Inorganic Chemistry

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Achiral and Chiral PNP-Pincer Ligands with a Carbazole Backbone: Coordination Chemistry with d^8 Transition Metals

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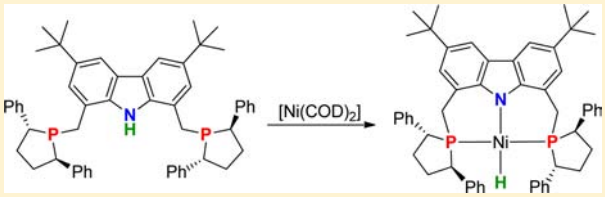
Supporting Information

ABSTRACT: Two new monoanionic PNP pincer type ligands have been synthesized, the achiral 3,6-di-*tert*-butyl-1,8-bis-((diphenyl-phosphino)methyl)-9*H*-carbazole CbzdiphosH (**5**) and the chiral 3,6-di-*tert*-butyl-1,8-bis(((2*R*,5*R*)-2,5-diphenylphospholan-1-yl)methyl)-9*H*-carbazole CbzdipholH (**7**), both of which were initially prepared as their borane complexes. The synthesis of CbzdiphosH is based on the reaction between the key intermediate 1,8-bis(bromomethyl)-3,6-di-*tert*-butyl-9*H*-carbazole (**3**) and lithium diphenylphosphide-borane complex. The chiral ligand CbzdipholH was prepared by treating **3** with lithium (2*R*,5*R*)-2,5-diphenylphospholanide-borane complex and subsequent deprotection with diethylamine. The complexation of the two ligands with nickel, palladium and rhodium was investigated, for which the conformational behavior of the ligands was found to be different. Although the arrangement of the donor atoms in all crystallographically characterized complexes is approximately square planar, the carbazole plane in Cbzdiphos complexes is inclined relative to the coordination plane. On the other hand, a helical twist is observed in Cbzdiphol complexes.



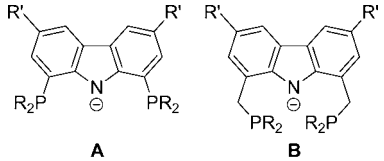
INTRODUCTION

Monoanionic meridionally coordinating tridentate ligands, so-called "pincers", have attracted much attention over the past three decades.[1−10] They provide a robust ancillary ligand system which may stabilize unusual complex structures and thus give rise to remarkable stoichiometric and catalytic reactivity. Particularly notable is the direct involvement of the ligand backbone in the transformations at the metal center. This particular feature enables many recently discovered catalytic transformations reported by Milstein and co-workers.[11−13]

Of special interest are ligands containing both soft and hard donors, a combination which has proved beneficial to a variety of chemical transformations.[14−18] One remarkable example is the PNP system bearing two phosphorus and one nitrogen donor atom. The first monoanionic PNP pincer ligand containing a $-CH_2CH_2NCH_2CH_2-$ backbone was synthesized by Sacconi and co-workers,[19,20] and a number of late transition metal complexes of this ligand have been reported in recent years.[21−24]

The amido phosphine ligands extensively studied in Fryzuk's group have given rise to significant breakthroughs in the activation of small molecules.[25−28] To avoid undesired reactivity involving the PNP ligand, a more robust and rigid system was developed by Liang and co-workers.[29,30] This ligand containing an *o*-phenylene-derived backbone was further studied by Ozerov and Mindiola.[31−33] We have recently reported the synthesis of a new monoanionic PNP ligand incorporating a pyrrole backbone and investigated its Ni^{I} and Ni^{II} coordination chemistry, which is different from other existing systems.[34]

A very interesting PNP pincer ligand (**A**) has been reported by Cui, Hou, and co-workers.[35] In this case the *o*-phenylene derived framework is formally replaced by a carbazole ring. This change led to enhanced rigidity and a larger bite angle. Since their work focused on coordination chemistry of rare-earth metals, these features were favorable, but the orientation of the three donor atoms disfavors meridional complexation of most d-block metals.



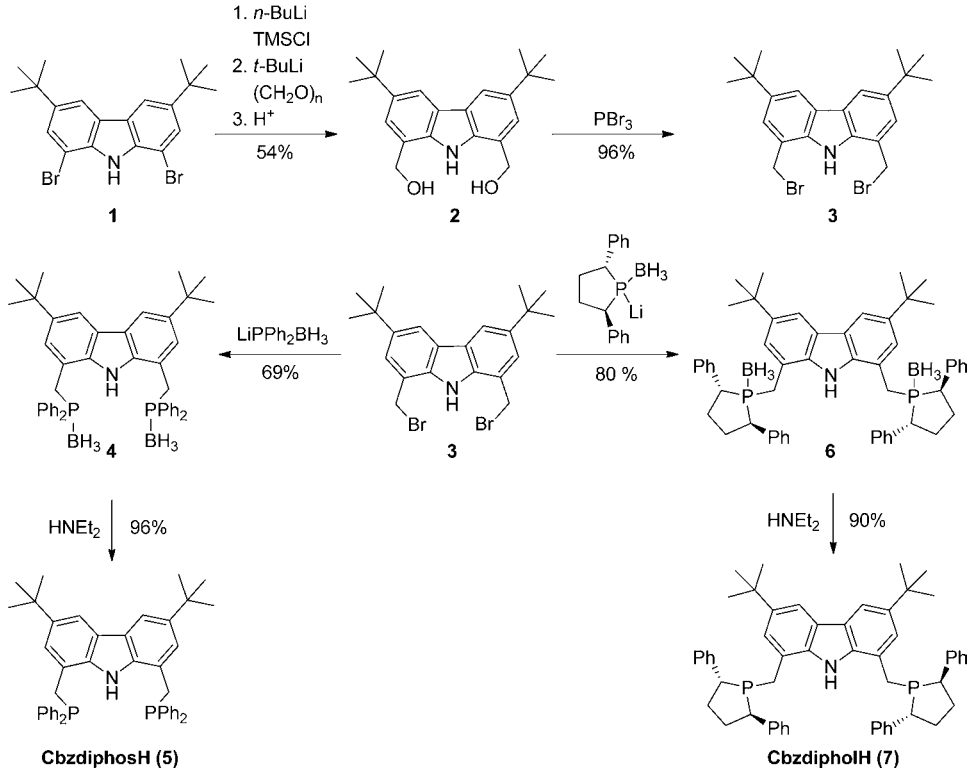
Cui & Hou 2011

Herein we report the synthesis of a new achiral and chiral PNP ligand (**B**) which is designed to combine the advantages of the ligands described above. The achiral ligand 3,6-di-*tert*-butyl-1,8-bis((diphenyl-phosphino)-methyl)-9*H*-carbazole **CbzdiphosH** bears two diphenylphosphine groups linked by a methylene bridge. In the chiral ligand 3,6-di-*tert*-butyl-1,8-bis(((2*R*,5*R*)-2,5-diphenylphospholan-1-yl)methyl)-9*H*-carbazole **CbzdipholH** the phosphine unit is represented by 1,3-diphenyl-phospholane.

The key difference between ligands **A** and **B** is the increased chelate-ring size of the latter because of the insertion of the methylene group. This changes the position and orientation of the phosphine units at the "wingtips" of the tridentate ligand

Received: November 9, 2012
Published: January 30, 2013

Scheme 1. Synthesis and Characterization of the PNP-Pincer Protio-Ligands CbzdiphosH (5) and CbzdipholH (7)



and allows the coordination of the whole range of d-block metals.

We note that despite recent advances in PNP ligand design, chiral monoanionic PNP pincer ligands are still poorly explored. To the best of our knowledge, the only existing system is a modification of Sacconi's ligand, which was first synthesized by Burk and co-workers[36] and further developed by Abdur-Rashid.[37] These ligands contain a $-CH_2CH_2NCH_2CH_2-$ backbone and are thus probably less robust than the chiral ligand described herein.

RESULTS AND DISCUSSION

Synthesis and Characterization of the PNP-Pincer Protio-Ligands CbzdiphosH (5) and CbzdipholH (7). The syntheses of the two protio-ligands are depicted in Scheme 1. The required starting material 1,8-dibromo-3,6-di-*tert*-butyl-9*H*-carbazole (**1**) was synthesized starting from carbazole following literature procedures.[38] Using TMS as an N-protection group,[38] the bromine in **1** was substituted by a hydroxymethylene group introduced by lithiation and subsequent reaction with *p*-formaldehyde. The alcohol (3,6-di-*tert*-butyl-9*H*-carbazole-1,8-diyl)dimethanol (**2**) was then treated with PBr_3 to yield 1,8-bis(bromomethyl)-3,6-di-*tert*-butyl-9*H*-carbazole (**3**), which is a key intermediate in the synthesis of both the chiral and the achiral ligand. The achiral borane protected ligand was prepared by reaction of **3** with the lithium diphenylphosphide-BH_3 adduct, which was generated in situ. After deprotection with diethylamine the protio-ligand CbzdiphosH (**5**) was obtained and characterized by multinuclear NMR spectroscopy and high resolution mass spectrometry. The preparation of the borane protected chiral protio-ligand **6** was achieved by reaction of the enantiopure lithium (2*R*,5*R*)-2,5-diphenylphopholanide-borane complex[39] with **3**. In a similar procedure its enantiomer was obtained using lithium (2*S*,5*S*)-2,5-diphenylphopholanide-borane complex[39] as starting material. Deprotection of **6** with diethylamine gave CbzdipholH (**7**) in 96% yield.

