skeletal mode of $(CH_3)_2Te$ (526 cm^{-1}). This excellent correlation allows the assignment of this peak in the spectrum of ion **1** to the symmetric stretching vibration ν_6 for the $C–I^+–C$ skeleton.

Acknowledgment. Support of this work by grants from the U.S. Army Research Office (Durham) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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A New Method of Forming the Carbon–Silicon Bond. Reductive Silylation of Aromatic Acids

Sir:

It is well recognized that only a limited number of chemical reagents are available which can bring about the reduction of a carboxyl group.[1] Previously[2,3] we described the potency of certain trichlorosilane–tertiary amine combinations as reducing agents. We now wish to report a novel reaction in which the latter effects the reduction of benzoic acid and certain of its derivatives to benzylic trichlorosilanes in good yields.

The overall process, which can again be termed a "reductive silylation,"[3] can be represented as follows

$$RCO_2H + SiHCl_3 + R_3N \xrightarrow[\Delta]{CH_3CN} RCH_2SiCl_3 + R_3\overset{+}{N}H\overset{-}{Cl} + (SiCl_2O)_x$$

In a typical experiment, 1 equiv of benzoic acid and 5 equiv of trichlorosilane were dissolved in 100 ml of acetonitrile and refluxed for 1 hr.[4] Two equivalents of tri-*n*-propylamine was added at this point and the resulting mixture was refluxed at 79–86° for 14 hr. Treatment with dry ether caused the precipitation of tri-*n*-propylamine hydrochloride (95%). Distillation of the filtrate gave benzyltrichlorosilane (58%) boiling at 82–84° (8 mm). The pot residue was a resinous material whose ir spectrum was dominated by Si–O absorption at 8.5–9.5 μ. Data for the transformation of a series of aromatic acids are summarized in Table I.

Table I. Reductive Silylation of Aromatic Acids by Trichlorosilane–Tri-*n*-propylamine

Run	Reactants[a]	Conditions[b]	Products[c,d]
1	$C_6H_5CO_2H$	14 hr, 77–82°	$C_6H_5CH_2SiCl_3$ (58%)
2	*p*-$ClC_6H_4CO_2H$	16 hr, 73–77°	*p*-$ClC_6H_4CH_2SiCl_3$[e] (69%)
3	*p*-$BrC_6H_4CO_2H$	15 hr, 72–79°	*p*-$BrC_6H_4CH_2SiCl_3$ (58%)
4	*p*-$CH_3C_6H_4CO_2H$	16 hr, 71–77°	*p*-$CH_3C_6H_4CH_2SiCl_3$ (56%)
5	3,5-$(CH_3)_2C_6H_3CO_2H$	18 hr, 75–82°	3,5-$(CH_3)_2C_6H_3CH_2SiCl_3$ (51%)

[a] In every case, the mole ratio of acid:$SiHCl_3$:$(n\text{-}C_3H_7)_3N$ was 1:5:2. [b] In all cases, about 100 ml of acetonitrile was used as solvent. [c] In every instance, the percentage given in parentheses represents the *isolated* yield of organosilane based upon the weight of the starting acid. In addition, isolated yields of tri-*n*-propylamine hydrochloride ranging from 86 to 98% were obtained. [d] In the case of the silanes resulting from runs 1, 2, and 4, identification was made by matching their spectra (ir and nmr) with authentic samples. Satisfactory elemental analyses and spectral data (ir and nmr) were obtained for the silanes resulting from runs 3 and 5. [e] It is likely that tri-*n*-butylamine can be substituted for the tri-*n*-propylamine in every case. A 65% yield of *p*-chlorobenzyltrichlorosilane was realized when such a substitution was made in this run.

When a mixture of *p*-nitrobenzoic acid, trichlorosilane, and tri-*n*-propylamine was refluxed for 2 hr, a gelatinous colored material was formed which did not contain *p*-nitrobenzyltrichlorosilane. Further work is presently underway to delineate the effects of aromatic substituents on the course of the reaction as well as to ascertain whether it can be extended to aliphatic acids.

