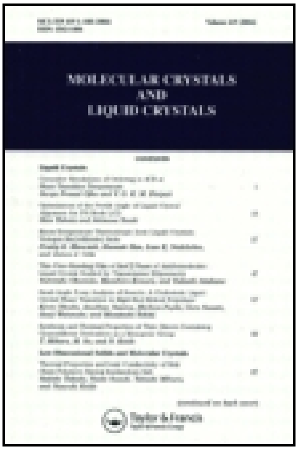

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Color Tuning of Iridium Complexes through Heteroleptic Tris-cyclometallated Ligands

In June Kim [a] & Young Sik Kim [a] [b]

[a] Department of Information Display, Hongik University, Seoul, Korea

[b] Department of Science, Hongik University, Seoul, Korea

Version of record first published: 10 Nov 2009

To cite this article: In June Kim & Young Sik Kim (2009): Color Tuning of Iridium Complexes through Heteroleptic Tris-cyclometallated Ligands, Molecular Crystals and Liquid Crystals, 514:1, 55/[385]-63/[393]

To link to this article: http://dx.doi.org/10.1080/15421400903217801

Mol. Cryst. Liq. Cryst., Vol. 514, pp. 55/[385]–63/[393], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903217801

Color Tuning of Iridium Complexes through Heteroleptic Tris-cyclometallated Ligands

In June Kim[1] and Young Sik Kim[1,2]
[1]Department of Information Display, Hongik University, Seoul, Korea
[2]Department of Science, Hongik University, Seoul, Korea

White organic light-emitting devices (WOLEDs) consist of a fluorescent blue material doped in a region spatially separate from the phosphorescent dopant iridium complex. This study evaluated two potential new phosphorescent materials, the heteroleptic tris-cyclometallated iridium complexes $Ir(tpy)_2(btp)$ *and* $Ir(btp)_2(tpy)$*, where tpy and btp are "2-(p-tolyl)pyridine" and "2-(2′-benzothienyl) pyridine", respectively. The luminescence mechanism in heteroleptic iridium complexes is determined by the rates of decay from two different species of ligands. The quantum yields (lifetime) of* fac-$Ir(tpy)_3$ *and* fac-$Ir(btp)_3$ *were reported as 0.5 (2.0 μs) and 0.12 (4.0 μs), respectively. Thus, the radiative decay rate* (k_r) *of* fac-$Ir(tpy)_3$ *and* fac-$Ir(btp)_3$ *can be calculated as* $2.5 \times 10^5/s$ *and* $3.0 \times 10^4/s$*, respectively. Heteroleptic tris-cyclometallated iridium complexes were able to tune the color for white phosphorescent materials, by controlling the radiative decay rate of ligands and number of ligands in complexes.*

Keywords: cyclometallated iridium (III) complex; organic light-emitting devices (OLEDs)

INTRODUCTION

Recently interest in next-generation displays and lighting technologies has stimulated research on white organic light-emitting devices (WOLEDs) employing phosphorescent materials which have led to significant improvements in efficiency. Various strategies to fabricate WOLEDs include the manufacture of multilayer OLEDs by consecutive evaporation, and the manufacture of single layer polymer blend

---

This work was supported by the Korea Research Foundation Grant Funded by the Korean Government (MOEHRD) (KRF-2007-313-D00290).

Address correspondence to Prof. Young Sik Kim, Department of Science, Hongik University, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea (ROK). E-mail: youngkim@hongik.ac.kr

devices, where all the emitting components are mixed in one layer [1–4]. However, the emission color in both devices is sensitive to features of the device structure, such as layer thickness and doping concentration. Furthermore, the use of charge blockers to confine the charges and excitons causes high driving voltage and low efficiencies in multilayer white devices and colors are dependent on the driving voltage in the single layer polymer devices. Most of problems seem avoidable if a single component material can be used as the emitting species, for example, heteroleptic complexes has more than two kind of N^C ligands avoid able to saturated quenching. Although a few single emitting component WOLEDs have been reported in which white electroluminescence comes from the individual lumophore and excimer (or electromer), no single emitting component WOLED has yet been reported [5,6].

