

fluoromethyl)cyclopentadienone]tricarbonyl iron¹² being 95° and 96.6° respectively. It seems reasonable to believe that a similar model to that which we have elaborated here will rationalise these results.

SUMMARY

The bonding electron distribution in allyl complexes of transition metal ions is discussed and related to the observed stereochemistries of π -allylpalladium-chloride and -acetate. Some general comments are made on the application of the theory to the bonding in other organometallic molecules.

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SHORT COMMUNICATIONS

PMR spectra of some neopentyl derivatives of mercury. Long-range ¹⁹⁹Hg-¹H coupling

Recently we reported^{1,2} spin-spin coupling between protons and phosphorus through four σ bonds. In continuation of our work on the long-range interaction of protons with hetero nuclei, we have now found that mercury (isotope ¹⁹⁹Hg, spin 1/2, 16.86% natural abundance) couples strongly with protons over four single bonds. A very recent communication by Kiefer and Waters³ on the coupling of mercury with γ protons prompts us to report our findings on this subject.

Neopentyl derivatives, prepared by the usual methods*, were used as model compounds because of the simplicity of their PMR spectra. The ¹⁹⁹Hg-H _{γ} coupling could be measured easily as the two peaks of the split γ protons were located symmetrically about the resonance of the corresponding unsplit protons (Fig. 1). The pertinent data are summarized in Table 1.

* The preparation of neopentylmagnesium chloride and its further reactions with appropriate mercuric halides were carried out in dry tetrahydrofuran².

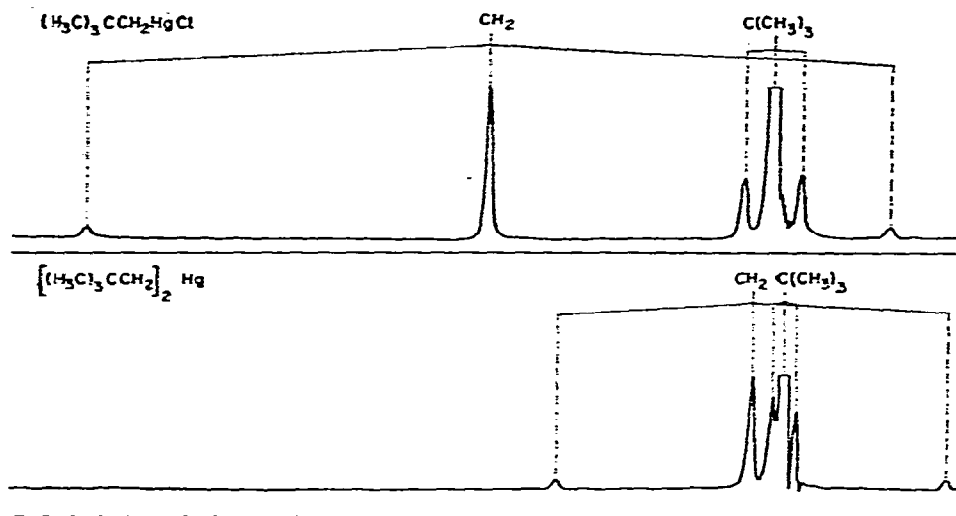


Fig. 1. Proton magnetic resonance spectra of trineopentylmercuric chloride and dineopentylmercury in deuteriochloroform solutions

Effect of substituent

The coupling constant of mercury with α protons in dineopentylmercury lies well within range of the corresponding values for other dialkylmercury compounds⁴. More than two-fold increase in its value in the case of neopentylmercuric halides clearly indicates that the replacement of electron-donating neopentyl group by more electronegative chlorine and bromine atoms results in diverting considerable amount of *s*-character into the mercury-carbon bond. Hatton *et al.*⁵ observed the same substituent effect on $J(^{199}\text{Hg}-\text{H}_\alpha)$ in methyl (and ethyl) derivatives of mercury and ascribed it to the change $\text{Hg}(6s6p) \rightarrow \text{Hg}^-(6s)$. In other words, the fractional *s*-character of the valence orbital of mercury involved in bonding with carbon increases from 1/2 in the case of dialkylmercury to 1 in ionic alkylmercuric compounds such as alkylmercuric perchlorates. Also the hyperfine structure constant, which is ap-

