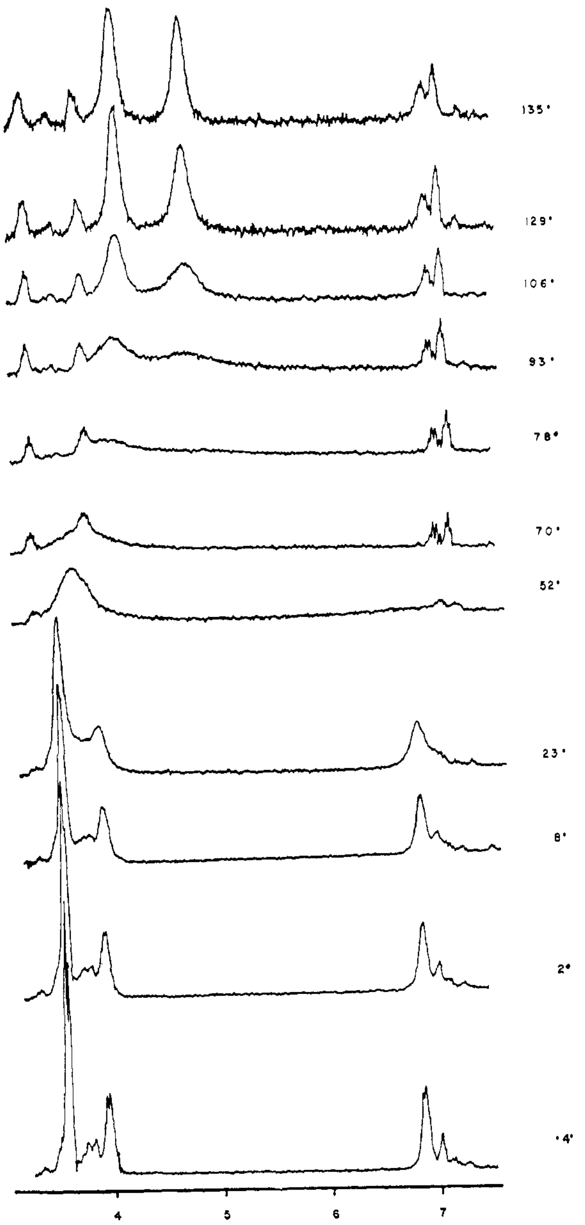
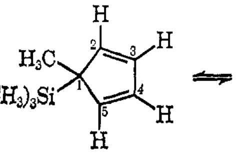
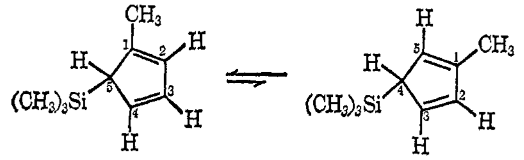


Figure 2. Proton nmr spectra of $(CH_3)_3SiC_5H_4CH_3$ in the region τ 3 to 7. The peaks at τ 3.3, 3.8, 7.1, and 7.2 appear irreversibly at temperatures above 0°. They are not present in a freshly distilled sample of $(CH_3)_3SiC_5H_4CH_3$. All other features of these spectra are completely reversible.

resonance. Thus the fine structure is due to coupling of the ring olefinic protons to the methyl group and not simply three separate methyl resonances from isomers I, II, and III. We ascribe the complex, low-temperature spectrum to the three isomers rearranging slowly on the nmr time scale. The simultaneous appearance of resonances at τ 6.9 and 7.0, assigned to the tertiary hydrogens H(5) and H(4) in structures II and III, respectively, lends support to our claims.[8]



