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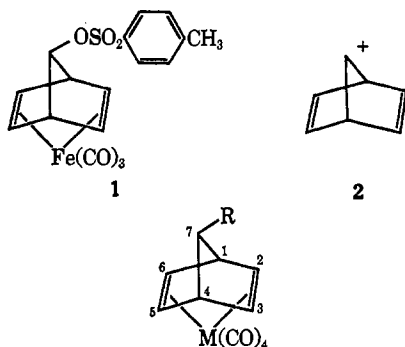
Solvolysis and Dissociation of 7-Substituted Norbornadiene Group VIb Metal Tetracarbonyls¹

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Chromium-, molybdenum-, and tungsten-tetracarbonyl complexes of 7-chloronorbornadiene and chromium- and molybdenum-tetracarbonyl complexes of 7-benzoyloxynorbornadiene have been prepared. Solvolysis of the 7-chloro compounds in 80% aqueous acetone at 25° proceeds *via* a prior rapid dissociation to a solvated metal tetracarbonyl species and 7-chloronorbornadiene, which then solvolyzes. These norbornadiene complexes, which are undissociated in deuteriochloroform, have been shown to dissociate reversibly in acetone and aqueous-acetone mixtures by nmr spectroscopy. Per cent dissociation of norbornadiene metal carbonyl complexes decreases in the series Mo > Cr, W > Fe and increases with increasing electron pair donor power of the solvent. The 7-substituted norbornadiene metal tetracarbonyls are more highly dissociated than their corresponding parent norbornadiene complexes.

Solvolysis studies on 7-tosyloxynorbornadienetetracarbonyliron (1) indicated that the 7-norbornadienyl cation (2) was greatly destabilized when coordinated to



- 3, R = Cl, M = Cr
4, R = Cl, M = Mo
5, R = Cl, M = W
6, R = OCOC₆H₅, M = Cr
7, R = OCOC₆H₅, M = Mo
8, R = OH, M = Mo
9, R = H, M = Cr
10, R = H, M = Mo
11, R = H, M = W

a tricarbonyliron group.² In an effort to examine the effect of group VIb metals on the stability of the 7-norbornadienyl cation, we have studied the solvolysis reactions of 7-chloronorbornadienetetracarbonylchromium (3),³ -molybdenum (4), and -tungsten (5). 7-Benzoyloxynorbornadienetetracarbonylchromium (6) and -molybdenum (7) have also been synthesized.

Compounds 4, 6, and 7 were prepared by refluxing either 7-chloronorbornadiene (12)² or 7-benzoyloxynorbornadiene⁴ with excess metal hexacarbonyl in methylcyclohexane. Compound 3 could not be prepared by

this procedure but was obtained in 17% yield by treating 7-chloronorbornadiene in methylcyclohexane with a more reactive chromium carbonyl derivative, triaminetricarbonylchromium.⁵ A reaction of 7-chloronorbornadiene and excess triacetoneitriletricarboxyltungsten⁶ in refluxing methylcyclohexane gave a 5% yield of 5.⁷ Infrared and nmr data for these 7-substituted norbornadiene complexes are summarized in Table I.

