A Study of the Development of CVD Precursors III-Synthesis and Properties of New Lead β-Diketonate Derivatives

Jong Tae Lim, Joong Cheol Lee,[†] Wan In Lee, and Ik-Mo Lee*

Department of Chemistry, Inha University, Inchon 402-751, Korea
[†]Daejung Laboratory, Inchon 405-310, Korea
Received September 17, 1998

To improve the volatility and stability of lead complexes, the principle of stabilization by saturating the metal coordination sphere by intramolecular coordination through a β-diketonates with an ethereal group has was tested. Several new lead complexes with alkoxyalkyl-substituted β-diketonates, $Pb(R^1C(O)CHC(O)(CH_2)_3\text{-}OR^2)_2$ (R^1=t-Bu, Me, OMe, i-Pr, R^2=Me, Et), or carboxylate, $Pb(OC(O)(CH_2)_3OEt)_2$, were prepared by the reaction between $Pb(OAc)_2$ and corresponding alkoxyalkyl-substituted β-diketonates, and they were found to have a viscous liquid phase. The nature of the head (β-diketonate or carboxylate) or tails and substituents of β-diketonates appeared not to be important for the formation of the liquid phase. It is worth mentioning that $Pb(OAc)_2$, which has limited use due to its low solubility, was successfully adopted as a starting material for the preparation of new lead complexes. Easy hydrolysis, reaction with HCl, and ^{13}C NMR spectra indicated that tail portions were not coordinated to the metal as a copper derivative, $Cu(t\text{-}BuC(O)CHC(O)(CH_2)_3OMe)_2$. All these complexes were not volatile enough for the MOCVD experiments, but a methyl derivative, $Pb(MeC(O)CHC(O)(CH_2)_3OEt)_2$, showed some sublimation. The methoxy derivative, $Pb(MeOC(O)CHC(O)(CH_2)_3OEt)_2$, was thermally unstable due to possible equilibrium between species coordinating with a keto oxygen atom and an ethereal atom of a methoxy group, which was confirmed by IR and ^{13}C NMR spectra.

Introduction

Due to their interesting properties, which can be applicable to nonvolatile ferroelectric random access memories (RAMs), optoelectronic devices, sensors, and transducers,[1] lead titanate (PT, $PbTiO_3$) based ceramics have received much attention. Promising characteristics of metal organic chemical vapor deposition (MOCVD) such as better step coverage, easy scale-up, easy control of composition and thickness, and limited diffusion of substrate have led to the conclusion that this MOCVD technique may be the best suited for the commercial production of thin films of these ceramics.[2] This technique, however, relies largely on the availability of precursors of high volatility, low toxicity, and adequate stability. We have reported the preparation of lanthanum and titanium β-diketonate complexes and studied the characteristics and pyrolysis mechanism to confirm the possibility of potential sources of lead lanthanum titanate (PLT) precursors.[3]

For the lead precursors, lead alkyls such as lead tetraethyl have been utilized for their high volatility, but the toxicities of these complexes prevented further application. Lead alkoxides and carboxylates are known to hydrolyze easily. Lead β-diketonates are rather stable and less toxic, but also less volatile. In the reported MOCVD experiments, Pb (dpm)$_2$ (dpm: dipivaloylmethane) was generally chosen as a lead source material, but it is not very volatile. Even though the lead precursor material is not quite satisfactory, research activity in this area has been limited.

Meanwhile, investigations into the volatile alkaline earth metal source material are very active mainly due to rapidly

growing interest in layered perovskites such as BST $((Ba,Sr)TiO_3)$, SBT $(SrBi_2Ta_2O_9)$, and SBNT $(SrBi_2(Nb, Ta)_2O_9)$.[4] Noticeable advances in this area have been reported. Fragala reported one-pot synthesis of second-generation alkaline-earth metal precursors such as $M(hfa)_2$·tetraglyme (M=Ba, Sr, Ca and hfa=1,1,1,5,5,5-hexafluoro-2,4-pentadionate; tetraglyme=$CH_3(OCH_2CH_2)_4OMe$), which is monomeric, water-free, highly stable, and volatile.[5] Igumenov studied the effect of sterically hindered methoxy-β-diketonates on the volatility of Ba complexes, which induced increased thermal stability but little improvement in volatility.[6] Rees prepared several new ligands such as $C_5H_4(CH_2)_nER_m$ (n=2,3; ER_m=OMe, OEt, NMe_2),[7] $O(CH_2CH_2O)_nR$ (n=2,3; R=Me, Et),[8] and t-$BuCOCH_2CO(CH_2)_3OMe$[9] to improve the stabilities and volatilities of the CVD precursors, and synthesized some new liquid barium complexes with these ligands. Marks[10] also introduced new ligands: β-ketoiminate containing appended polyether "lariats" to prepare the barium complexes, one of which was volatile enough for MOCVD experiments.

In this research, the principle of stabilization by saturating the metal coordination sphere through formation of adducts with Lewis bases was utilized. It is interesting that no attempt to increase the volatility of lead complexes by formation of Lewis base adducts has been made even though this methodology has proved effective in increasing the volatility of complexes containing large metal ions.

Since the ionic radius of Pb^{2+} (119 pm) is not much smaller than that of Ba^{2+} (135 pm)[11] and the coordination number of lead β-diketonates is mostly 4, intramolecular stabilization through a β-diketonates with an ethereal group

356 *Bull. Korean Chem. Soc.* **1999**, Vol. 20, No. 3

Jong Tae Lim et al.

would improve the stability and volatility of lead complexes as mentioned above. In this paper, we report the applicability of this principle to the lead complexes and the effect of substituents in alkoxyalkyl-substituted β-diketones on the properties of lead complexes.

Experimental Section

All procedures were performed under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Solvents were reagent grade, distilled under a nitrogen atmosphere from appropriate drying agents before use. Reagent grade chemicals were purchased from Aldrich Chemical Co., Inc. and used without further purification unless stated otherwise. 4-Methoxy-1-butanol[12] and 4-methoxybutanoic acid[13] were prepared by the modified literature procedures. Infrared spectra were recorded on a Nicolet MX-1E, Shimadzu IR-435 and Bruker IFS-66, and the IR samples were prepared as neat liquid. ^{1}H and ^{13}C NMR spectra were recorded using 5 mm tube on a Bruker AC-250 FT NMR spectrometer operating at 250.133 MHz and 62.896 MHz, respectively, and referenced to tetramethylsilane (TMS). Thermal analyses were performed on a TA Instrument, DSC 2010 (DSC) and a TA Instrument, SDT 2960 (TGA, DTA). Elemental analyses were performed on a EA 1110 (C,H,N,S-O Model), CE Instrument. Mass spectral analyses were recorded on a HP 5890A GC/HP 5917A MS detector equipped with a 30 m-long capillary column packed with liquid methylsilicon.

