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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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Electronic Supplementary Information

ESI Table 1. ES-MS, 300 MHz ^{1}H NMR and 121 MHz ^{31}P{^{1}H} NMR data for the mononuclear complexes.

Complex	Positive-ion ES-MS *m/z* found[a] (*m/z* calcd[a]) [ion]$^{z+}$	^{1}H NMR solvent: δ_H	^{31}P{^{1}H} NMR solvent; δ_P (J_{PX}/Hz)
$[Cu(L^1)][PF_6]$	564.0 (564.0) $[Cu(L^1)]^+$	$(CD_3)_2CO$: 8.85 (2 H, br s), 7.94 (2 H, t), 7.61 (1 H, t), 7.60–7.35 (12 H, m), 7.30–7.20 (4 H, m), 6.92 (1 H, t), 3.91 (2 H, s), 3.10–2.50 (8 H, m)	$(CD_3)_2CO$: –10 (br s; fwhh = 1600 Hz), –142.03 (J_{PF} 707)
$[Cu(L^2)][PF_6]$	550.0 (550.0) $[Cu(L^2)]^+$	$(CD_3)_2CO$: 7.65–7.50 (8 H, m), 7.50–7.45 (5 H, m), 6.94 (1 H, t), 3.88 (2 H, s), 3.39 (2 H, sept), 3.15–2.55 (12 H, m), 1.47 (6 H, d), 1.13 (6 H, d)	$(CD_3)_2CO$: –0.3 (br s; fwhh = 700 Hz), –142.00 (J_{PF} 707)
$[ZnCl(L^2)][PF_6]$	588.0 (588.0) $[ZnCl(L^2)]^+$	$CDCl_3$: 7.63 (1 H, m), 7.55–7.32 (12 H, m), 6.99 (1 H, t), 4.14 (2 H, s), 3.51 (2 H, sept), 3.25–3.10 (2 H, m), 3.03 (6 H, m), 2.95–2.70 (4 H, m), 1.25 (6 H, d), 1.21 (6 H, d)	$CDCl_3$: –17.71 (s), –143.76 (J_{PF} 707)
$[PtCl(L^1)][PF_6]$	732.0 (732.0) $[PtCl(L^1)]^+$	$(CD_3)_2CO$: 8.67 (2 H, br s), 8.20–7.20 (18 H, br m), 7.07 (2 H, t), 4.76 (2 H, br m), 3.95 (2 H, br s), 3.29 (6 H, br m)	$(CD_3)_2CO$: –0.78 (J_{PPt} 3624), –142.03 (J_{PF} 707)
$[PtCl(L^2)][PF_6]$	718.0 (718.0) $[PtCl(L^1)]^+$	$CDCl_3$: 7.81 (2 H, t), 7.70–7.30 (48 H, m), 6.88 (2 H, t), 4.50–3.30 (16 H, m), 3.30–2.80 (26 H, m), 1.20 (14 H, d), 0.9 (10 H, m)	$CDCl_3$: –0.71 (J_{PPt} 3752), –143.50 (J_{PF} 707)
trans-$[PtCl_2(H_3L^1)_2](ClO_4)_6$	1369.0 (1369.0) $[PtCl_2(HL^1)_2 + ClO_4]^+$, 635.0 [b] (635.0) $[PtCl_2(HL^1)_2]^{2+}$	$CDCl_3$: 8.98 (4 H, d), 8.74 (4 H, t), 8.21 (4 H, t), 8.10–7.00 (32 H, m), 5.05 (4 H, s), 3.58 (16 H, m)	$CDCl_3$: 18.42 (J_{PPt} 2567)
trans-$[PtCl_2(HL^2)_2][PF_6]_2$	1387.0 (1387.0) $[PtCl_2(HL^2)_2 + PF_6]^+$, 621.0 [b] (621.0) $[PtCl_2(HL^2)_2]^{2+}$	$(CD_3)_2CO$: 7.95–7.75 (10 H, m), 7.65–7.45 (14 H, m), 7.29 (2 H, t), 7.09 (2 H, q), 4.50 (4 H, s), 3.35 (4 H, sept), 3.27 (4 H, m), 3.10–2.60 (20 H, m), 1.30 (12 H, d), 1.18 (12 H, d)	$(CD_3)_2CO$: 15.44 (J_{PPt} 2597), –142.05 (J_{PF} 707)
cis-$[PtCl_2(L^3)_2]$	1235.0 (1235.0) $[PtCl(L^3)_2]^+$, 617.5 [b] (617.5) $[PtCl(HL^3)_2]^{2+}$	$CDCl_3$: 8.44 (4 H, d), 7.70–6.90 (40 H, br m), 3.55 (4 H, s), 2.86 (16 H, s)	$CDCl_3$: 15.03 (J_{PPt} 3674)

