Selective hydrocarbon activation and functionalization has long been identified as a major challenge to synthetic chemists. The search for practical methods in this regard has thus far led to extensive investigation in systems predominantly focused on second- and third-row transition metals. The preference for the heavier metals instead of their corresponding first-row congeners is due likely to comparatively stronger M–H and M–C bond strengths for the former. Notably, while detailed examinations on Pt(II)- and Pd(II)-mediated C–H activation processes emerge significantly, parallel studies involving Ni(II) remain relatively unexplored. The pursuit of feasible methods for hydrocarbon activation by Ni(II) is attractive, particularly from an economic viewpoint, as compared to the current alternatives of more expensive and thus the corresponding intermolecular steric repulsion of phenyl and pentafluorophenyl complexes are known, intermolecular arene C–H activation mediated by a divalent nickel complex is virtually unprecedented.

Inspired by Fryzuk’s pioneering work in (SiMe2)CH3-derived amido phosphate compounds, we became interested in exploratory chemistry of diarylamido phosphate compounds. It has been demonstrated that Pt(II) complexes of [N(o-C6H4PR2)2]2− (R = Pr, Cy) are active for intermolecular benzene C–H activation. Ni(II) complexes of [R–NP]− (R = Ph, Pr, Cy) effectively promote the C–X (X = Cl, Br, I) bond cleavage of a variety of halogenated hydrocarbons. Encouraged by these results, we envision that intermolecular arene C–H activation may also be accessed by [R–NP]− complexes of inexpensive Ni(II). In this contribution, we describe the reactivity studies of [R–NP]NiX (X = R, Pr, Cy; Scheme 2). The 1H and 31P NMR spectroscopy; only the disappearance of [R–NP]NiH and the formation of [R–NP]Ni(C6F5) throughout the reaction period as indicated by the 31P NMR spectroscopy. The concomitant formation of the major [R–NP]Ni(C6F5) and the minor [R–NP]NiPh is indicative of competitive reactions between C6F5 transfer and intermolecular benzene C–H activation, respectively. Both phenyl and pentafluorophenyl complexes are presumably evolved from the putative [Pr–NP]Ni(μ-H)B(C6F5)3 intermediate. The transfer of C6F5 from B(C6F5)3 to a transition metal has also been reported in some cases. As anticipated for the inherent thermal stability of pentafluorophenyl complexes of late transition metals, [Pr–NP]Ni(C6F5) can be efficiently isolated by heating the reaction mixture at 110 °C for 1 day. Similar phenomena were also observed for reactions involving [Cy–NP]NiH, although at a much slower rate (>7 days at room temperature), consistent with the larger steric size of cyclohexyl than isopropyl and thus the corresponding intermolecular steric repulsion of [R–NP]NiH with B(C6F5)3. The putative [Cy–NP]Ni(μ-H)B(C6F5)3 intermediate was observed at 43 ppm in the 31P(1H) NMR spectroscopy.

Red crystals of [Cy–NP]Ni(C6F5) suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. Figure S1 (see Supporting Information) illustrates the X-ray structure of this molecule in which the C6F5 group is trans to the amido nitrogen donor in a square-planar geometry. The Ni–N distance in [Cy–NP]Ni(C6F5) (1.912(6) Å) is slightly shorter than that in [Cy–NP]NiMe (1.947(5) Å), suggesting that the trans influence of the pentafluorophenyl ligand is somewhat lower than that of methyl. The C6F5 ring in [Cy–NP]Ni(C6F5) lies approximately perpendicular to the mean coordination plane with a dihedral angle of 79.5°.

Interestingly, addition of 1 equiv of AlMe3 to a benzene solution of [R–NP]NiH at room temperature led exclusively to the formation of the corresponding benzene C–H activation product [R–NP]NiPh (R = Pr, Cy; Scheme 2). The 1H and 31P(1H) NMR spectroscopy indicates that these reactions are complete in 4 h, a rate that is notably much faster than that employing B(C6F5)3. No intermediate was observed as indicated by 31P(1H) NMR spectroscopy; only the disappearance of [R–NP]NiH and the formation of [R–NP]NiPh could be detected. The identity of byproducts was periodically monitored by 31P(1H) NMR spectroscopy. After 40 h, the 31P(1H) NMR spectrum of the homogeneous reaction aliquot indicates the concurrent presence of the starting material [Pr–NP]NiH (29%), an intermediate (30%) that we tentatively formulate as zwitieronic [Pr–NP]Ni(μ-H)B(C6F5)3 (δp 51 ppm), the desired benzene C–H activation product [Pr–NP]NiPh (12%, vide infra), and [Pr–NP]Ni(C6F5) (29%, vide infra) (Scheme 1). Unsatisfactorily, the relative ratio of the desired [Pr–NP]NiPh is consistently low (up to 20%) over a period of 110 h as compared to the other components present in the reaction mixture. Selective isolation of the presumed [Pr–NP]Ni(μ-H)B(C6F5)3 seems unlikely as it is always accompanied by a significant amount of [Pr–NP]NiH and/or [Pr–NP]Ni(C6F5) throughout the reaction period as indicated by the 31P(1H) NMR spectroscopy. The reaction was periodically monitored by 31P(1H) NMR spectroscopy.
formed from these reactions is currently under investigation. Analysis of the 1H NMR spectra of reactions performed in a J. Young NMR tube in C₆D₆ led us to propose the production of methane and dimethylamine. No hydrogen gas, however, was detected. Remarkably, reactions employing a substoichiometric amount (e.g., 0.2 equiv) of AlMe₃ also afforded quantitatively the corresponding [R—PNP]NiH. The identity of these phenyl complexes was further confirmed by independent preparation of these molecules from the reactions of [R—PNP]NC(Ph = Pr, Cy)[p] with PhMgCl in ethereal solutions at −35 °C. It is worth noting that the reactivity of [R—PNP]NiH toward intermolecular benzene C—H activation is somewhat better than that of [Ph—PNP] complexes of Pt(II), which cleave benzene C—H bonds in 3 h at room temperature in the presence of a Lewis acid. 8

The intermolecular activation of toluene and xylenes was subsequently investigated. The reaction of [Pr—PNP]NiH with AlMe₃ in toluene at room temperature produced quantitatively a mixture of [Pr—PNP]Ni(m-tolyl) and [Pr—PNP]Ni(p-tolyl) in a 2:1 ratio. Neither [Pr—PNP]Ni(o-tolyl) nor [Pr—PNP]Ni(CHPh)₂ was observed in the reaction mixture as judged by 1H and 31P{1H} NMR spectroscopy. The identity of these possible Cₛ—H or Cₛₛ—H activation products was verified by independent preparation of these compounds from the reactions of [Pr—PNP]Ni[C₆F₅] with appropriate Grignard reagents. Complex [Pr—PNP]Ni(p-tolyl) was further characterized by X-ray crystallography (see Supporting Information), which revealed a core structure that is very similar to that of [Cy—PNP]Ni(C₆F₅). The dihedral angle between the C₆F₅ ring and the mean coordination plane around Ni(II) is 79.0°. The selective formation of [Cy—PNP]NiH toward intermolecular benzene C—H activation is therefore more efficient than methyl C—H activation: (c) van der Boom, M. E.; Liou, J. A.; Bercaw, J. E. Angew. Chem., Int. Ed. 2005, 14, 10235.

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Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic data in CIF format for [Cy—PNP]Ni(C₆F₅) and [Pr—PNP]Ni(p-tolyl). This material is available free of charge via the Internet at http://pubs.acs.org.

References


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