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.

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

BY R. G. HAYTER

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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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tained using a Varian Associates A-60 instrument. Melting points were determined on a heated Kofler block. All manipulations of the phosphine ligands were carried out in an atmosphere of nitrogen; unless otherwise specified, the complexes were sufficiently stable to be crystallized without exclusion of air.

Dichlorotetrakis(diethylphosphine)ruthenium(II).—Ruthenium trichloride (0.32 g., 1.24 mmoles), diethylphosphine (0.56 g., 6.20 mmoles), and ethanol (50 ml.) were refluxed for 2 hr. to give a yellow-green solution. After filtration, cooling gave yellow plates of the pure complex (m.p. 175–190°, yield 67%).

Anal. Calcd. for $C_{16}H_{44}Cl_2P_4Ru$: C, 36.1; H, 8.3; Cl, 13.3; mol. wt., 532. Found: C, 36.2; H, 8.0; Cl, 13.3; mol. wt. (C_6H_6), 500.

Dichlorotetrakis(diphenylphosphine)ruthenium(II) was similarly prepared, yellow crystals precipitating from the reaction mixture. Recrystallization from chloroform–hexane gave yellow-orange needles (m.p. 245–255°, with decomposition setting in above 200°, yield 29%).

Anal. Calcd. for $C_{48}H_{44}Cl_2P_4Ru$: C, 62.9; H, 4.8; Cl, 7.7. Found: C, 62.65; H, 4.8; Cl, 6.7.

Trichlorotris(diethylphosphine)rhodium(III).—$RhCl_3 \cdot 3H_2O$ (0.52 g., 1.965 mmoles) in ethanol (50 ml.) was treated with diethylphosphine (0.53 g., 5.9 mmoles) to give an immediate crystalline precipitate. After standing overnight the precipitated solid was filtered and crystallized from nitromethane–methanol to give orange prisms (m.p. 212–215° dec., yield 21%).

Anal. Calcd. for $C_{12}H_{33}Cl_3P_3Rh$: C, 30.05; H, 6.9; Cl, 22.2. Found: C, 30.3; H, 6.5; Cl, 21.4.

Trichlorotris(diphenylphosphine)rhodium(III) (Isomers A and B).—$(C_6H_5)_2PH$ (1.05 g., 5.63 mmoles) was added to a solution of $RhCl_3 \cdot 3H_2O$ (0.50 g., 1.88 mmoles) in ethanol (50 ml.) to give a yellow-brown precipitate which was filtered and dried. The crude product was extracted with hot acetone and addition of hexane to the filtrate precipitated pure isomer A as a yellow-brown microcrystalline powder (m.p. 150–170° dec., yield 40%).

Anal. Calcd. for $C_{36}H_{33}Cl_3P_3Rh$: C, 56.3; H, 4.3; Cl, 13.85; P, 12.1; mol. wt., 768. Found: C, 54.2; H, 4.9; Cl, 13.4; P, 11.8; mol. wt. (CH_2Br_2), 790.

The residue from the acetone extraction was crystallized from chloroform–hexane to give isomer B as pale yellow needles (m.p. 150–170° dec., yield 7%).

Anal. Found: C, 56.4; H, 4.5; Cl, 14.4; P, 11.5; mol. wt. (CH_2Br_2), 528.

Chlorotris(diphenylphosphine)rhodium(I).—$[RhCl(C_2H_4)_2]_2$[3] (0.20 g., 0.355 mmole), diphenylphosphine (0.53 g., 2.84 mmoles), and benzene (20 ml.) were stirred together for 15 hr. to give a slight yellow precipitate and an orange-red solution. After filtration under nitrogen, addition of hexane to the solution caused the slow separation of yellow-brown crystals which were filtered and washed with hexane (m.p. 173–175°, yield 52%).

Anal. Calcd. for $C_{36}H_{33}ClP_3Rh$: C, 62.0; H, 4.8; Cl, 5.1; P, 13.3; Rh, 14.8; mol. wt., 697. Found: C, 61.9; H, 4.7; Cl, 3.4; P, 12.9; Rh, 15.5; mol. wt. (C_6H_6), 680.

