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Towards co-operative reactivity in conjoint classical-organometallic heterometallic complexes: the co-ordination chemistry of novel ligands with triphenylphosphine and bis(pyridylethyl)amine or triazacyclononane domains †

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With a view towards later studies of co-operativity in heteronuclear complexes with hard classical (oxygen-activating) and soft organometallic (organic-substrate binding) metal centres, four novel ditopic N_3P-donor ligands (L^1–L^4), each comprising triphenylphosphine tethered to an *N*,*N*′-bis(2-pyridyl-2-ethyl)amine (bpea) or a 1,4-diisopropyl-1,4,7-triazacyclononane (tacn*) N_3-donor group, have been designed and prepared by reductive aminations of *ortho*- and *meta*-(diphenylphosphino)benzaldehydes with bpea (for L^1 and L^3) and tacn* (for L^2 and L^4). A range of $\kappa N_n,\kappa P$-chelate mononuclear complexes have been isolated from the reactions of the *ortho*-substituted ligands, L^1 and L^2, with Cu(I), Zn(II) and Pt(II) sources, and the X-ray crystal structures of $[Cu(L^1)][PF_6]$, $[Cu(L^2)][PF_6]$ (communicated in: S. E. Watkins, D. C. Craig and S. B. Colbran, *J. Chem. Soc., Dalton Trans.*, 1999, 1539) and $[PtCl(L^1)][PF_6]$ have been determined. Six complexes with the phosphine of L^1–L^4 co-ordinated to a softer [Pt(II), Ir(I) or W(0)] metal centre and with dangling, metal-free N_3-donor domains have been prepared: for the *ortho*-substituted ligands L^1 and L^2, it was necessary to protect the hard, more basic N_3-donor domains by protonation (pH control) to prevent formation of $\kappa N_n,\kappa P$-chelate mononuclear complexes; for the *meta*-substituted ligands L^3 and L^4, pH control was unnecessary as the phosphine group selectively binds to the softer metal ions. The complex *trans*-$[IrCl(CO)(L^3)_2]$ reversibly forms a dioxygen adduct. An Ir(III)Cu(II)$_2$ and four Pt(II)Cu(II)$_2$ heterometallic complexes were prepared by adding hard Cu(II) ions to the Ir(I) and Pt(II) complexes with metal-free N_3-donor domains, and the full characterisation of these is described. The tungsten(0) carbonyl complex $[W(CO)_5(L^3)]$, with a metal-free N_3-bpea domain, was prepared for a study of metal ion recognition. No perturbation of the carbonyl region of the IR spectrum was observed when metal ions were added. The effect of submolar quantities of heterometallic complexes, obtained by adding a first d-series metal(II) ion (2 equivalents) to $[IrCl(CO)(L^3)_2]$, on the oxidation of styrene by oxygen in methylethyl ketone has been assayed: inhibition of the oxidation is observed with the %conversion and the product selectivity dependant on the metal(II) ion.

Introduction

Heterometallic systems offer prospects for advantageous synergistic effects where the reactivity of the whole is greater than the sum of the parts. The goal of the research described in this paper was to design, synthesise and characterise heterometallic complexes comprised of two different types of reactive metal centres linked by a ditopic ligand to provide the means for the study of such co-operative bimetallic reactivity.[1] One possible combination of reactive metal centres, and the one which provided the main impetus for this work, is to couple an oxygen binding and activating, classical centre, akin to those found in oxygen-activating proteins, to an organometallic centre known to bind and activate organic substrates. The combination of these two types of centres offers the possibility of affording artificial oxidases or oxygenases, complexes which employ the clean and abundant oxidant, oxygen, in the co-operative oxidations or oxygenations of organic substrates.

The ditopic ligands, L^1–L^4, were targeted for this study for the following reasons. First, over the last decade or so major advances have been made in our understanding of the structures and function of biological oxygen-activating centres.[2–5] Modelling studies have greatly contributed to this knowledge. For example, simple copper(I) complexes of ligands with *N*,*N*′-bis(2-pyridyl-2-ethyl)amine (bpea) or 1,4-diisopropyl-1,4,7-triazacyclononane (tacn*) N_3-donor groups are able to bind oxygen to afford $Cu(II)_2(\mu\text{-peroxo}) \leftrightarrow Cu(III)_2(\mu\text{-oxo})_2$ dimeric species, which closely model the active sites in oxygen-binding proteins with dicopper active sites such as hemocyanin, tyrosinsase and catechol oxidase, and are able to hydroxylate appropriately situated arene or alkyl groups within the ligands and to oxidise exogenous hydrocarbon substrates.[2–5] We therefore chose to incorporate the bpea and tacn* groups into the targeted ditopic ligands. Following a similar line of thought, Nolte has prepared a diphenylglycouril receptor substituted by two (bpea)Cu centres for use as a catechol oxidase mimic—to date, however, oxidation of exogenous substrates has not been observed using this particular system.[5]

Second, triphenylphosphine is one of the more commonly used ligands in inorganic chemistry and is one of the most common ligands found in homogeneous transition metal catalysts for the binding and transformations of organic substrates.[6] For this reason, the triphenylphosphine group was chosen as the second metal-binding domain in the targeted ditopic ligands. Moreover, we anticipated that use of ditopic ligands with *P*- and N_3-donors would provide a useful degree of

† Electronic supplementary information (ESI) available: NMR and FTIR spectra; table of ES-MS and NMR spectral data for the mononuclear complexes; table of analytical and EPR and electronic spectral data for heteronuclear complexes; table of FTIR spectral data for $[W(CO)_5(L^3)]$ solutions in thf following addition of transition metal salts. See http://www.rsc.org/suppdata/dt/b2/b201720m/

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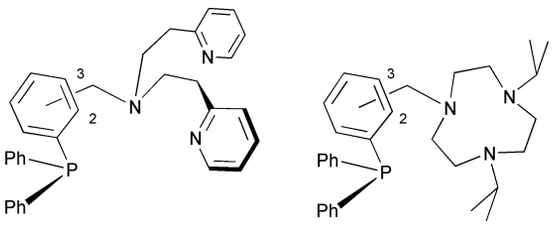


L^1 = 2-isomer
L^3 = 3-isomer

L^2 = 2-isomer
L^4 = 3-isomer

selectivity when constructing the targeted heteronuclear metal complexes—phosphines are soft donors and should preferentially bind to soft metal ions whereas the harder bpea and tacn* donors should prefer hard metal ions.[7] At the outset of this work and presently, Schiff-base (imine) derivatives of 2-diphenylphosphinobenzaldehyde are the most common N_n,*P*-donor ligands.[8–13] We discounted use of Schiff-base ligands in our work because these are susceptible to hydrolysis (imine formation is reversible). Other ligands with N_n- and *P*-donor domains[14–25] have either long or not readily adaptable preparations,[17–19,21,22] or alkyl "linkers" that would be too flexible for our purposes (see below);[14–16,19,20,22] and only a handful have macrocyclic N_n-sets.[14–16,18,20,23,24] These problems are overcome in L^1–L^4 which we thought should be readily available from reductive aminations[24–26] of the corresponding diphenylphosphinobenzaldehydes; moreover, this methodology had the attraction of potentially being applicable to the preparations of a wide variety of phosphinoamine derivatives.

Third, it was important that the metal centres in the heteronuclear ensemble should retain their individual reactivities. Here, we were particularly mindful of Bosnich and co-workers' extensive studies of a series of hetero-bimetallic species, which revealed the oxidation of one metal centre to invariably cause deactivation of the other.[1] The deactivation followed from ligand designs that allowed (mechanical, electronic or electrostatic) coupling between the metal centres. We thought that the *meta*-benzyl "linker" in ligands L^3 and L^4 should keep the metal centres sufficiently apart for these to maintain their individual reactivities but at the same time should allow an organic substrate bound and activated at the organometallic centre to approach close to the oxygen-binding classical centre. Considerably more interactions between metal centres are expected in heterometallic species bridged by the *ortho*-benzyl substituted ligands L^1 and L^2, which would provide interesting comparisons.

For the organometallic centres, analogues of $[PtCl_2(PPh_3)_2]$ and $[Ir(CO)Cl(PPh_3)_2]$, Vaska's complex,[27–29] were targeted in this preliminary study. Such complexes are relatively easily prepared, have diamagnetic, square-planar d^8 metal centres that facilitate their NMR characterisation, and most importantly, exhibit extensive organometallic chemistries.[30] Also targeted were $[W(CO)_5(\kappa P\text{–L})]$ (L = L^1, L^3), analogues of $[W(CO)_5(PPh_3)]$ with a dangling bpea group, because any changes to the carbonyl IR bands upon binding of a second metal ion would provide a useful measure of inter-metal centre interactions. Moreover, if the carbonyl IR bands were perturbed by the addition of a second metal, then the $[W(CO)_5(L)]$ complexes could be considered to be "IR metal ion sensors",[31] with the dangling bpea group acting as the recognition centre and the tungsten(0) carbonyl moiety acting as the IR signal transducer.

Results and discussion

Ligands

Our proposal that direct reductive amination of phosphinobenzaldehydes is a simple route to phosphinoamine ligands was tested by the syntheses of the targeted triphenylphosphine-derivatives, L^1–L^4. The 2- and 3-isomers of diphenylphosphinobenzaldehyde were required. The Hoot–Rauchfuss modification[32] of Schiemenz and Kaack's original synthesis[33] of the 2-isomer proceeded as reported. However, in our hands the yellow oil(s) repeatedly obtained following Schiemenz and Kaack's procedure to the 3-isomer,[33] contained at best 45% of phosphinobenzaldehyde product (as ascertained from ^{1}H and ^{31}P NMR spectra; it is perhaps noteworthy that the only characterisation data for this product in the original report[33] is from a 60 MHz ^{1}H NMR spectrum). Although the yellow oil could be further purified by chromatography [silica support; petroleum ether–ethyl acetate (2 : 1) eluent] to afford 3-isomer that was pure by ^{1}H and ^{31}P NMR spectroscopy, considerable material was always lost leading to an overall yield (from 3-bromobenzaldehyde) less than 20%.

As anticipated, the reductive aminations[26] of 2- and 3-phosphinobenzaldehydes with bis(2-pyridylethyl)amine (bpea) and 1,4-diisopropyl-1,4,7-triazacyclononane (tacn*) using sodium triacetoxyborohydride (1.6 equivalents) in 1,2-dichloroethane afforded the four new N_3,*P*-donor ligands, L^1–L^4, as thick yellow–orange oils. The crude products obtained following neutralisation, extraction into dichloromethane and evaporation of this solvent were generally quite clean by NMR spectroscopy and were used in subsequent reactions. Although giving "purer" ligands, column chromatography [silica support; petroleum ether–ethyl acetate (2 : 1) eluent] resulted in considerable losses and is not recommended. The "purer" ligands tenaciously retain traces of solvent and, as a result, elemental analyses were not acquired. However, ES-MS and NMR spectroscopic data (see Experimental) are entirely consistent for the ligands, and the subsequent successful syntheses of metal complexes (see below) further attest to their successful preparations. Ligands L^3 and L^4 are the first derivatives of 3-diphenylphosphinobenzaldehyde to be reported, a fact perhaps explained by the difficulties in purifications of these compounds and the starting aldehyde.

Protonation of bis(2-pyridylethyl)amine and 1,4,7-triazacyclononane derivatives, which are most often oils, may give tractable solids.[34] Accordingly, the crude products from the preparations of L^1 and L^2 (see above) were dissolved in methanol and treated with excess ammonium hexafluorophosphate to afford white precipitates of the monoprotonated derivatives, $[HL][PF_6]$ (L = L^1, L^2), in 55 and 60% yield (overall from 2-phosphinobenzaldehyde). NMR spectra of the protonated derivatives show relatively large shifts in δ_H for the proton peaks of the N_3-domains and relatively small shifts in δ_P for the phosphine (for data, see Experimental) suggesting that protonation occurs at only the more basic N_3-domains and not at the phosphine group. Notable in the ^{1}H NMR spectra of L^2 and $[HL^2]^+$ are the methyl resonances of the isopropyl groups which appear as a doublet for L^2 and two sharp doublets for $[HL^2]^+$, indicating that monoprotonation is sufficient to lock the macrocyclic ring and prevent ring inversion within the NMR timescale. In an attempt to obtain a more highly protonated derivative of L^1, 70% perchloric acid was added to L^1 in methanol; a white precipitate formed, which shows $^{31}P\{^1H\}$ NMR peaks at δ_P −16.87 (relative integrated intensity: 1.00) typical of a "free" phosphine and at δ_P 34.8 (0.08), 35.5 (0.08) and 40.7 (0.07) typical of phosphine oxide species. The peak at δ_P 40.7 grows upon standing and attempted recrystallisations of the original white precipitate afforded this species, a colourless crystalline solid which analyses as the triprotonated or tris(hydronium ion) complex of the phosphine oxide, $[H_3L^1O](ClO_4)_3\cdot 3H_2O$ or $(L^1O)[H_3O]_3(ClO_4)_3$ respectively. The positive-ion ES-MS spectrum of the original white precipitate shows a single strong peak at *m*/*z* 502.0 corresponding to the $[HL^1]^+$ ion and products from reactions with metal ions suggest it is principally tris-protonated ligand, $[H_3L^1](ClO_4)_3$, in which the phosphine group is unprotonated (see below). It is noteworthy that oxidation of $[H_nL^1]^{n+}$ to phosphine oxide-containing

species was only observed when (oxidising) perchlorate was the counter-anion.

Mononuclear N_n,P-chelated complexes of L^1 and L^2

For the *ortho*-substituted triphenylphosphine derivatives, L^1 and L^2, it seemed likely that the *P*- and N_3-ligand domains could simultaneously bind to the same metal. To explore this possibility, reactions of these ligands with sources of copper(I), zinc(II) and platinum(II) ions were investigated.

