

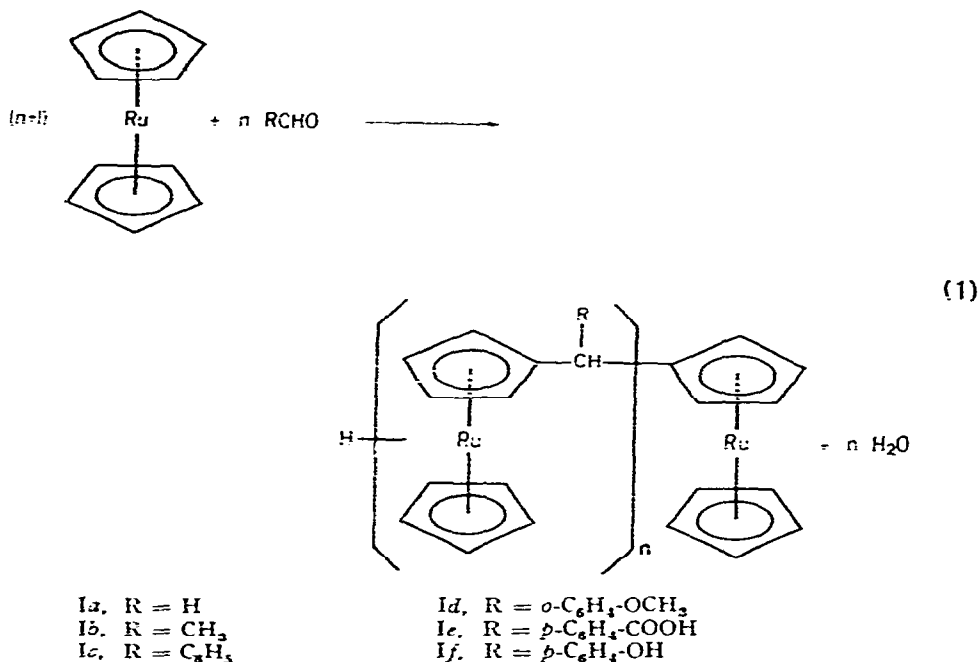
## SHORT COMMUNICATIONS

## Metallocene polymers

## XV. Polymers containing the ruthenocene system\*

During the last few years, numerous publications dealing with polymers that contained ferrocenylene ( $C_{10}H_9Fe$ ) units in the backbone have appeared in the literature. To our knowledge, however, no polymeric compounds possessing the analogous ruthenocenylene ( $C_{10}H_9Ru$ ) units have been described to this date.

It is the purpose of this communication to report the preparation of ruthenocene-containing polymers I, having a structure in which 1,2-, 1,3- and 1,1'-ruthenocenylene groups are interlinked in a random sequence distribution by methylene or variously substituted methinyl bridges. These polymers were obtained by zinc chloride-catalyzed melt condensation of ruthenocene<sup>1</sup> with aldehydes according to equation 1, using the



conventional techniques employed in earlier ferrocene-aldehyde condensations<sup>2-4</sup>. The aldehydes used were formaldehyde (as its dimethyl acetal), acetaldehyde, benzal-

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dehyde, *o*-methoxy-, *p*-carboxy- and *p*-hydroxybenzaldehyde. Molar reactant ratios and other reaction variables for representative condensations are summarized in Table I, as are the analytical data for the soluble polymers isolated from the crude reaction products by washing with water for catalyst removal, followed by reprecipitation from benzene (Nos. 1-4) or dioxane (Nos. 5, 6) solutions.

A comparison of the tabulation with the corresponding data from previous investigations on ferrocene polymers<sup>2-6</sup> shows that more rigorous reaction conditions, such as higher temperatures, higher catalyst concentrations and/or longer heating periods were required to achieve yields and molecular weights comparable with the earlier results, thus pointing to diminished reactivity of the metallocene reactant in the present study. This trend is consistent with the decrease in nucleophilicity in Friedel-Crafts reactions observed in going from ferrocene to ruthenocene (and, further, to osmocene)<sup>1,7</sup>. This decreased susceptibility of the  $\pi$ -cyclopentadienyl rings to electrophilic substitution is convincingly manifested in the condensation of ruthenocene with *o*-anisaldehyde as exemplified in experiment No. 4. Here, in contrast to the corresponding ferrocene case<sup>2</sup>, the methoxyphenyl moiety competed effectively with the metallocene in the overall reaction, causing early side-chain and crosslink formation as reflected in both the relatively low soluble polymer yield and the concomitant isolation of nearly 15% insolubles. Still more strikingly, this effect is seen in No. 6 involving *p*-hydroxybenzaldehyde as co-reactant, where the insolubles amounted to almost 30%. (Analogous condensations of ferrocene with the same aldehyde over 1.3 h at 135° gave 69.2% soluble polymer and less than 5% insoluble product.) Presumably, a factor contributing to the results in these two cases is the increased stability of the intermediary  $\alpha$ -ruthenocenyl cations resulting from greater metal back-side participation<sup>7,8</sup>, which would be expected to lead to enhanced selectivity in the ensuing substitution steps.

