der aber bei weiterer Zugabe wieder in Lösung ging. Nach beendeter Reaktion wurde das Lösungsmittel im Vakuum abgezogen, es hinterblieb ein Gemisch aus Festsubstanz und ölig-zäher Flüssigkeit. Dieses wurde mit absol. Äther versetzt, das darin unlösliche Festprodukt abgesaugt und aus Methanol/Äther umgefällt. Man erhält farblose Kristalle von Tetraäthylammonium-tetrafluoroborat, Schmp. 375–377°. (Gef.: N, 6.36. $C_8H_{20}BF_4N$ ber.: N, 6.45%.) Die filtrierte Ätherlösung wurde eingeengt und der Rückstand über eine Feststoff-Destillationsanordnung bei 180°/0.01 mm destilliert; man erhält eine farblose Festsubstanz, Tributylzinn-tetrafluoroborat, Schmp. 265–270°, gut löslich in Äther, mässig in Methanol, Aceton und schlecht löslich in Pentan/Petroläther. Die Verbindung hat einen unscharfen Schmelzpunkt und sintert/schmilzt über einen Bereich von ca. 20°. (Gef.: Sn, 33.1. $C_{12}H_{27}BF_4Sn$ ber.: Sn, 31.7%.)

Reaktion von $(n\text{-}C_4H_9)_3SnN(C_2H_5)_2$ *mit Borfluorid-Ätherat*

(XIV) (35 g, 97 mMol), gelöst in 40 ml absol. Äther, wurde auf −80° gekühlt und unter Rühren tropfenweise mit 22 g (155 mMol) Bortrifluorid-ätherat versetzt. Dabei wurde die Reaktionslösung zunächst zähflüssig-fest, erst nach weiterer Zugabe wurde die hochviskose Masse wieder klarflüssig. Nach beendeter Reaktion wurde Äther im Vakuum abgezogen, dabei fanden sich in der mit fl. Luft gekühlten Falle farblose, hydrolyseempfindliche Kristalle, $[F_2B\text{–}N(C_2H_5)_2]_2$, Schmp. 55°. Ausb. 6 g. (Gef.: C, 38.6; H, 8.45; N, 11.43; Mol.-Gew., 230. $C_8H_{20}B_2F_4N_2$ ber.: C, 39.7; H, 8.27; N, 11.55%; Mol.-Gew., 242.) Der zähflüssige Kolbeninhalt wurde wie im vorhergehenden Versuch destilliert und ergab als identisches Produkt Tributylzinn-tetrafluoroborat, Schmp. 245–255°, unscharf. Ausbeute nach Resublimation 26.5 g. (Gef.: Sn 31.93. $C_{12}H_{27}BF_4Sn$ ber.: Sn, 31.7%.)

Reaktion von $(n\text{-}C_4H_9)_3SnN(C_2H_5)_2$ *mit* CH_3MgBr

(XIV) (12 g, 33 mMol) wurde unter Kühlung tropfenweise mit einer Lösung von 10 g (84 mMol) CH_3MgBr in absol. Äther versetzt. Nach Beendigung der sehr heftig verlaufenden Reaktion wurde mit 2 *N* HCl hydrolysiert und die ätherische Lösung fraktioniert destilliert. Man erhielt 8 g einer farblosen Flüssigkeit, Tributylmethylstannan, Sdp. 75–80°/0.1 mm (Lit.[33] Sdp. 121°/12 mm). (Gef.: C, 51.68; H, 10.03; Sn, 38.53. $C_{13}H_{30}Sn$ ber.: C, 51.2; H, 9.85; Sn, 39.0%.)

DANK

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LITERATUR

1 K. Jones und M. F. Lappert, *Organometal. Chem. Rev.*, 1 (1966) 67.
2 J. G. A. Luijten, F. Rijkens und G. J. M. van der Kerk, *Advan. Organometal. Chem.*, 3 (1965) 413.
3 W. P. Neumann, *Die organische Chemie des Zinns*, F. Enke Verlag, Stuttgart, 1967.
4 J. Lorberth, unveröffentlicht.
5 D. Schmid, Dissertation, Univ. München, 1962.
6 H. Schumann, H Köpf und M. Schmidt, *J. Organometal. Chem.*, 2 (1964) 150.

7 H. Schumann, P. Jutzi, A. Roth, P. Schwabe und E. Schauer, *J. Organometal. Chem.*, 10 (1967) 71.
8 K. Jones und M. F. Lappert, *J. Organometal. Chem.*, 3 (1965) 295.
9 H. Weingarten und W. A. White, *J. Amer. Chem. Soc.*, 88 (1966) 2885.
10 C. R. Noller, *Lehrbuch der organischen Chemie*, Springer-Verlag, Heidelberg, 1960, p. 276.
11 E. W. Randall, C. H. Yoder und J. J. Zuckermann, *Inorg. Nucl. Chem. Lett.*, 1 (1966) 105.
12 A. G. Davies und T. N. Mitchell, *J. Organometal. Chem.*, 6 (1966) 568.
13 W. Kuchen und H. Buchwald, *Chem. Ber.*, 92 (1959) 227.
14 R. Okawara, B. J. Hathaway und D. E. Webster, *Proc. Chem. Soc.*, (1963) 13.
15 A. B. Burg und J. R. Spielmann, *J. Amer. Chem. Soc.*, 83 (1961) 2667.
16 H. Nöth und H. Vahrenkamp, *Chem. Ber.*, 99 (1966) 2757; 100 (1967) 3353.
17 T. A. George und M. F. Lappert, *Chem. Commun.*, (1966) 463.
18 O. J. Scherer, *Organometal. Chem. Rev.*, 3 (1968) 281.
19 E. A. V. Ebsworth und H. J. Emeléus, *J. Chem. Soc.*, (1958) 2150.
20 M.-R. Kula, J. Lorberth und C. G. Kreiter, *Chem. Ber.*, 97 (1964) 1294.
21 J. Lorberth und M.-R. Kula, *Chem. Ber.*, 98 (1965) 520.
22 J. Lorberth und H. Vahrenkamp, *J. Organometal. Chem.*, 11 (1968) 111.
23 E. B. Baker, *J. Chem. Phys.*, 26 (1957) 960.
24 J. P. Maher und D. F. Evans, *Proc. Chem. Soc.*, (1961) 208.
25 O. Yamamoto, *J. Chem. Phys.*, 36 (1963) 1463.
26 P. T. Narasimhan und M. T. Rogers, *J. Chem. Phys.*, 31 (1959) 1431.
27 P. T. Narasimhan und M. T. Rogers, *J. Chem. Phys.*, 34 (1961) 1049.
28 P. T. Narasimhan und M. T. Rogers, *J. Amer. Chem. Soc.*, 82 (1960) 34.
29 H. Bürger und H. Goetze, *Angew. Chem.*, 80 (1968) 192; *Angew. Chem. Int. Ed. Engl.*, 7 (1968) 212.
30 E. W. Abel und D. B. Brady, *J. Organometal. Chem.*, 11 (1968) 145.
31 A. J. Leusink, H. A. Budding und J. W. Marsmann, *J. Organometal. Chem.*, 13 (1968) 155.
32 E. V. van den Berghe, D. F. van de Vondel und G. P. van der Kelen, *Inorg. Chim. Acta*, 1 (1967) 97.
33 R. K. Ingham, S. D. Rosenberg und H. Gilman, *Chem. Rev.*, 39 (1960) 459.
34 J. Lorbeth, H. Krapf und H. Nöth, *Chem. Ber.*, 100 (1967) 3511.
35 H. Nöth und I. Geisler, persönliche Mitteilung.
36 F. E. Brinckman, H. S. Haiss und R. A. Robb, *Inorg. Chem.*, 4 (1965) 936.
37 O. J. Scherer und M. Schmidt, *J. Organometal. Chem.*, 3 (1965) 156.
38 O. J. Scherer und P. Hornig, *J. Organometal. Chem.*, 8 (1967) 465.
39 O. J. Scherer, J. Schmidt, J. Wokulat und M. Schmidt, *Z. Naturforsch.*, 20b (1965) 183.
40 I. Schumann-Ruidisch und B. Jutzi-Mebert, *J. Organometal. Chem.*, 11 (1968) 77.

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HALOMETHYL–METAL COMPOUNDS
XXII*. THE PREPARATION OF TRIHALOMETHYL AND OTHER HALOGENATED ORGANOTIN COMPOUNDS**

DIETMAR SEYFERTH AND FRANK M. ARMBRECHT, JR.***
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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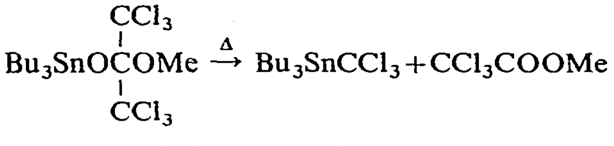
SUMMARY

The compounds Me_3SnCCl_3, Me_3SnCCl_2H, Me_3SnCCl_2Ph and Me_3SnCCl_2-Me have been prepared by reaction of the appropriate organolithium reagent with trimethyltin chloride at low temperature. The reaction of phenyl(bromodichloromethyl)mercury with trimethyltin bromide in refluxing benzene solution produced Me_3SnCCl_2Br in 63% yield. An experiment in which this mercury reagent was allowed to react with trimethyltin chloride gave both Me_3SnCCl_3 and Me_3SnCCl_2Br, which suggests that this route to trihalomethyl–tin compounds proceeds both by CCl_2 insertion into the Sn–X bond and by substituent exchange between mercury and tin.

INTRODUCTION

For an investigation of the possible general utility of trihalomethyl and other halogenated organotin compounds as potential carbene transfer reagents, compounds of type R_3SnCX_3 and R_3SnCX_2R' (X = Cl, Br) were required. At the time this work was initiated, (monohalomethyl)tin compounds were well-known[3], but the only (polyhalomethyl)tin derivative to have been prepared was trimethyl(trifluoromethyl)tin[4,5]. During the course of our work, however, other workers reported the preparation of (trihalomethyl)tin compounds by routes other than those used in the present investigation:



$$Bu_3SnO\overset{CCl_3}{\underset{CCl_3}{C}}OMe \xrightarrow{\Delta} Bu_3SnCCl_3 + CCl_3COOMe$$

(ref. 6)

$$R_3SnNR'_2 + HCX_3 \rightarrow R_3SnCX_3 + R'_2NH$$ (ref. 7, 8)

(X = Cl, Br; R = Me, Bu; R' = Me, Et)

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* Part XXI: ref. 1.

** Preliminary communication: ref. 2.

*** National Institutes of Health Predoctoral Fellow, 1964–1968.

RESULTS AND DISCUSSION

Most of our preparations of (α-polyhaloalkyl)tin compounds were accomplished using the organolithium route:

$$RCCl_2Li + Me_3SnX \rightarrow Me_3SnCCl_2R + LiX$$
$$(R = Cl, H, CH_3, Ph)$$

This was made possible by the development of useful synthetic polyhaloalkyllithium chemistry by several groups in recent years[9-11]. (For a review of this area, see ref. 12.) The most notable feature of the preparation and utilization of polyhaloalkyllithium reagents is the fact that they are stable only at low (−60° to −120°) temperatures. Tetrahydrofuran has been found to stabilize such lithium reagents (compared to diethyl ether), but systems containing only THF as solvent tend to freeze at −100° even when vigorously stirred. Köbrich and coworkers[11,13] used a solvent system containing THF, diethyl ether and pentane in 4/1/1 volume ratio with good success, and another system, THF, pentane, diethyl ether and methylal (dimethoxymethane), also has been employed for low temperature organolithium work[14]. We have made extensive use of these solvent systems, but during the later stages of the present study we developed still another solvent system for low temperature organolithium synthesis and reactions: 3/1 by volume THF/dimethyl ether. It is, in our opinion, superior to the other systems in terms of ease of formulation, low viscosity and low freezing point. Only one solvent, THF, requires prior purification by drying and distillation. Gaseous (b.p. −23.7°) dimethyl ether was prepared for use simply by passing it through a drying tower containing activated alumina, anhydrous calcium sulfate and phosphorus pentoxide and condensing it in a cold trap.

The preparation of trimethyl(trichloromethyl)tin in 62% yield was accomplished by quenching a solution of trichloromethyllithium[13] at −100° in Köbrich's solvent system with an equimolar amount of trimethyltin chloride. The extremely labile $Cl_3C{-}Sn$ bond made isolation and purification of this compound difficult. Trimethyl(trichloromethyl)tin is very moisture-sensitive; small samples hydrolyze rapidly and quantitatively to trimethyltin hydroxide and chloroform when exposed to atmospheric moisture. The compound sublimes readily but it decomposed when distillation was attempted. The usual methods for separating unconverted trimethyltin chloride from Me_3SnR preparations failed: alcoholic potassium fluoride and anhydrous ammonia in diethyl ether also destroyed trimethyl(trichloromethyl)tin. The lithium chloride formed in the coupling reaction interfered in the purification of trimethyl(trichloromethyl)tin and had to be removed by a nonaqueous procedure, precipitation with 1,4-dioxane. It is clear that where it is applicable, the $Me_3SnNR_2/RCHCl_2$ procedure[7,8] is preferable to the organolithium route.

(α,α-Dichlorobenzyl)trimethyltin, a distillable liquid prepared in 53% yield via α,α-dichlorobenzyllithium[10,13], appeared to be sensitive to both moisture and oxygen, the slightest exposure to the atmosphere immediately producing a yellow coloration. 1,1-Dichloroethyllithium, a new reagent prepared by reaction of n-butyllithium with 1,1-dichloroethane at −115°, was used to prepare trimethyl(1,1-dichloroethyl)tin (49%), a volatile, moisture-sensitive solid. Trimethyl(dichloromethyl)tin, a distillable liquid which was stable to atmospheric moisture, was obtained in 66%

yield by reaction of dichloromethyllithium[11,15] with trimethyltin chloride. Subsequently, (dichloromethyl)tin compounds were prepared by other workers using two different procedures: insertion of sodium trichloroacetate-derived dichlorocarbene into the Sn–H bond of triethyl- and tri-n-butyltin hydride[16] and reduction of trialkyl(trichloromethyl)tin compounds with organotin hydrides[17].