To gain insight into the structural details of this new chiral ligand, single crystals of **6** were grown and subjected to X-ray diffraction (Figure 1). The carbazole backbone is planar and both phosphine units are located at the same side of the carbazole plane. The P−B distances of P(1)−B(1) 1.91 Å are similar to those reported for other phosphine/borane

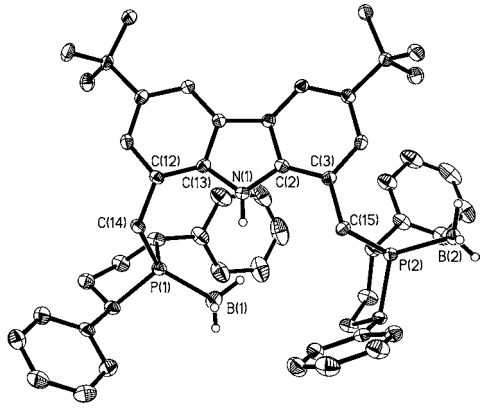


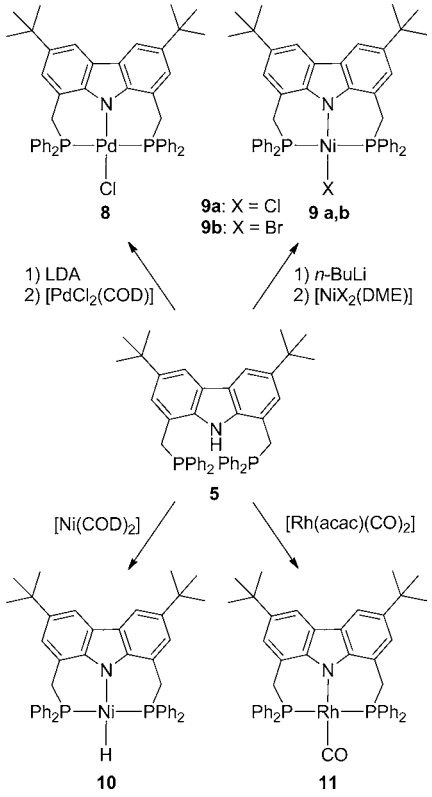
Figure 1. Molecular structure of (*R*)-**6** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon are omitted for clarity. Selected distances (Å) and angles (deg): N(1)−C(2) 1.391(2), N(1)−C(13) 1.396(3), C(2)−C(3) 1.400(3), C(12)−C(13) 1.394(3), C(3)−C(15) 1.513(3), C(12)−C(14) 1.514(3), P(2)−C(15) 1.833(2), P(1)−C(14) 1.836(2); C(2)−C(3)−C(15) 120.1(2), C(13)−C(12)−C(14) 123.4(2), C(3)−C(15)−P(2) 117.7(1), C(12)−C(14)−P(1) 114.1(1).

dx.doi.org/10.1021/ic302454n | Inorg. Chem. 2013, 52, 2050−2059

adducts.[40] All other metric parameters are as expected for carbazole derivatives.[40]

Synthesis and Structural Characterization of Cbzdiphos Transition-Metal Complexes. The coordination chemistry of ligand **5** was investigated for square-planar d^8 transition metal complexes. Reaction with the appropriate metal complex precursors yielded the nickel, palladium, and rhodium compounds shown in Scheme 2.

Scheme 2. Synthesis of the Complexes with Cbzdiphos



The palladium(II) complex **8** was synthesized by salt metathesis of [(Cbzdiphos)Li] with [$PdCl_2$(COD)] at ambient temperature. The complex was fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum displays one singlet at 42.7 ppm [$\delta(^{31}P)$ = −18.5 ppm for the protio-ligand]. This shift is in the range of palladium complexes with other monoanionic PNP ligands.[41]

A single crystal X-ray structure analysis of compound **8** was carried out to establish its structural details and the way this novel ligand system binds to the metal center. Two views of its molecular structure are depicted in Figure 2. As noted above, Cbzdiphos was designed to chelate metals in a tridentate motif and adopts this coordination mode which is approximately square planar around the palladium center [P(1)−Pd−P(2) 173.39(2), N(1)−Pd−Cl 171.60(5)]. The best planes spanned by the four donor atoms, on the one hand, and the carbazole ring, on the other, are inclined relative to each other by an angle of 41.83(3)°. This inclination is due to the structural flexibility of the bridging methylene groups which allow the donor functions to adapt to the size of the central metal atom. Furthermore the ligand offers the possibility of adjusting the P(1)−M−P(2) angle, and thus a certain flexibility in its coordination to metals with different radii.

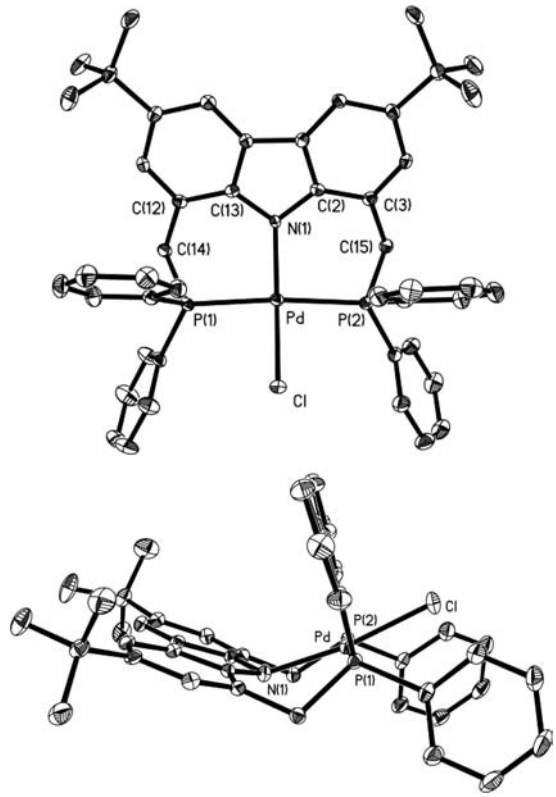


Figure 2. Two representations for the molecular structure of **8** (thermal ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Pd−N(1) 2.079(2), Pd−P(1) 2.3075(6), Pd−P(2) 2.3191(6), Pd−Cl 2.3264(6), N(1)−C(2) 1.405(3), C(2)−C(3) 1.403(4), C(3)−C(15) 1.505(3), P(2)−C(15) 1.831(2); P(1)−Pd−P(2) 173.39(2), N(1)−Pd−Cl 171.60(5), C(12)−C(14)−P(1) 107.5(2), C(3)−C(15)−P(2) 108.9(2).

In view of the nonequivalence of the two faces of the square planar complexes because of the inclination of the ligand backbone in the solid state, the methylene protons were expected to be diastereotopic. The NMR spectrum, however, revealed only one signal for all four methylene protons, indicating a rapid exchange between two conformers in solution. Attempts to freeze out the interconversion between both conformers on the NMR time scale at low temperature were unsuccessful.

Deprotonation of **5** with *n*-BuLi and subsequent reaction with [$NiCl_2$(DME)] or [$NiBr_2$(DME)] yielded the square planar nickel(II) complexes **9a** or **9b**, respectively. The formation of both complexes was confirmed by elemental analysis, NMR spectroscopy and mass spectrometry. Single crystal X-ray structure analyses display notable differences between the two nickel(II) complexes. The angles between the coordination plane spanned by the four donor atoms and the carbazole ring are 47.98(3)° (**9a**) and 42.81(5)° (**9b**) and the P(1)−Ni−P(2) angles are 159.99(2)° (**9a**) and 170.62(5)° (**9b**). Furthermore the distances *d*(Ni−N1) = 1.934(2) Å (**9a**) and *d*(Ni−N1) = 1.948(4) Å (**9b**) differ significantly (see Supporting Information). These differences most likely result from the different *trans* influences of the chloro and the bromo ligand.[42,43]

As previously observed with other PNP ligands oxidative addition of the N−H bond of the protio-ligand **5** to Ni^0 led to the nickel(II) hydrido complex [(Cbzdiphos)NiH] **10**.[30,44,45]

dx.doi.org/10.1021/ic302454n | *Inorg. Chem.* 2013, 52, 2050−2059

Its formulation and structure were confirmed by NMR spectroscopy, high resolution mass spectrometry, elemental analysis, and single crystal X-ray structure analysis. The formation of complex **10** was monitored by ^{1}H NMR spectroscopy and was indicated by the disappearance of the N−H signal and the appearance of a triplet for the hydrido ligand at −18.5 ppm ($^{2}J_{PH}$ = 69.9 Hz). The ^{31}P{^{1}H} NMR spectrum revealed one singlet at 33.4 ppm.

The detailed structure of complex **10** was established by X-ray diffraction (Figure 3). The position of the hydrido ligand could be directly detected in the electron density map. The coordination geometry around the nickel center is again distorted square planar with a N(1)−Ni−H angle of 169(1)° and a P(1)−Ni−P(2) angle of 164.12(3)°. As a consequence, the angle between the carbazole moiety and the plane spanned by all four donor atoms is 33.5(3)° and thus smaller than in the complexes described above.

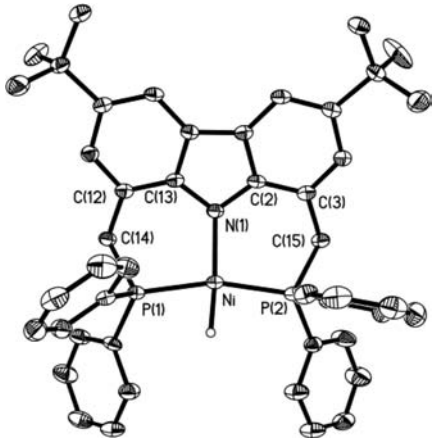


Figure 3. Molecular structure of complex **10** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon are omitted for clarity. Selected distances (Å) and angles (deg): Ni−N(1) 1.934(2), Ni−P(1) 2.1403, Ni−P(2) 2.1384(6), Ni−H 1.40(3), N(1)−C(2) 1.396(3), C(2)−C(3) 1.406(3), C(3)−C(15) 1.504(3), P(2)−C(15) 1.832(2); N(1)−Ni−H 169(1), P(1)−Ni−P(2) 164.12(3), C(12)−C(14)−P(1) 110.8(1), C(3)−C(15)−P(2) 109.7(1).

