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Synthesis and Characterization of a New Thiophene-Bridged Diamidophosphine [NPN] Donor Set and Its Coordination Chemistry with Zirconium(IV): Unexpected Deprotonation−Lithiation Sequence with a Mesitylaminothiophene Precursor

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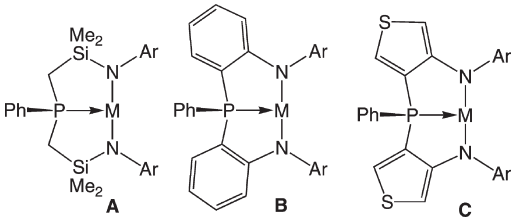
The synthesis and characterization of the thiophene-bridged diamidophosphine proligand $[NPN]^SH_2$ (**2**) (where $[NPN]^SH_2 = \{[N\text{-}(2,4,6\text{-}Me_3C_6H_2)(3\text{-}NH\text{-}SC_4H_2\text{-}2\text{-})]_2PPh\}$) along with several $[NPN]^SZrX_2$ (X = NMe_2, Cl, I) complexes are presented. The ligand precursor $[NPN]^SH_2$ was prepared from *N*-(2,4,6-$Me_3C_6H_2$)(3-NH-4-Br-SC_4H_2) (**1**), ^{t}BuLi, and $PhPCl_2$ in Et_2O in 50% yield; the stereochemistry of the ligand precursor was unexpected and likely resulted from a competitive bromine−lithium exchange and deprotonation sequence with the thiophene starting material **1** and ^{t}BuLi. A mechanism to rationalize the observed stereochemistry of the product is proposed following deuteration experiments. $[NPN]^SZr(NMe_2)_2$ (**8**) can be prepared in 80% yield by the direct reaction of $[NPN]^SH_2$ and $Zr(NMe_2)_4$ in toluene. Both $[NPN]^SZrCl_2$ (**9**) and $[NPN]^SZrI_2$ (**10**) are prepared in high yield by the reaction of **8** with excess Me_3SiCl or Me_3SiI, respectively.

Introduction

Our interest in tailoring the coordination environment around metal centers to make them suitable for dinitrogen activation has been focused on combinations of amido (NR_2) and phosphine (PR_3) donors arranged in multidentate arrays.[1−11] In particular, we have achieved considerable success with a tridentate combination involving two amido donors flanking a central phosphine unit, which we term NPN.[1,4,6,12,13] We have examined two modifications that differ in the linker groups as shown generically below; in **A** we have CH_2SiMe_2 linkers[6] that build off of our earlier ligand design work, and we have also initiated more robust systems that involve *o*-phenylene connectors,[4] as shown in **B**, which are common motifs in recent ligand designs.[14,15]



As both of these systems (**A** and **B**) have shown success in their ability to support N_2 activation, we have continued to examine changes in the linker to monitor what effect this might have on the stability and reactivity of the resultant metal complexes. It is well known that rather small changes in the ancillary ligands can evoke rather dramatic changes in coordination mode and reactivity of group 4 dinitrogen complexes.[16−18] We anticipated that this change would result in slightly different bite angles in the two chelate rings for **C** as compared to **B** and that the phosphine donor in **C** would be more electron rich than in **B**. How these

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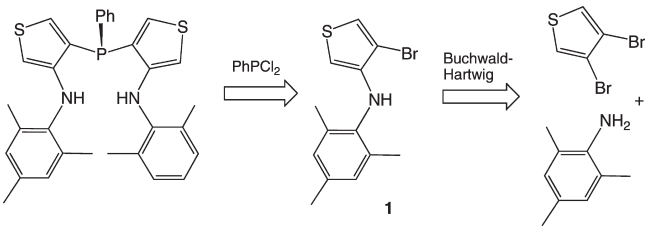
two changes would manifest in dinitrogen activation was not easily predictable, and so we initiated an exploration of the synthesis of this modified ligand system. In this study, we document our attempts to replace the *o*-phenylene linker of **B** with a 3,4-thiophene unit as shown in **C**. One of the surprising aspects of this work was the unanticipated stereochemistry of the final product that likely results from a competitive deprotonation−lithiation sequence. We also include the coordination chemistry of this new ligand system with zirconium(IV).

Results and Discussion

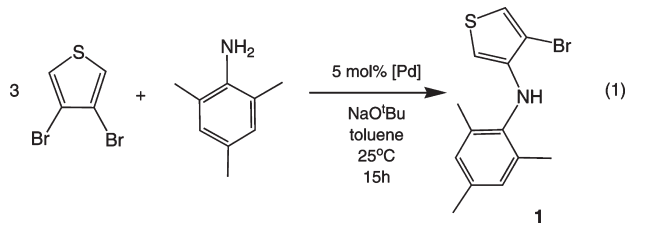
Synthesis of $[NPN]^{S}H_2$. The proposed retrosynthetic analysis for the synthesis of a new $[NPN]^{S}$-type system that has a 3,4-thiophene-type linker is shown in Scheme 1; the key intermediate is 3-mesitylamino-4-bromothiophene (mesityl = 2,4,6-trimethylphenyl = Mes) (**1**), which could be obtained by a selective Buchwald−Hartwig *N*-aryl amination[19,20] of 3,4-dibromothiophene.

Scheme 1



This amination reaction to yield **1** was optimized by screening several different Pd catalysts and reagent ratios; the results with the approximate gas chromatography−mass spectrometry (GC-MS) results are shown in Table S1 in the Supporting Information.

The N-heterocyclic carbene Pd complex (SIPr)Pd(allyl)Cl (SIPr = [*N*,*N*′-bis(2,6-diisopropylphenyl)4,5-dihydroimidazol)-2-ylidene])[21] provided the most promising initial results. Optimal conditions were found to be with a 5% catalyst loading at room temperature; higher catalyst loadings yielded little improvement in yield, and higher temperatures led to the production of small amounts of the disubstituted N^3,N^4-dimesitylthiophene-3,4-diamine byproduct. Complete conversion to yield **1** could be achieved using 3 equiv of 3,4-dibromothiophene (eq 1). Separation of the product **1** from the excess 3,4-dibromothiophene is easily accomplished by silica gel column chromatography (R_f values of 0.19 and 0.71 in hexanes, respectively); the unreacted 3,4-dibromothiophene can then be recycled.



Compound **1** was obtained in 74% isolated yield and fully characterized by NMR spectroscopy, elemental analyses, and X-ray crystallography. The product is somewhat photo- and thermally sensitive, turning red gradually over time in the solid state. However, it can be stored indefinitely without any color change in the dark at −35 °C under N_2.