The discovery in these Laboratories that dihalocarbenes will insert into the mercury–halogen linkage[18] suggested to us that a similar route might be preparatively useful for (trihalomethyl)tin compounds. We had our first indication that CX_2 insertion into the tin–halogen bond could occur during the organolithium work referred to above. It was found that the reaction of trimethyltin bromide with trichloromethyllithium at −100° gave not only Me_3SnCCl_3 but also an equal amount of a second trimethyltin compound which was moisture-sensitive, had a similar IR spectrum and which tentatively was identified as trimethyl(bromodichloromethyl)tin. This compound might have arisen from insertion of lithium chloride-complexed dichlorocarbene (produced upon warming the reaction mixture containing unreacted trichloromethyllithium) into the Sn–Br bond of trimethyltin bromide.

The thermolysis of phenyl(bromodichloromethyl)mercury, an excellent dichlorocarbene source[19], in the presence of trimethyltin bromide (50% excess) in refluxing benzene solution did indeed produce the desired trimethyl(bromodichloromethyl)tin in 63% yield. The presence of unconverted trimethyltin bromide rendered the isolation of this product quite difficult; preparative GLPC with a specially designed cell-bypass was required to achieve separation. The IR spectrum of the product was identical with that of the by-product of the CCl_3Li/Me_3SnBr reaction, thus confirming that the latter was Me_3SnCCl_2Br.

While the premise upon which our $PhHgCCl_2Br/Me_3SnBr$ experiment was based was that mercurial-derived dichlorocarbene should be capable of inserting into the Sn–Br bond, another mechanism for this Me_3SnCCl_2Br-producing reaction was possible: substituent exchange between tin and mercury, in which the intact CCl_2Br moiety is transferred from mercury to tin. In order to obtain information concerning the mechanism of this reaction, the analogous reaction of phenyl(bromodichloromethyl)mercury and trimethyltin *chloride* was examined. In this case, the insertion process should give trimethyl(trichloromethyl)tin (in the absence of complicating halogen exchange reactions) and the substituent exchange process should give trimethyl(bromodichloromethyl)tin. When this reaction was carried out, the total product yield was only 16%, probably as a result of a lesser reactivity of the Sn–Cl bond. However, the important fact which emerged upon GLPC analysis of the reaction mixture was that a 1.5/1 mixture of Me_3SnCCl_3 and Me_3SnCCl_2Br had been formed. A possible explanation for this result, the formation of trimethyltin bromide by reaction of phenylmercuric bromide with trimethyltin chloride (then followed by CCl_2 insertion into the Sn–Br bond) was excluded by experiment. From these results it would appear that trimethyl(bromodichloromethyl)tin could have been formed by both possible routes in the $PhHgCCl_2Br/Me_3SnBr$ reaction. The preparation of tri-n-butyl(trichloromethyl)tin by Chinese workers via reaction of dichlorocarbene with tri-n-butyltin chloride has been alluded to in ref. 7, but no details of this work are available to us.

The availability of Me_3SnCCl_3, Me_3SnCCl_2Br, Me_3SnCCl_2H, Me_3SnCCl_2Ph and of the compounds $Me_3SnCX_2SnMe_3$ (X = Cl, Br)[20] has made possible the study of (α-polyhaloalkyl)tin compounds as divalent carbon transfer agents, and the results of this investigation will be presented in a later paper of this series.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Methyltin compounds were obtained from M&T Chemicals, Inc., n-butyllithium from the Foote Mineral Co. Phenyl(bromodichloromethyl)mercury was prepared as described by us previously, either in benzene medium[21] or in diethyl ether[22]. (Note, however, our improved procedure for this mercurial[23].) Elemental analyses were performed by Dr. S. M. Nagy (M.I.T.) and by the Galbraith Laboratories, Knoxville, Tennessee. IR spectra were recorded using a Perkin–Elmer 337 grating spectrophotometer, NMR spectra with a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal TMS.

The low temperature organolithium reactions were carried out in a three-necked Morton (creased) flask (usually a 500 ml flask) equipped with a high speed stirrer, pressure-equalizing dropping funnel, pentane thermometer (or thermocouple connected to a recorder) and a gas inlet tube. Of the solvents used, THF was purified by distillation from lithium aluminum hydride, diethyl ether and pentane from calcium hydride, methylal from lithium aluminum hydride.

Trimethyl(trichloromethyl)tin

Into the 500 ml reaction flask (*cf.* section above) was placed 13.85 g (0.115 mole) of chloroform (dried over calcium chloride and passed through Woelm neutral activated alumina immediately before use) and 240 ml of a 4/1/1 mixture of THF, diethyl ether and pentane under an atmosphere of dry nitrogen. The solution was cooled to −100° and then 72.3 ml (0.112 mole) of 1.55 *N* n-butyllithium in hexane was added with stirring over a 1 h period. After an additional 2 h period of vigorous stirring, 19.84 g (0.10 mole) of trimethyltin chloride in ether was added over a 25 min period. The mixture was stirred at −100° for 2 h, then was allowed to warm to room temperature. Fifty ml of 1,4-dioxane was added to precipitate the lithium halide; the 7.3 g of whitish-brown solid thus obtained was filtered under nitrogen and the filtrate was concentrated at 60 mm using a rotary evaporator. The residue was trap-to-trap distilled at 0.01 mm (70° pot temperature). Two fractions were taken; the second was collected when sublimed solid began to appear on the cooler surfaces of the apparatus and it was essentially pure trimethyl(trichloromethyl)-tin, 17.92 g (62%). Its m.p. after recrystallization from pentane at −80° was 61–63° (sintering at 40–42°). Davies and Mitchell[7] reported a m.p. of 54–59°; Chivers[8] reported 41–42°. (Found: C, 17.05; H, 3.62. $C_4H_9Cl_3Sn$ calcd.: C, 17.00; H, 3.22%.) NMR (in CS_2): singlet at 0.50 ppm [$J(^{117}Sn-^{1}H)$ 51 cps; $J(^{119}Sn-^{1}H)$ 55 cps]. IR spectrum (in CS_2): 2985 m; 2915 m; 1380 m; 1193 (sh); 775 vs; 698 vs; 642 (sh); 583 s, cm^{-1}.

Exposure of a small sample of the product to atmospheric moisture gave trimethyltin hydroxide, m.p. 116–118° (lit.[24] m.p. 118°). Cleavage of another sample with an excess of bromine gave methyl bromide, bromotrichloromethane and tin tetrabromide.

Trimethyl(dichloromethyl)tin

Dichloromethyllithium was prepared at −100° under nitrogen from 10.04 g (0.118 mole) of dichloromethane and 0.112 mole of n-butyllithium solution in 245 ml of the THF/diethyl ether/pentane mixture. To this solution was added with stirring at −100° 20.12 g (0.101 mole) of trimethyltin chloride over a 20 min period. The reaction mixture was stirred for 2 h at −100°, warmed to room temperature, treated with 50 ml of dioxane and filtered from 29.56 g of white solid. Solvents were removed from the filtrate at reduced pressure and the residue was trap-to-trap distilled at 0.02 mm (room temperature) to give 23.00 g of clear liquid. Redistillation through a 12″ Vigreux column gave 16.40 g (66%) of trimethyl(dichloromethyl)tin, b.p. 86–87° (38 mm), n_D^{25} 1.5030. (Found: C, 19.34; H, 4.04; Cl, 29.00; Sn, 47.51. $C_4H_{10}Cl_2Sn$ calcd.: C, 19.39; H, 4.07; Cl, 28.62; Sn, 47.92%.) NMR spectrum (in CCl_4): singlets at 0.3 ppm [$J(^{117}Sn-^1H)$ 53.5 cps; $J(^{119}Sn-^1H)$ 56.5 cps] and at 5.4 ppm [$J(Sn-H)$ 15 cps]. IR spectrum (liquid film): 2980 m; 2910 m; 2340 w; 1480 w; 1410 w; 1198 (sh); 1194 m; 1095 w; 778 vs; 725 m; 688 vs; 540 vs, cm^{-1}.

(α,α-Dichlorobenzyl)trimethyltin

α,α-Dichlorobenzyllithium was prepared at −100° by reaction of 20.16 g (0.10 mole) of benzotrichloride and 0.10 mole of n-butyllithium solution in a solvent mixture of 180 ml of THF and 60 ml of dimethyl ether (purified as mentioned in the discussion section). During the course of the addition, during which the mixture gradually turned deep red, the temperature was lowered to below −120°. After the reagent solution had been stirred at this temperature for 30 min, 19.64 g (0.099 mole) of trimethyltin chloride in 6 ml of ether was added. A change in color to light orange resulted. The reaction mixture was stirred for 95 min at low temperature, then was warmed to room temperature, treated with 50 ml of dioxane and filtered to remove 11.75 g of white solid. The filtrate was concentrated at 15 mm and the residue trap-to-trap distilled at 0.05 mm. The first fraction (no external heating) was discarded; the second fraction (pot temperature to 120°) was redistilled (*acid-washed* short path distillation unit) to give 16.80 g (53%) of product, b.p. 77–80° (0.06 mm). (α,α-Dichlorobenzyl)trimethyltin, a colorless liquid when freshly distilled, was extremely sensitive to moisture and apparently also to oxygen. (Found: C, 36.99; H, 4.21; Sn, 36.39. $C_{10}H_{14}Cl_2Sn$ calcd.: C, 37.09; H, 4.36; Sn, 36.66%.) NMR spectrum (in CCl_4): singlet at 0.25 ppm [$J(^{117}Sn-^1H)$ 52 cps; $J(^{119}Sn-^1H)$ 54 cps]; multiplet at 6.80 to 7.40 ppm. IR spectrum (in CCl_4): 3080 (sh); 3060 m; 3030 (sh); 3005 (sh); 2985 m; 2910 m; 2350 w; 1950 w; 1880 w; 1770 m; 1730 w; 1680 (sh); 1650 w; 1590 m; 1485 s; 1465 w; 1445 s; 1385 (sh); 1380 w; 1325 (sh); 1312 w; 1226 w; 1205 (sh); 1195 m; 1178 w; 1078 w; 1035 m; 998 w; 913 w; 871 w; 845 w; 830–730 (obscured by solvent); 708 vs; 690 vs; 668 (sh); 645 (sh); 615 (sh); 605 m; 533 vs, cm^{-1}.

Trimethyl(1,1-dichloroethyl)tin

1,1-Dichloroethyllithium was prepared at −115° from 5.00 g (50.5 mmoles) of 1,1-dichloroethane and 49.6 mmoles of n-butyllithium solution in 98 ml of 3/2/1/1 THF/diethyl ether/pentane/methylal mixture. The reagent solution was stirred at −115° for 2 h and then 9.65 g (46.3 mmoles) of trimethyltin chloride was added. The reaction mixture was stirred at −115° for 1.5 h, warmed to room temperature, treated with 10 ml of dioxane and filtered. The filtrate was trap-to-trap distilled at 0.02 mm to give a solvent fraction at room temperature and another fraction (heating with a heat lamp), 25.23 g, shown by gas chromatography (General Electric Co. SE-30 silicone rubber gum on Chromosorb P at 80–185°; tetralin internal standard; F&M 700 instrument) to contain solvent, trimethyltin chloride, n-butyltrimethyltin (20% yield) and trimethyl(1,1-dichloroethyl)tin (49% yield). An analytical sample of the latter, a crystalline solid, m.p. 58–59° (sealed tube) was collected by GLPC. (Found: C, 23.26; H, 4.86; Cl, 27.38. $C_5H_{12}Cl_2Sn$ calcd.: C, 22.94; H, 4.62; Cl, 27.09%) NMR spectrum (in chloroform): singlets at 0.36 ppm [$J(^{117}Sn-^{1}H)$ 53.5 cps; $J(^{119}Sn-^{1}H)$ 56 cps] and at 2.20 ppm [$J(^{117}Sn-^{1}H)$ 35 cps; $J(^{119}Sn-^{1}H)$ 37 cps] in an area ratio of 3/1. IR spectrum (in CS_2): 2970 s; 2955 s; 2905 s; 2840 m; 2350 m; 1720 w; 1695 w; 1440 s (in $CHCl_3$); 1430 s (in $CHCl_3$); 1365 s; 1104 w; 1057 s; 1020 s; 775 vs; 719 (sh); 695 s; 642 vs; 530 s, cm^{-1}.

Trimethyl(bromodichloromethyl)tin

Into a dried 500 ml, three-necked flask equipped with magnetic stirring unit, reflux condenser and gas inlet tube, under an atmosphere of dry nitrogen was placed 44.04 g (0.10 mole) of phenyl(bromodichloromethyl)mercury, 37.40 g (0.154 mole) of trimethyltin bromide and 250 ml of benzene (freshly distilled from calcium hydride). The solution was heated at reflux and stirred for 3 h. The phenylmercuric bromide which precipitated, 33.75 g (95%), m.p. 284–287°, was filtered off under nitrogen. The filtrate was concentrated at 20 mm on a rotary evaporator and the residue was trap-to-trap distilled at 0.02 mm (pot temperature to 70°). Analysis of the distillate by GLPC (20% SE-30 on Chromosorb P; M.I.T. isothermal unit, 70° column temperature, benzotrichloride internal standard) showed the presence of trimethyl(bromodichloromethyl)tin in 63% yield and of tetrachloroethylene in 17% yield. Analytical and preparative samples of the product, a white, crystalline solid, m.p. (sealed tube) 103.5–105°, were isolated by GLPC using a cell by-pass system (described in the thesis of F.M.A., M.I.T., 1968). (Found C, 14.77; H, 3.05; AgX, 9.040 mg from a 6.805 mg sample. $C_4H_9Cl_2BrSn$ calcd.: C, 14.69; H, 2.77%; AgX, 9.079 mg.) NMR spectrum (in CS_2): singlet at 0.49 ppm [$J(^{117}Sn-^{1}H)$ 52 cps; $J(^{119}Sn-^{1}H)$ 55 cps]. IR spectrum (in CS_2): 2980 m; 2915 m; 1385 m; 1193 s; 778 vs; 700 vs; 641 vs; 534 vs, cm^{-1}.

