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

Nathan R. Paisley,‡ Melanie W. Lui,‡ Robert McDonald, Michael J. Ferguson and Eric Rivard*

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, [IPr=CH–, ([IPr=CH– = ([HCNDipp]2C=CH)–]; Dipp = 3,6-iPr2C6H2) is linked to terminally bound phosphine and amine donors. Preliminary coordination chemistry is presented involving phosphine ([IPr=CH]PR2 (R = iPr and Ph) and amine ([IPr=CH])NMe2 ligands and the Lewis acids BH3 and AuCl. Interestingly, ([IPr=CH])NMe2 binds AuCl through an exocyclic olefin unit, while the softer phosphorus centers in ([IPr=CH]PR2 coordinate to yield Au–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 C=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 organocatalysts 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 ([IPr=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 Pd(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; E = 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; Ar = aryl; Dipp = 2,6-iPr2C6H3.

Department of Chemistry, University of Alberta 11227 Saskatchewan Drive, Edmonton, AB, T6G 2G2 Canada. E-mail: erivard@ualberta.ca

‡These authors contributed equally to this study.

†Electronic supplementary information (ESI) available: NMR spectra for all compounds and refined structure of 11. CCDC 1448842-1448851. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00299d

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

Synthesis of N-heterocyclic olefin phosphines (NHOs)

We began our studies by exploring the synthesis of the diisopropylphosphine-capped N-heterocyclic olefin (IPr=CH)PPr₂ 2 (IPr= [(HCNDipp)₂C]; Dipp = 2,6-iPr₂C₆H₃). In line with prior work from our group,⁹ the readily available NHO, IPr=CH₂ 1,¹⁰ was combined with CIPPr₂ in a 1:1 ratio in THF (Scheme 1) with the intention of first isolating the imidazolium salt [IPr-CH₂-PPr₂]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 IPr=CH₂ 1 was sufficiently basic to deprotonate [IPr-CH₂-PPr₂]Cl to give 2 and the known by-product [IPrCH₃]Cl.⁹ Fortunately 2 and [IPrCH₃]Cl have quite different solubilities, allowing for their easy separation. By altering the ratio between IPr=CH₂ 1 and CIPPr₂ to 2:1 (eqn (1)) and conducting the reaction in THF at room temperature for 20 h, we were able to isolate pure (IPr=CH)PPr₂ 2 in 81% yield after extracting 2 from the product mixture (containing [IPrCH₃]Cl) with hexanes. Following a similar procedure, the phenyl-substituted NHO (IPr=CH)PPh₂ 3 was prepared in an isolated yield of 83% (eqn (1)). The new NHOs 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).

![Scheme 1](image)

Scheme 1  In the reaction of IPr=CH₂ (1) and PPr₂PCI in a 1:1 ratio, we observe the formation of the imidazolium-alkylphosphine salt [IPr-CH₂-PPr₂]Cl as well as the desired neutral NHO-appended phosphine 2.

The refined structure of (IPr=CH)PPr₂ 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 C=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 C=C bond length of 1.332(4) Å in free IPr=CH₂.²⁴ As expected, the crystallographically determined C(sp³)→P linkages in 2 [C(4)=P(1) = 1.780(3) to 1.788(2) Å] are contracted with respect to the C(sp³)→P bonds involving the 1Pr substituents [1.835(4) to 1.896(4) Å]. For comparison the C(olefin)→P distances in cis-Ph₂P-CH=CH-PPh₂ are 1.817(3) and 1.825(3) Å,¹¹ suggesting a possible increase in C(π)→P–C(σ*) hyperconjugation in 2, leading to shorter C(sp³)→P bonds. The overall metrical parameters in (IPr=CH)PPh₂ 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)°, compared to a range of 126.9(2) to 129.8(2)° in 2.

