Journal of Organometallic Chemistry, 320 (1987) 211–216
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF PENTACARBONYL(η^1-2,4-PENTADIENYL)MANGANESE

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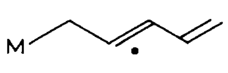
(Received April 14th, 1986; in revised form August 25th, 1986)

Summary

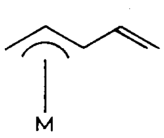
Reaction of $NaMn(CO)_5$ with *trans*-1-bromopenta-2,4-diene in tetrahydrofuran at −78°C gives (η^1-2,4-pentadienyl)$Mn(CO)_5$ (**1**) in excellent yield. Compound **1** undergoes $\eta^1 \rightarrow syn\text{-}\eta^3 \rightarrow \eta^5$ transformation and, yields (*syn*-η^3-2,4-pentadienyl)$Mn(CO)_4$ (**2**) and (η^5-pentadienyl)$Mn(CO)_3$ (**3**), respectively. The reactions of **1** with the electrophiles tetracyanoethylene (TCNE) and sulfur dioxide (SO_2) were investigated. Compound **1** undergoes a [4 + 2] cycloaddition with TCNE and an insertion reaction with SO_2. The products are characterized by elemental analysis and spectroscopic data.

Introduction

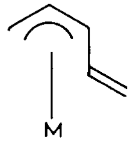
The chemistry of transition-metal acyclic pentadienyl complexes has recently attracted considerable attention [1,2]. A series of pentadienyl alkaline-metal salts C_5H_7M (M = Li, Na, K) or its higher analogues [3] have been used for the synthesis of these complexes. For the pentadienyl compounds, η^1, *syn*-η^3, and η^5 configurations are possible and the bonding mode varies depending on the nature of metal and ligand. For example, $Cp_2Zr(4\text{-}CH_3C_5H_6)_2$ assumes an η^1 configuration [4], and $(PR_3)(C_5H_7)Mn(CO)_3$ prefers the *anti*-η^3 [5], and a variety of η^5 compounds are known for the open metallocenes [1]. Recently we have prepared acyclic pentadienyl complexes of iron [6], cobalt [7] and molybdenum [8] from 1-halopenta-2,4-diene.



η^1



syn-η^3



anti-η^3

η^5

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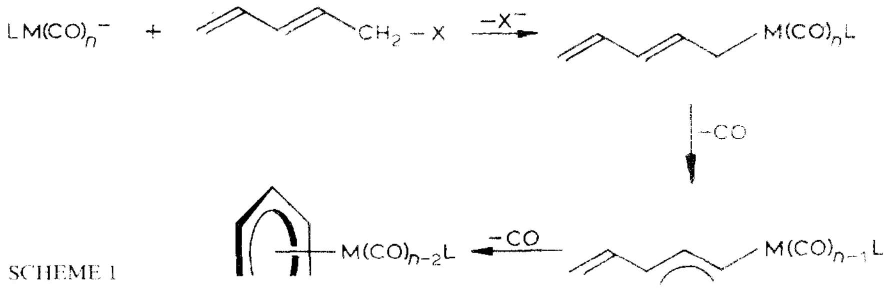


SCHEME 1

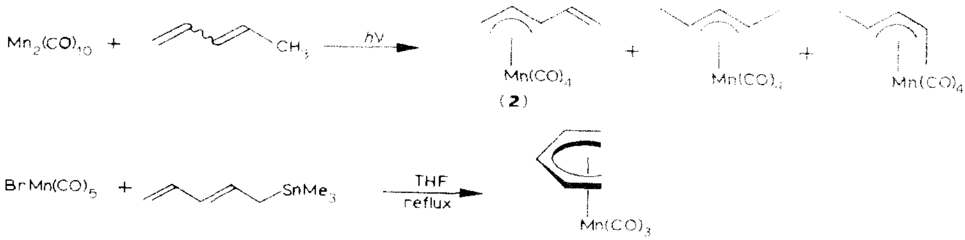
1-Halopenta-2,4-diene seems to be of greater benefit than pentadienyl alkaline-metal salts in the synthetic pathway because it reacts with metal carbonyl anions e.g. $CpFe(CO)_2^-$ [6], $Co(CO)_4^-$ [7] and $CpMo(CO)_3^-$ [8] in a more controllable pathway as depicted in Scheme 1.

Further ligand modification of the compounds in principle is made possible since the remaining CO groups have the potential to be exchanged.