Copper(I) complexes. Reactions of $[Cu(MeCN)_4][PF_6]$ with L (L = L^1 or L^2) or $[HL][PF_6]$ in dichloromethane afforded the corresponding copper(I) complex, $[CuL][PF_6]$, which are air stable. ES-MS spectra, see Table 1 of the ESI, † show prominent peaks for the $[CuL]^+$ molecular ions at *m/z* 564 (L = L^1) and 551 (L = L^2) respectively. NMR spectra are presented in Fig. 1 and 2 of the ESI.† Marked changes are observed between the ^1H NMR spectra of the free or protonated ligand and the corresponding copper(I) complex characteristic for co-ordination to copper, and $^{31}P\{^1H\}$ NMR spectra in $(CD_3)_2CO$ show a broad peak centred at $\delta_P \approx -10$ (fwhh ≈ 1600 Hz) for $[CuL^1]^+$ and at $\delta_P \approx -0.3$ (fwhh ≈ 700 Hz) for $[CuL^2]^+$ as well as the distinctive sharp peaks of the hexafluorophosphate septet (δ_P −142.0, J_{PF} 707 Hz). The ^{31}P NMR peaks are broad due to quadrupolar relaxation [$^{63,65}Cu$, I = 3/2] and are indicative of the asymmetric charge distributions about copper.[35]

Recrystallisation of both copper(I) complexes from acetonitrile–diethyl ether gave clear, colourless crystals suitable for X-ray crystallography. The crystal structure of $[Cu(L^2)][PF_6]$ is reported in a communication.[24] In the crystal structures of $[CuL][PF_6]$ (L = L^1, L^2) there are no significant interion interactions. The structure determinations confirm the copper(I) ion in both complexes is $\kappa^3N,\kappa P$-bound by the ligand, *e.g.* Fig. 1 and

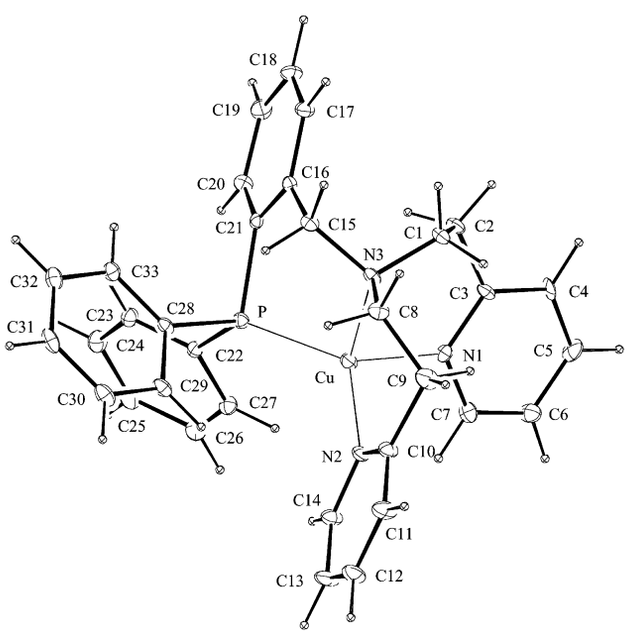


Fig. 1 View of the cation from the crystal structure of $[Cu(L^1)][PF_6]$ (10% thermal ellipsoids).

ref. 24. The co-ordination geometry for the copper(I) ion is best described as distorted tetrahedral for both complexes; the sum of the six bond angles about the copper(I) ion is 649° for $[Cu(L^1)]^+$ (Table 1) and 631° for $[Cu(L^2)]^+$[24] compared to 657° for a perfect tetrahedron.

For $[Cu(L^1)]^+$, the ligand design constrains the N(3)–Cu–P bond angle to 97.7(1)° (compared to 107.5° for a perfect tetrahedron), whilst the P–Cu–N(pyridyl) bond angles are greater than 120° (Table 1), which minimises the steric interactions between the pyridyl and phenyl rings. The geometry about

Table 1 Selected bond lengths (Å) and angles (°) for $[Cu(L^1)][PF_6]$

Cu–P	2.197(1)	P–Cu–N(1)	125.6(1)
Cu–N(1) (pyridyl)	2.034(4)	P–Cu–N(2)	122.5(1)
Cu–N(2) (pyridyl)	2.055(4)	P–Cu–N(3)	97.7(1)
Cu–N(3) (amine)	2.159(4)	N(1)–Cu–N(2)	105.2(2)
		N(1)–Cu–N(3)	97.9(2)
		N(2)–Cu–N(3)	100.4(2)

$[Cu(L^2)]^+$ is more distorted due to the dual constraints of the *ortho*-phosphino-benzylamine linkage [P–Cu–N(benzylamine): 100.6(1)°] and the macrocyclic ring which prevents the two remaining amine donors from splaying outward toward the phosphorus atom [P–Cu–N(*iso*-propylamine): 133.6(1), 138.9(1)°].[24] Comparable Cu–P bond lengths are found in $[Cu(L^1)]^+$ [2.197(1) Å] and $[Cu(L^2)]^+$ [2.141(1) Å].[24] The two Cu–N(pyridyl) bonds in $[Cu(L^1)]^+$ average 2.045 Å, significantly shorter than the Cu–N(amine) bond [2.159(4) Å], which is consistent with copper(I) ions forming stronger bonds with the softer, pyridyl nitrogens. These Cu–N(pyridyl), Cu–N(amine) and Cu–P bond lengths are similar to those reported for Cu(I) complexes of bpea-based ligands with triphenylphosphine as a co-ligand.[36]

The electrochemistries of the copper(I) complexes and the ligands L^1 and L^2 were examined by cyclic voltammetry experiments. Cyclic voltammograms (CVs) of L^1 and L^2 show an anodic peak for an irreversible oxidation at ≈+1.1 V *vs.* ferrocenium–ferrocene (Fc^+–Fc) couple; the number of electrons transferred in the processes were not ascertained by coulometry. CVs of $[Cu(L^1)][PF_6]$, Fig. 2, exhibit an electro-

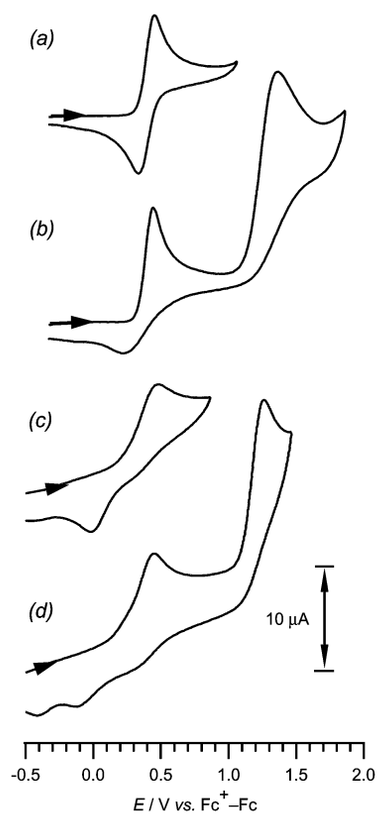
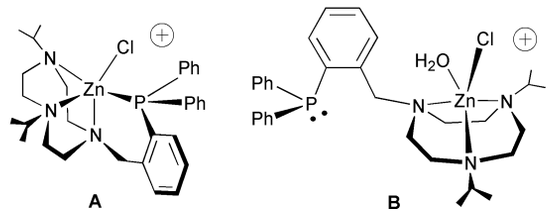


Fig. 2 Cyclic voltammograms of $[Cu(L^1)][PF_6]$ (*a, b*) and $[Cu(L^2)][PF_6]$ (*c, d*). Conditions: 0.1 M $[NBu_4][PF_6]$-acetonitrile; 295 K; 1 mm diameter Pt disk electrode; scan rate = 100 mV s^{-1}.

chemically quasireversible Cu(II)–Cu(I) couple at +0.40 V [$i_{pc}/i_{pa} \approx 0.85$ and ΔE_p = 110 mV at scan rate (v) = 100 mV s^{-1} *cf.* $\Delta E_p(Fc^+–Fc)$ = 65 mV; ΔE_p increases with v], suggesting that rate-limiting structural changes accompany the forward and reverse electron transfer processes. Coulometry at +0.60 V confirmed that the +0.4 V couple is a one-electron process. In

CVs of $[Cu(L^2)][PF_6]$ the Cu(II)–Cu(I) couple is less electrochemically reversible with an anodic peak at +0.48 V for oxidation of the Cu(I) complex that gives rise to a cathodic peak in the reverse sweep at +0.22 V for reduction of the thus-produced Cu(II) species. In the CVs of both complexes at more positive potential an irreversible oxidation is observed, at +1.36 V for $[Cu(L^1)][PF_6]$ and at +1.27 V for $[Cu(L^2)][PF_6]$, which on the basis of relative peak currents is a two-electron process. For $[Cu(L^2)][PF_6]$, the irreversible oxidation at +1.27 V gives rise to "daughter" cathodic peaks at −0.12 and −0.41 V in the reverse negative sweep. The irreversible two-electron oxidations are tentatively attributed to a phosphine-centred oxidation process, possibly to the corresponding phosphine oxide, with the two-electron nature of the process somewhat unexpected as, despite some controversies, it has been established that triphenylphosphine undergoes a one-electron oxidation above +1.0 V.[37] One possibility is that the copper centres assist in the two-electron oxidation of the phosphine. The low affinity of copper(II) for phosphine donors[19,38] suggests that the phosphine should dissociate in the copper(II) species and oxidation of the dangling, dissociated phosphine group is consistent with the loss of chemical reversibility for the Cu(I)–Cu(II) redox couples after the two-electron oxidation is traversed in the CVs. The low affinity of copper(II) for phosphine ligands[19,38] also accounts for the relatively high Cu(II)–Cu(I) couples for these complexes [as recently discussed by Rorabacher *et al.*,[39] Cu(II)–Cu(I) couples are determined largely by the stabilities of the copper(II) complexes, with the stabilities of the copper(I) congeners being relatively invariant and having little effect].

A zinc(II) complex. Each of the ligands was treated with anhydrous zinc(II) chloride in ethanol, followed by excess ammonium hexafluorophosphate: for L^1 the monoprotonated ligand, $[HL^1][PF_6]$, precipitated (see above), and for L^2 an off-white precipitate formed. This was recrystallised but crystals of quality sufficient for X-ray crystallography could not be obtained. A partial elemental analysis of the precipitate is consistent with the formulation "$ZnCl(H_2O)(L^2)(PF_6)$". The ES-MS spectrum exhibits a single strong peak at *m*/*z* 588 for the $[ZnCl(L^2)]^+$ ion (see Table 1 of the ESI †), consistent with this being the molecular ion. An electrical conductivity measurement reveals the complex is a 1 : 1 electrolyte in dichloromethane also consistent with chloride binding to the zinc(II) ion. The ^{1}H NMR spectrum of the zinc complex (see Table 1 of the ESI †) shows significant differences to those of L^2 and $[HL^2]^+$: for example, the benzyl peak shifts downfield from $\delta(CDCl_3)$ 3.97 for $[HL^2]^+$ to $\delta(CDCl_3)$ 4.14, the macrocyclic alkyl proton resonances are more spread, and the characteristic *iso*-propyl C–H septet shifts from $\delta(CDCl_3)$ 3.11 for $[HL^2]^+$ to $\delta(CDCl_3)$ 3.51. These data provide compelling evidence for the co-ordination of the zinc(II) ion to the N_3-donor set. The $^{31}P\{^1H\}$ NMR spectrum shows the expected hexafluorophosphate septet and a phosphine singlet at δ_P ($CDCl_3$) −17.72 only slightly upfield of $[HL^2]^+$ [δ_P ($CDCl_3$): −14.22]. In the complex cation $[Zn_2(\kappa^3N,\kappa P\text{-}L^5)_2Cl_3]^+$ [L^5 = *N*-(diphenylphosphinopropyl)-1,4,7-triazacyclononane, a ligand closely related to L^2], one zinc is N_3PCl_2-pseudo-octahedral and the other is formally five (N_3PCl-) co-ordinate but with a weak interaction (2.91 Å) to one of the two chlorides of the pseudo-octahedral zinc centre.[20] The change in ^{31}P chemical shift upon co-ordination of L^5 to zinc is small ($\Delta\delta_P = -3.2$),[20] typical for other examples of phosphine co-ordination to zinc(II) ion.[20,40] Thus the ^{31}P data for "$ZnCl(H_2O)(L^2)(PF_6)$" are consistent with structures for the cation in which the phosphine binds zinc such as $[ZnCl(\kappa N_3,\kappa P\text{-}L^2)]^+$ (**A**). However, the ^{31}P data are also consistent with structures having a dangling phosphine group such as in $[ZnCl(H_2O)(\kappa N_3\text{-}L^2)]^+$ (**B**), in which case the proximate zinc(II) centre could cause δ_P to shift upfield from that of L^2. Overall the present data highlight the difficulties in assigning authentic zinc(II) phosphine complexes; zinc-phosphine co-ordination chemistry is not extensive and assignments of genuine zinc-phosphine complexes are considered somewhat controversial[41] with only a handful of crystallographically characterised examples reported to date.[20]



Platinum(II) complexes. Pale yellow crystalline $[PtCl(L^1)][PF_6]$ was obtained in 43% yield from the reaction of $[PtCl_2(PhCN)_2]$ with $[HL^1][PF_6]$ and excess triethylamine in 1,2-dichloroethane at reflux, followed by recrystallisation from $MeCN–Et_2O$.

