$C_{14}H_{22}O_2Si_2$: C, 60.38; H, 7.96. Found: C, 60.21; H, 7.77. *m*-$Me_3SiC_6H_4COSiMe_3$: ^1H NMR δ 0.30 (s), 0.49 (s), 7.26–8.13 (m); IR (neat) 1610 cm^{-1}. Anal. Calcd for $C_{13}H_{22}OSi_2$: C, 62.34; H, 8.85. Found: C, 62.12; H, 8.78. *m*-$HCOC_6H_4COSiMe_3$: ^1H NMR δ 0.40 (s), 7.46–8.52 (m), 10.21 (s); IR (neat) 1700, 1620 cm^{-1}. β-$C_{10}H_7COSiMe_3$: ^1H NMR δ 0.44 (s), 7.43–8.42 (m); IR (neat) 1600, 1590 cm^{-1}. (2-C_4H_3O)$COSiMe_3$: bp 130 °C (27 torr); ^1H NMR δ 0.35 (s), 6.48 (dd), 7.03 (d), 7.53 (m); IR (neat) 1610 cm^{-1}. $C_7H_{15}COSiMe_3$: ^1H NMR (CCl_4) δ 0.16 (s), 0.89 (t), 1.26 (br s), 2.48 (t); IR (neat) 1620 cm^{-1}. $C_6H_5CH_2COSiMe_3$: bp 110 °C (3 torr); ^1H NMR (CCl_4) 0.04 (s), 3.69 (s), 7.17 (m); IR (CCl_4) 1640 cm^{-1}.

Palladium Complex Catalyzed Competitive Benzoylation of Bimetallic Compounds. All reactions were carried out under the standard conditions (entry 6, Table I), and respective yields of benzoylated derivatives are indicated in eq 3–7. Some Physical data are given below. $PhCOGeMe_3$:[31] ^1H NMR ($CDCl_3$) δ 0.50 (s), 7.34–7.92 (m); IR (neat) 1625, 1595 cm^{-1}. $C_7H_{15}COGeMe_3$: ^1H NMR δ 0.33 (s), 0.87 (t, J = 4.8 Hz), 1.07–1.91 (m), 2.60 (t, J = 6.9 Hz); IR (neat) 1660 cm^{-1}. $PhCOSiMe_2Ph$:[32] ^1H NMR 0.63 (s), 7.08–7.90 (m). $PhCOGeMe_2Ph$:[33] ^1H NMR δ 0.72 (s), 7.20–7.85 (m).

Controlled Reactions of Benzoyl Chloride with Triethyl Phosphite or Diethyl Trimethylsilyl Phosphite. Authentic Samples. (1) Preparation of Diethyl Trimethylsilyl Phosphite. To a solution of diethyl phosphite (19.4 mL, 0.15 mol) and triethylamine (25.2 mL, 0.18 mol) in dry ether (100 mL) was added dropwise chlorotrimethylsilane (22.8 mL, 0.18 mol) over a period of 45 min. The reaction mixture was stirred at room temperature for 5 h and refluxed for additional 4 h. Voluminous precipitates were filtered, and the filtrate was concentrated. Distillation of the residue gave $(EtO)_2P(OSiMe_3)$ (26.6 g, 84% yield), bp 55–57 °C (12 torr). **(2) Preparation of Diethyl Benzoylphosphonate.** To a solution of diethyl trimethylsilyl phosphite (8.42 g, 40 mmol) in benzene (20 mL) was added benzoyl chloride (4.4 mL, 38 mmol). The mixture was stirred for 2.5 h and then concentrated in vacuo. The residue was distilled, bp 154 °C (6 torr), to give $PhCOP(O)(OEt)_2$ (4.9 g, 54% yield).

Attempted Arbuzov Reaction. An equimolar mixture of triethyl phosphite and palladium complex 1 (0.2 mmol) in dry benzene (0.5 mL) was heated at 100 °C for 7 h with benzoyl chloride (0.2 mmol) under argon. No diethyl benzoylphosphonate was detected by GLC analysis.