A small sample gave trimethyltin hydroxide (m.p. 114°) and bromodichloromethane (identified by GLPC retention time) when exposed to the atmosphere. Cleavage of another sample with an excess of bromine gave methyl bromide, dibromodichloromethane and tin tetrabromide.

Reaction of phenyl(bromodichloromethyl)mercury with trimethyltin chloride.

A similar reaction was carried out using 10.0 mmoles each of the mercurial and trimethyltin chloride and 25 ml of benzene. The reaction mixture was stirred at reflux for 3 h. Phenylmercuric bromide, 2.34 g (66% yield), was removed by filtration. GLPC analysis of the filtrate (SE-30; benzotrichloride internal standard) showed that trimethyl(trichloromethyl)tin (9.4%) and trimethyl(bromodichloromethyl)tin (6.6%) had been produced. The products were identified by comparison of their GLPC retention times and their IR spectra with those of authentic samples.

In a similar experiment (8 h reflux period), the yields of the (trichloromethyl)- and (bromodichloromethyl)tin compounds were 11% and 4.8%, respectively.

Reaction of phenyl(trichloromethyl)mercury with trimethyltin chloride

Using the general procedure described above, a reaction was carried out between 19.7 mmoles of trimethyltin chloride and 30 mmoles of phenyl(trichloromethyl)-mercury in 50 ml of benzene, at 80° for 80 h. Phenylmercuric chloride (4.12 g, 66%) was filtered off, the filtrate was concentrated at reduced pressure and the residue trap-to-trap distilled at 0.02 mm. A moist, crystalline solid was thus obtained (1.92 g). Its analysis by GLPC showed the presence of trimethyl(trichloromethyl)tin in 6.4% yield. The product was identified by means of its GLPC retention time and its IR spectrum. A distillation residue of 3.53 g remained.

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REFERENCES

1 D. Seyferth, J. D. H. Paetsch and R. S. Marmor, *J. Organometal. Chem.*, 16 (1969) 185.
2 D. Seyferth, F. M. Armbrecht, Jr., B. Prokai and R. J. Cross, *J. Organometal. Chem.*, 6 (1966) 573.
3 D. Seyferth, *Chem. Rev.*, 55 (1955) 1155.
4 H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *J. Amer. Chem. Soc.*, 82 (1960) 6228.
5 H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, 82 (1960) 1888.
6 A. G. Davies and W. R. Symes, *J. Organometal. Chem.*, 5 (1966) 394.
7 A. G. Davies and T. N. Mitchell, *J. Organometal. Chem.*, 6 (1966) 568.
8 T. Chivers and B. David, *J. Organometal. Chem.*, 10 (1967) P35; 13 (1968) 177.
9 W. T. Miller and D. M. Whalen, *J. Amer. Chem. Soc.*, 86 (1964) 2089.
10 D. F. Hoeg, D. I. Lusk and A. L. Crumbliss, *J. Amer. Chem. Soc.*, 87 (1965) 4147.
11 G. Köbrich, K. Flory and W. Drischel, *Angew. Chem.*, 76 (1964) 536.
12 G. Köbrich, *Angew. Chem.*, 79 (1967) 15.
13 G. Köbrich, K. Flory and R. H. Fischer, *Chem. Ber.*, 99 (1966) 1793.
14 M. Schlosser and V. Ladenberger, *Angew. Chem.*, 78 (1966) 547.
15 G. Köbrich and H. R. Merkle, *Chem. Ber.*, 99 (1966) 1782.
16 C.-L. Tseng, J.-H. Cho and S.-C. Ma, *K'o Hsueh T'ung Pao*, 17 (1966) 77; *Chem. Abstr.*, 66 (1967) 2755.
17 A. G. Davies, T. N. Mitchell and W. R. Symes, *Abstracts, Third International Symposium on Organometallic Chemistry*, München, 28. August–1. September 1967, p. 154.
18 M. E. Gordon, K. V. Darragh and D. Seyferth, *J. Amer. Chem. Soc.*, 88 (1966) 1831; *J. Organometal. Chem.*, 14 (1968) 43.
19 D. Seyferth, *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds*, Robert A. Welch Foundation, Houston, Texas, 1966, pp. 89–135 (review).
20 D. Seyferth and F. M. Armbrecht, Jr., *J. Amer. Chem. Soc.*, 89 (1967) 2790.
21 D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, 4 (1965) 127.
22 D. Seyferth, J. Y.-P. Mui and J. M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 4953.
23 D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, 16 (1969) 21.
24 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60 (1960) 459.

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PREPARATION AND PROPERTIES OF ORGANO(ACETYLACETONATO)-ANTIMONY(V) COMPOUNDS

H. A. MEINEMA AND J. G. NOLTES
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

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SUMMARY

Organo(acetylacetonato)antimony(V) compounds of the types R_2SbCl_2Acac, $R_4SbAcac$, $PhSbCl_3Acac$ and $Cl_4SbAcac$ have been synthesized. The compounds are monomeric in solution. IR and PMR data of these compounds, which contain a chelated Acac ligand have been discussed. Ph_2SbCl_2Acac shows abnormal behaviour, in that in chloroform solution a non-chelated configuration in which the Acac group is probably C-bonded, is also present.

INTRODUCTION

Recently the structure of pentavalent organoantimony compounds has received considerable attention[1]. The coordination behaviour of compounds R_n-$SbX_{(5-n)}$ ($n = 1$–4), in which X is a potentially bidentate ligand, is of special interest. Two groups have studied the IR spectra of trimethylantimony(V) derivatives Me_3-SbX_2 containing such ligands[2a,b]. Japanese workers have reported the synthesis and properties of tetrachloro(acetylacetonato)antimony $Cl_4SbAcac$ and of phenyltrichloro(acetylacetonato)antimony $PhSbCl_3Acac$[3,4].

The present paper deals with the preparation of some novel organo(acetylacetonato)antimony compounds of the type R_2SbCl_2Acac and $R_4SbAcac$*.

RESULTS AND DISCUSSION

Preparation

Organo(acetylacetonato)antimony(V) compounds R_2SbCl_2Acac (R = Me and Et) were prepared by dissolving the corresponding dialkylhydroxo(oxo)antimonies[5] in a mixture of concentrated hydrochloric acid and acetylacetone and extracting this solution with methylene chloride (*cf.* ref. 3b). The corresponding phenyl derivative was easily obtained by refluxing diphenyltrichloroantimony with acetylacetone in carbon tetrachloride.

Organo(acetylacetonato)antimony(V) compounds of the type $R_4SbAcac$ were obtained in quantitative yield by reacting acetylacetone with the corresponding R_4SbOMe derivatives (R = Ph[6a,b], Me, Et[7]).

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* After this paper had been completed a recent study of $Ph_4SbAcac$ has come to our attention[15].

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR SOME ORGANO(ACETYLACETONATO)ANTIMONY(V) COMPOUNDS

Compound	M.p. (°C)	Molecular weight		Sb (%)		Cl (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
$\mathrm{Cl_4SbAcac}$	131[a]	367	363	32.71	33.57	39.78	39.10
$\mathrm{PhSbCl_3Acac}$	176–178(dec.)[b]	409	405	30.30	30.11	25.32	25.40
$\mathrm{Ph_2SbCl_2Acac}$	180–190(dec.)	484	446	27.55	27.35	16.25	15.92
$\mathrm{Me_2SbCl_2Acac}$	~ 150(dec.)	369[c]	322	38.21	37.88	22.85	22.05
$\mathrm{Et_2SbCl_2Acac}$	102–104	364	350	34.99	34.85	20.87	20.20
$\mathrm{Ph_4SbAcac}$	205–209(dec.)	522	529	22.32	23.06		
$\mathrm{Me_4SbAcac}$	47–48[d]	291	281	43.68	43.32		
$\mathrm{Et_4SbAcac}$	[e]	340	337	36.64	36.11		

[a] Reported[3b] 131°. [b] Reported[3b] 176–178°. [c] Difficult to determine because of limited solubility in benzene. [d] B.p. 102–103° (19 mm). [e] B.p. 84° (0.12 mm).

$\mathrm{Cl_4SbAcac}$ and $\mathrm{PhSbCl_3Acac}$ have been prepared as reported[3b].

Attempts to prepare compounds of the type $\mathrm{R_3SbClAcac}$ were unsuccessful.

All organo(acetylacetonato)antimony(V) compounds, including the two reported by Okawara *et al.*[3b], were found to be monomeric in benzene solution at room temperature.

Melting points, analytical and molecular weight data for the various compounds prepared are given in Table 1.

Infrared spectra

Infrared spectral data in the region 2000–400 cm^{-1} for the various compounds are given in the experimental part. Table 2 shows the IR absorptions in the C=O, C=C stretching region.

For each of the organo(acetylacetonato)antimony(V) compounds described in this paper the position of the absorptions connected with the acetylacetonate ligand is very similar to the values reported for other metal acetylacetonates in which the

TABLE 2

INFRARED ABSORPTIONS OF SOME ORGANO(ACETYLACETONATO)ANTIMONY(V) COMPOUNDS IN THE 2000–1500 cm^{-1} REGION[a]

Compound	C=O	C=C
$\mathrm{Cl_4SbAcac}$[b]	1548	1546
$\mathrm{PhSbCl_3Acac}$[b]	1563, 1555	1546
$\mathrm{Ph_2SbCl_2Acac}$[c]	1563	1537
$\mathrm{Me_2SbCl_2Acac}$	1563	1527
$\mathrm{Et_2SbCl_2Acac}$	1565	1527
$\mathrm{Ph_4SbAcac}$	1587, 1575	1527
$\mathrm{Me_4SbAcac}$	1587	1511, 1503
$\mathrm{Et_4SbAcac}$	1585	1506, 1499

[a] The Sb–Acac absorptions have been tentatively assigned according to Behnke and Nakamoto[8]. [b] The IR data obtained for $\mathrm{Cl_4SbAcac}$ and $\mathrm{PhSbCl_3Acac}$ differ only slightly from the reported values[3a,4]. [c] An additional C=O absorption at 1715 cm^{-1} was observed in the chloroform solution spectrum.

acetylacetonate group acts as a bidentate ligand[9a,b]. These results indicate the presence of hexa-coordinated antimony in these compounds (*cf.* ref. 3a and 4).

One would expect the strength of the Sb–O coordinate bond to increase and ν(C=O) to decrease upon increasing the number of electron-withdrawing substituents at antimony. Indeed, as can be seen from Table 2 the C=O stretching frequency decreases when the organic ligands around antimony are successively replaced by chlorine. Okawara *et al.*[3a] observed the same phenomenon in their study of organotin acetylacetonates.

A rather interesting result is the difference between the spectrum of Ph_2SbCl_2-Acac in nujol and in chloroform solution. Whereas the nujol spectrum shows only one strong band at 1563 cm^{-1}, the $CHCl_3$ spectrum displays an additional weak band at 1715 cm^{-1}. This result indicates that whereas in the solid state Ph_2SbCl_2Acac occurs only in the hexa-coordinate form a penta-coordinate form with a non-chelating acetylacetonate group [ν(C=O) 1715 cm^{-1}] is also present to some extent in chloroform solution.

The assignments of the absorption bands in the region 600–400 cm^{-1} have to be tentative, as coupled vibrations will occur. In the spectra of the phenyl derivatives the strong phenyl absorptions at approximately 460 cm^{-1} (see also ref. 10) partly obscure the Sb–O stretching mode. The Sb–C stretching modes for Me_2SbCl_2Acac are most probably obscured by the strong acetylacetonate π-band[9a] at 564 cm^{-1}.

It seems reasonable to assume, that in the R_2SbCl_2Acac compounds, the R groups will occupy equatorial positions, whereas the two chlorine atoms occupy the axial positions. A structure with two phenyl groups occupying equatorial positions has been established for Ph_2SbCl_3 using X-ray spectroscopy[11]. The appearance of two absorption bands of weak intensity at 553 and 493 cm^{-1} in the nujol spectrum of Et_2SbCl_2Acac, which are assigned to the antisymmetric and the symmetric Sb–C stretching frequency respectively, further supports this assumption.

In $PhSbCl_3Acac$ it has been established that the phenyl group, together with one chlorine atom and the Acac group occupy the equatorial positions[4].

The tetramethyl- and tetraethyl(acetylacetonato)antimony compounds show a very broad band at about 520 cm^{-1}. This band, which could not be resolved, is assigned to the Sb–C stretching frequencies. The Sb–O stretching absorption for these compounds, which was not observed, probably occurs below 400 cm^{-1}.

PMR spectra

PMR spectral data for organo(acetylacetonato)antimony(V) compounds in deuterochloroform are tabulated in Table 3.

For the methyl- and ethylantimony derivatives single signals were observed for the methyl and methylene resonances.

With the exception of the spectra of $PhSbCl_3Acac$[3b,4] and Ph_2SbCl_2Acac, all compounds show one singlet due to the Acac methyl protons at δ 1.76–2.31 and one singlet due to the γ-H protons at δ 4.94–5.99 ppm.

The CH_3(Acac) and γ-H proton resonances appear at progressively lower field upon increasing the number of electron-withdrawing chlorine atoms at antimony. This reflects the increasing strength of the Sb–O coordinate bond in the order $R_4SbAcac < R_2SbCl_2Acac < RSbCl_3Acac < Cl_4SbAcac$ and agrees with the IR data.

