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

Sebastian J. K. Forrest, Paul G. Pringle,* Hazel A. Sparkes and Duncan F. Wass*

The ligands 1,2-C₆H₄(CH₂P₄tBu₂)₂ (La) and 1,2-C₆H₄(P₄tBu₂)(CH₂P₄tBu₂) (Lb) displace norbornene (nbe) from [Pt(η²-nbe)₃] to give [Pt(L)(η²-nbe)] where L = La (1a) or Lb (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 Lb (2b) which then react further, and reversibly, to give the dicarbonyls [PtL(CO)₂] where L = La (3a) or Lb (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 (Lf).

Introduction

The bulky o-xylene 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 hydromethoxy-carbonylation (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 Lb–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 carbonylation 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(η) intermediates while the corresponding Pd–La cycle is not similarly inhibited because of the lower affinity of Pd(η) for CO.

School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, UK.
E-mail: paul.pringle@bristol.ac.uk, duncan.wass@bristol.ac.uk
* CCDC 1015609. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02303j

Received 28th July 2014,
Accepted 9th September 2014
DOI: 10.1039/c4dt02303j
www.rsc.org/dalton

© The Royal Society of Chemistry 2014

Dalton Trans., 2014, 43, 16335–16344 | 16335

Open Access Article. Published on 10 September 2014. Downloaded on 5/21/2022 3:33:33 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.
View Article Online | View Journal | View Issue
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 La to toluenediyl in Lb led to a more active Pd-catalyst. This has prompted us to investigate and compare the coordination chemistry of La and Lb, particularly that which may be relevant to the ethene hydromethoxycarbonylation catalysis (eqn (1)).

The dichloroplatinum(II) complexes of La and Lb have been shown to be fluxional on the NMR timescale. The conformations of the chelate rings in [PtCl2(L)]2, as determined by X-ray crystallography, are depicted as A (L = La) and B (L = Lb) 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 La and Lb, 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 Lf. The reactions of the carbonyl complexes of La and Lb with ethene, H2 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 La and Lb is summarised in Scheme 2. Addition of 1 equiv. of La or Lb to [Pt(η2-nbe)3] (nbe = norbornene) gave the corresponding [Pt(L)(η2-nbe)] (1a, L = La; 1b, L = Lb). The 31P NMR spectrum of the previously reported 1a at −60 °C in toluene, showed 2 singlets in the ratio of ca. 7:3 (δ 49.2 ppm J PtP = 3325 Hz and δ 47.3 ppm J PtP = 3308 Hz) which coalesce at 0 °C, consistent with the interchange of the diastereoisomeric rotamers 1a and 1a′ shown in eqn (2). The 1H NMR spectrum of 1a at −40 °C shows two multiplets for the diphos CH2 which coalesce at −20 °C and appear as a broad singlet (w1/2 = 23 Hz) at room temperature; only one A2XX′ 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–La chelate ring inversion on the NMR timescale8-11 and slow rotation about the Pt–nbe bonds in [Pt(Ld)(η2-nbe)], a complex of the xylenediyl ligand Ld (Chart 1), has been observed.12
In the case of 1b, its 31P 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 1H NMR spectrum of 1b showed 2 multiplets for the diphos CH2 and 4 sharp A9XX′ 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 ν(CO) band at 1907 and 1898 cm$^{-1}$ respectively, (cf. for [Pt(PCy3)2(CO)], ν(CO) = 1916 cm$^{-1}$). The 31P NMR spectrum of 2a shows the expected singlet at 70.0 ppm with a $^{3}J$(PPt) of 3647 Hz and its 1H NMR spectrum shows one broad signal for the diphos CH2 group and one AXX′ multiplet for the tBu groups, as expected for a conformationally labile chelate.8−10 Unexpectedly, the 31P NMR spectrum of 2b showed a single broad signal ($\nu_{1/2} = 40$ Hz) at 78.5 ppm with $^{3}J$(PPt) of 3450 Hz which below −20 °C is resolved into an AB pattern with δ 77.9 and 76.4, $^{3}J$(PP) = 93 Hz and $^{1}J$(PtP) = 3556 and 3250 Hz respectively (see Fig. 1).

