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Preparation and Wittig Reactivity of Organotransition-Metal-Substituted Phosphonium Salts

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Summary: The reaction of $[(C_6H_6)Mn(CO)_3]^+$ *with* $CHR{=}PPh_3$ *produces* $[(Ph_3PCHR\text{-}\eta^5\text{-}C_6H_6)Mn(CO)_3]^+$ *(**2**). **2** reacts with LDA to produce a manganese-substituted ylide, which reacts with aldehydes to yield substituted olefinic compounds **3** and after oxidation to yield compound **6**.*

Phosphorus ylides have become one of the most effective arsenals in synthetic organic chemistry before inorganic chemists begin to take an increased interest in them. As powerful electron donors, ylides form with almost all metals a wide range of complexes having surprisingly stable metal–carbon bonds. The coordination chemistry of phosphorus ylides has been reviewed by Schmidbaur[2] and Kaska.[3]

The Wittig reactivity of the phosphonium-substituted six- and seven-membered-ring dienyl complexes of $Fe(CO)_3$ has been demonstrated by the work of Lewis et al.,[4] and the work of Howell[5] has shown how such complexes may be used as precursors in the preparation of alkyl-substituted six-membered-ring dienyl complexes of $Fe(CO)_3$. However, to our knowledge there have been no reports on the use of phosphorus ylides as nucleophiles the π-coordinated ring.

Nucleophilic attack on $(arene)Mn(CO)_3^+$ complexes can follow different paths, depending upon the nucleophiles.[6] Therefore, the broad spectrum of nucleophilicity of ylides can offer a chance to observe nucleophilic attack on the metal center or on the coordinated arene group. This report will describe the preparation of organometallic-substituted phosphonium salts and their reaction with aldehydes and oxidation.

The reaction of nonstabilized ylides such as $CHR{=}PPh_3$ (R = H, Me, OMe, Et, OCH_2Ph) with $(C_6H_6)Mn(CO)_3^+$ (**1**) give the organometallic-substituted ylide complexes **2** in moderate yield (Scheme I).[7] However, for the reaction between **1** and $CHPh{=}PPh_3$, only $[PhCH_2PPh_3]PF_6$ was isolated. The reactions of stabilized ylides such as $PPh_3{=}C(COR)H$ (R = H, Me, OMe, OEt, Ph) with compound **1** do not give any organometallic-substituted ylide complexes. Compounds **2** have been characterized by IR, ^{1}H NMR, elemental analysis, and/or mass spectroscopy, and all data are consistent with their formulations as complex **2**. One noticeable thing is that, due to the introduction of the phosphorus ylide, the molecule lost

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[1] X-ray analysis for **3**(benzaldehyde).

[2] Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

[3] Kaska, W. *Coord. Chem. Rev.* **1983**, *48*, 1.

[4] Hackett, P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1247. Jaouen, G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1982**, *231*, C21.

[5] Howell, J. A. S.; Thomas, M. J. *Organometallics* **1985**, *4*, 1054.

[6] Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677, 1683. Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* **1977**, *15*, 258. Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621. Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053.

[7] Typical procedure: A freshly prepared solution of $CH_2{=}PPh_3$ (0.50 mmol) was added to the suspension of $[(C_6H_6)Mn(CO)_3]PF_6$ (0.181 g, 0.5 mmol) in 30 mL of THF at 0 °C. After it was stirred for 1 h, the reaction mixture was treated with CH_2Cl_2/H_2O. The CH_2Cl_2 extracts were dried ($CaCl_2$) and evaporated to give the crude product (86%). The analytically pure compound **2**(H) was obtained by column chromatography by eluting with THF/Et_2O (4:5 v/v). Mp: 178 °C dec. IR: ν(CO) 2010, 1925 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.5–8.0 (m, 15H, Ph), 5.94 (t, J = 5.37 Hz, 1H, H^3), 4.88 (t, J = 5.86 Hz, 2H, $H^{2,4}$), 3.01 (m, 1H, H^6), 2.79 (t, J = 6.6 Hz, 2H, $H^{1,5}$), 2.56 (dd, J_{HH} = 6.34 Hz, J_{PH} = 12.20 Hz, 2H, CH_2) ppm. Anal. Calcd for $C_{28}H_{23}F_6MnO_3P_2$: C, 52.68; H, 3.63. Found: C, 52.87; H, 4.55.