To the best of our knowledge, the synthesis of **1** is the first high-yielding Pd-catalyzed *N*-aryl amination coupling of 3,4-dibromothiophene to selectively yield the monosubstituted product under mild reaction conditions. Although the analogous reaction of diphenyl amine and 3,4-dibromothiophene to yield the monosubstituted product has been reported,[22] this product was not isolated, and a yield of 12% determined by GC-MS was reported. Similar reactions to produce either C−C bonded species, such as 3-benzyl-4-bromothiophene from 3,4-dibromothiophene,[23] or C−N bonded species, using monobromothiophenes[24−26] or polysubstituted monobromothiophenes,[27] are well documented.

Figure 1 displays the typical numbering scheme for thiophenes as well as the characteristic H−H coupling constants found for thiophene aromatic protons in appropriately substituted systems.[28] This numbering scheme is also applied to **1**, as it will become important in the following sections.

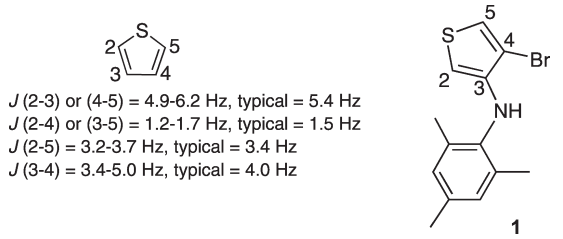


Figure 1. Typical numerical assignments and H−H coupling constants for different unsymmetrically disubstituted thiophenes shown on the left (without substituents); on the right, the assignments that will be used for **1**.

The assignment of the stereochemistry of bromo-amine **1** having the substituents in the 3,4-positions was made on the basis of the NMR coupling constant, $J(2-5) = 3.6$ Hz, which agrees with the values summarized in Figure 1; as already mentioned, this was confirmed by a solid-state X-ray crystal structure of **1**, which is reported in the Supporting Information. Thus it was expected that upon lithiation and quenching with 0.5 equiv of $PhPCl_2$, the PhP fragment would be installed in the 4-position of each ring, in accordance with our retrosynthetic analysis shown above in Scheme 1.

Not the Expected Stereochemistry. The details for the synthesis of the $[NPN]^{S}H_2$ ligand precursor, **2**, are shown in eq 2. All steps are done *in situ* beginning with the

(19) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348–1350.
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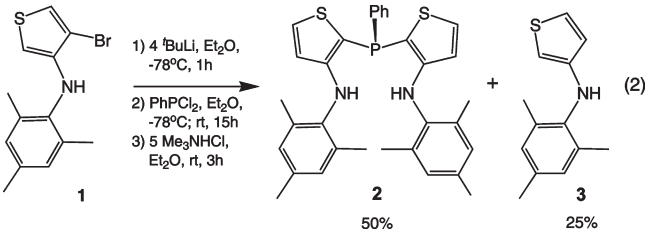
deprotonation−lithiation reaction using *tert*-butyllithium (^{t}BuLi), followed by the addition of $PhPCl_2$, and finally protonation using excess trimethylammonium hydrochloride (Me_3NHCl); the isolated yield of **2** is 50%. Also formed in this reaction is the debrominated 3-mesitylaminothiophene **3** in 25% yield. ^{t}BuLi was used rather than ^{n}BuLi since the latter generated considerable quantities of unreacted **1**, which complicated the purification of the product.

The PhP fragment, as shown in the retrosynthetic analysis in Scheme 1, was expected to be in the 4-position of both thiophene rings since bromine−lithium exchange is known to lead to C−Li bonds in those positions. For example, the reaction of 3,4-dibromothiophene with successive BuLi additions and quenches with various electrophiles[29,30] such as Pr^iSSPr^i leads regiospecifically to the formation of 3,4-disubstituted thiophene derivatives with no evidence of the formation of 2- or 5-isomers. Thus, we were surprised to find that the anticipated 3,4-product was not formed; instead, the PhP moiety was determined to be in the 2-position of each thiophene ring, as shown in eq 2.



The $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 shows one singlet at −55.5 ppm, which only indicates that it is a single compound. At first glance, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** were consistent with the proposed 3,4-disubstituted structure. However, upon more detailed analysis of the coupling constants on the thiophene unit in the ^1H NMR spectrum (see Figure 2), evidence mounted that the 2-substituted isomer (eq 2) was in fact the product of this reaction.

Two thiophene signals were observed: a doublet at 6.88 ppm and a doublet of doublets at 6.19 ppm (due to coupling to both H and P) with J_{H-H} values of 5.2 Hz (the dd also had J_{P-H} = 2.6 Hz). As shown in Figure 1, this H−H coupling constant value is indicative of two protons side-by-side in the 4,5-positions of the thiophene ring *and not* across the sulfur of the ring as in the expected 2,5-positions.[28] Unequivocal confirmation of the structure was obtained by single-crystal X-ray diffraction studies. The solid-state structure of the compound is shown in Figure 3.

Deuteration Studies Related to $[NPN]^SH_2$ Formation. In an effort to try to understand how the PhP fragment could have ended up in the 2-position rather than the 4-position, a series of deprotonation−lithiation, deuterium-quench

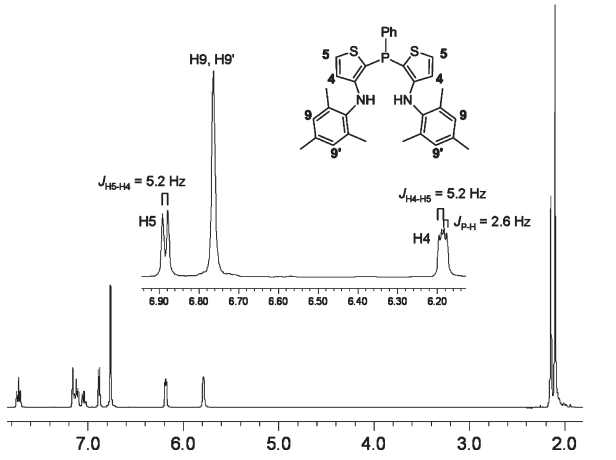


Figure 2. 400 MHz ^1H NMR spectrum (C_6D_6) of **2**. The vicinal coupling constant of 5.2 Hz between H4 and H5 is consistent with the PhP fragment in the 2-position.

