system by boron-11 nmr showed that intermediate species were present; further work resulted in the isolation of the new compound sodium bis(borane)dimethylamide(1−), $Na(CH_3)_2N(BH_3)_2$.[2] This paper describes the nmr investigation of the course of eq 1 and the role of $Na(CH_3)_2N(BH_3)_2$ as a reaction intermediate.

Experimental Section

General Information.—Conventional high-vacuum and glovebag techniques were used throughout this investigation. The solvents monoglyme (1,2-dimethoxyethane) and diglyme (bis(2-methoxyethyl) ether) were purified by standard methods and stored over lithium aluminum hydride in evacuated vessels. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer equipped with a 32.1-MHz probe and standard accessories. Chemical shifts are in ppm relative to diethyl ether–boron trifluoride. Nmr studies were performed in nmr reaction vessels equipped with Kontes Teflon high-vacuum stopcocks for the easy addition of reagents and the removal of products for separation and characterization.

$Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ was prepared by the reaction of dimethylamine-borane with sodium hydride in monoglyme followed by crystallization with dioxane.[3] μ-$(CH_3)_2NB_2H_5$ was prepared according to eq 1 as previously described.[1]

Study of the Addition of Diborane to Sodium Dimethylamidotrihydroborate(1−).—In a dry nitrogen atmosphere an nmr reaction vessel was loaded with a 0.103-g (0.82-mmol) sample of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$. The vessel was evacuated and 1 ml of monoglyme was added. The boron-11 nmr spectrum of this solution was recorded to confirm the purity of the reactant. Diborane was then added to the system in approximately 0.4-mmol increments and the nmr spectrum of the resulting solution was recorded after each addition.

The spectrum obtained after addition of the first 0.4 mmol of diborane (Figure 1) consisted of a strong quartet centered at +11.0 ppm, characteristic of $Na(CH_3)_2N(BH_3)_2$[2], and a considerably weaker triplet at −3.0 ppm and quintet at +42.0 ppm, assigned to $(CH_3)_2NBH_2$ and $NaBH_4$, respectively. The low intensity of the $NaBH_4$ resonance is caused by saturation effects. In addition, a weak unidentified signal was present on the low-field side of the $(CH_3)_2NBH_2$ resonance. The unidentified signal disappeared upon further addition of diborane. The formation of $(CH_3)_2NBH_2$ was confirmed by isolation and identification (infrared spectrum) in a separate experiment in which diglyme was employed as the solvent. Addition of further increments of diborane caused no change in the $(CH_3)_2NBH_2$ triplet but resulted in the appearance of signals due to dioxane–borane and to μ-$(CH_3)_2NB_2H_5$ and NaB_2H_7, which are products characteristic of the reaction of $Na(CH_3)_2N(BH_3)_2$ with diborane.[2] Attempts to isolate the small amount of unidentified byproduct associated with the lowest field nmr signal were unsuccessful.

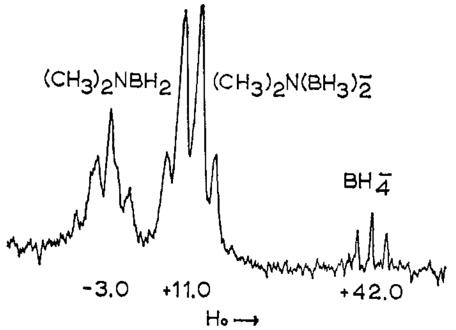

Figure 1.—Boron-11 nmr spectrum of a solution resulting from the reaction $Na(CH_3)_2NBH_3 + 0.5B_2H_6$.

Reaction of μ-Dimethylaminodiborane with Sodium Dimethylamidotrihydroborate(1−).—In a dry nitrogen atmosphere an nmr reaction vessel was loaded with 0.155 g (1.24 mmol) of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$. The vessel was evacuated and cooled to −196°, and 1 ml of monoglyme followed by 1.25 mmol of μ-$(CH_3)_2NB_2H_5$ was added. The boron-11 nmr spectrum of the clear colorless solution formed after warming to room temperature showed a well-resolved triplet (−5.0 ppm) and quartet (+11.2 ppm) of intensity ratio 1:2, respectively. Assignment of the quartet to $Na(CH_3)_2N(BH_3)_2$[2] was confirmed by addition of diborane to the reaction vessel and subsequent isolation of μ-$(CH_3)_2NB_2H_5$ by high-vacuum methods. The presence of $(CH_3)_2NBH_2$ was confirmed by the boron-11 nmr spectrum of the monoglyme fraction of the volatile products.

