bridge (*e.g.* $[(CH_3)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$) does not make the two diastereotopic methyl groups in such a $(CH_3)_2PCH_2CH_2$ unit sufficiently different for their nonequivalence to be detected by proton nmr spectroscopy.

The phosphorus-31 nmr resonances from $(C_6H_5)_2PCH_2CH_2$-, $C_6H_5P(CH_2CH_2-)_2$, and $P(CH_2CH_2-)_3$ units in methylated poly(tertiary phosphines) (Table II) occur at +13.1 to +13.2, +17.4 to +17.6, and +19.5 to +19.6 ppm, respectively, consistent with the previously observed[4] ranges in the phenylated poly(tertiary phosphines) except for some upfield shifts arising from the effects of such units being bonded to phosphorus atoms bearing some methyl groups rather than only phenyl groups as in the phenylated poly(tertiary phosphines). Units of the types $CH_3P(CH_2CH_2-)_2$ and $(CH_3)_2PCH_2CH_2-$ exhibit characteristic phosphorus-31 resonances at +32.6 to +34.3 and at +46.5 to +48.8 ppm, respectively. In $(CH_3)_2PCH_2CH_2P<$ units the ^2J(PH) methyl–phosphorus coupling of ~2 Hz is so small relative to the ^3J(PP) phosphorus–phosphorus coupling of ~20 Hz, that even without proton decoupling the phosphorus resonances are clear doublets.

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Organometallic Chemistry of the Transition Metals. XXIX. Redox Systems in Hexamethylbenzene Cluster Compounds of Niobium and Tantalum[1-3]

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Abstract: Oxidation of the hexamethylbenzene niobium and tantalum clusters $[(Me_6C_6)_3M_3X_6]^+$ (M = Nb, X = Cl and Br; M = Ta, X = Cl) with reagents such as cerium(IV), *N*-bromosuccinimide, iodine, or air in acid solution or by electrochemical methods gives the corresponding diamagnetic clusters $[(Me_6C_6)_6M_6X_{12}]^{4+}$ isolable as their hexafluorophosphate or thiocyanate salts. The electrochemical reversibility of these redox systems is demonstrated by triangular voltammetry. All of the hexamethylbenzene niobium and tantalum clusters exhibit characteristic maxima in their electronic spectra which can be used for their identification in solution.

Since 1955 Fischer and coworkers have developed the "reducing Friedel-Crafts synthesis" for the preparation of bisarenemetal complexes of chromium,[6] molybdenum,[7] tungsten,[7] vanadium,[8] technetium,[9] rhenium,[10] iron,[11] ruthenium,[12] cobalt,[13] and rhodium[13] by reactions of the appropriate metal halides with an aromatic hydrocarbon in the presence of an anhydrous aluminum halide with aluminum powder as a reducing agent when necessary. However, when Fischer and Röhrscheid[14] attempted a similar method for the synthesis of hexamethylbenzene complexes of the early transition metals titanium, zirconium, niobium, and tantalum, they obtained products with only one rather than two arene units for each metal atom. All four of these metals thus gave apparent trimetallic cations of the stoichiometry $[(Me_6C_6)_3M_3Cl_6]^+$ (M = Ti, Zr, Nb, and Ta).

The niobium and tantalum compounds of Fischer and Röhrscheid[14] attracted our attention for several reasons. Their trimetallic formulas correspond to half of the well-known clusters containing M_6X_{12} units with an octahedron of six metal atoms bridged by halogen atoms across each of its 12 edges.[18] Indeed, at the time we began our work, the available data did not exclude unambiguously a hexametallic formulation for the niobium and tantalum hexamethylbenzene clusters although somewhat ambiguous molecular weight determinations made a trimetallic formulation more probable than a hexametallic one.[14] Furthermore, the or-

