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Studies of the Reactions between P-donors and [(exo-6-R-η^5-2-MeO-C$_6$H$_5$)Mn(CO)$_2$NO]PF$_6$

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Synthetic studies have been carried out for the addition or substitution of phosphorus nucleophiles to the cation [(exo-6-R-η^5-2-MeO-C$_6$H$_5$)Mn(CO)$_2$NO]PF$_6$, 2. PPh$_3$ reacts with 2 to yield the CO displaced product and MePPh$_2$ attacks the dienyl ring of 2 to yield the phosphonium adduct or the metal to give the CO displaced depending upon the reaction temperatures. Nucleophilic addition of HPPh$_2$ to the dienyl ring of 2 gives a neutral substituted product. P(OMe)$_3$ reacts with 2 to yield a mixture of ring adduct and CO displaced product at room temperature. At -20 °C, P(OMe)$_3$ attacks the dienyl ring of 2 to give a posphonium adduct, which underwent Arbuzov reaction. This reaction affords a new route to the phosphonate complexes.

Introduction

Tertiary phosphines and phosphites have been proved to be particulary convenient nucleophiles for mechanistic investigations because they generally undergo clean addition to the π–hydrocarbon ligands to yield stable phosphonium adducts[1]. Apart from their intrinsic interest, these phosphonium adducts are potential precursors for synthetically useful organometallic ylides. The phosphonium adducts have been used successfully in preparing new derivatives of (benzene) tricarbonylchromium[2], ferrocene[3], and six- and seven-membered ring dienyl complexes of Fe(CO)$_3^+$. As part of a systematic study of the mechanism of nucleophilic attack on π–hydrocarbon ring ligands, Sweigart and Chung[5] reported the kinetic data for the addition of phosphorus and nitrogen donor to [(C$_6$H$_6$R)Mn(CO)(NO)(L)]$^+$ (R = Me, Ph; L = CO, PPh$_3$) complexes, 1, to give cyclohexadiene complexes. The present paper reports further synthetic studies of the reaction of [(exo-6-R-η^5-2-MeOC$_6$H$_5$)Mn(CO)$_2$NO]$^+$ (R = Me, Ph, and CH$_2$C(O) CH$_3$), 2, with phosphines RPPh$_2$ (R = H, Me, and Ph) and P(OMe)$_3$. The synthesis of [(exo-5-dimethylphosphino-exo-6-R-η^5-cyclohexadiene)Mn (CO)$_2$NO] (R = Me, Ph, and CH$_2$C(O)CH$_3$), 7, has been the subject of a preliminary communication[6].

Experimental

Elemental analyses were performed by Yanaco, MT-2 Elemental Analyzer at the chemical Analytic Center of the College of Engineering, Seoul National University. ^{1}H and ^{13}C-NMR spectra were measured on either Bruker AC 80 or Varian XL-200. Infrared spectra were recorded on a Perkin-Elmer 782 spectrometer and mass spectra were recorded on a VG ZAB-E double focusing mass spectrometer.

All solvents were purified by standard methods and all synthetic procedures were done under a nitrogen atmosphere. The [(arene)Mn(CO)$_3$]PF$_6$, [(cyclohexadienyl)Mn(CO)$_3$], and [(cyclohexadienyl)Mn(CO)$_2$NO]PF$_6$ were synthesized as previously described[7].

Preparation of 3. A 2 mole excess of PPh$_3$ was added to the corresponding compound in CH$_2$Cl$_2$. After stirring for 1 hr, an excess of diethyl ether was added to the reaction mixture to precipitate the product. The precipitate was filtered and washed several times with diethyl ether. The yield was 90% (R = Ph). R = Me: IR ν(CO and NO) 2040, 1778 cm^{-1}. R = Ph: IR ν(CO and NO) 2044, 1784 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.47 (d, J = 5 Hz, H^3), 4.83 (m, H^4), 3.86 (m, H^6), 3.52 and 3.11 (m, H^1 and H^5), 3.74 (s, OMe), 7.2–7.6 (m, Ph). Anal. Calcd for C$_{32}$H$_{28}$F$_6$MnNO$_3$P$_2$: C, 54.48; H, 4.00; N, 1.99. Found: C, 55.11; H, 3.79; N, 1.79.

