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New Type of Photoluminescent Iridium Complex: Novel Synthetic Route for Cationic *trans*-Bis(2-phenylpyridinato)iridium(III) Complex

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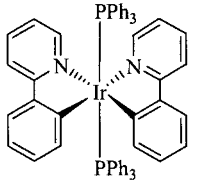
A new type of iridium(III) complex [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**) has been prepared by a novel synthetic method and its structural and photoluminescent characteristics have been compared with those of the *cis* analogue, [*cis*-Ir(ppy)$_2$(PPh$_3$)(P(OPh)$_3$)]$^+$ (**2**) which has also been newly prepared in this study.

Introduction

Studies on iridium(III) complexes of 2-phenylpyridinato (ppy) and related ligands have been extensively carried out as their characteristic luminescent properties seem to be utilizable in the display industry.[1] There are three different types of compounds reported thus far: tris-ppy complexes, *fac-* and *mer*-Ir(ppy)$_3$;[1c,2] bis-ppy complexes, *cis*-Ir(ppy)$_2$(L)(L′);[3] and mono-ppy complexes, *trans,cis*-Ir(ppy)(PR$_3$)$_2$(L)(L′) [*trans*-(PR$_3$)$_2$, *cis*-(L)(L′)].[1a] Emission characteristics such as $\lambda_{\max}$, Φ_{PL}, and τ are somewhat successfully controlled by modifying the ppy ligand and by introducing diverse ancillary ligands (L and L′).[1–4]

There has been no report of *trans*-Ir(ppy)$_2$(L)(L′) containing two ppy ligands *trans* to each other probably because of the lack of the established synthetic procedures, although these *trans* bis-ppy complexes are expected to show emission properties that are comparable with those of *cis*-Ir(ppy)$_2$(L)(L′); the properties may also be tunable by modifying the ppy ligand and by varying ancillary ligands. The *trans*-M(ppy)$_2$ moiety is only observed in four-coordinate Pt(ppy)$_2$[5,6] and Pd(ppy)$_2$,[6] which also emit strongly in the visible region.

We now report the synthesis of new complexes [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**) with the two nitrogen atoms *cis* to each other and [*cis*-Ir(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$ (**2**) and their emission characteristics.



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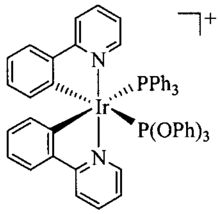

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Results and Discussion

Synthesis

Complex **1**, [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$(OTf), is synthesized in high yield following the procedure depicted in Equation (1) where the ppy ligands are added to the metal one by one. Complex **3** was chosen as the starting material because of its unique reactivity that results from the four equatorial ligands (H)$_2$(MeCN)$_2$. These equatorial ligands can be readily replaced by two anionic hydrocarbyls and two other neutral ligands.[7] The mono-ppy complex [Ir(ppy)(H)(NCMe)(PPh$_3$)$_2$]$^+$ (**4**) has to be isolated in good purity for the next step (**4**→**5**) to obtain **1** in high purity and yield. An analogous mono-ppy complex [Ir(ppy)(H)(OCMe$_2$)(PPh$_3$)$_2$]$^+$ was previously prepared.[8] The two ligands (H)(MeCN) of **3** are readily replaced with one ppy ligand to give complex **4** by facile dissociation of the MeCN ligand along with H$_2$ evolution. Complex **4**, however, does not react further with ppyH in refluxing toluene. The reaction mixture of **4** and ppyH in C$_3$H$_7$OC$_2$H$_4$OH (b.p. 150 °C) heated at reflux affords **1** with unknown materials, whereas the reaction in refluxing C$_2$H$_5$OC$_2$H$_4$OH (b.p. 133 °C) gives a stable complex [*trans*-Ir(ppy)(ppyH)(H)(PPh$_3$)$_2$]$^+$ (**6**) [Equation (2)] which does not undergo further reaction. Replacement of the labile MeCN ligand by ppyH was also

