Preparation of $[(C_2H_5)_3NH]_3B_{20}H_{19}$. Method A.—To 30 ml of 0.436 *M* $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was added 30 ml of 2.1 *M* $FeCl_3$ and the two were thoroughly mixed. After 3 hr at room temperature, the reaction mixture was filtered and the solid washed repeatedly with cold water until the washings were free of Fe(II) and Fe(III) ions. Subsequently, the wet solid was washed with four 25-ml aliquots of methanol, removed from the filter paper, stirred for 15 min with 50 ml of acetone, and separated by filtration. The resulting white solid weighed 0.5623 g and melted at 163–164° after being kept for 24 hr over P_2O_5 *in vacuo;* its ultraviolet spectrum showed no evidence of $B_{20}H_{18}^{2-}$. Elemental analysis indicated that the water of hydration amounted to no more than 0.4% by weight. The filtrate and the washings were combined, reduced to half the initial volume on a steam bath, allowed to cool to room temperature, and left standing for 24 hr. Filtration of the resulting mixture yielded 2.0932 g of $[(C_2H_5)_3NH]_2B_{20}H_{18}$.

Method B.—With the aid of a pipet 10 ml of 4 *M* $FeCl_3$ was introduced underneath 15 ml of 0.872 *M* $[(C_2H_5)_3NH]_2B_{10}H_{10}$, contained in a medium size Petri dish (8 cm in diameter). The two aqueous layers remained undisturbed for 20 hr; then the remaining clear liquid phases were siphoned out, and the residual wet solid was separated by filtration and washed with five 25-ml aliquots of cold water. After drying for 24 hr over P_2O_5 the crude product weighed 2.4378 g. Since its ultraviolet spectrum still exhibited a weak band at 293 mμ the solid was washed with four 25-ml aliquots of acetone and dried. The resulting product was white, mp 163–164°, and its ultraviolet spectrum showed no evidence of absorption at either 293 or 232 mμ. The weight of the washed material, 2.0252 g, indicated that $[(C_2H_5)_3NH]_3B_{20}H_{19}$ made up over 80% (by mole) of the crude product.

Preparation of $[(C_2H_5)_3NH]_5(B_{20}H_{18}\cdot B_{20}H_{19})$.—A 0.2230-g sample of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ was dissolved in 50 ml of boiling methanol and the solution immediately allowed to cool to room temperature. After 24 hr 0.0942 g of very clear large crystals, melting at 203–204°, was isolated. The product was identified as the double salt by means of its ultraviolet and infrared spectra.[2,3]

Preparation of $[(CH_3)_4N]_3B_{20}H_{19}$.—A 0.5725-g sample of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ in 25 ml of acetonitrile was stirred with 5 ml of 1 *M* tetramethylammonium chloride for 30 min and filtered. The precipitate was first washed with 10 ml of water, then with two 25-ml aliquots of acetonitrile, and dried over P_2O_5 for 12 hr. The dry product, which was characterized by its ultraviolet and infrared spectra,[2,3] weighed 0.3835 g.

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Nuclear Magnetic Resonance in Polycyclic Compounds. III. Evidence for P^{31}–H^1 Spin–Spin Sign Changes in the PCH Bonds of a New Polycyclic Phosphine

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Received June 26, 1967

There exists a substantial body of evidence which suggests strongly that the absolute sign of the phosphorus–hydrogen coupling constant is positive in compounds such as $P(CH_3)_3$ and $P(CH_2CH_3)_3$ and negative in phosphonium salts and trialkylphosphine chalcogenides such as PR_4^+ and OPR_3, respectively.[2] That a change in sign of J_{PCH} from three- to four-coordinate phosphorus compounds of this type takes place has been known with fair certainty for some time.[3] Such a sign change was demonstrated recently by the observation that J_{PCH} for $P(CH_3)_3$ passed through zero as $Al(CH_2CH_3)_3$ was added to form the labile but slightly dissociated 1:1 adduct.[4]

We present evidence here which is consistent with a decrease in the absolute magnitude of J_{PCH} to zero as the new polycyclic phosphine $P(CH_2O)_3CCH_3$[5] (I) is converted to $Fe(CO)_4(I)$ or *trans*-$[Fe(CO)_3(I)_2]$ followed by a progressive increase upon oxidation of I to $SP(CH_2O)_3CCH_3$ (II) and $OP(CH_2O)_3CCH_3$ (III). Moreover, these changes parallel those we observed earlier for J_{POCH} in the analogous derivatives of $P(OCH_2)_3CCH_3$.[6]

Experimental Section

Preparation of $P(CH_2O)_3CCH_3$ (I).—This polycycle was synthesized following a preparation we reported earlier for $P(CH_2O)_3CH$ (IV)[7] except that the methanol produced was removed by a nitrogen flush as soon as the temperature of the reaction mixture reached 90°. The oily residue which solidified on cooling was sublimed twice under vacuum at 60° to give a 60% yield of colorless crystals.