ESI Table 1 *continues on the next page…..*

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Complex	Positive-ion ES-MS[a] *m/z* found[a] (*m/z* calcd[a]) [ion]$^{z+}$	^{1}H NMR solvent: δ_H	^{31}P{^{1}H} NMR solvent; δ_P (J_{PX}/Hz)
trans-$[PtCl_2(HL^4)_2][PF_6]_2$	621.0 [b] (621.0) $[PtCl_2(HL^4)_2]^{2+}$	$(CD_3)_2CO$: 8.10 (2 H, m), 7.90–7.60 (20 H, m), 7.60–7.20 (32 H, m), 3.92 (4 H, s), 3.56 (2 H, q), 3.39 (2 H, q), 3.13 (12 H, m), 2.89 (16 H, m), 2.73 (10 H, m), 1.09 (24 H) — includes peaks for significant benzonitrile contaminant (≈20 %)	$(CD_3)_2CO$: 22.93 (J_{PPt} 2643), –142.04 (J_{PF} 707)
trans-$[IrCl(CO)(L^3)_2]$ [c]	630.0 [b] (630.0) $[IrCl(CO)(L^3)_2]^{2+}$	$CDCl_3$: 8.45 (4 H, d), 7.66 (10 H, br s), 7.53 (2 H, br s), 7.40 (4 H, t), 7.35–7.30 (12 H, m), 7.25–7.20 (4 H, m), 7.00 (4 H, t), 6.94 (4 H, d), 6.60 (0.001 H, d), 3.66 (4 H, s), 2.84 (16 H, s) — includes peaks for trace *p*-toluidine (≈ 0.2%)	$CDCl_3$: 24.68; thf: 25.55
$[W(CO)_5(L^3)]$ [d]	825.0 (825.0) $[W(CO)_5(HL^3)]^{+}$	$CDCl_3$: 8.45 (2 H, d), 7.60–7.35 (12 H, m), 7.26 (4 H, m), 7.08 (2 H, m), 6.98 (2 H, d), 3.73 (2 H, s), 2.90 (8 H, s)	$CDCl_3$: 21.49 (J_{PW} 243)

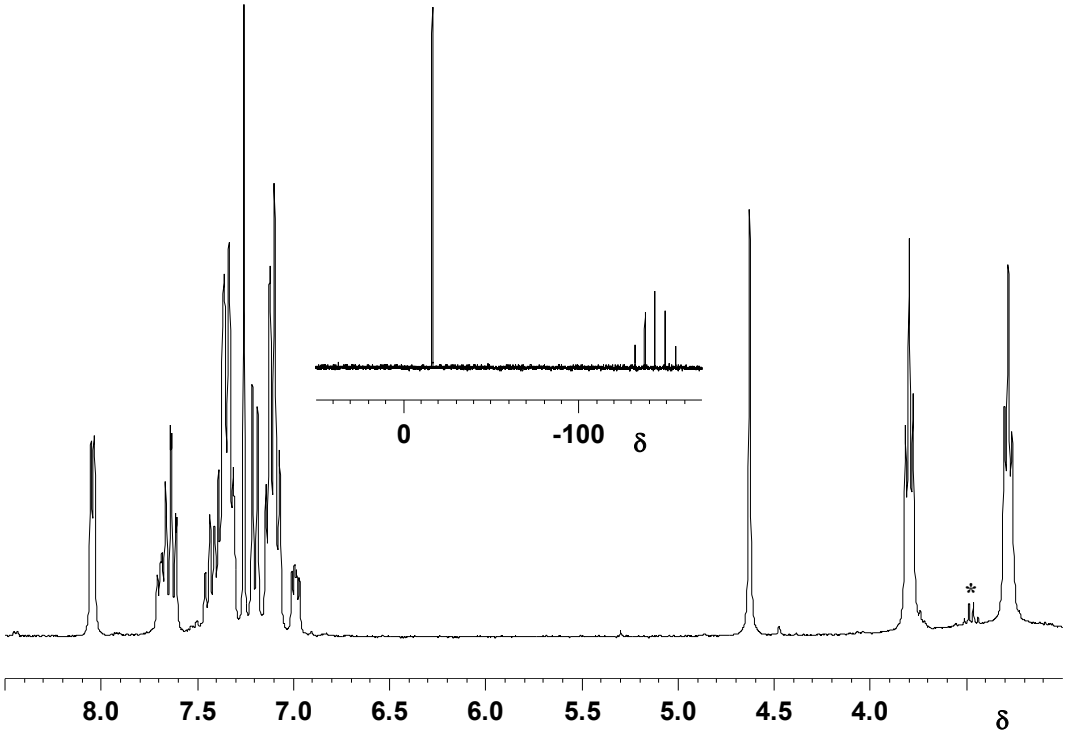
[a] Peak for the most abundant isotopomer of each ion. [b] Half-integer spacing between isotopomer peaks for ion observed.
[c] IR: ν_{CO} (thf) 1965s cm^{-1}. [d] IR: ν_{CO} ($CDCl_3$) 2071m, 1983w, 1939vs cm^{-1}.

