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Electron rich bidentate phosphinimine-imine ligands: Synthesis and reactivity of late transition metal complexes†

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Electron rich phosphinimine-imine proligands $Ph_3PN(C_6H_4)C(Ph)(NAr)$ ($\mathbf{L_{Ar}}$) (Ar = 4-(OEt)C_6H_4 (OEt), 3,5-$Me_2C_6H_3$(Xyl)) were synthesized in three steps from 2-aminobenzophenone. These compounds, along with previously reported $\mathbf{L_{Mes}}$ and $\mathbf{L_{Tol}}$ (Mes = 2,4,6-$Me_3C_6H_2$, Tol = 4-MeC_6H_4) were used to synthesize a series of tetracarbonyltungsten(0) complexes: $\mathbf{L_{Mes}}W(CO)_4$ (**1**), $\mathbf{L_{Tol}}W(CO)_4$ (**2**), $\mathbf{L_{OEt}}W(CO)_4$ (**3**), and $\mathbf{L_{Xyl}}W(CO)_4$ (**4**). The ligands were evaluated by analysis of the carbonyl stretching frequencies of the tungsten complexes and were shown to be better σ-donors and poorer π-acceptors compared to similar ligands in the literature. The coordination chemistry of the proligands was expanded to other late transition metals and $\mathbf{L_{Mes}}CoCl_2$ (**5**), $\mathbf{L_{Tol}}CoCl_2$ (**6**), $\mathbf{L_{Mes}}NiBr_2$ (**7**), $\mathbf{L_{Tol}}NiBr_2$ (**8**), $\mathbf{L_{Mes}}ZnCl_2$ (**9**), and $\mathbf{L_{Tol}}ZnCl_2$ (**10**) were synthesized by the direct reaction of $\mathbf{L_{Mes}}$ and $\mathbf{L_{Tol}}$ with the respective metal dihalide precursors. The complexes were fully characterized and the molecular structures of complexes **3**, **6**, **7**, and **10** were reported. The synthesis of zinc complexes **9** and **10** was dependent on the steric bulk of the ligand. Complex **10** proved to be resistant to derivatization *via* a number of routes.

Introduction

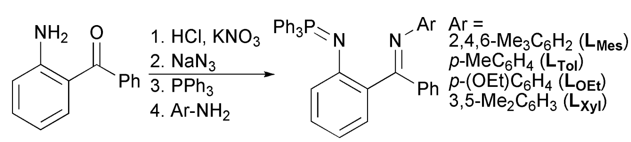
In the last decade the chemistry of bidentate phosphinimine ligands has expanded to encompass early[1] and late[2] transition metals as well as main group elements and a variety of transformations involving these compounds have been reported.[3] Bisphosphinimine complexes of rhodium and palladium incorporating a ferrocene backbone have shown interesting reactivity and catalytic behaviour.[2] Phosphinimines derived from 1,1-diphosphinomethanes have been used to generate carbenoids for a variety of metals.[4] Bidentate phosphinimine-donor systems incorporating pyridine, imidazole,[5] and pyrazole[6] donor moieties, and a tridentate bisphosphinimine-pyridine[7] system have also been studied and in most cases their activity in ethylene polymerization[8] was investigated. Orthopalladation of phosphinimines offers a facile route to asymmetric pincer complexes and has been studied in some detail.[9]

We have recently reported palladium complexes bearing bidentate phosphinimine-imine ligands and elucidated a method for their orthopalladation and the direct and controlled reverse reaction.[10] In the context of our work with phosphinimine ligands, as well as our efforts to develop catalysts for the controlled polymerization of lactide,[11] we were inspired by reports of cationic zinc catalysts supported by bidentate phosphinimines for polymerization of lactide.[12] In this report we present our investigations into expanding the family of phosphinimine-imine proligands, probe their electronic properties *via* synthesis of carbonyl complexes, evaluate their viability as ligands for late transition metals, and ultimately investigate the synthesis and reactivity of their zinc complexes.

Results and discussion

Tunable bidentate phosphinimine-imine ligands

We have reported a facile and modular route for the synthesis of a family of proligands $Ph_3PN(C_6H_4)C(Ph)(NAr)$ ($\mathbf{L_{Ar}}$) with a range of steric and electronic characteristics.[10] The reported compounds, $\mathbf{L_{Mes}}$ and $\mathbf{L_{Tol}}$ (Mes = 2,4,6-$Me_3C_6H_2$, Tol = p-MeC_6H_4) and the new compounds $\mathbf{L_{OEt}}$ and $\mathbf{L_{Xyl}}$ (OEt = p-(OEt)C_6H_4, Xyl = 3,5-$Me_2C_6H_3$) are synthesized in four steps from 2-aminobenzophenone *via* a 2-(triphenylphosphinimine)benzophenone intermediate (Scheme 1). The imine moieties are installed *via* condensation reactions of this intermediate with *p*-ethoxy and 3,5-dimethylanilines to yield $\mathbf{L_{OEt}}$ and $\mathbf{L_{Xyl}}$ as air and moisture stable yellow solids in 85 and 81% yield, respectively. The condensation reaction is more facile with less hindered anilines: $\mathbf{L_{Tol}}$ and $\mathbf{L_{OEt}}$ are synthesized in 24 h, while $\mathbf{L_{Xyl}}$ and $\mathbf{L_{Mes}}$ require 48 h reaction time with a Dean–Stark apparatus. We reported that the molecular structure of $\mathbf{L_{Mes}}$ shows hindered rotation around the N–Ar bond and in solution two magnetically nonequivalent *ortho* methyl groups are observed in the ^{1}H NMR spectrum.[10] A similarly hindered rotation is not observed for $\mathbf{L_{OEt}}$ or $\mathbf{L_{Xyl}}$; the ^{1}H NMR spectrum of $\mathbf{L_{OEt}}$ does not show asymmetric -OCH_2CH$_3$ protons and only one signal



Scheme 1

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† CCDC reference numbers 738462–738465. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b912783f

Table 1 Comparison of $^{31}\{^{1}H\}$ NMR and IR spectroscopic characteristics of compounds in this work and literature compounds

Entry	Compound	$^{31}P\{^{1}H\}$ (ppm)	ν_{PN} (cm^{-1})	ν_{CO} (cm^{-1})
1	$\mathbf{L_{Mes}}$	1.16	1339	
2	$\mathbf{L_{Tol}}$	0.87	1360	
3	$\mathbf{L_{OEt}}$	1.64	1345	
4	$\mathbf{L_{Xyl}}$	2.18	1328	
5[a]	$Ph_2PCH_2(Ph)_2P{=}N(SiMe_3)$	−1.38	1310	
6	**1**	27.36	1228	1994, 1870, 1845, 1808.
7	**2**	25.34	1242	1996, 1870, 1846, 1805.
8	**3**	28.6	1231	1995, 1879, 1852, 1802.
9	**4**	25.09	1241	1998, 1874, 1842, 1808.
10[a]	$Ph_2PCH_2(Ph)_2P{=}N(SiMe_3)W(CO)_4$	40.02	1120	2007, 1920, 1884, 1866.
11[b]	Terpyridine$W(CO)_4$			2008, 1990, 1891, 1842.
12[c]	2,2′-Biquinoline$W(CO)_4$			2005, 1920, 1870, 1812.
13	**5**		1238	
14	**6**		1234	
15[d]	Pyridine-phosphinimine$CoCl_2$		1260	
16	**7**		1241	
17	**8**		1246	
18[d]	Pyridine-phosphinimine$NiBr_2$		1280	
19[d]	Imidazole-phosphinimine$NiBr_2$		1225	
20	**9**		1241	
21	**10**		1238	