Table I. New Hexamethylbenzene Niobium and Tantalum Derivatives

Compound	Color		Analyses, % C	H	Other
$[(Me_6C_6)_3Nb_3Cl_6][BPh_4]$	Green	Calcd	56.0	5.8	
		Found	56.6	5.7	
$[(Me_6C_6)_3Ta_3Cl_6][BPh_4]$	Brown-violet	Calcd	46.1	4.8	
		Found	46.0	4.7	
$[(Me_6C_6)_6Nb_6Cl_{12}][PF_6]_4$	Dark green	Calcd	34.1	4.3	16.8 (Cl)
		Found	34.4	4.4	16.8 (Cl)
$[(Me_6C_6)_6Nb_6Cl_{12}][BPh_4]_4$	Brown–green	Calcd	62.4	5.9	
		Found	63.2	5.9	
$[(Me_6C_6)_6Nb_6Cl_{12}][SCN]_4$	Brown	Calcd	41.7	5.0	2.6 (N)
		Found	41.4	4.9	2.5 (N)
$[(Me_6C_6)_6Nb_6Cl_{12}][I_3]_4$	Brown	Calcd	24.9	3.1	
		Found	25.1	3.1	
$[(Me_6C_6)_6Nb_6Cl_{12}][Ce(NO_3)_6]_2$	Green	Calcd	29.0	3.6	5.6 (N)
		Found	28.8	3.5	5.1 (N)
$[(Me_6C_6)_6Ta_6Cl_{12}][PF_6]_4$	Green-brown	Calcd	28.2	3.5	
		Found	28.1	3.6	
$[(Me_6C_6)_6Ta_6Cl_{12}][SCN]_4$	Green-brown	Calcd	31.5	3.8	1.9 (N)
		Found	32.7	3.9	2.3 (N)
$[(Me_6C_6)_3Nb_3Br_6]Br$	Brown	Calcd	32.7	4.2	42.1 (Br)
		Found	33.5	4.6	42.0 (Br)
$[(Me_6C_6)_6Nb_6Br_{12}][PF_6]_4$	Brown	Calcd	28.2	3.5	
		Found	27.1	3.6	

Table II. Electronic Spectra of Hexamethylbenzene Niobium and Tantalum Derivatives

Compound	Electronic spectrum Solvent	Maxima, 475–275 nm
$[(Me_6C_6)_3Nb_3Cl_6]Cl$	MeOH	419 (37,000), 338 (11,000)
$[(Me_6C_6)_3Nb_3Cl_6]Cl$	Me_2CO	420 (36,000), 339 (10,000)
$[(Me_6C_6)_3Nb_3Cl_6][BPh_4]$	Me_2CO	419 (44,000), 339 (12,000)
$[(Me_6C_6)_6Nb_6Cl_{12}][PF_6]_4$	MeOH	396 (54,000), 344 (19,000)
$[(Me_6C_6)_3Ta_3Cl_6]Cl$	MeOH	364 (39,000), 288 (21,000)
$[(Me_6C_6)_3Ta_3Cl_6][BPh_4]$	Me_2CO	365 (40,000) *a*
$[(Me_6C_6)_6Ta_6Cl_{12}][PF_6]_4$	MeOH	354 (58,000) *a*
$[(Me_6C_6)_3Nb_3Br_6]Br$	MeOH	453 (28,000), 378 (8,000)
$[(Me_6C_6)_6Nb_6Br_{12}][PF_6]_4$	MeOH	432 (47,000), 378 (17,000)
$[(Me_6C_6)_6Nb_6Br_{12}][PF_6]_4$	Me_2CO	430 (49,000), 382 (20,000)

[a] The expected second maximum was apparently obscured by other absorptions.

ganometallic chemistry of niobium and tantalum is still considerably more limited than that of neighboring elements such as molybdenum and tungsten. Reactions of the Fischer-Röhrscheid hexamethylbenzene niobium and tantalum clusters could expand the scope of organoniobium and -tantalum chemistry since the Me_6C_6M (M = Nb and Ta) units are isoelectronic with the C_5H_5M (M = Mo and W) units which form extensive series of metal complexes.