The labelled compounds [Pt(L)[13CO]] (2a*, L = L1a; 2b*, L = L1b) were prepared in order to confirm their structures and to probe further the apparent fluxionality of 2b. Treatment of 2a and 2b with 13CO gave the labelled complexes 2a* and 2b*. The 31P NMR spectrum of 2a* at ambient temperature is a doublet with $^{3}J$(PC) = 45 Hz and its 13C NMR spectrum shows a triplet at 229 ppm with $^{1}J$(PtC) = 2096 Hz and the same $^{3}J$(PC) of 45 Hz; these spectra support the monocarbonyl structure assigned to 2a. The 31P NMR spectrum of 2b* at −90 °C showed an ABX pattern with $^{195}$Pt satellites (see Fig. 1) and its 13C NMR spectrum showed a doublet of doublets at 235 ppm with $^{2}J$(PC) = 52 and 41 Hz and $^{1}J$(PtC) = 2136 Hz; again, these spectra are consistent with the monocarbonyl structure assigned to 2b. The ambient temperature 31P and 13C NMR spectra of 2b* resembled the spectra for the unlabelled 2b, being broad and unresolved. Above room temperature, the 31P NMR spectrum of 2b* broadens progressively until at +100 °C, $\nu_{1/2} \sim 400$ Hz. In the 13C 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 31P and 13C NMR spectra reassumed their original forms.

It is not obvious what the source of the line-broadening is in the 31P and 13C 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

![Scheme 2](image)

**Scheme 2** When diphos = L$_{1a}$ the complex is denoted na, and when diphos = L$_{1b}$, the complex is denoted nb.

![Fig. 1](image)

**Fig. 1** Variable temperature 31P NMR spectra: top, 2b, room temperature; middle, 2b, −90 °C; bottom, 2b*, −90 °C.
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 °C). Nevertheless, one explanation for the NMR behaviour is that at elevated temperatures, CO exchange is taking place perhaps via an analogue of $[\text{Pt}(_2\text{CO})(\mu-\text{CO})(\text{L}_2)_2]$ (see Chart 1 for structure of $\text{L}_4$) reported by Mezaillès et al.$^{14}$ which is in equilibrium with $2b$.

The dicarbonyl complexes, $[\text{PtL}(\text{CO})_2]_3$ ($3a$, $L = \text{L}_a$; $3b$, $L = \text{L}_b$) were generated when solutions of $2a$ and $2b$ were pressurised with 2 atm of CO. The solid state IR spectrum of $3a$ showed $\nu$(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 discernible resonances but at −90 °C, a singlet at 35.3 ppm with $J_{(PPt)}$ of 3107 Hz was observed. At +40 °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 $[\text{Pt}(\text{L}_a)-\left(\text{13CO}\right)_2]_3(3a^*)$ was prepared from $3a$ and $13\text{CO}$ and its $^{13}$C NMR spectrum at −90 °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 $J_{(PC)}$ 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 $\nu$(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 $^1$C NMR spectrum of the labelled complex $[\text{Pt}(\text{L}_a)(\text{13CO})_2]_3(3b^*)$ 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 dicarbons $3a/3b$ 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 $[\text{Pt}(\text{CO})_2(\text{PR}_3)_2]^{13,15}$ and $[\text{Pt}(\text{CO})_2(\text{diphos})]^{14,16}$ including the complex where diphos = $\text{L}_a$(see Chart 1) which has $\nu$(CO) values (1912, 160 cm$^{-1}$) closely similar to those for $3b$ (see eqn (3)); the bulk and bite angles of $\text{L}_a$ and $\text{L}_b$ should be similar. However there is only one previously reported example of a 16-electron $[\text{Pt}(\text{CO})(\text{diphos})]$ 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 $\pi$-acceptor capacity of the fluorophos ligand $\text{L}_f$ efficiently de-localises the electron-density on the Pt(0); this is supported by the high $\nu$(CO) values for $2f$ and $3f$ (see eqn (3)). A similar argument is not tenable for $2a/2b$ since $\text{L}_a/\text{L}_b$ are strong $\sigma$-donors, as reflected in the low $\nu$(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 $\text{L}_a/\text{L}_b$. This steric argument can be extended to explain why CO dissociation from $3a$ appears to be more facile than from $3b$, since $\text{L}_a$ is more sterically demanding than $\text{L}_b$. The complementary explanations for the equilibria shown in eqn (3) for $\text{L}_a/\text{L}_b$ vs. $\text{L}_f$ exemplify how ligands with very different stereoelectronic properties can produce complexes with similar properties.

