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Preliminary communication

SYNTHESES OF (*exo*- AND *endo*-DIALKYLPHOSPHONATE-η^5-CYCLOHEXADIENYL)MANGENESE TRICARBONYL COMPOUNDS

HYE KYUNG BAE, IL NAM JUNG, and YOUNG KEUN CHUNG*

Inorganic Chemistry Laboratory, Korea Advanced Institute of Science and Technology P.O. Box 150, Cheongryang, Seoul, 131 (Korea)

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Summary

$[(C_6H_6)Mn(CO)_3]^+$ reacts with $NaP(O)(OR)_2$ (R = Me, Et) to give the phosphonate complex, $[exo\text{-}(RO)_2P(O)\text{-}\eta^5\text{-}C_6H_6]Mn(CO)_3$ which on treatment with n-BuLi and H_2O undergoes stereospecific rearrangement to $[endo\text{-}(RO)_2P(O)\text{-}\eta^5\text{-}C_6H_6]Mn(CO)_3$.

(Arene)manganese tricarbonyl cations have been and continue to be the topic of extensive investigation. This is due in part to the rich chemistry associated with nucleophilic attack at the aromatic ring leading to formation of cyclohexadienylmanganese tricarbonyl compounds [1]. Addition to the arene ring occurs with hydride [2], phenide [3], cyanide [4], Grignard reagents [5], ketone enolates [5], and some other nucleophiles [6].

Phosphonate carbanions are used to form a carbon–carbon double bond in the Horner–Emmons reaction [7]. These phosphonate carbanions have several advantages compared to alkylidenephosphoranes. The carbanion is further sufficiently stable to prevent self-condensation during carbanion preparation, and weaker bases may be used. The elimination of phosphonate occurs rapidly under mild conditions without rearrangements [8]. To our knowledge there are no reports on the use of phosphate as a nucleophile to the π-coordinated ring. We report here phosphate addition to the $[(C_6H_6)Mn(CO)_3]^+$ cation and its reaction with n-BuLi and water.

Sodium dialkylphosphates were synthesized as previously described [9]. These phosphates, $NaP(O)(OR)_2$ (R = Me, Et), were synthesized from NaH and the corresponding dialkylphosphite in tetrahydrofuran (THF) at room temperature under an inert atmosphere. Sodium dialkylphosphate was used in situ without isolation.

A 2/1 molar excess of sodium dialkylphosphate was added to a stirred suspension of $[(benzene)Mn(CO)_3]PF_6$ in THF using a syringe at room temperature under N_2. After 30 min, the reaction mixture was quenched with water to destroy the excess of sodium dialkylphosphate. Excess diethyl ether was added to extract the

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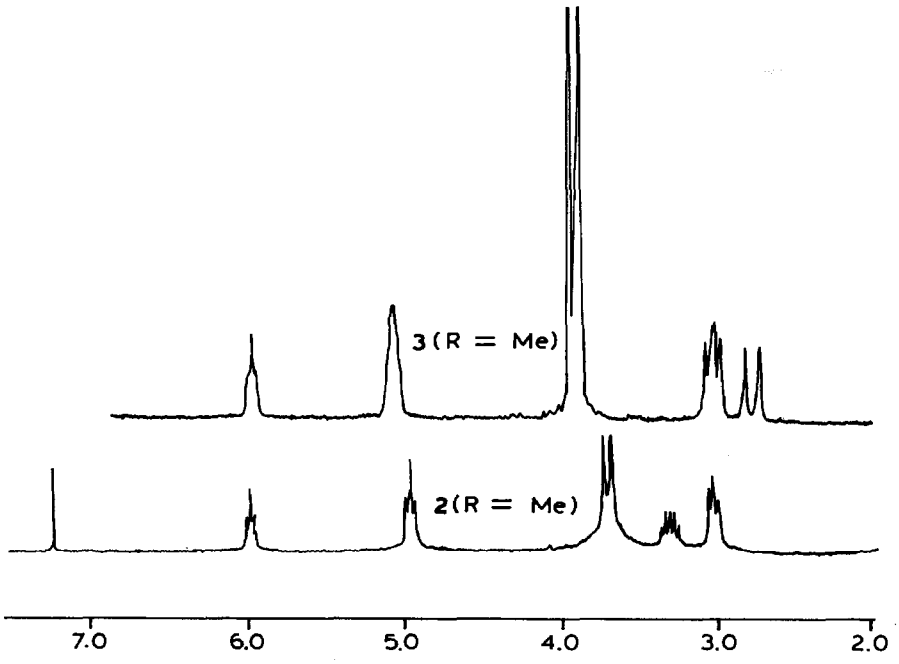
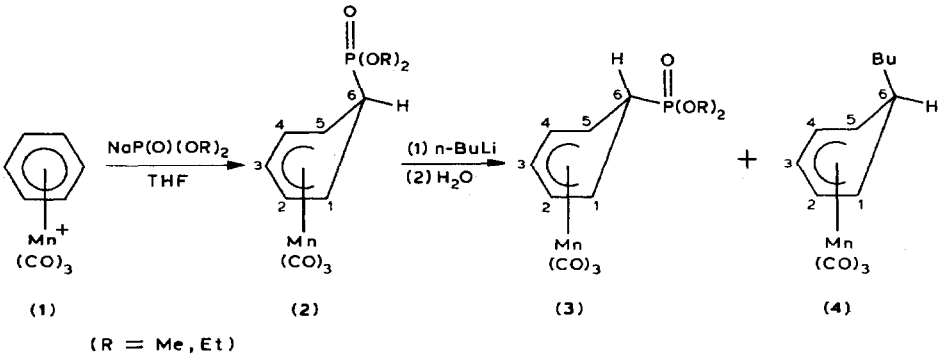