[a] ref. 1a [b] ref 13. [c] ref 14 [d] ref 5.

is observed for the meta-CH_3 groups of $\mathbf{L_{Xyl}}$. The $^{31}P\{^{1}H\}$ NMR spectra of $\mathbf{L_{OEt}}$ and $\mathbf{L_{Xyl}}$ show singlets at 1.4 and 2.1 ppm and the IR spectra show characteristic ν_{PN} stretches of 1345 and 1328 cm^{-1}. Although the values are similar for all the proligands, there is a 32 cm^{-1} difference between $\mathbf{L_{Tol}}$ and $\mathbf{L_{Xyl}}$ which may indicate conjugation in the molecules affected by slight changes in the aryl substituent (Table 1, entries 1-4).[1a] Despite being sterically unhindered, the newly synthesized proligands have the advantage of being air and moisture stable ($\mathbf{L_{Tol}}$ is air and moisture sensitive).

Tetracarbonyltungsten complexes

We probed the electronic properties of the $\mathbf{L_{Ar}}$ proligands by studying the corresponding tungsten tetracarbonyl complexes. Complexes $\mathbf{L_{Ar}}W(CO)_4$ (Ar = Mes (**1**), Tol (**2**), OEt (**3**), Xyl (**4**)) were synthesized by refluxing a THF solution of the desired proligand $\mathbf{L_{Ar}}$ with (THF)$W(CO)_5$ for 18 h and were isolated as red air and moisture stable solids. The $^{31}P\{^{1}H\}$ NMR spectra of **1–4** show a characteristic signal at ~28 ppm indicative of coordinated phosphinimine. The IR spectra of **1–4** show characteristic ~100 cm^{-1} decreases in ν_{PN} compared to the free ligands indicating a decrease in the P–N bond order (Table 1, entries 6–9). There are no significant differences in the ν_{CO} values of **1–4**, which are some of the lowest reported for bidentate nitrogen-based donor ligands on tetracarbonyltungsten(0) moieties (*cf*. Table 1, entries 10–12).[13,14] This suggests that the $\mathbf{L_{Ar}}$ ligands exhibit strong σ-donor and unusually poor π-acceptor characteristics.

The differences in the steric bulk imparted by the ligands are clearly seen by comparing the ^{1}H NMR spectra of the respective complexes. Complex **1** shows restricted rotation of the mesityl imine moiety as observed in $\mathbf{L_{Mes}}$. The two inequivalent *ortho* methyl groups are observed at 1.82 and 2.50 ppm. In contrast the xylyl derivative **4**, which shows no sign of hindered rotation in the free ligand, shows two inequivalent peaks for the *meta* methyl groups at 2.06 and 2.29 ppm. The less sterically encumbered complexes **2** and **3** show no signs of hindered rotation upon coordination to the tetracarbonyltungsten(0) moiety.

The molecular structure of **3**, obtained *via* single crystal X-ray crystallography, shows distorted octahedral geometry around the tungsten centre (Fig. 1, Table 2).[15] The strained geometry of the ligand is apparent in the twist in the ligand backbone and in the N1–W–N2 bond angle of 76.2°, the W–N2–C1–C6 torsion angle of 8.5°, and the C1–C6–C7–N2 torsion angle of 42.1°. The W–N1 and W–N2 bond lengths are identical (2.260 Å) and are consistent with literature values.[14,16]

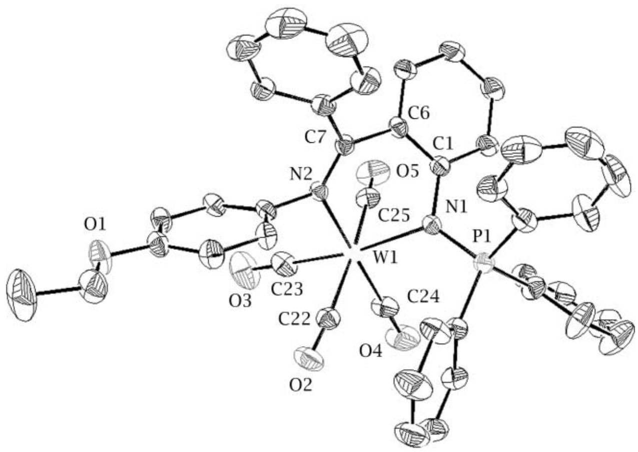


Fig. 1 Molecular structure of **3** (depicted with 35% probability ellipsoids, H atoms are omitted for clarity). Selected bond distances (Å) and angles (°): P(1)–N(1) = 1.606(5); N(1)–W(1) = 2.260(4); N(2)–W(1) = 2.260(4); C(23)–W(1) = 1.944(7); C(24)–W(1) = 1.952(6); N(2)–W(1)–N(1) = 76.21(16); N(1)–W(1)–C(23) = 171.3(2); N(2)–W(1)–C(24) = 173.5(2); C(23)–W(1)–C(24) = 87.6(3).

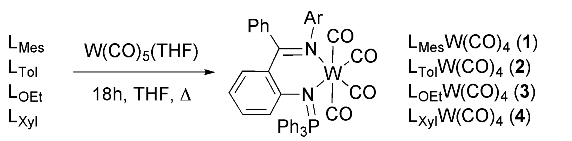
Cobalt and nickel complexes of $\mathbf{L_{Mes}}$ and $\mathbf{L_{Tol}}$

The $\mathbf{L_{Ar}}$ proligands are versatile supports for late transition metals. Dichlorocobalt(II) complexes, $\mathbf{L_{Mes}}CoCl_2$ (**5**) and $\mathbf{L_{Tol}}CoCl_2$ (**6**), were synthesized by the reaction of $\mathbf{L_{Mes}}$ or $\mathbf{L_{Tol}}$ with anhydrous $CoCl_2$ in THF at room temperature and isolated as paramagnetic air and moisture stable green solids (Scheme 3). The μ_{eff} for **5** and **6** were measured using a magnetic susceptibility balance and calculated to be 5.32 μB and 4.26 μB respectively.[5] The ν_{PN} stretching frequencies of **5** and **6** are consistent for coordinated phosphinimines (Table 1, entries 13, 14). The molecular structure of **6** shows a pseudo-tetrahedral geometry with Co–N1 phosphinimine and Co–N2 imine bond lengths of 2.012(1) Å and 2.035(1) Å respectively and are comparable to those of a similar dichlorocobalt(II) complex (Fig. 2).[5]

