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Preparation and Characterization of Ordered Perovskite (CaLa) (MgMo) O_6

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The polycrystalline powder of (CaLa) (MgMo)O_6 has been prepared at 1350 °C in H_2/H_2O and N_2 flowing atmosphere. The powder X-ray diffraction pattern indicates that (CaLa) (MgMo)O_6 has a monoclinic perovskite structure with the lattice constants $a_o = b_o = 7.901(1)$ Å, $c = 7.875(1)$ Å and $\gamma = 89° 16'(1')$, which can be reduced to orthorhombic unit cell, $a = 5.551(1)$ Å, $b = 5.622(1)$ Å and $c = 7.875(1)$ Å. The infrared spectrum shows two strong absorption bands with their maxima at 590(ν_3) and 380(ν_4) cm, which are attributed to $2T_{1u}$ modes indicating the existence of highly charged molybdenum octahedron MoO_6 in the crystal lattice. According to the magnetic susceptibility measurement, the compound follows the Curie-Weiss law below room temperature with the effective magnetic moment 1.83(1) μ_B, which is well consistent with that of spin only value (1.73 μ_B) for Mo^{5+} with $4d^1$-electronic configuration within the limit of experimental error. From the thermogravimetric analysis, it has been confirmed that (CaLa) (MgMo)O_6 decomposes gradually into $CaMoO_4$, MoO_3, MgO, La_2O_3 and unidentified phases due to the oxidation of Mo^{5+} to Mo^{6+}.

Introduction

In perovskite type compounds $\{A_2(BB')O_6\}$ and $\{(AA')(BB')O_6\}$, the B and B′ cations are coordinated with six oxygen ions to form octahedron in the crystal lattice. It is well known that the differences in charges and ionic radii between B and B′ are the major factor that determine the ordered structure[1] and the structural phase transition of solid solution $(ABO_3)_{1-x}(AB'O_3)_x$[2]. Therefore, it is expected that the electrical and magnetic properties of perovskite type oxide should be dependent upon the valency pair (B,B′).

A complete ordered structure of B and B′ cation is shown in Figure 1, where the unit cell is doubled along all three axes, compared to a primitive unit cell of ABO_3.

Sleight and Weiher[3] reported the valency pairs (M, Re) (M = Mn, Fe, Co, Ni) in the ordered perovskites $Ba_2(MRe)O_6$, where they confirmed the valency of ions from the structural point of view rather than physical characterizations.

When A cation is divalent and A′ trivalent in (AA′) (BB′)O_6, the valency pair (B, B′) should be one of three possible pairs (1+, 6+), (2+, 5+) and (3+, 4+) by charge neutrality condition. For all the compounds with the formula of (SrLa) (BB′)O_6 where {B(II), B′(V)} = (Co^{2+}, Nb^{5+}), (Co^{2+}, Sb^{5+}), (Co^{2+}, Ta^{5+}), (Ni^{2+}, Nb^{5+}), (Ni^{2+}, Sb^{5+}), (Ni^{2+}, Ta^{5+}), (Cu^{2+}, Nb^{5+}), (Cu^{2+}, Sb^{5+}) and (Cu^{2+}, Ta^{5+}), the ordered

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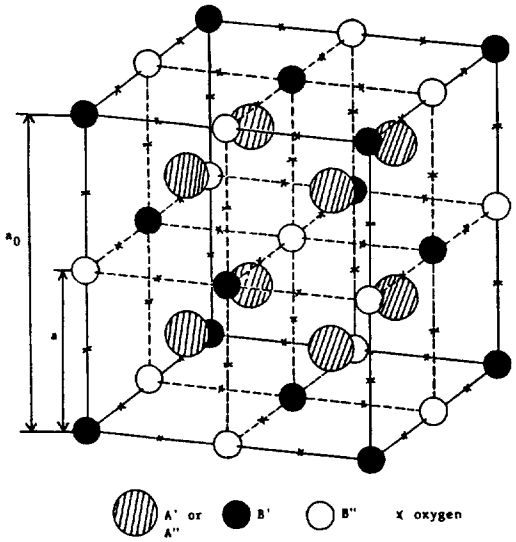