TABLE I

INFRARED AND NMR DATA ON NORBORNADIENETETRACARBONYL COMPLEXES OF CHROMIUM, MOLYBDENUM, TUNGSTEN, AND IRON

Compound	Ir, cm ⁻¹ ^a	Nmr, τ^a		
		C=C	H ₇	H _{1,4} H _{2,3} H _{5,6}
C ₇ H ₈	1543	8.01	6.43	3.23
C ₇ H ₈ Cr(CO) ₄ (9)	1438	8.66	6.33	5.53
C ₇ H ₈ Mo(CO) ₄ (10)	1438	8.62	6.24	5.06
C ₇ H ₈ W(CO) ₄ (11) ^b	1420			
C ₇ H ₈ Fe(CO) ₃		8.75	6.65	6.85
C ₇ H ₇ Cl (12)	1545	5.80	6.37	3.37 3.23
C ₇ H ₇ ClCr(CO) ₄ (3)	1445	6.38	6.23	5.78 5.63
C ₇ H ₇ ClMo(CO) ₄ (4)	1445	6.35	6.18	5.36 5.21
C ₇ H ₇ ClW(CO) ₄ (5)	1427	6.56	6.09	5.64 5.50
C ₇ H ₇ OCOC ₆ H ₅		5.15	6.32	3.38 3.28
C ₇ H ₇ OCOC ₆ H ₅ Cr(CO) ₄ (6)		5.51	6.03	5.70 5.58
C ₇ H ₇ OCOC ₆ H ₅ Mo(CO) ₄ (7)		5.52	6.00	5.30 5.19
C ₇ H ₇ OCOC ₆ H ₅ Fe(CO) ₃ ^c		5.50	6.45	7.08 6.91

^a Spectra were recorded in deuteriochloroform solution. ^b Reference 6. ^c Reference 2.

7-Chloronorbornadienetetracarbonylchromium, -molybdenum, and -tungsten were solvolyzed in 80% aqueous acetone.⁸ The solvolyses were rapid and

(1) Presented in part at the Third International Symposium on Organometallic Chemistry, Munich, Germany, Aug 28-Sept 1, 1967; Abstracts of Papers, p 204.

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(3) Ethanolsis of this compound has been reported previously: R. S. Bly and M. S. Kablaoui, Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1-3, 1967, No. 312.

(4) H. Tanida and T. Tsuiji, *J. Org. Chem.*, **29**, 849 (1964).

(5) V. W. Hieber, W. Abeck, and H. K. Platzer, *Z. Anorg. Allgem. Chem.*, **280**, 255 (1955).

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(7) This procedure was only successful on one occasion.

(8) During the solvolysis reactions, the color of the solutions darkened rapidly and a considerable amount of gas was evolved, even when the solvolysis experiments were carried out under nitrogen using degassed solvents. Despite considerable decomposition of the organometallic derivatives, the total amount of acid generated in the reactions never differed by more than 10% from the theoretical amount expected.

