TABLE I
YIELDS OF BORANES FROM VARIOUS MAGNESIUM BORIDE SAMPLES

Expt.	Type of boron	Comp. of mixture	Temp. of heating, °C.	Time of heating, min.	% yield of hydrides (based on boron)			
					B_4H_{10}	B_5H_9	B_6H_{10}	Total
1	Tech. amorph.	Mg_3B_2	640	120	5.0	0.4	4.5	9.9
2	Tech. amorph.	Mg_3B_2	770	30	4.7	0.4	5.5	10.6
3	Tech. amorph.	Mg_3B_2	770	240	3.4	0.7	6.0	10.1
4	Tech. amorph.	MgB_2	770	30	1.1	0.4	2.7	4.2
5	Tech. amorph.	Mg_3B	770	30	6.6	0.3	5.5	12.4
6	99.5% pure cryst.	Mg_3B_2	770	40	1.8	0.2	2.2	4.2

its melting point (found −62.2°, reported −65°,[2] −63.4°,[7] −62.3°[8]), and its vapor pressure at 0° (found 7.2 mm., lit.[2,8] 7.2 mm.).

When a 3:1 by weight mixture of 98% pure magnesium powder and about 80% pure technical amorphous boron was heated to 780° for 30 min. in a covered alumina boat in a stream of pure hydrogen, a boride was formed which yielded 5.5% of its boron content as hexaborane on hydrolysis with 8 M phosphoric acid.[9] The total yield of hydrides was about 11% based on the boron. Table I shows the yields of tetraborane, pentaborane B_5H_9, and hexaborane from samples of magnesium boride prepared under different conditions. Appreciable amounts of decaborane were also formed but were not estimated in the total hydride yield. Trace amounts of unstable pentaborane B_5H_{11} were obtained from borides prepared at the higher temperatures.

The hydrolysis reaction was carried out in a 1-l. flask. In a typical experiment 5 g. of the powdered boride was tamped into five or six 1-cm. bore cylinders of very thin aluminum foil and these were added to 200 ml. of acid over a period of about 15 min. The foil dissolved away quickly, liberating the boride into the acid at a convenient rate. A flow of 600 ml./min. of hydrogen was passed for 1 hr. through the acid to carry the hydrides through a phosphorus pentoxide drying tube into a trap cooled in liquid oxygen.

The yields of hexaborane were reduced if the temperature of the phosphoric acid rose above about 80° during the hydrolysis. Temperature control was facilitated and the yields of hexaborane improved by using the high ratio of acid volume to boride weight of 200 ml.:5 g. Where the cost of boron is not limiting, the alloy of composition MgB_2 can be used to advantage (see experiment 4, Table I). It gives more hexaborane per weight of boride than Mg_3B_2 and evolves much less heat in reaction with the acid, so that larger samples of hexaborane can be made at one time. It is interesting that the relative yields of hydrides are the same from borides made with amorphous and crystalline boron (compare experiments 2 and 6, Table I) although the total hydride yield is much lower from the latter.

In our system the trapped hydrides were separated by injection onto a 12 ft. × 1 cm. column packed with 10% tritolyl phosphate on Celite. The detector was a katharometer (Pretzel Cell, Gow-Mac Instrument Co.) and the column flow was 600 ml./min. of oxygen-free hydrogen. Relative to n-hexane the retention times for tetraborane, pentaborane, and hexaborane on tritolyl phosphate at 20° are approximately 0.5, 3.7, and 49.5. At room temperature on our column the start of the peak from a 250-mg. sample of hexaborane emerged 2.5 hr. after the other boron hydrides and possible silane and phosphine impurities. This suggests that a 3 ft. × 1 cm. column would probably adequately purify samples of up to 250 mg. of hexaborane.

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[7] S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

[8] A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

[9] B. D. Steele and J. E. Mills, *J. Chem. Soc.*, 74 (1930).

