Reversible CO exchange at platinum(0). An example of similar complex properties produced by ligands with very different stereoelectronic characteristics†

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The ligands 1,2-C₆H₄(CH₂P₄ᵗBu₂)₂ (Lₐ) and 1,2-C₆H₄(P₄ᵗBu₂)(CH₂P₄ᵗBu₂) (L₉) displace norbornene (nbe) from [Pt(n²-nbe)]₂ to give [Pt(Ln²-nbe)] where L = Lₐ (1a) or L₉ (1b). 1a is fluxional on the NMR timescale. Reaction of 1a,b with CO gives the corresponding monocarbonyls [PtL(CO)] where L = Lₐ (2a) or L₉ (2b) which then react further, and reversibly, to give the dicarbonyls [PtL(CO)₂] where L = Lₐ (3a) or L₉ (3b). The CO interchange between 2a,b and 3a,b is compared with the only other such system (2f and 3f), which are complexes of (C₂F₅)₂PCH₂CH₂P(C₂F₅)₂ (L₇). Ethene reacts smoothly with 2a to give (4a) and H₂ with 2a generates some [PtH₂(Lₐ)]. Protonation of 2a gives [Pt(Lₐ)(H)(CO)][B(C₆F₅)₄] (5a) whose crystal structure has been determined. Similarly protonation of 2b gives [Pt(L₉)(H)(CO)][B(C₆F₅)₄] as a mixture of geometric isomers 5b–6b.

Introduction

The bulky o-xylenyl diphosphine Lₐ (Chart 1) was first prepared in 1976 by Shaw et al. who also reported cis-[PtH₂(Lₐ)], the first example of a cis-dihydridoplatinum(II) complex.1 Spencer et al. later reported that treatment of complexes of the type [Pt(Lₐ)-(η²-alkene)] with a Brønsted acid produced the first examples of β-agostic C–H–Pt complexes.2,3 More recently, Lₐ has been used in the commercialised Pd-catalysed ethene hydromethoxycarbonylation (Lucite Process) for the production of methyl methacrylate, shown in eqn (1).4

This application has galvanised academic interest in the Pd and Pt chemistry of Lₐ and related ligands (e.g. ligands L₉–Lₑ shown in Chart 1)5–10 with the aim of understanding the special qualities of the Lₐ chelate. For example, using isotopically labelled MeOD and ¹³CH₂=CH₂, Iggo et al.6,7 identified by NMR the key intermediates in the carboxylation cycle with Pd–Lₐ and Pt–Lₐ catalysts; they determined that the Pt-catalysis (Scheme 1) is inhibited by the reversible binding of CO to the Pt(n) intermediates while the corresponding Pd–Lₐ cycle is not similarly inhibited because of the lower affinity of Pd(n) for CO.
It has been established that the activity and longevity of the Pd-catalyst for carbonylation can be improved by ligand modification. For example, we have shown that changing the backbone from xylenediyl in $L_a$ to toluenediyl in $L_b$ led to a more active Pd-catalyst. This has prompted us to investigate and compare the coordination chemistry of $L_a$ and $L_b$, particularly that which may be relevant to the ethene hydromethoxycarbonylation catalysis (eqn (1)).

The dichloroplatinum(II) complexes of $L_a$ and $L_b$ have been shown to be fluxional on the NMR timescale. The conformations of the chelate rings in [PtCl$_2$(L)]$_2$, as determined by X-ray crystallography, are depicted as A (L = $L_a$) and B (L = $L_b$) in Chart 2 and the observed fluxionality is associated with ring inversion.

Here we present the characterisation of Pt(0)–carbonyl complexes of the electron-rich, bulky ligands $L_a$ and $L_b$, that have the property of reversible CO-interchange between three- and four-coordinate complexes, only previously observed with Pt(0) complexes of the electron-poor $L_d$. The reactions of the carbonyl complexes of $L_a$ and $L_b$ with ethene, H$_2$ and H$^+$ are also described and the relevance of this chemistry to the carbonylation catalysis shown in Scheme 1 is discussed.