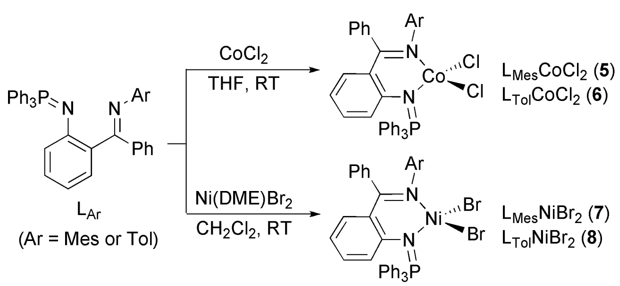
Dibromonickel(II) complexes $\mathbf{L_{Mes}}NiBr_2$ (**7**) and $\mathbf{L_{Tol}}NiBr_2$ (**8**) were synthesized by reaction of $\mathbf{L_{Mes}}$ or $\mathbf{L_{Tol}}$ with Ni(DME)Br_2 in CH_2Cl_2 at room temperature and were isolated as paramagnetic air and moisture stable blue solids with μ_{eff} values of 3.51 and 2.24 μB respectively (Scheme 2).[5] The IR spectra of **7** and **8** show

Table 2 Crystallographic data for the X-ray structure determinations of **3**, **6**, **7**, and **10**

	$L_{OEt}W(CO)_4$ (**3**)	$L_{Tol}CoCl_2$ (**6**)	$L_{Mes}NiBr_2$ (**7**)	$L_{Tol}ZnCl_2$ (**10**)
empirical formula	$C_{46}H_{39}N_2O_5PCl_6W$	$C_{38}H_{31}N_2PCl_2Co$	$C_{41}H_{37}N_2PCl_2Br_2Ni$	$C_{39}H_{33}N_2PCl_4Zn$
fw	1127.31	676.45	878.13	767.81
T (K)	173	173	173	173
a (Å)	12.1621(6)	10.935(4)	21.2062(12)	12.3640(9)
b (Å)	13.8626(7)	13.014(3)	13.2498(7)	17.4916(14)
c (Å)	15.8963(13)	13.330(4)	13.7667(8)	16.9571(13)
α (°)	101.352(4)	118.200(10)	90	90
β (°)	102.052(4)	94.80(2)	90	99.222(3)
γ (°)	112.080(3)	95.250(10)	90	90
volume (Å^3)	2314.0(2)	1647.3(8)	3868.1(4)	3619.8(5)
Z	2	2	4	4
crystal system	triclinic	triclinic	orthorhombic	monoclinic
space group	P -1	P -1	$P\,na2_1$	$P\,2_1/n$
d_{calc} (g/cm^3)	1.618	1.364	1.508	1.409
μ (MoKα) (cm^{-1})	29.24	7.61	27.79	10.49
$2\theta_{max}$ (°)	55.0	46.8	55.8	56.0
absorption correction (T_{min}, T_{max})	0.483, 0.704	0.788, 0.846	0.642, 0.846	0.762, 0.837
total no. of reflections	39908	26521	42494	42130
no. of indep reflections (R_{int})	10320 (0.037)	7653 (0.039)	9177 (0.043)	8741 (0.036)
residuals (refined on F^2, all data): R_1; wR_2	0.058; 0.126	0.037; 0.072	0.044; 0.055	0.047; 0.081
GOF	1.06	1.03	0.98	1.03
no. observations [$I > 2\sigma(I)$]	9053	6505	7601	7001
residuals (refined on F): R_1; wR_2	0.047; 0.118	0.028; 0.068	0.029; 0.052	0.031; 0.074

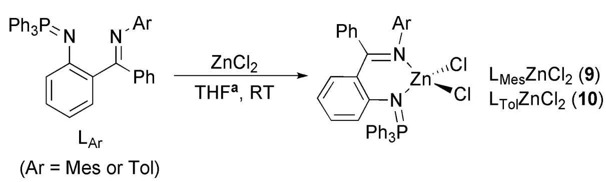


Scheme 2



Scheme 3

characteristic ν_{PN} stretching frequencies (Table 1, entries 16, 17). The molecular structure of **7** shows a slightly distorted tetrahedral geometry, with identical Ni–N(1) and Ni–N(2) bond lengths of 1.997(2) Å comparable to those of similar phosphinimine dibromonickel(II) complexes.[5]



Scheme 4 In reactions with L_{Mes} a saturated solution is required to form **10**

Zinc complexes of L_{Mes} and L_{Tol}

Previously, we have described the significant effects of ligand sterics on the orthopalladation of L_{Mes} and L_{Tol}.[10] In studying the analogous zinc complexes we again observe a significant difference in reactivity based on ligand sterics. The dichlorozinc complexes $L_{Mes}ZnCl_2$ (**9**) and $L_{Tol}ZnCl_2$ (**10**) were synthesized by reaction of L_{Mes} or L_{Tol} with anhydrous $ZnCl_2$ in THF at room temperature (Scheme 4). Complex **9** was isolated as an air and moisture stable pale yellow solid with a signature $^{31}P\{^1H\}$ NMR peak at 29 ppm. Interestingly, the ^1H NMR spectrum of **9** shows only one signal at 2.02 ppm for the *ortho* methyl groups on the mesityl moiety indicating fast rotation at room temperature on the NMR time scale. As discussed above, in the proligand L_{Mes}, tungsten complex **1**, and the previously reported palladium analogue we observed restricted rotation of the aryl group. Likely, in **9** the tetrahedral geometry of the complex allows for a less hindered system and free rotation of the mesityl moiety.

Control of the reaction conditions is very important in obtaining complex **9** in pure form. Only a minimum amount of THF must be used to induce the complex to precipitate upon formation. If the complex remains soluble when stirred overnight at room temperature, secondary peaks are observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra of the isolated yellow material.

Synthesis of the tolyl derivative $L_{Tol}ZnCl_2$ (**10**) was carried out without similar complications to yield air and moisture stable yellow solid. Complex **10** is insoluble in THF and thus precipitated out of solution upon reaction. The $^{31}P\{^1H\}$ NMR spectrum of **10** shows a characteristic signal at 27 ppm and the ^1H NMR spectrum shows the tolyl CH_3 protons as a singlet at 2.30 ppm. The ν_{PN} of 1238 cm^{-1} is consistent with other compounds in the series (Table 1, entry 21). The molecular structure of **10**, obtained *via* single crystal X-ray crystallography, shows distorted tetrahedral geometry around the zinc centre (Fig. 2). A comparison of the structural parameters for **6**, **7** and **10** shows no major differences between the three structures in terms of bond lengths or bond