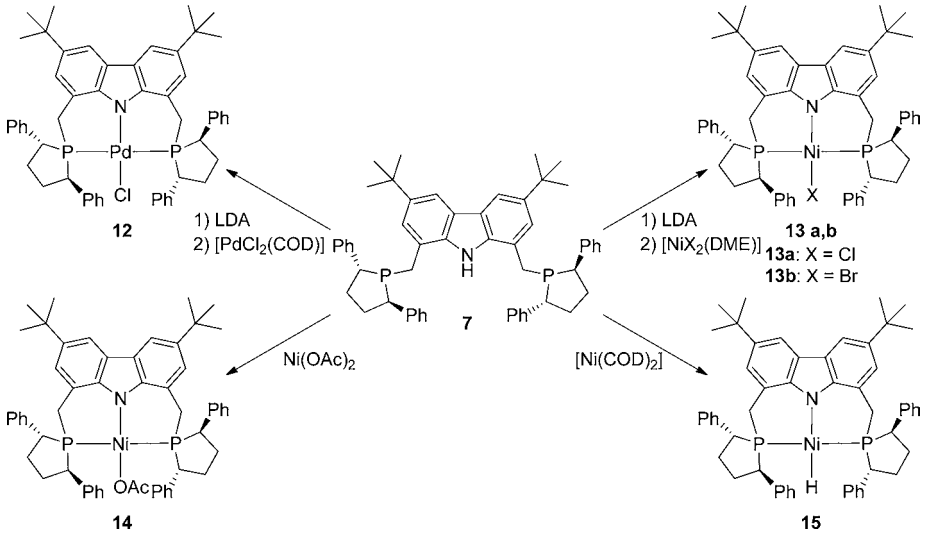
Following a synthetic pathway that avoids lithiation of the protio-ligand, compound **5** was treated with [Rh(acac)(CO)$_2$]. Acetylacetonate acts as an internal base, and gas evolution was observed upon formation of complex **11** indicating displacement of CO. The formulation of the rhodium(I) complex was established by elemental analysis and mass spectrometry. Similar to the complexes described above, the ^{1}H, ^{13}C, and ^{31}P NMR spectra indicate effective C_{2v}-symmetry in solution. The molecular geometry in the crystal structure is closely related to that of the complexes described above, with a square-planar arrangement of the donor atoms [P(2)−Rh−P(1) 178.21(2) and C(48)−Rh−N(1) 179.67(7)]. The angle between the coordination plane and the carbazole ring is 30.48(4)° and thus the smallest among the complexes described here. (See Supporting Information)

Synthesis and Structural Characterization of Cbzdiphol Transition-Metal Complexes. To explore the coordination chemistry of the chiral ligand Cbzdiphol five different complexes were prepared (Scheme 3).

Deprotonation of the protio-ligand **7** with LDA and subsequent reaction with [PdCl$_2$(COD)] gave the palladium(II) complex **12**. The formation of the complex was confirmed by elemental analysis and high resolution mass spectrometry, and the ^{1}H, ^{13}C, and ^{31}P NMR spectra are consistent with effective C_2-symmetry in solution.

The nickel(II) halogenido complexes **13a** and **13b** were prepared by salt metathesis with [Li(Cbzdiphol)] and [NiCl$_2$(DME)] or [NiBr$_2$(DME)], respectively, and fully characterized by elemental analysis, high resolution mass spectrometry, and NMR spectroscopy. The NMR spectra indicate C_2-symmetry in solution as in the case of the palladium(II) complex **12**. To gain insight into the structural details of the complex geometry in the solid state, a single crystal X-ray structure analysis of **13b** was carried out (Figure 4). The C_2-symmetry of the solution structure, indicated by NMR spectroscopy, is only approximately retained in the solid state with a near molecular C_2 axis along the N(1)−Ni−Br vector. The coordination geometry around the nickel center is nearly ideal square planar with a N(1)−Ni−Br angle of

Scheme 3. Synthesis of the Complexes with Cbzdiphol



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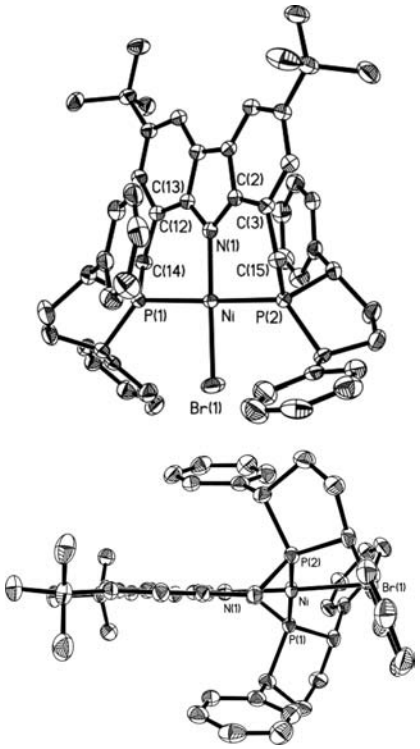

Figure 4. Two representations of the molecular structure of (*S*)-**13b** (thermal ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni−N(1) 1.937(2), Ni−P(1) 2.1940(8), Ni−P(2) 2.1921(8), Ni−Br 2.3073(5), N(1)−C(2) 1.391(4), C(2)−C(3) 1.409(4), C(3)−C(15) 1.506(4), P(2)−C(15) 1.823(3); N(1)−Ni−Br 177.75(8), P(1)−Ni−P(2) 175.61(4), C(12)−C(14)−P(1) 111.4(2), C(3)−C(15)−P(2) 108.4(2).

177.8(1) and a P(1)−Ni−P(2) angle of 175.61(5), thus close to 180°. The nickel center is shielded by one phenyl group of each phospholane which are facing in opposite directions.

To adapt to the radius of the central metal ion the coordination plane is twisted with respect to the carbazole ring. As a consequence, the two phospholane groups point to opposite faces of the carbazole plane. The angle between these planes is 27.70°, and the distances between the plane spanned by the carbazole atoms and the two phosphorus atoms are 1.080 Å and 0.929 Å.

The preparation of the nickel complexes **13a** and **13b** was based on the initial lithiation of the chiral ligand CbzdipholH **7** and the use of the lithium carbazolides as ligand transfer reagents. As an alternative route to nickel compounds, we treated the protio-ligands directly with nickel(II) acetate, the acetate anion acting as an internal base. The formation of the acetato complex **14** was confirmed by elemental analysis, mass spectrometry, and NMR spectroscopy. Single crystals were obtained from a pentane solution, and the molecular structure of a pentane solvate in the solid state was established by X-ray diffraction (Figure 5).

The coordination geometry around the nickel center is approximately square planar with the metal ion surrounded by the Cbzdiphol ligand and a disordered acetate moiety. The acetate is bound in a monodentate (κ^1) fashion in a trans disposition to the central anionic carbazolato ring, the two disordered positions of the nickel bound oxygen O(1A)/O1(B) (population 0.76 and 0.24, respectively) being slightly above

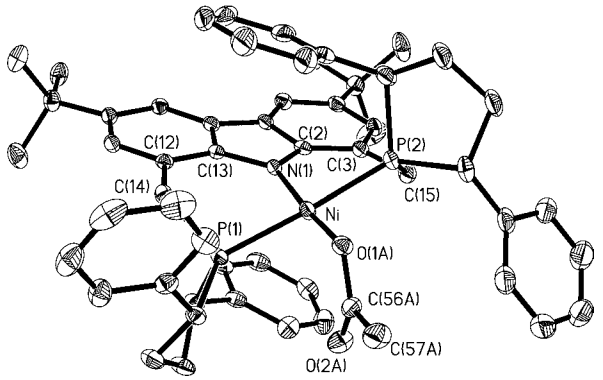

Figure 5. Molecular structure of (*R*)-**14** (thermal ellipsoids at 50% probability level). Hydrogen atoms and the less populated of the disordered acetate moieties are omitted for clarity. Selected distances (Å) and angles (deg): Ni−N(1) 1.911(1), Ni−P(1) 2.1882(5), Ni−P(2) 2.1959(4), Ni−O(1A) 1.877(2), N(1)−C(2) 1.401(2), C(2)−C(3) 1.410(2), C(3)−C(15) 1.507(2), P(1)−C(14) 1.815(2), P(2)−C(15) 1.820(2); N(1)−Ni−O(1A) 172.09(8), P(1)−Ni−P(2) 176.89(2), C(12)−C(14)−P(1) 108.8(1), C(3)−C(15)−P(2) 109.8(1).

and below the N(1)NiP(1)P(2) plane [N(1)−Ni−O(1A)/O(1B) 172.09(8)/ 163.2(2)°, P(1)−Ni−P(2) 176.89(2)°]. The helical twist between the carbazolide ring and the plane spanned by the ligating atoms of Cbzdiphol is 29.08(2)° [30.68(4)°, respectively] and thus slightly larger than in complex **13b**.

Following the same route as described above for the synthesis of the nickel(II) hydrido complex **10** the protio-ligand **7** was treated with [Ni(COD)$_2$] yielding complex **15** via oxidative addition of the N−H bond to Ni^0. The hydrido complex was isolated in 69% yield and characterized by elemental analysis, mass spectrometry, and NMR spectroscopy. The ^{1}H NMR spectrum revealed a triplet resonance at −19.77 ppm for the hydride ($^2J_{PH}$ = 73.3 Hz) which is very similar to the spectral characteristics of complex **10**.

CONCLUSION

In this work, we developed an efficient synthesis for two new monoanionic PNP ligands containing a carbazole backbone. Both ligands were prepared by reacting the borane protected lithium salt of the phosphine unit with the key intermediate **3**.