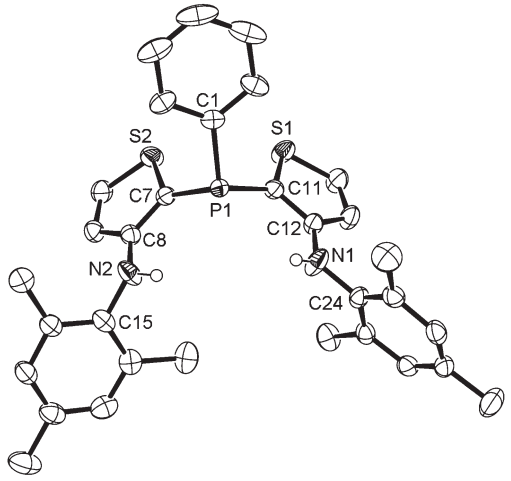


Figure 3. ORTEP drawing of the solid-state molecular structure of **2** (ellipsoids drawn at the 50% probability level). All hydrogen atoms, except the N−H bonds, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−P1 1.8172(17), C7−P1 1.7893(17), C11−P1 1.7889(17), C7−S2 1.7307(17), C11−S1 1.7316(16), C8−N2 1.375(2), C12−N1 1.382(2), N2−C15 1.426(2), N1−C24 1.414(2), C1−P1−C7 101.70(8), C1−P1−C11 105.03(8), C7−P1−C11 105.76(8), C12−N1−C24 123.97(16), C8−N2−C15 121.92(15).

experiments were performed. The first involved addition of 2 equiv of ^{t}BuLi[31−33] to **1** followed by quenching with 2 equiv of CF_3COOD; the reaction times, temperatures, and concentrations used were identical to those used to prepare **2**, except that instead of quenching with $PhPCl_2$, deuterated trifluoroacetic acid was added. The averaged results of two runs, with H/D ratios integrated by ^1H NMR spectroscopy in C_6D_6, are accurate to ±5% (eq 3); clearly evident is the fact that the starting bromo-amine **1** was consumed and partially deuterated 3-mesitylaminothiophene **3** was the only product observed. Deuterium was incorporated at the amine and both the 2- and 4-positions in the ratios indicated; the fact that a total of approximately 2 equiv of deuterium was detected in **3(H/D)** is consistent with a mixture of dilithio species being present.

(29) Reddinger, J. L.; Reynolds, J. R. *J. Org. Chem.* **1996**, *61*, 4833–4834.
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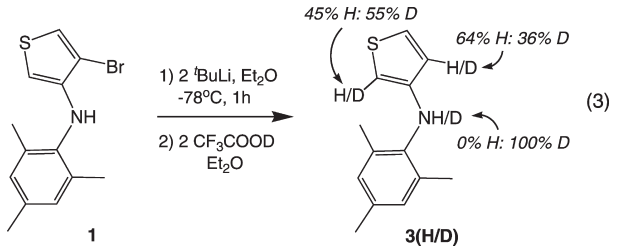
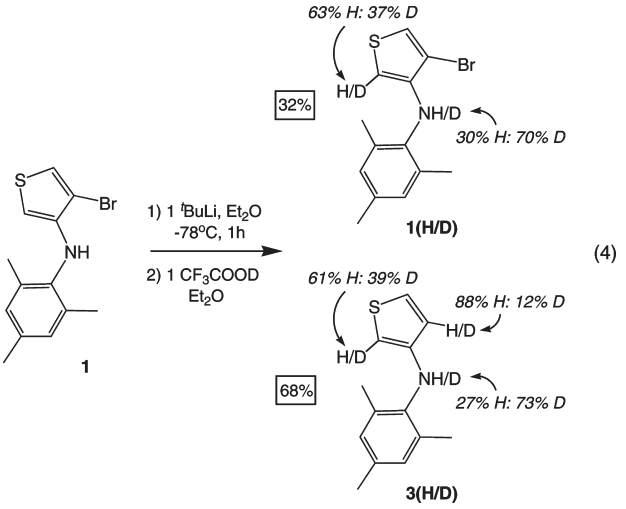


Most interestingly, deuterium was detected at the 2-position, which is consistent with the formation of phosphine substitution at this position.

An identical experiment using just 1 equiv of ^{t}BuLi, and quenching with 1 equiv of CF_3COOD, generates two products, as shown in eq 4 (ratios accurate to ±5%).



The major product (68%) is the debrominated 3-mesitylaminothiophene **3(H/D)**, which is the only observed product in the reaction of **1** with 2 equiv of ^{t}BuLi (eq 3), and the minor product (32%) is the starting 4-bromo-3-mesitylaminothiophene (**1**) with deuterium incorporation at the N-H position and at the 2-position (indicated as **1(H/D)** in eq 4). This last experiment indicates that bromine−lithium exchange is a competitive process with deprotonation of the N-H moiety;[34,35] interestingly, the presence of deuterium in the 2-position of **1(H/D)** in eq 4 suggests that deprotonation at this position may also be occurring to some extent. This all suggests that these processes may be under kinetic control since thermodynamic control would have only deuterium at the most acidic site, the amine N-H. The actual percentages of deuterium incorporation are not easily interpreted due to various intermolecular and intramolecular deprotonation−protonation processes; nevertheless, both products show that there is deuterium incorporation at the 2-position.

Scheme 2 tries to rationalize the results of the deuteration studies by considering the reaction of **1** with ^{t}BuLi in a stepwise manner. The first equivalant of ^{t}BuLi could generate two monolithio species, **1-NLi** and **3-CLi**, which result from competitive N-H deprotonation and bromine−lithium exchange reactions. Both of these species would be expected to proceed further to generate the dilithio species **4**. However, while **4** is the expected dilithio species, the deuteration experiments and the observation of the stereochemistry of **2** require other processes to be occurring. One likely reaction is the intramolecular transfer of the N-H proton in **3-CLi** to generate **3-NLi**, which subsequently could react further with ^{t}BuLi in competition with or concurrently with the formation of **4** to generate dilithio **5**; this is the key species that is the presumed precursor to generate **2** by further reaction with $PhPCl_2$. We can rationalize the formation of **5** from **3-NLi** as being due to the influence of two cooperative effects: the first is that the deprotonated amine acts as a strong ortho-directing group[36,37] for deprotonation at both the 2- and 4-positions; the preference for deprotonation at the 2-position over the 4-position is a result of the second effect, which is that the C−H bonds at the 2,5-positions of thiophene are approximately 6 orders of magnitude more acidic that the C−H bonds at the 3,4-positions (pK_a values of 33 and 39, respectively).[38,39] This helps explain the formation of **5** from **3-NLi** by reaction with ^{t}BuLi; furthermore, the expected dilithio product **4** can rearrange via intermolecular deprotonation to generate **5**. Because there is deuterium incorporation at the 4-position (see eq 3), the fact that no phosphine substitution is observed at this position may be kinetic in origin, as the 2-Li species **5** may react more quickly than the 4-Li isomer **4**. If any unreacted **4** remains at the end of the reaction with $PhPCl_2$, it would be protonated by the added Me_3NHCl and generate **3** (Scheme 2), the only other product observed (eq 2); it should also be noted that **3** could arise via protonation of other lithio species such as **3-NLi** or **5** that do not react with $PhPCl_2$. The fact that no deuterium is incorporated at the 5-position (eqs 3 and 4) is consistent with the cooperative ortho-directing effect of the deprotonated amine; if this were just a result of the more acidic C−H bonds at the 2- and 5-positions as compared to the 3- and 4-positions, then deuterium incorporation should be observed at both of the 2- and the 5-positions α to the sulfur heteroatom of the thiophene ring. Most importantly, it is the ortho-directing effect of the lithium mesitylamide in the 3-position that changes the course of the reaction to regioselectively produce **2** with the phosphine moiety in the 2-position.

