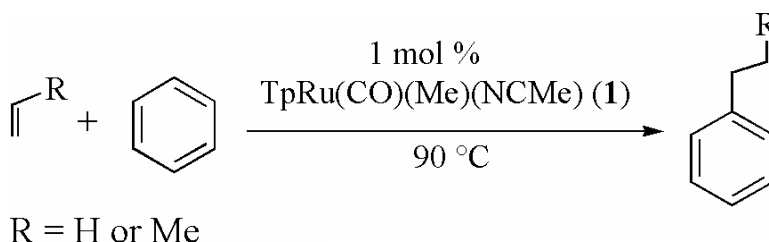


Addition of Arenes to Ethylene and Propene Catalyzed by Ruthenium

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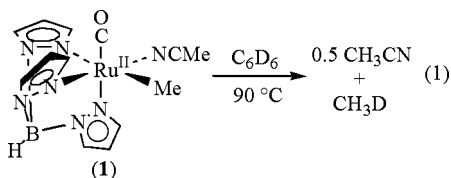
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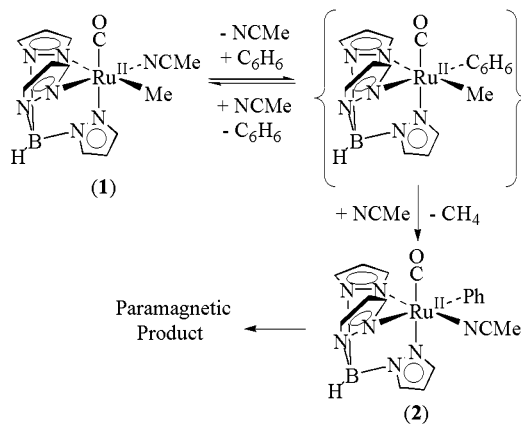
Due to the potential synthetic utility of hydrocarbon functionalization reactions, transition-metal-mediated C–H activation sequences have attracted considerable attention.^{1,2} Although many transition metal complexes that initiate C–H oxidative addition have been reported,^{3–5} efficient chemical synthesis via *catalytic* C–H bond activation and subsequent C–C bond formation remains a challenging goal.^{6–8} Significant recent advancements in the arena of catalytic C–H activation have been reported for aromatic systems;⁹ however, such reactions are primarily limited to aromatic systems with heteroatomic functionality. For example, ruthenium- or rhodium-catalyzed C–H activations of aromatic ketones and subsequent C–C bond formation with alkenes or alkynes have been reported.^{10–15} Low-valent ruthenium systems have been demonstrated to catalyze carbonylation reactions of pyridylbenzenes and other heteroaromatics.^{16–18} Analogous transformations of nonfunctionalized aromatics are more difficult to achieve. Rhodium, palladium, and ruthenium catalysts that convert aromatics and olefins to styrenes in the presence of a sacrificial hydrogen reservoir or via oxidative coupling have been reported.^{19–23} Pd or Pt systems can catalyze electrophilic metalation of aromatic C–H bonds followed by C–C coupling with alkynes.²⁴ Another strategy for aromatic C–H functionalization involves the formation of B–C coupled products.^{25–28} Most germane here are recent reports of Ir-catalyzed olefin arylation reactions that occur at 180 °C.^{29,30}

Heating a benzene solution (90 °C) of TpRu(CO)(Me)(NCMe) (1) (Tp = hydridotris(pyrazolyl)borate) results in the conversion of the TpRu system to NMR-silent ruthenium products, and Evans NMR experiments reveal that the reaction product is paramagnetic. Although the identity of the product has not been determined, performing the reaction in C₆D₆ indicates that the transformation involves benzene C–H activation and methane elimination. The ¹H NMR spectrum of the reaction in C₆D₆ reveals an upfield 1:1:1 triplet (2 Hz) at 0.16 ppm due to the formation of CH₃D (eq 1).

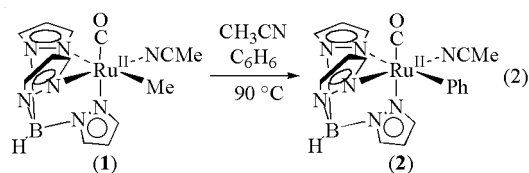


There is no evidence of deuterium incorporation into the methyl, Tp, or NCMe ligands of complex 1. Thus, the arene C–H activation is apparently irreversible under the reaction conditions. Free acetonitrile is observed in the final reaction solution. A plausible reaction pathway involves initial CH₃CN/C₆H₆ ligand exchange followed by C–H activation and methane elimination (Scheme 1). Consistent with this notion, the addition of 10 equiv of acetonitrile suppresses the rate of disappearance of complex 1 in C₆D₆ at 90 °C (*t*_{1/2} ≈ 80 min versus *t*_{1/2} ≈ 15 min in the absence of added acetonitrile). The closely related Ru(II) complex TpRu(PPh₃)(NCMe)(H) has recently been reported to activate C–H bonds,³¹ and a ruthenium–neopentyl complex has been reported to undergo

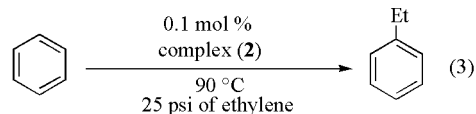
Scheme 1. Plausible Reaction Pathway for the Conversion of Complex 1 and Benzene to Methane and Paramagnetic Product



aromatic C–H activation reactions.³² The reaction of complex 1 in a 1.4:1.0 molar mixture of benzene and acetonitrile at 90 °C allows isolation of TpRu(CO)(NCMe)(Ph) (2) (eq 2). Complex 2 has been characterized by ¹H and ¹³C NMR and IR spectroscopy as well as elemental analysis.

