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SYNTHESES OF NEW TETRAFLUOROARYL DERIVATIVES OF PHOSPHORUS AND SULFUR

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SUMMARY

A number of polydentate phosphorus and sulfur ligands, containing one or two 1,2,3,4-tetrafluorophenyl connecting groups, were readily synthesised from the lithium derivatives of diphenyl(*o*-bromotetrafluorophenyl)phosphine and 2,3,4,5-tetrafluorothioanisole. The latter molecules were prepared from the monolithium derivatives of 1,2-dibromotetrafluorobenzene and 1,2,3,4-tetrafluorobenzene, respectively.

RESULTS AND DISCUSSION

In connection with our interests in the design of new polydentate phosphorus, arsenic, and sulfur ligands to promote formation of complexes with unusual coordination numbers and stereochemistries, we have been interested in obtaining fluorine-substituted compounds of Groups V and VI. The monolithium derivatives of 1,2-dibromotetrafluorobenzene and 1,2,3,4-tetrafluorobenzene have been reported recently and have been used in the preparations of tetrafluorophenyl derivatives of silicon[1,2], germanium[3], tin[4,5], sulfur[3,4,6,7], and mercury[2-4]. We have used 2-bromo-3,4,5,6-tetrafluorophenyllithium (I), as well as 1,2,3,4-tetrafluorophenyllithium (II) to prepare polyfunctional sulfur and phosphorus tetrafluorophenyl compounds relatively easily and in good yields as depicted in the schemes below.

Diphenyl(2-bromotetrafluorophenyl)phosphine (III) can be prepared conveniently by adding chlorodiphenylphosphine to (I) at −78°. Compound (III) can serve as a stable intermediate for the synthesis of many 2-(diphenylphosphino)tetrafluorophenyl derivatives. For example, the crystalline, air-stable di- and tri-phosphines (IV) and (V) were prepared from the lithium derivative of (III) and the appropriate chlorophosphine.

Attempts to prepare the analogous tetraphosphine $\{o\text{-}[P(C_6H_5)_2]C_6H_4\}_3P$ by use of (III) has given only (VI) to date. Compound (VI) is the expected product after hydrolysis if only two of the three chlorines in phosphorous trichloride were replaced by perfluoroaryl substituents. Examination of an accurate molecular model of the desired tetraphosphine indicates that severe crowding occurs between fluorine

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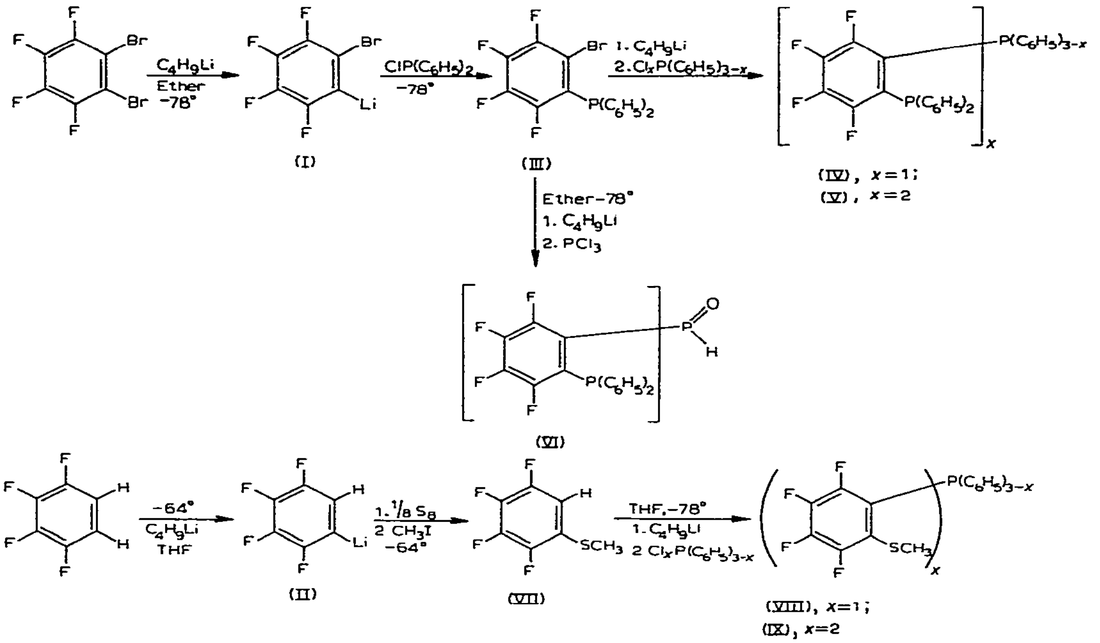