### Results and discussion

The platinum(0) chemistry of $L_a$ and $L_b$ is summarised in Scheme 2. Addition of 1 equiv. of $L_a$ or $L_b$ to [Pt(η$_2$-nbe)$_3$] (nbe = norbornene) gave the corresponding [Pt(L)(η$_2$-nbe)] ($1_a$, L = $L_a$; 1$b$, L = $L_b$). The $^{31}$P NMR spectrum of the previously reported $^{31}$P NMR spectrum of the previously reported $1_a$ at −60 °C in toluene, showed 2 singlets in the ratio of ca. 7:3 ($\delta$ 49.2 ppm $J_{PtP} = 3325$ Hz and $\delta$ 47.3 ppm $J_{PtP} = 3308$ Hz) which coalesce at 0 °C, consistent with the interchange of the diastereoisomeric rotamers $1_a$ and $1_a'$ shown in eqn (2). The $^1$H NMR spectrum of $1_a$ at −40 °C shows two multiplets for the diphos CH$_2$ which coalesce at −20 °C and appear as a broad singlet ($\omega_{1/2} = 23$ Hz) at room temperature; only one $A_2XX'$ signal for the tBu groups was discerned across the temperature range −40 to +20 °C indicating the insensitivity of this signal to the inequivalence of these groups. Two mechanisms can be postulated for the interchange shown in eqn (2): chelate ring inversion and Pt–nbe bond rotation. Both are plausible since there is precedent for Pt–$L_a$ chelate ring inversion on the NMR timescale$^{8-11}$ and slow rotation about the Pt–nbe bonds in [Pt(L)(η$_2$-nbe)], a complex of the xylenediyl ligand $L_d$ (Chart 1), has been observed.
In the case of 1b, its $^{31}$P NMR spectrum shows sharp doublets over the whole temperature range of +23 to −90 °C which we interpret as due to there being a thermodynamic preference for one of the rotamers analogous to those shown in eqn (2). The $^1$H NMR spectrum of 1b showed 2 multiplets for the diphos CH$_2$ and 4 sharp $A_9XX'$ multiplets for the tBu groups, consistent with the presence of a predominant isomer.

The displacement of the nbe from 1a and 1b to give the monocarbonyls 2a and 2b was achieved by bubbling CO through their toluene solutions and removing the solvent with the displaced nbe by evaporation to dryness. The colourlessness of 1a/1b contrasts with the vivid orange-red of 2a/2b.

Complexes 2a and 2b exhibit one $\nu$(CO) band at 1907 and 1898 cm$^{-1}$ respectively, (cf. for [Pt(PCy$_3$)$_2$(CO)], $\nu$(CO) = 1916 cm$^{-1}$).$^{11}$ The $^{31}$P NMR spectrum of 2a shows the expected singlet at 70.0 ppm with a $^1$$J$(PPT) of 3647 Hz and its $^1$H NMR spectrum shows one broad signal for the diphos CH$_2$ group and one $A_9XX'$ multiplet for the tBu groups, as expected for a conformationally labile chelate.$^{8-10}$ Unexpectedly, the $^{31}$P NMR spectrum of 2b showed a single broad signal ($\omega_{1/2} = 40$ Hz) at 78.5 ppm with $^1$$J$(PPT) of 3450 Hz which below −20 °C is resolved into an AB pattern with $\delta$ 77.9 and 76.4, $^2$$J$(PP) = 93 Hz and $^1$$J$(PPT) = 3556 and 3250 Hz respectively (see Fig. 1).

The labelled compounds [Pt(L)([13$CO$]) (2a*, L = La; 2b*, L = Lb) were prepared in order to confirm their structures and to probe further the apparent fluxionality of 2b. Treatment of 2a and 2b with $^1$CO gave the labelled complexes 2a* and 2b*. The $^{31}$P NMR spectrum of 2a* at ambient temperature is a doublet with $^2$$J$(PCC) = 45 Hz and its $^{13}$C NMR spectrum shows a triplet at 229 ppm with $^1$$J$(PtC) = 2096 Hz and the same $^2$$J$(PCC) of 45 Hz; these spectra support the monocarbonyl structure assigned to 2a. The $^{31}$P NMR spectrum of 2b* at −90 °C showed an AB pattern with $^1$$J$(PCC) = 2096 Hz and the same $^2$$J$(PCC) of 45 Hz; these spectra are consistent with the monocarbonyl structure assigned to 2b. The ambient temperature $^{31}$P and $^{13}$C NMR spectra of 2b* resembled the spectra for the unlabelled 2b, being broad and unresolved. Above room temperature, the $^{31}$P NMR spectrum of 2b* broadens progressively until at +100 °C, $\omega_{1/2} \sim 400$ Hz. In the $^{13}$C NMR spectra of 2b* measured between +40 and +100 °C, no CO signal was observed at all presumably because of its broadness. When the high temperature NMR samples were cooled to ambient temperature, the $^{31}$P and $^{13}$C NMR spectra reassumed their original forms.

