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Structurally versatile phosphine and amine donors constructed from N-heterocyclic olefin units†

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A general strategy for the synthesis of hindered N- and P-based donors is presented whereby the strongly electron releasing N-heterocyclic olefin (NHO) unit, $\text{IPr}=\text{CH}-$, ($\text{IPr}=\text{CH}- = [(\text{HCNDipp})_2\text{C}=\text{CH}]^-$; $\text{Dipp} = 3,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_2$) is linked to terminally bound phosphine and amine donors. Preliminary coordination chemistry is presented involving phosphine ($\text{IPr}=\text{CH})\text{PR}_2$ ($\text{R} = ^i\text{Pr}$ and Ph) and amine ($\text{IPr}=\text{CH})\text{NMe}_2$ ligands and the Lewis acids BH_3 and AuCl . Interestingly, $(\text{IPr}=\text{CH})\text{NMe}_2$ binds AuCl through an exocyclic olefin unit, while the softer phosphorus centers in $(\text{IPr}=\text{CH})\text{PR}_2$ coordinate to yield $\text{Au}-\text{P}$ linkages; thus the reported NHO-based ligands exhibit tunable binding modes to metals.

Introduction

Sterically encumbered phosphines and N-heterocyclic carbenes (NHCs) are effective ligands for supporting a variety of catalytic bond-forming processes,¹ and can stabilize highly reactive molecular entities *via* strong coordinative interactions.² Common traits between these two ligand classes are the presence of a strongly σ -donating atom, ease of synthesis, and a high level of structural tunability. A related ligand group that is attracting increasing attention of late are N-heterocyclic olefins (NHOs),³ which contain considerable nucleophilic character due to the highly polarized nature of the exocyclic $\text{C}=\text{C}$ double bond, allowing these species to be strong neutral 2-electron donors (Chart 1; left). Accordingly, NHOs are now being used to intercept reactive inorganic species,^{4,5} as organo-

catalysts for various polymerization strategies,⁶ and as a component of pincer-type ligands.⁷

In this paper, we present efficient routes to phosphine and amine donors that contain an NHO moiety $[\text{IPr}=\text{CH}]^-$ directly linked to P- and N-donor sites. As shown in Chart 2, there is a possibility of coordination through either the NHO (*via* carbon-ligation) or the terminal P/N atoms. Our current study was motivated in part by the prior work of Beller who demonstrated that imidazolium-alkylphosphines (Chart 1; right) when combined with $\text{Pd}(\text{II})$ sources and base, afforded active catalysts (*in situ*) for the hydroxylation of arylhalides, and for both C–N (Buchwald–Hartwig) and C–C (Sonogashira) coupling reactions.⁸ Despite the possible formation of neutral NHO-linked phosphines (NHOPs; Chart 2; $\text{E} = \text{P}$) during Beller's catalytic processes, such ligands were not isolated, nor were any well-defined metal complexes with these ligands reported. As a result, we decided to explore this ligand class in more detail and consequently uncovered divergent coordination behavior towards AuCl , depending if hard amine- or soft-phosphine groups are appended to an NHO unit.

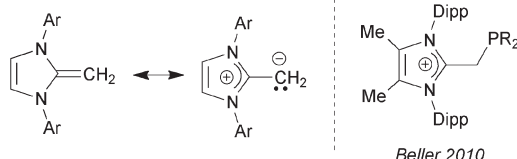


Chart 1 (Left) Canonical forms for a generic N-heterocyclic olefin (NHO); (Right) Beller's imidazolium alkylphosphines; $\text{Ar} = \text{aryl}$; $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$.

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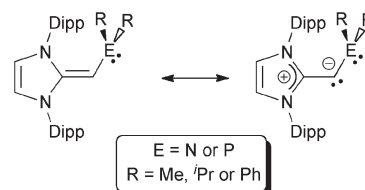


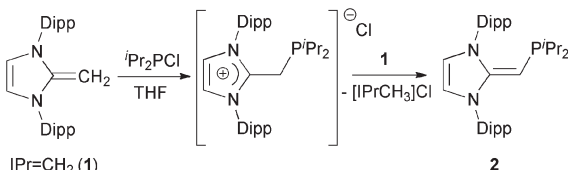
Chart 2 N-Heterocyclic olefin-phosphines (NHOP) or -amines (NHON) discussed in this paper.



Results and discussion

Synthesis of N-heterocyclic olefin phosphines (NHOPs)

We began our studies by exploring the synthesis of the diisopropylphosphine-capped N-heterocyclic olefin ($\text{IPr}=\text{CH}$) P^iPr_2 **2** ($\text{IPr} = [(\text{HCNDipp})_2\text{C}]$; $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$). In line with prior work from our group,⁹ the readily available NHO, $\text{IPr}=\text{CH}_2$ **1**,^{3d} was combined with ClP^iPr_2 in a 1:1 ratio in THF (Scheme 1) with the intention of first isolating the imidazolium salt $[\text{IPr}-\text{CH}_2-\text{P}^i\text{Pr}_2]\text{Cl}$, which would be isostructural to Beller's pre-ligands shown in Chart 1. While there was spectroscopic evidence for the formation of the desired imidazolium salt, the starting material $\text{IPr}=\text{CH}_2$ **1** was sufficiently basic to deprotonate $[\text{IPr}-\text{CH}_2-\text{P}^i\text{Pr}_2]\text{Cl}$ to give **2** and the known by-product $[\text{IPrCH}_3]\text{Cl}$.⁹ Fortunately **2** and $[\text{IPrCH}_3]\text{Cl}$ have quite different solubilities, allowing for their easy separation. By altering the ratio between $\text{IPr}=\text{CH}_2$ **1** and ClP^iPr_2 to 2:1 (eqn (1)) and conducting the reaction in THF at room temperature for 20 h, we were able to isolate pure ($\text{IPr}=\text{CH}$) P^iPr_2 **2** in 81% yield after extracting **2** from the product mixture (containing $[\text{IPrCH}_3]\text{Cl}$) with hexanes. Following a similar procedure,



Scheme 1 In the reaction of $\text{IPr}=\text{CH}_2$ (**1**) and $^i\text{Pr}_2\text{PCl}$ in a 1:1 ratio, we observe the formation of the imidazolium-alkylphosphine salt $[\text{IPr}-\text{CH}_2-\text{P}^i\text{Pr}_2]\text{Cl}$ as well as the desired neutral NHO-appended phosphine **2**.

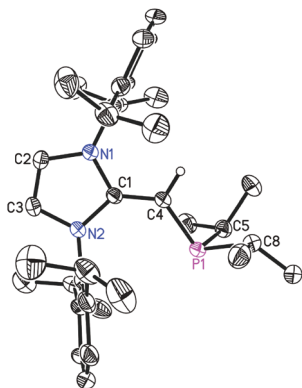


Fig. 1 Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Only one of the four crystallographically-independent molecules in the unit cell is presented. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P–C(4) 1.780(3)–1.788(3), P–C(5) 1.835(4)–1.883(3), P–C(8) 1.859(4)–1.896(4), C(1)–C(4) 1.364(4)–1.366(4); P–C(4)–C(1) 126.9(2)–129.8(2), N(1)–C(1)–N(2) 104.0(2), C(4)–P–C(5) 101.03(14)–105.72(18), C(4)–P–C(8) 99.71(15)–104.29(17), C(5)–P–C(8) 99.12(14)–101.57(17).

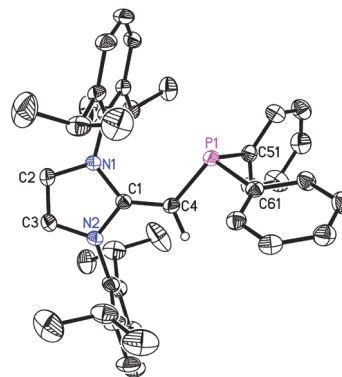
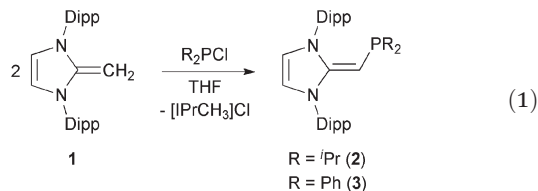


Fig. 2 Molecular structure of **3** with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) with values corresponding to a second molecule in the asymmetric unit in square brackets: P(1)–C(4) 1.7762(15) [1.782(2)], P(1)–C(51) 1.8411(16) [1.839(2)], P(1)–C(61) 1.8406(15) [1.8448(18)], C(1)–C(4) 1.365(2) [1.377(2)], C(4)–P(1)–C(51) 104.37(7) [104.50(9)], C(4)–P(1)–C(61) 99.75(6) [99.70(8)], P(1)–C(4)–C(1) 126.25(11) [126.16(16)], N(1)–C(2)–N(2) 104.08(12) [104.29(12)].

the phenyl-substituted NHOP ($\text{IPr}=\text{CH}$) PPh_2 **3** was prepared in an isolated yield of 83% (eqn (1)). The new NHOPs **2** and **3** were each characterized by NMR spectroscopy, elemental analysis and X-ray crystallography (colorless crystals grown from hexanes at -30°C ; Fig. 1 and 2).