CONTRIBUTION FROM THE RESEARCH LABORATORIES
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Tetracarbonylcyclopentadienyl Compounds of the Group V Transition Metals

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Although several organometallic compounds belonging to the classes of "double sandwich" and "half-sandwich" π-complexes of vanadium are known,[2] very few fully characterized organometallic[3] complexes of tantalum and niobium have been reported. The latter group is represented by the tetracyclopentadienyl complexes of niobium and tantalum,[4a] bis-cyclopentadienyltantalum trihydride,[4b] and the recently reported tetracarbonylcyclopentadienylniobium.[5] We now wish to report the preparation and properties of tetracarbonylcyclopentadienyltantalum, as well as a new and more efficient procedure for the vanadium and niobium homologs.

The reductive carbonylation of group V metal chlorides has previously been shown to furnish the

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[1] To whom all communications should be addressed.

[2] (a) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **9b**, 503 (1954); (b) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 5263 (1959); (c) R. P. M. Werner and S. A. Manastyrskyj, *ibid.*, **83**, 2023 (1961); (d) E. O. Fischer and H. P. Kögler, *Chem. Ber.*, **90**, 250 (1957); (e) R. L. Pruett, J. E. Wyman, D. R. Rink, and L. Parts, U. S. Patent 3,007,954 (Nov. 7, 1961).

[3] Defined here as those complexes which do not contain metal–oxygen or metal–halogen bonds.

[4] (a) E. O. Fischer and A. Treiber, *Chem. Ber.*, **94**, 2193 (1961); (b) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

[5] R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).

respective hexacarbonylmetalates(−I).(6) Further elucidation of this reaction, which can be carried out in diglyme(7) or dimethoxyethane using excess sodium as the reducing agent, has demonstrated that the use of a catalyst is quite advantageous. Whereas VCl_3 does not undergo reaction with the polydentate ether beyond formation of simple adducts such as VCl_3–diglyme, it was found that both $NbCl_5$ and $TaCl_5$ gradually cleaved the polyethers, presumably giving rise to compounds of the type Cl_4MOR (M = Nb, Ta). It is believed that the metal–oxygen bonds in these alkoxy metal halides or in the oxyhalides resulting from their decomposition are not readily disrupted under the conditions of the reductive carbonylation; for this reason the ether cleavage by $NbCl_5$ and $TaCl_5$ is rather detrimental to obtaining a high yield of the corresponding hexacarbonylmetalate. It was found that the rate of reductive carbonylation could be greatly increased by the presence of compounds of iron, ruthenium, or osmium, suggesting that the active carbonylating agent in the homogeneous reaction is one of the carbonyl derivatives of these metals which are, under the conditions chosen, readily formed and regenerated.

Since the formal oxidation state of the transition metals in the bis(diglyme)sodium hexacarbonylmetalates of Nb and Ta is Nb(−I) and Ta(−I), respectively, an oxidizing agent had to be provided in order to facilitate formation of the respective tetracarbonylcyclopentadienyl metal(+I) complex from the available hexacarbonylmetalate(−I). The oxidizing agent (mercury(II) chloride) was selected from those metal halides which can be readily reduced and do not form cyclopentadienyl compounds of exceeding stability.

The reaction of an equimolar mixture of mercury(II) chloride and cyclopentadienylsodium with the hexacarbonylmetalates of vanadium, niobium, or tantalum was usually carried out in dimethoxyethane, at room temperature. The bis(diglyme)sodium salts as well as the similar tris(dimethoxyethane)sodium hexacarbonylmetalates were used. Two moles of carbon monoxide were smoothly evolved over a short period of time, according to the equation

$$[\mathrm{Na\cdot diglyme_2}]^+[\mathrm{M(CO)_6}]^- + \mathrm{C_5H_5Na} + \mathrm{HgCl_2} \longrightarrow \mathrm{C_5H_5M(CO)_4} + 2\mathrm{CO} + 2\mathrm{NaCl} + \mathrm{Hg} + 2\ \mathrm{diglyme}$$

$$(\mathrm{M} = \mathrm{V, Nb, Ta})$$

Filtration to remove the solids containing the Hg metal yielded clear orange solutions. Removal of the solvent followed by sublimation at about 80–100° (0.05 mm.) furnished the tetracarbonylcyclopentadienyl compounds of vanadium, niobium, and tantalum in yields of 78, 41, and 63%, respectively. Removal of traces of cosublimed Hg was accomplished by ether extraction of the crude sublimates followed by filtration and resublimation, or it was avoided by hydrolyzing the reaction mixture prior to the first sublimation.