One characteristic of the octahedral metal halide clusters of niobium and tantalum[15] is the multiplicity of oxidation states related by reversible redox systems. For example, the tetraanion $[(Nb_6Cl_{12})Cl_6]^{4-}$ can be oxidized[16] successively to the trianion $[(Nb_6Cl_{12})Cl_6]^{3-}$ and the dianion $[(Nb_6Cl_{12})Cl_6]^{2-}$. Operating under the hypothesis since disproven by X-ray crystallography[17] that the Fischer-Röhrscheid hexamethylbenzene niobium and tantalum clusters might be hexametallic like the M_6X_{12} clusters, we subjected the niobium chloride complex $[(Me_6C_6)_3Nb_3Cl_6]Cl$ to chlorine oxidation in the presence of concentrated hydrochloric acid, conditions suitable[16] for converting $[(Nb_6Cl_{12})Cl_6]^{4-}$ to $[(Nb_6Cl_{12})Cl_6]^{2-}$. This led to the discovery of salts of a cation of stoichiometry $[(Me_6C_6)_3Nb_3Cl_6]^{2+}$. Subsequent work discussed in detail in this paper indicated that all of the cations of the type $[(Me_6C_6)_3M_3X_6]^+$ (X = Cl, M = Nb and Ta; X = Br, M = Nb) can be oxidized to similar products, which are formulated as the hexametallic derivatives $[(Me_6C_6)_6M_6X_{12}]^{4+}$, since their diamagnetism excludes the simpler trimetallic formulation.

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microlab, Inc., Atlanta, Ga., and by the microanalytical laboratory within the Chemistry Department at the University of Georgia. Electronic spectra (ultraviolet and visible) (Table II) were taken in the indicated solvents under nitrogen and recorded on a Cary Model 15 spectrometer. A nitrogen atmosphere was normally provided for the following operations: (1) carrying out reactions of organometallic compounds, (2) handling solutions of organometallic compounds, (3) filling evacuated vessels containing organometallic compounds.

Several techniques normally used in organometallic chemistry were of little value for this work. Attempts to take melting points of the niobium and tantalum derivatives in capillaries by usual methods led to gradual decomposition which could not be followed because of the deep colors of both the original compounds and their decomposition products. The infrared spectra of several compounds in the 4000-600-cm^{-1} region were essentially identical since complexed hexamethylbenzene is the only stuctural feature of the metal clusters giving bands in this region. The various hexafluorophosphate salts exhibited the characteristic strong infrared ν(P-F) band of PF_6^- at 830-840 cm^{-1}. The proton nmr spectra of several compounds showed only the expected single sharp resonance of hexamethylbenzene, which was of little diagnostic value other than confirming their diamagnetism.

Anhydrous niobium and tantalum pentahalides (Alfa Inorganics, Inc., Beverly, Mass., or Research Inorganic Chemical Corp., Sun Valley, Calif.), hexamethylbenzene (Columbia Organic Chemicals, Inc., Columbia, S. C.), and anhydrous aluminum halides (Fischer Scientific, Atlanta, Ga.) were purchased from the indicated commercial sources.

Preparations of $[(Me_6C_6)_3M_3Cl_6]Cl$ (M = Nb and Ta). The procedure of Fischer and Röhrscheid[14] was followed closely for the preparation of these compounds including the construction of the reaction vessel and the helical stirrer. We obtained 10-31% yields of the niobium complex $[(Me_6C_6)_3Nb_3Cl_6]Cl$ (reported[14] 21% yield) and 15-20% yields of the corresponding tantalum complex (reported[14] 12% yield). An attempt to prepare the niobium complex $[(Me_6C_6)_3Nb_3Cl_6]Cl$ using cyclohexane as a solvent in "normal" apparatus gave only a 5% yield.

Preparation of $[(Me_6C_6)_3Nb_3Br_6]Br$. An intimate mixture of 21.5 g (44 mmol) of niobium pentabromide, 66 g (247 mmol) of aluminum bromide, 1.44 g (50 mmol) of aluminum powder, and 8.5 g (50 mmol) of hexamethylbenzene was prepared by shaking these reactants in a dry nitrogen-filled jar. This mixture was then heated at 130° for 20 hr in the Fischer–Röhrscheid reaction vessel[14] using the helical stirrer for agitation. A brown-green oil was obtained with much hydrogen bromide evolution. The apparatus containing the product was cooled in liquid nitrogen for 4 hr and then broken. The finely ground solid was added to a mixture of 200 ml of degassed water and 300 ml of degassed chloroform. The insoluble product was washed with more chloroform as long as it dissolved. The combined chloroform solutions were dried over anhydrous sodium sulfate and then filtered through 75 mm of glass wool. Concentration of the chloroform filtrate with addition of hexane to aid precipitation of the product gave 5.8–8.9 g (30–46% yield) of brown $[(Me_6C_6)_3Nb_3Br_6]Br$. The analytical sample was obtained by crystallization from a mixture of chloroform and hexane.

