$TCNQ^-$. In the region 300–600 nm, the brown solid shows strong bands at 345 and 492 nm (compared with 365 and 500 nm for the green $TCNQ^-$ salt).

Thus the brown product is formulated as the $[Co(acacen)(py)_2]^+$ salt of $TCNQ^{2-}$, rather than as a nitrile-bonded dimer similar to those of TCNE described earlier.[1] This compound is the first salt of the $TCNQ^{2-}$ anion to be reported. The $TCNQ^{2-}$ anion has only been previously known in solution from the electrochemical reduction of TCNQ.[13] As shown above, this anion is diamagnetic and does not show any electronic transitions in the visible region. The ir spectrum of the brown complex shows only two C≡N stretches at 2151 and 2102 cm^{-1}, whereas Crumbliss and Basolo[1] found five such bands for the nitrile-bonded TCNE dimers. The lowering of the frequency of these two bands from those of $TCNQ^-$ (at 2171 and 2145 cm^{-1} in solid $[Co(acacen)(py)_2]TCNQ$; at 2177 and 2144 cm^{-1} in acetone solution) is consistent with the $TCNQ^{2-}$ formulation, where a further electron has been placed in the antibonding orbitals, thereby weakening the C≡N bonds.

The behavior of TCNQ with [Co(acacen)py] in the presence of pyridine summarized in Scheme I contrasts markedly with that observed for TCNE.[1] The analogous $[Co(acacen)(py)_2]TCNE$ salt is not isolated from 1:1 mixtures of [Co(acacen)py] and TCNE in the presence of pyridine, but the nitrile-bonded dimers precipitate. However, these dimers in CH_2Cl_2 solution do give the $TCNE^-$ radical anion, a reaction analogous to that of the brown 2:1 adduct of TCNQ. The structures of the 2:1 adducts are very different in the TCNQ case (containing a second mole of coordinated pyridine and ionic $TCNQ^{2-}$) and the TCNE cases (the species contain Co—N≡C– linkages). These differences in behavior can be rationalized by considering the different redox properties of the two compounds TCNQ and TCNE (see Table I).

Table I

Reduction Potentials ($E_{1/2}$, V) *vs.* Standard Calomel Electrode

TCNQ[a]	TCNE[a]	$[Co^{III}(acacen)(py)_2]^+$ [b]
+0.10	+0.14	−0.47
−0.39	−0.75	

[a] Solvent CH_3CN, with 0.1 *M* Et_4NClO_4 as supporting electrolyte. [b] From ref 14.

From the reduction potential for $[Co^{III}(acacen)(py)_2]^+$, it is clear that the production of $TCNQ^{2-}$ in the third step of Scheme I would have an equilibrium constant of ~0.5 in 1 *M* solutions and could be driven to the right by the insolubility of the product (and reversed on solution of the product). A similar reaction forming the analogous $TCNE^{2-}$ salt would have an equilibrium constant of 10^{-7} and hence does not occur, the product obtained containing the Co—N≡C– linkages rather than the free dianion.

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The Slow Isomerization of 2-[Trifluoromethyl(trifluoromethylthio)-phosphino]pentaborane. Other New Phosphinopentaboranes[1]

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Compounds of the type 2,3-μ-$R_3MB_5H_8$ (M = Si, Ge, Sn, Pb) have been reported to isomerize slowly (usually by heating) to 2-$R_3MB_5H_8$,[2] convertible with even more difficulty to 1-$R_3MB_5H_8$.[3] However, the known phosphinopentaboranes have either persisted as 2,3-μ-$R_2PB_5H_8$ or appeared only as 1-$R_2PB_5H_8$.[4]

We now have made some new phosphinopentaboranes, one of which was isolated first as 2-$(CF_3SPCF_3)B_5H_8$, slowly convertible at 25° to 1-$(CF_3SPCF_3)B_5H_8$. The others involved more strongly basic phosphine groups, which remained in the 2,3-bridge position.

This study required the synthesis of the new compound $(CF_3S)_2PCF_3$, which was made quantitatively by the cleavage of $(CF_3P)_4$ by $(CF_3S)_2$ at 200°. This process, as well as the new quantitative synthesis of the known compound $CF_3SP(CF_3)_2$ from $P_2(CF_3)_4$ and $(CF_3S)_2$, might be regarded as analogous to the nucleophilic action of CH_3S–SCH_3 on the P–P bond[5] or perhaps more appropriately as a pseudohalogen action by CF_3S–SCF_3, like the long known cleavage of $(CF_3P)_4$ or $P_2(CF_3)_4$ by iodine. Both trifluoromethylthiophosphines seemed to have excellent stability, having been formed without loss at 200°. The reported instability of $CF_3SP(CF_3)_2$[6] presumably was an effect of catalytic impurities, not excluded by the original method of synthesis.