The two compounds, $C_5H_5Nb(CO)_4$ and $C_5H_5Ta(CO)_4$, were more stable, thermally and oxidatively, than $C_5H_5V(CO)_4$. They were soluble in most common organic solvents, their orange solutions being fairly stable under nitrogen, but gradually decomposing in air. Some of their properties are summarized in Table I.

TABLE I

PROPERTIES OF TETRACARBONYLCYCLOPENTADIENYL COMPOUNDS OF THE GROUP V TRANSITION METALS

Compound	M.p.	Principal CO stretching freq. (cm.$^{-1}$) in CS_2	Color
$C_5H_5V(CO)_4$	139°	1890, 1982	Orange
$C_5H_5Nb(CO)_4$	144–146°	1901, 2000	Red
$C_5H_5Ta(CO)_4$	171–173°	1900, 2020	Red

Further comparative studies of these three tetracarbonylcyclopentadienyl compounds, particularly of their reactive behavior toward various unsaturated hydrocarbons,(8) are currently being carried out at these laboratories, and results will be published in the near future.

Experimental

All solvents used were carefully de-aerated; diglyme and dimethoxyethane were distilled from sodium benzophenone ketyl. Sodium dispersions in mineral oil of 50% sodium content were used for the reductive carbonylations. $NbCl_5$ and $TaCl_5$ were supplied from a commercial source and freshly sublimed for each run. Melting points given are uncorrected.

Preparation of Bis(diglyme)sodium Hexacarbonylniobium(−I).—A sealed glass tube containing 54 g. (0.2 mole) of $NbCl_5$ was inserted into a 2-l. autoclave of 10,000-p.s.i. capacity in such a fashion as to facilitate complete breaking of the glass vessel upon commencement of stirrer action. An excess of 55.2 g. (2.4 g.-atoms) of sodium suspended in 800 ml. of diglyme was added together with 2 g. of anhydrous $FeCl_3$ and/or 2 g. of iron pentacarbonyl. The autoclave was pressurized with CO to 4000 p.s.i., stirring was initiated, and the contents were heated to 105° for about 20 hr., during which time an uptake of about 1000 p.s.i. CO took place. After cooling the mixture to room temperature, the autoclave was vented and the contents discharged, always maintaining a protective blanket of purified nitrogen. Addition of petroleum ether to the filtered clear and deeply yellow solution, which showed a strong infrared absorption at 1830 cm.$^{-1}$, furnished an oily precipitate of the salt, which subsequently solidified on further trituration with petroleum ether. The yield was 29 g., corresponding to 26.2%. Upon heating in a sealed nitrogen-filled capillary, the yellow solid decomposed at 145° without melting.

Anal. Calcd. for $C_{18}H_{28}NaNbO_{12}$: C, 39.14; H, 5.11; Nb, 16.82. Found: C, 38.3; H, 5.25; Nb, 16.5. The salt did not contain any iron.

The preparation of bis(diglyme)sodium hexacarbonylvanadium and bis(diglyme)sodium hexacarbonyltantalum was similarly carried out, as described elsewhere.(6) The corresponding Na dimethoxyethane salts were obtained in the same fashion, using dimethoxyethane as a medium for the reductive carbonylation.