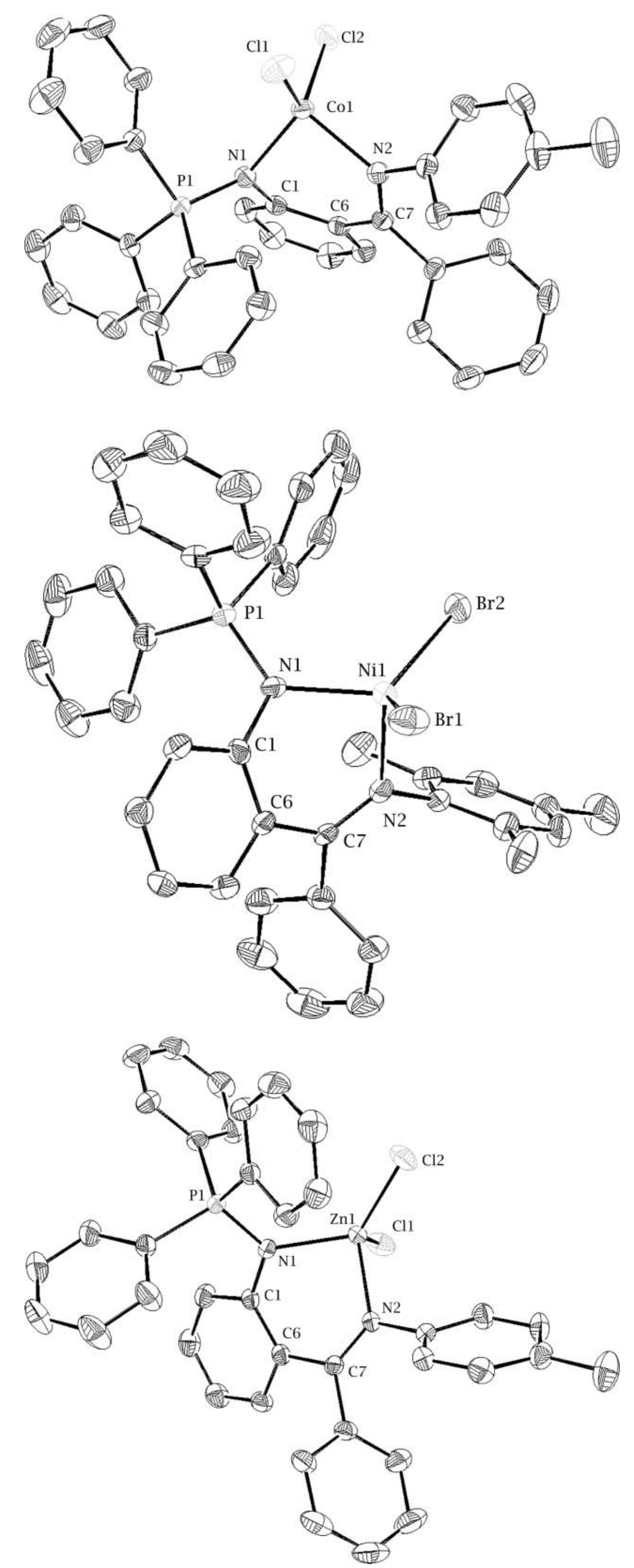
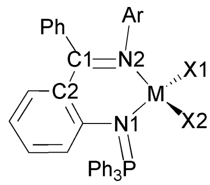


Fig. 2 Molecular structures of **6** (top), **7** (middle) and **10** (bottom) (depicted with 35% probability ellipsoids, H atoms are omitted for clarity).

angles around the metal centre (Table 3). It is worth noting that in complex **10** the Zn–Cl bond lengths differ by 0.05 Å, perhaps due to amplified steric differences around the smaller zinc centre.

Table 3 Structural details for complexes **6**, **7**, and **10**



6: M = Co; Ar = Tol; X = Cl
7: M = Ni; Ar = Mes; X= Br
10: M = Zn; Ar =Tol; X = Cl

	6	7	10
Bond lengths (Å)			
C1–N2	1.294(2)	1.286(3)	1.292(2)
P–N1	1.609(1)	1.619(2)	1.6079(14)
M–N1	2.012(1)	1.997(2)	2.0212(14)
M–N2	2.035(1)	1.997(2)	2.0587(14)
M–X1	2.2289(8)	2.3854(4)	2.2462(5)
M–X2	2.2259(7)	2.3429(4)	2.1929(5)
Bond angles (°)			
N1–M–N2	91.42(5)	89.81(9)	88.04(6)
N1–M–X1	117.64(4)	103.08(5)	103.82(4)
N2–M–X2	108.71(4)	113.06(6)	117.13(4)
X1–M–X2	116.35(3)	119.40(2)	114.83(2)

The dichlorozinc complex $\mathbf{L_{Tol}}ZnCl_2$ (**10**) proved to be resistant to further derivatization. Attempts to form alkoxy, alkyl, or amido derivatives of **10** were unsuccessful. Reaction of **10** with 2 equiv. NaOEt in THF either at room temperature or at −10 °C forms pale yellow solutions with one $^{31}P\{^1H\}$ NMR signal at 1 ppm, suggesting that the phosphinimine moiety is no longer coordinated. The ^1H NMR spectrum shows peaks in the aromatic region near 8.2 ppm and characteristic signals for a coordinated THF molecule are observed at 3.56 and 1.42 ppm. This spectrum is not consistent with either the free ligand or complex **10** and may be indicative of dissociation of the phosphinimine moiety while the imine remains attached. Similar results were observed when only one equiv. of NaOEt was used. When the reaction was carried out at room temperature or in refluxing CH_2Cl_2, $CHCl_3$ or CH_3CN the result was unreacted starting material. Addition of MeMgBr to complex **10** in THF at −10 °C forms a pale yellow solution followed by formation of a precipitate after the reaction mixture has been stirred at room temperature overnight. The $^{31}P\{^1H\}$ and ^1H NMR spectra of the solution are consistent with free ligand. Reaction of complex **10** with 1 equiv. of $KN(TMS)_2$ at −10 °C in THF followed by overnight stirring at room temperature resulted in a pale yellow solution with the NMR characteristics of a complex with dissociated phosphinimine moiety and a coordinated imine. These compounds were not isolable. The reaction of $\mathbf{L_{Tol}}$ with $Zn(N(TMS)_2)_2$ yielded only free ligand.

Conclusions

We have synthesized a family of bidentate phosphinimine-imine proligands with different aryl groups on the imine moiety which can easily be changed to tune the electronic or steric requirements upon coordination to metal centres. Coordination of the proligands to a tetracarbonyltungsten(0) fragment formed complexes **1–4** which exhibit some of the lowest ν_{CO} stretching frequencies for compounds of this type, suggesting that the $\mathbf{L_{Ar}}$ system is predominately σ-donating with minimal π-acceptor capability. The differences in steric bulk imparted by the ligand systems was demonstrated by the hindered rotation around the N–Ar bond for the bulkier mesityl and xylyl derivatives, **1** and **4**.

We explored the reactivity of the $\mathbf{L_{Ar}}$ proligands with late transition metals and showed that, despite the lack of π-acceptor capability, they were able to form the dichlorocobalt(II) (**5**, **6**), dibromonickel(II) (**7**, **8**) and the dichlorozinc(II) complexes (**9**, **10**) *via* reactions with dihalide metal precursor at room temperature. In the case of the mesityl derivative **9** the reaction conditions are vital, as the utilization of too much solvent prevents the product from precipitating and leads to the formation of impurities. Complex **10** resisted all our attempts at derivatization and was either inert under the studied reaction conditions, released free ligand, or formed intractable decomposition products. We can only conclude that these bulky ligands are not effective in stabilizing neutral Zn(II) alkoxide, alkyl or amide complexes. Investigations are currently underway to produce cationic analogues as potential catalysts for the ring opening polymerization of cyclic esters.

