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SUBSTITUTION OF CHLORIDE IN $[PtCl_2(dppe)]$ BY THE CHIRAL ANIONIC LIGAND $[Mo(CO)_5(PPhH)]^-$: SYNTHESIS AND X-RAY STRUCTURE OF $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ AND A $^{31}P\{^1H\}$ NMR ANALYSIS OF ITS ISOMERIC PRODUCTS AND FLUXIONALITY

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Abstract—Reaction of the chiral anionic ligand $[Mo(CO)_5(PPhH)]^-$ with $[PtCl_2(L\text{-}L)]$ affords the neutral trimetallic monophosphido bridged complexes $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(L\text{-}L)]$ (L-L = dppe, $Ph_2PCH_2CH_2PPh_2$, **2**; dpae, $Ph_2AsCH_2CH_2AsPh_2$, **3**; dppe′, *cis*-$Ph_2PCH{=}CHPPh_2$, **4**). Compounds **2**–**4** are the first examples of heterometallic complexes that contain two chiral primary phosphido bridges existing as pairs of diastereoisomers. $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**) has been characterized spectroscopically and by a single-crystal X-ray analysis. The molecular structure of **2** can be considered either as Mo_2Pt phosphido-bridged trimer or a square-planar Pt^{II} complex bonded to one chelating dppe and two anionic phosphine ligands. The latter PtP_4 description successfully accounts for the line broadening observed in the $^{31}P\{^1H\}$ NMR spectra of **2**–**4**, which can be understood in terms of the existence of several interconverting rotameric forms arising from restricted rotation about the Pt–phosphido bond. The Pt—P—Mo angles of 122.1(1) and 123.5(1)° are some of the largest ever to be reported for phosphido-bridged heterometallics, reflecting the long Pt—Mo separations [4.349(2) and 4.320(2) Å] and the electronic and structural flexibility of the phosphido bridge. The PtMo compound $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**), comprised of one neutral and one dianionic chelate ligand, was prepared from $[Li]_2[Mo(CO)_5(PPhH)_2]$ and $[PtCl_2(dppe)]$ and was shown to contain a conformationally rigid PtP_4 structure with characteristically sharp ^{31}P resonances. The $^{31}P\{^1H\}$ NMR spectrum of **5** is rich with information analysing as two overlapping AA′XX′ spin systems together with their AA′XX′M (M = ^{195}Pt) counterparts. The values of $^2J(P\text{—}P)$ and $^1J(^{195}Pt\text{—}P)$ are significantly lower for $PPhH\{Mo(CO)_5\}^-$ than dppe, a difference that cannot be accounted for solely on the basis of bond length variations. *Meso*-$[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**) is thermodynamically unstable, undergoing a rapid intramolecular elimination of $[Mo(CO)_6]$ to generate $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**), while its racemic diastereoisomer, that which was observed in the crystal, decomposes to unidentified phosphorus-containing products.

Early–late heterobimetallic complexes capable of reacting with organic substrates in a cooperative manner have long been sought after.[1] Unfortunately, of the large number of such complexes, few exhibit the desired cooperatively,[2] reactions often occurring preferentially at a single metal centre.[3] Despite their limited applications the synthesis of heterobimetallic complexes continues to attract interest and has been accomplished in vari-

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ous ways including: (i) displacement of CO or weakly coordinated ligands,[4] (ii) anion substitution,[5] (iii) formation and elimination of small molecules,[6] (iv) bridge assisted reactions[7] and (v) reactions of unsaturated compounds.[8] Although successful cooperativity between electron-poor early transition metals and electron-rich late transition metal centres is rare, this area of chemistry continues to attract attention from researchers in the areas of substrate activation and catalysis.[9] Some of the more notable recent examples are the elegant studies of Bergman *et al.* on the synthesis of an imido-bridged zirconium-iridium heterobimetallic dimer which exhibits a cooperatively in its reaction with both polar and non-polar X—H bonds.[10] Braunstein *et al.* recently reported that the reactivity of platinum–iron heterometallics depends markedly on the nature of the bridging ligand. Those bridged by phosphido ligands underwent a unique CO induced silyl migration from one metal centre to the adjacent metal, whilst their dppm-bridged counterparts formed a siloxycarbene via silyl migration to an acyl ligand.[11] These studies serve to underlie the importance of designed synthesis to achieve participation from both metals centres in the reaction of a heterobimetallic with organic substrates.