It is not obvious what the source of the line-broadening is in the $^{31}$P and $^{13}$C NMR spectra of 2b at ambient temperature and above. If the conformation of the 6-membered chelate in 2b is $B/B'$-like (see Chart 2), then 2b would exist as a pair of...
enantiomers (with identical $^{31}$P shifts) and therefore interchange between such conformers would not contribute to the line broadening. If intermolecular CO exchange were taking place, P–C coupling would be lost in the labelled $2b^*$ which apparently it is, but this observation is inconclusive because the large observed NMR line-width would swamp the $J$(PC) of 52 and 41 Hz (measured at $-90 \, ^\circ\mathrm{C}$). Nevertheless, one explanation for the NMR behaviour is that at elevated temperatures, CO exchange is taking place perhaps via an analogue of [Pt$_2$(CO)$_2$(μ-CO)(L)$_2$]$_2$] (see Chart 1 for structure of L) reported by Mezailess et al.$^{14}$ which is in equilibrium with $2b$.

The dicarbonyl complexes, [PtL(CO)$_2$] ($3a$, L = L$_a$; $3b$, L = L$_b$) were generated when solutions of $2a$ and $2b$ were pressurised with 2 atm of CO. The solid state IR spectrum of $3a$ showed ν(CO) bands at higher frequencies (1971 and 1931 cm$^{-1}$) than the 1907 cm$^{-1}$ for $2a$, consistent with the two CO ligands in $3a$ sharing the electron density from the platinum(0). The $^{31}$P NMR spectrum of $3a$ at room temperature showed no discernable resonances but at $-90 \, ^\circ\mathrm{C}$, a singlet at 35.3 ppm with $J$(PPT) of 3107 Hz was observed. At $+40 \, ^\circ\mathrm{C}$, the only $^{31}$P NMR signal observed was for $2a$, showing that CO dissociation from $3a$ occurs readily and this explains the great broadness of the signal at ambient temperatures. The labelled complex [Pt(L$_a$)-($^{13}$CO)$_2$] ($3a^*$) was prepared from $3a$ and $^{13}$CO and its $^{13}$C NMR spectrum at $-90 \, ^\circ\mathrm{C}$ had multiplets at 187.1 and 186.6 ppm with $J$(CP) of 1832 and 1900 Hz respectively which were assigned to inequivalent Pt–CO ligands. The $J$(CP) coupling was approximately 4 Hz, leading to multiplets in the $^{31}$P and $^{13}$C NMR spectra. The inequivalence of the CO ligands detected in the low temperature $^{13}$C NMR spectrum of $3a^*$ is consistent with an A-type conformation of the 7-membered chelate (see Chart 2) giving rise to CO ligands being syn and anti to the phenylene of the chelate.

The solid state IR spectrum of $3b$ showed ν(CO) bands at higher frequencies (1961 and 1915 cm$^{-1}$) than the 1898 cm$^{-1}$ in $2b$. The $^{31}$P NMR spectrum of $3b$ at ambient temperatures showed 2 sets of broad singlets at 44.4 and 42.7 ppm with $J$(PPT) = 3106 and 3818 Hz respectively. The $^{13}$C NMR spectrum of the labelled complex [Pt(L$_a$)-($^{13}$CO)$_2$] ($3b^*$) had two signals at 187.1 and 186.0 ppm with $J$(CP) of 1930 and 1850 Hz respectively; the C–P coupling was not resolved in the $^{31}$P or $^{13}$C NMR spectra of $3b^*$. According to solid-state IR spectroscopy (see Fig. 2), when red solid monocarbonyl $2b$ was subjected to a CO atmosphere, it was converted to yellow $3b$ and this was reversed upon application of a vacuum to powdered $3b$.

Dissociation of CO from the dicarboxyls $3a/3b$ to give $2a/2b$ occurred slowly when their solutions were stirred under a N$_2$ atmosphere and rapidly when solutions were put under vacuum, presumably due to the dissolved CO being removed under the reduced pressure. The uptake of CO by $2a/2b$ (eqn (3)) is notable because of its rarity$^{13}$ and reversibility.$^{14}$ There are several examples of 18-electron complexes of the type [Pt(CO)$_2$(PR)$_3$]$^{13,15}$ and [Pt(CO)$_2$(diphos)]$^{14,16}$ including the complex where diphos = L$_a$,$^{17}$ (see Chart 1) which has ν(CO) values (1912, 1960 cm$^{-1}$) closely similar to those for $3b$ (see eqn (3)); the bulk and bite angles of L$_b$ and L$_a$ should be similar. However there is only one previously reported example of a 16-electron [Pt(CO)(diphos)] complex, $2f$, which Roddick et al.$^{18}$ reported undergoes a similar CO interchange between $2f$ and $3f$ (eqn (3)). The explanation that was given for the stability of $2f$ relative to $3f$ was that the high π-acceptor capacity of the fluorophos ligand L$_f$ efficiently delocalises the electron-density on the Pt(0); this is supported by the high ν(CO) values for $2f$ and $3f$ (see eqn (3)). A similar argument is not tenable for $2a/2b$ since L$_a$/L$_b$ are strong σ-donors, as reflected in the low ν(CO) values for their carbonyl complexes (see eqn (3)). The stability of the coordinatively unsaturated $2a/2b$ is therefore associated with the large bulk of L$_a$/L$_b$. This steric argument can be extended to explain why CO dissociation from $3a$ appears to be more facile than from $3b$, since $L_a$ is more sterically demanding than $L_b$.$^{11}$ The complementary explanations for the equilibria shown in eqn (3) for L$_a/\text{L}_b$ vs. L$_f$ exemplify how ligands with very different stereoelectronic properties can produce complexes with similar properties.