In this paper, we studied new heteroleptic tris-cyclometallated iridium complexes, $Ir(tpy)_2(btp)$ and $Ir(btp)_2(tpy)$, where tpy and btp are "2-(*p*-tolyl)pyridine" and "2-(2′-benzothienyl)pyridine", respectively, as phosphorescent materials for WOLEDs, by tuning the color which consist of a fluorescent blue material doped in a region spatially separate from the phosphorescent dopant iridium complex [7,8]. Emission wavelengths (the radiative decay rate) of *fac*-$Ir(tpy)_3$ (*fac* = facial) and *fac*-$Ir(btp)_3$ were reported as 512 nm (2.0 μs) and 596 nm (4.0 μs), respectively [9,10]. By controlling radiative decay rates and the number of ligands, we caused the material to emit each ligand at the same time, tune the color and improve quantum efficiency.

EXPERIMENTAL

All reagents were purchased from Aldrich Co., except iridium (III) trichloride hydrate ($IrCl_3 \cdot nH_2O$) which was purchased from Strem Co., and all were used without further purification. All reactions were carried out under a nitrogen or argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-Mesh, Merck Co.). The synthesis methods used for heteroleptic and homoleptic iridium complexes are modified from Nonoyama's works [11] and are shown in Figure 1. In order to examine the purity of the products, Gas Chromatography–Mass Spectrometry (GC/MS) was performed by the DIP method on a Varian 3800GC/1200 L single quadruple mass in dilute CH_2Cl_2 at room temperature.

Ultraviolet-visible (UV-Vis) absorption spectra were measured on a Hewlett Packard 8425A spectrometer. The PL spectra were obtained on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of

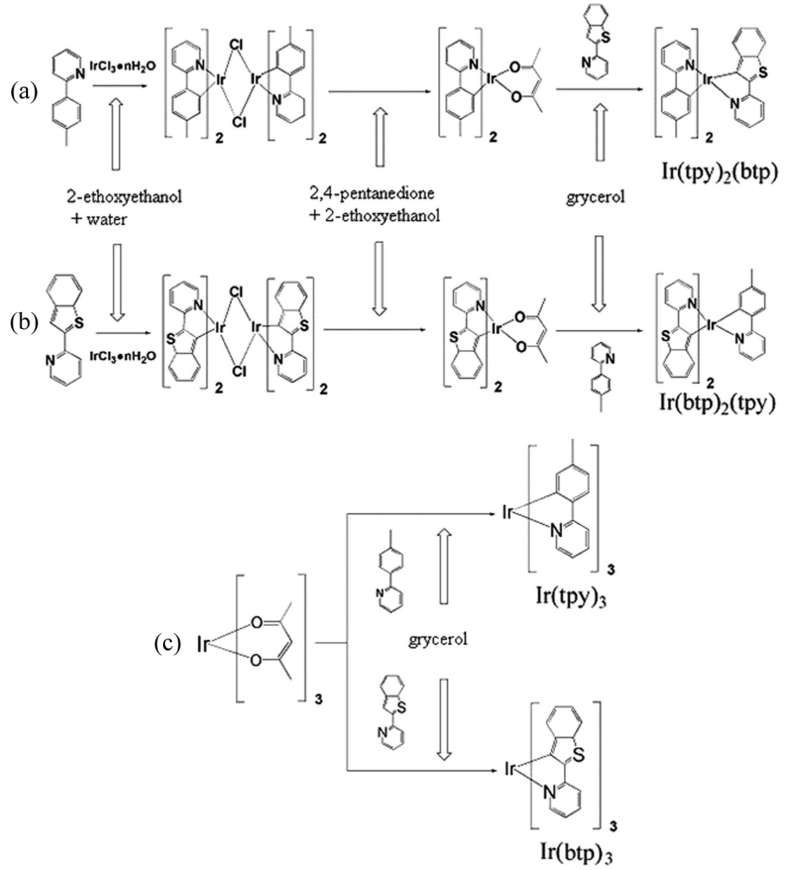

FIGURE 1 Synthesis of heteroleptic iridium complexes containing two different kinds of C^N ligands are shown in part (a) and (b). Synthesis of homoleptic iridium complexes containing one kind of C^N ligand are shown in part (c).

$Ir(tpy)_3$, $Ir(tpy)_2(btp)$, $Ir(btp)_2(tpy)$, and $Ir(btp)_3$ were measured with a 10^{-5} M dilute solution in methylene chloride(CH_2Cl_2).

