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| Title: | Hg(ii) and Pd(ii) complexes with a new selenoether bridged biscarbene ligand: efficient mono- and bis-arylation of methyl acrylate with a pincer biscarbene Pd(ii) precatalyst† |
| Authors: | Rishu (/jspui/browse?type=author&value=Rishu) Prashanth, B. (/jspui/browse?type=author&value=Prashanth%2C+B.) Bawari, D. (/jspui/browse?type=author&value=Bawari%2C+D.) Verma, Aditya (/jspui/browse?type=author&value=Verma%2C+Aditya) Choudhury, A.R. (/jspui/browse?type=author&value=Choudhury%2C+A.R.) Singh, Sanjay (/jspui/browse?type=author&value=Singh%2C+Sanjay) |
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| Abstract: | Two equivalents of 1-benzyl-3-bromoethylbenzimidazolium bromide couple with Na ₂ Se to produce the first selenoether bridged bis-benzimidazolium salt (LH ₂)Br ₂ . The nitrate (LH ₂)(NO ₃) ₂ and tetrafluoroborate (LH ₂)(BF ₄) ₂ salts were also synthesized from (LH ₂)Br ₂ . The reaction of Hg(OAc) ₂ with (LH ₂)Br ₂ gave the first pseudo pincer carbene mercury complex, [Hg(L-κ ² C)] [HgBr ₄] (C1). Different complexes of Pd(II) with selenoether bridged carbene were obtained using (LH ₂)Br ₂ and (LH ₂)(NO ₃) ₂ . Syntheses of these complexes were dependent on the counter anion and the temperature. Thus, the pincer type ionic complex [PdBr(L-κ ³ CSeC)]Br (C2) was isolated at 80 °C and the pseudo pincer type neutral complex cis-[PdBr ₂ (L-κ ² C)] (C3) was isolated at room temperature from (LH ₂)Br ₂ and Pd(OAc) ₂ in DMSO. The nitrate precursor (LH ₂)(NO ₃) ₂ on palladation with Pd(OAc) ₂ afforded [Pd(L-κ ⁴ CBzCSeC)]NO ₃ (C4) showing an unprecedented intramolecular metallation at the ortho position of the benzyl wingtip of the benzimidazole moiety. The ligand salts and metal complexes have been characterized using HRMS, heteronuclear NMR and IR spectroscopy. Single crystal X-ray structures of the ligand salts (LH ₂)Br ₂ and (LH ₂)(BF ₄) ₂ and complexes C1–C4 have also been elucidated. Complex C2 showed good activity for C–C coupling in the mono-Heck reaction of methyl acrylate and arylbromides. Interestingly, the less common bis-arylation was also observed with deactivated arylbromides as the result of double-Heck coupling. |
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