Attempted Palladium Complex Catalyzed Reaction of Diethyl Benzoylphosphonate with Hexamethyldisilane. An equimolar (3-mmol each) mixture of hexamethyldisilane, benzoyl chloride, and diethyl benzoylphosphonate prepared above in dry toluene (2 mL) was heated at 110 °C under an argon atmosphere in the presence of 1 (0.15 mmol, 5 mol %). Gradual decomposition of 1 took place, and no appreciable reaction to form benzoyltrimethylsilane was observed by GLC analysis.

Acknowledgment. Support of the Grant-in-Aid from the Ministry of Education, Japan (No. 555341), is gratefully acknowledged. We thank Toshiba Silicone Co. Ltd. for a gift of chlorosilanes.

---

(31) Yates, K.; Agolini, F. *Can. J. Chem.* **1966**, *44*, 2229.

(32) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102.

(33) Mochida, K.; Ishikawa, K.; Okui, S.; Sakaguchi, Y.; Hayashi, H. *Chem. Lett.* **1985**, 1433.

Substituent Effects of Substituted Benzoyltrimethylsilanes on Their Ultraviolet Spectral Properties

Keiji Yamamoto,* Atsushi Hayashi, Shigeaki Suzuki, and Jiro Tsuji

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Received September 2, 1986

A series of meta- and para-substituted benzoyltrimethylsilanes have been prepared, and their ultraviolet spectra are recorded. Correlation of the wavenumber of the n → π^* absorption maxima with the dual substituent parameters (DSP) has been examined, giving the susceptibility parameters $\lambda = \rho_R/\rho_I = 2.54$. Implication of this treatment has briefly been discussed.

Table I. Solvent Effect on the Absorption Maxima of Benzoyltrimethylsilane

		absorptn maxima			
solv	concn × 10^5,[a] mol/L	$\pi \to \pi^*$, nm	$10^{-4}\epsilon$	$n \to \pi^*$,[b] nm	ϵ
hexane	5.65	250.0	1.13	423.0	119
cyclohexane	5.83	250.5	1.18	423.0	130
THF	8.47			420.0	116
ethanol	5.77	252.5	0.95	415	101
$PhCOCMe_3$ in hexane		238	0.88	320	103

[a] For $n \to \pi^*$ measurements; diluted as 1/100 for $\pi \to \pi^*$. [b] The most intense peak in a fine structure.

One of the outstanding features of α-silyl ketones is their yellow color, which stems from the long wavelength (~420 nm) absorption.[1] These transitions have been assigned as n → π^*.[2] Bock et al.[2d] have discussed the remarkable long-wavelength shifts of the n → π^* transition of benzoylsilanes mainly in terms of strong electron-releasing effects of R_3Si groups on the oxygen lone pair n_0. Also, the importance of metal–carbon bond mixing with adjacent

---

(1) (a) Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373. (b) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102. (c) Brook, A. G.; Kivisikk, R.; LeGraw, G. E. *Can. J. Chem.* **1965**, *43*, 1175. (d) For a review, Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(2) (a) West, R. *J. Organomet. Chem.* **1965**, *3*, 314. (b) Agolini, F.; Klemenko, S.; Csizmadia, J. G.; Yates, K. *Spectrochim. Acta, Part A* **1968**, *24A*, 169. (c) Peddle, G. J. D. *J. Organomet. Chem.* **1966**, *5*, 48. (d) Bock, H.; Alt, H.; Seidl, H. *J. Am. Chem. Soc.* **1969**, *91*, 355. (e) Bruns, R. E.; Kuznesof, P. M. *J. Organomet. Chem.* **1973**, *56*, 131. (f) Reuter, M. J.; Damrauer, R. *J. Organomet. Chem.* **1974**, *82*, 201. (g) Dextheimer, E. M.; Buell, G. R.; Le Croix, C. *Spectrosc. Lett.* **1978**, *11*, 751. (h) For reviews, see: Ramsey, B. R. *Electronic Transition in Organometalloids*; Academic: New York, 1969. Ramsey, B. R. *Spectroscopy in Inorganic Chemistry*; Rao, C. N. R., Ferraro, J. R., Eds.; Academic: New York, 1970; Vol. 2.