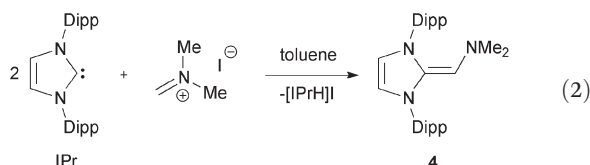


The refined structure of ($\text{IPr}=\text{CH}$) P^iPr_2 **2** is presented in Fig. 1 with only one of the four crystallographically-independent molecules in the unit cell shown; thus, selected bond lengths and angles are provided as a range. The exocyclic $\text{C}=\text{C}$ bonds in **2** [C(1)–C(4) = 1.364(4) to 1.366(4) Å] are considerably shorter than the typical C–C single bond length of *ca.* 1.530 Å,¹⁰ and is only slightly elongated compared to the exocyclic $\text{C}=\text{C}$ bond length of 1.332(4) Å in free $\text{IPr}=\text{CH}_2$.^{3c} As expected, the crystallographically determined $\text{C}(\text{sp}^2)\text{--P}$ linkages in **2** [C(4)–P(1) = 1.780(3) to 1.788(2) Å] are contracted with respect to the $\text{C}(\text{sp}^3)\text{--P}$ bonds involving the ^iPr substituents [1.835(4) to 1.896(4) Å]. For comparison the $\text{C}(\text{olefin})\text{--P}$ distances in *cis*- $\text{Ph}_2\text{P}-\text{CH}=\text{CH}-\text{PPh}_2$ are 1.817(3) and 1.825(3) Å,¹¹ suggesting a possible increase in $\text{C}(\pi) \rightarrow \text{P}-\text{C}(\sigma^*)$ hyperconjugation in **2**, leading to shorter $\text{C}(\text{sp}^2)\text{--P}$ bonds. The overall metrical parameters in ($\text{IPr}=\text{CH}$) PPh_2 (**3**) (Fig. 2) are quite similar to that of **2** with an average C(4)–P(1) distance of 1.780(2) Å in **3** and average C(1)–C(4)–P(1) angles of $126.0(2)^\circ$, compared to a range of $126.9(2)$ to $129.8(2)^\circ$ in **2**.



Synthesis of the N-heterocyclic olefin amine (IPr=CH)NMe₂ 4

In addition to preparing NHOPs, we wanted to see if a harder amine donor could be incorporated onto an NHO scaffold. The dimethylamino-substituted NHO, (IPr=CH)NMe₂ 4, was prepared by combining two equivalents of the commercially available carbene IPr with one equivalent of Eschenmoser's salt [H₂C=NMe₂]⁺I[−] in toluene (eqn (2)). In this process, the first equivalent of IPr is believed to undergo a nucleophilic attack on the iminium moiety to form [IPr-CH₂-NMe₂]⁺I[−] which is then subsequently deprotonated by a second equivalent of IPr to yield (IPr=CH)NMe₂ 4 and the imidazolium by-product [IPrH]⁺I[−] (which can be recycled for the preparation of IPr) (eqn (2)). In a similar fashion as the syntheses of 2 and 3, the salt by-product [IPrH]⁺I[−] is much less soluble than the target ligand 4, thus separation could be achieved by filtering the reaction mixture. One drawback with this synthesis is that the crude samples of 4 occasionally contains *ca.* 5–10% of unreacted IPr (as determined by ¹H NMR), which is difficult to separate from (IPr=CH)NMe₂ 4 due to their similar solubilities in common organic solvents. However, a successful way to remove the IPr contaminant involves adding a small amount of BPh₃ to form the known adduct IPr-BPh₃,¹³ which is much less soluble in hexanes than 4.



The structure of (IPr=CH)NMe₂ 4 was authenticated by X-ray crystallography (Fig. 3) and this study revealed an exocyclic C(1)–C(4) bond length of 1.3463(14) Å which is slightly shorter than the corresponding distances in the NHOPs 2 and 3, suggesting the retention of substantial C–C π -bonding in this

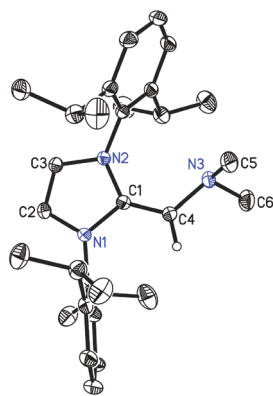


Fig. 3 Molecular structure of 4 with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.4024(12), N(2)–C(1) 1.4009(12), C(1)–C(4) 1.3463(14), C(4)–N(3) 1.4299(13), N(3)–C(5) 1.4563(16), N(3)–C(6) 1.4570(16); N(1)–C(1)–N(2) 104.44(8), N(1)–C(1)–C(4) 125.71(9), C(1)–C(4)–N(3) 122.98(9), C(4)–N(3)–C(6) 110.19(10).

unit. The C(1)–C(4)–N(1) angle was also consistent with sp²-hybridization at C(4) [122.98(9)°], while the nitrogen atom of the –NMe₂ group is significantly pyramidalized [$\Sigma\angle(N) = 333.35(17)^\circ$] consistent with a lack of substantial N(3)–C(4) π -bonding.

Coordination of the NHOPs 2 and 3 to BH₃ and AuCl

With the new NHOPs in hand, we first tested their reactivity with the Lewis acid source THF·BH₃. When either (IPr=CH)-PⁱPr₂ 2 or (IPr=CH)PPh₂ 3 was combined with THF·BH₃ in hexanes (eqn (3)), the reaction mixture went from yellow to colorless after 90 min at room temperature. After the volatiles were removed, the respective phosphine–borane adducts (IPr=CH)ⁱPr₂P·BH₃ 5 and (IPr=CH)Ph₂P·BH₃ 6 were isolated as colorless crystals in 52 and 56% yields after recrystallization from cold (−30 °C) hexanes or toluene (slow evaporation), respectively. As expected, coordination of a BH₃ unit was evident by NMR spectroscopy, which showed broad ¹¹B NMR resonances at −42.0 and −35.8 ppm for 5 and 6, respectively, consistent with the presence of four-coordinate boron environments. In addition, considerable downfield shifts in the ³¹P resonances were noted within the NHOPs upon BH₃ coordination: from −17.4 ppm in 2 to 21.9 ppm in (IPr=CH)ⁱPr₂P·BH₃ 5; from −31.4 ppm in 3 to 7.3 ppm in (IPr=CH)-Ph₂P·BH₃ 6. Such a substantial change in ³¹P NMR chemical shift indicated the likely presence of BH₃ units bound to the phosphorus centers; this postulate was confirmed by performing single-crystal X-ray crystallography (5: Fig. 4; 6: Fig. 5).

As shown in Fig. 4, (IPr=CH)ⁱPr₂P·BH₃ 5 contains a P-bound borane residue with a P–B bond length of 1.9166(18) Å; for comparison, the dialkylphosphine–borane adduct ^tBu₂PH·BH₃ has a P–B bond length of 1.936(2) Å.¹⁴ In the case of (IPr=CH)ⁱPr₂P·BH₃ 5, the P(1)–C(4) length [1.7504(14) Å] is contracted in comparison to the corresponding distance in the free phosphine (IPr=CH)PⁱPr₂ 2 [1.780(3) to 1.788(2) Å]. The

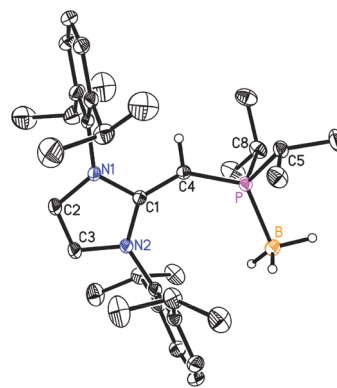


Fig. 4 Molecular structure of 5 with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P–B 1.9166(18), P–C(4) 1.7504(14), C(1)–C(4) 1.3749(18), P–C(5) 1.8486(14), P–C(8) 1.8495(16); C(4)–P–B 124.56(7), P–C(4)–C(1) 138.02(11), C(4)–P–C(5) 102.07(7), C(4)–P–C(8) 106.76(7), B–P–C(5) 110.56(8), B–P–C(8) 107.50(8).