Synthesis of Complexes

Synthesis of Ir(C^N)$_2$(acac): [Ir(tpy)$_2$(acac), Ir(btp)$_2$(acac)]

To a flask containing $IrCl_3 \cdot nH_2O$ (1.49 g, 5 mmol) and a cyclometallating ligand (C^N = tpy or btp, 12.5 mmol (2.5 eq)), we added a 3:1 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 15 hr and cooled to room temperature. The solution mixture was slowly evaporated to obtain the crude product $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2$.

The yellow and dark red solid was filtered and washed with ethanol. This chloride-bridged dimer (2 mmol) was then placed in a 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL). 2,4-pentanedione (0.68 ml, d = 0.975, 6.8 mmol (3.4 eq)) was added and the reaction mixture was refluxed for 2 hr at 120°C. The solution was cooled to room temperature and poured into 30 ml of 2N HCl. The yellow solid was filtered and washed with water, followed by purification by silica gel column chromatography, using CH_2Cl_2 to afford a yellow powder and red powder.

$Ir(tpy)_2(acac)$: Yield (1.192 g, 47.5%).

$Ir(btp)_2(acac)$: Yield (1.212 g, 42.5%).

Synthesis of Heteroleptic Ir(III) Complexes [Ir(C^N)$_2$(C^N)′]

$Ir(C^{\wedge}N)_2(acac)$ 1 mmol and a cyclometallating ligand ((C^N)', 2.3 mmol (2.3 eq)) were dissolved in 20 mL of glycerol in a 50 ml flask. The mixture was refluxed for 10 hr at 210°C. The reaction mixture was poured into 30 ml of 2N HCl to give the crude solid. Column chromatography on silica followed by recrystallization in methylene chloride/hexanes yielded an orange powder and red powder of the hetero Ir complex.

$Ir(tpy)_2(btp)$: Yield (0.231 g, 31.2%), GC/MS: calcd.739.47; found 739.41.

$Ir(btp)_2(tpy)$: Yield (0.254 g, 32.5%), GC/MS: calcd.780.00; found 780.45.

Synthesis of Homoleptic Ir(III) Complexes [fac-Ir(tpy)$_3$, fac-Ir(btp)$_3$]

These complexes were prepared from $Ir(acac)_3$ and the corresponding (C^N) ligand by a reported procedure. $Ir(acac)_3$ (245 mg, 0.5 mmol) and (C^N) ligands (tpy or btp, 2 mmol) were dissolved in 20 ml of glycerol and the mixture was refluxed for 10 hr at 210°C. After cooling, 20 ml of 1N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography, using CH_2Cl_2 and then recrystallized in methylene chloride/hexanes.

fac-$Ir(tpy)_3$: Yield (0.194 g, 55.7%).

fac-$Ir(btp)_3$: Yield (0.184 g, 44.7%).

RESULTS AND DISCUSSION

New heteroleptic tris-cyclometallated iridium complexes, $Ir(tpy)_2(btp)$ and $Ir(btp)_2(tpy)$ have been studied to tune the color by controlling radiative decay rates and the number of ligands. To protect the heteroleptic tris-cyclometallated iridium complexes from impurities, we used a method of recrystallization and repeated column chromatography. GC/MS data of the Ir(tpy)$_2$(btp) is shown in Figure 2. The highest mass spectrum and the calculated molecular weight of Ir(tpy)$_2$(btp) complex are 739.41 and 739.47, respectively. It provide evidence that complex have been synthesized without impurities. Due to the GC/MS measurement method, the ligand is easily taken off from the iridium complex. Second and third mass peaks represent the cations of Ir(tpy)(btp) and Ir(tpy)$_2$ and their calculated molecular weight are 571.25 and 528.65, respectively.