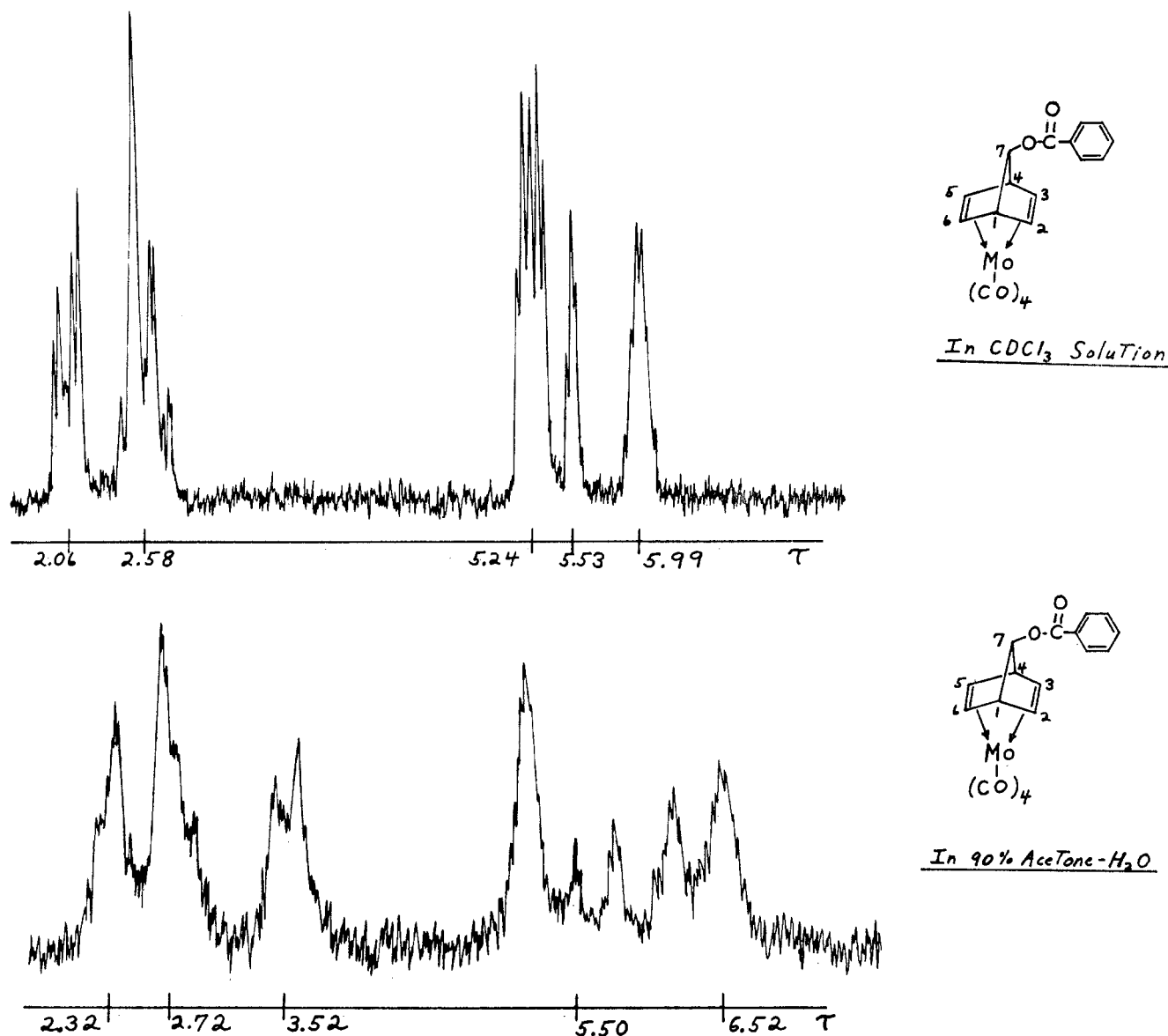


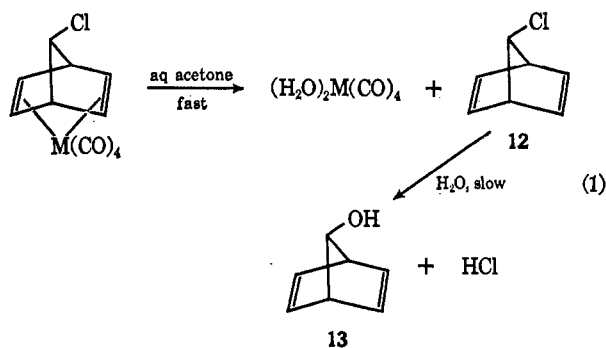
Figure 1.—Nmr spectra of 7-benzoyloxynorbornadienetetracarbonylmolybdenum (7): top, in deuteriochloroform (no dissociation); bottom, in 90% aqueous acetone. Signals for uncomplexed 7-benzoyloxynorbornadiene appear at τ 2.32 and 2.72 (aromatic hydrogens), τ 3.52 (H_2, H_3, H_5, H_6), τ 5.75 (H_7), and τ 6.52 (H_1, H_4).

followed first-order rate laws to more than 75% completion. The rate constants listed in Table II were all within a factor of 2 of the rate constant for 7-chloronorbornadiene itself.

Product analysis performed directly on the reaction mixture by means of thin layer chromatography and nmr spectroscopy showed that solvolysis of 4 produced, instead of the expected alcohol 8, 7-norbornadienol (13) and two organometallic compounds^{9,10} which decomposed on attempted isolation.

