of metal thiocyanates with decaborane in ethereal media is precisely described as

$$x R_2O + M^+SCN^- + B_{10}H_{14} \longrightarrow H_2 + M^+B_{10}H_{12}NCS(OR_2)_x{}^-$$
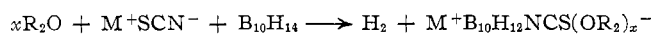
Earlier[1] we reported that such $B_{10}H_{12}X^-$ salts can be recrystallized from water; however, we find now that this is not a general property of these salts. Dissolution of the isothiocyanate derivative in water is accompanied by vigorous hydrogen evolution, and the only anionic species we have successfully isolated from aqueous solutions is $B_9H_{13}NCS^-$. We also found that this ion can be alternatively prepared in high yield through the reaction of decaborane with an aqueous dioxane solution of potassium thiocyanate.

Formation of $B_9H_{13}NCS^-$ in water–dioxane media must proceed through initial reaction of thiocyanate ion and decaborane. The alternative of decaborane ionization to $B_{10}H_{13}^-$ followed by thiocyanate ion addition can be rigorously excluded. We found no evidence of reaction between thiocyanate ion and $B_{10}H_{13}^-$ in *aqueous* dioxane. For example, dissolution of $(CH_3)_4$-$N^+B_{10}H_{13}^-$ in water–dioxane and in water solutions of thiocyanate ion did not yield any borane species containing the NCS group. Salts of $B_{10}H_{13}^-$ were recovered on short solution exposures and $B_9H_{14}^-$ salts[2] on long (>1 min.) exposures. Thiocyanate ion does, however, add to $B_{10}H_{13}^-$ in *anhydrous* ethereal media to give $B_{10}H_{13}NCS^{2-}$.

This behavior of thiocyanate ion contrasts sharply with that of aqueous BH_4^-, CN^-, NH_3, and OH^-, which react with $B_{10}H_{14}$ to yield $B_{10}H_{14}^{2-}$, $B_{10}H_{13}$-CN^{2-}, $B_{10}H_{13}NH_3^-$, and $B_{10}H_{13}OH^{2-}$, respectively.[3-6] Moreover, we found that addition of $B_{10}H_{13}^-$ salts to aqueous solutions of CN^-, BH_4^-, and OH^- gave $B_{10}H_{13}CN^{2-}$, $B_{10}H_{14}^{2-}$, and $B_{10}H_{13}OH^{2-}$, respectively.[7] The rate of addition to $B_{10}H_{13}^-$ is very high for cyanide ion and relatively low for the other species.

Experimental

Potassium thiocyanate (0.02 mole) which had been rigorously dried under vacuum and decaborane (0.02 mole) were added to 60 ml. of dimethoxyethane, and the reaction mixture was stirred for 2 hr. During this time, hydrogen evolved (*ca.* 0.02 mole). Dioxane (60 ml.) was added, and the reaction mixture was concentrated until solid began to form. The solid was redissolved in warm dioxane which contained about 10% dimethoxyethane. This solution was filtered and then concentrated at about 10°

(2) $B_{10}H_{13}^-$ hydrolysis to $B_9H_{14}^-$ is relatively fast.
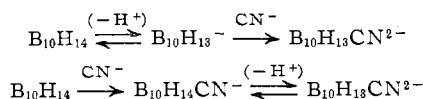
(3) E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

(4) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(5) E. L. Muetterties, to be published.

(6) L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Am. Chem. Soc.*, **85**, 2674 (1963).