![Diagram](https://example.com/diagram.png)

When a toluene solution of $2a$ was stirred under an atmosphere of H$_2$ for 5 days, the cis-$[\text{PtH}_2(\text{L}_a)]$ was formed in approximately 50% NMR yield (along with other uncharacterised products), as shown by the close matching of the NMR data
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 characterized by matching of the NMR data with those previously reported for this complex.\textsuperscript{19} Under similar conditions to those used to generate 4a, 2b reacted with ethene but the product, according to the \textsuperscript{31}P NMR spectrum at −90 °C, was a mixture containing 2b (50%), 3b (30%) and a third species (20%) whose \textsuperscript{31}P 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 \([\text{Et}_2\text{O}]_2\text{H}\)[B(C$_6$F$_5$)$_4$]\textsuperscript{20} in chlorobenzene gave a product assigned structure 5a (Scheme 2) on the basis of its \textsuperscript{1}H NMR spectrum which showed a signal at −4.7 ppm with $J$(PPh) = 736 Hz characteristic of a hydride. A band at 2102 cm$^{-1}$ in its IR spectrum is typical of a cationic Pt(II)−CO.\textsuperscript{21} The NMR spectroscopic data for 5a match well those reported by Iggo \textit{et al.}\textsuperscript{7} for the trflate salt of 5a which they characterized in solution only.

Crystals of 5a suitable for X-ray crystallography grew from its CH$_2$Cl$_2$ solution, crystallising in the triclinic space group P$ar{1}$ with two [Pt(L$_a$)(H)(CO)][B(C$_6$F$_5$)$_4$] 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 P1–Pt1–P2 bite angle is 104.00(12)$^\circ$ and the P3–Pt2–P4 bite angle is 104.74(12)$^\circ$ and all four of the half cone angles are $\sim$117$^\circ$.

The chelate conformations for xylenediyl diphos chelates can be described in terms of the two M−P−C−C(Ph) torsion angles. There are currently 12 Pt and 26 Pd xylenediyl diphos chelates in the Cambridge Crystallographic Database (CSD)\textsuperscript{22}, 35 of which have structures where the two M−P−C−C(Ph) torsion angles have similar absolute values and the ring conformation is half-chair-like with an essentially coplanar MP$_2$C$_2$ component as depicted as A in Chart 2. In the remaining 3 structures (HUXCIN\textsuperscript{23}, HUXCEJ\textsuperscript{23} and IHETOF\textsuperscript{24}) the chelate rings adopt a twist-boat-like conformation, with two different Pt−P−C−C(Ph) torsion angles of approximately ±50$^\circ$ and ±14$^\circ$.

Protonation of 2b gave a mixture of geometric isomers of hydridocarbonyl complexes where the position of the H ligand relative to the P-aryl is cis (5b) or trans (6b). Evidence for the two isomers in solution comes from the \textsuperscript{1}H NMR spectrum which showed 2 hydride signals at −2.3 and −4.3 ppm in a 1:4 ratio and the \textsuperscript{31}P NMR spectrum showed two sets of signals; the NMR data for the two species are similar and therefore it was not possible to assign the major isomer (see Experimental for the data). The solid state IR spectrum of the 5b–6b mixture shows 2 ν(CO) bands at 2102 and 2094 cm$^{-1}$.