Most popular is the preparation of heterobimetallics from terminal phosphido complexes[12] and in a recent report of diphosphido-bridged early–late transition metal heterobimetallics, Baker *et al.* provide a thorough literature survey.[12(f)] The role played by the phosphido ligand in facilitating the synthesis of these compounds can be attributed, at least in part, to stabilization of the metal frameworks as well as the ^{31}P nuclei, which are useful for probing solution state structures and fluxionality.[13] For some time it has been argued that the phosphido ligand is capable of enhancing metal–metal bond stability and maintaining the integrity of polynuclear metal framework during chemical transformations since their flexibility allows a large variation from bonding to non-bonding metal–metal interactions.[14] However, recently reports of some quite remarkable and/or facile transformations of these ligands confirm that they should no longer be considered as innocent and cast doubt on their value as metal framework stabilizing fragments.[15]

Recent activity has focused on the preparation of monophosphido-bridged complexes without metal–metal bonds or other bridging ligands.[16] The enhanced nucleophilicity of pyramidal terminal phosphido complexes[17] has played an important role in synthesis and Kubicki and co-workers have exploited this approach to prepare $[Cp_2MH(PR_2)M'(CO)_4]$ (M = Mo, W; M′ = Cr, Mo, W) from the bent metallocene complex $[Cp_2M(PPh_2)(H)]$, and $[M'(CO)_5(THF)]$, a monophosphido bridged complex which boats the largest reported M—P—M′ (M = W, M′ = W) angle to date.[16(a)]

We have been prompted to report our investigations into the synthesis and characterization of phosphido-bridged complexes by the appearance of several recent articles. Powell *et al.* reported the oxidative addition of the P—H bond of a secondary phosphine complex to zero-valent platinum centres leading to singly-bridged heterobimetallic complexes.[18] Shortly afterwards Mathieu published the synthesis of homo- and heterometallic complexes containing diphenylphosphido ligands and evaluated their catalytic properties.[19] An FeRu diphenylphosphido-bridged compound is an effective catalytic precursors for the hydroformylation of styrene, while the hydrogenation of cyclohexanone was catalysed by a RuMo compound.

Herein we report the synthesis, X-ray structure and solution-state $^{31}P\{^1H\}$ NMR studies of the trimetallic monophosphido-bridged complex $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ **2** and it has been possible to determine the crystal structure of its racemic form. The *meso* diasteroisomer of **2** is revealed to be thermally unstable decomposing to $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ **5** via a facile intramolecular elimination reaction. The $^{31}P\{^1H\}$ NMR spectrum of **5** is rich with information, providing values of $^1J(^{195}Pt—P)$ for both neutral phosphine ligands and phosphido bridges.

RESULTS AND DISCUSSION

Synthesis and characterization of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**)

The reactive nucleophilic ligand $[Mo(CO)_5(PPhH)]^-$ is formed cleanly and quantitatively by treating a THF solution of $[Mo(CO)_5(PPhH_2)]$ (**1a**) with DBU (1,8-diazabicyclo[450]undec-7-ene). Deprotonation was observed to go to completion by the appearance of low frequency carbonyl absorption bands characteristic of a negatively charged complex. Addition of $[PtCl_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to a solution of the anion resulted in facile nucleophilic substitution of both chloride ligands. Purification by thin layer chromatography revealed three products; a minor quantity of $[Mo(CO)_6]$, a major product identified as $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**) and $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**) as a minor product (*vide infra*). The ^1H NMR spectrum of **2**, although generally uninformative, served to confirm the presence of both dppe (δ CH_2 = 2.1) and P—H fragments, the signal for the latter characterized by a large phosphorus–hydrogen coupling constant [^1J(P—H) = 295 Hz], consistent with previous literature reports.[20] In contrast, the $^{31}P\{^1H\}$ NMR spectrum of **2** gave considerable insight into its structure and aspects of a fluxional process in solution. The $^{31}P\{^1H\}$ NMR spectrum of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**) shown in Fig. 1(a) contains two sets of resonances, each consisting of signals for a chelating dppe ligand [δ = 44.8, 46.0 ppm],[21] as well as a signal at much higher field [δ = −33.6, −53.0 ppm] assigned to the bridging phosphido ligand. The proton-coupled ^{31}P NMR spectrum of **2** confirmed our assignment of the $\mu\text{-}PPhH\{Mo(CO)_5\}$ ligand.