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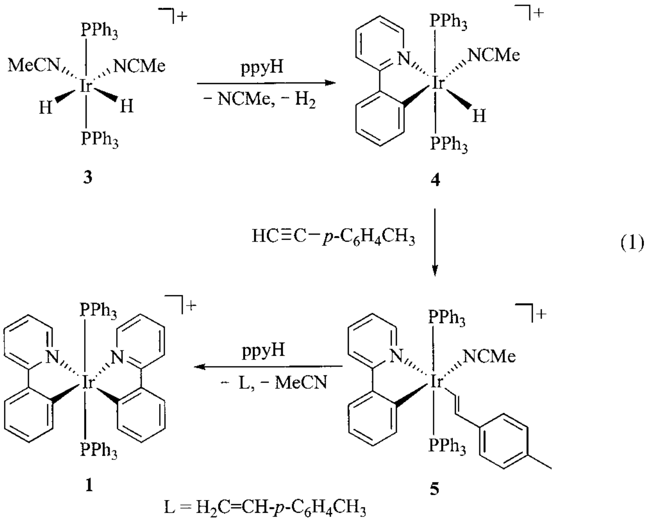
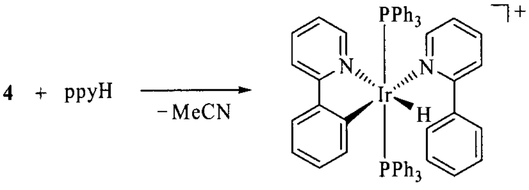
observed in the reaction of $[Ir^I(NCMe)(CO)(PPh_3)_2]^+$ at 25 °C to give $[Ir^I(CO)(ppyH)(PPh_3)_2]^+$ which undergoes oxidative addition of ppyH to produce $[Ir(ppy)(H)(CO)(PPh_3)_2]^+$ at the elevated temperature.[9] Insertion of a bulky alkyne into the Ir–H bond of **4** makes abstraction of the bulky alkenyl ligand, –CH=CH–*p*-$C_6H_4CH_3$, of **5** facile to give **1**. Alkyne insertion into the Ir–H bond of **6** has not been observed yet. Formation of stable hydrocarbon CH_2=CH–*p*-$C_6H_4CH_3$ may facilitate the production of **1** from **5**. Attempts to replace one PPh_3 of **1** with $P(OPh)_3$ to prepare [*trans*-Ir(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$ have been unsuccessful thus far.



(1)



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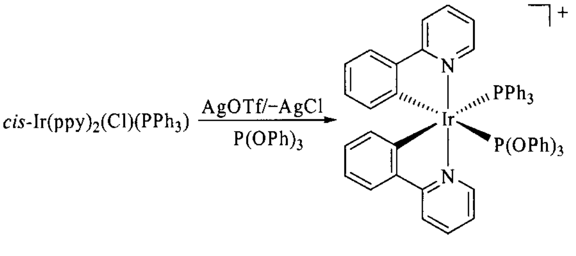
(2)

Complex **2**, [*cis*-Ir(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$(OTf), has been synthesized [Equation (3)] in order to compare its properties with those of **1**. Attempts to prepare [*cis*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ have been unsuccessful, probably because PPh_3 is too large for the *cis*-Ir(ppy)$_2$ moiety to have two PPh_3 in the *cis* position[10] (see below for the crystal structure of **2**). Although monophosphorus ligand complexes such as *cis*-Ir(ppy)$_2$(PR$_3$)(X) (X = Cl, CN; R = Ph, *n*Bu, OPh)[3c] have been previously prepared, no report of a bis(phosphorus base ligand) complex such as [*cis*-Ir(ppy)$_2$(PR$_3$){P(OPh)$_3$}]$^+$ (**2**) has been made.

Complexes **1**F$_2$, **1**F$_2$Me, **2**F$_2$, and **2**F$_2$Me have also been prepared by the same procedures shown in Equations (1) and (3) to investigate the effects that modification of the ppy ligand would have on the emission characteristics of complexes **1** and **2**.



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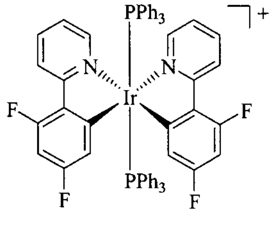
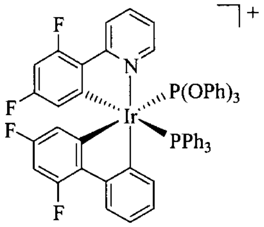
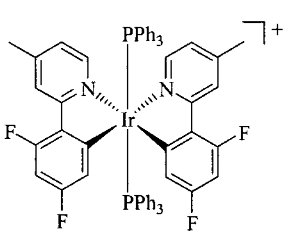
(3)



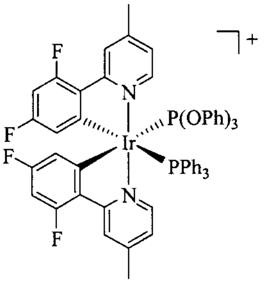
1F$_2$



2F$_2$



1F$_2$Me



2F$_2$Me

Newly prepared complexes **1**, **1**F$_2$, **1**F$_2$Me, **2**, **2**F$_2$, **2**F$_2$Me, **4**, **5**, and **6** have been unambiguously characterized by detailed spectral (^{1}H-, ^{13}C-, ^{31}P NMR, IR, TOF mass) and elemental analysis data and also crystal X-ray diffraction data analysis for **1** and **2**. Assignment of the spectral signals is mostly straightforward (see Supporting Information for spectra and detailed assignments).