Anal. Calcd for $C_5H_9O_3P$: C, 40.54; H, 6.07. Found: C, 40.27; H, 5.90. The mass spectrum obtained at a source temperature of 200° exhibited a parent peak corresponding to mass 148 as expected.

Preparation of $SP(CH_2O)_3CCH_3$ (II).—A mixture of 1.0 g of I (6.7 mmoles) and 0.20 g of sulfur (6.7 mg-atoms) was heated in a sealed tube for 1 hr at 110°. An acetone extract of the residue upon concentration and addition of methanol gave a white solid which sublimed at 60° under vacuum to give a 33% yield of II as colorless crystals. A medium band at 744 cm^{-1} characteristic of the P=S group was observed in Nujol in the infrared spectrum.

Anal. Calcd for $C_5H_9O_3PS$: C, 33.22; H, 5.00. Found: C, 33.28; H, 5.07.

Preparation of $OP(CH_2O)_3CCH_3$ (III).—To 1.0 g of I (6.7 mmoles) dissolved in 10 ml of absolute ethanol containing about 3 g of Linde 4A Molecular Sieve was added 0.8 g of 30% hydrogen peroxide (6.7 mmoles of H_2O_2). After standing 15 min at room temperature, the mixture was filtered and the solution concentrated under vacuum to 5 ml. Cooling this solution to 0° gave a 20% yield of III as colorless crystals after several hours. A strong infrared band at 1200 cm^{-1} observed in $CHCl_3$ is assigned to the P=O stretching mode.

Anal. Calcd for $C_5H_9O_4P$: C, 36.59; H, 5.49. Found: C, 37.18; H, 5.48.

Preparation of $P(CH_2O)_3CH$ (IV), $SP(CH_2O)_3CH$ (V), and $OP(CH_2O)_3CH$ (VI).—Compounds IV and VI were prepared as described earlier.[7] The thiophosphine V was prepared in the same way as was II. The product sublimed at 40° under vacuum to give a 28% yield of colorless crystals.

Preparation of $Ni(CO)_2(I)_2$.—This complex was prepared by

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[1] Alfred P. Sloan Fellow.

[2] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966), and references therein.

[3] G. Mavel in "Progress in N.M.R. Spectroscopy," Vol. 1, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N. Y., 1966, p 251.

[4] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966).

[5] The new compound $P(CH_2O)_3CCH_3$ (I) is named 4-methyl-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane. The names of the derivatives $SP(CH_2O)_3CCH_3$ (II) and $OP(CH_2O)_3CCH_3$ (III) are the same except they are preceded by 1-sulfo and 1-oxo, respectively.

[6] J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

[7] E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Am. Chem. Soc.*, **88**, 1140 (1966).

adding 2.5 g of I (17 mmoles) to 3.2 ml of $Ni(CO)_4$ (24 mmoles) dissolved in 20 ml of $CHCl_3$. After stirring the mildly exothermic reaction mixture for 2 hr at room temperature, the solution was filtered and evaporated under vacuum to give a light brown solid. Recrystallization from pentane gave a 73% yield of colorless complex. The infrared spectrum in CH_2Cl_2 revealed two strong peaks due to the CO groups at 2030 and 1978 cm^{-1}.

Anal. Calcd for $Ni(CO)_2(I)_2$: C, 35.06; H, 4.38. Found: C, 35.32; H, 4.42.

The following reactions were used to prepare $Ni(CO)(I)_3$ and $Ni(I)_4$ which could only be partially characterized because of their poor stability to decomposition and oxidation. To a solution of 1.0 g (2.4 mmoles) of $Ni(CO)_2(I)_2$ in 20 ml of ethylbenzene was added 0.36 g (2.4 mmoles) of I. Refluxing the solution for 3 hr, followed by concentration and cooling, gave a 79% yield of the $Ni(CO)(I)_3$ as colorless crystals. A similar procedure with a 2.5:1.1 mole ratio of $Ni(CO)_2(I)_2$ to I yielded a 56% yield of the $Ni(I)_4$ as colorless crystals. Attempts to isolate the monosubstituted complex were fruitless. The formulation of these compounds as the tri- and tetrasubstituted complexes was consistent with their infrared spectra in CH_2Cl_2 which showed a strong CO band at 1971 cm^{-1} and the absence of a CO mode, respectively.