Figure 1. Unit cell of ordered perovskite-type (AA')(BB')O_6, where A and A' are distributed at random.

perovskite structures were reported[4], but on the other hand, random distribution was observed where {B(III), B'(IV)} = (Mn^{3+}, Ti^{4+}), (Mn^{3+}, Ir^{4+}), (Fe^{3+}, Ti^{4+}) and (Fe^{3+}, Ir^{4+}).

In this study the stable Mg^{2+} ion has been chosen as a B cation in order to stabilize Mo^{5+} in the octahedral site as a B' and a new perovskite compound (CaLa) (MgMo)O_6 has been synthesized and characterized by the crystallographic, infrared absorption spectroscopic, thermogravimetric analyses and magnetic susceptibility measurement.

Experimental

The polycrystalline sample of (CaLa) (MgMo)O_6 were prepared from high purity $CaCO_3$, La_2O_3, Mg $(CH_3COO)_2{\cdot}4H_2O$ and MoO_3. The stoichiometric mixture was ground thoroughly in agate mortar with small amounts of ethanol, dried, pelleted and prefired in an alumina boat at 1100 °C for 10 hours under a wet hydrogen flowing atmosphere. The sample was reground, repelleted and heated at 1350 °C for several hours under a nitrogen flowing atmosphere The above process has been repeated until a homogeneous product was obtained.

The identification of the resultant phases and the determination of the lattice constants were carried out a powder X-ray diffraction method with nickel-filtered Cu-K_α radiation (wavelenth = 1.5418Å), using Jeol X-ray diffractometer.

Infrared absorption spectrum was obtained in the wavenumber range from 200 cm^{-1} to 3000 cm^{-1}, using a CsBr pellet with Jasco Diffraction grating Infrared Spectrophotometer.

Thermogravimetric analysis was from room temperature to 1000 °C under air atmosphere with Rigaku Thermal Analsis Station Tas 100.

Magnetic susceptibility was measured with a Faraday-type magnetobalance in the temperature range from liquid nitrogen boiling temperature to room temperature.

Results and Discussion

1. Preparation. In the preparation of complex perovskite (CaLa) (MgMo)O_6 no single phase could be isolated under air atmosphere. The major phase in the X-ray diffraction pattern was $CaMoO_4$, which has the scheelite structure[5] where Mo^{6+} ion is stabilized in a tetrahedral site as MoO_4^{2-} tetrahedron.

In order to stabilize Mo^{5+} ion into octahedral site in the perovskite, the starting material Mo^{6+} in MoO_3 had to be reduced to Mo^{5+} ion. The synthesis could be achieved only under the reducing condition, that is, nitrogen or wet hydrogen flowing atmosphere.

2. Crystallographic analysis. The X-ray powder diffraction pattern (Figure 2) indicates that (CaLa) (MgMo)O_6 has perovskite structure with superlattice lines (111, 111, 311, 113, 3$\bar{1}$1 and 1$\bar{1}$3) caused by the rock-salt arrangement

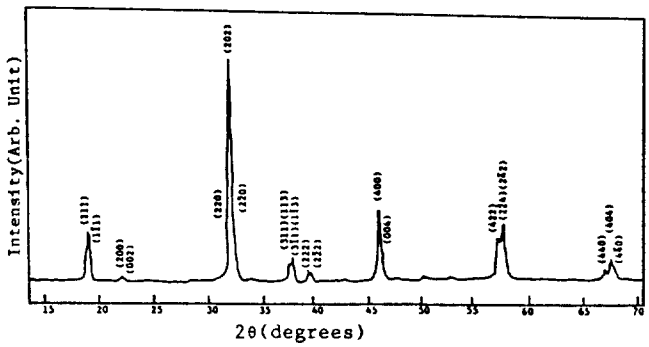

Figure 2. Powder X-ray diffraction pattern for (CaLa)(MgMo)O_6; monoclinic indexation.