![Fig. 1](image)

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 (°) with values corresponding to a second molecule in the asymmetric unit in square brackets: P(1)–C(4) = 1.780(15) [1.782(15)], P(1)–C(51) = 1.8411(16) [1.839(16)], P(1)–C(61) = 1.8406(15) [1.8484(18)], C(1)–C(4) = 1.365(2) [1.377(2)], C(1)–P(1)–C(51) = 104.37(7) [104.50(9)], C(4)–P(1)–C(61) = 99.75(6) [99.70(6)], P(1)–C(4)–C(1) = 126.25(11) [126.16(16)], N(1)–C(2)–N(2) = 104.08(12) [104.29(12)].
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=NHMe]⁺ [12] 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]⁺ which is then subsequently deprotonated by a second equivalent of IPr to yield (IPr=CH)NMe₂ 4 and the imidazolium by-product [IPrH]²⁻ (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]²⁻ 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 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 [Σ(NO) = 333.35(17)°] 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)-PPr₂ 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)²⁻PPr₂·BH₃ 5 and (IPr=CH)PPh₂·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 ³¹P NMR resonances at −4.0 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)²⁻PPr₂·BH₃ 5; from −31.4 ppm in 3 to 7.3 ppm in (IPr=CH)²⁻PPh₂·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)²⁻PPr₂·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 t-Bu₂PH·BH₃ has a P–B bond length of 1.936(2) Å.¹⁴ In the case of (IPr=CH)²⁻PPr₂·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)²⁻PPr₂ 2 [1.780(3) to 1.788(2) Å].

![Fig. 3](image1.png) 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(5) 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(5) 122.98(9), C(4)–N(3)–C(6) 110.19(10).

![Fig. 4](image2.png) 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 [1.36(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)PiPr2·BH3 6 [138.31(9)°] (Fig. 5) is wider than in the free phosphine (IPr=CH)PiPr2 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.

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 –PPr2 unit in (IPr=CH)PPr2 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 Pr(0) complex Pt(PBu3)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 = νC9H7CCHCH(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)PPr2 2. When 2 was mixed with [PdCl(cinnamyl)] 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(n) complex (IPr=CH)PPr2·PdCl(cinnamyl) 7 (Fig. 6).

Upon closer inspection of the structure of 7 (Fig. 6) it is clear that the –PPr2 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)PPr2·PdCl(cinnamyl) 7 the phosphorus bound Pr substituents are positioned toward one Dipp group, enabling the more hindered Pd(cinnamyl) array to occupy a more open side of the NHOP ligand coordination sphere. Therefore despite the bulk of (IPr=CH)PPr2, 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)PPr2 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-
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). A toluene solution of [IPr=CH]Pr2 2 was added to a molar equivalent of Me2S·AuCl, and after stirring at room temperature for 2 h, [IPr=CH]Pr2P·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]Pr2P·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 −PPr2 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 arenen−Au(I) interactions have been noted within a series of 1.304−2.19 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)°.

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[BArF4] [BArF4]− = (3,5-(F3C)2C6H3)4B) in toluene. This reaction afforded a gummy orange precipitate from which a product of [BArF4]− anion activation [IPr−CH2−PPh2·Au(3,5-(F3C)2C6H3)P·AuCl 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, along with the removal of one ArF unit from the generally unreactive weakly coordinating [BArF4]− 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 ArF from the [BArF4]− anion; although rare, related pro-

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 2.2914(10), P−C(4) 1.7442(19), C(1)−C(4) 1.376(3), P−C(5) 1.848(2), P−C(8) 1.864(4), Au−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 hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au−P 2.2334(8), Au−Cl 2.2914(10), P−C(4) 1.7413(5), C(1)−C(4) 1.3814(4), P−C(5) 1.8313(5), P−C(61) 1.8265(3), P−Au−Cl 168.72(4), P−C(4)−Au 128.48(11), P−C(4)−C(1) 136.9(3), C(4)−P−C(5) 96.84(15), (4)−P−C(61) 109.43(15), Au−P−C(51) 106.45(11), Au−P−C(61) 106.46(11).

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 have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au−P 2.2798(8), Au−Cl 2.2914(10), P−C(4) 1.7442(19), C(1)−C(4) 1.376(3), P−C(5) 1.848(2), P−C(8) 1.864(4), Au−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).
cesses have been noted with both phosphine and NHC-bound Au(i) centers.\textsuperscript{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)\textsuperscript{+}P–AuCl \textsuperscript{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 sp\textsuperscript{2} in 8 to sp\textsuperscript{3} in 10. No reaction was observed when [IPr=CH] Ph\textsubscript{2}P·AuCl 9 was treated with Na[SbF\textsubscript{6}].