atoms that are *ortho* to the apical, pyramidal phosphorus because of the bulkiness of the large *ortho* diphenylphosphino groups. Since tris(pentafluorophenyl)phosphine is known[8], the additional steric interaction resulting from the diphenylphosphino groups may be sufficient to preclude addition of the third *o*-(diphenylphosphino)tetrafluorophenyl substituent.

The thioether intermediate (VII) can be prepared in 80% yield and provides a convenient route to numerous mixed sulfur–organometallic compounds. The air-stable, crystalline bidentate and tridentate ligands (VIII) and (IX) were isolated in ~60% yield.

It should be noted that both series of tetrafluorophenylphosphines form stable transition metal complexes. One interesting reaction of the coordinated sulfur-phosphorus ligands (VIII) and (IX) is the facile *S*-demethylation to produce coordination compounds of the corresponding phosphine-mercaptide ligand. The characterization and properties of the complexes will be reported elsewhere[9].

EXPERIMENTAL

All reactions were carried out under a dry nitrogen atmosphere. All reagents were distilled or recrystallized before use. Proton NMR spectra were obtained on a Varian A-60 instrument with all resonance positions reported relative to TMS. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The melting points are uncorrected.

(2-*Bromo*-3,4,5,6-*tetrafluorophenyl*)*diphenylphosphine* (*III*)

A solution of 20.0 g (0.065 mole) of 1,2-dibromotetrafluorobenzene in 200 ml of anhydrous diethyl ether was cooled to −78° by immersion of the reaction flask into a Dry-Ice/isopropanol bath. To the cold, stirred solution was added dropwise 40.2 ml of a 15.22% solution of n-butyllithium in hexane (0.065 mole). After the reaction mixture was stirred for 30 min, 14.3 g (0.065 mole) of diphenylchlorophosphine was added slowly. The resulting amber slurry was stirred for an additional 45 min and then removed from the low temperature bath and allowed to warm to room temperature, whereupon a white solid separated. After 30 min at room temperature, no further change in the reaction mixture was observed. The reaction mixture was hydrolyzed with water; the pale amber organic layer was separated and dried (Na_2SO_4) overnight. The solvents were removed by aspiration, yielding a yellowish, gummy solid. The solid was recrystallized from 30 ml of hot methanol to give 23.8 g (89% yield) of white crystals, m.p. 65–66°. (Found: C, 53.71; H, 2.48; P, 7.59. $C_{18}H_{10}BrF_4P$ calcd.: C, 52.32; H, 2.42; P, 7.50%.)

The quaternary methyl iodide derivative was prepared by refluxing (III) in a solution of ethanol and methyl iodide for 20 min. The white solid, which precipitated from the solution upon cooling, was collected on a filter and recrystallized from ethanol, m.p. 192–193°. (Found: C, 41.4; H, 2.4. $C_{19}H_{13}BrF_4IP$ calcd.: C, 41.1; H, 2.35%.)

1,2-*Bis(diphenylphosphino)tetrafluorobenzene* (*IV*)

A solution of 17.0 g (0.0411 mole) of (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine in 250 ml of diethyl ether was cooled to −78° by immersion of the reaction vessel into a Dry-Ice/isopropanol mixture. To the cold, stirred solution was added dropwise 25.5 ml of a 15.22% solution of n-butyllithium in hexane (0.0411 mole), and the resulting mixture was allowed to stir for 15 min. A solution of 9.08 g (0.0411 mole) of chlorodiphenylphosphine was added slowly and the reaction mixture was allowed to stir for 1 h; a pale yellow slurry resulted. The reaction mixture was then removed from the −78° bath and allowed to warm to room temperature as it stirred, producing an orange slurry over a period of 4 h. The reaction mixture was hydrolyzed with water; the orange organic layer was separated and dried ($CaSO_4$) overnight. The solvents were removed by an aspirator to give an orange syrup, which deposited a light pink solid on addition of cold ethanol. Light yellow crystals 15.9 g (74.7% yield) were obtained on recrystallization from ethanol. The slight yellow color persisted throughout repeated recrystallizations, m.p. 108–109°. (Found: C, 69.71; H, 3.90; P, 11.61. $C_{30}H_{20}F_4P_2$ calcd.: C, 69.50; H, 3.89; P, 11.95%.)