Since it is well known that benzylic silanes are readily cleaved by base,[5] the method herein described holds promise as a procedure for converting benzoic acids to substituted toluenes. It has already been shown that the benzyltrichlorosilane resulting from run 1 (Table I) can be cleaved readily to toluene.[6] Further experiments are currently underway in our laboratory to determine the generality and feasibility of such a two-step process for reducing a carboxyl group to methyl.

We must reemphasize that the mechanism of "reductive silylations," such as described here and previously,[3] remains speculative. The current thrust of our program has been directed solely at illustrating the preparative value of the method.

Acknowledgment. The authors are grateful to the Purdue Research Foundation whose financial assistance made this work possible.

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(2) R. A. Benkeser and W. E. Smith, *ibid.*, **90**, 5307 (1968).

(3) R. A. Benkeser and W. E. Smith, *ibid.*, **91**, 1556 (1969).

(4) It should be emphasized that the stoichiometry of the reactants has not been ascertained nor any attempt made to optimize reaction conditions.

(5) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 143–146.

(6) Unpublished studies by J. M. Gaul and K. M. Foley of these laboratories.

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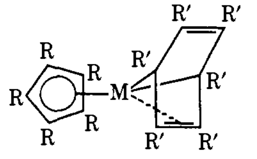
Fluxional Behavior in *Tetrahapto*benzene–Rhodium and –Iridium Complexes

Sir:

We report the first example of fluxional behavior in a benzene–metal complex. Fluxional behavior in cyclic π- and σ-bonded organometallic systems, where the metal atom usually moves along the periphery of a ring by a series of 1,2 shifts, is a well-established phenomenon.[1] It has been observed for cyclooctatetraene[1]

(1) This topic has recently been reviewed: F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

and cycloheptatrienyl complexes,[2] but not, until now, for a π-benzene complex.



1a, M = Rh; R = Me; R′ = COOMe
b, M = Ir; R = Me; R′ = COOMe
c, M = Rh; R = H; R′ = CF_3

We have prepared the 1,2,3,4-*tetrahapto*hexakiscarbomethoxybenzene(*pentahapto*pentamethylcyclopentadienyl)rhodium and -iridium complexes[3,4] **1a** and **1b** by reaction of the diacetato complexes **2**[5] with dimethyl acetylenedicarboxylate in benzene in the presence of hydrogen.

$$\underset{\mathbf{2}}{C_5Me_5M(OAc)_2H_2O} + MeOOCC{\equiv}CCOOMe + H_2 \longrightarrow \underset{\mathbf{1}}{C_5Me_5MC_6(COOMe)_6} + 2HOAc$$

(**a**, M = Rh; **b**, M = Ir)

The structures **1a** and **1b** were assigned to the complexes on the basis of their analyses, molecular weights, mass and nmr spectra, and their obvious analogy to the complex **1c**. This has been prepared by Dickson and Wilkinson from dicarbonylcyclopentadienylrhodium and hexafluoro-2-butyne,[6] and the structure determined by Churchill and Mason.[7] These authors formulated the bonding in valence-bond terms as **1c**, involving two σ and one π bond (Rh(III), as shown). A more realistic description is the molecular orbital one, also discussed by Churchill and Mason,[7,8] in which four carbon atoms of the benzene are π bonded to the metal, **3** (Rh(I)); in this case the nonplanarity of the benzene arises from considerable back-donation of metal d electrons to vacant orbitals of the π-*cis*-butadiene moiety of the benzene ring.

The nmr spectrum of the rhodium complex **1a** showed the presence of the pentamethylcyclopentadienyl ring, τ 8.51 (s, 15 H), and of three different types of carbomethoxy protons at 6.29 (s, 6 H), 6.41 (s, 6 H), 6.50 (s, 6 H).[9] An alternative formulation, π-$C_5Me_5RhC_4(COOMe)_4$(π-$MeOOCC_2COOMe$), is ruled out by the mass spectrum which shows the molecular ion peak (*m/e* 664) followed by loss of methoxycarbonyl groups (*m/e* 605, 546) as well as peaks due to hexamethyl mellitate (*m/e* 426) and $C_5Me_5Rh^+$ (*m/e* 238). No peaks arising from loss of dimethyl acetylenedicarboxylate from **1a** were observed.