Ligand Syntheses.

Me$_3$CC(O)CH$_2$C(O)(CH$_2$)$_3$OCH$_3$: 3.06 g (23.1 mmol) of 5-methoxy-1-methylbutanoate, 1.01 g (41.9 mmol) of sodium hydride, and 100 mL of dimethoxyethane (DME) were placed in a flame-dried 250 mL three-neck flask, and 3.06 g (23.1 mmol) of pinacolone were added dropwise for 30 min at room temperature. After addition, the solution was refluxed for 24 hr while stirring vigorously. After cooling, the reaction was quenched with 5 mL of concentrated HCl aqueous solution, and an orange suspension was obtained. 50 mL of water were added and the solution was extracted with 100 mL of methylene chloride 5 times. The organic fraction was dried over anhydrous sodium sulfate and filtered. The solvent was removed by a rotary evaporator at 50 °C. The remaining compound was distilled to produce a pale yellow liquid at 120 °C under reduced pressure. The compound was further purified with a silica column eluting with 10% ethylacetate/hexane. Yield: 2.68 g (58.0%). ^{1}**H NMR** (CDCl$_3$); keto form; δ 5.55 (s, 2H, -C(O)**CH$_2$**-C(O)), 3.30 (t, 2H, -**CH$_2$**OCH$_3$), 3.26 (s, 3H, -OCH$_3$), 2.34 (t, 2H, -C(O)-**CH$_2$**CH$_2$-), 1.85 (p, 2H, -CH$_2$**CH$_2$**CH$_2$), 1.09 (s, 9H, -C(**CH$_3$**)$_3$), enol form; δ 3.58 (s, 1H, -C(O)**CH**C(OH)), 2.53 (t, 2H, -**CH$_2$**OCH$_3$), 3.23 (s, 3H, -OCH$_3$), 2.45 (t, 2H, -C(OH)-**CH$_2$**CH$_2$-), 1.85 (p, 2H, -CH$_2$**CH$_2$**CH$_2$), keto/enol= 6.72, ^{13}**C NMR** (CDCl$_3$); δ 198.1 (Me$_3$**C**C(O)CH$_2$-), 193.8 (-CH$_2$**C**-(O)CH$_2$-), 93.5 (C(O)**CH$_2$**C(O)), 69.9 (**CH$_3$**OCH$_2$), 56.6 (CH$_3$O**CH$_2$**), 37.1 (**C**(O)**C**Me$_3$), 33.6 (C(O)**CH$_2$**CH$_2$), 25.5

(C(**CH$_3$**)$_3$), 23.8 (-CH$_2$**CH$_2$**CH$_2$), **IR** (neat); 2970.4, 2933.3, 2874.1, 2733.3, 1700.7, 1600.9, 1479.0, 1456.8, 1360.7, 1275.8, 1194.5, 1116.9, 958.0, 891.4, 788.0, 751.0 cm^{-1}, **GC/MS (EI)**; 200 (M$^+$), 168 (M$^+$-OMe-1), 155 (M$^+$-CH$_2$OMe), 143 (M$^+$-CMe$_3$), 127 (M$^+$-(CH$_2$)$_3$OMe), 111 (M$^+$-CMe$_3$-OMe-1), 85 (M$^+$-CMe$_3$-(CH$_2$)$_2$OMe+1), 69 (C(O)-CHC(O)), 57 (Me$_3$C), 45 (CH$_2$OCH$_3$), **Anal.** Calc. (Found): C, 65.97 (66.47); H, 10.06 (10.12)

MeOC(O)CH$_2$C(O)(CH$_2$)$_3$OCH$_2$CH$_3$: 0.23 g (9.35 mmol) of sodium hydride and 15 mL of tetrahydrofuran (THF) were placed in a flame-dried 250 mL three-neck flask, and 1.00 mL (9.35 mmol) of methylacetoacetate in 15 mL of THF was added dropwise via a cannula for 30 min at room temperature. After completion of hydrogen evolution, 5.40 mL (11.2 mmol) of n-butyllithium (2.5 M in hexane) were added dropwise to this solution. After addition, 1.17 mL (9.35 mmol) of 2-bromoethyl ethyl ether was introduced dropwise via a cannula and stirred for 30 min. The reaction was quenched with HCl solution (concentrated HCl 3 mL in 5 mL of H$_2$O), and the solution was stirred for 10 min. The solvent was removed under reduced pressure. 50 mL of water was added, and the solution was extracted with 50 mL of methylene chloride 5 times. The organic fraction was dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure. The remaining compound was distilled, producing a yellow liquid at 140 °C under reduced pressure. The compound was further purified with a silica column eluting with 10% ethylacetate/hexane. Yield: 1.14 g (64.8%). ^{1}**H NMR** (CDCl$_3$); keto form; δ 3.46 (s, 2H, -C(O)**CH$_2$**C (O)), 3.43 (q, 2H, -Me**CH$_2$**OCH$_2$), 3.41 (t, 2H, -**CH$_2$**OEt), 3.72 (s, 3H, -OCH$_3$), 2.63 (t, 2H, -C(O)**CH$_2$**CH$_2$-), 1.86 (p, 2H, -CH$_2$**CH$_2$**CH$_2$), 1.16 (t, 3H, -OCH$_2$**CH$_3$**), ^{13}**C NMR** (CDCl$_3$); δ 200.9 (-CH$_2$**C**(O)CH$_2$-), 166.1 (MeO**C**(O)CH$_2$-), 67.5 (-O**CH$_2$**CH$_2$), 64.4 (-O**CH$_2$**CH$_3$), 50.5 (**CH$_3$**OC(O)), 47.3 (C(O)**CH$_2$**C(O)), 38.1 (C(O)**CH$_2$**-CH$_2$), 22.0 (-CH$_2$**CH$_2$**-CH$_2$), 13.3 (OCH$_2$**CH$_3$**), **IR** (neat); 2976.7, 2860.5, 2798.5, 1751.5, 1716.5, 1650.5, 1627.2, 1436.9, 1316.5, 1266.0, 1200.0, 1001.9 cm^{-1}, **GC/MS (EI)**; 189 (M$^+$+1), 157 (M$^+$-OMe), 143 (M$^+$-OEt or M$^+$-OMe-Me+1), 129 (M$^+$-CH$_2$-OEt), 116 (M$^+$-CH$_2$CH$_2$OEt+1), 101 (MeOC(O)CH$_2$C(O)), 87 ((CH$_2$)$_3$OEt), 74 ((CH$_2$)$_2$OEt+1), 59 (CH$_2$OEt), 45 (OCH$_2$-CH$_3$), **Anal.** Calc. (Found): C, 57.43 (57.43); H, 8.57 (8.86).

