$ is an analog of the type reported by Richardson, Wagner, and Sands;[4] (pyH)$_2$Ln(hfa)$_5$, where py is pyridine and Ln either La, Pr, or Nd. We agree with their speculation that the lanthanide in these compounds may be ten-coordinated.

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