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Reaction of tricarbonyl(η^6-cycloheptatriene)manganese cation with phosphorus ylides

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Abstract

The phosphonium salt $[(\eta^5\text{-}C_7H_8\text{–}CH_2PPh_3)Mn(CO)_3]ClO_4$ (**2**) has been prepared by the reaction of $[(\eta^6\text{-}C_7H_8)Mn(CO)_3]ClO_4$ (**1**) with $CH_2{=}PPh_3$. Deprotonation of **2** generated presumably $[(\eta^5\text{-}C_7H_8\text{–}CHPPh_3)Mn(CO)_3]$ (**3**), which reacts with several kinds of aldehydes RCHO to yield olefin-containing complexes, $[(\eta^5\text{-}C_7H_8\text{–}CH{=}CHR)Mn(CO)_3]$ (**4**) (R = Me, Et, $CH{=}CH_2$, Ph, $C_6H_4CH_3$-*p*, $C_6H_4NO_2$-*p*, C_6H_4OMe-*p*). Reaction of **1** with stabilized ylides $R\text{–}C(O)CH{=}PPh_3$ (R = Ph, Me, H, EtO, MeO) produces compounds $[\eta^5\text{-}C_7H_8\text{–}C{=}PPh_3\{\text{–}C(O)R\}]Mn(CO)_3$ (**5**) (R = Ph, Me, H, EtO, MeO) in high yields, which are too stable to react with aldehydes. An X-ray crystal structure of **4** (Ph) has been determined.

Keywords: Manganese; Cycloheptatriene; Ylide; Olefinated; Phosphonium; Cycloheptadienyl

1. Introduction

We recently described the use of ylide as a nucleophile to $(arene)Mn(CO)_3^+$ [1]. The chemistry involves the phosphonium salt formation of $(arene)Mn(CO)_3^+$, followed by trapping of the resulting phosphorus ylide by an electrophile to give substituted olefinic compounds. This procedure provides one of the methods to form the carbon–carbon bond and effect the olefination of coordinated π-arene rings. We are currently exploring the applicability of this olefination procedure to (cycloheptatriene) $Mn(CO)_3^+$ (**1**). In this report we describe some relevant chemistry of $(cycloheptatriene)Mn(CO)_3^+$ and the molecular structure of olefinated cycloheptadienyl manganese complex. We find that complex **1** reacts with stabilized- and non-stabilized ylides to give the corresponding organomanganese substituted phosphonium salts (**2** and **5**).

2. Experimental section

All reactions were conducted under nitrogen using standard Schlenk flask and cannula techniques. Work-up procedures were done in air.

Elemental analyses were done at the Korea Basic Science Center. ^1H NMR were obtained on a Varian XL-200 instrument. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer (spectra measured as films on NaCl by evaporation of the solvent). Mass spectra were recorded on a VG ZAB-E double focusing mass spectrometer.

Compound **1** was synthesized according to the published procedure [2]. Freshly prepared solutions of ylides were used in all experiments. The ylides used in this study were as follows: $CH_2{=}PPh_3$, $\{PhC(O)\}HC{=}PPh_3$, $\{MeC(O)\}HC{=}PPh_3$, $\{HC(O)\}HC{=}PPh_3$, $\{EtOC(O)\}HC{=}PPh_3$, $\{MeOC(O)\}HC{=}PPh_3$.

2.1. Synthesis of 2

A freshly prepared solution of $CH_2{=}PPh_3$ (generated in situ by reaction of LDA (2.4 mmol) with CH_3PPh_3Br (0.856 g, 2.4 mmol)) was added to the suspension of **1** (0.660 g, 2 mmol) in 30 ml of THF at

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0°C. After stirring for 1 h, the reaction mixture was extracted by using CH_2Cl_2/H_2O. The extracts of CH_2Cl_2 were dried ($CaCl_2$), and evaporated to give the crude product (67%). The analytically pure compound was obtained by column chromatography by eluting with ethyl acetate.

Mp. 103°C. IR (NaCl): ν (CO) 2008, 1928 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.88 (t, $J = 6.34$ Hz, 1H, H^3), 5.34 (dd, $J = 8.30$, 5.12 Hz, 1H, H^2), 4.87 (dd, $J = 9.76$, 6.83 Hz, 1H, H^4), 3.44–3.18 (m, 5H, CH_2 and $H^{1,5,6}$), 1.75–1.50 (m, 1H, $H^{7\text{-endo}}$), 0.90–0.81 (m, 1H, $H^{7\text{-exo}}$) ppm.