Complex	Partial EA data (%)			ICP-AES element ratios [a]			X-Band EPR (77 K)			*d*–*d* Bands (400–1400 nm)
	C	H	N	Cu	Pt	P	$g_{\|\|}$	$A_{\|\|}$/G	$g_{\perp}$	λ_{max}/nm (ε/M^{-1} cm^{-1})
$[PtCl_2\{(L^1)Cu(OAc)\}_2](ClO_4)_2$ [b]	49.11	4.44	5.15	2.1	1.0	2.7	2.26	166	2.06	664 (300)
	(49.07)	(4.12)	(4.91)	(2)	(1)	(2)				
$[PtCl_2\{(L^2)Cu(OAc)\}_2][PF_6]_2\cdot H_2O$ [b]	44.08	4.99	4.43	2.2	1.0	4.0	2.25	164	2.07	661 (80), 1081 (20)
	(44.17)	(5.17)	(4.68)	(2)	(1)	(4)				
$[PtCl_2\{(L^4)Cu(OAc)\}_2][PF_6]_2$ [b]	45.71	5.18	5.06	1.7	1.0	4.1	2.26	160	2.07	647 (60), 1072 (40)
	(44.62)	(5.11)	(4.73)	(2)	(1)	(4)				
$[PtCl_2\{(L^3)CuCl_2\}_2]\cdot 3H_2O$ [c]	49.61	4.25	5.16	2.6	1.0	2.2	2.23	121	2.10	776 (190), 988 (140)
	(49.79)	(4.43)	(5.28)	(2)	(1)	(2)				
$[IrCl(CO)\{(L^3)CuCl_2\}_2]\cdot 6H_2O$ [c]	47.24	3.96	4.82		*d*		2.23	125	2.10	771 (160), 988 (120)
	(47.15)	(4.49)	(4.92)							

