This article is published as part of the Dalton Transactions themed issue entitled:

Pincers and other hemilabile ligands

Guest Editors Dr Bert Klein Gebbink and Gerard van Koten

Published in issue 35, 2011 of Dalton Transactions



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Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 8950

PAPER

Unsymmetrical ^RPNP^{R'} pincer ligands and their group 10 complexes[†]

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Received 18th February 2011, Accepted 6th April 2011 DOI: 10.1039/c1dt10265f

Two new unsymmetrical ^RPNP^{R'}-type pincer ligands based on a *bis*(tolyl)amine framework have been synthesized and characterized by a variety of techniques, including X-ray crystallography. These ligands have been coordinated to Ni, Pd, and Pt precursors to provide a number of well-characterized group 10 halides. Conversion of these metal halides to metal hydrides was accomplished using borohydride reagents, or by direct interaction of the ligand with the zerovalent metal precursor. The insertion of oxygen into these hydrides in an attempt to prepare metal hydroperoxides has been examined; however, we were unable to obtain stable and isolable hydroperoxide species.

Introduction

The search for new ligands that can direct specific electronic or steric effects upon metal ions is one that continues unabated. Pincer ligands, which are multidentate ligands that afford increased thermal and kinetic stabilities to metal complexes, have been highly-developed over the past decades; however, new types of pincer ligands are still desired.^{1,2} Pincer ligands have been synthesized with a wide range of donor atoms to serve as attachment points to metals, and these pincer-metal complexes have been used in a variety of applications, most importantly in catalytic chemistry.³⁻⁶ In this current submission we restrict ourselves to a family of ^RPNP^{R'}-pincer ligands based on a backbone framework recently investigated by Kaska,7 Liang,8 Mindiola,9-11 and Ozerov.4,12-16 In the vast majority of these ^RPNP^{R'}-pincer ligands, both R and R' are the same alkyl or aryl fragment, thus producing PNP ligands with symmetrical ends (Fig. 1). However, very recently the group of Liang has shown that an unsymmetrical ^RPNP^{R'}-pincer (R =Ph, $R' = {}^{i}Pr$) ligand based on a phenyl backbone (R = H) can be prepared and coordinated to Ni and Al.^{17,18} We have been interested in expanding the range of unsymmetrical ^RPNP^{R'}-pincer ligands for application in the preparation of new late transition metal complexes of Ni, Pd, and Pt.

Our research groups have had long-standing efforts in the syntheses, characterization, and use of pincer-containing metal compounds.¹⁹⁻²² In a more focused application, we have been examining the insertion of O_2 into transition metal hydrides containing various symmetric phosphine- and carbene-based



X = H, Me, F

Fig. 1 Symmetrical versions of the PNP-framework.

pincer ligands. We have recently demonstrated the first direct insertion of O_2 into a Pd–H bond to form the Pd–OOH complex,²³ and have examined this reaction computationally.²⁴ Therefore, in order to learn more about these O_2 reactions it was of interest to us to expand our approaches and prepare new unsymmetrical ^RPNP^{R'}-pincer ligands, as well as to examine their abilities to form new late metal halide and hydride complexes. We report herein the detailed syntheses and characterization of two new unsymmetrical ligands based on the *bis*(tolyl)amine backbone (R = Me in Fig. 1). Also reported are the preparations of new Ni, Pd, and Pt halide complexes utilizing these ligands, and the conversion of these halides into the corresponding metal hydrides. Lastly, the reactivities of O_2 with these metal hydrides are also briefly presented.

Results and discussion

Synthesis and characterization of unsymmetrical ligands 1 and 2

The unsymmetrical *bis*(tolyl)amine ligands **1** and **2** were both prepared similarly to the method employed by Liang (Scheme 1).¹⁷ The same dibromo-substituted amine precursor was used in each preparation.²⁵ The key step in the syntheses of the unsymmetrical ligands **1** and **2** is to add the dialkylchlorophosphine first, prior to the addition of the diphenylchlorophosphine, due to the higher electrophilic character of the diphenylchlorophosphine. If the

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[†] CCDC reference numbers: 812749 (1), 812750 (3), 812751(4), 812752 (5), 812753 (6), 812754 (7), and 812755 (10). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10265f



Scheme 1 Preparation of unsymmetrical ligands 1 and 2.

order of addition is reversed, mixtures of products including the symmetrically-substituted ligands are formed.^{17 Ph}PNP^{iPr} ligand 1 can be isolated in 39% yield as an off-white solid after precipitation from a diethyl ether/pentane mixture at -35 °C.

Ligand 1 was completely characterized by ¹H, ¹³C, and ³¹P multinuclear NMR spectra, elemental analysis, and single crystal X-ray diffraction studies. The ³¹P{¹H} NMR spectrum as expected showed two distinct resonances for the two non-equivalent P atoms present. A single crystal suitable for X-ray diffraction analysis was grown from a concentrated solution of 1 in diethyl ether at -30 °C, and the molecular structure of 1 is shown in Fig. 2. The structure of 1 largely resembles the structure seen by Liang in his related ^RPNP^R-ligand,¹⁷ and as such requires little need for extensive discussion. Even though the two tolyl rings attached to N1 that make up the ligand backbone are twisted by 54.9° relative to each other, the Ph- and ¹Pr-substituents are large enough to lead to a somewhat crowded environment around the location of the N1–H1A bond.



Fig. 2 Molecular structure of **1** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon omitted for clarity.

The ^{ph}PNP^{Cy} ligand **2** can be prepared in an analogous fashion to **1** in 33% isolated yield as an off-white solid after deposition from a diethyl ether/pentane mixture at -30 °C. **2** was also fully characterized by multinuclear NMR spectra and elemental analysis. The ¹³C{¹H} NMR spectra for **1** and **2** both showed fewer resonances than expected, presumably due to overlapping and broadened peaks. Inequivalent P atoms were again seen in the ³¹P NMR spectrum, and the ¹H NMR spectrum was more complex than in **1** as the Cy groups replaced the ⁱPr groups. As the X-ray structure of **1** so resembled the prior structure reported by Liang,¹⁷ we saw no compelling reason to obtain the single-crystal structure of 2.