2.2. Synthesis of 4

Typical procedure: compound **2** (0.20 g, 0.33 mmol) in a mixed solvent of Et_2O (20 ml) and THF (5 ml) was treated with LDA at −78°C for 30 min. The resulting solution was allowed to warm to 0°C, and then treated with excess CH_3CHO for 2 h. The reaction mixture was extracted with Et_2O/H_2O. The ether extract was dried ($MgSO_4$), concentrated, and column chromatographed by eluting with hexane. After evaporation of solvent, compound **4** (Me) was obtained in a yield of 31%. The isomer ratio of *cis*- and *trans*-**4** (Me) was determined to be 1.6:1 by comparing the integration of the characteristic protons of *cis*- and *trans*-**4** (Me) of the ^1H NMR spectrum.

Mp. 45°C. IR (NaCl): ν(CO) 2008, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.81 (t, $J = 5.61$ Hz, 1H, H^3) 5.33 (dd, $J = 9.0$, 5.0 Hz, 1H, H^2), 5.5–5.2 (m, *cis* and *trans* H^9), 4.92 (ddd, $J = 15.13$, 8.17, 1.58 Hz, *trans* H^8), 4.81 (dd, $J = 10.37$, 6.46 Hz, 1H, H^4), 4.79 (td, $J = 10.61$, 1.83 Hz, *cis* H^8), 4.04–3.88 (m, 1H, H^6), 3.76 (dd, $J = 10.25$, 4.03 Hz, 1H, H^5), 3.60 (tq, $J = 9.40$, 1.70 Hz, 1H, H^1), 2.01–1.84 (m, 1H, $H^{7\text{-endo}}$), 1.67 (dd, $J = 6.84$, 1.71 Hz, *cis* CH_3), 1.56 (dd, $J = 6.47$, 1.58 Hz, *trans* CH_3), 0.80–0.65 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: M^+ calc. 272.0242, obsd. 272.0245.

2.2.1. Synthesis of 4 (Et)

Yield: 34%. The *cis*:*trans* ratio was 3:1. Mp. 35°C. IR (NaCl): ν (CO) 2008, 1934 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.81 (t, $J = 6.34$ Hz, 1H, H^3), 5.43 (dt, $J = 15.38$, 6.25 Hz, *trans* H^9), 5.31 (t, $J = 8.54$ Hz, 1H, H^2), 5.19 (dt, $J = 10.74$, 7.07, *cis* H^9), 4.89 (dd, $J = 16.84$, 8.06 Hz, *trans* H^8), 4.81 (dd, $J = 10.25$, 6.59 Hz, 1H, H^4), 4.74 (t, $J = 10.25$, *cis* H^8), 4.0–3.8 (m, 1H, H^6), 3.74 (dd, $J = 9.76$, 3.42 Hz, 1H, H^5), 3.65–3.50 (m, 1H, H^1), 2.10 (quint. $J = 7.57$ Hz, H, H), 2.00–1.84 (m, 1H, $H^{7\text{-endo}}$, 0.98 (t, $J = 7.56$ Hz, *cis* CH_3), 0.91 (t, $J = 7.56$ Hz, *trans* CH_3), 0.78–0.65 (m, 1H, $H^{7\text{-exo}}$) ppm. Anal: Found: C, 59.24; H, 5.37. $C_{14}H_{15}MnO_3$ calc.: C, 58.75; H, 5.28%.

2.2.2. Synthesis of 4 ($C_6H_4NO_2$-p)

Yield: 28%. The cis:*trans* ratio was 1:2. Mp. 128°C. IR (NaCl): ν (CO) 2016, 1930 cm^{-1}, ν(C=C) 1590 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.24 (d, $J = 8.54$ Hz, 2H, *cis* Ph), 8.13 (d, $J = 8.54$ Hz, 2H, Ph), 7.41 (d, $J = 8.00$ Hz, 2H, *cis* and *trans* Ph), 6.40 (d, $J = 16.11$ Hz, 1H, *trans* H^{10}), 6.27 (d, $J = 11.47$ Hz, 1H, cis H^{10}), 5.87 (t, $J = 5.61$ Hz, 1H, H^3), 5.37 (dd, $J = 8.54$, 5.61 Hz, 1H, H^2), 5.19 (t, $J = 10.18$ Hz, 1H, H^8), 4.91 (dd, $J = 9.76$, 6.59 Hz, 1H, H^4), 4.09 (m, $J = 10.00$, 3.66 Hz, 1H, H^6), 3.74 (dd, $J = 9.52$, 3.17 Hz, 1H, H^5), 3.65 (br t, $J = 7.56$ Hz, H, H), 2.14–1.88 (m, 1H, $H^{7\text{-endo}}$), 0.96–0.79 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: M^+ calc. 379.0252, obsd. 379.0259.