At the magnet temperature (27°) the PMR spectrum of Ph_2SbCl_2Acac shows

TABLE 3

PMR SPECTRAL DATA FOR SOME ORGANO(ACETYLACETONATO)ANTIMONY COMPOUNDS IN DEUTEROCHLOROFORM AT 27°

Compound	Chemical shifts (ppm[a])					
	–CH=	CH_3(Acac)	Ph(–Sb)	CH_3(–Sb)	–CH_2(–Sb)	CH_3(–CH_2Sb)
HAcac (enol form)	5.51[12]	2.01[12]				
$Cl_4SbAcac$[b]	5.99	2.31				
$PhSbCl_3Acac$[c]	5.91	2.23	7.51			
		2.28	8.06			
Ph_2SbCl_2Acac	5.35	1.96	7.38			
	5.79	2.13	7.90			
Me_2SbCl_2Acac	5.62	2.15		2.38		
Et_2SbCl_2Acac	5.63	2.15			2.81	1.51
$Ph_4SbAcac$	5.19	1.80	7.21			
			7.46			
$Me_4SbAcac$	5.09	1.76		1.09		
$Et_4SbAcac$	4.94	1.64			1.51	1.01

[a] Downfield from TMS, which is used as an internal standard. [b] Reported[3b,4] –CH= at 6.06, CH_3(Acac) at 2.43 ppm. [c] Reported[3b,4]–CH=at 5.85, CH_3(Acac) at 2.25 ppm (doublet).

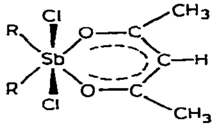
two singlets at δ 1.96 and 2.13 ppm respectively, due to the Acac methyl protons and two singlets at δ 5.35 and 5.79 ppm due to the corresponding γ-H protons. The singlets at δ 1.96 and 5.35 ppm belong to one type of Acac group, while the singlets at δ 2.13 and 5.79 ppm belong to another, as for both sets an intensity ratio of 6/1 was observed. The two different Acac groups were observed to be present in a ratio 3/1. Heating the sample to 55° causes a change of this ratio to ~2.5/1, while no variation in chemical shift is observed. This change was shown to be reversible. Measurements at lower temperatures were prevented by the low solubility of Ph_2SbCl_2Acac in $CDCl_3$ or in other suitable solvents. These results combined with the observations from the IR spectrum, indicate that in $CHCl_3$ solution Ph_2SbCl_2Acac exists for about 75% in the chelated configuration (I) (Acac proton resonance signals at 1.96 and 5.35 ppm), which is in slow equilibrium with the non-chelated configuration (II) (signals at 2.13 and 5.79 ppm).

(I) (II)

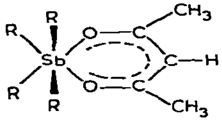
The PMR data suggest, that for the non-chelated configuration, (II), the Acac group is symmetrically bonded to antimony by the γ-carbon atom, rather than by oxygen, because the methyl protons give rise to only one sharp singlet, which occurs at even lower field than the corresponding singlet of the chelated Acac group in (I) (*cf.* ref. 13 for a discussion of the PMR spectra of C-bonded platinum acetylacetonates). The two phenyl groups in (I) are either in equatorial or in axial positions, as an unsymmetrical arrangement of these groups around antimony would result in the appearance of two singlets for the two non-equivalent methyl groups of the chelated Acac group. Assuming that the chlorine atoms occupy axial positions[11] the structures (I) and (II) are proposed for the chelated and the non-chelated configuration.

Combined IR and PMR spectral evidence suggests a symmetrical structure (III) for R_2SbCl_2Acac (R = Me and Et).

The $R_4SbAcac$ derivatives (IV) (R = Me, Et, Ph) according to the IR and PMR data occur only in the chelated configuration.



(III)



(IV)

Non-equivalence of the equatorial and axial organic groups could not be observed. The PMR spectrum of $Me_4SbAcac$ in chloroform showed even at −40° only one CH_3–Sb resonance indicating the presence of a non-rigid structure for this molecule in solution (*cf.* ref. 14).

EXPERIMENTAL PART

General

The IR spectra measured in the range 2000–400 cm^{-1} were run as mulls in nujol between KBr disks for the solid compounds [$Cl_4SbAcac$, $PhSbCl_3Acac$, R_2SbCl_2Acac (R = Me, Et and Ph) and $Ph_4SbAcac$] and as a liquid between AgCl disks for $R_4SbAcac$ (R = Me and Et). In order to obtain a better resolution in the range 1800–1400 cm^{-1} the spectra were also recorded as solutions in chloroform. All IR spectra were run on a Grubb–Parsons Spectromaster.

The PMR spectra were measured as solutions in deuterochloroform at 27° using a Varian Associates HA-100 spectrometer.

Molecular weights were measured on ~5% solutions in benzene, using a Mechrolab dynamic vapour pressure osmometer.

Analytical and physical data are given in Table 1.

Tetrachloro(acetylacetonato)antimony and phenyltrichloro(acetylacetonato)-antimony were prepared as reported in the literature[3b,4].

Preparation of organo(acetylacetonato)antimony(V) compounds

Diphenyldichloro(acetylacetonato)antimony

Diphenyltrichloroantimony 4.05 g (10.5 mmoles) was dissolved in a mixture of carbon tetrachloride (25 ml) and acetylacetone (1.05 g, 10.5 mmoles).

The reaction mixture was kept at reflux temperature for 15 min, after which the solvent was evaporated. The remaining yellow-brown solid afforded after repeated recrystallization from chloroform. 2.19 g of Ph_2SbCl_2Acac as a colourless crystalline solid. Yield 44.8%.

IR spectrum [s = strong, m = medium, w = weak, vw = very weak, (sh) =

shoulder, (br) = broad]: 1715* w, 1563 s, 1537 s, 1351 m, 1282 m, 1183 m, 1164 vw, 1160 vw, 1099 vw, 1070 vw, 1064 vw, 1058 vw, 1031 m, 1020 m, 999 m, 935 m, 917 (sh), 817 m, 736 s, 686 s, 655 vw, 649 vw, 574 m, 465 s, 462 (sh), 458 (sh), 421 m.

Dimethyldichloro(acetylacetonato)antimony

Dimethylhydroxo(oxo)antimony (1.3 g, 7.0 mmoles) was dissolved in a mixture of concentrated hydrochloric acid (25 ml) and acetylacetone (2 ml). The reaction mixture was extracted with methylenechloride. After evaporation of the solvent the remaining yellow-brown solid afforded after repeated recrystallization from chloroform/pentane, Me_2SbCl_2Acac (0.7 g) as a colourless crystalline solid. Yield 31.8%.

IR spectrum: 1563 s, 1527 s, 1429 w, 1351 s, 1282 m, 1022 s, 935 s, 859 m (br), 813 s, 770 vw, 722 vw, 670 m, 653 m, 584 w, 564 s, 431 m (br), 408 m (br).

Diethyldichloro(acetylacetonato)antimony

This compound was isolated in 38.4% yield as a colourless crystalline solid, by essentially the same procedure.

IR spectrum: 1565 s, 1527 s, 1410 w, 1340 s, 1282 m, 1190 m, 1031 m, 980 w, 961 w, 937 m, 813 m, 787 vw, 725 m, 669 m, 653 w, 566 m, 553 w, 495 w (br), 427 m (br), 409 m (br).

Tetraphenyl-, tetramethyl- and tetraethyl(acetylacetonato)antimony

These compounds were obtained in quantitative yield upon addition of acetylacetone in a 1/1 molar ratio to a benzene solution of the corresponding tetraphenyl- or tetraalkylmethoxoantimony compounds.

$Ph_4SbAcac$. IR spectrum: 1587 s, 1575 s, 1527 s, 1488 m, 1435 s, 1376 s, 1337 w, 1312 w, 1263 m, 1190 w, 1161 vw, 1099 vw, 1066 m, 1020 m, 999 w–m, 972 vw, 926 m, 857 vw, 795 m, 787 m, 740 (sh), 737 s, 733 s, 695 s, 664 w, 657 w, 643 w, 617 vw, 568 w, 537 w, 475 m, 465 m, 458 (sh), 454 m.

$Me_4SbAcac$. IR spectrum: 1587 s, 1503 s, 1449 s, 1375 s, 1299 w, 1235 m, 1199 m, 1163 w (sh), 1010 s, 970 m, 948 w (sh), 912 m, 836 vw, 810 w, 763 m, 704 m–s, 680 m (sh), 649 m, 621 vw, 602 vw, 534 m, 515 m (br).

$Et_4SbAcac$. IR spectrum: 1585 s, 1506 s (br), 1449 s (br), 1290 m, 1235 m, 1205 m, 1171 m, 1000 s (br), 948 m, 914 w, 823 vw, 775 m (br), 714 m–s (br), 680 w, 648 vw, 621 w (br), 531 m (br).

Attempts to prepare compounds of the type $R_3SbClAcac$

After keeping a mixture of R_3SbCl_2 (R = Me, Ph) and acetylacetone in carbon tetrachloride at reflux temperature for several hours R_3SbCl_2 was recovered almost quantitatively.

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* Only observed in a chloroform solution spectrum.

REFERENCES

1 K. Shen, W. E. McEwen, S. J. La Placa, W. C. Hamilton and A. P. Wolf, *J. Amer. Chem. Soc.*, 90 (1968) 1718.
2 (a) H. C. Clark and R. G. Goel, *Inorg. Chem.*, 5 (1969) 998;
(b) M. Shindo and R. Okawara, *J. Organometal. Chem.*, 5 (1966) 537.
3 (a) Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta*, 22 (1966) 1571;
(b) Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jap.*, 40 (1967) 1562.
4 Y. Kawasaki and R. Okawara, *Bull. Chem. Soc. Jap.*, 40 (1967) 428.
5 H. A. Meinema and J. G. Noltes, to be published.
6 (a) G. H. Briles and W. E. McEwen, *Tetrahedron Lett.*, 42 (1966) 5191.
(b) G. O. Doak, G. G. Long and L. D. Freedman, *J. Organometal. Chem.*, 12 (1968) 443.
7 Y. Takashi, *J. Organometal. Chem.*, 8 (1967) 225.
8 G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 7 (1968) 330.
9 (a) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963, p. 216.
(b) F. Bonati, *Organometal. Chem. Rev.*, 1 (1966) 379.
10 G. O. Doak, G. G. Long and L. D. Freedman, *J. Organometal. Chem.*, 4 (1965) 82.
11 T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 2 (1961) 477; *Chem. Abstr.*, 56 (1962) 8107 i.
12 T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, 7 (1968) 502.
13 (a) J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.*, (1965) 6740.
(b) J. Lewis and C. Oldham, *J. Chem. Soc., A*, (1966) 1456.
14 (a) S. R. Berry, *J. Chem. Phys.*, 32 (1960) 933.
(b) R. J. Gillespie, *J. Chem. Soc.*, (1963) 4672.
15 Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 521.

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THE FORMATION OF GASEOUS IONS FROM DICYCLOPENTADIENYLTITANIUM DICHLORIDE AND DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE UPON ELECTRON IMPACT*

JOHN G. DILLARD** AND ROBERT W. KISER***
Department of Chemistry, Kansas State University, Manhattan, Kansas 66502 (U.S.A.)
(Received September 20th, 1968)

SUMMARY

The mass spectra of dicyclopentadienyltitanium dichloride and dicyclopentadienylzirconium dichloride are characterized by a unique fragmentation scheme involving the removal and fragmentation of the cyclopentadienyl groups in the molecular ions. From heats of combustion the heat of formation of $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s) were determined to be −145 and −153 kcal/mole, respectively. The measured ionization potentials are $I[Ti(C_5H_5)_2Cl_2] = 8.9_8 \pm 0.1_6$ and $I[Zr(C_5H_5)_2Cl_2] = 9.3_7 \pm 0.2_5$ eV, respectively. Metastable transitions observed were used together with clastogram data to identify the fragmentation routes of the principal ionic species.

INTRODUCTION

Electron impact processes associated with positive fragment ions produced from metal "sandwich" compounds have been considered by several investigators[1-4]. The fragmentation patterns and energetic measurements have been determined for some dicyclopentadienylmetal compounds[1] and a group of cyclopentadienylmetal carbonyls[4-5]. The mass spectrum of cyclopentadienyltitanium trichloride has been measured[6] and the fragmentation pattern reported was similar to the mass spectrum of the cyclopentadienylmetal carbonyls[4-5]. For $Ti(C_5H_5)Cl_3$ the primary fragment ions were formed by the loss of chlorine atoms. Ions corresponding to the loss of C_5H_5 were quite low in abundance as was the intensity of the metal ion. No energetic measurements for the $Ti(C_5H_5)Cl_3$ molecule were given. The mass spectrum of dicyclopentadienylzirconium dichloride has been determined[7], but no energetic measurements were reported.

The present work presents an examination of the energetic processes involved in ion formation and suggests a probable unimolecular decomposition process based on observed metastable transitions and supported by clastogram curves. This in-

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* This study is a portion of a dissertation presented by J. G. Dillard to the Graduate School of Kansas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1967.

** Present address: Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia (U.S.A.).

*** Present address: Department of Chemistry, University of Kentucky, Lexington, Kentucky (U.S.A.).

vestigation has been conducted to introduce information which may aid in the effort to better understand ionization processes and the unimolecular decomposition reactions of molecules containing transition metal atoms upon electron impact.

EXPERIMENTAL

Dicyclopentadienyltitanium dichloride, a red solid, and dicyclopentadienylzirconium dichloride, a white crystalline solid, were purchased commercially. The materials were used in the mass spectrometric study without further purification since low voltage mass spectrometry indicated no impurities which would interfere with the studies.

The Bendix time-of-flight (TOF) mass spectrometer, the AEI MS-9 double focusing mass spectrometer, and the experimental procedures used in this study have already been described in detail[8,9]. Mass spectra determined with the TOF and the MS-9 instruments agreed to within a few percent of the relative intensities. Where possible energetic measurements were made at the *m/q* values for atom combinations which included the most abundant titanium, zirconium, and chlorine isotopes (48, 90, and 35 amu, respectively).

The heats of combustion of $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s) were determined using a Parr series 1200 adiabatic calorimeter and a double valve Parr bomb made of a nickel–chromium alloy. The heat equivalent of the calorimeter was determined by burning samples of reagent grade benzoic acid.

