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PAPER

Pincer ligands with an all-phosphorus donor set: subtle differences between rhodium and palladium†

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The synthesis of a new, all-phosphorus pincer $PP^{NEt2}P$ ligand **L3^{NEt2}**, which is derived from 2-indolylphosphine and features a central $N_2P(NEt_2)$ core, is described. This 'PPP' species shows coordination toward Rh as a neutral trisphosphine ligand. Tridentate diphenylphosphine-derived $PP^{H}P$ ligands **L1^{H}** and **L2^{H}**, featuring a secondary phosphine core, show 'ambivalent' coordination, acting as persistent neutral triphosphine ligands with Rh, and as easily-formed monoanionic phosphido(bisphosphine) pincer ligands toward Pd. These subtle differences, which might be more general for group 9 and 10 metal complexes with this ligand set, are explained by comparative DFT calculations (BP86; def2-TZVP level of theory) for the Rh and Pd species involved, including those with the structurally related $PN^{H}P$ ligands. The optimized structure for complex PdCl(**L2**) indicates minimal overlap of available Pd d-orbitals with the lone pair of the central, deprotonated phosphorus atom (formally a phosphido fragment), suggesting that it behaves predominantly like a bulky phosphine instead of a phosphido fragment.

Introduction

Diphosphorus "PEP" pincer ligands have attracted substantial interest and shown significant merits in studies of fundamental C–H, C–C and C–N bond-activation processes, coordination chemistry, metal-mediated reactivity and homogeneous catalysis applications.[1] Some of the characteristic ligand design features include i) a rigid, tridentate binding pocket, ii) compatibility with a large number of transition metals, iii) a high degree of synthetic tunability, and iv) modularity in the coordinating bridgehead atom E. Besides the archetypical, monoanionic carbon-based frameworks such as **A**,[2,3] novel backbones incorporate amido (**B**),[4] silyl (**C**)[5] or boryl (**D**)[6] units that function as pivotal heterodonor systems (Fig. 1). Furthermore, various *neutral* pincer ligands with phosphorus side-groups have been intensively studied, including noninnocent, cooperative systems based on pyridine as the central fragment.[7] These systems undergo facile and reversible charge-switching from a neutral to a monoanionic state, which can be used to selectively activate substrates and catalyse novel reactions efficiently,[8] even with first row transition metals.[9,10]

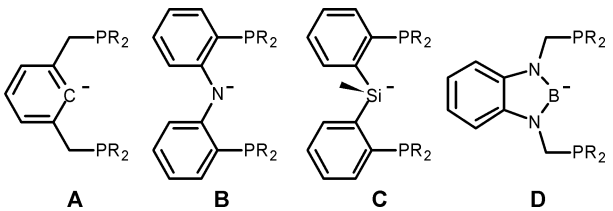

Fig. 1 Generic representations of monoanionic "PEP" pincer ligands; **A**: classic PC^{-}P framework; B–D: various scaffolds with a central deprotonated heteroatom.

Interest in the design of novel pincer systems is spurred by recent developments in the field of E–H bond activation processes. For instance, the selective N–H bond cleavage of ammonia is one of the most sought-after proponents.[11] Successful metal-mediated N–H activation of ammonia has been reported for a small number of mononuclear late transition metal complexes, *i.e.* Ir(PC^{-}P) (**E**),[12] Ir(PSi^{-}P) (**F**),[13] and Ru(PN^{-}P) (**G**),[14] all featuring a pincer type ligand (Fig. 2). Additionally, we have preliminary data to suggest that Ir-species (**H**), bearing a novel hybrid PN^{-}N pincer ligand, is also amenable to N–H bond activation.[15]

We wondered if the rich coordination chemistry displayed by the versatile monoanionic frameworks with a central heteroatom donor **B–D** and the resulting reactivity with group 9 metals could be extended to all-phosphorus based donor sets, of which there are surprisingly few reports (Fig. 3).

Neutral triphosphorus ligands that induce a characteristic *mer*-coordination are relatively rare[16] compared to systems such as 'triphos' (**I**) that prefer a *fac* arrangement,[17] whilst there are

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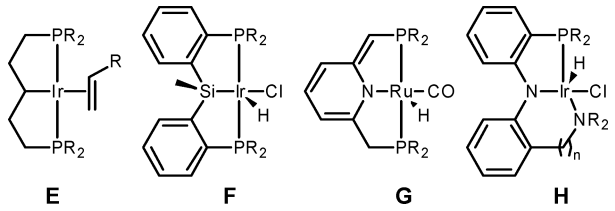


Fig. 2 Recent pincer complexes capable of NH_3 activation.

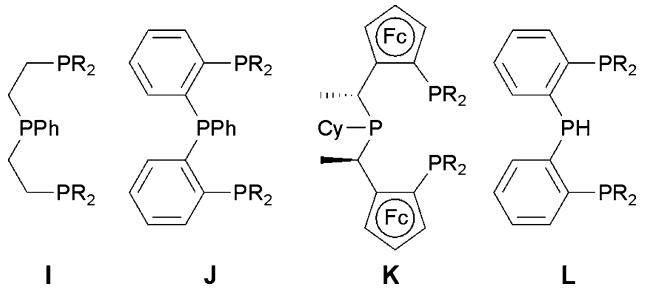


Fig. 3 Overview of known PPP pincer ligand systems.

