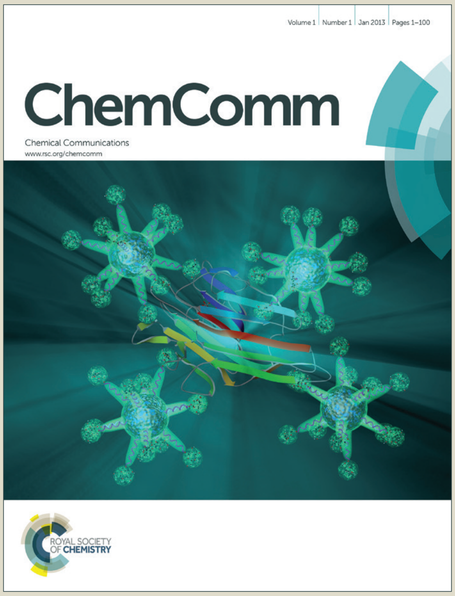
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

RSCPublishing

COMMUNICATION

Stable Bis(trifluoromethyl)Nickel(III) Complexes

Cite this: DOI: 10.1039/x0xx00000x

Fengzhi Tang,[a] Nigam P. Rath,[b] and Liviu M. Mirica[a,*]

Received 00th January 2012,
Accepted 00th January 2012

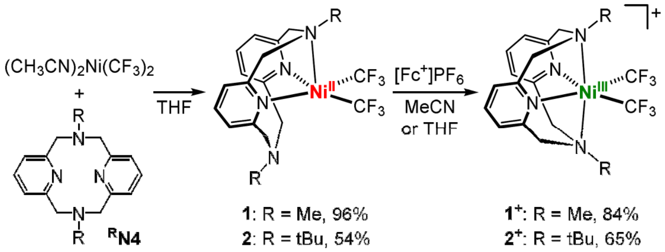
DOI: 10.1039/x0xx00000x

www.rsc.org/

Organometallic Ni(III) intermediates have been proposed in several Nickel-catalyzed cross-coupling reactions, yet no isolated bis(hydrocarbyl)Ni(III) complexes have been reported to date. Herein we report the synthesis and detailed characterization of stable organometallic Ni(III) complexes that contain two trifluoromethyl ligands and are supported by tetradentate N-donor ligands ^{R}N4 (R = Me or tBu). Interestingly, the corresponding Ni(II) precursors undergo facile oxidation, including aerobic oxidation, to generate uncommonly stable organometallic Ni(III) complexes that exhibit limited reactivity.

For more than three decades, Nickel complexes have been employed as catalysts in Negishi, Kumada, and Suzuki cross-coupling reactions.[1] In these catalytic systems, bis(hydrocarbyl) Ni^{III} species have been proposed as the reactive intermediates that undergo reductive elimination and C-C bond formation.[2] However, to the best of our knowledge no such bis(hydrocarbyl)Ni^{III} complexes have been isolated to date. Moreover, only a few other organometallic Ni^{III} complexes have been isolated and characterized in detail.[3]

We have recently employed the tetradentate N-donor ligands N, N'-dialkyl-2,11-diaza[3.3](2,6)pyridinophane (^{R}N4, R = Me, iPr, tBu) to stabilize the first organometallic mononuclear Pd^{III} complexes and investigate their C-C/C-heteroatom bond formation reactivity.[4] In those studies, we have proposed that the macrocyclic nature and the flexibility of the ^{R}N4 ligands account for their observed ability to stabilize the distorted octahedral geometry of Pd^{III} d^7 centers, while the ligand steric effects have been shown to dramatically influence the structure and reactivity of the corresponding high-valent Pd complexes. Moreover, we have also reported the isolation and characterization of organometallic Ni^{III}-aryl species that can undergo C-C and C-heteroatom bond formation reactions and are efficient catalysts for Kumada and Negishi cross-coupling reactions.[5] While a Ni^{III}(aryl)alkyl intermediate was spectroscopically characterized therein, that complex undergoes rapid reductive elimination and could not be isolated. In order to further stabilize such organometallic Ni^{III} complexes, we hypothesized that the use of perfluoroakyl ligands will slow down the reductive elimination reactivity of these species. Such an approach has been elegantly used recently by Vicic et al. to detect spectroscopically a terpyridine-supported bis(trifluoromethyl)Ni^{III} complex.[6] Herein, we report the isolation and detailed characterization of uncommonly stable mononuclear bis(trifluoromethyl)Ni^{III} complexes supported by the pyridinophane ligands ^{Me}N4 and ^{tBu}N4. Interestingly, these Ni^{III} complexes can be generated upon facile oxidation of the Ni^{II} precursors, including aerobic oxidation, and surprisingly they exhibit a very limited reactivity. Overall, these studies strongly suggest the ^{R}N4 tetradentate ligand system is capable of stabilizing various bis(hydrocarbyl)Ni^{III} complexes that would allow for their isolation and detailed investigation of their reactivity relevant to cross-coupling reactions.