Preparation of $Fe(CO)_4(I)$.—A solution containing 2.0 g (14 mmoles) of I and 1.8 ml (14 mmoles) of $Fe(CO)_5$ in 25 ml of ethylbenzene was irradiated in a quartz tube with a Hanovia No. 658 A lamp for 2 hr. Filtration and evaporation of the solution produced a pale yellow solid which was recrystallized from pentane to give a 20% yield of $(I)Fe(CO)_4$ as pale yellow crystals. The infrared spectrum in the CO region taken in CH_2Cl_2 revealed bands at 2059 (s), 1988 (s), and 1949 (vs) cm^{-1}.

Anal. Calcd for $Fe(CO)_4(I)$: C, 34.25; H, 2.84. Found: C, 34.75; H, 2.76.

Preparation of *trans*-$Fe(CO)_3(I)_2$.—A preparation similar to the preceding using a 2:1 mole ratio of I to $Fe(CO)_5$ and irradiating for 5 hr produced a brown solid upon cooling the reaction mixture. Concentration of a CH_2Cl_2 extract of the solid gave a 39% yield of $Fe(CO)_3(I)_2$ as pale yellow crystals. Its infrared spectrum in CH_2Cl_2 showed a very strong band in the CO region at 1904 cm^{-1}.

Anal. Calcd for $Fe(CO)_3(I)_2$: C, 35.82; H, 4.04. Found: C, 36.12; H, 4.28.

Preparation of $C_5H_{12}O_3PB$.—Absorption of diborane by an ether solution of I (0.84 *M*) was carried out by techniques described earlier.[8] The stirred mixture was allowed to equilibrate at −78° overnight after which the solid was filtered off and washed with ether while on the vacuum line. An infrared spectrum in Nujol revealed peaks in the BH stretching region at 2368 (m) and 2342 (m) cm^{-1}.

Anal. Calcd for $C_5H_{12}O_3PB$: C, 37.08; H, 7.47; P, 19.13; B, 6.68. Found: C, 36.92; H, 7.50; P, 19.27; B, 6.62.

Attempts to prepare the $B(CH_3)_3$ adduct of I in $n\text{-}C_5H_{12}$ at −45° were unsuccessful. Two moles of BF_3 was absorbed by I in CH_2Cl_2 at −78° producing a white unstable solid. No 1:1 adduct could be isolated despite presence of excess I. The orthoformate $CH_3C(CH_2O)_3CH$[7] also absorbed 2 moles of BF_3 under the same conditions but decomposition of the reaction mixture prevented further characterization. Attempts to make phosphonium salts of I with $[(CH_3CH_2)_3O]BF_4$ or $[(C_6H_5)_3C]BF_4$ resulted in intractable oils.

Nmr Spectra.—Proton nmr spectra were observed in 10–20% solutions in the solvents specified in Table I on a Varian A-60 instrument using tetramethylsilane as an internal standard.

Results and Discussion

It is not obvious why I was not observed to absorb $B(CH_3)_3$. Isolation of the stable adduct $(CH_3)_3BP(OCH_2)_3CCH_3$ reported earlier[9] suggests that the more distant electronegative oxygens in I should decrease the basicity of phosphorus even less than those in $P(OCH_2)_3CCH_3$. Furthermore $(CH_3CH_2)_3BP(CH_3)_3$ has been found to be stable at 0°.[10] It is tentatively suggested that I is a poor base because the phosphorus is at the positive end of the molecular dipole and hence is not easily polarized by the relatively weak Lewis acid $B(CH_3)_3$. This is substantiated by the fact that subtraction of 1.19 D. (the dipole moment of $P(CH_3)_3$[11] for the $P(CH_2)_3$ moiety of I from the total dipole moment of 2.71 D. for $CH_3C(CH_2O)_3CCH_3$ leaves 1.52 D. for the moment of I compared with its measured value of 1.53 D.[12] The lack of formation of a tractable 1:1 adduct of I with BF_3 is probably due to the behavior of two of the oxygens as basic sites and the poor polarizability of phosphorus for reasons cited above. The absorption of 2 moles of BF_3 by $CH_3C(CH_2O)_3CH$ under the same conditions supports the postulated function of the oxygens in I. Absorption of 3 moles of BF_3 was followed by decomposition even at −78°. Phosphonium salt formation could also have been prevented by the poor polarizability of phosphorus.