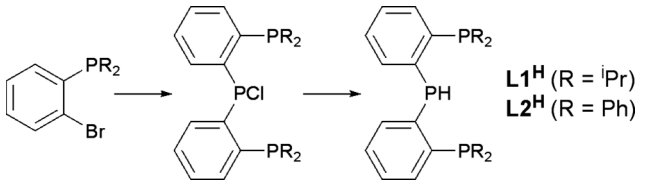
also intermediate cases (**J**).[18] Togni developed various chiral PPP ligands, termed Pigiphos (**K**), which were successfully applied in the Ni-catalyzed hydroamination of electron-poor olefins.[19] Only very recently scaffold $\mathbf{L^H}$ was described, and it was shown to act as a monoanionic bridging ligand to Cu^I.[20] Subsequently, $\mathbf{L^H}$ was found to coordinate as a monoanionic pincer ligand to Pd.[21]

To date, group 9 metal complexes of diphenylphosphine-derived PP^HP ligands $\mathbf{L1^H}$ and $\mathbf{L2^H}$ have not been reported, whereas the coordination chemistry and reactivity with analogous diphenylamine-derived PN^HP ligands have been very successfully investigated and exploited.[4,22] Grützmacher has shown that the acidity of secondary amines is significantly increased upon coordination to group 9 metals.[23] The difference in acidity of $HPPh_2$ (pK_a: exp. 21.7; calc. 22.9) *vs.* $HNPh_2$ (pK_a: exp. 25.0; calc. 26.4),[24] which may be assumed to persist after *ortho*-functionalization of the phenyl rings, suggests that extension of the amine-based noninnocent reactivity to secondary phosphine derived skeletons might be possible. This could lead to similar rich coordination chemistry and reversible deprotonation behaviour for PP^HP-type ligands such as $\mathbf{L1^H}$ and $\mathbf{L2^H}$, especially with group 9 transition metals. For instance, E–H bond splitting might be promoted *via* similar cooperative ligand–metal activation mechanisms as observed for certain neutral, tridentate PNP systems,[8–10] and monoanionic PNP ligand frameworks.[25] To facilitate spectroscopic characterization, we focused on Rh complexes with these all-phosphorus tridentate donor ligands, which also enabled a direct comparison with its group 10 congener Pd.[21]

Results and discussion

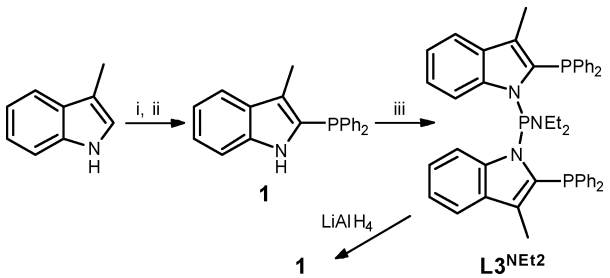
Ligand synthesis

Tridentate PP^HP ligands $\mathbf{L1^H}$ and $\mathbf{L2^H}$ were prepared as previously described in the literature (Scheme 1).[20] Furthermore, we developed a new all-phosphorus pincer ligand based on the recently described 'indolylphosphine' building block,[26] which is easily prepared from 3-methylindole using a convenient two-step protocol involving *in situ* CO_2 protection of the indole nitrogen.



Scheme 1 Generic synthesis route to PP^HP ligands $\mathbf{L^H}$.[20]

This scaffold has previously been utilized for the construction of tripodal tetradentate frameworks.[27] Deprotonation of **1** with ^{n}BuLi followed by treatment with 0.5 equiv Cl_2PNEt_2 led to the new tridentate PPP pincer ligand $\mathbf{L3^{NEt2}}$ (Scheme 2), which was isolated as a pure white solid in good yield after purification by chromatography. The ^{31}P NMR spectrum exhibited a triplet at δ 96.1 ppm ($PNEt_2$) and a doublet at –29.4 ppm, (PPh_2), both with a coupling constant $^3J_{PP}$ of 168.5 Hz.



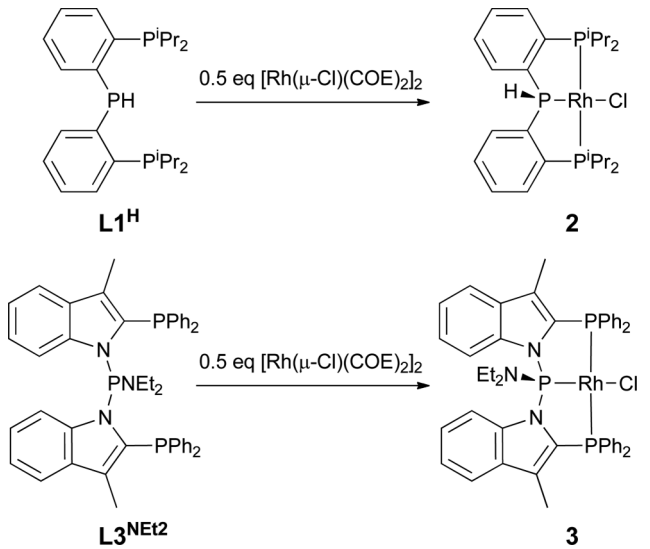
Scheme 2 Synthesis of novel triphosphorus ligand $\mathbf{L3^{NEt2}}$. Reaction conditions: i) 1 equiv ^{n}BuLi, CO_2; ii) 1 equiv ^{t}BuLi, $ClPR_2$; iii) 1 equiv ^{n}BuLi, 0.5 equiv $P(NEt_2)Cl_2$.