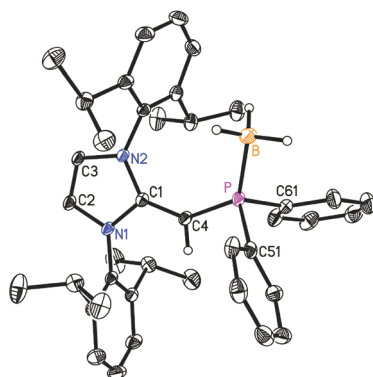
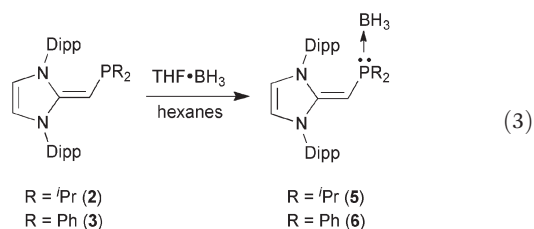


Fig. 5 Molecular structure of **6** with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): P–B 1.9242(18), P–C(4) 1.7479(11), C(1)–C(4) 1.3811(15), P–C(51) 1.8292(12), P–C(61) 1.8300(13); C(4)–P–B 125.76(6), P–C(4)–C(1) 138.31(9), C(4)–P–C(51) 101.10(5), C(4)–P–C(61) 107.67(6), B–P–C(51) 109.21(7), B–P–C(61) 108.15(7).

exocyclic C(1)–C(4) double bond within the NHO unit in **5** [1.3749(18) Å] is essentially the same length within experimental error as the exocyclic C=C bond distances in the phosphine **2** [1.364(4) to 1.366(4) Å]. The main structural change noted upon coordination of BH₃ is a widening of the P–C(4)–C(1) from 126.9(2)° in the free ligand **2** to 138.02(11)° in adduct **5**. Similarly, the P–C(4)–C(1) angle in the phenyl analogue (IPr=CH)Ph₂P·BH₃ (**6**) [138.31(9)°] (Fig. 5) is wider than in the free phosphine (IPr=CH)PPh₂ (**3**) [126.0(2)° *avg.*]. In both compounds **5** and **6**, the BH₃ unit is oriented in an *anti*-fashion with respect to the exocyclic olefinic C–H group, placing the BH₃ group in close proximity to one of the flanking Dipp aryl groups of the NHO ligand; such a coordination mode could enhance aryl...metal interactions within NHOP–metal complexes.^{1e}



After demonstrating the successful coordination of the small Lewis acid BH₃ to the NHOPs **2** and **3**, we decided to expand our studies to include transition metals. Our initial explorations focused on the noble metals Pd and Pt since complexes bearing these elements in conjunction with bulky phosphines¹⁵ and NHCs¹⁶ are often used in metal-mediated cross-coupling reactions. Despite the presence of a potentially strongly coordinating terminal –PⁱPr₂ unit in (IPr=CH)PⁱPr₂ **2**, no discernable reaction was noted when excess **2** (2–3 equiv.) was combined with either Pd(PPh₃)₄ or Pt(PPh₃)₄ in hot C₆D₆ (50 °C) for 4 days (monitored by ³¹P NMR spectroscopy). A similar lack of reactivity was found with the two coordinate Pt(0) complex Pt(PⁱBu₃)₂. Attempts to form a bis NHOP–PdCl₂

pre-catalyst¹⁷ by treating PdCl₂(NCPh)₂ with two equiv. of **2** in toluene, led to an immediate color change of the reaction mixture from yellow to dark red, however ³¹P NMR analysis revealed the formation of six spectroscopically distinct products from which a single clean product could not be isolated.

Reports of using [PdCl(cinnamyl)]₂ (cinnamyl = η³-H₂CCHCH(Ph)) as a palladium source to generate active L–Pd(cinnamyl) pre-catalysts (L = ligand)¹⁸ in cross-coupling reactions led us to combine [PdCl(cinnamyl)]₂ with (IPr=CH)PⁱPr₂ **2**. When **2** was mixed with [PdCl(cinnamyl)]₂ in toluene several new species were found by ³¹P NMR spectroscopy. In one case, layering of the crude reaction mixture with hexanes, followed by cooling to –30 °C gave a small batch of yellow crystals (2–3 mg) that were identified by X-ray crystallography as the target Pd(II) complex (IPr=CH)PⁱPr₂–PdCl(cinnamyl) **7** (Fig. 6).

Upon closer inspection of the structure of **7** (Fig. 6) it is clear that the –PⁱPr₂ unit is free to rotate with respect to the bulky IPr=CH– group. In the BH₃ adduct **5**, the isopropyl groups are rotated away from the IPr unit, while in (IPr=CH)PⁱPr₂–PdCl(cinnamyl) **7** the phosphorus bound ⁱPr substituents are positioned toward one Dipp group, enabling the more hindered PdCl(cinnamyl) array to occupy a more open side of the NHOP ligand coordination sphere. Therefore despite the bulk of (IPr=CH)PⁱPr₂, there exists sufficient torsional flexibility to allow different coordination pockets to be formed (a useful property for catalysis when various intermediates need to be stabilized). The Pd–cinnamyl bonding interactions in **7** range from 2.113(6) Å to 2.261(5) Å with the longest Pd–C bond to C(53) positioned *trans* to the phosphine donor. In the NHC complex IPr–PdCl(cinnamyl), the related *trans*-positioned Pd–C bond length (with respect to the IPr donor) is 2.201(17) Å,¹⁹ indicating that the ligand (IPr=CH)PⁱPr₂ exerts a similar degree of *trans*-influence as IPr.

Given the difficulties faced in introducing an NHOP as a ligand to Pd and Pt centers, we decided to explore the coordi-

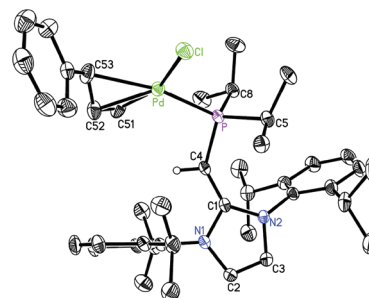


Fig. 6 Molecular structure of (IPr=CH)PⁱPr₂–PdCl(cinnamyl) **7** with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P 2.3086(12), Pd–Cl 2.3582(12), Pd–C(51) 2.113(6), Pd–C(52) 2.143(5), Pd–C(53) 2.261(5), P–C(4) 1.765(4), C(1)–C(4) 1.386(6), P–C(5) 1.847(5), P–C(8) 1.863(5); P–Pd–Cl 102.23(4), C(4)–P–Pd 103.85(15), P–C(4)–C(1) 136.1(3), C(4)–P–C(5) 105.8(2), C(4)–P–C(8) 110.7(2), Pd–P–C(5) 117.51(16), Pd–P–C(8) 113.69(18), C(51)–C(52)–C(53) 120.4(6).



nation of this ligand class to gold(i) centers. Added motivation for this work stems from the rapidly growing use of Au(i) complexes in catalysis (*e.g.* in the hydroamination of alkynes).²⁰ A toluene solution of (IPr=CH)PⁱPr₂ **2** was added to a molar equivalent of Me₂S·AuCl, and after stirring at room temperature for 2 h, (IPr=CH)ⁱPr₂P·AuCl **8** was obtained as a pale yellow solid in an 85% yield after filtration of the reaction mixture and removal of the volatiles (eqn (4)); the resulting product was analytically pure as judged by satisfactory C, H and N analyses. Compound **8** was characterized by X-ray crystallography and the refined molecular structure is shown in Fig. 7. The metrical parameters within the IPr=CH- unit in **8** are similar to those in the BH₃ adduct (IPr=CH)ⁱPr₂P·BH₃ **5**, with comparable P–C(4) and exocyclic C(1)–C(4) bond lengths [1.7742(19) and 1.376(3) Å, respectively]. Interestingly, the –PⁱPr₂ unit in **8** is rotated in such a fashion as to place the hindered isopropyl groups away from the Dipp groups within the IPr=CH- unit; as a result the Au(i) center lies over the π -face of a Dipp substituent (Au...C(*ipso*) distance = 3.507 Å), and accordingly the P–Au–Cl angle [171.40(2)°] is distorted from the expected linear geometry. For comparison, shorter arene...Au(i) interactions have been noted within a series of Buchwald biarylphosphine–Au(i) complexes L·Au(NCMe)⁺ (3.04–3.19 Å).²¹ The corresponding diphenylphosphine-capped NHO complex (IPr=CH)PPh₂·AuCl **9** was prepared (98% yield) in a similar straightforward manner as **8**, and exhibited the same overall geometry as in **8** (Fig. 8) with a slightly narrower P–Au–Cl angle of 168.72(4)°.

