

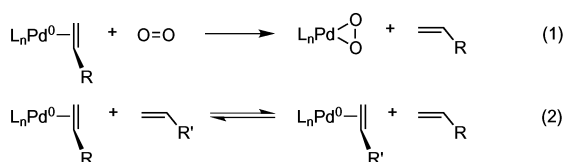
“Inverse-Electron-Demand” Ligand Substitution in Palladium(0)–Olefin Complexes

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Palladium(0) participates in numerous catalytic reactions, including carbon–carbon and carbon–heteroatom cross-coupling, alkyne reductive coupling, and carbonylation reactions.¹ Our interest in the reactivity of palladium(0) derives from its proposed role in dioxygen-coupled oxidation reactions.^{2,3} Mechanistic studies of the reaction between molecular oxygen and a palladium(0) species, (bc)-Pd(dba),^{3a} (bc = bathocuproine, i.e., 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; dba = dibenzylidene acetone) indicated that this reaction proceeds by an associative mechanism, resembling associative olefin substitution at palladium(0) (eqs 1 and 2).⁴ The comparison between these two related reactions belies the distinct electronic structures of the substrates: olefins have well-defined donor (filled π) and acceptor (empty π^*) orbitals, whereas dioxygen has two singly occupied π^* orbitals resulting in a triplet electronic ground-state. In this context, we have undertaken an investigation of olefin substitution reactions at bathocuproine–palladium(0) complexes, (bc)Pd(ns^X) (ns^X = *trans*- β -nitrostyrene derivative) to probe their mechanistic details. We describe here the initial results of this study that contradict the general model for ligand substitution reactions, specifically the description of the incoming ligand and the metal as nucleophilic and electrophilic reaction partners, respectively. The associative substitution reactions described below proceed by an “inverse-electron-demand” pathway involving nucleophilic attack of the metal on the external ligand. The principles revealed in this study should apply to numerous other electron-rich transition-metal systems, which are finding growing application in homogeneous catalysis.



Previous studies of zerovalent, group 10 transition metals have revealed a relatively flat energy landscape for two-, three-, and four-coordinate complexes.⁵ Consequently, both associative and dissociative ligand substitution mechanisms have been characterized. To permit a direct comparison between oxygenation and olefin substitution, a systematic series of palladium(0)–olefin complexes was prepared by addition of 1.2 equiv of a para-substituted *trans*- β -nitrostyrene derivative (ns^X), $\text{XC}_6\text{H}_4\text{CH}=\text{CHNO}_2$ ($X = \text{CH}_3\text{O}$, CH_3 , H , Br , CF_3), to (bc)Pd(dba) in dichloromethane. Single crystals suitable for X-ray diffraction were obtained for several of the analogues ($X = \text{H}$, Br , CH_3), and the molecular geometry exhibits the trigonal planar structure expected for palladium(0)–olefin complexes (Figure 1).

In solution at room temperature, the (bc)Pd(ns^X) complexes are nonfluxional on the NMR time scale; however, upon addition of a nitrostyrene derivative to this solution, rapid exchange takes place

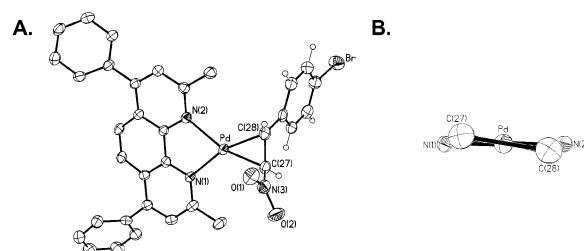


Figure 1. (A) ORTEP drawing of the *p*-bromo- β -nitrostyrene adduct of palladium(0). (B) Frontal view reflecting the nearly planar palladium(0) coordination environment. Thermal ellipsoids are shown at the 30% probability level.

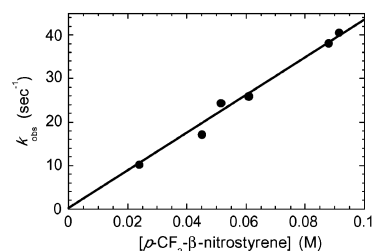
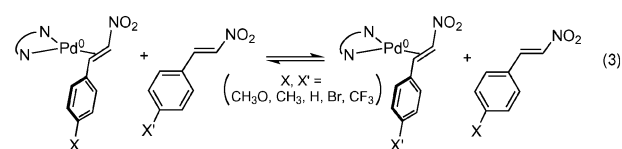


Figure 2. Olefin concentration dependence of the intermolecular exchange rate between (bc)Pd(ns^{CF_3}) and ns^{CF_3} based on ¹H NMR line-broadening kinetics. Reaction conditions: [Pd] = 10 mM, [ns^{CF_3}] = 24–91 mM, CD_2Cl_2 , 286 K.

to achieve an equilibrium mixture of the palladium(0)–olefin complexes (eq 3). Temperature-dependent equilibrium constants



were obtained for individual pairs of olefins. The relative binding constants for the entire series of olefins yields a linear Hammett correlation with a positive slope ($\rho = 3.9$), that is, derivatives with more electron-withdrawing substituents exhibit greater stability.⁶