2.2.3. Synthesis of 4 (C_6H_4Me-p)

Compound **2** (0.20 g, 0.33 mmol) in a mixed solvent of Et_2O (20 ml) and THF (5 ml) was treated with LDA at −78°C for 30 min. The resulting solution was allowed to warm to 0°C, and then treated with excess p-$CH_3C_6H_4CHO$ for 2h. The reaction mixture was extracted with Et_2O/H_2O. The ether extract was dried ($MgSO_4$), concentrated, and flash-column chromatographed by eluting with hexane. The first light yellow band was a *cis*-isomer and the second was a *trans*-isomer (colourless). After evaporation of solvent, *cis*- and *trans*-isomers were obtained in a ratio of 6:1 (total yield: 31%).

The isomeric mixture has the following physical properties: IR (NaCl): ν(CO) 2016, 1926 cm^{-1}. HRMS: M^+ calc. 348.0558, obsd. 348.0550.

^1H NMR ($CDCl_3$) of *cis*-isomer: δ 7.2–7.0 (m, 4H, Ph), 6.19 (d, $J = 12.8$ Hz, H^9), 5.85 (t, $J = 6.20$ Hz, 1H, H^3), 5.35 (dd, $J = 8.5$, 5.6 Hz, 1H, H^2), 4.96 (t, $J = 10.2$ Hz, H^8), 4.88 (dd, $J = 10.00$, 6.59 Hz, 1H, H^4), 4.30–4.13 (m, 1H, H^6), 3.85 (dd, $J = 10.0$, 3.7 Hz, 1H, H^5), 3.61 (br t, $J = 8.3$ Hz, 1H, H^1), 2.37 (s, Me, 3H), 2.16–1.97 (m, 1H, $H^{7\text{-endo}}$), 0.87–0.70 (m, 1H, $H^{7\text{-exo}}$) ppm.

^1H NMR ($CDCl_3$) of *trans*-isomer: δ 7.19–7.05 (m, Ph, 4H), 6.30 (d, $J = 15.6$ Hz, 1H, H^9), 5.84 (t, $J = 6.6$ Hz, 1H, H^3), 5.61 (dd, $J = 15.6$, 8.2 Hz, 1H, H^8), 5.36 (dd, $J = 8.8$, 5.9 Hz, 1H, H^2), 4.89 (dd, $J = 10.0$, 6.6 Hz, 1H, H^4), 3.84 (dd, $J = 10.5$, 3.7 Hz, 1H, H^5), 3.81–3.67 (m, 1H, H^6), 3.62 (br t, $J = 8.30$ Hz, 1H, H^1), 2.31 (s, Me, 3H), 2.10–1.94 (m, 1H, $H^{7\text{-endo}}$), 0.92–0.78 (m, 1H, $H^{7\text{-exo}}$) ppm.

2.2.4. Synthesis of 4 (Ph)

Yield: 34%. The *cis*:*trans* ratio was 3:1. Mp. 89°C. IR (NaCl): ν (CO) 2008, 1922 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7–7.2 (m, 5H, Ph), 6.33 (dd, $J = 15.87$, Hz, *trans* H^9), 6.23 (d, $J = 11.47$ Hz, *cis* H^9), 5.83 (t, $J = 6.59$ Hz, 1H, H^3), 5.66 (dd, $J = 16.52$, 8.05 Hz, *trans* H^8), 5.33 (dd, $J = 8.79$, 5.85 Hz, 1H, H^2), 5.00 (t, $J = 11.23$ Hz,

cis H^8), 4.88 (dd, $J = 10.01$, 6.59 Hz, 1H, H^4), 4.3–4.1 (m, 1H, H^6), 3.83 (dd, $J = 10.01$, 3.17 Hz, 1H, H^5), 3.61 (br t, $J = 8.54$ Hz, 1H, H^1), 2.08–1.90 (m, 1H, $H^{7\text{-endo}}$), 0.95–0.85 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: calc. 334.0398, obsd. 334.0401.