The combustion of the organometallic halides was complicated by the fact that some of the combustion products (probably HCl) reacted with the bomb walls. Examination and analysis of the contents of the bomb after combustion indicated that molecular chlorine was not one of the primary products. It is suggested that HCl is the product which reacts with the bomb walls and that the reaction in the combustion of the dicyclopentadienylmetal dichlorides is

$$M(C_5H_5)_2(s)+13\ O_2(g) \rightarrow MO_2(s)+2\ HCl(aq)+10\ CO_2(g)+4\ H_2O\,(l) \qquad (1)$$

Since HCl reacted with the bomb walls, an appropriate correction must be made so that correct heats of combustion for the $M(C_5H_5)_2Cl_2$ compounds can be evaluated.

To evaluate the energy released in the reaction of HCl, samples of chlorobenzene were burned in the calorimeter. In these combustions the heat evolved in excess of the known heat of combustion of chlorobenzene[10] (−6604.0 cal/g) was taken as the heat of reaction of HCl with the bomb walls. For repeated combustions of chlorobenzene the excess energy evolved was 66.6 ± 2.3 kcal/g-atom of chlorine. It was assumed that the excess energy evolved in the combustion of the organometallic chlorides was equal to that given off when an equivalent amount of chlorobenzene was burned.

If reaction with the walls was the same for combustions with chlorobenzene and the organometallic chlorides, the ratio of the individual metal ion concentrations to the total chlorine in the sample should be constant. From an analysis of total chlorine (Cl) as chloride and a determination of the respective metal ion concentration by atomic absorption[11], the metal to chlorine (Cl) ratio was constant for combustions of chlorobenzene and the dicyclopentadienylmetal dichlorides.

After adiabatic combustion, gaseous products were removed from the bomb and the bomb contents washed into vessels for subsequent chemical analysis. In all combustions the total chlorine (Cl) recovered as chloride ion was 100%. In combustion of the organometallic chlorides the metal dioxide recovered corresponded to the quantity expected based on the weight of the sample burned. The heats of combustion of $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s) were -1366 ± 5 and -1398 ± 5 kcal/mole, respectively. Calculated heats of formation of the crystalline compounds determined from the heat of combustion according to reaction (1) were -145 ± 7 and -153 ± 7 kcal/mole for $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s), respectively. Heats of formation employed in the calculations were:

$\Delta H_f(CO_2(g)) = -94.05$ (ref. 12) $\Delta H_f(ZrO_2(s)) = -258.2$ (ref. 13)
$\Delta H_f(H_2O(l)) = -68.32$ (ref. 12) $\Delta H_f(HCl(aq)) = -39.55$ kcal/mole (ref. 10)
$\Delta H_f(TiO_2(s)) = -218$ (ref. 13)

RESULTS AND DISCUSSION

The results for this investigation of the positive ions produced from dicyclopentadienyltitanium dichloride and dicyclopentadienylzirconium dichloride are presented in Tables 1 and 2. The relative abundances of the positive ions represent the monoisotopic intensity and as such include contributions from all the isotopes for a given ion at 70 eV. Several hydrocarbon ions of the type $C_xH_y^+$ have been omitted from the tables. The appearance potentials determined are given in column 3. The calculated heats of formation for the positive ions are reported in column 5. Heats of formation of the gaseous species used to evaluate the heats of formation of the ions are (in kcal/mole):

TABLE 1

APPEARANCE POTENTIALS AND HEATS OF FORMATION FOR POSITIVE IONS PRODUCED FROM DICYCLOPENTADIENYLTITANIUM DICHLORIDE

Ion	Relative abundance at 70 eV	Appearance potential (eV)	Probable process $Ti(C_5H_5)_2Cl_2 \rightarrow$	ΔH_f(ion) (kcal/mole)
$Ti(C_5H_5)_2Cl_2^+$	29.1	$8.9_8 \pm 0.1_6$	$Ti(C_5H_5)_2Cl_2^+$	85
$Ti(C_5H_5)_2Cl^+$	8.9	10.8 ± 0.3	$Ti(C_5H_5)_2Cl^+ + Cl$	98
$Ti(C_5H_5)Cl_2^+$	100.0	11.8 ± 0.2	$Ti(C_5H_5)Cl_2^+ + C_5H_5$	100
$Ti(C_5H_5)Cl^+$	38.7	16.3 ± 0.3	$Ti(C_5H_5)Cl^+ + C_5H_5 + Cl$	175
$Ti(C_3H_3)Cl_2^+$	0.8			
$Ti(C_3H_3)Cl^+$	6.7	(19.5)[a]	$Ti(C_3H_3)Cl^+ + C_5H_5 + C_2H_2 + Cl$	(194)[a]
$Ti(C_3H_3)^+$	1.9			
$Ti(C_2H_2)Cl^+$	2.3			
$TiCl_2^+$	21.3	19.7 ± 0.4	$TiCl_2^+ + C_5H_5 + C_3H_3 + C_2H_2$	144
$TiCl^+$	28.8	21.6 ± 0.4	$TiCl^+ + C_5H_5 + C_3H_3 + C_2H_2 + Cl$	159
Ti^+	2.5			
$C_5H_5^+$	26.6	13.0 ± 0.4	$C_5H_5^+ + Ti(C_5H_5)Cl_2$	(−62)[b]
$C_3H_3^+$	38.3	18.0 ± 0.5	?	

[a] Estimated values; see text. [b] Heat of formation of $Ti(C_5H_5)Cl_2$.

TABLE 2

APPEARANCE POTENTIALS AND HEATS OF FORMATION FOR POSITIVE IONS PRODUCED FROM DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE

Ion	Relative abundance at 70 eV	Appearance potential (eV)	Probable process $Zr(C_5H_5)_2Cl_2 \rightarrow$	ΔH_f(ion) (kcal/mole)
$Zr(C_5H_5)_2Cl_2^+$	50.6	$9.3_7 \pm 0.2_5$	$Zr(C_5H_5)_2Cl_2^+$	87
$Zr(C_5H_5)_2Cl^+$	11.3	12.3 ± 0.2	$Zr(C_5H_5)_2Cl^+ + Cl$	125
$Zr(C_5H_5)Cl_2^+$	100.0	12.5 ± 0.2	$Zr(C_5H_5)Cl_2^+ + C_5H_5$	109
$Zr(C_5H_5)Cl^+$	10.0	19.8 ± 0.4	$Zr(C_5H_5)Cl^+ + C_5H_5 + Cl$	248
$Zr(C_3H_3)Cl_2^+$	29.3			
$Zr(C_3H_3)Cl^+$	10.1	(19.9)[a]	$Zr(C_3H_3)Cl^+ + C_5H_5 + C_2H_2 + Cl$	(196)[a]
$Zr(C_3H_3)^+$	4.5			
$Zr(C_2H_2)Cl^+$	3.5			
$ZrCl_2^+$	9.4	20.9 ± 0.5	$ZrCl_2^+ + C_5H_5 + C_3H_3 + C_2H_2$	164
$ZrCl^+$	8.6	24.3 ± 0.5	$ZrCl^+ + C_5H_5 + C_3H_3 + C_2H_2 + Cl$	214
Zr^+	0.3			
$C_5H_5^+$	12.1	13.6 ± 0.2	$C_5H_5^+ + Zr(C_5H_5)Cl_2$	(-56)[b]
$C_3H_3^+$	16.2	19.5 ± 0.4	?	

[a] Estimated values; see text. [b] Heat of formation of $Zr(C_5H_5)Cl_2$.

$Ti(C_5H_5)_2Cl_2$, -122.0★
$Zr(C_5H_5)_2Cl_2$, -129.9★
Cl, 29.08 (ref. 12)
C_5H_5, 50 (ref. 14)
C_3H_3, 84 (ref. 15)
C_2H_2, 54.2 (ref. 13)
$C_5H_5^+$, 240 (ref. 16)

Because of the overlap of m/q values for the MCl_2^+ and $M(C_3H_3)Cl^+$ ions it was not feasible to determine accurately the appearance potentials of the $M(C_3H_3)Cl^+$ ions using normal experimental procedures. The appearance potentials were estimated from the clastograms by noting the relative position of the $M(C_3H_3)Cl^+$ ion curves at low values of the fractional abundance relative to the position of the curves in this region for the MCl_2^+ and MCl^+ ions. The estimated appearance potentials are 19.5 and 19.9 eV for $Ti(C_3H_3)Cl^+$ and $Zr(C_3H_3)Cl^+$, respectively.

The most abundant ion, $M(C_5H_5)Cl_2^+$, is formed from the parent molecule-ion by the loss of a cyclopentadienyl group. This decomposition scheme is distinctly different from that observed for the cyclopentadienylmetal carbonyls[4,5] and cyclopentadienyltitanium trichloride[6] where the difficulty of removing the cyclopentadienyl group was great compared with the loss of CO or Cl. This preferential elimination of C_5H_5 in the dicyclopentadienylmetal dichlorides is indicative of the probable greater bond strength and ionic character of the chlorine–metal bond. For other fragment ions removal and fragmentation of the cyclopentadienyl group is favored, and ions retaining the chlorine substituent are the most abundant ions of a given series.

Two series of ions, $Zr(C_3H_3)Cl_n^+$ and $Zr(C_2H_2)Cl_m^+$ ($n=0, 1, 2$; $m=1, 2$), were detected in the 70 eV mass spectrum of the zirconium compound. The production of $Zr(C_3H_3)Cl_n^+$ and $Zr(C_2H_2)Cl_m^+$ ions occurs by fragmentation of the cyclopentadienyl

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★ $\Delta H_f[Ti(C_5H_5)_2Cl_2(s)]$ and $\Delta H_f[Zr(C_5H_5)_2Cl_2(s)]$ were determined in this work (see text); the heats of sublimation of these compounds have been reported previously[9].

TABLE 3

METASTABLE TRANSITIONS IN DICYCLOPENTADIENYLTITANIUM DICHLORIDE

m^* obsd.	m^* calcd.	Metastable transition
185.0	184.90	$Ti(C_5H_5)_2Cl_2^+(250) \rightarrow Ti(C_5H_5)_2Cl^+(215) + Cl(35)$
183.0	182.94	$Ti(C_5H_5)_2Cl_2^+(248) \rightarrow Ti(C_5H_5)_2Cl^+(213) + Cl(35)$
181.5	181.48	$Ti(C_5H_5)_2Cl_2^+(250) \rightarrow Ti(C_5H_5)_2Cl^+(213) + Cl(37)$
136.9	136.90	$Ti(C_5H_5)_2Cl_2^+(250) \rightarrow Ti(C_5H_5)Cl_2^+(185) + C_5H_5(65)$
135.1	135.04	$Ti(C_5H_5)_2Cl_2^+(248) \rightarrow Ti(C_5H_5)Cl_2^+(183) + C_5H_5(65)$
121.6	121.62	$Ti(C_5H_5)Cl_2^+(185) \rightarrow Ti(C_5H_5)Cl^+(150) + Cl(35)$
119.7	119.69	$Ti(C_5H_5)Cl_2^+(183) \rightarrow Ti(C_5H_5)Cl^+(148) + Cl(35)$
118.5	118.40	$Ti(C_5H_5)Cl_2^+(185) \rightarrow Ti(C_5H_5)Cl^+(148) + Cl(37)$
102.5	102.51	$Ti(C_5H_5)Cl^+(150) \rightarrow Ti(C_3H_3)Cl^+(124) + C_2H_2(26)$
100.5	100.57	$Ti(C_5H_5)Cl^+(148) \rightarrow Ti(C_3H_3)Cl^+(122) + C_2H_2(26)$
23.5	23.40	$C_5H_5^+(65) \rightarrow C_3H_3^+(39) + C_2H_2(26)$

group probably forming the neutral species C_2H_2 and C_3H_3 while the ion retains either one or two chlorine atoms. In previous mass spectrometric studies[3-5] of cyclopentadienyl-containing metal compounds, fragmentation of the cyclopentadienyl group to produce the $M(C_3H_3)^+$ ions was observed, but ions containing $M(C_2H_2)$ were not detected. The formation of $M(C_2H_2)Cl_m^+$ ions appears novel for the dicyclopentadienylmetal dichlorides.

TABLE 4

METASTABLE TRANSITIONS IN DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE

m^* obsd.	m^* calcd.	Metastable transitions
184.0	183.90	$Zr(C_5H_5)Cl_2^+(233) \rightarrow Zr(C_3H_3)Cl_2^+(207) + C_2H_2(26)$
182.0	181.93	$Zr(C_5H_5)Cl_2^+(231) \rightarrow Zr(C_3H_3)Cl_2^+(205) + C_2H_2(26)$
180.1	179.95	$Zr(C_5H_5)Cl_2^+(229) \rightarrow Zr(C_3H_3)Cl_2^+(203) + C_2H_2(26)$
178.3	177.98	$Zr(C_5H_5)Cl_2^+(227) \rightarrow Zr(C_3H_3)Cl_2^+(201) + C_2H_2(26)$
176.3	176.00	$Zr(C_5H_5)Cl_2^+(225) \rightarrow Zr(C_3H_3)Cl_2^+(199) + C_2H_2(26)$
182.0	182.18	$Zr(C_5H_5)_2Cl_2^+(298) \rightarrow Zr(C_5H_5)Cl_2^+(233) + C_5H_5(65)$
180.1	180.27	$Zr(C_5H_5)_2Cl_2^+(296) \rightarrow Zr(C_5H_5)Cl_2^+(231) + C_5H_5(65)$
178.3	178.37	$Zr(C_5H_5)_2Cl_2^+(294) \rightarrow Zr(C_5H_5)Cl_2^+(229) + C_5H_5(65)$
176.3	176.47	$Zr(C_5H_5)_2Cl_2^+(292) \rightarrow Zr(C_5H_5)Cl_2^+(227) + C_5H_5(65)$
174.6	174.57	$Zr(C_5H_5)_2Cl_2^+(290) \rightarrow Zr(C_5H_5)Cl_2^+(225) + C_5H_5(65)$
147.4	147.45	$Zr(C_5H_5)Cl^+(196) \rightarrow Zr(C_3H_3)Cl^+(170) + C_2H_2(26)$
146.5	146.47	$Zr(C_5H_5)Cl^+(195) \rightarrow Zr(C_3H_3)Cl^+(169) + C_2H_2(26)$
145.5	145.48	$Zr(C_5H_5)Cl^+(194) \rightarrow Zr(C_3H_3)Cl^+(168) + C_2H_2(26)$
144.4	144.50	$Zr(C_5H_5)Cl^+(193) \rightarrow Zr(C_3H_3)Cl^+(167) + C_2H_2(26)$
143.5	143.52	$Zr(C_5H_5)Cl^+(192) \rightarrow Zr(C_3H_3)Cl^+(166) + C_2H_2(26)$
142.5	142.54	$Zr(C_5H_5)Cl^+(191) \rightarrow Zr(C_3H_3)Cl^+(165) + C_2H_2(26)$
141.6	141.56	$Zr(C_5H_5)Cl^+(190) \rightarrow Zr(C_3H_3)Cl^+(164) + C_2H_2(26)$
23.5	23.40	$C_5H_5^+(65) \rightarrow C_3H_3^+(39) + C_2H_2(26)$

Other ions detected in the mass spectrum of the zirconium compound, but not included in Table 2, were $Zr(C_2H_x)Cl^+$ (8.7%), $Zr(C_2H_x)Cl_2^+$ (36.5%), $Zr(C_3H_2)Cl^+$ (14.2%) and small amounts of $Zr(C_4H_x)Cl_2^+$ and $Zr(C_5H_5)(C_2H_2)Cl^+$. Very low intensities of $Zr(C_3H_3)_2^+$ and $Zr(C_5H_5)_2^+$ ions were observed.