Scheme 1 Synthesis of (^{R}N4)Ni^{II}(CF$_3$)$_2$ and [(^{R}N4)Ni^{III}(CF$_3$)$_2$]PF$_6$ complexes.

The Ni^{II} complexes (^{R}N4)Ni^{II}(CF$_3$)$_2$ (R = Me: **1**, R = tBu: **2**) were synthesized by mixing the Ni^{II} precursor[6] (MeCN)$_2$Ni^{II}(CF$_3$)$_2$ with the corresponding ^{R}N4 ligand to afford complexes **1** and **2** in 96% and 54% yield, respectively (Scheme 1).[7] Both **1** and **2** are diamagnetic, suggesting an S = 0 ground state. Interestingly, the ^{1}H NMR spectra reveals two signals corresponding to the N-substituent and four different doublets corresponding to the methylene protons, suggesting a κ^3 conformation with two pyridine donors and one amine donor of the ^{R}N4 ligand coordinating to the metal center.[7] Moreover, the ^{1}H NMR spectrum of complex **2** is very similar to that of the reported complex (^{tBu}N4)Pd^{II}Cl$_2$ in which ^{tBu}N4 also adopts a κ^3 conformation.[8] The crystal structure of **2** indeed confirms the expected κ^3 conformation, with the Ni center found in a distorted square pyramidal geometry (Fig. 1). The axial Ni-N$_{amine}$ bond distance (2.537 Å) is substantially longer than the average equatorial Ni-N$_{py}$ bond distance (1.966 Å), likely due to the small ring size and the bulky *t*-butyl N-substituents. The

Ni-CF_3 distance (1.910 Å) is similar to other reported Ni-perfluoroalkyl bond distances (1.853 - 2.046 Å).[6,9]

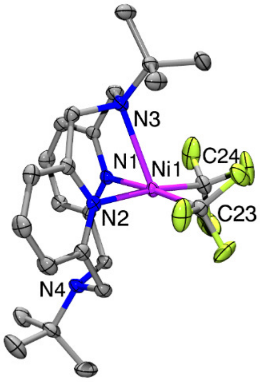
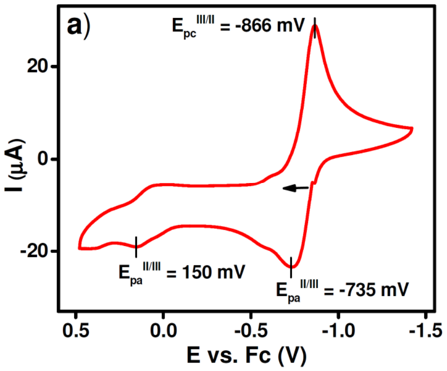


Fig. 1 ORTEP representation (50% probability thermal ellipsoids) of **2** (hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (°): Ni1-N1 1.939(2), Ni1-N2 1.994(2), Ni1-N3 2.537(3), Ni1-C23 1.905(3), Ni1-C24 1.915(3), N1-Ni1-N2 86.7(1).