Reaction of Tantalum Pentabromide with Hexamethylbenzene, Aluminum Bromide, and Aluminum. Reaction of 25 g (42 mmol) of tantalum pentabromide, 80 g (300 mmol) of aluminum bromide, 1.3 g (44 mmol) of aluminum powder, and 8.0 g (49 mmol) of hexamethylbenzene by a procedure similar to that described above for the preparation of $[(Me_6C_6)_3Nb_3Br_6]Br$ did not give the corresponding $[(Me_6C_6)_3Ta_3Br_6]Br$ but instead gave 10.9 g (51% yield) of a brown solid only slightly soluble in chloroform or dichloromethane which analyzed for $[Me_6C_6TaBr_2]_n$.

Anal. Calcd for $C_{12}H_{18}TaBr_2$: C, 28.7; H, 3.6; Br, 31.8. Found: C, 28.6, 28.4; H, 3.5, 3.6; Br, 32.2, 32.2.

The electronic spectrum of a saturated dichloromethane solution of this product exhibited maxima at 405 (sh), 365 (sh), and 314 nm.

Preparation of the Tetraphenylborates $[(Me_6C_6)_3M_3Cl_6][B(C_6H_5)_4]$. Metathesis of the chlorides $[(Me_6C_6)_3M_3Cl_6]Cl$ (M = Nb and Ta) with sodium tetraphenylborate in tetrahydrofuran in which $[(Me_6C_6)_3M_3Cl_6][B(C_6H_5)_4]$ is soluble or in water in which $[(Me_6C_6)_3M_3Cl_6][B(C_6H_5)_4]$ is insoluble gave the corresponding tetraphenylborates which could be recrystallized from mixtures of dichloromethane and diethyl ether or acetone and ethanol.

Oxidations of the Halides $[(Me_6C_6)_3M_3X_6]X$ (M = Nb and Ta, X = Cl; M = Nb, X = Br) with Ammonium Hexanitratocerate(IV). A solution of 2.0 g (2.0 mmol) of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ in 100 ml of methanol was treated dropwise with a solution of 2.16 g (4.0 mmol) of ammonium hexanitratocerate(IV) in 50 ml of methanol. The originally dark green solution became dark brown and a brown-green precipitate separated after about half of the cerium(IV) solution had been added. This precipitate was filtered, washed with diethyl ether, and dried to give 2.44 g (82% yield) of $[(Me_6C_6)_6Nb_6Cl_{12}][Ce(NO_3)_6]_2$.

A filtered aqueous solution of 1.0 g (0.34 mmol) of $[(Me_6C_6)_6Nb_6Cl_{12}][Ce(NO_3)_6]_2$ was treated with a solution of 1.0 g (6.1 mmol) of ammonium hexafluorophosphate in 10 ml of water. The green precipitate was filtered, washed twice with water, and dried. Recrystallization of the crude product from a mixture of acetone and diethyl ether followed by drying at 60° (0.1 mm) for 4 hr gave 0.50 g (58% yield) of green $[(Me_6C_6)_6Nb_6Cl_{12}][PF_6]_4$.

Similar metathesis reactions were used to prepare the corresponding thiocyanate and tetraphenylborate salts, which were recrystallized from mixtures of dichloromethane and diethyl ether.

The tantalum derivative $[(Me_6C_6)_3Ta_3Cl_6]Cl$ was oxidized similarly with ammonium hexanitratocerate(IV) in methanol. The resulting green precipitate was converted to the thiocyanate $[(Me_6C_6)_6Ta_6Cl_{12}][SCN]_4$ by reaction with sodium thiocyanate in aqueous solution; the thiocyanate was purified by crystallization from a mixture of acetone and diethyl ether.

