JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Scandium Arene Inverted-Sandwich Complexes Supported by a Ferrocene Diamide Ligand

Wenliang Huang, Saeed I. Khan, and Paula L. Diaconescu*

Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095, United States

S *Supporting Information*

ABSTRACT: The synthesis and characterization of the first scandium arene inverted-sandwich complexes supported by a ferrocene diamide ligand (NN^{fc}) are reported. Through the use of $(NN^{fc})ScI(THF)_2$ as a precursor and potassium graphite (KC_8) as a reducing agent, the naphthalene and anthracene complexes $[(NN^{fc})Sc]_2(\mu\text{-}C_{10}H_8)$ and $[(NN^{fc})Sc]_2(\mu\text{-}C_{14}H_{10})$, respectively, were synthesized and isolated in moderate to high yields. Both molecular structures feature an inverted-sandwich geometry and exhibit short Fe−Sc distances. DFT calculations were employed to gain understanding of the electronic structures of these new scandium arene complexes. A variable-temperature NMR spectroscopic study of $[(NN^{fc})Sc]_2(\mu\text{-}C_{14}H_{10})$ indicated that two different structures are accessible in solution. Reactivity studies showed that the naphthalene complex $[(NN^{fc})Sc]_2(\mu\text{-}C_{10}H_8)$ can be converted to the corresponding anthracene species $[(NN^{fc})Sc]_2(\mu\text{-}C_{14}H_{10})$ and that $[(NN^{fc})Sc]_2(\mu\text{-}C_{10}H_8)$ can act as either a reductant or a proton acceptor. The reaction of $[(NN^{fc})Sc]_2(\mu\text{-}C_{10}H_8)$ with excess pyridine led to a rare example of C−C bond formation between two pyridine rings at the para position.

Complexes of rare-earth metals (REMs) (i.e., group-3 metals and lanthanides) and reduced arenes have long been targeted because of their fundamental importance and their potential as multielectron reagents.[1] Arenes have outstanding stability because of their aromaticity, but the accessibility of both their π and π^* orbitals allows them to serve as multielectron neutral or anionic ligands. REMs, because of their large ionic radii and high positive charges, can have high coordination numbers without sacrificing the strength of interactions with a ligand. As a consequence, arenes serve as excellent ligands for REM complexes.[1] The first authentic lanthanide arene complex was synthesized in 1986,[2] and this was followed by reports of numerous other REM arene complexes. Among them, naphthalene complexes are the most studied and have been synthesized and characterized for almost all REMs.[1]

The series of REM naphthalene complexes is missing examples of scandium compounds. The synthesis of scandium arene sandwich complexes has been limited to the cocondensation of scandium metal vapors with benzene derivatives having bulky substituents (1,3,5-$^tBu_3C_6H_3$)[3] or aromatic heterocycles (2,4,6-$^tBu_3C_5H_2N$, $^tBu_3C_3P_3$) to give formally zero-valent scandium complexes;[4−6] the gas-phase reaction of scandium ions with benzene and its derivatives led to products that could only be characterized by mass spectrometry.[7]

Scandium has the smallest ionic radius among REMs, a feature that enables special properties and reactivity of its complexes[8,9] but destabilizes its reduced arene complexes. Cationic scandium(III) arene complexes supported by β-diketiminato ligands have been isolated and structurally characterized.[10,11] These compounds feature metal−arene interactions; however, these interactions are mainly electrostatic, and the arene is not reduced.