Crystal Structures

Figures 1 and 2 show the two nitrogen atoms that are *cis* to each other in *trans*-isomer **1** but *trans* to each other in *cis*-isomer **2**. Figure 2 shows the two ppy groups being pushed away from the two phosphorus ligands, which results in a notable difference between the two Ir–N distances (2.089 and 2.042 Å) and the N–Ir–N bond angle (164°), which is far smaller than 180°. It seems less likely for *cis*-bis(ppy) complex **2** to maintain two bulky PPh_3 groups in the *cis* position without severe steric hindrance. Density function theory calculations suggest that the HOMO of Ir(ppy)$_3$,[1c,11] Ir(ppy)$_2$L$_2$,[1f,11] and Pt(ppy)L$_2$[12] involve dπ-orbitals of the metal and whose energy level is closely related to the bond lengths between the metal and the ligands. Both Ir–N and Ir–C distances for **1** are very close to those of *fac*-Ir(ppy)$_3$ and *fac*-Ir(tpy)$_3$ (see Table 1) where all N atoms are *trans* to the C atoms. The Ir–N distances are longer in *trans* complex **1** than those in *cis* complexes **2** and *cis*-Ir(tpy)$_2$(P–P) (Table 1). The Ir–P [phosphite, P(OPh)$_3$] distances are shorter than those in Ir–P [phosphane, PPh$_3$, (PPh$_2$CH$_2$)$_2$BPh$_2$] (see Table 1).

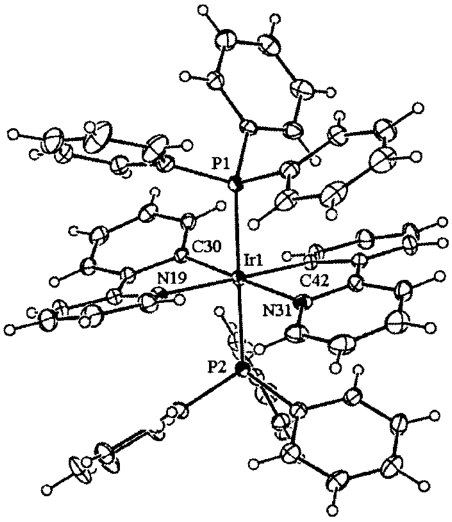


Figure 1. ORTEP drawing of [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å]: Ir1–C42 = 2.050(5); Ir1–C30 = 2.052(5); Ir1–N31 = 2.160(4); Ir1–N19 = 2.168(4); Ir1–P2 = 2.3802(12); Ir1–P1 = 2.3891(12). Selected bond angles [°]: C30–Ir–N31 = 178.99(16); C42–Ir–N19 = 178.81(17); P1–Ir–P2 = 179.19(4).

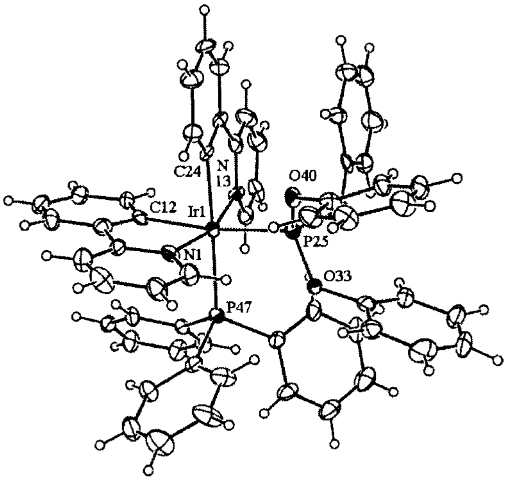


Figure 2. ORTEP drawing of [*cis*-Ir(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å]: Ir–N1 = 2.089(11); Ir–N13 = 2.042(11); Ir–C12 = 2.072(13); Ir–C24 = 2.071(12); Ir–P25 = 2.307(3); Ir–P47 = 2.433(3). Selected bond angle [°]: N1–Ir–N13 = 164.3(4); C12–Ir–P25 = 169.3(4); C24–Ir–P47 = 177.0(4).