The positive-ion ES-MS mass spectrum of $[PtCl(L^1)][PF_6]$ shows only peaks for the $[PtCl(L^1)]^+$ ion centred at *m*/*z* 732.0 (see Table 1 of the ESI †). The ^{1}H NMR spectrum exhibits extremely broad peaks suggestive for fluxional behaviour in solution, and the large downfield shift of the pyridyl H^6 peak from δ 8.22 [$(CD_3)_2CO$] for $[HL^2]$ to δ 8.67 [$(CD_3)_2CO$] (see ESI Table 1 and ESI Fig. 3 †) is indicative for one of the pyridyl groups binding to platinum. Although not pursued further, it is likely that exchange of the metal-free, dangling and the bound pyridyl groups (see below) on the NMR timescale is the underlying process leading to the broad peaks; the bound pyridyl is expected to be labile as it lies opposite the phosphine (see below) which exerts a strong *trans* effect. The $^{31}P\{^1H\}$ NMR spectrum [in $(CD_3)_2CO$; see inset to Fig. 3 of the ESI †] exhibits the hexafluorophosphate septet (δ_P −142.0, J_{PF} 707 Hz) and a "triplet" at δ_P 0.78 (J_{PPt} 3624 Hz) due to coupling to ^{195}Pt (^{195}Pt: I = 1/2, 33% natural abundance) for the phosphine group bonded to platinum.[35]

The X-ray structure of $[PtCl(L^1)][PF_6]$ confirms that in the cation the platinum(II) ion is bound by the phosphine, the amine and one pyridyl of L^1, and by a chloride co-ligand in the position *trans* to the amine, Fig. 3. A dangling pyridyl lies

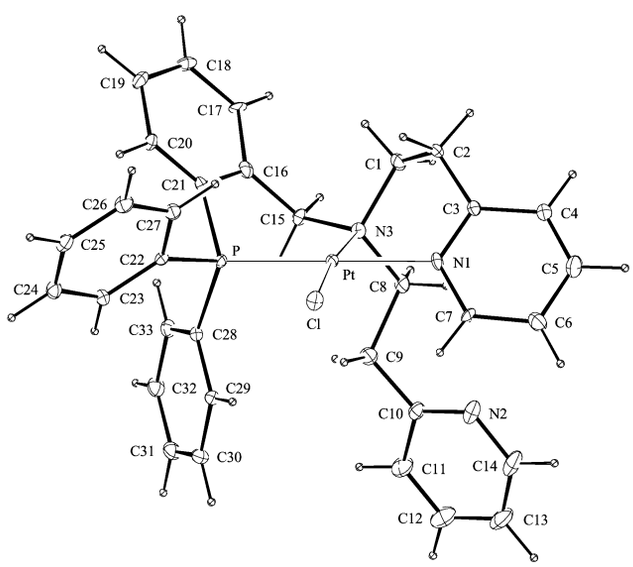


Fig. 3 View of the cation from the crystal structure of $[PtCl(L^1)][PF_6]$ (10% thermal ellipsoids).

orientated away from the platinum centre. Perhaps most remarkable about the structure is that it is entirely undistorted compared to related phosphine and pyridyl platinum(II) complexes: the co-ordination geometry about the platinum(II) centre is square planar (the sum of the eight bond angles about the metal centre is 713°, close to the value of 720° expected for a

Table 2 Selected bond lengths (Å) and angles (°) for $[PtCl(L^1)][PF_6]$

Pt–P	2.234(1)	Cl–Pt–P	91.9(1)
Pt–Cl	2.285(1)	Cl–Pt–N(1)	89.2(1)
Pt–N(1)	2.105(3)	Cl–Pt–N(3)	174.0(1)
Pt–N(3)	2.120(3)	P–Pt–N(1)	178.7(1)
		P–Pt–N(3)	93.3(1)
		N(1)–Pt–N(3)	85.6(1)

perfect square planar structure), the Pt–N and Pt–Cl bond lengths (Table 2) are in the ranges established for similar platinum(II) complexes, and the Pt–P [2.234(1) Å] bond length is typical of those reported for other platinum(II) compounds with *transoid* phosphine and pyridyl groups.[42–44] Likewise the P–Pt–N(3) bond angle [93.3(1)°] is only slightly greater than the 90° expected for a perfect square planar structure. Clearly L^1 can comfortably accommodate tetrahedral and square planar co-ordination geometries.

Noteworthily, $[PtCl(L^1)][PF_6]$ is completely air stable and survives heating in ethanol solution at 60 °C under oxygen. Under the latter conditions *cis*-$[PtCl_2(\kappa^2N\text{-tacn})]$ is rapidly oxidised to the peroxo-bridged platinum(IV) dimer, $[Pt_2Cl_2(\kappa^3N\text{-tacn})_2(\mu\text{-}O_2)_2]$, a reaction proposed to be facilitated by the binding of the non-co-ordinated *N*-donor group of the tacn to platinum.[45] The failure of $[PtCl(L^1)][PF_6]$, which has a similarly placed dangling pyridyl arm, to react with oxygen highlights the importance of the ligand(s) influence upon the electronic properties of the metal centre.

Although reaction of $[PtCl_2(PhCN)_2]$ with $[HL^2][PF_6]$ and excess triethylamine in 1,2-dichloroethane heated at reflux afforded a yellow solid, this unfortunately could not be further purified—attempted recrystallisations and chromatography always lead to oily product containing trace solvent. The positive-ion ES-MS mass spectrum of the solid is remarkably simple exhibiting only a peak for the $[PtCl(L^2)]^+$ ion (*m*/*z* 717.0; calc. *m*/*z* 717.25), and the $^{31}P\{^1H\}$ NMR spectrum shows a "triplet" at δ_P −0.71 (J_{PPt} 3752 Hz), values remarkably similar to those for $[PtCl(L^1)]^+$, and the hexafluorophosphate septet. These data are consistent with $[PtCl(L^2)][PF_6]$ having formed. However the ^1H NMR spectrum (see Table 1 of the ESI †) is complicated with more than the expected number of sharp peaks—there was no evidence for fluxional behaviour—and could not be fully assigned.

Heteronuclear complexes

We reasoned that pH control should allow selective preparations of heteronuclear complexes from ligands, L^1–L^4. Reactions of the protonated ligands, in which the N_3-domains are effectively "tied-up" and unavailable for metal binding, with sources of softer metal ions in solvents with little or no Brønsted basicity should allow mononuclear phosphine complexes with dangling, metal-free N_3-donor domains, so-called "complex ligands",[46,47] to be prepared. If they could be made, these would be useful precursors to heteronuclear complexes—deprotonation of the dangling N_3-domain followed by addition of harder metal ions could be used to selectively prepare hard–soft heteronuclear trimeric complexes. For the reasons outlined in the Introduction, these ideas were tested using platinum(II) and iridium(I) as softer metal centres and copper(II) as a harder metal centre.

Mononuclear precursors with dangling, metal-free N_3-domains. Six such complexes were isolated. The platinum(II) examples with dangling monoprotonated tacn-based domains, *trans*-$[PtCl_2(HL)_2][PF_6]_2$ (L = L^2, L^4), were obtained from reactions of $[PtCl_2(PhCN)_2]$ with $[HL][PF_6]$ (2 equivalents) in dichloromethane. Attempts to prepare the analogous platinum(II) complex using $[HL^1][PF_6]$, which has a bpea-domain, always resulted in a mixture of products (as judged by the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures) with the predominant product always being $[PtCl(\kappa^3N,\kappa P\text{-}L^1)][PF_6]$. Monoprotonation of L^1 apparently leaves the amine and one pyridyl donor "free" for complex formation and is therefore insufficient to prevent the N_3-domain from binding to platinum. For L^1, however, triple protonation served to protect the N_3-domain; thus reaction of $[PtCl_2(PhCN)_2]$ and $[H_3L^1](ClO_4)_3$ (2 equivalents) in acetonitrile cleanly afforded the complex *trans*-$[PtCl_2(H_3L^1)_2](ClO_4)_6$ with dangling triply-protonated bpea domains. The *meta*-substitution of the triphenylphosphine moiety in L^3 and L^4 prevents the phosphine and N_3-domains from simultaneously binding to a metal and, in this case, protonation of the ligand to protect the N_3-domain is unnecessary. Thus, the direct reactions of L^3 (2 equivalents) with $[PtCl_2(PhCN)_2]$ in dichloromethane and *cis*-$[IrCl(CO)_2(4\text{-}NH_2C_6H_4CH_3)]$ in tetrahydrofuran gave *cis*-$[PtCl_2(L^3)_2]$ and *trans*-$[IrCl(CO)(L^3)_2]$, respectively, also with dangling bpea domains.

To test for interactions between the metal centres in dimers, tungsten(0) carbonyl complexes of L^1 and L^3 were also sought. Reactions of $[W(CO)_5(thf)]$ with L^1 or L^3 always produced mixtures, the $^{31}P\{^1H\}$ NMR spectra of which showed many singlets, all with no discernable satellites from ^{183}W coupling (^{183}W: I = 1/2, 14.4% natural abundance), suggestive for multiple products in which the phosphine is not bound to tungsten. As an alternative route to the targeted complexes, the complexes $[W(CO)_5(L)]$ (L = 2- and 3-diphenylphosphinobenzaldehyde) were prepared and reductive aminations with bpea using triacetoxyborohydride in 1,2-dichloroethane attempted. The reactions of $[W(CO)_5(2\text{-}Ph_2PC_6H_4CHO)]$,[48] including using forcing conditions such as heating or addition of excess acetic acid, all failed with the starting complex recovered, presumably because of steric protection of the aldehyde group by the bulky $W(CO)_5$ moiety. Reductive amination of $[W(CO)_5(3\text{-}Ph_2PC_6H_4CHO)]$ with bpea using triacetoxyborohydride in 1,2-dichloroethane, however, proceeded as expected and afforded $[W(CO)_5(L^3)]$, isolated as a thick yellow–orange oil in 37% yield after purification by flash chromatography (silica support; eluent: ethyl acetate).

Of these six complexes, only $[PtCl_2(H_3L^1)_2](ClO_4)_6$ and $[PtCl_2(HL^2)_2][PF_6]_2$ with protonated N_3-donor domains were solids and partial elemental analyses of these were consistent with the formulations. The remaining four complexes could not be obtained free from trace solvent(s) and were viscous oils or solids that tended to oil upon attempts to recrystallise them. As a result, elemental analyses were not measured. However, the ES-MS and MALDI-MS, NMR and IR data (see Table 1 of the ESI †) along with their subsequent reactions (see below) provide compelling evidence for their suggested structures. All of the positive-ion ES-MS spectra show only peaks for ions that are consistent for the proposed metal centre, having the correct (number of) co-ligands and N_3,*P*-ligands, and with protonation of one or two of the dangling N_3-domains. MALDI-MS spectra were also recorded for $[W(CO)_5(L^3)]$ (observed: *m*/*z* 826.50; calc. *m*/*z* 826.99 for $[W(CO)_5(HL^3)]^+$) and $[IrCl(CO)(L^3)_2]$ (observed: *m*/*z* 1259.86, 1223.43; calc. *m*/*z* 1259.89, 1223.32 for $[IrCl(CO)\{H(L^3)_2\}]^+$ and $[Ir(CO)(L^3)_2]^+$, respectively). The CO bands in infrared spectra of $[W(CO)_5(L^3)]$ and $[IrCl(CO)(L_3)_2]$ (see footnotes, Table 1 of the ESI †) are within 5 cm^{-1} of those for the corresponding triphenylphosphine complex.[27,49]

The ^1H NMR spectra of these six complexes exhibit large co-ordination shifts for the benzylic resonances and shifts and changes in the phenyl peaks, while the peaks for the bpea or tacn* groups (depending on the ligand) are little changed from those in the spectrum of the ligand (L) or protonated ligand salt $\{[H_nL]^{n+}\}$ (as appropriate). These observations are consistent with phosphine co-ordination and dangling, metal-free N_3-donor domains. Fig. 4 and 5 of the ESI † reproduce the ^1H and $^{31}P\{^1H\}$ NMR spectra for *trans*-$[PtCl_2(\kappa P\text{–}HL^2)_2][PF_6]_2$ and $[W(CO)_5(\kappa P\text{–}L^3)]$, which show the same general features as

those of the other κ*P*–L complexes. The $^{31}P\{^{1}H\}$ NMR spectrum of each of the six complexes exhibits only one phosphine resonance (and, when expected, a hexafluorophosphate septet) consistent in each case with a single phosphine-containing species in solution. For $[W(CO)_5(L^3)]$ the phosphine peak at δ_P ($CDCl_3$) 21.49 is flanked by a satellite doublet due to ^{31}P–^{183}W coupling (J_{PW} 243 Hz); these data compare with δ_P (CH_2Cl_2) 26.6 (J_{PW} 280 Hz) for $[W(CO)_5(PPh_3)]$.[49] Likewise the phosphine resonances of the platinum(II) complexes appear as "triplets" because of ^{31}P–^{195}Pt couplings, which are characteristic for *cis*- or *trans*-co-ordination geometries (*trans*-$[PtCl_2(PR_3)_2]$: J_{PPt} < 2800 Hz; *cis*-$[PtCl_2(PR_3)_2]$: J_{PPt} > 3200 Hz).[35] Interestingly $^{31}P\{^{1}H\}$ NMR spectra acquired early during syntheses of $[PtCl_2(L^3)_2]$ reveal a "triplet" at δ 21.61 (J_{PPt} 2632 Hz) for the *trans*-isomer which is only slowly replaced on standing in solution overnight by the "triplet" at δ 15.03 (J_{PPt} 3674 Hz) for the *cis*-isomer. This reproducible, thermodynamic preference for *cis* over *trans* co-ordination geometry is typical for $[PtCl_2P_2]$ (*P* = non-bulky phosphine) complexes, and the isomerisation from *trans* kinetic product to *cis* thermodynamic product can be catalysed by extra ligand in the solution such as free halide or phosphine.[50] The fact that the three other *trans*-platinum(II) complexes did not isomerise may be attributable to the bulk of the *ortho*-substituted triphenylphosphines L^1 and L^2 and to the protonation of the N_3-donor domains rendering these unavailable to catalyse isomerisation.