MeC(O)CH$_2$C(O)(CH$_2$)$_3$OCH$_2$CH$_3$: 5.20 mL (49.9 mmol) of 2,4-pentanedione and 50 mL of THF were placed in a flame-dried 250 mL three-neck flask, and 4.35 g (99.5 mmol) of sodium amide in 100 mL of THF were added dropwise by a cannula at room temperature. After addition, the solution was stirred for 2 hr at 50 °C. After cooling to 0 °C, 6.25 mL (49.9 mmol) of 2-bromoethylethyl ether were added slowly to this solution via a cannula, producing an orange slurry. The solution was stirred for an additional 3 hr, and the reaction was quenched with 100 mL of HCl aqueous solution. The solvent was removed under reduced pressure. 50 mL of water were added, and the solution was extracted with 100 mL of methylene chloride 5 times. The organic fraction was dried over anhydrous magnesium sulfate and

filtered. The solvent was removed by a rotary evaporator at 50 °C. The remaining red liquid was distilled, producing a pale yellow liquid at 90 °C-120 °C under reduced pressure. The compound was further purified with a silica column eluting with 10% ethylacetate/hexane. Yield: 4.78 g (55.6%). **¹H NMR** (CDCl₃); keto form; δ 5.46 (s, 2H, -C(O)C**H₂**C(O)), 3.41 (t, 2H, -C**H₂**OEt), 2.88 (q, 2H, -OC**H₂**CH₃), 2.32 (t, 2H, -C(O)C**H₂**CH₂-), 1.99 (s, 3H, C**H₃**C(O)-), 1.81 (p, 2H, -CH₂C**H₂**CH₂-), 1.13 (t, 3H, -OCH₂C**H₃**), **¹³C NMR** (CDCl₃); δ 192.7 (-CH₂**C**(O)CH₂-), 189.2 (Me**C**(O)CH₂-) 98.2 (C(O)**C**H₂C(O)), 67.7 (EtO**C**H₂), 64.4 (CH₃**C**H₂-OCH₂), 33.3 (C(O)**C**H₂CH₂), 23.9 (C(O)**C**H₃), 23.0 (-CH₂-**C**H₂CH₂), 13.4 (OCH₂**C**H₃), **IR** (neat); 2977.8, 2933.3, 2866.7, 2807.4, 1722.9, 1704.4, 1623.1, 1442.0, 1419.9, 1375.5, 1353.4, 1301.6, 1238.8, 1109.5, 1031.9, 935.8, 873.0, 780.6 cm⁻¹, **GC/MS (EI)**; 172 (M⁺), 126 (M⁺-OEt +1), 113 (M⁺-CH₂OEt), 100 (M⁺-(CH₂)₂OEt+1), 85 (M⁺-(CH₂)₃OEt), 72 ((CH₂)₂OEt-1), 69 (C(O)CHC(O)), 59 (CH₂-OEt), 45 (OCH₂CH₃), **Anal.** Calc. (Found): C, 61.40 (61.43); H, 9.47 (9.37).

Me₂CHC(O)CH₂C(O)(CH₂)₃OMe: 1.73 g (13.1 mmol) of 4-methoxy-1-methylbutanoate, 0.78 g (32.6 mmol) of sodium hydride, and 80 mL of DME (1,2-dimethoxyethane) were placed in a flame-dried 250 mL three-neck flask, and 1.54 g (17.9 mmol) of 3-methyl-2-butanone was added dropwise via a cannula at room temperature for 10 min. After addition, the solution was refluxed for 24 hr. After cooling to 0 °C, the reaction was quenched with 5 mL of concentrated HCl solution, resulting in an orange suspension. 30 mL of water were added, and the solution was extracted with 100 mL of methylene chloride 5 times. The organic fraction was dried over anhydrous magnesium sulfate and filtered. The solvent was removed by a rotary evaporator at 40 °C. The remaining liquid was distilled, producing a pale yellow liquid at 90 °C under reduced pressure. The compound was further purified with a silica column eluting with 5% ethylacetate/hexane. Yield: 0.78 g (32.0%). **¹H NMR** (CDCl₃); keto form; δ 5.49 (s, 2H, -C(O)C**H₂**C (O)), 3.38 (t, 2H, -C**H₂**OMe), 3.31 (s, 3H, -OC**H₃**), 2.58 (h, 1H, Me₂C**H**-), 2.36 (t, 2H, -C(O)C**H₂**CH₂-), 1.85 (p, 2H, -CH₂C**H₂**CH₂-), 1.12 (d, 6H, -OCH(C**H₃**)₂), enol form; δ 3.60 (s, 1H, -C(O)C**H**C(OH)), 2,44 (t, 2H, -C**H₂**OCH₃), 3.28 (s, 3H, -OC**H₃**), 2.40 (t, 2H, -C(OH)C**H₂**CH₂-), 1.85 (p, 2H, -CH₂C**H₂**CH₂-), 1.08 (d, 6H, -CH(C**H₃**)₂), keto/enol=2.67, **¹³C NMR** (CDCl₃); δ 196.4 (-CH₂**C**(O)CH₂-), 189.2 (Me₂-CH**C**(O)CH₂-) 95.4 (C(O)**C**H₂C(O)), 69.8 (MeO**C**H₂), 56.7 (**C**H₃OCH₂), 33.3 (C(O)**C**H₂CH₂), 34.7 (C(O)**C**H(CH₃)₂), 23.7 (-CH₂**C**H₂CH₂), 17.4 (C(O)CH(**C**H₃)₂), **IR** (neat); 2970.4, 2918.5, 2874.1, 2829.6, 1726.6, 1704.4, 1615.7, 1456.8, 1449.4, 1209.2, 1116.9, 928.4, 784.3 cm⁻¹, **GC/MS (EI)**; 186 (M⁺), 154 (M⁺-OMe-1), 143 (M⁺-i-Pr), 128 (M⁺-CH₂CH₂OMe+1), 111 (M⁺-i-Pr-OMe-1), 101 (C(O)(CH₂)₃-OMe), 85 (C(CH₂)₃OMe), 72 ((CH₂)₃OMe-1), 69 (C(O)-CHC(O)), 59 (CH₂CH₂OMe), 46 (CH₂OCH₃), **Anal.** Calc. (Found): C, 64.49 (63.95); H, 9.74 (10.20).