0276-7333/87/2306-0979$01.50/0

Table II. UV Spectral Data of Substituted Benzoyltrimethylsilanes in Cyclohexane

R	absorptn maxima[a]			
	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	
	λ_{max}, nm	$10^{-4}\epsilon$	λ_{max},[b] nm	ϵ
	Para Substituents			
H	250.5	1.18	423	130
Me	261	1.45	420.5	136
t-Bu	262	1.63	420.5	137
OMe	278	1.61	413	149
NMe_2	240	0.65	408.5	194
Cl	261	1.52	425.5	122
Br	264	1.63	426.5	115
CF_3	242	1.24	435	99
CO_2Me	257	1.88	438	104
CO_2Et	257.5	1.90	439	98
CN	254	1.87	(423) 440	(96) 96
NO_2	265	1.57	(431) 444	(95) 96
$COSiMe_3$	268	2.23	(424) 438	(204) 202
$SiMe_3$[c]	259.5	1.82	426.5	125
	Meta Substituents			
Me	253.5	1.11	422.5	120
OMe	255	0.87	421.5	123
NMe_2	249	2.49	(418)	
Cl	249	0.78	428	90
Br	250	0.96	427.5	111
CF_3	242	1.12	429	109
CO_2Me	247	0.99	426.5	116
CO_2Et	247	1.00	425.5	119
NO_2	232	2.17	432	110
$COSiMe_3$	239	2.41	427.5	208
$SiMe_3$	254.5	1.09	423.5	119
CHO	231.5	(2.56)	427.5	(90)

[a] Error within ±0.5 nm. [b] The most intense peak in a fine structure. [c] See ref 2b.

oxygen lone pair, σ_{Si-C}–n_O, is suggested.[3,4]

The longest wavelength transitions, $n \rightarrow \pi^*$, of benzoylsilanes are clearly separated from by far the strongest $\pi \rightarrow \pi^*$ absorptions. We are, therefore, expected to look at precise substituent effects on the absorption maxima of substituted benzoylsilanes. In fact, an interesting correlation between the wavelength of the most intense $n \rightarrow \pi^*$ band and the Hammett σ constant was noted for six para-substituted benzoyltriphenylsilanes.[1c] However, the marked deviation arising from resonance effects has not been discussed in detail but rather appears to be an open question.

In this paper, we wish to describe and discuss briefly the ultraviolet spectral data of 23 meta- and parap-substituted benzoyltrimethylsilanes, most of which are newly obtained in the preceding paper.[5]

Results and Discussion

Most meta- and para-substituted benzoyltrimethylsilanes have been prepared by a novel, general reaction of the corresponding benzoyl chloride with hexamethyldisilane in the presence of a (π-allyl)palladium complex with added triethyl phosphite as a catalyst.[5] One exception was *m*- and *p*-*N*,*N*-dimethylamino derivatives, which were prepared by way of dithiane procedures.[6]

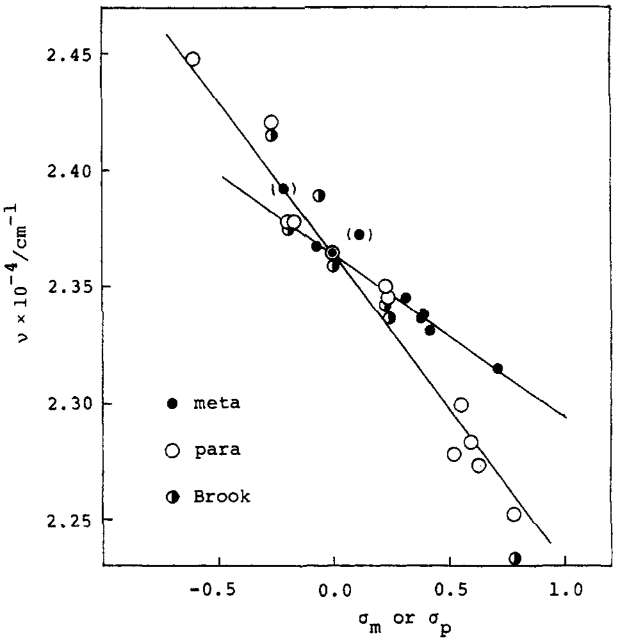

Figure 1. A plot of Hammett σ vs. wavenumbers (ν) from Table II for meta and para substituents in cyclohexane.

The ultraviolet spectra of analytically pure samples were measured in cyclohexane and, in a few cases, in ethanol and in THF. The positions and intensities of the absorption maxima are listed in Tables I and II.