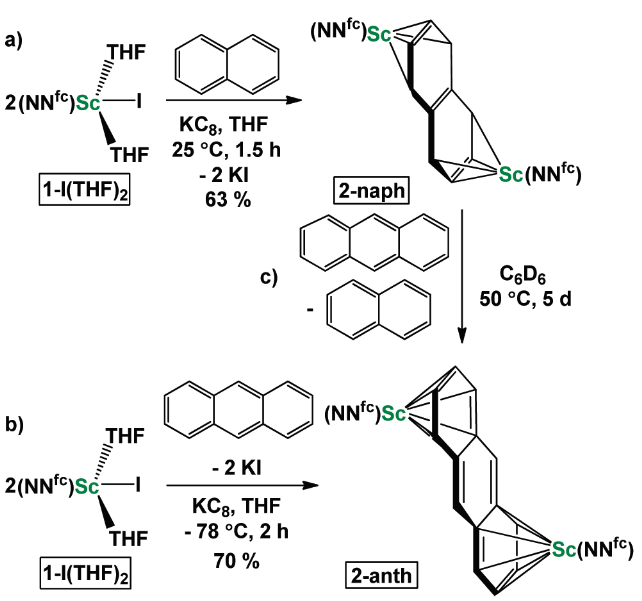
Although dinuclear inverted-sandwich complexes of yttrium/lutetium and reduced naphthalene with the general formula $(\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Ln)_2(\mu\text{-arene})$ (arene = $C_{10}H_8$, $C_{10}H_7Me$; Ln = Y, Lu) have been prepared by the reaction of a mixture of potassium graphite (KC_8) and naphthalene or 1-methylnaphthalene with the yttrium complex $(\{PhP[CH_2(SiMe_2)N(SiMe_2)CH_2]_2PPh\}Y)_2(\mu\text{-}Cl)_2$ or its lutetium analogue[12] and homoleptic or mixed-halide naphthalene complexes of larger lanthanides are known,[13−26] no analogous scandium naphthalene complexes have been reported. The same situation applies to anthracene and other polyaromatic hydrocarbons.[1] Herein we describe the synthesis and characterization of the first scandium arene inverted-sandwich complexes, which are supported by the ferrocene (fc) diamide ligand 1,1′-$(NSi^tBuMe_2)_2fc$ (NN^{fc}).

We anticipated[27] that NN^{fc} could serve as a suitable ancillary ligand to support a scandium precursor to be employed in reduction chemistry. The scandium iodide complex $(NN^{fc})ScI(THF)_2$ [**1-I(THF)$_2$**] was synthesized by heating $(NN^{fc})Sc(CH_2Ar)(THF)$ [**1-(CH$_2$Ar)(THF)**, Ar = 3,5-$Me_2C_6H_3$] with 10 equiv of MeI in toluene at 85 °C [see the Supporting Information (SI) for details]. Treatment of **1-I(THF)$_2$** with 1.2 equiv of KC_8 and 0.5 equiv of naphthalene in THF (Scheme 1a) caused an immediate color change from yellow to dark-purple; in the absence of **1-I(THF)$_2$**, the color of KC_8 and naphthalene in THF was dark-green. After the mixture was stirred for 1.5 h at ambient temperature, the volatiles were removed, affording a red-to-purple oily film. Surprisingly, when this oily film was extracted with toluene, the filtrate had a very dark blue color. Single-crystal X-ray diffraction was used to determine the solid-state structure of this scandium naphthalene complex, $[(NN^{fc})Sc]_2(\mu\text{-}C_{10}H_8)$ (**2-naph**) (Figure 1).

The molecular structure of **2-naph** is reminiscent of previously reported yttrium naphthalene complexes.[12] The naphthalene is distorted from planarity, with C2/C3 and C2′/C3′ displaced in

Received: May 10, 2011
Published: June 10, 2011

Scheme 1. (a) Synthesis of **2-naph**; (b) Synthesis of **2-anth**; (c) Conversion of **2-naph** to **2-anth**