2.2.5. Synthesis of **4** *(C_6H_4OMe-p)*

Yield: 40%. The *cis trans* ratio was 3:1. Mp. 93°C. IR (NaCl): ν (CO) 2004, 1926 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.3–7.2 (m,), 6.95–6.83 (m, Ph), 6.28 (d, $J = 16.0$ Hz, *trans* H^9), 6.17 (d, $J = 11.47$ Hz, *cis* H^9), 5.84 (t, $J = 5.61$ Hz, 1H, H^3), 5.53 (dd, $J = 16.00$, 9.00 Hz, *trans* H^8), 5.35 (dd, $J = 8.54$, 5.85 Hz, 1H, H^2), 4.92 (t, $J = 10.74$ Hz, *cis* H^8), 4.88 (dd, $J = 10.5$, 6.84 Hz, 1H, H^4), 4.3–4.15 (m, 1H, H^6), 3.84 (s, 3H, OMe), 3.92–3.78 (m, 1H, H^5), 3.63 (br t, $J = 7.08$ Hz, 1H, H^1), 2.10–1.90 (m, 1H, $H^{7\text{-endo}}$), 1.00–0.78 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: M^+ calc. 364.0507, obsd. 364.0507.

2.2.6. Synthesis of **4** *($CH{=}CH_2$)*

Yield: 27%. The *cis*:*trans* ratio was 2.3:1. IR (NaCl): ν (CO) 2008, 1922 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.72 (dt, $J = 15.60$, 10.49 Hz, 1H, *cis* H^{10}), 6.18 (dt, $J = 17.09$, 10.50 Hz, *trans* H^{10}), 6.04–5.74 (m, *cis* and *trans* H^9), 5.82 (t, $J = 5.85$ Hz, 1H, H^3), 5.33 (dd, $J = 7.56$, 6.60 Hz, 1H, H^2), 5.6–5.4 (br, *trans* H^8), 5.28–4.93 (m, 2H, $H^{11,12}$), 4.87 (dd, $J = 9.76$, 5.37 Hz, 1H, H^4), 4.82 (t, $J = 9.76$ Hz, *cis* H^8), 4.17–4.01 (m, 1H, H^6), 3.79 (br d, $J = 6.10$ Hz, 1H, H^5), 3.61 (br t, $J = 8.05$ Hz, 1H, H^1), 2.07–1.84 (m, 1H, $H^{7\text{-endo}}$), 0.92–0.7 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: M^+ calc. 284.0242, obsd. 284.0247.

2.3. Synthesis of **5**

Typical procedure: freshly prepared solution of $RCH{=}PPh_3$ (0.56 mmol) was added to a suspension of **1** (0.170 g, 0.51 mmol) in 30 ml of THF at 0°C. After stirring for 0.5 h, the solution was evaporated and concentrated to the volume of 5 ml. To the reaction mixture 100 ml of Et_2O/H_2O (v/v, 1:1) was added. In order to deprotonate the phosphonium salt, the water layer was titrated by aqueous NaOH (0.1 N) solution using a drop of phenolphthalein as an indicator. At the endpoint, the colour of the water layer became bright pink. The extract of Et_2O was dried ($MgSO_4$), and evaporated to give the crude product. The analytically pure compound was obtained by column chromatography by eluting with ethyl acetate.

2.3.1. Synthesis of **5** *(C(O)Ph)*

Yield: 94.7%. Due to the overlapping of the ^1H NMR spectra, we failed to determine the *cis*/*trans* isomer ratio in $CDCl_3$. Mp. 98°C. IR (NaCl): ν (CO) 2000, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7–7.3 (m, 15H, Ph), 4.96 (dd, $J = 5.86$, 5.37 Hz, 1H, H^2), 4.86 (t, $J = 5.13$ Hz, 1H, H^3), 3.98 (dd, $J = 9.76$, 6.10 Hz, 1H, H^4), 4.0–3.8 (m, 2H, $H^{5,6}$), 3.11 (br t, $J = 8.30$ Hz, 1H, H^1), 1.7–1.6 (m, 1H, $H^{7\text{-endo}}$), 0.83–0.72 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: M^+ calc. 610.1106, obsd. 610.1088.