The New Thiophosphine.—A sample of $(CF_3P)_4$[7] (purified by recrystallization from hexane in the absence of air) was exposed to a fivefold proportion of $(CF_3S)_2$ in a sealed Pyrex tube at 200°. The reaction progressed only moderately during 1 day but was complete after 3 days. The millimolar stoichiometry of a typical run is shown as follows.

$$\begin{array}{ccccc} (CF_3P)_4 & + & 4(CF_3S)_2 & \longrightarrow & 4(CF_3S)_2PCF_3 \\ 1.78 & & 8.5 & & 7.1 \\ & & \underline{-1.4} & & \\ & & 7.1 & & \end{array}$$

The product was isolated by high-vacuum fractional condensation, using U traps at −23, −78, and −196°. No $(CF_3P)_4$ or $(CF_3P)_5$ was found in the −23° trap. For isolation and measurement of the unused $(CF_3S)_2$, the last of it was removed from the product by a small reflux column at −78°.

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The pure compound $(CF_3S)_2PCF_3$ melted at −93.5° (Stock magnetic plunger method). Vapor-phase molecular weights were 300, 302, and 298 (calcd 302). Its vapor-tension values at 0.0° (14.25 mm) and 23.3° (53.0 mm) and three points between were given very accurately by the equation $\log P(\text{mm}) = 8.4030 - 1980/T$. Since this equation implies a high Trouton constant (25.3 eu), the extrapolated boiling point (85.5°) probably is about 5° too low.

The infrared frequencies (cm^{-1}, Beckman IR7 instrument) of $(CF_3S)_2PCF_3$ are listed as follows, with relative intensities in parentheses: C–F stretching, 1175 (15), 1154 (7.4), 1117 (9.6), 1098 (8.0); CF_3 symmetric deformation, 762 (5.9), 748 (0.9), 745 (0.7); CF_3 asymmetric deformation, 568 (1.0), 544 (0.7); P–S stretching, 505 (3.9); S–CF_3 or P–CF_3 stretching, 433 (2.4); CF_3 rocking, 342 (0.8). A moderate peak at 1136 cm^{-1} is not assigned. The laser-Raman spectrum of this compound (kindly recorded for us by Dr. Robert Fenner of our Department of Physics) showed a peak at 1125 cm^{-1} (both polarized and depolarized); polarized only were 766, 263, and 165 cm^{-1}.

The ^{19}F nmr spectrum confirmed the formula $(CF_3S)_2PCF_3$. It was recorded by the HA-100 instrument (Cl_3CF substitution standard). The doublet of quartets at +36.0 ppm ($J_1 = 22$ cps, $J_2 = 1.1$ cps) belonged to CF_3S; half as intense was the CF_3P doublet of septets at +59.2 ppm ($J_1 = 80$ cps; J_2 consistent). The ^{31}P spectrum (centered at 47 ppm downfield of H_3PO_4) could be understood as a quartet of septets on the basis of the J values determined from the fluorine spectrum.

The mass spectrum of $(CF_3S)_2PCF_3$ showed the parent ion at m/e 302, confirmed by the sulfur isotope pattern. A metastable peak at 180 corresponded to the mass spectral reaction

$$\underset{302}{(CF_3S)_2PCF_3} \longrightarrow \underset{69}{CF_3^+} + \underset{233}{P(SCF_3)_2^+}$$

in terms of the calculation $180 = (233)^2/302$.[8]

The compound $(CF_3S)_2PCF_3$ failed to react at 100° with HCl (12 hr) or diborane (5 hr).

The Thiophosphinopentaborane.—The compound LiB_5H_8 (2.4 mmol) was formed in ether at −78° as usual[9] and treated with 2.5 mmol of $(CF_3S)_2PCF_3$ at −45°. The resulting light yellow liquid $CF_3SPCF_3B_5H_8$ was easily purified by a single fractional condensation at −33°; yield, 1.33 mmol (53%). Its vapor tension was 0.7 mm at 22° or 1.3 mm at 32°.

The ^{11}B nmr spectrum of this product was observed at 32.1 Mc. Initially, it was remarkably similar to that of $2\text{-}BrB_5H_8$:[10] the 2-B singlet at 27.2 ppm upfield of $(CH_3O)_3B$ overlapped the low-field peak of the 3,5-B doublet (δ 27; $J = 155$), and the 4-B doublet appeared only as an upfield shoulder from which δ could be estimated as 33 if $J = 170$ cps. The 1-B doublet was at δ 70.2 ppm; $J = 180$ cps. Beyond doubt, then, this was a 2-phosphinopentaborane.