The UV-Vis absorption spectra of Ir(tpy)$_3$, Ir(tpy)$_2$(btp), Ir(btp)$_2$(tpy), and Ir(btp)$_3$ in 10^{-5} M CH_2Cl_2 at room temperature are shown in Figure 3. The absorption peaks of Ir(tpy)$_3$ are located at 380, 410, 460, and 490 nm. The absorption bands below 380 nm can be assigned to the spin-allowed $^1\pi$-π^* transition, the band around 410 nm to a spin-allowed ^{1}MLCT (metal to ligand charge transfer) band, and the bands around 460 and 490 nm can be assigned to a spin-forbidden ^{3}MLCT band. MLCT absorption is allowed by the strong mixing of the π character of the ligand with the 5d character of the centric iridium atom in the highest occupied molecular orbitals (HOMOs). MLCT absorption peaks of Ir(btp)$_3$ are observed at 411, 427, and 485 nm. The overall profile of the absorption spectrum and the peak position of the MLCT absorption of the heteroleptic Ir(btp)$_2$(tpy) are very similar to those of Ir(btp)$_3$. This provides evidence that MLCT

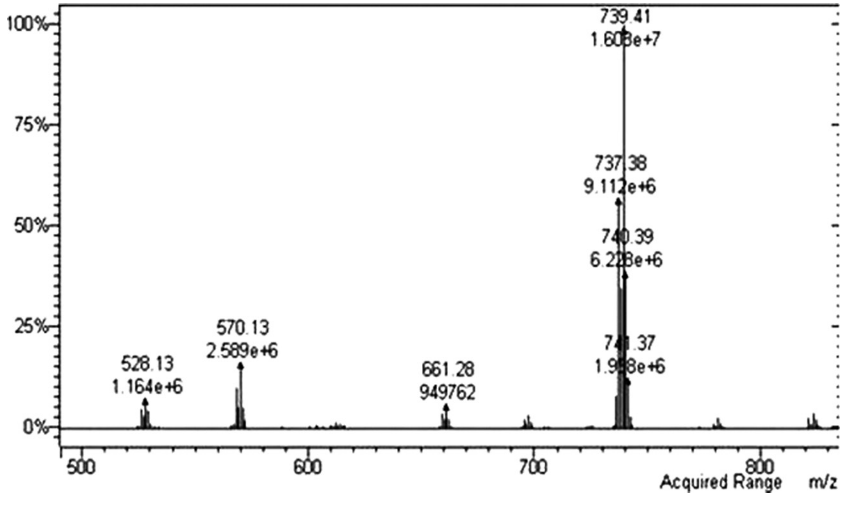

FIGURE 2 GC/MS data of the heteroleptic complex: Ir(tpy)$_2$(btp) mass data shown at 739.41 point.

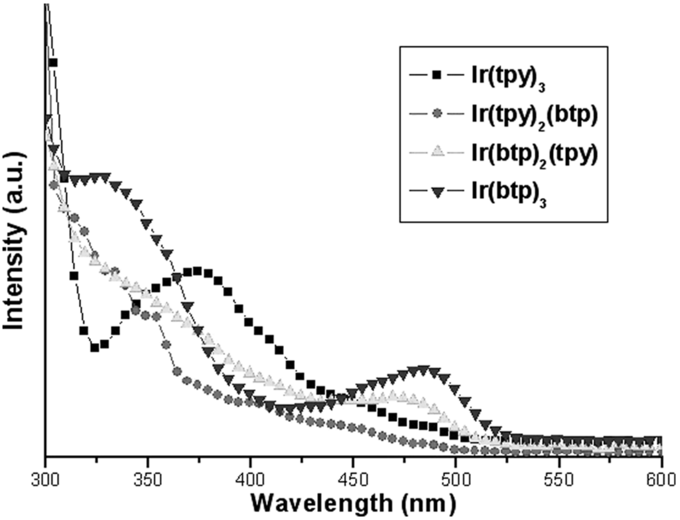

FIGURE 3 UV-Vis absorption spectra of Ir(tpy)$_3$, Ir(tpy)$_2$(btp), Ir(btp)$_2$(tpy), and Ir(btp)$_3$ in a 10^{-5} M dilute solution in methylene chloride(CH$_2$Cl$_2$).

absorption of the heteroleptic Ir(btp)$_2$(tpy) occurs mainly at the btp ligand. Because the energy level of the HOMOs and LUMOs (lowest occupied molecular orbitals) of btp ligand are located between those of the tpy ligand, and the electronic population of the HOMOs of Ir(btp)$_2$(tpy) is mainly located in the btp moiety, MLCT absorption is allowed only by the btp ligand. While at the same time, MLCT absorption peaks of Ir(tpy)$_2$(btp) are observed at 410, 455, and 490 nm. MLCT absorption peaks of Ir(tpy)$_2$(btp) are similar to those of Ir(tpy)$_3$., It is due to the strong MLCT characteristic of tpy ligand.