The oxidation of the niobium bromide complex $[(Me_6C_6)_3Nb_3Br_6]Br$ with ammonium hexanitratocerate(IV) was conducted in a mixture of dichloromethane and acetone since the niobium bromide complex was unstable in methanol solution. The oxidized niobium bromide cation was isolated as the hexafluorophosphate salt $[(Me_6C_6)_6Nb_6Br_{12}][PF_6]_4$ by reaction of the originally precipitated hexanitratocerate(IV) salt with ammonium hexafluorophosphate in aqueous solution followed by rapid recrystallization of the precipitate from acetone. Reactions and crystallizations of the niobium bromide complexes had to be performed rapidly because of their instability in solution.

Oxidation of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ with *N*-Bromosuccinimide. A solution of 0.5 g (2.8 mmol) of *N*-bromosuccinimide in 50 ml of anhydrous methanol was treated at room temperature with 0.3 g (0.30 mmol) of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ while the mixture was stirred. The resulting dark brown solution was filtered. The filtrate was treated with a solution of 0.5 g (3.1 mmol) of ammonium hexafluorophosphate in 25 ml of methanol. The precipitate was filtered, dried, and recrystallized from a mixture of acetone and diethyl ether to give 0.18 g (47% yield) of green $[(Me_6C_6)_6Nb_6Cl_{12}][PF_6]_4$.

Oxidation of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ with Iodine. A dichloromethane solution of 0.2 g (0.2 mmol) of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ was treated with an excess of a dichloromethane solution of iodine. The resulting precipitate was filtered, washed with alternate portions of diethyl ether and dichloromethane, and dried at 60° (0.1 mm) for 4 hr to give 0.27 g (78% yield) of brown insoluble $[(Me_6C_6)_6Nb_6Cl_{12}][I_3]_4$.

Air Oxidation of $[(Me_6C_6)_3Nb_3Cl_6]Cl$. An absolute methanol solution of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ was treated with sufficient 12 *M* aqueous hydrochloric acid to make the solution 3 *M* in hydrogen ion. Air was passed through the resulting solution for 3 hr. Addition of excess methanolic ammonium hexafluorophosphate gave a brown precipitate, which, after washing with methanol and drying, was shown to be $[(Me_6C_6)_6Nb_6Cl_{12}][PF_6]_4$ by the maximum at 396 nm in its electronic spectrum.

Repetition of this reaction of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ with methanolic hydrochloric acid without introducing any air gave after precipitation with methanolic ammonium hexafluorophosphate the salt $[(Me_6C_6)_3Nb_3Cl_6][PF_6]$ identified by the maximum at 421 nm in its electronic spectrum.

Electrochemical Studies on Hexamethylbenzene Niobium and Tantalum Chloride Complexes. The electrochemical studies were done in Professor R. E. Dessy's laboratory at the Virginia Polytechnic Institute, Blacksburg, Va., using equipment described in previous papers from his group.[18] Polarography was done with a dropping mercury electrode and a 0.001 *M* $AgClO_4$ (0.1 *M* $[(C_4H_9)_4N][ClO_4]$)|Ag wire reference electrode. A hanging mercury drop was used for the triangular voltammetry. Controlled potential electrolyses were done using a mercury pool electrode. All electrochemical experiments were done on 0.001 *M* solutions in an argon filled Vacuum Atmospheres glove box with redistilled and degassed 1,2-dimethoxyethane as a solvent and tetra-*n*-butylammonium perchlorate as a supporting electrolyte.

(a) $[(Me_6C_6)_3Nb_3Cl_6][B(C_6H_5)_4]$. Polarography, oxidation at $E_{1/2} = -0.21$ V, complex reduction wave below −1.8 V; triangular voltammetry, $E_{p,c} = -0.32$ V, $E_{p,a} = -0.07$ V. Controlled potential electrolysis at −0.1 V resulted in the removal of 1.4 electrons with the originally green-brown solution becoming yellow-brown. The polarogram of the oxidized solution exhibited two reduction waves of approximate equal heights at −1.10 and −0.28 V in addition to the complex reduction wave below −1.8 V.