Bis[2-(diphenylphosphino)-3,4,5,6-tetrafluorophenyl]phenylphosphine (*V*)

To a solution of 14.24 g (0.0345 mole) of (2-bromo-3,4,5,6-tetrafluorophenyl)-diphenylphosphine in 150 ml of diethyl ether, precooled to −78°, was added 21.3 ml of a 15.22% solution of n-butyllithium in hexane (0.0345 mole). After the reaction mixture was stirred for 50 min, a solution of dichlorophenylphosphine (6.60 g, 0.0369 mole) in 25 ml of diethyl ether was added. After the mixture was stirred for an additional 50 min, the amber slurry was removed from the low-temperature bath and allowed to warm to room temperature. After 30 min at room temperature, the resultant yellow slurry was hydrolyzed with water; the amber organic phase was separated and dried ($CaSO_4$) overnight. The solvents were removed by an aspirator to give a yellow oil which, on addition of ethanol and cooling, deposited a yellow, crystalline solid. The solid was recrystallized twice by dissolving it in a minimum quantity of dichloromethane, filtering, adding ethanol to the filtrate, and allowing the dichloromethane to evaporate. Yellow, crystalline needles of the triphosphine (V) were obtained, m.p. 173.5–174.5°. (Found: C, 64.87; H, 3.16; P, 12.08. $C_{42}H_{25}F_8P_3$ calcd.: C, 65.14; H, 3.25; P, 11.99%.)

Attempted preparation of tris[2-(diphenylphosphino)-3,4,5,6-tetrafluorophenyl]phosphine. Preparation of (VI)

A solution of 16.4 g (0.0397 mole) of (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine in 150 ml of diethyl ether was converted to the lithium derivative as described above. A solution of 5.44 g (0.0397 mole) of phosphorous trichloride in 50 ml of diethyl ether was added and the resulting mixture was stirred for 1 h. The resulting pale yellow slurry was then removed from the cold temperature bath and allowed to warm to room temperature. After 30 min, no further change was observed and the slurry was hydrolyzed with 0.2 *M* hydrochloric acid. The fluffy white solid, which formed at the diethyl ether–water interface, was collected by filtration. The organic phase was dried ($CaCl_2$) overnight and the volume of solvent reduced, producing an additional quantity of fluffy white solid. The combined portions of the solid were then recrystallized from a hot 70% ethanol/30% benzene mixture to give 7.4 g of white solid, m.p. 185–186°.

The IR spectrum of this compound contained a medium intensity, fairly sharp peak at 2390 cm^{-1}, characteristic of a P–H stretching frequency. The absence of any strong O–H bands near 3500 cm^{-1} precludes a P–OH structure. The compound is formulated as the aryl secondary phosphine oxide (VI), $C_{36}H_{21}F_8OP_3$*. (Found: C, 60.65; H, 3.15; P, 13.34. $C_{36}H_{21}F_8OP_3$ calcd.: C, 60.52; H, 2.96; P, 13.00%.)

Synthesis of 2,3,4,5-tetrafluorophenyl methyl sulfide (VII)

