TABLE I

PROTON NMR DATA FOR POLYCYCLIC PHOSPHORUS COMPOUNDS[a]

Compound	J_{PCH} or J_{POCH}	δ(CH₃)	δ(CH₂)	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)	. . .[c]	1.40	4.48	CCl_4
$Fe(CO)_3(I)_2$	. . .[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	. . .[e]	4.47	$CDCl_3$
$OP(OCH_2)_3C(CH_2)_4CH_3$	6.6	. . .[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).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, ENGLAND

Nuclear Magnetic Resonance Spectra of Cobalt Ammine Complexes with Isomeric Ligands

BY M. LACY AND L. PRATT(1)

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.

---

(1) To whom any correspondence should be addressed.

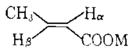
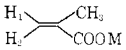
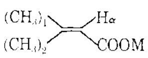
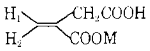
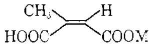
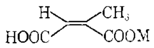
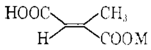
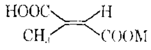
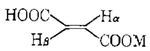
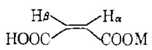
(2) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964); R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

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

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

TABLE I

PROTON RESONANCE LINE POSITIONS FOR OLEFINIC CARBOXYLATO LIGANDS IN PENTAAMMINE COBALTIC COMPLEXES[a,b]

Complex	Structural formula[c]	Proton group	Line position, $\tau^{d,i}$ pH ≈1	Line position, $\tau^{d,i}$ pH ≈7[e,f]
trans-Crotonato		H_α H_β CH_3	4.18 3.30 8.20	Same at both pH values
Methacrylato[g]		H_1 H_2 CH_3	4.57 4.17 8.17	
β,β-Dimethyl-acrylato[g]		H_α $(CH_3)_1$ $(CH_3)_2$	4.37 8.17 8.04	
Itaconato[g]		H_1 H_2 CH_2	4.44 3.94 6.66	4.59 4.08 6.87
Citraconato A		H CH_3	4.11 8.01	4.75 8.06
Citraconato B		H CH_3	4.28 8.01	4.09 8.17
Mesaconato C		H CH_3	3.49 7.90	3.34 8.14
Mesaconato D		H CH_3	3.26 8.01	3.74 8.00
Fumarato[h]		H_α H_β	3.21 3.45	3.59 3.40
Maleato[h]		H_α H_β	3.56 3.88	4.39 3.62

[a] The NH_3 protons give two broad lines, similar in appearance to those illustrated in ref 3, whose positions are approximately the same for each complex, with the *cis*-NH_3 at τ 6.0–6.1 and the *trans*-NH_3 at τ 7.0–7.1. These lines disappear at pH 7 as each NH_3 is converted to ND_3. [b] The solutions were 0.2–2 *M* in D_2O. [c] M = $Co^{III}(NH_3)_5$; hence, each formula shown represents a cation with an over-all charge of +2. At pH 7, the complexes from dibasic acids, having lost the carboxyl proton, have an over-all charge of +1. [d] Line positions were measured relative to the methyl line of the internal reference, *t*-butyl alcohol; this line was taken to have τ 8.75[i] in converting the measured positions to the τ scale. The errors in the quoted values are about ±0.015. [e] The line positions have reached constant values by pH 7; hence, the free carboxylate groups can be taken as being completely ionized. [f] To check for the absence of appreciable hydrolysis during the measurements at pH 7, the pH was afterward lowered to 1, when the lines were observed to go back to their previous positions; any lines from free acid would have had a different pH dependence. [g] The line assignments for groups 1 and 2 are assumed to be the same as for the free acids.[4] [h] Measurements at intermediate values of pH confirm that the two lines cross over and are coincident at one pH. [i] R. A. Y. Jones, A. R. Katritzky, J. N. Murrell, and N. Sheppard, *J. Chem. Soc.*, 2576 (1962); M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *ibid.*, 4854 (1961); R. J. Abraham and W. A. Thomas, *ibid.*, 3739 (1964).

The citraconate product gives two sets of lines which are attributed to the two isomeric complexes; they can be distinguished by the different intensities of lines in the two sets. One isomer (A) can be isolated by repeated recrystallization of the product from water; its spectrum at a given pH coincides with one of the sets of lines at the same pH. It was assigned the structure shown in the table since, on ionization, the =CH proton moves to a considerably higher τ value, suggesting that it is β to the free carboxyl, whereas the CH_3 proton line moves only slightly, suggesting that it is α to the free carboxyl. In contrast, ionization of isomer B makes the =CH line move (to a lesser extent) to lower τ while the τ of the CH_3 line increases by an amount typical of a β-methyl group in a monobasic olefinic acid.

Similar behavior is found for the mesaconate product; again, one isomer (C) could be isolated. With itaconic acid, only one isomer could be detected. It is assigned the structure with the side chain carboxyl free, since on ionization the $=CH_2$ protons move only slightly, yet the τ of the CH_2 group increases by 0.21, about the same as is found for the α-CH_2 protons in simple aliphatic carboxylic acids. With the maleato and fumarato complexes, no isomers are possible, but the two =CH protons can be distinguished. The changes on ionization are similar for both complexes; one proton moves to lower τ and is assigned as the proton α to the free carboxyl, whereas the β proton moves to a greater extent in the opposite direction.

Presumably the isomeric monodentate complexes formed from other dibasic acids could be distinguished in a similar manner, once the pH dependence of the proton resonance lines of the appropriate simple acids was known.

Acknowledgment.—We thank the Lancashire County Council Education Committee for a maintenance award to M. L.

CONTRIBUTION FROM THE INSTITUTE OF INORGANIC CHEMISTRY,
UNIVERSITY OF WUERZBURG, WUERZBURG, GERMANY

(Trimethylarsine)methylene

BY HUBERT SCHMIDBAUR AND WOLFGANG TRONICH

Received July 11, 1967

In a recent communication[1] the preparation and properties of (trimethylphosphine)methylene, $(CH_3)_3PCH_2$, the basic member of the phosphorus ylid series have been described. Using a similar synthetic procedure, we were now able to isolate the corresponding arsenic analog, (trimethylarsine)methylene $(CH_3)_3AsCH_2$ (I). Though the existence of this compound, at least in solution and at low temperatures, seemed to be rather likely, no successful attempt of isolation has been documented.[2,3]

---

(1) H. Schmidbaur and W. Tronich, *Angew. Chem.*, **79**, 412 (1967); *Angew. Chem. Intern. Ed. Engl.*, **5**, 448 (1967).

(2) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966.

(3) S. O. Grim and D. Seyferth, *Chem. Ind.* (London), 849 (1959); M. C. Henry and G. Wittig, *J. Am. Chem. Soc.*, **82**, 563 (1960); D. Seyferth and H. M. Cohen, *J. Inorg. Nucl. Chem.*, **20**, 73 (1961).