The relative PL spectra of the homoleptic and heteroleptic complexes in CH$_2$Cl$_2$ are shown in Figure 4. The PL spectrum of Ir (tpy)$_2$(btp) exhibits mainly at 512 nm from the tpy ligand. However, the PL spectrum of Ir(btp)$_2$(tpy) shows a large broad emission band at 512 and 598 nm from the tpy and btp ligands, respectively. In the theoretical analysis, the PL spectra of heteroleptic complexes having different kinds of ligands can be determined by the differences in the decay rate, the energy level of triplet state and the number of the ligand. The luminescent mechanism of heteroleptic complexes that have a similar energy level of triplet states are decided by the decay rates and the number of ligand. The radiative and nonradiative decay rate constants, k_r and k_{nr}, are calculated from the phosphorescence quantum yield, ϕ, and the phosphorescence lifetime, by the following

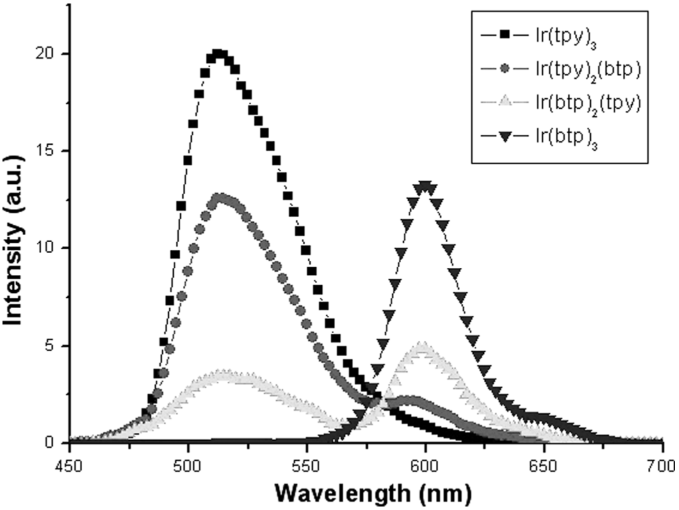

FIGURE 4 Relative PL spectra of $Ir(tpy)_3$, $Ir(tpy)_2(btp)$, $Ir(btp)_2(tpy)$, and $Ir(btp)_3$ in a 10^{-5} M dilute solution in methylene chloride(CH_2Cl_2).

equations: $\phi = \frac{k_r}{k_r + k_{nr}}$, and $\tau = \frac{1}{k_r + k_{nr}}$. The quantum yield (lifetime) of $Ir(tpy)_3$ and $Ir(btp)_3$ were reported as 0.5 (2.0 μs) and 0.12 (4.0 μs), respectively. Thus, the radiative decay rate (k_r) of $Ir(tpy)_3$ and $Ir(btp)_3$ can be calculated as 2.5×10^5/s and 3.0×10^4/s, respectively [9,10]. The PL spectra of heteroleptic iridium complexes tend to show these relationships. $Ir(tpy)_2(btp)$ has about 6 times stronger characteristics of $Ir(tpy)_3$ than that of $Ir(btp)_3$. Thus, MLCT absorption and the luminescence occur mainly at the same tpy ligand because of their strong MLCT characteristics. A small amount of partial excitation energy can be transfer to the btp ligand because of the inter-ligand energy transfer (ILET) time from dfppy to tpy within the ns time scale. The quantum yield of $Ir(tpy)_3$ and $Ir(tpy)_2(btp)$ were found to be 0.5 and 0.35, respectively, as shown in Table 1.