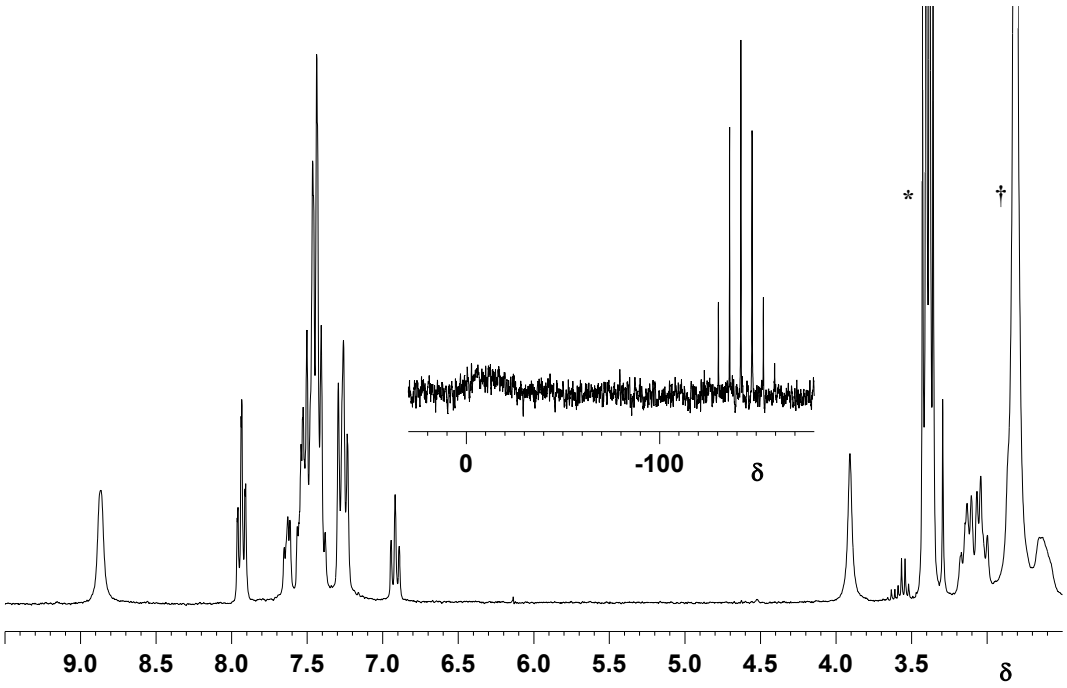
[a] Calculated from measurements of individual element concentrations that were reproducible to ±10%.

[b] Spectra for complex in MeCN solution. [c] Spectra for complex in $CHCl_3$ solution. [d] Not measured (see text).

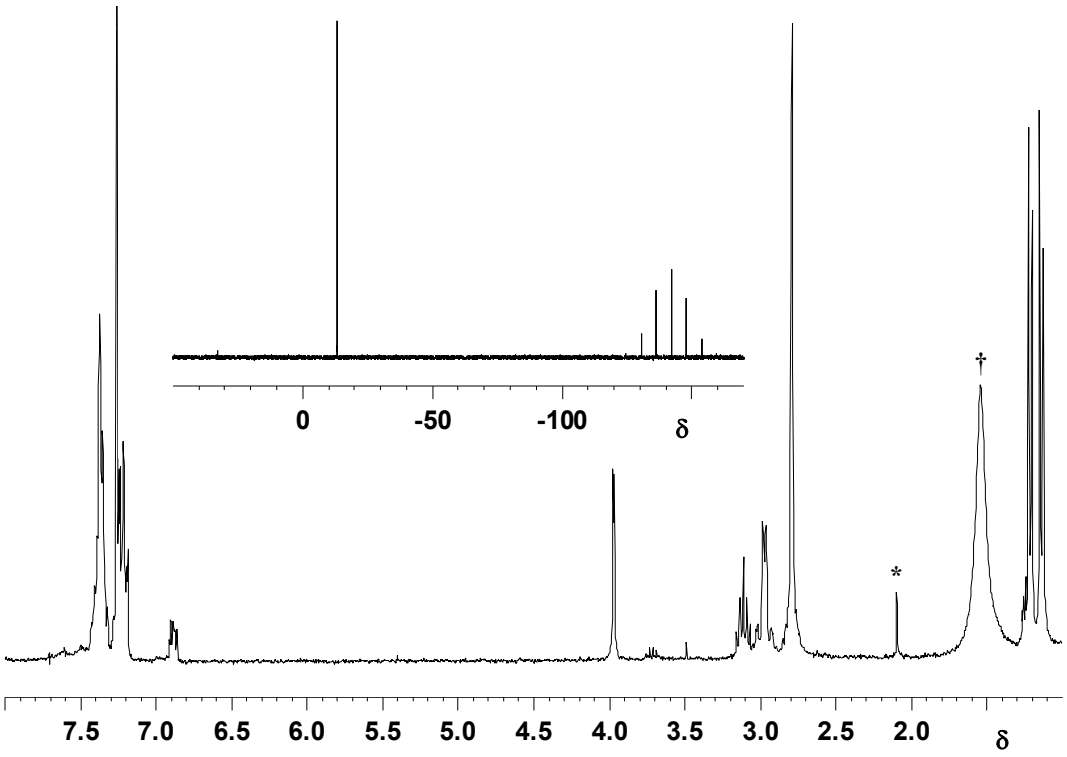
ESI Table 2. Found (and calculated) analytical and X-band EPR and electronic spectral data for multinuclear complexes.