When a toluene solution of $2a$ was stirred under an atmosphere of H$_2$ for 5 days, the cis-[PtH$_2$(L$_a$)] was formed in approximately 50% NMR yield (along with other uncharacterised products), as shown by the close matching of the NMR data...
(1H: δ = -3.8 ppm, J_{PH} = 1004 Hz; 31P: δ = 45.7 ppm, J_{PP} = 2109 Hz) with the literature values for this compound.1

The CO ligands in 2a were displaced by ethene to give 4a by repeated vacuum/ethene-addition cycles (see Experimental) and this transformation was readily reversed by the application of a CO atmosphere to 4a (Scheme 2). Complex 4a was characterised by matching of the NMR data with those previously reported for this complex.29 Under similar conditions to those used to generate 4a, 2b reacted with ethene but the product, according to the 31P NMR spectrum at -90 °C, was a mixture containing 2b (50%), 3b (30%) and a third species (20%) whose 31P NMR parameters (60.9 with J(PPt) = 3288 Hz, J(PP) = 45 Hz; 57.9 J(PPt) = 3288 Hz) led us to tentatively assign this minor product to 4b, although we have not isolated it.

In the carbonylation catalytic cycle shown in Scheme 1, neutral species are not involved in the core cycle because the reaction is carried out in an acidic medium. For this reason, we investigated the protonation of the monocarbonyl complex 2a. Treatment of the monocarbonyl complex 2a with 1 equivalent of [(Et₂O)₂][B(C₆F₅)₄] in chlorobenzene gave a product assigned structure 5a (Scheme 2) on the basis of its 1H NMR spectrum which showed a signal at -4.7 ppm with J(PtH) = 736 Hz characteristic of a hydride. A band at 2092 cm⁻¹ in its IR spectrum is typical of a cationic Pt(II)–CO.21 The NMR spectroscopic data for 5a match well those reported by Iggo et al.7 for the trflate salt of 5a which they characterized in solution only.

Crystals of 5a suitable for X-ray crystallography grew from its CH₂Cl₂ solution, crystallising in the triclinic space group P1 with two [Pt(L)(H)(CO)][B(C₆F₅)₄] moieties in the asymmetric unit, i.e. Z’ = 2. Both of these moieties have essentially the same geometrical conformation and selected bond lengths and angles are listed below Fig. 3. The location of the hydride was not determined directly from the data, but its position was inferred from the metal geometry and located accordingly. The Pt1–Pt1–P2 bite angle is 104.00(12)° and the P3–Pt2–P4 bite angle is 104.74(12)° and all four of the half cone angles are ~117°.

The chelate conformations for xylenediyl diphos complexes 2a/2b and 3a/3b are readily formed and interconvert.

**Conclusion**

We have shown here that the mono- and dicarbonylplatinum(0) complexes 2a/2b and 3a/3b are readily formed and interconvert.

**Fig. 3** Crystal structure of [Pt(L)(H)(CO)][B(C₆F₅)₄] (5a). The view on the right shows the chelate ring conformation. Only one of the two Pt-containing moieties in the asymmetric unit is shown and only one position of the disordered CO/H combination. For clarity all of the hydrogen atoms (apart from the hydride H1D) are omitted along with the [B(C₆F₅)₄] counterions. Selected bond lengths (Å) and angles (°): Pt1–P1 2.366(3); Pt1–P2 2.328(3); Pt1–C25 1.900(14); Pt1–H1D 1.660(5); P1–C4 1.886(13); P1–C5 1.869(12); P1–C9 1.818(11); P2–C16 1.835(13); P2–C20 1.888(12); P2–C21 1.886(14); P1–Pt1–P2 104.00(12); C25–P1–P1 157.5(5); C25–P1–P2 157.5(5).
The stability of the coordinatively unsaturated \([\text{Pt(CO)(diphos)}]\) species \(2a/2b\) relative to \(3a/3b\) is associated with the steric congestion provided by the bulky diphos ligands \(L_a\) and \(L_b\). The only related \([\text{Pt(CO)}_n(\text{diphos})]\) species reported (\(2f/3f\)) feature the electron-poor fluorinated diphos ligand \(L_f\) (which has modest steric bulk)\(^{25}\) where the explanation given for the stability of the monocarbonyl is electronic – the \(\pi\)-acceptor properties of the diphos ligand destabilises the corresponding \([\text{Pt(CO)}_2(\text{diphos})]\). This is a textbook example of ligands with very different stereoelectronic properties producing similar outcomes in terms of the properties of their complexes.