The PL spectrum of $Ir(btp)_2(tpy)$ shows a similar intensity from tpy and btp ligands. However, the calculated radiative decay rate of $Ir(btp)_2(tpy)$ shows 4 times stronger characteristics of $Ir(tpy)_3$ than that of $Ir(btp)_3$. Moreover, the radiative lifetime of $Ir(btp)_3$ is longer than that of $Ir(tpy)_3$ and the energy transfer time from btp to tpy is shorter than the radiated time. This discrepancy comes from the difficulty of the endothermic ILET from btp to tpy ligand. Because the HOMO and LUMO energy levels of the btp ligand are located between those of tpy ligand, and the electronic population of the HOMO of

TABLE 1 Emission Wavelength λ_{em}(nm), Quantum Yield Φ_{PL}, Lifetime τ, Radiative Decay Rate k_r (10^5/s) and Nonradiative Decay Rate k_{nr} (10^5/s) of Homoleptic and Heteroleptic Iridium Complexes

	λ_{em} (nm)	Φ_{PL}	τ (μs)	k_r (10^5/s)	k_{nr} (10^5/s)
$Ir(tpy)_3$	512	0.5	2.0	2.5	2.5
$Ir(btp)_3$	598	0.12	4.0	0.3	2.2
$Ir(tpy)_2(btp)$	512, 592	0.35	–	–	–
$Ir(btp)_2(tpy)$	512, 598	0.18	–	–	–

$Ir(btp)_2(tpy)$ is mainly located in the btp moiety, dominant emission mainly occurs in the btp moiety. However, ILET can occur partially from btp to tpy ligand because of a fast ILET time.

Therefore PL spectra of $Ir(btp)_2(tpy)$ shows a broad emission band from both tpy and btp ligands. The quantum yield of $Ir(btp)_2(tpy)$ and $Ir(btp)_3$ were determined to be 0.18 and 0.12, respectively. As a result, the PL spectrum of $Ir(btp)_2(tpy)$ shows quite similar intensity from tpy and btp ligands. Therefore, the heteroleptic tris-cyclometallated Ir(III) complexes were found to be good candidates for white phosphorescent materials, assuming control of the decay rate, the energy level of the triplet state and the number of ligands in the iridium complex.

CONCLUSIONS

We studied two new heteroleptic tris-cyclometallated iridium complexes, $Ir(tpy)_2(btp)$ and $Ir(btp)_2(tpy)$, as potential phosphorescent materials for WOLEDs, which consist of a fluorescent blue material doped in a region spatially separate from the phosphorescent dopant iridium complex. The luminescence mechanism in the heteroleptic iridium complex is determined by the rates of decay from two different species of ligands. As a result, heteroleptic iridium complexes can be tune the color for white phosphorescent materials, assuming control of the radiative decay rate of the ligands and number of ligands in the iridium complexes.

REFERENCES

[1] Berggren, M., Gustafsson, G., Inganäs, O., Andersson, M. R., Hfertberg, T., & Wennerstrom, O. (1994). *J. Appl. Phys.*, *76*, 7530.

[2] Jordan, R. H., Dodabalapur, A., Strukel, M. J., & Miller, T. M. (1996). *Appl. Phys. Lett.*, *68*, 1192.

[3] Granstrom, M. & Inganas, O. (1996). *Appl. Phys. Lett.*, *68*, 147.

[4] Chao, C. I. & Chen, S. A. (1998). *Appl. Phys. Lett.*, *73*, 426.

[5] Kido, J., Kimura, M., & Nagai, K. (1995). *Science*, *267*, 1332.

[6] Strukelj, M., Jordan, R. H., & Dodabalapur, A. (1996). *J. Am. Chem. Soc.*, *118*, 1213.

[7] Rho, H. H., Park, G. Y., Ha, Y. K., & Kim, Y. S. (2006). *Jpn. J. App. Phys.*, *45*, 563.

[8] Lee, Y. H., Park, G. Y., & Kim, Y. S. (2007). *J. Korean Phys. Soc.*, *50*, 1722.

[9] Tamayo, A. B., Alleyne, B. D., Djurovich, P. I., Lamansky, S., Tsyba, I., Ho, N. N., Bau, R., & Thompson, M. E. (2003). *J. Am. Chem. Soc.*, *125*, 7377.

[10] Tsuboyama, A., Iwawaki, H., Furugori, M., Mukaide, T., Kamatani, J., Igawa, S., Moriyama, T., Miura, S., Takiguchi, Y., Okada, S., Hoshino, M., & Ueno, K. (2003). *J. Am. Chem. Soc.*, *125*, 12971.

[11] Nonoyama, M. J. (1975). *Organomet. Chem.*, *86*, 263.