The series of unimolecular reactions for the formation of the fragment ions was established from the metastable transitions observed and the general shapes of the clastogram curves. The fragmentation scheme consists of competitive reactions involving the parent molecule-ion and a series of consecutive and competitive reactions where fragment ions decompose via elimination and fragmentation of C_5H_5 or by loss of chlorine atoms. The observed and calculated "metastable masses" and their associated transitions are presented in Tables 3 and 4.

The initial unimolecular reactions clearly indicated by the metastable transitions involve competitive loss of C_5H_5 and Cl from the parent molecule-ion. A unique "metastable isotopic pattern" was observed corresponding to removal of ^{35}Cl or ^{37}Cl isotopes from the titanium or zirconium ion which was composed of the most abundant metal isotope and the chlorine isotopic combinations: ^{35}Cl: ^{35}Cl; and ^{35}Cl : ^{37}Cl. The intensity of the metastable peak for elimination of ^{37}Cl from the metal chlorine combination ^{37}Cl : ^{37}Cl was too low to be detected. In a similar fashion a characteristic metastable isotopic pattern was noted for the process involving loss of the cyclopentadienyl group from the parent molecule-ion. The reaction processes which occur following the formation of the $M(C_5H_5)Cl_2^+$ ion are confirmed from the observed metastable transitions. The processes leading to the formation of the most abundant ions in the mass spectrum are:

$$\begin{tikzcd} Ti(C_5H_5)_2Cl_2^+ \arrow[r] \arrow[dr] & Ti(C_5H_5)Cl_2^+ \arrow[r] & Ti(C_5H_5)Cl^+ \arrow[r] & Ti(C_3H_3)Cl^+ \\ & Ti(C_5H_5)_2Cl^+ & C_5H_5^+ \arrow[r] & C_3H_3^+ \end{tikzcd} \qquad (2)$$

and

$$\begin{tikzcd} Zr(C_5H_5)_2Cl_2^+ \arrow[r] \arrow[ddr] & Zr(C_5H_5)Cl_2^+ \arrow[r] \arrow[dr] & Zr(C_3H_3)Cl_2^+ & \\ & & Zr(C_5H_5)Cl^+ \arrow[r] & Zr(C_3H_3)Cl^+ \\ & Zr(C_5H_5)_2Cl^+ & C_5H_5^+ \arrow[r] & C_3H_3^+ \end{tikzcd} \qquad (3)$$

In the above reactions, decomposition pathways for which metastable transitions were observed are indicated by solid arrows. Processes deduced from the clastogram data are signified by broken lines and are discussed below. Although two processes:

$$Zr(C_5H_5)_2Cl^+ \rightarrow Zr(C_5H_5)Cl^+ + C_5H_5 \qquad (4)$$

$$Zr(C_5H_5)Cl^+ \rightarrow Zr(C_3H_3)Cl^+ + C_2H_2 \qquad (5)$$

are indicated by the 141.6–147.4 metastable ions, it is suggested that these metastable ions result from reaction (5). Comparison with the transitions observed in $Ti(C_5H_5)_2Cl_2$ supports this suggestion for $Zr(C_5H_5)_2Cl_2$. Since the metastable transitions for the processes:

$$Zr(C_5H_5)_2Cl_2^+ \rightarrow Zr(C_5H_5)Cl_2^+ + C_5H_5 \qquad (6)$$

and

$$Zr(C_5H_5)Cl_2^+ \rightarrow Zr(C_3H_3)Cl_2^+ + C_2H_2 \qquad (7)$$

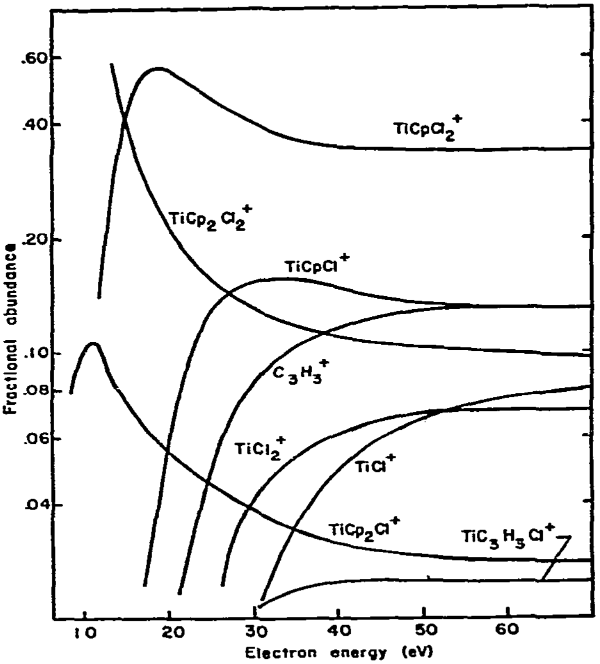

Fig. 1. Logarithmic clastogram for singly-charged positive ions from $Ti(C_5H_5)_2Cl_2$.

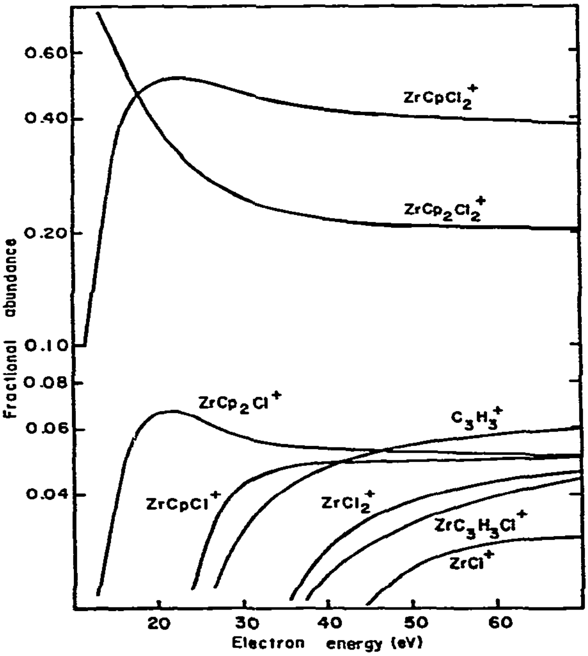

Fig. 2. Logarithmic clastogram for singly-charged positive ions from $Zr(C_5H_5)_2Cl_2$.

overlap somewhat in the mass spectrum, the identity of each transition was deduced from an analysis of the observed isotopic abundances for zirconium and chlorine in the respective metastable ions.

The logarithm of the fractional abundance of the ions as a function of the uncorrected ionizing electron energy is plotted in the clastograms shown in Figs. 1 and 2. The curve shapes are indicative of the unimolecular decomposition processes occurring in the ion source[4,9,17]. The parent molecule-ion is the most abundant ion at low electron energies and decreases in intensity as the electron energy is increased due to fragmentation of the parent ion. The primary fragment ions, $M(C_5H_5)Cl_2^+$ and $M(C_5H_5)_2Cl^+$, appear at low energies, reach a maximum intensity, and then decrease at higher energy.

This behavior in the clastogram curve is indicative of a consecutive reaction occurring in the ion source. This conclusion is confirmed by the metastable transitions observed. For the titanium compound a metastable transition was observed for the process $Ti(C_5H_5)Cl_2^+ \rightarrow Ti(C_5H_5)Cl^+ + Cl$. In the clastogram curve it is noted that the $Ti(C_5H_5)Cl^+$ ion begins to increase in abundance as the fractional intensity of the $Ti(C_5H_5)Cl_2^+$ ion decreases. From the clastogram data it is evident that $Ti(C_5H_5)Cl^+$ is not formed from $Ti(C_5H_5)_2Cl^+$ by loss of C_5H_5, since the intensity of the $Ti(C_5H_5)_2Cl^+$ ion is low when the abundance of $Ti(C_5H_5)Cl^+$ begins to increase. This interpretation of the clastogram is in agreement with the metastable data.

Similar arguments and correlations are applicable in the zirconium compound. From the curves it is evident that the intensity of the parent molecule-ion decreases as the abundance of the $Zr(C_5H_5)_2Cl^+$ and $Zr(C_5H_5)Cl_2^+$ ions increase. Similarly, the $Zr(C_5H_5)Cl^+$ ion increases as the $Zr(C_5H_5)Cl_2^+$ ion abundance decreases suggesting that the primary mode of formation of $Zr(C_5H_5)Cl^+$ is $Zr(C_5H_5)Cl_2^+ \rightarrow Zr(C_5H_5)Cl^+ + Cl$. Complementary arguments based on clastogram data and metastable transitions support the decomposition process presented above.

The ionization potentials of $8.9_8 \pm 0.1_6$ and $9.3_7 \pm 0.2_5$ eV for $Ti(C_5H_5)_2Cl_2$ and $Zr(C_5H_5)_2Cl_2$, respectively, are greater than the ionization potentials measured for a series of dicyclopentadienylmetal molecules[1,4]. The values are also higher than the corresponding metal ionization potentials[18] but approximate the ionization potential of the cyclopentadienyl radical[19].

A molecular orbital description of the electronic structure of $Ti(C_5H_5)_2Cl_2$ has been presented by Chien[20]. According to the molecular orbital representation the electron removed in ionization occurred from the a_2^* anti-bonding orbital, which is anti-bonding among all the metal–ligand bonds. Although Chien assigns no weighted contributions to the orbital from the ligands, it would appear from our results that the contribution by chlorine is somewhat larger than the contribution by cyclopentadienyl since the ionization potentials are greater than for $M(C_5H_5)_2$ molecules[1,4]. Thus the inference is that the electron removed in ionization occurs from the molecular orbital composed predominantly of contributions from the metal and chlorine.

The heats of formation of the ions presented are calculated according to the reactions given in Tables 1 and 2 using the heats of formation of gaseous neutral species given above. Selection of the products accompanying the formation of the ions is based on the processes indicated from the metastable transitions and the clastogram curves. Although the metastable transitions were observed at 70 eV, the close correlation with the clastogram curves, which were determined by measuring the mass spectrum at a range of electron energies, indicates the neutral species suggested in the reactions of Tables 1 and 2 are the products formed at the threshold energy for production of the fragment ions.

The calculated heat of formation of $TiCl_2^+$ from dicyclopentadienyltitanium dichloride compares favorably with the value $\Delta H_f(TiCl_2^+) = 145$ kcal/mole calculated[9] for this ion from $TiCl_4$. However, the heat of formation of $TiCl^+$ determined here is somewhat less than the "best" value $\Delta H_f(TiCl^+)=206$ kcal/mole calculated[9] from $TiCl_4$. The magnitudes of the heats of formation of the $ZrCl_n^+$ ions and $M(C_5H_5)_mCl_n^+$ $\{M=Ti, Zr; m=n=1, 2\}$ are taken as acceptable values since no measurements have been reported previously.

Studies are currently being carried out to establish the identity of the negative ions observed in the mass spectrum and to measure the energy associated with electron capture processes.

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REFERENCES

1 L. FRIEDMAN, A. P. IRSA AND G. WILKINSON, *J. Amer. Chem. Soc.*, 77 (1955) 3689.
2 F. W. MCLAFFERTY, *Anal. Chem.*, 28 (1956) 306.
3 E. SCHUMACHER AND R. TAUBENEST, *Helv. Chim. Acta*, 47 (1964) 1525.
4 R. E. WINTERS, *Mass Spectrometric Study of Some Organometallic Compounds*, Kansas State University, 1965.
5 R. E. WINTERS AND R. W. KISER, *J. Organometal. Chem.*, 4 (1965) 190.
6 A. N. NESMEYANOV, W. A. DUBOVITSKII, O. V. NOGINA AND V. N. BOCHKAREV, *Dokl. Akad. Nauk SSSR.*, 165 (1965) 125.
7 A. F. REID, J. A. SHANNON, J. M. SWAN AND P. C. WAILES, *Aust. J. Chem.*, 18 (1965) 173.
8 E. J. GALLEGOS AND R. W. KISER, *J. Amer. Chem. Soc.*, 83 (1961) 733; *J. Phys. Chem.*, 65 (1961) 1177.
9 R. W. KISER, J. G. DILLARD AND D. L. DUGGER, *Advan. Chem. Ser.*, 72 (1968) 153.
10 W. N. HUBBARD, J. W. KNOWLTON AND H. M. HUFFMAN, *J. Phys. Chem.*, 58 (1954) 396.
11 C. W. FRANK, *Studies in Analytical Chemistry, Part I. Source Units for Atomic Absorption Spectrophotometry. Part II. Indium and Antimony Polarography*, Kansas State University, 1965.
12 D. D. WAGMAN, W. H. EVANS, I. HALOW, V. B. PARKER, S. M. BAILEY AND R. H. SCHUMM, *Selected Values of Chemical Thermodynamic Properties. Part I.*, National Bureau of Standards, Technical Note 270–1, U.S. Government Printing Office, Washington, D.C., 1965.
13 F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE AND I. H. JAFFE, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards, Circular 500, U.S. Government Printing Office, Washington, D.C., 1952.
14 F. A. COTTON AND G. WILKINSON, *J. Amer. Chem. Soc.*, 74 (1952) 5764.
15 J. B. FARMER AND F. P. LOSSING, *Can. J. Chem.*, 33 (1955) 361.
16 J. L. FRANKLIN, J. G. DILLARD, H. M. ROSENSTOCK, J. T. HERRON, K. DRAXAL AND F. H. FIELD, *Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions*, National Standard Reference Data System, Washington, D.C., to be published.
17 A. B. KING AND F. A. LONG, *J. Chem. Phys.*, 29 (1958) 374.
18 C. E. MOORE, *Atomic Energy Levels*, National Bureau of Standards, Circular 467, volumes 1, 2, and 3, U.S. Government Printing Office, Washington D.C., 1949, 1952 and 1958.
19 A. G. HARRISON, L. R. HONNEN, H. J. DAUBEN AND F. P. LOSSING, *J. Amer. Chem. Soc.*, 82 (1960) 5593.
20 J. C. W. CHIEN, *J. Phys. Chem.*, 67 (1963) 2477.