It should be noted that the two dilithio species **4** and **5** shown in Scheme 2 are not the only intermediates that are possible; the 4-bromo-dilithio derivative **6** could also be formed by reaction of **1-NLi** with ^{t}BuLi by deprotonation of the 2-C-H instead of bromine for lithium exchange. Indeed, bromine−lithium exchange of dilithio **6** could generate the trilithio species **7**, which could also be formed to some extent by the reaction of ^{t}BuLi with **4**. How important these other species are to the formation of **2** is not known. Interestingly, the reaction of **6** with CF_3COOD can account for the observed deuterium distribution found in **1(H/D)** shown in eq 4.

(34) Beak, P.; Musick, T. J.; Chen, C. W. *J. Am. Chem. Soc.* **1988**, *110*, 3538–3542.
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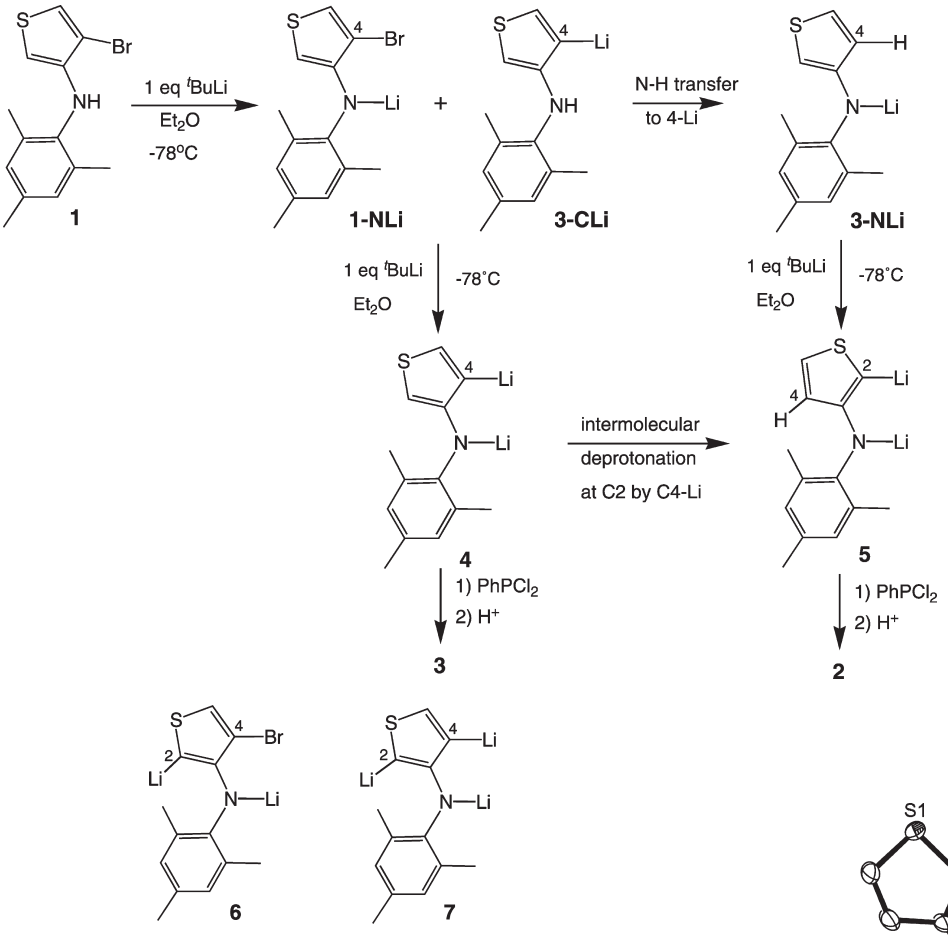
(39) Shen, K.; Fu, Y.; Li, J. N.; Liu, L.; Guo, Q. X. *Tetrahedron* **2007**, *63*, 1568–1576.

Scheme 2



Synthesis of $[NPN]^{S}ZrX_2$ (X = NMe_2, Cl, or I) Compounds. The coordination chemistry of this new thiophene-derived tridentate ligand is still of interest even though the stereochemistry is not what was initially targeted. The synthesis of a series of zirconium complexes can be easily undertaken starting from the ligand precursor **2** and using transamination procedures as shown in Scheme 3. The $[NPN]^{S}Zr(NMe_2)_2$ (**8**), $[NPN]^{S}ZrCl_2$ (**9**), and $[NPN]^{S}ZrI_2$ (**10**) complexes are all isolated in high yields and have been fully characterized.

The synthesis of **8** involves the transamination of a 1:1 mixture of **2** and tetrakis(dimethylamido)zirconium(IV), $Zr(NMe_2)_4$, in toluene to generate an 80% yield of a yellow solid. The $^{31}P\{^1H\}$ NMR spectrum of **8** in C_6D_6 shows a new peak downfield from the free ligand precursor **2** (−55.5 ppm) at −41 ppm, and the ^1H NMR spectrum shows five singlets in the aliphatic region, three of which can be assigned to two inequivalent sets of mesityl *o*-methyl groups due to hindered rotation, and the corresponding *p*-methyls, while the remaining two singlets correspond to the inequivalent NMe_2 groups. The thiophene protons in **8** display the same pattern as in **2** of a doublet and a doublet of doublets (due to H−H and P−H coupling). The solution NMR data suggest a C_s symmetric trigonal-bipyramidal complex with NMe_2 groups in both the equatorial and apical positions. These results are analogous to the related [NPN]*Zr$(NMe_2)_2$ ([NPN]* = {[*N*-(2,4,6-$Me_3C_6H_2$)(*o*-N-C_6H_4)]$_2$PPh}) complex previously reported[12] and are also consistent with the solid-state structure as shown in Figure 4.