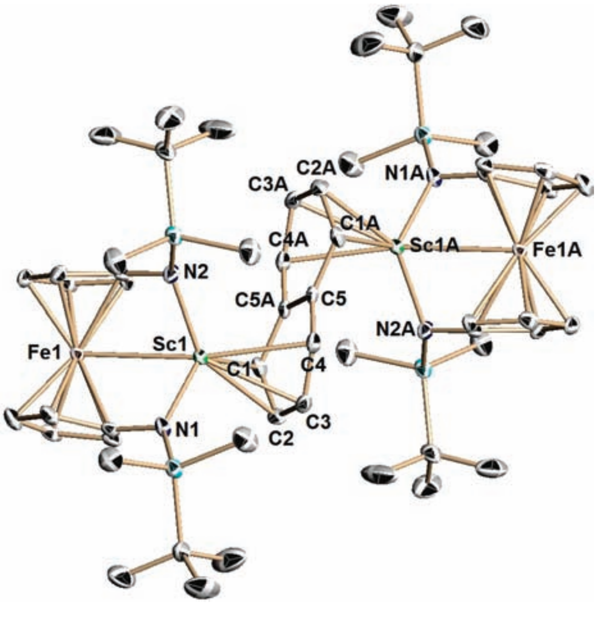


Figure 1. Molecular structure of **2-naph**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Sc1−N1, 2.056(4); Sc1−N2, 2.090(4); Sc1−C1, 2.511(4); Sc1−C2, 2.503(4); Sc1−C3, 2.506(5); Sc1−C4, 2.536(5); Sc1−Fe1, 2.831(1); C1−C5A, 1.421(6); C1−C2, 1.428(7); C2−C3, 1.368(7); C3−C4, 1.425(7); C4−C5, 1.426(6); C5−C5A, 1.445(9); Fe1−Sc1−C1, 105.1(1); Fe1−Sc1−C4, 167.0(1); C5A−C1−C2, 120.3(4); C4−C5−C5A, 117.0(5).

opposite directions with respect to the plane composed of the other six carbon atoms (~20° torsion angle). The bonds in the naphthalene are best described as two isolated double bonds (C2═C3 and C2′═C3′) with short distances averaging 1.37 Å and an eight-electron−six-center delocalized π system formed by the other six carbons. Scandium binds in an η^4 fashion to C1−C4 with similar distances averaging 2.51 Å. These features are also reminiscent of the lithium naphthalene dianion $[Li(TMEDA)]_2$-(μ-$C_{10}H_8$),[28] except that in that case, the localization of the double bond between C2 and C3 was more prominent.

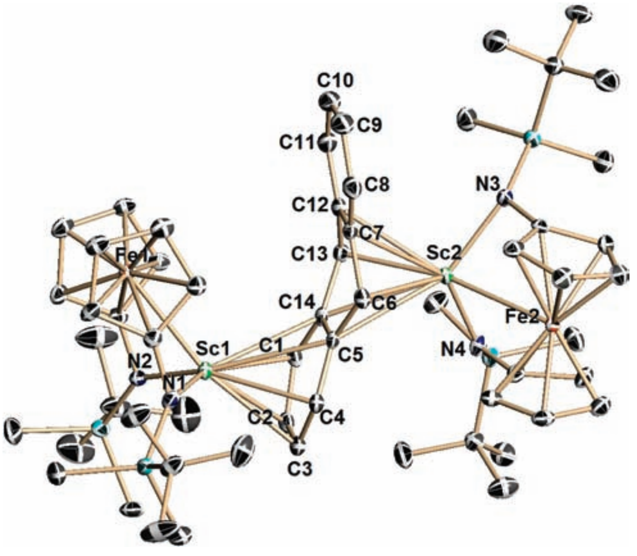
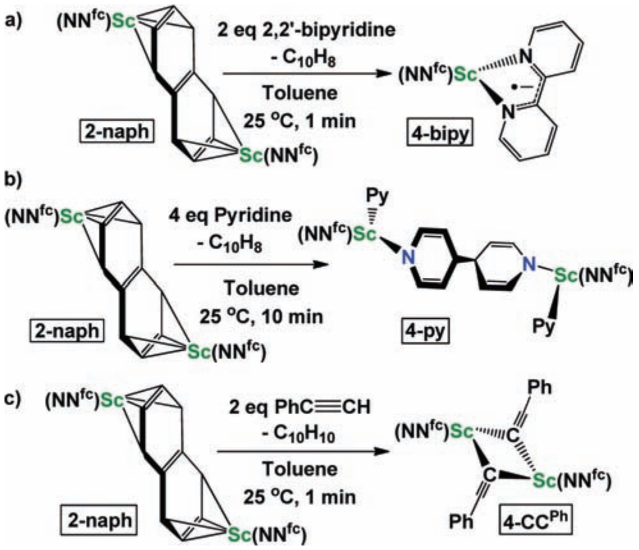


