

The Reaction Of Metal Trialkyls With Benzo[H]Quinolin-10-ol

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Abstract: The reaction of the trialkyl metals (R_3M , $R = \text{Me, Et}$; $M = \text{Ga, In}$) with benzo[h]quinolin-10-ol (HO-BQ) in a 1:1 molar ratio gave intramolecular N coordinated complexes $R_2M\text{-O-BQ}$ ($M = \text{Ga, R} = \text{Me}$ **1**, Et **2**) and $(R_2\text{In-O-BQ})_2$ ($M = \text{In, R} = \text{Et}$ **3**,) in 80-90% yield. The molecular structures of complexes **1** and **3** have been established by X-ray crystallography.

Keywords: Metal trialkyls, gallium, indium, MOCVD precursors, X-ray crystal structure.

Introduction

The chemistry of organoaluminum, organogallium and organoindium complexes has attracted much attention due not only to their interesting structural and chemical properties but also their application in semiconductor materials¹⁻⁵. In the course of our studies on exploring volatile MOCVD precursors that have the properties of lower toxicity and higher stability, we have recently reported on the synthesis and characterization of intermolecular adducts⁶⁻⁸, novel bonding mode complexes^{9,10}, and the complexes in which N/O mixed-donor crown ethers as ligands^{11,12}. As an extension of these studies, here we describe the synthesis and characterization of above gallium and indium complexes.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a drybox. Benzene and cyclohexane were dried by distillation over sodium under nitrogen prior to use. Metal trialkyls (Me_3Ga , Et_3Ga , and Et_3In) were provided by the National High-Tec MO Precursors R&D Centre of China, Nanjing University. Benzo[h]quinolin-10-ol (HO-BQ) was synthesized according to the literature¹³. ¹H-NMR spectra were obtained on a Bruker AM500 or JEOL PMX-60 spectrometer using SiMe_4 as internal reference. IR spectra were recorded on an IR-440 spectrometer. Mass spectra were obtained on a VG-ZAB-MS instrument. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer.

*Preparation of $\text{Me}_2\text{Ga-O-BQ}$ **1**.* HO-BQ (0.97 g, 5 mmol) was dissolved in 10 ml of benzene. To the stirred solution, a benzene (5 ml) solution of Me_3Ga (5 mmol) was

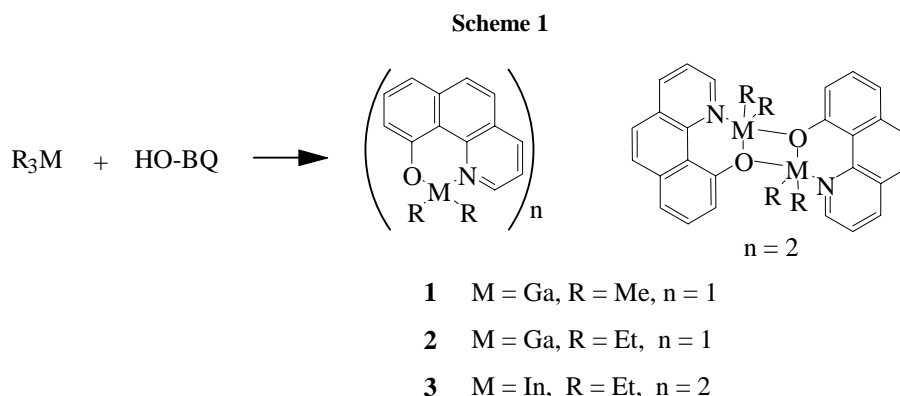
added slowly. The reaction took place immediately with gas evolution. The mixture was continuously stirred for 10mins at room temperature and 30mins at 50°C. Solvent was removed *in vacuum* and the solid residue was recrystallized from benzene, yellow crystals were obtained. Yield 90%, m.p.141-142°C. Anal. Found: C, 60.66; H, 4.84; N, 4.62%. Calc. for C₁₅H₁₄NOGa: C, 61.28; H, 4.80; N, 4.76%. ¹H-NMR (500MHz, CDCl₃): -0.01 (6H, s, AlMe₂); 7.42 (2H, t, ArH); 7.69 (1H, d, ArH); 7.79 (2H, t, ArH); 7.99 (1H, d, ArH); 8.50 (1H, d, ArH); 8.64 (1H, s, ArH). IR (cm⁻¹): 3054, 2954 (νC-H); 1627, 1578, 1430, 1402 (νC=C or νC=N); 630 (νGa-O or νGa-C). MS (% intensity, m/z): 293.0 (5.73, M⁺); 278.1 (100, [M-Me]⁺); 263.0 (29.21, [M-2Me]⁺); 68.9 (47.98, Ga⁺).

