oxides such as $SrTiO_3$[5,6] ($g=1.994\pm0.001$), calcium zirconate ($g=1.994$)[7], $\alpha$-$Al_2O_3$ ($g=1.994$)[8], $SrLa_3NiMnO_8$ ($g=1.995\pm0.001$)[9] and (BaLa)$(MgMn)O_{5.5}$ ($g=1.995$)[10]. There are no additional signal which might be attributed to Mn(II), Mn(V), or Mn(VI) ions. The $g$-values of Mn(II) in various oxides are ranging from 1.998 to 2.003[11] at room temperature, which is not found in our spectrum. In case of Mn(III), however, its relaxation time is so short that any signal cannot be found at room temperature. Thus, considering the results of redox titration and EPR spectrum, it is concluded that a small amount of Mn(III) ions are stabilized in $(CaLa)(MgMn)O_{6-x}$, which can therefore be formulated as $(CaLa)(MgMn^{III}_{0.1}Mn^{IV}_{0.9})O_{5.45}$. Goodenough[12] postulated that Mn(III) hybridizes the stable $dsp^2$ lattice orbitals (favoring the square planar symmetry) and Mn(IV) the stable $d^2sp^3$ orbitals (favoring the octahedral symmetry). Based on this postulate, it is most probable that Mn(III) ions in $(CaLa)(MgMn^{III}_{0.1}Mn^{IV}_{0.9})O_{5.45}$ favor the oxygen vacant site having square planar symmetry. In order to confirm the valence states of manganese ions, the magnetic susceptibility was measured as a function of temperature. The variation of $X_m^{-1}$ *vs* $T$ is shown in Figure 2. Diamagnetic contribution of every ion in $(CaLa)(MgMn)O_{5.45}$ to $X_m$ is corrected according to Selwood[13]. $(CaLa)(MgMn)O_{5.45}$ follows the Curie-Weiss law above 200 K with Curie constant $C=2.32$, Weiss constant $\theta=29$ K and effective magnetic moment $\mu_{eff}=2.828\sqrt{C}=4.31$ $\mu_B$. The Curie and Weiss constants were obtained from the least square fit of $X_m^{-1}=(T-\theta)/C$ in the temperature domain from 200 K to 400 K. Generally the orbital motions of 3d electrons in crystal lattice are quite quenched by ligand ions[14]. Thus, in the absence of magnetic interaction between 3d metal ions, the observed moments are well consistent with the spin-only values. Therefore, the effective magnetic moment of $(CaLa)(MgMn^{III}_{0.1}Mn^{IV}_{0.9})O_{5.45}$ can be calculated as the followings: $\mu_{eff}^2=0.1\times\mu_{eff}^2(Mn^{III})+0.90\times\mu_{eff}^2(Mn^{IV})=0.1\times(4.90)^2+0.9\times(3.87)^2=15.9$ or $\mu_{eff}\simeq4.0$ $\mu_B$. Then it should be noted that the observed moment of 4.31 is somewhat larger than the spin-only value, which implies the existence of magnetic coupling between manganese ions in the crystal lattice. There might be two kinds of possible magnetic interactions in the lattice: Mn(III)-O-Mn(IV) and Mn(IV)-O-Mn(IV). According to Goodenough[12], the manganese ions can ferromagnetically coupled in the former case, and antiferromagnetically coupled in the latter case. Therefore the somewhat larger value of observed magnetic moment might result from the possible ferromagnetic interaction between Mn(III) and Mn(IV) ions in $(CaLa)(MgMn^{III}_{0.1}Mn^{IV}_{0.9})O_{5.45}$, which is consistent with the positive value of the observed Weiss constant. But the antiferromagnetic coupling (Mn(IV)-O-Mn(IV)) at low temperature could not be excluded completely, because of the small positive curvature, indicating the antiferro-paramagnetic transition, in the $X_m^{-1}$ *vs* $T$ plot (Figure 2) below 200 K.