These rate and product data strongly suggest that 3-5

dissociate rapidly in 80% aqueous acetone to give metal tetracarbonyl species and 7-chloronorbornadiene (12), which then solvolyzes to give 7-norbornadienol (13). This process is illustrated below



(9) Analogous compounds were also detected by tlc in the solvolysis mixtures of 3 and 5.

(10) Tlc indicated that the same three compounds were obtained when the preparation of an authentic sample of 8 was attempted by hydrolyzing 7 with either dilute sodium hydroxide solution or methanolic sodium methoxide.

TABLE II
SOLVOLYSIS RATES OF 7-CHLORONORBORNADIENEMETAL
TETRACARBONYLS IN 80% AQUEOUS ACETONE AT 25°

Compound	10 ³ k, sec ⁻¹	E _a , kcal/mol	ΔS [‡] , eu
C ₇ H ₇ Cl ^a (12)	1.33 ± 0.04	15 ± 1.5	-22.4 ± 4
C ₇ H ₇ ClMo(CO) ₄ (4)	1.51 ± 0.10	15 ± 1.5	-23 ± 4
C ₇ H ₇ ClCr(CO) ₄ (3)	0.83 ± 0.05		
C ₇ H ₇ ClW(CO) ₄ (5)	1.61 ± 0.2 ^b		

^a 7-Chloronorbornadiene.² ^b One determination only.

TABLE III
PER CENT DISSOCIATION OF THE GROUP VIb METAL
TETRACARBONYL COMPLEXES IN AQUEOUS ACETONE SOLUTIONS

Compound	% disson of 0.80 M soln ^a		
	Acetone-d ₆	95% acetone-d ₆ - 5% D ₂ O	
		90% acetone-d ₆ - 10% D ₂ O	90% acetone-d ₆ - 10% D ₂ O
C ₇ H ₇ Cr(CO) ₄ (9)	<3	<3	<3
C ₇ H ₇ Mo(CO) ₄ (10)	4	10	17
C ₇ H ₇ W(CO) ₄ (11)	<3	<3	<3
C ₇ H ₇ OCOC ₆ H ₅ Cr(CO) ₄ (6)	9	22	30
C ₇ H ₇ OCOC ₆ H ₅ Mo(CO) ₄ (7)	12	27	50
C ₇ H ₇ ClMo(CO) ₄ (4)	11	24	50

^a Data are accurate to ±3%.

To test for dissociation in the solvolysis medium, an excess of norbornadiene was added to the solvolysis reactions of 3 and 4 in an effort to trap the solvated metal carbonyl species. Norbornadienetetracarbonylchromium (9) and -molybdenum (10), respectively, were detected immediately and were identified by comparison of their nmr spectra with those of authentic samples.¹¹

Qualitative estimates concerning the degree of dissociation of norbornadienetetracarbonyl derivatives of the group VIb metals in aqueous acetone solutions were made with the aid of nmr spectroscopy. Nmr spectra of these norbornadiene complexes exhibit signals for both complexed and uncomplexed norbornadienes (Figure 1). Integration of the vinylic hydrogen signals, which are shifted to higher field by complexation,¹² gives relative amounts of the complexed and uncomplexed norbornadiene derivatives. These data are summarized in Table III.

With either chromium or molybdenum, the degree of dissociation is enhanced by electronegative substituents at C₇ in the norbornadiene ligand. In agreement with this trend, we find that equimolar amounts of 7-benzoyloxynorbornadienetetracarbonylmolybdenum and norbornadiene in acetone-d₆ give an equilibrium mixture in which the ratio of norbornadiene complex to 7-benzoyloxynorbornadiene complex is 2.3:1. An identical mixture was obtained by starting with equimolar amounts of 7-benzoyloxynorbornadiene and norbornadienetetracarbonylmolybdenum. These findings are understandable, since electron-attracting groups at C₇ would be expected to withdraw

electrons from the π cloud of the double bond, thereby weakening the diene-metal bond and facilitating the dissociation of the norbornadiene ligand. Infrared data in Table I support this conclusion. Generally, coordination of a diene to a metal lowers the energy required to stretch a double bond, sometimes by as much as 180 cm⁻¹.¹³ Since the above absorption occurs at higher frequency in the norbornadiene ligand bearing electronegative substituents at C₇ than it does in the norbornadiene ligand itself, the carbon-metal bond in the former species is presumed to be the weaker of the two.