Preparation of Et₂Ga-O-BQ 2. Complex **2** was prepared in a manner similar to **1**. Yield 81%, yellow crystals, m.p.73-75°C. Anal. Found: C, 63.61; H, 5.38; N, 5.10%. Calc. for C₁₇H₁₈NOGa: C, 63.40; H, 5.63; N, 4.35%. ¹H-NMR (60MHz, CDCl₃): 0.6 (4H, q, Ga(CH₂CH₃)₂); 1.01 (6H, t, Ga(CH₂CH₃)₂); 7.1-7.8 (6H, m, ArH); 8.2-8.4 (2H, m, ArH). IR (cm⁻¹): 3020, 2900-2960 (νC-H); 1580, 1430, 1400 (νC=C or νC=N); 640 (νGa-O or νGa-C). MS (% intensity, m/z): 291.9 (0.68, [M-Et]⁺); 194.9 (100, [HO-BQ]⁺); 69.0 (1.37, Ga⁺).

Preparation of [Et₂In-O-BQ]₂ 3. Complex **3** was prepared in a manner similar to **1**. Yield 85%, yellow crystals, m.p.120-122°C. Anal. Found: C, 55.97; H, 4.06; N, 3.98%. Calc. for C₃₄H₃₆N₂O₂Ga₂: C, 55.62; H, 4.94; N, 3.82%. ¹H-NMR (60MHz, C₆H₆): 1.1 (4H, q, In(CH₂CH₃)₂); 1.4 (6H, t, In(CH₂CH₃)₂); 7.1-8.2 (8H, m, ArH). MS (% intensity, m/z): 195 (100,HO-BQ⁺); 114.0 (3.0, In⁺).

Results and Discussion

Preparation and characterization of the complexes: The reaction of the trialkyl metals (R₃M, M = Ga, R = Me, Et; M = In, R = Et) with benzo[h]quinolin-10-ol (HO-BQ) in a 1:1 molar ratio gave intramolecular N coordinated monomer complexes R₂M-O-BQ (M = Ga, R = Me **1**, Et **2**) and dimer complexes (R₂In-O-BQ)₂ (M = In, R = Et **3**) in high yields as shown in **Scheme 1**.



These complexes are much less sensitive toward air and moisture than those of metal trialkyls. The elemental analysis (C, H, N) of these complexes showed that they

have the composition as in **Scheme 1**. The $^1\text{H-NMR}$ spectra of these complexes are listed in experimental section. The chemical shifts of the metal alkyls in these complexes are shifted downfield compared with their respective R_3M parents. This phenomenon is also observed in other complexes^{6,10}. The mass spectra of these complexes show their corresponding fragments but no parent molecular ions $[\text{M}]^+$ except for complex **3** (the intensity is very low- 5.7%). This means that these complexes are unstable with electron impact ionization (EI).

X-ray structure determination of complexes of 1 and 3

Figure 1

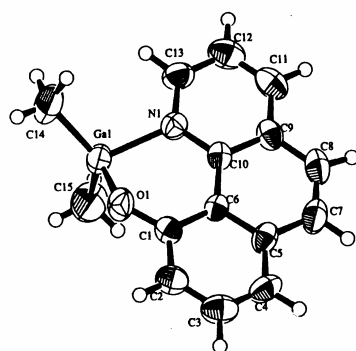
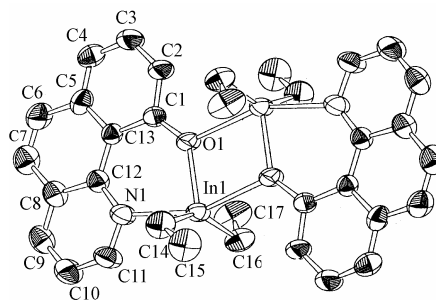