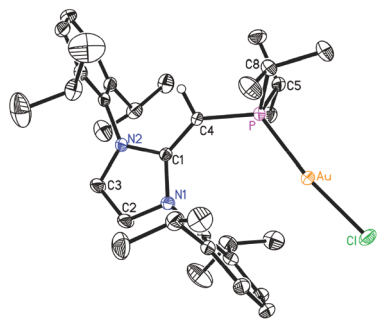
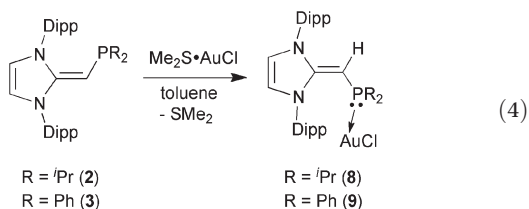


Fig. 7 Molecular structure of **8** with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au–P 2.2348(5), Au–Cl 2.2991(5), P–C(4) 1.7442(19), C(1)–C(4) 1.376(3), P–C(5) 1.848(2), P–C(8) 1.845(2), P–Au–Cl 171.40(2), C(4)–P–Au 122.82(7), P–C(4)–C(1) 136.20(15), C(4)–P–C(5) 105.69(10), C(4)–P–C(8) 104.31(10), Au–P–C(5) 106.89(7), Au–P–C(8) 110.83(7).

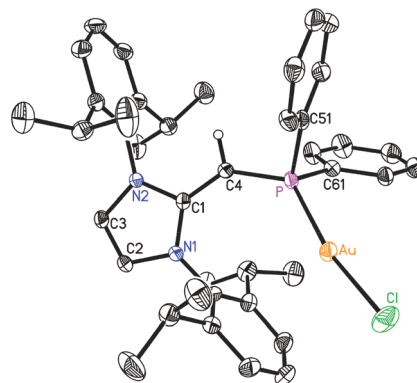


Fig. 8 Molecular structure of **9** with thermal ellipsoids at the 30% probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au–P 2.2334(8), Au–Cl 2.2914(10), P–C(4) 1.741(3), C(1)–C(4) 1.381(4), P–C(51) 1.831(3), P–C(61) 1.826(3), P–Au–Cl 168.72(4), C(4)–P–Au 128.48(11), P–C(4)–C(1) 136.9(3), C(4)–P–C(51) 99.84(15), C(4)–P–C(61) 109.43(15), Au–P–C(51) 106.45(11), Au–P–C(61) 106.46(11).

In an attempt to prepare a more reactive Au(i) complex for future catalytic trials,^{20d} the NHO–Au complex (IPr=CH)–Ph₂P·AuCl **9** was treated with Na[BAR^F₄] ([BAR^F₄][–] = (3,5-(F₃C)₂C₆H₃)₄B) in toluene. This reaction afforded a gummy orange precipitate from which a product of [BAR^F₄][–] anion activation [IPr–CH₂–PPh₂·Au(3,5-(F₃C)₂C₆H₃)₄][–] **10** could be isolated and structurally characterized (eqn (5); Fig. 9). While the mechanism of this process is under investigation, protonation of the exocyclic olefin within the NHO unit occurred to yield an imidazolium-alkylphosphine ligand,⁸ along with the removal of one Ar^F unit from the generally unreactive weakly coordinating [BAR^F₄][–] anion. One possible source of the proton would be C–H activation of the backbone olefin within the IPr unit.²² The generation of a highly electron deficient Au(i) center during the reaction process could facilitate the abstraction of Ar^F from the [BAR^F₄][–] anion; although rare, related pro-

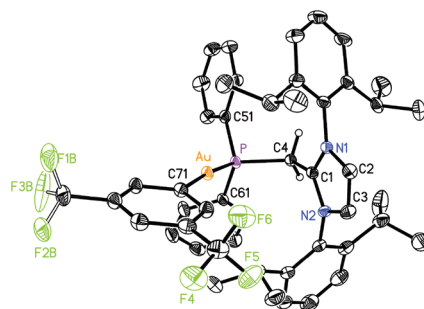
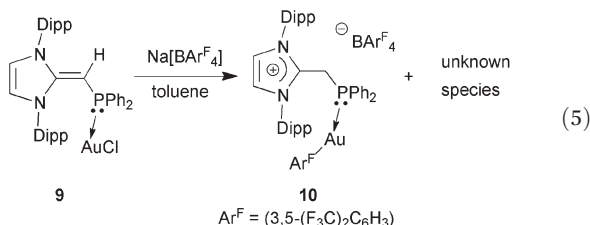


Fig. 9 Molecular structure of **10** with thermal ellipsoids at the 30% probability level. The hydrogen atoms attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms and the B(3,5-(F₃C)₂C₆H₃)₄[–] anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au–P 2.2798(8), Au–C(71) 2.070(23), P–C(4) 1.864(4), C(1)–C(4) 1.487(4); P–Au–C(71) 174.82(11), C(4)–P–Au 112.43(11), C(1)–C(4)–P 116.5(2).



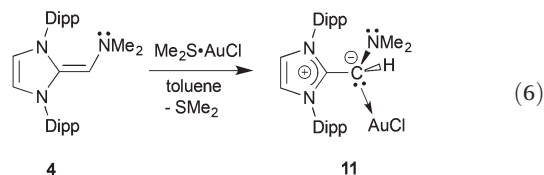
cesses have been noted with both phosphine and NHC-bound Au(I) centers.²³ The structure of **10** is shown in Fig. 9 and, as expected, a nearly linear coordination geometry exists at the Au(I) center [P–Au–C(71) angle = 174.82(11)°]. The coordinative Au–P interaction in **10** [2.2798(8) Å] is only marginally elongated in relation to the Au–P distance in (IPr=CH)ⁱPr₂P–AuCl **8** [2.2348(5) Å], while the adjacent P–C(4) bond length in **10** is longer by *ca.* 0.12 Å when compared to the P–C(4) distance in **8** as a result of a hybridization change at carbon from sp² in **8** to sp³ in **10**. No reaction was observed when (IPr=CH)Ph₂P–AuCl **9** was treated with Na[SbF₆].



To further evaluate the donation abilities of the new phosphines, we targeted the preparation of NHOP–Rh(CO)₂Cl complexes with the hope of obtaining informative $\nu(\text{CO})$ IR data.^{3d} When the NHOPs **2** and **3** were each combined with 0.5 equiv. of [RhCl(CO)₂]₂, three different Rh–P containing products were found, as evidenced by ³¹P{¹H} NMR spectroscopy in the form of doublet resonances due to coupling to Rh (*I* = 1/2). Despite multiple attempts, we could not separate the products due to their similar solubilities in common organic solvents, and as such further investigations were not pursued.

Divergent coordination chemistry of (IPr=CH)NMe₂ **4**

As presented above, the NHOPs **2** and **3** exclusively bind to Lewis acidic units through the terminal phosphine residues. However in the corresponding amine-capped NHOs (such as **4**) featuring hard N-donor sites, there exists a chance that olefin coordination could transpire with soft Lewis acids (Chart 1). Somewhat to our surprise, (IPr=CH)NMe₂ **4** did not yield clean reactivity with THF–BH₃, with multiple products identified by ¹¹B NMR spectroscopy. In contrast, an isolable 1 : 1 complex (IPr=CH)NMe₂–AuCl **11** formed as a yellow solid in 89% yield when **4** was combined with Me₂S–AuCl in toluene (eqn (6)). The most drastic change in the ¹³C{¹H} NMR spectra of the (IPr=CH)NMe₂ units was the upfield shift of the olefinic CHNMe₂ carbon from 89.0 ppm in free (IPr=CH)NMe₂ **4** to a position of 58.4 ppm in **11**; this latter spectroscopic signature suggested possible olefin coordination to gold in **11**. Crystals of **11** were obtained for X-ray crystallographic analysis and despite the lower quality of the data, (IPr=CH)NMe₂ coordination through a C–Au linkage was confirmed with a distance of 2.044(15) Å; moreover a nearly linear geometry was present at gold [C(3)–Au–Cl angle = 177.6(4)°; see Fig. S32 in the ESI†]. Therefore one can see direct evidence for the two possible binding modes of NHO-supported amines and phosphines in this study (Chart 2).



Conclusion

We have reported efficient syntheses of neutral N-heterocyclic olefin-appended phosphines and amine donors, and present preliminary coordination behavior with the Lewis acids BH₃ and AuCl. Interestingly, modulation of the donor properties enables either NHO-based coordination (*via* an olefinic carbon atom) or standard phosphine binding modes to be adopted. As a result, we are exploring these coordinatively versatile ligands within the context of late metal-mediated catalysis.