Halide-containing Pd and Pt metal complexes prepared from 1 and 2

After the new unsymmetrical ligands 1 and 2 were prepared we next investigated the coordination chemistry of these ligands to Ni, Pd, and Pt. Treatment of (COD)PdCl₂ with either 1 or 2 in THF in the presence of NEt₃ for one hour gave (^{Ph}PNP^{iPr})PdCl (3) or (PhPNP^{Cy})PdCl (4), respectively (Scheme 2). The synthesis of 3 required one hour of reflux at 80 °C, resulting in a 96% yield of a red solid. The ${}^{31}P{}^{1}H$ NMR spectrum of **3** reveals two signals corresponding to the two distinct phosphorus environments within the molecule. A doublet exists at 54.0 ppm with $J_{PP} = 437.2$ Hz, corresponding to the -PiPr2 phosphorus atom, and another doublet is found further upfield at 25.7 ppm with $J_{PP} = 437.2$ Hz, corresponding to the –PPh₂ phosphorus environment. The large $J_{\rm PP}$ values for the two signals are characteristic of phosphines in the trans-orientation, which suggests that the binding mode is similar to other PNP metal halides (square planar geometry). The solid-state structure of 3 was determined using X-ray diffraction analysis. A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a benzene solution at room temperature. The structure of 3 is depicted in Fig. 3, along with selected bond lengths and angles. As shown, the geometry of 3 is confirmed to be approximately square planar around the metal center. The P-Pd-P angle is 163.724(15)°. The two Pd-P



Scheme 2 Preparation of halide-containing Pd and Pt complexes.



Fig. 3 Molecular structure of **3** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon omitted for clarity. Selected distances (Å) and angles (°): Pd1–Cl1 2.314(4); Pd1–P1 2.300(4); Pd1–P2 2.278(4), Pd1–N1 2.028(1); P1–Pd1–P2 163.72(1); N1–Pd1–Cl1 179.12(4).

bond lengths are 2.278(4) and 2.300(4) Å, and the Pd–N bond length is 2.028(1) Å. The N–Pd–Cl bond angle is expected to be 180° and experimentally is found to be so (179.12(4)°). The other bond lengths and angles show no remarkable differences from previously-characterized related complexes, and so no further discussion is warranted.

Similarly, the ³¹P{¹H} NMR spectrum of **4** exhibits two resonances for the inequivalent phosphorus environments. A doublet at 46.5 ppm ($J_{PP} = 437.5$ Hz, $-PCy_2$) and another doublet at 25.7 ppm ($J_{PP} = 437.4$ Hz, $-PPh_2$) are present, consistent with the spectrum of **3**. Again, the coupling constant values are consistent with earlier complexes and suggests a square planar geometry. The solid-state structure of **4** was determined by X-ray diffraction analysis (Fig. 4). A single crystal suitable for X-ray study was grown from the slow evaporation of a benzene solution at room temperature. A list of selected bond lengths and angles for **4** are shown in Fig. 4. The environment around the central Pd atom is very similar to **3** in terms of Pd–P, Pd–N, and Pd–Cl bond lengths; however, the N–Pd–Cl angle of **4** deviates slightly more from linearity (176.23(4)°) than was seen in **3**.



Fig. 4 Molecular structure of **4** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon omitted for clarity. Selected distances (Å) and angles (°): Pd1–Cl1 2.3171(4); Pd1–P1 2.2843(4); Pd1–P2 2.3046(4), Pd1–N1 2.0229(13); P1–Pd1–P2 164.233(16); N1–Pd1–Cl1 176.23(4).

The Pt-containing analogs of 3 and 4 were also prepared via similar synthetic routes (Scheme 2). (PhPNPiPr)PtCl (5) was generated in 75% yield as a yellow solid. The ³¹P{¹H} NMR spectrum of 5 reveals two signals for the two inequivalent phosphorus environments, both containing Pt satellites-a doublet at 43.7 ppm ($J_{PPt} = 2754.5$ Hz and $J_{PP} = 401.6$ Hz) for the $-P^{i}Pr_{2}$ phosphorus atom, and a second doublet at 24.7 ppm (J_{PPt} = 2673.9 Hz and J_{PP} = 401.9 Hz) for the –PPh₂ environment. In both cases, the J_{PPt} coupling constants are consistent with other similar structures, and the large J_{PP} values are characteristic of phosphines binding in the trans-orientation, in an approximate square-planar motif. The proposed molecular structure of 5 was confirmed by X-ray diffraction analysis. A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a benzene solution at room temperature. The crystal structure confirmed a distorted square-planar geometry around the metal center. The two Pt-P bond lengths are 2.282(9) and 2.272(1) Å, the Pt-N bond length is 2.028(3) Å, and the Pt-Cl bond length is 2.321(1) Å, very close to the values found in the structure of the Pd analogue 3. Other bond distances and angles showed no remarkable differences from 3. As the structure of 5 visually resembled 3 closely, no separate figure is shown although the structural files have been deposited in the Cambridge Structural Database (CSD) (see Supplementary Information[†]). (^{Ph}PNP^{Cy})PtCl (6) was prepared analogously, and exhibited similar NMR spectra to 5 with details presented in the Experimental section. X-ray quality crystals of 6 were deposited from the gradual evaporation of solvent from a concentrated solution of 6 in benzene. The crystal structure confirmed the expected distorted square-planar geometry around the metal center. All other bond distances and angles around Pt were not significantly different from the Pd analogue 4. As with 5, no separate figure is shown although the structural files for 6 have been deposited in the CSD (see Supplementary Information[†]). Crystallographic data for all compounds are in Tables 1 and 2.

Hydrido-containing group 10 metal complexes prepared from 1 and 2

New metal hydrides containing these new ligands 1 and 2 were prepared from all three Group 10 metals—Ni, Pd, and Pt, albeit by different synthetic routes. Due to the reactivity of the N–H bond, it is possible to directly prepare the M(II)– H complex *via* direct oxidative addition of the ligand to a M(0) precursor. Previously, Ozerov has shown that this N–H oxidative addition reaction to M(0) can occur, but due to the demanding conditions often required for Group 10 metals it can be difficult to obtain pure products.¹³ We decided to approach the preparation of unsymmetrical PNP-ligated Ni–H complexes *via* this direct one-step, oxidative route rather than attempting to convert (^RPNP^{R'})NiCl precursor complexes using hydride sources. We have previously documented the difficulty in determining the optimal hydride reagent to use to obtain analytically-pure products in the conversion of pincer-Ni halides to hydrides.¹⁹

The syntheses of the unsymmetric metal hydrides, (^{Ph}PNP^{iPr})NiH (7) and (^{Ph}PNP^{Cy})NiH (8), were performed *via* the oxidative addition route using either 1 or 2 as the starting amine. Harsh, forcing conditions were fortunately not required. Equimolar amounts of the starting amine and Ni(COD)₂ were stirred at room temperature for 15 min, and the volatiles removed to form brown solids in both cases (Scheme 3). The ³¹P{¹H} NMR spectrum of 7 revealed two doublets, corresponding to the two different phosphorus environments. The first doublet appeared at 58.9 ppm with a $J_{PP} = 244.2$ Hz (-PⁱPr₂) and the second doublet appeared at 31.4 ppm with a $J_{PP} = 244.1$ Hz



Scheme 3 Preparation of Ni hydrides using direct addition route.