The data in Table III indicate that molybdenum compounds dissociate more completely than do the corresponding chromium compounds, and the solvolysis data are consistent with a degree of dissociation for tungsten compounds which is at least comparable to that of the corresponding chromium derivatives. Since 7-tosyloxynorbornadienetetracarbonyliron has been found not to dissociate in 80% aqueous acetone,² we can list metal carbonyl derivatives of norbornadienes in decreasing order of dissociation: Mo > Cr, W > Fe. It is interesting to note that the degree of dissociation correlates with nmr chemical shifts of vinylic hydrogens (Tables I and III). Within this series, the stronger the metal-olefin bond, the larger the upfield shift of the vinylic hydrogens on complex formation.

Increases in per cent dissociation as the solvent is changed from deuteriochloroform to acetone to 95% acetone to 90% acetone can be explained in terms of better solvation of the metal tetracarbonyl moiety. Thus, in deuteriochloroform, where the metal tetracarbonyl moiety would be virtually unsolvated, little or no dissociation occurs. As the donor strength of the solvent increases, the per cent dissociation increases. In aqueous acetone, the metal tetracarbonyl moiety presumably exists as a species of the type (H₂O)₂M(CO)₄.

Support for dissociation of these group VIb metal-norbornadienetetracarbonyl complexes can be found in the recent literature. Facile displacement of the norbornadiene ligand from complexes of chromium and molybdenum by a variety of nucleophilic amines and some π organic ligands have been reported by Prinz and Werner.¹⁴ Bennett, *et al.*, have made use of the lability of the norbornadiene ligand to prepare olefinic complexes of molybdenum and chromium.¹⁵

These dissociations are facile reactions. In all cases, equilibrium had been established before nmr spectra could be recorded (*ca.* 2 min). Rapid equilibration is consistent with the first-order behavior of the chloro complexes in solvolysis. Points recorded as early as 20 sec after addition of water to an acetone solution of the substrate lay on the straight line of the

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first-order plot. These data are consistent only with a reaction scheme in which dissociation is faster than solvolysis (eq 1). The solvolysis reaction has a half-life of *ca.* 1 min at 25°. Of the solvolysis rate constants for 3–5, only that for the chromium derivative 3 is significantly different from that of 7-chloronorbornadiene itself. This low value of $0.83 \times 10^{-3} \text{ sec}^{-1}$ compared to $1.33 \times 10^{-3} \text{ sec}^{-1}$ for the free ligand may be caused by incomplete dissociation of 7-chloronorbornadienetetracarbonylchromium under solvolysis conditions. Unfortunately, this point could not be checked by nmr spectroscopy, owing to insufficient solubility of 3 in 80% aqueous acetone at 25°.

Experimental Section

Melting points were determined using a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded using a Beckman IR-10 instrument and were calibrated with polystyrene (accuracy $\pm 3 \text{ cm}^{-1}$). Nmr spectra were obtained on a Varian A-60 spectrometer. They were referenced with tetramethylsilane as an internal standard and are accurate to $\pm 0.02 \text{ ppm}$. All microanalyses were performed by the Schwarzkopf Micro-analytical Laboratory, Woodside, N. Y. Experimental details of the kinetic procedure can be found in ref 2.