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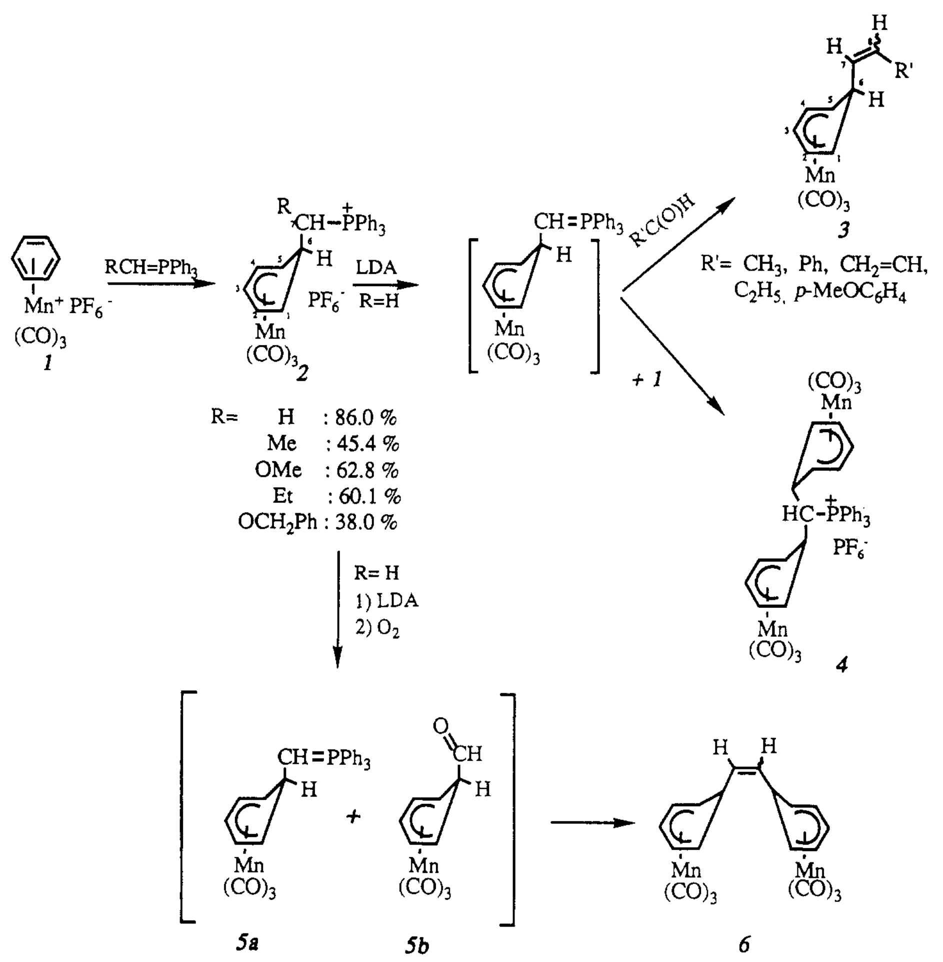
Scheme I



the plane symmetry and the protons on the cyclohexadienyl ring appeared in different positions in the ^{1}H NMR spectra.

The methyne proton of the ylide-substituted complex **2**(H) is acidic and can be easily deprotonated to yield presumably the organotransition-metal-substituted ylide. The organometallic-substituted ylides react with aldehydes such as CH_3COH, PhCOH, $CH_2{=}CHC(O)H$, $C_2H_5C(O)H$, and *p*-anisaldehyde to give olefinic compound **3** (Table I).[8] We have succeeded in solving the molecular structure of **3**(benzaldehyde).[9] An ORTEP drawing of the molecular structure of **3**(benzaldehyde) is shown in Figure 1. The manganese center displays a distorted-octahedral geometry, formed by cyclohexadienyl and three carbonyl ligands. The structure analysis shows that the crystal is a *cis* form. It seems likely that the mixture of *cis* and *trans* isomers is separated during crystallization, toward the crystallization of the *cis* form. The ratio of *cis*- and *trans*-**3** was determined by the integration of peaks of protons of characteristic *cis*- and *trans*-**3** complexes, respectively. However, in the cases of complexes **3**(benzaldehyde) and **3**(*p*-anisaldehyde), separation of the *cis*- and *trans*-**3** species was achieved by column chromatography. Thus, *cis*:*trans* ratios were found to be 9:4 and 2.1:1 for **3**(benzaldehyde) and **3**(*p*-anisaldehyde), respectively. Table I shows that the ratio of *cis*- and *trans*-**3** was dependent upon the aldehyde.