The ligands which are best categorized as monoanionic pincers, readily coordinate to transition metals such as nickel, palladium, and rhodium. The coordination modes of the two ligand systems differ in that the carbazole backbone is inclined in the Cbzdiphos complexes whereas the Cbzdiphol compounds display a helical twist between the coordination plane and the carbazole ring. Studies focusing on potential applications as ancillary ligands in molecular catalysis are ongoing in our laboratory.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations were carried out under inert gas conditions by using standard Schlenk and glovebox techniques. Argon 5.0, purchased from Messer Group GmbH, was used after drying over Granusic phosphorus pentoxide (granulated). Solvents were dried according to literature procedures[46] and stored in glass ampules under an argon atmosphere. Et_2O and *n*-pentane were distilled from sodium/potassium alloy, benzene and *n*-hexane from potassium, CH_2Cl_2 and $CHCl_3$ from calcium hydride, and toluene from sodium. The same procedures were used to dry the deuterated

dx.doi.org/10.1021/ic302454n | *Inorg. Chem.* 2013, 52, 2050−2059

solvents. Degassed solvents were obtained by three successive freeze−pump−thaw cycles. The ligand precursor was synthesized according to literature.[38] All other chemicals were used as received without further purification. NMR spectra were recorded on Bruker Avance III (600 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual proton solvent signals or carbon resonances.[47] H_3PO_4 (^{31}P) was used as an external standard. The following abbreviations were used: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad signal). High-resolution mass spectra were acquired on JEOL JMS-700 magnetic sector (FAB, EI) spectrometers at the mass spectrometry facility of the Institute of Organic Chemistry, the University of Heidelberg. Elemental analysis was carried out in the Microanalysis Laboratory of the Heidelberg Chemistry Department.

Preparation of (3,6-Di-*tert*-butyl-9*H*-carbazole-1,8-diyl)-dimethanol (2). *n*-BuLi (6.0 mL, 2.5 M in *n*-hexane, 15.2 mmol) was added to a solution of 1,8-dibromo-3,6-di-*tert*-butyl-9*H*-carbazole (**1**) (5.0 g, 11,4 mmol) in 100 mL of diethyl ether at 0 °C. After stirring for 1 h, trimethylsilyl chloride (2.0 mL, 15.8 mmol) was added, and the reaction mixture was allowed to warm to ambient temperature. After stirring for 1 h, the suspension was cooled to −78 °C, and *t*-BuLi (37 mL, 1.9 M in *n*-pentane, 70 mmol) was added. After completed addition, the reaction mixture was stirred at 0 °C for 3 h. At −78 °C, paraformaldehyde (1.25 g, 41.6 mmol) was added, and the reaction mixture was allowed to warm to room temperature overnight. The resulting suspension was heated to 55 °C. Hydrolysis was performed by the addition of 25 mL of H_2O. The organic phase was washed with 25 mL of saturated $NaHCO_3$ and 25 mL of brine, dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (gradient elution from dichloromethane to methanol) to yield the product as a white solid (2.1 g, 6.2 mmol, 54%). ^{1}H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 1.44 (s, 18H, $C(CH_3)_3$), 4.97 (s, 4H, CH_2), 7.29 (s, 2H, $CH^{Carb\text{-}2}$), 8.01 (s, 2H, $CH^{Carb\text{-}4}$), 9.24 (br, 1H, N*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 32.0 (s, $C(CH_3)_3$), 34.6 (s, $C(CH_3)_3$), 64.4 (s, CH_2), 116.0 (s, $CH^{Carb\text{-}4}$), 122.1 (s, $C^{Carb\text{-}1}$), 122.3 (s, $CH^{Carb\text{-}2}$), 123.6 (s, $C^{Carb\text{-}4a}$), 137.0 (s, $C^{Carb\text{-}9a}$), 141.9 (s, $C^{Carb\text{-}3}$). HRMS (EI) *m*/*z* (%) calcd: 339.2198. Found: 339.2210 (100) (M^+). Anal. Calcd. for $C_{22}H_{29}NO_2$: C 77.84; H 8.61; N 4.13. Found: C 77.41; H 8.67; N 4.11.

Preparation of 1,8-Bis(bromomethyl)-3,6-di-*tert*-butyl-9*H*-carbazole (3). PBr_3 (1.22 mL, 13.0 mmol) was added to a solution of (3,6-di-*tert*-butyl-9*H*-carbazole-1,8-diyl)dimethanol (**2**) (2.0 g, 5.89 mmol) in 40 mL of dichloromethane at 0 °C. After stirring for 1 h, hydrolysis was performed at 0 °C. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and dried in vacuo to afford a white solid (2.63 g, 5.65 mmol, 96%). ^{1}H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 1.45 (s, 18H, $C(CH_3)_3$), 4.90 (s, 4H, CH_2), 7.42 (s, 2H, $CH^{Carb\text{-}2}$), 8.05 (s, 2H, $CH^{Carb\text{-}4}$), 8.44 (br, 1H, N*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 31.9 (s, CH_2), 32.0 (s, $C(CH_3)_3$), 34.7 (s, $C(CH_3)_3$), 117.6 (s, $CH^{Carb\text{-}4}$), 119.0 (s, $C^{Carb\text{-}1}$), 124.2 (s, $CH^{Carb\text{-}2}$), 124.4 (s, $C^{Carb\text{-}4a}$), 137.2 (s, $C^{Carb\text{-}9a}$), 143.0 (s, $C^{Carb\text{-}3}$). HRMS (EI) *m*/*z* (%) calcd: 465.0490. Found: 465.0472 (42.4) (M^+). Anal. Calcd. for $C_{22}H_{27}Br_2N$: C 56.79; H 5.85; N 3.01. Found: C 57.20; H 6.08; N 3.01.

Preparation of 3,6-Di-*tert*-butyl-1,8-bis((diphenylphosphino)methyl)-9*H*-carbazole-borane Complex (4). *n*-BuLi (5.16 mL, 2.5 M in *n*-hexane, 12.9 mmol) was added to a solution of borane diphenylphosphine complex (2.58 g, 12.9 mmol) in 60 mL of thf at −78 °C. After stirring for 45 min, the reaction mixture was treated with a solution of 1,8-bis(bromomethyl)-3,6-di-*tert*-butyl-9*H*-carbazole (**3**) (2.0 g, 4.3 mmol) in 50 mL of thf at −78 °C. After stirring overnight, the solvent was removed in vacuo. The resulting solid was dissolved in dichloromethane and was washed with H_2O and saturated brine, dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was recrystallized from diethyl ether to yield the product as a white solid (2.10 g, 2.99 mmol, 69%). ^{1}H{^{31}P} NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 0.71−1.50 (br, 6H, B*H*3), 1.20 (s, 18H, $C(CH_3)_3$), 3.78 (s, 4H, CH_2), 6.75 (s, 2H, $CH^{Carb\text{-}2}$), 7.37 (t, $^3J_{HH}$ = 7.5 Hz 8H, $CH^{m\text{-}Ph}$), 7.45 (t, ^3J = 7.3 Hz, 4H, $CH^{p\text{-}Ph}$), 7.63 (d, ^3J = 7.9 Hz, 8H, $CH^{o\text{-}Ph}$), 7.82 (s, 2H, $CH^{Carb\text{-}4}$), 8.03 (br, 1H, N*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 31.1 (d, $^1J_{CP}$ = 33.0 Hz, CH_2), 31.7 (s, $C(CH_3)_3$), 34.4 (s, $C(CH_3)_3$), 113.6 (d, $^2J_{CP}$ = 4.6 Hz, $CH^{Carb\text{-}1}$), 115.1 (d, $^5J_{CP}$ = 2.9 Hz, $C^{Carb\text{-}4}$), 123.6 (d, $^4J_{CP}$ = 2.1 Hz, $C^{Carb\text{-}4a}$), 126.2 (d, $^3J_{CP}$ = 5.0 Hz, $CH^{Carb\text{-}2}$), 128.7 (d, $^3J_{CP}$ = 10.0 Hz, $CH^{m\text{-}Ph}$), 128.7 (d, $^1J_{CP}$ = 54.0 Hz, C^{Ph}), 131.3 (d, $^4J_{CP}$ = 2.4 Hz, $CH^{p\text{-}Ph}$), 132.7 (d, $^2J_{CP}$ = 8.8 Hz, $CH^{o\text{-}Ph}$), 137.7 (d, $^3J_{CP}$ = 3.6 Hz, $C^{Carb\text{-}9a}$), 142.0 (d, $^4J_{CP}$ = 2.7 Hz, $C^{Carb\text{-}3}$). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) 16.9. ^{11}B{^{1}H} NMR (182.3 MHz, $CDCl_3$, rt): δ (ppm) −37.9. HRMS (ESI) *m*/*z* (%) calcd: 704.39137. Found: 704.39267 (12.5) ($M+H^+$). Anal. Calcd. for $C_{46}H_{53}B_2NP_2$: C 78.54; H 7.59; N 1.99. Found: C 78.07; H 7.67; N 2.21.

Preparation of 3,6-Di-*tert*-butyl-1,8-bis((diphenylphosphino)methyl)-9*H*-carbazole (5). 3,6-Di-*tert*-butyl-1,8-bis-((diphenylphosphino)methyl)-9*H*-carbazole-borane complex (**4**) (1.50 g, 2.13 mmol) was dissolved in degassed diethylamine. After stirring for 4 days, the solvent was removed in vacuo to yield the product as a white solid (1.38 g, 2.04 mmol, 96%). ^{1}H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 1.31 (s, 18H, $C(CH_3)_3$), 3.63 (s, 4H, CH_2), 6.92 (s, 2H, $CH^{Carb\text{-}2}$), 7.31−7.35 (m, 12H, $CH^{p\text{-}Ph}$, $CH^{m\text{-}Ph}$), 7.41−7.46 (m, 8H, $CH^{o\text{-}Ph}$), 7.81 (br, 1H, N*H*), 7.88 (s, 2H, $CH^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 31.9 (s, $C(CH_3)_3$), 32.9 (s, CH_2), 34.5 (s, $C(CH_3)_3$), 114,1 (s, $CH^{Carb\text{-}4}$), 118.7 (m, $C^{Carb\text{-}1}$), 123.7 (s, $C^{Carb\text{-}4a}$), 125.0 (m, $CH^{Carb\text{-}2}$), 128.4 (m, $CH^{m\text{-}Ph}$), 128.8 (s, $CH^{p\text{-}Ph}$), 133.0 (m, $CH^{o\text{-}Ph}$), 137.3 (m, C^{Ph}), 138.4 (m, $C^{Carb\text{-}9a}$), 142.3 (s, $C^{Carb\text{-}3}$). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) −18.5. HRMS (EI) *m*/*z* (%) calcd: 675.3184. Found: 675.3163 (42.0) (M^+).