Syntheses of Pb Complexes.

Pb(Me₃CC(O)CHC(O)(CH₂)₃OCH₃)₂ (1): In a flame-dried 250 mL flask, 1.95 g (6.00 mmol) of lead acetate trihydrate was dried for 2 hr at 50 °C under reduced pressure, to which 30 mL of methylene chloride were then introduced. In another flame-dried 250 mL flask, 0.24 g (9.99 mmol) of sodium hydride and 100 mL of methylene chloride were placed and cooled at 0 °C. 30 mL of methylene chloride solution containing 2.00 g (9.99 mmol) of 2,2-dimethyl-8-methoxyoctane-3,5-dione were then added to the sodium hydride slurry solution dropwise for 3 hr by a cannula, producing a white slurry. This solution was added to the lead acetate solution by a cannula for 10 min and stirred for 3 hr. The solvent was removed under reduced pressure and 50 mL of hexane added. The resulting solution was filtered with a celite-packed frit and the solvent was removed under reduced pressure again. The residue was distilled at 120 °C under reduced pressure to remove unreacted ligand and a yellow oil was obtained. Yield: 5.45 g (90.1%). **¹H NMR** (CDCl₃); δ 5.33 (s, H, -C(O)C**H**C(O)), 3.37 (t, 2H, -C**H₂**-OMe), 3.32 (s, 3H, -OC**H₃**), 2.27 (t, 2H, -C(O) C**H₂**CH₂-), 1.82 (p, 2H, -CH₂C**H₂**CH₂-), 1.08 (s, 9H, -C(O) (C**H₃**)₃), **¹³C NMR** (CDCl₃); δ 198.2 (-**C**HC(O)CH₂-), 192.1 (*t*-Bu**C**-(O)CH₂-), 97.8 (C(O)**C**HC(O)), 72.2 (MeO**C**H₂), 58.4 (**C**H₃-OCH₂), 41.4 (C(O)**C**H₂CH₂), 38.9 (-**C**H₂CH₂CH₂-), 29.6 (**C**Me₃), 28.3 (C(**C**H₃)₃), **IR** (neat); 2955.6, 1567.7, 1497.5, 1379.7, 1353.4, 1116.9, 773.2 cm⁻¹, **GC/MS (EI)**; 606 (M⁺), 548 (M⁺-t-Bu), 490 (M⁺-2t-Bu), 448 (M⁺-t-Bu-C(O)(CH₂)₃-OMe+1), 407 (M⁺-L), 207 (Pb), 168 (L-OMe), 143 (L-*t*-Bu), 127 (L-(CH₂)₃OMe), 111 (L-*t*-Bu-OMe), 85 (t-BuC(O)), 57 (*t*-Bu), **Anal.** Calc. For PbC₂₂H₃₈O₆ (Found): C, 43.62 (44.43); H, 6.32 (6.65), **TGA**; (Variable Temperature) 242.7 °C, complex-2 (*t*-Bu+CH₂OMe), Calc. (Found), 66.34 (67.07), 370.8 °C, Pb²⁺(C(O)CH), Calc. (Found), 47.69 (47.29), 700.5 °C, PbO, Calc. (Found) 36.9% (35.7%); (Isotherm, 1 hr, 8 mL/min N₂) 80 °C, 0.30% loss/10 min, yellow liquid, 110 °C, 1.27% loss/10 min, yellow liquid, 140 °C, 2.68%/10 min, black solid, **DSC**; 247.5 °C, 367.2 °C (Endothermic).

Pb(MeC(O)CHC(O)(CH₂)₃OCH₂CH₃)₂ (2): This complex was prepared by the same procedure as above except 2.08 g (6.39 mmol) of lead acetate trihydrate and 2.00 g (11.6 mmol) of 1-methyl-7-ethoxyoctane-3,5-dione were used. Yield: 4.99 g (78.2%). **¹H NMR** (CDCl₃); δ 5.07 (s, H, -C(O)C**H**C(O)), 3.34 (q, 2H, CH₂OC**H₂**Me), 3.28 (t, 2H, -C**H₂**OEt), 2.13 (t, 2H, -C(O) C**H₂**CH₂-), 1.84 (s, 3H, C**H₃**C(O)), 1.68 (p, 2H, -CH₂C**H₂**-CH₂), 1.07 (s, 3H, -C(O)CH₂C**H₃**), **¹³C NMR** (CDCl₃); δ 190.0 (-**C**HC(O)-CH₂-), 187.7 (Me**C**(O)CH₂-), 101.0 (C(O) **C**HC(O)), 68.1 (EtO**C**H₂), 64.2 (CH₃**C**H₂OCH₂), 36.7 (C(O) **C**H₂CH₂), 26.9 (**C**H₃C(O)), 24.9 (-CH₂**C**H₂CH₂), 13.4 (OCH₂**C**H₃), **IR** (neat); 2970.4, 2925.9, 2859.3, 1586.1, 1515.9, 1442.0, 1394.0, 1357.0, 1109.5, 776.9 cm⁻¹, **GC/MS (EI)**; 550 (M⁺+1), 478 (M⁺-2Et-Me+1), 449 (M⁺-(CH₂)₂-OEt-Et+1), 377 (M⁺-L+1), 208 (Pb+1), 171 (L-1), 126 (L-OEt-1), 100 (L-(CH₂)₂OEt+2), 85 (L-(CH₂)₂OEt-Me+2), 72 ((CH₂)₂OEt-1), 59 (CH₂OEt), 45 (OEt), **Anal.** Calc. for PbC₁₈H₃₀O₆ (Found): C, 39.33 (38.50); H, 5.50 (5.51), **TGA**; (Variable

Temperature) 284.8 °C, Pb+C(O)CHC(O)CH$_2$, Calc. (Found), 52.73 (53.10), 379.8 °C, PbO, Calc. (Found), 40.55 (38.70), 700.0 °C, PbO, Calc. (Found) 40.55 (33.18); (Isotherm, 1 hr, 8 mL/min N$_2$) 90 °C, 0.06% loss/10 min, yellow liquid, 120 °C, 2.55% loss/10 min, yellow liquid, 150 °C, 4.62%/10 min, gray solid, **DSC**; 298.6 °C-330 °C (Endothermic).