The hydromethoxycarbonylation of ethene is efficiently catalysed by Pd-complexes of \(L_a\) and \(L_b\) and Iggo et al.\(^7\) have shown that the analogous organoplatinum chemistry is relevant in the study of the mechanism of the catalysis. Ethene reacts with the coordinatively unsaturated \(2a\) to give \(4a\) presumably via the 18-electron tetrahedral intermediate \(X\) (Scheme 3). The protonation of the \(2a/2b\) to give the cationic hydridocomplexes \(5a/5b\) (and the geometric isomer \(6b\)) is pertinent because the catalysis is carried out at low pH. It is possible that complexes of the type \(2–5\) described above are present in non-productive equilibria during the Pt-catalysed carbonylation shown in Scheme 1; their place is shown in Scheme 3.

**Experimental**

Unless otherwise stated, all reactions were carried out using standard Schlenk line and dry box techniques. Dry \(\text{N}_2\)-saturated solvents were collected from a Grubbs system in flame and vacuum-dried glassware. Deuterated solvents were dried and distilled from CaH\(_2\). Pentane was dried over 4 Å molecular sieves and \(\text{N}_2\)-saturated by repeated freeze, vacuum and thawing cycles. The complex \([\text{Pt}(\eta^2-\text{nbe})]\)\(^{26}\) was prepared by literature methods. Ligand \(L_a\) was obtained from Lucite International. Ligand \(L_b\) was prepared as previously described.\(^{11}\) CO, \(\text{C}_2\text{H}_4\), and \(\text{H}_2\), were used as obtained from BOC and \(\text{CO}\) was used as obtained from Aldrich. NMR spectra were recorded on a Jeol ECP (Eclipse) 300 or a Varian VNMR S500 spectrometer. Chemical shifts are referenced relative to high frequency of \(\text{Si(CH}_3)_4\) (\(\text{H}\) or \(\text{C}^1\text{H}_3\)), 85% \(\text{H}_2\text{PO}_4\) (\(\text{P}^{31}\)) and \(\text{CF}_3\text{Cl}\) (\(\text{F}\)). Infrared spectra were obtained using a Perkin Elmer 1600 series FTIR. Mass spectrometry was carried out by the Mass Spectrometry Service at the University of Bristol. Elemental analyses were carried out by the Microanalytical Laboratory at the University of Bristol.

**Preparation of \([\text{Pt}(L_a)(\eta^2-\text{nbe})]\) (1a)**

This was made according to the method of Spencer et al. and characterised by comparison of the NMR spectra with the reported data.\(^3\) The spectra at low temperature have not been previously reported. \(\text{P}^{31}\)[H] NMR (202 MHz, \(\text{C}_6\text{D}_5\text{CD}_3\), –60 °C): \(\delta\) 49.2 (s, \(J(\text{PtP}) = 3251\) Hz), \(\delta\) 47.3 (s, \(J(\text{PtP}) = 3308\) Hz).

**Preparation of \([\text{Pt}(L_b)(\eta^2-\text{nbe})]\) (1b)**

A solution of \(L_b\) (0.089 g, 0.26 mmol) in toluene (5 mL) was added in one portion to a solution of \([\text{Pt}(\eta^2-\text{nbe})]\) (0.125 g, 0.262 mmol) in toluene (5 mL) at –78 °C and the resulting mixture was stirred for 2 h, allowed to warm to room temperature and then stirred for a further 16 h. The volatiles were then removed under reduced pressure to yield an off-white solid that was dissolved in pentane (1 mL) and the product crystallized at –78 °C. The supernatant was removed by cannula and the white solid dried under vacuum (0.149 g, 0.222 mmol,
Preparation of [Pt(La)(CO)] (2a)