Experimental

General procedure

Unless otherwise specified all procedures were carried out using standard Schlenk techniques. A Bruker Avance 300 MHz spectrometer and Bruker Avance 400dir MHz spectrometer were used to record the ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectra. ^{1}H NMR chemical shifts are given in ppm *versus* residual protons in deuterated solvents as follows: δ 5.32 for CD_2Cl_2, and δ 7.27 for $CDCl_3$. ^{13}C{^{1}H} NMR chemical shifts are given in ppm *versus* residual ^{13}C in solvents as follows: δ 54.00 for CD_2Cl_2, and δ 77.23 for $CDCl_3$. ^{31}P{^{1}H} NMR chemical shifts are given in ppm *versus* 85% H_3PO_4 set at 0.00 ppm. A Waters/Micromass LCT mass spectrometer equipped with an electrospray (ESI) ion source and a Kratos-50 mass spectrometer equipped with an electron impact ionization (EI) source were used to record low-resolution and high-resolution spectra. A Nicolet 4700 FT-IR spectrometer was used to record infrared spectra. Magnetic susceptibility measurements were made with a Johnson Matthey magnetic susceptibility balance.[17] All measurements for X-ray crystallographic data were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo-Kα radiation.

All solvents were degassed and dried using 3 Å molecular sieves in an mBraun Solvent Purification System. The THF was further dried over Na and distilled under N_2. CD_2Cl_2 and $CDCl_3$ were dried over CaH_2 and degassed through a series of freeze-pump-thaw cycles. Ni(DME)Br_2 and W(CO)$_6$ were purchased from Strem Chemicals and used without further purification. W(CO)$_5$THF was made by the UV photolysis of a THF solution of the desired amount of W(CO)$_6$ for 4 h. Anhydrous $CoCl_2$,[18] $\mathbf{L_{Mes}}$, and $\mathbf{L_{Tol}}$ were made *via* literature procedures.[10] All other chemicals were obtained from Aldrich and used without further purification.

(Ph)$_3$PN(C$_6$H$_4$)C(Ph)(=N(4-OEtC$_6$H$_5$)), $\mathbf{L_{OEt}}$. A round bottom flask was charged with a spatula head of *p*-toluidinesulfonic acid (0.1–0.2 g), 2-(triphenylphosphinimine)benzophenone (2.0 g, 4.6 mmol), *p*-phenetidine (0.63 g, 4.6 mmol), and toluene (50 mL). A standard Dean–Stark apparatus topped with a Dryrite drying column was assembled, and the reaction mixture was refluxed for 24 h. Ether was added to the resulting dark yellow solution to precipitate a bright yellow solid. The solid was filtered and then dried *in vacuo*, yielding $\mathbf{L_{OEt}}$ as a pale yellow solid, which was recrystallized from CH_2Cl_2 (2.25 g, 85%). ^{1}H NMR (300.1 MHz; $CDCl_3$): δ 1.35 (t, $J_{H\text{-}H}$ = 7.0 Hz, 3H, OCH$_2$CH_3); 3.91 (q, $J_{H\text{-}H}$ = 6 Hz, 2H, OCH_2CH$_3$); 6.37 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1H, Ar-H); 6.57-6.49 (m, 5H, Ar-H); 6.92-6.80 (m, 4H, Ar-H); 7.41–7.27 (m, 8H, Ar-H); 7.59–7.46 (m, 8H, Ar-H); 7.90–7.87 (m, 2H, Ar-H). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 15.33 (s, OCH$_2$$CH_3$); 63.93 (s, O$CH_2CH_3$); 114.40 (s, CH); 116.00 (s, CH); 121.27 (d, $J_{C\text{-}P}$ =10.4 Hz, CH); 122.50 (s, CH); 128.35 (s, CH); 128.87 (s, CH); 129.00 (s, CH); 129.13 (s, CH); 130.09 (s, CH); 130.88 (s, C); 131.87 (s, C); 132.21 (d, $J_{C\text{-}P}$ = 2.6 Hz, CH); 132.91 (s, CH); 133.00 (s, CH) 141.17 (s, C); 146.16 (s, C); 150.49 (s, C); 155.67 (s, C); 170.80 (s, C). ^{31}P{^{1}H} NMR (121.5 MHz; $CDCl_3$): δ 1.64 (s). IR (Nujol®, cm^{-1}): 1622 (ν_{CN}), 1345 (ν_{NP}). MS (ESI, *m/z*): Calc. Mass: 577.2390; Obs. Mass: 577.2409 (M^{+}). Anal. Calcd for $C_{39}H_{33}N_2OP$ (576.67): C, 81.23; H, 5.77; N, 4.86. Found: C, 81.14; H, 5.77; N, 4.86.

(Ph)$_3$PN(C$_6$H$_4$)C(Ph)(=N(3,5-Me$_2$C$_6$H$_4$)), $\mathbf{L_{Xyl}}$. The proligand $\mathbf{L_{Xyl}}$ was synthesised in an identical manner to $\mathbf{L_{OEt}}$, except 3,5-dimethylaniline (0.56 g, 4.6 mmol) was used instead of 2,4,6-trimethylaniline, and the reaction was refluxed for 48 h. The reaction yielded $\mathbf{L_{Xyl}}$ as a yellow solid (2.09 g, 81%). ^{1}H NMR (300.1 MHz; $CDCl_3$): δ 2.08 (s, 6H, CH_3); 6.31 (d, $^{3}J_{H\text{-}H}$ = 6 Hz, 1H, *p*-NCC$_6$$H_5$); 6.50 (t, $^{3}J_{H\text{-}H}$ = 5.7 Hz, 2H, *m*-NCC$_6$$H_5$); 6.63 (s, 2H, Ar-$H$); 6.85–6.77 (m, 2H, Ar-$H$); 7.37–7.27 (m, 10H, Ar-H); 7.46 (t, $J_{H\text{-}H}$ = 5.7 Hz, 3H, Ar-H); 7.57–7.55 (m, 5H, Ar-H); 7.88 (d, $^{3}J_{H\text{-}H}$= 6 Hz, 2H, *o*-NCC$_6$$H_5$). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 21.63 (s, Ar-*m*-CH$_3$); 116.82 (s, CH); 118.66 (s, CH); 121.08 (s, CH); 124.93 (s, CH); 128.34 (s, CH); 128.88 (s, CH); 129.01 (s, CH); 129.13 (s, CH); 130.19 (s, CH); 130.86 (s, C); 131.85 (s, C); 132.19 (d, $J_{C\text{-}P}$= 2.7 Hz, CH); 132.91 (s, CH); 133.00 (s, CH); 138.11 (s, C); 140.91 (s, C); 150.39 (s, C); 153.19 (s, C); 170.65 (s, C). ^{31}P{^{1}H} NMR (121.5 MHz; $CDCl_3$): δ 2.18 (s). IR (Nujol®, cm^{-1}): 1623 (ν_{CN}), 1328 (ν_{NP}). MS (ESI, *m/z*): Calc. Mass: 561.2476; Obs. Mass: 561.2460 (M^{+}). Anal. Calcd for $C_{39}H_{33}N_2P$ (560.67): C, 83.55; H, 5.93; N, 5.00. Found: C, 83.10; H, 5.89; N, 4.98.