Results and Discussion

Boron-11 nmr studies show that $Na(CH_3)_2NBH_3$ reacts with diborane to produce two principal sets of products. The first reaction (eq 2) results in addition of a borane group to produce $Na(CH_3)_2N(BH_3)_2$; the second

$$Na(CH_3)_2NBH_3 + 0.5B_2H_6 \longrightarrow Na(CH_3)_2N(BH_3)_2 \quad (2)$$

lesser reaction (eq 3) results in formation of $(CH_3)_2NBH_2$ and $NaBH_4$. The latter products arise through the interaction of the starting reagents, possibly by a

$$Na(CH_3)_2NBH_3 + 0.5B_2H_6 \longrightarrow (CH_3)_2NBH_2 + NaBH_4 \quad (3)$$

simple hydride ion transfer, and not by a process like eq 4; $Na(CH_3)_2N(BH_3)_2$ has not been observed to de-

$$Na(CH_3)_2N(BH_3)_2 \not\longrightarrow (CH_3)_2NBH_2 + NaBH_4 \quad (4)$$

compose in this manner.[2] The formation of μ-$(CH_3)_2NB_2H_5$ does not occur until more diborane is allowed to react with the $Na(CH_3)_2N(BH_3)_2$ (eq 5).

$$(CH_3)_2N(BH_3)_2^- + B_2H_6 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + B_2H_7^- \quad (5)$$

The reaction of $Na(CH_3)_2NBH_3$ with μ-$(CH_3)_2NB_2H_5$ suggests an alternate route to the formation of $(CH_3)_2NBH_2$ proceeding through the formation of a

$$Na(CH_3)_2NBH_3 + \mu\text{-}(CH_3)_2NB_2H_5 \longrightarrow (CH_3)_2NBH_2 + Na(CH_3)_2N(BH_3)_2 \quad (6)$$

small quantity of μ-$(CH_3)_2NB_2H_5$ *via* eq 2 and 5 followed by reaction 6. This pathway seems less likely than eq 3, since $(CH_3)_2NBH_2$ always appears even when $Na(CH_3)_2NBH_3$ is in excess and since, as demonstrated by eq 5, diborane is superior to μ-$(CH_3)_2NB_2H_5$ when the two compounds are allowed to compete for a hydride ion.

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Some Fluorocarbon-Bridged Ditertiary Phosphine Derivatives of Triosmium Dodecacarbonyl

BY J. P. CROW AND W. R. CULLEN*

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The development of a high-yield synthesis of triosmium dodecacarbonyl has stimulated research in this area.[1] Lewis and coworkers[2] have recently investi-

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gated the reactions of triosmium dodecacarbonyl with monodentate tertiary phosphine ligands: one, two, or three carbonyl groups were displaced depending on the reaction conditions. In all cases the triangular metal atom skeleton remained intact. Treatment of triosmium dodecacarbonyl and its phosphine-substitution products with halogens did, however, cause rupture of the osmium–osmium bonds leading to breakdown of the metal atom skeleton. With acetylenes[3] triosmium dodecacarbonyl breaks down fairly easily to give complexes containing one or more osmium tricarbonyl moieties.

We have recently described the reactions of various ditertiary fluoroorganophosphines and arsines with triiron[4,5] and triruthenium[6] dodecacarbonyls; here we shall describe the reactions of triosmium dodecacarbonyl with the ligands 1,2-bis(diphenylphosphino)tetrafluorocyclobutene, $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2CF_2CF_2}$ (f$_4$fos), 1,2-bis(diphenylphosphino)octafluorocyclohexene, $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2CF_2CF_2CF_2CF_2}$ (f$_8$fos), and 1,2-bis(dimethylarsino)tetrafluorocyclobutene (ffars).