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## Synthesis of $[\{\eta^6\text{-}C_6H_5NPhC(O)R'\}Mn(CO)_3]PF_6$ and Its Reactivity toward Nucleophiles

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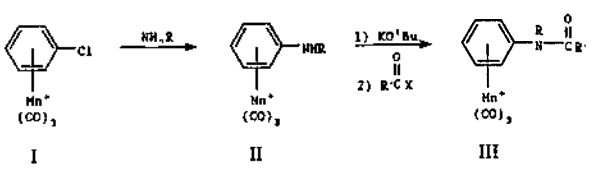
$[(Halobenzene)Mn(CO)_3]^+$ is a versatile starting compound. The high reactivity of the manganese complex is utilized in the preparation of other functionally substituted arene complexes by substitution of chloride with anionic or neutral nucleophiles[1].

Several years ago, (aromatic amide)$FeCp^+$ cations were made by using (haloarene)$FeCp^+$ cations[2]. However, no attempts were made to synthesize (aromatic amide)$Mn(CO)_3^+$ cations. When we compared the electrophilicity of $FeCp^+$ and $Mn(CO)_3^+$, we expected that the (aromatic amide)$Mn(CO)_3^+$ compounds would be potentially more versatile synthetic reagents. We decided to make the (aromatic amide)$Mn(CO)_3^+$ and to study the reaction between (aromatic amide)$Mn(CO)_3^+$ and nucleophiles. In this note, we report the formation of $[\{\eta^6\text{-}C_6H_5NPhC(O)R'\}Mn(CO)_3]PF_6$ (R'=Ph and Me) and its reaction with $H^-$, PhMgBr, MeMgBr, $LiCH_2CN$, and $LiCMe_2CN$.

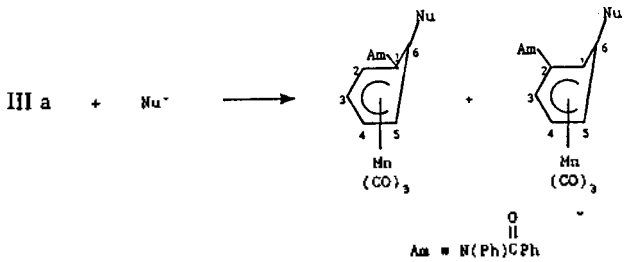
$[\{\eta^6\text{-}C_6H_5\text{-}NPhC(O)R'\}Mn(CO)_3]PF_6$ was prepared according to the following scheme. The first step was reported




I II III

(a, R' = Ph ; b, R' = Me)

by Pauson and Segal in 1975[1]. When we used ammonia gas as an amine, the expected compound (aniline)$Mn(CO)_3^+$ was easily obtained. However, the next step with (aniline)$Mn(CO)_3^+$ was not easy to follow. After all, the expected final product was not obtained. When we used $NH_2Ph$ as an amine, we could get the expected final product, **III**. The yields were not high due to the side reaction. The side product was the imine compound, $[(C_6H_5{=}NPh)Mn(CO)_3]$. The overall yield was 34% for R=Ph and 52% for R=Me[3]. Compounds **III** were stable in the air, but rather unstable in the polar solvent suchas acetone and acetonitrile. In order to evaluate the possible effects of various factors that may influence the site of nucleophilic addition, we have examined the reaction of hydride and some carbanions with **IIIa**.




Hydride addition to **IIIa** was studied by using three kinds of hydride sources. For the addition of $NaBH_4$ or $NaBH_3CN$, the hydride attacked the coordinated arene ring. The product gives typical $^1$H-NMR spectrum for coodinated cyclohexadienyl compound. The ortho and meta-adducts were obtained in the ratio of 10:1[4]. For the addition of $LiAlH_4$, $(C_6H_7)Mn(CO)_3$ was obtained as a sole product. This compound was an unexpected and might be produced as follows: the hydride of $LiAlH_4$ substituted the amide group, and then hydride reattacked the coordinated arene ring to give $(C_6H_7)Mn(CO)_3$[5].

For the addition of MeMgBr to **IIIa**, the ortho-and-meta-adducts were obtained in the ratio of 4:1[6]. For the addition of PhMgBr to **IIIa**, the ortho-, meta-, and para-adducts were obtained in the ratio of 2:30:1[7].