Preparation of {3,6-Di-*tert*-butyl-1,8-bis(((2*R*,5*R*)-2,5-diphenylphospholan-1-yl)methyl)-9*H*-carbazole}borane Complex (6). *n*-BuLi (1.4 mL, 2.5 M in *n*-hexane, 3.5 mmol) was added to a solution of (2*R*,5*R*)-2,5-diphenylphospholane-borane complex (0.86 g, 3.4 mmol) in 20 mL of thf at −78 °C. After stirring for 1 h, the reaction mixture was treated with a solution of **3** (0.53 g, 1.1 mmol) in 20 mL of thf at −78 °C. The solution was stirred overnight, and the solvent was removed in vacuo. The resulting solid was dissolved in dichloromethane and was washed with H_2O and brine, dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, dichloromethane/pentane 1:2) yielding the product as a white solid (0.73 g, 0.90 mmol, 80%). ^{1}H{^{31}P} NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 0.55−1.11 (bs, 6H, BH_3), 1.33 (s, 18H, $C(CH_3)_3$), 2.05−2.12 (m, 2H, CH_2^{Phos}), 2.27−2.34 (m, 2H, CH_2^{Phos}), 2.43−2.55 (m, 4H, CH_2^{Phos}), 2.71−2.78 (m, 4H, CH_2), 3.14 (m, 2H, CH^{Phos}), 3.78 (dd, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, CH^{Phos}), 6.11 (d, $^3J_{HH}$ = 7,4 Hz, 4H, $CH^{o\text{-}Ph}$), 6.63 (t, $^3J_{HH}$ = 7,3 Hz, 2H, $CH^{p\text{-}Ph}$), 6.75 (t, $^3J_{HH}$ = 7,4 Hz, 4H, $CH^{m\text{-}Ph}$), 7.25 (s, 2H, $CH^{Carb\text{-}2}$), 7.33 (t, $^3J_{HH}$ = 7,3 Hz, 2H, $CH^{p\text{-}Ph}$), 7.47 (t, $^3J_{HH}$ = 7,4 Hz, 4H, $CH^{m\text{-}Ph}$), 7.60 (d, $^3J_{HH}$ = 7,6 Hz, 4H, $CH^{o\text{-}Ph}$), 7.92 (s, 2H, $CH^{Carb\text{-}4}$), 8.41 (s, 1H, N*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 27.0 (d, $^1J_{CP}$ = 24.5 Hz, CH_2), 29.6 (s, CH_2^{Phos}), 31.9 (s, $C(CH_3)_3$), 33.0 (d, $^2J_{CP}$ = 4.4 Hz, CH_2^{Phos}), 34.6 (s, $C(CH_3)_3$), 43.6 (d, $^1J_{CP}$ = 28.0 Hz, CH^{Phos}), 47.2 (d, $^1J_{CP}$ = 29.1 Hz, CH^{Phos}), 113.4 (d, $^2J_{CP}$ = 4.2 Hz, $C^{Carb\text{-}1}$), 115.2 (d, $^5J_{CP}$ = 2.5 Hz, $CH^{Carb\text{-}4}$), 124.1 (d, $^4J_{CP}$ = 2.1 Hz, $C^{Carb\text{-}4a}$), 126.1 (d, $^3J_{CP}$ = 4.7 Hz, $CH^{Carb\text{-}2}$), 126.3 (d, $^5J_{CP}$ = 2.6 Hz, $CH^{p\text{-}Ph}$), 127.3 (d, $^5J_{CP}$ = 2.4 Hz, $CH^{p\text{-}Ph}$), 127.5 (d, $^4J_{CP}$ = 2.0 Hz, $CH^{m\text{-}Ph}$), 127.8 (d, $^3J_{CP}$ = 3.5 Hz, $CH^{o\text{-}Ph}$), 128.1 (d, $^3J_{CP}$ = 4.7 Hz, $CH^{o\text{-}Ph}$), 128.9 (d, $^4J_{CP}$ = 1.8 Hz, $CH^{m\text{-}Ph}$), 135.6 (d, $^2J_{CP}$ = 4.4 Hz, $C^{q\text{-}Ph}$), 136.5 (s, $C^{q\text{-}Ph}$), 137.5 (d, $^3J_{CP}$ = 3.6 Hz, $C^{Carb\text{-}9a}$), 142.9 (d, $^4J_{CP}$ = 2.2 Hz, $C^{Carb\text{-}3}$). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) 38.4. HRMS (ESI) *m*/*z* (%) calcd: 834.4673. Found: 834.4688 (31) ($M+Na^+$). Anal. Calcd. for $C_{54}H_{65}B_2NP_2$: C 79.91; H 8.07; N 1.73. Found: C 79.43; H 8.08; N 2.23.

Preparation of 3,6-Di-*tert*-butyl-1,8-bis(((2*R*,5*R*)-2,5-diphenylphospholan-1-yl)methyl)-9*H*-carbazole (7). **6** (0.30 g, 0.37 mmol) was suspended in 30 mL of degassed diethylamine. After stirring for 48 h, the solvent was removed in vacuo, and the crude product dissolved in toluene. After filtration through alumina the product was obtained as a white solid (0.26 g, 0.33 mmol, 90%). ^{1}H{^{31}P} NMR (600.1 MHz, C_6D_6, rt): δ (ppm) 1.40 (s, 18H, $C(CH_3)_3$), 1.67−1.77 (m, 2H, CH_2^{Phos}), 2.09−2.28 (m, 6H, CH_2^{Phos}), 2.56 (d, $^2J_{HH}$ = 13.7 Hz, 2H, CH_2), 2.69 (d, $^2J_{HH}$ = 13.9 Hz, 2H, CH_2),

dx.doi.org/10.1021/ic302454n | *Inorg. Chem.* 2013, 52, 2050−2059

3.17 (dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, CH^{Phos}), 3.60 (dd, $^3J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 5.3 Hz, 2H, CH^{Phos}), 6.74 (d, $^3J_{HH}$ = 7,8 Hz, 4H, C$H^{o\text{-}Ph}$), 6.77 (t, $^3J_{HH}$ = 7,3 Hz, 2H, C$H^{p\text{-}Ph}$), 6.89 (t, $^3J_{HH}$ = 7,6 Hz, 4H, C$H^{m\text{-}Ph}$), 7.07 (t, $^3J_{HH}$ = 7,3 Hz, 2H, C$H^{p\text{-}Ph}$), 7.21 (t, $^3J_{HH}$ = 7,6 Hz, 4H, C$H^{m\text{-}Ph}$), 7.24 (s, 2H, C$H^{Carb\text{-}2}$), 7.35 (d, $^3J_{HH}$ = 7,7 Hz, 4H, C$H^{o\text{-}Ph}$), 8.06 (s, 2H, C$H^{Carb\text{-}4}$), 8.36 (s, 1H, N*H*). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 29.0 (d, $^1J_{CP}$ = 26.9 Hz, CH_2), 31.4 (d, $^2J_{CP}$ = 3.1 Hz, CH_2^{Phos}), 32.0 (s, C$(CH_3)_3$), 34.5 (s, $C(CH_3)_3$), 36.2 (s, CH_2^{Phos}), 46.4 (m, CH^{Phos}), 49.0 (m, CH^{Phos}), 114.4 (s, C$H^{Carb\text{-}4}$), 119.2 (vt, $C^{Carb\text{-}1}$), 124.1 (s, $C^{Carb\text{-}4a}$), 124.4 (vt, C$H^{Carb\text{-}2}$), 125.6 (s, C$H^{p\text{-}Ph}$), 126.0 (s, C$H^{p\text{-}Ph}$), 127.6 (m, 2C, C$H^{o\text{-}Ph}$), 128.3 (s, C$H^{m\text{-}Ph}$), 128.6 (s, C$H^{m\text{-}Ph}$), 137.6 (s, $C^{Carb\text{-}9a}$), 139.0 (s, $C^{q\text{-}Ph}$), 142.1 (s, $C^{Carb\text{-}3}$), 144.2 (m, $C^{q\text{-}Ph}$). ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 6.8. ^{11}B{^{1}H} NMR (182.3 MHz, $CDCl_3$, rt): δ (ppm) −36.6. HRMS (FAB) *m*/*z* (%) calcd: 784.4196. Found: 784.4253 (100) (M+H$^+$). Anal. Calcd. for $C_{54}H_{59}NP_2$: C 82.73; H 7.59; N 1.79. Found: C 82.74; H 7.16; N 1.70.

Preparation of Chloro{3,6-di-*tert*-butyl-1,8-bis-((diphenylphosphino)methyl)carbazole}palladium(II) (8). LDA (0.087 mg, 0.81 mmol) was added to a solution of CbzdiphosH (**5**) (0.50 g, 0.74 mmol) in 20 mL of thf. After stirring for 1 h at ambient temperature, the resulting solution was added to a solution of $PdCl_2COD$ (0.25 g, 0.89 mmol) in 10 mL of thf. The reaction mixture was stirred overnight. The solvent was removed in vacuo, dissolved in toluene, and filtered. After drying in vacuo, the crude product was washed with *n*-pentane to give the product as a pink solid (0.47 g, 0.58 mmol, 78%). ^{1}H NMR (600.1 MHz, C_6D_6, rt): δ (ppm) 1.41 (s, 18H, $C(CH_3)_3$), 3.60 (m, 4H, CH_2), 6.91−6.98 (m, 2H, C$H^{p\text{-}Ph}$, C$H^{m\text{-}Ph}$), 7.01 (s, 2H, C$H^{Carb\text{-}2}$), 7.76−7.80 (m, 8H, C$H^{o\text{-}Ph}$), 8.15 (s, 2H, C$H^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 29.1 (vt, CH_2), 32.0 (s, C$(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 115.5 (s, C$H^{Carb\text{-}4}$), 118.2 (s, $C^{Carb\text{-}1}$), 124.4 (vt, C$H^{Carb\text{-}2}$), 127.0 (s, $C^{Carb\text{-}4a}$), 128.2 (vt, C$H^{m\text{-}Ph}$), 130.3 (vt, C^{Ph}), 130.5 (s, C$H^{p\text{-}Ph}$), 133.9 (vt, C$H^{o\text{-}Ph}$), 139.9 (s, $C^{Carb\text{-}3}$), 148.9 (vt, $C^{Carb\text{-}9a}$). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) 42.7. HRMS (FAB) *m*/*z* (%) calcd: 817.1835. Found: 817.1804 (100) (M$^+$). Anal. Calcd. for $C_{50}H_{54}ClNOP_2Pd$: C 67.57; H 6.12; N 1.58. Found: C 67.47; H 6.20; N 1.77.