\textbf{Conclusion}

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

\textbf{Fig. 3} Crystal structure of [Pt(L$_a$)(H)(CO)][B(C$_6$F$_5$)$_4$] (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(C$_6$F$_5$)$_4$] counterions. Selected bond lengths (Å) and angles (°): P1–Pt1 2.366(3); P1–Pt2 2.328(3); P1–C25 1.900(14); P1–H1D 1.660(3); 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–Pt1–P1 98.4(5); C25–Pt1–P2 157.5(5).
The stability of the coordinatively unsaturated [Pt(CO)(diphos)] species 2a/2b relative to 3a/3b is associated with the steric congestion provided by the bulky diphos ligands La and Lb. The only related [Pt(CO)n(diphos)] species reported (2f/3f) feature the electron-poor fluorinated diphos ligand Lf (which has modest steric bulk) where the explanation given for the stability of the monocarbonyl is electronic – the π-acceptor properties of the diphos ligand destabilises the corresponding [Pt(CO)2(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 La and Lb 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 N2-saturated solvents were collected from a Grubbs system in flame and vacuum-dried glassware. Deuterated solvents were dried and distilled from CaH2. Pentane was dried over 4 Å molecular sieves and N2-saturated by repeated freeze, vacuum and thawing cycles. The complex [Pt(η2-nbe)]26 was prepared by literature methods. Ligand La was obtained from Lucite International. Ligand Lb was prepared as previously described.11 CO, C2H4 and H2, were used as obtained from BOC and 13CO 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 Si(CH3)4 (1H or 13C), 85% H3PO4 (31P), and CF3Cl (19F). 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 [Pt(La)(η2-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.31P{H} NMR (202 MHz, C6D5CH3, −60 °C): δ 49.2 (s, 1J(PtP) = 3251 Hz), δ 47.3 (s, 1J(PtP) = 3308 Hz).

**Preparation of [Pt(Lb)(η2-nbe)] (1b)**

A solution of Lb (0.089 g, 0.26 mmol) in toluene (5 mL) was added in one portion to a solution of [Pt(η2-nbe)]2 (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 L₄ (0.158 g, 0.415 mmol) in toluene (5 mL) was added in one portion to a solution of [Pt(η³-nbE)₃] (0.198 g, 0.415 mmol) in toluene (5 mL) at −78 °C, the resulting mixture was stirred for 2 h, allowed to warm to room temperature and then stirred overnight. CO was then bubbled through the solution for 30 min to give an orange solution which was filtered and then the volatiles removed under reduced pressure. The residue was redissolved in toluene (5 mL) and CO was bubbled through solution again. The vacuum/CO cycle was repeated twice more to ensure that all of the norbornene had been displaced. The solvent was 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, 58%): C: 54.17, H: 7.83 (7.39). ESI accurate mass spectrum: (calcd for C₂₄H₄₃OP₂Pt 604.2431) M⁺: 610.2431.

IR: νCO 1907 cm⁻¹. ²³P{H} NMR (162 MHz, C₆D₆): δ 78.5 (br, 1J(PPt) = 3450 Hz), δ 77.9 (d, 1J(PPP) = 3556 Hz, 2J(PPP) = 93 Hz), 76.4 (d, 1J(PP) = 3250 Hz, 2J(PP) = 93 Hz). ¹³C{H} NMR (121 MHz, C₆D₅CD₃): δ 137.9 (s), 133.7 (s), 125.6 (s), 36.8 (br, CH₂), 123.4 (m, C₆H₂), 29.3 (br, C₃H₃).