Acyclic pentadienyl manganese complexes (*syn*-η^3-pentadienyl)$Mn(CO)_4$ (**2**) [9] and (η^5-pentadienyl)$Mn(CO)_3$ (**3**) [10] have been prepared before, but from the following independent routes. In this paper, beside the report on the synthesis of (η^1-2,4-pentadienyl)$Mn(CO)_5$ (**1**), we also describe its photo-induced conversion to **2**, and its thermal conversion to **3**. The reactions of **1** with the electrophiles tetracyanoethylene (TCNE) and sulfur dioxide were investigated and are discussed.

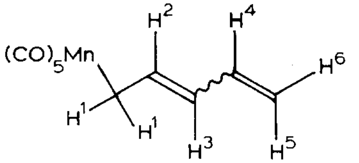
Results and discussion

When a tetrahydrofuran solution of *trans*-1-bromopenta-2,4-diene was stirred with one equivalent of $NaMn(CO)_5$ at −78°C for 3 h, a smooth reaction occurred to yield (η^1-2,4-pentadienyl)$Mn(CO)_5$ (**1**). After the solvent was removed, and the residues vacuum distilled, the yellow oil of **1** was obtained in high yield (82%). Both elemental analysis and mass spectrum conform to the formula. The pentadienyl group is linked to the manganese center in an η^1 configuration as shown by its ^1H NMR spectrum (100 MHz, C_6D_6): δ 1.98(d, H1, 2H, J_{12} 6 Hz), 5.00(dd, H6, 1H, J_{46} 11 Hz, J_{56} 1 Hz), 5.16(dd, H5, 1H, J_{45} 17 Hz, J_{56} 1 Hz), 6.08–6.60(complex m, H2, H3 and H4, 3H) ppm. Moreover, the IR spectrum in pentane shows a weak ν(C=C) band at 1628 cm^{-1}, and strong ν(C≡O) bands at 2108, 2080, 2025 and 2000 cm^{-1}. The four observed carbonyl frequencies are in good agreement with the data reported for compounds of the type $RMn(CO)_5$ (R = alkyl, allyl) [11]. These



SCHEME 2

spectroscopic data suggest the structure of **1** as represented below:



(**1**)

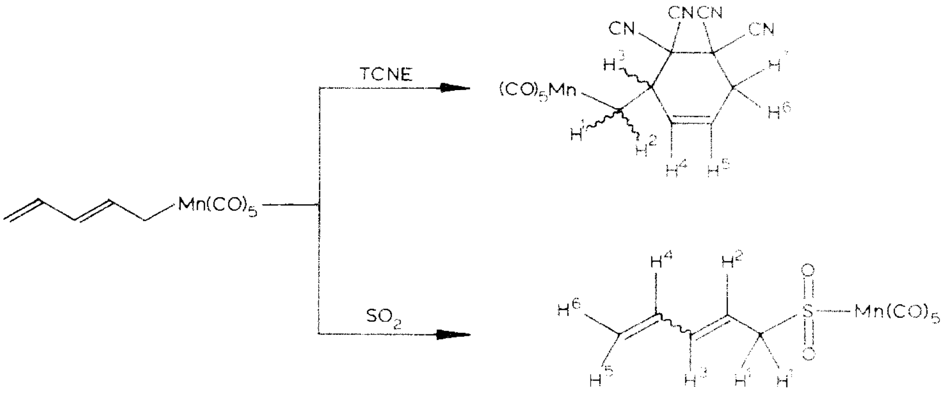
Photolysis of an ethereal solution of **1** at −20°C for 12 h gave (*syn*-η^3-pentadienyl)Mn(CO)$_4$ (**2**) in excellent yield (79%). No η^5-pentadienylmanganese compound (**3**) was formed under prolonged irradiation. Thermolysis of **1** in cyclohexane at reflux failed to produce **2** in significant amounts owing to the facile conversion to **3** (vide infra). The ^{1}H NMR, IR and mass spectroscopic data of **2** show that the pentadienyl group is bound to the manganese center in a *syn*-η^3 configuration. Although compound **2** can be prepared by photolysis of Mn$_2$(CO)$_{10}$ with *cis*- and *trans*-pentadiene as depicted in Scheme 2, the yields were low owing to the presence of (η^3-*E*,*E*-3-penten-2-yl)Mn(CO)$_4$ and (η^3-*Z*,*E*-3-penten-2-yl)Mn(CO)$_4$. Our method for synthesis of **2** appears to be more productive and selective.