Table 1 Crystallographic data for the structures of 1, 3, and 4

	1	3	4
Empirical formula	$C_{32}H_{37}NP_{2}$	C ₃₅ H ₃₉ ClNP ₂ Pd	C44H50ClNP2Pd
Formula weight	497.57	677.46	796.64
T/K	228(2)	183(2)	188(2)
Crystal size/mm	$0.45 \times 0.19 \times 0.16$	$0.60 \times 0.43 \times 0.28$	$0.50 \times 0.23 \times 0.11$
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pna2_1$	$P2_1/n$	$P\overline{1}$
a/Å	15.4380(11)	9.6912(6)	11.3446(3)
b/Å	22.8418(16)	11.5459(7)	11.7317(3)
c/Å	8.1278(5)	28.3155(17)	15.4507(4)
α (°)	90	90	93.6470(10)
$\beta(\tilde{c})$	90	98.821(3)	109.9500(10)
γ (°)	90	90	93.1420(10)
Volume/Å ³	2866.1(3)	3130.8(3)	1922.61(9)
Ζ	4	4	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.153	1.437	1.376
$\mu(Mo-K\alpha)/mm^{-1}$	0.172	0.805	0.667
F(000)	1064	1396	828
Total reflections	36855	107611	56344
Unique reflections	5539	15154	16083
Parameters	316	361	442
$R_{\rm int}$	0.039	0.0297	0.0289
GOF on F^2	1.121	1.239	1.142
Final R_1 , wR_2 ($I >$	0.0373, 0.0980	0.0325, 0.0856	0.0348, 0.0929
$2\sigma(I)$), (all data)	0.0579, 0.1208	0.0411, 0.0962	0.0461, 0.0929

Table 2Crystallographic data for the structures of 5, 6, 7, and 10

	5	6	7	10
Empirical formula	C ₃₅ H ₃₉ ClNP ₂ Pt	C44H50ClNP2Pt	C ₃₂ H ₃₇ NNiP ₂	$C_{40.5}H_{45}NP_2Pd$
Formula weight	766.15	885.32	556.28	714.12
T/K	183(2)	183(2)	228(2)	183(2)
Crystal size/mm	$0.21 \times 0.09 \times 0.06$	$0.32 \times 0.16 \times 0.09$	$0.51 \times 0.46 \times 0.34$	$0.25 \times 0.12 \times 0.07$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\overline{1}$
a/Å	9.7018(3)	11.3219(5)	12.3808(8)	11.3866(5)
b/Å	11.5256(4)	11.7353(5)	14.9010(10)	11.4791(5)
c/Å	28.4989(10)	15.5010(6)	18.6532(11)	14.9377(7)
α (°)	90	93.810(2)	90	91.051(2)
β (°)	100.733(2)	110.178(2)	122.533(4)	108.575(2)
γ (°)	90	92.996(2)	90	94.265(2)
Volume/Å ³	3130.97(18)	1922.65(14)	2901.3(3)	1843.81(14)
Ζ	4	2	4	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.625	1.529	1.274	1.286
μ (Mo-K α)/mm ⁻¹	4.694	3.834	0.800	0.618
<i>F</i> (000)	1524	892	1176	742
Total reflections	47085	43159	31034	41162
Unique reflections	7789	13063	5933	10335
Parameters	367	442	328	392
R _{int}	0.0764	0.0381	0.0445	0.0375
GOF on F^2	1.024	1.157	1.063	1.162
Final R_1 , $w\mathbf{R}_2$ ($I > 2\sigma(I)$),	0.0320, 0.0601	0.0411, 0.1260	0.0447, 0.1158	0.0364, 0.1020
(all data)	0.0501, 0.0656	0.0514, 0.1336	0.0649, 0.1317	0.0445, 0.1162

(-PPh₂). The large J_{PP} values indicate that the phosphine donor atoms are coordinated to the metal in a *trans*-orientation. The ¹H NMR spectrum of **7** exhibits a doublet of doublets for the Ni–H resonance at -18.1 ppm with $J_{HP} = 58.2$ Hz (-PⁱPr₂) and $J_{HP} =$ 68.4 Hz (-PPh₂). The molecular structure of **7** was determined by X-ray diffraction analysis (Fig. 5). A single crystal suitable for X-ray study was grown from a concentrated solution of **7** in diethyl ether at -30 °C. A list of selected bond lengths and angles for **7** are also shown in Fig. 5. The crystal structure of **7** confirms the distorted square-planar geometry around the metal center. The P–Ni–P bond angle is 173.78°, which is also consistent with the other crystallographically-characterized compounds discussed above. The hydride ligand attached to Ni was located and refined; the process used to refine the H atom is discussed in the Experimental section. Interestingly, in previous work done by our group, the hydrides in a series of related (^RPCP)NiH complexes could also be located in the X-ray pattern and refined to give accurate Ni–H bond lengths.¹⁹

The ³¹P{¹H} NMR spectrum of **8** reveals a pair of doublets corresponding to the two significantly different phosphorus environments. The first doublet appeared at 49.6 ppm with a J_{PP} = 244.9 Hz (–PCy₂) and the second doublet appeared at 31.8 ppm



Fig. 5 Molecular structure of **7** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon omitted for clarity. Selected distances (Å) and angles (°): Ni1–P1 2.1353(8); Ni1–P2 2.1344(8), Ni1–N1 1.921(2); P1–Ni1–P2 173.77(3).

with a $J_{PP} = 244.2$ Hz (–PPh₂), with the large J_{PP} values indicating a *trans*-orientation of the two phosphine donor atoms. The ¹H NMR spectrum of **8** contains a doublet of doublets for the Ni–H at -18.15 ppm with $J_{HP} = 58.9$ Hz (–PCy₂) and $J_{HP} = 64.4$ Hz (–PPh₂). Unfortunately, even after multiple attempts to grow crystals, a sample for X-ray diffraction analysis was not obtained.

The Pd and Pt hydrides (PhPNPiPr)PdH (9), (PhPNPCy)PdH (10), and (PhPNPiPr)PtH (11) were prepared via conversion of the four (^RPNP^{R'})MCl precursors using Super-Hydride[®] reagent (LiEt₃BH in THF). Use of other traditional metal hydride sources was also attempted; however, none proved as effective as Super-Hydride solution. The general synthetic procedure to prepare these hydrides is shown in Scheme 4. The "PNP"-containing metal chloride precursor was treated with an equimolar amount of Super-Hydride solution in THF for 2-5 h at room temperature, and removal of the volatiles in all cases gave brown solids. These solids were redissolved in pentane, filtered through Celite[®] filter aid, and the volatiles again removed to give orangish-brown solids. Detailed NMR and characterization data for these compounds are given in the Experimental section. X-ray quality crystals could not be grown of either (^{Ph}PNP^{iPr})-containing complex (9 or 11); however, gradual deposition at -30 °C from a concentrated diethyl ether solution of the (^{Ph}PNP^{Cy})-containing 10 did produce highquality orangish-brown crystals. The ${}^{31}P{}^{1}H{}$ NMR of 10 exhibits a pair of doublets at 54.5 ppm ($J_{PP} = 354.5$ Hz, $-PCy_2$) and 31.5 ppm (J_{PP} = 354.5 Hz, -PPh₂) which showed the characteristic downfield shift from 4. The ¹H NMR spectrum of 10 displays



Scheme 4 Preparation of Pd and Pt hydrides using borohydride route.

a virtual triplet for the hydride ligand at -9.91 ppm. The X-ray structure of **10** is shown in Fig. 6. Interestingly, in the case of **10** we were able to locate and refine the hydride ligand at a Pd1–H1 distance of 1.55(3) Å (see discussion in Experimental section). The single crystal X-ray structure displays an approximate square planar geometry around the palladium center with a P–Pd–P angle of 165.11(2)° as compared to 164.23(2)° of **4**. The Pd–N bond distance of **10** (2.0833(19) Å) is slightly elongated from that of **4** (2.023(1) Å), which is due to the *trans*-influence of the hydride ligand. All other noted bond distances and angles are similar to earlier complexes that have been structurally-characterized.