Experimental

General

All reactions were performed in either an inert atmosphere glove box (Innovative Technology, Inc.) or using Schlenk techniques. Solvents were dried using a Grubbs-type solvent purification system²⁴ manufactured by Innovative Technologies, Inc. and stored under an atmosphere of nitrogen prior to use. Chlorodiisopropylphosphine, chlorodiphenylphosphine, *N,N*-dimethyliminium iodide [(Me₂N=CH₂)]I, borane tetrahydrofuran complex, dimethylsulfide gold(I) chloride, Na[SbF₆], and [PdCl(cinnamyl)]₂ were used as received from Sigma Aldrich. Na[(3,5-(F₃C)₂C₆H₃)₄B] was obtained from Sigma Aldrich and dried under vacuum at 100 °C for 12 h prior to use. IPr=CH₂ **1**^{3d} and IPr²⁵ were prepared according to literature procedures. ¹H, ¹H{³¹P}, ¹³C{¹H}, ³¹P{¹H}, ¹¹B, and ¹¹B{¹H} NMR spectra were recorded on a Varian VNMR-400 or Varian VNMR-500 spectrometer and referenced externally to SiMe₄, 85% H₃PO₄, or F₃B–OEt₂. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

X-ray crystallography

Crystals for X-ray diffraction studies were removed from a vial and immediately coated with thin a layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer. All data (Tables 1 and 2) were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo K α or Cu K α radiation with the crystals cooled to –80 °C or –100 °C. The data was corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using intrinsic phasing SHELXT²⁶ (**2**, **4**, **5**, **6**, **9** and **11**), direct methods (**3**), or Patterson/structure expansion (**7** and **8**)²⁷ and refined using full-matrix



Table 1 Crystallographic data for compounds 2–6

	(IPr=CH)P ⁱ Pr ₂ (2)	(IPr=CH)PPh ₂ (3)	(IPr=CH)NMe ₂ (4)	(IPr=CH) ⁱ Pr ₂ P·BH ₃ (5·0.5C ₆ H ₁₄)	(IPr=CH)Ph ₂ P·BH ₃ (6)
CCDC number	1448851	1448848	1448850	1448846	1448845
Formula	C ₃₄ H ₅₁ N ₂ P	C ₄₀ H ₄₇ N ₂ P	C ₃₀ H ₄₃ N ₃	C _{35.50} H _{57.50} BN ₂ P	C ₄₀ H ₅₀ BN ₂ P
Formula weight	518.73	586.76	445.67	554.11	600.60
Cryst. dimens. (mm)	0.34 × 0.17 × 0.17	0.21 × 0.18 × 0.07	0.20 × 0.15 × 0.08	0.49 × 0.08 × 0.06	0.24 × 0.20 × 0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Trigonal	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>R</i> 3̄	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions					
<i>a</i> (Å)	21.3382(6)	10.7803(2)	9.3774(2)	42.1750(6)	10.7033(2)
<i>b</i> (Å)	18.3587(5)	16.7651(3)	20.2169(4)		18.7813(3)
<i>c</i> (Å)	17.2832(4)	39.0845(6)	20.2169(4)	10.4933(2)	17.9853(3)
β (°)	33.3817(9)	95.7606(9)	100.0916(11)		92.3243(8)
<i>V</i> (Å ³)	13053.4(6)	7028.2(2)	2799.90(10)	16164.1(6)	3612.46(11)
<i>Z</i>	16	8	4	18	4
ρ calcd (g cm ⁻³)	1.056	1.109	1.057	1.025	1.104
μ (mm ⁻¹)	0.897	0.894	0.463	0.835	0.874
Temperature (°C)		–100	–100	–100	–100
2 θ_{\max} (°)	146.35	146.98	148.31	148.11	145.02
Total data	75117	48 771	108 108	38 050	24 968
Unique data (<i>R</i> _{int})	25 575 (0.0449)	13 861 (0.0370)	5659 (0.0433)	7292 (0.0561)	7118 (0.0257)
Obs [<i>I</i> > 2 σ (<i>I</i>)]	17 632	11 433	5104	6290	6558
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2 σ (<i>F</i> _o ²)] ^a	0.0698	0.0461	0.0417	0.0497	0.0371
<i>wR</i> ₂ [all data]	0.2012	0.1292	0.1151	0.1428	0.1037
Max/min $\Delta\rho$ (e Å ⁻³)	0.954/–0.511	0.444/–0.299	0.238/–0.256	0.552/–0.453	0.311/–0.366

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

Table 2 Crystallographic data for compounds 7–10

	(IPr=CH) ⁱ Pr ₂ P·PdCl(cinnamyl) (7)	(IPr=CH) ⁱ Pr ₂ P·AuCl (8)	(IPr=CH)Ph ₂ P·AuCl (9·0.5C ₇ H ₈)	[IPr-CH ₂ -PPh ₂ ·AuAr ^F]-BAr ^F ₄ (10)
CCDC number	1448843	1448847	1448849	1448844
Formula	C ₅₀ H ₆₈ ClN ₂ PPd	C ₃₄ H ₅₁ AuClN ₂ P	C _{43.50} H ₅₁ AuClN ₂ P	C ₈₀ H ₆₃ AuBF ₃₀ N ₂ P
Formula weight	869.88	751.15	865.25	1861.07
Cryst. dimens. (mm)	0.14 × 0.13 × 0.10	0.32 × 0.18 × 0.16	0.19 × 0.18 × 0.06	0.48 × 0.13 × 0.01
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell				
<i>a</i> (Å)	10.3535(3)	10.4781(4)	9.7488(6)	14.0570(4)
<i>b</i> (Å)	12.5649(4)	16.3684(6)	20.0872(13)	25.1328(6)
<i>c</i> (Å)	18.9321(6)	20.9256(7)	20.8717(14)	22.7564(7)
α (°)	72.828(2)			
β (°)	100.0916(11)	101.6635(4)	98.4585(10)	102.1003(18)
γ (°)	89.231(2)			
<i>V</i> (Å ³)	2304.58(13)	3514.8(2)	4042.8(5)	7861.0(4)
<i>Z</i>	2	4	4	4
ρ calcd (g cm ⁻³)	1.254	1.419	1.422	1.573
μ (mm ⁻¹)	4.357	4.330	3.776	4.750
Temperature (°C)	–100	–80	–80	–100
2 θ_{\max} (°)	147.88	56.66	55.22	148.42
Total data	87 008	32 818	36 511	55 754
Unique data (<i>R</i> _{int})	8901 (0.1174)	8717 (0.0238)	9373 (0.0430)	12 419(0.0808)
Obs [<i>I</i> > 2 σ (<i>I</i>)]	7672	7584	7578	7672
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2 σ (<i>F</i> _o ²)] ^a	0.0566	0.0200	0.0316	0.0420
<i>wR</i> ₂ [all data]	0.1547	0.0532	0.0855	0.1156
Max/min $\Delta\rho$ (e Å ⁻³)	1.436/–1.103	1.076/–0.505	1.671/–1.292	1.078/–2.636

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

least-squares on *F*². The assignment of hydrogen atoms positions were based on the sp² or sp³ hybridization of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Special refinement conditions

(IPr=CH)PⁱPr₂·BH₃ 5. Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexane carbon atoms were unsuccessful. The data were cor-



rected for disordered electron density through use of the SQUEEZE procedure as implemented in PLATON.²⁸ A total solvent-accessible void volume of 1145 Å³ with a total electron count of 212 (consistent with 4.24 molecules of solvent hexane, or ~0.25 molecules per formula unit of 5) was found in the unit cell.

(IPr=CH)PⁱPr₂·PdCl(cinnamyl) 7. The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program CELL_NOW (Bruker AXS, Inc., Madison, WI, 2004). The second twin component can be related to the first component by a 7.4° rotation about the [0.2 1 –0.35] axis in real space and about the [0.1 1 –0.4] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a SHELXL-2014²⁶ HKLF 5 reflection file with the data integration program SAINT (version 8.34A), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (SHELXL-2014 BASF parameter) was 0.3198(17).

(IPr=CH)PPh₂·AuCl 9. Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent toluene or hexane carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in PLATON.²⁸ A total solvent-accessible void volume of 517 Å³ with a total electron count of 110 (consistent with 2 molecules of solvent toluene, or 0.5 molecules per formula unit of the Au complex) was found in the unit cell.