Unfortunately, selective P–N bond cleavage was not possible when indolyl-based phosphine $\mathbf{L3NEt_2}$ was subjected to standard hydride reduction methodologies used for the conversion of diethylaminophosphines or chlorophosphines to the corresponding secondary phosphines, and only the initial indolylphosphine **1** was recovered. Selective removal of the diethylamino group *via* alcoholysis or protonation was also not successful.

Coordination chemistry to Rh and comparison with Pd

Reaction of $\mathbf{L1^H}$ with $[Rh(\mu\text{-}Cl)(COE)_2]_2$ (COE = cyclooctene) in THF or toluene resulted in the formation of a light orange solid (Scheme 3, top). Strikingly, the ^{31}P NMR spectrum of the corresponding Rh-complex showed a doublet-of-triplets at 48.9 ppm for the central P atom (free $\mathbf{L1^H}$: $\delta_P{}^H$ = –49.2 ppm[20]) and a doublet-of-doublets at 65.5 ppm for the diisopropylphosphine groups (free $\mathbf{L1^H}$: $\delta_P{}^{iPr}$ = 0.0 ppm), which results in substantial $\Delta\delta$ shifts of up to 98.1 ppm upon complexation. The $^1J_{Rh\text{-}P}$ coupling constants of 136 Hz (P^{iPr}-Rh) and 167 Hz (P^H-Rh) and a $^3J_{PP}$ coupling constant of 32 Hz (free $\mathbf{L1^H}$: $^3J_{PP}$ = 131 Hz) reveal the coordination of phosphines to Rh to yield complex **2**. This implies that deprotonation of the central -PH fragment of the pincer ligand, to generate a phosphido-unit, does not occur. Genuine terminal rhodium-phosphido species are very rare; to the best of our knowledge only rhodium complexes with bridging phosphides are well-characterized.[28]

Notably, upon closer inspection of the ^{1}H NMR spectrum, a doublet was observable at δ 6.30 ppm, with a $^1J_{PH}$ coupling of 342 Hz (free ligand: δ 6.02 ppm, $^1J_{PH}$ = 219 Hz), which is



Scheme 3 Synthesis of neutral Rh complexes **2** (top, with **L1^H**) and **3** (bottom, with **L3^{NEt2}**).

strong evidence for the existence of a species with the overall formulation Rh(**L1^H**)Cl, species **2**.[29] To confirm this, we also measured the IR spectrum of species **2**, which showed a band at ν 2272 cm^{-1} for the P–H moiety (free HP(P^{iPr})$_2$ ligand: 2282 cm^{-1}). Unfortunately, we were unable to recrystallize compound **2** as it proved very unstable, with significant decomposition after 24 h and complete decomposition within 7 days at 4 °C; it was therefore only characterized spectroscopically. Complexation of the diphenylphosphine analogue **L2^H** to Rh or Ir led to multiple species, as determined by ^{31}P NMR spectroscopy, with no indication for P–H activation.

Ligand **L1^H** was subjected to several Rh sources‡ under varying conditions, in order to achieve insertion into the P–H bond but none of these reactions led to a well-defined product. Deprotonation of the PP^{H}P ligand with ^{n}BuLi at –78 °C, evidenced by the characteristic bright red/pink colour of the THF solution, and subsequent treatment with [Rh(μ-Cl)(COE)$_2$]$_2$ did not result in the formation of the desired product either, but rather led to decomposition with no detectable ^{31}P NMR signals. Reaction of *in situ* prepared Rh complex **2** with strong bases such as NaO^{t}Bu, ^{n}BuLi or KHMDS only resulted in decomposition of the ligand, as indicated by ^{31}P NMR spectroscopy, whereas LiNH$_2$, LiNHPh, and triethylamine did not noticeably react with the Rh species. These results are remarkable, given the higher intrinsic acidity of R$_2$PH *vs.* R$_2$NH in their free form,[24] and the reported effect on the –NH acidity upon amine coordination to Rh.[23] This must mean that the acidity of the P–H bond of unactivated secondary phosphines is not substantially altered upon coordination to Rh.

Abstraction of the chloride ligand from complex **2** using silver salts such as AgSbF$_6$ in either THF or CH$_2$Cl$_2$ resulted in decomposition of the complex. Chloride abstraction from the initial Rh reagent, prior to addition of pincer ligand **L1^H**,[30] also resulted in unwanted side-reactions. Treatment of Rh complex **2** with 2.0 M HCl in diethylether at 0 °C afforded a hydride signal (doublet-of-doublet-of-triplets) at δ –16.91 ppm in the ^{1}H NMR spectrum, with J_{PH} coupling constants of 6.7 (-*P*iPr) and 10.1 Hz (-*P*H). We propose that oxidative addition of HCl has occurred, leading to octahedral Rh^{III}-hydride species **2HCl** with the hydride acting as axial ligand, *i.e. cis* to all phosphorus groups, although this was not investigated further.

The tridentate all-phosphorus ligand **L3^{NEt2}**, which bears a stronger P–N bond at the bridging atom, also acts as a neutral ligand when complexed with Rh. Treatment of **L3^{NEt2}** with [Rh(μ-Cl)(COE)$_2$]$_2$ or [Rh(μ-Cl)(CO)$_2$]$_2$ in THF resulted in the facile and clean formation of complex **3** as an orange solid (Scheme 3, bottom). Both Rh reagents form the same pincer complex, as evidenced from the spectral data, *e.g.* signals at 142.4 ppm (dt, $^1J_{RhP}$ = 223.9 Hz; $^2J_{PP}$ = 42.6 Hz) and 17.1 ppm (dd, $^1J_{RhP}$ = 144.6 Hz; $^2J_{PP}$ = 42.6 Hz) in the ^{31}P NMR spectrum. In this case, the chemical shift differences were more moderate and typical for archetypical phosphine coordination with $\Delta\delta$'s of up to 46.3 ppm.