Fig. 6 Molecular structure of **10** (thermal ellipsoids at 50% probability level). Hydrogen atoms bound to carbon omitted for clarity. Selected distances (Å) and angles (°): Pd1–P1 2.2692(6); Pd1–P2 2.2614(6), Pd1–N1 2.0833(19); Pd1–H1 1.55(3); P1–Pd1–P2 165.11(2); N1–Pd1–H1 179.5(13).

Reactions of Group 10 hydrides with oxygen

Examining the interaction of metal hydrides with O_2 is of interest with respect to the discovery of new partial oxidation catalysts.²⁶ We have previously shown that O_2 can insert into a Pd–H bond to form a Pd–OOH species, which we fully characterized by Xray crystallography.²³ In an attempt to prepare new, isolable metal hydroperoxides, each of the Group 10 metal hydrides prepared in this work (7–11) were treated with gaseous O_2 under pressure in a medium-wall NMR tube fitted with a J. Young valve. This technique is similar to that previously described by us.²³

The two nickel PNP-based hydrides 7 and 8 were first investigated in these oxygen reactions. Compounds 7 and 8 were each treated with O_2 at 70 psig (4.76 atm.) in toluene- d_8 and an immediate color change from brown to green was noted. These complexes reacted much faster with O₂ than the Pd ^RPNP^{R'}-based metal hydrides 9 and 10 (vide infra). In the ${}^{31}P{}^{1}H{}$ NMR spectra, the peaks corresponding to either 7 or 8 disappeared followed by the formation of several new peaks. In the ¹H NMR spectra, the Ni-H peak disappears with no formation of resonances that can be confidently assigned to either a Ni-OH or Ni-OOH species. Attempts to grow crystals of components of the reaction mixture were unsuccessful. Unfortunately, the formation of a number of products is reminiscent of our previous work using ^RPCP–NiH complexes with O_2 , in which we observed attack on and destruction of the R groups of the ^RPCP-ligand framework, presumably by highly reactive Ni-OOH species.27

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The two new Pd-based hydrides **9** and **10** were also examined using similar conditions. Each compound was treated with O_2 under pressure, and after a day the reaction turned from dark brown to an orange/red solution. As in the Ni–H cases above, the ³¹P{¹H} NMR spectrum showed disappearance of the starting Pd–H complexes and formation of a mixture of new, unidentified compounds. These new compounds are likely the Pd–OOH and Pd–OH species, as we have seen these species in our ^RPCP– PdH work earlier. The ¹H NMR spectrum of each reaction also showed disappearance of the respective Pd–H resonance. Unfortunately, despite much effort, single crystals suitable for X-ray diffraction analysis could not be isolated for any of these presumed hydroperoxides or hydroxides.

The platinum ^{Ph}PNP^{iPr}-based hydride **11** was also treated with O₂ under identical conditions as above. The NMR tubes were pressurized with 70 psig (4.76 atm.) of O₂ in toluene- d_8 with no immediate color change observed. The system was closely monitored over several days with no change in the color in either solution, nor in the NMR chemical shifts of the Pt–H complex. The lack of reactivity with O₂ is likely attributable to the stronger M–H bond strength of Pt relative to Pd.

Conclusions

In this submission we report the synthesis and characterization of two new unsymmetrically-substituted examples of the ^RPNP^{R'} pincer ligands based on the *bis*(tolyl)amine backbone which should prove useful to a wide range of chemists. The coordination chemistry of these unsymmetric ligands has been demonstrated *via* the preparation of Group 10 metal halides and hydrides. While the Pd(II) and Pt(II) hydrides were prepared *via* borohydride reduction of the metal halide complexes, the Ni hydrides were prepared using direct interaction of the ligands with a Ni(0) precursor. Full characterization of these products, including Xray crystallography, is reported. Lastly, the Group 10 hydrides were treated with gaseous oxygen in attempts to isolate metal hydroperoxides. Unfortunately, only mixtures of products were obtained and individual products could not be isolated.

Experimental

General procedures

All procedures and manipulations were carried out under argon using an MBRAUN glove box or by standard Schlenk techniques. All solvents used were of high purity (anhydrous) or were dried by using standard methods. All reagents were purchased from Acros, Aldrich, Alfa Aesar, or Strem and were used as received. The starting *bis*(2-bromo-4-methylphenyl)amine was prepared according to the literature procedure.²⁵ NMR spectra were obtained at room temperature on a Bruker AMX 250 MHz spectrometer or on a Bruker AC 250 MHz spectrometer with a Tecmag MacSpect upgrade. All chemical shifts are reported in (δ) ppm with ¹H and ¹³C spectra referenced to tetramethylsilane or to their respective residual solvent peaks.³¹P NMR spectra were referenced externally using 85% H₃PO₄ at δ 0 ppm. All coupling constants are given in Hz. Elemental analyses were performed by Columbia Analytical Services of Tucson, AZ.