(Ph)$_3$PN(C$_6$H$_4$)C(Ph)(=N(2,4,6-Me$_3$C$_6$H$_2$))W(CO)$_4$, $\mathbf{L_{Mes}}$W-(CO)$_4$ (1). A solution of tungsten pentacarbonyl (0.20 g, 0.57 mmol) in THF, (15 ml) was added to a suspension of the proligand $\mathbf{L_{Mes}}$ (0.18 g, 0.57 mmol) in THF (10 ml). The reaction mixture was refluxed for 18 h yielding a crimson solution. The solution was concentrated, and diethyl ether (10 ml) was added to precipitate a brown solid. Filtration and drying *in vacuo* yielded complex **1** as a reddish-brown solid, (0.28 g, 58%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.82 (s, 3H, CH_3); 2.17 (s, 3H, CH_3); 2.50 (s, 3H, CH_3); 6.50 (s, 1H, Ar-H); 6.79–6.59 (m, 3H, Ar-H); 6.88–6.82 (m, 2H, Ar-H); 7.06 (d, $J_{H\text{-}H}$ = 9.0 Hz, 2H, Ar-H); 7.33–7.20 (m, 3H, Ar-H); 7.71–7.58 (m, 10H, Ar-H); 7.97–7.90 (m, 6H, Ar-H). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 19.66 (s, *o*-CH$_3$); 19.94 (s, *o*-CH$_3$); 21.00 (s, *p*-CH$_3$); 120.50 (s, CH); 124.11 (d, $J_{C\text{-}P}$ = 10.4 Hz, CH); 126.25 (s, CH); 128.83 (s, CH); 129.33 (s, CH); 129.40 (s, CH); 129.45 (s, CH); 129.78 (s, CH); 130.22 (s, CH); 131.11 (s, CH); 133.65 (d, $J_{C\text{-}P}$ = 2.75 Hz, CH); 134.25 (s, C); 134.86 (s, C); 135.51 (s, C); 135.60 (s, C); 138.14 (s, C); 149.36 (s, C); 154.53 (s, C); 173.72 (s, C); 204.46 (s, CO); 204.71 (s, CO); 212.07 (s, CO); 215.76 (s, CO). ^{31}P{^{1}H} NMR (121.5 MHz;

$CDCl_3$): δ 27.36 (s). IR (Nujol®, cm^{-1}): 1994 (ν_{CO}), 1870 (ν_{CO}), 1845 (ν_{CO}), 1808 (ν_{CO}), 1550 (ν_{CN}), 1228 (ν_{NP}). MS (ESI, *m/z*): 842.0 ((M – CO)$^+$). Anal. Calcd for $C_{44}H_{35}N_2O_4PW$ (870.57): C, 60.70; H, 4.05; N, 3.22. Found: C, 61.12; H, 4.24; N, 3.25.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(4\text{-}MeC_6H_4))W(CO)_4$, $L_{Tol}W(CO)_4$ (2). Complex **2** was synthesised in an identical manner to complex **1** using the proligand L_{Tol} (0.31 g, 0.57 mmol) instead. Complex **2** was isolated as a brown solid, (0.34 g, 70%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 2.23 (s, 3H, C*H*$_3$); 6.68–6.65 (m, 4H, Ar-*H*); 6.77 (dt, $J_{H\text{-}H}$= 8.4, 1.8 Hz, 2H, Ar-*H*); 6.90 (td, $J_{H\text{-}H}$= 8.7 Hz, 1.8, 2H, Ar-*H*); 7.28–7.04 (m, 7H, Ar-*H*); 7.69–7.55 (m, 8H, Ar-*H*); 7.97–7.90 (m, 5H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 21.13 (s, *C*H$_3$); 120.93 (s, CH); 124.05 (d, $J_{C\text{-}P}$ = 10.7 Hz, CH); 126.37 (s, C); 127.37 (s, C); 128.25 (s, CH); 129.00 (s, CH); 129.38 (s, CH); 129.46 (s, CH); 129.59 (s, CH); 130.72 (s, CH); 131.53 (s, CH); 133.66 (d, $J_{C\text{-}P}$ = 2.7 Hz, CH); 134.18 (s, C); 134.99 (s, CH); 135.08 (s, CH); 138.05 (s, C); 152.27 (s, C); 154.51 (s, C); 174.44 (s, C); 204.23 (s, CO); 205.79 (s, CO); 214.18 (s, CO); 216.46 (s, CO). ^{31}P{^{1}H} NMR (121.5 MHz; CD_2Cl_2): δ 25.34 (s). IR (Nujol®, cm^{-1}): 1996 (ν_{CO}), 1870 (ν_{CO}), 1846 (ν_{CO}), 1805 (ν_{CO}), 1553 (ν_{CN}), 1242 (ν_{NP}). MS (ESI, *m/z*): 814.2 ((M – CO)$^+$). We were not able to purify this compound.[19]

$(Ph)_3PN(C_6H_4)C(Ph)(=N(4\text{-}OEtC_6H_4))W(CO)_4$, $L_{OEt}W(CO)_4$ (3). Complex **3** was synthesised in an identical manner to complex **1** using the proligand L_{OEt} (0.18 g, 0.57 mmol) instead. Complex **3** was isolated as a light reddish-brown solid, and was recystralised from DCM and hexane, (0.33 g, 66%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.33 (t, $J_{H\text{-}H}$ = 5.4 Hz, 3H, OCH$_2$C*H*$_3$); 3.93 (q, $J_{H\text{-}H}$ = 5.4 Hz, 2H, OC*H*$_2$CH$_3$); 6.68–6.61 (m, 3H, Ar-*H*); 6.774 (dt, $J_{H\text{-}H}$ = 6.0, 1.5 Hz, 2H, Ar-*H*); 6.91 (dt, $J_{H\text{-}H}$ = 5.7, 1.5 Hz, 2H, Ar-*H*); 7.05 (dd, $J_{H\text{-}H}$ = 6.0, 1.2 Hz, 2H, Ar-*H*); 7.29–7.22 (m, 4H, Ar-*H*); 7.68–7.56 (m, 9H, Ar-*H*); 7.95-7.90 (m, 6H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 15.17 (s, OCH$_2$*C*H3); 64.08 (s, O*C*H$_2$CH$_3$); 120.94 (s, CH); 124.02 (d, $J_{C\text{-}P}$= 9.3 Hz, CH); 126.37 (s, C); 127.38 (s, C); 128.31 (s, CH); 129.40 (s, CH); 129.47 (s, CH); 129.60 (s, CH); 130.80 (s, C); 131.53 (s, C); 133.67 (d, $J_{C\text{-}P}$= 2.6 Hz, CH); 134.15 (s, CH); 134.98 (s, CH); 135.08 (s, CH); 138.18 (s, C); 148.43 (s, C); 154.54 (s, C); 156.56 (s, C); 174.61 (s, C); 204.12 (s, CO); 205.88 (s, CO); 214.36 (s, CO); 216.46 (s, CO). ^{31}P{^{1}H} NMR (121.5 MHz; $CDCl_3$): δ 28.60 (s). IR (Nujol®, cm^{-1}): 1995 (ν_{CO}), 1879 (ν_{CO}), 1852 (ν_{CO}), 1802 (ν_{CO}), 1533 (ν_{CN}), 1231 (ν_{NP}). MS (ESI, *m/z*): Calc. Mass: 844.1659; Obs. Mass: 844.1687 ((M – CO)$^+$). Anal. Calcd for $C_{43}H_{33}N_2O_5PW$ (872.55): C, 59.19; H, 3.81; N, 3.21. Found: C, 58.43; H, 3.85; N, 3.19.