2.3.2. Synthesis of **5** *(C(O)Me)*

Yield: 87%. We were not certain which isomer was abundant in $CDCl_3$. Thus, the *cis*:*trans* ratio was either 1:4 or 4:1. Mp. 180–185°C dec. IR (NaCl): ν (CO) 2000, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7–7.3 (m, 15H, Ph), 5.58 (br d, $J = 5.12$ Hz, 1H, H^3), 5.24 (dd, $J = 8.29$, 5.37 Hz, 1H, H^2), 4.88 (dd, $J = 4.88$, 4.15 Hz, 1H, H^4), 3.95 (br d, $J = 10.0$ Hz, 1H, H^5), 3.40–3.10 (m, 2H, $H^{1,6}$), 1.92 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.8–1.55 (m, 1H, $H^{7\text{-endo}}$), 1.5–1.05 (m, 1H, $H^{7\text{-exo}}$) ppm. Anal. Found: C, 67.40; H, 4.88. $C_{31}H_{26}MnO_4P$ calc.: C, 67.89; H, 4.78%.

2.3.3. Synthesis of **5** *(CHO)*

Yield: 60.2%. The *cis*:*trans* ratio in $CDCl_3$ was 2.5:1. Mp. 68°C. IR (NaCl): ν (CO) 2000, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.89 (d, $J = 32$ Hz, *cis* C(O)*H*), 8.82 (s, *trans* C(O)*H*), 7.80–7.25 (m, 15H, Ph), 5.70 (br t, 1H, H^3), 5.33 (dd, $J = 7.56$, 5.61 Hz, 1H, H^2), 4.83 (dd, $J = 6.59$, 5.83 Hz, 1H, H^4), 4.03 (br d, $J = 5.83$ Hz, 1H, H^5), 3.5–3.3 (br m, 1H, H^6), 3.30–3.10 (br m, 1H, H^1), 1.75–1.55 (br m, 1H, $H^{7\text{-endo}}$), 1.05–0.85 (br m, 1H, $H^{7\text{-exo}}$) ppm. Anal. Found: C, 66.98; H, 4.99. $C_{30}H_{24}MnO_4P$ calc.: C, 67.42; H, 4.53%.

2.3.4. Synthesis of **5** *(C(O)OEt)*

Yield: 95%. The *cis*:*trans* ratio in $CDCl_3$ was 1:2.7. Mp. 66°C. IR (NaCl): ν (CO) 2000, 1930 cm^{-1}. ^1H NMR ($CDCl_3$); δ 7.73–7.4 (m, 15H, Ph), 5.8–5.6 (br t, 1H, H^3), 5.22 (dd, $J = 8.3$, 5.37 Hz, 1H, H^2), 5.05–4.85 (m, 1H, H^4), 3.97 (q, 2H, *cis* CH_3CH_2O), 3.77 (br d, $J = 10.0$ Hz, 1H, H^5), 3.58 (q, J = 6.83 Hz, 2H, *trans* CH_3CH_2O), 3.25 (br t, $J = 6.59$ Hz, 1H, H^1), 3.15–2.9 (m, 1H, H^6), 1.8–1.6 (m, 1H, $H^{7\text{-endo}}$), 1.44 (t, $J = 7.81$ Hz, 3H, *cis* CH_3), 1.3–1.0 (m, 1H, $H^{7\text{-exo}}$), 0.33 (t, $J = 6.83$ Hz, 3H, *trans* CH_3) ppm. Anal: Found: C, 66.52; H, 4.97. $C_{32}H_{28}MnO_5P$ calc.: C, 66.44; H, 4.88%.

2.3.5. Synthesis of **5** *(C(O)OMe)*

Yield: 91%. The *cis*:*trans* ratio in $CDCl_3$ was 1:3.4. Mp. 165°C dec. IR (NaCl): ν (CO) 2000, 1925 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7–7.25 (m, 15H, Ph), 5.74 (t, $J = 5.37$ Hz, 1H, H^3), 5.23 (dd, $J = 8.05$, 5.61 Hz, 1H, H^2), 4.98 (dd, $J = 9.76$, 6.83 Hz, 1H, H^4), 3.80 (br d, $J = 10.25$ Hz, 1H, H^5), 3.50 (s, 3H, *cis* CH_3O), 3.25 (br t, $J = 5.80$ Hz, 1H, H^1), 3.1–2.9 (m, 1H, H^6), 2.98 (s, 3H, *trans* CH_3O), 1.72–1.58 (m, 1H, $H^{7\text{-endo}}$), 1.48–1.38 (m, 1H, $H^{7\text{-exo}}$) ppm. HRMS: M^+ calc. 564.0840, obsd. 564.0855.