Preparation of PhPNPiPr 1

"BuLi (2.4 mL, 6.03 mmol, 2.5 M in hexane) was added dropwise to a solution of bis(2-bromo-4-methylphenyl)amine (1.07 g, 3.02 mmol) in diethyl ether (50 mL) at -35 °C. The solution was allowed to warm to room temperature (RT) and was stirred for 3 h. The reaction mixture was cooled back to -30 °C and a diethyl ether (5 mL) solution of diisopropylchlorophosphine (0.460 g, 3.02 mmol) was added dropwise. The reaction mixture was stirred at RT overnight. The yellow solution was cooled down to -35 °C and "BuLi (0.71 mL, 1.76 mmol, 2.5 M in hexane) was added dropwise. The solution was stirred at RT for 3 h. The reaction mixture was cooled down to -35 °C and a diethyl ether (5 mL) solution of diphenylchlorophosphine (0.390 g, 1.76 mmol) was added dropwise. The reaction mixture was stirred at RT overnight, filtered through Celite® filter aid, and evaporated to dryness under reduced pressure, resulting in an orange residue. The orange residue was dissolved into diethyl ether (20 mL) and 5 mL of degassed deionized water was added. The solution was then dried with MgSO₄, filtered through Celite, and evaporated to dryness under reduced pressure resulting in an orange oil. The oil was dissolved into a solution of diethyl ether and layered with pentane (3:1) and cooled to -35 °C. This resulted in an off-white solid of 1 (0.590 g, 39%). ¹H NMR (C₆D₆, 250.13 MHz): δ 7.66 (dd, 1H, $J_{\rm HP}$ = 10.51 and $J_{\rm HP}$ = 3.25, NH), 7.49 (dt, 4H, Ar) 7.40 (dd, 1H, Ar) 7.24 (dd, 1H, Ar), 7.09 (m, 7H, Ar), 6.90 (m, 3H, Ar), 2.16 (s, 3H, Ar-Me), 1.96 (s, 3H, Ar-Me), 1.88 (m, 2H, CHMe₂), 1.02 (dd, 6H, CHMe₂), 0.88 (dd, 6H, CHMe₂). ${}^{31}P{}^{1}H{}$ NMR $(C_6D_6, 101.26 \text{ MHz})$: $\delta -14.5$ (bs, P^iPr_2), -16.5 (d, $J_{PP} = 8.10$, PPh₂). Observable ${}^{13}C{}^{1}H$ NMR (C₆D₆, 62.89 MHz): δ 147.7 (d, $J_{\rm CP} = 19.0, \text{ C}$), 144.9 (d, $J_{\rm CP} = 19.9, \text{ C}$), 136.9 (d, $J_{\rm CP} = 11.1, \text{ C}$), 134.7 (s, CH), 134.3 (d, J_{CP} = 19.9, CH), 133.7 (s, CH), 131.3 (s, CH), 130.7 (d, *J*_{CP} = 7.4, CH), 128.8 (s, CH), 128.7 (s, CH) 122.1 $(d, J_{CP} = 15.7, C), 119.7 (s, CH), 116.9 (s, CH), 23.6 (d, J_{CP} = 11.1, CH)$ CHMe₂), 20.9 (s, Ar-Me), 20.8 (s. Ar-Me) 20.5 (d, $J_{CP} = 19.0$, $CHMe_2$), 19.3 (d, $J_{CP} = 9.2$, $CHMe_2$). Anal. Calcd for $C_{32}H_{37}NP_2$: C, 77.24; H, 7.49; N, 2.81. Found: C, 77.49; H, 7.85; N, 2.68.

Preparation of PhPNPCy 2

"BuLi (8.15 mL, 20.37 mmol, 2.5 M in hexane) was added dropwise to a solution of *bis*(2-bromo-4-methylphenyl)amine (3.62 g, 10.19 mmol) in diethyl ether (80 mL) at -5 °C. The solution was stirred at RT for 3 h. The reaction mixture was cooled down to -35 °C and a diethyl ether (5 mL) solution of dicyclohexylchlorophosphine (2.37 g, 10.19 mmol) was added dropwise. The reaction mixture was stirred at RT overnight. The yellow solution was cooled down to -30 °C and "BuLi (4.08 mL, 10.19 mmol, 2.5 M in hexane) was added dropwise. The solution was stirred at RT for 3 h. The reaction mixture was cooled down to -35 °C and a diethyl ether (5 mL) solution of diphenylchlorophosphine (2.25 g, 10.19 mmol) was added dropwise. The reaction mixture was stirred at RT overnight, filtered through Celite, and evaporated to dryness under reduced pressure resulting in an orange residue. The orange residue was redissolved into diethyl ether (20 mL) and 5 mL of degassed DI water was added. The solution was dried with MgSO₄, filtered through Celite, and evaporated to dryness under reduced pressure resulting in an orange oil. The orange oil was redissolved into a solution of diethyl ether and layered with pentane (1:3) and cooled to -35 °C. This resulted in an off-white solid of **2** (1.92 g, 33%). ¹H NMR (C₆D₆, 250.13 MHz): δ 7.70 (dd, 1H, J_{HP} = 10.13 and J_{HP} = 3.25, NH), 7.49 (m, 5H, Ar) 7.28 (m, 2H, Ar), 7.11 (m, 6H, Ar), 6.91 (m, 3H, Ar), 2.18 (s, 3H, Me), 1.96 (s, 3H, Me), 1.88–1.38 (m, Cy), 1.38–0.95 (m, Cy). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ -16.5 (d, J_{PP} = 7.7, PPh₂), -23.5 (bs, PCy₂). Observable ¹³C{¹H} NMR (C₆D₆, 62.89 MHz): δ 148.0 (d, J_{CP} = 19.0, C), 144.1 (d, J_{CP} = 19.5, C), 137.1 (d, J_{CP} = 10.6, C), 134.7 (s, CH), 134.4 (d, J_{CP} = 19.9, CH), 134.0 (s, CH), 131.4 (s, CH), 130.7 (d, J_{CP} = 7.9, CH), 128.8 (s, CH), 128.7 (s, CH) 121.8 (d, J_{CP} = 16.2, C), 119.5 (s, CH), 116.9 (s, CH), 33.6 (d, J_{CP} = 11.6, CH), 30.9 (J_{CP} = 17.6, CH₂), 29.2 (d, J_{CP} = 7.4, CH₂), 27.4 (d, J_{CP} = 12.5, CH₂), 27.3 (d, J_{CP} = 7.4, CH₂), 26.8 (s, CH₂), 21.0 (s, Ar–*Me*), 20.9 (s, Ar–*Me*). Anal. Calcd for C₃₈H₄₅NP₂: C, 79.00; H, 7.85; N, 2.42; Found: C, 78.82; H, 7.93; N, 2.22.

Preparation of (PhPNPiPr)PdCl 3

PhPNPiPr (1) (0.051 g, 0.180 mmol) and (COD)PdCl2 (0.089 g, 0.180 mmol) were placed into a round bottom flask along with 20 mL of THF and one equiv. of NEt₃. The red solution was refluxed for 1 h, filtered through Celite, and the volatiles were removed under reduce pressure, resulting in a red solid. The red solid was washed with cold pentane and dried under vacuum to give 3 (0.110 g, 96%). A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a benzene solution at room temperature. ¹H NMR (C₆D₆, 250.13 MHz): δ 7.96 (m, 4H, Ar), 7.78 (dd, 1H, Ar) 7.68 (dd, 1H, Ar) 6.99 (m, 7H, Ar), 6.78 (td, 3H, Ar), 2.28 (m, 2H, CHMe₂), 2.11 (s, 3H, Ar-Me), 1.91 (s, 3H, Ar-Me), 1.43 (dd, 6H, CHMe2), 1.07 (dd, 6H, CHMe₂). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 54.0 (d, $J_{PP} = 437.2, P^{i}Pr_{2}), 25.7 (d, J_{PP} = 437.2, PPh_{2}). Observable {}^{13}C{}^{1}H{}$ NMR (C₆D₆, 62.89 MHz): δ 161.8 (d, J_{CP} = 20.4, C), 161.5 (d, J_{CP} = 25.1, C), 135.2 (s, CH), 134.0 (d, J_{CP} = 12.1, CH), 133.1 (s, CH), 132.5 (s, CH), 131.5 (d, J_{CP} = 43.1 and J_{CP} = 3.7, C), 130.5 (s, CH), 129.0 (s, CH), 128.8 (s, CH), 126.9 (d, J_{CP} = 7.0, CH), 126.3 (d $J_{\rm CP} = 7.0$, CH), 121.3 (d, $J_{\rm CP} = 46.5$, C), 119.2 (d, $J_{\rm CP} = 39.4$, C), 116.9 (d, J_{CP} = 13.0, CH), 116.5 (J_{CP} = 14.3, CH), 25.2 (d, J_{CP} = 21.3, CHMe₂), 20.4 (s, Ar–Me), 20.2 (s, Ar–Me), 18.8 (d, J_{CP} = 3.7, CHMe₂), 18.1 (s, CHMe₂). Anal. Calcd for $C_{32}H_{36}ClNP_2Pd$: C, 60.20; H, 5.68; N, 2.19; Found: C, 60.55; H, 5.69; N, 2.08.