There are several notable features of the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**), the first of which is two sets of exchange-broadened resonances for two compounds in unequal abundance (5:2). Both sets resemble doublets flanked by platinum-195 satellites, confirming that only a single platinum atom is bonded to any one phosphorus nucleus. A close examination of Fig. 1(c) reveals that the $^{31}P\{^1H\}$ NMR spectrum of the major product is a non-first-order AA′XX′ spin system. In contrast, the expected fine structure associated with the minor isomer was masked by line broadening. Secondly, the high-field chemical shifts of these phosphido ligands are consistent with the presence of non-bonded metal atoms.[13] Downfield (δ +50 to +300 ppm) resonances are characteristic of phosphido ligand that bridge metal–metal bonds, while higher field (δ +50 to −200 ppm) signals are typically associated with ligands that span non-bonded metal atoms.[3(a),13,22(b)] This correlation is evident on comparing the data for **2** (δ −33.6 ppm) with that reported for $[(CO)_4W(\mu\text{-}PPh_2)_2Pt(PPh_3)]$ (δ +175 ppm), a difference that can only be accounted for by the presence of a Pt—W bond.[22(a)]

We also note a substantial difference between $^1J(^{195}Pt—P)$ for the bridging phosphido and chelating phosphine ligands. The values of the $^1J(^{195}Pt—P)$ for dppe *trans* to a phosphido ligand [$^1J(^{195}Pt—Pdppe)$ = 2323.0 and 2187.0 Hz for the major and minor isomers, respectively] are substantially lower than for dppe *trans* to chloride in $[PtCl_2(dppe)]$ [$^1J(^{195}Pt—Pdppe)$ = 3500 Hz]. There is therefore a significant reduction in $^1J(^{195}Pt—P)$ for dppe upon replacing the *trans*-chloride by the anionic ligand $PPhH\{Mo(CO)_5\}^-$. Moreover, $^1J(^{195}Pt—P\mu)$ (where $P\mu = PPhH\{Mo(CO)_5\}$) is substantially lower than expected based on values for simple tertiary phosphine complexes with similar *trans* ligands. For instance, the value of $^1J(^{195}Pt—P\mu)$ (1400 Hz) for $PPhH\{Mo(CO)_5\}$ *trans* to dppe in **2** is substantially lower than 2500 Hz commonly encountered in *trans* tertiary phosphine complexes.[23] These differences in $^1J(^{195}Pt—P)$ are also reflected in vastly disparate *trans*-^2J(P—P) values. *Trans* tertiary phosphine complexes typically have ^2J(P—P) values of 320–340 Hz. However, placing $PPhH\{Mo(CO)_5\}^-$ *trans* to dppe reduces this values to 213 Hz in **2** and 222 Hz in $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ **5**. These observations support a lower *s*-orbital contribution to the Pt–phosphido bond compared with Pt–phosphine bonds of similar length.

Powell correlated Pt—P bond lengths reasonably well with $^1J(^{195}Pt—P)$ values, the longer Pt—P bonds being associated with a decrease in *J*.[18(b,c)] we believe this is only correct if ligands of the same type are compared, that is, we have to distinguish between tertiary and anionic phosphines in order to obtain credible correlations. The value of $^1J(^{195}Pt—P)$ for tertiary phosphines do then reflect the Pt—P distances as do those of $^1J(^{195}Pt—P\mu)$, which are, in general, considerably lower than their tertiary phosphine counterparts with similar bond lengths.[23] Our structural and spectroscopic studies of the complexes $[Pt(Cl)(PEt_3)_2(\mu\text{-}PPhH)\{Mo(CO)_5\}]$ and *cis*- and *trans*-$[Pt(PEt_3)_2(\mu\text{-}PPhH)\{Mo(CO)_5\}_2]$ support this trend and will be reported elsewhere.[24]