Figure 2. Molecular structure of **2-anth**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Sc1−N1, 2.057(3); Sc1−N2, 2.061(3); Sc1−Fe1, 2.743(1); Sc2−N3, 2.072(3); Sc2−N4, 2.078(3); Sc2−Fe2, 2.851(1); Sc1−C1, 2.583(3); Sc1−C2, 2.523(3); Sc1−C3, 2.543(3); Sc1−C4, 2.605(3); Sc1−C14, 2.833(3); Sc2−C5, 2.844(3); Sc2−C6, 2.442(3); Sc2−C7, 2.679(3); Sc2−C12, 2.707(3); Sc2−C13, 2.464(3); Sc2−C14, 2.863(3); C14−C1, 1.403(4); C1−C2, 1.428(5); C2−C3, 1.385(5); C5−C14, 1.452(4); C5−C6, 1.436(4); C6−C7, 1.470(4); C7−C12, 1.416(4); N1−Sc1−N2, 112.0(1); N3−Sc2−N4, 114.3(1); Fe1−Sc1−C1, 121.1(1); Fe2−Sc2−C6, 101.3(1); Fe2−Sc2−C13, 167.6(1); C4−C5−C6, 124.6(3); C6−C7−C8, 123.6(3).

Despite the usual structural parameters shared with other REM or alkali-metal naphthalene dianion complexes, **2-naph** features a unique interaction between scandium and the ferrocene backbone. The Fe−Sc distance is 2.83 Å, which is significantly shorter than that in **1-I(THF)$_2$** (3.12 Å) and among the shortest Fe−Sc distances observed by us,[27,29] indicating a relatively strong interaction between scandium and iron that might be essential for the stability of **2-naph**. We previously proposed[27] that the ferrocene diamide ligand behaves as a pincer with two hard, inflexible amide donors and one soft, flexible Fe(II) donor that can act as an electron reservoir and engage in a donor−acceptor interaction with the electrophilic metal center as needed. In addition, the short Fe−Sc distance allows the ferrocene backbone to shield the scandium center and provide steric protection. This proposal is supported by the fact that when $[(Me_3Si)_2N]_2ScI(THF)$ [**3-I(THF)**] was used, the formation of a scandium naphthalene complex was not observed (see the SI for details).

To explore further the scope of the scandium arene synthesis, anthracene was employed as well. Reaction of 0.5 equiv of anthracene and 1.5 equiv KC_8 with **1-I(THF)$_2$** at −78 °C led to the corresponding anthracene complex $[(NN^{fc})Sc]_2(\mu$-$C_{14}H_{10})$ (**2-anth**) in 70% yield (Scheme 1b). Single crystals of **2-anth** (Figure 2) were grown from a concentrated diethyl ether solution stored at −35 °C for a week. The molecular structure of

Scheme 2. (a) Reaction of **2-naph** with 2 equiv of 2,2′-Bipyridine To Form **4-bipy**; (b) Reaction of **2-naph** with 4 equiv of Pyridine To Form **4-py**; (c) Reaction of **2-naph** with 2 equiv of Phenylacetylene To Form **4-CC^{Ph}**



2-anth is similar to that of ({PhP[$CH_2(SiMe_2)N(SiMe_2)CH_2]_2$PPh}Y)$_2$($\mu$-$C_{14}H_{10}$),[12] featuring an unsymmetrical coordination mode. The two scandium moieties are η^6-bound to the middle ring and an outer ring on opposite sides of the anthracene plane. ^{1}H NMR spectroscopy, however, indicated that the solution structure of **2-anth** is symmetrical at 25 °C (see the SI for details). In order to study the dynamics of **2-anth** in solution, a variable-temperature NMR experiment was performed (see the SI for details). Cooling a toluene-d_8 solution of **2-anth** resulted in peak broadening; coalescence took place at −15 °C. Further cooling led to the appearance of new, sharp peaks consistent with the presence of the unsymmetrical molecular structure obtained by X-ray crystallography.