The cyclic voltammetry (CV) analysis of the Ni^{II} complexes **1** and **2** reveals anodic peaks at low potentials that were assigned to the $Ni^{II/III}$ redox couples. For example, **1** exhibits an $E_{1/2}^{II/III}$ value of -805 mV (ΔE_p = 130 mV) vs Fc^+/Fc, while the CV of **2** reveals a similar oxidation wave at -220 mV (ΔE_p = 110 mV) vs Fc^+/Fc (Fig. 2). These low oxidation potentials are proposed to be due to the flexible ^{R}N4 ligand that can greatly stabilize d^7 ions in a distorted octahedral geometry, as shown recently for both Pd^{III} and Ni^{III} systems.[4-5] Interestingly, the CVs of both **1** and **2** exhibit additional anodic waves observed at higher potentials that become more prominent at higher scan rates (Figs. S5 and S6).[7] Based on our previous electrochemical studies of analogous (^{R}N4)Pd^{II} complexes, we attribute these oxidation waves to two interconverting conformations present in solution for both **1** and **2**: a predominant κ^3 conformer in which ^{R}N4 acts as a tridentate ligand – as observed for **2** by X-ray diffraction, and a minor κ^4 conformer in which ^{R}N4 acts as a tetradentate ligand.[10] These κ^4 conformers for both **1** and **2** are expected to be more easily oxidized due to the presence of two axial N donors that raise the energy of the highest occupied molecular orbital (HOMO) d_{z^2} and thus lower the corresponding $Ni^{II/III}$ oxidation potential.[10]



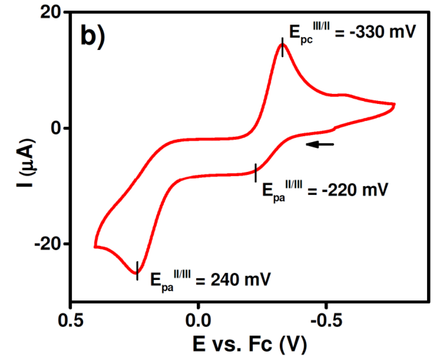


Fig. 2 Cyclic voltammograms (CVs) of **1** (a) and **2** (b) in 0.1 M Bu_4NClO_4/MeCN (scan rate 100 mV/s).

Since both Ni^{II} complexes **1** and **2** have low oxidation potentials, they can be easily oxidized by mild oxidants. For example, addition of 1 equiv [Fc^+]PF_6 to **1** or **2** in MeCN generates purple or orange solutions of the Ni^{III} complexes [(^{Me}N4)Ni^{III}(CF_3)$_2$]$^+$ (**1**$^+$) or [(^{tBu}N4)Ni^{III}(CF_3)$_2$]$^+$ (**2**$^+$, Scheme 1), respectively. Both [**1**$^+$]PF_6 and [**2**$^+$]PF_6 were isolated and characterized by X-ray crystallography to reveal Ni^{III} centers that adopt a distorted octahedral geometry. Interestingly, 6-coordinate[3a,d,5] organometallic Ni^{III} complexes are less common than 3-[3f,h,11] and 5-coordinate[3b,c,e,12] Ni^{III} species. In [**1**$^+$]PF_6 and [**2**$^+$]PF_6 the Ni-N_{axial} distances of 2.21-2.42 Å, Ni-$N_{equatorial}$ distances of 1.92-1.96 Å, and Ni-C distances of 1.91-1.97 Å (Fig. 3) are similar to the other recently reported organometallic (^{tBu}N4)Ni^{III} complexes.[5] The Ni-N_{axial} distances in **2**$^+$ are ~0.2 Å longer than those in **1**$^+$, and the ^{tBu}N4 ligand in **2**$^+$ is drastically twisted and no longer adopts a C_{2v} symmetry, as observed for ^{Me}N4 in **1**$^+$ (see front views of **1**$^+$ and **2**$^+$ in Fig. S21).[7] Such structural differences have also been observed in the (^{R}N4)Pd^{III} complexes and are likely caused by the larger *t*-butyl vs. methyl N-substituents in **2**$^+$ vs. **1**$^+$ and their steric clash with the CF_3 groups.[4d] Importantly, complexes [**1**$^+$]PF_6 and [**2**$^+$]PF_6 are stable at room temperature, both in solution and the solid state, and constitute to the best of our knowledge the first isolable organometallic Ni^{III} complexes with two exogenous organic ligands.