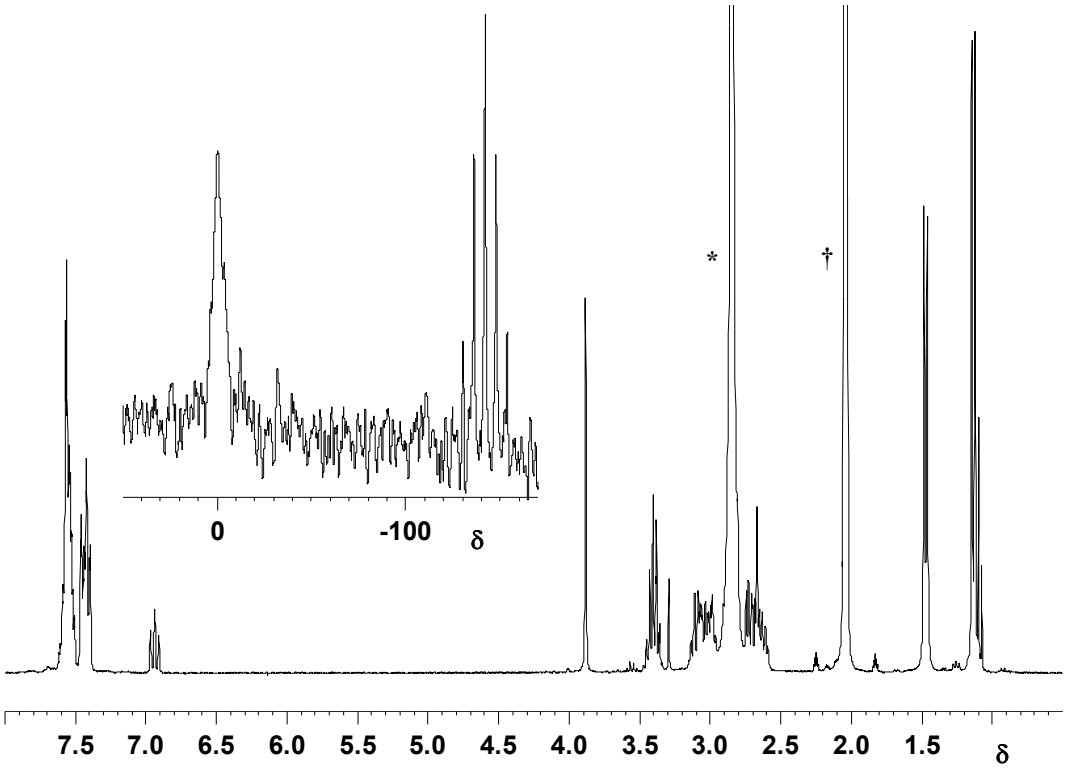
ESI Fig. 1(a). 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of $[HL^{1}][PF_6]$ in $CDCl_3$ at 300 K (* diethyl ether).