Preparation of 4. A 1.5 mole excess of MePPh$_2$ was added to the suspension of the corresponding compound in CH$_2$Cl$_2$ at -20 °C. After stirring for 1 hr, an excess of diethyl ether was added to precipitate the unreacted salt and the CO–displaced one. After removal of the precipitates, the filtrate was concentrated and column chromatographed on basic alumina with diethyl ether, and then with CH$_2$Cl$_2$. The first coming out was PMePh$_2$ and the second one is the pro-

duct. The yield was 90% (R = Ph). R = Me: IR ν(CO and NO) 2056, 1977, 1750 cm^{-1}. EI-MS, m/z, 200 (PMePh$_2^+$), 122 (m-MeOC$_6$H$_4$Me$^+$). R = Ph: IR ν(CO and NO) 2053, 1998, 1749 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 5.83 (d, J = 5.9 Hz, H^3), 4.29 (m, H^5), 4.15 (m, H^6), 3.79 (s, OMe), 3.73 (m, H^1), 3.55 (m, H^4), 2.20 (d, J = 12.9 Hz, CH$_3$), 6.68–7.61 (m, Ph). Because compound **3** is very hygroscopic, we could not obtain good elemental analysis data.

Preparation of 5. A 5 mole excess of HPPh$_2$ was added to the corresponding compound in CH$_2$Cl$_2$ at 0 °C under N$_2$. After stirring for 1 hr, the solvent was evaporated the column chromatographed on silica gel with hexane, and then with benzene. The first coming out is the oxidized phosphine compound and the second one is the product. The yield was 63% (R = Ph). R = Me: IR (CO and NO) 2037, 1983, 1734 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 5.29 (d, J = 5 Hz, H^3), 3.63 (m, H^5), 2.78 (m, H^1 and H^6), 2.09 (m, H^4), 3.58 (s, OMe), 1.17 (d, J = 6 Hz, CH$_3$), 7.29–7.39 (m, Ph). R = Ph: IR ν(CO and NO) 2035, 1977, 1735 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ 5.34 (d, J = 5.2 Hz, H^3), 4.06 (m, H^5), 3.76 (m, H^1), 3.52 (m, H^6), 3.25 (s, Ome), 2.84 (m, H^4), 7.09–7.79 (m, Ph). Anal. Calcd for C$_{27}$H$_{23}$MnNO$_4$P: C, 63.41; H, 4.53; N, 2.74. Found: C, 63.51; H, 4.51; N, 2.57.

Preparation of 6. A 1.5 mole excess of P(OMe)$_3$ was added to the suspension of the corresponding compound in CH$_2$Cl$_2$ at room temperature. After stirring for 1 hr, an excess of diethyl ether was added to precipitate the CO-displaced compound. The precipitates wer filtered and washed several times with diethyl ether to remove the contaminant, P(OMe)$_3$. R = Ph: IR ν(CO and NO) 2040, 1790 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.82 (m, H^3), 6.25 (m, H^4), 5.28 (m, H^5), 4.13 (m, H^1 and H^6), 3.83 (s, OMe), 3.97 (d, J = 11 Hz, OMe), 7.1–7.3 (m, Ph). Anal Calcd for C$_{17}$H$_{22}$F$_6$MnNO$_6$P$_2$: C, 35.99; H, 3.90; N, 2.47. Found: C, 36.08; H, 4.32; N, 2.43.