Preparation of Chloro{3,6-di-*tert*-butyl-1,8-bis-((diphenylphosphino)methyl)carbazole}nickel(II) (9a). *n*-BuLi (0.20 mL, 2.5 M in *n*-hexane, 0.50 mmol) was added to a solution of CbzdiphosH (**5**) (0.31 g, 0.45 mmol) in 10 mL of thf at −78 °C. After stirring for 0.5 h at ambient temperature, $NiCl_2DME$ (0.14 g, 0.63 mmol) was added at −78 °C. The reaction mixture was stirred overnight. The solvent was removed in vacuo, dissolved in dichloromethane and filtered through a pad of Celite. After drying in vacuo, the crude product was washed with *n*-pentane to give the product as a red solid (0.32 g, 0.41 mmol, 91%). ^{1}H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 1.33 (s, 18H, $C(CH_3)_3$), 3.60 (t, $^2J_{HP}$ = 3.2 Hz, 4H, CH_2), 6.95 (s, 2H, C$H^{Carb\text{-}2}$), 7.31 (t, $^3J_{HH}$ = 7.5 Hz, 8H, C$H^{m\text{-}Ph}$), 7.41 (t, $^3J_{HH}$ = 7.4 Hz, 4H, C$H^{p\text{-}Ph}$), 7.84−7.87 (m, 8H, C$H^{o\text{-}Ph}$), 7.88 (s, 2H, C$H^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 28.8 (vt, CH_2), 31.9 (s, C$(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 114,5 (s, C$H^{Carb\text{-}4}$), 118.6 (s, $C^{Carb\text{-}1}$), 123.2 (vt, C$H^{Carb\text{-}2}$), 126.9 (s, $C^{Carb\text{-}4a}$), 128.3 (vt, C$H^{m\text{-}Ph}$), 130.4 (s, C$H^{p\text{-}Ph}$), 130.6 (vt, C^{Ph}), 133.5 (vt, C$H^{o\text{-}Ph}$), 140.5 (s, $C^{Carb\text{-}3}$), 147.9 (vt, $C^{Carb\text{-}9a}$). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) 23.0. HRMS (FAB) *m*/*z* (%) calcd: 767.2147. Found: 767.2139 (19.2) (M$^+$). Anal. Calcd. for $C_{46}H_{46}ClNNiP_2$: C 71.85; H 6.03; N 1.82. Found: C 71.29; H 6.32; N 1.70.

Preparation of Bromo{3,6-di-*tert*-butyl-1,8-bis-((diphenylphosphino)methyl)carbazole}nickel(II) (9b). *n*-BuLi (0.065 mL, 2.5 M in *n*-hexane, 0.16 mmol) was added to a solution of CbzdiphosH (**5**) (0.10 g, 0.15 mmol) in 15 mL of thf at −78 °C. After stirring for 0.5 h at ambient temperature, $NiBr_2DME$ (0.064 g, 0.21 mmol) was added at −78 °C. The reaction mixture was stirred overnight. The solvent was removed in vacuo, dissolved in dichloromethane, and filtered through a pad of Celite. After drying in vacuo, the crude product was washed with *n*-pentane to give the product as a red solid (0.063 g, 0.078 mmol, 52%). ^{1}H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 1.34 (s, 18H, $C(CH_3)_3$), 3.58 (t, $^2J_{HP}$ = 3.5 Hz, 4H, CH_2), 6.90 (s, 2H, C$H^{Carb\text{-}2}$), 7.33 (t, $^3J_{HH}$ = 7.5 Hz, 8H, C$H^{m\text{-}Ph}$), 7.41 (t, $^3J_{HH}$ = 7.5 Hz, 4H, C$H^{p\text{-}Ph}$), 7.84−7.88 (m, 8H, C$H^{o\text{-}Ph}$), 7.93 (s, 2H, C$H^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 29.4 (vt, CH_2), 31.9 (s, C$(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 114,5 (s, C$H^{Carb\text{-}4}$), 118.7 (s, $C^{Carb\text{-}1}$), 123.0 (s, C$H^{Carb\text{-}2}$), 126.7 (s, $C^{Carb\text{-}4a}$), 128.1 (s, C$H^{m\text{-}Ph}$), 130.4 (s, C$H^{p\text{-}Ph}$), 131.1 (vt, C^{Ph}), 133.7 (s, C$H^{o\text{-}Ph}$), 140.6 (s, $C^{Carb\text{-}3}$), 148.2 (m, $C^{Carb\text{-}9a}$). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) 28.8. HRMS (FAB) *m*/*z* (%) calcd: 813.1622. Found: 813.1606 (100) (M$^+$). Anal. Calcd. for $C_{46}H_{46}BrNNiP_2$: C 67.92; H 5.70; N 1.72. Found: C 68.14; H 6.03; N 1.52.

Preparation of Hydrido{3,6-di-*tert*-butyl-1,8-bis-((diphenylphosphino)methyl)carbazole}nickel(II) (10). A solution of CbzdiphosH (**5**) (0.16 g, 0.23 mmol) in 5 mL of thf was added to a solution of Ni(COD)$_2$ (0.063 g, 0.23 mmol) in 5 mL of thf. After stirring for 1 h the solvent was removed in vacuo, and the residue was washed with *n*-pentane to yield a yellow solid (0.14 g, 0.18 mmol, 80%). ^{1}H NMR (600.1 MHz, C_6D_6, rt): δ (ppm) −18.5 (t, $^2J_{HP}$ = 69.9 Hz), 1.52 (s, 18H, $C(CH_3)_3$), 3.65−3.67 (m, 4H, CH_2), 6.91−6.97 (m, 2H, C$H^{p\text{-}Ph}$, C$H^{m\text{-}Ph}$), 7.29 (s, 2H, C$H^{Carb\text{-}2}$), 7.61−7.66 (m, 8H, C$H^{o\text{-}Ph}$), 8.36 (s, 2H, C$H^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 29.3 (vt, CH_2), 32.3 (s, C$(CH_3)_3$), 34.4 (s, $C(CH_3)_3$), 115.6 (s, C$H^{Carb\text{-}4}$), 118.6 (s, $C^{Carb\text{-}1}$), 123.9 (vt, C$H^{Carb\text{-}2}$), 126.5 (s, $C^{Carb\text{-}4a}$), 128.4 (vt, C$H^{m\text{-}Ph}$), 130.0 (s, C$H^{p\text{-}Ph}$), 133.0 (vt, C$H^{o\text{-}Ph}$), 133.8 (m, C^{Ph}), 138.5 (s, $C^{Carb\text{-}3}$), 148.2 (vt, $C^{Carb\text{-}9a}$). ^{31}P NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 33.4 (d, $^2J_{PH}$ = 68.8). HRMS (FAB) *m*/*z* (%) calcd: 733.2537. Found: 733.2513 (100) (M$^+$). Anal. Calcd. for $C_{46}H_{47}NNiP_2$: C 75.22; H 6.45; N 1.91. Found: C 75.79; H 6.39; N 2.05.

Preparation of {3,6-Di-*tert*-butyl-1,8-bis((diphenylphosphino)methyl)carbazole}carbonyl-rhodium(I) (11). A solution of CbzdiphosH (**5**) (1.00 g, 1.48 mmol) in 20 mL of toluene was added to a solution of rhodium(I)dicarbonyl-2,4-pentanedionate (Rh(acac)(CO)$_2$) (0.38 g, 1.5 mmol) in 20 mL of toluene. After stirring overnight the resulting suspension was filtered, and the residue was washed with toluene. After drying in vacuo, the product was obtained as a gray solid (1.06 g, 1.32 mmol, 89%). ^{1}H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 1.30 (s, 18H, $C(CH_3)_3$), 3.91 (t, $^2J_{HP}$ = 3.0 Hz, 4H, CH_2), 6.99 (s, 2H, C$H^{Carb\text{-}2}$), 7.31−7.38 (m, 2H, C$H^{p\text{-}Ph}$, C$H^{m\text{-}Ph}$), 7.70−7.74 (m, 8H, C$H^{o\text{-}Ph}$), 7.85 (s, 2H, C$H^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 30.5 (vt, CH_2), 32.0 (s, C$(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 114.3 (s, C$H^{Carb\text{-}4}$), 118.0 (s, $C^{Carb\text{-}1}$), 123.9 (vt, C$H^{Carb\text{-}2}$), 125.1 (s, $C^{Carb\text{-}4a}$), 128.4 (vt, C$H^{m\text{-}Ph}$), 130.2 (s, C$H^{p\text{-}Ph}$), 133.0 (vt, C$H^{o\text{-}Ph}$), 133.4 (vt, C^{Ph}), 139.0 (s, $C^{Carb\text{-}3}$), 147.9 (vt, $C^{Carb\text{-}9a}$), 192.3 (vt, CO). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, rt): δ (ppm) 37.5 (d, $^1J_{RhP}$ = 134 Hz). HRMS (FAB) *m*/*z* (%) calcd: 805.2104. Found: 805.2062 (100) (M$^+$). Anal. Calcd. for $C_{47}H_{46}NOP_2Rh$: C 69.97; H 5.87; N 1.74. Found: C 70.17; H 5.87; N 1.85. IR (dichloromethane): $\tilde{\nu}$ = 1970 cm^{-1} (br, CO).