Heteronuclear Ir(I)–Cu(II)$_2$ and Pt(II)–Cu(II)$_2$ trimers. Treating the mononuclear complexes *trans*-$[PtCl_2(H_3L^1)_2]^{6+}$ and *trans*-$[PtCl_2(HL)_2]^{2+}$ (L = L^2, L^4), which have dangling protonated N_3-domains, with $[Cu_2(OAc)_4(H_2O)_2]$ in the presence of excess triethylamine as base in acetonitrile afforded the corresponding $[PtCl_2\{(L)Cu(OAc)\}_2]^{2+}$ complex (isolated in 55–80% yield). Addition of $CuCl_2{\cdot}2H_2O$ (2 equivalents) to thf solutions of *cis*-$[PtCl_2(L^3)_2]$ or *trans*-$[IrCl(CO)(L^3)_2]$, in which the dangling N_3-domains are unprotonated, caused immediate precipitation of $[PtCl_2\{(L^3)CuCl_2\}_2]$ (78% yield) and *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$ (47% yield) respectively. The yield of the latter complex (less than 50%) is consistent with the stoichiometry shown in eqn. 1, but was not increased by adding $CuCl_2{\cdot}2H_2O$ (4 equivalents) to *trans*-$[IrCl(CO)(L^3)_2]$. Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$, is likewise oxidised by $CuCl_2$ to afford *mer*-$[IrCl_3(CO)(PPh_3)_2]$.[51] The $PtCu_2$ complexes of L^1 and L^2, the *ortho*-substituted triphenylphosphine ligands, decomposed on prolonged standing in solution during attempted recrystallisations; *e.g.* over several weeks a mixture of colourless crystals of $[Cu(L^2)][PF_6]$ and green "flowers" of an unidentified species[52] grew from *trans*-$[PtCl_2\{(L^2)Cu(OAc)\}_2][PF_6]_2$ in MeCN–Et_2O. In distinct contrast, the $IrCu_2$ and two $PtCu_2$ trimers from the *meta*-substituted triphenylphosphine ligands L^3 and L^4 were indefinitely stable in solution. Unfortunately the crystals of these complexes obtained from recrystallisations were of insufficient quality for X-ray crystallography.

$$\textit{trans}\text{-}[IrCl(CO)(L^3)_2] + 4CuCl_2 \longrightarrow \textit{mer}\text{-}[IrCl_3(CO)\{(L^3)CuCl_2\}_2] + 2CuCl \quad (1)$$

Partial elemental analyses (for C, H and N) and elemental ratios for Cu, P and Pt calculated from ICP-AES analyses are presented in Table 2 of the ESI.† The carbon contents of the $CuCl_2$-containing complexes are low which is consistent with lattice waters as is often found for Cu–Cl containing species.[34,53] ICP-AES analyses were not obtained for *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$ because all attempted digestions of this complex (*e.g.* with hot 20% nitric acid or hot *aqua regia*) produced insoluble iridium-containing precipitates. Frustratingly, the ES-MS spectra of these heteronuclear complexes show only peaks for the protonated ligands, ligand fragments and fragment ions containing Pt or Ir or Cu but never the molecular ions, and with poor reproducibility—repeat acquisitions sometimes produced differing spectra. Constable *et al.* likewise report that they could not obtain reproducible ES-MS spectra of heteronuclear complexes based on a similar N_3,*P*-ditopic phosphinoterpyridine ligand.[21]

The EPR and electronic absorption spectra of the $PtCu_2$ and $IrCu_2$ complexes are characteristic for a single type of copper(II) centre in each complex. In each case the electronic absorption and EPR spectra of the complex are markedly different from the spectra of the corresponding copper(II) source $\{[Cu_2(OAc)_4(H_2O)_2]$ or $CuCl_2{\cdot}2H_2O\}$ in the same solvent,[38] which is evidence for co-ordination of copper(II) ions by the dangling N_3-domains of the mononuclear Pt or Ir precursor. The EPR spectra are all axial and no half-field transitions are observed [which would have indicated exchange-coupled copper(II) centres[38]], Fig. 4 (data are in Table 2 of the ESI†). For the

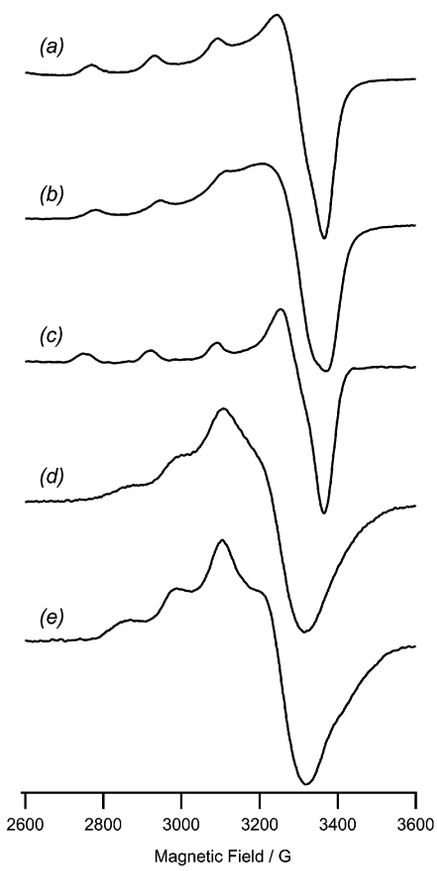


Fig. 4 X-Band EPR spectra (at ν = 9.52 GHz) of heteronuclear complexes at 77 K: (*a*) $[PtCl_2\{(L^1)Cu(OAc)\}_2](ClO_4)_2$, (*b*) $[PtCl_2\{(L^2)Cu(OAc)\}_2][PF_6]_2$, (*c*) $PtCl_2\{(L^4)Cu(OAc)\}_2][PF_6]_2$, (*d*) $[PtCl_2\{(L^3)CuCl_2\}_2]$, (*e*) $[IrCl(CO)\{(L^3)CuCl_2\}_2]$; frozen acetonitrile solution for spectra (*a*)–(*c*) and frozen chloroform solution for (*d*), (*e*).

$[PtCl_2\{(L)Cu(OAc)\}_2]^{2+}$ (L = L^1, L^2, L^4) complexes: $g_{||}$ (≈ 2.25–2.26) > $g_\perp$ (≈ 2.06–2.07) and $A_{||}$ ≈ 160–166 G, parameters indicative for square pyramidal or tetragonally-distorted octahedral copper(II) complexes with a $d_{x^2-y^2}$ ground-state.[34,38] The parameters for $[PtCl_2\{(L^3)CuCl_2\}_2]$ and *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$, $g_{||}$ (= 2.23) > $g_\perp$ (= 2.10) and a lower $A_{||}$ value (121 G and 125 G), are identical within experimental error to those for [Cu(Bzbpea)Cl_2] [Bzbpea = benzylbis(2-pyridylethyl)-amine)] (see Experimental),[34] which we prepared for comparative purposes. The observation of axial EPR spectra and the absence of half-field transitions argue against structures containing exchange-coupled dicopper(II) centres, *e.g.* with bridging acetato, hydroxo or chloro ligands.[38]

The electronic absorption spectra of the five heteronuclear complexes show intense ligand-centred absorptions below 340 nm (ε > 3000 $dm^3\ mol^{-1}\ cm^{-1}$) and characteristic, weak d–d

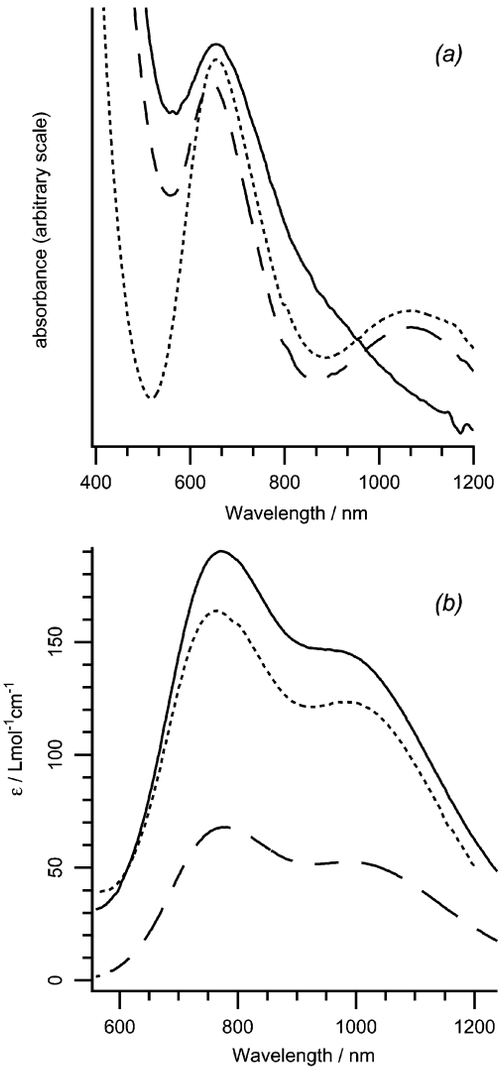
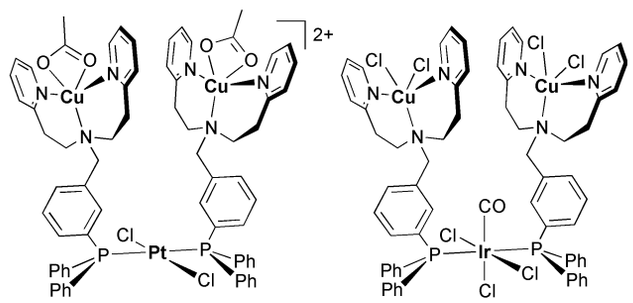


Fig. 5 Vis-NIR spectra of the heteronuclear complexes: (*a*) $[PtCl_2\{(L^1)Cu(OAc)\}_2](ClO_4)_2$ (——), $[PtCl_2\{(L^2)Cu(OAc)\}_2][PF_6]_2$ (· · · · · ·) and $PtCl_2\{(L^4)Cu(OAc)\}_2][PF_6]_2$ (– – –) in acetonitrile solution; (*b*) $[PtCl_2\{(L^3)CuCl_2\}_2]$ (——) and $[IrCl(CO)\{(L^3)CuCl_2\}_2]$ (· · · · · ·) along with $[Cu(Bzbpea)Cl_2]$ (– – –) in chloroform solution.

bands in the 500–1200 nm region, Fig. 5 and ESI† Table 2. Briefly, $[PtCl_2\{(L^1)Cu(OAc)\}_2](ClO_4)_2$ with (bpea)Cu(OAc) centres shows a band at 664 nm (ε = 300 M^{-1} cm^{-1}) with a prominent low energy tail, whilst $[PtCl_2\{(L)Cu(OAc)\}_2][PF_6]_2$ (L = L^2, L^4) with (tacn*)Cu(OAc) centres exhibit almost identical spectra—distinct Cu(II) d–d bands at ≈650 nm ($\varepsilon \approx 70$ M^{-1} cm^{-1}) and ≈1080 nm ($\varepsilon \approx 30$ M^{-1} cm^{-1}). These data are similar to those reported for comparable square pyramidal Cu(II) complexes bound by a N_3-donor ligand and a chelating (κ^2O–)-acetate co-ligand such as $[Cu(\kappa^3N\text{-dpt})(\kappa^2O\text{–OAc})](ClO_4)$ [dpt = dipropylenetriamine; λ_{max} (solid): 641 nm],[54] $[Cu(\kappa^3N\text{–}Pr^i_3tacn)(\kappa^2O\text{–OAc})](CF_3SO_3)$ [λ_{max} (MeOH): 672 nm (the spectrum above 680 nm was not recorded)],[55] and $[Cu(\kappa^3N\text{–L})(\kappa^2O\text{–OAc})](ClO_4)$ [L = 2,4,4′-trimethyl-1,5,9-triazacyclododec-1-ene; λ_{max} (acetone): 694 nm (ε = 99 M^{-1} cm^{-1}), 1150 nm (ε = 99 M^{-1} cm^{-1})].[56] Spectra of $[PtCl_2\{(L^3)CuCl_2\}_2]$ and *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$ with (bpea)$CuCl_2$ centres reveal a band at ≈775 nm and high energy shoulder at ≈990 nm, d–d bands typical of a square pyramidal N_3Cl_2–Cu(II) centre[34,38] and identical to those of $[CuCl_2(Bzbpea)]$ but with double the extinction coefficient as is expected for two copper centres in each trimer. Finally the infrared spectrum of *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$ shows a single strong carbonyl band at ν_{CO} ($CHCl_3$) = 2074 cm^{-1}, which compares with ν_{CO} ($CHCl_3$) = 2075 cm^{-1} for *mer*-$[IrCl_3(CO)(PPh_3)_2]$.[29]

Probable structures for $[PtCl_2\{(L^3)Cu(OAc)\}_2]^{2+}$ and *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$ deduced from the geometry of the mononuclear Pt or Ir precursor, from the stoichiometry established by analyses, and from the EPR, Vis/NIR and IR spectroscopic properties are drawn below. The copper centres are representative of those in the other trimers. Given the limited stabilities of the trimers spanned by the *ortho*-substituted triphenylphosphines L^1 and L^2, which may be related to the ability of these ligands to form mononuclear chelate complexes, our subsequent studies were concentrated on the more stable heteronuclear complexes of L^3, which is much the more economically made (in terms of both money and time spent) *meta*-substituted triphenylphosphine ligand.