Preparation of 7. A 10 mole excess of P(OMe)$_3$ was added to the suspension of the corresponding compound in CH$_2$Cl$_2$ at -20 °C. After stirring for 1 hr, the resulting solution was warmed to room temperature, and stirred for an additional 1 hr. The resulting solution was poured into the excess of diethyl ether, and the ether soluble fraction was column chromatographed on neutral alumina using THF after diethyl ether as an eluant to give the product in a yield of 80%. R = Me: IR ν(CO, NO) 2038, 1979, 1739 cm^{-1}. ^{13}C NMR (CDCl$_3$) δ 54.76, 68.9, 65.75, 38.93, 54.70 (OMe), 52.14 (P(OMe)$_2$), 22.32 (CH$_3$), 221.15, 224.22 (CO). EI-MS, m/z, 345 (M$^+$-CO), 317 (M$^+$-2CO), 287 (M$^+$-2CO-NO), 232 (M$^+$-2CO-NO-Mn). R = Ph: IR ν(CO, NO) 2042, 1984, 1742 cm^{-1}. ^{13}C NMR (CDCl$_3$) δ 52.76, 68.94, 62.57, 55.01 (OMe), 48.03, 51.74 (P(OMe)$_2$), 127.06, 127.93, 129.81, 129.83(Ph), 220.92, 224.50 (CO). EI-MS, m/z, 379 (M$^+$-2CO), 349 (M$^+$-2CO-NO), 294 (M$^+$-2CO-NO-Mn). R = CH$_2$C(O)CH$_3$: IR ν(CO, NO) 2041, 1983, 1740, 1715 cm^{-1}. ^{13}C NMR (CDCl$_3$) δ 48.98, 67.47, 62.52, 54.37 (OMe), 51.82 (P(OMe)$_2$), 35.50 (-CH$_2$-), 206.0 (-C(O)-), 29.85 (-CH$_3$), 220.40, 223.50C(O). EI-MS, m/z, 359 (M$^+$-2CO), 271 (M$^+$-2CO-NO-CH$_2$C(O)CH$_3$-Mn).

Attempts to do the Wittig reaction with Compound 4. Compound **4** (R = Me, 0.20g, 0.33 mmol) was dissolved in 30 ml THF and cooled to -78 °C. "BLi (0.52 mmol) was added dropwise to the compound **4** at -78 °C. The color turned deep red. Acetaldehyde (0.06 ml, 1 mmol) was added and the reaction mixture was stirred for 1 hr. While stirring, the color of

the solution turned brownish red. The reaction mixture was allowed to warm to room temperature and an excess of diethyl ether and water were added. The ether layer was separated, dried over anhydrous MgSO$_4$, and column chromatographed on silicagel with hexane and ether. The IR spectrum of the products shows 2030(VS), 1960(S), 1920 (VS), and 1780 cm^{-1}. According to the IR spectrum, the product consists of two kinds of compounds, and one of them is a tricarbonyl compound. No further investigation was carried out.

When the above reaction was carried out with compound **4** (R = Ph) and benzaldehyde, the reactant was recovered.

When the above reaction was carried out with compound **4** (R = Ph) and propionaldehyde, the reaction product was not characterized. The ^{1}H NMR spectrum of the product was different from what we expected.

Demetallation of Compound 5. A mixture of compound **5** (0.040g, mmol) and Me$_3$NO(0.13g, mmol) in 50 ml benzene was refluxed for 4 hrs. After cooled to room temperature, the solvent was evaporated. The organic compound was extracted with diethyl ether. After removal of the solvent, the white solid was left. ^{1}H NMR (CDCl$_3$) δ 3.90 (s, OME), 6.95–7.80 (m, Ph).