Preparation of (PhPNPCy)PdCl 4

^{ph}PNP^{Cy} (2) (0.191 g, 0.330 mmol) and (COD)PdCl₂ (0.094 g, 0.330 mmol) were placed into a round bottom flask along with 20 mL of THF and one equiv. of NEt₃. The red solution was refluxed for 1 h, filtered through Celite, and the volatiles were removed under reduced pressure resulting in a red solid. The red solid was washed with cold pentane and dried under vacuum to give **4** (0.129 g, 84%). A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a benzene solution at room temperature. ¹H NMR (C₆D₆, 250.13 MHz): *δ* 8.00 (m, 4H, Ar), 7.83 (dd, 1H, Ar) 7.74 (dd, 1H, Ar) 6.99 (m, 8H, Ar), 6.77 (td, 2H, Ar), 2.13 (s, 3H, Ar–Me), 1.91 (s, 3H, Ar–Me), 2.48–0.91 (m, 22H, Cy). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): *δ* 46.5 (d, J_{PP} = 437.5, PCy₂), 25.7 (d, J_{PP} = 437.4, PPh₂). Observable ¹³C{¹H} NMR (C₆D₆, 62.89 MHz): *δ* 162.0 (d, J_{CP} = 10.3, CH), 161.6 (d, J_{CP} = 25.7, C), 135.2 (s, CH), 134.0 (d, J_{CP} = 11.3, CH),

133.9 (d, $J_{CP} = 30.1$, CH), 132.5 (s, CH), 131.4 (dd, $J_{CP} = 43.0$ and $J_{CP} = 3.8$, C), 130.6 (s, CH), 129.0 (s, CH), 128.8 (d, $J_{CP} = 5.0$, CH), 126.9 ($J_{CP} = 6.0$, CH), 126.3 (d, $J_{CP} = 6.8$, CH), 121.3 (d, $J_{CP} = 47.5$, C), 119.5 (d, $J_{CP} = 40.0$, C), 117.0 (d, $J_{CP} = 12.8$, CH), 116.5 ($J_{CP} = 14.3$, CH), 34.4 (d, $J_{CP} = 21.3$, CH), 28.7 (s, CH₂), 28.3 (s, CH₂), 27.1 (s, CH₂), 27.0 (s, CH₂), 25.8 (s, CH₂), 20.4 (s, Ar–*Me*), 20.0 (s, Ar–*Me*). Anal. Calcd for C₃₈H₄₄CINP₂Pd: C, 63.51; H, 6.17; N, 1.95; Found: C, 63.14; H, 6.16; N, 1.87.

Preparation of (PhPNPiPr)PtCl 5

PhPNPiPr (1) (0.093 g, 0.190 mmol) and (COD)PtCl2 (0.070 g, 0.190 mmol) were placed into a round bottom flask along with 20 mL of THF and one equiv. of NEt₃. The yellow solution was refluxed for 2.5 h, filtered through Celite, and the volatiles were removed under reduced pressure resulting in a yellow solid. The solid was washed with cold pentane and dried under vacuum to give 5 (0.102 g, 75%). A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a benzene solution at room temperature. ¹H NMR (C₆D₆, 250.13 MHz): δ 8.00 (m, 4H, Ar), 7.78 (dd, 1H, Ar) 7.68 (dd, 1H, Ar) 6.99 (m, 8H, Ar), 6.78 (td, 2H, Ar), 2.52 (m, 2H, CHMe₂), 2.13 (s, 3H, Ar-Me), 1.94 (s, 3H, Ar-Me), 1.43 (dd, 6H, CHMe₂), 1.08 (dd, 6H, CHMe₂). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 43.7 (d, J_{PPt} = 2754.5 and $J_{\rm PP} = 401.6$, PⁱPr₂), 24.7 (d, $J_{\rm PPt} = 2673.9$ and $J_{\rm PP} =$ 401.9, PPh₂). Observable ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 62.89 MHz): δ 162.0 (d, $J_{CP} = 18.1$, C), 161.6 (d, $J_{CP} = 20.4$, C), 135.1 (s, CH), 134.0 (d, $J_{CP} = 10.6$, CH), 132.6 (d, $J_{CP} = 45.3$, C), 132.4 (s, CH), 131.6 (d, J_{CP} = 52.1 and J_{CP} = 3.0, C), 130.6 (s, CH), 128.9 (s, CH), 128.7 (s, CH), 127.3 (s, CH), 126.7 (d J_{CP} = 6.8, CH), 121.5 (d, J_{CP} = 55.8, C), 119.5 (d, *J*_{CP} = 48.3, C), 116.8 (d, *J*_{CP} = 11.3, CH), 116.4 $(J_{CP} = 12.1, CH), 25.3 (d, J_{CP} = 28.0, CHMe_2), 20.3 (s, Ar-Me),$ 20.0 (s, Ar-Me), 18.4 (s, CHMe₂), 17.9 (s, CHMe₂). Anal. Calcd for C₃₂H₃₆ClNP₂Pt: C, 52.86; H, 4.99; N, 1.93; Found: C, 52.46; H, 5.14; N, 1.71.

