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P-H/Ru-Cl migration by triphosphine pincer-ruthenium complexes

By: Mandal, Souvik; Malakar, Santanu; Emge, Thomas J.; Hughes, Russell Profit; Goldman, Alan Stuart

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Metal ligand cooperativity (MLC) has revealed a plethora of unusual reactivity in catalysis in the last couple of decades. Since Milstein's report of aromatization-dearomatization of the pincer backbone of pyridine-based-pincer complexes, ruthenium has played a particularly important role in the development of MLC. We have recently reported a (H-P_3)Ir complex which is the fastest known catalyst for alkane-transfer dehydrogenation. The active species results from P-to-Ir migration of H in this system. We further explored the possibility of MLC in an analogous Ru system. Surprisingly, when metalating the same H-P_3 ligand with a $RuCl_2$ precursor we only isolated a (Cl-P_3)Ru(H)Cl complex where H had migrated to Ru from P, and Cl to P from Ru ("P-H/M-X exchange"). We have demonstrated that the thermodynamically favored direction of such exchanges depends strongly on the ancillary ligands, with particular driving force for formation of 5-coordinate (pincer)MHCl complexes (M = d6 metal center). However, for 6-coordinate Ru complexes (H-pincer)MXYL, the electronic nature of L appears to determine if P-H/M-X exchange occurs. Strongly pi-accepting ligands promote P-X/M-H exchange with the reaction observed for L = CO, xylylisonitrile and NO^+, but not for L = N_2, CH_3CN, or PMe_3. While exchange at 5-coordinate (16e$^-$) Ru centers appears to proceed through initial P-to-Ru migration of X or H, to give a phosphide intermediate, in the case of 6-coordinate (18e$^-$) Ru centers exchange is believed to proceed through phosphoranyl intermediates. DFT and intrinsic bond orbital anal. has been used to better understand this reactivity.

Conference

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