Demetallation of Compound 7. A 2 mole excess of Me$_3$NO was added to the corresponding comound **7** in benzene, and refluxed for 4 hr under nitrogen. The resulting solution was cooled to room temperature, and diethyl ether and water was added. The ther soluble organic compound was extracted. The extract was dried over anhydrous MgSO$_4$. The solvent was evaporated and the residue was column chromatographed on silica gel using THF : ether = 1:1 as an eluant to obtain compound **8** and **9**. Compound **8** (R = Ph) ^{1}H NMR (CDCl$_3$) H^1 3.66, H^3 5.14 (d, 6 Hz), H^4 3.44 (m), H^5 2.28 (d, J(P-H) = 18 Hz), H^6 2.97 (m), OMe 3.52 (s), P(OMe)$_2$ 3.17 (d, 10.5 Hz), 3.54 (d, 10.5 Hz), Ph 7.07–7.32 ppm. ^{13}C NMR (CDCl$_3$) C^1 129.0, C^2 129.90, C^3 162.35, C^4 141.66, C^5 35.59, C^6 38.56, OMe 54.92, P(OMe)$_2$ 51.70, Ph 126–129 ppm. EI-MS, m/z, 294 (M$^+$), 217 (M$^+$-Ph), 185 (M$^+$-P(O)(OME)$_2$). Compound **9** (R = Me) ^{1}H NMR (CDCl$_3$) H^2 5.05 (d, 6 Hz), H^3 6.85 (dd, 19, 6 Hz) H^5 2.73 (m), H^{6exo} 2.19(m), H^{6endo} 2.73(m), Me 1.06 (d, 6.7 Hz), OMe 3.65(s), P(OMe)$_2$ 3.74 (d, 14.7 Hz) ppm. ^{13}C NMR (CDCl$_3$) C^1 150.87 (d, 2.73 Hz), C^2 139.79 (d, 10.3 Hz), C^3 97.65 (d, 14 Hz), C^4 129.46 (d, 154 Hz), C^5 29.47 (d, 17.2 Hz), C^6 31.45 (d, 12 Hz), OMe 53.22, P(OMe)$_2$ 51.88 (d, 9.5 Hz), Me 21.96 ppm. EI-MS, m/z, 232 (M$^+$), 217 (M$^+$-,e), 123 (M$^+$-P(O)(OMe)$_2$). Compound **8** (R = CH$_2$C(O)CH$_3$) ^{1}H NMR (CDCl$_3$) H^1 4.72 (m), H^3 5.24 H^4 2.88(m), H^5 3.19 (d, 13 Hz), H^6 2.88(m) CH$_2$ 2.16 (d, 6 Hz), -C(O)CH$_3$ 2.06(s), OMe 3.58(s), P(OMe)$_2$ 3.76 (d, 11.8 Hz) ppm. EI-MS, m/z, 274 (M$^+$), 217 (M$^+$-CH$_2$C(O)CH$_3$), 165 (M$^+$-P(O)(OMe)$_2$).

Results and Discussion

When PPh$_3$ reacts with **1** in polar solvent, the reaction does not go to completion. Usually the equilibrium mixture is obtained and the product is a phosphonium salt. However, when PPh$_3$ reacts with **2** in polar solvent such as CH$_2$Cl$_2$ and CH$_3$CN, the CO-displaced product **3** is obtained as a sole product (eq. 1).

(eq. 1)
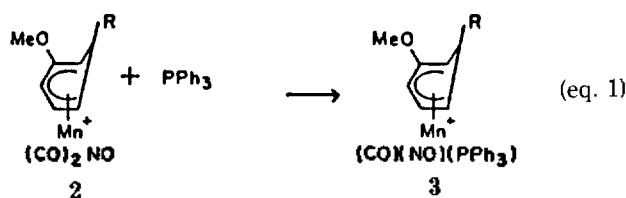
This would be understandable if we consider the inductive influence of methoxide group. Kane-Maguire studied[8,9] the influence of ring substituents on the rate of PPh_3 addition to dienyl ring of $[(RC_6H_6)Fe(CO)_3][BF_4]$. According to his study, $[(C_6H_6OMe)Fe(CO)_3][BF_4]$ is generally 5–10 times slower than the parent cation $[(C_6H_7)Fe(CO)_3][BF_4]$. Due to the inductive effect of methoxide group the cyclohexadienyl ring of 2 would lose some of the electrophilicity and can not react with PPh_3 to yield a phosphonium salt. Finally the product, 3, is obtained.