In the present study, the transition that is of principal interest is the symmetry-forbidden $n \rightarrow \pi^*$ band. In cyclohexane, the 423-nm band of benzoyltrimethylsilane appears as three main peaks with two additional shoulders at lower wavelengths (a fine structure),[2b] whereas in ethanol the ketone shows one unresolved peak with shoulders on each side, the peak shifting 8 nm to a shorter wavelength from that in cyclohexane (Table I).

Then, it is hoped to find a clear-cut correlation between the substituent effects at the meta and para positions of the benzoyl group and the positions of the $n \rightarrow \pi^*$ transition bands, provided that the most intense peak in the fine structure, mostly corresponding to the second longest wavelength one, refers to the position of the transition.

It is noted that derivatives with such strong electron-withdrawing substituents as nitro and nitrile groups exhibit a rather ambiguous fine structure, where the second longest wavelength peak becomes almost even with the third one. We took consistently the former peak to define the position of the $n \rightarrow \pi^*$ transition bands in looking for the correlation with these substituent effects.

In Figure 1 are shown attempted Hammett σ correlations with wavenumbers (ν) of $n \rightarrow \pi^*$ bands of meta- and para-substituted benzoyltrimethylsilanes (closed and open circles, respectively). Also, plotted are the correlations of para-substituted benzoyltriphenylsilanes (semi-open circles), data cited from Brook et al.[1c]

Apparently the ν_p/σ_p correlation (correlation coefficient (r) = 0.987) differs from ν_m/σ_m (r = 0.991). Breakdown of the single substituent parameter (Hammett) treatment is often encountered in physical property measurements that pertain to a specific state of the substituents.[7]

---

(3) Ramsey, B. R.; Brook, A. G.; Bassindale, A. R.; Bock, H. *J. Organomet. Chem.* **1974**, *74*, C41.

(4) However, there seems to be controversy. Estimation of the energy levels of σ_{M-C} must be Ge > Si; so far as the π^* level does not change significantly, α-germyl ketones would have lower transition energy than α-silyl ketones. This is not the case. See Table III and the Experimental Section. Also: Hassner, A. *J. Am. Chem. Soc.* **1980**, *102*, 1577.

(5) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics*, preceding paper in this issue. Also, Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653.

(6) (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (b) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.

(7) In this context, an ab initio (STO-3G) calculation of benzoyltrimethylsilane and four para-substituted derivatives (MeO, Me, Cl, and CO_2Me) have been carried out. A change in the total electron density at the ipso position with respect to the trimethylsilylcarbonyl group correlates well with a change in observed wavenumbers (ν_p): Nagase, S.; Yamamoto, K., unpublished results.

Table III. UV Spectral Data of Other Acylsilanes and -germanes in Cyclohexane

compound	concn × 10^5, mol/L	absorptn maxima			
		$\pi \rightarrow \pi^*$, nm	$10^{-4}\epsilon$	$n \rightarrow \pi^*$,[a] nm	ϵ
o-$MeC_6H_4COSiMe_3$	5.20	251	0.95	410.5	113
o-$MeOC_6H_4COSiMe_3$	6.29	254	0.77	407.5	117
o-$ClC_6H_4COSiMe_3$	4.89	244	0.51	(387) 403	(123) 125
o-$BrC_6H_4COSiMe_3$	4.59	246	0.42	(387) 403.5	(151) 143
2-$(C_4H_3O)COSiMe_3$[b]	5.88	278.5	1.40	421.5	143
$PhCOSiMe_2Ph$[c]	4.87	253.5	1.05	421.5	242
$PhCOGeMe_3$[c]	10.14	246.5	1.24	417.5	134
$PhCOGeMe_2Ph$[c]	4.63	249	1.19	415.5	(186)

[a] The most intense peak in a fine structure. [b] 2-Furyl. [c] See ref 4.

It is evident, however, that para substituents without an appreciable resonance effect (t-Bu, Me, Cl, and Br) is well-correlated with the same slope as that determined by meta substituents.