Table 1. Powder X-ray diffraction data for (CaLa) (MgMo)O_6

h k l	H K L	$d_{obs.}$ (Å)	d_{cal} (Å)	$I_{obs.}$	I_{cal}
0 1 1	1 1 1	4.575	4.575	13	13
1 0 1	1 $\bar{1}$ 1	4.537	4.537	6	12
1 1 0	2 0 0	3.950	3.950	4	4
0 0 2	0 0 2	3.937	3.398		
0 2 0	2 $\bar{2}$ 0	2.811	2.811	23	25
1 1 2	2 0 2	2.788	2.789	100	100
2 0 0	2 2 0	2.776	2.776	21	24
1 2 1	3 1 1	2.387	2.390	5	5
0 1 3	1 1 3	2.378	2.379		2.4
2 1 1	3 $\bar{1}$ 1	2.373	2.373	11	4.7
1 0 3	1 $\bar{1}$ 3	2.379	2.373		2.3
0 2 2	2 $\bar{2}$ 2	2.288	2.288	7	9
2 0 2	2 2 2	2.269	2.269	7	8
2 2 0	4 0 0	1.975	1.975	49	39
0 0 4	0 0 4	1.968	1.969		19.3
1 3 2	4 2 2	1.618	1.619	27	19.5
2 0 4	2 $\bar{2}$ 4	1.606	1.606	30	9.5
3 1 2	2 $\bar{4}$ 2	1.605	1.605		19
0 4 0	4 4 0	1.405	1.406	4	5
2 2 4	4 0 4	1.394	1.394	18	22
4 0 0	4 $\bar{4}$ 0	1.388	1.388	1	1
2 4 0	6 2 0	1.254	1.254	4	4
3 3 2	6 0 2	1.249	1.249	13	8
1 1 6	2 0 6	1.245	1.246		8
4 2 0	6 $\bar{2}$ 0	1.244	1.244	5	4

Indices(hkl) and (HKL) are attributed to the orthorhombic and monoclinic cells, respectively.

Table 2. Lattice constants and perovskite parameter $a = \sqrt[3]{Vp}$ of perovskite-type compounds (CaLa)(BB')O_6 used in this work.

(BB')	lattice parameter a(Å)	b(Å)	c(Å)	ā(Å)	remarks
MgMo	5.551(1)	5.622(1)	7.785(1)	3.959	this work (Mg^{2+}, Mo^{5+}) ordered
MgRu	5.513	5.44	7.89(9)	3.941	(Mg^{2+}, Ru^{5+})
MgIr	5.533	5.573	7.83(9)	3.943	(Mg^{2+}, Ir^{5+})
CaTa	5.654	5.899	8.164	4.061	(Ca^{2+}, Ta^{5+})
MnMo	5.596(2)	5.766(2)	7.976(1)	4.005	(Mn^{2+}, Mo^{5+})
MnTa	5.597(4)	5.741(4)	7.994(2)	4.003	(Mn^{2+}, Ta^{5+})
MnTi	3.912(α=90° 12R)				(Mn^{3+}, Ti^{4+})

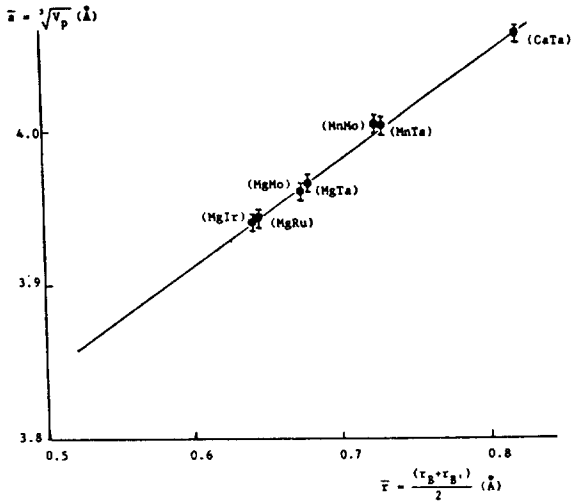

Figure 3. The linear relation between cube root of cell volume versus mean ionic radius of (BB') ions for perovskites (CaLa)(BB')O_6.

