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A new preparation of tricarbonyl(η^5-pentadienyl)manganese

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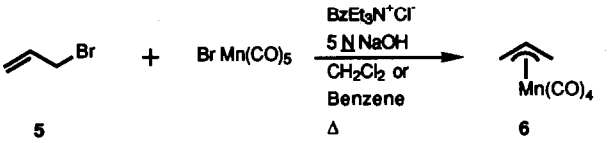
Abstract

Tricarbonyl(η^5-pentadienyl)manganese has been prepared by the reaction of 5-bromo-1,3-pentadiene with bromopentacarbonyl manganese under phase transfer catalysis conditions in the presence of a base. A comparison of phase transfer catalysts, solvents, bases and reaction conditions is described.

1. Introduction

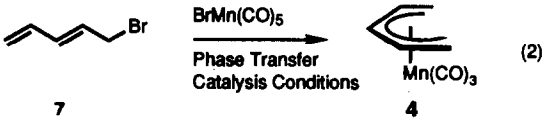
The chemistry of η^5-pentadienyl transition metal complexes has attracted considerable interest in recent years, with particular emphasis on their preparation and reactivity [1–4]. Our interest in the chemistry of tricarbonyl(η^5-pentadienyl)manganese complexes [4b] prompted us to investigate economical and safe methods for their preparation. The literature contains two routes to complex **4** (Fig. 1). The preparation by Seyferth *et al.* [5] utilizes the reaction of pentadienyllithium and chlorotrimethylstannane to generate the dienylstannane **2**, followed by reaction with bromopentacarbonyl manganese in refluxing tetrahydrofuran to generate tricarbonyl(η^5-pentadienyl)manganese (**4**). Although this route is relatively simple to carry out, 1,4-pentadiene is expensive [6*], and chlorotrimethylstannane is both expensive [7*] and highly toxic. The method of Lee and Liu [8] consists of the reaction of sodium pentacarbonylmanganate, prepared by the reaction of Na–Hg with $Mn_2(CO)_{10}$, with 5-bromo-1,3-pentadiene (**3**). This preparation proved difficult to carry out as the overall yields were low and the desired product **4** was always contaminated with significant amounts of manganese-containing by-products.

Our approach to the synthesis of complex **4** followed the work of Gibson *et al.* [9] who have reported the preparation of π-allyl manganese complex **6** by the reaction of allyl bromide (**5**) with bromopentacarbonyl manganese under phase transfer catalysis conditions (eqn. (1)). It was expected that the analogous approach



5 6 (1)

to (η^5-pentadienyl)manganese complex **4** would therefore involve the reaction of 5-bromo-1,3-pentadiene (**7**) [10] with bromopentacarbonyl manganese [11] under similar conditions (eqn. (2)). Formation of the η^5-com-



7 4 (2)

plex would require only the replacement of one additional carbon monoxide group with the second olefin group. Initial experiments utilizing Gibson's conditions provided promising results (Table 1, entries 1–3), although with relatively low yields. Therefore, a survey of phase transfer catalysts, solvents, bases and reaction conditions was undertaken (Table 1). It was determined that a yield of 82% of tricarbonyl(η^5-pentadienyl)manganese (**4**) could be achieved using $^nBu_4NBr$ as the phase transfer catalyst, dichloromethane as the organic solvent, and sodium hydroxide as the base (entry 12). The optimal reaction time was approximately 24 hours, with longer reaction times leading to

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* Reference number with asterisk indicates a note in the list of references.

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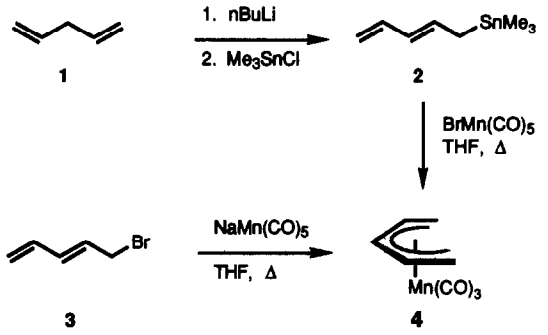
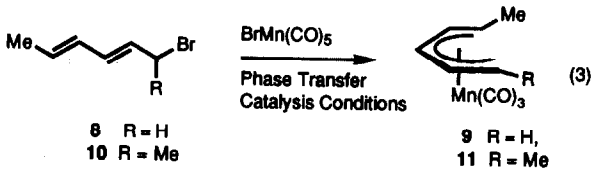