Fig. 1. ^{1}H NMR spectra (200 MHz) in $CDCl_3$ of (*exo*-dimethylphosphonate-η^5-cyclohexadienyl)manganese tricarbonyl (**2**) and (*endo*-dimethylphosphonate-η^5-cyclohexadienyl)manganese tricarbonyl (**3**).

neutral compound. The clear yellow extract was dried over anhydrous $MgSO_4$ and slowly evaporated to give compound **2** as a pale yellow solid in moderate to high yield *. Support for the structure of compound **2** is given by its ^{1}H NMR spectrum (Fig. 1), which is typical for a coordinated cyclohexadienyl group [1,5]. For compound **2** (R = Me) a complicated splitting pattern is expected for the 6-*endo*-hydrogens, due to coupling to the two adjacent olefinic hydrogens as well as to phosphorus (J 18 Hz). When compound **2** (R = Et) was treated with n-BuLi so as to deprotonate, the solution turned red and upon quenching with water, the solution turned yellow. After work-up, two compounds were isolated, a butylated compound (**4**) with the phosphate group replaced (yield 14%) and a phosphonate compound (yield 65%), (see Scheme 1) **. Much to our surprise the ^{1}H NMR spectrum of the

* Spectral properties of **2** (R = Me): ^{1}H NMR ($CDCl_3$): δ 2.98(t, H(1,5). $J_{1,2}$ 6 Hz), 3.24(m, H(6), $J_{6,P}$ 18 Hz, $J_{1,6}$ 5 Hz), 3.67(d, OMe, J(P,OMe) 10.5 Hz), 4.96(t, H(2,4), $J_{1,2}$ 5.6 Hz), 6.00(t, H(3), $J_{2,3}$ 5.1 Hz) ppm. IR(ν(CO)): 2013(s), 1925(s) cm^{-1}. M.p. 125–126.2°C. Anal. Found: C, 40.7; H, 3.67. $C_{11}H_{12}O_6PMn$ calc.: C, 40.5; H, 3.70%. Spectral properties of **2** (R = Et): ^{1}H NMR ($CDCl_3$): δ 1.29(CH_3), 3.03(t, H(1,5), $J_{1,2}$ 6 Hz), 3.22(m, H(6)), 4.01 (OCH_2), 4.95(t, H(2,4), $J_{2,3}$ 5.6 Hz), 5.98(t, H(3), $J_{3,4}$ 5.0 Hz) ppm. IR(ν(CO)): 2017(s), 1928(s) cm^{-1}. ^{13}C NMR ($CDCl_3$): 16.69(CH_3), 47.60(OCH_2), 62.39(C(1,6)), 80.25(C(2,4)), 97.95(C(3)), 220.05 (CO) ppm. Anal. Found: C, 44.5; H, 4.75. $C_{13}H_{16}O_6PMn$ calc.: C,441; H, 4.56%.

** Spectral properties of **3** (R = Et): ^{13}C NMR($CDCl_3$): 16.69(CH_3), 47.60(OCH_2), 62.39(C(1,5)), 80.25(C(2,4)), 97.95 (C(3)), 220.25(CO) ppm. Spectral properties of **3** (R = Me): ^{1}H NMR ($CDCl_3$): δ 2.58(d, 6-*exo*-H, $J_{6,P}$ 17.7 Hz), 2.83(t, H(1,5), $J_{5,P}$ 10.4 Hz, $J_{4,5}$ 7.1 Hz), 3.84(d, OMe, J(P,OMe) 10.7 Hz), 4.96(q, H(2,4)), 5.82(t, H(3), $J_{3,4}$ 5 Hz). IR(ν(CO)) 2007(s), 1928(s) cm^{-1}. M.p. 72.0–72.4°C.



SCHEME 1.

phosphonate compound obtained is very different from that of compound **2** (R = Me). Figure 1 shows that 6-*endo*-H is absent in compound **3** (R = Me), and a new peak appears as a doublet at δ 2.58 ppm, arising from coupling to phosphorus (J 17.7 Hz). If the hydrogen was situated in the *exo* position, coupling of 6-*exo*-H to the olefinic hydrogens should be negligible because of its nearly perpendicular orientation, and 6-*exo*-H must appear as a doublet.

Examples of initial *exo* products that can transform to *endo* species in (η^4-diene)Fe(CO)$_3$ complexes upon standing are reported [10,11]. To our knowledge, the reaction discussed herein is the first example of *endo*-hydrogen-to-*exo*-hydrogen isomerization on the coordinated cyclic ring. When compound **3** (R = Me) was treated with n-BuLi and quenched with water, only compound **3** (R = Me) was recovered. After deprotonation with n-BuLi one *p*-orbital was left which was perpendicular to the planar (C(1),C(6),C(5)). Due to greater steric hindrance of the manganese tricarbonyl moiety, a proton was picked up from water molecules in an *exo* fashion.

There are two pathways in the above reaction, alkylation and isomerization in basic solution. The alkylation pathway is believed to proceed with a different intermediate from the deprotonated species. Proof of this must await further study. X-ray structural determination of **2** and **3** are in progress [12].

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