7-Chloronorbornadienetetracarbonylmolybdenum (4).—A mixture of molybdenum hexacarbonyl (6.6 g, 25 mmol) and 7-chloronorbornadiene² (2.52 g, 20 mmol) in 60 ml of methylcyclohexane was heated at reflux under nitrogen for 18 hr. Evaporation of the solvent at 25° (15 mm) left a brown solid which was sublimed at 60° (0.3 mm) to remove unchanged molybdenum hexacarbonyl. Continued heating at 95° (0.3 mm) afforded 3.6 g (54%) of 4 as a pale yellow solid, mp 109.5–110.5° under nitrogen. Bands due to terminal carbonyl groups (CCl_4) occurred at 2050 (s), 1965 (s), and 1915 (s) cm^{-1} . *Anal.* Calcd for $\text{C}_{11}\text{H}_7\text{ClMoO}_4$: C, 39.48; H, 2.11; Cl, 10.60; Mo, 28.68. Found: C, 39.33; H, 2.21; Cl, 10.77; Mo, 28.92.

7-Chloronorbornadienetetracarbonylchromium (3).—Triaminetricarbonylchromium⁵ (1.87 g, 10 mmol) and 7-chloronorbornadiene² (0.63 g, 5 mmol) were heated at reflux in 20 ml of methylcyclohexane for 16 hr under nitrogen. The solvent was evaporated at room temperature (15 mm) and the residue was sublimed at 60° (0.3 mm) to remove chromium hexacarbonyl. Continued heating at 80° (0.2 mm) afforded 0.24 g (17%) of 3 as a bright yellow solid, mp 104–104.5° under nitrogen. Bands due to terminal carbonyl groups (CCl_4) were found at 2038 (s), 1965 (s), 1950 (s), and 1920 (s) cm^{-1} . *Anal.* Calcd for $\text{C}_{11}\text{H}_7\text{ClCrO}_4$: C, 45.46; H, 2.43; Cl, 12.20; Cr, 17.90. Found: C, 45.44; H, 2.45; Cl, 12.48; Cr, 17.67.

7-Chloronorbornadienetetracarbonyltungsten (5).⁷—Triacetonitriletetracarbonyltungsten⁸ (4.0 g, 10 mmol) and 7-chloronorbornadiene² (0.63 g, 5 mmol) were placed in 20 ml of methylcyclohexane and the resulting solution was heated at reflux under nitrogen for 24 hr. Following evaporation of the solvent at 25° (15 mm), the residue was sublimed at 100° (0.3 mm) to give 0.4 g of crude 5. The product was recrystallized from Skelly F at –78° and subsequently sublimed at 70° (0.3 mm) to afford 0.1 g (5%) of 5 as a pale yellow solid. Bands due to terminal carbonyl groups (CDCl_3) occurred at 2050 (s), 1965 (s), and 1905 (s) cm^{-1} . *Anal.* Calcd for $\text{C}_{11}\text{H}_7\text{ClO}_4\text{W}$: C, 31.27; H, 1.67; Cl, 8.39; W, 43.52. Found: C, 31.24; H, 1.57; Cl, 8.44; W, 43.36.

7-Benzoyloxynorbornadienetetracarbonylmolybdenum (7).—A mixture of molybdenum hexacarbonyl (16.5 g, 62.5 mmol) and 7-benzoyloxynorbornadiene⁴ (10.6 g, 50 mmol) in 150 ml of methylcyclohexane was heated at reflux under nitrogen for 16 hr. The tan solution was then cooled to –78° and filtered to collect the dark precipitate. The latter material was sublimed at 60° (0.2 mm) to remove molybdenum hexacarbonyl and then at 80° (0.2 mm) to remove unreacted 7-benzoyloxynorbornadiene. The residue was dissolved in benzene and chromatographed on Florisil. The first yellow band was eluted with benzene and furnished 15.0 g (71%) of 7 as a bright yellow solid. Recrystallization of the latter from methylene chloride–Skelly F at –78° afforded an analytically pure sample, mp 119–121° under nitrogen. Bands due to terminal carbonyl groups (CHCl_3) occurred at 2040 (s), 1965 (s), and 1900 (s) cm^{-1} . *Anal.* Calcd for $\text{C}_{18}\text{H}_{12}\text{MoO}_6$: C, 51.44; H, 2.88; Mo, 22.84. Found: C, 51.41; H, 3.04; Mo, 23.00.

