

Intermolecular Arene C–H Activation by Nickel(II)

Lan-Chang Liang,* Pin-Shu Chien, and Yu-Lun Huang

Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

Received July 31, 2006; E-mail: lcliang@mail.nsysu.edu.tw

Selective hydrocarbon activation and functionalization has long been identified as a major challenge to synthetic chemists.¹ 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.^{2,3} 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,^{2,4} parallel studies involving Ni(II) remain relatively unexplored.^{1c} 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 4d and 5d metals. We note that, although examples of well-defined Ni(0)-mediated and chelate-assisted hydrocarbon activation processes are known,⁵ intermolecular arene C–H activation mediated by a divalent nickel complex is virtually unprecedented.

Inspired by Fryzuk's pioneering work in $-\text{SiMe}_2\text{CH}_2-$ derived amido phosphine complexes,⁶ we became interested in exploratory chemistry of diarylamido phosphine compounds.⁷ It has been demonstrated that Pt(II) complexes of $[\text{N}(o\text{-C}_6\text{H}_4\text{PR}_2)_2]^-$ ($[\text{R}-\text{PNP}]^-$; $\text{R} = \text{Ph}$) are active for intermolecular benzene C–H activation.⁸ Ni(II) complexes of $[\text{R}-\text{PNP}]^-$ ($\text{R} = \text{Ph}$, ^iPr , Cy) effectively promote the C–X ($\text{X} = \text{Cl}$, Br , I) bond cleavage of a variety of halogenated hydrocarbons.^{9a} Encouraged by these results, we envision that intermolecular arene C–H activation may also be accessed by $[\text{R}-\text{PNP}]^-$ complexes of inexpensive Ni(II). In this contribution, we describe the reactivity studies of $[\text{R}-\text{PNP}]\text{NiR}'$ ($\text{R} = ^i\text{Pr}$, Cy ; $\text{R}' = \text{H}$, Me) in this aspect, which represents a rare example of Ni(II)-mediated intermolecular arene C–H activation under extremely mild conditions.

Complexes $[\text{Pr}-\text{PNP}]\text{NiH}$ and $[\text{Cy}-\text{PNP}]\text{NiH}$ were readily prepared in high yield by oxidative addition reactions of $\text{Ni}(\text{COD})_2$ with $\text{H}[\text{R}-\text{PNP}]^{9a}$ in benzene at room temperature. Alternatively, metathetical reactions of $[\text{R}-\text{PNP}]\text{NiCl}^{9a}$ with LiBHEt_3 in THF at -35°C also afforded the corresponding $[\text{R}-\text{PNP}]\text{NiH}$. A similar nickel hydride complex supported by a tolyl-derived amido diphosphine ligand was also reported very recently.¹⁰ Surprisingly, attempts to isolate $[\text{Ph}-\text{PNP}]\text{NiH}$ by identical synthetic routes were not successful. Reminiscent of the previously reported $[\text{R}-\text{PNP}]\text{NiX}$ ($\text{X} = \text{halide or alkyl}$),⁹ complexes $[\text{Pr}-\text{PNP}]\text{NiH}$ and $[\text{Cy}-\text{PNP}]\text{NiH}$ display solution C_{2v} symmetry on the NMR time scale, indicating a square-planar geometry for these molecules. The nickel-bound hydride ligand appears as a characteristic triplet resonance at -18.5 ppm with $^2J_{\text{HP}}$ of 63 Hz in the ^1H NMR spectroscopy.

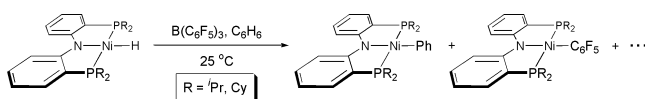
Strong Lewis acidic boron and aluminum compounds are often effective to abstract an alkyl or hydride ligand from transition metal complexes.¹¹ Addition of 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ to a benzene solution of $[\text{Pr}-\text{PNP}]\text{NiH}$ at room temperature led immediately to a change in color from yellow to red. No precipitate was observed from the reaction mixture even after a prolonged period of time (>5 days).