Experimental Section

All reactions were done under nitrogen. Chromatography was done on Florisil columns using 30–60° petroleum ether–diethyl ether solvent mixtures. Products were crystallized by dissolving the concentrated eluate in a small amount of dichloromethane, adding 2–5 ml of *n*-hexane, and cooling to 0° for 2–10 hr. Analyses were carried out by Mr. P. Borda of this department. Mass spectra were run on an AEI MS9 spectrometer with direct introduction of solid samples. Molecular weights were determined osmometrically in benzene.

(1) **Preparation of f$_4$fosOs$_3$(CO)$_{11}$ and f$_4$fosO$_3$(CO)$_{10}$.**—Triosmium dodecacarbonyl (0.20 g, 2.2 mmol) and f$_4$fos (0.10 g, 2.0 mmol) were stirred in 10 ml of refluxing toluene for 4 hr. The solvent was removed at reduced pressure and the reaction mixture was chromatographed. A red band which eluted from the column in 10:1 petroleum ether–ether gave, after crystallization, f$_4$fosOs$_3$(CO)$_{10}$ (0.20 g, 65%) as a red crystalline solid. *Anal.* Calcd for $(F_2C)_2C_2P_2(C_6H_5)_4Os_3(CO)_{10}$: C, 33.9; H, 1.4; F, 5.7. Found: C, 33.6; H, 1.5; F, 5.9. Molecular weight: calcd, 1345; found, 1300 ± 50. A second band eluted by 1:1 petroleum ether–ether gave yellow f$_4$fosOs$_3$(CO)$_{11}$ (0.05 g, 16%) on crystallization. *Anal.* Calcd for $(F_2C)_2C_2P_2(C_6H_5)_4Os_3(CO)_{11}$: C, 34.1; H, 1.5; F, 5.5. Found: C, 34.0; H, 1.6; F, 5.8.

(2) **Preparation of f$_4$fosOs$_2$(CO)$_6$ and (f$_4$fos)$_2$Os$_3$(CO)$_8$.**—The ligand f$_4$fos (0.45 g, 9 mmol) and triosmium dodecacarbonyl (0.45 g, 5 mmol) were stirred in refluxing xylene for 8 hr. The solvent was removed at reduced pressure, and the reaction mixture was chromatographed. Many bands were observed, only some of which could be characterized. The first complex to be eluted from the column by 50:1 petroleum ether–ether after crystallization yielded 0.08 g (15%) of white f$_4$fosOs$_2$(CO)$_6$. *Anal.* Calcd for $(CF_2)_2C_2P_2(C_6H_5)_4Os_2(CO)_6$: C, 39.1; H, 1.9; F, 7.3. Found: C, 39.3; H, 1.9; F, 7.1. A dark red band eluted from the column by 1:3 petroleum ether–ether yielded after crystallization (f$_4$fos)$_2$Os$_3$(CO)$_8$ (0.20 g, 22%) a dark red solid soluble only in fairly polar solvents. *Anal.* Calcd for $[(CF_2)_2C_2P_2(C_6H_4)_4]_2Os_3(CO)_8$: C, 43.0; H, 2.2; F, 8.5. Found: C, 42.5; H, 2.3; F, 8.3. Molecular weight: calcd, 1783; found, 1920 ± 200. The other bands were eluted from the column by ether, but these produced only traces of solid on crystallization. Reaction of a 3:1 mole ratio of ligand to metal carbonyl resulted in a slightly greater proportion of (f$_4$fos)$_2$Os$_3$(CO)$_8$ being produced.

(3) **Preparation of f$_8$fosOs$_3$(CO)$_{11}$.**—Triosmium dodecacarbonyl (0.36 g, 4 mmol) and f$_8$fos (0.25 g, 4 mmol) were stirred in refluxing xylene for 10 hr. On cooling, the reaction mixture deposited some unreacted metal carbonyl (0.30 g). The solution was decanted, concentrated, and chromatographed. One yellow band was eluted by 2:1 petroleum ether–ether which on crystallization yielded yellow f$_8$fosOs$_3$(CO)$_{11}$ (0.01 g, 16%). *Anal.* Calcd for $(CF_2)_4C_2P_2(C_6H_4)_4Os_3(CO)_{11}$: C, 33.4; H, 1.4. Found: C, 33.6; H, 1.5.