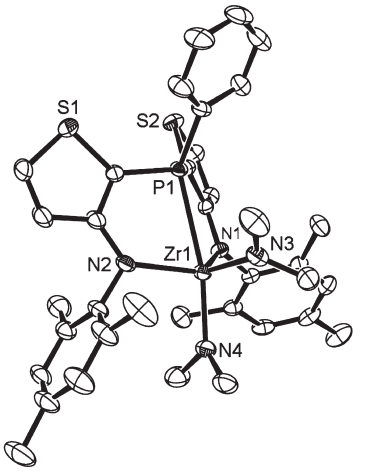


Figure 4. ORTEP drawing of the solid-state molecular structure of **8** (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−N1 2.1663(18), Zr1−N2 2.1464(19), Zr1−N3 2.022(2), Zr1−N4 2.0430(19), Zr1−P1 2.8410(6), N1−Zr1−N2 117.97(7), N3−Zr1−N4 99.19(8), N1−Zr1−P1 74.80(5), N2−Zr1−P1 72.24(5), N1−Zr1−N3 114.64(7), P1−Zr1−N3 88.78(6), P1−Zr1−N4 169.62(5).

As seen in Figure 4, the solid-state structure is indeed trigonal bipyramidal but distorted. The $[NPN]^{S}$ ligand binds facially to the metal center as expected since the phosphine donor is trigonal pyramidal. The N1−Zr1−P1 and N2−Zr1−P1 angles are noticeably smaller than 90°, which make the amide donors hinged out of the equatorial plane. Furthermore, the angles around N1 and N2 add up to 359.59° and 359.72°, respectively, consistent with sp^2 hybridization at the amide donors.

The dichloride $[NPN]^{S}ZrCl_2$ (**9**) can be readily synthesized from **8** using an excess of trimethylsilyl chloride (Me_3SiCl) in toluene and isolated in 80% yield. The $^{31}P\{^1H\}$ NMR

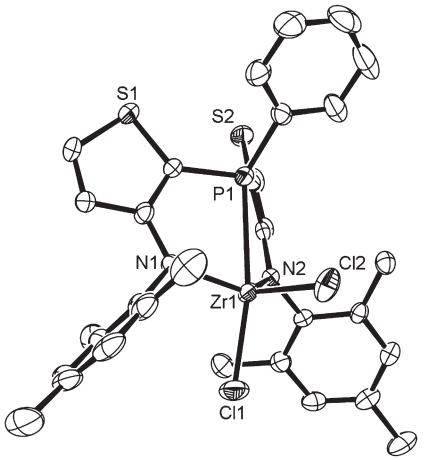


Figure 5. ORTEP drawing of the solid-state molecular structure of **9** (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−N1 2.072(3), Zr1−N2 2.070(3), Zr1−Cl1 2.3773(12), Zr1−Cl2 2.3909(16), Zr1−P1 2.8352(12), N1−Zr1−N2 121.28(11), Cl1−Zr1−Cl2 101.27(5), N1−Zr1−P1 72.64(8), N2−Zr1−P1 72.90(8), N1−Zr1−Cl2 115.28(9), P1−Zr1−Cl2 91.88(5), P1−Zr1−Cl1 166.84(4).

spectrum in C_6D_6 shows a singlet at −36 ppm. Similar to compound **8**, three peaks in the aliphatic region of the ^{1}H NMR spectrum can be assigned to the three separate methyl groups on the mesityl rings, thus suggesting hindered rotation. The solution NMR data are consistent with a C_s symmetric trigonal-bipyramidal complex, which was also the structure found in the solid state as shown in Figure 5.

The solid-state structure of dichloride **9** displayed in Figure 5 is largely analogous to the one shown in Figure 4. The structure is again distorted trigonal bipyramidal with the amide donors hinged out of the equatorial plane. One of the expected differences in changing from NMe_2 ligands to less bulky Cl ligands is the N1−Zr1−N2 angle, which increases slightly from approximately 118° to 121°, respectively. The Zr−N (average 2.09 Å for **8** and 2.07 Å for **9**), Zr−Cl (average 2.38 Å), and Zr−P (2.84 Å) bonds in both **8** and **9** are typical.[40,41]

The diiodide complex [NPN]^{S}ZrI_2 (**10**) can also be synthesized in high yield using an excess of trimethylsilyl iodide (TMSI). As shown in Scheme 3, this compound can be synthesized via two different routes. The cleanest route to this synthesis is by using **8** as the starting material and treating it with excess TMSI. After 3 h, a pure orange solid can be obtained following workup in 82% yield. The ^{31}P{^{1}H} NMR spectrum in C_6D_6 shows a singlet at −35 ppm, slightly shifted from the −36 ppm peak for the dichloride **9**. The ^{1}H NMR data are analogous to those for **9** and also suggest a C_s symmetric trigonal-bipyramidal complex. The solid-state structure, seen in Figure 6, shows this type of structure. As in both **8** and **9**, the structure is again distorted trigonal bipyramidal with the amide donors hinged out of the equatorial plane. The Zr−N (average 2.07 Å), Zr−I (average 2.78 Å), and Zr−P (2.84 Å) bonds are also typical in this complex.[40−42]

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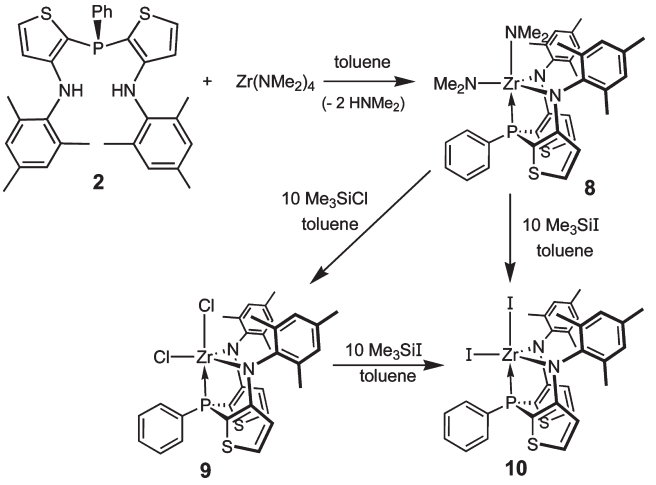
(41) Chien, P. S.; Liang, L. C. *Inorg. Chem.* **2005**, *44*, 5147–5151.
(42) King, W. A.; Di Bella, S.; Gulino, A.; Lanza, G.; Fragala, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 355–366.