For the addition of $LiCMe_2CN$, the meta-adduct was obtained as a major-product[8]. For the addition of $LiCH_2CN$, the ortho-adduct was obtained as a major product[9]. For the addition of $LiCH_2C(O)CH_3$, it was very difficult to separate the isomers. We could not determine which one was the major product. However, the formation of the expected product was inferred from its spectroscopic and elemental analysis data[10]. For the addition of NaCN or $NaCH(CO_2Me)_2$, the yield of the products was very poor. We could only confirm the formation of the product by checking the infrared spectral data. For the addition of $BrZnCH_2CO_2Me$ or KF, we could confirm the formation of the product. However, the crude product was very unstable and readily decomposed while taking $^1$H-NMR spectrum in $CDCl_3$. We failed to characterize the cyclohexadienyl compound in detail. According to the inductive effect of the amide group in compound **IIIa**, we expected the exclusive formation of meta-adduct. However, we could see the formation of ortho-adduct and even the para-adduct. From the above results, the position of attacking site would be largely related to the bulkyness of the nucleophile instead of the inductive effect of amide group.

In conclusion, we could synthesize $[\{\eta^6\text{-}C_6H_5NPhC(O)R'\}Mn(CO)_3]^+$ cations from $[(C_6H_5Cl)Mn(CO)_3]^+$. The inductive effect of the amide group was not great. The steric effect of the amide group would be considerable. Therefore, the site of nucleophilic attack would be largely controlled by the size of nucleophiles. For the addition of $H^-$, $^-CH_2CN$, and $Me^-$, the ortho-adducts were obtained as major products. For the additions of $Ph^-$ and $^-CMe_2CN$, the meta-adducts were obtained as major products. The directive effect of amide group was rather small compared to other substituents, such as -OMe[11]and $-Si(OCH_2CH_2)N$[12]. This diminishes the utility of compound **III** in the synthetic application.

## Experimental

A typical procedure for the preparation of **IIIa**. $[(C_6H_5NHPh)Mn(CO)_3]PF_6$ (0.75g, 1.7 mmol) and Bu'OK (0.19 g, 1.7 mmol) were placed in a dried Schlenk type flask under nitrogen. Anhydrous THF (30 m*l*) was added to the flask. The solution was cooled to ice temperature. Benzoyl chloride (3.4 mmol) was added to the yellow solution. the color of the resulting solution turned to light brown. After being stirred for 0.5 h, the yellow solution was allowed to warm to room temperature. The solution was stirred for another 1 h. The yellow solution was filtered and the filtrate was evaporated to dryness. The yellow residue was washed with diethyl ether (30 m*l*×5). The crude product was recrystallized in diethyl ether/THF solution. The product was dried (yield: 0.31 g, 34%). IR $\nu_{CO}$ 2064, 2003 cm$^{-1}$, $\nu_{C=O}$ 1684 cm$^{-1}$. Anal. Calcd. for $C_{22}H_{15}F_6MnNO_4P$: C, 47.42; N, 2.71; N, 2.51. Found: C, 46.73; H, 2.75; N, 2.44.

A typical procedure for the reaction of **IIIa** with Grignard reagents. To a stirred solution of complex **IIIa** (0.20 g, 0.36 mmol) in THF (25 m*l*) at 0℃ was added PhMgBr (0.7 m*l* in hexane, 1.1 mmol). The color of the solution turned to brownish yellow. After being stirred for 0.5 h, the reaction mixture was allowed to warm to room temperature. Several drops of 0.1 N HCl solution was added to destroy the unreacted PhMgBr. Diethyl ether (40 m*l*) and water (30 m*l*) were added to the solution. The organic layer was separated and dried over anhydrous $MgSO_4$. The organic layer was concentrated and column chromatographed on silica gel with benzene (0.15 g, 85%), $^1$H-NMR($CDCl_3$) δ 6.43(d, 7 Hz, $H^3$), 5.18(t, 6.4 Hz, $H^4$), 3.87(t, 6.4 Hz, $H^5$), 3.43(d, 6 Hz, $H^1$), 3.39(t, 6 Hz, $H^6$) ppm. IR $\nu_{CO}$ 2010, 1920 cm$^{-1}$, $\nu_{C=O}$ 1657 cm$^{-1}$. Anal. Calcd. for $C_{28}H_{20}MnNO_4$:C, 68.72; H, 4.12; N, 2.86. Found: C, 68.37; H, 4.24; N, 2.81.