The self-exchange reactions between (bc)Pd(ns^X) and the corresponding ns^X derivative are amenable to study by dynamic NMR spectroscopy. Line-widths of ¹H NMR resonances of the bound olefin were monitored as a function of temperature ($ns^{\text{CF}_3, \text{OCH}_3, \text{CH}_3}$) and the concentration of added olefin (ns^{CF_3}). Eyring plots derived from the temperature-dependence data reveal similar activation parameters for each of the three olefins: $\Delta H^\ddagger = 7.3$, 8.2, 7.2 kcal/mol and $\Delta S^\ddagger = -21$, -20 , and -24 eu for ns^{CF_3} , ns^{OCH_3} , and ns^{CH_3} , respectively. The [olefin]-dependence study with ns^{CF_3} (Figure 2) revealed a first-order fit that intersects the y-axis at the origin. Together, these data support an associative ligand substitution pathway with essentially no contribution from a parallel dissociative pathway.

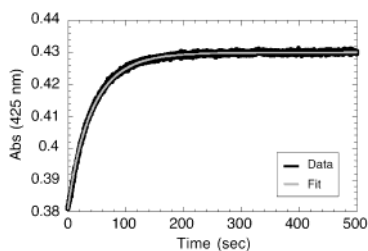


Figure 3. Approach-to-equilibrium absorbance data for the intermolecular exchange between (bc)Pd(ns^{CH_3}) and ns^H . Reaction conditions: [(bc)Pd(ns^{CH_3})] = 100 μ mol, [ns^H] = 140 μ mol, 2.5 mL CH_2Cl_2 , 300 K.

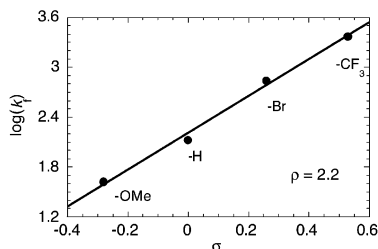


Figure 4. Hammett plot reflecting electronic effects on ligand substitution of ns^{CH_3} from (bc)Pd(ns^{CH_3}) by p -substituted nitrostyrene derivatives.

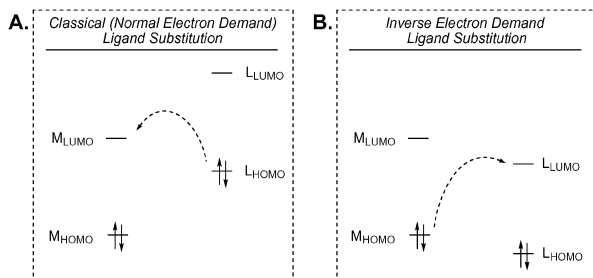


Figure 5. Qualitative molecular orbital representations of normal- and inverse electron demand "associative" ligand substitution reactions.

The nondegenerate exchange between (bc)Pd(ns^X) and different olefins, $ns^{X'}$, for which $X \neq X'$, is too rapid to monitor by NMR methods. Instead, the reaction between (bc)Pd(ns^{CH_3}) and four different para-substituted nitrostyrene derivatives was studied by UV–visible spectroscopy. Kinetics data for these bimolecular exchange reactions (e.g., Figure 3) were analyzed by numerical integration to obtain forward and backward rate constants. The Hammett analysis (Figure 4) of the forward rate constants reveals that exchange rates are faster with more electron-withdrawing substituents on the incoming olefin, namely *less nucleophilic substrates react more readily in the associative ligand substitution reaction*. This observation implicates an "inverse-electron-demand" ligand substitution pathway in which the primary electronic interaction in the transition state occurs between a filled palladium orbital donating into the empty olefin π^* orbital (Figure 5).⁷ Such orbital energetics are favored by the use of palladium(0), which has fully occupied 4d orbitals, together with an electron-deficient olefin bearing a low-lying LUMO. This transition-state argument is linked to thermodynamic considerations via the Hammond postulate, namely ligands with enhanced π -acidity might be expected to stabilize a high-energy tetrahedral intermediate and thereby promote the substitution reaction.

π -Acceptor contributions to ligand substitution reactions, for example, in the trans-effect, have been recognized since the early seminal studies of ligand substitution at platinum(II).^{8,9} However,

the results described here appear to be the first demonstration of an inverted electronic dependence in ligand substitution.^{10,11} Mechanistically, this reactivity is closely related to oxidative addition reactions that proceed by nucleophilic attack of the metal on the substrate, as in the addition of methyl iodide to iridium(I) in Vaska's complex.¹² We have initiated computational studies to probe details of the orbital interactions in these reactions, in particular to compare the reactivity between olefins and dioxygen with palladium(0). The data described herein, in addition to their fundamental value, have implications for the design and development of electron-rich transition-metal catalysts, which find widespread application in catalytic transformations.

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Supporting Information Available: Synthesis and characterization details (including crystallographic data) for (bc)Pd(ns^X) derivatives and description of kinetics experiments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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