If the representation of the structure **3**, involving a π-bonded *tetrahapto*benzene as suggested by Churchill and Mason, is correct, then this complex should show fluxional behavior. This was indeed the case (Figure 1); on heating the complex to 155° a complete averaging of the carbomethoxy peaks was observed, giving a sharp singlet at τ 6.37 (*o*-$C_6H_4Cl_2$) or 6.20 (DMSO-d_6). The C_5Me_5 remained a singlet. On cooling, these changes were quite cleanly reversed.

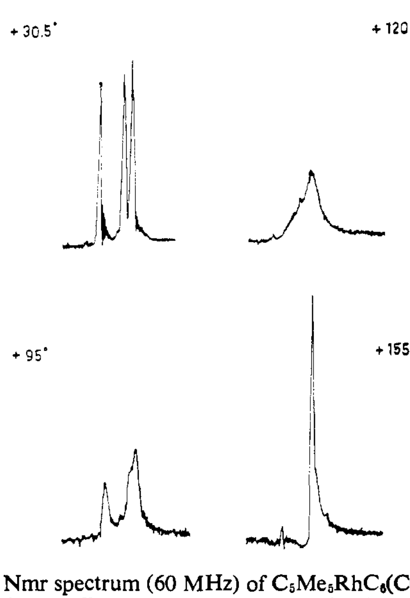
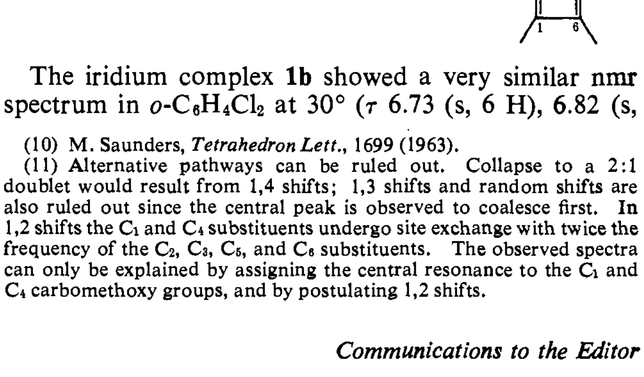


Figure 1. Nmr spectrum (60 MHz) of $C_5Me_5RhC_6(COOMe)_6$ (**1a**) in *o*-$C_6H_4Cl_2$ at different temperatures. Only the carbomethoxy methyl groups are shown.

Using a Saunders many-site nmr line-shape program[10] line shapes of the carbomethoxy methyl groups were calculated and plotted for a range of different rate constants. Very good duplication of the observed spectra was obtained when it was assumed that the central peak of the three resonances was due to carbomethoxy groups at C_1 and C_4 and that a series of 1,2 shifts of the metal occurred.[11] A rate constant, *k*, of 2 sec^{-1} was obtained at 81° and one of 50 sec^{-1} at 120°, corresponding to $\Delta F^{\ddagger}$ of 20.3 and 20.1 kcal mol^{-1}, respectively. There was no significant difference in rates between the two solvents (DMSO-d_6 and *o*-$C_6H_4Cl_2$) used; this rules out a solvent-assisted reaction. Apart from a very small amount (*ca.* 1%) of decomposition to hexamethyl mellitate, the spectrum of **1a** was regenerated cleanly on cooling of the solution.



3

The iridium complex **1b** showed a very similar nmr spectrum in *o*-$C_6H_4Cl_2$ at 30° (τ 6.73 (s, 6 H), 6.82 (s,

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[2] M. A. Bennett, R. Bramley, and R. Watt, *J. Amer. Chem. Soc.*, **91**, 3089 (1969).

[3] For a description of the *hapto* nomenclature, see F. A. Cotton, *Ibid.*, **90**, 6230 (1968).

