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Amine Boranes Dehydrogenation Mediated by an Unsymmetrical Iridium Pincer Hydride: (PCN) vs (PCP) Improved Catalytic Performance

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Abstract

© 2018 American Chemical Society. The IrIII hydride (tBuPCN)IrHCl (1) containing the tridendate unsymmetrical pincer ligand tBuPCN- {tBuPCN(H) = 1-[3-[(di-t-rt-butylphosphino)methyl]phenyl]-1H-pyrazole} has been exploited as ammonia borane (NH3BH3, AB) and amine boranes dehydrogenation catalyst in THF solution at ambient temperature. 1 releases one H2 equivalent per AB equivalent, with concomitant cyclic poly(aminoboranes) formation [B-(cyclotriborazanyl)-amine-borane (BCTB) and cyclotriborazane (CTB)] as the final "spent fuel". 1 has been found to have superior catalytic activity than its symmetrical analogue (tBuPCP)IrHCl, with recorded TOF values of 580 h-1 (AB in THF) and 401 h-1 (DMAB in toluene) at ambient temperature. The reaction has been analyzed experimentally through multinuclear [11B, 31P{1H}, 1H] NMR and IR spectroscopy, kinetic rate measurements, and kinetic isotope effect determination with deuterated AB isotopologues. The hydride/borohydride intermediate (tBuPCN)IrH(η2-BH4) (2) is the catalyst resting state formed during the dehydrogenation process; it is detected by a variableerature multinuclear NMR of the reaction course (in the 190-323 K range). A DFT modeling of the reaction mechanism using DMAB as substrate has been performed with the geometry optimization in toluene at the M06 level of theory. The combination of the kinetic and computational data reveals that a simultaneous B-H/N-H activation occurs in the presence of 1, after the preliminary amine borane coordination to the metal center.

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