These lower $^1J(^{195}Pt—P\mu)$ coupling constants are not simply a consequence of the ligand occupying the *trans* coordination site, because $^1J(^{195}Pt—P\mu)$ for $PPhH\{Mo(CO)_5\}^-$ *trans* to chloride in $[PtCl(PEt_3)_2(\mu\text{-}PPhH)\{Mo(CO)_5\}]$ [$^1J(^{195}Pt—P\mu)$ = 2135 Hz] is far lower than expected based on the value of 3500 Hz reported for $^1J(^{195}Pt—PEt_3)$ in *cis*-$[PtCl_2(PEt_3)_2]$. There is a similar effect in the complex *trans*-$[Pt(PEt_3)_2(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2]$ for which $^1J(^{195}Pt—PEt_3)$ (2526 Hz) is similar in magnitude to $^1J(^{195}Pt—PEt_3)$ in *trans*-$[PtCl_2(PEt_3)_2]$ (2400 Hz), while $^1J(^{195}Pt—P\mu)$ (1110.0 Hz) in the same complex is less than half this value, a reduction that cannot be attributed solely to bond length variations. These reduced $^1J(^{195}Pt—P)$ values are also paralleled by lower ^2J(P—P) values with $^2J(PEt_3—P\mu)$ and $^2J(PEt_3—PEt_3)$ 200 and 360 Hz, respectively.[24] These observations suggests that $[Mo(CO)_5(PPhH)]^-$ should not be treated naively as an anionic phosphine.

Finally, complex **2** represents the first example of a heterometallic trimer containing two chiral primary phosphido ligands and therefore should exist in *meso* and racemic forms which accounts for the two sets of resonances in the $^{31}P\{^1H\}$ NMR spectrum illustrated in Fig. 1(a).