Direct conversion of **1** to the η^5-pentadienylmanganese compound (**3**) was achieved by refluxing **1** in a cyclohexane solution for 24 h. Solution IR spectroscopic studies indicated that a minor amount of **2** was present as the solution intermediate. Pale-yellow crystals off **3** were obtained in good yield (71%) after workup. The spectroscopic data of **3** were identical to those of the authentic sample [8].

The reaction of NaRe(CO)$_5$ with 1-bromopenta-2,4-diene failed to produce the expected product (η^1-2,4-pentadienyl)Re(CO)$_5$, giving a mixture of Re$_2$(CO)$_{10}$ and 1,3,7,9 decatetraene. The products may have arisen from the thermal decomposition of (η^1-2,4-pentadienyl)Re(CO)$_5$ which occurs too rapidly at ambient temperatures to allow isolation. Powell and coworkers [12] have recently reported the synthesis of (η^5-pentadienyl)Re(CO)$_3$ from the reaction of (η^1-2,4-pentadienyl)Me$_3$Sn and Re(CO)$_5$Br. The rhenium η^1-pentadienylrhenium complex is an unlikely reaction intermediate because of its high thermal instability. The mechanism is most likely to be similar to that of the reaction of Re(CO)$_5$Br with (η^1-allyl)Me$_3$Sn where double bond coordination is a prerequisite [13].

Transition-metal η^1-allyl complexes have been used extensively in many organic reactions, the most notable example of which is [3 + 2] cycloaddition to many different electrophiles [14]. One of our aims for the synthesis of transition-metal η^1-pentadienyl complexes was to explore their potential in organic reactions because of their close resemblance to metal η^1-allyl compounds.

The reaction of **1** with the electrophiles SO$_2$ and TCNE has thus been investigated. Stirring a dichloromethane solution of **1** with tetracyanoethylene at 23°C for 1 h gave the [4 + 2] cycloaddition adduct in good yield (80%) after the solvent had been removed. A more convenient preparation involved benzene as the solvent, which gave complete precipitation of the product within one hour at 23°C. After recrystallization from acetone/hexane, pale white crystals were obtained in good yield (80%). The elemental analyses conform to the formulated structure. The proposed structure is easily confirmed from its ^{1}H NMR spectrum (acetone-d_6)



SCHEME 3

which shows the resonances of H1 and H2 as an AB quartet at δ 0.8 – 1.4 ppm, further split by H3. The IR spectrum (KBr) gives the absorption bands $\nu(C=C)$ at 1655(w) cm^{-1} and $\nu(C\equiv N)$ at 2230(w) cm^{-1}, which are consistent with the structure.

Slow bubbling of SO_2 through a rapidly stirring hexane solution of **1** at 23°C for 6 h gave a yellow precipitate. After crystallization from $CHCl_3$/hexane, the pale yellow crystals were obtained in moderate yield (51%). The compound contains the *S*-sulfinate group as inferred from its IR spectrum which shows the bands of $\nu(C=C)$ at 1600 cm^{-1}, $\nu_{as}(SO)$ and $\nu_{as}(SO)$ at 1190(vs) and 1048(vs) cm^{-1} respectively. The observed $\nu(SO)$ bands are in good agreement with the data for compounds of the type $(CO)_5Mn-SO_2R$ (R = methyl, benzyl and allyl) [15]. In the ^1H NMR spectrum, the doublet centered at δ 4.06 ppm of the methylene group shows that the pentadienyl group is bound to the SO_2 group [15]. The elemental analyses conform to the structure formulated.

Here we present the first example of transition-metal pentadienyl compounds which undergo Diels–Alder reactions and SO_2 insertion. Previously, only the [4 + 2] cycloaddition and electrophilic reactions of metal pentadienyl complexes of main group compounds such as (η^1-2,4-pentadienyl)Me_3M (M = Si, Sn) [16] were studied. The metal–carbon bonds of many transition-metal complexes often undergo carbonylation and insertion reactions. In principle, compound **1** could become a very useful reagent in organic synthesis if its reactivities with dienophiles were to be extensively studied.

Experimental

All reactions were carried out under dry nitrogen using Schlenk tube techniques. *trans*-1-Bromopenta-2,4-diene was synthesized by treatment of penta-1,4-dien-3-ol with HCl (aq) at 0°C [17]. The preparation of $NaMn(CO)_5$ followed the procedure reported in the literature [18]. NMR spectra were recorded on a JEOL FX-100 spectrometer. Microanalyses were performed by the Microanalytic Laboratory at the National Taiwan University.