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

A solution of 2a* (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 the ¹²CO 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 ¹³C NMR spectrum of 2b* was essentially the same as for 2b. ³¹P{H} NMR (121 MHz, C₆D₅CD₃, −90 °C): δ 77.9 (dd, 1J(PPP) = 3556 Hz, 2J(PPP) = 93 Hz, 2J(PC) = 52 Hz), 76.4 (d, 1J(PP) = 3250 Hz, 2J(PP) = 93 Hz, 2J(PC) = 41 Hz). ¹³C{H} NMR (75 MHz, C₆D₅CD₃, −90 °C): δ 234.6 (dd, 1J(CPP) = 2189 Hz, 2J(CP) = 41 Hz, 2J(PC) = 52 Hz, CO).

Preparation of [Pt(Lb)(CO)₂] (3a)

A solution of 2a (10.2 mg, 0.0165 mmol) in d₅-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, C₆D₅CD₃, −90 °C): δ 35.3 (s, 1J(PPP) = 3107 Hz). ¹³C NMR (300 MHz, C₆D₅CD₃): δ 7.1 (m, 2H), 6.9 (m, 2H), 3.3 (br, 4H, CH₂), 1.2 (m, 36H, C₃H₃). ¹³C{H} NMR (100 MHz, C₆D₅CD₃): δ 142.9 (s), 138.7 (s), 130.5 (s), 41.8 (br, CH₂), 37.3 (br, C₃H₃), 34.8 (m, C₃H₃). 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 solution was then saturated with N2 to remove the excess of 13CO. 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, J(PtP) = 3107 Hz). 13C{H} NMR (75 MHz, C6D5CD3, −90 °C): δ 187.1 (m, J(CP) = 1832 Hz, CO), 186.6 (m, J(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. 31P{H} NMR (121 MHz, C6D5CD3): 60.9 (d, J(PtP) = 3106 Hz, J(P) = 20 Hz), 42.7 (d, J(P) = 3818 Hz, J(P) = 20 Hz). 1H NMR (300 MHz, C6D5CD3): δ 7.8 (m, 1H), 7.0 (m, 2H), 6.9 (m, 1H), 3.2 (m, 2H, CH2), 1.3 (d, J(PP) = 13 Hz, 18H, CCH3), 1.1 (d, J(PP) = 13 Hz, 18H, CCH3). 13C{H} NMR (126 MHz, C6D5CD3): δ 143.8 (d, J(CP) = 15 Hz), 134.5 (d, J(CP) = 8 Hz, J(CP) = 5 Hz), 134.4 (d, J(CP) = 2 Hz), 129.0 (s), 125.4 (s), 124.3 (s), 36.9 (m, CCH3), 34.8 (m, CCH3), 32.4 (m, CCH3), 30.1 (br, CH3), 29.8 (m, CCH3), 28.8 (d, CCH3). vCO 1961, 1915 cm−1.

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

A solution of 2b (9.9 mg, 0.0164 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 then the resulting mixture allowed to react for 30 min. The vacuum/CO cycle was repeated twice more to ensure that all 12CO had been displaced. The product was not isolated because it reverted to 2b* upon removal of solvent and was identified in solution by NMR. The 1H NMR spectrum of 3b* was essentially the same as for 3b. 31P{H} NMR (121 MHz, C6D5CD3, −90 °C): δ 43.0 (m, J(PtP) = 3046 Hz), 40.3 (m, J(P) = 2788 Hz). 13C{H} NMR (75 MHz, C6D5CD3, −90 °C): δ 187.1 (m, J(CP) = 1903 Hz, CO), 186.0 (m, J(CP) = 1850 Hz, CO).

Preparation of [Pt(La)(C2H4)] (4a)

A solution of 2a (12.2 mg, 0.0194 mmol) in d8-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 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.15 ESI mass spectrum: (calcd for C25H48P2Pt 617.3 M+ 617.3. 31P{H} NMR (121 MHz, C6D5CD3): δ 48.9 (J(PtP) = 3548 Hz). 1H NMR (300 MHz, C6D5CD3): δ 7.1–6.9 (m, 4H), 3.4 (br, 4H, CCH2), 2.2 (br, J(PP) = 54 Hz, 4H, PtCH2), 1.3 (d, J(PP) = 13 Hz, 36H, CCH3).