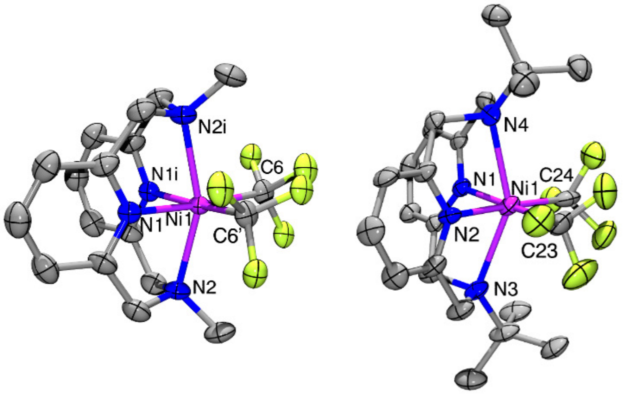


Fig. 3 ORTEP representation of the cations of [**1**$^+$]PF_6 (left, 30% probability thermal ellipsoids) and [**2**$^+$]PF_6 (right. 50% probability thermal ellipsoids). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): **1**$^+$, Ni1-N1 1.962(7), Ni1-N2 2.212(8), Ni1-C6 1.912(2), N1-Ni1-N1i 84.5(4), N2-Ni1-N2i 156.2(5); **2**$^+$, Ni1-N1 1.946(5), Ni1-N2 1.924(5), Ni1-N3 2.431(6), Ni1-N4 2.399(5), Ni1-C23 1.969(8), Ni1-C24 1.949(8), N1-Ni1-N2 89.3(2), N3-Ni1-N4 148.0(2).

Complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ are paramagnetic and their effective magnetic moments μ_{eff} were determined as 2.06 and 2.15 μ_b, respectively, corresponding to one unpaired electron. The presence of a Ni^{III} center was further confirmed by the EPR spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ (77 K, 3:1 PrCN:MeCN glass) that reveal g_{ave} values of 2.105 and 2.143, respectively (Fig. 4). In addition, superhyperfine coupling to the two axial N atoms (I=1) is observed in the g_z direction for both complexes. The larger coupling constant observed in the pseudo-axial EPR spectrum of $\mathbf{1}^+$ (A_{2N} = 18.5 G) than that observed in the rhombic spectrum of $\mathbf{2}^+$ (A_{2N} = 14.3 G) strongly supports the shorter Ni-N_{axial} distances found in $\mathbf{1}^+$, as well as the more distorted geometry of the bulkier ^{tBu}N4 ligand in $\mathbf{2}^+$ that gives rise to the observed rhombic EPR spectrum (Fig. 4). Similar differences in the EPR spectra have been observed for the related (^{R}N4)Pd^{III} complexes.[4d]

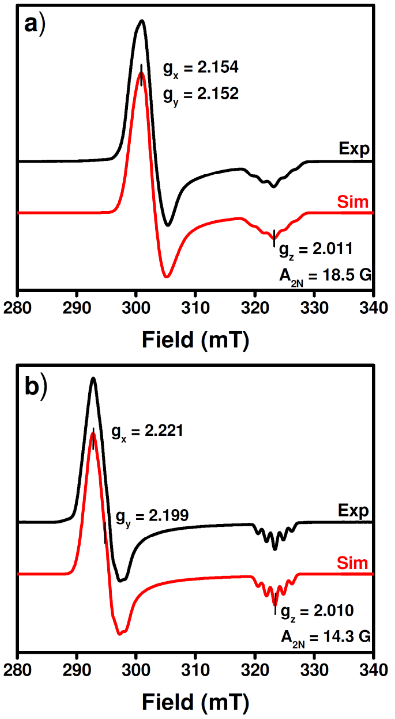
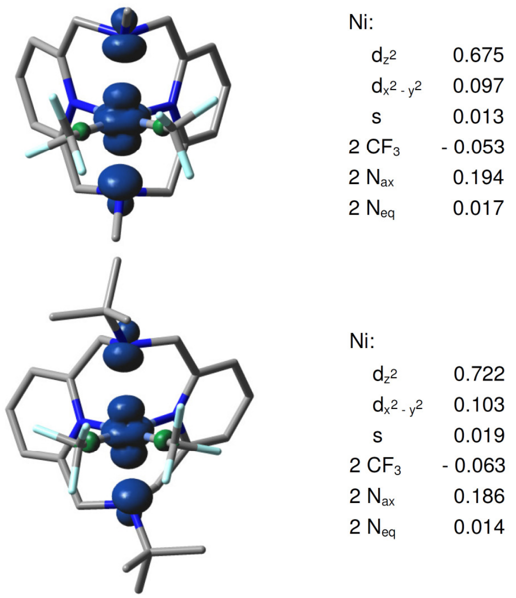