[4] Satisfactory analyses were obtained for all new compounds described.

[5] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **91**, 5970 (1969).

[6] R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).

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[9] In *o*-dichlorobenzene. The resonances appeared at τ 6.11, 6.27, 6.32, and 8.30 (C_5Me_5) in DMSO-d_6.

[10] M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

[11] Alternative pathways can be ruled out. Collapse to a 2:1 doublet would result from 1,4 shifts; 1,3 shifts and random shifts are also ruled out since the central peak is observed to coalesce first. In 1,2 shifts the C_1 and C_4 substituents undergo site exchange with twice the frequency of the C_2, C_3, C_5, and C_6 substituents. The observed spectra can only be explained by assigning the central resonance to the C_1 and C_4 carbomethoxy groups, and by postulating 1,2 shifts.

6 H), 6.90 (s, 6 H), and 8.35 (s, 15 H)). No significant line broadening was observed up to 167° though there appeared to be a slight high-field shift of the central carbomethoxy resonance again at this temperature. A rearrangement with $k \leq 3$ sec^{-1} could have been detected. The $\Delta F^{\ddagger}$ for the iridium complex is therefore at least 25 kcal mol^{-1}, and this rearrangement occurs much less readily here.[12]

It is intriguing to speculate that a process involving formation of an intermediate corresponding to **1** ($R' =$ Me) but with Cl and π-bonded hexamethyl(Dewar benzene) (HMDB) in place of C_5Me_5, may be involved in the $[(HMDB)RhCl]_2$-catalyzed isomerization of HMDB to hexamethylbenzene recently reported by Volger and Hogeveen.[15]

Acknowledgment. We thank the National Research Council of Canada and the Petroleum Research Fund administered by the American Chemical Society (Grant 1796-Al) for support of this work.

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[12] We have also compared the rates of rotation of ethylene about the ethylene–metal axis for $C_5Me_5M(C_2H_4)_2$ and find this to be slower for M = Ir than for M = Rh. This appears to be a general phenomenon for 4d and 5d metals; Cotton, *et al.*, have shown that fluxional behavior is slower, and ΔH higher, for $C_8H_4Me_4W(CO)_3$ than for $C_8H_4Me_4Mo(CO)_3$,[13] and Bruce, *et al.*, have observed the same for $C_8H_8Os(CO)_3$ and $C_8H_8Ru(CO)_3$.[14]

[13] F. A. Cotton, J. W. Faller, and A. Musco, *J. Amer. Chem. Soc.*, **90**, 1438 (1968).

[14] M. I. Bruce, M. Cooke, and M. Green, *Angew. Chem. Intern. Ed. Engl.*, 7, 639 (1968).

[15] H. C. Volger and H. Hogeveen, *Rec. Trav. Chim. Pays-Bas*, **86**, 831 (1967).

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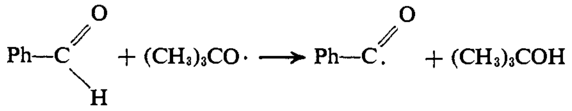
Electron Spin Resonance Study of Benzoyl σ Radicals in Solution

Sir:

In sharp contrast to the voluminous literature concerned with the electron spin resonance (esr) of π radicals, there exist very few experimental[1] or theoretical[2] studies on organic σ radicals. In such radicals the unpaired electron is mainly localized in an orbital with nonvanishing amplitude at the nucleus of the radical center. Most of these investigations, moreover, were carried out in rigid matrices, except for the vinyl and methylvinyl radicals[3] and a few aliphatic acyl radicals derived from formamide and substituted formamides[4] by abstraction of the aldehyde hydrogen atom. In this report we present an esr study of a number of benzoyl radicals in solution.[5] The esr spectra of these radicals permit the study of the delocalization of unpaired spin density from the σ system of the acyl moiety into the adjacent phenyl substituent.