$(Ph)_3PN(C_6H_4)C(Ph)(= N(3,5 - Me_2C_6H_3))W(CO)_4$, $L_{Xyl}W$ - $(CO)_4$ (4). Complex **4** was synthesised in an identical manner to complex **1** using the proligand L_{Xyl} (0.18 g, 0.57 mmol) instead. Complex **4** was isolated as a light brown solid, (0.30 g, 62%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 2.06 (s, 3H, C*H*$_3$); 2.29 (s, 3H, C*H*$_3$); 6.05 (s, 1H, Ar-*H*); 6.67–6.59 (m, 3H, Ar-*H*); 6.78 (dt, $J_{H\text{-}H}$ = 6.3, 1.8 Hz, 1H, Ar-*H*); 6.90 (td, $J_{H\text{-}H}$= 7.5, 1.8 Hz, 1H, Ar-*H*); 7.01 (s, 1H, Ar-*H*); 7.11–7.08 (m, 2H, Ar-*H*); 7.28–7.23 (m, 3H, Ar-*H*); 7.69-7.55 (m, 9H, Ar-*H*); 7.97–7.90 (m, 6H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 21.57 (s, *m*-CH$_3$); 31.15 (s, *m*-CH$_3$); 119.47 (s, CH); 120.94 (s, CH); 124.08 (d, $J_{C\text{-}P}$ = 9.2 Hz, CH); 126.37 (s, CH); 126.74 (s, CH); 127.38 (s, C); 128.17 (s, CH); 129.43 (s, CH); 129.55 (s, CH); 130.61 (s, C); 131.47 (s, C); 133.64 (d, $J_{C\text{-}P}$ = 2.7 Hz, CH); 134.09 (s, CH); 134.98 (s, CH); 135.07 (s, CH); 137.89 (s, C); 154.20 (s, C); 154.43 (s, C); 173.91 (s, C); 204.26 (s, CO); 205.89 (s, CO); 214.15 (s, CO); 216.51 (s, CO). ^{31}P{^{1}H} NMR (121.5 MHz; CD_2Cl_2): δ 25.09 (s). IR (Nujol®, cm^{-1}): 1998 (ν_{CO}), 1874 (ν_{CO}), 1842 (ν_{CO}), 1808 (ν_{CO}), 1549 (ν_{CN}), 1241 (ν_{NP}). MS (ESI, *m/z*): 828.1 ((M – CO)$^+$). Anal. Calcd for $C_{43}H_{33}N_2O_4PW.CH_2Cl_2$: C 56.13, H 3.75, N 2.98. Found (%): C 56.04, H 4.00, N 2.96.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(2,4,6\text{-}Me_3C_6H_2))CoCl_2$, $L_{Mes}CoCl_2$ (5). A Schlenk flask was loaded with proligand L_{Mes} (0.5 g, 0.87 mmol) and anhydrous $CoCl_2$ (0.12 g, 0.96 mmol), and THF (20 ml) was added. The reaction mixture was stirred for 18 h at room temperature, which resulted in the formation of a green suspension. Ether (20 ml) was added to further precipitate the green solid, and after filtration, washing with ether (3 × 5 ml) and drying under vacuum yielded **5** (0.47 g, 76%). IR (Nujol®, cm^{-1}): 1553 (ν_{CN}), 1238 (ν_{NP}). μ_{eff} = 5.32 μB. MS (EI, *m/z*): Calc. Mass: 703.1260; Obs. Mass: 703.1247 (M); Calc. Mass: 667.1461; Obs. Mass: 667.1480 (M – HCl). Anal. Calcd for $C_{40}H_{35}N_2PCl_2Co$ (704.53): C, 68.19; H, 5.01; N, 3.98. Found: C, 68.27; H, 4.97; N, 3.97.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(4\text{-}MeC_6H_4))CoCl_2$, $L_{Tol}CoCl_2$ (6). Complex **6** was made in an identical manner to **5**, using proligand L_{Tol} (0.5 mg, 0.91 mmol), and $CoCl_2$ (0.13 g, 1.01 mmol). Yielding a green solid of **6** (0.46 g, 74%). A single crystal suitable for X-ray crystallography was grown from cooling a solution of DCM and hexane. IR (Nujol®, cm^{-1}): 1547 (ν_{CN}), 1234 (ν_{NP}). μ_{eff} = 4.26 μB. MS (EI, *m/z*): Calc. Mass: 675.0924; Obs. Mass: 675.0934 (M); Calc. Mass: 640.1252; Obs. Mass: 640.1245 (M – Cl). Anal. Calcd for $C_{38}H_{31}N_2PCl_2Co$ (676.48): C, 67.47; H, 4.62; N, 4.14. Found: C, 67.47; H, 4.73; N, 4.01.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(2,4,6\text{-}Me_3C_6H_2))NiBr_2$, $L_{Mes}NiBr_2$ (7). A yellow solution of proligand L_{Mes} (0.5 g, 0.87 mmol) in DCM (10 ml) was added to a suspension of Ni(DME)Br_2 (0.3 g, 0.96 mmol) in DCM (10 ml). The reaction mixture immediately turns green and was stirred at room temperature for 18 h. The resulting dark green solution was concentrated *in vacuo* and ether (20 ml) was added to precipitate a blue solid. Filtration, washing with ether (3 × 5 ml), and drying under vacuum yielded a blue solid of **7** (0.49 g, 71%). A single crystal suitable for X-ray crystallography was grown from slow cooling a solution of DCM and hexane. IR (Nujol®, cm^{-1}): 1558 (ν_{CN}), 1242 (ν_{NP}). μ_{eff} = 3.51 μB. MS (EI, *m/z*): Calc. Mass: 713.1042; Obs. Mass: 713.1054 for $C_{40}H_{35}N_2P^{58}Ni^{81}Br$ and 713.1029 for $C_{40}H_{35}N_2P^{60}Ni^{79}Br$ (M – Br). Calc. Mass: 711.1093; Obs. Mass: 711.1075 for $C_{40}H_{35}N_2P^{58}Ni^{79}Br$ (M – Br). Anal. Calcd for $C_{40}H_{35}N_2PBr_2Ni$ (793.20): C, 60.57; H, 4.45; N, 3.53. Found: C, 60.48; H, 4.45; N, 3.51.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(4\text{-}MeC_6H_4))NiBr_2$, $L_{Tol}NiBr_2$ (8). Complex **8** was made in an identical manner to **7**, using proligand L_{Tol} (0.5 g, 0.91 mmol), and Ni(DME)Br_2 (0.31 g, 1.01 mmol). Yielding a blue solid of **8** (0.48 g, 69%). IR (Nujol®, cm^{-1}): 1548 (ν_{CN}), 1247 (ν_{NP}). μ_{eff} = 2.24 μB. MS (EI, *m/z*): Calc. Mass: 685.0742; Obs. Mass: 685.0741 for $C_{38}H_{31}N_2P^{58}Ni^{81}Br$, and 685.0716 for $C_{38}H_{31}N_2P^{60}Ni^{79}Br$ (M – Br). Calc. Mass: 683.077; Obs. Mass: 683.0762 for $C_{38}H_{31}N_2P^{58}Ni^{79}Br$ (M – Br). Anal. Calcd for $C_{38}H_{31}N_2PBr_2Ni$ (765.15): C, 63.89; H, 4.69; N, 3.73. Found: C, 64.12; H, 4.78; N, 3.72.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(2,4,6\text{-}Me_3C_6H_2))ZnCl_2$, $L_{Mes}ZnCl_2$ (9). A Schlenk flask was loaded with proligand **1a** (0.5 g, 0.87 mmol) and anhydrous $ZnCl_2$ (0.13 g, 0.96 mmol), and THF (5 ml) was added. The reaction mixture was stirred for 18 h at room temperature, which resulted in the formation of a yellow suspension. After filtration, washing with hexanes (3 × 5 ml) and drying under vacuum **9** was isolated as a pale yellow solid, (0.53 g, 86%). ^{1}H NMR (400.2 MHz; CD_2Cl_2): δ 2.02 (s, 6H, *o*-CH_3); 2.18 (s, 3H, *p*-CH_3); 6.68 (m, 3H, Ar-*H*); 6.75 (t, $J_{H\text{-}H}$= 8.0 Hz, 1H, Ar-*H*); 6.91 (m, 2H, Ar-*H*); 7.08 (d, $J_{H\text{-}H}$ = 4.0 Hz, 2H, Ar-*H*); 7.26 (t, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar-*H*); 7.36 (t, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar-*H*); 7.57 (dt, $^dJ_{H\text{-}H}$ = 4.0 Hz, $^tJ_{H\text{-}H}$ = 8.0 Hz, 6H, Ar-*H*); 7.68 (t, $J_{H\text{-}H}$ = 8.0 Hz, 3H, Ar-*H*); 7.88 (q, $J_{H\text{-}H}$= 8.0 Hz, 6H, Ar-*H*). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 19.42 (s, *o*-CH_3); 21.07 (s, *p*-CH_3); 121.06 (s, CH); 125.53 (d, C); 126.53 (s, C); 127.23 (d, $J_{C\text{-}P}$= 11.1 Hz, CH); 128.23 (s, CH); 129.03 (s, CH); 129.54 (s, C); 129.63 (s, CH); 129.78 (d, $J_{C\text{-}P}$ = 5.0 Hz, CH); 130.70 (s, CH); 131.86 (CH); 133.97 (d, $J_{C\text{-}P}$ = 3.0 Hz, CH); 134.79 (d, $J_{C\text{-}P}$ = 11.1 Hz, CH); 135.15 (s, CH); 135.58 (s, C); 137.95 (s, C); 143.08 (s, C); 150.05 (s, C); 175.95 (s, C). ^{31}P NMR (161.2 MHz; CD_2Cl_2): δ 29.87 (s). IR (Nujol®, cm^{-1}): 1556 (ν_{CN}), 1241 (ν_{NP}). MS (EI, *m*/*z*): 673.0 (M – Cl)$^+$. Anal. Calcd for $C_{40}H_{35}N_2PCl_2Zn$ (710.86): C, 67.57; H, 4.69; N, 3.94. Found: C, 67.49; H, 4.88; N, 4.05.