Preparation of Chloro{3,6-di-*tert*-butyl-1,8-bis(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl)methyl)-carbazole}palladium(II) (12). A solution of LDA (0.034 g, 0.32 mmol) in 10 mL of thf was added to a solution of CbzdipholH (**7**) (0.20 g, 0.26 mmol) in 10 mL of thf at −78 °C. After stirring for 1 h at ambient temperature, the resulting solution was added to a solution of $PdCl_2COD$ (0.10 g, 0.35 mmol) in 5 mL of thf. The reaction mixture was stirred overnight. The solvent was removed in vacuo, dissolved in pentane, and filtered. The filtrate was cooled to −78 °C and filtered again. The residue was dried in vacuo to give the product as a red solid (0.19 g, 0.21 mmol, 79%). ^{1}H{^{31}P} NMR (600.1 MHz, C_6D_6, rt): δ (ppm) 1.51 (s, 18H, $C(CH_3)_3$), 1.67−1.75 (m, 2H, CH_2^{Phos}), 1.82−1.88 (m, 2H, CH_2^{Phos}), 1.90−1.96 (m, 2H, CH_2^{Phos}), 1.96−2.04 (m, 2H, CH_2^{Phos}), 2.46 (d, $^2J_{HH}$ = 15.0 Hz, 2H, CH_2), 2.70 (d, $^2J_{HH}$ = 15.8 Hz, 2H, CH_2), 2.89 (dd, $^3J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 5.6 Hz, 2H, CH^{Phos}), 5.01 (dd, $^3J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, CH^{Phos}), 6.56 (t, $^3J_{HH}$ = 7,3 Hz, 2H, C$H^{p\text{-}Ph}$), 6.70 (t, $^3J_{HH}$ = 7,6 Hz, 4H, C$H^{m\text{-}Ph}$), 6.76 (d, $^3J_{HH}$ = 7,6 Hz, 4H, C$H^{o\text{-}Ph}$), 6.94 (s, 2H, C$H^{Carb\text{-}2}$), 7.16 (t, $^3J_{HH}$ = 7,7 Hz, 2H, C$H^{p\text{-}Ph}$), 7.27 (t, $^3J_{HH}$ = 7,6 Hz, 4H, C$H^{m\text{-}Ph}$), 7.53 (d, $^3J_{HH}$ = 7,6 Hz, 4H, C$H^{o\text{-}Ph}$), 8.22 (s, 2H, C$H^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 25.5 (vt, CH_2), 29.9 (s, CH_2^{Phos}), 32.2 (s, C-CH_3), 33.9 (vt, CH_2^{Phos}), 34.2 (s, *C*-CH_3), 40.0 (vt, CH^{Phos}), 47.3 (vt, CH^{Phos}), 114.9

dx.doi.org/10.1021/ic302454n | *Inorg. Chem.* 2013, 52, 2050−2059

(s, $CH^{Carb\text{-}4}$), 116.3 (s, $C^{Carb\text{-}1}$), 124.1 (vt, $CH^{Carb\text{-}2}$), 125.7 (s, $C^{Carb\text{-}4a}$), 125.9 (s, $CH^{p\text{-}Ph}$), 126.8 (s, $CH^{p\text{-}Ph}$), 127.6 (s, $CH^{m\text{-}Ph}$), 128.4 (s, 2C, $CH^{o\text{-}Ph}$), 128.6 (s, $CH^{m\text{-}Ph}$), 136.8 (vt, $C^{q\text{-}Ph}$), 138.1 (s, $C^{Carb\text{-}3}$), 139.9 (vt, $C^{q\text{-}Ph}$), 144.5 (vt, $C^{Carb\text{-}9a}$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 50.1. HRMS (FAB) m/z (%) calcd: 923.2784. Found: 923.2772 (100) (M^+). Anal. Calcd. for $C_{54}H_{58}ClNP_2Pd$: C 70.13; H 6.32; N 1.51. Found: C 70.29; H 6.41; N 1.74.

Preparation of Chloro{3,6-di-*tert*-butyl-1,8-bis(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl)methyl)carbazole}nickel(II) (13a). A solution of LDA (0.039 g, 0.37 mmol) in 10 mL of thf was added to a solution of CbzdipholH (7) (0.26 g, 0.33 mmol) in 10 mL of thf at −78 °C. After stirring for 0.5 h at ambient temperature, the resulting solution was added to a solution of $NiCl_2DME$ (0.094 g, 0.43 mmol) in 5 mL of thf at −78 °C. The reaction mixture was stirred overnight. The solvent was removed in vacuo, dissolved in *n*-pentane, and filtered. The filtrate was cooled to −78 °C and filtered again. The residue was dried in vacuo to give the product as a green solid (0.26 g, 0.30 mmol, 90%). $^1H\{^{31}P\}$ NMR (600.1 MHz, C_6D_6, rt): δ (ppm) 1.51 (s, 18H, $C(CH_3)_3$), 1.63−1.69 (m, 2H, CH_2^{Phos}), 1.70−1.78 (m, 4H, CH_2^{Phos}), 1.82−1.89 (m, 2H, CH_2^{Phos}), 2.26 (d, $^2J_{HH}$ = 15.4 Hz, 2H, CH_2), 2.40 (m, 2H, CH^{Phos}), 3.02 (d, $^2J_{HH}$ = 15.2 Hz, 2H, CH_2), 4.63 (dd, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 6.9 Hz, 2H, CH^{Phos}), 6.43 (t, $^3J_{HH}$ = 7,4 Hz, 2H, $CH^{p\text{-}Ph}$), 6.59 (t, $^3J_{HH}$ = 7,5 Hz, 4H, $CH^{m\text{-}Ph}$), 6.70 (d, $^3J_{HH}$ = 7,5 Hz, 4H, $CH^{o\text{-}Ph}$), 6.99 (s, 2H, $CH^{Carb\text{-}2}$), 7.22 (t, $^3J_{HH}$ = 7,3 Hz, 2H, $CH^{p\text{-}Ph}$), 7.39 (t, $^3J_{HH}$ = 7,7 Hz, 4H, $CH^{m\text{-}Ph}$), 7.78 (d, $^3J_{HH}$ = 7,8 Hz, 4H, $CH^{o\text{-}Ph}$), 8.11 (s, 2H, $CH^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 24.5 (vt, CH_2), 30.1 (s, CH_2^{Phos}), 32.2 (s, $C(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 34.7 (vt, CH_2^{Phos}), 38.3 (vt, CH^{Phos}), 46.0 (vt, CH^{Phos}), 114.2 (s, $CH^{Carb\text{-}4}$), 116.0 (s, $C^{Carb\text{-}1}$), 123.6 (vt, $CH^{Carb\text{-}2}$), 125.5 (s, $CH^{p\text{-}Ph}$), 126.7 (s, $CH^{p\text{-}Ph}$), 126.8 (s, $C^{Carb\text{-}4a}$), 127.4 (s, $CH^{m\text{-}Ph}$), 128.0 (vt, $CH^{o\text{-}Ph}$) 128.6 (s, $CH^{m\text{-}Ph}$), 128.9 (s, $CH^{o\text{-}Ph}$), 137.6 (vt, $C^{q\text{-}Ph}$), 138.1 (s, $C^{Carb\text{-}3}$), 141.1 (vt, $C^{q\text{-}Ph}$), 143.3 (vt, $C^{Carb\text{-}9a}$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 36.6. HRMS (FAB) m/z (%) calcd: 875.3087. Found: 875.3107 (100) (M^+). Anal. Calcd. for $C_{54}H_{58}ClNNiP_2$: C 73.94; H 6.66; N 1.60. Found: C 73.67; H 6.90; N 1.46.

Preparation of Bromo{3,6-di-*tert*-butyl-1,8-bis(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl)methyl)carbazole}nickel(II) (13b). A solution of LDA (0.031 g, 0.31 mmol) in 10 mL of thf was added to a solution of CbzdipholH (7) (0.22 g, 0.28 mmol) in 10 mL of thf at −78 °C. After stirring for 0.5 h at ambient temperature, the resulting solution was added to a solution of $NiBr_2DME$ (0.11 g, 0.36 mmol) in 5 mL of thf at −78 °C. The reaction mixture was stirred overnight. The solvent was removed in vacuo, dissolved in pentane, and filtered. The filtrate was cooled to −78 °C and filtered again. The residue was dried in vacuo to give the product as a green solid (0.23 g, 0.25 mmol, 89%). $^1H\{^{31}P\}$ NMR (600.1 MHz, C_6D_6, rt): δ (ppm) 1.51 (s, 18H, $C(CH_3)_3$), 1.59−1.67 (m, 2H, CH_2^{Phos}), 1.69−1.75 (m, 4H, CH_2^{Phos}), 1.83−1.88 (m, 2H, CH_2^{Phos}), 2.28 (d, $^2J_{HH}$ = 15.5 Hz, 2H, CH_2), 2.42 (t, $^3J_{HH}$ = 9.5 Hz, 2H, CH^{Phos}), 3.01 (d, $^2J_{HH}$ = 15.2 Hz, 2H, CH_2), 4.90 (dd, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 6.5 Hz, 2H, CH^{Phos}), 6.46 (t, $^3J_{HH}$ = 7,3 Hz, 2H, $CH^{p\text{-}Ph}$), 6.61 (t, $^3J_{HH}$ = 7,5 Hz, 4H, $CH^{m\text{-}Ph}$), 6.69 (d, $^3J_{HH}$ = 7,3 Hz, 4H, $CH^{o\text{-}Ph}$), 6.99 (s, 2H, $CH^{Carb\text{-}2}$), 7.21 (t, $^3J_{HH}$ = 7,3 Hz, 2H, $CH^{p\text{-}Ph}$), 7.36 (t, $^3J_{HH}$ = 7,7 Hz, 4H, $CH^{m\text{-}Ph}$), 7.79 (d, $^3J_{HH}$ = 7,7 Hz, 4H, $CH^{o\text{-}Ph}$), 8.14 (s, 2H, $CH^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 25.7 (vt, CH_2), 30.7 (s, CH_2^{Phos}), 32.2 (s, $C(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 34.7 (vt, CH_2^{Phos}), 40.2 (vt, CH^{Phos}), 46.2 (vt, CH^{Phos}), 114.2 (s, $CH^{Carb\text{-}4}$), 116.2 (s, $C^{Carb\text{-}1}$), 123.5 (vt, $CH^{Carb\text{-}2}$), 125.5 (s, $CH^{p\text{-}Ph}$), 126.7 (s, $CH^{p\text{-}Ph}$), 126.9 (s, $C^{Carb\text{-}4a}$), 127.4 (s, $CH^{m\text{-}Ph}$), 128.0 (vt, $CH^{o\text{-}Ph}$) 128.5 (s, $CH^{m\text{-}Ph}$), 129.0 (s, $CH^{o\text{-}Ph}$), 137.8 (vt, $C^{q\text{-}Ph}$), 138.2 (s, $C^{Carb\text{-}3}$), 141.0 (vt, $C^{q\text{-}Ph}$), 143.3 (vt, $C^{Carb\text{-}9a}$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 37.8. HRMS (FAB) m/z (%) calcd: 921.2565. Found: 921.2571 (100) (M^+). Anal. Calcd. for $C_{54}H_{58}BrNNiP_2$: C 70.38; H 6.34; N 1.52. Found: C 70.17; H 6.64; N 1.46.