Table 1
Crystal data and refinement for **4** (Ph)

Empirical formula	$C_{18}H_{15}O_3Mn$
Formula weight	334.24
Crystal stem	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	$a = 12.391(3)$ Å
	$b = 10.014(4)$ Å
	$c = 13.322(2)$ Å
	$\beta = 107.17(2)°$
Radiation	Mo Kα, $\lambda = 0.071069$ Å
Absorption coefficient	0.84 mm^{-1}
Crystal size	0.50×0.35×0.15 mm
Volume	1579.4(5) $Å^3$
Z	4
Density (calculated)	1.406 g cm^{-3}
Instrument	Rigaku AFC4 diffractometer
$F(000)$	688
Measured reflections	2917
Independent reflections	2780
Observed reflections	1793 [$F > 4\sigma(F)$]
R(int)	0.0329
θ max. for data collection	25.09°
Refinement method	Full-matrix least-squares on F
Data/parameters	1793/259
S, Goodness-of-fit on F	1.213
Final R indices	$R = 0.0514$, $wR = 0.0517$

2.4. X-ray structure determination of 4 (Ph)

Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in hexane. The crystal was mounted on a Rigaku AFC4 diffractometer, and the unit cell parameters were obtained from a least-squares fit of the 22 centred reflections ($10.52° < 2\theta < 25.80°$). Data were collected with Mo Kα radiation by using the $\omega/2\theta$ scan mode. The crystal structure was solved by the use of the conventional heavy-atom method as well as Fourier difference technique and refined by means of full-matrix least-squares procedures using SHELX-76. Non-hydrogen atoms were found by SHELXS 86 and refined anisotropically; all hydrogen atoms were located by difference Fourier synthesis and refined isotropically in the final refinement. The last cycle of refinement converged with $R = 5.14\%$ and $R_w = 5.17\%$. Crystal data, details of the data collection, and refinement parameters for **4** (Ph) are listed in Table 1. The final atomic parameters for **4** (Ph) are given in Table 2. Selected bond distances and angles are given in Table 3. Complete bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and tables of observed and calculated factors are available from the authors.

Table 2
Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å×10^3) for **4** (Ph)

	x	y	z	U_{eq}
Mn	3216(1)	1282(1)	1193(1)	35
O(1)	4790(4)	3275(5)	794(4)	85
O(2)	4893(4)	−748(5)	1063(4)	79
O(3)	1822(4)	997(5)	−995(3)	82
C(1)	4174(5)	2508(6)	952(4)	51
C(2)	4240(5)	37(6)	1133(4)	49
C(3)	2388(4)	1108(6)	−147(4)	48
C(4)	1915(4)	2693(5)	1329(4)	40
C(5)	2798(5)	2615(6)	2263(4)	47
C(6)	3278(5)	1461(7)	2804(4)	54
C(7)	2931(5)	176(7)	2446(5)	53
C(8)	1967(5)	−34(6)	1605(5)	46
C(9)	878(5)	650(6)	1562(5)	51
C(10)	758(4)	2047(6)	1080(4)	40
C(11)	−27(4)	2884(6)	1491(4)	42
C(12)	−994(5)	3448(5)	982(4)	43
C(13)	−1566(4)	3513(5)	−145(4)	38
C(14)	−1001(4)	3704(5)	−906(4)	39
C(15)	−1583(5)	3789(6)	−1955(4)	51
C(16)	−2740(5)	3963(6)	−2292(5)	57
C(17)	−3308(5)	3522(7)	−1564(5)	62
C(18)	−2743(5)	3462(7)	−514(5)	56

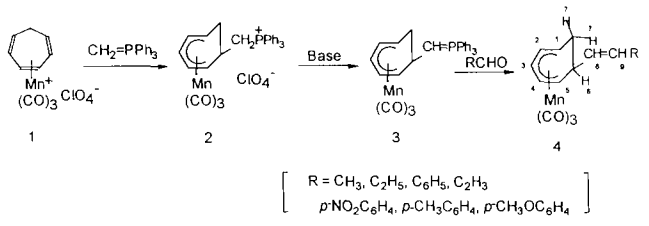
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij}.

