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η^5-PENTADIENYLTRICARBONYLMANGANESE, AN "OPEN" ANALOG OF CYMANTRENE

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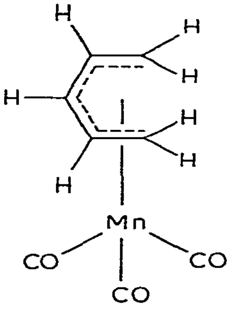
Summary

2,4-Pentadienyltrimethyltin, obtained by the reaction of pentadienyllithium with trimethyltin chloride, reacted with bromopentacarbonylmanganese in refluxing tetrahydrofuran to give η^5-pentadienyltricarbonylmanganese in 52% yield.

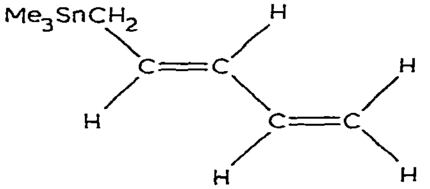
The report by Wilson, DiLullo and Ernst [1] of the synthesis and characterization of several bis(η^5-pentadienyl)iron complexes ("open ferrocenes") prompts us to provide details of our preparation of η^5-pentadienyltricarbonylmanganese, I, the "open" analog of cymantrene, η^5-cyclopentadienyltricarbonylmanganese.



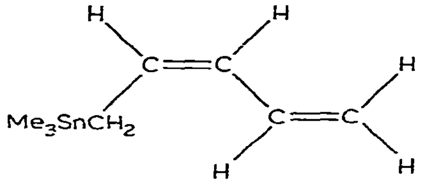
(I)

We were led to our synthesis of I by our studies of the preparation and utilization in organic synthesis of 2,4-pentadienyltrimethylsilane, $Me_3SiCH_2CH=CHCH=CH_2$ [2]. The latter reagent was obtained by the action of pentadienyllithium [3] on trimethylchlorosilane. A similar reaction of pentadienyllithium, with trimethyltin chloride provided 2,4-pentadienyltrimethyltin,

$Me_3SnCH_2CH{=}CHCH{=}CH_2$, in high yield, as a mixture containing 4 parts of the *E* isomer, II*E*, and 1 part of the *Z* isomer, II*Z*.



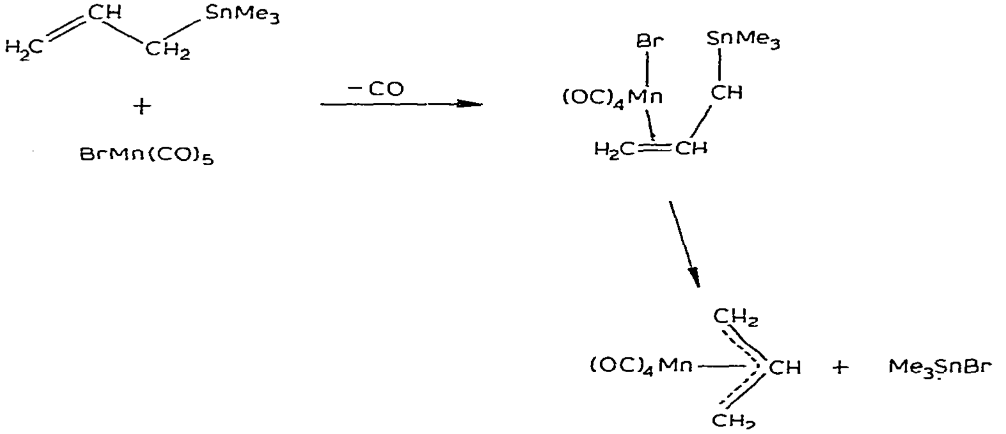
(II *E*)



(II *Z*)

Allylsilanes are known to undergo Lewis acid-induced allylation of the C=O function of aldehydes and ketones [4]. Our application of 2,4-pentadienyltrimethylsilane as a carbonyl pentadienylation reagent had been developed by considering this compound as an extended allylsilane and it seemed of interest to search for useful applications of 2,4-pentadienyltrimethyltin using the same allyl/pentadienyl analogy.

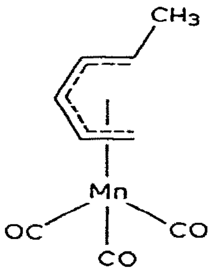
Allylic tin compounds have been demonstrated to be useful reagents for the preparation of π-allyl derivatives of transition metals [5,6]. For instance, the reaction of allyltrimethyltin with bromopentacarbonylmanganese gave η^3-allyltetracarbonylmanganese (eq. 1). It was of particular interest that Abel and Moorhouse [5] claimed the isolation of a methyl-substituted η^5-pentadienyltricarbonylmanganese complex, III, which was formed in the reaction of hexadienyltrimethyltin (a mixture of 3-trimethylstannylhexa-1,5-diene and 1-trimethylstannylhexa-2,5-diene) with bromopentacarbonylmanganese. The claimed product, however, was characterized only by analysis and the statement that its IR and NMR spectra showed the presence of a methyl group.



