Abstract:
Irradiation with light (UV and visible) increases the rate of the Heck reaction using homogeneous (palladium(II) acetate) and heterogeneous (Pd/Al2O3 and Pd/TiO2) catalysts. The rate of the coupling of bromobenzene, chlorobenzene, and 4-chloroacetophenone with styrene was increased under light irradiation at temperatures between 90 and 160 degrees C. Detailed investigations showed that light irradiation accelerates the reduction of the Pd(II) precursor, as confirmed by 31P NMR spectroscopy, in which the in situ reduction of [Pd(OAc)2(PPh3)2] to [Pd(PPh3)(n)] (n=2-4) in the presence of PPh3 took only minutes under visible light irradiation and several hours in the dark. The role of light is, however, complex since it also influences other Pd(II) reduction steps in conjunction with catalyst deactivation (Pd black formation).
31P NMR spectroscopy showed the same active species, anionic palladium halide complexes, in both irradiated and unirradiated reactions. UV/Vis absorption spectroscopy of Pd(OAc)2 and DFT calculations, theoretical UV/Vis spectra, and orbital calculations of [PdI4]2-, [PdBr4]2-, and [PdCl4]2-, showed that ligand-to-metal charge transfer (LMCT) is responsible for the accelerated reduction of Pd(0) to Pd(0) under light irradiation.
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