After standing for 1 day at 25°, however, the sample showed the spectrum of a 1-phosphinopentaborane: the four basal boron atoms showed one large doublet at δ 31.5 ppm ($J = 156$ cps) and the 1-B a small singlet at δ 68 ppm, very much like $1\text{-}(CF_3)_2PB_5H_8$.[4] The ^{19}F nmr spectrum of this 1-B isomer was recorded at 94.1 Mc: δ 33 ppm ($J_{FCSP} = 16$ cps) and δ 66 ppm ($J_{FCP} = 82$ cps) for two equal doublets with δ measured upfield of Cl_3CF.

The vapor-phase molecular weight of an 8.5-mg sample of this compound was 255 (calcd 263). Its pure-water hydrolysis (sample 18.4 mg or 0.070 mmol) gave 0.78 mmol of H_2; expected, 0.77 mmol. Then a basic hydrolysis at 60° liberated 0.069 mmol of HCF_3 corresponding to one CF_3 on phosphorus. For this result to occur, it seems that the P–B connection would not have been destroyed by the pure-water hydrolysis, for the resulting $CF_3P(H)OH$ would have yielded half as much HCF_3 from the basic hydrolysis.

The volatility of $1\text{-}CF_3SPCF_3B_5H_8$ was not appreciably different from that of the 2 isomer.

Diphenylphosphinopentaborane.—A solution of 3.3 mmol of LiB_5H_8 in 20 ml of ether was treated with 0.58 ml of $(C_6H_5)_2PCl$ (kindly donated by Stauffer Chemical Co.), which was introduced by means of a measuring syringe, under dry N_2. The mixture was stirred for some hours at −78°. After most of the ether had been removed by vacuum evaporation, the viscous liquid was filtered through a sintered plate into an nmr tube.

The ^{11}B nmr spectrum of the product consisted of three doublets, δ_1 21 ($J_1 = 166$ cps), δ_2 44 ($J_2 = 156$ cps), and δ_3 66 ($J_3 = 200$ cps), measured in ppm upfield from $(CH_3O)_3B$. The intensity ratio was 2:2:1. It is reasonable to assign δ_3 to 1-B, δ_1 to 4,5-B, and δ_2 to a phosphorus-bridged 2,3-B pattern. This feature is atypical of μ-phosphinopentaboranes, earlier examples of which[4] had P–B and adjacent B–H couplings so similar that the feature near δ 44 ppm was a pseudotriplet. It is suggested that the phosphorus employs much of its s-electron character for bonding to carbon sp^2 orbitals of the two phenyl groups, so that the P–B coupling in $(C_6H_5)_2PB_5H_8$ is unusually small. On this basis, the B–H doublet would include unresolved P–B coupling.

Although $(C_6H_5)_2PB_5H_8$ was not more fully characterized, the standard method of synthesis and the nmr data leave no serious question of its existence.

Methylchlorophosphinopentaborane.—A solution of 3.2 mmol of LiB_5H_8 was treated with 3.3 mmol of CH_3PCl_2 (kindly donated by Ethyl Corp.), with low-temperature stirring. After 6 hr at −45°, the mixture yielded 2.9 mmol of $CH_3PClB_5H_8$ (90%, based on LiB_5H_8). The vapor tension of this product at 0° was 0.5 mm. Its mass spectrum showed the correct isotopic pattern for $CH_3PClB_5H_8^+$.

The analysis of a 58-mg sample of this compound was done by pure-water hydrolysis at 90–100° to yield, per molecule, 10.83 H_2 (expected, 11), 0.95 Cl^-, and 6.07 H^+ by titration to the phenolphthalein end point in the presence of mannitol. This acid would consist of HCl + $5B(OH)_3$. A separate experiment, employing an aqueous solution made from known amounts of $B(OH)_3$ and CH_3PCl_2, proved that the expected $CH_3P(OH)_2$ did not interfere with either the total-acid titration or the chloride determination by the Mohr method.

The new compound $CH_3PClB_5H_8$ proved to be unstable at 25°, showing resin formation within a few days. Its ^{11}B nmr spectrum was similar to that of

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$(CH_3)_2PB_5H_8$:[4] with $(CH_3O)_3B$ as the reference, there was a doublet at 18.9 ppm (J = 158 cps), an equally intense pseudotriplet at 41.5 ppm ("J" = 113 cps), and a doublet half as intense at 63.4 ppm (J = 153 cps). These features would correspond, respectively, to the 4,5-B, the 2,3-P-bridged B, and the 5-B atoms. Possible isomers, like those of $CH_3CF_3PB_5H_8$,[4] were not observed.