Scheme 3



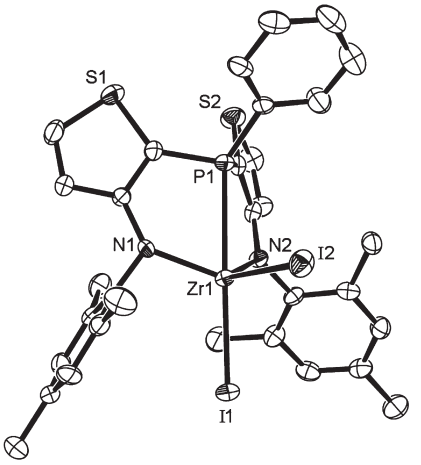


Figure 6. ORTEP drawing of the solid-state molecular structure of **10** (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−N1 2.054(4), Zr1−N2 2.081(5), Zr1−I1 2.7812(8), Zr1−I2 2.7757(15), Zr1−P1 2.8357(16), N1−Zr1−N2 116.80(17), I1−Zr1−I2 95.51(3), N1−Zr1−P1 70.08(12), N2−Zr1−P1 73.56(12), N1−Zr1−I2 114.40(12), P1−Zr1−I2 85.27(4), P1−Zr1−I1 177.40(4).

Diiodide **10** can also be readily synthesized from the dichloride species [NPN]^{S}ZrCl_2 (**9**). The reaction is performed in an analogous way using TMSI, but a longer reaction time of approximately 15 h is required. The yield is 88%. Although this may seem like the highest yielding route, the overall yield is lower since this is a two-step procedure. Finally, this complex can also be synthesized using a one-pot protocol. Mixing [NPN]^SH_2 (**2**) with Zr$(NMe_2)_4$ in toluene for 1 h, followed by the direct addition of excess TMSI, yields the desired product. The overall yield is 73%. Although this route provides the highest overall yield, this reaction is often complicated by the appearance of intractable impurities, requiring an extra filtration step. The NMR analysis also tends to show trace impurities. Thus, although convenient, this method does not yield the purest product: the optimal method for synthesizing **10** is by the first method described.

The effect of changing the *o*-phenylene linker in the original [NPN]* ligand system to a 2,3-thiophene moiety as

found in $[NPN]^S$ can be seen in some of the bond angles and bond distances of analogous complexes.[12] In [NPN]*$ZrCl_2$ the N−Zr−N bond angle is 113.96(9)°, whereas in **9** N1−Zr1N2 is 121.28(11)°; the Zr−P bond length in [NPN]*$ZrCl_2$ is 2.7229(8) Å, while for **9**, this bond lengthens to 2.8352(12) Å, a full 0.1 Å longer. While it is clear that these linkers do generate differences in the coordination complexes, the ramifications of these changes to the chemistry of these Zr(IV) complexes are currently under investigation.

Conclusions

In this report, the synthesis of $[NPN]^SH_2$ (**2**), a new tridentate mixed donor ligand precursor with 2,3-thiophene moieties linking mesityl amido and phosphine units, and its coordination chemistry with Zr(IV) are reported. The stereochemistry of **2** has the PhP fragment in the 2-position, which was unexpected, as the 3,4-dibromothiophene precursor should have led to the PhP moiety in the 4-position. Preliminary mechanistic investigations suggest a mechanism involving competitive deprotonation and bromine−lithium exchange reactions in which the ortho-directing effect of the deprotonated aryl amine in the 3-position can override the usually regiospecific bromine−lithium exchange process. A series of Zr(IV) complexes of this new ligand were synthesized. The $[NPN]^SZr(NMe_2)_2$ (**8**) complex is synthesized via transamination of $Zr(NMe_2)_4$ with **2**. The related $[NPN]^SZrCl_2$ and $[NPN]^SZrI_2$ complexes can be prepared by deamination of **8** with trimethylsilyl chloride or trimethylsilyl iodide, respectively. We are currently investigating the reduction of these halide complexes for the activation of N_2.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free N_2 or Ar by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a −35 °C freezer). Hexanes, toluene, pentane, and diethyl ether were purchased anhydrous from Aldrich, sparged with N_2, and passed through columns containing activated alumina and Ridox catalyst. C_6D_6 was dried on activated 5 Å molecular sieves and freeze−pump−thaw degassed three times. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV-300, a Bruker AV-400, or a Bruker AV-400inv spectrometer, operating at 300.1, 400.0, and 400.0 MHz for ^1H spectra, respectively. All spectra were recorded at room temperature. ^1H NMR spectra were referenced to residual protons in the deuterated solvent, C_6D_6 (7.16 ppm). $^{31}P\{^1H\}$ NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). $^{13}C\{^1H\}$ NMR spectra are referenced to residual solvent, C_6D_6 (128.0 ppm). Chemical shifts (δ) listed are in ppm, and absolute values of the coupling constants are in Hz. GC-MS spectra were recorded on an Agilent series 6890 GC system with a 5973 mass selective detector. Mass spectrometry (EI-MS), elemental analysis (C, H, N), and X-ray crystallography were all performed at the Department of Chemistry at the University of British Columbia.

Mesitylamine and $PhPCl_2$ (Aldrich) were both distilled prior to use. 3,4-Dibromothiophene (Alfa) was degassed by freeze−pump−thaw and mixed with activated molecular sieves (5 Å). CF_3COOD (purchased in sealed glass ampules), Me_3NHCl, NaO^{t}Bu, TMSCl, and TMSI were purchased from Aldrich and used without further purification. $Zr(NMe_2)_4$ was purchased from Strem and used without further purification. (SIPr)Pd(allyl)Cl was prepared by literature methods.[21] ^{t}BuLi (~1.7 M in pentane) was doubly titrated using a known literature procedure.[43] All other compounds were purchased from commercial suppliers and were used as received.

