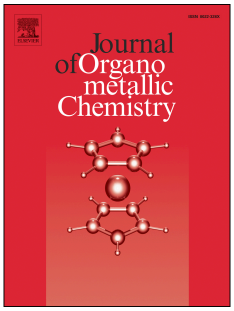

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PII: S0022-328X(17)30701-5

DOI: 10.1016/j.jorganchem.2017.12.016

Reference: JOM 20211

To appear in: *Journal of Organometallic Chemistry*

Received Date: 7 July 2017

Revised Date: 7 December 2017

Accepted Date: 12 December 2017

Please cite this article as: M. Zanganeh, S.J. Hoseini, M. Rashidi, S.M. Nabavizadeh, M.R. Halvagar, 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, *Journal of Organometallic Chemistry* (2018), doi: 10.1016/j.jorganchem.2017.12.016.

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

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ABSTRACT

Reaction of the known cyclometallated platinum(II) complexes [PtMe(C^N)(PPh_2Me)], 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, CH_2=CH-CH_2Br, in acetone gave the thermodynamic Pt(IV) product complex *cis*-[PtMe(CH_2-CH=CH_2)Br(ppy-H)(PPh_2Me)], **2a**, or *cis*-[PtMe(CH_2-CH=CH_2)Br(bhq-H)(PPh_2Me)], **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 ^{1}H, ^{13}C and ^{31}P 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)(PPh_2Me)], **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 ºC gradually gave the Pt(II) complex [PtBr(bhq-

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[*] Corresponding authors: (S. J. Hoseini) E mail: jhosseini@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.