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Infrared Spectroscopic Evidence for Palladium Tetracarbonyl

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Binary carbonyls are known for a wide range of transition metals,[1] but although nickel tetracarbonyl was one of the first to be characterized, there appears to be very little evidence for the corresponding palladium carbonyl $Pd(CO)_4$. This is presumably because attempts to prepare this compound by routine methods have failed. Quite recently, however, Timms[2] has demonstrated that zerovalent organometallic compounds can readily be prepared by a new synthetic route in which metal atoms are cocondensed at low temperatures with a suitable ligand. If cocondensation takes place at 4°K in the presence of an inert gas, then this method closely resembles a typical matrix-isolation experiment, and, in particular, DeKock[3] has shown that when nickel atoms are cocondensed with Ar–CO mixtures in this way, nickel carbonyls are obtained.

We have been studying the parallel reaction between palladium atoms and Ar–CO mixtures deposited at cryogenic temperatures, and this note describes the characterization of palladium tetracarbonyl.

Experimental Section

A detailed description of the apparatus used for this work is described elsewhere.[4] In these experiments, palladium atoms were produced by heating palladium wire (99.99% pure) to ~1800°K and were cocondensed with a large excess (~1000-fold) of Ar–CO mixture on a cesium iodide window cooled to ~20°K. High-purity (Grade "X") argon and carbon monoxide ($C^{16}O$) were supplied by the British Oxygen Co., while samples of 90 atom % ^{18}O-enriched carbon monoxide were obtained from Miles Laboratories, Inc.

In a series of preliminary experiments, the mixtures of argon and carbon monoxide were varied in composition from 99% Ar–1% CO to 90% Ar–10% CO, and the window temperature was also varied. These experiments established that a number of different palladium carbonyl species could be formed depending mainly upon the Ar:CO ratio and to a lesser extent upon the temperature of the cesium iodide window. Thus the spectrum obtained from cocondensing Pd atoms with 99% Ar–1% CO at 15°K was quite different from that obtained using 90% Ar–10% CO at 27°K. Deposition rates were held constant at ~5 mmol/hr.

A detailed discussion of all the possible palladium carbonyls produced under different experimental conditions is beyond the scope of this note and will be presented in a future paper. However, a very simple spectrum was always obtained using a 95% Ar–5% CO mixture deposited at 27°K, and the results described here refer specifically to these conditions.

Results

Figure 1a shows part of the infrared spectrum obtained when palladium atoms are cocondensed at 27°K with a large excess of Ar–$C^{16}O$ (95% Ar–5% CO). A single palladium carbonyl peak is observed at 2070.3 cm^{-1}, and no other absorptions were noted apart from a strong band due to unreacted carbon monoxide and traces of CO_2 and H_2O. When we condensed nickel atoms under these conditions in a separate experiment, a prominent band was observed at 2050 cm^{-1} which is assigned by DeKock[3] to $Ni(CO)_4$. This suggests that the single peak in the Pd–Ar–CO experiment arises from the corresponding palladium tetracarbonyl, and this assignment is confirmed in experiments using Ar–$C^{16}O$–$C^{18}O$ mixtures.

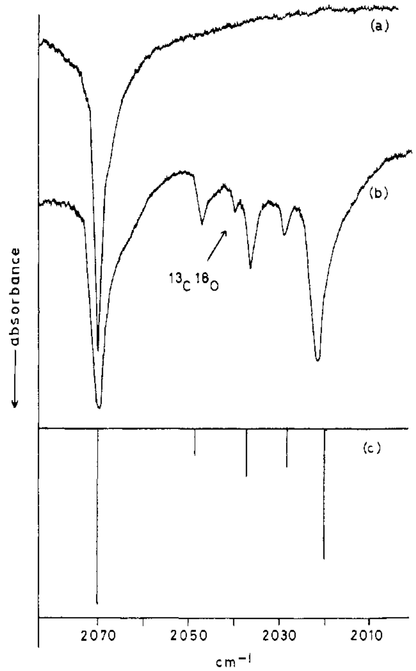

Figure 1.—(a) Infrared spectrum obtained from cocondensation of Pd atoms with Ar–$C^{16}O$ at 27°K. (b) Infrared spectrum obtained from cocondensation of Pd atoms with Ar–$C^{16}O$–$C^{18}O$ at 27°K. (c) Calculated spectrum for $Pd(C^{16}O)_n(C^{18}O)_{4-n}$ species.

Figure 1b shows the corresponding spectrum obtained when palladium atoms are condensed with a mixture of 95% Ar–2.7% $C^{16}O$–2.3% $C^{18}O$. This spectrum shows five prominent bands at 2070.3, 2047.5, 2037.0, 2029.0, and 2022.0 cm^{-1} due to Pd–$C^{16}O$–$C^{18}O$ species together with a weak feature at 2039.8 cm^{-1} which is due to matrix-isolated $^{13}C^{18}O$.

Discussion

If one assumes that the terminal C–O stretching vibrations in metal carbonyls may be "factored off" from the remaining vibrations of the molecule, it is then fairly straightforward[5] to calculate both the vibration frequencies and relative infrared band intensities for all

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