I



II III

To further verify the assumption that methyl substitution on the cyclopentadienyl ring does not grossly affect the nonrigid behavior of these systems, we have prepared trimethyltinpentamethylcyclopentadiene, $(CH_3)_3SnC_5(CH_3)_5$, which shows two singlets in the nmr at τ 10.03 and 8.19 in the ratio 3:5.[9] [By comparison, hexamethylcyclopentadiene exhibits two peaks at τ 9.09 and 8.30 in the ratio 2:1.[10]] These are assigned to the trimethyltin unit and a σ-pentamethylcyclopentadienyl group undergoing rapid intramolecular rearrangement by direct analogy to the $(CH_3)_3SnC_5H_5$ system. The presence of Sn to ring methyl hydrogen coupling at the rapid exchange limit gives clear evidence that the predominant path for rearrangement is *intra*molecular and not *inter*molecular exchange, and rearrangement *via* hydride shift[5,6] is unlikely in these systems since it cannot account for the behavior of $(CH_3)_3SnC_5(CH_3)_5$ where no ring hydrogens are present. Although significant broadening of both the ring methyl and Sn–methyl resonances occur at −100°, complete collapse is not observed. Further studies are in progress on other members of the general class of group IVA compounds indicated above. A detailed report of their systematic behavior will be published soon.

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(8) Either peak may be due to either isomer. We are not able at present to decide between the two alternative assignments.

(9) ^{117,119}Sn–H coupling = 50.0 and 48.0 Hz for the τ 10.03 peak. ^{117,119}Sn–H coupling (isotopes not resolved) average is 19.7 Hz for the τ 8.19 peak.

(10) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

(11) Alfred P. Sloan Foundation Fellow, 1967–1969.

(12) National Science Foundation, Predoctoral Fellow, 1966–1968.

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The Reactivity of Hydroxy Groups in Metal Complexes

Sir:

A recent communication[1] on the complexes of N-2-hydroxyethylethylenediamine (etolen) with cobalt(III), palladium(II), and platinum(II) prompts the author to report work on the general question of hydroxy group reactivity in these systems.

The behavior of 2-hydroxyethyl groups in complexes has been somewhat enigmatic. Apart from a low reactivity of the OH group observed in bis(N-2-hydroxyethyliminodiacetato)chromate(III),[2] studies in other complexes have suggested a total resistance to electrophilic attack.[3,4] The initial studies of Keller and Edwards[3] described the preparation of $[Co(etolen)_3]^{3+}$ by oxidation of the corresponding cobalt(II) complex. The last-mentioned reaction has since been shown to

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(1) B. Das Sarma, G. J. Tennenhouse, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **90**, 1362 (1968).

(2) R. A. Krause and S. D. Goldby, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 143.

(3) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 215 (1952).

(4) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960).

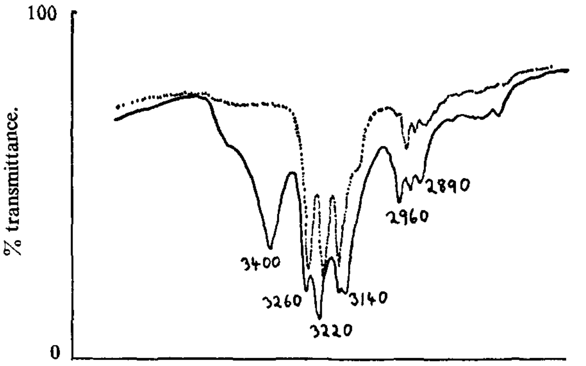

Figure 1. Infrared spectra of $[Co(NO_2)_3etoldien]$ and halogenation product (dotted curve) in the 4000–2500-cm^{-1} region for hexachlorobutadiene mulls between sodium chloride disks.