Fig. 1.

decomposition of the desired product (entry 12 *vs.* entry 13). It should be noted that, in general, use of $^nBu_4NBr$ as the phase transfer catalyst led to significantly higher yields compared to other phase transfer catalysts. Although the use of dichloromethane or toluene gave similar results, workup was much simpler using dichloromethane. Use of sodium hydroxide or potassium hydroxide as the base gave comparable yields (entry 1 *vs.* entry 8; entry 10 *vs.* entry 11), but attempts to utilize sodium carbonate as the base gave less satisfactory results (entries 5, 6, 14, 15). Finally, it should be noted that large excesses of 5-bromo-1,3-pentadiene failed to increase the overall yield of the reaction, and in fact in some cases led to lower yields (entry 9 *vs.* entry 10).

This method could also be applied to the preparation of tricarbonyl(η^5-hexadienyl)manganese (**9**), by replacing 5-bromo-1,3-pentadiene (**7**) with 1-bromo-2,4-hexadiene (**8**) [10] (eqn. (3), R = H). In this case, however, utilizing the optimized reaction conditions determined for complex **4** ($^nBu_4NBr$ as the phase transfer catalyst, dichloromethane as the solvent, and sodium hydroxide as the base, reflux for 24 h), complex **9** was produced in only 36% yield. Variation of these reaction conditions failed to increase the yield. Attempts to prepare the disubstituted complex **11** by reaction of 6-bromo-2,4-heptadiene (**10**) provided only trace amounts of the desired product. Apparently these more substituted bromides are sensitive to the strongly basic conditions utilized in this procedure.



A procedure has therefore been developed which allows for the preparation of tricarbonyl(η^5-pentadienyl)manganese (**4**) in good yields without the use of expensive or toxic starting materials. Attempts are underway to extend this general procedure to more complicated substrates.

TABLE 1. Reaction conditions for preparation of tricarbonyl(η^5-pentadienyl)manganese (**1**)

Entry	PTC [a]	Solvent	Base [b]	Method [c]	Time (h)	Yield (%)
1	TEBA	CH_2Cl_2	NaOH	A	18	28
2	TEBA	Benzene	NaOH	A	18	28
3	TEBA	Benzene	NaOH	B	18	31
4	TEBA	Toluene	NaOH	A	18	35
5	TEBA	CH_2Cl_2	Na_2CO_3	C	18	21
6	TEBA	CH_2Cl_2	Na_2CO_3	B	18	32
7	TEBA	CH_2Cl_2	NaOH	D	18	24
8	TEBA	CH_2Cl_2	KOH	A	18	33
9	$^nBu_4Br$	CH_2Cl_2	NaOH	B	18	36
10	$^nBu_4Br$	CH_2Cl_2	NaOH	C	18	57
11	$^nBu_4Br$	CH_2Cl_2	KOH	C	18	56
12	$^nBu_4Br$	CH_2Cl_2	NaOH	C	24	82
13	$^nBu_4Br$	CH_2Cl_2	NaOH	C	42	70
14	$^nBu_4Br$	CH_2Cl_2	Na_2CO_3	A	18	26
15	$^nBu_4Br$	Toluene	Na_2CO_3	A	18	25
16	TMBA	CH_2Cl_2	NaOH	C	24	46

[a] TEBA is triethylbenzylammonium chloride, $^nBu_4Br$ is tetrabutylammonium bromide, TMBA is trimethylbenzylammonium chloride.
[b] In each case the concentration of the base was 5 m.
[c] Reaction conditions were as follows: (A) 5.0 eq. diene, 1.0 eq. bromopentacarbonyl manganese, 0.5 eq. phase transfer catalyst; (B) 5.0 eq. diene, 1.0 eq. bromopentacarbonyl manganese, 2.5 eq. phase transfer catalyst; (C) 2.0 eq. diene, 1.0 eq. bromopentacarbonyl manganese, 2.8 eq. phase transfer catalyst; (D) Concentrations identical to (C) but diene added dropwise to reaction mixture during reflux.