A solution of L (0.158 g, 0.415 mmol) in toluene (5 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with CO (2 bar) and the resulting mixture allowed to react for 30 min. The vacuum/C0 cycle was repeated twice more to ensure that all of the CO had been displaced. The solvents were then removed under reduced pressure to give a yellow solid which turned red under prolonged exposure to vacuum. The solid was extracted with pentane (3 mL) and the product crystallized at -78 °C. The supernatant was removed via cannula and the red solid dried under vacuum (0.108 g, 0.179 mmol, 88%). Elemental analysis (calcd for C25H44OP2Pt, 70.2 (d, 1J(Pt) = 3647 Hz). 1H NMR (500 MHz, C6D6): δ 7.1–8.9 (m, 1H, CHH), 3.3 (m, 2H, CCH2), 2.5–2.2 (m, 2H, CPh), 2.0 (m, 2H, CCHH), 1.7 (m, 2H, CCHH), 1.4 (d, 1J(Pt) = 13 Hz, 9H, CCHH), 1.3 (d, 1J(Pt) = 13 Hz, 9H, CCHH), 1.2 (d, 1J(Pt) = 12 Hz, 9H, CCHH), 0.8 (m, 1H, CHH bridge), 0.7 (m, 1H, CHH bridge).

Preparation of [Pt(La)(13CO)] (2a*)

A solution of L (0.135 g, 0.202 mmol) in toluene (10 mL) for 30 min to give a yellow solid which was filtered and then the volatiles removed under reduced pressure. The residue was redissolved in toluene (5 mL) and CO was bubbled through the solution again. The vacuum/CO cycle was repeated twice more to ensure that all of the norbornene had been displaced. The solvent was then removed under reduced pressure to give a yellow solid which turned red under prolonged exposure to vacuum. The solid was extracted with pentane (3 mL) and the product crystallized at -78 °C. The supernatant was removed via cannula and the red solid dried under vacuum (0.108 g, 0.179 mmol, 88%). Elemental analysis (calcd for C25H44OP2Pt, 70.2 (d, 1J(Pt) = 3647 Hz). 1H NMR (500 MHz, C6D6): δ 7.1–8.9 (m, 1H, CHH), 3.3 (m, 2H, CCH2), 2.5–2.2 (m, 2H, CPh), 2.0 (m, 2H, CCHH), 1.7 (m, 2H, CCHH), 1.4 (d, 1J(Pt) = 13 Hz, 9H, CCHH), 1.3 (d, 1J(Pt) = 13 Hz, 9H, CCHH), 1.2 (d, 1J(Pt) = 12 Hz, 9H, CCHH), 0.8 (m, 1H, CHH bridge), 0.7 (m, 1H, CHH bridge).

Preparation of [Pt(Lb)(CO)] (2b)

A solution of 2b (11.2 mg, 0.0185 mmol) in benzene (1.2 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with 13CO (2 bar) and the resulting mixture allowed to react for 30 min. The vacuum/CO cycle was repeated twice more to ensure that all of the 13CO had been displaced. The volatiles were removed under reduced pressure to yield a yellow solid that turned red under prolonged exposure to vacuum. The product was identified in solution by NMR only. The 1H NMR spectrum of 2b* was essentially the same as for 2b. 31P{H} NMR (121 MHz, C6D6CD3, -90 °C): δ 77.9 (dd, 1J(PPT) = 3556 Hz, 1J(PC) = 52 Hz), 76.4 (d, 1J(PPT) = 3250 Hz, 1J(PC) = 93 Hz), 13C{H} NMR (101 MHz, C6D6): δ 134.6 (m), 129.0 (m), 128.9 (s), 128.8 (s), 125.6 (s), 125.0 (m), 35.7 (br, CH2), 30.9 (br, CCHH), 29.3 (br, CCH3).

Preparation of [Pt(Lb)(13CO)] (2b*)

A solution of 2b (11.2 mg, 0.0185 mmol) in benzene (1.2 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with 13CO (2 bar) and the resulting mixture allowed to react for 30 min. The vacuum/CO cycle was repeated twice more to ensure that all of the 13CO had been displaced. The volatiles were removed under reduced pressure to yield a yellow solid that turned red under prolonged exposure to vacuum. The product was identified in solution by NMR only. The 1H NMR spectrum of 2b* was essentially the same as for 2b. 31P{H} NMR (121 MHz, C6D6CD3, -90 °C): δ 77.9 (dd, 1J(PPT) = 3556 Hz, 1J(PC) = 52 Hz), 76.4 (d, 1J(PPT) = 3250 Hz, 1J(PC) = 93 Hz), 13C{H} NMR (75 MHz, C6D6CD3, -90 °C): δ 234.6 (dd, 1J(CP) = 2189 Hz, 1J(PC) = 41 Hz, 1J(PC) = 52 Hz, CO).