Single crystals suitable for X-ray diffraction were obtained from toluene and the resulting molecular structure is depicted in Fig. 4. The four-coordinate Rh–Cl pincer complex, which shows a distorted square-planar geometry around the Rh-center, features a central trisamidophosphine group (connectivity around atom P$_1$). The distortion is evident from the $\angle$P$_2$–Rh–P$_3$ of 154.301(17)°, which is induced by the tetrahedral geometry around the sp^3-hybridized P^{NEt2}-atom that pushes both indole-fragments below the P^{NEt2}-Rh–Cl plane (angle N$_2$–P$_1$–N$_3$ is 111.30(7)°). There is a pseudo-helical out-of-plane twist of the indole-heterocycles due to steric constraints, similar to what was observed in tetradentate analogues.[27a] The intramolecular Rh–P$_1$ distance is slightly shorter than for Rh–P$_2$ and Rh–P$_3$, which could be an electronic effect of PN$_3$ *vs.* PC$_3$ substitution.

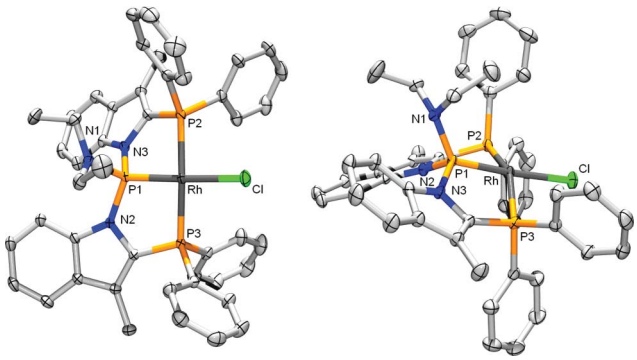


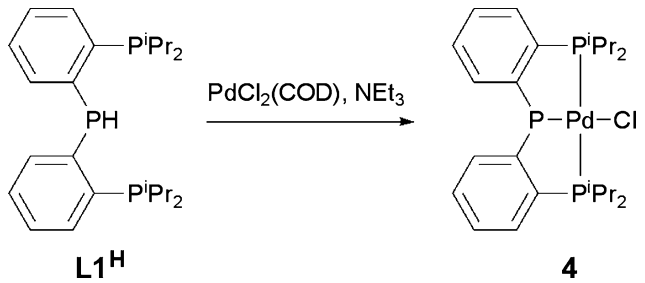
Fig. 4 ORTEP plot (50% probability displacement ellipsoids) of complex **3**, [RhCl(**L3^{NEt2}**)]; left–top view; right–side view. Hydrogen atoms and disordered toluene solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–P$_1$ 2.1516(4); Rh–P$_2$ 2.2677(4); Rh–P$_3$ 2.2514(4); Rh–Cl 2.3948(4); P$_1$–N$_1$ 1.6774(14); P$_1$–N$_2$ 1.7271(14); P$_1$–N$_3$ 1.7298(14); P$_1$–Rh–P$_2$ 83.620(16); P$_1$–Rh–P$_3$ 87.092(16), P$_2$–Rh–P$_3$ 154.301(17), P$_1$–Rh–Cl 176.474(17), Rh–P$_1$–N$_1$ 126.06(5); N$_1$–P$_1$–N$_2$ 99.56(7), N$_1$–P$_1$–N$_3$ 100.78(7), N$_2$–P$_1$–N$_3$ 111.30(7).

As encountered with complex **2**, attempts to obtain a cationic species from **3** *via* Ag$^+$-induced halide abstraction led to ill-defined products, presumably involving undesired redox-chemistry. Treating Rh complex **3** with 2.0 M HCl in ether at 0 °C did not appear to result in protonation of the diethylamino-group and subsequent P–N rupture, prohibiting this ligand from acting as an *in situ* generated monoanionic analogue of **L^H**, also when already

‡ Other precursors employed to induce P–H cleavage were [Rh(cod)$_2$]BF$_4$, [Rh(μ-OH)(coe)$_2$]$_2$, Rh(acac)(CO)$_2$, [Rh(CO)$_2$Cl]$_2$, [Rh(cod)(MeCN)$_2$]-BF$_4$, [Rh(OAc)$_2$]$_2$ and RhCl$_3$·3H$_2$O.

coordinated to Rh. This further illustrates the propensity of both types of tridentate PPP-compounds to act as neutral triphosphine ligands to Rh.

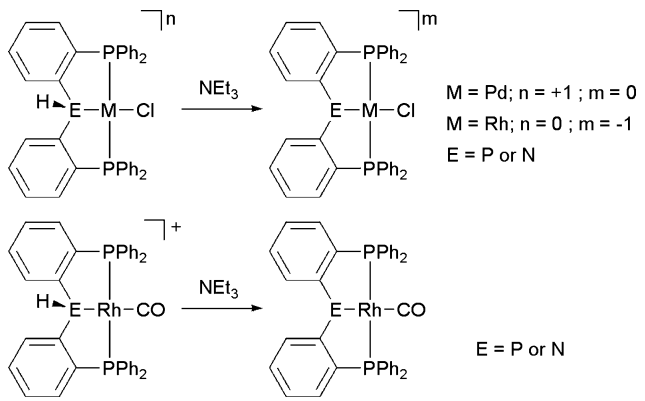
These results markedly contrast the facile way by which Pd coordinates to the tridentate monoanionic PP⁻P ligand. The palladium complex PdCl(**L2**) **4** can be prepared simply by heating PP^{H}P ligand **L2^{H}** with $PdCl_2$(COD) and Hünig's base in THF at 50 °C (Scheme 4).[21] The ^{1}H NMR signal for a secondary phosphine is absent (no $^1J_{P\text{-}H}$ coupling detected), and no P–H stretch is observed in the IR spectrum. The molecular structure for complex **4** has been reported before.[21]



Scheme 4 Synthesis of Pd complex **4** featuring deprotonated monoanionic ligand **L1**.