$[PtCl_2\{(L^3)Cu(OAc)\}_2]^{2+}$ $[Ir(CO)Cl_3\{(L^3)CuCl_2\}_2]$

Inter-metal centre interaction. Two results point to the near independence of the Ir and Cu centres in *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$: 1. The EPR and Vis-NIR spectroscopic properties of *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$, which characterise the Cu(II) centres, are identical to those of $[CuCl_2(Bzbpea)]$ (see Table 2 of the ESI†). 2. The ν_{CO} band energies of *mer*-$[IrCl_3(CO)\{(L^3)CuCl_2\}_2]$ and *mer*-$[IrCl_3(CO)(PPh_3)_2]$ are near identical (see above) indicating that *meta*-substitution of the triphenylphosphine ligands in the latter complex by Cu(bpea) centres to give the former complex does not perturb the electronic properties of the Ir centre. Likewise, the CO bands in the IR spectrum of $[W(CO)_5(L^3)]$ in thf were not perturbed upon addition of a 10-fold molar excess of $M(ClO_4)_2{\cdot}6H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn), see ESI Fig. 6 and ESI Table 3.† Clearly "*meta*-substituted" $[W(CO)_5(L^3)]$ does not act as an IR-metal ion sensor of the type proposed in the Introduction; greater inter-metal ion interactions are expected in metal complexes of "*ortho*-substituted" $[W(CO)_5(L^1)]$, but this complex could not be prepared (see above) to test for these.

Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$, cleanly and reversibly forms a dioxygen adduct.[28] Substitutions to afford analogues of Vaska's complex critically affect the oxygen reactivity; for example, alkylphosphine and Rh(I) analogues are unreactive and $[Ir(CO)I(PPh_3)_2]$ is irreversibly oxidised by oxygen.[57,58] Since the oxidation of *trans*-$[IrCl(CO)(L^3)_2]$ by $CuCl_2$ prevented the preparation and study of an Ir(I) complex with pendant (bpea)Cu(II) centres, the reaction of *trans*-$[IrCl(CO)(L^3)_2]$ with oxygen was investigated. Fig. 6 shows IR spectra collected as oxygen was bubbled through a solution of *trans*-$[IrCl(CO)(L^3)_2]$. The spectra show a quantitative conversion to the dioxygen adduct *trans*-$[IrCl(CO)(L^3)_2(O_2)]$ (ν_{CO}: 2006 cm^{-1}), that is cleanly reversed by heating the solution at reflux (inset to Fig. 6).[59] The conversion was also clean by $^{31}P\{^1H\}$ NMR spectroscopy [δ_P (adduct): 5.2] and the ES-MS spectrum of the adduct shows a strong peak at *m*/*z* 1291.0 (calc. 1291.0) for the $[IrCl(CO)\{H(L^3)\}_2(O_2)]^+$ ion. The *meta*-substitution of the triphenylphosphine ligands in *trans*-$[IrCl(CO)(L^3)_2]$ has little affected the reactivity with oxygen compared to Vaska's complex.

A preliminary "catalysis" study: styrene oxidation. The oxidation of styrene by oxygen is catalysed by Vaska's complex and close Ir-analogues, and affords acetophenone, benzaldehyde or

Table 3 Oxidation of styrene by oxygen in MEK. Reagents and conditions: solutions were prepared containing styrene (500 mM), the iridium complex (1 mM) and the added metal ion as the perchlorate salt, $[M(ClO_4)_2 \cdot 6H_2O]$ [2 mM (two equiv./Ir)]. The solutions were bubbled with oxygen whilst heated at 80 °C for 16 h and then analysed directly by gas chromatography. The %conversion refers to the number of moles of products relative to the number of moles of styrene added and was determined by comparison of the gas chromatograms of reaction mixtures with calibration curves for authentic samples of the products

Iridium complex	Added metal ion	Products	%Conversion
trans-[IrCl(CO)(PPh_3)$_2$]	—	benzaldehyde (54%), styrene oxide (42%), acetophenone (4%)	6.1
trans-[IrCl(CO)(L^3)$_2$]	—	no products	0
trans-[IrCl(CO)(L^3)$_2$]	Mn(II)	benzaldehyde	2.3
trans-[IrCl(CO)(L^3)$_2$]	Fe(II)	no products	0
trans-[IrCl(CO)(L^3)$_2$]	Co(II)	benzaldehyde	<0.2
trans-[IrCl(CO)(L^3)$_2$]	Ni(II)	benzaldehyde	0.9
trans-[IrCl(CO)(L^3)$_2$]	Cu(II)	benzaldehyde	5.3
trans-[IrCl(CO)(L^3)$_2$]	Zn(II)	benzaldehyde	24
—	—	benzaldehyde (90%), styrene oxide (10%)	19

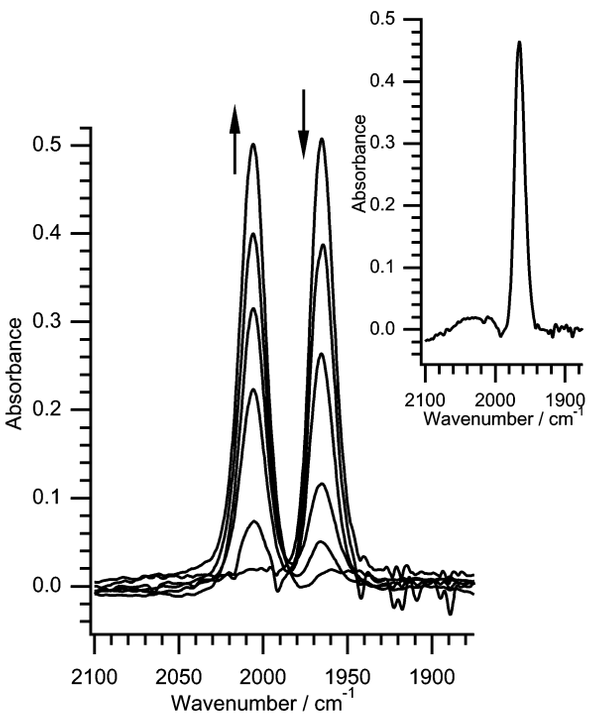


Fig. 6 FTIR spectra recorded at approx. 3 h intervals as a tetrahydrofuran solution of *trans*-[IrCl(CO)(L^3)$_2$] was bubbled with oxygen at 295 K showing conversion to *trans*-[IrCl(CO)(L^3)$_2$(O_2)]. Inset: the FTIR spectrum of the same solution after heating at reflux under nitrogen to regenerate *trans*-[IrCl(CO)(L^3)$_2$].

styrene oxide in proportions that depend on the exact conditions.[60–63] It has been shown that the reactions proceed by a radical process with the role of the Ir centre not to activate oxygen but to decompose organic peroxides and thereby initiate radical formation.[61,63] Since either *trans*-[IrCl(CO)(L^3)$_2$] or its metal adducts [formed *in situ* by adding $M(ClO_4)_2 \cdot 6H_2O$ (2 equivalents)] were not soluble in the solvents such as toluene, ethanol, acetic acid and dioxane that had been previously used for Ir-catalysed oxidations of styrene, we chose methylethyl ketone (MEK) as the solvent for its ability to keep all of the metal species used in this work in solution and because it is readily oxidised in air to the peroxide (MEKP), which is a reason for the extensive use of this solvent in radical-initiated polymerisations.[64] Reagents, reaction conditions and our results are summarised in Table 3. Despite the previous claims of solvent independence in Ir-catalysed styrene oxidations,[60–63] it is clear that this is not so[65] and that MEK is a solvent *par excellence* for this reaction and, moreover, that in MEK the metal complexes are inhibitors of the reaction. Perhaps most astonishing is the dependence of the inhibition on the metal ion added to *trans*-[IrCl(CO)(L^3)$_2$]. Since MEKP will form at constant rate under the identical conditions employed in the parallel reactions, the order of inhibition of styrene oxidation is: *trans*-[IrCl(CO)(L^3)$_2$] ≈ +Fe(II) ≈ +Co(II) (complete inhibition) ≥ +Ni(II) > +Mn(II) > +Cu(II) ≈ [IrCl(CO)(PPh_3)$_2$] ⩾ +Zn(II) (no inhibition; at least the same %conversion as with no metal) {where + (metal ion) indicates the metal ion added to *trans*-[IrCl(CO)(L^3)$_2$]}. The complete inhibition of styrene oxidation by *trans*-[IrCl(CO)(L^3)$_2$] may represent the ability of the N_3-donor domain in this complex to scavenge trace metal ion (*e.g.* Fe^{2+}) from glassware. At present we have no explanation for the distinct and interesting differences in %conversion and selectivity when [IrCl(CO)(PPh_3)$_2$] or [IrCl(CO)(L^3)$_2$] + $2Zn^{2+}$ are employed.

Summary and conclusions

Towards our goal of demonstrating co-operativity between metal centres in conjoint classical-organometallic heterometallic complexes we have prepared the new ligands L^1–L^4 with triphenylphosphine and bis(2-pyridylethyl)amine or triazacyclononane N_3-donor domains, and have undertaken preliminary studies of their co-ordination chemistry. We believe the research demonstrates the following:

1. Reductive amination is a convenient method for linking a phosphinobenzaldehyde and a secondary amine substituted with metal co-ordinating groups; it should prove to be a powerful, general route to a wide range of ditopic ligands with soft phosphine and hard N_n-metal-binding donor domains, including asymmetric examples from chiral amines. The major difficulty may be the synthesis of the appropriate phosphinobenzaldehyde.

2. The N_n-donor domains can be selectively protonated, which may facilitate purification and handling of the ligands.

3. Ligands with an *ortho*-benzyl "linker" such as L^1 and L^2 can act as $\kappa N_n,\kappa P$-chelate ligands supporting tetrahedral and square planar metal centres. Although not tested in this work, there are no geometrical constraints to these ligands forming square pyramidal and octahedral metal complexes. A rich $\kappa N_n,\kappa P$-chelate co-ordination chemistry is predicted.

4. The *meta*-benzyl "linker" (in L^3 and L^4) is sufficiently rigid to prevent the N_n- and *P*-domains from binding to the same metal ion. This control over co-ordination is not matched in those previous N_n,*P*-ligands with flexible alkyl "linkers".[14–16,18,19,20,23]

5. Mononuclear complexes in which the phosphine group is selectively bound to a soft metal leaving the N_n-donor domain dangling and metal-free are directly available by addition of a *meta*-substituted ligand such as L^3 or L^4 to a source of a softer metal ion. For the *ortho*-substituted ligands, L^1 and L^2, protonation (pH control) protects the N_n-donor domain, preventing $\kappa N_n,\kappa P$-chelate monomers from forming, and thereby enables the selective binding of the phosphine group to soft metals. The physical characteristics of these mononuclear complexes reflect those of their dangling N_3-donor domains: those

with the unprotonated N_3-donor domains tend to be oils and protonation may lead to more tractable compounds.

6. Addition of hard metal ions to the mononuclear complexes with dangling, metal-free N_3-donor domains (when these are protonated, with a weakly co-ordinating Brønsted base also added) affords the targeted hard-soft heteronuclear complexes. The heteronuclear complexes of the *meta*-substituted ligands, L^3 and L^4, were more stable than those of their analogues from the *ortho*-substituted ligands, L^1 and L^2, perhaps because decomposition pathways leading to $\kappa N_n,\kappa P$-chelate monomers are unavailable to the former heteronuclear complexes. The protection/deprotection of the N_n-donor domain by protonation/deprotonation under pH control route appears well suited to the combinatorial syntheses of libraries of heteronuclear complexes.

7. The available evidence for the heteronuclear complexes of *meta*-substituted L^3 and L^4 suggests that the hard and soft metal centres retain their individual reactivities and only weakly perturb each other's spectroscopic properties. That is not to say co-operative behaviour will not lead to new reactivitity beyond that for the individual metal centres: for example, the results for styrene oxidation, particularly those with $[IrCl(CO)(PPh_3)_2]$ added compared to $[IrCl(CO)(L^3)_2] + 2Zn^{2+}$ added, are intriguing in this regard. However, it remains to be definitely demonstrated that co-operativity between the metal centres in these or similar heteronuclear systems can result in new and advantageous reactivity for the complex as whole.

Experimental

Physical measurements

Elemental analyses for C, H and N were determined by the Australian National University Microanalytical Unit. Elemental ratios for Cu, Fe and S are calculated from inductively-coupled plasma-atomic emission spectroanalysis (ICP–AES) data. Samples for ICP–AES were prepared by digestion of the complex with 10% nitric acid overnight; the individual concentrations of P, Cu and/or Pt, in the samples were then simultaneously determined (to ±10%) using a GBC Integra ICP-AES instrument fitted with a 22-channel polychromator. Electrospray mass spectra (ES-MS) were acquired on a VG Quattro mass spectrometer with a capillary voltage of 4 kV and a cone voltage of 30 V. The solvent system was 50 : 50 acetonitrile–water with 1% acetic acid. MALDI-MS spectra were obtained at the Biomedical Mass Spectroscopy Centre, UNSW, using a Voyager DE-STR MALDI-time-of-flight mass spectrometer and samples in an α-cyano-4-hydroxycinnamic acid matrix. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AC 300F (300 MHz) or Bruker DPX (300 MHz) spectrometer. Molar conductivity measurements were made on ≈1 mM solutions of the complexes in MeCN or CH_2Cl_2 at 25 °C. The molar conductivity of the 1 : 1 electrolyte tetra-*n*-butylammonium hexafluorophosphate was determined to be 157 S cm^2 mol^{-1} in MeCN and 28 S cm^2 mol^{-1} in CH_2Cl_2 under these conditions. Electronic spectra of complexes were recorded between 200 and 1400 nm on a CARY 5 spectrometer in the dual beam mode (1 nm resolution); solution spectra were recorded in sealed 1 cm quartz cuvettes. EPR spectra of frozen solutions (at 77 K; liquid nitrogen dewar) were recorded using a Bruker EMX 10 EPR spectrometer ($\nu \approx 9.52$ GHz). Infrared spectra were recorded in the quoted solvents in a solution cell with CaF_2 windows using a Mattson Genesis FTIR spectrometer (± 1.0 cm^{-1} resolution).