Pb(MeOC(O)CHC(O)(CH$_2$)$_3$OCH$_2$CH$_3$)$_2$ (3): This complex was prepared by the same procedure as above except 1.00 g (3.07 mmol) of lead acetate trihydrate and 1.00 g (5.31 mmol) of 1-methoxy-6-ethoxyhexane-3,5-dione were used. Yield: 2.37 g (76.7%). **^{1}H NMR** (CDCl$_3$); δ 4.60 (s, H, -C(O)C**H**C(O)), 3.44 (s, 3H, -OC**H$_3$**), 3.29 (s, 3H, -C**H$_2$**OEt), 3.38 (q, 2H, -OC**H$_2$**-Me), 2.03 (br, 2H, -C(O)C**H$_2$**CH$_2$-), 1.71 (br, 2H, -CH$_2$-C**H$_2$**CH$_2$-), 1.10 (t, 3H, -OCH$_2$C**H$_3$**), **^{13}C NMR** (CDCl$_3$); δ 185.0 (-C**H**C(O)CH$_2$-), 169.5 (MeO**C**(O)CH$_2$-) 84.3 (C(O) **C**HC(O)), 68.3 (EtO**C**H$_2$), 64.2 (CH$_3$**C**H$_2$OCH$_2$), 48.3 (C(O) O**C**H$_3$), 36.8 (-C(O)**C**H$_2$CH$_2$CH$_2$), 25.6 (-CH$_2$**C**H$_2$CH$_2$-), 13.4 (OCH$_2$**C**H$_3$), **IR** (neat); 2985.2, 2940.7, 2859.3, 1634.2, 1515.9, 1445.7, 1216.6, 1161.2, 1105.8, 1043.0, 791.7, 736.3 cm^{-1}, **GC/MS (EI)**; 582 (M$^+$), 510 (M$^+$-(CH$_2$)$_2$OEt+1), 393 (M$^+$-(CH$_2$)$_3$OEt-(CH$_2$)$_2$OEt-OMe+2), 363 (M$^+$-C(O)(CH$_2$)$_3$-OEt-(CH$_2$)$_2$OEt-OMe), 208 (Pb+1), 187 (L-1), 157 (L-OMe), 143 (L-OEt), 129 (L-CH$_2$OEt), 116 (L-(CH$_2$)$_2$OEt), 84 (OC(O)CHC(O)), **Anal.** Calc. for PbC$_{18}$H$_{30}$O$_8$·0.38C$_6$H$_{14}$ (Found): C, 39.65 (39.65); H, 5.79 (6.05) , **TGA**; (Variable Temperature) 218.8 °C, complex-2 ((CH$_2$)$_2$OEt), Calc. (Found), 74.91 (76.19), 371.3 °C, Pb+2(C(O)CHC(O)), Calc. (Found), 59.28 (59.54), 699.9 °C, Pb^{+4} (C(O)), Calc. (Found) 54.81% (54.28%); (Isotherm, 1 hr, 8 mL/min N$_2$) 90 °C, 0.29% loss/10 min, gray liquid, 120 °C, 1.54% loss/10 min, gray solid, **DSC**; 247.5 °C, 367.2 °C (Endothermic).

Pb(Me$_2$CHC(O)CHC(O)(CH$_2$)$_3$OCH$_3$)$_2$ (4): This complex was prepared by the same procedure as above except 0.34 g (1.05 mmol) of lead acetate trihydrate and 0.30 g (1.61 mmol) of 2-methyl-8-methoxyoctane-3,5-dione were used. Yield: 0.47 g (67.0 %). **^{1}H NMR** (CDCl$_3$); δ 5.10 (s, H, -C(O)C**H**C(O)), 3.30 (t, 2H, -C**H$_2$**OMe), 3.25 (s, 3H, -OC**H$_3$**), 2.27 (h, H, Me$_2$C**H**C (O)-), 2.15 (t, 2H, -C(O)C**H$_2$**-CH$_2$-), 1.73 (p, 2H, -CH$_2$C**H$_2$**-CH$_2$), 0.96 (d, 6H, -C(O)CH-(C**H$_3$**)$_2$), **^{13}C NMR** (CDCl$_3$); δ 195.4 (-C**H**C(O)CH$_2$-), 190.3 (i-Pr**C**(O)CH-), 97.4 (C(O) **C**HC (O)), 70.5 (MeO**C**H$_2$), 56.6 (**C**H$_3$OCH$_2$), 38.0 (C(O)**C**H$_2$CH$_2$), 36.8 (C(O)**C**HMe$_2$), 24.9 (-CH$_2$**C**H$_2$CH$_2$-), 18.5 (CH(**C**H$_3$)$_2$), **IR** (neat); 2955.6, 2918.5, 2866.7, 1674.8, 1582.5, 1508.6, 1412.5, 1357.0, 1320.1, 1116.9, 1024.5, 958.0, 928.4, 776.9 cm^{-1}, **GC/MS (EI)**; 578 (M$^+$), 520 (M$^+$-4Me+2), 393 (M$^+$-L+1), 208 (Pb), 154 (L-OMe-1), 143 (L-CH$_2$OMe+2), 129 (L-(CH$_2$)$_2$-OMe+2), 111 (L-i-Pr-OMe+1), 85 (L-i-Pr-(CH$_2$)$_2$-OMe+1), 71 (C(O)CHC(O)+2), **Anal.** Calc. for PbC$_{20}$H$_{34}$-O$_6$·2H$_2$O (Found): C, 39.14 (39.04); H, 6.24 (5.58), **TGA**; (Variable Temperature) 266.1 °C, complex-2 (i-Pr+CH$_2$CH$_2$OMe), Calc. (Found), 64.69 (66.59), 375.9 °C, Pb^{+2}(C(O)C), Calc. (Found), 50.29 (48.80), 600 °C, Pb^{+2}(C(O)), Calc. (Found), 45.56 (47.39); (Isotherm, 1 hr, 8 mL/min N$_2$) 60 °C, 0.10% loss/10 min, yellow liquid, 90 °C, 0.48% loss/10 min, yellow

liquid, 120 °C, 2.23%/10 min, mixture of gray solid and yellow liquid, **DSC**; 260.4 °C (Endothermic).