The reaction was periodically monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 40 h, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the homogeneous reaction aliquot indicates the concurrent presence of the starting material $[\text{Pr}-\text{PNP}]\text{NiH}$ (29%), an intermediate (30%) that we tentatively formulate as zwitterionic $[\text{Pr}-\text{PNP}]\text{Ni}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ (δ_{p} 51 ppm), the desired benzene C–H activation product $[\text{Pr}-\text{PNP}]\text{NiPh}$ (12%, *vide infra*), and $[\text{Pr}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ (29%, *vide infra*) (Scheme 1). Unsatisfactorily, the relative ratio of the desired $[\text{Pr}-\text{PNP}]\text{NiPh}$ 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 $[\text{Pr}-\text{PNP}]\text{Ni}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ seems unlikely as it is always accompanied by a significant amount of $[\text{Pr}-\text{PNP}]\text{NiH}$ and/or $[\text{Pr}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ throughout the reaction period as indicated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The concomitant formation of the major $[\text{Pr}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ and the minor $[\text{Pr}-\text{PNP}]\text{NiPh}$ is indicative of competitive reactions between C_6F_5 transfer and intermolecular benzene C–H activation, respectively. Both phenyl and pentafluorophenyl complexes are presumably evolved from the putative $[\text{Pr}-\text{PNP}]\text{Ni}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ intermediate. The transfer of C_6F_5 from $\text{B}(\text{C}_6\text{F}_5)_3$ to a transition metal has also been reported in some cases.¹² As anticipated for the inherent thermal stability of pentafluorophenyl complexes of late transition metals, $[\text{Pr}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ can be efficiently isolated by heating the reaction mixture at 110°C for 1 day. Similar phenomena were also observed for reactions involving $[\text{Cy}-\text{PNP}]\text{NiH}$, 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 $[\text{R}-\text{PNP}]\text{NiH}$ with $\text{B}(\text{C}_6\text{F}_5)_3$. The putative $[\text{Cy}-\text{PNP}]\text{Ni}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ intermediate was observed at 43 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

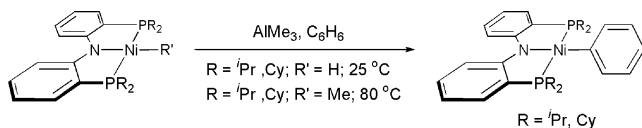
Red crystals of $[\text{Cy}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at -35°C . Figure S1 (see Supporting Information) illustrates the X-ray structure of this molecule in which the C_6F_5 group is *trans* to the amido nitrogen donor in a square-planar geometry. The Ni–N distance in $[\text{Cy}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ (1.912(6) Å) is slightly shorter than that in $[\text{Cy}-\text{PNP}]\text{NiMe}$ (1.947(5) Å),^{9a} suggesting that the *trans* influence of the pentafluorophenyl ligand is somewhat lower than that of methyl. The C_6F_5 ring in $[\text{Cy}-\text{PNP}]\text{Ni}(\text{C}_6\text{F}_5)$ lies approximately perpendicular to the mean coordination plane with a dihedral angle of 79.5° .

Interestingly, addition of 1 equiv of AlMe_3 to a benzene solution of $[\text{R}-\text{PNP}]\text{NiH}$ at room temperature led exclusively to the formation of the corresponding benzene C–H activation product $[\text{R}-\text{PNP}]\text{NiPh}$ ($\text{R} = ^i\text{Pr}$, Cy ; Scheme 2). The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicates that these reactions are complete in 4 h, a rate that is notably much faster than that employing $\text{B}(\text{C}_6\text{F}_5)_3$. No intermediate was observed as indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; only the disappearance of $[\text{R}-\text{PNP}]\text{NiH}$ and the formation of $[\text{R}-\text{PNP}]\text{NiPh}$ could be detected. The identity of byproducts

Scheme 1



Scheme 2



formed from these reactions is currently under investigation. Analysis of the 1H NMR spectra of reactions performed in a J. Young NMR tube in C_6D_6 led us to propose the production of methane and dimethylalane. No hydrogen gas, however, was detected. Remarkably, reactions employing a substoichiometric amount (e.g., 0.2 equiv) of $AlMe_3$ also afforded quantitatively the corresponding $[R-PNP]NiPh$. The identity of these phenyl complexes was further confirmed by independent preparation of these molecules from the reactions of $[R-PNP]NiCl$ ($R = ^iPr, Cy$)^{9a} with $PhMgCl$ in ethereal solutions at $-35\text{ }^\circ\text{C}$. 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 31 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 $[^iPr-PNP]NiH$ with $AlMe_3$ in toluene at room temperature produced quantitatively a mixture of $[^iPr-PNP]Ni(m\text{-tolyl})$ and $[^iPr-PNP]Ni(p\text{-tolyl})$ in a 2:1 ratio. Neither $[^iPr-PNP]Ni(o\text{-tolyl})$ nor $[^iPr-PNP]Ni(CH_2Ph)$ was observed in the reaction mixture as judged by 1H and $^{31}P\{^1H\}$ NMR spectroscopy. The identity of these possible $C_{sp^2}\text{-H}$ or $C_{sp^3}\text{-H}$ activation products was verified by independent preparation of these compounds from the reactions of $[^iPr-PNP]NiCl$ ^{9a} with appropriate Grignard reagents. Complex $[^iPr-PNP]Ni(p\text{-tolyl})$ was further characterized by X-ray crystallography (see Supporting Information), which revealed a core structure that is very similar to that of $[Cy-PNP]Ni(C_6F_5)$. The dihedral angle between the $p\text{-tolyl}$ ring and the mean coordination plane around Ni(II) is 79.0° . The selective formation of $[^iPr-PNP]Ni(m\text{-tolyl})$ and $[^iPr-PNP]Ni(p\text{-tolyl})$ rather than $[^iPr-PNP]Ni(o\text{-tolyl})$ is consistent with the steric accessibility of the corresponding $C_{sp^2}\text{-H}$ bonds upon competitive activation. The preference for meta to para by a factor of 2 is in good agreement with the statistical availability of these C–H bonds. Consistent with these results, the reaction of $[^iPr-PNP]NiH$ with $AlMe_3$ in m -xylene at room temperature afforded exclusively $[^iPr-PNP]Ni(3,5\text{-xylyl})$. Similar phenomena were also found for reactions involving $[Cy-PNP]NiH$ in toluene and m -xylene, respectively.