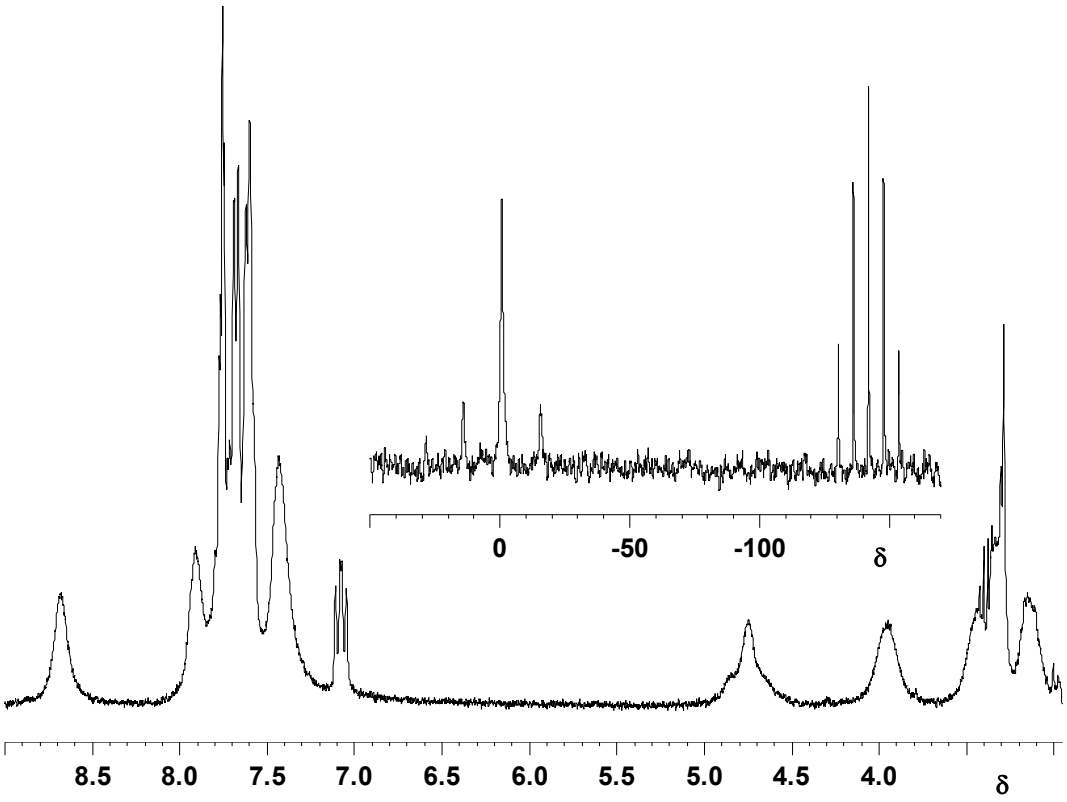
ESI Fig. 1(b). 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of $[Cu(L^{1})][PF_6]$ in $(CD_3)_2CO$ at 300 K (* diethyl ether, † H_2O).



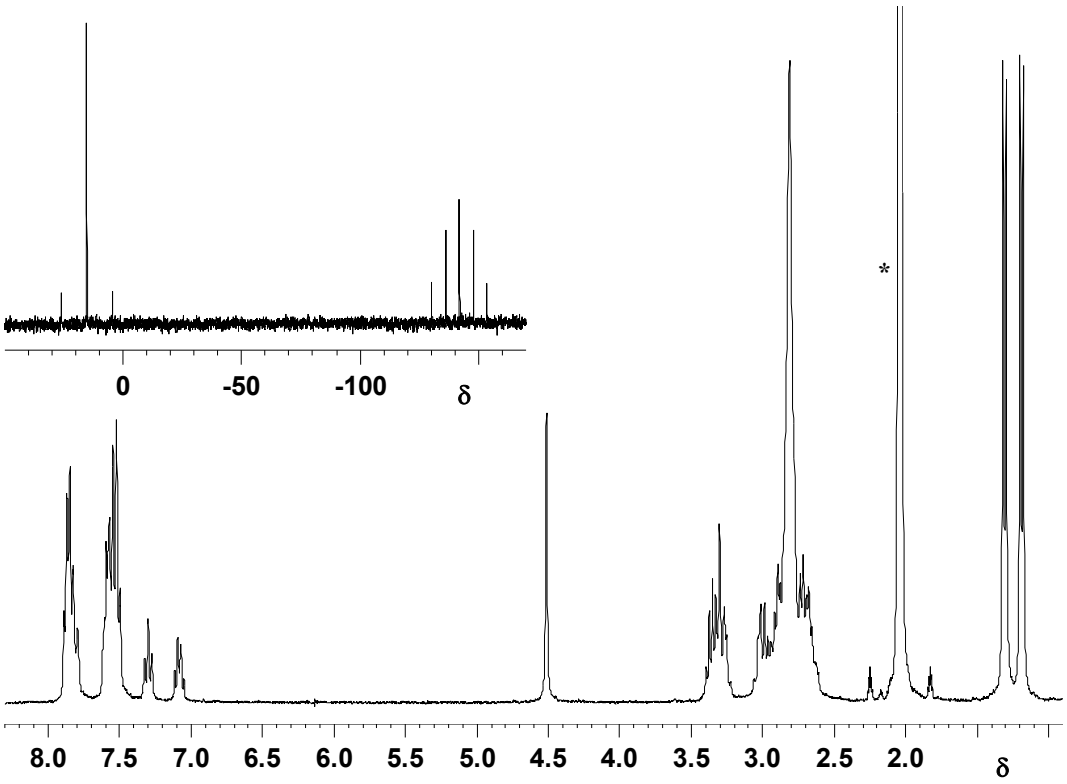
ESI Fig. 2(a). 300 MHz ^{1}H (in $CDCl_3$) and 121 MHz $^{31}P\{^{1}H\}$ [inset in $(CD_3)_2CO$] nmr spectra of $[HL^2][PF_6]$ at 300 K (* CH_3COOH, † H_2O).