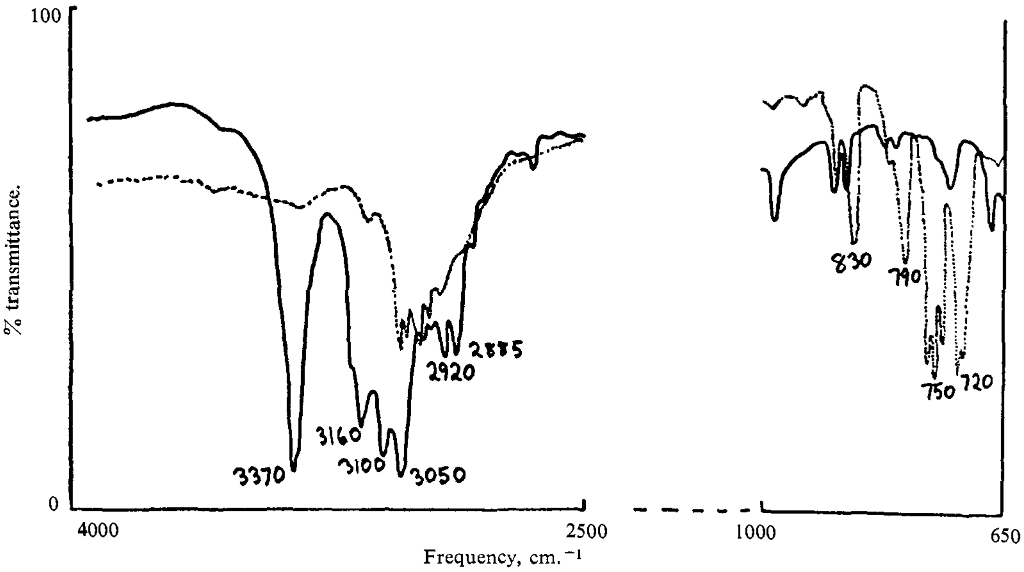

Figure 2. Infrared spectra of $[Pt(etolen)_2]Cl_2$ and halogenation product $[Pt(Cl\text{-}etolen)_2]Cl_2$ (dotted curve) in the 4000–2500-cm^{-1} region for hexachlorobutadiene mulls and in the 1000–650-cm^{-1} region for Nujol mulls between sodium chloride disks.

lead to carbon–nitrogen bond cleavage, giving ethylenediamine (en), formaldehyde, ammonia, and other products.[5] It was suggested that the lack of reactivity of the orange product obtained by Keller and Edwards with OH group reagents such as thionyl chloride, acetyl chloride, acetic anhydride, phosphorus tribromide, and benzoyl chloride was due to the presence of $[Co(en)_3]^{3+}$ rather than $[Co(etolen)_3]^{3+}$. To avoid the ligand degradation associated with the oxidation of the cobalt(II) complex, later workers[4] used the hexaamminecobalt(III) cation to synthesize a red, glass-like compound believed to contain $[Co(etolen)_3]^{3+}$, though it was incompletely characterized. The fact that this red complex gave no reaction of the OH group was first attributed to repulsion of the electrophilic reagents by the positive charge of the cobalt(III) complex but has recently been related to the coordination of the OH group attended by proton loss.[1] To investigate the role of complex charge, the neutral compounds $[Co(NO_2)_3dietoldien]$ and $[Co(NCS)_3dietoldien]$ (dietoldien = $HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2OH$) were synthesized but unfortunately decomposed in attempts to react their OH groups.[4] This point bears reinvestigation since both $[Co(NO_2)_3dietoldien]$ and $[Co(NCS)_3dietoldien]$ were characterized only by analysis which would not detect isomers such as $[Co(dietoldien)_2][Co(NO_2)_6]$ and $[Co(dietoldien)_2][Co(NCS)_6]$.