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ÜBERGANGSMETALL-CARBEN-KOMPLEXE
XIII*. UNTERSUCHUNGEN ZUR *cis–trans*-ISOMERIE VON KOMPLEXGEBUNDENEM (METHYLAMINO)METHYLCARBEN

E. MOSER UND E. O. FISCHER
Anorganisch-Chemisches Laboratorium der Technischen Hochschule, München (Deutschland)

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SUMMARY

cis(Methylamino)methylcarbene, which is bound to the pentacarbonylchromium(0), the pentacarbonyltungsten(0), or the (triphenylphosphine)tetracarbonyltungsten(0) group, can be isomerized to the *trans*-isomer. The isomerization proceeds completely to the *trans*-isomer with the pentacarbonyltungsten(0) group, however only partially with the other groups. A corresponding isomerization has not been observed with the (triphenylphosphine)tetracarbonylchromium(0) group. The isomers can be recognized by their ^{1}H-NMR and IR spectra.

ZUSAMMENFASSUNG

An den Pentacarbonylchrom(0)-, den Pentacarbonylwolfram(0)- oder den (Triphenylphosphin)tetracarbonylwolfram(0)-Rest gebundenes *cis*-(Methylamino)-methylcarben kann in das *trans*-Isomere übergeführt werden. Die Isomerisierung verläuft vollständig zum *trans*-Isomeren beim Pentacarbonylwolfram(0)-Rest, jedoch nur teilweise bei den anderen Resten. Beim (Triphenylphosphin)tetracarbonylchrom(0)-Rest konnte eine entsprechende Isomerisierung nicht beobachtet werden. Die Isomeren können an ihren ^{1}H-NMR- und IR-Spektren erkannt werden.

EINLEITUNG

Vor kurzem haben wir über die *cis–trans*-Isomerie von an den Pentacarbonylchrom(0)-Rest gebundenem (Methylamino)methylcarben berichtet[2]. Um weitere Informationen und Vergleichsmöglichkeiten zu gewinnen, wurden nun auch die entsprechende Verbindung des Wolframs und die [(Methylamino)methylcarben]-(triphenylphosphin)tetracarbonyl-Komplexe von Chrom(0) und Wolfram(0) untersucht.

PRÄPARATIVE ERGEBNISSE

Die Umsetzung von [*trans*-(Methoxy)methylcarben]pentacarbonylwolfram(0)[3,4,5] mit Methylamin gemäss

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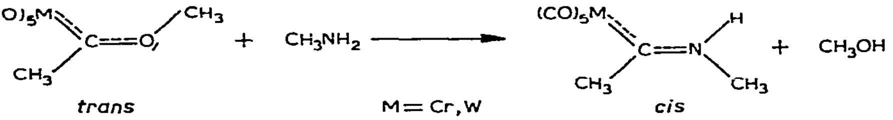
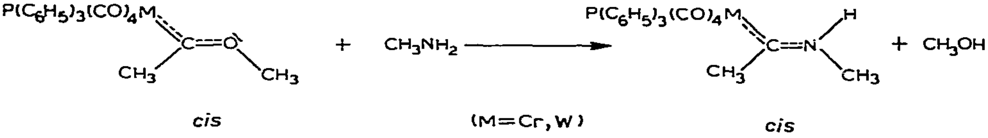
* XII. Mitteilung siehe Ref. 1.



führte zu [*cis*-(Methylamino)methylcarben]pentacarbonylwolfram(0). Ebenso hatte die Reaktion von [*trans*-(Methoxy)methylcarben]pentacarbonylchrom(0)[4,5] und von [(Trimethylsiloxy)methylcarben]pentacarbonylchrom(0)[6], dessen Struktur noch unbekannt ist, mit Methylamin [*cis*-(Methylamino)methylcarben]pentacarbonylchrom(0) geliefert[2].

Die analogen Triphenylphosphin-tetracarbonyl-Komplexe[7,8], in denen das komplexgebundene (Methoxy)methylcarben in der *cis*-Konfiguration vorliegt[5], reagierten mit Methylamin gemäss



zu [*cis*-(Methylamino)methylcarben](triphenylphosphin)tetracarbonyl-Komplexen*. Die Konfiguration des komplexgebundenen Carbens in der Ausgangsverbindung scheint demnach für die Konfiguration im Produkt ohne Bedeutung zu sein.

Die Aminolyse wurde vorteilhaft durch Einleiten des Amins in Äther durchgeführt – wobei eine Farbänderung das rasche Fortschreiten der Reaktion anzeigte –, da in Pentan, das früher hierfür verwendet worden war, nur langsame Umsetzung eintritt[8] (Vergl. hierzu auch Ref. 9).

Durch Behandlung von [*cis*-(Methylamino)methylcarben]pentacarbonylchrom(0) mit Natrium-tert-Butylat in tert-Butanol war es uns gelungen, eine weitgehende Isomerisierung zu erzielen[2]. Unter entsprechenden Bedingungen konnte nun [*cis*-(Methylamino)methylcarben]pentacarbonylwolfram(0) vollständig in das *trans*-Isomere übergeführt werden. Hingegen entstand bei [*cis*-(Methylamino)-methylcarben](triphenylphosphin)tetracarbonylwolfram(0) nur ein Gemisch, das *cis*- und *trans*-Isomere etwa im Verhältnis 1 : 3 enthielt. Die analoge Chromverbindung liess sich demgegenüber unter vergleichbaren Bedingungen (bei den triphenylphosphinhaltigen Komplexen musste wegen ihrer Schwerlöslichkeit ziemlich viel Äther zugesetzt werden) überhaupt nicht in das *trans*-Isomere umwandeln.

Es liegt nahe, versuchsweise das unterschiedliche Verhalten räumlich gedrängten Verhältnissen zuzuschreiben, da unseres Erachtens der Triphenylphosphin-Ligand am Koordinationsoktaeder relativ zum komplexgebundenen Carben eine Nachbarstellung einnehmen dürfte, wie dies bei den Ausgangsverbindungen IR-spektroskopisch[7], beim Chromkomplex auch röntgenographisch[10], festgestellt worden ist. Ein Platzwechsel von Liganden unter den milden Bedingungen der Aminolyse scheint jedenfalls recht unwahrscheinlich. Entsprechende sterische Wechselwirkungen mögen bewirken, dass bei (Methoxy)methylcarben-Komplexen die Einführung von Triphenylphosphin die Bevorzugung der *cis*-Konfiguration zur Folge hat[5].

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* Die Bezeichnung *cis* oder *trans* bezieht sich in dieser Arbeit nur auf die Konfiguration des komplexgebundenen Carbens, nicht aber auf die Stellung von Liganden am Koordinationsoktaeder.

^{1}H-NMR-SPEKTREN

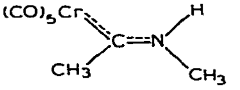
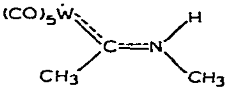
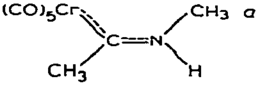
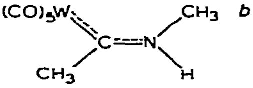
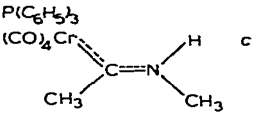
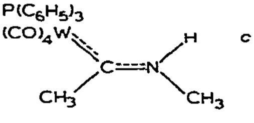
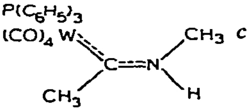
Die Konfiguration der Isomeren wurde mittels ihrer ^{1}H-NMR-Spektren bestimmt; als Kriterium dienten wie früher[2,12] lösungsmittelabhängige chemische Verschiebungen und Homoallyl-Kopplungskonstanten J(H–C–N=C–C–H). Tabelle 1 enthält die ermittelten Parameter (bei den phosphinhaltigen Komplexen waren wegen ihrer Schwerlöslichkeit keine eingehenderen Untersuchungen möglich).

Das Spektrum von [*cis*-(Methylamino)methylcarben]pentacarbonylwolfram(0) zeigt im Methylgruppenbereich zwei Quartetts (NCH_3) und ein Sextett (CCH_3), das der *trans*-Verbindung zwei Quartetts (NCH_3) und ein Quintett (CCH_3). Die beiden Quartetts kommen durch vicinale Kopplung (H–C–N–H) und Homoallylkopplung(H–C–N=C–C–H) zustande. Das Auftreten des Sextetts lässt sich mit der

TABELLE 1

NMR-PARAMETER VON KOMPLEXGEBUNDENEM (METHYLAMINO)METHYLCARBEN

Die τ-Werte sind auf das Signal des jeweiligen Lösungsmittels bezogen.

Verbindung		τ(CCH_3)		τ(NCH_3)		J (Hz)	
		$HCCl_3$	C_6H_6	$HCCl_3$	C_6H_6		
	[a]	7.30	7.95	6.79	8.20	CH_3–CH_3 HN–C–CH_3 H–N–CH_3	~ 0.3[e] ~ 0.8[e] 5.1 ±0.1
	[b]	7.25	7.90	6.84	8.21	CH_3–CH_3 HN–C–CH_3 H–N–CH_3	0.45±0.1 0.9 ±0.1 5.1 ±0.1
	[a]	7.19	7.85	6.35	7.20	CH_3–CH_3 HN–C–CH_3 H–N–CH_3	0.85±0.1 0.85±0.1 4.9 ±0.1
	[b]	7.08	7.76	6.45	7.32	CH_3–CH_3 HN–C–CH_3 H–N–CH_3	0.95±0.1 0.95±0.1 4.9 ±0.1
	[c]	7.60	7.91	7.33	8.32	H–N–CH_3	~ 5
	[c]	7.83	8.00	7.60	8.40	H–N–CH_3	5.3 ±0.1
	[c]	[d]	7.89	[d]	7.30	H–N–CH_3	5.0 ±0.1

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[a] 20%ige Lösungen (aus Ref. 2). [b] 25%ige Lösungen. [c] Gesättigte Lösungen. [d] Zu wenig löslich in $HCCl_3$. [e] Aus der Linienbreite geschätzt.

Annahme deuten, dass hier die Homoallyl-Kopplungskonstante halb so gross wie die Allyl-Kopplungskonstante J(H–N=C–C–H) ist (vergl. hierzu Ref. 13), während das Quintett durch gleiche Grösse von J(H–C–N=C–C–H) und J(H–N=C–C–H) hervorgerufen wird. Im Spektrum von [*trans*-(Methylamino)methylcarben]pentacarbonylchrom(0) lassen sich ebenfalls zwei Quartetts und ein Quintett beobachten. Beim *cis*-Isomeren hingegen konnte eine Auflösung der Feinstruktur nicht erzielt werden, doch machen Signalform und Halbwertsbreite, sowie das übrige analoge Verhalten das Vorliegen derselben Verhältnisse wie bei der entsprechenden Wolframverbindung wahrscheinlich. Die Tatsache, dass die Allyl-Kopplungskonstanten J(H–N=C–C–H) in beiden Isomeren praktisch gleich gross sind (siehe Tabelle 1), unabhängig davon, ob es sich um eine *cis*- oder *trans*-Kopplung handelt, ist recht überraschend, da wir in [(Amino-^{15}N)methylcarben]pentacarbonylchrom(0) zwei verschiedene Allylkopplungen gefunden hatten[11,12]. Es ist jedoch aus eingehenden Untersuchungen bekannt, dass *cis*-Allyl-Kopplungskonstanten J(H–C=C–C–H) grösser, gleich gross oder kleiner als die entsprechenden *trans*-Kopplungen sein können, da ihre Grösse nicht nur von der geometrischen Anordnung an der Doppelbindung, sondern auch von Substituenteneinflüssen und der Besetzung der Rotameren bezüglich der C–C-Einfachbindung abhängt[14–23].

IR-SPEKTREN

Tabelle 2 und 3 geben die IR-Spektren zwischen 4000 und 600 cm^{-1} wieder.