Electrochemical measurements were recorded using a Pine Instrument Co. AFCBP1 Bipotentiostat interfaced to and controlled by a Pentium computer. For cyclic voltammetry measurements, a standard three electrode configuration was used with a quasi-reference electrode comprised of a commercial Ag–AgCl mini-reference electrode (Cyprus Systems, Inc. EE008) but filled with the same electrolyte solution as used in the experiment [rather than saturated AgCl in 3 M KCl(aq) solution], a freshly polished platinum disk (1 mm diameter) working electrode and a platinum wire as the auxiliary electrode. Solutions of the compounds were 1.0 mM in anhydrous acetonitrile (Aldrich, used as received) with 0.1 M $[NBu^n_4][PF_6]$. Solutions were de-oxygenated by bubbling with high purity nitrogen (pre-saturated with solvent) and then blanketed with a cover of nitrogen for the duration of the experiment. Data are reported from cyclic voltammograms recorded at a scan rate of 100 mV s^{-1}. The electrochemical potentials quoted are relative to the ferrocene–ferrocenium (Fc^+–Fc) couple measured under the same experimental conditions (same concentrations, solvent, support electrolyte, electrodes, temperature and scan rate). Controlled-potential electrolysis (coulometry) of $[Cu(L^1)][PF_6]$ was carried out in a conventional three-compartment "H"-cell adapted so that it could be loaded and sealed under an inert atmosphere (high purity nitrogen). An acetonitrile-filled Ag/AgCl quasi-reference electrode (the same as used in CV experiments) was placed in the working compartment along with the Pt gauze (5 × 2 cm^2) working electrode. The counter electrode was a Pt gauze (4 × 2 cm^2) and was separated from working compartment by two fine-porosity glass frits. During the electrolysis the potential of the working electrode was fixed at +0.60 V and the solution in the working compartment was stirred magnetically with a Teflon-coated stirring bar. Anhydrous acetonitrile (Aldrich) was used as the solvent, and the concentration of $[Cu(L^1)][PF_6]$ was 2.0 mM and the support electrolyte was 0.2 M $[NBu^n_4][PF_6]$.

Gas chromatographic analyses employed a Shimadzu GC-17A gas chromatograph equipped with a hydrogen flame ionisation detector interfaced to a Macintosh computer. The column used was an Alltech Econocap™ carbowax column, #19654, 30 m × 0.32 mm ID, FSOT, 0.25 micron. The carrier gas was nitrogen. The gas chromatograph settings used are given below.

Syntheses

Reactions were routinely carried out under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques. Dry solvents were obtained by routine distillations from the appropriate drying agent under nitrogen immediately prior to use: methanol and ethanol from magnesium turnings activated with iodine; thf, diethyl ether and toluene from sodium benzophenone ketyl; MeCN, CH_2Cl_2 and 1,2-dichloroethane from CaH_2; chloroform from P_2O_5; triethylamine from BaO; and dimethylformamide under reduced pressure from CaH_2. Styrene was purified before use by passage through a neutral alumina (Brockmann I) column (eluent: dichloromethane) and the solvent removed under vacuum. Flash chromatography was carried out using Merck silica gel 7730 $60GF_{254}$. Columns were packed with dry gel; solvent was applied to the column before a concentrated solution of the sample in the appropriate solvent. Table 1 of the ESI † presents ES-MS, NMR and IR data for the monomeric (diamagnetic) complexes. Partial elemental analyses, elemental ratios from ICP-AES, and EPR and electronic spectral data for the heteronuclear (paramagnetic) complexes are given in Table 2 of the ESI. †

The following substances were prepared according to methods in the literature: 2-(diphenylphosphino)benzaldehyde,[31] *N*,*N*-bis(2-pyridyl-2-ethyl)amine (bpea),[66] 1,4-diisopropyl-1,4,7-triazacyclononane (tacn*),[67] bis(benzonitrile)-platinum(II) dichloride,[68] *cis*-dicarbonylchloro(*p*-toluidine)-iridium(I),[69] pentacarbonyl(phenyl-2-carbaldehyde diphenylphosphine-κ*P*)tungsten[48] and tetrakis(acetonitrile)copper(I) hexafluorophosphate.[70]

Warning: Although no problems were encountered in this work, perchlorate salts of metal complexes are potentially explosive and should be treated with due care.

[2-(Diphenylphosphino)benzyl]-*N*,*N*-bis(2-pyridyl-2-ethyl)-amine, L^1. A solution of bpea (1.49 g, 6.56 mmol) and 2-diphenylphosphinobenzaldehyde (1.92 g, 6.56 mmol) in 1,2-dichloroethane (40 cm^3) was treated with solid sodium triacetoxyborohydride (2.21 g, 10.4 mmol). The mixture was stirred under nitrogen at room temperature for 18 h and then neutralised with a saturated aqueous solution of sodium hydrogen carbonate (20 cm^3). The organic phase was separated and the aqueous phase extracted with dichloromethane (2 × 20 cm^3). The combined organic extracts were dried with magnesium sulfate and concentrated to give crude L^1 as a thick orange oil (2.86 g), $\delta_P[(CD_3)_2CO]$ −14.23; $\delta_H[(CD_3)_2CO]$ 8.42 (2 H, d), 7.70–7.00 (18 H, m), 6.87 (2 H, t), 3.93 (2 H, d), 2.90–2.70 (8 H, m); *m*/*z* (ES-MS) 502 ($[HL^1]^+$).

Protonation of L^1: $[HL^1][PF_6]$. A solution of crude L^1 (0.83 g, 1.7 mmol) was dissolved in methanol (10 cm^3) and treated with an excess of ammonium hexafluorophosphate (4.2 g) in methanol (20 cm^3). The solution was stirred at room temperature for 5 h and the volume reduced to 25 cm^3 whereupon scratching of the flask resulted in immediate precipitation. The solution was cooled in a −15 °C freezer for 2 h to complete precipitation followed by filtration of the yellow powder (0.94 g, 87%). An analytically pure sample was obtained by recrystallisation from dichloromethane–diethyl ether, (Found: C, 59.58; H, 5.12; N, 6.36. $C_{33}H_{33}F_6N_3P_2\cdot H_2O$ requires C, 59.55; H, 5.30; N, 6.31%); $\delta_P[(CD_3)_2CO]$ −15.38 (s), −142.02 [sept, *J*(PF) 708 Hz]; $\delta_P(CDCl_3)$ −16.46 (s), −143.42 [sept, *J*(PF) 713 Hz]; $\delta_H[(CD_3)_2CO]$ 8.22 (2 H, d), 7.90–7.10 (19 H, m), 7.07 (1 H, t), 4.97 (2 H, s), 3.98 (4 H, t), 3.47 (4 H, t); $\delta_H(CDCl_3)$ 8.04 (2 H, d), 7.70–7.60 (3 H, m), 7.50–7.30 (8 H, m), 7.20 (2 H, d), 7.10 (6 H, m), 6.99 (1 H, m), 4.63 (2 H, s), 3.80 (4 H, t), 3.28 (4 H, t); *m*/*z* (ES-MS) 502 $\{[HL^1]^+\}$.

Protonation of L^1 with perchloric acid. A solution of L^1 (1.31 g, 2.61 mmol) in methanol (40 cm^3) was treated with perchloric acid (70%, 12 cm^3). The solution was stirred at room temperature for 2 h and then diluted with water (5 cm^3) until just cloudy. The solution was then cooled in a −15 °C freezer overnight and the white precipitate was collected by filtration, washed with diethyl ether and dried under vacuum (1.48 g), $\delta_P[(CD_3)_2CO]$ −16.87 (s); $\delta_H[(CD_3)_2CO]$ 9.00 (2 H, d), 8.73 (2 H, t), 8.18 (4 H, m), 7.92 (1 H, t), 7.70–7.50 (2 H, m), 7.39 (6 H, m), 7.27 (4 H, m), 7.16 (1 H, m), 5.18 (2 H, s), 4.21–4.09 (8 H, m); *m*/*z* (ES-MS) 502 $\{[HL^1]^+\}$. Subsequent reactions (see below) are consistent with the solid being $[H_nL^1](ClO_4)_n$ with $n \approx 3$. Recrystallisation of a small sample of $[H_nL^1](ClO_4)_n$ from methanol in air over a period of days gave colourless crystals of a phosphine oxide derivative, $[H_3L^1O](ClO_4)_3\cdot 3H_2O$, (Found: C, 45.60; H, 3.95; N, 4.84. $C_{33}H_{35}Cl_3N_3O_{13}P\cdot 3H_2O$ requires C, 45.40; H, 4.73; N, 4.81%); $\delta_P[(CD_3)_2CO]$ 40.74 (s); $\delta_H[(CD_3)_2CO]$ 9.00 (2 H, d), 8.68 (2 H, t), 8.21 (2 H, d), 8.13 (2 H, t), 8.04 (1 H, m), 7.87 (1 H, t), 7.78–67 (11 H, m), 7.32 (1 H, m), 4.82 (2 H, s), 4.11 (4 H, m), 3.92 (4 H, m); *m*/*z* (ES-MS) 518 $\{[HL^1O]^+\}$.

1-[2-(Diphenylphosphino)benzyl]-4,7-diisopropyl-1,4,7-triazacyclononane, L^2. Solid sodium triacetoxyborohydride (4.61 g, 21.8 mmol) was added to a stirred solution of tacn* (2.90 g, 13.6 mmol) and 2-diphenylphosphinobenzaldehyde (3.95 g, 13.6 mmol) in 1,2-dichloroethane (60 cm^3). The mixture was stirred under nitrogen for 24 h, and then neutralised with a saturated aqueous solution of sodium hydrogen carbonate (20 cm^3). The organic phase was separated and the aqueous phase further extracted with dichloromethane (2 × 40 cm^3). The combined organic extracts were dried with magnesium sulfate and the solvent removed to yield crude L^2 as a thick orange oil (5.32 g), $\delta_P(CDCl_3)$ −14.66 (s); $\delta_H(CDCl_3)$ 7.48 (1 H, m), 7.35–7.19 (8 H, m), 6.88 (1 H, m), 3.94 (2 H, d), 3.09 (2 H, t), 3.00 (4 H, s), 2.90 (8 H, s), 1.13 (12 H, d); *m*/*z* (ES-MS) 488 $\{[HL^2]^+\}$.

Protonation of L^2: $[HL^2][PF_6]$. A solution of L^2 (0.60 g, 1.2 mmol) in methanol (15 cm^3) was treated with a solution of ammonium hexafluorophosphate (2.0 g, 12 mmol) in methanol (10 cm^3). The solution was stirred at room temperature for 1 h and the white precipitate collected by filtration. Further product was obtained by concentration of the filtrate. The product was recrystallised from MeCN–diethyl ether to give a white powder (0.55 g, 72%), (Found: C, 57.91; H, 6.47; N, 6.60. $C_{31}H_{43}F_6N_3P_2\cdot 0.5H_2O$ requires C, 57.94; H, 6.90; N, 6.54%); $\delta_P(CDCl_3)$ −14.22 (s), −143.78 [sept, *J*(PF) 707 Hz]; $\delta_H(CDCl_3)$ 7.37–7.32 (8 H, m), 7.24–7.17 (5 H, m); 6.90–6.85 (1 H, m), 3.97 (2 H, d), 3.11 (2 H, sept), 3.00–2.93 (4 H, m), 2.79 (8 H, br s), 1.21 (6 H, d), 1.14 (6 H, d); *m*/*z* (ES-MS) 488 $\{[HL^2]^+\}$.

Preparation of 3-(diphenylphosphino)benzaldehyde. *(a) 2-(3-Bromophenyl)-1,3-dioxolane.* A solution of 3-bromobenzaldehyde (25.1 g, 0.136 mol), ethylene glycol (11.5 cm^3, 0.206 mol) and *p*-toluenesulfonic acid (0.14 g, 0.74 mmol) in toluene (150 cm^3) was heated at reflux for 45 h with the water produced by the reaction collected through the use of a Dean–Stark condenser. The solution was cooled and washed with a saturated aqueous solution of sodium hydrogen carbonate (50 cm^3) and then a saturated aqueous solution of sodium chloride (50 cm^3). The combined organic layers were dried with potassium carbonate, concentrated and distilled at 94–99 °C at 0.4 mmHg to give a yellow oil (25.1 g, 80%), $\delta_H(CDCl_3)$ 7.65 (1 H, s), 7.49 (1 H, d), 7.39 (1 H, d), 7.24 (1 H, t), 5.77 (1 H, s), 4.04 (4 H, m).

(b) [3-(1,3-Dioxolan-2-yl)phenyl]diphenylphosphine. A mixture of magnesium turnings (2.8 g, 0.12 mol) in thf (160 cm^3) was prepared in a 250 cm^3 flask equipped with a condenser and a dropping funnel under nitrogen. A crystal of iodine was added and the mixture was then slowly treated with a solution of 2-(3-bromophenyl)-1,3-dioxolane (25.0 g, 0.11 mol) in thf (30 cm^3) *via* the dropping funnel. The grey mixture was heated at reflux for 0.5 h and then cooled to room temperature (little magnesium remained). The mixture was then cooled in an ice bath and treated with a solution of chlorodiphenylphosphine (19.1 cm^3, 0.11 mmol) in thf (40 cm^3) *via* the dropping funnel over about 2 h with the temperature maintained below 5 °C. The solution was warmed to room temperature, heated at 40 °C for 3 h and then stirred under nitrogen for a further 11 h. The solution was then cooled to −10 °C and treated with a 40% aqueous solution of ammonium chloride. The organic layer was separated and the aqueous phase washed with diethyl ether (100 cm^3). The combined organic layers were dried with sodium sulfate and the solvent removed *in vacuo* to give a thick yellow oil (22.1 g, 61%), $\delta_P(CDCl_3)$ −4.44 (s); $\delta_H(CDCl_3)$ 7.90–7.40 (4 H, m), 7.40–7.00 (10 H, m), 5.75 (1 H, s), 4.04 (4 H, m).