$(Ph)_3PN(C_6H_4)C(Ph)(=N(4\text{-}MeC_6H_4))ZnCl_2$, $L_{Tol}ZnCl_2$ (10). A Schlenk flask was loaded with proligand **L_{Tol}** (0.48 g, 0.87 mmol) and anhydrous $ZnCl_2$ (0.13 g, 0.96 mmol), and THF (10 ml) was added. The reaction mixture was stirred for 18 h at room temperature, which resulted in the formation of a yellow suspension. Ether (10 ml) was added to further precipitate the yellow solid, and after filtration, washing with ether (3 × 5 ml) and drying under vacuum yielded **10** as a yellow solid (0.53 g, 89%). ^{1}H NMR (400.2 MHz; CD_2Cl_2): δ 2.30 (s, 3H, *p*Tol-CH_3); 6.55 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar-*H*); 6.76 (t, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar-*H*); 6.86 (t, $J_{H\text{-}H}$ = 8.0 Hz, 3H, Ar-*H*); 6.95 (t, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar-*H*); 7.02 (d, $J_{H\text{-}H}$ = 4.0 Hz, 2H, Ar-*H*); 7.08 (d, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar-*H*); 7.27 (t, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar-*H*); 7.36 (t, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar-*H*); 7.52 (t, $J_{H\text{-}H}$ = 8.0 Hz, 6H, Ar-*H*); 7.65 (t, $J_{H\text{-}H}$ = 4.0 Hz, 3H, Ar-*H*); 7.79 (dd, $J_{H\text{-}H}$ = 8.0, 4.0 Hz, 6H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz; CD_2Cl_2): δ 21.34 (s, *C*H_3); 121.82 (s, *C*H); 124.02 (s, *C*H); 126.11 (s, *C*); 127.11 (s, *C*); 128.29 (d, $J_{C\text{-}P}$ = 8.1 Hz, *C*H); 128.63 (s, *C*H); 129.70 (t, $J_{C\text{-}P}$ = 13.1 Hz, *C*H); 130.28 (s, *C*H); 130.51 (s, *C*H); 132.14 (s, *C*H); 133.91 (d, $J_{C\text{-}P}$ = 3.0 Hz, *C*H); 134.31 (s, *C*H); 134.41 (s, *C*H); 134.82 (s, *C*H); 136.36 (s, *C*); 137.26 (s, *C*); 144.64 (s, *C*); 148.60 (s, *C*); 176.10 (s, *C*). ^{31}P{^{1}H} NMR (162.0 MHz; CD_2Cl_2): δ 27.52 (s). IR (Nujol®, cm^{-1}): 1551 (νCN), 1238 (νNP). MS (Maldi-TOF, *m*/*z*): 645.2 (M – Cl)$^+$. Anal. Calcd for $C_{38}H_{31}N_2PCl_2Zn \cdot CH_2Cl_2$ (767.61): C, 61.87; H, 4.69; N, 3.52. Found: C, 61.59; H, 4.43; N, 3.51.

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