$MePPh_2$ reacts with 1 to yield a phosphonium adduct. However, with 2, $MePPh_2$ attacks the dienyl ring to yield a phosphonium salt or the metal to give the CO-displaced compound depending upon the reaction condition. When the reaction was carried out in CH_3CN at room temperature, the CO-displaced was obtained as a sole product. However, when the reaction was carried out in CH_2Cl_2 at $-20\,°C$, the phosphonium adduct was obtained as a major product (eq. 2).


(eq. 2)
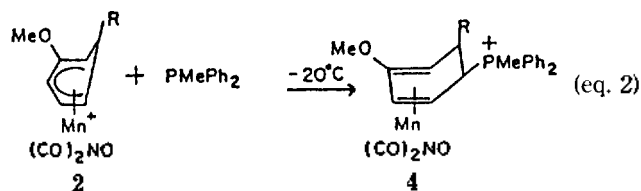
When we compare the cone angle (136°) of $PMePh_2$ to that (145°) of PPh_3[10], there would be less steric conjestion for $PMePh_2$ addition than for PPh_3 addition.

The reaction of $PMePh_2$ addition to 2 is governed by either kinetic or thermodynamic factors. If the reaction conditions are carefully adjusted it will be possible for the phosphonium adduct to accumulate and not proceed to the CO-displaced compound. Under such conditions phosphonium will be dominant product and the reaction can be said to be under kinetic control. Under slightly more energetic conditions the phosphonium adduct will be transformed to the CO-displaced. When this occurs the CO-displaced will be dominant product since it is more stable. The phosphine substituent in compound 4 is in an exo-position by analogy with the established structures of phosphino-product $[Bu_3P-C_6H_5Me)(Mn(CO)_2NO]\,PF_6$[11].

To do the Wittig reaction, the phosphonium adduct 4 was deprotonated by using several kinds of bases, and the resulting ylide was reacted with acetaldehyde or benzaldehyde or propionaldehyde. The expected product was not obtained. Instead, the phosphonium adduct or (cyclohexadienyl)Mn(CO)$_3$ was obtained depending upon R and aldehyde. This would be understandable. There are several positions which can be deprotonated. Even if the hydrogen situated at the sp^3 carbon was deprotonated, there was some steric crowdness around carbanion center to be approached by aldehyde. There are some possibilities of electron transfer. When carbon nucleophiles (MeLi, $CdMe_2$, MeMgCl, $LiCuMe_2$, and KCH_2NO_2) in THF react with compound 1, large amounts of (cyclohexadienyl)

$Mn(CO)_3$ are produced[7]. Most likely this is due to initial electron transfer from the carbanion to compound 1 followed by loss of NO and attack by a second molecule of 1. The same kind electron transfer reaction might occur with compound 2.

Nucleophilic addition of $HPPh_2$ to the dienyl ring of 2 in polar solvents gives neutral substituted product 5 in a reasonable yield (eq. 3).

(eq. 3)
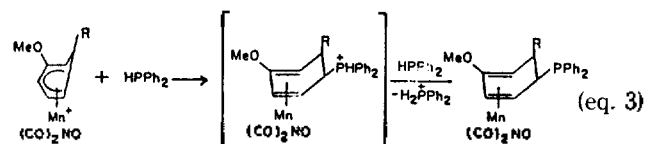
This reaction is very similar to the nucleophilic addition of aniline to the dienyl ring of $[(C_6H_7)Fe(CO)_3][BF_4]$ giving neutral substituted products of the type $[1-4-\eta-5-exo-N-anilinocyclohexa-1,3-diene]Fe(CO)_3^8$. Considering the basicity of $RPPh_2$ (R = H, Me, and Ph), $HPPh_2$ is the least basic. In spite of the low basicity of $HPPh_2$, the final product was the ring-attacked cyclohexadiene complex. This means that the reaction product of the reaction between $RPPh_2$ and 2 is dependent largely upon the size of the nucleophile and the presence of proton which can be deprotonated. Infrared spectra $\nu(CO)$ of the equimolar mixtures of $HPPh_2$ and 2 show two additional shoulders (R = Ph: 2051 and 1998 cm^{-1}) besides those of the reactant (R = Ph: 2111 and 2078 cm^{-1}) and the neutral product (R = Ph: 2035 and 1977 cm^{-1}). These bands can be assigned to the intermediate cationic species. The cationic species would undergo rapid proton loss to yield the neutral product. This observation supports the general step-wise mechanism. The complex 5 was demetallated by refluxing with Me_3NO in benzene. The aromatized product was obtained as a sole product. We expect that by changing the reaction conditions or oxidizing agents cyclohexadiene compound would be liberated and the cyclohexadiene compound would be undergone electrophilic attack by MeI, and can be used to difunctionalize.