(c) 3-(Diphenylphosphino)benzaldehyde. A solution of [3-(1,3-dioxolan-2-yl)phenyl]-diphenylphosphine (11.06 g, 33.1 mmol) and *p*-toluenesulfonic acid (0.5 g, 2.6 mmol) in toluene (250 cm^3) was heated at reflux for 16 h. The hot solution was diluted with water (50 cm^3) and allowed to cool. The organic layer was separated and the aqueous phase extracted with benzene (2 × 50 cm^3). The combined organic layers were dried with sodium sulfate and the solvent removed *in vacuo* to give a thick yellow oil (10.11 g), δ_P 31.99 (0.22), 31.64 (0.13), 29.90 (0.10), 28.76 (0.23), −4.36 (0.28), −4.47 (0.23), −4.79 (1.00). The oil was judged to be about 45% pure by ^{31}P NMR and was used "as is" in subsequent reactions. However, further purification of 2.00 g of the crude oil was achieved by flash chromatography [eluent: 60–80 °C petroleum ether–ethyl acetate (2 : 1)] to afford the product, a pale yellow oil (0.74 g), $\delta_P(CDCl_3)$ −4.80; $\delta_H(CDCl_3)$ 9.94 (1 H, s), 7.85 (1 H, d), 7.80 (1 H, d), 7.49 (2 H, m), 7.35 (10 H, m); *m*/*z* (ES-MS) 292 $\{[H(3\text{-}Ph_2PC_6H_4CHO)]^+\}$.

[3-(Diphenylphosphino)benzyl]-*N*,*N*-bis(2-pyridyl-2-ethyl)-amine, L^3. A solution of bpea (1.66 g, 7.27 mmol) and crude 3-diphenylphosphinobenzaldehyde (2.32 g, 8.00 mmol) in 1,2-dichloroethane (30 cm^3) was treated with solid sodium triacetoxyborohydride (2.47 g, 11.6 mmol). The mixture was stirred under nitrogen at room temperature for 19 h and then neutralised with a saturated aqueous solution of sodium hydrogen carbonate (20 cm^3). The organic phase was separated and the aqueous phase extracted with dichloromethane (2 × 20 cm^3). The combined organic extracts were dried with magnesium sulfate and concentrated to give crude L^3 as a thick orange oil. The crude oil was further purified by flash chromatography (eluent: ethyl acetate) giving L^3 as an orange oil (1.14 g, 31%), $\delta_P(CDCl_3)$ −4.50; $\delta_H(CDCl_3)$ 8.46 (2 H, d), 7.48 (2 H, t), 7.30–7.00 (16 H, m), 6.97 (2 H, d), 3.67 (2 H, s), 2.88 (8 H, s); *m*/*z* (ES-MS) 502 $\{[HL^1]^+\}$.

1-[3-(Diphenylphosphino)benzyl]-4,7-diisopropyl-1,4,7-triazacyclononane, L^4. Solid sodium triacetoxyborohydride (3.00 g, 14.1 mmol) was added to a stirred solution of tacn* (2.16 g, 10.1 mmol) and crude 3-diphenylphosphinobenzaldehyde (2.94 g, 10.1 mmol) in 1,2-dichloroethane (50 cm^3). The mixture was stirred under nitrogen for 17 h, and then neutralised with a saturated aqueous solution of sodium hydrogen carbonate (40 cm^3). The organic phase was separated and the aqueous phase further extracted with dichloromethane (6 × 20 cm^3). The combined organic extracts were dried with magnesium sulfate and the solvent removed to yield crude L^4 as a thick brown–red oil (4.70 g), $\delta_P(CDCl_3)$ −32.11 (0.19), −28.98 (0.12), −4.44 (0.33), −4.47 (0.33), −4.87 (1.00); $\delta_H(CDCl_3)$ 7.90–7.30 (4 H, m), 7.30–7.10 (9 H, m), 7.14 (1 H, t), 3.73 (2 H, s), 3.20–2.70 (14 H, m), 1.07 (12 H, t); *m*/*z* (ES-MS) 488 $\{[HL^4]^+\}$.

Protonation of L^4: $[HL^4][PF_6]$. A solution of ammonium hexafluorophosphate (1.8 g, 11 mmol) in methanol (10 cm^3) was added to a stirred solution of L^4 (0.50 g, 1.0 mmol) in methanol (10 cm^3). After stirring for 2 h at room temperature, water (2 cm^3) was added and the solution cooled in a −15 °C freezer overnight. The orange solid was collected by filtration and washed with a small amount of diethyl ether, (0.40 g), $\delta_P(CDCl_3)$ −4.86 (s), −143.59 [sept, *J*(PF) 712 Hz]; $\delta_H(CDCl_3)$ 7.50–7.20 (13 H, m), 7.16 (1 H, t), 3.74 (2 H, s), 3.10–2.80 (6 H, m), 2.80–2.60 (6 H, m), 1.08 (12 H, t); *m*/*z* (ES-MS) 488 $\{[HL^4]^+\}$. Subsequent reactions (see below) are consistent with the solid being $[HL^4][PF_6]$.

Benzyl{*N*,*N*-bis(2-pyridyl-2-ethyl)amine} (Bzbpea). The synthesis of this ligand has previously been reported by Karlin *et al.*[71] In this work, an alternative synthetic method was adopted. A solution of bpea (0.121 g, 0.533 mmol), benzaldehyde (0.057 g, 0.53 mmol) and glacial acetic acid (0.048 g, 0.80 mmol) in 1,2-dichloroethane (10 cm^3) was treated with solid sodium triacetoxyborohydride (0.181 g, 0.850 mmol). The mixture was stirred at room temperature for 19 h and then neutralised with a saturated aqueous solution of sodium hydrogen carbonate (10 cm^3). The organic phase was separated and the aqueous phase extracted with dichloromethane (2 × 20 cm^3). The combined organic extracts were dried with magnesium sulfate and concentrated to give a thick orange oil (0.145 g, 86%), $\delta_H(CDCl_3)$ 8.46 (2 H, d), 7.51 (2 H, t), 7.40–6.90 (9 H, m), 3.70 (2 H, s), 2.93 (8 H, s); *m*/*z* (ES-MS) 318 $\{[HL^5]^+\}$. Lit.:[71] $\delta_H(CDCl_3)$ 8.35 (2 H, br d), 7.40–6.70 (11 H, br m), 3.60 (2 H, br s), 2.85 (8 H, br s).

$[Cu(L^1)][PF_6]$. A solution of $[HL^1][PF_6]$ (0.086 g, 0.13 mmol) in dichloromethane (5 cm^3) was added to a solution of $[Cu(MeCN)_4][PF_6]$ (0.050 g, 0.13 mmol) in dichloromethane (5 cm^3). The solution immediately turned cloudy and stirring was continued for 4 h. The solvent was removed and the crude yellow–green powder was dissolved in MeCN (5 cm^3) which was allowed to slowly evaporate overnight (to 1 cm^3) yielding yellow microcrystals which were collected by filtration (0.046 g, 49%), (Found: C, 55.25; H, 4.89; N, 5.80. $C_{33}H_{32}CuF_6N_3P_2 \cdot 0.5H_2O$ requires C, 55.16; H, 4.56; N, 5.85%). A small portion of the sample was recrystallised from MeCN–diethyl ether to yield colourless crystals suitable for X-ray analysis.

$[Cu(L^2)][PF_6]$. A solution of $[HL^2][PF_6]$ (0.287 g, 0.454 mmol) and $[Cu(CH_3CN)_4][PF_6]$ (0.169 g, 0.454 mmol) in dichloromethane (20 cm^3) were stirred under nitrogen for 16 h. The light yellow solution was concentrated to 10 cm^3 and precipitated with diethyl ether to give a white powder (0.270 g, 86%), (Found: C, 52.62; H, 6.41; N, 6.10. $C_{31}H_{42}CuF_6N_3P_2 \cdot 0.5H_2O$ requires C, 52.80; H, 6.15; N, 5.96%). A small portion of the sample was recrystallised from MeCN–diethyl ether to yield colourless crystals suitable for X-ray analysis.[24]

$[ZnCl(L^2)][PF_6]$. Solid zinc dichloride was added to a stirred solution of crude L^2 (0.155 g, 0.318 mmol) in ethanol (25 cm^3). The solution was warmed gently to get all of the reactants into solution following which solid ammonium hexafluorophosphate (0.207 g, 1.27 mmol) was added and the solution allowed to stir at room temperature for 3 h. The solution was cooled in a −15 °C freezer and the off white precipitate that formed collected by filtration (0.163 g, 70%), (Found: C, 49.86; H, 6.32; N, 5.78. $C_{31}H_{42}ClF_6N_3P_2Zn \cdot H_2O$ requires C, 49.54; H, 5.90; N, 5.59%).

$[PtCl(L^1)][PF_6]$. A solution of $[PtCl_2(PhCN)_2]$ (0.095 g, 0.20 mmol) in 1,2-dichloroethane (10 cm^3) was treated dropwise with a solution of $[HL^1][PF_6]$ (0.130 g, 0.20 mmol) and triethylamine (0.020 g, 0.20 mmol) in 1,2-dichloroethane (10 cm^3). The solution was heated at reflux for 3 h, then cooled and a yellow powder precipitated by the addition of diethyl ether. The powder was recrystallised from MeCN–diethyl ether to give yellow microcrystals, (0.076 g, 43%), (Found: C, 45.38; H, 3.41 N; 4.68. $C_{33}H_{32}ClF_6N_3PPt$ requires C, 45.19; H, 3.68; N, 4.79%). A second recrystallisation of a small portion of the sample from MeCN–diethyl ether yielded colourless crystals suitable for X-ray analysis.

$[PtCl(L^2)][PF_6]$. A solution of $[PtCl_2(PhCN)_2]$ (0.048 g, 0.10 mmol) in 1,2-dichloroethane (5 cm^3) was treated with a solution of $[HL^2][PF_6]$ (0.064 g, 0.10 mmol) in 1,2-dichloroethane (5 cm^3) and triethylamine (0.014 cm^3, 0.10 mmol). The solution was heated at reflux for 2 h. The solvent was removed under vacuum and redissolved in dichloromethane. Layering of the solution with *n*-pentane gave a sticky yellow solid (0.110 g).

***trans*-$[PtCl_2(H_3L^1)_2][ClO_4]_6$.** A solution of $[H_nL^1][ClO_4]_n$ (0.706 g, 0.880 mmol if $n = 3$) in MeCN (20 cm^3) was treated with a solution of $[PtCl_2(PhCN)_2]$ (0.238 g, 0.503 mmol) in MeCN (40 cm^3) and stirred at room temperature for 4.5 h. The solvent was removed *in vacuo* and the crude oil dissolved in a solution of MeCN (5 cm^3), methanol (30 cm^3) and diethyl ether (5 cm^3) which was cooled in a −15 °C freezer overnight to give $[PtCl_2(H_3L^1)_2][ClO_4]_6$ as a yellow microcrystalline solid (0.800 g, 85% based on Pt). An analytically pure sample was obtained by recrystallisation from acetone–dichloromethane, (Found: C, 42.21; H, 3.89; N, 4.19. $C_{66}H_{70}Cl_8N_6O_{24}P_2Pt \cdot 4H_2O$ requires C, 42.12; H, 4.18; N, 4.47%).

***trans*-$[PtCl_2(HL^2)_2][PF_6]_2$.** A solution of $[PtCl_2(PhCN)_2]$ (0.30 g, 0.63 mmol) in dichloromethane (25 cm^3) was added to a solution of $[HL^2][PF_6]$ (0.80 g, 1.3 mmol) in dichloromethane (25 cm^3). The solution was stirred at room temperature for 3 h, concentrated to 25 cm^3, layered with diethyl ether (10 cm^3) and allowed to stand in a −15 °C freezer overnight. The yellow microcrystalline solid was collected by filtration and washed with diethyl ether, (0.84 g, 87%), (Found: C, 48.07; H, 5.33; N,

5.13. $C_{62}H_{86}Cl_2F_{12}N_6P_4Pt\cdot H_2O$ requires C, 48.06; H, 5.72; N, 5.42%).

***cis*-[PtCl$_2$(L^3)$_2$].** A solution of L^3 (0.270 g, 0.539 mmol) in dichloromethane (20 cm^3) was treated with a solution of [PtCl$_2$(PhCN)$_2$] (0.121 g, 0.257 mmol) in dichloromethane (10 cm^3) and stirred at room temperature overnight by which time the *trans*-isomer [δ_P(dichloromethane) 21.61 {s, *J*(PPt) 2632 Hz}] had all been converted to the *cis*-isomer as evidenced by $^{31}P\{^1H\}$ NMR. Addition of diethyl ether to the cooled solution gave a sticky yellow powder which was washed with diethyl ether and dried under vacuum (0.182 g, 56%).

***trans*-[PtCl$_2$(HL^4)$_2$][PF$_6$]$_2$.** A solution of [PtCl$_2$(PhCN)$_2$] (0.049 g, 0.10 mmol) in dichloromethane (5 cm^3) was added to a solution of [HL^4][PF$_6$] (0.130 g, 0.21 mmol) in dichloromethane (10 cm^3). The solution was stirred at room temperature for 2 h and the solvent removed under vacuum. The resultant orange oil was washed with *n*-pentane and then dried *in vacuo* to give a sticky yellow solid (0.130 g). Although clearly contaminated by excess benzonitrile (≈20%), no additional resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum and the product was of sufficient purity for further reactions.