Table I. Reaction of the Ylide Complex with Aldehydes

aldehyde	product distribn *cis*	product distribn *trans*	total yield (%)
$CH_3C(O)H$	13	4	66
$C_2H_5C(O)H$	7	1	49
$CH_2{=}CHC(O)H$	5	1	53
PhC(O)H	9	4	60
4-$MeOC_6H_4(O)H$	2.1	1	42

Deprotonation of **2**(H) by LDA followed by treatment with $(C_6H_6)Mn(CO)_3^+$ gave complex **4**.[10] Formulation of compound **4** was verified by IR, ^{1}H NMR, and high-resolution mass spectra.

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[8] Typical procedure: Compound **2**(H) (0.683 g, 1 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 warmed to 0 °C and then treated with CH_3COH (10 mmol) for 2 h. The reaction mixture was extracted with Et_2O/H_2O. The ether extracts was dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel with ethyl acetate/hexane (1:4 v/v) as eluent. After evaporation of the solvent, compound **3**(acetaldehyde) was obtained in a yield of 66% (0.170 g). **3**(acetaldehyde): mp 55 °C dec; IR (NaCl) ν_{CO} 2000, 1995, 1920 cm^{-1}; ^{1}H NMR ($CDCl_3$) spectrum of *cis*-**3**(acetaldehyde) δ 5.79 (t, J = 5.37 Hz, H, 3H), 4.99 (dd, J = 11.2, 6.8 Hz, 1 H, H^7), 4.80 (t, J = 6.1 Hz, 2 H, $H^{2,4}$), 4.60 (t, J = 9.27 Hz, 1 H, H^8), 3.40 (m, 1 H, H^6), 3.17 (t, J = 6.34 Hz, 2 H, $H^{1,5}$), 1.54 (dd, J_{HH} = 1.46, 6.83 Hz, 3H, H) ppm; ^{1}H NMR ($CDCl_3$) of *trans*-**3**(acetaldehyde) δ 5.79 (t, J = 5.37 Hz, 1 H, H^3), 5.0–5.2 (m, 1 H, H^7), 4.80 (t, J = 6.1 Hz, 2 H, $H^{2,4}$), 5.12 (dd, J = 15.6, 6.6 Hz, 1 H, H^8), 3.17 (t, J = 6.34 Hz, 2 H, $H^{1,5}$), 3.05 (m, 1H, H^6), 1.54 (dd, J_{HH} = 1.46, 6.83 Hz, 3H, Me) ppm; MS m/z (M^+) calcd 258.0089, obsd 258.0077.

[9] Single crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2/hexane solution of **3**(benzaldehyde): triclinic; a = 9.231(5) Å, b = 10.434(7) Å, c = 8.606(5) Å, α = 97.97(7)°, β = 110.40(6)°, γ = 101.41(7)°; space group $P\bar{1}$; Z = 2, D_{calcd} = 1.433 g cm^{-3}; 2213 independent reflections (5° < 2θ < 120°, Cu Kα radiation, Rigaku AFC diffractometer); solution of the structure by the conventional heavy-atom method (SHELXS 86); hydrogen positions calculated according to ideal geometry with a C–H bond length of 1.05 Å. Refinement by use of SHELX 76 with anisotropic temperature factors for all non-hydrogen atoms gave R = 0.081 and R_w = 0.087 for 1827 unique reflections with $F_o \geq 4\sigma(F_o)$.

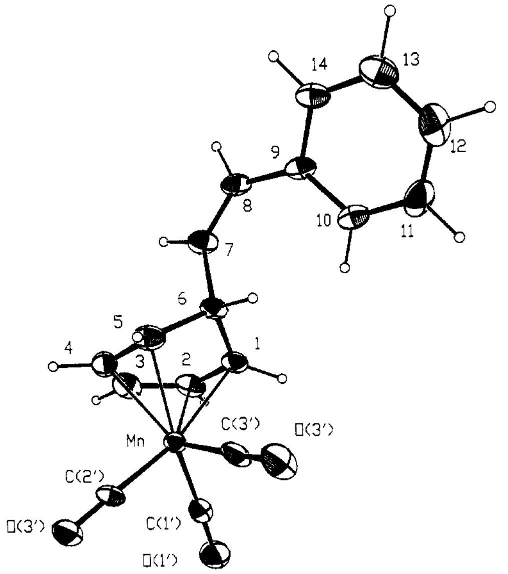

Figure 1. ORTEP drawing of the **3**(benzaldehyde) molecule with the atom numbering. Selected bond distances (Å): C1–Mn, 2.233(6); C5–Mn, 2.246(7); C3–Mn, 2.112(7); C6–C7, 1.493(9); C7–C8, 1.331(9); C8–C9, 1.473(10); C1′–Mn, 1.771(7). Selected bond angles (deg): C5–C6–C1, 103(5); C2–C3–C4, 118.7(7); C6–C7–C8, 130.2(7); C7–C8–C9, 128.0(6); C10–C9–C14, 118.4(6); C11–C12–C13, 118.8(8).