(1)

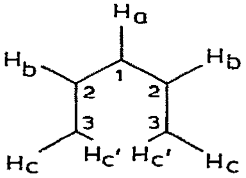
In analogy to the reaction of allyltrimethyltin shown in eq. 1, we found that 2,4-pentadienyltrimethyltin reacts with bromopentacarbonylmanganese to give a yellow, crystalline, sublimable organomanganese carbonyl, m.p. 101—101.5°C, in 52% yield (eq. 2). The C, H analysis and the mass spectrum agreed with the

$$Me_3SnCH_2CH{=}CHCH{=}CH_2 + BrMn(CO)_5 \xrightarrow[4\ h]{THF,\ reflux} (C_5H_7)Mn(CO)_3 + Me_3SnBr \quad (2)$$



(III)

formulation shown for the product. That it has the structure shown in I was demonstrated clearly by its proton and ^{13}C NMR spectra. In both the symmetrical structure of the C_5H_7 ligand was evident:



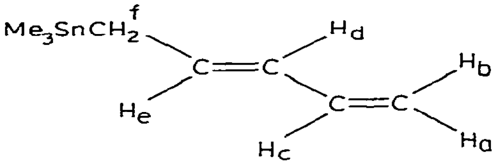
^{13}C NMR spectrum (in $CDCl_3$): δ_C 57.52 (t of d, C_3, $J(CH) = 161$ Hz, $J(CH_b) = 9$ Hz); 83.34 (d of t, C_1, $J(CH) = 170$ Hz, $J(CH_b) = 11$ Hz); 100.14 (d of d, C_2, $J(CH) = 163$ Hz, $J(CH_{a,c}) = 10$ Hz); 221.90 ppm (broad, CO). ^1H NMR spectrum (in $CDCl_3$) (90 MHz): δ 0.61 (d, $J = 12$ Hz, 2 H, $H_{c'}$); 2.95 (d, $J = 10$ Hz, 2 H, H_c); 5.15 (m, 2 H, H_b); 5.67 ppm (m, 1 H, H_a). The similarity of I and its "closed" analog, η^5-cyclopentadienyltricarbonylmanganese, is noteworthy. The latter is a pale yellow, crystalline solid which sublimes readily a little above room temperature in vacuum [7] and as the solid it is stable to air and light. Compound I, on the other hand, appears to be less robust; its crystals decompose slowly in air.

In principle, there should exist an open η^5-pentadienyl complex for every known η^5-cyclopentadienyl-metal derivative. It would be of interest to probe this possibility in depth and to compare the physical and chemical properties of each "closed" and "open" pair.

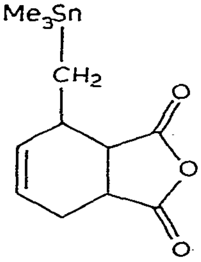
Experimental

Preparation of 2,4-pentadienyltrimethyltin

A 250 ml three-necked, round-bottomed flask fitted with a nitrogen inlet tube, a magnetic stir-bar, a pressure-equalizing addition funnel and a serum cap was flame-dried under a brisk stream of nitrogen, which was continued while the apparatus was cooling. The flask was charged with 28.2 ml of 2.3 *M* (0.065 mol) of n-butyllithium in hexane (Alfa/Ventron) and 10 ml of dry tetrahydrofuran (THF). The solution was cooled immediately to —78°C and then 4.27 g (6.46 ml, 0.065 mol) of 1,4-pentadiene (Chemical Samples) was added by syringe. The reaction mixture was stirred and was allowed to warm slowly to room temperature. After the resulting yellow-orange solution of pentadienyllithium [3] had been stirred for 1 h, it was cooled to 0°C and a solution of 12.47 g (0.063 mol) of trimethyltin chloride in 10 ml of THF was added dropwise. After the addition had been completed a cloudy white solution was present. The mixture was stirred at room temperature for 3 h, and then was hydrolyzed by the addition of 30 ml of saturated aqueous ammonium chloride. The aqueous layer was separated and washed with three 30 ml portions of diethyl ether. The washings and the organic layer were combined, dried over anhydrous potassium carbonate, filtered and concentrated at reduced pressure. Short-path distillation of the residue gave 12.34 g (0.053 mol, 82%) of the title compound, b.p. 78°C at 23 mm, n_D^{25} 1.5141. Anal. Found: C, 41.57; H, 7.02. Calcd. for $C_8H_{16}Sn$: C, 41.61; H, 6.98%. The 270 MHz proton NMR spectrum (CCl_4) showed that a mixture of the *E* and *Z* isomers was present. Integration of the $SnCH_2$ signals (*E* isomer at 1.89 ppm, *Z* isomer at 2.00 ppm) showed the *E*/*Z* ratio = 4. The ^1H NMR spectrum of the *E* isomer showed: δ 0.16 (s, 9 H, Me_3Sn, with ^{117}Sn and ^{119}Sn satellites), 1.89 (d, *J*(fe) = 9.2 Hz, CH_2), 4.78 (d, *J*(ac) = 10.3 Hz, H_a), 4.93 (d, *J*(bc) = 16.8 Hz, H_b), 5.88 (d of d, *J*(dc) = 10.3 Hz, *J*(de) = 16.2 Hz, H_d), 6.28 (d of t, *J*(ed) = 16.2 Hz, *J*(ef) = 9.2 Hz, H_e) and 6.59 ppm (d of d of d, *J*(ca) = 10.3 Hz, *J*(cb) = 16.8 Hz, *J*(cd) = 10.3 Hz, H_c).