![Diagram](image1)

To further evaluate the donation abilities of the new phosphines, we targeted the preparation of NHOP-Rh(CO)\textsubscript{2}Cl complexes with the hope of obtaining informative ν(CO) IR data.\textsuperscript{14} When the NHOPs 2 and 3 were each combined with 0.5 equiv. of [RhCl(CO)\textsubscript{2}], three different Rh–P containing products were found, as evidenced by \textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy in the form of doublet resonances due to coupling to Rh (J = 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)NMe\textsubscript{2} 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). As presented above, the NHOPs were identified as a result of a hybridization change at carbon from sp\textsuperscript{2} to sp\textsuperscript{3}. The most drastic change in the 13C{\textsuperscript{1}H} NMR spectra of the (IPr=CH)NMe\textsubscript{2} units was the upfield shift of the olefinic CHNMe\textsubscript{2} carbon from 89.0 ppm in free (IPr=CH)NMe\textsubscript{2} to 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)NMe\textsubscript{2} 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 ESIf]. 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 BH\textsubscript{3} 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 system\textsuperscript{24} manufactured by Innovative Technologies, Inc. and stored under an atmosphere of nitrogen prior to use. Chlorodisopropylphosphine, chlorodiphenylphosphine, N,N-dimethyliminium iodide ([Me\textsubscript{2}N=CH\textsubscript{2}])\textsubscript{2}, borane tetrahydrofuran complex, dimethylsulfide gold(i) chloride, Na[SbF\textsubscript{6}], and [PdCl (cinnamyl)]\textsubscript{2} were used as received from Sigma Aldrich. Na([3,5-\text{F\textsubscript{2}}C\textsubscript{6}H\textsubscript{3})\textsubscript{4}B] was obtained from Sigma Aldrich and dried under vacuum at 100 °C. The data was corrected for absorption 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)\textsuperscript{27} and refined using full-matrix
least-squares on $F^2$. The assignment of hydrogen atoms positions were based on the sp$^2$ or sp$^3$ hybridization of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Special refinement conditions (IPr=CH)PPr$_2$-BH$_3$. 5. Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexane carbon atoms were unsuccessful. The data were cor-

### Table 1 Crystallographic data for compounds 2–6

<table>
<thead>
<tr>
<th>Compound</th>
<th>CCDC number</th>
<th>Formula</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Crystallographic Data</th>
<th>Crystallographic Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>(IPr=CH)PPr$_2$</td>
<td>1448851</td>
<td>C$<em>{34}$H$</em>{52}$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/n$</td>
<td>$a$ (Å): 21.3382(6)</td>
<td>$b$ (Å): 16.3765(6)</td>
</tr>
<tr>
<td>(IPr=CH)PPr$_2$</td>
<td>1448848</td>
<td>C$<em>{40}$H$</em>{67}$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/n$</td>
<td>$c$ (Å): 18.9321(6)</td>
<td>$β$ (°): 95.7606(9)</td>
</tr>
<tr>
<td>(IPr=CH)NMe$_2$</td>
<td>1448850</td>
<td>C$<em>{30}$H$</em>{43}$N$_3$</td>
<td>Monochinic</td>
<td>$P2_1/n$</td>
<td>$α$ (°): 89.231(2)</td>
<td>$γ$ (°): 100.0916(11)</td>
</tr>
<tr>
<td>(IPr=CH)PPr$_2$-BH$_3$ (S-0.5C$<em>6$H$</em>{12}$)</td>
<td>1448846</td>
<td>C$<em>{35.50}$H$</em>{57.50}$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/n$</td>
<td>$λ$ (°): 100.0916(11)</td>
<td>$μ$ (mm$^{-1}$): 0.897</td>
</tr>
<tr>
<td>(IPr=CH)PPr$_2$-BH$_3$</td>
<td>1448845</td>
<td>C$<em>{40}$H$</em>{50}$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/n$</td>
<td>$ρ$ (g cm$^{-3}$): 1.056</td>
<td>$ρ_{calcd}$ (g cm$^{-3}$): 1.057</td>
</tr>
</tbody>
</table>