DFT calculations on Rh and Pd species with L2^{H} and L2

To shed more light on the fact that the Rh complexes of ligands **L1^{H}** and **L2^{H}** are difficult to deprotonate, while the corresponding phosphido Pd complexes are easily obtained, we calculated the optimized geometries of the PP^{H}P phosphine and PPP phosphido complexes [M(**L2^{H}**)(L)]^{n} and [M(**L2**)(L)]$^{n-1}$ (M = Rh, Pd; L = Cl, CO; n = +1, 0) with DFT (BP86, def2-TZVP). For comparison, we also optimized the analogous PN^{H}P amine and PNP amido complexes, as both Rh(PNP) and Pd(PNP) complexes are known.[31] A comparative analysis of the relative energies for deprotonation of the ligand backbone by triethylamine was performed using a full geometry optimization (BP86, def2-TZVP) of all the species involved (Scheme 5).



Scheme 5 Computed (DFT) deprotonation of the PP^{H}P and PN^{H}P ligands in the complexes [MCl(**PE^{H}P**)]^{n} and [Rh(**PE^{H}P**)(CO)]$^{+}$ (M = Rh, Pd; E = P, N) with NEt_3 to give the corresponding **PE⁻P** complexes.

Quite similar geometries were obtained for the four PP^{H}P based complexes Rh(**L2^{H}**)(CO)-cation, Rh(**L2**)(CO), Pd(**L2^{H}**)Cl-cation and Pd(**L2**)Cl (Table 1). The geometric data obtained for complex **4** when optimized at the BP86, def2-TZVP level agree well with the X-ray structural data available, with the Pd-P^{-} intramolecular distance being slightly shorter than the Pd-P^{R} bond lengths (Pd-P^{-}: ~2.25 Å; Pd-P^{R} ~2.30 Å).[21,32] Improved energies were obtained with single point calculations employing COSMO (ε = 7.58; tetrahydrofuran) dielectric solvent corrections, using both BP86/def2-TZVP and b3lyp/def2-TZVP level of theory for each of the PP^{H}P and PN^{H}P complexes (Table 2). The computed data clearly confirm that deprotonation is much less favorable for the PP^{H}P based species. For both PP^{H}P and PN^{H}P, deprotonation of the RhCl complexes is disfavored relative to deprotonation of the corresponding PdCl complexes. To balance the effect of comparing complexes with different overall charges (neutral *vs.* monoanionic), the corresponding rhodium-carbonyl complexes were included in the analysis. However, even after elimination of charge differences *and* introducing the π-accepting carbonyl ligand (which should stabilise the amido-metal interaction through push-pull charge delocalisation[33]), deprotonation of the Pd complexes is still favored (Table 2). This is most likely a local charge effect resulting from the higher metal oxidation state of Pd (Rh^{I} *vs.* Pd^{II}). The calculations agree with our experimental observations that a monoanionic framework is easily accessed for Pd^{II}, but difficult to achieve for Rh^{I}.

Table 1 Selected structural data for the DFT optimized geometries (BP86, def2-TZVP) of Rh and Pd complexes with **L2^{H}** and **L2**

	Rh(**L2^{H}**)	Rh(**L2**)	Pd(**L2^{H}**)	Pd(**L2**)
M-P^{H} (Å)	2.2952	2.3399	2.2267	2.2882
M-P^{Ph} (Å)	2.3155	2.2931	2.3300	2.2985
	2.3242	2.3036	2.3346	2.3144
P^{H}-M-*L* (°)	174.03	174.35	178.67	172.11
P^{H}-M-P^{Ph} (°)	82.03	81.82	84.66	83.62
	84.21	83.75	85.31	85.84
C-P^{H}-C (°)	113.77	108.98	116.27	107.82
P^{Ph}-M-P^{Ph} (°)	162.81	159.25	168.46	162.45

From inspection of the geometries and orbitals of the deprotonated PN⁻P and PP⁻P complexes it is clear that the nitrogen atom of the PN⁻P complexes readily adopts an sp^2 hybridisation, thus allowing a clear π-interaction between the nitrogen atom p-orbital and the metal orbitals (Fig. 6). Although these are weakly attractive interactions, they do contribute to some stabilisation of the amido complexes. Similar stabilising interactions cannot be achieved for the corresponding PP⁻P phosphido complexes, because the P-atom does not rehybridise from sp^3 to sp^2, and thus the lone pair on the central phosphorus atom points away from the metal (Fig. 5 and 6), giving the P-atom considerable phosphine character. Taken together with the higher electronegativity of nitrogen, this explains why the R_2PH ligand complexes are weaker acids than the corresponding R_2NH ligand complexes.

This observation opens up the interesting possibility to use these phosphido-palladium complexes as sterically encumbered metallo-ligands for other metals.