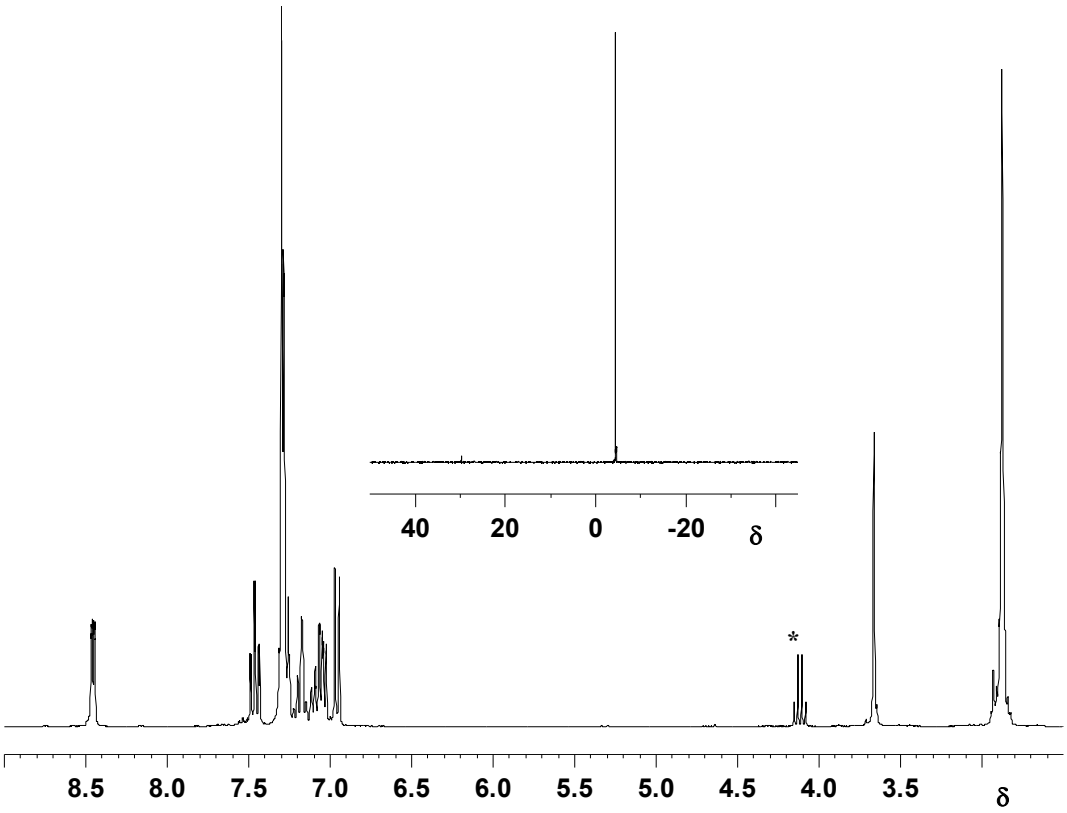
ESI Fig. 2(b). 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of $[Cu(L^2)][PF_6]$ in $(CD_3)_2CO$ at 300 K (* H_2O, † acetone).