### Table 2 Crystallographic data for compounds 7–10

<table>
<thead>
<tr>
<th>Compound</th>
<th>CCDC number</th>
<th>Formula</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Crystallographic Data</th>
<th>Crystallographic Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>(IPr=CH)PPr$_2$-PdCl(cinnamyl)</td>
<td>1448843</td>
<td>C$<em>{31}$H$</em>{49}$Cl$_2$N$_2$Pd</td>
<td>Triclinic</td>
<td>$P1$</td>
<td>$a$ (Å): 10.3535(3)</td>
<td>$b$ (Å): 16.3766(4)</td>
</tr>
<tr>
<td>(IPr=CH)PPr$_2$-AuCl</td>
<td>1448847</td>
<td>C$<em>{31.30}$H$</em>{52}$Cl$_2$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/c$</td>
<td>$c$ (Å): 18.9321(6)</td>
<td>$β$ (°): 95.7606(9)</td>
</tr>
<tr>
<td>(IPr=CH)Ph$_2$P-AuCl</td>
<td>1448849</td>
<td>C$<em>{31.30}$H$</em>{52}$Cl$_2$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/c$</td>
<td>$α$ (°): 90.0916(11)</td>
<td>$γ$ (°): 100.0916(11)</td>
</tr>
<tr>
<td>(IPr=CH)PPh$_2$-AuArF$_4$</td>
<td>1448850</td>
<td>C$<em>{35.00}$H$</em>{57.00}$N$_2$P</td>
<td>Monochinic</td>
<td>$P2_1/c$</td>
<td>$V$ (Å$^3$): 3514.58(13)</td>
<td>$R_1$ (all data): 0.1547</td>
</tr>
</tbody>
</table>

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

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

---

Open Access Article. Published on 18 February 2016. Downloaded on 9/19/2020 6:19:35 AM. This journal is © The Royal Society of Chemistry 2016
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)PPr2-PdC1(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-2014 26 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)PPh3-AuC9** 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.

**Synthesis details**

**Synthesis of (IPr=CH)PPr2 2.** 1Pr2P(I) (100 µL, 0.77 mmol) was added dropwise to IPr=CH 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, δJHH = 2.4 Hz, δJHH = 0.8 Hz, 1H, NCHCHN), 5.85 (dd, δJHH = 2.4 Hz, δJHH = 0.8 Hz, 1H, NCHCHN), 3.28 (overlapping septets, 4H, ArCH(CH3)2), 2.66 (dd, δJHP = 5.6 Hz, 1H, CHFPr2), 1.45 (d, δJHH = 7.2 Hz, 6H, ArCH(Ch3)2), 1.33 (d, δJHH = 7.2 Hz, 6H, ArCH(Ch3)2), 1.25 (broad septet, δJHH = 6.8 Hz, 2H, PCH(Ch3)2), 0.96 (dd, δJHH = 7.2 Hz, δJHH = 1.6 Hz, 6H, CH(CH3)-CH3), 0.90 (dd, δJHH = 6.8 Hz, δJHH = 12.8 Hz, 6H, PC(=O)(CH3)-CH3), 11C[1H] (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 (HCCN), 115.0 (HCCN), 51.4 (d, δJCP = 114.7 Hz, HCPPr2), 29.1 (ArCH(Ch3)2), 28.7 (ArCH(Ch3)2), 26.5 (d, δJCP = 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 122.2. Anal. Calcld for C40H47N2P: C, 81.87; H, 8.07; N, 4.77. Found: C, 81.84; H, 8.33; N, 4.55.