Table 3
Selected bond distances (Å) and angles (°) for **4** (Ph)

Mn–C(1)	1.801(6)	Mn–C(4)	2.191(5)
Mn–C(5)	2.126(6)	Mn–C(6)	2.132(5)
O(1)–C(1)	1.145(8)	C(4)–C(5)	1.396(7)
C(5)–C(6)	1.398(9)	C(4)–C(10)	1.518(7)
C(9)–C(10)	1.528(8)	C(10)–C(11)	1.504(7)
C(11)–C(12)	1.317(8)	C(12)–C(13)	1.317(8)
Mn–C(1)–O(1)	179.1(5)	C(1)–Mn–C(2)	87.4(3)
C(4)–C(5)–C(6)	127.4(5)	C(5)–C(6)–C(7)	123.0(5)
C(6)–C(7)–C(8)	121.3(6)	C(4)–C(10)–C(9)	109.3(4)
C(9)–C(10)–C(11)	110.5(4)	C(10)–C(11)–C(12)	129.7(5)
C(11)–C(12)–C(13)	129.8(5)	C(12)–C(13)–C(14)	123.6(5)

3. Results and discussion

The reaction of a nonstabilized ylide such as CH_2=PPh_3 with $(C_7H_8)Mn(CO)_3^+$ (**1**) gives the organometallic-substituted phosphonium salt **2** (Scheme 1). The NMR assignments were generally made by comparison with other spectra and consideration of coupling constants. Due to the introduction of the phosphorus ylide, the molecule lost its plane symmetry. Thus, the ^1H NMR spectrum was rather more complicated than



Scheme 1.

Table 4
Product distribution of reaction of the ylide complex **3** with aldehyde

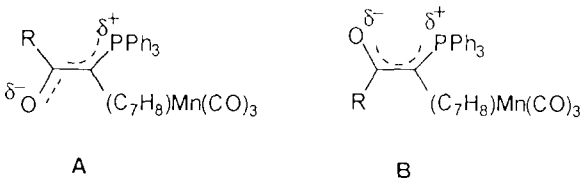
aldehyde	*cis*	*trans*	total yield (%)
$CH_3C(O)H$	1.6	1	31
$C_2H_5C(O)H$	3	1	34
$CH{=}CH_2C(O)H$	2.3	1	27
$PhC(O)H$	3	1	34
p-$CH_3C_6H_4C(O)H$	5	1	31
p-$O_2NC_6H_4C(O)H$	1	2	28
p-$MeOC_6H_4C(O)H$	3	1	40

that of $(C_7H_9)Mn(CO)_3$ [3]. Complex **2** has been also characterized by IR and elemental analysis, and all data are consistent with its formulation as complex **2**.

The methyne proton of the phosphonium salt **2** is acidic and can be easily deprotonated by LDA to yield what is presumably the oragnotransition-metal-substituted ylide, **3**. Addition of a solution of LDA to the suspension of **2** in THF/diethyl ether (v/v, 1:5) at −78°C under nitrogen gives rise to a yellowish orange unstable solution of **3**.

When acetaldehyde is added to the solution of **3** at 0°C, triphenylphosphine oxide is precipitated and both *cis*- and *trans*- $[(C_7H_8CH{=}CHMe)Mn(CO)_3]$ (3:1) (**4** (Me)) can be isolated from the solution in 34% yield. Similarly, treatment of the yellowish orange solution of **3** with aldehydes such as CH_3CHO, C_2H_5CHO, *p*-nitrobenzaldehyde, *p*-tolualdehyde, PhCHO, CH=CHCHO, and *p*-anisaldehyde, gives both *cis*- and *trans*-olefinic complex **4** in yields from 27% to 40%. The ratio of *cis* and *trans* isomers was determined by the integration of peaks of protons of characteristic *cis*-and *trans*-**4** complexes, respectively. However, in the case of **4** (*p*-tolualdehyde), the separation of the *cis* and *trans* isomer was achieved by flash chromatography. The *cis*:*trans* isomer ratio varied according to the aldehyde (Table 4). We have succeeded in solving the molecular structure of *cis*-**4** (Ph) (see below). It seems likely that the mixture of *cis* and *trans* isomers is separated during crystallization, towards the crystallization of the *cis* form.

Lewis et al. [4] used similar strategies to prepare six-, seven-, and eight-membered ring iron compounds containing an exocyclic double bond. However, they did not use organophosphorus ylide as nucleophiles. Instead, they made phosphonium salt by treatment of coordinated carbonium with tertiary phosphines or by dehydration of $[Fe(CO)_3(C_8H_7CH_2OH)]$ and subsequent addition of PPh_3. The reaction of stabilized ylide such as $CHR{=}PPh_3$ (R = PhC(O), MeC(O), HC(O), EtOC(O), MeOC(O)) with $(C_7H_8)Mn(CO)_3^+$ (**1**) gave the organometallic phosphonium salt and the deprotonation of the resulting phosphonium salt by NaOH gave organometallic-substituted ylide complexes **5** in high ylides (Scheme 2). Due to the hindered internal rotation about the $R(O)C{-}C(PPh_3)(C_7H_8)Mn(CO)_3$



Scheme 2.

bond [5], the *cis* and *trans* conformational isomers A and B can be distinguished by their ^1H NMR spectra. In $CDCl_3$, compounds **5** exist as a mixture of *cis* and *trans* isomers.