Synthesis of *N*-3-(NHMes)-4-Br-SC_4H_2 (1). A 500 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with (SIPr)Pd(allyl)Cl (1.17 g, 2 mmol), NaO^{t}Bu (4.33 g, 45 mmol), and toluene (300 mL). The reaction mixture was stirred for 5 min; then 3,4-dibromothiophene (13.7 mL, 124 mmol) and mesitylamine (5.8 mL, 41 mmol) were added all at once. The solution quickly turned dark green-brown and was allowed to stir overnight (15 h). The mixture was then poured on 300 mL of water in open air. The organic phase was separated and washed with another 2 × 300 mL of water. The combined aqueous extracts were washed with 2 × 100 mL of toluene. The organics were combined and dried with $MgSO_4$. The mixture was filtered and the toluene was removed by rotoevaporation. Column chromatography using silica gel of the resulting crude black liquid separated the excess 3,4-dibromothiophene (R_f = 0.71) from the desired product (R_f = 0.19) using hexanes as the solvent. Once the 3,4-dibromothiophene is separated, the polarity of the eluent can be increased to 2% Et_2O in hexanes. The total weight of the pure white product was 9.0 g (74% yield). Slow evaporation of a hexanes solution of the compound yielded single crystals suitable for X-ray crystallography.

^1H NMR (400 MHz, C_6D_6): δ 6.77 (s, 2H, Mes-H), 6.75 (d, J = 3.6 Hz, H_5), 5.29 (d, J = 3.6 Hz, H_2), 5.07 (bs, N-H), 2.16 (s, 3H, *p*-CH_3), 2.03 (s, 6H, *o*-CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 143.3, 137.2, 135.4, 135.2, 129.6, 122.4, 102.8, 96.8, 21.0 (*p*-CH_3), 17.9 (*o*-CH_3). Anal. Calcd for $C_{13}H_{14}BrNS$: C, 52.71; H, 4.76; N, 4.73. Found: C, 53.00; H, 4.95; N, 4.96. EI-MS (*m*/*z*): 297 $[M]^+$, 216 $[M - Br]^+$.

Synthesis of $[NPN]^SH_2$ (2). A 1 L, two-necked round-bottom Schlenk flask was equipped with a magnetic stirbar and two dropping funnels. One was charged with 2.04 equiv of ^{t}BuLi (1.74 M in pentane, 60 mL, 104 mmol) and the other with a dilute solution of 0.5 equiv of $PhPCl_2$ (3.38 mL, 25 mmol) in 250 mL of Et_2O. The round-bottom flask was loaded with 15 g (50 mmol) of **1** in 300 mL of Et_2O. The solution was stirred and was cooled to −78 °C (dry ice/acetone bath) on the Schlenk line. The ^{t}BuLi solution was added dropwise to the solution. The pale yellow solution was kept at −78 °C while stirring for 1 h following the addition. The $PhPCl_2$ solution was then added dropwise at −78 °C over 5 h. The solution gradually went from pale yellow to dark orange-brown. The solution was allowed to warm to room temperature overnight. The following morning, an excess of Me_3NHCl (11.95 g, 125 mmol) was added all at once to the stirring solution. The solution was stirred for 3 h, after which time the Et_2O was removed *in vacuo*. The brown residue was dissolved in ca. 200 mL of toluene and was filtered on a glass frit with Celite. The Celite was then washed with toluene. The toluene was thoroughly removed *in vacuo* to obtain a viscous dark blackish-brown residue. The residue was mixed with ca. 200 mL of hexanes. A pale beige solid precipitated and was filtered on a glass frit. Repeated trituration using hexanes yielded 6.8 g (50% yield) of pure product. Slow evaporation of a hexanes solution of the compound yielded single crystals suitable for X-ray crystallography.

^1H NMR (400 MHz, C_6D_6): δ 7.75−7.71 (m, 2H), 7.14−7.11 (m, 2H), 7.06−7.02 (m, 1H), 6.88 (d, J = 5.2 Hz, 2H), 6.76 (s, 4H), 6.19 (dd, J_{H-H} = 5.2 Hz, J_{P-H} = 2.6 Hz, 2H), 5.79 (*N-H*) (d, J_{P-H} = 3.2 Hz, 2H), 2.15 (s, 6H), 2.10 (s, 12H). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ −55.5. ^{13}C NMR (100 MHz, C_6D_6): δ 153.7 (d, J = 74.4 Hz), 138.0, 137.8, 135.6, 135.2, 132.2 (d, J = 70.8 Hz), 131.3 (d, J = 11.2 Hz), 129.5, 128.8 (d, J = 25.6), 128.4, 119.3 (d, J = 14.8 Hz), 103.8 (d, J = 61.2 Hz), 20.9, 18.4. Anal. Calcd for $C_{32}H_{33}N_2PS_2$: C, 71.08; H, 6.15; N, 5.18. Found: C, 71.31; H, 6.29; N, 5.51. EI-MS (*m*/*z*): 540 $[M]^+$, 525 $[M - CH_3]^+$.

(43) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447–454.

Isolation of 3. This air-sensitive compound was extracted from the reaction mixture in the synthesis of **2** following the Celite filtration and removal of toluene. The Schlenk flask containing the residue was fitted with a distillation bridge attached to a flask submerged in liquid N_2. The apparatus was attached to the high-vacuum line, and the pressure was reduced to 10 mTorr. The oily compound was distilled off by heating the flask to 125−135 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 6.82 (dd, J = 3.2 Hz, J = 5.2 Hz, 1H), 6.80 (s, 2H), 6.37 (dd, J = 1.6 Hz, J = 5.2 Hz, 1H), 5.59 (dd, J = 1.6 Hz, J = 3.2 Hz, 1H), 4.56 (bs, 1H), 2.17 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 146.9, 138.3, 134.7 (2 overlapping carbons), 129.6, 125.2, 120.0, 98.3, 20.9, 18.1. Anal. Calcd for $C_{13}H_{15}NS$: C, 71.84; H, 6.96; N, 6.44. Found: C, 72.22; H, 7.02; N, 6.38. EI-MS (m/z): 217 $[M]^+$, 202 $[M - CH_3]^+$.