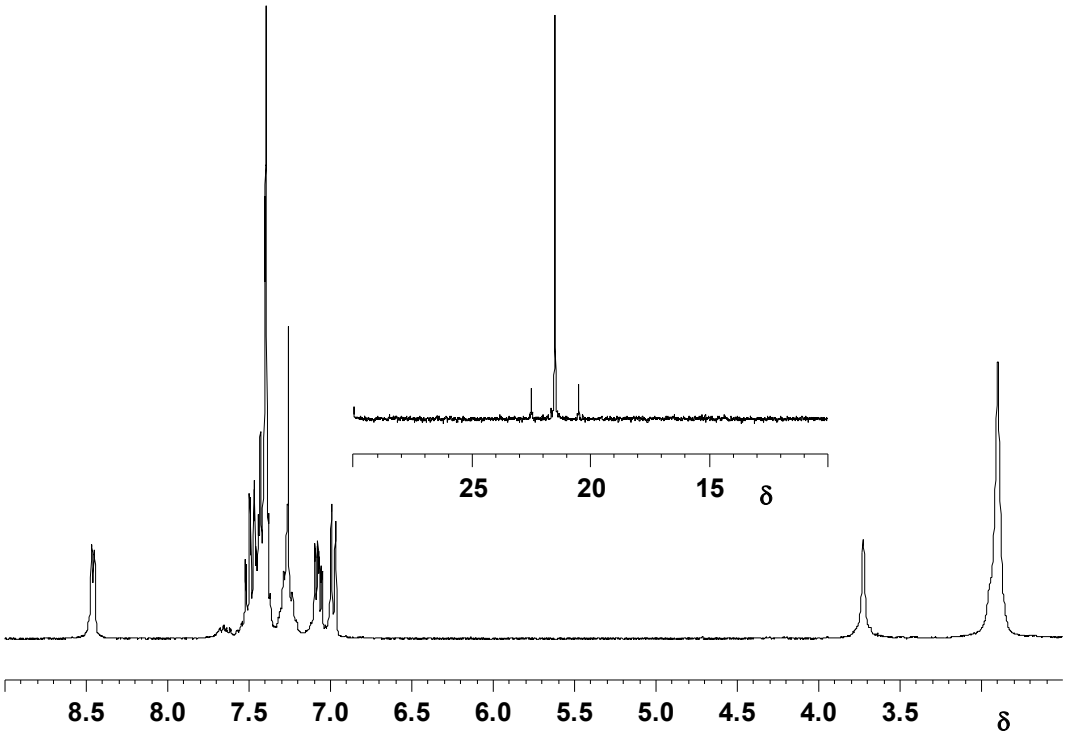
ESI Fig. 3. 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of $[PtCl(L^{1})][PF_6]$ in $(CD_3)_2CO$ at 300 K.



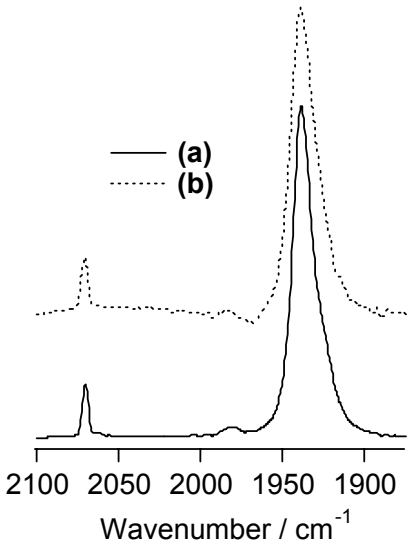
ESI Fig. 4. 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of $[PtCl_2(HL^{2})_2][PF_6]_2$ in $(CD_3)_2CO$ at 300 K (* acetone).



ESI Fig. 5(a). 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of L^3 in $CDCl_3$ at 300 K (* ethyl acetate).



ESI Fig. 5(b). 300 MHz ^{1}H and 121 MHz $^{31}P\{^{1}H\}$ (inset) nmr spectra of $[W(CO)_5(L^3)]$ in $CDCl_3$ at 300 K.



ESI Fig. 6. The FTIR spectrum in the CO region of a tetrahydrofuran solution of $[W(CO)_5(L^3)]$ prior to (a) and after (b) the addition of 10 molar equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ (s).

Added metal salt	ν_{CO} / cm^{-1} (absorbance)	
—	2070 (0.015)	1939 (0.075)
$Mn(ClO_4)_2 \cdot 6H_2O$	2071 (0.011)	1940 (0.057)
$Fe(ClO_4)_2 \cdot 6H_2O$	2071 (0.013)	1940 (0.063)
$Co(ClO_4)_2 \cdot 6H_2O$	2071 (0.014)	1940 (0.070)
$Ni(ClO_4)_2 \cdot 6H_2O$	2071 (0.014)	1939 (0.072)
$Cu(ClO_4)_2 \cdot 6H_2O$	2071 (0.014)	1940 (0.069)
$Zn(ClO_4)_2 \cdot 6H_2O$	2071 (0.014)	1939 (0.068)

ESI Table 3. FTIR spectral data for a solution of $[W(CO)_5(L^3)]$ in tetrahydrofuran prior to and following the addition of transition metal salts (10 molar equivalents).