Fig. 4 EPR spectra (black lines) of [$\mathbf{1}^+$]PF_6 (a) and [$\mathbf{2}^+$]PF_6 (b) in 3:1 PrCN:MeCN at 77 K, and the simulated EPR spectra (red lines) using the following parameters: $\mathbf{1}^+$, g_x = 2.154; g_y = 2.152; g_z = 2.011 (A_{2N} = 18.5 G); $\mathbf{2}^+$, g_x = 2.221; g_y = 2.199; g_z = 2.010 (A_{2N} = 14.3 G).

Density functional theory (DFT) calculations were employed to provide additional insight into the electronic properties of these unique organometallic Ni^{III} complexes. The calculated spin densities for $\mathbf{1}^+$ and $\mathbf{2}^+$ support the presence of a Ni^{III} center, with the unpaired electron residing mostly (>80%) on the metal center, along with a significant contribution (~19%) from the two axial N atoms (Fig. 5). The calculated spin density has a slightly higher contribution from the Ni^{III} center for $\mathbf{2}^+$ vs. $\mathbf{1}^+$, likely due to the more distorted structure leading to less orbital overlap for $\mathbf{2}^+$. Importantly, calculation of the g tensors and the superhyperfine coupling constants using the ORCA sofware program[13] that takes into account the spin-orbit coupling contribution nicely reproduces the experimental results (Table S7),[7] and also validates the theoretical model employed for analyzing the electronic properties of these uncommon organometallic Ni^{III} complexes.

The UV-vis spectrum of $\mathbf{1}^+$ in MeCN reveals a visible absorption band at 568 nm (ε = 330 $M^{-1}cm^{-1}$) along with a shoulder at ~680 nm, while $\mathbf{2}^+$ exhibits a transition at 422 nm (ε = 930 $M^{-1}cm^{-1}$) and a weak, low energy transition at 930 nm (ε = 40 $M^{-1}cm^{-1}$, Figs. S9 and S10).[7] Time-dependent DFT (TD-DFT) calculations of the UV-vis spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ reveal similar transition energies and suggest these absorption bands are ligand-to-metal charge transfer transitions (Tables S5 and S6 and Figs. S19 and S20). In addition, the higher transition energy observed for $\mathbf{2}^+$ (422 nm) vs. $\mathbf{1}^+$ (568 nm) is likely due to the more distorted structure of $\mathbf{2}^+$ that diminishes the bonding character of the Ni-N_{axial} interactions and lowers the energy of the corresponding antibonding HOMO (Tables S3 and S4).[7] Overall, the observed differences in the structural and electronic properties of $\mathbf{1}^+$ and $\mathbf{2}^+$ seem to be mainly due to the increased steric bulk of the ^{tBu}N4 ligand and this is expected to also affect the reactivity of these two systems.



Ni:	
d_{z^2}	0.675
$d_{x^2-y^2}$	0.097
s	0.013
2 CF_3	- 0.053
2 N_{ax}	0.194
2 N_{eq}	0.017

Ni:	
d_{z^2}	0.722
$d_{x^2-y^2}$	0.103
s	0.019
2 CF_3	- 0.063
2 N_{ax}	0.186
2 N_{eq}	0.014

Fig. 5 DFT calculated Mulliken spin densities for $\mathbf{1}^+$ (top) and $\mathbf{2}^+$ (bottom) – shown as 0.005 isodensity contour plots, and the relevant atomic and Ni orbital contributions to the spin densities.