Preparation of (PhPNPCy)PtCl 6

PhPNP^{Cy} (2) (0.056 g, 0.096 mmol) and (COD)PtCl₂ (0.036 g, 0.096 mmol) were placed into a round bottom flask along with 20 mL of THF and one equiv. of NEt₃. The yellow solution was refluxed for 2.5 h, filtered through Celite, and the volatiles were removed under reduced pressure resulting in a yellow solid. The yellow solid was washed with cold pentane and dried under vacuum to give 6 (0.067 g, 87%). A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a benzene solution at room temperature. ¹H NMR (C₆D₆, 250.13 MHz): δ 8.03 (m, 4H, Ar), 7.90 (dd, 1H, Ar) 7.81 (dd, 1H, Ar) 6.97 (m, 8H, Ar), 6.75 (td, 2H, Ar), 2.15 (s, 3H, Ar-Me), 1.93 (s, 3H, Ar–Me), 2.60–0.99 (m, 22H, Cy). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 36.2 (d, J_{PPt} = 2749.2 and J_{PP} = 402.4, PCy₂), 24.4 (d, $J_{PPt} = 2673.0$ and $J_{PP} = 402.3$, PPh₂). Observable ¹³C{¹H} NMR (C₆D₆, 62.89 MHz): δ 162.0 (d, J_{CP} = 17.4, C), 161.6 (d, J_{CP} = 19.6, C), 135.1 (s, CH), 134.0 (d, J_{CP} = 10.6, CH), 132.7 (d, J_{CP} = 52.0, C), 132.6 (s, CH), 132.3 (s, CH₂), 131.7 (d, J_{CP} = 53.6, C), 130.6 (s, CH), 128.9 (s, CH), 128.7 (s, CH), 127.3 (d, $J_{CP} = 7.5$, CH), 126.8 (d, $J_{CP} = 6.7$, C), 121.5 (d, $J_{CP} = 55.8$, C), 119.7 (d, J_{CP} = 46.0, C), 116.9 (d, J_{CP} = 10.6, CH), 116.4 $(J_{CP} = 11.3, CH), 34.7 (d, J_{CP} = 27.9, CH), 28.4 (s, CH₂), 28.3 (d, J_{CP} = 11.3, CH), 28.4 (s, CH₂), 28.3 (d, J_{CP} = 27.9, CH), 28.4 (s, CH₂), 28.3 (d, J_{CP} = 27.9, CH), 28.4 (s, CH₂), 28.3 (d, J_{CP} = 27.9, CH), 28.4 (s, CH₂), 28.4 (s,$ $J_{CP} = 6.3$, CH₂), 27.2 (s, CH₂), 27.0 (d, $J_{CP} = 6.2$, CH₂), 26.1 (s, CH₂), 20.4 (s, Ar–*Me*), 20.0 (s, Ar–*Me*). Anal. Calcd for C₃₈H₄₄ClNP₂Pt: C, 56.54; H, 5.49; N, 1.74; Found: C, 56.98; H, 6.35; N, 1.98.

Preparation of (PhPNPiPr)NiH 7

PhPNPiPr (1) (0.103 g, 0.160 mmol) and Ni(COD)2 (0.160 mL, 0.160 mmol) were placed into a round bottom flask along with 20 mL of benzene and stirred at RT for 15 min. The volatiles were removed under reduced pressure, resulting in a brown residue. The brown residue was washed with cold pentane and dried under vacuum to give 7 as a brown solid (0.081 g, 84%). A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a diethyl ether solution at -30 °C. ¹H NMR (C₆D₆, 250.13 MHz): δ 7.95–7.75 (m, 6H, Ar), 7.10–6.85 (m, 10H, Ar) 2.05 (m, 2H, CHMe₂), 2.21 (s, 3H, Ar-Me), 2.02 (s, 3H, Ar-Me), $1.23 (dd, 6H, CHMe_2), 0.95 (dd, 6H, CHMe_2) - 18.1 (dd, 1H, J_{HP} =$ 68.4 and $J_{\rm HP}$ = 58.9, Ni–H). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 58.9 (d, $J_{PP} = 244.2$, $P^{i}Pr_{2}$), 31.4 (d, $J_{PP} = 244.1$, PPh_{2}). Observable ¹³C{¹H} NMR (C₆D₆, 62.89 MHz): δ 161.4 (dd, J_{CP} = 21.4 and $J_{\rm CP}$ = 3.5, C), 160.9 (dd, $J_{\rm CP}$ = 25.1 and $J_{\rm CP}$ = 2.3, C), 134.5 (s, CH), 133.8 (d, J_{CP} = 12.5, CH), 133.0 (s, CH), 132.5 (s, CH), 130.0 (s, CH), 128.6 (d, $J_{CP} = 9.9$, CH), 128.5 (s, CH), 124.6 (d, $J_{CP} = 7.0$, C), 124.5 (d, J_{CP} = 42.3, C), 124.1 (d, J_{CP} = 5.4, CH), 122.5 (d, J_{CP} = 34.2, C), 115.6 (d, J_{CP} = 10.8, CH), 115.0 (J_{CP} = 11.1, CH), 23.7 $(d, J_{CP} = 25.7, CHMe_2), 20.5 (s, Ar-Me), 20.3 (s, Ar-Me), 19.5 (d, Me_2))$ $J_{CP} = 5.7$, CHM e_2), 18.3 (s, CHM e_2). Anal. Calcd for C₃₂H₃₇NP₂Ni: C, 69.09; H, 6.70; N, 2.52; Found: C, 69.27; H, 6.88; N, 2.27.

Preparation of (PhPNPCy)NiH 8

^{Ph}PNP^{Cy} (2) (0.100 g, 0.104 mmol) and Ni(COD)₂ (0.140 mL, 0.140 mmol) were placed into a round bottom flask along with 20 mL of benzene and stirred at RT for 15 min. The volatiles were removed under reduced pressure resulting in a brown solid. The brown solid was washed with cold pentane and dried under vacuum to give 8 as a brown solid (0.083 g, 87%). ¹H NMR (C_6D_6 , 250.13 MHz): δ 8.00–7.78 (m, 6H, Ar) 7.14–6.85 (m, 10H, Ar), 2.22 (s, 3H, Ar-Me), 2.02 (s, 3H, Ar-Me), 2.22-0.85 (m, Cy), -18.15 (dd, $J_{\rm HP} = 58.9$ and $J_{\rm HP} = 68.4$, Ni–H). ³¹P{¹H} NMR $(C_6 D_6, 101.26 \text{ MHz})$: δ 49.6 (d, J_{PP} = 244.9, PCy₂), 31.8 (d, J_{PP} = 244.2, PPh₂). Observable ¹³C{¹H} NMR (C₆D₆, 62.89 MHz): δ 161.6 (dd, J_{CP} = 21.9 and J_{CP} = 3.6, C), 160.9 (dd, J_{CP} = 25.3 and $J_{\rm CP}$ = 2.4, C), 134.4 (s, CH), 133.8 (d, $J_{\rm CP}$ = 12.4, CH), 132.7 (d, J_{CP} = 31.0, CH), 132.4 (s, CH), 129.9 (s, CH), 128.8 (s, CH), 128.6 (s, CH), 124.6 (d, J_{CP} = 6.1, C), 124.6 (d, J_{CP} = 42.0, C), 124.2 (d, $J_{\rm CP} = 5.4$, CH), 122.6 (d, $J_{\rm CP} = 34.3$, C), 115.6 (d, $J_{\rm CP} = 10.4$, CH), 115.1 ($J_{CP} = 11.7$, CH), 33.3 (d, $J_{CP} = 26.0$, CH), 29.8 (d, $J_{CP} = 4.1$, CH₂), 28.6 (s, CH₂) 27.4 (s, CH₂), 27.0 (s, CH₂), 26.6 (s, CH₂), 20.6 (s, Ar-Me), 20.3 (s, Ar-Me).