Synthetic details

Synthesis of (IPr=CH)PⁱPr₂ 2. ⁱPr₂PdCl (100 μL, 0.77 mmol) was added dropwise to IPr=CH₂ **1** (0.508 g, 1.26 mmol) in 8 mL of THF. The resulting mixture was stirred for 20 h to give an orange suspension. The mixture was then filtered and the volatiles were removed from the filtrate to afford an orange solid that was extracted with 4 mL of hexanes and filtered again. Removal of the volatiles from the filtrate gave **2** as a light brown solid (0.267 g, 81%). Crystals suitable for X-ray crystallography were obtained by cooling (–30 °C) a saturated solution of **2** in hexanes. ¹H NMR (400 MHz, C₆D₆): δ 7.26–7.11 (m, 6H, ArH), 5.88 (dd, ³J_{HH} = 2.4 Hz, ⁵J_{HH} = 0.8 Hz, 1H, NCHCHN), 5.85 (dd, ³J_{HH} = 2.4 Hz, ⁵J_{HH} = 0.8 Hz, 1H, NCHCHN), 3.28 (overlapping septets, 4H, ArCH(CH₃)₂), 2.66 (d, ²J_{HP} = 5.6 Hz, 1H, CHPⁱPr₂), 1.45 (d, ³J_{HH} = 7.2 Hz, 6H, ArCH(CH₃)₂), 1.33 (d, ³J_{HH} = 7.2 Hz, 6H, ArCH(CH₃)₂), 1.25 (broad septet, ³J_{HH} = 7.2 Hz, 2H, PCH(CH₃)₂), 1.18 (d, ³J_{HH} = 6.8 Hz, 6H, ArCH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.8 Hz, 6H, ArCH(CH₃)₂), 0.96 (dd, ³J_{HH} = 7.2 Hz, ³J_{HP} = 11.6 Hz, 6H, PCH(CH₃)-CH₃), 0.90 (dd, ³J_{HH} = 6.8 Hz, ³J_{HP} = 12.8 Hz, 6H, PCH(CH₃)-CH₃). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 154.5 (Ar-C), 154.3 (Ar-C), 148.7 (Ar-C), 148.1 (Ar-C), 134.6 (NCN), 129.7 (Ar-C), 129.4 (Ar-C), 124.6 (Ar-C), 123.9 (Ar-C), 117.8 (HCCH), 115.0 (HCCH), 51.4 (d, ¹J_{CP} = 114.7 Hz, HCPⁱPr₂), 29.1 (ArCH(CH₃)₂), 28.7 (ArCH(CH₃)₂), 26.5 (d, ²J_{CP} = 11.1 Hz, PCH(CH₃)₂), 25.9 (ArCH(CH₃)₂), 24.9 (ArCH(CH₃)₂), 23.4 (ArCH(CH₃)₂), 22.6 (ArCH(CH₃)₂). ³¹P{¹H} NMR (160 MHz, C₆D₆): δ –17.4. Mp

(°C): 132–135. Anal. Calcd for C₃₄H₅₁N₂P: C, 78.72; H, 9.91; N, 5.40. Found: C, 77.76; H 9.85; N, 5.21.

Synthesis of (IPr=CH)PPh₂ 3. Ph₂PdCl (41.2 μL, 0.16 mmol) was added dropwise to a solution of IPr=CH₂ **1** (0.150 g, 0.37 mmol) in 3 mL of THF. The resulting mixture was stirred overnight to give an orange suspension. The precipitate was allowed to settle and the mother liquor was isolated after filtration. The volatiles were removed from the mother liquor to afford (IPr=CH)PPh₂ **3** as a brown solid (0.078 g, 83%). Crystals suitable for X-ray crystallography were obtained by cooling (–30 °C) a saturated solution in hexanes. ¹H NMR (400 MHz, C₆D₆): δ 7.35–6.92 (m, 16H, ArH and PhH), 5.92 (s, 2H, N(CH₂)₂N), 3.34 (d, ³J_{HP} = 5.6 Hz, 1H, CHPPh₂), 3.26 (overlapping septets, 4H, ArCH(CH₃)₂), 1.33 (d, ³J_{HH} = 7.2 Hz, 6H, ArCH(CH₃)₂), 1.19 (d, ³J_{HH} = 7.0 Hz, 6H, ArCH(CH₃)₂), 1.18 (d, ³J_{HH} = 7.0 Hz, 6H, ArCH(CH₃)₂), 1.12 (d, ³J_{HH} = 7.2 Hz, 6H, ArCH(CH₃)₂). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 154.0 (d, ¹J_{CP} = 35 Hz, Ph-C), 148.5 (Ar-C), 147.9 (Ar-C), 146.2 (d, ²J_{CP} = 13 Hz, Ph-C), 136.6 (Ar-C), 134.2 (Ar-C), 132.3 (d, ²J_{CP} = 20 Hz, Ph-C), 130.0 (Ar-C), 129.7 (Ar-C), 127.7 (Ar-C), 126.8 (Ar-C), 124.5 (d, ¹J_{CP} = 41 Hz, Ph-C), 117.1 (HCCH), 115.5 (HCCH), 52.7 (HCPPh₂), 29.1 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 22.5 (CH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ –31.4. Mp (°C): 172–176. Anal. Calcd for C₄₀H₄₇N₂P: C, 81.87; H, 8.07; N, 4.77. Found: C, 81.34; H 8.33; N, 5.05.

Synthesis of IPr=CHNMe₂ 4. A solution of IPr (0.481 g, 1.24 mmol) in 3 mL of toluene was added to finely ground [H₂C=N(CH₃)₂]I (0.115 g, 0.62 mmol). The resulting mixture was stirred overnight to give a cloudy yellow reaction mixture. The mother liquor was isolated after filtration. The volatiles were then removed from the mother liquor to afford a yellow solid that was extracted with 2 mL of hexanes and filtered. Removal of the volatiles from the filtrate afforded **4** as a yellow solid (227 mg, 82%, product also contained 7% of unreacted IPr). Further purification can be performed by adding BPh₃ (ca. 2 mg) to **4** (0.050 g) in minimal amount of benzene (ca. 0.5 mL). The solution was stirred for 15 min and 2 mL of hexanes was added to yield a white precipitate. The mother liquor was isolated after filtration and the volatiles were removed from the filtrate to afford **4** (0.040 g) containing <1% of unreacted IPr. Crystals suitable for X-ray crystallography were obtained by cooling (–30 °C) a saturated solution in hexanes. ¹H NMR (500 MHz, C₆D₆): δ 7.23 (t, ³J_{HH} = 7.5 Hz, 2H, ArH), 7.14 (d, ³J_{HH} = 8.0 Hz, 4H, ArH), 5.86 (dd, ³J_{HH} = 2.5 Hz, ⁵J_{HH} = 1.0 Hz, 1H, HCCH), 5.77 (d, ³J_{HH} = 2.0 Hz, 1H, HCCH), 3.51 (septet, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂), 3.47 (s, 1H, CHN(CH₃)₂), 3.36 (septet, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂), 1.97 (s, 6H, N(CH₃)₂), 1.41 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂), 1.38 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂), 1.27 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂), 1.22 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 149.0 (Ar-C), 148.1 (Ar-C), 145.0 (Ar-C), 138.1 (NCN), 129.1 (Ar-C), 128.3 (Ar-C), 124.6 (Ar-C), 123.1 (Ar-C), 117.4 (HCCH), 114.4 (HCCH), 89.0 (HCN(CH₃)₂), 49.8 (CH(CH₃)₂), 28.7 (N(CH₃)₂), 28.6 (N(CH₃)₂), 25.6 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 22.9 (CH(CH₃)₂). Mp (°C): 89–94. Anal. Calcd for C₃₀H₄₃N₃: C, 80.85; H, 9.72; N, 9.43.



Found: C, 79.04; H 9.43; N, 8.52. Despite repeated attempts, analyses were consistently low in the carbon content. See Fig. 7 and 8 in the ESI† for a copy of the NMR spectra of 4.

Preparation of (IPr=CH)PⁱPr₂-BH₃ 5. 106 μL of THF·BH₃ (1.0 M solution in THF, 0.11 mmol) was added dropwise to a solution of IPr=CHPⁱPr₂ 2 (50 mg, 0.096 mmol) in 2 mL of hexanes. The reaction mixture was stirred for 1.5 h and then filtered. The volatiles were removed from the filtrate and the resulting solid was dissolved in approximately 0.5 mL of hexanes and cooled (−30 °C) to afford (IPr=CH)PⁱPr₂-BH₃ as a white microcrystalline solid (27 mg, 52%). Crystals suitable for X-ray crystallography were obtained by cooling (−30 °C) a saturated solution in hexanes. ¹H NMR (500 MHz, C₆D₆): δ 7.24 (t, ³J_{HH} = 7.5 Hz, 2H, ArH), 7.17 (d, ³J_{HH} = 8.0 Hz, 4H, ArH), 5.87 (s, 2H, N(CH)₂N), 3.16 (septet, ³J_{HH} = 7.0 Hz, 4H, ArCH(CH₃)₂), 2.09 (d, ²J_{HP} = 10.0 Hz, 1H, CHPⁱPr₂), 1.44 (d, ³J_{HH} = 6.5 Hz, 12H, CH(CH₃)₂), 1.44 (broad septet, 2H, P(CH(CH₃)₂)₂), 1.14 (d, ³J_{HH} = 6.5 Hz, 12H, ArCH(CH₃)₂), 1.06 (dd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 14.5 Hz, 6H, PCH(CH₃)₂), 0.93 (dd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 13.5 Hz, 6H, PCH(CH₃)₂), 0.25 (broad d, ²J_{HP} = 15.0 Hz, 3H, BH₃). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 154.3 (d, ²J_{CP} = 11.6 Hz, NCN), 147.9 (Ar-C), 130.2 (Ar-C), 128.4 (Ar-C), 128.2 (Ar-C), 128.0 (Ar-C), 124.8 (N(CH)₂N), 40.2 (d, ¹J_{CP} = 73.8 Hz, HCPⁱPr₂), 28.8 (ArCH(CH₃)₂), 26.7 (d, ²J_{CP} = 39.5 Hz, P(CH(CH₃)₂)₂), 25.3 (ArCH(CH₃)₂), 22.9 (ArCH(CH₃)₂), 17.2 (d, ¹J_{CP} = 58.9 Hz, P(CH(CH₃)₂)₂). ¹¹B{¹H} NMR (160 MHz, C₆D₆): δ −42.0. ³¹P{¹H} NMR (201 MHz, C₆D₆): δ 21.9. Mp (°C): 154–156. Anal. Calcd for C₃₄H₅₄BN₂P: C, 76.67; H, 10.22; N, 5.26. Found: C, 75.94; H 10.10; N, 5.42.