(1:1 ordering) of Mg and Mo ions in the B-sites of the perovskite structure ABO_3.

(CaLa) (MgMo)O_6 prepared in this study was found to have monoclinically distorted perovskite structure with lattice constants $a_o = b_o = 7.901(1)$ Å, c = 7.875(1) Å and $\gamma = 89°$ 16′ (1′), which can be reduced to a body-centered orthorhombic unit cell, a = 5.551(1) Å, b = 5.622(1) Å and c = 7.875(1) Å. Indices (hkl) and (HKL) in Table 1 are attributed to the body-centered orthorhombic cell and the face-centered (monoclinic) cell with the doubled edges of the perovskite unit, respectively. In Table 1 the observed lattice spacings and diffraction intensities are compared with those calculated. The intensity calculation was based on the assumptions that the Ca^{2+} and La^{3+} ions are distributed at random in the oxygen-cuboctahedral A-sites, the Mg^{2+} and Mo^{5+} ions are completely ordered over the oxygen-octahedral B-sites, and all the other ions are located at their ideal positions in the perovskite structure. Agreement between the intensities is good as can be seen in Table 1. Reliability factor in this calculation was 7.6%.

For all the other compounds reported previously in the literature[6-8] with the fomula of (CaLa)(BB')O_6 where {B(II), B'(V)} = (MaTa), (MgRu), (MgIr), (CaTa), (MnMo) and (MnTa), the superlattice lines caused by an ordered arrangement of B and B' ions in the oxygen-octahedral sites were also found in the X-ray diffraction patterns (Table 2).

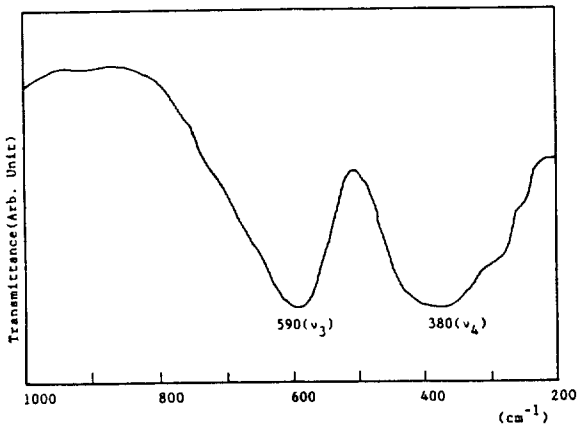

Figure 4. IR spectrum of (CaLa)(MgMo)O_6 with a CsBr pellet.

As shown in Figure 3, the perovskite parameter ā (see Table 2) defined as the cube root of cell volume of the perovskite unit, was plotted against the mean ionic radius $\bar{r} = \frac{1}{2}\{r_B + r_{B'}\}$ in order to check whether they follow the linear relationship of ā vs.f($\bar{r}$) or not. Perhaps it will be a simple and rough measure to predict the ordering of valency pair (BB') for the first approximation. Figure 3. indicates clearly that all the Ca-compounds with ordered valency pair of {B(II), B'(V)} follow the linear relationship as well as (CaLa) (MgMo)O_6. This can be one evidence indicating the ordered arrangement of Mg and Mo ions due to the relatively large charge difference.[1]

3. IR spectrum. In order to confirm that Mo^{5+} ions are distributed in the B-site of perovskite lattice ABO_3, infrared absorption spectrum was obtained. The IR spectrum shows two strong absorption band with their maxima at 590 and 380 cm^{-1} (Figure 4).