The reaction of **2-naph** with anthracene at 50 °C in C_6D_6 led to its complete conversion to **2-anth** and free naphthalene (Scheme 1c). No significant decomposition of either **2-anth** or **2-naph** was observed after heating at 70 °C for 1 day; however, both decomposed rapidly in THF at 70 °C, leading to free naphthalene or anthracene as well as an intractable mixture of scandium products. We propose that the conversion of **2-naph** to **2-anth** occurs because the reduction potential of naphthalene is more negative than that of anthracene;[30] therefore, **2-naph** could reduce anthracene to its dianion to form **2-anth** and generate free naphthalene. We do not presently understand the difference in behavior between **2-naph**/**2-anth** and the analogous yttrium complexes reported by the Fryzuk group that do not show such behavior.[12]

REM arene complexes are considered to be good precursors for other difficult-to-synthesize REM complexes;[1] therefore, we became interested in exploring the reactivity of these new scandium arene complexes. The addition of 2,2′-bipyridine to a C_6D_6 solution of **2-naph** was associated with an immediate color change from dark-blue to dark-green (Scheme 2a). The formation of the previously characterized bipyridyl radical anion complex (NN^{fc})Sc($C_{10}H_8N_2$) (**4-bipy**)[31] was confirmed by ^{1}H NMR spectroscopy, which also indicated that **4-bipy** was the only scandium product formed, with free naphthalene as the byproduct. This reaction shows that **2-naph** can act as a two-electron reductant.

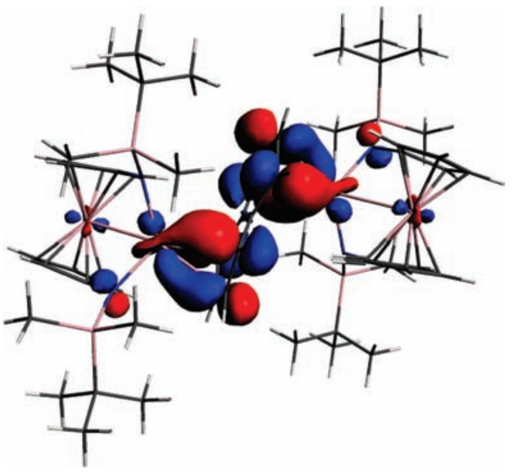


Figure 3. HOMO of **2-naph**.

Although 2,2′-bipyridine is known to react with reducing agents to form scandium bipyridyl radical anion complexes,[32] no reaction of REM arene complexes with pyridine has been reported to date. The reaction of **2-naph** with excess pyridine was fast and clean (Scheme 2b). The color of the solution changed immediately from dark-blue to pale-yellow after the addition of excess pyridine. X-ray crystallography corroborated the isolation of a rare, reductively 4,4′-coupled diamide linker bridging the two scandium fragments (see the SI for details). This type of reduction has been observed only in the reactions of divalent thulium complexes with pyridine.[33,34]

The reduced nature of the diamide linker was clearly demonstrated by the metrical parameters of **4-py**: the two carbons at the 4 and 4′ positions were sp^3-hybridized (average angle of 111° and average distances of 1.53 Å to the neighboring carbon atoms); the average distance between scandium and the amide nitrogens was 2.10 Å, which is 0.14 Å shorter than that to the pyridine nitrogen and close to the average distance to the ferrocene diamide nitrogens (2.08 Å). These structural features are comparable to those of previously reported thulium complexes.[33,34] Another interesting feature is the rather short distance of 2.96 Å between scandium and iron; short scandium−iron distances were not observed by us previously in the presence of a strong σ donor such as pyridine.[35,36]

Another common substrate used with REM arene complexes is phenylacetylene.[1] The reaction of **2-naph** with 2 equiv of phenylacetylene led to the immediate formation of **4-CC^{Ph}** (Scheme 2c); a mixture of $C_{10}H_{10}$ isomers was also observed. X-ray crystallography confirmed the isolation of the phenylacetylide-bridged dimer with short Sc−Fe and Sc−Sc distances (see the SI for details). The average Sc−Fe distance was 2.89 Å, which is close to that in **2-naph**, indicating a relatively strong Sc−Fe interaction. The Sc−Sc distance was 3.45 Å, which is close to the sum of the covalent radii (3.40 Å).[37] The latter distance likely does not indicate any bonding interaction between the two scandium centers but is rather a consequence of the small size of the acetylide ligand.