A generalized treatment of substituent effects in the benzoyltrimethylsilane series with adequate substituents sets is then examined by the dual substituent parameter (DSP) equation:[8]

$$\text{substituent property } (P) = \rho_I\sigma_I + \rho_R\sigma_R$$

A clean correlation of wavenumbers (ν_m) of the n → π^* band in meta-substituted benzoyltrimethylsilanes with σ_I was found to be represented by eq 1, with one exception for the m-MeO group, the plot of which deviated to extraordinarily high wavenumbers.

$$\nu_m/\text{cm}^{-1} = -7.080 \times 10^2\sigma_I + 2.367 \times 10^4 \ (r = 0.977) \quad (1)$$

Consequently, the correlation of $\nu_p - \nu_m$ vs. σ_R^0 rather than σ_R can easily be examined by using eight para-substituted benzoyltrimethylsilanes and shown in Figure 2. Also the correlation is represented by eq 2, the correlation coefficient being 0.968.

$$\nu_p/\text{cm}^{-1} = -7.080 \times 10^2\sigma_I - 1.798 \times 10^3\sigma_R^0 + 2.335 \times 10^4 \ (r = 0.968) \quad (2)$$

It should be pointed out that of these eight substituents examined the σ_R^0 value differs significantly from the σ_R value in only two cases, i.e., NMe_2 and OMe groups. The fact that the substituent effects appeared to be well correlated by σ_R^0 values implies the specific state of substituted benzoylsilanes for which no electron-donating substituent effects from the para position are enhanced by quinoidal resonance effect.[7]

Finally, by definition, the susceptibility parameter, $\lambda = \rho_R/\rho_I$, was calculated to be 2.54. It is concluded that the change in wavenumbers (ν_p) of the n → π^* band of para-substituted benzoyltrimethylsilanes is ca. 2.5 times more sensitive to a resonance effect of the substituent than to an inductive effect, provided that the transmission of the latter effect from either the meta or para position does not vary significantly.[9]

It follows that any electron-withdrawing group on the para position of benzoyltrimethylsilane lowers effectively the energy level of carbonyl π^* orbital by the resonance effect and vice versa in the case of an electron-releasing one.

In conclusion, we have presented a new, clear-cut example of the DSP treatment of the UV spectral properties of meta- and para-substituted benzoyltrimethylsilanes.[10]

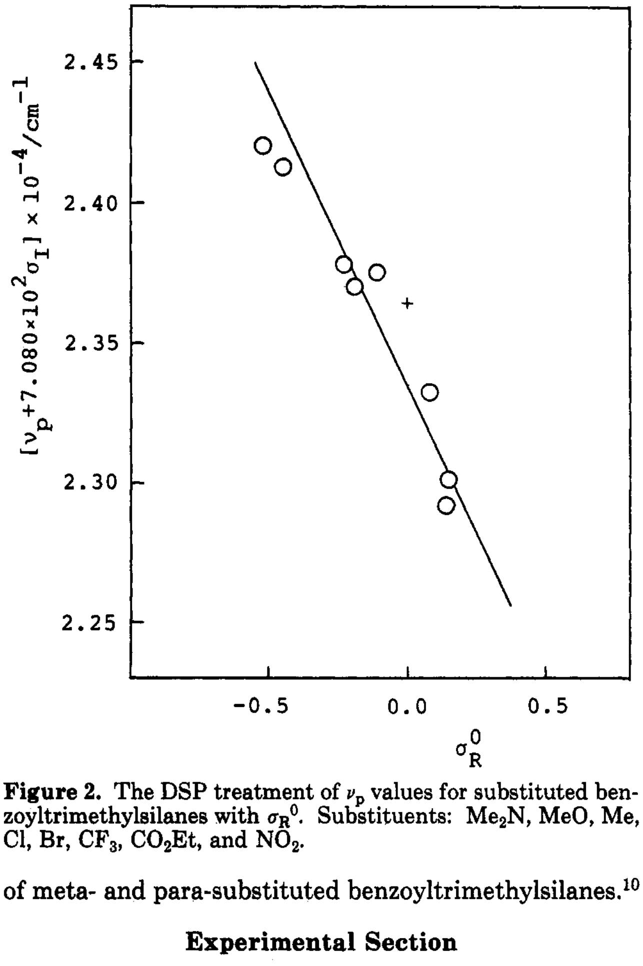

Figure 2. The DSP treatment of ν_p values for substituted benzoyltrimethylsilanes with σ_R^0. Substituents: Me_2N, MeO, Me, Cl, Br, CF_3, CO_2Et, and NO_2.