Conclusions

In summary, the preparation and coordination chemistry of the neutral, tridentate all-phosphorus ligand **L1^{H}** and **L3^{NEt2}** to group 9 metals is described, including a molecular structure for RhCl(**L3^{NEt2}**). In contrast to the known reactivity of structurally

Table 2 Computed proton transfer energies (kcal mol^{-1})[a]

	BP86	BP86 + cosmo[b]	b3-lyp + cosmo[b]
[(PP*H*P)**M**L]^{m} + [(PNP)**M**L]^{n} → [(PN*H*P)**M**L]^{n} + [(PPP)**M**Cl]^{m}			
M = Rh, L = Cl	+18.0	+16.3	+15.8
M = Rh, L = CO	+12.9	+11.0	+11.1
M = Pd, L = Cl	+12.4	+10.2	+9.5
[(PN*H*P)**M**L]^{n} + NEt_3 → [(PNP)**M**L]$^{n-1}$ + $[HNEt_3]^+$			
M = Rh, L = Cl	+74.4	+6.3	+10.3
M = Rh, L = CO	+6.7	−13.8	−10.3
M = Pd, L = Cl	+1.4	−18.2	−16.2
[(PP*H*P)**M**L]^{n} + NEt_3 → [(PPP)**M**L]$^{n-1}$ + $[HNEt_3]^+$			
M = Rh, L = Cl	+92.4	+22.6	+26.2
M = Rh, L = CO	+19.6	−2.8	+0.8
M = Pd, L = Cl	+13.9	−8.0	−6.7

[a] def2-TZVP basis set. [b] ε = 7.58 (tetrahydrofuran)

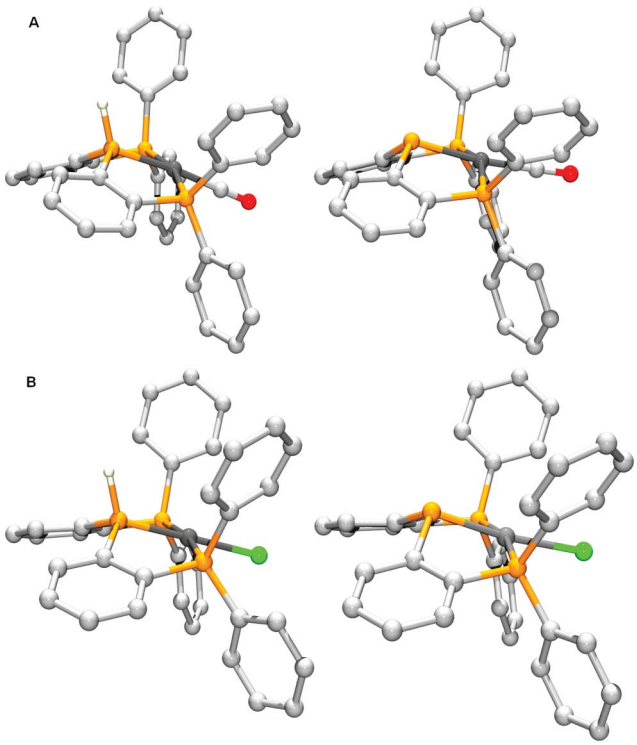


Fig. 5 DFT optimized geometry of complexes (A) [Rh(CO)(**L2**^{H})]-cation (left) and [Rh(CO)(**L2**)] (right) and (B) [PdCl(**L2**^{H})]-cation (left) and [PdCl(**L2**)] (right) (DFT; BP86 functional; def2-TVZP). Color code: orange – P; red – O; green – Cl, dark gray – metal.

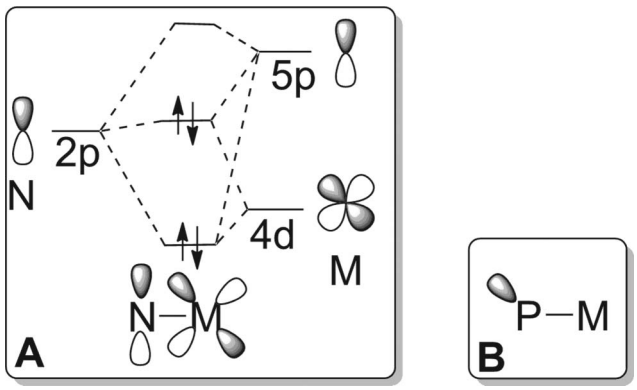


Fig. 6 Simplified orbital interaction scheme explaining the stabilisation of the amido complexes (A) relative to the phosphido complexes (B).