Preparation of [Pt(Lb)(CO)2] (3a)

A solution of 2a (10.2 mg, 0.0165 mmol) in d6-toluene (1 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with CO (2 bar) and the resulting mixture allowed to react for 30 min. The product was not isolated because it reverted to 2a upon removal of solvent and was identified in solution by NMR. 31P{H} NMR (121 MHz, C6D6CD3, -90 °C): δ 35.3 (s, 1J(PPT) = 3017 Hz). 1H NMR (300 MHz, C6D6CD3): δ 7.1 (m, 2H), 6.9 (m, 2H), 3.3 (br, 4H, CH2), 1.2 (m, 36H, CCH3), 13C{H} NMR (100 MHz, C6D6CD3): δ 142.9 (s), 138.7 (s), 130.5 (s), 41.8 (br, CH2), 37.3 (br, CCH3), 34.8 (m, CCH3). νCO 1971, 1931 cm⁻¹.
Preparation of [Pt(La)(13CO)2] (3a*)

A solution of 2a (10.0 mg, 0.0162 mmol) in d8-toluene (1.2 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with 13CO (2 bar) and the resulting mixture allowed to react for 30 min. The vacuum/CO cycle was repeated twice more to ensure that most of the 12CO had been displaced. The product was not isolated because it reverted to 2a* upon removal of solvent and was identified in solution by NMR. The 1H NMR spectrum of 3a* was essentially the same as for 3a. 31P{H} NMR (121 MHz, C6D5CD3, −90 °C): δ 35.3 (m, 3J(Ppt) = 3107 Hz). 13C{H} NMR (75 MHz, C6D5CD3, −90 °C): δ 187.1 (m, 3J(Cp) = 1832 Hz, CO) 186.6 (m, 3J(Cp) = 1900 Hz, CO).

Preparation of [Pt(Lb)(13CO)2] (3b*)

A solution of 2b (8.7 mg, 0.014 mmol) in d8-toluene (1 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with CO (2 bar) and the resulting mixture allowed to react for 30 min. The product was not isolated because it reverted to 2b upon removal of solvent and was identified in solution by NMR.

Reaction of [Pt(La)(CO)] with ethene

A solution of 2a (10.0 mg, 0.0175 mmol) in d8-toluene (1.2 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with C2H4 (2 bar) and the resulting mixture allowed to react for 30 min. The vacuum/C2H4 cycle was repeated twice more to ensure that most of the CO had been displaced. The product was identified by comparison of its NMR spectra with the literature data for this previously reported complex. 19F ESI mass spectrum: (calcd for C38H14O2P2Pt 617.35 M, 617.3. 31P{H} NMR (121 MHz, C6D6): δ 48.9 (3J(Ppt) = 3548 Hz). 1H NMR (300 MHz, C6D6, C6D5CD3, −90 °C): δ 7.1−6.9 (m, 4H), 3.4 (br, 4H, PhCH2), 2.2 (br, 3J(PP) = 54 Hz, 4H, PhCH2), 1.3 (d, 3J(PP) = 13 Hz, 36H, CH3).

Preparation of [Pt(La)(CO)][B(C6F5)4] (5a)

A solution of [(Et2O)2H][B(C6F5)4] (12.5 mg, 0.0151 mmol) in PhCl (0.5 mL) was added in one portion to a solution of 3a* (9.2 mg, 0.015 mmol) in PhCl (0.5 mL) and the resulting mixture was left for 16 h. The solution was layered with pentane (3 mL) to give colourless crystals (17.8 mg, 90 °C). IR: νCO 1961, 1915 cm−1. Satisfactory C, H elemental analyses for 5a were not obtained even when a sample from the crystals used for the X-ray crystallography were submitted. 31P{H} NMR (162 MHz, CD2Cl2): δ 43.4 (d, 3J(Ppt) = 3046 Hz), 40.3 (m, 3J(Cp) = 2788 Hz). 13C{H} NMR (75 MHz, C6D5CD3, −90 °C): δ187.1 (m, 3J(Cp) = 1903 Hz, CO), 186.0 (m, 3J(Cp) = 1850 CO).