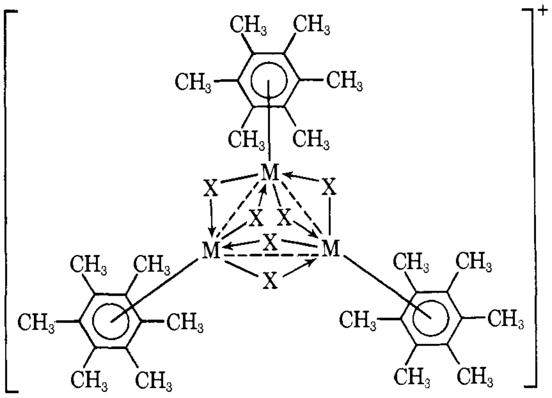
(b) $[(Me_6C_6)_3Ta_3Cl_6][B(C_6H_5)_4]$. Polarography, oxidation at $E_{1/2} = -0.18$ V, complex reduction wave below −2.3 V, triangular voltammetry, $E_{p,c} = -0.40$ V, $E_{p,a} = -0.11$ V. Controlled potential electrolysis at −0.1 V resulted in an ill-defined curve which could not be integrated precisely. During this oxidation the original brown solution became more reddish.

Magnetic Susceptibility Observations. The compounds $[(Me_6C_6)_6M_6Cl_{12}][PF_6]_4$ (M = Nb and Ta) were found to be diamagnetic by the Faraday method on an Alpha Scientific Model 9500 magnetic balance located at the University of Georgia until summer 1972.

Exploratory Reactions of $[(Me_6C_6)_3Nb_3Cl_6]Cl$. The following reagents did not give tractable new organoniobium compounds upon reaction with $[(Me_6C_6)_3Nb_3Cl_6]Cl$: (a) sodium cyclopentadienide in tetrahydrofuran, (b) dipotassium cyclooctatetraenediide in boiling tetrahydrofuran, (c) pentafluorophenyllithium in diethyl ether, (d) zinc in boiling ethanol either in a nitrogen or carbon monoxide atmosphere (The infrared spectrum of the mixture from the reaction in a carbon monoxide atmosphere failed to exhibit any ν(CO) frequencies.), (e) sodium borohydride in 1,2-dimethoxyethane (Hexamethylbenzene was isolated from this reaction.), (f) piperidinodifluorophosphine in boiling diethyl ether, (g) triphenylphosphine in boiling ethanol or 2-methoxyethanol (In both cases unchanged $[(Me_6C_6)_3Nb_3Cl_6]Cl$ was recovered after the reaction.), (h) trimethyltin chloride in boiling tetrahydrofuran (The electronic spectrum of the product indicated the absence of reaction.), (i) benzyl chloride in tetrahydrofuran at room temperature (Again the electronic spectrum of the resulting solution indicated the absence of reaction.).

Discussion

The "reduced" forms of the hexamethylbenzene niobium and tantalum halide clusters appear to be trimetallic derivatives $[(Me_6C_6)_3M_3X_6]X$ (I: M = Nb, X = Cl and Br; M = Ta, X = Cl) on the basis of the reported[17] X-ray crystal structure of the niobium chloride complex $[(Me_6C_6)_3Nb_3Cl_6]Cl$. On the other hand, the "oxidized" forms of the hexamethylbenzene niobium and tantalum halide clusters of the stoichiometry $[(Me_6C_6)_3M_3X_6]X_2$ must be an even multiple of this formula on the basis of the observed diamagnetism of the hexafluorophosphate salts of the niobium and tantalum chloride derivatives. These compounds are formulated in this paper as the hexametallic derivatives $[(Me_6C_6)_6M_6X_{12}]X_4$, although more complex, but far less likely, formulas with 12, 18, 24, or other multiples of six metal atoms cannot be excluded on the basis of the available information.