(7) This establishes that these species can add to $B_{10}H_{13}^-$ but it does not distinguish between the two possible reaction sequences for the aqueous decaborane reactions, *e.g.*,

$$B_{10}H_{14} \underset{(-H^+)}{\rightleftharpoons} B_{10}H_{13}^- \xrightarrow{CN^-} B_{10}H_{13}CN^{2-}$$

$$B_{10}H_{14} \xrightarrow{CN^-} B_{10}H_{14}CN^- \underset{(-H^+)}{\rightleftharpoons} B_{10}H_{13}CN^{2-}$$

In the cyanide and borohydride ion reactions there is no detectable yellow coloration attributable to a $B_{10}H_{13}^-$ intermediate but there is in the KOH reaction. The rate of CN^- addition to $B_{10}H_{13}^-$ is so fast that these data are not definitive. However, borohydride ion addition to $B_{10}H_{13}^-$ is slow. Therefore, we suggest that in the $B_{10}H_{14}$–BH_4^- reaction $B_{10}H_{15}^-$ is the important intermediate.

until a crystalline phase separated. The solid was collected by filtration and vacuum dried for 24 hr. *Anal.* Calcd. for KB_{10}-$H_{12}NCS \cdot 2.25OC_4H_8O$: C, 28.9; H, 7.28; K, 9.41; B, 26.1; N, 3.38; S, 7.70. Found: C, 29.0; H, 7.47; K, 8.72; B, 26.1; N, 3.41; S, 7.52.

The above reaction procedure was followed, and the reaction product was dissolved in water. There was an immediate and brisk evolution of hydrogen. A concentrated solution of tetramethylammonium chloride was added to the solution, and an oil formed. On warming, the oil solidified. The solid was collected by filtration and recrystallized from a hot water–methanol mixture. *Anal.* Calcd. for $(CH_3)_4NB_9H_{13}NCS$: C, 25.0; H, 10.4; B, 40.4; S, 13.3. Found: C, 25.2; H, 10.6; B, 40.1; S, 13.3. Major infrared absorptions of $(CH_3)_4NB_9H_{13}NCS$ in a Nujol mull, exclusive of Nujol bands, are at ~2500 (BH), 2150 (CN), 1470, 1060, 1040, 1020, 1005, 980, 950, 860, 735, and 715 cm.$^{-1}$.

Decaborane (0.02 mole) was added to a mixture of 50 ml. of a saturated potassium thiocyanate solution in water and 35 ml. of water. Then 45 ml. of dioxane was added. On addition of the ether, decaborane dissolved rapidly with much hydrogen evolution to give a yellow solution. After 1 hr., the solution was diluted with 100 ml. of water and filtered. To the filtrate was added tetramethylammonium chloride solution to give a precipitate. The precipitate was collected and was recrystallized from hot water containing a small amount of methanol. *Anal.* Calcd. for $(CH_3)_4NB_9H_{13}NCS$: C, 25.0; H, 10.4; N, 11.6; B, 40.4; S, 13.3. Found: C, 25.4; H, 10.4; N, 11.6; B, 40.1; S, 13.4.

Anhydrous potassium thiocyanate (3.9 g., 0.02 mole) and the tetramethylammonium salt of $B_{10}H_{13}^-$ (1.94 g., 0.02 mole) were added to a mixture of dimethoxyethane (200 ml.) and dioxane (200 ml.). As the slurry was stirred, the B_{10} salt rapidly went into solution, leaving behind the large potassium thiocyanate crystals. After about 10 min. of stirring, the thiocyanate crystals were not visible, and a white solid had separated. Stirring was continued for 1 hr. and then the slurry was filtered. The solid was washed thoroughly with dimethoxyethane and dioxane. The solid was recrystallized from hot water containing a small amount of methanol, m.p. 295–300°. *Anal.* Calcd. for $[(CH_3)_4$-$N]_2B_{10}H_{13}NCS$: C, 33.0; H, 11.4; B, 33.1; N, 12.8; S, 9.78. Found: C, 33.5; H, 11.5; B, 33.4; N, 12.8; S, 9.78. The infrared spectrum of this salt is quite rich; absorptions exclusive of the Nujol region are at ~2500 (BH), 2160 (CN), 1480, 1405, 1280, 1175, 1106, 1005, 970, 945, 793, 725, 698, and 665 cm.$^{-1}$. This derivative of $B_{10}H_{14}^{2-}$ degrades in acidic media to B_9H_{13}-NCS^-.[8]

(8) Analogous degradations in acidic media have been reported by B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