Preparation of Tetracarbonylcyclopentadienyltantalum.—To a clear brown solution of 1.65 g. (0.0188 mole) of C_5H_5Na in 100 ml. of dimethoxyethane, a solution of 5.1 g. (0.0188 mole) of $HgCl_2$ in 50 ml. of dimethoxyethane was added with stirring, whereupon the original brown color changed to beige and a precipitate formed. The unfiltered solution of 8 g. (0.0125 mole) of [Na(dimethoxyethane)$_3$][Ta(CO)$_6$] in 100 ml. of dimethoxyethane was added slowly through a dropping funnel to the stirred mixture at 25°. The addition was completed after 2 hr., during which time 850 ml. (STP, 0.038 mole) of gas was collected. The

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(6) R. P. M. Werner and H. E. Podall, *Chem. Ind.* (London), 144 (1961).

(7) Diethylene glycol dimethyl ether.

(8) For example, see E. O. Fischer, H. P. Kögler, and P. Kuzel, *Chem. Ber.*, **93**, 3006 (1960).

solvent was then removed, using a rotary evaporator, and the residual solids were extracted with water in order to hydrolyze any cyclopentadienyl derivatives of sodium or mercury. The mixture was filtered under nitrogen, and the precipitate was washed several times with water. Subsequent extraction of the solid with ether furnished, after filtration through fluted paper in a nitrogen-filled funnel, a clear orange solution. Evaporation of the ether and subsequent sublimation at 105° (0.1 mm.) afforded large red crystals which were washed with a few ml. of cold petroleum ether and dried. The yield was 2.8 g. (68%) of pure compound which did not require resublimation. In another run, the procedure was slightly modified. The unfiltered solution of 12 g. (0.0187 mole) of $[Na(diglyme)_2][Ta(CO)_6]$ in 100 ml. of dimethoxyethane was added to the stirred mixture of 2.0 g. (0.0228 mole) of C_5H_5Na and 6.2 g. (0.0228 mole) of $HgCl_2$ in 50 ml. of dimethoxyethane. After filtration and removal of solvent under vacuum, the residual solids were sublimed to yield 4.6 g. of crude compound (68.8%) which, however, contained traces of mercury. This material was further purified by dissolving it in ether, filtering, removing solvent, and resubliming. The ruby-red crystals were stable in air for several days and melted, in a sealed capillary under nitrogen, at 171–173°. The compound was soluble in most common organic solvents and sublimed readily at 30–40° (10^{-4} mm.); its solutions decomposed upon exposure to air. In CS_2, its infrared spectrum exhibited bands at 1900 and 2020 cm.$^{-1}$; measurement of its magnetic susceptibility[9] showed the complex to be diamagnetic.

Anal. Calcd. for $C_9H_5O_4Ta$: C, 30.19; H, 1.41; Ta, 50.52. Found: C, 29.9; H, 1.48; Ta, 50.6.

Preparation of Tetracarbonylcyclopentadienylniobium.—The compound was prepared in a like fashion by treating $[Na(diglyme)_2][Nb(CO)_6]$ (9.0 g., 0.0163 mole) in dimethoxyethane with cyclopentadienylsodium (1.7 g., 0.019 mole) and mercury(II) chloride (5.5 g., 0.019 mole). After extracting the crude solids with water, ruby-red crystals were obtained by sublimation (1.8 g., 41%), melting at 144–146° under nitrogen. The compound was soluble in organic solvents and exhibited CO absorptions in its infrared spectrum at 1901 and 2000 cm.$^{-1}$, in CS_2.

Anal. Calcd. for $C_9H_5NbO_4$: C, 40.03; H, 1.87; Nb, 34.40. Found: C, 39.8; H, 2.09; Nb, 33.7.

Preparation of Tetracarbonylcyclopentadienylvanadium.—This compound was obtained analogously in 78% yield. It had a melting point of 139° (reported,[2a] 138°); its infrared spectrum, showing CO bands at 1890 and 1982 cm.$^{-1}$, was similar to the spectra of the niobium and tantalum complexes.

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[9] We wish to thank Prof. S. Kirschner of Wayne State University, Detroit, Mich., for carrying out the magnetic susceptibility measurement.