Treatment of the II*E*/II*Z* mixture with maleic anhydride (4.3 mmol each) in 1 ml of toluene under argon for 1 h at 80°C, gave, after removal of the solvent, the expected Diels-Alder adduct, IV, in 65% yield. Recrystallization from hexane gave material with m.p. 51°C. Anal. Found: C, 44.21; H, 5.48. Calcd. for $C_{12}H_{18}O_3Sn$: C, 43.81; H, 5.50. ^1H NMR (60 MHz, in CCl_4): δ 0.10 (s, 9 H, Me_3Sn, with ^{117}Sn and ^{119}Sn satellites), 1.05—1.45 (m, 2 H, $SnCH_2$), 2.20—3.60 (m, 5 H, aliphatic ring H) and 5.80—6.10 ppm (m, 2 H, CH=CH).



(IV)

Preparation of η^5-pentadienyltricarbonylmanganese, I

A 100 ml, three-necked flask equipped with a nitrogen inlet tube, a magnetic stir-bar, a Claisen condenser and a serum cap was flame-dried, flushed with nitrogen and charged with 2.07 g (7.53 mmol) of bromopentacarbonylmanganese [8], 1.88 g (8.14 mmol) of 2,4-pentadienyltrimethyltin and 20 ml of dry THF. The reaction mixture was stirred and heated at reflux under nitrogen for 4 h. During this time the color of the solution changed from red to orange-yellow. The reaction mixture then was allowed to cool to room temperature and 35 ml of deaerated distilled water was added. A yellow-orange oil separated. The mixture was extracted with 30 ml of anhydrous diethyl ether. The ether solution was dried ($MgSO_4$), filtered and evaporated at reduced pressure. The yellow oil which remained was sublimed at 35°C and 0.07 mmHg to give 0.81 g (3.93 mmol, 52%) of yellow crystals of the title compound. Resublimation gave an analytical sample with m.p. 101.0—101.5°C. Anal. Found: C, 46.32; H, 3.47. Calcd. for $C_8H_7O_3Mn$: C, 46.63; H, 3.42%. IR spectrum (Perkin Elmer 457A, in CCl_4): 2016vs, 2007(sh), 1957vs, 1940(sh), 1937vs, 1678m, 1613m, 1489w, 1353(br) cm^{-1}. Mass spectrum (Varian MAT-44, 70 eV), m/e: 206 (9.97, M^+), 178 (26, $[M - CO]^+$), 150 (26, $[M - 2\ CO]^+$), 122 (100, $[M - 3\ CO]^+$), 67 (34.3, $C_5H_7^+$), 55 (86, Mn^+).

The NMR spectra were recorded using a JEOL FX-90Q NMR spectrometer, at 25.2 MHz for ^{13}C NMR spectra and 90 MHz for ^1H NMR spectra. Chemical shifts are given in δ_C and δ, ppm downfield from internal tetramethylsilane.

Acknowledgements

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References

1 D.R. Wilson, A.A. DiLullo and R.D. Ernst, J. Amer. Chem. Soc., 102 (1980) 5928.
2 D. Seyferth and J. Pornet, J. Org. Chem., 45 (1980) 1722.
3 R.B. Bates, D.W. Gosselink and J.A. Kaczynski, Tetrahedron Lett., (1967) 199, 205.
4 J.A. Mangravite, J. Organometal. Chem. Library, 7 (1979) 45.
5 E.W. Abel and S. Moorhouse, J. Chem. Soc. Dalton Trans., (1973) 1706.
6 (a) P.L. Maxfield, Inorg. Nucl. Chem. Lett., 6 (1970) 707; (b) M. Fishwick and M.G.H. Wallbridge, J. Organometal. Chem., 25 (1970) 69.
7 T.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 165.
8 R.B. King, Vol. 1, in J.J. Eisch and R.B. King (Ed.), Organometallic Syntheses, Academic Press, New York, 1965, pp. 174—175.