related PN^{H}P, PN^{H}N, PSi^{H}P, and PC^{H}P ligand backbones, **L1**^{H} displays neither oxidative addition nor proton-transfer activation of the central P–H bond under various reaction conditions with several Rh^{I} precursors, and only neutral tridentate PP^{H}P ligation is seen. This is mirrored by the reactivity of the electronically and sterically related, novel tridentate ligand **L3**^{NEt2}. To understand the apparent dichotomy of the reactivity of the PP^{H}P scaffold to group 9 (Rh) and previously reported group 10 (Pd) precursors, we performed DFT calculations on both cationic Rh^{I} and Pd^{II} complexes with **L2**^{H} and the related neutral complexes with the deprotonated monoanionic analogue **L2**. Related PN^{H}P analogs were included in the analysis as well. The computations reveal that in all cases deprotonation of the PN^{H}P ligand complexes is favored over deprotonation of the PP^{H}P ligand complexes, which is partly due to the higher electronegativity of nitrogen and partly due to a stabilising π-interaction between the amido fragment and the metal. In all cases deprotonation of the palladium complexes is favored over deprotonation of the rhodium complexes. This is most likely due to a better stabilisation of the negative charge of the ligand by the divalent palladium centre. Furthermore, the HOMO of the resulting complex PdCl(**L2**) displayed a high degree of P lone pair character, implying that the pivotal phosphorus atom of the PP^{H}P scaffold **L**^{H}, which is formally a phosphido unit when coordinated to Pd as a monoanionic ligand, is actually more like a metallophosphine fragment that should be amenable to form (hetero)bimetallic complexes. We foresee very interesting applications for catalysis with these very bulky, electron-rich monophosphines. Furthermore, in light of the increased interest in adaptive catalyst systems, it is worthwhile to investigate if complex PdCl(**L2**), **4**, or (other group 10 metal) analogues thereof are susceptible to reversible protonation of the pivotal 'phosphido' unit, as has previously been described for Pd-complexes with a structurally related PN^{H}P ligand.[25a]

Experimental section

General

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Reagents were purchased

from commercial suppliers and used without further purification. The following compounds were prepared following literature procedures: **L1^{H}** and **L2^{H}**,[20] 2-diphenylphosphino-3-methylindole **1**,[26] and [{Rh(μ-OH)(COE)$_2$}$_2$].[34] THF, pentane, hexane and Et$_2$O were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2, toluene and NEt_3 from sodium under nitrogen. NMR spectra (^{1}H, ^{31}P and ^{13}C) were measured on a Varian INOVA 500 MHz or a Varian MERCURY 300 MHz. IR spectra (in C_6D_6) were measured on a FT-IR Vertex-70 (Bruker).

Preparation of *N*,*N*′-bis(2-(diphenylphosphino)-3-(methyl)-indolyl)diethylaminophosphine (L3^{NEt2}). To a THF solution (10 mL, −78 °C) of indolylphosphine **1** (1.0 g, 3.17 mmol) was added 2.5 M ^{n}BuLi (1.27 mL, 3.17 mmol) dropwise. The solution was removed from the cold bath for 25 min, then cooled to −78 °C and treated dropwise with Et_2NPCl_2 (231 μL, 1.59 mmol). The solution was slowly allowed to warm up to r.t. and stirred for 16 h, whereafter volatiles were removed *in vacuo* and the crude material chromatographed through neutral alumina using a gradient elution from 15% to 25% CH_2Cl_2 in hexanes to obtain **L3^{NEt2}** as a white solid (858 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.0 Hz, 2H); 7.27–7.20 (m, 10H); 7.15 (t, J = 7.6 Hz, 2H); 7.11–7.04 (m, 8H); 7.04–6.93 (m, 6H); 3.49–3.31 (m, 4H); 1.67 (s, 6H); 0.86 (t, J = 7.3 Hz, 6H). ^{13}C APT (100 MHz, $CDCl_3$): δ 10.7 (s, CH_3); 14.5 (s, CH_3); 45.4 (d, J = 23 Hz, CH_2); 113.1 (s, CH_{ar}); 119.0 (s, CH_{ar}); 119.8 (s, CH_{ar}); 123.5 (s, CH_{ar}); 124.9 (br, C_{Ar}); 127.4 (s, CH_{ar}); 127.8 (s, CH_{ar}); 128.0 (dd, J_a = 37 Hz, J_b = 6 Hz, $CH_{o\text{-phenyl}}$); 132.1 (br, C_{Ar}); 132.5 (dd, J_a = 19 Hz, J_b = 3 Hz, CH_{ar}); 135.0 (br, C_{Ar}); 136.0 (br, C_{Ar}); 140.0 (br, C_{Ar}). ^{31}P{H} NMR (162 MHz, $CDCl_3$): δ 95.6 (t, $^3J_{PP}$ = 163.0 Hz); −30.2 (d, $^3J_{PP}$ = 163.0 Hz). ^{31}P{H} NMR (162 MHz, $CDCl_3$): δ 95.6 (t, $^3J_{PP}$ = 163.0 Hz); −30.2 (d, $^3J_{PP}$ = 163.0 Hz).

Complex RhCl(PP^{H}P) (2). To a stirred solution of **L1^{H}** (82.8 mg, 198.0 μmol) in THF (10 mL) was added [{Rh(μ–Cl)(COE)$_2$}$_2$] (71 mg, 99 μmol) at r.t. and the reaction mixture was stirred for 10 min to generate an orange-colored solution. Evaporation of the solvent *in vacuo* yielded **1** with persistent COE[29] in near-quantitative yield as an orange powder. Complex **1** decomposes significantly within 24 h under inert atmosphere. ^{1}H NMR (300 MHz, C_6D_6): δ 7.90–7.82 (m, 2H), 7.47–7.40 (m, 2H), 7.26–7.03 (m, 4H), 6.30 (d, $^1J_{PH}$ = 342 Hz, P*H*), 3.13 (br sept, 2H), 2.37 (br sept, 2H), 1.24 (app q, J = 7.1 Hz, 12H), 0.90 (app q, J = 7.1 Hz, 12H). ^{31}P{H} NMR (121 MHz, C_6D_6): δ 65.5 (dd, $^1J_{RhP}$ = 136.4 Hz; $^3J_{PP}$ = 32.0 Hz); 48.9 (dd, $^1J_{RhP}$ = 167.1 Hz; $^3J_{PP}$ = 32.0 Hz). ^{31}P NMR (121 MHz, C_6D_6): δ 65.5 (dd); 48.9 (ddt, $^1J_{PH}$ = 341.7 Hz). IR (THF): ν = 2271 cm^{-1}. The analogous complex with **L2^{H}** was prepared using the same procedure.[30]