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

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 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 then the resulting mixture allowed to react for 30 min. The vacuum/C2H4 cycle was repeated twice. The product was a mixture of 2b, 3b and a species tentatively assigned to 4b on the basis of its 31P NMR parameters. 31P{H} NMR (121 MHz, C6D5CD3): 60.9 (d, J(PtP) = 3288 Hz, J(P) = 45 Hz), 57.9 (d, J(PtP) = 3288 Hz, J(P) = 45 Hz).

Preparation of [Pt(La)(H)(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 to one portion to a solution of 2a (10.5 mg, 0.0169 mmol) in chlorobenzene (0.5 mL) and the resulting mixture was left for 16 h. The solution was layered with pentane (3 mL) resulting in the slow formation of colourless crystals suitable for X-ray crystallography (14.8 mg, 0.012 mmol, 71%). ESI accurate mass spectrum: (calcd for C25H14OP2Pt 618.6655 M+ 618.2589. IR: νCO 2092 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, J(PtP) = 2994 Hz, J(P) = 19 Hz), 34.2 (d, J(PtP) = 2018 Hz, J(P) = 19 Hz). 1H NMR (400 MHz, CD2Cl2): δ 7.4 (m, 2H), 7.3 (m, 2H), 3.9 (br, 4H, CH2), 1.4 (m, 36H, CCH3), −47.4 (d, J(PP) = 145 Hz, J(P) = 15 Hz, J(PH) = 736 Hz, 1H, PtH), 11B{H} NMR (128 MHz, CD2Cl2): δ −17.7 (s). 19F NMR (376 MHz, CD2Cl2): δ −130.3 (m, 8F, p-C6F5), −162.3 (t, 4F, p-C6F5), −166.2 (m, 8F, m-C6F5).

Preparation of [Pt(La)(CO)(H)][B(C6F5)3] (5b/6b)

A solution of [(Et2O)2H][B(C6F5)3] (12.5 mg, 0.0151 mmol) in PhCl (0.5 mL) was added in one portion to a solution of 2b (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, 0.014 mmol, 93%). The product was a mixture of 2 geometric isomers. 31P{H} NMR (202 MHz, CD2Cl2): δ 54.9 (d, J(PtP) = 2948 Hz, J(P) = 22 Hz), 53.5 (d, J(PtP) = 2978 Hz, J(P) = 22 Hz) 49.8 (d, J(PtP) = 1879 Hz, J(P) = 22 Hz), 49.7 (d, J(PtP) = 1879 Hz, J(P) = 22 Hz)
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-Kα radiation (λ = 0.71073 Å). Absorption corrections were based on equivalent reflections using SADABS.27 The structure was solved by direct methods in SHELXS and refined by full matrix least squares, while the CO thermal parameters were located geometrically and refined using a riding model with the exception of H1D, H1E, H2D, H2E. The structure was refined anisotropically and all of the hydrogen atoms (H1D, H1E, H2D, H2E) were located on the basis of 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 Uiso values were fixed at 1.5 × Ueq(Pt). Crystal structure and refinement data are given in Table 1.