Synthesis of $[NPN]^SZr(NMe_2)_2$ (8). $Zr(NMe_2)_4$ (0.989 g, 3.70 mmol) and **2** (2.00 g, 3.70 mmol) were mixed together, and toluene (40 mL) was added to obtain a lemon yellow solution, which was stirred for 1 h. The reaction mixture was taken to dryness to obtain a yellow residue. Upon addition of minimal hexanes, a bright yellow precipitate formed that was collected on a frit and dried (2.11 g). Slow cooling to −35 °C of a concentrated Et_2O solution of the compound yielded single crystals suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_6D_6): δ 7.86−7.81 (m, 2H), 7.15−7.10 (m, 2H), 7.05−7.01 (m, 1H), 6.97 (d, J = 5.2 Hz, 2H), 6.89 (bs, 2H), 6.87 (bs, 2H), 5.92 (dd, J_{H-H} = 5.2 Hz, J_{P-H} = 4.0 Hz, 2H), 2.99 (s, 6H), 2.36 (s, 6H), 2.26 (s, 6H), 2.25 (s, 6H), 2.17 (s, 6H). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ −41.4. ^{13}C NMR (100 MHz, C_6D_6): δ 168.6 (d, J = 138.8 Hz), 146.4 (d, J = 8.4 Hz), 135.31, 135.29, 134.9, 133.8, 133.7, 133.4, 131.9 (d, J = 53.2 Hz), 129.7, 129.2, 128.7 (d, J = 36.8 Hz), 120.1 (d, J = 41.6 Hz), 99.4 (d, J = 84.0 Hz), 43.0, 42.8 (d, J = 18.8 Hz), 20.9, 19.3, 19.2. Satisfactory EA values for this compound could not be obtained due to persistent residual solvents. EI-MS (m/z): 716 $[M]^+$, 672 $[M - NMe_2]^+$.

Synthesis of $[NPN]^SZrCl_2$ (9). To a stirred yellow toluene solution (85 mL) of **8** (2.55 g, 3.56 mmol) was added trimethylsilyl chloride (4.52 mL, 35.6 mmol) dropwise. The clear yellow solution was stirred for 5 h. The reaction mixture was taken to dryness to obtain a yellow powder that was collected on a frit, washed with pentane (3 × 5 mL), and dried (2.0 g, 2.85 mmol, 80%). Slow evaporation of an Et_2O solution of the compound yielded single crystals suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_6D_6): δ 7.89−7.84 (m, 2H), 7.07−7.04 (m, 2H), 7.00−6.96 (m, 1H), 6.88 (bs, overlapping singlet and doublet, 4H), 6.74 (bs, 2H), 5.72 (dd, J_{H-H} = 5.2 Hz, J_{P-H} = 3.2 Hz, 2H), 2.46 (s, 6H), 2.36 (s, 6H), 2.08 (s, 6H). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ −36.2. ^{13}C NMR (100 MHz, C_6D_6): δ 166.6 (d, J = 145.2 Hz), 140.7 (d, J = 13.6 Hz), 137.6, 137.4, 136.4, 135.8, 131.6 (d, J = 53.2 Hz), 131.2, 130.7 (d, J = 8.8 Hz), 130.6, 130.5, 129.3 (d, J = 42.4 Hz), 118.5 (d, J = 46.0 Hz), 105.8 (d, J = 127.6 Hz), 21.0, 19.3, 19.1. Anal. Calcd for $C_{32}H_{31}Cl_2N_2PS_2Zr$: C, 54.84; H, 4.46; N, 4.00. Found: C, 54.69; H, 4.65; N, 3.88. EI-MS (m/z): 700 $[M]^+$.

Synthesis of $[NPN]^SZrI_2$ (10) from $[NPN]^SZr(NMe_2)_2$ (8). To a stirred yellow toluene solution (50 mL) of **8** (1.60 g, 2.23 mmol) was added trimethylsilyl iodide (3.18 mL, 22.3 mmol) dropwise. The solution rapidly turned orange and was stirred for 3 h. The reaction mixture was taken to dryness to obtain an orange powder that was collected on a frit, washed with pentane (3 × 5 mL), and dried (1.61 g, 1.82 mmol, 82%). Slow evaporation of an Et_2O solution of the compound yielded single crystals suitable for X-ray crystallography.

Synthesis of $[NPN]^SZrI_2$ (10) from $[NPN]^SZrCl_2$ (9). To a stirred yellow toluene solution (50 mL) of **9** (0.9 g, 1.28 mmol) was added trimethylsilyl iodide (1.83 mL, 12.8 mmol) dropwise. The solution turned orange and was stirred overnight. The reaction mixture was taken to dryness to obtain an orange powder that was collected on a frit, washed with pentane (3 × 5 mL), and dried (1.00 g, 1.13 mmol, 88%).

Synthesis of $[NPN]^SZrI_2$ (10) from $[NPN]^SH_2$ (2) and $Zr(NMe_2)_4$: One-Pot Synthesis. $Zr(NMe_2)_4$ (0.495 g, 1.85 mmol) and **2** (1.00 g, 1.85 mmol) were mixed together, and toluene (40 mL) was added to obtain a lemon yellow solution, which was stirred for 1 h. Trimethylsilyl iodide (2.63 mL, 18.5 mmol) was added dropwise to the yellow solution. The solution rapidly turned orange and was stirred for 3 h. The reaction mixture was taken to dryness to obtain an orange powder that was collected on a frit with Celite. The solids were washed on the Celite with pentane (3 × 10 mL). The product was then extracted from the Celite by washing it with excess toluene into an empty round-bottom flask. Removal of the toluene *in vacuo* produced 1.20 g (1.36 mmol, 73%) of product.

^{1}H NMR (400 MHz, C_6D_6): δ 7.81−7.76 (m, 2H), 7.10−7.05 (m, 2H), 7.02−6.98 (m, 1H), 6.85 (bs, overlapping singlet and doublet, 4H), 6.78 (bs, 2H), 5.69 (dd, J_{H-H} = 5.2 Hz, J_{P-H} = 3.6 Hz, 2H), 2.60 (s, 6H), 2.25 (s, 6H), 2.09 (s, 6H). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ −35.3. ^{13}C NMR (100 MHz, C_6D_6): δ 167.0 (d, J = 144.4 Hz), 138.9 (d, J = 14.0 Hz), 138.6, 137.9, 136.9, 136.6, 132.0, 131.6 (d, J = 48.0 Hz), 130.95, 130.92, 130.8 (d, J = 9.6 Hz), 129.1 (d, J = 44.4 Hz), 118.3 (d, J = 46.8 Hz), 106.6 (d, J = 118.4 Hz), 21.2, 20.8, 20.4. Anal. Calcd for $C_{32}H_{31}I_2N_2PS_2Zr$: C, 43.49; H, 3.54; N, 3.17. Found: C, 43.39; H, 3.72; N, 3.08. EI-MS (m/z): 882 $[M]^+$, 755 $[M - I]^+$.

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Supporting Information Available: Optimization of conditions for the preparation of bromo-amine **1**; crystallographic data for **1**, **2**, and **8**−**10** (CIFs); experimental details for X-ray structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.