***trans*-[IrCl(CO)(L^3)$_2$].** A solution of *cis*-[IrCl(CO)$_2$(*p*-toluidine)] (0.187 g, 0.506 mmol) in deoxygenated thf (10 cm^3) was added to a stirred solution of L^3 (0.533 g, 1.06 mmol) in deoxygenated thf (10 cm^3). The red–brown solution was stirred under nitrogen for 2 h whereupon its IR spectrum revealed the complete disappearance of carbonyl peaks for the starting complex: ν_{CO}/cm^{-1} 1967s, 1928s (thf); δ_P(thf) 25.19 (0.01, s), 21.78 (1.00, br), 4.86 (0.01, s). The solvent was removed *in vacuo*. In order to remove the *p*-toluidine (bp 200 °C at 760 mmHg), the oil was redissolved in thf (10 cm^3) and the solvent again removed under high vacuum (0.01 mmHg) to give a thick orange oil (0.626 g, 98%), which contained only a trace amount of *p*-toluidine (≈ 0.2%) as judged by the ^{1}H NMR spectrum; *m*/*z* (MALDI-MS) for $C_{67}H_{65}ClIrN_6OP_2$ $(MH)^+$, calc. 1259.89, found 1259.86; for $C_{67}H_{64}IrN_6OP_2$ $(M–Cl)^+$, calc. 1223.43, found 1223.32.

Pentacarbonyl(phenyl-3-carbaldehyde diphenylphosphine-κP)tungsten. A solution of tungsten hexacarbonyl (1.99 g, 5.67 mmol) in thf (160 cm^3) was stirred at room temperature in a flask fitted with a quartz cased mercury UV lamp. The solution was photolysed for 2 h whilst being bubbled with nitrogen. This solution was then added *via* a cannula to a solution of crude 3-diphenylphosphinobenzaldehyde (1.83 g) in thf (50 cm^3) and the yellow solution stirred under nitrogen overnight. The solvent was removed under vacuum and the resultant yellow oil purified twice by flash chromatography [eluent: 60–80 °C petroleum ether–dichloromethane (3 : 7) then 60–80 °C petroleum ether–dichloromethane (6 : 4)] to give a thick orange oil (1.07 g, 31% based on W), ν_{CO}/cm^{-1} 2072m, 1984w, 1941vs (chloroform); $\delta_P(CDCl_3)$ 22.16 [s, *J*(PW) 246 Hz]; $\delta_H(CDCl_3)$ 9.98 (1 H, s), 7.94 (2 H, m), 7.72 (1 H, m), 7.63 (1 H, m), 7.47 (10 H, m); *m*/*z* (EI-MS) 614 (M^+), 586 (M − CO), 558 (M − 2CO), 530 (M − 3CO), 502 (M − 4CO), 474 (M − 5CO).

[W^0(CO)$_5$(L^3)]. Solid sodium triacetoxyborohydride (0.238 g, 1.12 mmol) was added to a stirred solution of bpea (0.159 g, 0.700mmol)andpentacarbonyl(phenyl-3-carbaldehydediphenylphosphine-κP)tungsten (0.430 g, 0.700 mmol) in 1,2-dichloroethane (15 cm^3). The mixture was stirred under nitrogen for 22 h and then neutralised with a saturated aqueous solution of sodium hydrogen carbonate (10 cm^3). The organic phase was separated and the aqueous phase extracted with dichloromethane (3 × 10 cm^3). The combined organic extracts were dried with magnesium sulfate, filtered and the solvent removed *in vacuo* to give an orange oil. The crude product was purified by flash chromatography (eluent: ethyl acetate) to give an orange oil (0.213 g, 37%); *m*/*z* (MALDI-MS) for $C_{38}H_{32}N_3O_5$-PW (MH^+), calc. 826.50, found 826.99.

[CuCl$_2$(Bzbpea)]. A solution of Bzbpea (0.027 g, 0.085 mmol) in methanol (5 cm^3) was treated with a solution of $CuCl_2\cdot 2H_2O$ in methanol (2 cm^3) and the dark green solution was stirred for 2 h. Addition of diethyl ether (15 cm^3) and cooling in a −15 °C freezer overnight resulted in the formation of blue–green needles which were collected by filtration, washed with diethyl ether and dried under vacuum (0.023 g, 60%), (Found: C, 53.27; H, 5.56; N, 8.45. $C_{21}H_{23}Cl_2CuN_3\cdot H_2O$ requires C, 53.68; H, 5.36; N, 8.94%); λ_{max}/nm (ε/M^{-1} cm^{-1}) (chloroform) 778 (68), 987 (52); EPR (chloroform, 77 K): $g_{||}$ 2.22 ($A_{||}$ 127 G), $g_\perp$ 2.12; *m*/*z* (ES-MS) 439 {[Cu(OAc)(Bzbpea)]$^{2+}$} (Note: the acetate anion observed in the ES mass spectrum is due to exchange between the chloride ligand of the complex and acetic acid in the feed solvent used).

[PtCl$_2${(L^1)Cu(OAc)}$_2$][ClO$_4$]$_2$. A solution of *trans*-[PtCl$_2$(H$_3$L^1)$_2$](ClO$_4$)$_6$ (0.0528 g, 0.028 mmol) in MeCN (10 cm^3) was treated with triethylamine (0.017 g, 0.17 mmol) and then stirred at room temperature for 40 min by which time a cloudy precipitate had formed. The mixture was then diluted with MeCN (5 cm^3) and ethanol (5 cm^3). The cloudy solution was then treated with a solution of [Cu$_2$(OAc)$_4$(H$_2$O)$_2$] (0.0112 g, 0.028 mmol) in MeCN (5 cm^3). After 6 h stirring at room temperature the solution remained slightly cloudy and stirring was therefore continued overnight resulting in a clear, light green solution. The solution was then concentrated to 8 cm^3 and diluted with diethyl ether (2 cm^3) until just cloudy. This cloudy solution was then warmed gently to give a clear, green solution which upon standing in a −15 °C freezer overnight resulted in light green microcrystals which were collected by filtration, (0.030 g, 62%).

[PtCl$_2${(L^2)Cu(OAc)}$_2$][PF$_6$]$_2$. A solution of [Cu$_2$(OAc)$_4$(H$_2$O)$_2$] (0.095 g, 0.24 mmol) in MeCN (20 cm^3) was added to a stirred solution of *trans*-[PtCl$_2$(HL^2)$_2$][PF$_6$]$_2$ (0.37 g, 0.24 mmol) and triethylamine (0.066 cm^3, 0.48 mmol) in MeCN (20 cm^3). The green solution was allowed to stir at room temperature for 24 h and a green powder was precipitated by the addition of diethyl ether. The powder was recrystallised from MeCN–diethyl ether to give a light green powder, (0.24 g, 56%); *m*/*z* (ES-MS) 743 {[PtCl$_2${(L^2)Cu(OAc)}$_2$]$^{2+}$}.

[PtCl$_2${(L^3)CuCl$_2$}$_2$]. A warm solution of *cis*-[PtCl$_2$(L^3)$_2$] (0.048 g, 0.038 mmol) in thf (30 cm^3) was treated with a solution of $CuCl_2\cdot 2H_2O$ (0.012 g, 0.072 mmol) in thf (4 cm^3). This resulted in the immediate formation of a precipitate and stirring was continued for a further 1 h. The light green precipitate was collected by filtration and washed with diethyl ether (0.043 g, 78% based on Cu).

[PtCl$_2${(L^4)Cu(OAc)}$_2$][PF$_6$]$_2$. A solution of *trans*-[PtCl$_2$(HL^4)$_2$][PF$_6$]$_2$ (0.130 g, 0.085 mmol) in MeCN (10 cm^3) was treated with triethylamine (0.024 cm^3, 0.09 mmol) and a solution of [Cu$_2$(OAc)$_4$(H$_2$O)$_2$] (0.034 g, 0.085 mmol) in MeCN (20 cm^3). The solution was stirred at room temperature for 1.5 h and the solvent was removed *in vacuo*. The remaining green oil was dissolved in dichloromethane (5 cm^3). The solution was layered with diethyl ether and allowed to stand resulting in the formation of a brown–green precipitate which was collected by filtration (0.083 g, 55%). An analytically pure sample was obtained by slow evaporation of a methanol–ethanol solution.

***mer*-[IrCl$_3$(CO){(L^3)CuCl$_2$}$_2$].** A solution of $CuCl_2\cdot 2H_2O$ (0.016 g, 0.095 mmol) in deoxygenated thf (10 cm^3) was added *via* a cannula to a solution of [IrCl(CO)(L^3)$_2$] (0.066 g, 0.053 mmol) in deoxygenated thf (15 cm^3). The solution was stirred under nitrogen and began to turn cloudy within 5 min. Stirring

Table 4 Numerical crystal and refinement data for the X-ray crystal structures

Complex	$[Cu(L^1)][PF_6]$	$[PtCl(L^1)][PF_6]$
Formula (sum)	$C_{33}H_{32}CuF_6N_3P_2$	$C_{33}H_{32}ClF_6N_3P_2Pt$
M	710.1	877.1
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	10.979(7)	18.910(3)
b/Å	11.717(7)	10.098(1)
c/Å	13.848(11)	19.429(3)
α/°	71.18(6)	90
β/°	78.57(5)	118.93(1)
γ/°	70.04(6)	90
V/Å^3	1577(2)	3247.1(8)
Z	2	4
μ/cm^{-1} (Cu-Kα)	24.98	104.7
Reflections collected	4680	6341
R_{merge} (no. of equiv. reflections)	0.039 (3)	0.020 (192)
Observed reflections [$I/\sigma(I) > 3$]	2879	5250
No. of parameters	298	288
Observed reflections/no. parameters	9.7	18.3
Final R, R_w [$I/\sigma(I) > 3$]	0.042, 0.057	0.027, 0.043
Goodness-of-fit	1.85	1.64
Max., min. peaks in final difference map/e Å^{-3}	0.74, −0.80	1.58, −0.93

was continued for 2 h and the cloudy mixture was left in a −15 °C freezer overnight. The green–brown powder was collected by filtration. Additional product (which gave identical IR and electronic spectra) was obtained by concentration of the filtrate and layering with diethyl ether (0.038 g, 47%); ν_{CO}/cm^{-1} 2074s (chloroform).

$[IrCl(CO)(O_2)(L^3)_2]$. A solution of *trans*-$[IrCl(CO)(L^3)_2]$ (0.048 g, 0.038 mmol) in thf (10 cm^3) was bubbled with oxygen and the IR spectrum recorded at various intervals over a 24 h period. After 24 h almost the entire product had been converted to the dioxygen adduct, $[IrCl(CO)(O_2)(L^3)_2]$, as judged by IR and $^{31}P\{^1H\}$ NMR spectroscopy: ν_{CO}/cm^{-1} 2006s (thf); δ_P(thf) 27.38 (0.04, s), 25.72 (0.06, s), 25.65 (0.03, s), 25.36 (0.03, s), 4.96 (1.00, s); *m*/*z* (ES-MS) 1291.0 ($[IrCl(CO)(O_2)(HL^3)_2]^{2+}$). The solution was then heated at reflux under nitrogen for 2.5 h to cleanly regenerate the starting complex as judged by IR and $^{31}P\{^1H\}$ NMR spectroscopy.

Metal ion sensing experiment with $[W^0(CO)_5(L^3)]$

Separate aliquots (0.15 cm^3 each) of a 1.00 mM solution of $[W^0(CO)_5(L^3)]$ (0.0207 g, 0.0251 mmol) in thf (25.0 cm^3) were treated with an approximately 10 fold molar excess of solid $M(ClO_4)_2{\cdot}6H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn). The IR spectra of the solutions before and after the addition of the metal ions were recorded and the results are summarised in ESI Table 3 and ESI Fig. 6.†

Styrene oxidations

In a typical reaction, a measured aliquot (≈150 × 10^{-3} cm^{-3}) of freshly purified styrene was added to a solution of *trans*-$[IrCl(CO)(L^3)_2]$ in the solvent (2 cm^3) and the solution was bubbled with oxygen using a glass pipette whilst being heated at 80 °C for 16 h. The solution was sampled at various time intervals and an aliquot (1 × 10^{-3} cm^3) injected directly into the gas chromatograph. Reactions with heterometallic catalysts involved the addition of a solution (2 cm^3) containing two molar equivalents (with respect to the iridium complex) of the added metal ions [as the perchlorate salt $\{M(ClO_4)_2{\cdot}6H_2O\}$]. For some reactions *o*-dichlorobenzene (50 × 10^{-3} cm^3) was added after the completion of the reaction as an internal standard.

The following gas chromatograph settings were used: column temperature: 115 °C, injector temperature: 200 °C, detector temperature: 200 °C, column inlet pressure: 42 kPa, total flow rate: 42 cm^3 min^{-1}, split ratio: (1 :) 43, range: 0. Under these conditions the following retention times were observed for authentic samples: thf (2.5 min), MEK (2.5 min), toluene (2.6 min), MeCN (2.6 min), styrene (3.0 min,), *o*-dichlorobenzene (4.3 min), benzaldehyde (4.8 min,), styrene oxide (5.9 min), acetophenone (6.7 min). The results of the styrene oxidation reactions are summarised in Table 3.

X-Ray crystallography

Relevant crystal and refinement data are collected in Table 4.

CCDC reference numbers 179667 and 179668.

See http://www.rsc.org/suppdata/dt/b2/b201720m/ for crystallographic data in CIF or other electronic format.

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