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.

Acknowledgment.—The authors wish to thank Dr. W. E. Burt for helpful suggestions during the course of this work.

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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.

CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT,
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Perfluorophenyl Derivatives of the Transition Metals

BY MARVIN D. RAUSCH

Received August 26, 1963

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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product (6% in deuteriochloroform) exhibits a single sharp peak at 5.04 τ; the corresponding peak for π-cyclopentadienyliron dicarbonyl iodide (10% in deuteriochloroform) occurs at 4.96 τ. The F^{19} n.m.r. spectrum (20% in benzene) of π-cyclopentadienylperfluorophenyliron dicarbonyl is similar to the spectrum of the manganese derivative, with multiplet resonances occurring at 28.6 ($\pm$0.1) and 85.4 ($\pm$0.1) p.p.m., and a triplet resonance [J_{F-F} = 20.6 ($\pm$1.0) c.p.s.] at 82.5 ($\pm$0.1) p.p.m. In analogy to similar reactions involving phenylmagnesium bromide,[12] appreciable amounts of the reduction product bis(π-cyclopentadienyliron) tetracarbonyl were isolated, as well as lesser amounts of perfluorobiphenyl.

Treatment of a methylene chloride solution of bis-(π-cyclopentadienyl)titanium dichloride with approximately two equivalents of perfluorophenylmagnesium bromide in ether produced a mixture of π-cyclopentadienylperfluorophenyltitanium derivatives.

The H^1 n.m.r. spectrum (deuteriochloroform solution) of the reaction products exhibits peaks at 3.30, 3.52, and 3.58 τ. By means of chromatographic separation of the reaction products in tetrahydrofuran solution and subsequent recrystallization from n-heptane, one of the reaction products (3.58 τ) was isolated and identified as bis(π-cyclopentadienyl)perfluorophenyltitanium chloride, m.p. 187–188°. *Anal.* Calcd.: C, 50.49; H, 2.65; Cl, 9.31; F, 24.96; Ti, 12.59; mol. wt., 381. Found: C, 50.39; H, 2.67; Cl, 9.30; F, 25.65; Ti, 12.20; mol. wt., 369. The other products of the reaction have not yet been separated into pure compounds, although elemental analyses indicate the product of 3.52 τ to be bis(π-cyclopentadienyl)-perfluorophenyltitanium bromide, resulting from halogen interchange. It is striking that the proton resonance absorptions for both bis(π-cyclopentadienyl)-perfluorophenyltitanium chloride and the product of 3.52 τ appear as triplets, with J equal to *ca.* 0.4 c.p.s. for each triplet. In contrast, a single sharp proton resonance peak is observed for bis(π-cyclopentadienyl)-titanium dichloride (deuteriochloroform solution) at 3.42 τ. These triplets may well arise from through-space coupling[13,14] of the cyclopentadienyl ring protons with the *ortho* fluorine atoms of the perfluorophenyl group.

In general, these new perfluorophenyl derivatives of the transition metals exhibit remarkable thermal and oxidative stabilities compared to their hydrocarbon analogs.[12,15,16] Similar enhanced stabilities have been noted previously for perfluoroalkyl–transition metal compounds. The electronegative perfluorophenyl group may inductively polarize the carbon–transition metal bond and increase the energy required for irreversible decomposition. This feature may make possible the isolation and characterization of perfluorophenyl–transition metal compounds for which hydrocarbon analogs are unattainable. Our studies along these lines are continuing.

Acknowledgment.—The author wishes to thank Mr. Claude Dungan for his assistance in obtaining and interpreting the F^{19} n.m.r. spectra.

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Transition Metal Complexes of Secondary Phosphines. IV. Some Complexes of Ruthenium, Rhodium, and Palladium

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Received August 30, 1963

In continuation of our study of secondary phosphine complexes of the group VIII transition metals,[1] we have prepared a number of ruthenium and rhodium chloro complexes and have attempted to convert them into phosphorus-bridged complexes by reaction with p-toluidine or triethylamine.[2] These attempts were unsuccessful, there being either no reaction (ruthenium) or reaction with the production of ill-defined products (rhodium). The chloro complexes are of well-known types and usually contain octahedral Ru(II) or Rh(III). $[RhCl_3\{HP(C_6H_5)_2\}_3]$ was isolated in two isomeric forms, presumably *cis* and *trans*. $[RhCl(C_2H_4)_2]_2$[3] reacts with diphenylphosphine to give a square-planar complex of Rh(I), $[RhCl\{HP(C_6H_5)_2\}_3]$. Attempts to prepare this complex by other routes, for example, from $[RhCl(CO)_2]_2$, were unsuccessful.

We also describe the preparation of $[PdCl_2\{HP(CH_3)_2\}_2]$ and its conversion into the phosphorus-bridged complex $[PdCl\{P(CH_3)_2\}\{HP(CH_3)_2\}]_2$.[2] The proton n.m.r. spectrum of the dimeric complex shows that the methyl resonance of the bridging $(CH_3)_2P$ group is a doublet. This is in contrast to the 1:2:1 triplet which is usually observed in the spectra of complexes containing four-membered rings involving a transition metal and $(CH_3)_2P$ groups.[4]

Experimental[5]

Diphenyl- and diethylphosphine were prepared as previously described.[2] Dimethylphosphine was prepared by reduction of tetramethylbiphosphine disulfide with $LiAlH_4$[6] and was used directly for complex formation. The n.m.r. spectrum was ob-

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