| Crystal data and structure refinement for 5a |
|---------------------------------------------|
| **Empirical formula**                       |
| C₄₂H₄₂Br₂O₂P₂Pt                            |
| **Formula weight**                         |
| 1297.69                                     |
| **Temperature/K**                          |
| 100(2)                                     |
| **Crystal system**                         |
| Triclinic                                   |
| **Space group**                            |
| P1                                          |
| **a/Å**                                     |
| 14.3193(7)                                  |
| **b/Å**                                     |
| 15.3989(8)                                  |
| **c/Å**                                     |
| 23.2615(11)                                 |
| **α°**                                      |
| 93.138(4)                                   |
| **β°**                                      |
| 106.589(4)                                  |
| **γ°**                                      |
| 90.129(4)                                   |
| **Volume/Å³**                               |
| 4907.5(4)                                   |
| **Z**                                       |
| 2                                           |
| **μ/Mg/cm³**                                |
| 1.756                                       |
| **μ/mm⁻¹**                                  |
| 3.039                                       |
| **F(000)**                                  |
| 2560.0                                      |
| **Crystal size/mm³**                       |
| 0.10 × 0.15 × 0.17                          |
| **Radiation**                               |
| MoKa (λ = 0.71073)                          |
| **2θ range for data collection/°**          |
| 3.01 to 51.36                               |
| **Index ranges**                            |
| -17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28  |
| **Rint**                                    |
| 0.1485                                      |
| **Reflections collected**                   |
| 53729                                       |
| **Independent reflections**                 |
| 17979                                      |
| **Data/restraints/parameters**              |
| 17979/76/1406                              |
| **Goodness-of-fit on F²**                   |
| 0.981                                       |
| **Final R indexes [I > 2σ(I)]**             |
| R1   = 0.0789, wR2 = 0.1490                  |
| **Final R indexes [all data]**              |
| R1   = 0.1290, wR2 = 0.1877                 |
| **Largest diff. peak/hole/e Å⁻³**           |
| 1.62/−1.61                                 |

References

1 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1976, 365.
2 N. Carr, B. J. Dunne, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1988, 926.
3 L. Mole, J. L. Spencer, N. Carr and A. G. Orpen, *Organometallics*, 1991, 10, 49.
4 (a) R. F. M. J. Parton and M. C. C. Janssen, WO2013030344 (A1), 2013; (b) R. P. Tooze, G. R. Eastham, W. Keith and X. L. Wang, WO9619434 (A1), 1996; (c) J. M. Pearson and R. A. Hadden, WO9841945 (A1), 1998; (d) J. G. De Vries, N. Sereinig, E. W. M. Van de Vondervoort and M. C. J. Janssen, WO2012131027 (A1), 2012; (e) G. R. Eastham, R. P. Tooze, X. L. Wang and K. Whiston, US6335471 (B1), 1996; (f) W. Clegg, M. R. J. Elsegoud, G. R. Eastham, R. P. Tooze, X. Lan Wang and K. Whiston, *Chem. Commun.*, 1999, 1877.
5 (a) R. I. Pugh, E. Drent and P. G. Pringle, *Chem. Commun.*, 2001, 1476; (b) S. Doherty, E. G. Robins, J. G. Knight, C. R. Newman, B. Rhodes, P. A. Champkin and W. Clegg, *J. Organomet. Chem.*, 2001, 640, 182; (c) J. G. Knight, S. Doherty, A. Harriman, E. G. Robins, M. Betham, G. R. Eastham, R. P. Tooze, M. R. J. Elsegoud, P. Champkin and W. Clegg, *Organometallics*, 2000, 19, 4957; (d) O. V. Gusev, A. M. Kalsin, M. G. Peterleitner, P. V. Petrovskii, K. A. Lyssenko, N. G. Akhmedov, C. Bianchini, A. Meli and W. Oberhauser, *Organometallics*, 2002, 21, 3637; (e) C. Bianchini, A. Meli, W. Oberhauser, M. A. Zudeveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev and A. M. Kal’sin, *Organometallics*, 2003, 22, 2409; (f) O. V. Gusev, A. M. Kalsin, P. V. Petrovskii, K. A. Lyssenko, Y. F. Oprunenko, C. Bianchini, A. Meli and W. Oberhauser, *Organometallics*, 2003, 22, 913; (g) N. R. Vautravers and D. J. Cole-Hamilton, *Dalton Trans.*, 2009, 2130; (h) E. Drent, J. A. M. Van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, 417, 235; (i) S. J. Dossett, A. Gillon, A. G. Orpen, S. J. Fleming, P. G. Pringle, D. F. Wass and M. D. Jones, *Chem. Commun.*, 2001, 699; (j) C. Bianchini, H. M. Lee, A. Meli, S. Moneti, F. Vizza, M. Fontani and P. Zanello, *Macromolecules*, 1999, 32, 4183; (k) C. Bianchini, H. Man Lee, P. Barbaro, A. Meli, S. Moneti and F. Vizza, *New J. Chem.*, 1999, 23, 929; (l) E. Lindner, M. Schmid, J. Wald, J. A. Queisser,
M. Geprägs, P. Wegner and C. Nachtigal, *J. Organomet. Chem.*, 2000, **602**, 173; (m) P. W. N. M. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. L. Spek, *J. Am. Chem. Soc.*, 2003, **125**, 5523.