**Synthesis of (IPr=CH)PF3Ph 3.** 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 3 as a yellow solid (227 mg, 82%, product also contained 7% of unreacted IPr). Further purification can be performed by adding BpPh3 (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, δJHH = 7.5 Hz, 2H, ArH), 7.14 (d, δJHH = 8.0 Hz, 4H, ArH), 5.86 (dd, δJHH = 2.5 Hz, δJHH = 1.0 Hz, 1H, HCCN), 5.77 (d, δJHH = 2.0 Hz, 1H, HCCN), 3.51 (septet, δJHH = 7.0 Hz, 2H, CH(CH3)2), 3.47 (s, 1H, CHN(Ch3)2), 3.36 (septet, δJHH = 7.0 Hz, 2H, CH(CH3)2), 1.97 (s, 6H, N(Ch3)2), 1.41 (d, δJHH = 7.0 Hz, 6H, CH(Ch3)2), 1.38 (d, δJHH = 7.0 Hz, 6H, CH(Ch3)2), 1.27 (d, δJHH = 7.0 Hz, 6H, CH(Ch3)2), 1.22 (d, δJHH = 7.0 Hz, 6H, CH(Ch3)2). 13C[1H] NMR (126 MHz, C6D6): δ 149.0 (Ar-C), 148.1 (Ar-C), 138.1 (Ncn), 129.1 (Ar-C), 128.3 (Ar-C), 124.6 (Ar-C), 123.1 (Ar-C), 117.4 (HCCN), 114.4 (HCCN), 109.0 (H(Ch3)2), 94.8 (CH(Ch3)2), 28.7 (N(Ch3)2), 28.6 (N(Ch3)2), 25.6 (CH(Ch3)2), 24.4 (CH(Ch3)2), 22.6 (CH(Ch3)2).
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)PPr2·BH3. 106 μL of THF-BH3 (1.0 M solution in THF, 0.11 mmol) was added dropwise to a solution of IPr=CHPPr2·2 (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)PPr2·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, 3JHH = 7.5 Hz, 2H, ArH), 7.17 (d, 3JHH = 8.0 Hz, 4H, ArH), 5.87 (s, 2H, N(CH3)2), 3.16 (septet, 3JHH = 7.0 Hz, 4H, ArCH(CH3)2), 2.09 (d, 3JHP = 10.0 Hz, 1H, CHPPr2), 1.44 (d, 3JHP = 6.5 Hz, 12H, CH(C(CH3)2)2), 1.14 (d, 3JHP = 6.5 Hz, 12H, ArCH(C(CH3)2)2), 1.06 (dd, 3JHH = 7.0 Hz, 3JHP = 14.5 Hz, 6H, PCH(CH3)2), 0.93 (dd, 3JHH = 7.0 Hz, 3JHP = 13.5 Hz, 6H, PCH(CH3)2), 0.25 (broad d, 3JHP = 15.0 Hz, 3H, BH3). 13C{1H} NMR (126 MHz, C6D6): δ 117.6 (Ar–C), 78.8 (Ar–C), 58.9 Hz, P(CH3)2), 28.8 (Ar–C), 25.1 (Ar–CH2), 22.8 (CH(CH3)2), 23.2 (CH(CH3)2), 1.14 (d, 3JCP = 73.8 Hz, 13C{1H} NMR (126 MHz, C6D6): δ 25.2 (CH(CH3)2), 1.12 (d, 3JCP = 10.3 Hz, 13C{1H} NMR (126 MHz, C6D6): δ 147.0 (Ar–C), 131.2 (Ar–C), 125.4 (Ar–C), 117.5 (N(CH3)2), 117.6 (Ar–C), 44.2 (d, 3JCP = 84.8 Hz, HCPPr2), 29.0 (CH(CH3)2), 25.2 (CH(CH3)2), 22.8 (CH(CH3)2). 11B{1H} NMR (126 MHz, C6D6): δ −35.8. 31P{1H} NMR (162 MHz, C6D6): δ 7.3. Mp (°C): 154–156. Anal. Calcd for C34H51AuClN2P: C, 79.99; H, 8.39; N, 3.73. We did not have enough sample to record a meaningful 11B{1H} NMR spectrum.