Emission Spectral Data

Both *trans*- and *cis*- complexes (**1** and **2**, respectively) display relatively strong emission in the green–blue color region (see $\lambda_{\max}$ in Table 2). *trans*-Bis(PPh$_3$) complex **1** shows the $\lambda_{\max}$ emission at a somewhat longer wavelength than that of *cis*-(PPh$_3$)[P(OPh)$_3$] complex **2**. This small difference in $\lambda_{\max}$ may be due to the P(OPh)$_3$ in **2** since *cis*-Ir(ppy)$_2$-X(PPh$_3$) complexes show their emission at longer wavelengths than do *cis*-Ir(ppy)$_2$X[P(OPh)$_3$] complexes.[3c]

Table 2. Photoluminescence spectroscopic data in degassed MeCN at 25 °C for [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**), [*trans*-Ir(F$_2$ppy)$_2$-(PPh$_3$)$_2$]$^+$ (**1**F$_2$), [*trans*-Ir(F$_2$Meppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**F$_2$Me), [*cis*-Ir-(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$ (**2**), [*cis*-Ir(F$_2$ppy)$_2$(PPh$_3$)$_2$]$^+$ (**2**F$_2$) and [*cis*-Ir(F$_2$Meppy)$_2$ (PPh$_3$)$_2$]$^+$ (**2**F$_2$Me). [Ir] = $1\cdot10^{-5}$ M.

Complex	$\lambda_{\max}$ [nm]	Φ_{PL}	τ [μs]
1	470, 497	0.24	4.4
1F$_2$	452, 479	0.36	4.8
1F$_2$Me	450, 475	0.37	3.5
2	458, 488	0.18	0.31
2F$_2$	444, 473	0.91	2.8
2F$_2$Me	442, 470	0.72	2.9

It is well-established that $\lambda_{\max}$ emission bands for *cis*-Ir(ppy)$_2$(L)(L′) are shifted to shorter wavelengths when the ppy ligand is F-substituted on the phenyl ring and Me-substituted on the pyridyl ring.[1c,g,3b,4] It is noticed that the blueshifts, which result from the exchange of a ppy ligand to either a F$_2$ppy or F$_2$Meppy ligand, are greater for the *trans* complexes (**1**, **1**F$_2$, **1**F$_2$Me) than they are for the *cis* complexes (**2**, **2**F$_2$, **2**F$_2$Me) (see Table 2). It is also noticed that quantum yields are significantly larger for F$_2$ppy (**1**F$_2$) and F$_2$Meppy (**1**F$_2$Me) complexes than for ppy (**1**) complexes. A striking increase in Φ_{PL} is observed when the ppy ligand of **2** is replaced with either a F$_2$ppy or F$_2$Meppy ligand (Table 2).

In conclusion, a new type of iridium(III) complex [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**) has been prepared by a novel synthetic method and its structural and photoluminescent characteristics have been compared with those of the *cis* analogue, [*cis*-Ir(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$ (**2**), which has also been newly prepared in this study. No significant differences have been found for their photoluminescent properties because of the geometric differences between *trans*-**1** and *cis*-**2**. Sky

Table 1. Structural and Photoemission data for [*trans*-Ir(ppy)$_2$(PPh$_3$)$_2$]$^+$ (**1**), [*cis*-Ir(ppy)$_2$(PPh$_3$){P(OPh)$_3$}]$^+$ (**2**) and related complexes.

Complex	Ir–C [Å]	Ir–N [Å]	Ir–P [Å]	$\lambda_{\max}$ [nm]
[*trans*-(ppy)$_2$Ir(PPh$_3$)$_2$]$^+$ (**1**)	2.050, 2.052	2,160, 2.168	2.380, 2.389	470, 497
[*cis*-(ppy)$_2$Ir(PPh$_3$){P(OPh)$_3$}]$^+$ (**2**)	2.072, 2.071	2.089, 2.042	2.307, 2.433	458, 488
fac-Ir(ppy)$_3$[1d]	2.035	2.167		545
fac-Ir(tpy)$_3$[a],[1c]	2.024	2.132		510
mer-Ir(tpy)$_3$[a],[1c]	2.076, 2.086, 2.020[c]	2.151,[d] 2.044, 2.065		512
cis-(tpy)$_2$Ir(P–P)[a,b],[1f]	2.047, 2.057	2.082, 2.083	2.420, 2.431	468