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Perfluorophenyl Derivatives of the Transition Metals

BY MARVIN D. RAUSCH

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In recent years a variety of compounds have been reported in which a perfluoroalkyl group is attached by means of a σ-bond to a transition metal.[1] We wish to report several examples of another new class of compounds, *viz.*, perfluorophenyl derivatives of the transition metals. These compounds are conveniently prepared by the reaction of perfluorophenylmagnesium bromide[2,3] with various transition metal halides Perfluorophenyl derivatives of phosphorus,[4] silicon,[4] lithium,[5] mercury,[5,6] and tin[7] have been described previously.

Treatment of a suspension of manganese pentacarbonyl bromide in ether with perfluorophenylmagnesium bromide followed by chromatography of the reaction products in benzene solution on alumina and subsequent vacuum sublimation produced pale yellow crystals of perfluorophenylmanganese pentacarbonyl, m.p. 121–122°, in 47% yield. *Anal.* Calcd.: C, 36.50; F, 26.24; Mn, 15.18; mol. wt., 362. Found: C, 36.61; F, 25.99; Mn, 14.94; mol. wt., 383. The F^{19} n.m.r. spectrum[8] of this product (saturated solution in benzene) exhibits a multiplet centered at 25.87 (±0.02) p.p.m., a triplet [J_{F-F} = 26 (±2) c.p.s.] at 79.16 (±0.02) p.p.m., and a multiplet centered at 83.06 (±0.06) p.p.m.

On the basis of the relative intensities and splitting patterns of the peaks as well as comparison of the spectrum with the F^{19} n.m.r. spectrum of bis(perfluorophenyl)mercury,[9] these resonances are assigned to the *ortho, para,* and *meta* fluorine atoms, respectively, of the perfluorophenyl group. Strong metal carbonyl stretching vibrations occur at 4.68, 4.87, 5.00, and 5.08 μ in the infrared spectrum (KBr pellet) of perfluorophenylmanganese pentacarbonyl, and the remainder of the spectrum is consistent with the presence of a perfluorophenyl group.[10]

From the reaction of perfluorophenylmagnesium bromide and π-cyclopentadienyliron dicarbonyl iodide in ether, followed by chromatographic separation of the reaction products, golden yellow crystals of π-cyclopentadienylperfluorophenyliron dicarbonyl, m.p. 144.5–145°, were obtained in *ca.* 7% yield. *Anal.* Calcd.: C, 45.39; H, 1.46; Fe, 16.23; F, 27.62; mol wt., 344. Found: C, 45.46; H, 1.55; Fe, 16.35; F, 27.42; mol wt., 366. The H^1 n.m.r. spectrum[11] of this

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[1] For reviews, see: H. J. Emeléus, *Angew. Chem. Intern. Ed. Engl.*, **1**, 129 (1962); R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, "Proceedings of the Sixth International Conference on Coordination Chemistry," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 619.

[2] W. J. Pummer and L. A. Wall, *J. Res. Natl. Bur. Std.*, **63A**, 167 (1959).

[3] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

[4] L. A. Wall, R. E. Donadio, and W. J. Pummer, *J. Am. Chem. Soc.*, **82**, 4846 (1960).

[5] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3227 (1962).

[6] R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *ibid.*, 4367 (1962).

[7] J. M. Holmes, R. D. Peacock, and J. C. Tatlow, *Proc. Chem. Soc.*, 108 (1963).

[8] F^{19} n.m.r. spectra were determined on a Varian Model HR-60 spectrometer at 27° and at a frequency of 56.444 Mc. Peaks are referenced to trifluoroacetic acid as an external standard, using either the superposition technique or by calibration of the trace by the side-band method.

[9] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, submitted for publication.

[10] J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, 13 (1959); 3719 (1961).

[11] H^1 n.m.r. spectra were determined on a Varian Model A-60 spectrometer at 36° and at a frequency of 60.000 Mc. Peaks are referenced to tetramethylsilane as an internal standard.