Synthesis of (IPr=CH)PPr2·AuCl8. A solution of (IPr=CH)-PPr2 (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)-PPr2·AuCl8 as a pale yellow solid (121 mg, 85%). Crystals suitable for X-ray crystallography were obtained by cooling (−30 °C) a saturated solution in toluene/hexanes. Data for (IPr=CH)PPr2·AuCl8: 1H NMR (400 MHz, C6D6): δ 11.2 Hz, 2H, ArH), 7.22–7.00 (m, 8H, PhH and ArH), 5.39 (s, 2H, N(CH3)2), 5.41 (dd, 3JHH = 13.2 Hz, JHH = 9.2 Hz, JHH = 9.2 Hz, 1H, CH, CH3), 4.98 (3H, 3JHH = 11.2 Hz, 3H, PCH(CH3)2). 3.23 (broad septet, 4H, ArCH(CH2)2), 2.79 (broad s, (IPr=CH)PPr2), 2.44 (broad d, 3JHH = 12.0 Hz, 3H, PCH(CH2)3), 1.38 (broad m, 12H, ArCH(CH2)3), 1.14 (broad m, 1H, PCH(CH2)3), 1.06 (dd, 3JHH = 6.8 Hz, 12H, ArCH(CH2)3), 3.15 (H, N(CH3)2), 1.15 (broad m, 1H, PC(CH3)2), 0.87 (dd, 3JHH = 7.0 Hz, 4H, ArCH(CH2)3), 2.22 (d, 3JHP = 6.0 Hz, 1H, PCH(CH2)3), 1.38 (d, 3JHP = 7.0 Hz, 12H, ArCH(CH2)3), 1.28 (septet, 3JHH = 8.0 Hz, 2H, P(CH(CH3)2)), 1.07 (d, 3JHH = 7.0 Hz, 12H, ArCH(CH2)3), 0.87 (dd, 3JHH = 7.0 Hz, 3JHP = 18.0 Hz, 6H, PCH(CH2)3), 0.80 (dd, 3JHH = 7.0 Hz, 3JHP = 16.0 Hz, 6H, PCH(CH2)3). 11C{1H} NMR (126 MHz, C6D6): δ 153.7 (d, 3JCP = 10.3 Hz, 13C{1H} NMR (126 MHz, C6D6): δ 147.0 (Ar–C), 134.3 (Ar–C), 129.3 (Ar–C), 125.4 (Ar–C), 117.5 (N(CH3)2), 40.7 (d, 3JCP = 81.3 Hz, HCPPr2), 29.3 (d, 3JCP = 41.6 Hz, PCH(CH2)3), 28.8 (ArCH(CH2)3), 25.0 (ArCH(CH2)3), 23.2 (ArCH(CH2)3), 19.1 (d, 3JCP = 3.8 Hz, P(CH(CH3)2)), 18.3 (ArCH(CH2)3), 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·AuCl9. A solution of (IPr=CH)-PPh2 (78 mg, 0.13 mmol) in 5 mL of toluene was slowly
added to solid Me₆S·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 [IPr=CH]PMPh₂·AuCl as a pale yellow solid (108 mg, 98%). Crystals suitable for X-ray crystallography were obtained by cooling (−30 °C) a saturated solution in 2:1 mixture of toluene/hexanes. ¹H NMR (400 MHz, C₆D₆): δ 7.47–7.49 (m, 4H, PhH), 7.41 (t, J_HH = 8.0 Hz, 2H, ArH), 7.18 (d, J_HH = 8.0 Hz, 4H, ArH), 6.86–6.87 (m, 6H, 6H, PhH), 5.83 (s, 2H, N(CH₃)₂), 3.00 (septet, J_HH = 6.8 Hz, 4H, CH(CH₃)₂), 2.80 (d, J_HP = 6.4 Hz, 1H, CH₂PPh₂), 1.20 (d, J_HH = 6.8 Hz, 12H, CH(CH₃)₂), 1.08 (d, J_HH = 6.8 Hz, 12H, CH(CH₃)₂).

C¹{H} NMR (126 MHz, C₆D₆): δ 152.3 (d, J_CP = 13.6 Hz, NCN), 146.9 (Ar–C), 139.1 (d, J_CP = 63.9 Hz, Ph–C), 137.8 (Ar–C), 133.7 (Ar–C), 132.6 (d, J_CP = 14.1 Hz, Ph–C), 131.4 (N(CH₃)₂), 129.7 (d, J_CP = 2.3 Hz, Ph–C), 117.5 (Ar–C), 44.6 (d, J_CP = 92.6 Hz, HCPPh₂), 29.0 (CH(CH₃)₂), 24.6 (CH₂CH₃), 23.1 (CH(CH₃)₂).


Reaction of [IPr=CH]PMPh₂·AuCl and Na[BAr₄]²⁻: isolation of [IPr=CH]·PMPh₂·AuCl[BAr₄]²⁻ 10. [IPr=CH]·PMPh₂·AuCl[BAr₄]²⁻

Notes and references
Paper

Dalton Transactions