Experimental Section

Materials. All meta- and para-substituted benzoyltrimethylsilanes but the N,N-dimethylamino derivatives were prepared by a palladium complex catalyzed reaction of the corresponding benzoyl chloride with hexamethyldisilane, the detailed procedure for the preparation being described in the preceding paper.[5]

Preparation of (m-(Dimethylamino)benzoyl)- and (p-(Dimethylamino)benzoyl)trimethylsilanes. 2-(p-(Dimethylamino)phenyl)-1,3-dithiane was prepared in a 46% yield from p-(dimethylamino)benzaldehyde (2.98 g, 20 mmol) and propane-1,3-dithiol (2.0 mL, 20 mmol) in $CHCl_3$ (20 mL) in the presence of $BF_3 \cdot OEt_2$ (0.25 mL, ca. 2 mmol).

According to the literature method,[6] lithiation of the dithiane (recrystallized from AcOEt) (2.20 g, 9.2 mmol) in THF (35 mL) with n-BuLi (2.4 M in hexane, 4.1 mL, 9.7 mmol) at −40 °C, followed by silylation with $ClSiMe_3$ (1.3 mL, 10.2 mmol), afforded 2-(p-(dimethylamino)phenyl)-2-(trimethylsilyl)-1,3-dithiane in a 96% yield. The latter (0.27 g, 0.87 mmol) was carefully hydrolyzed with $HgCl_2$ (0.50 g, 2.2 mmol), HgO (0.32 g, 1.5 mmol), and 90%

---

[8] Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog Phys. Org. Chem.* **1973**, *10*, 1–80. See also: Bromolow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.

[9] Vorpagel, E. R.; Streitweiser, A., Jr.; Alexandratos, S. D. *J. Am. Chem. Soc.* **1981**, *103*, 3777.

[10] For a review on the use of DSP concepts for the properties of organosilicon compounds, see: Mileshkevich, T. P.; Novikova, N. F. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 49.

aqueous MeOH (10 mL) to give a low-melting yellow solid. Purification of the product by column chromatography afforded 0.11 g (55%) of (*p*-(dimethylamino)benzoyl)trimethylsilane: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.33 (s), 4.03 (s), 6.67 and 7.81 (d, AA′BB′, J = 9.0 Hz); IR (KBr) 1610 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{19}NOSi$: C, 65.11; H, 8.65; N, 6.33. Found: C, 64.97; H, 8.51; N, 6.35.

Essentially in the same manner as described above, (*m*-(dimethylamino)benzoyl)trimethylsilane was obtained as a yellow oil: ^{1}H NMR δ 0.33 (s), 2.96 (s), 6.55–7.59 (m); IR (neat) 1605 cm^{-1}. Anal. Found: C, 65.08; H, 8.65; N, 6.47.

Measurements of Ultraviolet Spectra. Spectroscopic grade solvents (cyclohexane, hexane, ethanol, and THF) were used as received. UV spectra were recorded on a Shimadzu UV-200 spectrophotometer, concentration for $n \rightarrow \pi^*$ bands being in a range of (2.84–7.22) × 10^{-5} mol/L. Solvent effects on the absorption maxima were examined for the parent benzoyltrimethylsilane, and data are shown in Table I.

All data for meta- and para-substituted benzoyltrimethylsilanes measured in cyclohexane are given in Table II.

For an examination of the substituent effect with respect to the observed wavenumbers of the $n \rightarrow \pi^*$ band, σ values are taken from Jaffe's review[11] and σ_I and $\sigma_R{}^0$ values are from ref 8.

In addition, UV spectral data of other acylsilanes and -germanes, preparation of which was also reported in the preceding paper,[5] are listed in Table III.[4]

Acknowledgment. This work was supported by the Grant-in-Aid from the Ministry of Education, Japan (No. 555341), to which our thanks are due. We thank Prof. Morikawa of this department for the measurements of UV spectra.