Given the uncommonly low oxidation potential of $\mathbf{1}$, a mild oxidant such as O_2 can rapidly oxidize $\mathbf{1}$ in 5% H_2O/MeCN to generate a purple solution of the Ni^{III} complex $\mathbf{1}^+$ in up to 80% yield within 10 min at RT, as monitored by UV-vis spectroscopy (Fig. 6). The formation of $\mathbf{1}^+$ is further supported by the EPR spectrum of the oxidized solution that is identical to the EPR spectrum of the isolated [$\mathbf{1}^+$]PF_6 (Fig. S17). A similar aerobic oxidation was observed for $\mathbf{2}$, although at a much slower rate likely due to the higher oxidation potential of this complex. Overall, these aerobic oxidation studies suggest that organometallic Ni^{III} complexes supported by ^{R}N4 ligands can be generated using mild oxidants such as O_2 instead of the hazardous oxidants currently used in many transition metal-catalyzed oxidative C-C and C-heteroatom bond formation reactions.[1i]

Strikingly, unlike other reported organometallic Ni^{III} complexes, complexes [$\mathbf{1}^+$]PF_6 and [$\mathbf{2}^+$]PF_6 are indefinitely stable at RT under N_2. Heating these complexes at 80 °C for 24 h or photolysis with visible light at RT produces only trace amounts of the decomposition products CF_3H (<7%) and C_2F_6

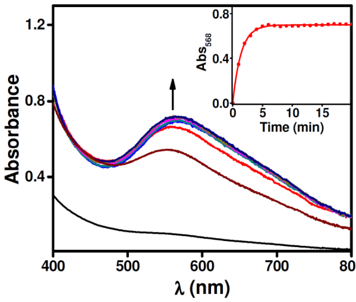


Fig. 6 Formation of 1^+ during aerobic oxidation of **1** (3 mM) in 5% H_2O/MeCN, as monitored by UV-vis spectroscopy (Δt = 5 min). Inset: time course of the formation of 1^+ and the first-order fit of the absorption data at 568 nm, corresponding to a pseudo-first order rate constant of 0.71 ± 0.02 min^{-1}.

(< 2%), with [$\mathbf{2}^+$]PF_6 being more reactive than [$\mathbf{1}^+$]PF_6 likely due to its distorted structure caused by the bulkier ^{tBu}N4 ligand. In order to probe the mechanism of products formation, the photolysis of [$\mathbf{2}^+$]PF_6 was performed for 24 h in the presence of 5 equiv of the radical trapping agent *N-tert-butyl*-α-phenylnitrone (PBN). The EPR spectrum of the reaction mixture supports the formation of a CF_3-PBN adduct (A_N = 14.10 G, A_H = 1.20 G, $A_F(CF_3)$ = 1.85 G, Fig. S15), strongly suggesting the transient generation of •CF_3 radicals.[6] However, spin integration of the EPR signal for the CF_3-PBN adduct corresponds to an yield of ~5%, corresponding to a very limited Ni-CF_3 bond homolysis that occurs upon irradiation.[7] Overall, the reduced reactivity of the bis(trifluoromethyl)Ni^{III} species $\mathbf{1}^+$ and $\mathbf{2}^+$ strongly supports our hypothesis that the ^{R}N4 ligands can dramatically stabilize organometallic Ni^{III} complexes, which can now be isolated and should allow for the detailed investigation of their reactivity. While the bis(trifluoromethyl)Ni^{III} complexes described herein are indeed too stable, it is expected that analogous bis(alkyl)Ni^{III} species will exhibit enhanced organometallic reactivity.

In conclusion, we have reported herein the isolation and detailed characterization of uncommonly stable bis(hydrocarbyl)Ni^{III} complexes containing two trifluoromethyl ligands. In addition to the use of an organic ligand that exhibits limited reactivity, these organometallic Ni^{III} species are further stabilized by the tetradentate N-donor ligands ^{tBu}N4 and ^{Me}N4. Therefore, these ligands seem to be optimally suited for taming the reactivity of organometallic high-valent Ni complexes that are particularly relevant to Ni-mediated C-C and C-heteroatom bond formation reactions. Current efforts are aimed at the isolation, characterization, and detailed reactivity studies of bis(alkyl)Ni^{III} complexes that are reactive intermediates in various cross-coupling reactions.