In this study $[Co(NO_2)_3etoldien]$ (etoldien = $HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) has been synthesized by a method analogous to that described for $[Co(NO_2)_3dietoldien]$.[4] The orange crystalline product has the correct analysis and gives a conductivity in water of 4 ohm^{-1} cm^2 mole^{-1}, corresponding to that of a nonelectrolyte. The infrared spectrum (Figure 1, lower curve) clearly shows the presence of the OH group at 3400 cm^{-1}. For comparison, literature values[2] for alcoholic OH groups in metal complexes give the OH stretching mode as 3380 and 3300 cm^{-1}. Though $[Co(NO_2)_3etoldien]$ is almost insoluble in reagents such as thionyl chloride, it dissolves readily in dimethylformamide. Cold (<10°) solutions in this solvent react with cold, premixed thionyl chloride–dimethylformamide, and a red crystalline compound can be isolated. The infrared spectrum of this product shows complete removal of the OH stretching band (Figure 1, dotted curve) though the NH_2 (3300–3100 cm^{-1}) and CH_2 (~2900 cm^{-1}) modes are still evident. New bands at 816 (s), 780 (vw), and 665 (m) cm^{-1} also appear, but correlation with C–Cl stretching vibrations is made ambiguous by the occurrence of ONO deformation frequencies in this general region. Elemental analysis suggests that the red product is a mixture of $[Co(NO_2)_2Cl(Cl\text{-}etoldien)]$ and $[Co(NO_2)_3(Cl\text{-}etoldien)]$, where Cl-etoldien = $ClCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$. The special nature of the thionyl chloride–dimethylformamide reagent has been discussed by Eilingsfeld.[6]

In view of the above information concerning anionic and neutral complexes, the question of OH group reactivity in cationic complexes remains of interest. Accordingly, the new complex $[Pt(etolen)_2]Cl_2$ was synthesized by reaction of $PtCl_2$ with the ligand in dimethyl-

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(5) D. Huggins and W. C. Drinkard in ref 2, p 181.

(6) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, 72, 836 (1960).

formamide and subsequent treatment of the solution with hydrochloric acid. The white product gives the expected C, H, N, and Cl analyses and is a 2:1 electrolyte in water. The infrared spectrum (Figure 2) shows the strong, sharp OH frequency at 3370 cm^{-1}. It is possible to deuterate selectively the OH group by treatment of the complex with D_2O–DCl, thus confirming the OH assignment by the band shift to 2506 cm^{-1}. The ratio $\gamma_{OH}/\gamma_{OD} = 1.34$ is in good agreement with the theoretical value of 1.41.

Though $[Pt(etolen)_2]Cl_2$ is of low solubility in dimethylformamide, it is readily soluble as the tetraphenylborate salt in this solvent and reacts in the cold with the thionyl chloride–dimethylformamide reagent. The tetraphenylborate anion is decomposed in the reaction, and the white product crystallizes as the chloride salt whose infrared spectrum is shown in Figure 2 (dotted curve). The OH absorption at 3370 cm^{-1} has been removed, while new bands appear in the 700–800-cm^{-1} region.

No attempt has been made to separate the various isomers expected with these complexes. Nevertheless, the results serve to demonstrate that OH groups in neutral $[Co(NO_2)_3etoldien]$ and in positively charged $[Pt(etolen)_2]^{2+}$ are certainly capable of undergoing reaction.

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A Cogwheel Effect in the Internal Rotations of Highly Hindered Systems

Sir:

Several recent references to hindered rotations in diarylcarbonium ions[1,2] prompts us to report the results of pmr studies in closely related systems. In particular, we are concerned with these properties of the dimesitylcarbonium ions and the respective substrates from which they can be generated in strong acid solutions (see Table I).

Table I. Pmr Data

Structure	Chemical shifts,[b] (Hz), of protons: *o*-Methyl	*p*-Methyl	Aromatic[f]	Methinyl	Temp, °C	References
$(Mes)_2CH^+$, **1**	7.80	7.70	3.09[a]	2.37	−52, −60, and +25	This work
$(Mes)_2COH^+$, **2**[b]	7.78	7.63	2.99		−52 and +25	This work
$MesC^+$, **3**[b]	7.62	7.72	3.08		−60 and +25	This work
$(C_6H_5)_2CH^+$, **4**			2.02[a]	0.19		*e*
$(C_6H_5)_2COH^+$, **5**			2.17			*e*
$MesCH^+CH_3$, **6**	±7.2 (doublet)	7.45	2.60	±1.30 (quartet)	−60	1
MesCOOH, **3a**	7.57[d]	7.71[d]	3.17		+40	This work
$(Mes)_2CHOH$, **1a**	7.87[d]	7.81[d]	3.35[d]	3.80[d]	+40	This work
$(Mes)_2C{=}O$, **2a**	7.81[d]	7.64[d]	3.10[d]		+40	This work
Mesitylene	7.75		3.22			*c*
Toluene	7.68					*c*

