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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

IV*. η^5-PENTADIENYLTRICARBONYLRHENIUM

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Summary

η^5-Pentadienyltricarbonylrhenium has been prepared by reacting 2,4-pentadienyltributyltin with bromopentacarbonylrhenium in refluxing tetrahydrofuran.

The recent report by Seyferth, Gollman and Pornet [2] of the synthesis of η^5-pentadienyltricarbonylmanganese prompts us to describe our results on the rhenium analogue (I). We had also independently prepared the manganese derivative by a similar method to that used by Seyferth, prior to the appearance of his paper. We find good agreement between our characterising data and his observations.

2,4-Pentadienyltributyltin, prepared by the reaction between pentadienyllithium and tributyltin chloride reacts with bromopentacarbonylrhenium in refluxing tetrahydrofuran according to the equation

$$\mathrm{Bu_3SnCH_2CH{=}CHCH{=}CH_2 + BrRe(CO)_5 \xrightarrow[\text{reflux}\ 9\ \text{h}]{\text{THF}} \underset{\text{(I)}}{(C_5H_7)Re(CO)_3} + Bu_3SnBr}$$

The product I was isolated from the reaction mixture by chromatography on alumina followed by vacuum sublimation. It is a white crystalline material which, like its manganese analogue, decomposes slowly in air. The ^{1}H NMR spectrum (in C_6D_6) (250 MHz) is consistent with a symmetrical structure for the η^5pentadienyl ligand.

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* For part III, see ref. 1.

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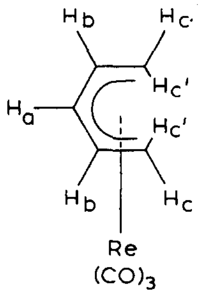

(I)

^{1}H NMR: δ 0.40 [d, $H_{c'}$, $J(H_bH_{c'})$ = 11.3 Hz]; 2.35 [d, H_c, $J(H_bH_c)$ = 10.3 Hz]; 4.42 [m, H_b]; 4.68 ppm [t, H_a, $J(H_aH_b)$ = 6.3 Hz]. Each resonance possesses fine structure indicating coupling constants $J(H_cH_{c'}) \sim$ 2.5 Hz, and long range couplings $J(H_aH_c)$ and $J(H_aH_{c'}) \sim$ 0.9 Hz.

Experimental

All operations were conducted under dry nitrogen. Solvents were dried by standard methods before use.

Preparation of 2,4-pentadienyltributyltin

To a solution of pentadienyllithium [3] (74 mmol) in tetrahydrofuran (125 cm^3) tributyltin chloride (24.1 g, 74 mmol) was added with stirring at —70°C. The reaction mixture was allowed to warm up to room temperature over 40 min and the solvents were removed in vacuo. Hexane (30 cm^3) was added and the precipitate of lithium chloride was filtered off. Distillation of the filtrate afforded the title compound (24.6 g, 94%) b.p. 102—105°C at 0.1 mm Hg. Anal. Found: C, 56.77; H, 9.16. Calcd. for $C_{17}H_{34}Sn$: C, 57.17; H, 9.60%.

The ^{1}H NMR spectrum (250 MHz in $CDCl_3$) showed the presence of two isomers, in the approximate ratio 4 : 1. The major isomer is assigned the *E* configuration on account of the similarity of its NMR spectrum with that of *E*-1-trimethylsilyl-2,4-pentadiene [3].

^{1}H NMR (*E* isomer): δ 0.89 (m, 15H), 1.31 (m, 6H), 1.49 (m, 6H), 1.81 (d, *J* 7.7 Hz, 1H), 4.78 (dd, *J* 9.8, 2.0 Hz, 1H) 4.94 (dd, *J* 16.8, 2.0 Hz, 1H), 5.70 (m, 1H), 5.90 (m, 1H), 6.27 ppm (dt, *J* 17.0, 9.6 Hz, 1H). The minor isomer showed resonances at 1.91 (d, *J* 7.7 Hz), 4.95 (dd, *J* 9.8, 2.2 Hz) 5.06 (dd, *J* 16.9, 2.2 Hz), 6.61 ppm (dt, *J* 16.9, 10.1 Hz). We prefer to assign a multiplet at δ 5.70 ppm to the *E* isomer rather than the one at δ 6.61 ppm on the basis of intensity measurements. (Compare Seyferth's assignments for 2,4-pentadienyltrimethyltin) [2].)

Preparation of η^5-pentadienyltricarbonylrhenium, I

Bromopentacarbonylrhenium [4] (5.9 g 14.5 mmol) in tetrahydrofuran (150 cm^3) was heated under reflux with 2,4-pentadienyltributyltin (5.2 g, 14.5 mmol) until no further change in the infrared spectrum of the mixture was observed (9 h). The pale yellow solution was evaporated to small bulk and filtered from a white precipitate. The filtrate was taken up in hexane and chromatographed on alumina using petroleum ether (b.p. below 40° C). The first colourless band afforded white crystals (1.23 g) which were purified by sublimation at 60°C and 0.3 mm Hg to give 0.73 g (15%) of the title compound, m.p. 70—72°C.

Anal. Found: C, 28.49; H, 1.90. Calcd. for $C_8H_7O_3Re$: C, 28.48; H, 2.09%. Mass spectrum, *m/e*: 338 (M^+); 310 ($M^+ - CO$); 282 ($M^+ - 2\ CO$); 254 ($M^+ - 3\ CO$).

Raman spectrum (solid): 2018m, 1946m, 1935m, 1915s, 1510w, 1098w, 1008m, 940s, 530m, 525(sh). 500vs, 385s, 345s, 310m, 285m, 120s cm^{-1}.

IR spectrum (in $CHCl_3$) (νCO): 2030vs, 2018(sh), 1945vs, 1922vs cm^{-1}.

Raman spectrum (solid) $[Mn(\eta^5\text{-}C_5H_7)(CO)_3]$: 2018m, 1946s, 1935s, 1918vs, 1915w, 1518w, 1468w, 1458w, 1240w, 1098(br), 1012m, 1003m, 978s, 950s, 918s, 902w, 670s, 658w, 640w, 535s, 528s, 500vs, 497s, 468s, 385vs, 355vs, 318vs, 305vs, 162s cm^{-1}.

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