Preparation of (η^1-2,4-pentadienyl)Mn(CO)$_5$ (1)

A tetrahydrofuran solution of NaMn(CO)$_5$ (2.0 g, 9.18 mmol) was stirred with *trans*-1-bromopenta-2,4-diene (1.46 g, 10.0 mmol) at −78°C for 4 h. After the insoluble sodium amalgam residues had been filtered off at −78°C, the solution was warmed to 0°C, the solvent removed under reduced pressure leaving a red residue. Repeated purification of this residue by vacuum distillation (4×10^{-3} Torr) at 23°C into a 0°C cold trap several times afforded the yellow oil of **1** (1.97 g, 7.52 mmol). Mass spectrum, m/e: 262(M^+), Anal. Found: C, 45.55; H, 2.89. $C_{10}H_7MnO_5$ calc: C, 45.83; H, 2.68%.

Preparation of (syn-η^3-2,4-pentadienyl)Mn(CO)$_4$ (2) from 1

A vacuum-sealed pyrex tube containing a 20 ml ether solution of **1** (1.00 g, 3.80 mmol) was irradiated by a 400 watt mercury lamp for 12 h. The solvent was removed in vacuo at 0°C leaving an oil. Further vacuum distillation of the oil at 23°C into a −25°C cold trap gave the yellow oil of **2** (0.71 g, 3.00 mmol). The ^{1}H NMR, IR and mass spectra of **2** were identical to those of the authentic sample reported by Kreiter et al. [9].

Preparation of (η^5-pentadienyl)Mn(CO)$_3$ (3) from 1

A cyclohexane solution of **1** (1.00 g, 3.80 mmol) was heated under reflux for 24 h. The solvent was removed in vacuo at 0°C to give yellow a residue. Further sublimation of the residue at 40°C gave yellow crystals of **3** (0.57 g, 2.70 mmol). The ^{1}H NMR, IR and mass spectra of **3** were identical to those of the authentic sample reported by Seyferth et al. [10].

Reaction of 1 with tetracyanoethylene

Tetracyanoethylene (0.25 g, 2.00 mmol) and compound **1** (0.48 g, 1.85 mmol) were dissolved in 20 ml benzene and stirred at 23°C for 1 h. The white precipitate that formed during this period was collected by filtration, and recrystallized from hexane/acetone to give white crystals (0.62 g, 1.60 mmol). Anal. Found: C, 48.89; H, 1.78; N, 15.07. $C_{16}H_7MnN_4O_5$ calc: C, 48.25; H, 1.80; N, 14.36%. IR spectrum (KBr) ν(C≡N): 2230(w); ν(CO): 2121(s), 2049(s), 2004(br,vs) cm^{-1}; ν(C=C) 1655(w) cm^{-1}. ^{1}H NMR spectrum (100 MHz, acetone-d_6) δ 0.84 (dd, 1H, H1, J_{12} 13 Hz, J_{13} 11 Hz), 1.32 (dd, 1H, H2, J_{12} 13 Hz, J_{23} 2 Hz), 3.00 – 3.60 (complex m, 3H, H3 + H6 + H7), 5.92 (br s, 2H, H4 + H5) ppm.

Reaction of 1 with SO$_2$

SO$_2$ was slowly bubbled through a 20 ml hexane solution of **1** (0.5 g, 1.90 mmol) at 23°C and the mixture was rapidly stirred for 6 h. The yellow precipitate that formed during this period was collected by filtration. Recrystallization from chloroform/hexane gave yellow crystals (0.32 g, 0.98 mmol). Anal. Found: C, 36.52; H, 2.01. $C_{10}H_7MnO_7S$ calc: C, 36.81; H, 2.14%. IR spectrum (KBr): ν(CO): 2142(s), 2094(s), 2040(br,vs), 2004(s) cm^{-1}; ν(C=C): 1600(w) cm^{-1}; ν(SO): 1190(vs), 1048(vs) cm^{-1}. NMR spectrum (CDCl$_3$): δ 4.06 (br d, 2H, H1, J_{12} 7 Hz), 5.00 – 5.40 (br m, 2H, H5 + H6), 5.6 – 6.5 (br m, 3H, H2 + H3 + H4) ppm.

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