A solution of 25.0 g (0.167 mole) of freshly distilled 1,2,3,4-tetrafluorobenzene in 100 ml of purified tetrahydrofuran was cooled to −64° by immersion of the reaction vessel into a chloroform slush bath. Over a 20 min interval, 103 ml of a 15.22% solution of n-butyllithium in hexane (0.167 mole) was added, and the reaction mixture was allowed to stir for an additional 5 min. A slight excess of elemental sulfur (6.4 g, 0.200 mole) was added directly to the reaction mixture and stirred for 15 min before adding 31.1 ml (0.500 mole) of methyl iodide. After the black reaction mixture had been stirred for 40 min, it was removed from the cold bath and allowed to warm to room temperature. After 45 min of stirring at room temperature, the reaction mixture had changed into a yellow-white slurry. The slurry was hydrolyzed with 100 ml of aqueous ammonium chloride solution, and the organic phase was separated and dried ($CaSO_4$) overnight. Solvents were removed by an aspirator and the remaining dark amber liquor was filtered to remove unreacted sulfur. The filtrate was dissolved in 30 ml of methanol, cooled to −78°, and filtered through a funnel which was maintained at −78°. A light brown solid (28.5 g) was obtained. This product was recrystallized twice from methanol at −78° to give a light amber, crystalline, lachrymatory solid which melted near 20°. The proton NMR spectrum showed a complex multiplet centered at τ 7.52 (S–CH_3 protons) and a broad complex multiplet at τ 3.20 (aryl proton) in relative intensities of 3.0 to 0.92.

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* Unfortunately, (VI) is insufficiently soluble in suitable solvents for a proton NMR spectrum.

The compound (VII) can also be vacuum distilled [b.p. 62.0°(0.6 mm)] for purification. (Found: C, 43.02; H, 2.06; S, 16.52. $C_7H_4F_4S$ calcd.: C, 42.85; H, 2.05; S, 16.34%.)

Diphenyl[2-(methylthio)-3,4,5,6-tetrafluorophenyl]phosphine (VIII)

A solution of 20.3 g (0.104 mole) of 2,3,4,5-tetrafluorophenyl methyl sulfide (VII) in 200 ml of anhydrous diethyl ether was cooled to −78° by immersion of the reaction vessel in a Dry-Ice/isopropanol bath. To the cold stirred solution was added 64.0 ml of a 15.22% solution of n-butyllithium in hexane (0.104 mole) over a 20 min interval, producing a brown-black solution. After 20 additional min, 22.9 g (0.104 mole) of chlorodiphenylphosphine dissolved in 25 ml of diethyl ether was added slowly to the black solution. The resulting mixture was stirred for 20 min and then removed from the −78° bath and allowed to warm to room temperature. The reaction mixture became a dark amber slurry on warming and after 1 h at room temperature, no additional change was noted. The reaction mixture was hydrolyzed with an aqueous ammonium chloride solution and the amber-red organic phase was separated. Solvents were removed with an aspirator to give a brown oil which, on addition of 50 ml of 95% ethanol, deposited 27.6 g (70.3% yield) of a crystalline, light tan solid. The compound was recrystallized from 95% ethanol and dried *in vacuo*. The proton NMR spectrum showed a singlet at τ 7.70 (S–CH_3 protons) and a multiplet centered at τ 2.72 (aryl protons), integrating in the ratio 3.0/10.0, m.p., 70–71°. (Found: C, 59.93; H, 3.45; P, 8.17. $C_{19}H_{13}F_4PS$ calcd.: C, 60.00; H, 3.44; P, 8.15%.)

Preparation of the methyl iodide derivative of (VIII)

A solution of 0.30 g of (VIII) in methyl iodide was refluxed for 2 h. The white crystals which precipitated as the solution cooled, were collected on a filter and washed with diethyl ether. The compound was recrystallized by dissolving it in hot ethanol, filtering the solution and adding diethyl ether to the filtrate. The resulting colorless needles were collected on a filter, washed with diethyl ether, and dried *in vacuo*, m.p., 173–174°. (Found: C, 46.22; H, 3.18. $C_{20}H_{16}F_4IPS$ calcd.: C, 46.17; H, 3.10%.)

Bis[2-(methylthio)-3,4,5,6-tetrafluorophenyl]phenylphosphine (IX).

Compound (IX) was prepared by the same procedure as (VIII), using dichlorophenylphosphine instead of chlorodiphenylphosphine*. A white, crystalline solid was obtained in 50% yield. The proton NMR spectrum showed a singlet at τ 7.59 (S–CH_3 protons) and a multiplet at τ 2.57 (aryl protons), integrating in the ratio 6.03/5.00, m.p. 97.0°. (Found: C, 47.70; H, 2.48; S, 13.55. $C_{20}H_{11}F_8PS_2$ calcd.: C, 48.19; H, 2.23; S, 12.87%.)

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* Specific details on the synthesis of (IX), along with its complexes, will be reported in *Inorg. Chem.* We thank J. Riker for these data.

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