7-Benzoyloxynorbornadienetetracarbonylchromium (6).—Chromium hexacarbonyl (13.8 g, 62.5 mmol) and 7-benzoyloxynorbornadiene⁴ (10.6 g, 50 mmol) were mixed with 200 ml of methylcyclohexane and the resulting mixture was heated at reflux for 70 hr under nitrogen. The solution was then cooled to –78° to precipitate 6 as a yellow solid. Rapid filtration gave a crude sample of 6 which was sublimed at 60° (0.2 mm) to remove chromium hexacarbonyl. Unchanged 7-benzoyloxynorbornadiene was separated by sublimation at 80° (0.2 mm). The remaining nonvolatile material was chromatographed on Florisil with benzene as the eluent. The first band contained 3.12 g (17%) of 6. Recrystallization from methylene chloride–Skelly F at –78° afforded an analytical sample of 6 as a bright yellow solid, mp 109–111° under nitrogen. Bands due to terminal carbonyl groups (CHCl_3) were found at 2030 (s), 1945 (s), and 1910 (s) cm^{-1} . *Anal.* Calcd for $\text{C}_{18}\text{H}_{12}\text{CrO}_6$: C, 57.45; H, 3.21; Cr, 13.82. Found: C, 57.78; H, 3.06; Cr, 13.61.

Representative Procedure for Measuring the Degree of Dissociation of Group VIb Metal Tetracarbonyl Complexes of Norbornadienes.—An example involving 7-benzoyloxynorbornadienetetracarbonylmolybdenum (7) in 95% aqueous acetone is given. 7-Benzoyloxynorbornadienetetracarbonylmolybdenum (7) (20 mg, $48 \times 10^{-6} \text{ mol}$) was dissolved in a solvent mixture composed of 58 μl of acetone-*d*₆ and 3 μl of deuterium oxide. Following the addition of tetramethylsilane, the solution was transferred to a 25- μl nmr tube with the aid of a disposable micro glass pipet. Several nmr spectra were recorded over a period of 1 hr. The relative amounts of 7 and the dissociated ligand, 7-benzoyloxynorbornadiene, were determined by integrating the signals due to the olefin protons in both the complexed and uncomplexed ligand. Compound 7 was found to be 27% dissociated in 95% aqueous acetone solution. Although the per cent dissociation appeared to be time independent during the hour in which measurements were recorded, the formation of insoluble material in the nmr tube, accompanied by broadening of the nmr signals, indicated that some decomposition was occurring in the above medium.

Ligand Exchange between 7-Benzoyloxynorbornadienetetracarbonylmolybdenum (7) and Norbornadiene.—A solution of 7-benzoyloxynorbornadienetetracarbonylmolybdenum (7) (20 mg, $48 \times 10^{-6} \text{ mol}$) and norbornadiene (4.4 mg, $48 \times 10^{-6} \text{ mol}$) dissolved in 60 μl of acetone-*d*₆ was transferred to a micro nmr tube and the spectrum was recorded a number of times over a period of 2 hr. In the case of the two above compounds, a state of equilibrium was reached between the time of mixing and the time at which the first spectrum was recorded (*ca.* 5 min). Integration of the signals due to the 7-protons in both 7-benzoyloxynorbornadiene and the corresponding molybdenum complex 7 provided an estimate of the relative amounts of the two compounds present in the reaction mixture. Alternatively, the signals corresponding to the 7-protons in norbornadiene and norbornadienetetracarbonylmolybdenum (10) were integrated, providing a check on the results obtained in the first procedure. On the basis of these measurements, the ratio of 10 to 7 was found to be 2.3:1. Exactly the same ratio was obtained when the above

(16) Bly and Kablaoui's data³ on ethanolysis of 3 are consistent with a scheme in which direct solvolysis of 3 proceeds at a measurable rate and dissociation of 3 is slower than solvolysis of 7-chloronorbornadiene. Our subsequent data² showing that 7-tosyloxynorbornadienetetracarbonyliron is very unreactive make direct solvolysis of 3 unlikely, however.

procedure was repeated, starting with 10 and 7-benzoyloxy-norbornadiene.