[a] tpy = 2-(*p*-tolyl)pyridinato. [b] P–P = (PPh$_2$CH$_2$)$_2$BPh$_2$. [c] *trans* to N. [d] *trans* to C.

blue color emission can be obtained by replacing the ppy ligands of **1** or **2**, which produce greenish–blue light, with either F_2ppy or F_2Meppy ligands. New synthetic methods are currently under investigation to replace the PPh_3 axial ligand of **1** with a variety of ligands to prepare [*trans*-Ir(ppy)$_2$(L)(L$'$)]$^{+,0}$ (L, L$'$ = neutral or anionic C, N, P, O-base) which would show diverse luminescent characteristics. Finally, we wish this study to open a new research field that deals with light emitting iridium complexes containing two ppy ligands and related cyclometalated ligands *trans* to each other.

Supporting Information (see footnote on the first page of this article): ^{1}H-, ^{13}C-, ^{31}P NMR spectra for **1**–**6**. Experimental details with ^{1}H-, ^{13}C-, ^{31}P NMR, FTIR, TOF-Mass spectral and EA data. PL decay diagrams. CCDC-617305 (**1**) and -617304 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[1] a) N. Herron, N. S. Radu, E. M. Smith, Y. Wang, *US Patent* **2005**/0048312 A1; b) S. Lamansky, M. E. Thompson, V. Adamovich, P. I. Djurovich, C. Adachi, M. A. Baldo, S. R. Forrest, R. Kwong, *US Patent* **2002**/0182441 A1; c) A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377–7387; d) J. Breu, P. Stössel, S. Schrader, A. Starukhin, W. J. Finkenzeller, H. Yersin, *Chem. Mater.* **2005**, *17*, 1745–1752; e) M. K. Nazeeruddin, R. Humphrey-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, *J. Am. Chem. Soc.* **2003**, *125*, 8790–8797; f) J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 1713–1727.

[2] K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1985**, *107*, 1431–1432.

[3] a) W. J. Finkenzeller, P. Stößel, H. Yersin, *Chem. Phys. Lett.* **2004**, *397*, 289–295; b) C. Adachi, R. C. Kwong, P. I. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 2082–2084; c) C.-L. Lee, R. R. Das, J.-J. Kim, *Curr. Appl. Phys.* **2005**, *5*, 309–313; d) Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, F. Li, T. Yi, C. Haung, *Inorg. Chem.* **2006**, *45*, 6152–6160.

[4] a) C.-H. Yang, K.-H. Fang, C.-H. Chen, I.-W. Sun, *Chem. Commun.* **2004**, 2232–2233; b) R. Ragni, E. A. Plummer, K. Brunner, J. W. Hofstraat, F. Babudri, G. M. Farinola, F. Naso, L. De Cola, *J. Mater. Chem.* **2006**, *16*, 1161–1170; c) T. Tsuzuki, N. Shirasawa, T. Suzuki, S. Tokito, *Adv. Mater.* **2003**, *15*, 1455–1458.

[5] a) L. Chassot, E. Müller, A. von Zelewsky, *Inorg. Chem.* **1984**, *23*, 4249–4253; b) M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet, A. von Zelewsky, *Chem. Phys. Lett.* **1985**, *122*, 375–379; c) L. Chassot, A. von Zelewsky, *Inorg. Chem.* **1987**, *26*, 2814–2818.

[6] P. Jolliet, M. Gianini, A. von Zelewsky, G. Bernadinelli, H. Stoeckli-Evans, *Inorg. Chem.* **1996**, *35*, 4883–4888.

[7] a) C. S. Chin, H. Lee, S. Noh, H. Park, M. Kim, *Organometallics* **2003**, *22*, 2119–2123; b) C. S. Chin, M. Kim, H. Lee, S. Noh, K. M. Ok, *Organometallics* **2002**, *21*, 4785–4793.

[8] X. Li, T. Vogel, C. D. Incarvito, R. H. Crabtree, *Organometallics* **2005**, *24*, 62–76.

[9] F. Neve, M. Ghedini, G. De Munno, A. Crispini, *Organometallics* **1991**, *10*, 1143–1148.

[10] [*cis*-Ir(ppy)$_2$(PPh$_2$Me)$_2$]$^+$ will be reported elsewhere.

[11] P. J. Hay, *J. Phys. Chem. A* **2002**, *106*, 1634–1641.

[12] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovivh, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055–3066.

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