Preparation of Acetato{3,6-di-*tert*-butyl-1,8-bis(((2*R*,5*R*)-2,5-diphenylphospholan-1-yl)methyl)carbazole}nickel(II) (14). A solution of CbzdipholH (7) (0.10 g, 0.13 mmol) in 2 mL of methanol was added to a solution of $Ni(OAc)_2$ (0.032 g, 0.13 mmol) in 2 mL of methanol. After stirring for 1 h the solvent was removed in vacuo, and the resulting solid washed with 2 mL of pentane. The residue was dried in vacuo to yield a green solid (0.077 g, 0.086 mmol, 66%). $^1H\{^{31}P\}$ NMR (600,1 MHz, C_6D_6, rt): δ (ppm) 1.49 (s, 18H, $C(CH_3)_3$), 1.57−1.66 (m, 2H, CH_2^{Phos}), 1.81−1.87 (m, 2H, CH_2^{Phos}), 1.91−1.97 (m, 2H, CH_2^{Phos}), 2.06−2.13 (m, 2H, CH_2^{Phos}), 2.13−2.18 (m, 5H, CH_2, $OC(O)CH_3$), 2.35 (dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, CH^{Phos}), 2.42 (d, $^2J_{HH}$ = 15.1 Hz, 2H, CH_2), 3.96 (dd, $^3J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 6.5 Hz, 2H, CH^{Phos}), 6.40 (t, $^3J_{HH}$ = 7,3 Hz, 2H, $CH^{p\text{-}Ph}$), 6.65 (t, $^3J_{HH}$ = 7,5 Hz, 4H, $CH^{m\text{-}Ph}$), 6.94 (s, 2H, $CH^{Carb\text{-}2}$), 7.11 (d, $^3J_{HH}$ = 7,5 Hz, 4H, $CH^{o\text{-}Ph}$), 7.22 (t, $^3J_{HH}$ = 7,4 Hz, 2H, $CH^{p\text{-}Ph}$), 7.43 (t, $^3J_{HH}$ = 7,6 Hz, 4H, $CH^{m\text{-}Ph}$), 7.62 (d, $^3J_{HH}$ = 7,7 Hz, 4H, $CH^{o\text{-}Ph}$), 8.02 (s, 2H, $CH^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 25.2 (s, $OC(O)CH_3$), 25.3 (vt, CH_2), 30.3 (s, CH_2^{Phos}), 32.2 (s, $C(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 34.8 (vt, CH_2^{Phos}), 38.9 (vt, CH^{Phos}), 46.2 (vt, CH^{Phos}), 114.0 (s, $CH^{Carb\text{-}4}$), 115.8 (s, $C^{Carb\text{-}1}$), 123.5 (vt, $CH^{Carb\text{-}2}$), 125.4 (s, $CH^{p\text{-}Ph}$), 126.9 (s, $CH^{p\text{-}Ph}$), 127.3 (s, $CH^{m\text{-}Ph}$), 128.1 (vt, $CH^{o\text{-}Ph}$) 128.5 (s, $CH^{o\text{-}Ph}$), 126.9 (s, $C^{Carb\text{-}4a}$), 128.9 (s, $CH^{m\text{-}Ph}$), 137.8 (s, $C^{q\text{-}Ph}$), 138.0 (s, $C^{Carb\text{-}3}$), 141.0 (s, $C^{q\text{-}Ph}$), 142.9 (vt, $C^{Carb\text{-}9a}$). 176.1 (s, $OC(O)CH_3$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 32.6. HRMS (FAB) m/z (%) calcd: 899.3531. Found 899.3539 (44) (M^+). Anal. Calcd. for $C_{56}H_{61}NNiO_2P_2$: C 74.67; H 6.83; N 1.56. Found: C 74.33; H 6.54; N1.66 .

Preparation of Hydrido{3,6-di-*tert*-butyl-1,8-bis(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl)methyl)carbazole}nickel(II) (15). A solution of CbzdipholH (7) (0.23 g, 0.30 mmol) in 5 mL of pentane was added to a solution of $Ni(COD)_2$ (0.11 g, 0.38 mmol) in 5 mL of pentane at −78 °C. After stirring for 4 h the resulting solution was filtered, the filtrate was cooled to −78 °C, and filtered again. The residue was dried in vacuo to yield a gray solid (0.17 g, 0.21 mmol, 69%). $^1H\{^{31}P\}$ NMR (600.1 MHz, C_6D_6, rt): δ (ppm) −19.77 (s, 1H, Ni*H*), 1.54 (s, 18H, $C(CH_3)_3$), 1.94−2.02 (m, 8H, CH_2^{Phos}), 2.59 (d, $^2J_{HH}$ = 15.1 Hz, 2H, CH_2), 2.66 (d, $^2J_{HH}$ = 14.5 Hz, 2H, CH_2), 3.26 (dd, $^3J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, CH^{Phos}), 3.58 (dd, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 6.1 Hz, 2H, CH^{Phos}), 6.77 (d, $^3J_{HH}$ = 6.7 Hz, 4H, $CH^{o\text{-}Ph}$), 6.81−6.85 (m, 4H, $CH^{Carb\text{-}2}$, $CH^{p\text{-}Ph}$), 6.94−7.02 (m, 14H, $CH^{o\text{-}Ph}$, $CH^{m\text{-}Ph}$, $CH^{p\text{-}Ph}$,), 8.26 (s, 2H, $CH^{Carb\text{-}4}$). ^{13}C NMR (150.9 MHz, C_6D_6, rt): δ (ppm) 26.2 (vt, CH_2), 30.4 (s, CH_2^{Phos}), 32.5 (s, $C(CH_3)_3$), 32.7 (s, CH_2^{Phos}), 34.3 (s, $C(CH_3)_3$), 47.2 (vt, CH^{Phos}), 48.1 (vt, CH^{Phos}), 114.9 (s, $CH^{Carb\text{-}4}$), 117.9 (s, $C^{Carb\text{-}1}$), 123.1 (vt, $CH^{Carb\text{-}2}$), 125.7 (s, $C^{Carb\text{-}4a}$), 126.5 (s, $CH^{p\text{-}Ph}$), 126.6 (s, $CH^{p\text{-}Ph}$), 127.7 (s, $CH^{o\text{-}Ph}$) 128.0−128.3 (m, 3C, $CH^{m\text{-}Ph}$, $CH^{o\text{-}Ph}$), 136.5 (s, $C^{q\text{-}Ph}$), 137.4 (s, $C^{Carb\text{-}3}$), 141.0 (s, $C^{q\text{-}Ph}$), 147.2 (vt, $C^{Carb\text{-}9a}$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6, rt): δ (ppm) 54.2. HRMS (FAB) m/z (%) calcd: 841.3491. Found: 841.3471 (100) (M^+). Anal. Calcd. for $C_{54}H_{59}NNiP_2$: C 76.96; H 7.06; N 1.66. Found: C 76.87; H 6.91; N1.83 .

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are listed in Supporting Information, Tables 1 and 2. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, sealed tube, graphite monochromator) or an Agilent Technologies Supernova-E CCD diffractometer (Cu-K_α radiation, microfocus tube, multilayer mirror optics). Data were corrected for air and detector absorption, Lorentz and polarization effects;[48,49] absorption by the crystal was treated analytically[50] (compound **9b**), numerically (Gaussian grid)[51] (complexes **8** and **13b**), or with a semiempirical multiscan method[50,52,53] (all others). The structures were solved by direct methods with dual-space recycling (VLD procedure)[54] (complex **9b**) or by the charge flip procedure[55] (all others) and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[56] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model.[56] The position of the hydride ligand in **10** was taken from a difference Fourier synthesis and fully refined. When possible, disorder of solvent (chloroform, complex **9b**), *t*-butyl (compound **6**), and acetate (complex **14**) was resolved with split atom models. When necessary, adp and/or geometrical similarity restraints were applied to these moieties during refinement. Because of severe disorder and/or fractional occupancy, electron density attributed to solvent of crystallization was removed from the structures (and the correspond-

dx.doi.org/10.1021/ic302454n | *Inorg. Chem.* 2013, 52, 2050−2059

ing F_{obs}) of **9a** (two of three molecules of $CDCl_3$) and **10** (thf) with the BYPASS procedure,[57] as implemented in PLATON (SQUEEZE).[58]

CCDC 908483−908490 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structures of **9a**, **9b**, and **11**. Crystallographic data and details of the structure determinations for **6**, **8**, **9a**, **9b**, **10**, **11**, **13b**, and **14**. NMR spectra of compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to Bianca Pokrandt and Sabine Stolz for experimental help in developing this class of ligands and complexes. We thank the Deutsche Forschungsgemeinschaft for financial support of this work (SFB 623, TP B6) and the Fundación Ramón Areces for the award of a postdoctoral fellowship to L.I.R.

■ ABBREVIATIONS

COD, cyclooctadiene; DME, dimethoxyethane; TMS, trimethylsilyl; LDA, lithium diisopropylamide

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