Similar exchange studies in the chromium series indicated a ratio of norbornadienetetracarbonylchromium (9) to 7-benzoyloxy-norbornadienetetracarbonylchromium (6) of 2.3:1 under equilibrium conditions in acetone- d_6 . In these studies, however, the time required to reach equilibrium was *ca.* 30 min.

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The Preparation and Properties of Pentafluorosilicates

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The preparation of quaternary ammonium and arsonium pentafluorosilicates is described. It is shown that SiF_5^- is a relatively weak acceptor, forming an unstable 1:1 ammonia adduct and interacting only weakly with other Lewis bases. The infrared and Raman absorptions due to SiF_5^- are not inconsistent with a trigonal-bipyramidal geometry. Many spectroscopic similarities with phosphorus pentafluoride are apparent.

Introduction

Although the chemistry of silicon tetrafluoride and of hexafluorosilicates has been extensively studied, the existence of pentafluorosilicates containing the SiF_5^- ion has not been considered likely. Indeed, it is only recently that five-coordinate derivatives of silicon have been fully characterized.¹⁻³ Recently, we reported⁴ the first formation of a pentafluorosilicate in a complex reaction involving silica, tetrafluoroethylene, and a platinum hydride. We have since been able to show that pentafluorosilicates can be prepared by a simple and convenient method,⁵ and we now wish to describe some detailed chemical and spectroscopic investigations of these salts. Since our initial report, several other workers have described studies^{3,6,7} leading to the isolation and characterization of pentafluorosilicates.

Synthesis and Properties

For appropriate cations, pentafluorosilicates may be prepared readily by the treatment of a mixture of silica and the appropriate chloride with aqueous hydrofluoric acid. Tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium pentafluorosilicates and tetraphenylarsonium pentafluorosilicate have thus been obtained. Interestingly, the tetramethylammonium salt could not be prepared by this method, the product being the SiF_6^{2-} derivative. Apparently, the cation size required

to stabilize SiF_5^- in the solid state is somewhat larger than $(\text{CH}_3)_4\text{N}^+$ but smaller than $(\text{C}_2\text{H}_5)_4\text{N}^+$, although even the latter gives a rather unstable pentafluorosilicate. Other than this restriction, this general synthetic route should be applicable to the preparation of many additional pentafluorosilicates. It is also somewhat more convenient than the reaction of silicon tetrafluoride with quaternary ammonium fluoride as described³ by Klanberg and Muettterties and is presumably essentially the same method as that used by Behrends and Kiel.⁶ Certainly the dehydrofluorination reactions of Harris and Rudner⁷ are less suitable for the synthesis of pentafluorosilicates. It is also surprising that these latter authors claimed to have isolated the trimethylammonium pentafluorosilicate, whereas the above simple reaction led to only tetramethylammonium hexafluorosilicate and not the pentafluorosilicate. This point is discussed in detail later.

While the analytical data for the above quaternary ammonium and tetraphenylarsonium derivatives show the Si:F ratio to be 1:5, further evidence is necessary to establish that discrete, singly charged SiF_5^- ions exist. This is provided first by preliminary X-ray structural studies⁸ of tetraphenylarsonium pentafluorosilicate which show that the silicon-silicon distances are too great for the presence of any bridged species, such as $\text{Si}_2\text{F}_{10}^{2-}$. Second, the conductance data of Table I clearly show that these are 1:1 electrolytes in nitromethane solution although in aqueous solution there is extensive hydrolysis. The conclusion that discrete SiF_5^- ions are present, therefore, is reasonable; it remains to determine their stereochemistry.

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