We thank the American Chemical Society Petroleum Research Fund (52988-ND3), the Department of Energy, BES Catalysis Science Program (DE-FG02-11ER16254), and the National Science Foundation (CHE-1255424) for support. L.M.M. is also supported by a Sloan Research Fellowship.

Notes and references

[a] Department of Chemistry, Washington University, One Brookings Drive, St. Louis, Missouri 63130-4899, mirica@wustl.edu

[b] Department of Chemistry and Biochemistry, One University Boulevard, University of Missouri – St. Louis, Missouri 63121-4400.

† Electronic Supplementary Information (ESI) available: Experimental details, spectroscopic characterization, computational details, and X-ray crystallographic data. See DOI: 10.1039/c000000x/

1. a) A. d. Meijere, F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, New York, 2004; b) M. R. Netherton, G. C. Fu, *Adv. Synth. Catal.*, 2004, **346**, 1525; c) A. C. Frisch, M. Beller, *Angew. Chem. Int. Ed.*, 2005, **44**, 674; d) J. Terao, N. Kambe, *Acc. Chem. Res.*, 2008, **41**, 1545; e) F. Glorius, *Angew. Chem. Int. Ed.*, 2008, **47**, 8347; f) V. B. Phapale, D. J. Cardenas, *Chem. Soc. Rev.*, 2009, **38**, 1598; g) A. Rudolph, M. Lautens, *Angew. Chem. Int. Ed.*, 2009, **48**, 2656; h) P. Knochel, T. Thaler, C. Diene, *Isr. J. Chem.*, 2012, **50**, 547; i) J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito, 2010.
2. a) T. T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.*, 1978, **100**, 1634; b) T. T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 7547; c) C. Amatore, A. Jutand, *Organometallics*, 1988, **7**, 2203; d) D. A. Powell, T. Maki, G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 510; e) F. Gonzalez-Bobes, G. C. Fu, *J. Am. Chem. Soc.*, 2006, **128**, 5360; f) A. S. Dudnik, G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 10693; g) S. L. Zultanski, G. C. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 624; h) G. D. Jones, C. McFarland, T. J. Anderson, D. A. Vicic, *Chem. Commun.*, 2005, 4211; i) G. D. Jones, J. L. Martin, C. McFarland, O. R. Allen, R. E. Hall, A. D. Haley, R. J. Brandon, T. Konovalova, P. J. Desrochers, P. Pulay, D. A. Vicic, *J. Am. Chem. Soc.*, 2006, **128**, 13175; j) A. Klein, Y. H. Budnikova, O. G. Sinyashin, *J. Organomet. Chem.*, 2007, **692**, 3156; k) V. B. Phapale, E. Bunuel, M. Garcia-Iglesias, D. J. Cardenas, *Angew. Chem. Int. Ed.*, 2007, **46**, 8790; l) V. B. Phapale, M. Guisan-Ceinos, E. Bunuel, D. J. Cardenas, *Chem. Eur. J.*, 2009, **15**, 12681; m) H. G. Gong, M. R. Gagné, *J. Am. Chem. Soc.*, 2008, **130**, 12177; n) O. Vechorkin, X. Hu, *Angew. Chem. Int. Ed.*, 2009, **48**, 2937; o) O. Vechorkin, V. r. Proust, X. Hu, *J. Am. Chem. Soc.*, 2009, **131**, 9756; p) X. Hu, *Chem. Sci.*, 2011, **2**, 1867; q) D. A. Everson, R. Shrestha, D. J. Weix, *J. Am. Chem. Soc.*, 2010, **132**, 920; r) S. Biswas, D. J. Weix, *J. Am. Chem. Soc.*, 2013, **135**, 16192; s) A. Joshi-Pangu, C. Y. Wang, M. R. Biscoe, *J. Am. Chem. Soc.*, 2011, **133**, 8478; t) X. L. Yu, T. Yang, S. L. Wang, H. L. Xu, H. G. Gong, *Org. Lett.*, 2011, **13**, 2138; u) J. C. Tellis, D. N. Primer, G. A. Molander, *Science*, 2014, **345**, 433; v) Z. W. Zuo, D. T. Ahneman, L. L. Chu, J. A. Terrett, A. G. Doyle, D. W. C. MacMillan, *Science*, 2014, **345**, 437; w) Y. Aihara, M. Tobisu, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.*, 2014, **136**, 15509.