In order to understand the nature of the bonding in **2-naph**, density functional theory (DFT) calculations were carried out on the full molecule, and the optimized structural parameters matched well with those of the solid-state structure (see the SI for details). The results indicated that the electronic structure of **2-naph** bears similarities to that of other REM naphthalene complexes.[1] As expected, the HOMO is composed mostly of naphthalene orbitals, consistent with its dianionic nature (Figure 3). Charge calculations showed that the negative charge is located mainly on C1 and C4 (average −0.02), while the other naphthalene carbon atoms bear slightly positive charges (average for C2 and C3, +0.17; C5, +0.22). More interestingly, a Mayer bond order of 0.41 was calculated for the iron−scandium interaction; this value is larger than the average Mayer bond order for the Sc−C1 and Sc−C4 bonds (0.24). The Mulliken charges (Sc, +1.02; Fe, −0.04) indicated a donor−acceptor interaction from iron to scandium, in agreement with earlier proposals.[27] DFT calculations on **2-anth** were also carried out. The calculated Mayer bond orders for the Fe−Sc interactions were 0.44 and 0.41 for the end- and middle-ring Sc atoms, respectively. The Mulliken charges for Sc1, Sc2, Fe1, and Fe2 were +1.04, +1.07, −0.05, and −0.05, respectively, which are similar to the values in **2-naph**. The calculated bond orders together with the short Fe−Sc distances determined experimentally support the existence of relatively strong interactions between iron and scandium in **2-naph** and **2-anth**.

In summary, we successfully synthesized and structurally characterized the first scandium arene inverted-sandwich complexes. DFT calculations on the scandium naphthalene and anthracene complexes shed light on their electronic structures as well as the importance of the ferrocene backbone in stabilizing these motifs. On the basis of variable-temperature NMR spectroscopy studies, the scandium anthracene complex adopts a symmetrical structure at ambient temperature in solution but an unsymmetrical structure at lower temperatures. The solid-state structure determined by X-ray crystallography at 100 K matched the unsymmetrical structure found in solution. The reactivity of the scandium naphthalene complex was explored; in addition to its reactions with 2,2′-bipyridine and phenylacetylene, the reaction with pyridine led to a rare example of reductive C−C coupling of pyridine. Our current efforts are focused on further exploring the reactivity of the scandium arene complexes and applying the C−C bond formation to organic synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data (CIF) and experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

pld@chem.ucla.edu

■ ACKNOWLEDGMENT

This work was supported by UCLA, the Sloan Foundation, and the NSF (CAREER Grant).

■ REFERENCES

(1) Bochkarev, M. N. *Chem. Rev.* **2002**, *102*, 2089.

(2) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657.

(3) Cloke, F. G. N.; Khan, K.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 1372.

(4) Cloke, F. G. N. *Chem. Soc. Rev.* **1993**, *22*, 17.

(5) Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7630.

(6) Arnold, P. L.; Cloke, F. G. N.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1998**, 797.

(7) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346.

(8) Moeller, T.; Martin, D. F.; Thompson, L. C.; Ferrús, R.; Feistel, G. R.; Randall, W. J. *Chem. Rev.* **1965**, *65*, 1.

(9) Zimmermann, M.; Anwander, R. *Chem. Rev.* **2010**, *110*, 6194.

(10) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622.

(11) Hayes, P. G.; Piers, W. E.; Parvez, M. *Chem.—Eur. J.* **2007**, *13*, 2632.