In ordered perovskites of the type $A_2(BB')O_6$ studied by Blasse *et al.*[9-10], the highly charged B ion octahedra such as $W^{4+}O_6$, $Mo^{6+}O_6$, $Nb^{5+}O_6$ and $Ti^{4+}O_6$ act as independent groups. The vibrational spectrum arises from such BO_6 octahedra. Assuming that the binding forces in the MoO_6 octahedron are large compared with the crystal-binding forces, the frequencies of the internal vibrations of this group in the solid must be close to the freqencies of the free-ion modes. Furthermore, the external modes ought to lie at lower freqencies than the internal modes. Group theoretical considerations represent the normal vibrations of an octahedral molecule as

$$A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$$

Since the two modes T_{1u} are IR-active and there is only one BO_6 group per primitive unit cell, we expect two bands in IR spectra.

In the IR spectra of ABO_3 or $A_2(BB')O_6$ perovskites, two strong absorption band around 600 and 400cm^{-1} have been reported, which are assigned to the ν_3 and ν_4 modes of the octahedra.[9-13] In addition the week band around 300 cm^{-1} are ascribed to the vibrations due to external vibrations.[10] The relatively broad ν_3 vibrational mode might be resulted from the slightly distorted structure from cubic one.

From our IR study we conclude that local symmetry of

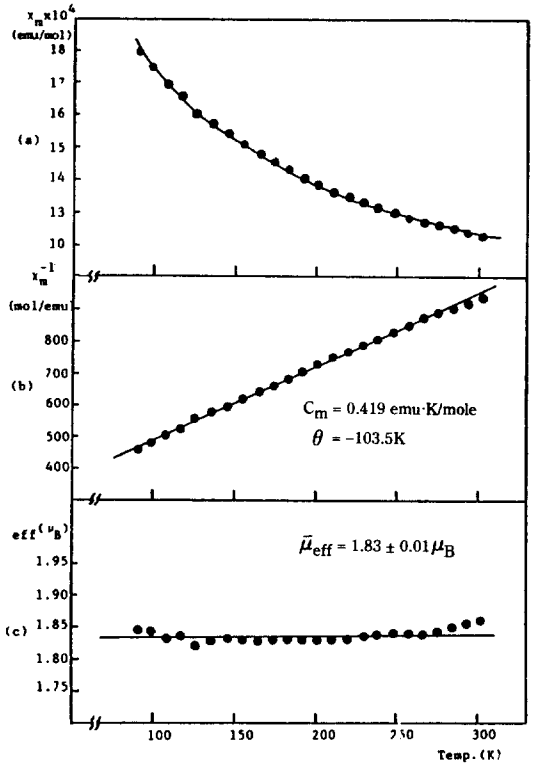

Figure 5. Temperature dependence of molar magnetic susceptibility χ_m(a), its inverse χ_m^{-1}(b), and effective magnetic moment μ_{eff}(c) of (CaLa)(MgMo)O_6.

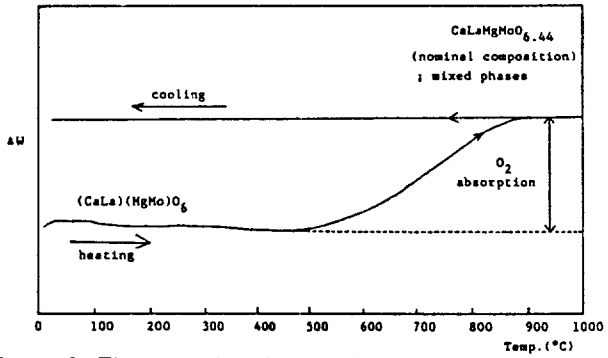

Figure 6. Thermogravimetric analysis of (CaLa)(MgMo)O_6 under an ambient atmosphere.

Mo ion in the oxide lattice (CaLa)(MgMo)O_6 is a slightly distorted octahedral one, which is well commensurate with the results of structural analysis (monoclinic distortion).