Preparation of (PhPNPiPr)PdH 9

 $(^{Ph}PNP^{iPr})PdCl$ (3) (0.103 g, 0.160 mmol) and Super-Hydride[®] solution (LiEt₃BH in THF, 0.160 mL, 0.160 mmol) were placed into a round bottom flask with 20 mL of THF and stirred at RT for 5 h. The volatiles were removed under reduced pressure, resulting in a brown residue. The brown residue was redissolved into pentane and filtered through Celite resulting in a brown solution. The volatiles were removed under reduced pressure, resulting in a brown solution.

brown solid. The brown solid was dried under vacuum to give **9** (0.081 g, 84%). ¹H NMR (C₆D₆, 250.13 MHz): δ 7.96 (m, 2H, Ar), 7.83 (m, 4H, Ar) 6.98 (m, 8H, Ar), 2.05 (m, 2H, CHMe₂), 2.21 (s, 3H, Ar–Me), 2.00 (s, 3H, Ar–Me), 1.22 (dd, 6H, CHMe₂), 0.90 (dd, 6H, CHMe₂) –9.97 (vt, 1H, J_{HP} = 5.25, Pd–H). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 63.4 (d, J_{PP} = 354.2, PⁱPr₂), 31.4 (d, J_{PP} = 354.3, PPh₂).

Preparation of (PhPNPCy)PdH 10

(^{Ph}PNP^{Cy})PdCl (**4**) (0.100 g, 0.140 mmol) and Super-Hydride solution (0.140 mL, 0.140 mmol) were placed into a round bottom flask along with 20 mL of THF and stirred at RT for 3 h. The volatiles were removed under reduced pressure, resulting in a brown residue. The brown residue was redissolved into pentane and filtered through Celite, again resulting in a brown solution. The volatiles were removed under reduced pressure to give a brown solid. The brown solid was dried under vacuum to give **10** (0.083 g, 87%). A single crystal suitable for X-ray diffraction analysis was grown from the slow evaporation of a diethyl ether solution at -30 °C. ¹H NMR (C₆D₆, 250.13 MHz): δ 7.99 (m, 4H, Ar), 7.90–7.75 (m, 2H, Ar), 7.14–6.86 (m, 10H, Ar), 2.23 (s, 3H, Ar–Me), 2.16 (s, 3H, Ar–Me), 2.01–0.95 (m, 22H, Cy), –9.91 (vt, 1H, J_{HP} = 4.75, Pd–H). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 54.5 (d, J_{PP} = 354.5, PCy₂), 31.5 (d, J_{PP} = 354.5, PPh₂).

Preparation of (PhPNPiPr)PtH 11

(^{Ph}PNP^{iPr})PtCl (**5**) (0.043 g, 0.060 mmol) and Super-Hydride solution (0.060 mL, 0.060 mmol) were placed into a round bottom flask along with 20 mL of THF and stirred at RT for 2 h. The volatiles were removed under reduced pressure resulting in a brown residue. The brown residue was redissolved into pentane and filtered through Celite to again give a brown solution. The volatiles were removed under reduced pressure, resulting in a brown solid. The brown solid was dried under vacuum to give **11** (0.035 g, 85%). ¹H NMR (C₆D₆, 250.13 MHz): δ 8.05–7.71 (m, 6H, Ar), 7.11–6.96 (m, 10H, Ar), 2.13 (m, 2H, CHMe₂), 2.11 (s, 3H, Ar–Me), 2.00 (s, 3H, Ar–Me), 1.18 (dd, 6H, CH*Me*₂), 0.93 (dd, 6H, CH*Me*₂), -11.6 (vt, 1H, J_{HP} = 14.1 and J_{HPt} = 1031.8, Pt–H). ³¹P{¹H} NMR (C₆D₆, 101.26 MHz): δ 59.8 (d, J_{PPt} = 2860.3 and J_{PP} = 361.4, PⁱPr₂), 34.5 (d, J_{PPt} = 2824.0 and J_{PP} = 361.3, PPh₂).

Reactions of (PhPNPR')MH with O2

An approximate 0.04 mmol sample of the metal hydride **7**, **8**, **9**, **10**, or **11** was placed into a medium-walled NMR tube fitted with a J. Young valve. Approximately 0.6 mL of C_7D_8 was added to dissolve the metal hydride. The sample was degassed using several freeze-pump-thaw cycles, and then pressurized to 70 psig (4.76 atm.) O_2 for 30 min. The tube was shaken several times during this period. The reaction progress was monitored by ³¹P and ¹H NMR spectra taken during the reaction. The tube was then placed in a -35 °C freezer in order to attempt to isolate the crystallized product(s).

X-ray data collection

Data for X-ray crystallographic determination were collected and solved with the assistance of Dr. Diane Dickie of the University of New Mexico. Crystallographic data were collected on a Bruker X8

APEX CCD-based X-ray diffractometer using monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The single crystals were coated in oil (Paratone-NTM) and mounted on nylon cryoloops (Hampton Research). Bruker APEX2 was used to collect and process the data.²⁸ The structures were solved by either the direct or Patterson method with XSHEL and were refined by full matrix leastsquares method on F² with SHELXTL.²⁹ All non-hydrogens were refined anisotropically and hydrogen atoms were fixed at calculated geometric positions with the exception of hydrogens attached to metals. All H atoms were refined in calculated positions with the exception of the M-H bonds in 7 and 10. We initially allowed the hydrogen attached to the metal atom to vary in position. However, when doing this, two large residual electron density peaks appeared at a distance of approximately 0.8–0.9 Å from the metal. We believe that the large residual electron density is likely due to the Fourier series truncation effect because of a lack of collected data as the two residual electron density peaks are located on a symmetry axis containing the metal atoms.³⁰ To solve this issue, we initially constrained the Ni-H bond length to be 1.50 Å, and the Pd-H bond length to be 1.7 Å and then allowed the M-H bond to vary during refinement. The value of the M-H bond lengths resulting from this model treatment at 1.95(3) Å for 7 and 1.55(3) Å for 10, within the range seen earlier for other M-H bonds. SQUEEZE in PLATON was used to treat disordered solvent molecules.³¹ Crystallographic figures were generated using Diamond 3.1g.³² All crystallographic data are located in Tables 1 and 2.

Acknowledgements

This work was financially supported by the Department of Energy *via* a grant (DE-FG02-06ER15765) to RAK and KIG. The Bruker X-ray diffractometer was purchased *via* a National Science Foundation CRIF:MU award to the University of New Mexico (CHE-0443580). We thank Dr. Diane Dickie of UNM for assistance with the X-ray data analysis. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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