(12) Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Rettig, S. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 767.

(13) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749.

(14) Kirillov, E. N.; Trifonov, A. A.; Nefedov, S. E.; Eremenko, I. L.; Edelmann, F. T.; Bochkarev, M. N. *Z. Naturforsch.* **1999**, *54b*, 1379.

(15) Bochkarev, M. N.; Fedushkin, I. L.; Larichev, R. B. *Russ. Chem. Bull., Int. Ed.* **1996**, *45*, 2443.

(16) Fedushkin, I. L.; Bochkarev, M. N.; Schumann, H.; Esser, L.; Kociok-Kohn, G. *J. Organomet. Chem.* **1995**, *489*, 145.

(17) Basalgina, T. A.; Kalinina, G. S.; Bochkarev, M. N. *Organomet. Chem. USSR* **1989**, *2*, 606.

(18) Bochkarev, M. N.; Trifonov, A. A.; Cherkasov, V. L.; Razuvaev, G. A. *Organomet. Chem. USSR* **1988**, *1*, 216.

(19) Bochkarev, M. N.; Fagin, A. A.; Fedushkin, I. L.; Trifonov, A. A.; Kirillov, E. N.; Eremenko, I. L.; Nefedov, S. E. *Mater. Sci. Forum* **1999**, *315−317*, 144.

(20) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Schumann, H.; Demtschuk, J. J. *J. Chem. Soc., Chem. Commun* **1997**, 1783.

(21) Fedushkin, I. L.; Nevodchikov, V. K.; Cherkasov, V. K.; Bochkarev, M. N.; Schumann, H.; Girgsdies, F.; Gorlitz, F. H.; Kociok-Köhn, G.; Pickardt, J. *J. Organomet. Chem.* **1996**, *511*, 157.

(22) Arakawa, T.; Shimada, S.; Adachi, G.-Y.; Shiokawa, J. *Inorg. Chim. Acta* **1988**, *145*, 327.

(23) Fedorova, E. A.; Glushkova, N. V.; Bochkarev, M. N.; Schumann, H.; Hemling, H. *Russ. Chem. Bull., Int. Ed.* **1996**, *45*, 1996.

(24) Bochkarev, M. N.; Trifonov, A. A.; Cherkasov, V. K.; Razuvaev, G. A. *J. Gen. Chem. USSR* **1988**, *58*, 637.

(25) Bochkarev, M. N. *Proc. Indian Natl. Sci. Acad.* **1989**, *55A*, 170.

(26) Bochkarev, M. N.; Trifonov, A. A.; Fedorova, E. A.; Emelyanova, N. S.; Basalgina, T. A.; Kalinina, G. S.; Razuvaev, G. A. *J. Organomet. Chem.* **1989**, *372*, 217.

(27) Diaconescu, P. L. *Acc. Chem. Res.* **2010**, *43*, 1352.

(28) Melero, C.; Guijarro, A.; Yus, M. *Dalton Trans.* **2009**, 1286.

(29) Huang, W.; Carver, C. T.; Diaconescu, P. L. *Inorg. Chem.* **2011**, *50*, 978.

(30) Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1989**, *111*, 2325.

(31) Williams, B. N.; Huang, W.; Miller, K. L.; Diaconescu, P. L. *Inorg. Chem.* **2010**, *49*, 11493.

(32) Beetstra, D. J.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2003**, *22*, 4372.

(33) Fedushkin, I. L.; Nevodchikov, V. I.; Bochkarev, M. N.; Dechert, S.; Schumann, H. *Russ. Chem. Bull.* **2003**, *52*, 154.

(34) Jaroschik, F.; Nief, F.; Goff, X.-F. L.; Ricard, L. *Organometallics* **2007**, *26*, 3552.

(35) Carver, C. T.; Williams, B. N.; Ogilby, K. R.; Diaconescu, P. L. *Organometallics* **2010**, *29*, 835.

(36) Carver, C. T.; Diaconescu, P. L. *J. Alloys Compd.* **2009**, *488*, 518.

(37) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.