Deprotonation of **2**(H) by LDA followed by oxidation with O_2 gave complex **6**.[11] Complex **6** would be formed by the reaction between **5a** and **5b**, which might be generated under the reaction conditions. Complex **6** is a mixture of *cis* and *trans* isomers. The ratio *cis*:*trans* was determined to be 4:1.

This work provides an example of the use of ylides as nucleophiles on the π-coordinating benzene ring. Surprisingly, this is the first example, though many phosphonium salts have been prepared. The present results clearly show that the ylides are easily added to the π-coordinating benzene ring and the organotransition-metal-substituted phosphonium salts are as easily olefinated as the usual phosphonium salts. We are continuing to explore the potentially fascinating chemistry of organotransition-metal-substituted phosphonium salts. Preliminary studies[12] show that (cycloheptatrienyl)$Mn(CO)_3^+$ reacts cleanly with stabilized ylides.

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Supplementary Material Available: Tables of Crystallographic data, atomic positional parameters and thermal parameters, and bond lengths and angles for **3**(benzaldehyde) and text giving the physical properties of compounds **2**–**4** and the experimental procedures for **2**–**4** (13 pages). Ordering information is given on any current masthead page.

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(10) To the suspension of **2**(H) (0.270 g, 0.5 mmol) in 10 mL of THF was added 5 mL of LDA solution (0.75 mmol, generated *in situ* in THF) at –78 °C. After it was stirred for 30 min, the ylide solution was warmed to 0 °C and then added to a suspension of $[(C_6H_6)Mn(CO)_3]PF_6$ (0.181 g, 0.5 mmol) in 20 mL of THF at 0 °C. The reaction mixture was stirred for 1 h and then extracted with CH_2Cl_2/H_2O. After column chromatography of the CH_2Cl_2 extracts with ethyl acetate/hexane (2.5:1 v/v) as eluent, **4** was obtained in a yield of 22%. **4** slowly decomposed to **2**(H) while the ^1H NMR spectrum was taken. Thus, we failed to see the splitting patterns of each hydrogen and observed a rather broad ^1H NMR spectrum. Mp: 191 °C dec. IR: ν_{CO} 2015, 1925 cm^{-1}. ^1H NMR (CD_3CN): δ 7.4–8.0 (br m, Ph), 5.7 (br, 2H), 5.13 (br, 2H), 4.32 (br, 2H), 4.07 (m, 1H), 3.21 (br, 4H), 2.53 (br, 2H) ppm. Anal. Calcd for $C_{37}H_{28}F_6Mn_2O_6P_2$: C, 52.01; H, 3.30. Found: C, 52.93; H, 4.15.

(11) Compound **2**(H) (0.380 g, 0.595 mmol) in a mixed solvent of THF (5 mL) and Et_2O (20 mL) was treated with LDA at –78 °C for 30 min. The resulting solution was warmed to 0 °C and then bubbled with O_2 for 1 h. The reaction mixture was extracted with Et_2O/H_2O. The ether extracts were dried ($MgSO_4$), concentrated, and column chromatography by eluting with ethyl acetate/hexane (1:4 v/v). After evaporation of the solvent, compound **6** was obtained in a yield of 17.7%. Mp: 174 °C. IR (NaCl): ν_{CO} 2010, 1960, 1900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.76 (t, J = 5.37 Hz, 1 H, H^3), 4.78 (t, J = 5.61 Hz, 2 H, $H^{2,4}$), 4.32 (d, J = 14.6 Hz, 1 H, $H^{trans\text{-}7}$), 4.10 (dd, J = 1.76, 10 Hz, 1 H, $H^{cis\text{-}7}$), 3.4–3.2 (m, 1 H, H^6), 3.07 (t, J = 5.85 Hz, 2 H, $H^{1,5}$) ppm. MS: m/z (M^+) calcd 460.203, obsd 459.9552.

(12) Lee, S.-G.; Chung, Y. K. Unpublished results.