Complex Rh(H)Cl$_2$(L1^{H}) (2HCl). To a stirred THF solution (2 mL, 0 °C) of **L1^{H}** (24.5 mg, 58.5 μmol) and [{Rh(μ-Cl)(COE)$_2$}$_2$] (21 mg, 29.2 μmol) was added HCl in ether (35 μL, 2.0 M, 0.070 mmol). After 16 h at room temperature, volatiles were removed under vacuum to afford the product, which is stable in solution with no evidence of decomposition for 3 days. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.31–8.20 (br s, 2H); 7.91–7.78 (br s, 2H); 7.75–7.55 (br m, 4H); 6.96 (d, $^1J_{PH}$ = 393 Hz, 1H); 3.25 (br sept, 2H); 2.82 (br sept, 2H); 1.40–1.18 (m, 18H); 1.09 (d, J = 6.8 Hz, 6H); −16.91 (ddt, $^1J_{RhH}$ = 10.1 Hz; $^2J_{PH}$ = 10.1 Hz (PH);$^2J_{PH}$ = 6.7 Hz (P^{i}Pr$_2$), 1H). ^{31}P{H} NMR (121 MHz, CD_2Cl_2): δ 71.1 (ddd, $^1J_{RhP}$ = 97 Hz; $^2J_{PP}$ = 11.0 Hz;); 64.5 (ddt, $^1J_{RhP}$ = 120 Hz; $^2J_{PP}$ = 11.0 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 64.5 (br dd, $^1J_{PP}$ = 393 Hz).

Complex RhCl(PP^{NEt2}P) (3). To a stirred THF solution (4 mL) of **L3^{NEt2}** (211 mg, 0.29 mmol) was added solid [Rh(μ–Cl)(COE)$_2$]$_2$ (103.5 mg, 0.14 mmol). After 1 h the volatiles were removed under vacuum; washing with hexanes removed COE to yield a pure orange powder (216 mg, 86%). Complex **3** was recrystallized from toluene at −4 °C to afford orange crystals suitable for X-ray analysis. ^{1}H NMR (300 MHz, C_6D_6): δ 8.17–8.04 (m, 6H); 7.87–7.78 (m, 4H); 7.32 (d, J = 7.4 Hz, 2H); 7.23–7.03 (m, 8H); 7.02–6.89 (m, 8H); 2.41–2.18 (m, 4H); 1.93 (s, 6H); 0.69 (t, J = 7.5 Hz, 6H). ^{31}P NMR (121 MHz, C_6D_6): δ 142.4 (dt, $^1J_{RhP}$ = 223.9 Hz; $^2J_{PP}$ = 42.6 Hz); 17.1 (dd, $^1J_{RhP}$ = 144.6 Hz; $^2J_{PP}$ = 42.6 Hz). HR-MS (FAB) calcd. for [M + H] $C_{46}H_{45}N_3ClP_3Rh$, 869.1492; found 869.1498. Upon addition of a 2.0 M HCl solution, these signals shift to δ 134.4 (*P*Ph$_2$) and 22.1 ppm (*P*NEt$_2$), indicating that P–N rupture by protonation did not occur.

DFT geometry optimizations and spectral parameter calculations. Geometry optimizations were carried out with the Turbomole program[35a,b] coupled to the PQS Baker optimizer.[36] All geometries were fully optimized as minima at the BP86[37] level using the polarized triple-ξ def2-TZVP basis[38] (small-core pseudopotential[39] on Rh or Ir). Solvent corrections from single point cosmo calculations (ε = 7.58; thf) were applied for all species as well.[40] For comparison, single point calculations (using the optimized geometries obtained at the BP86/def2-TZVP level) using the b3-lyp[41] and the same def2-TZVP basis set and cosmo corrections were performed as well. Thus obtained (SCF) energies (kcal mol^{-1}) are reported in Table 2. Optimized geometries of all species are supplied as separate files in .pdb and .xyz format in the supporting information.†

X-ray crystal structure determination of 3. $C_{46}H_{44}ClN_3P_3Rh{\cdot}1.5(C_7H_8)$, Fw = 1008.31, orange blocks, 0.21 × 0.27 × 0.33 mm, triclinic, $P\bar{1}$(no. 2), a = 11.4830(6), b = 12.4619(4), c = 18.6500(6) Å, α = 90.887(2), β = 99.603(2), γ = 109.560(2)°, V = 2472.24(17) Å^3, Z = 2, D_c = 1.355 g cm^{-3}, μ = 0.537 mm^{-1}. 47552 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150(2) K. The crystal appeared to be cracked into two fragments. Therefore two orientation matrices were used for the intensity integration with Eval15.[42] TWINABS[43] was used for absorption correction and scaling based on multiple measured reflections (0.69–0.71 correction range). 11346 Reflections were unique (R_{int} = 0.02), of which 10282 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97.[44] The structure was refined with SHELXL-97[44] against F^2 of all reflections taking the presence of two fragments into account.[45] Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. The toluene solvent molecules were disordered on inversion centers. 681 Parameters were refined with 420 restraints concerning the disordered toluene molecules. R_1 [$I > 2\sigma(I)$] = 0.0255; wR_2 [all refl.] = 0.0647; S = 1.04. Residual electron density between −0.43

and 0.56 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[46]

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