Preparation of (IPr=CH)PPh₂-BH₃ 6. 93.8 μL of THF·BH₃ (1.0 M solution in THF, 0.094 mmol) was added dropwise to a solution of IPr=CHPPh₂ 3 (50.0 mg, 0.085 mmol) in 2 mL of hexanes. The reaction mixture was stirred for 90 min. The solvent volume was reduced *in vacuo* until the mixture just turned cloudy and then cooled (−30 °C) to afford 6 as an off-white microcrystalline solid (29 mg, 56%). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a saturated solution of (IPr=CH)PPh₂-BH₃ 6 in toluene at room temperature. ¹H NMR (500 MHz, C₆D₆): δ 7.69–7.71 (m, 4H, PhH), 7.72 (t, ³J_{HH} = 7.5 Hz, 2H, ArH), 7.12 (d, ³J_{HH} = 8.0 Hz, 4H, ArH), 6.98–6.95 (m, 6H, PhH), 5.93 (s, 2H, N(CH)₂N), 3.15 (septet, ³J_{HH} = 7.0 Hz, 4H, CH(CH₃)₂), 2.83 (d, ²J_{HP} = 9.5 Hz, 1H, CHPPH₂), 1.24 (d, ³J_{HH} = 7.0 Hz, 12H, CH(CH₃)₂), 1.12 (d, ³J_{HH} = 7.0 Hz, 12H, CH(CH₃)₂), 0.98 (broad d, ²J_{HP} = 16.0 Hz, 3H, BH₃). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 153.2 (d, ²J_{CP} = 15.6 Hz, NCN), 147.7 (Ar-C), 137.7 (d, ¹J_{CP} = 58.7 Hz, Ph-C), 132.0 (d, ¹J_{CP} = 9.3 Hz, Ph-C), 130.4 (ArC), 129.1 (d, ¹J_{CP} = 2.0 Hz, Ph-C), 128.3 (Ar-C), 128.0 (d, ¹J_{CP} = 9.5 Hz, Ph-C), 125.0 (N(CH)₂N), 117.6 (Ar-C), 44.2 (d, ¹J_{CP} = 84.8 Hz, HCPPh₂), 29.0 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 22.8 (CH(CH₃)₂). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ −35.8. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 7.3. Mp (°C): 164–170. Anal. Calcd for C₄₀H₅₀BN₂P: C, 79.99; H, 8.39; N, 4.66. Found: C, 79.36; H 8.38; N, 4.68.

Reaction of IPr=CHNMe₂ with THF·BH₃. 63.8 μL of THF·BH₃ (1.0 M solution in THF, 0.058 mmol) was added dropwise to a solution of IPr=CHNMe₂ 4 (26 mg, 0.058 mmol)

in 1 mL of hexanes. Once THF·BH₃ was added the yellow solution became colorless. The reaction was stirred for approximately 2 hours and then the volatiles were removed. ¹¹B NMR analysis showed that there was no THF·BH₃ remaining, however 5 new unidentifiable products were formed; attempts to obtain pure products were not successful.

Reaction of (IPr=CH)PⁱPr₂ with [PdCl(cinnamyl)]₂. [PdCl(cinnamyl)]₂ (0.024 g, 0.046 mmol) was combined with (IPr=CH)PⁱPr₂ 2 (0.048 g, 0.093 mmol) in 2 mL of toluene. The reaction mixture rapidly became yellow in color. The solution was left to stir overnight to yield a red solution and the volatiles were removed. ¹H and ³¹P NMR spectroscopy showed a mixture of several products. On one occasion, yellow crystals (2–3 mg) suitable for X-ray crystallography were obtained by cooling (−30 °C) a saturated solution of the reaction mixture in toluene/hexanes. Data for (IPr=CH)PⁱPr₂-PdCl(cinnamyl) 7. ¹H NMR (400 MHz, C₆D₆): δ 7.55 (d, ³J_{HH} = 8.0 Hz, 2H, ArH), 7.22–7.00 (m, 8H, PhH and ArH), 5.90 (s, 2H, N(CH)₂N), 5.41 (ddd, ³J_{HH} = 13.2 Hz, ³J_{HH} = 9.2 Hz, ³J_{HH} = 9.2 Hz, 1H, CH₂CHCHPh), 4.98 (m, 3H, CH₂CHCHPh), 4.01 (broad d, ³J_{HP} = 11.2 Hz, 3H, PCH(CH₃)₂), 3.49 (broad d, ³J_{HP} = 6.8 Hz, 3H, PCH(CH₃)₂), 3.23 (broad septet, 4H, ArCH(CH₃)₂), 2.79 (broad s, (IPr=CH)PⁱPr₂), 2.44 (broad d, ³J_{HH} = 12.0 Hz, 3H, PCH(CH₃)₂), 1.88 (broad s, 3H, PCH(CH₃)₂), 1.38 (broad m, 12H, ArCH(CH₃)₂), 1.14 (broad m, 1H, PCH(CH₃)₂), 1.06 (d, ³J_{HH} = 6.8 Hz, 12H, ArCH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 34.0. We did not have enough sample to record a meaningful ¹³C{¹H} NMR spectrum.

Synthesis of (IPr=CH)PⁱPr₂-AuCl 8. A solution of (IPr=CH)-PⁱPr₂ 2 (99 mg, 0.19 mmol) in 5 mL of toluene was added dropwise to solid Me₂S·AuCl (56 mg, 0.19 mmol) to give a yellow solution. This reaction mixture was stirred at room temperature for 2 hours and a small amount of metallic precipitate was observed. The mixture was then filtered and the volatiles were then removed from the filtrate to afford (IPr=CH)-PⁱPr₂-AuCl 8 as a pale yellow solid (121 mg, 85%). Crystals suitable for X-ray crystallography were obtained by cooling (−30 °C) a saturated solution in a 1:1 mixture of toluene/hexanes. ¹H NMR (500 MHz, C₆D₆): δ 7.49 (t, ³J_{HH} = 7.0 Hz, 2H, ArH), 7.23 (d, ³J_{HH} = 8.0 Hz, 4H, ArH), 5.78 (s, 2H, N(CH)₂N), 3.01 (septet, ³J_{HH} = 7.0 Hz, 4H, ArCH(CH₃)₂), 2.22 (d, ²J_{HP} = 6.0 Hz, 1H, CHPⁱPr₂), 1.38 (d, ³J_{HH} = 7.0 Hz, 12H, ArCH(CH₃)₂), 1.28 (septet, ³J_{HH} = 8.0 Hz, 2H, P(CH(CH₃)₂)₂), 1.07 (d, ³J_{HH} = 7.0 Hz, 12H, ArCH(CH₃)₂), 0.87 (dd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 18.0 Hz, 6H, PCH(CH₃)₂), 0.80 (dd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 16.0 Hz, 6H, PCH(CH₃)₂). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 153.7 (d, ²J_{CP} = 10.3 Hz, NCN), 147.0 (Ar-C), 134.3 (Ar-C), 131.2 (Ar-C), 129.3 (Ar-C), 125.4 (Ar-C), 117.5 (N(CH)₂N), 40.7 (d, ¹J_{CP} = 81.3 Hz, HCPⁱPr₂), 29.3 (d, ²J_{CP} = 41.6 Hz, P(CH(CH₃)₂)₂), 28.8 (ArCH(CH₃)₂), 25.0 (ArCH(CH₃)₂), 23.2 (ArCH(CH₃)₂), 19.1 (d, ¹J_{CP} = 3.8 Hz, P(CH(CH₃)₂)₂), 18.3 (ArCH(CH₃)₂). ³¹P{¹H} NMR (201 MHz, C₆D₆): δ 28.7. Mp (°C): 90 (decomp., turned black). Anal. Calcd for C₃₄H₅₁AuClN₂P: C, 54.36; H, 6.84; N, 3.73. Found: C, 54.82; H 6.86; N, 3.61.