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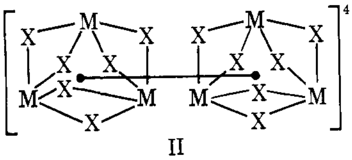

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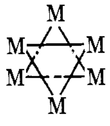

III

The metal triangle in the structure of the reduced cations $[(Me_6C_6)_3M_3X_6]X$ appears[17] to have an average metal-metal bond order of ⅓. The metal triangle can thus be considered to contain only one metal-metal bond which resonates between the three edges of the triangle. Oxidation of $[(Me_6C_6)_3M_3X_6]X$ to $[(Me_6C_6)_6M_6X_{12}]X_4$ must involve the following two successive steps: (1) removal of one of the two bonding electrons in the niobium triangle of $[(Me_6C_6)_3M_3X_6]X$ (I) to give a species $[(Me_6C_6)_3M_3X_6]X_2$ with only a single odd electron in the metal triangle; (2) coupling of two such $[(Me_6C_6)_3M_3X_6]X_2$ units through the formation of an intertriangle metal-metal bond as in structure II (the hexamethylbenzene rings are omitted for clarity). In order to have enough space to accommodate the 12 bridging chlorines in structure II with a reasonably short intertriangle metal-metal bond distance, the two metal triangles have to be staggered as depicted in III. More specific suggestions concerning the structures of the $[(Me_6C_6)_6M_6X_{12}]X_4$ derivatives must await a successful X-ray crystal structure determination on one of these derivatives, but preliminary indications suggest considerable difficulty in obtaining suitable single crystals of a $[(Me_6C_6)_6M_6X_{12}]X_4$ derivative.

Electrochemical studies indicate that the oxidations of $[(Me_6C_6)_3M_3Cl_6]^+$ to $[(Me_6C_6)_6M_6Cl_{12}]^{4+}$ (M = Nb and Ta) occur at potentials around −0.2 V and are reversible by triangular voltammetry. This electrochemical reversibility may relate to a trimetallic oxidized product $[(Me_6C_6)_3M_3Cl_6]^{2+}$ which dimerizes to the isolated $[(Me_6C_6)_6M_6Cl_{12}]^{4+}$ at a rate slow relative to the triangular voltammetry time scale (~0.01 sec), since electrochemical studies on solutions of $[(Me_6C_6)_6M_6Cl_{12}]^{4+}$ obtained either from $[(Me_6C_6)_6M_6Cl_{12}][PF_6]_4$ or by controlled potential electrolysis of $[(Me_6C_6)_3M_3Cl_6]^+$ at −0.1 V exhibit reduction waves not found in the polarogram of $[(Me_6C_6)_3M_3Cl_6]^+$ (*i.e.*, one at −1.10 V in $[(Me_6C_6)_6Nb_6Cl_{12}]^{4+}$).

The oxidation of $[(Me_6C_6)_3Nb_3Cl_6]^+$ to $[(Me_6C_6)_6Nb_6Cl_{12}]^{4+}$ has been accomplished by several chemical reagents including cerium (IV), *N*-bromosuccinimide, iodine, and even air in acid solution. The oxidation with the cerium(IV) derivative ammonium hexanitratocerate(IV) gives directly the hexanitratocerate(IV) salt of the oxidized niobium cluster, which is soluble in water and thus can be converted to water-insoluble salts of the $[(Me_6C_6)_6Nb_6Cl_{12}]^{4+}$ cation by simple metathesis. For this reason, ammonium hexanitratocerate(IV) was used for the oxidations of the hexamethylbenzene tantalum chloride and niobium bromide derivatives to the corresponding $[(Me_6C_6)_6M_6X_{12}]^{4+}$ cations, which were isolated as both hexafluorophosphates and thiocyanates by simple metatheses of the originally precipitated hexanitratocerates(IV). Iodine oxidation of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ resulted in the direct precipitation of the brown triiodide salt of the oxidized cation $[(Me_6C_6)_6Nb_6Cl_{12}][I_3]_4$.