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3. **IIIb**: IR $\nu_{CO}$ 2070, 2000 cm$^{-1}$, $\nu_{C=O}$ 1693 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2.05(s, Me), 6.25-7.65(m, Ph) ppm; Anal. Calcd. for $C_{17}H_{13}F_6MnNO_4P$: C, 41.23; H, 2.65; N, 2.83. Found: C, 42.01; H, 2.67; N, 2.62.
4. To a stirred suspension of **IIIa** (0.20 g) in 15 m*l* of THF

at −5℃ was added a slight excess of $NaBH_4$ or $NaBH_3CN$. After it was stirred for 1 h, the solution was evaporated to dryness extracted with diethyl ether (100 ml). Evaporation of the ether gave a yellow crystalline solid of the ortho and meta adducts (80 % yield). The ratio of ortho- and meta-adduct was determined by comparing the integration of $^1$H-NMR spectrum. The mixture has the following spectral properties: IR $\nu_{CO}$ 2015, 1920 cm$^{-1}$, $\nu_{C=O}$ 1655 cm$^{-1}$. Anal. Calcd. for $C_{22}H_{11}MnNO_4$: C, 63.93; H, 3.90; N, 3.39. Found: C, 63.11; H, 4.18; N, 3.49. Ortho-adduct: $^1$H-NMR($CDCl_3$) δ 2.54(t, 6 Hz, $H^5$), 2.58(d, 13.7 Hz, $H^{6\text{-exo}}$), 3.04(dd, 13.7 Hz, 6 Hz, $H^{6\text{-endo}}$), 4.13(t, 6 Hz, $H^4$), 4.46(d, 6 Hz, $H^2$), 4.97(t, 6 Hz, $H^3$) 6.71−7.40(m, Ph) ppm. Meta-adduct: $^1$H-NMR($CDCl_3$) δ 1.86(d, 11.6 Hz, $H^{6\text{-exo}}$), 2.32(m, $H^{1\text{ and }5}$), 3.05(ddd, 11.6 Hz, $H^{6\text{-endo}}$), 4.26(t, 6 Hz, $H^4$), 6.19(d, 6 Hz, $H^3$), 6.68-7.28(m, Ph) ppm.

5. (a) The reaction was studied by using a slight excess of $LiAlH_4$ in THF at 0℃. Ms, m/z, 218($M^+$), 190($M^+$-CO), 134($M^+$-2CO). (b) G. Winkhaus and G. Wilkinson, *Proc. Chem. Soc.*, 31 (1960); G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961).
6. A 52% isolated yield of ortho- and meta-adduct was obtained. The ratio of ortho- and meta-adduct was determined to be 75:25. The mixture has the following spectral properties: IR $\nu_{CO}$ 2000, 1920 cm$^{-1}$, $\nu_{C=O}$ 1650 cm$^{-1}$. Ms, m/z, 427($M^+$), 399($M^+$-CO), 371($M^+$-2CO), 343($M^+$-3CO), 287($M^+$-$Mn(CO)_3$-H). Ortho-adduct: $^1$H-NMR($CDCl_3$) δ 0.73 (d, 6.4 Hz, Me), 3.43-3.53(t+m, $H^{5\text{ and }6}$), 4.76(t, 5.7 Hz, $H_4$), 5.00(d, 5.8 Hz, $H^2$), 5.66(t, 5.8 Hz, $H^3$), 6.91-7.60 (m, Ph) ppm. Meta-adduct: $^1$H-NMR($CDCl_3$), 0.50(d, 6.5 Hz, Me), 2.64(m, $H^6$), 3.10(m, $H^{1\text{ and }5}$), 4.82(t, 5.6 Hz, $H^4$), 6.36(d, 5.6 Hz, $H^3$), 7.00-7.80(m, Ph) ppm.
7. The isomer ratio was determined by the integration of $^1$H-NMR spectrum.
8. A 70% isolated yield of meta-adduct was obtained. IR $\nu_{CO}$ 2020, 1925 cm$^{-1}$, $\nu_{C-O}$ 1655 cm$^{-1}$, $\nu_{CN}$ 2230 cm$^{-1}$. Ms, m/z, 480($M^+$), 452($M^+$-CO), 424($M^+$-2CO), 396($M^+$-3CO), 340($M^+$-$Mn(CO)_3$-H). $^1$H-NMR($CDCl_3$) δ 1.05(d, 5.8 Hz, Me), 2.56(t, 5.9 Hz, $H^5$), 3.19(t, 5.9 Hz, $H^6$), 3.51(d, 5.7 Hz, $H^1$), 5.05(t, 6.2 Hz, $H^4$), 6.17(d, 6.2 Hz, $H^3$), 7.16-7.34(m, Ph) ppm.
9. A 50% isolated yield of ortho-adduct was obtained. IR $\nu_{CO}$ 2010, 1910 cm$^{-1}$, $\nu_{C-O}$ 1640 cm$^{-1}$, $\nu_{CN}$ 2240 cm$^{-1}$. $^1$H-NMR($C_6D_6$) δ 1.29(d, 7.7 Hz, $CH_2$), 2.51(t, 6.4 Hz, $H^5$), 3.55(tt, 6.4 Hz, $H^6$), 3.96(t, 5.8 Hz, $H^4$), 4.60(d, 5.9 Hz, $H^2$), 4.70(t, 5.8 Hz, $H^3$), 6.80-7.50(m, Ph) ppm. Anal. Calcd. for $C_{23}H_{17}MnN_2O_4$: C, 63.73; H, 3.79; N, 6.19. Found: C, 63.69; H, 4.55; N, 5.45.
10. IR $\nu_{CO}$ 2107, 1920 cm$^{-1}$, $\nu_{C-O}$ 1710, 1655 cm$^{-1}$. Ms, m/z, 413($M^+$-2CO), 385($M^+$-3CO), 342($M^+$-3CD-$CH_3CO$). Anal. Calcd. for $C_{25}H_{20}MnNO_5$: C, 63.97; H, 4.30; N, 2.98. Found: C, 64.65; H, 5.68; N, 2.87.
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## Antibody for L-Mandelate. Kinetic Assay of Monoclonal Antibody and Optical Resolution with Antibody