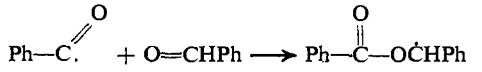
Photolysis of a stationary cyclopropane solution of benzaldehyde in the presence of di-*t*-butyl peroxide[6] gives an esr spectrum consisting of a 1:2:1 triplet of 1.16-G separation (g value = 2.0014) over a wide temperature range. An extremely weak identical spectrum was obtained in the absence of the peroxide.[7] We assign the spectrum (*vide infra*) to the benzoyl radical, formed by abstraction of the aldehyde hydrogen atom by *t*-butoxy radical (eq 1). No esr evidence was obtained for the α-hydroxybenzyl radical which would be formed by photoreduction of benzaldehyde[8,9] (eq 2) or



$$\mathrm{Ph{-}C(=O)H} + (\mathrm{CH_3})_3\mathrm{CO}\cdot \longrightarrow \mathrm{Ph{-}\dot{C}{=}O} + (\mathrm{CH_3})_3\mathrm{COH} \qquad (1)$$

$$\mathrm{PhCHO}^{3}(\mathrm{n},\pi^{*}) + \mathrm{RH} \longrightarrow \mathrm{Ph\dot{C}HOH} + \dot{\mathrm{R}} \qquad (2)$$

for the ester radical I, which was postulated as an intermediate in the thermal decomposition of di-*t*-butyl peroxide in the presence of benzaldehyde.[10]



$$\mathrm{Ph{-}\dot{C}{=}O} + \mathrm{O{=}CHPh} \longrightarrow \underset{\mathbf{I}}{\mathrm{Ph{-}C(=O){-}O\dot{C}HPh}} \qquad (3)$$

Under the same conditions, benzaldehyde-2,4,6-d_3 also gave the same triplet (Figure 1), but with narrower line widths (Table I). Since both benzaldehyde-3,5-d_2 and benzaldehyde-2,3,4,5,6-d_5 show collapse of the triplet into a single unresolved line, which is of greater line width than the lines of either the undeuterated or the 2,4,6-d_3 species, we conclude that *the major proton hyperfine splitting (1.16 G) is due to the meta hydrogens*

Table I. Hyperfine Coupling Constants of Benzoyl Radicals[a]

Starting compound	Type of spectrum	Temp, °C	Coupling Constants, G a_{mH}	$a_{^{13}\mathrm{C}}$[c]	ΔH,[b] G
Benzaldehyde	Triplet	−86	1.16	128.2	0.35
Benzaldehyde-2,4,6-d_3	Triplet	−89	1.17		0.21
Benzaldehyde-3,5-d_2	Singlet	−103			0.65
Benzaldehyde-2,3,4,5,6-d_5	Singlet	−83			0.63

[a] From photolysis of cyclopropane solutions of substituted benzaldehydes in the presence of di-*t*-butyl peroxide (1/1/1, v/v/v). [b] Peak-to-peak line width. [c] From benzaldehyde-7-^{13}C (50 atom %).

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[1] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962); **43**, 462 (1965); E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964); **44**, 4626 (1966); J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965); *Proc. Roy. Soc.* (London), **A293**, 246 (1966); J. E. Bennett, B. Mile, and B. Ward, *Chem. Commun.*, 13 (1969); H. J. Bower, J. A. McRae, and M. C. R. Symons, *ibid.*, 542 (1967); I. Miyogawa and W. Gordy, *J. Chem. Phys.*, **30**, 1590 (1959); M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963); Y. Kurita, *J. Chem. Soc. Jap.*, **86**, 581 (1965); H. Hayashi, K. Itoh, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **40**, 284 (1967); R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); N. Cyr and W. C. Lin, *J. Chem. Phys.*, **50**, 3701 (1969).

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[6] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968).

[7] Benzoyl radicals formed under these conditions were probably formed by adventitious peroxides.

[8] R. Wilson, *J. Chem. Soc.*, *B*, 84 (1968).

[9] Previous studies (*cf.* ref 6) have shown that cyclopropane is a poor hydrogen donor. It has been, therefore, widely used as "inert" solvent in these experiments.

[10] F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 70, 3258 (1948).