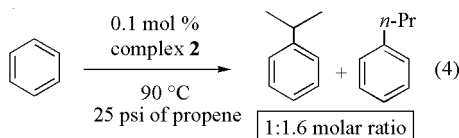


Under a dinitrogen atmosphere, the combination of 0.1 mol % TpRu^{II}(CO)(NCMe)(Ph) (2) in dry benzene under 25 psi of ethylene at 90 °C results in the formation of ethylbenzene (eq 3). In addition



to the formation of ethylbenzene, small amounts of 1,3- and 1,4-diethylbenzene are produced. After 4 h of reaction, approximately 51 catalytic turnovers are observed per mole of catalyst, with TOF = 3.5 × 10⁻³ mol⁻¹ s⁻¹. Catalyst decomposition after 4 h is evident by a decrease in reaction turnover. Approximately one turnover of 1,3-diethylbenzene production is observed, and a negligible amount of 1,4-diethylbenzene is produced. No evidence of 1,2-diethylbenzene or higher alkyl substitution (e.g., trisubstituted benzenes) has been found. Setting up the reaction in air using benzene that has not been predried results in approximately 23 catalytic turnovers after 4 h. Placing the benzene/catalyst solution under 25 psi of propene results in the addition of benzene to propene within 30 min at 90 °C. Analysis by gas chromatography reveals a 1.6:1.0 ratio of *n*-propyl to isopropylbenzene, with 14 catalytic

turnovers after 19 h. Thus, the catalyst system is mildly selective for the linear alkylbenzene (eq 4). Similar catalytic reactions are



observed when complex **1** is used as the catalyst precursor (see Supporting Information); however, the rate is faster for complex **2** versus using **1** as the catalyst precursor. Formation of the paramagnetic complex that results from the reaction of **1** with benzene (see above and Scheme 1) is not observed for catalysis with **2**, and it is unlikely that the paramagnetic complex is the catalyst.

Lewis acid catalysts are known to initiate olefin arylation reactions including the coupling of benzenes with ethylene (Friedel–Crafts reactions).^{33,34} However, the ruthenium-catalyzed reactions reported herein exhibit characteristics that are inconsistent with a Friedel–Crafts mechanism and that are consistent with a metal-mediated C–H activation pathway. Friedel–Crafts reactions typically produce 1,2-dialkyl products in addition to 1,3- and 1,4-dialkylbenzenes. Presumably, the lack of formation of 1,2-diethylbenzene with **1** or **2** is due to steric selectivity in the C–H activation step, similar to that directly observed in stoichiometric aromatic C–H oxidative addition reactions.³⁵ Heating (90 °C) a 1:1 molar mixture of 1,4-diethylbenzene and benzene in the presence of **1** does not result in the formation of ethylbenzene (after 24 h) as is observed for Friedel–Crafts catalysts. *In contrast to catalysis with 1 or 2, Lewis acid activation of propene in the presence of arenes yields the production of branched alkyl products exclusively.* Finally, attempted catalysis using Ru^{III}Cl₃·trihydrate or TpRu^{II}(CO)₂(Me) fails to produce ethylbenzene. If the reactions were Lewis acid catalyzed, it might be anticipated that similar (or enhanced) reactivity would be observed for the Ru(III) chloride system. The lack of activity for TpRu^{II}(CO)₂(Me) (the immediate precursor to complex **1**) indicates that minor amounts of impurities from commercial starting reagents are not responsible for the catalysis.

Taken together, our studies indicate that TpRu(CO)(Me)(NCMe) (**1**) reacts with arenes to initiate C–H activation and loss of methane via initial arene/acetonitrile ligand exchange (Scheme 1). This reaction produces the active catalyst TpRu(CO)(NCMe)(Ph) (**2**), and a plausible catalytic cycle involves olefin/acetonitrile ligand exchange followed by olefin insertion into the Ru–aryl bond, which provides a pathway for C–C bond formation. Subsequent C–H activation of another equivalent of arene allows elimination of alkylbenzene and re-formation of the catalyst. Although we have not yet definitively established the mode of C–H activation, an electrophilic reaction similar to that reported by Milstein et al. seems likely.²¹ Electrophilic attack of Ru on an arene could lead to a σ -metathesis type transition state. Closely related Cp*Ir^{III}(PMe₃)-(R) systems have been suggested to activate CH bonds via oxidative addition, and a similar mechanism cannot be definitively eliminated from consideration.³⁶ In addition, a bis-acac Ir(III) complex has recently been proposed to be the active species of an Ir system that catalyzes the addition of arenes across C=C bonds,^{29,30,37} and the comparable selectivities of this Ir catalyst and the Ru systems reported herein imply potential mechanistic similarities. Periana et

al. have suggested a catalytic cycle that involves olefin binding to an Ir(III)–aryl complex, followed by insertion and reaction with another equivalent of arene.³⁷ We are presently working to further discern mechanistic details, explore the scope of the reaction, and improve catalyst activity and selectivity.

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Supporting Information Available: Details of experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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