The polymers I showed solubility in a number of organic solvents (dioxane, pyridine for *Ic, f*; in addition, benzene and halohydrocarbons for the less polar *Ia-d*) and, in contrast to the yellow to dark brown ferrocene analogs, were off-white to light gray in color as a result of transparency of the ruthenocene system in the visible spectral range. The latter characteristic renders these ruthenocene polymers particularly useful in such applications that require stability toward high-energy ultraviolet radiation (as encountered, *e.g.*, under extraterrestrial conditions), coupled with high reflectivity. In addition, the products proved superior in thermal and oxidative stability to the analogous ferrocene polymers. A sample of polymer *Ia*, for example, obtained by subfractionation ( $M_n$  2850), when subjected to thermogravimetric analysis at a heating rate of 15°/min., showed a relative weight loss of about 10% (20%, 35%) at 450° (500°, 600°) in argon environment, and 8% (15%, 20%) at the respective temperatures in air. In contrast, the analogous ferrocene polymer<sup>4</sup> of equal molecular weight gave corresponding weight loss figures of about 15% (35%, 45%) in argon and 8% (35%, 75%) in air. This enhanced stability behavior of the ruthenocene polymers is well in accord with chronopotentiometric, thermochemical and mass spectral evidence established earlier<sup>1,9,20</sup> for the monomeric metallocenes of the iron-ruthenium-osmium series.

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TABLE I  
POLYCONDENSATION OF RUTHENOCENE WITH ALDEHYDES

No.	Substituent R in equation 1	Molar ratio <sup>a</sup> Aldehyde : ZnCl <sub>2</sub>	Temp. (°C)	Time (hours)	Soluble polymer Yield <sup>b</sup> (%)	M <sub>n</sub> <sup>c</sup>	M.p. <sup>d</sup> (°C)	Anal. calcd. for 1			Anal. found for soluble polymer		
								C	H	Ru	C	H	Ru
1	H	1.6	180	5.0	21.3 (31.1)	1920	120	54.02	4.17	41.81	54.19	4.28	40.59
2	CH <sub>3</sub>	1.5	150	9.0	18.9 (28.7)	1270	130	55.62	4.02	40.36	56.01	4.30	39.88
3	C <sub>6</sub> H <sub>5</sub>	1.0	140	10.0	32.4 (55.3)	1860	140	62.29	4.40	33.31	62.72	4.17	32.79
4	2-C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub>	1.0	145	2.8	37.4 (47.6)	3600	180	61.19	4.60	29.95	61.49	4.60	28.99
5	4-C <sub>6</sub> H <sub>4</sub> -COOH	0.9	195	5.0	21.0 <sup>e</sup>	1310	> 280	58.17	3.97	---	57.69	4.20	---
6	4-C <sub>6</sub> H <sub>4</sub> -OH	0.9	145	1.5	4.9 <sup>f</sup>	---	> 280	60.88	4.21	---	61.91	4.17	---

<sup>a</sup> Per mole of ruthenocene. <sup>b</sup> In parentheses, total % soluble condensation product including oligomer collected from mother liquor (cf. refs. 2-6). <sup>c</sup> In dioxanomethane solution (pyridine for Nos. 5, 6). <sup>d</sup> Upper limit of melting range. <sup>e</sup> Total soluble condensation product, collected by precipitation from dioxane solution with water (starting materials removed by washing with hot water, followed by vacuum sublimation).

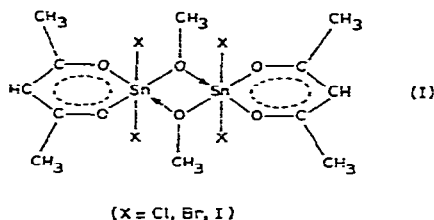
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### Infrared spectra of alkoxy-bridged tin complexes

Previously we have reported<sup>1</sup> the preparation and properties of methoxy-(acetylacetonato)tin dihalides  $[(\text{CH}_3\text{O})(\text{C}_5\text{H}_7\text{O}_2)\text{SnX}_2]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and on the basis of their infrared spectra and molecular weight determinations we have suggested a probable configuration (I).



In this paper, the infrared spectra in the 1600-400  $\text{cm}^{-1}$  region of these complexes and some new alkyl-substituted compounds of (I),  $[(\text{CH}_3\text{O})(\text{C}_5\text{H}_7\text{O}_2)\text{SnYX}]_2$ , will be described. These complexes belong to a series of typical compounds having a four-membered ring  $\text{Sn}-\text{O}-\text{Sn}$ . In the chemistry of organotin compounds, this is a structural feature of considerable importance<sup>2</sup>. The infrared spectra of these complexes are rather simple, and these results will be useful in the interpretation of more complicated spectra such as those of the dimeric tetraalkyl-1,3-disubstituted distannoxanes, which are known to have the four-membered ring<sup>3</sup>.

The spectra of these complexes are almost identical to those of the corresponding bis(acetylacetonato)tin complexes<sup>4</sup> except for additional strong bands appearing at 1020-970 and 530-480  $\text{cm}^{-1}$ . The former band is assigned to a perturbed  $\text{H}_3\text{C}-\text{O}$  stretching vibration and the latter to a ring vibration of the  $\text{Sn}-\text{O}$  four-membered ring. The frequencies of these two bands are listed in Table 1. Fig. 1 shows correlations of these bands with the sum of the Hammett's constant<sup>5</sup>  $\sigma^*$  of the substituents X and Y, and it is clear that there are linear relationships between  $\sigma^*$  and the wave numbers of these two bands. It is seen that the weaker the  $\text{H}_3\text{C}-\text{O}$  bond, the stronger is the