Preparation of [Pt(Lb)(CO)][B(C6F5)4] (5b)

A solution of 2b (10.6 mg, 0.0175 mmol) in d8-toluene (1.2 mL) was placed in a valved NMR tube. The solution was frozen with liquid N2 and then the NMR tube was evacuated and sealed. The solution was then thawed and the NMR tube backfilled with C2H4 (2 bar) and the resulting mixture allowed to react for 30 min. The vacuum/C2H4 cycle was repeated twice more to ensure that most of the CO had been displaced. The product was identified by comparison of its NMR spectra with the literature data for this previously reported complex. 19F ESI mass spectrum: (calcd for C38H14O2P2Pt 617.35 M, 617.3. 31P{H} NMR (121 MHz, C6D6): δ 48.9 (3J(Ppt) = 3548 Hz). 1H NMR (300 MHz, C6D6, C6D5CD3, −90 °C): δ 7.1−6.9 (m, 4H), 3.4 (br, 4H, PhCH2), 2.2 (br, 3J(PP) = 54 Hz, 4H, PhCH2), 1.3 (d, 3J(PP) = 13 Hz, 36H, CH3).
= 1918 Hz, $\delta$([PP] = 22 Hz). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.1 (m, 1H), 7.6 (m, 2H), 7.5 (m, 1H), 3.6 (m, 2H, CH$_2$), overlapping $^1$Bu peaks: 1.5 (d, $\delta$([PH] = 15 Hz, CH$_3$), 1.5 (d, $\delta$([PH] = 16 Hz, CH$_3$) (total integration 18H), overlapping $^1$Bu peaks: 1.3 (d, $\delta$([PH] = 15 Hz, CH$_3$), 1.3 (d, $\delta$([PH] = 16 Hz, CH$_3$) (total integration 18H). $^2$F (−2.3 (dd, $\delta$([PH] = 777 Hz, $\delta$([PH] = 147 Hz, $\delta$([PH] = 11 Hz, 0.2H, Pt$^{\text{III}}$), −4.3 (dd, $\delta$([PH] = 810 Hz, $\delta$([PH] = 148 Hz, $\delta$([PH] = 10 Hz, 0.8H, Pt$^{\text{III}}$). $^{13}$B([H]) NMR (128 MHz, CD$_2$Cl$_2$): $\delta$ = −14.41 (s). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ = 13.81 (s), 16.49 (s), 167.51 (m, 8F, P-C$_6$F$_5$). ESI accurate mass spectrum: (calcd for C$_{24}$H$_{43}$OP$_2$Pt 604.2431) $M_0$ = 604.2429. Elemental analysis (calcd for C$_{24}$H$_{43}$OP$_2$Pt 50.41%, H 3.10%, C 46.45%).

**Crystal structure determination**

A single crystal of 5a was mounted on a glass fibre and X-ray diffraction data were collected at 100 K on a Bruker APEX II CCD diffractometer using graphite monochromatised Mo-K$_{\alpha}$ radiation (λ = 0.71073 Å). Absorption corrections were based on equivalent reflections using SADABS. The structure was solved by direct methods in SHELXS and refined by full matrix least squares on $F^2$ in SHELXL. All of the non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms were located geometrically and refined using a riding model. The Pt metal centres were redefined by refining them on equivalent reflections using SADABS.27 The structure was solved by direct methods in SHELXS and refined by full matrix least squares on $F^2$ in SHELXL.28 All of the non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms were located geometrically and refined using a riding model with the exception of H1D, H1E, H2D, H2E. The structure showed a small amount of disorder in the positions of the CO group and hydride attached to the Pt metal centres. The occupancy of each CO group was determined by refining them against a free variable with the sum of the occupancies for the two CO sites attached to each Pt set to equal one, prior to fixing the occupancy at the refined values. The hydrogen atoms (H1D, H1E, H2D, H2E) were located on equivalent reflections using SADABS and their occupancy fixed to that of the related CO occupancy. Restraints were applied to maintain chemically sensible geometries (DFIX, SADI, DANG) for the disordered sections, while the CO thermal parameters were restrained to similar values using SIMU and the H $U_{eq}$ values were fixed at 1.5 × $U_{eq}$(Pt). Crystal structure and refinement data are given in Table 1.

### Table 1  Crystal data and structure refinement for 5a

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Empirical formula</td>
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<tr>
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<td>c/Å</td>
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<td>α/°</td>
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<td>ρcalcd/g cm$^{-3}$</td>
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<td>μ/mm$^{-1}$</td>
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<td>ϕ(000)</td>
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<tr>
<td>Index ranges</td>
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<td>Goodness-of-fit on $F^2$</td>
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<tr>
<td>Final R indexes [I ≥ 2σ(I)]</td>
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<tr>
<td>Final R indexes [all data]</td>
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<tr>
<td>Largest diff. peak/hole/e Å$^{-3}$</td>
<td>1.62/−1.61</td>
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</table>

**References**


20 P. Jutzi, C. Muller, A. Stammler and H.-G. Stammler, Organometallics, 2000, 19, 1442.


25 M. F. Ernst and D. M. Roddick, Organometallics, 1990, 9, 1586.