In order to better assess the influence of the $[R-PNP]^-$ ligands on the reactivity of Ni(II) toward intermolecular arene C–H activation, a parallel study involving $[R-PNP]NiMe$ ($R = Ph, ^iPr, Cy$) was attempted. The reactions of $[R-PNP]NiMe$ ($R = ^iPr, Cy$)^{9a} with 1 equiv of $AlMe_3$ in benzene at $80\text{ }^\circ\text{C}$ produced the corresponding $[R-PNP]NiPh$ (Scheme 2) quantitatively in 1 day as indicated by 1H and $^{31}P\{^1H\}$ NMR spectroscopy. Unlike what has been observed for $[R-PNP]NiH$, heating is necessary for $[^iPr-PNP]NiMe$ and $[Cy-PNP]NiMe$ to become reactive as these reactions do not proceed at all at room temperature for >3 days, highlighting the intrinsic discrepancy in reactivity between $[R-PNP]NiMe$ and $[R-PNP]NiH$. In contrast, no reaction was found when $[Ph-PNP]NiMe$ ⁹ was employed under similar conditions. The divergent reactivity of $[Ph-PNP]NiMe$ versus $[^iPr-PNP]NiMe$ and

$[Cy-PNP]NiMe$ likely underscores the significance of π basicity of Ni(II) in the latter complexes for rather sufficient back π bonding from formally electron-deficient Ni(II) to the σ^* orbital of the benzene C–H bond. The possibility of ineffective methyl abstraction from $[Ph-PNP]NiMe$ by $AlMe_3$, however, cannot be ruled out.

In summary, we have demonstrated an efficient intermolecular arene C–H activation process mediated by Ni(II) complexes of $[R-PNP]^-$ under extremely mild conditions. Of particular note is the remarkable reactivity of inexpensive Ni(II) as compared to the current alternatives of 4d and 5d metals. Studies directed to delineate the reaction mechanism and reactivity with applicable hydrocarbons are currently underway.

Acknowledgment. We thank the National Science Council of Taiwan for financial support (NSC 94-2113-M-110-004), and Mr. Ting-Shen Kuo (NTNU) for crystallographic assistance.

Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic data in CIF format for $[Cy-PNP]Ni(C_6F_5)$ and $[^iPr-PNP]Ni(p\text{-tolyl})$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (c) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Boston, 2000. (d) Das, S.; Incarvito, C. D.; Crabtree, R. H.; Brudvig, G. W. *Science* **2006**, *312*, 1941. (e) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 9071. (f) Ingleson, M. J.; Yang, X.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2005**, *127*, 10846. (g) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik, M.-H.; Mendiola, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16016.
- (a) Lersch, M.; Tilstet, M. *Chem. Rev.* **2005**, *105*, 2471. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181.
- (a) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475. (b) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (c) Chen, H. Y.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (d) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H. J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596. (e) Fan, L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 16772.
- (a) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (b) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. (c) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870.
- Examples of Ni(0)-mediated C–H activation: (a) Brunkan, N. M.; Brestensky, D. M.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 3627. (b) Keen, A. L.; Johnson, S. A. *J. Am. Chem. Soc.* **2006**, *128*, 1806. Examples involving chelate-assisted C–H activation: (c) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Inorg. Chim. Acta* **2004**, *357*, 4015. (d) Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2006**, *25*, 602. Examples involving Ni-crystal surfaces or clusters: (e) Davis, S. C.; Severson, S. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 3024 and references therein.
- (a) Fryzuk, M. D.; Macneil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918. (b) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
- (a) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152. (b) Chien, P.-S.; Liang, L.-C. *Inorg. Chem.* **2005**, *44*, 5147. (c) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471. (d) Liang, L.-C.; Chien, P.-S.; Huang, M.-H. *Organometallics* **2005**, *24*, 353.
- Liang, L.-C.; Lin, J.-M.; Lee, W.-Y. *Chem. Commun.* **2005**, 2462.
- (a) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399. (b) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007.
- Ozerov, O. V.; Guo, C. Y.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573.
- (a) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809. (c) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.
- (a) Woodman, T. J.; Thornton-Pett, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 4080. (b) Kalamarides, H. A.; Iyer, S.; Lipian, J.; Rhodes, L. F.; Day, C. *Organometallics* **2000**, *19*, 3983.

JA065505P