Discussion

In general triosmium dodecacarbonyl was found to be much less reactive toward the ligands used than either triiron or triruthenium dodecacarbonyls. This observation, in agreement with the results of Lewis[2] and other workers, is well illustrated by comparison of the conditions required to prepare the complexes f$_4$fosM$_2$(CO)$_6$ (M = Fe, Ru, Os) in maximum yield from the trinuclear cluster: M = Fe,[5] reflux in benzene for 6 hr, yield 76%; M = Ru,[6] reflux in toluene for 6 hr, yield 54%; M = Os, reflux in xylene for 8 hr, yield 18%.

Triosmium dodecacarbonyl failed to yield any complexes of 1,2-bis(dimethylarsino)perfluorocyclobutene (ffars) in contrast with triiron[4,5] and triruthenium[6] dodecacarbonyls which react with this ligand under fairly mild conditions to give a variety of products. Increasing the severity of the conditions (from 140° for 24 hr to 160° for 24 hr) merely caused decomposition of the ligand.

No trace of a complex such as LOs(CO)$_3$ was observed in any of the reactions. Our experience with LRu(CO)$_3$[6] indicates that species such as LOs(CO)$_3$ would have very limited existence.

The reaction between a 1:1 mole ratio of f$_4$fos and triosmium dodecacarbonyl in refluxing toluene gives, after chromatography, two compounds which we have formulated as f$_4$fosOs$_3$(CO)$_{11}$ and f$_4$fosOs$_3$(CO)$_{10}$. In the former complex the ligand has displaced one carbonyl group (presumably equatorial) and is behaving in a monodentate fashion; the latter complex is thought to contain the phosphine ligand bridging two osmium atoms, the ligand having displaced two equatorial carbonyl groups from triosmium dodecacarbonyl. Thus the phosphorus atoms and the triangle of osmium atoms would probably be coplanar or nearly so. This structure, illustrated in Figure 1A, is assigned to the complex by virtue of the remarkable similarity of its ir spectrum in the carbonyl stretching region to those of the anal-

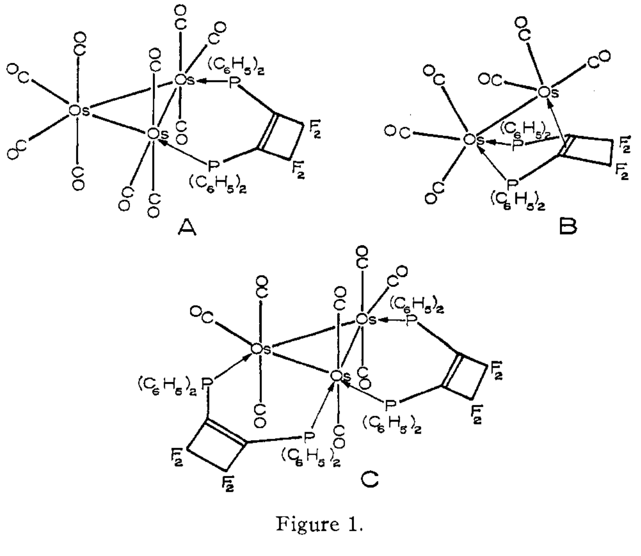

Figure 1.

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TABLE I

INFRARED SPECTRA OF THE OSMIUM COMPLEXES IN THE CARBONYL STRETCHING REGION[a]

$f_4fosOs_3(CO)_{11}$	2088 (10)	2063 (8)	2040 (1)	2020 (10)	2010 (10)	2006 (8) sh	1993 (8)	1982 (5)	1952 (6)
$f_4fosOs_3(CO)_{10}$	2097 (6)	2033 (4) sh	2023 (8)	2010 (10)	1984 (5)	1970 (4)	1960 (4)	1950 (1)	
$f_4fosOs_2(CO)_6$	2082 (9)	2050 (10)	2016 (8)	1992 (4)	1978 (8)	1972 (5)			
$(f_4fos)_2Os_3(CO)_8$[b]	2064 (2)	2008 (7)	2002 (6) sh	1982 (10)	1950 (4)	1932 (2)			
$f_8fosOs_3(CO)_{11}$	2100 (7)	2088 (5)	2048 (10)	2034 (8)	2025 (8)	2016 (4)	2009 (8)	1989 (6)	