The ratio of *cis* and *trans* isomers was determined by ^1H NMR. According to a previous report [5], the *cis*/*trans* ratio is strongly influenced by a change of solvent. However, we did not carry out further study.

In contrast with **2**, complexes **5** are very stable and resistant to electrophilic addition and oxidation. To do the Wittig reaction, complexes **5** were refluxed with benzaldehyde in benzene. However, after work-up, we only recovered the reactant. To get diketone substituted complexes, **5** was treated with $[Bu_4N]IO_4$ in methylene dichloride [6]. Again, we only recovered the reactant. To obtain the O-alkylated product, **5** was treated with $[Me_3O]BF_4$, but we could not obtain the expected product. We even tried ozonolysis of **5**, but during the reaction, **5** was completely destroyed. Thus, we have been unable to find any way to functionalize **5**.

3.1. Molecular structure of 4 (Ph)

The single-crystal X-ray structure of **4** (Ph) confirms the *cis*-disubstituted olefin. An ORTEP drawing of the molecule is shown in Fig. 1. The dienyl carbon atoms, C(4), C(5), C(6), C(7), and C(8) define a plane (maximum deviation 0.068 Å). The carbon atoms C8–C9–C10–C4 are roughly planar. The dihedral angle between these two planes is 49.7°, which is typical for seven-membered dienyl rings [7]. The metal–carbon distances in the cycloheptadienyl ring show a pattern in which the metal is significantly closer to C5–C7 of the

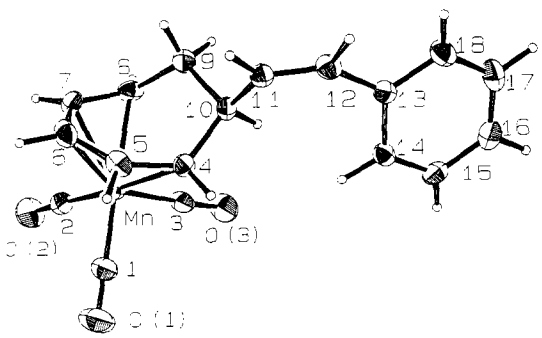


Fig. 1. ORTEP drawing of compound **4** (Ph).

delocalized set than to the two terminal carbon atoms, C4 and C8 [Mn–C5 = 2.126(6), Mn–C6 = 2.132(5), Mn–C4 = 2.191(5), and Mn–C8 = 2.221(6) Å] [8]. The carbon–carbon distances in the bent back portion have normal single bond lengths (1.518(7), 1.528(8), and 1.499(8) Å). In contrast to the cyclohexadienyl complexes, the carbon–carbon distances (av. 1.393 Å) in the cycloheptadienyl are almost same. The carbon atoms C10–C11–C12–C13 define a plane (maximum deviation 0.0168(5) Å) and the dihedral angle between this plane and the phenyl ring is 37.5°. The bond distance of C(13)–C(14) in the phenyl ring is 1.405(7) Å which is rather longer than the other carbon–carbon distances in the phenyl ring. Thus the bond angle of C(14)–C(13)–C(18) (116.2(5)°) is smaller than the usual bond angles in the phenyl ring. The bond angles of C(10)–C(11)–C(12) and C(11)–C(12)–C(13) (129.7(5)° and 129.8(5)°, respectively) are somewhat larger than the usual sp^2 bond, due to the steric bulkiness of the two substituents. However, the bond length of C=C (C11–C12) (1.317(8) Å) is similar to the value expected for *cis*- disubstituted olefinic compounds [9].

In conclusion, we have demonstrated that the ylides are easily added to the π-coordinating cycloheptatriene ring to yield the organotransition-metal-substituted phosphonium salt and the phosphonium salt derived from nonstabilized ylide is used to make olefinated cycloheptadienylmanganese compound. However, the ylide complexes derived from the stabilized ylides are too stable to react with aldehydes or oxidizing reagents.

Acknowledgment

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