3. a) D. M. Grove, G. van Koten, W. P. Mul, A. A. H. Vanderzeijden, J. Terheijden, M. C. Zoutberg, C. H. Stam, *Organometallics*, 1986, **5**, 322; b) D. M. Grove, G. van Koten, R. Zoet, N. W. Murrall, A. J. Welch, *J. Am. Chem. Soc.*, 1983, **105**, 1379; c) D. M. Grove, G. van Koten, P. Mul, R. Zoet, J. G. M. van der Linden, J. Legters, J. E. J. Schmitz, N. W. Murrall, A. J. Welch, *Inorg. Chem.*, 1988, **27**, 2466; d) L. A. van de Kuil, Y. S. J. Veldhuizen, D. M. Grove, J. W. Zwikker, L. W. Jenneskens, W. Drenth, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Organomet. Chem.*, 1995, **488**, 191; e) C. M. Lee, C. H. Chen, F. X. Liao, C. H. Hu, G. H. Lee, *J. Am. Chem. Soc.*, 2010, **132**, 9256; f) M. I. Lipschutz, X. Yang, R. Chatterjee, T. D. Tilley, *J. Am. Chem. Soc.*, 2013, **135**, 15298; g) M. I. Lipschutz, T. D. Tilley, *Angew. Chem. Int. Ed.*, 2014, **53**, 7290; h) V. M. Iluc, G. L. Hillhouse, *J. Am. Chem. Soc.*, 2014, **136**, 6479.
4. a) J. R. Khusnutdinova, N. P. Rath, L. M. Mirica, *J. Am. Chem. Soc.*, 2010, **132**, 7303; b) J. R. Khusnutdinova, N. P. Rath, L. M. Mirica, *J. Am. Chem. Soc.*, 2012, **134**, 2414; c) F. Tang, Y. Zhang, N. P. Rath, L. M. Mirica, *Organometallics*, 2012, **31**, 6690; d) F. Tang, F. Qu, J. R. Khusnutdinova, N. P. Rath, L. M. Mirica, *Dalton Trans.*, 2012, **41**, 14046; e) L. M. Mirica, J. R. Khusnutdinova, *Coord. Chem. Rev.*, 2013, 299; f) J. R. Khusnutdinova, N. P. Rath, L. M. Mirica, *Angew. Chem. Int. Ed.*, 2011, **50**, 5532; g) J. R. Khusnutdinova, F. Qu, Y. Zhang, N. P. Rath, L. M. Mirica, *Organometallics*, 2012, **31**, 4627.
5. B. Zheng, F. Tang, J. Luo, J. W. Schultz, N. P. Rath, L. M. Mirica, *J. Am. Chem. Soc.*, 2014, **136**, 6499.
6. C. P. Zhang, H. Wang, A. Klein, C. Biewer, K. Stimat, Y. Yarnaguchi, L. Xu, V. Gomez-Benitez, D. A. Vicic, *J. Am. Chem. Soc.*, 2013, **135**, 8141.
7. See Supporting Information. .
8. S. P. Meneghetti, P. J. Lutz, J. Kress, *Organometallics*, 2001, **20**, 5050.
9. a) Y. Yamaguchi, H. Ichioka, A. Klein, W. W. Brennessel, D. A. Vicic, *Organometallics*, 2012, **31**, 1477; b) G. G. Dubinina, W. W. Brennessel, J. L. Miller, D. A. Vicic, *Organometallics*, 2008, **27**, 3933.
10. J. R. Khusnutdinova, N. P. Rath, L. M. Mirica, *Inorg. Chem.*, 2014, DOI: 10.1021/ic5023054.
11. V. M. Iluc, A. J. M. Miller, J. S. Anderson, M. J. Monreal, M. P. Mehn, G. L. Hillhouse, *J. Am. Chem. Soc.*, 2011, **133**, 13055.
12. C. M. Lee, Y. L. Chuang, C. Y. Chiang, G. H. Lee, W. F. Liaw, *Inorg. Chem.*, 2006, **45**, 10895.
13. F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73.