2. Experimental details

2.1. General

Pentacarbonylmanganesebromide was prepared from dimanganese decacarbonyl (Strem Chemical) using the procedure of Munro and Pauson [11]. Tetrabutylammoniumbromide was purchased from Aldrich Chemical Company and used without purification. 5-Bromo-1,3-pentadiene and 1-bromo-2,4-hexadiene were prepared by the method of Mori [10]. 3,5-Heptadien-2-ol was prepared by the method of Frank *et al.* [22]. ^{1}H NMR data were obtained at 90 MHz using a JEOL FX90-Q Spectrometer, with tetramethylsilane as the reference. ^{13}C NMR data were obtained at 22.5 MHz using a JEOL FX90-Q Spectrometer with $CDCl_3$ (77.0 ppm) as the reference. Infrared spectra were obtained on a Perkin-Elmer 1600 FTIR.

2.2. Tricarbonyl(η^5-pentadienyl)manganese (4)

To a 250 ml round bottom flask was added 0.287 g (1.0 mmol) of $BrMn(CO)_5$, 50 ml of dichloromethane, 0.902 g (2.8 mmol) of $^nBu_4NBr$ in 50 ml of 5 N aqueous sodium hydroxide, and 0.294 g (2.0 mmol) of 5-bromo-1,3-butadiene. The mixture was degassed three times and left under argon. The reaction mixture was heated under reflux for 24 h and then allowed to cool to room temperature. The organic layer was separated and the aqueous layer washed with 25 ml of dichloromethane. The organic layers were combined, washed with 25 ml of water, dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was purified by radial chromatography (silica gel, elution with pentane), followed by recrystallization at −78°C from pentane, providing 0.170 g (82%) of tricarbonyl(η^5-pentadienyl)manganese (**4**) as large yellow needles, m.p. 100°C (ref. 5, m.p. 101–101.5°C). ^{1}H NMR ($CDCl_3$): δ 0.67 (d, J = 12.3 Hz, 2H, H_{1anti}), 2.68 (d, J = 9.4, 2H, H_{1syn}), 5.0–5.3 (m, 2H, H_2), 5.68 (apparent t, J = 6.4 Hz, 1H, H_3). ^{13}C NMR ($CDCl_3$): δ 57.7, 89.5, 100.3, 221.7 (broad CO peak). IR (COs only, CCl_4): 2025, 1956, 1937 cm^{-1}. It should be noted that the spectral properties of tricarbonyl(η^5-pentadienyl)manganese (**4**) generated by this method are identical to the same compound prepared by the method reported by Seyferth *et al.* [5].

2.3. Tricarbonyl(η^5-hexadienyl)manganese (9)

Complex **9** was obtained in 36% yield under the same conditions utilized for the preparation of complex **4** (replacing 5-bromo-1,3-pentadiene with 1-bromo-2,3-hexadiene): m.p. 32–33°C. ^{1}H NMR ($CDCl_3$): δ 0.64 (dd, J = 11.7, 2.7 Hz, 1H, H_{1anti}), 1.64 (overlapping s and m, 4H, $-CH_3$ and H_5), 2.48 (dd, J = 9.8, 2.7 Hz, 1H, H_{1syn}), 4.74–5.24 (m, 2H, H_2 and H_4), 5.54 (t, J = 6.6 Hz, 1H, H_3). ^{13}C NMR ($CDCl_3$): δ 20.4, 54.9, 86.2, 99.5, 102.0, 217 (br). IR (COs only, CCl_4): 2020, 1949, 1932 cm^{-1}.

2.4. 6-Bromo-2,4-heptadiene (10)

To a flame-dried 100 ml round bottom flask was added 2.0 g (0.178 mmol) of 3,5-heptadien-2-ol [10] followed by 25 ml of absolute ethyl ether. The mixture was degassed and left under argon, and cooled to 0°C in an ice–water bath. To this solution was added 2.6 g (0.0120 mol) of phosphorus tribromide dissolved in 5 ml of absolute ethyl ether. The reaction mixture was stirred at 0°C for 2 h and then poured over 50 ml of ice–water. The organic layer was separated and the aqueous phase extracted with 25 ml of ether. The organic layers were combined and washed with saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride, and then dried over anhydrous magnesium sulfate. Filtration and removal of the solvent under reduced pressure followed by distillation under reduced pressure in the presence of anhydrous sodium carbonate gave 2.0 g (64%) of **10**, b.p. 31°C at 1.7 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.72 (d, 3H), 1.83 (d, 3H), 4.79 (m, 1H), 5.4–6.2 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 18.3, 26.2, 50.7, 130.3, 131.3, 132.0, 132.8. This compound was stored at 0°C in the dark to avoid decomposition.

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