4. Magnetic susceptibility measurement. In order to determine the oxidation state of molybdenum ion in the lattice (CaLa)(MgMo)O_6, magnetic susceptibility were measured from 77K to room temperature. Temperature dependence of magnetic susceptibilities per mole of molybdenum ion is shown in Figure 5. Diamagnetic contribution of every ion to χ_m was corrected according to Selwood[14]. The χ_m's of (CaLa) (MgMo)O_6 obey the Curie-Weiss law below room temperture with magnetic moments per Mo ion of 1.83 ± 0.01 u_B. The Curie constant C_m and Weiss constant θ obtained from the least square fit of $\chi_m^{-1} = (T-\theta)/C_m$ for all the temperature data set are 0.419 (emu·K/mole) and −103.5K, respectively.

Although the observed effective moment 1.83 μ_B is slightly larger than the spin only value of Mo^{5+} (4d'-state), 1.73 μ_B, the moment is presumed to come from an Mo^{5+} in the oxide lattive within the experimental error. This slightly larger value of effective magnetic moment than spin-only value might be due to the spin-orbit coupling or over-correction of diamagnetism.

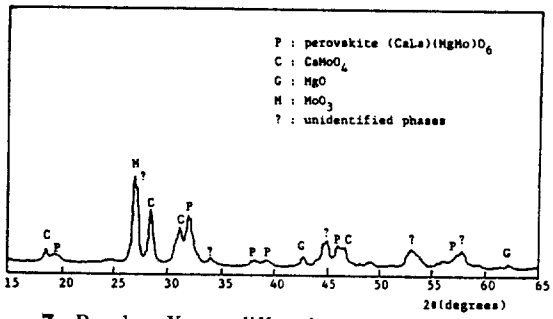

Figure 7. Powder X-ray diffraction pattern after oxidative decomposition of (CaLa)(MgMO)O_6 (The heat treated sample over 900 °C in TG analysis)

5. Thermogravimetric (TG) analysis According to TG analysis of (CaLa)(MgMo)O_6 under ambient atmosphere, oxygen absorption seems to be significant in the temeprature range from 25 °C to 1000 °C as shown in Figure 7, which might be attributed to the successive oxidation and decomposition reaction as follows:

$$(CaLa)(MgMo^{6+})O_6 + \frac{x}{4}O_2 \rightleftarrows \begin{matrix} CaLaMgMo^{5+}_{1-x}Mo^{6+}_{x}O_{6+x/2} \\ CaMo^{6+}O_4 + MgO + MoO_3 + La_2O_3 + \text{unidentified phases} \end{matrix}$$

The content of oxygen absorbed in TG analysis, 0.22 mole, is somewhat smaller than the calculated 0.25 mole which is based on the assumption of entire oxidation of Mo^{5+}. This descrepancy might be caused by the existence of small quantity of undecomposed perovskite phase in the oxidized product where small Mo^{5+} ion still remains, which is consistent with the XRD pattern of the oxidized product (Figure 7).

From the TG result, it could be concluded that the (CaLa)(MgMo)O_6 compound is only stable in a reducing atmosphere and the most probable oxidation state of molybdenum is pentavalent.

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Nucleophilic Addition of Phosphate to Coordinated (Arene)manganes Tricarbonyl Cations

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$[(Benzene)Mn(CO)_3]^+$ reacts with $NaP(O)(OR)_2$ (R = Me, Et, Ph) to give the phosphonate compound 1. Compound 1 reacts with R'Li (R = Me, Ph, ^{n}Bu, ^{t}Bu) to yield the isomerized compound 2 and the alkylated compound 3. $[(Toluene)Mn(CO)_3]^+$ reacts with $NaP(O)(OMe)_2$ to give the phosphonate complexes 1-A and 1-B. Treatment of 1-A with ^{t}BuLi in THF affords complexes 3-A and 3-B with the later major. With 1-B only the complex 3-C is formed. $[(Anisole)Mn(CO)_3]^+$ reacts with $NaP(O)(OMe)_2$ to give the phosphate complex 1-C, which on treatment with ^{t}BuLi and then H_2O yields compound 3-D. After demetallation of compound 3-D, meta-tertbutyl-anisole is obtained in a reasonable yield.