The coupling constants J_{PCH} among the proton nmr data in Table I are seen to range in absolute magnitude from an unobservable value near zero to 8.0 Hz for I and IV and their derivatives. In an earlier report[6] it was pointed out that J_{POCH} increased linearly with the methylene proton chemical shift in a series of σ-bonded adducts of the phosphite $P(OCH_2)_3CCH_3$ as the electronegativity of the Lewis acids increased in the order: electron pair < $B(CH_3)_3$ < BH_3 < $CH_3CH_2^+$ < $(C_6H_5)_3C^+$. The only σ-bonded adduct of I described here is the BH_3 compound and so no similar correlation could be made. It is noted that the J_{PCH} value decreased in absolute magnitude upon adduct formation although the methylene proton chemical shift moved downfield as expected.[13] This observation and the small and near-zero PCH coupling values measured for the nonlabile metal complexes of I show that the PCH spin interaction can pass through zero depending on the nature of the group attached to phosphorus. The existence of these complexes in which J_{PCH} is unobservable adds credence to the generally accepted supposition that a sign change occurs.

Assuming that a change in sign in J_{PCH} takes place in the above compounds, it is satisfying to note the parallel in the progression of J_{POCH} and J_{PCH} in analogous compounds of $P(OCH_2)_3CCH_3$ and I, respectively (Table I). Thus, regardless of whether the sign change from I to II and III is negative to positive or *vice versa*, the complexes and adduct of I possess J_{PCH} values which fall between I and the chalcogenides of I. A similar ordering is seen for $P(OCH_2)_3CCH_3$ and its derivatives.

Although the small PCH couplings in the BH_3 adduct and the dicarbonylnickel(0) complex of I may be

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[8] B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **6**, 173 (1967).

[9] C. W. Heitsch and J. G. Verkade, *ibid.*, **1**, 392 (1962).

[10] R. R. Holmes and R. P. Carter, *ibid.*, **2**, 1146 (1963).

[11] D. R. Lide, *J. Chem. Phys.*, **29**, 914 (1958).

[12] R. D. Bertrand, A. C. Vandenbroucke, and J. G. Verkade, submitted for publication.

[13] No exchange effects were observed in the nmr spectra of $(I)BH_3$ as was noted in the case of $(CH_3)_3PAl(CH_2CH_3)_3$.[4] Thus the J_{PCH} and chemical shift values cited for $(I)BH_3$ remained unchanged in the presence of excess ligand and the ligand spectrum was clearly visible.

TABLE I

PROTON NMR DATA FOR POLYCYCLIC PHOSPHORUS COMPOUNDS[a]

Compound	J_{PCH} or J_{POCH}	$\delta(CH_3)$	$\delta(CH_2)$	Solvent
$P(CH_2O)_3CCH_3$ (I)	8.0	1.23	4.30	CCl_4
$SP(CH_2O)_3CCH_3$ (II)	5.6	1.40	4.49	$(CH_3)_2CO$
$OP(CH_2O)_3CCH_3$ (III)	7.3	1.43	4.40	$CDCl_3$
$P(CH_2O)_3CH^b$ (IV)	8.5		4.33	CCl_4
$SP(CH_2O)_3CH^b$ (V)	5.3		4.46	$CDCl_3$
$OP(CH_2O)_3CH^b$ (VI)	7.4		4.42	$CDCl_3$
$Fe(CO)_4(I)$	$\dots^c$	1.40	4.48	CCl_4
$Fe(CO)_3(I)_2$	$\dots^c$	1.42	4.49	CH_2Cl_2
$Ni(CO)_2(I)_2{}^d$	1.8	1.34	4.38	CH_2Cl_2
$(I)BH_3$	0.8	1.13	4.46	$CDCl_3$
$SP(OCH_2)_3C(CH_2)_4CH_3$	7.2	$\dots^e$	4.47	$CDCl_3$
$OP(OCH_2)_3C(CH_2)_4CH_3$	6.6	$\dots^e$	4.49	$CDCl_3$
$P(OCH_2)_3CCH_3{}^f$	2	0.72	3.93	$CDCl_3$
$SP(OCH_2)_3CCH_3{}^f$	7	0.87	4.48	$CDCl_3$
$OP(OCH_2)_3CCH_3{}^f$	6	0.90	4.48	$CDCl_3$
$Fe(CO)_4(P(OCH_2)_3CCH_3)^g$	5.1	0.90	4.48	$(CH_3)_2CO$
$Fe(CO)_3(P(OCH_2)_3CCH_3)_2{}^g$	5.0	0.85	4.35	$(CH_3)_2CO$
$Ni(CO)_2(P(OCH_2)_3CCH_3)_2{}^g$	4.0	0.74	4.10	$CDCl_3$
$(CH_3C(CH_2O)_3P)BH_3{}^h$	4.2	0.80	4.30	CD_3CN