---

[11] Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

Fluoroorganometallic Chemistry: Synthesis, Structure, and Chemistry of the Cubane Cluster $[FRh(C_2H_4)(C_2F_4)]_4$[†]

Robert R. Burch,* Richard L. Harlow, and Steven D. Ittel

Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received September 23, 1986

The fluoro-bridged cluster $[FRh(C_2H_4)(C_2F_4)]_4$ was prepared by treatment of $[ClRh(C_2H_4)(C_2F_4)]_2$ with $AgBF_4$, followed by reaction with $[(CH_3)_2N]_3S^+(CH_3)_3SiF_2{}^-$. The cubanelike structure of the tetrameric complex was established by X-ray crystallography. Reaction of $[FRh(C_2H_4)(C_2F_4)]_4$ with $P(C_6H_5)_3$ yielded the new monometallic complex $FRh(C_2F_4)[P(C_6H_5)_3]_2$. The monometallic rhodium–fluoride complex can undergo reactions involving ligand substitution or fluoride extraction. In a ligand substitution reaction, solutions of $FRh(C_2F_4)[P(C_6H_5)_3]_2$ react with CO to give $FRh(CO)[P(C_6H_5)_3]_2$. Reaction with $(CH_3)_3SiO_3SCF_3$ yielded $CF_3SO_3Rh(C_2F_4)[P(C_6H_5)_3]_2$, derived from the fluoride extraction reaction.

Introduction

Although transition-metal complexes have wide utility in hydrocarbon transformations, the analogous chemistry of metal-bonded fluorocarbons is largely unexplored. Because of the importance of fluorocarbons as specialty chemicals, we have initiated a program aimed at elaborating the similarities and differences between organometallic and fluoroorganometallic chemistry. Hydrido–olefin complexes are cited as important intermediates in a variety of hydrocarbon transformations. We felt that an investigation of analogous fluoro–fluoroolefin complexes, a previously unknown structural type, would be of interest. While common in extended solid-state structures, fluorides are relatively unexplored as ligands in discrete molecular complexes compared to other halides. One reason is the ready solvolysis of the metal–fluorine bond.[1] In those cases where fluoride is observed as a bridging ligand, it is almost exclusively between two metal atoms; fluoride as a face-bridging ligand between three metal atoms is relatively rare.

An obvious route to a metal–fluoride fluoroolefin complex would be the metathesis reaction of fluoride for other halides in preformed fluoroolefin complexes. Many examples of complexes containing π-bonded fluoroolefins are known.[2] We chose to start by addition of fluoride sources to $[ClRh(C_2H_4)(C_2F_4)]_2$, a well-characterized chloro-bridged rhodium complex (1) first synthesized by Cramer.[3] The chemistry encountered in this approach was unexpectedly complex. Herein we report the synthesis and X-ray crystal

---

[†] Contribution No. 4087.

[1] Vaska, L.; Peone, J. *J. Chem. Soc. D* **1971**, 418–419.

[2] Representative examples of simple π complexes of tetrafluoroethylene with transition metals are given below. For Fe, Ru, Os: Cooke, M.; Green, M.; Kuc, T. A.; *J. Chem. Soc. A* **1971**, 1200–1203. Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. A* **1970**, 2975–2981. Cooke, M.; Green, M. *J. Chem. Soc. A* **1969**, 651–655. For Rh, Ir: Parshall, G. W.; Jones, F. W. *J. Am. Chem. Soc.* **1965**, *87*, 5356–5361. Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1975**, 1128–1137. Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1165–1169. For Ni, Pd, Pt: Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780–2788. Browning, J.; Cook, D. J.; Cundy, C. S.; Green, M.; Stone, F. G. A. *Chem. Commun.* **1968**, 929–930. Cundy, C. S.; Green, M.; Stone, F. G. A., *J. Chem. Soc. A* **1970**, 1647–1653. Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2828–2834. Maples, P. K.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 388–392. Mukhedkar, V. A.; Mukhedkar, A. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2801–2805. Green, M.; Osborn, R. B. L.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2525–2530. Fornies, J.; Green, M.; Laguna, A.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1515–1518. Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 449–451. Empsall, H. D.; Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3472–3476. Maples, P. K.; Green, M.; Stone, F. G. A.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1194–1198. Clark, H. C.; Manzer, L. E. *J. Chem. Soc., Chem. Commun.* **1973**, 870–871. Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1996–2004. See also: Booth, B. L.; Casey, S.; Haszeldine, R. N. *J. Organomet. Chem.* **1982**, *226*, 289–299. Simple π complexes of fluoroolefins of the early transition metal are exceedingly rare.

[3] Cramer, R.; Parshall, G. W. *J. Am. Chem. Soc.* **1965**, *87*, 1392–1393.

0276-7333/87/2306-0982$01.50/0