Contribution from the Department of Chemistry,
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Ligand Rearrangement in Cyclooctadiene by Palladium(II) and Platinum(II) π Complexes

By Herschel Frye, Ernest Kuljian, and James Viebrock

Information concerning the complexes of palladium-(II) and platinum(II) with 1,5-cyclooctadiene is available in the papers of Chatt[1] and of Fischer and

(1) L. Chatt, *J. Chem. Soc.*, 3340 (1949); see also J. Chatt and L. Duncanson, *ibid.*, 2239 (1953), and J. Chatt, L. Vallarino, and L. Venanzi, *ibid.*, 2496 (1957).

TABLE I

PHYSICAL AND ANALYTICAL DATA FOR COMPLEXES

Metal compound	Olefin	Formula of complex	Yield, %	M.p., °C.	Mol. wt. Calcd.	Mol. wt. Found	Calculated % C	Calculated % H	Found % C	Found % H
K$_2$PdCl$_4$	1,5-COD	(C$_8$H$_{12}$)PdCl$_2$	85	205 dec.	235.5	280	33.66	4.23	33.80	4.25
K$_2$PdCl$_4$	1,3-COD	(C$_8$H$_{12}$)PdCl$_2$	58	205 dec.	235.5	280	33.66	4.23	33.74	4.25
K$_2$PdBr$_4$	1,5-COD	(C$_8$H$_{12}$)PdBr$_2$	80	207 dec.	374.4	384	25.66	3.23	25.69	3.25
K$_2$PdBr$_4$	1,3-COD	(C$_8$H$_{12}$)PdBr$_2$	74	207 dec.	374.4	388	25.66	3.23	25.66	3.24
K$_2$PtCl$_4$	1,5-COD	(C$_8$H$_{12}$)PtCl$_2$	58	270 dec.	374.2	390	25.68	3.24	25.65	3.23
K$_2$PtCl$_4$	1,3-COD	(C$_8$H$_{12}$)PtCl$_2$	24	270 dec.	374.2	386	25.68	3.24	25.62	3.25
K$_2$PtBr$_4$	1,5-COD	(C$_8$H$_{12}$)PtBr$_2$	20	280 dec.	463.1	470	20.74	2.61	20.82	2.65
K$_2$PtBr$_4$	1,3-COD	(C$_8$H$_{12}$)PtBr$_2$	18	280 dec.	463.1	480	20.74	2.61	20.80	2.65

Frohlich.[2] Recent papers by Hüttel and co-workers,[3] by Rinehart and Lasky,[4] and by Robinson and Shaw[5] indicate that 1,3-cyclooctadiene yields different products with palladium(II) than does the 1,5- isomer. Research in this laboratory concerning the synthesis of the palladium(II) and platinum(II) complexes of 1,3-cyclooctadiene has produced excellent evidence of rearrangement of the ligand to the 1,5- isomer. Preparation of (C$_8$H$_{12}$)PdCl$_2$, (C$_8$H$_{12}$)PdBr$_2$, (C$_8$H$_{12}$)PtCl$_2$, and (C$_8$H$_{12}$)PtBr$_2$ with both isomers yielded compounds identical in appearance and melting point and with the same infrared spectra. Recovery of cycloolefin by decomposition of the supposed 1,3- complex yielded in every case a compound identical with the 1,5- isomer. Treatment of the 1,3- complex with potassium cyanide or dimethyl sulfoxide yielded pure 1,5-cyclooctadiene exclusively as established by vapor phase chromatography. This rearrangement appears to be identical with that reported by Rinehart and Lasky[4] *via* the rhodium(I) complex.