[a] The comparison of chemical shifts of the methinyl protons in **1** and **4** is only qualitatively valid since different media are used and bulk susceptibility corrections have not been made. [b] The carbonium ion species of the assigned structures were all generated in two solvents: concentrated sulfuric acid (45% or greater) and 10% CF_3COOH–90% $(CF_3CO)_2O$ solution (R. B. Moodie, T. M. Conner, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959)). The uv spectral and other characteristics by which these carbonium ions have heretofore been identified[3,4] were substantially the same in both media. These observations establish that the lowest temperature measurements (−60°) which could only be carried out in the CF_3COOH–$(CF_3CO)_2O$ solution were indeed taken on the carbonium ion and not on the trifluoroacetates. [c] Data from Varian catalog of nmr spectra taken in $CDCl_3$ solvent. [d] Data taken in CCl_4 at 40°. [e] D G. Farnum, *J. Am. Chem. Soc.*, **86**, 934 (1964). [f] *meta*.

The existence of ion **1** in sulfuric acid was first demonstrated by cryoscopic studies.[3] Its striking stability ($pK_{R^+} = -6.6$) was determined by means of uv spectral studies.[4] Deno and coworkers[4] have emphasized that the stability and spectral features of **1** cannot be understood on the basis of model examinations which reveal that the two mesityl rings are held rigidly at near right angles to each other, while their axes, and that of the (methinyl) hydrogen, join the cation center at 120° angles. However, the data given in Table I indicate that the models do not properly convey the rotational modes available both to dimesitylcarbonium ions or their respective tetracovalent precursors.

Pmr spectra of **1**, **2**, and **3** show sharp singlets for the methyl protons in both 60- and 100-Mc nmr measurements. The most distinctive features of these and other absorptions listed in Table I may be summarized as follows. (a) In **1**, **2**, and **3** the *o*-methyl protons are (all) magnetically equivalent and readily distinguished from the *p*-methyls. (b) In ions **1** and **2** (as well as the tetracovalent precursors) the *o*-methyls are more shielded than the *p*-methyls. (c) In the monomesitylcarbonium ions **3** and **6** the reverse is apparent: *i.e.*, the *p*-methyl protons are more shielded. (d) There is remarkably little difference in the chemical shifts (degree of shielding) of the *o*-methyl protons in all the mesitylcarbonium ions (**1**, **2**, and **3**), compared both to each other, to those of their precursors (**1a**, **2a**, and **3a**), or to the methyl-proton resonances in mesitylene and toluene. Moreover, the largest of these chemical shift differences (*ca.* 0.6 ppm between **1** and **6**) cannot be regarded as impressive. An entirely parallel situation prevails in a comparison among the corresponding *p*-methyl-proton resonances listed in Table I. (e) The (*meta*) aromatic protons in the mono- and dimesitylcarbonium ions **1**, **2**, and **3** are comparatively little deshielded in relation to those in the

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(1) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Am. Chem. Soc.*, **89**, 5259 (1967).

(2) R. van der Linde, J. W. Dornseiffen, J. R. Veenland, and Th. J. De Boer, *Tetrahedron Letters*, 525 (1968).

(3) M. S. Newman and N. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

(4) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); *J. Am. Chem. Soc.*, **77**, 3049 (1955); H. A. Smith and B. B. Stewart, *ibid.*, **79**, 3693 (1957).