[a] J and δ values are in Hz and ppm, respectively. [b] The methine proton resonance appears at 5.32, 5.67, and 5.54 ppm in IV, V, and VI, respectively. [c] No coupling observed. [d] Instability of the tri- and tetrasubstituted nickel(0) complexes prevented observance of their nmr spectra. [e] Complex multiplet in the regions 1.54–0.61 and 1.40–0.72 ppm in the 1-oxo and 1-sulfo derivatives, respectively. [f] J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962). The values for J_{POCH} in the chalcogenides in this reference are reversed but are given correctly in this table. [g] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *ibid.*, **4**, 228 (1965). [h] J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

either positive or negative, the signs in I and IV are positive and those in their respective chalcogenides are negative provided the arguments of Manatt, *et al.*,[2] apply. As the s character in the P–C bond increases, positive PCH coupling should become less positive.[2] As expected then, J_{PCH} is seen to decrease as the lone-pair electrons in I gain p character upon coordination and the P–C bonds gain s character. This argument can also be used to explain the observation that J_{PCH} in $P(CH_2OH)_3$ (2.3 Hz)[7] more than triples in I. The probable decrease in the CPC bond angle in forming the bicyclic system would decrease the s character in the P–C bonds and thus increase the PCH coupling.

Experimental evidence has been cited[2] which is consistent with the contention that as the s character in the P–C bond increases, negative PCH coupling should become less negative.[2] Thus the PCH coupling values[3] in $SP(CH_3)_3$ (13.0 Hz) and $SP(CH_2CH_3)_3$ (11.9 Hz) should be larger in magnitude than those in the corresponding phosphine oxides $OP(CH_3)_3$ (13.4 Hz) and $OP(CH_2CH_3)_3$ (11.3 Hz) if the greater electronegativity of oxygen is the predominating influence. The unexpected ordering in $SP(CH_2CH_3)_3$ and $OP(CH_2CH_3)_3$ is also seen in II and III and V and VI, respectively, where the relative differences are even greater. That these couplings are reversed by some other predominant factor is indicated by the same unexpected ordering of POCH coupling constants in $SP(OCH_2)_3CCH_3$ and $SP(OCH_2)_3C(CH_2)_4CH_3$ compared to their 1-oxo derivatives (see Table I) as well as in $SeP(OCH_3)_3$ (14.1 Hz) and $SP(OCH_3)_3$ (13.4 Hz), compared to $OP(OCH_3)_3$ (10.5 Hz).[3] The POCH coupling in phosphate derivatives is concluded to be positive in sign,[14] and its magnitude is expected to increase as the s character in the P–O bonds is increased.[6] Thus the unexpected trends in both J_{PCH} and J_{POCH} are perhaps attributable to some as yet unexplained effect associated with the π-bonding characteristics of the chalcogen.

(14) E. Duval and E. A. C. Lucken, *Mol. Phys.*, **10**, 499 (1966).

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Nuclear Magnetic Resonance Spectra of Cobalt Ammine Complexes with Isomeric Ligands

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Received July 13, 1967

Proton resonance data for some carboxylatopentaammine cobaltic complexes in solution in D_2O are given in Table I. The complexes were prepared following published methods,[2] except that they were isolated as the nitrates by the addition of nitric acid to the reaction mixtures. The large separations between the broad lines of the *cis*- and *trans*-NH_3 protons have been discussed previously.[3] The values of the coupling constants in the ligands were found to be similar to those found in the free acids.[4]

In the complexes formed from the monobasic acids, the line positions are independent of pH, as expected. In the complexes formed from dibasic acids, only one carboxylate group is bonded to the cobalt; the CH line positions at pH 1, where the free group is COOH, are different from those at pH 7, where the free group is COO^-, and at intermediate pH values the line positions (which are weighted averages) depend on the proportions of these two groups. It has been found previously for free monobasic olefinic carboxylic acids[4] that, on ionization, the τ values of $=CH$ and CH_3 protons in the position β to the carboxyl show a marked increase (since the withdrawal of electrons by COO^- is less than by COOH) whereas the τ values of corresponding protons in the α position show a smaller increase or decrease; here the effects due to electron redistribution may be canceled by changes in long-range shielding. Assuming that this criterion applies to these ligands, structures can be assigned to the complexes.

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(2) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964); R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

(3) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

(4) L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **63**, 2858 (1967).