Synthesis of (IPr=CH)PPh₂-AuCl 9. A solution of (IPr=CH)-PPh₂ 3 (78 mg, 0.13 mmol) in 5 mL of toluene was slowly



added to solid $\text{Me}_2\text{S}\cdot\text{AuCl}$ (40 mg, 0.14 mmol) to give a yellow solution. This reaction mixture was stirred at room temperature for 90 minutes and a small amount of metallic precipitate was observed. The mixture was filtered and the volatiles were then removed from the filtrate to afford $(\text{IPr}=\text{CH})\text{PPh}_2\cdot\text{AuCl}$ **9** as a pale yellow solid (108 mg, 98%). Crystals suitable for X-ray crystallography were obtained by cooling (-30°C) a saturated solution in a 2 : 1 mixture of toluene/hexanes. ^1H NMR (400 MHz, C_6D_6): δ 7.47–7.49 (m, 4H, PhH), 7.41 (t, $^3J_{\text{HH}} = 8.0$ Hz, 2H, ArH), 7.18 (d, $^3J_{\text{HH}} = 8.0$ Hz, 4H, ArH), 6.86–6.87 (m, 6H, PhH), 5.83 (s, 2H, $\text{N}(\text{CH}_2)_2\text{N}$), 3.00 (septet, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 2.80 (d, $^2J_{\text{HP}} = 6.4$ Hz, 1H, CHPPH_2), 1.20 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ 152.3 (d, $^2J_{\text{CP}} = 13.6$ Hz, NCN), 146.9 (Ar-C), 139.1 (d, $^1J_{\text{CP}} = 63.9$ Hz, Ph-C), 137.8 (Ar-C), 133.7 (Ar-C), 132.6 (d, $^2J_{\text{CP}} = 14.1$ Hz, Ph-C), 131.4 ($\text{N}(\text{CH}_2)_2\text{N}$), 129.7 (d, $J_{\text{CP}} = 2.3$ Hz, Ph-C), 117.5 (Ar-C), 44.6 (d, $^1J_{\text{CP}} = 92.6$ Hz, HCPPh_2), 29.0 ($\text{CH}(\text{CH}_3)_2$), 24.6 ($\text{CH}(\text{CH}_3)_2$), 23.1 ($\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ 8.1. Mp ($^\circ\text{C}$): 122 (decomp., turned black). Anal. Calcd for $\text{C}_{40}\text{H}_{47}\text{AuN}_2\text{P}$: C, 58.65; H, 5.78; N, 3.42. Found: C, 58.83; H 5.89; N, 3.13.

Reaction of $\text{IPr}=\text{CHPPH}_2\cdot\text{AuCl}$ and $\text{Na}[\text{BAR}^{\text{F}}_4]$: isolation of $[\text{IPr}-\text{CH}_2-\text{PPh}_2\cdot\text{Au}(3,5-(\text{F}_3\text{C})_2\text{C}_6\text{H}_3)]\text{BAR}^{\text{F}}_4$ **10.** $(\text{IPr}=\text{CH})\cdot\text{PPh}_2\cdot\text{AuCl}$ **9** (17 mg, 0.020 mmol) and $\text{Na}[\text{BAR}^{\text{F}}_4]$ (18 mg, 0.020 mmol) were combined in 2 mL of toluene and stirred at room temperature overnight. A pale orange solution formed along with a gummy orange precipitate. The mother liquor was decanted away and the precipitate was exposed to prolonged vacuum to yield an orange solid. This solid was then extracted with CH_2Cl_2 (2×1 mL) and the combined extracts were filtered. The filtrate was then layered with 2 mL of hexanes before cooling to -30°C , leading to colorless crystals of **10** (19 mg). ^1H NMR (500 MHz, CDCl_3): δ 7.42 (broad d, $^3J_{\text{HH}} = 5.5$ Hz, 2H, $\text{Ar}^{\text{F}}\text{-H}$), 7.69 (broad s, 8H, ArH in BAR^{F}_4), 7.66 (s, 2H, $\text{N}(\text{CH}_2)_2\text{N}$), 7.64 (broad s, 1H, $\text{Ar}^{\text{F}}\text{-H}$), 7.52 (m, 6H, Ph-H), 7.40 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H, ArH), 7.29 (d, $^3J_{\text{HH}} = 8.0$ Hz, 4H, ArH), 7.23–7.25 (m, 4H, Ph-H), 6.94–6.98 (m, 4H, ArH in BAR^{F}_4), 3.82 (d, $^2J_{\text{HP}} = 10.4$ Hz, 2H, CH_2PPh_2), 2.82 (br, 4H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.13 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.6. ^{19}F NMR (376 MHz, CDCl_3): δ -62.3 [$\text{BAR}^{\text{F}}_4^-$], -62.6 [$\text{Au}-\text{Ar}^{\text{F}}$]. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 34.4. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 161.7 (q, $^1J_{\text{CB}} = 49.6$ Hz, Ar-C in $\text{BAR}^{\text{F}}_4^-$), 146.7 (Ar-C), 144.9 (Ar-C), 137.9 (Ar-C in $\text{Au}-\text{Ar}^{\text{F}}$), 134.8 (Ar-C in $\text{BAR}^{\text{F}}_4^-$), 133.7 (Ar-C), 132.8 (Ar-C), 131.9 (d, $J_{\text{CP}} = 14.0$ Hz, Ar-C), 129.9 (d, $J_{\text{CP}} = 19.5$ Hz, Ar-C), 128.8 (q, $^1J_{\text{CB}} = 49.6$ Hz in $\text{BAR}^{\text{F}}_4^-$), 126.2 (Ar-C), 125.6 (d, $^2J_{\text{CP}} = 12.7$ Hz, Ar-C), 123.5 (Ar-C), 121.3 ($\text{N}(\text{CH}_2)_2\text{N}$), 119.9 (Ar-C), 117.5 (Ar-C in $\text{BAR}^{\text{F}}_4^-$), 30.0 ($\text{CH}(\text{CH}_3)_2$), 26.9 (HCPPh_2), 26.1 ($\text{CH}(\text{CH}_3)_2$), 22.7 ($\text{CH}(\text{CH}_3)_2$). The CF_3 groups in the $\text{Au}-\text{Ar}^{\text{F}}$ unit could not be located in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Mp ($^\circ\text{C}$): 97 (decomp.; turned brown). Anal. Calcd for $\text{C}_{80}\text{H}_{63}\text{AuBF}_3\text{N}_2\text{P}$: C, 51.63; H, 3.41; N, 1.51. Found: C, 51.31; H, 3.62; N, 1.52.

Synthesis of $(\text{IPr}=\text{CH})\text{NMe}_2\cdot\text{AuCl}$ **11.** A solution of $\text{IPr}=\text{CHNMe}_2$ **4** (98 mg, 0.22 mmol) in 5 mL of toluene was added dropwise to solid $\text{Me}_2\text{S}\cdot\text{AuCl}$ (65 mg, 0.22 mmol) to give

a dark yellow reaction mixture. This reaction mixture was stirred at room temperature for 90 minutes and a metallic precipitate was observed. The reaction mixture was then filtered and the volatiles were then removed from the filtrate to afford $(\text{IPr}=\text{CH})\text{NMe}_2\cdot\text{AuCl}$ as a pale yellow solid (133 mg, 89%). Crystals of **11** were obtained by cooling a 2 : 1 toluene/hexanes solution overnight to -30°C , however the low quality of the data prevents a detailed discussion of the metrical parameters (see Fig. S32 in the ESI†). ^1H NMR (400 MHz, C_6D_6): δ 7.13 (d, $^3J_{\text{HH}} = 9.0$ Hz, 2H, ArH), 7.01–7.04 (m, 4H, ArH), 6.10 (s, 2H, $\text{N}(\text{CH}_2)_2\text{N}$), 4.02 (s, 1H, CHNMe_2), 3.04 (septet, $^3J_{\text{HH}} = 6.4$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.79 (broad s, 6 H, $\text{N}(\text{CH}_3)_2$), 1.47 (d, $^3J_{\text{HH}} = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.47 (d, $^3J_{\text{HH}} = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ 161.0 (NCN), 147.5 (Ar-C), 145.3 (Ar-C), 132.2 (Ar-C), 131.2 (Ar-C), 124.7 (Ar-C), 124.5 (Ar-C), 120.8 (HCCCH), 58.4 ($\text{HCN}(\text{CH}_3)_2$), 29.8 ($\text{CH}(\text{CH}_3)_2$), 29.4 ($\text{CH}(\text{CH}_3)_2$), 26.0 ($\text{CH}(\text{CH}_3)_2$), 25.9 ($\text{CH}(\text{CH}_3)_2$), 23.2 ($\text{N}(\text{CH}_3)_2$), 23.1 ($\text{N}(\text{CH}_3)_2$). Mp ($^\circ\text{C}$): 123 (decomp., turned dark brown). Anal. Calcd $\text{C}_{30}\text{H}_{43}\text{AuN}_3$: C, 53.14; H, 6.39; N, 6.20. Found: C, 52.68; H, 6.33; N, 6.00.

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