Pb(OC(O)(CH$_2$)$_3$OCH$_3$)$_2$ (5): In a flame-dried 100 mL flask, 1.00 g (2.64 mmol) of lead acetate trihydrate was dried for 2 hr at 50 °C under reduced pressure and 20 mL of THF were then introduced. In another flame-dried 100 mL flask, 0.13 g (5.42 mmol) of sodium hydride and 15 mL of THF were placed, and 20 mL of THF solution containing 0.65 g (5.27 mmol) of 4-methoxybutanoic acid were added to the sodium hydride slurry solution dropwise for 10 min by a cannula, producing a white slurry solution. This solution was added to the lead acetate solution *via* a cannula for 10 min and was refluxed for 3 hr. The hot solution was filtered with a celite-packed frit, and the solvent removed under reduced pressure. The residue was further dried at 50 °C overnight to produce a pale yellow oil. Yield: 0.50 g (21.5%). **^{1}H NMR** (CDCl$_3$); δ 3.45 (t, 2H, -C**H$_2$**OMe), 3.32 (s, 3H, -OC**H$_3$**), 2.30 (b, 2H, -OC(O)C**H$_2$**CH$_2$-), 1.86 (b, 2H, -CH$_2$-C**H$_2$**CH$_2$), **^{13}C NMR** (CDCl$_3$); δ 181.4 (-O**C**(O)), 70.4 (CH$_3$-O**C**H$_2$), 56.7 (**C**H$_3$OCH$_2$), 33.9 (OC(O)**C**H$_2$CH$_2$), 23.5 (-CH$_2$-**C**H$_2$CH$_2$), **IR** (neat); 3457.4, 2930.2, 2868.2, 2744.2, 1770.9, 1732.0, 1557.3, 1405.8, 1258.3, 1168.9, 1118.5, 1021.4, 803.9, 664.1 cm^{-1}, **GC/MS (EI)**; 441 (M$^+$), 325 (M$^+$-2(CH$_2$CH$_2$-OMe)), 101 (L-1), 85 (L-OMe-2), 59 (CH$_2$C(O)OH), **Anal.** Calc. for PbC$_{10}$H$_{18}$O$_6$·0.13C$_6$H$_{14}$ (Found): C, 28.60 (28.58); H, 4.41 (4.10) , **TGA**; (Variable Temperature) 598 °C, PbO, Calc. (Found) 50.6% (49.4%), **DSC**; 328.9 °C, 355.3 °C, 499.4 °C (Endothermic).

Results and Discussion

Successful synthesis of the first liquid barium complex with 2,2-dimethyl-8-methoxyoctane-3,5-dione[9] underscored the importance of a properly designed ligand to enhance the performance of the MOCVD precursors. In a large metal ion such as Ba^{2+}, adoption of the strategy of intramolecular stabilization by alkoxyalkyl-substituted β-diketonates prevented the oligomerization by saturating the coordination sphere, and the liquid phase was obtained. Pb(β-diketonate)$_2$ is also known to form an adduct with bidentate bases such as 1,10-phenanthroline and 2,2′-bipyridine.[14] Therefore, it was expected that β-diketonates with an ethereal group might saturate the coordination sphere of lead(II) complexes, increasing the volatility of these complexes. We wanted to test the usefulness of these types of ligands in the lead complexes and explore the effect of substituents in these ligands on the properties of the complexes. We prepared various alkoxy-alkyl-substituted β-diketones using Claisen condensation with around 60% yields.

$$R^1C(O)CH_2C(O)CH_3 \xrightarrow{\text{1. Base 2. Br(CH}_2)_2OR^2}$$
$$R^1C(O)CH_2C(O)(CH_2)_3OR^2 \qquad (1)$$

$$Me_3CCOMe + MeO(CH_2)_3COOMe \xrightarrow{\text{1. NaH, DME 2. HCl}}$$
$$Me_3CC(O)CH_2C(O)(CH_2)_3OMe \qquad (2)$$
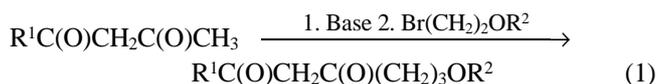
Lead complexes with these ligands were prepared by the following reactions.

$$Pb(acetate)_2 + 2\ Na[R^1C(O)CHC(O)(CH_2)_3OR^2] \rightarrow$$
$$Pb(R^1C(O)CHC(O)(CH_2)_3OR^2)_2 \quad (3)$$
$$(R^1= OMe, Me, i\text{-}Pr, t\text{-}Bu; R^2=Me, Et)$$

$$Pb(acetate)_2 + 2\ Na[OC(O)(CH_2)_3OMe] \rightarrow$$
$$Pb(OC(O)(CH_2)_3OMe)_2 \quad (4)$$
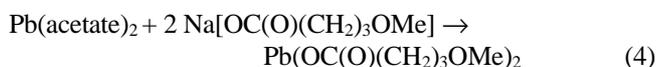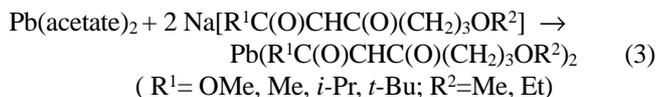
Generally, Pb(β-diketonate)$_2$ has been prepared by the reaction between lead halides or lead oxides and β-diketones. We tried to prepare Pb(β-diketonate)$_2$ using in-situ prepared lead alkyls, but it failed mainly due to the instability of lead alkyls, even at low temperatures. Metal acetates have been employed as a starting material in the synthesis of metal β-diketonates, but Pb(OAc)$_2$ is utilized only in limited cases such as sol-gel reactions[15] mainly due to its low solubility in most solvents except alcohols, DMSO and water. This low solubility comes from the polymeric nature with chelated bridging acetate groups.[16] Hubert-Pfalzgraf *et al.*[17] have also reported that Pb(OAc)$_2$ does not react with acetylacetone in isopropanol. We observed the same result in the refluxing toluene. Therefore, successful adoption of Pb(OAc)$_2$ as a starting material for the preparation of lead complexes in our study is worth mentioning.