TABLE I
PROTON MAGNETIC RESONANCE DATA^a

Compound	Solvent	δ^b	J (cps)		
			CH_2	$\text{C}(\text{CH}_3)_3$	$^{199}\text{Hg}-\text{H}_\alpha$
$(\text{H}_3\text{C})_3\text{CCH}_2\text{HgCl}^9$	CDCl_3	2.20	1.08	193.5 \pm 0.5	13.2 \pm 0.2 ^c
	$(\text{CD}_3)_2\text{CO}$	2.16	1.08	203.0 \pm 0.5	13.5 \pm 0.1
	$(\text{CD}_3)_2\text{SO}$	2.01	1.00	214.5 \pm 0.5	14.0 \pm 0.1
$(\text{H}_3\text{C})_3\text{CCH}_2\text{HgBr}^{10}$	CDCl_3	2.25	1.10	189.0 \pm 0.5	13.3 \pm 0.2
	$(\text{CD}_3)_2\text{CO}$	2.23	1.09	200.0 \pm 0.5	13.6 \pm 0.1
	$(\text{CD}_3)_2\text{SO}$	2.03	1.01	212.5 \pm 0.5	13.9 \pm 0.1
$[(\text{H}_3\text{C})_3\text{CCH}_2]_2\text{Hg}^{11}$	CDCl_3	1.16	1.01	94.0 \pm 0.5	5.5 \pm 0.2
	$(\text{CD}_3)_2\text{CO}$	1.14	1.00	94.5 \pm 0.5	5.5 \pm 0.2
	$(\text{CD}_3)_2\text{SO}$	1.12	0.98	95.0 \pm 0.2	5.6 \pm 0.1

^a Spectra were obtained on 2 molar solutions using a Varian A-60 spectrometer. ^b Chemical shifts are in ppm downfield from an internal standard of TMS. ^c Its field independence was checked by recording the spectrum at 200 Mc on a Varian HR-200 spectrometer.

proximately related to the spin-spin coupling through Fermi contact⁶, is greater for Hg⁺ than Hg⁷. The polarity of mercury-halogen bond (Hg^{δ+}-X^{δ-}) in neopentylmercuric chloride and bromide well explains the substituent effect on Hg-H coupling observed in the present case.

Of interest in the present study is that $J(^{199}\text{Hg-H}_\gamma)$ experiences the same substituent effect as $J(^{199}\text{Hg-H}_\alpha)$ [$J(^{199}\text{Hg-H}_\alpha)/J(^{199}\text{Hg-H}_\gamma) = \sim 15.5 \pm 1.5$]. It is tempting to conclude that both α and γ protons couple with mercury via the same mechanism. It has been shown previously⁵ that the dominant contribution to $J(^{199}\text{Hg-H}_\alpha)$ arises from the contact term. However, the coupling mechanism of mercury with gamma protons is complex³, and the possibility of any contribution through space cannot be excluded.

The substituents alter significantly the shielding of α protons; but have only little effect on the electronic environment of the γ protons.

Effect of solvent

It is interesting to note the effect of solvent on the chemical shifts of α and γ protons and their coupling constants with mercury. As expected, in neopentylmercuric halides, the coupling constants increase with the polarity of the solvent.

The greater shielding of protons in more polar solvents is readily explainable by the well-known fact of facile solvation of mercury compounds in polar solvents⁸. The mercury atom in RHg^{δ+} can easily accept one or more pairs of electrons into its empty 6p-orbitals from the solvents such as dimethyl sulfoxide-*d*₆ and thus cancel, at least partly, the partial charge on it. Consequently, depending upon the nature of the solvating media, the α and γ protons should be more shielded.

In the case of dineopentylmercury, there is only little solvent effect on $\delta(\text{H})$ and $J(^{199}\text{Hg-H})$. It is in line with the above explanation.

Effect of concentration

The proton chemical shifts and their coupling constants with mercury remained virtually unchanged when the molarity of the solution was reduced from 2 to 1.

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*Carothers Research Laboratory, Textile Fibers Department,
Experimental Station, E. I. du Pont de Nemours and Co., Inc.,
Wilmington, Delaware 19898 (U.S.A.)*

GURDIAL SINGH

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