6  
(a) G. R. Eastham, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *Chem. Commun.*, 2000, 609;  
(b) W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *Organometallics*, 2002, **21**, 1832.

7  
J. Wolowska, G. R. Eastham, B. T. Heaton, J. A. Iggo, C. Jacob and R. Whyman, *Chem. Commun.*, 2002, 2784.

8  
T. Fanjul, G. Eastham, N. Fey, A. Hamilton, A. G. Orpen, P. G. Pringle and M. Waugh, *Organometallics*, 2010, **29**, 2292.

9  
T. Fanjul, G. Eastham, M. F. Haddow, A. Hamilton, P. G. Pringle, A. G. Orpen, T. P. W. Turner and M. Waugh, *Catal. Sci. Technol.*, 2012, **2**, 937.

10 V. de la Fuente, M. Waugh, G. R. Eastham, J. A. Iggo, S. Castillón and C. Claver, *Chem. – Eur. J.*, 2010, **16**, 6919.

11 T. Fanjul, G. Eastham, J. Floure, S. J. K. Forrest, M. F. Haddow, A. Hamilton, P. G. Pringle, A. G. Orpen and M. Waugh, *Dalton Trans.*, 2013, **42**, 100.

12 P. G. Edwards, J. C. Knight and P. D. Newman, *Dalton Trans.*, 2010, **39**, 3851.

13 S. Bertsch, H. Braunschweig, M. Forster, K. Gruss and K. Radacki, *Inorg. Chem.*, 2011, **50**, 1816 and references therein.

14 E. Nicolas, G. Nocton and N. Mezailles, *Eur. J. Inorg. Chem.*, 2013, 4000.

15 (a) P. Chini and G. Longoni, *J. Chem. Soc. A*, 1970, 1542;  
(b) G. K. Anderson, H. C. Clark and J. A. Davies, *Organometallics*, 1982, **1**, 550; (c) V. V. Grushin, I. S. Akbem and M. E. Vol’pin, *J. Organomet. Chem.*, 1989, **371**, 403;  
(d) P. Giannocaro, A. Sacco and G. Vasapollo, *Inorg. Chim. Acta*, 1979, **31**, L455; (e) R. S. Paonessa and W. C. Trogler, *J. Am. Chem. Soc.*, 1982, **104**, 1138.

16 G. K. Anderson, G. J. Lumetta and J. W. Siria, *J. Organomet. Chem.*, 1992, **434**, 253.

17 T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 2063.

18 B. L. Bennett and D. M. Roddick, *Inorg. Chem.*, 1996, **35**, 4703.

19 N. Carr, L. Mole, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Dalton Trans.*, 1992, 2653.

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

21 D. Vuzman, E. Poverenov, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon and D. Milstein, *Dalton Trans.*, 2007, 5692.

22 F. H. Allen, *Acta Cryst.*, 2002, **B58**, 380.

23 P. G. Edwards, J. C. Knight and P. D. Newman, *Dalton Trans.*, 2010, **39**, 3851.

24 T. Weisheit, H. Petzold, H. Gorls, G. Mloston and W. Weigand, *Eur. J. Inorg. Chem.*, 2009, 3545.

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

26 S. Ogoshi, M. Morita, K. Inoue and H. Kurosawa, *J. Organomet. Chem.*, 2004, **689**, 662.

27 Bruker, SADAB-2012/1, *Absorption Correction*, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.

28 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.