Introduction

Activation of aromatic compounds toward nucleophilic attack represents an attractive method for the synthesis of polyfunctionalized derivatives. The use of arene chromium complex is now fairly well established[1], but these compounds undergo carbon-carbon bond formation only with very reactive nucleophiles[2], thereby limiting the degree to which deactivating substituents (-OR, $-NR_2$, etc.) may be attached to the ring.

(Arene) mangananese tricarbonyl cations have been and continue to be the topics of extensive investigation. This is due in part to the rich chemistry associated with nucleophilic attack at the aromatic ring leading to the formation of cyclohexadienyl manganese tricarbonyl compounds[3].

The reaction of aldehydes and ketones with phosphonium salts to produce olefins was developed in 1953 by Wittig and Geissler[4]. Since then the Wittig reaction has been widely used as a convenient high-yield synthesis of olefins, especially in the field of natural products[5]. Recently, much interest has been centered on the use of organometallic species in the synthesis of organic compounds not readily available otherwise. The use of the Wittig reaction in organometallic chemistry has been used successfully in preparing new derivatives of (benzene)dicarbonyl chromium[6], ferrocene[7], and six- and seven-membered ring dienyl complexes of $Fe(CO)_3$[8].

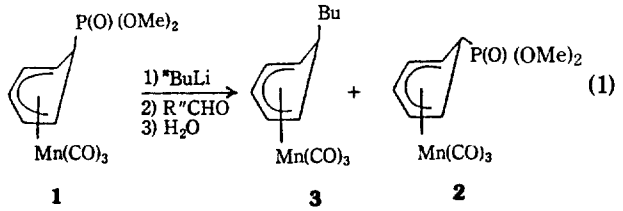
$[(Arene)Mn(CO)_3]^+$ has a low electrophilicity and cannot react with triphenylphosphine to yield a phosphonium salt. A very useful alternative method for the preparation of resonance stabilized phosphoranes for use in the Witting reaction proceeds from phosphonate esters[9]. So we tried to make organometallic phosphonate compounds.

We recently reported on the use of phosphate as a nucleophile to the $[(C_6H_6)Mn(CO)_3]^+$ cation[10]. To our knowledge there are no reports on the use of phosphate as a nucleophile to the π-coordinated ring. Our previous communication revealed that $[exo\text{-}(RO)_2P(O)\text{-}\eta^5\text{-}C_6H_6]Mn(CO)_3$ which on treatment with ^{n}BuLi and H_2O underwent stereospecific rearrangement to $[endo\text{-}(RO)_2P(O)\text{-}\eta^5\text{-}C_6H_6]Mn(CO)_3$. In this report we describe the reaction of [exo-(RO)$_2$P(O)-n^5-cyclohexadienyl]$Mn(CO)_3$ with R'Li (R' = Me, ^{n}Bu, ^{t}Bu, Ph) and related reactions.

Results and Discussion

(Exo-phosphonate-η^5-cyclohexadienyl) manganese tricarbonyl compounds were synthesized as previously described[10]. The compounds are soluble in organic solvent and stable in the air. The formation of the cyclohexadienyl compounds can be followed by checking the CO stretching bands and the reaction went completely within 30 min.

To do the Horner-Emmons reaction with compound 1, compound 1 was treated with ^{n}BuLi and aldehyde. After work-up, two compounds were obtained, one was butylated compound and the other isomerized phosphonate compound (eq. 1).



(1)

When the above reaction was carried without using aldehyde, the same reaction products were obtained. After deprotonation by ^{n}BuLi, the carbon which has a negative