It was found that all the complexes we prepared were liquid but viscous, as reported[9] in the case of Ba^{2+}. Even though these complexes were liquid, they were not very volatile. The nature of the heads (β-diketonate or carboxylate) and substituents at the β-diketonate head (Me, *i*-Pr, *t*-Bu, OMe) and the ethereal part (Me or Et) appeared not to be important for the liquid phase. From these observations, it appeared to have an ethereal group (or long chain) in the liquid phase. An ethereal part (or bulky group) might prevent the molecule from occupying the lattice site. It is generally known that liquid crystalline molecules have long rigid structures. Complex **2** froze at around -40 °C. Other complexes showed similar behavior. These melting points are extraordinarily low for the metal complexes, although it was not determined whether these solids were amorphous or not. Even though elemental analyses of these complexes were carefully and rapidly carried out, the results were not very satisfactory, possibly due to their viscous natures. Removing all the solvents and water molecules was difficult.

These compounds were not stable toward hydrolysis. Reactions with water or moisture in the air produced the white solid, possibly 3PbO·H$_2$O or Pb(OH)$_2$, the only known possible white lead solids. Reactions with HCl immediately produced free ligands almost quantitatively. Similar replacement reactions have been reported in the metal β-diketonates. No hydrolysis of scorpion tails was observed. These properties imply that scorpion tails may not be coordinated to the metal ion and thus, could not saturate the coordination sphere. Lindner *et al.*[18] reported that the signals of the carbon atoms adjacent to the ether oxygen were shifted to a lower field significantly in the ^{13}C{^{1}H} NMR spectra when the ether oxygen was coordinated to the metal. As shown in

Table 1. Chemical shifts of carbon atoms next to etheral oxygen in ligands and complexes

	δ (OC̲H$_3$) or δ (OC̲H$_2$CH$_3$)	δ (OC̲H$_2$CH$_2$CH$_2$-)
t-BuC(O)CH$_2$C(O)(CH$_2$)$_3$OMe	56.6	69.9
complex **1**	58.4	72.2
MeC(O)CH$_2$C(O)(CH$_2$)$_3$OEt	64.4	67.7
complex **2**	64.2	68.1
MeOC(O)CH$_2$C(O)(CH$_2$)$_3$OEt	64.4	67.5
complex **3**	64.2	68.3
i-PrC(O)CH$_2$C(O)(CH$_2$)$_3$OMe	56.7	69.8
complex **4**	56.6	70.5
HOC(O)(CH$_2$)$_3$OMe	56.5	69.7
complex **5**	56.7	70.4

Table 1, all the complexes prepared in this study did not show this tendency. Instability of the 7-membered metal-containing ring with scorpion tail fragments may be the reason. The noncoordinating nature of scorpion tails was also observed in the CuL$_2$ (L=alkoxyalkyl-substituted β-diketone) structure, but there was a weak interaction between an ethereal oxygen and the second copper atom (2.987 Å *vs.* 1.90 Å for the Cu-O single bond) in a unit cell.[9] Effect of the length of scorpion tails on the stability and volatility is under progress by preparing R^{1}C(O)CH$_2$C(O)(CH$_2$)$_2$OR^2.

Even though the exact vapor pressures of these complexes were not determined, isotherm TGA experiments showed the relative volatility under nitrogen flow conditions. The order of volatilities, although not greatly different, was as follows; **2** (Me, Et) > **1** (*t*-Bu, Me) > **4** (i-Pr, Me) > **3** (OMe, Et). Moreover, pyrolysis of complex **2** completed at the lowest temperature and the residue amounts (32.88%) were far less than the theoretical value of PbO (40.61%), indicating some sublimation occurred. Rationalization of this order is not straightforward, but it is worthwhile to note that complex **3** is thermally unstable. Generally, bulky substituents have been known to induce better thermal stability and volatility.[19] These behaviors cannot be explained; however, a combination of electronic and steric effects might induce the observed results. TGA thermograms and fragmentation patterns in mass spectra showed preferential decomposition of scorpion tail portions, indicating these fragments were not coordinated again. Bulky substituents such as t-Bu and i-Pr may interact with dangling scorpion tail, which induces less thermal stability than sterically less bulky methyl derivatives. TGA thermograms and mass spectra showed easy dissociation of these substituents. The thermal instability of methoxy derivative may be due to induced destabilization through the stopping resonance formed when the ligand coordinated through two oxygen atoms of carbonyl groups in β-diketonates (Scheme 1). No peaks above 1650 cm^{-1} in the IR spectrum of complex **3** indicated that canonical form A was predominant. There may be, however, an equilibrium between the two forms with the elevation of temperature, and destabilization with the formation of canonical form B may result in the easy dissociation of the ligand or thermal
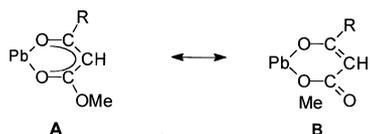
Scheme 1

Table 2. Conditions and results of PbO deposition with several Pb precursors by MOCVD (Substrate temperature: 500 °C; Substrate: Pt or pyrex glass; Carrier gas: N_2 100 sccm; Reactant gas: O_2 200 sccm, N_2 200 sccm; Reactor pressure: 3 torr)

Pb precursor	Bubbler temperature (°C)	PbO deposition rate (Å/30 min)
Complex **1**	110	50
Complex **2**	110	100
Pb(dpm)$_2$	140	600

decomposition. ^{13}C{^{1}H} NMR spectrum of complex **3** obtained at room temperature showed broad signals, indicating that an equilibrium between the two forms was actually established in the solution. This type of broadening was not observed in other lead complexes. The study of this behavior is under progress. A titanium complex, [Cp$_2$Ti(EtOC(O)CHC (O)Me)]ClO$_4$, was reported to have canonical form B, exhibiting bands at 1717, 1657, 1641, 1576, and 1566 cm^{-1}.[20] On the other hand, a vanadium derivative, [Cp$_2$V(EtOC(O)CHC (O)Me)]ClO$_4$, was found to have predominant canonical form A, exhibiting 1584 and 1563 cm^{-1}.[21]

These new lead complexes, especially complexes **1** and **2,** were tested as MOCVD precursors for the deposition of PbO film. For this experiment, the laboratory-made cold-wall type MOCVD equipment was employed. A 3-inch diameter silica tube was used as a film-growing reactor and the substrate was positioned on the graphite susceptor heated by RF induction coil. The flow rates of the carrier gas and reactant gases were controlled by mass flow controllers. All exposed tubings between the reactor and the bubbler, containing MOCVD precursor, were heated to about 150 °C by heating tapes. Deposition conditions for PbO films are described in Table 2. The deposition rate of PbO film was determined by measuring the weight change. It is considered that 110 °C is the optimized bubbler temperature for complexes **1** and **2**. The results of PbO film deposition with several precursors are also listed in Table 2. Even though complex **2** shows slightly better volatility than complex **1**, its volatility and thermal stability is still inferior to commercial solid complexes such as Pb(dpm)$_2$. When the bubbler temperature was higher than 110 °C, no PbO films were deposited. This indicates that complexes **1** and **2** are not thermally stable above this temperature.

