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Mahboobeh Zanganeh, S. Jafar Hoseini, Mehdi Rashidi, S. Masoud Nabavizadeh, Mohammad Reza Halvagar



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Reaction of allyl bromide with cyclometallated platinum(II) complexes: Unusual kinetic behavior and a novel case of methyl and allyl C-C bond reductive elimination

Mahboobeh Zanganeh,^a S. Jafar Hoseini,^{*,a} Mehdi Rashidi,^{*,b} S. Masoud Nabavizadeh,^b
 Mohammad Reza Halvagar^c

^a Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj 7591874831, Iran

^b Department of Chemistry, Faculty of Sciences, Shiraz University, Shiraz 7146413565, Iran

^c Department of Inorganic Chemistry, Chemistry and Chemical Engineering Research Center of Iran, Tehran, PO Box 14335-186, Iran

ABSTRACT

Reaction of the known cyclometallated platinum(II) complexes [PtMe(C[^]N)(PPh₂Me)], in which C[^]N is either 2-phenylpyridinate (abbreviated as ppy-H), **1a**, or benzo-h-quinolate (abbreviated as bhq-H), **1b**, with excess allyl bromide, CH₂=CH-CH₂Br, in acetone gave the thermodynamic Pt(IV) product complex *cis*-[PtMe(CH₂-CH=CH₂)Br(ppy-H)(PPh₂Me)], **2a**, or *cis*-[PtMe(CH₂-CH=CH₂)Br(bhq-H)(PPh₂Me)], **2b**, respectively, in which the phosphine and the allyl ligands are situated *trans* to each other. Although these Pt(IV) complexes may possibly take up other isomeric forms such as one in that allyl ligand being situated *trans* to N atom or one that allyl ligand is located *trans* to Br atom, our full characterization of the complexes using ¹H, ¹³C and ³¹P NMR spectroscopy, completely ruled out the latter possibilities. Our attempt to grow crystals of the Pt(IV) complex **2a** was ended up to give crystals of the Pt(II) complex [PtBr(ppy-H)(PPh₂Me)], **3a**, resulting from reductive elimination of Me and allyl from **2a**. Also the solution of the Pt(IV) bhq-H analogous complex **2b** in acetone at 60 °C gradually gave the Pt(II) complex [PtBr(bhq-

*Corresponding authors: (S. J. Hoseini) E mail: jhoseini@yu.ac.ir, sjhoseini54@yahoo.com, Tel: +98 74 33223048, fax: +98 74 33342172. Tragically, the second corresponding author, Professor Mehdi Rashidi, has passed away, while preparing this paper and we all miss him.

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