The reaction of $P(OMe)_3$ with a transition metal complex most often results in straightforward ligand substitution at the metal center. In some instances the final product contains a phosphonato rather than the phosphito ligand[12]. The phosphito ligand dealkylates to a phosphonate despite the absence of an apparent nucleophile.

$P(OMe)_3$ reacts with 1 to yield a mixture of ring adduct and CO displaced product, as already reported[7]. In the same way, $P(OMe)_3$ also reacts with 2 to yield a mixture of ring adduct and CO displaced product at room temperature, as judged from IR spectra. As described in Experimental section, we could isolate and characterize the CO displaced product. According to the preliminary experiment, the phosphite ligand of the CO displaced product dealkylated to a phosphonate (R = Ph: ν(CO and NO) 1960, 1710 cm^{-1}) under the reaction conditions of a large excess of $P(OMe)_3$ and UV irradiation (eq. 4). The synthesis and characterization of the metal-


(eq. 4)
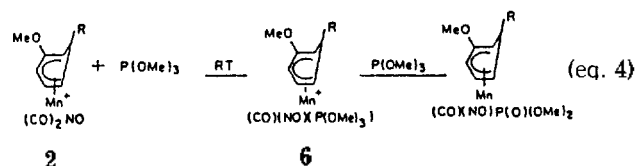
centered phosphonate compound will be published separately.

When the reaction temperatue was lowered to -20 °C and a large excess of P(OMe)$_3$ was used, P(OMe)$_3$ attached the dienyl ring of 2 to give a phosphonium adduct, which underwent Arbuzov reaction as already published[6]. The compound 7 was obtained in a reasonable yield (eq. 5). This reaction
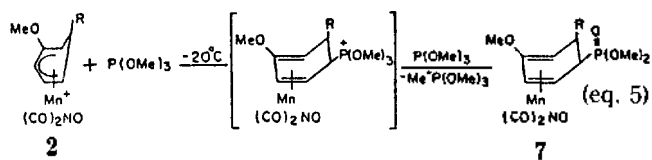
provides an easy and viable synthetic entry into the phosphonate complexes 7 which are analogues of the (5-dialkylphosphonocyclohexadiene) Fe(CO)$_3^{13}$. The phosphonate compounds 7 are moderately stable at room temperature.

Demetallation of compound 7 was performed to obtain a cyclohexadiene compound. The Mn(CO)$_2$NO group was easily removed by refluxing compound 7 with Me$_3$NO in benzene. After demetallation, compound 8 or 9 was isolated as a major product depending upon the R group (eq. 6). With
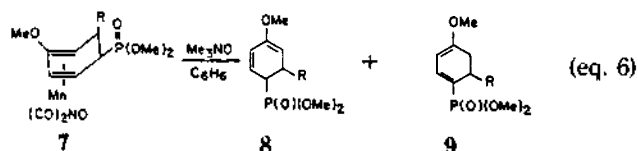
R = Ph and CH$_2$C(O)CH$_3$, the compound 8 was isolated as a major product. With R = Me the compound 9 resulting from double-bond migration was obtained as a major product. We expect that compound 8 or 9 would be good intermediates to make 4,5-disubstituted cyclohex-2-enones.

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