Dichlorobis(dimethylphosphine)palladium(II).—Dimethylphosphine was passed into a solution of $[PdCl_2\{P(C_4H_9)_3\}]_2$ (5.0 g., 6.60 mmoles) in dichloromethane (100 ml.) until the orange color faded to pale yellow. Removal of solvent at 15 mm. gave a yellow oil which formed a crystalline solid in acetone. Recrystallization from chloroform–hexane gave colorless prisms (dec. above 230°, yield 35%).

Anal. Calcd. for $C_4H_{14}Cl_2P_2Pd$: C, 15.9; H, 4.7; Cl, 23.5. Found: C, 16.4; H, 5.0; Cl, 23.1.

The acetone washings yielded yellow crystalline $[PdCl_2\{P(C_4H_9)_3\}_2]$. The reaction therefore takes place as follows

$$[PdCl_2\{P(C_4H_9)_3\}]_2 + 2(CH_3)_2PH \longrightarrow [PdCl_2\{HP(CH_3)_2\}_2] + [PdCl_2\{P(C_4H_9)_3\}_2]$$

The mixed complex is apparently unstable, in contrast to $[PdCl_2\{HP(C_2H_5)_2\}PR_3]$, R = C_2H_5, C_6H_5.[2]

Dichlorodi-μ-(dimethylphosphido)bis(dimethylphosphine)-dipalladium(II).—$[PdCl_2\{HP(CH_3)_2\}_2]$ (0.50 g., 1.13 mmoles), *p*-toluidine (0.12 g., 1.13 mmoles), and benzene (50 ml.) were refluxed together for 16 hr. to give a yellow solution and white precipitate. After filtration, the solution was evaporated leaving a yellow oil which crystallized in hexane. Recrystallization from benzene–hexane gave pale yellow needles (m.p. 150–154° dec., yield 45%).

Anal. Calcd. for $C_8H_{26}Cl_2P_4Pd_2$: C, 18.1; H, 4.9; Cl, 13.4; mol. wt., 530. Found: C, 18.4; H, 4.9; Cl, 13.9; mol. wt. (C_6H_6), 532.

The n.m.r. spectrum in $CDCl_3$ shows a singlet at 8.42 τ with a shoulder on the low field side and a doublet at 8.60 τ (J_{HP} = 6.4 c.p.s.). The resonance at 8.42 τ has a shape similar to that observed for the methyl resonance of $(CH_3)_2PH$ (at 8.85 τ) and is thus assigned to the terminal dimethylphosphine ligands. The doublet resonance is therefore due to the methyl groups attached to bridging phosphorus.

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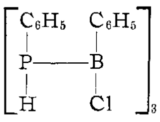
Correspondence

Phosphinoarylboranes

Sir:

On the basis of chemical composition, molecular weight, infrared spectra, and chemical reactions, the trimer



$$\left[\begin{array}{ll} C_6H_5 & C_6H_5 \\ | & | \\ P & \!\!\!-\!\!\!-\!\!\!-B \\ | & | \\ H & Cl \end{array}\right]_3$$

I

was identified as one of the products from the vacuum distillation of a solution prepared by adding $C_6H_5PH_2$ to a benzene solution containing excess $C_6H_5BCl_2$ and refluxing the mixture until evolution of HCl ceased.

The trimer (I) was a white, waxy solid (yield, about 15%) which sublimed at 60° under vacuum. The cryoscopic molecular weight in benzene was 680 and the chlorine content was 15.6 wt. % compared to the theoretical values of 697 for the molecular weight and 15.25 for the wt. % chlorine. The measured ratio of P:B in the trimer was 0.994 based on phosphorus and boron analysis of an air-hydrolyzed sample. The infrared spectrum of the trimer (in benzene) showed a sharp, moderately strong absorption band (probably P:H stretching) at 4.37 μ; relatively strong absorption bands also appeared at 6.21, 6.93, 7.25–7.50, 8.30, 8.78, 9.20, 10.35, 10.91, 11.15, 11.45, and 13.50 μ.

The trimer hydrolyzed rapidly in air. An air-hydrolyzed sample upon thermal decomposition under vacuum yielded a distillate which was approximately