Experimental

The cycloolefins used in this research were obtained from Cities Service Research and Development Co. and from K and K Laboratories. Each olefin was carefully redistilled in an efficient column; the middle fraction was retained and was stored over Drierite in the dark. Vapor phase chromatographic analysis of the retained fraction showed the purity of the 1,3-cyclooctadiene to be 98.7 mole %, and the purity of the 1,5-isomer to be 99.9 mole %. Vapor phase chromatograms showed that the 1,3-cyclooctadiene did not contain any 1,5- isomer as an impurity. Infrared spectra of the purified cycloolefins were made and were compared with those in the literature; all showed the characteristic strong absorbance at 1630 cm.$^{-1}$. The palladium(II) and platinum(II) halogenides were obtained from K and K Laboratories and were used without further purification.

The platinum(II) complexes were prepared according to the method of Chatt[1] involving the reaction of the potassium (better, sodium) salt of the type K$_2$PtX$_4$ with the cycloolefin in either methanol or 1-propanol. The palladium(II) complex using K$_2$PdCl$_4$ was prepared by displacement of the appropriate benzonitrilo complex with the cycloolefin in benzene as in the method of Kharasch.[6] A modification of this technique as reported by Frye, Kuljian, and Viebrock[7] was used to prepare the corresponding bromide. Synthetic procedures are given in the last named paper and are not repeated here. The benzonitrilo intermediates were recrystallized from benzene and benzonitrile, respectively, and were characterized by means of infrared spectra and ele-

mental analyses. The crystals were vacuum filtered, washed with petroleum ether, and stored over Drierite at atmospheric pressure; reduced pressure tended to pump off benzonitrile.

The platinum(II) complexes were crystallized directly from the methanol or 1-propanol reaction mixtures; palladium(II) complexes were obtained by allowing purified bis(benzonitrilo)-palladium(II) halogenide to react with cycloolefin in benzene. In each case good crystalline products were obtained which were carefully recrystallized from the appropriate solvent and were subsequently characterized by means of infrared and ultraviolet–visible spectra and elemental analyses. Molecular weight determinations by the Rast method using bromoform as solvent were made on all complexes. Data concerning the physical and analytical properties of the various complexes are presented in Table I.

Infrared spectra of the 1,5-cyclooctadiene complexes were checked with the rather sparse data in the literature. The infrared spectra of the complexes prepared with 1,3-cyclooctadiene were identical with those of the 1,5- analogs. The spectra were obtained using potassium bromide tablets. Ultraviolet–visible spectra were likewise identical.

Recovery of the cycloolefin by means of replacement of the ligand with cyanide ion or dimethyl sulfoxide yielded a material in all cases that was identical with the 1,5- isomer as established by means of infrared spectrophotometry and vapor phase chromatography. Absence of the strong absorbance at 1630 cm.$^{-1}$ indicated π bonding in the complex; the peak reappeared in the recovered cycloolefin, of course. Yield data for the various complexes are given in Table I.

The observed rearrangement is doubtless due to the more favorable placement for π bonding of the double bonds in the *cis-cis* (tub) form of the 1,5-cyclooctadiene; thus the rearrangement occurs in spite of the fact that the conjugated 1,3- isomer is the more stable olefin. Rinehart and Lasky[4] suggested a mechanism for the rearrangement *via* π complex formation followed by hydrogen transfer; this mechanism is, in our opinion, a valid one and is preferable to that proposed by Harrod and Chalk.[8]

(8) J. Harrod and A. Chalk, *J. Am. Chem. Soc.*, **86**, 1776 (1964).

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO

Lattice Constants of Some Alkali Metal Actinyl(V) Compounds[1]

BY T. K. KEENAN

Over the past few years, several new compounds have been reported which contain the doubly oxygen-

(2) E. Fischer and W. Frohlich, *Chem. Ber.*, **92**, 1423 (1959).
(3) R. Hüttel, H. Dietl, and H. Christ, *ibid.*, **97**, 2037 (1964).
(4) R. Rinehart and J. Lasky, *J. Am. Chem. Soc.*, **86**, 2516 (1964).
(5) S. Robinson and B. Shaw, *J. Chem. Soc.*, 5002 (1964).
(6) M. Kharasch, R. Seyler, and F. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).
(7) H. Frye, E. Kuljian, and J. Viebrock, *Z. Naturforsch.*, **20b**, 269 (1965).