All of the hexamethylbenzene metal halide cluster cations exhibit characteristic electronic spectra (Table II) which can be used for their identification in solution. The most intense maximum (extinction coefficients in the range 28,000-54,000) appear in the range 365-453 nm. A second maximum of about 25-40% of the relative intensity of the first maximum appears in the electronic spectrum of the niobium derivatives at 75-81 nm below the first maximum in the case of the reduced cations $[(Me_6C_6)_3Nb_3X_6]X$ and 48-54 nm below the first maximum in the case of the oxidized cations $[(Me_6C_6)_6Nb_6X_{12}]X_4$. Oxidation of a given $[(Me_6C_6)_3M_3X_6]^+$ cation to the corresponding $[(Me_6C_6)_6M_6X_{12}]^{4+}$ cation results in a hypsochromic shift of the most intense maximum in the electronic spectrum by 23 nm for the niobium derivatives and by 11 nm for the tantalum derivatives. A change from chlorine to bromine in the hexamethylbenzene niobium halide complexes results in a bathochromic shift of 30-35 nm for both maxima in the electronic spectra. The colors of solutions of these hexamethylbenzene niobium and tantalum halides are various shades of deep browns and greens with distinct differences for different systems consistent with these changes in their electronic spectra.

The original report of Fischer and Röhrscheid[14] described only the preparations of the niobium and tantalum chloride complexes $[(Me_6C_6)_3M_3Cl_6]^+$ (M = Nb and Ta). We have found that the corresponding niobium bromide complex $[(Me_6C_6)_3Nb_3Br_6]^+$ can be prepared as the bromide salt by a completely analogous reaction between niobium pentabromide, aluminum bromide, aluminum powder, and hexamethylbenzene. In our hands the yields of the niobium bromide complex (30-46%) were considerably better than those of the corresponding niobium and tantalum chloride complexes (10-31%) suggesting greater ease in the reduction of the bromide system relative to the chloride system consistent with the stabilization of lower oxidation states as the size of the halogen is increased. However, the niobium bromide complexes are much less stable in hydroxylic solvents such as methanol than are the corresponding niobium and tantalum chloride complexes. For this reason methanol was avoided as a solvent in the cerium(IV) oxidation of $[(Me_6C_6)_3Nb_3Br_6]Br$. An attempt to prepare a corresponding hexamethylbenzene tantalum bromide complex by reaction between tantalum pentabromide, aluminum bromide, aluminum powder, and hexamethylbenzene led instead to a relatively good yield (51%) of a brown product of stoichiometry $[(Me_6C_6TaBr_2]_n$, apparently a derivative with a still lower formal metal oxidation state. This tantalum bromide derivative was much less soluble in organic solvents than compounds of the types $[(Me_6C_6)_3M_3X_6]^+$ and $[(Me_6C_6)_6M_6X_{12}]^{4+}$. The maxima in the electronic spectrum of $[Me_6C_6TaBr_2]_n$ did not conform to the pattern established for the $[(Me_6C_6)_3M_3X_6]^+$ and $[(Me_6C_6)_6M_6X_{12}]^{4+}$ derivatives (Table II). The limited solubility of $[Me_6C_6TaBr_2]_n$ and the lack of applicable physical and spectroscopic techniques make data unavailable which provide a basis for postulation of a structure of this complex, although a structure containing Ta_3Br_6 triangles seems reasonable in view of the stuctures of the other compounds described in this paper. However, the alternative possibility that $[Me_6C_6TaBr_2]_n$ is an analog of the reported[14] $[Me_6C_6NbCl_2]_2$ cannot be excluded.

Numerous reactions of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ were investigated in order to prepare novel hexamethylbenzene niobium derivatives similar to known cyclopentadienylmolybdenum derivatives. These reactions were uniformly unsuccessful. Tertiary phosphines were unreactive toward the $[(Me_6C_6)_3Nb_3Cl_6]^+$ cation, which does not have an obvious position available for coordination by a Lewis base. Reactive organometallics (NaC_5H_5, $K_2C_8H_8$, LiC_6F_5) and other strongly reducing reagents such as zinc or sodium borohydride led to decomposition rather than the production of new organoniobium derivatives. This result is consistent with the irreversible reduction at potentials below −1.8 V found in the electrochemical studies. Strong reducing agents thus appear to cleave the hexamethylbenzene-niobium bond with resulting decomposition. Despite the low formal oxidation state of niobium in $[(Me_6C_6)_3Nb_3Cl_6]^+$, this cation showed no evidence for nucleophilic activity (*i.e.*, oxidative additions) in attempted reactions with the reactive halides benzyl chloride and trimethyltin chloride.

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