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During the past few years, the area of catalytic antibodies has emerged as a new field of both chemistry and biology.[1-3] In principle, tailor-made artificial enzymes can be obtained by designing antibodies capable of stabilization of the transition state of the target reaction. At present, efforts are primarily made on development of basic concepts and techniques for the enhancement of the efficiency of catalytic antibodies.

The primary biological function of antibodies is recognition of the structure of the antigen and very strong complex formation with the antigen. In order to develop a catalytic antibody, induction of the proper structure of the binding site of the antibody is attempted by using antigens resembling the transition state of the target reaction. Since antibodies are not readily produced against an antigen with a small size, the transition-state analogue is linked as a hapten to a large molecule such as proteins. When the resultant antigen with a large size is used for production of the antibody, a great number of antibodies are formed, each recognizing a small portion of the antigen. Then, monoclonal antibodies with correct catalytic behavior are slected from the polyclonal antibodies. In the study of catalytic antibodies, the design of the structure of the transition-state analogues and the selection of the right monoclonal antibodies are among the most crucial steps.

Several assay techniques are known for the selection of the monoclonal antibodies from the mixture of antibodies formed in immunological response to a single antigen. These include solid-phase assays such as ELISA (Enzyme Linked Immuno Sorbent Assay) or IRMA (Immuno Radio-Metric Assay), soluble-phase assay, immunodouble diffusion, cellular assay, biological assay, and immunocytochemical assay.[4] Monoclonal antibodies recognizing the hapten can be selected by using these techniques. Even if a monoclonal antibody specific for the hapten is selected, the chance that the antibody recognizes the functional group introduced to the hapten as the transition state analogue and, furthermore, catalyzes the target molecule is not large.

We have been interested in the development of kinetic methods for the selection process. If the ability to catalyze the target reaction is tested in the selection process, monoclonal antibodies with the desired catalytic ability can be, in principle, chosen at this stage. Toward this end, we have tested the kinetic assay method in the preparation of the monoclonal antibodies for L-mandelate(**L-1**). Hapten **L-1** was coupled to γ-globulin, the carrier protein, at pH 5.0 and 4℃ by using 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide, followed by exhaustive dialysis against 10 mM phosphate, 150