Conclusion

Liquid lead complexes were successfully prepared by employing the alkoxyalkyl-substituted β-diketone. Long scorpion tail with ethereal oxygen is believed to be essential for the liquid phase. Substituents at the head or tail did not change the state. Pb(OAc)$_2$, which has limited use due to low solubility, was successfully adopted as a starting material for the preparation of new lead complexes. Reactivities toward hydrolysis and HCl addition and ^{13}C NMR spectra indicated that the coordination of the tail portions was questionable. A methyl derivative showed higher volatility than bulkier derivatives such as *t*-butyl and *i*-Pr, which contradicts to the known trend, and this may represent the presence of interaction between bulky substituents and tail portions. Thermal instability of the methoxy derivative might be attributed to the stopping of resonance structure of β-diketonate by changing the keto oxygen to the ethereal oxygen as a coordinating atom. Film growth experiments showed that these complexes were not volatile enough for the deposition of PbO film.

References

1. (a) Eimori, T.; Ohno, Y.; Kimura, H.; Matsufusa, J.; Kishimura, S.; Yoshida, A.; Sumitani, H.; Maruyama, T.; Hayashide, Y.; Moriizumi, K.; Katayama, T.; Asakura, M.; Horikawa, T.; Shibano, T.; Itoh, H.; Sato, K.; Namba, K.; Nishimura, T.; Sato, S.; Miyoshi, H. *Tech. Dig. IEDM* **1993**, 631. (b) Kawahara, T.; Yamamuka, M.; Makita, T.; Naka, J.; Yuuki, A.; Mikami, N.; Ono, K. *Jpn. J. Appl. Phys.* **1994**, *33* (*part 1, No. 9B*), 5129.

2. (a) Moulson, A. J.; Herbert, J. M. In *Electroceramics: Materials, Properties and Applications*; Chapman and Hall: London, 1990; chapters 6-8. (b) Hendricks, W. C.; Desu, S. B.; Peng, C. H. *Chem. Mater.* **1994**, *6*, 1955.

3. (a) Hong, S. T.; Lim, J. T.; Lee, J. C.; Xue, M.; Lee, I. M. *Bull. Korean Chem. Soc.* **1996**, *17*, 637. (b) Lim, J. T.; Hong, S. T.; Lee, J. C.; Lee, I. M. *Bull. Korean Chem. Soc.* **1996**, *17*, 1023

4. (a) Sumi, T.; Moriwaki, N.; Nakane, G.; Nakakuma, T.; Judai, Y.; Uemoto, Y.; Nagano, Y.; Hayashi, S.; Azuma, M.; Otsuki, T.; Kano, G.; Cuchairo, J. D.; Scott, M.C.; McMillan, L. D.; Paz de Araujo, C. A. *Integrated Ferroelectrics* **1995**, *6*, 1. (b) Amanuma, K.; Hase, T.; Miyasaka, Y. *Appl. Phys. Lett.* **1995**, *66*, 221. (c) Arujo, C. A.; Cuchairo, J. D.; McMillan, L. D.; Scott, M. C.; Scott, J. F. *Nature* **1995**, *374*, 627. (d) Vijay, D. P.; Desu, S. B.; Nagata, M.; Zhang, X.; Chen, T. C. *Ferroelectric Thin Films IV*; Materials Research Society: Pittsburgh, 1995; pp 3-13.

5. Malandrino, G.; Castelli, F.; Fragala, I. L. *Inorg. Chim. Acta* **1994***, 224*, 203.

6. Igumenov, I. K.; Semyannikov, P. P.; Belaya, S. V.; Zanina, A. S.; Shergina, S. I.; Sokolov, I. E. *Polyhedron* **1996**, *15*, 4521.

7. Rees, Jr., W. S.; Dippel, K. A. In *Chemical Processing of Advanced Materials*; Hench, L. H., Ed.; Wiley: New York, 1992.

8. Rees, Jr., W. S.; Moreno, D. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1759.

9. Rees, Jr., W. S.; Caballero, C. R.; Hesse, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 735.

10. Schulz, D. L.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Inorg. Chem.* **1993**, *32*, 249.

11. Greenwood, N. N.; Earnshaw, A. In *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984: p 1497.

12. (a) Bennett, G. M. *J. Chem. Soc.* **1929**, 271. (b) Tallman, R. C. *J. Am. Chem. Soc.* **1934**, *56*, 128.

13. (a) Marel, C. S. *J. Am. Chem. Soc.* **1929**, *51*, 260. (b) Goto, G. *Chem. Pharm. Bull.* **1985**, *33*, 4422.

14. Mehrotra, R. C.; Bohra, R. In *Metal-diketonates and Allied Derivatives*; Academic Press: London, 1978; p 43.

15. Siccia, L.; West, B. O.; Zhang, Q. *Polyhedron* **1998**, *17*, 1851.

16. (a) Harrison, P. G.; Steel, A. T. *J. Organometal. Chem.* **1982**, *239*, 105.

17. Bryant, R. G.; Chacko, V. P.; Etter, M. C. *Inorg. Chem.* **1984**, *23*, 3580.

18. Hubert-Pfalzgraf, L. G.; Daniele, S.; Papiernik, R.; Massiani, M. C.; Septe, B.; Vaissermann, J.; Daran, J.-C. *J. Mater. Chem.* **1997**, *7*, 753.

19. Lindner, E.; Pautz, S.; Fawzi, R.; Steimann, M. *Organometallics* **1998**, *17*, 3006.

20. Hanusa, T. *Chem. Rev.* **1993**, *93*, 1023.

21. Doyle, G.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 2484.

22. ibid, **1968**, *7*, 2479.