[a] Run on a Perkin-Elmer 457 spectrometer in cyclohexane solution. Relative intensities are given in parentheses. [b] Run in dichloromethane.

ogous ruthenium complexes.[6] One of these, $ffarsRu_3(CO)_{10}$, has been shown by means of X-ray diffraction[7] to contain a triangle of metal atoms with the equatorial ligand bridging two of these atoms. The infrared spectra in the carbonyl stretching region of the new complexes are shown in Table I. It must be pointed out that there is much greater correlation between the infrared spectra of analogous complexes of ruthenium and osmium with the ligands used in this study than there is between different phosphine-ligand complexes of osmium carbonyl.[2]

Reaction of a 2:1 f₄fos:triosmium dodecacarbonyl mole ratio in refluxing xylene gives a small amount of a white solid, which has six sharp bands in the carbonyl stretching region of its infrared spectrum and has an elemental analysis corresponding to $f_4fosOs_2(CO)_6$. This complex we have assigned the structure shown in Figure 1B by analogy with the complexes $ffarsM_2(CO)_6$[5,6,8] (M = Fe, Ru) whose structures are well established. This type of complex $f_4fosM_2(CO)_6$ is the only one that can be isolated where M = Fe, Ru, and Os. Other complexes such as $f_4fosFe(CO)_3$ do not have ruthenium or osmium analogs, whereas $f_4fosOs_3(CO)_{10}$ does not have an iron counterpart. The complex $f_4fosM_2(CO)_6$ is particularly stable for the elements Fe, Ru, and Os, perhaps because it involves chelation and coordination of the double bond which might stabilize the iron complex, as well as a metal-metal bond which is particularly favored by osmium.

A dark red solid can also be obtained from the reaction of excess ligand with triosmium dodecacarbonyl in xylene; this solid has a carbonyl infrared spectrum closely resembling those of $(ffars)_2Ru_3(CO)_8$ and $(f_4fos)_2Ru_3(CO)_8$.[6] The structure of $(ffars)_2Ru_3(CO)_8$ is known[9] to consist of a ruthenium triangle bridged by two ffars ligands and we have assigned $(f_4fos)_2Os_3(CO)_8$ an analogous structure, as shown in Figure 1C. In this case as in $f_4fosOs_3(CO)_{10}$ (Figure 1A) the ligands have displaced equatorial carbonyl groups, so the four phosphorus atoms would be expected to lie near the plane of the triangle of osmium atoms.

Triosmium dodecacarbonyl and f₈fos react in xylene to give a very small amount of a yellow complex which is probably $f_8fosOs_3(CO)_{11}$. Here the phosphine is coordinated by one phosphorus atom only.

The mass spectra of all these new complexes showed no peaks at an m/e value expected for a parent ion; instead peaks with highest m/e corresponded to $Os_3(CO)_x{}^{n+}$ where $x = 0$–12 and $n = 1$ and 2. Under conditions employed (210°) to volatilize the samples in the mass spectrometer, rearrangement of the complexes must occur to give volatile triosmium dodecacarbonyl and other nonvolatile decomposition products.

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Complexes with Sulfur and Selenium Donors. VI. Electron Spin Resonance Spectra of Bis(*O,O'*-dialkyldithiophosphato)oxovanadium(IV) and -copper(II) Chelates[1,2]

BY JOHN R. WASSON

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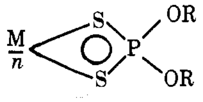
Since 1965 a number of papers[3-9] have appeared describing the electron spin resonance (esr) spectra of transition metal-*O,O'*-dialkyldithiophosphate complexes



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where n is the oxidation state of metal M and R is the alkyl group. A particularly unusual feature in the esr spectra of many of the complexes is the appreciable phosphorus-31 superhyperfine splitting which arises from metal-phosphorus interactions over distances of about 3 Å or longer. The present work was undertaken to confirm what initially appeared to be anomalously large ^{31}P superhyperfine splitting and to inquire into the mechanism(s) of the transferred superhyperfine interaction.

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