Figure 2



Crystals of $\text{Me}_2\text{Ga-O-BQ}$ **1** and $[\text{Et}_2\text{In-O-BQ}]_2$ **3** suitable for single-crystal X-ray structure determination were grown from hot benzene. The molecular structures are displayed in **Figures. 1** (**1**: one independent molecule only, the other being very similar

in geometry) and **2** (**3**). Complex **1** crystallized in triclinic with space group $\text{P}\bar{1}$ (#2). The geometry of the gallium coordination sphere can be described as a distorted tetrahedron. [Ga(1)-O(1), 1.865(3); Ga(1)-C(14), 1.946(7); Ga(1)-N(1), 2.029(4) and Ga(1)-C(15), 1.967(7) Å; $\angle\text{C}(14)\text{-Ga}(1)\text{-N}(1)$, 110.4(2); $\angle\text{O}(1)\text{-Ga}(1)\text{-N}(1)$, 91.4(1); $\angle\text{C}(14)\text{-Ga}(1)\text{-C}(15)$, 124.3(3); $\angle\text{Ga}(1)\text{-O}(1)\text{-C}(1)$, 122.6(3); $\angle\text{C}(14)\text{-Ga}(1)\text{-O}(1)$, 110.5(3) and $\angle\text{Ga}(1)\text{-N}(1)\text{-C}(10)$, 121.8(3)°]. Complex **3** crystallized in monoclinic with space group $\text{P}2_1/\text{n}$. The asymmetric unit comprises one half of the dimer, the other half being generated by the centre of symmetry on (0,0,0). Thus, the overall molecular symmetry is crystallographically constrained to be centrosymmetric with five-coordinated indium atoms. The two monomeric molecules are linked *via* oxygen bridges. The geometry of the indium coordination sphere can be described as a distorted trigonal bipyramid [In(1)-C(14), 2.161; C(14)-C(15), 1.47(1); In(1)-C(16), 2.156(7); C(16)-C(17), 1.487(9); In(1)-N(1), 2.386(5); O(1)-C(1), 1.332(6); In(1)-O(1), 2.435(4); N(1)-C(12), 1.360(7)Å; $\angle\text{C}(14)\text{-In}(1)\text{-N}(1)$, 93.1(2); $\angle\text{O}(1)\text{-In}(1)\text{-O}(1)^*$, 77.2(1); $\angle\text{C}(14)\text{-In}(1)\text{-C}(16)$, 146.9; $\angle\text{In}(1)\text{-O}(1)\text{-In}(1)^*$, 102.8(1); $\angle\text{C}(14)\text{-In}(1)\text{-O}(1)$, 95.1(2); $\angle\text{C}(1)\text{-O}(1)\text{-In}(1)^*$, 120.7(3);

$\angle C(15)-C(14)-In(1)$, 123.4(6); $\angle C(1)-O(1)-In(1)$, 136.5(3); $\angle C(17)-C(16)-In(1)$, 113.7(5); $\angle N(1)-In(1)-O(1)$, 156.2(1)]

Acknowledgments

The research was supported by the National Natural Science Foundation of China, the Science Foundation of Jiangsu Province and the National High Technology Program.

References

1. A.H. Cowley, R.A. Jones, *Angew. Chem. Int. Ed. Engl.*, **1989**, 28, 1208.
2. R.L. Wells, *Coord. Chem. Rev.*, **1992**, 112, 273.
3. G.H. Robinson, "Coordination Chemistry of Aluminum", VCH, New York, **1993**.
4. Downs A.J. "Chemistry of Aluminum Gallium Indium and Thallium", First Edition, Blackie Academic & Professional, **1993**.
5. Jones A. C and O'Brien P., "CVD of Compound Semiconductors: Precursor Synthesis, Development and Applications", VCH Verlagsgesellschaft mbH, **1997**.
6. H. Sun, X. You, X. Huang, *Polyhedron* **1995**, 14(15-16), 2159,.
7. H. Sun, X. Wang, X. Sun, X. You, J. Wang, *Acta Cryst.*, **1996**, C52,1184.
8. X. Huang, H. Sun, *Main Group Metal Chem.*, **1996**, 19(3), 161.
9. X. Wang, H. Sun, X. You and X. Huang, *Polyhedron* , **1996**, 15(20), 3543.
10. Q. Zhao, H. Sun, W. Chen, Y. Liu and X. You, *J. Organomet. Chem.*, **1998**, 556, 159.
11. Q. Zhao, H. Sun, W. Chen, C. Duan, Y. Liu, Y. Pan and X. You, *Organometallics*, **1998**, 17(2), 156,.
12. Q. Zhao, H. Sun and X. You, *J. Organomet. Chem.* **1999**, 572, 59.
13. H. Schenkel, M. Schenkel, *Helv. Chim. Acta*, **1944**, 27,1456.

Received 12 March 1999