TABELLE 2

IR-SPEKTREN DER [*cis*- UND *trans*-(METHYLAMINO)METHYLCARBEN]-PENTACARBONYL-KOMPLEXE VON CHROM(0) UND WOLFRAM(0)

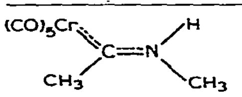
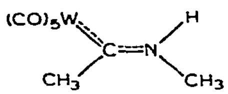
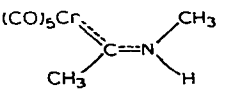
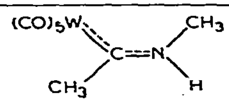
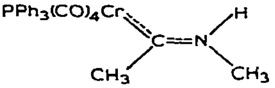
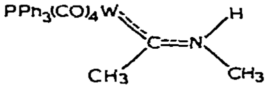
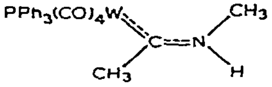
			
3400 m	3400 m	3330 m	3330 m
2941 vw	2932 vw	2941 vw	2932 vw
2857 vw	2857 vw	2857 vw	2857 vw
2058 s	2066 s	2060 s	2070 s
1974 w(sh)	1976 w(sh)	1980 (sh)	1980 (sh)
1950 w(sh)	1949 w(sh)		
1916 vs	1904 vs	1933 vs	1930 vs
1555 m	1555 m	1575 s	1576 s
1532 m	1532 m		
1449 w	1449 w		
1389 w	1389 w	1381 m	1381 m
1346 w	1342 w	1364 (sh)	1362 (sh)
1174 m	1179 m	1183 w	1186 w
		1171 (sh)	1170 (sh)
1059 w	1060 w	1081 w	1077 m
1034 m	1033 m	1044 w	1048 w
997 w	980 w	1000 m	1001 m
955 vw	935 w		
923 vw	917 vw	928 m	926 m
778 vs	775 vs	761 s	752 s
683 vs		671 vs	

TABELLE 3

IR-SPEKTREN VON [*cis*- UND *trans*-(METHYLAMINO)METHYLCARBEN](TRIPHENYLPHOSPHIN)TETRACARBONYLWOLFRAM(0), SOWIE VON [*cis*-(METHYLAMINO)METHYLCARBEN](TRIPHENYLPHOSPHIN)TETRACARBONYLCHROM(0)

		
3380 w	3380 w	3322 m
3067 vw	3067 vw	
2932 w	2932 w	2941 vw
2865 vw	2857 vw	2865 vw
2000 vs (2000 s)^a	2004 vs (2004 s)^a	2012 s (2008 s)^a
1938 w (sh)	1930 w (sh)	
1901 vs (1901(sh))	1894 vs (1901(sh))	1883 vs (1901 (sh))
1854 vs (1873 vs)	1850 vs (1873 vs)	1855 vs (1873 vs)
		1572 m
1533 m	1532 m	1547 (sh)
1484 m	1479 m	1481 m
1435 m	1433 m	1434 m
1381 w	1383 w	1381 w
1366 vw	1366 vw	1364 (sh)
1340 vw	1335 vw	1308 w
1171 w	1171 w	1181 w
1155 w(sh)	1155 w(sh)	1159 vw
1089 m	1089 m	1086 m
		1042 w
1025 w	1022 w	1028 w
1000 w	1000 w	1000 w
980 w	980 w	975 w
971 w(sh)	971 w(sh)	970 w(sh)
926 vw	926 vw	926 w
		773 m
752 s	752 s	752 m(sh)
746 s(sh)	746 s(sh)	746 s
719 w(sh)	725 w(sh)	
704 m(sh)	704 m(sh)	
699 s	694 s	694 vs
676 s		

^{a} 0.1 mm Benzollösung, LiF-Optik.

Die Spektren analoger Verbindungen entsprechen sich weitgehend. Als wesentlichen Unterschied gegenüber den Wolframkomplexen besitzen die Verbindungen des Chroms eine besonders tief liegende Absorption. Die jeweiligen Isomeren unterscheiden sich vor allem in drei Bereichen charakteristisch:

1. 3400–3300 cm^{-1}. Die Frequenz der N–H-Streckschwingung liegt bei den *cis*-Isomeren um 60-70 cm^{-1} höher als bei den entsprechenden *trans*-Formen. Die Einführung des Triphenylphosphin-Liganden hat in beiden Fällen eine geringe Verschiebung nach kleineren Wellenzahlen zur Folge.

2. 1600–1500 cm^{-1}. Bei den Carben-pentacarbonyl-Komplexen treten in diesem Bereich in den Spektren der *cis*-Isomeren zwei Banden auf, in den Spektren der *trans*-Verbindungen jedoch nur eine. Bei den phosphinhaltigen Komplexen ist es umgekehrt, doch spielen hier Schwingungen der Phenylreste mit herein. Beiden

Verbindungsgruppen gemeinsam ist aber die Tatsache, dass die höchste Absorption in diesem Bereich, nämlich bei *ca.* 1570 cm^{-1}, nur bei den *trans*-Formen auftritt.

3. 1000–600 cm^{-1}. In diesem Bereich sind deutliche Verschiebungen und Intensitätsunterschiede zu beobachten, doch verhindert das Vorhandensein der Phenylreste in einem Teil der Verbindungen vorläufig das Aufstellen einer Regel.

Die Unterschiede in den IR-Spektren der *cis*- und *trans*-Isomeren können vielleicht bei weiteren Aminocarben-Komplexen, bei denen eine Differenzierung mittels der Kernresonanzspektroskopie nicht möglich ist, wichtige Hinweise zur Zuordnung der Konfigurationen liefern.

Bei den phosphinhaltigen Komplexen besteht die Frage nach der relativen Stellung der beiden Substituenten am Koordinationsoktaeder. Bis jetzt lässt sich jedoch keine Antwort geben. [(Methoxy)methylcarben]-triphenylphosphin-tetracarbonyl-Komplexe zeigen nämlich in Hexanlösung vier ν(CO)-Banden[7,8], was für eine Nachbarstellung charakteristisch ist. Lösungsspektren der aus ihnen dargestellten (Methylamino)methylcarben-Komplexe, die wegen deren Schwerlöslichkeit allerdings in Benzol aufgenommen werden mussten, weisen hingegen nur drei ziemlich breite Banden auf. Ausgeschlossen ist damit eine Nachbarstellung noch keineswegs, da eine weitere Bande wegen mangelnder Auflösung verborgen geblieben sein kann.

EXPERIMENTELLER TEIL

Alle Arbeiten wurden unter Stickstoff und in stickstoffgesättigten Lösungsmitteln durchgeführt. Zur Aufnahme der ^{1}H-NMR-Spektren diente ein A 60 Spektrometer der Firma Varian. Die IR-Spektren wurden, wenn nicht anders vermerkt, in Nujol/Hostaflon mit einem IR-Spektrophotometer-Perkin-Elmer 21 mit NaCl-Optik aufgenommen. Zur Chromatographie wurde eine 10–15 cm lange Säule mit etwa 1 cm Durchmesser (Kieselgel Merck, 0.05–0.2 mm) verwendet.

(*a*) *Darstellung von [cis-(Methylamino)methylcarben]pentacarbonylwolfram*(0)

In eine konzentrierte ätherische Lösung von $(CO)_5WC(CH_3)OCH_3$[3,4] wurde unter Eiskühlung einige Minuten lang ein kräftiger Strom von Methylamin eingeleitet, wobei die Farbe der Lösung von orangegelb nach hellgelb umschlug. Nach Abziehen des Lösungsmittels wurde der gelbe Rückstand in Benzol aufgenommen und chromatographiert. Das Eluat wurde zur Trockne gebracht und soviel Benzol wieder zugegeben, wie zur Lösung des Rückstandes gerade nötig war. Durch tropfenweisen Zusatz von Pentan und Eiskühlung konnte das Produkt in kristalliner Form ausgefällt werden. Es wurde möglichst unter Lichtausschluss gearbeitet, da sonst rasche Zersetzung unter Braunfärbung der Lösungen eintrat. Ausbeute *ca.* 50% d.Th. Schmp. 81°. (Gef.: C,25.28; H,1.83; N,3.67; O,21.00; W,48.70. $C_8H_7NO_5W$ ber.: C,25.22; H, 1.85; N,3.68; O,21.00; W,48.26%.)

(*b*) *Darstellung von [trans-(Methylamino)methylcarben]pentacarbonylwolfram*(0)

cis-$(CO)_5WC(CH_3)NHCH_3$ (200 mg, *ca.* 0.55 mMol) wurde in 2 ml tert-Butanol gelöst, worin vorher 7 mg (*ca.* 0.3 mg-Atom)Natrium unter Erwärmen gelöst worden waren. Der Zusatz einiger Tropfen Äther sollte das Erstarren des Lösungsmittels verhindern. Nach 30-min. Stehen bei Raumtemperatur wurde Wasser zugesetzt, wodurch der Komplex ausfiel. Dieser wurde in Äther aufgenommen und nach Abziehen des Äthers in Benzol chromatographiert. Weiter wurde wie unter (*a*) verfahren. Ausbeute *ca.* 65% d.Th. Schmp. 89°. (Gef.: C,25.56; H,1.95; N,3.66; O,20.90; W,48.70. $C_8H_7NO_5W$ ber.: C,25.22; H,1.85; N,3.68; O,21.00; W,48.26%.)

(*c*) *Darstellung von* [*cis-(Methylamino)methylcarben*] (*triphenylphosphin*)*tetracarbonylwolfram*(0)

Ausgehend von orangegelbem $P(C_6H_5)_3(CO)_4WC(CH_3)OCH_3$[7] wurde die Darstellung von hellgelbem *cis*-$P(C_6H_5)_3(CO)_4WC(CH_3)NHCH_3$ wie unter (*a*) durchgeführt. Wegen der geringen Löslichkeit der triphenylphosphinhaltigen Komplexe waren die jeweiligen Lösungen gesättigt. Ausbeute *ca.* 60% d.Th. Schmp. 160–165° unter Zersetzung. (Gef.: C,49.13; H,3.64; N,2.40. $C_{25}H_{22}NO_4W$ ber.: C,48.80; H,3.62; N,2.28%.)

(*d*) *Umsetzung von* [*cis-(Methylamino)methylcarben*] (*triphenylphosphin*)*tetracarbonylwolfram*(0) *mit Natrium-tert-butylat*

cis-$P(C_6H_5)_3(CO)_4WC(CH_3)NHCH_3$ (32 mg, *ca.* 0.05 mMol) wurde in 2 ml Äther und 2 ml tert-Butanol gelöst, worin vorher unter Erwärmen 6 mg (*ca.* 0.25 mg-Atom) Natrium gelöst worden waren. Nach 30-min. Stehen bei Raumtemperatur wurde wie unter (*b*) aufgearbeitet. Wir erhielten dabei eine Mischung von *cis*- und *trans*-$P(C_6H_5)_3(CO)_4WC(CH_3)NHCH_3$ etwa im Verhältnis 1:3. Schmp. 180–183° unter Zersetzung. (Gef.: C, 48.68; H, 3.63; N, 2.27. $C_{25}H_{22}NO_4W$ ber.: C,48.80; H,3.62; N,2.28%.)

(*e*) *Umsetzung von* [*cis-(Methylamino)methylcarben*] (*triphenylphosphin*)*tetracarbonylchrom*(0) *mit Natrium-tert-butylat*

Ausgehend von orangerotem $P(C_6H_5)_3(CO)_4CrC(CH_3)OCH_3$[7,8] war wie unter (*c*) hellgelbes *cis*-$P(C_6H_5)_3(CO)_4CrC(CH_3)NHCH_3$ (siehe zur Darstellung auch Ref. 8) erhalten worden. 20 mg (*ca.* 0.04 mMol) des letzteren wurden in 4 ml Äther und 2 ml tert-Butanol gelöst, worin vorher 6 mg (*ca.* 0.25 mg-Atom) Natrium gelöst worden waren. Nach 30-min. Stehen bei Raumtemperatur wurde wie unter (*b*) aufgearbeitet. Dabei wurde unverändertes Ausgangsmaterial isoliert; eine Isomerisierung war nicht festzustellen.

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LITERATUR

1 J. A. CONNOR UND E. O. FISCHER, *J. Chem. Soc., A*, im Erscheinen.
2 E. MOSER UND E. O. FISCHER, *J. Organometal. Chem.*, 15 (1968) 147.
3 E. O. FISCHER UND A. MAASBÖL, *Angew. Chem.*, 76 (1964) 645.

4 E. O. FISCHER UND A. MAASBÖL, *Chem. Ber.*, 100 (1967) 2445.
5 E. MOSER UND E. O. FISCHER, *J. Organometal. Chem.*, 13 (1968) 209.
6 E. MOSER UND E. O. FISCHER, *J. Organometal. Chem.*, 12 (1968) P1.
7 R. AUMANN, Dissertation, Technische Hochschule München, 1967.
8 U. KLABUNDE, Dissertation, Northwestern University, Evanston, Ill., 1967.
9 B. HECKL, H. WERNER UND E. O. FISCHER, *Angew. Chem.*, 80 (1968) 847.
10 O. S. MILLS UND A. D. REDHOUSE, *Chem. Commun.*, (1966) 814.
11 E. MOSER UND E. O. FISCHER, *Naturwissenschaften*, 54 (1967) 615.
12 E. MOSER UND E. O. FISCHER, *J. Organometal. Chem.*, 13 (1968) 387.
13 E. W. RANDALL UND J. D. BALDESCHWIELER, *J. Mol. Spectrosc.*, 8 (1962) 365.
14 A. A. BOTHNER-BY UND C. NAAR-COLIN, *J. Amer. Chem. Soc.*, 83 (1961) 231.
15 R. R. FRASER UND D. E. MCGREER, *Can. J. Chem.*, 39 (1961) 505.
16 J. H. RICHARDS UND W. F. BEACH, *J. Org. Chem.*, 26 (1961) 623.
17 A. A. BOTHNER-BY, C. NAAR-COLIN UND H. GÜNTHER, *J. Amer. Chem. Soc.*, 84 (1962) 2748.
18 M. BARFIELD, *J. Chem. Phys.*, 41 (1964) 3825.
19 M. Y. DEWOLF UND J. D. BALDESCHWIELER, *J. Mol. Spectrosc.*, 13 (1964) 344.
20 S. STERNHELL, *Rev. Pure Appl. Chem.*, 14 (1964) 15.
21 J. W. EMSLEY, J. FEENEY UND L. H. SUTCLIFFE, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 1, Pergamon Press, Oxford, 1965, S. 176.
22 A. A. BOTHNER-BY, S. CASTELLANO, S. J. EBERSOLE UND H. GÜNTHER, *J. Amer. Chem. Soc.*, 88 (1966) 2466.
23 H. G. HECHT UND B. L. VICTOR, *J. Amer. Chem. Soc.*, 90 (1968) 3333.