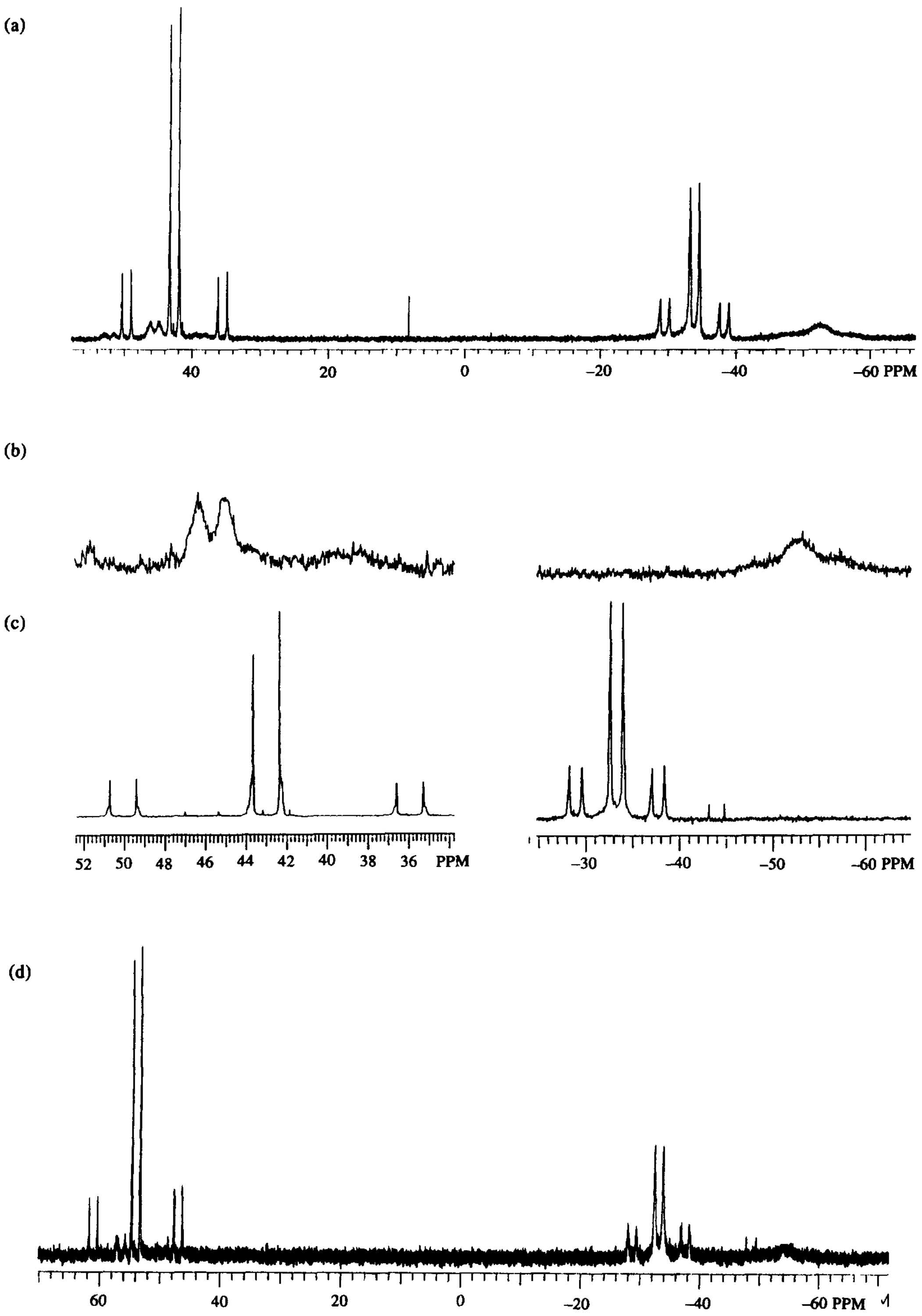


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectra in $CDCl_3$ of (a) the isomeric mixture of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**), (b) pure *meso*-$[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$, (c) pure racemic $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$, illustrating its non-first-order coupling and (d) the isomeric mixture of $Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe')$ (**4**)($dppe' = Ph_2PCH{=}CHPPh_2$).

Crystal structure of Pt(μ-PPhH)$_2${Mo(CO)$_5$}$_2$dppe (2)

The unusual ^{31}P{^{1}H} NMR spectroscopic features of [Pt(μ-PPhH)$_2${Mo(CO)$_5$}$_2$(dppe)] (**2**) described above coupled with the chirality of the phosphido bridges and the possibility of stereoisomers prompted a single-crystal X-ray structure study of a crystal which proved to be the racemic form. The molecular structure of **2** is shown in Fig. 2, identifying it as [Pt(μ-PPhH)$_2${Mo(CO)$_5$}$_2$(dppe)], a phosphido-bridged PtMo$_2$ trimer. An alternative projection in Fig. 3 shows that each phosphorus atom has two substituents on one side and one on the other side of the approximate PtP$_4$ plane that alternate around the molecule with substituents on *trans* ligands eclipsed. We have previously observed a similar situation in the coordination spheres of [IrCl$_2$(PMe$_2$Ph)$_4$][ClO$_4$],[25] [IrCl$_2$(PH$_2$)(PMe$_2$Ph)$_3$][26] and [IrCl$_2$(PMe$_3$)$_3$L][ClO$_4$] (L = PMe$_2$Ph, PMePh$_2$),[2] each of which contains an IrP$_4$ plane with a similar conformation of its substituents. In **2** the Mo(CO)$_5$ components of the anionic phosphines adopt an *anti* arrangement with the P—$\underline{\text{H}}$ substituents on opposite sides of the P$_4$ plane, although the H atoms were not located. Notable features of this structure are the exceptionally large M—P—M angles [Pt—P(1)—Mo(1) = 123.5(1) and Pt—P(2)—Mo(2) = 122.1(1)°], comparable to those recently reported by Kubicki for the unusual singly-bridging μ-phosphido in [Cp$_2$W(H)(μ-PPh$_2$)W(CO)$_5$], for which W—P—W = 124.5°. The vast majority of phosphido-bridged heterometallic complexes have more acute angles at phosphorus,[7,22,28] either because more than one bridging ligand constrains the two metal centres or because there are metal–metal bonding interactions.

The long Pt—Mo non-bonded distances in **2** [Pt—Mo(1) = 4.349(2) and Pt—Mo(2) = 4.320(2) Å] are responsible for the characteristically high-field shifted ^{31}P{^{1}H} NMR signal of the phosphido ligand. The platinum–phosphido bonds in **2** are among the longest to be reported [Pt—P(1) = 2.361(3) and Pt—P(2) = 2.363(2) Å], longer than Pt—P distances to the dppe ligand [Pt—P(3) = 2.300(3) and Pt—P(4) = 2.307(2) Å], presumably reflecting the greater *trans* influence of a dppe compared with PPhH{Mo(CO)$_5$}$^-$. We have demonstrated that Pt—Pμ bond distances are considerably shorter when the ligand in the *trans* coordination site exerts a weak *trans* influence, for instance, in *trans*-[PtCl(PEt$_3$)$_2$(μ-PPhH){Mo(CO)$_5$}][Pt—Pμ = 2.288(2) Å].[24]

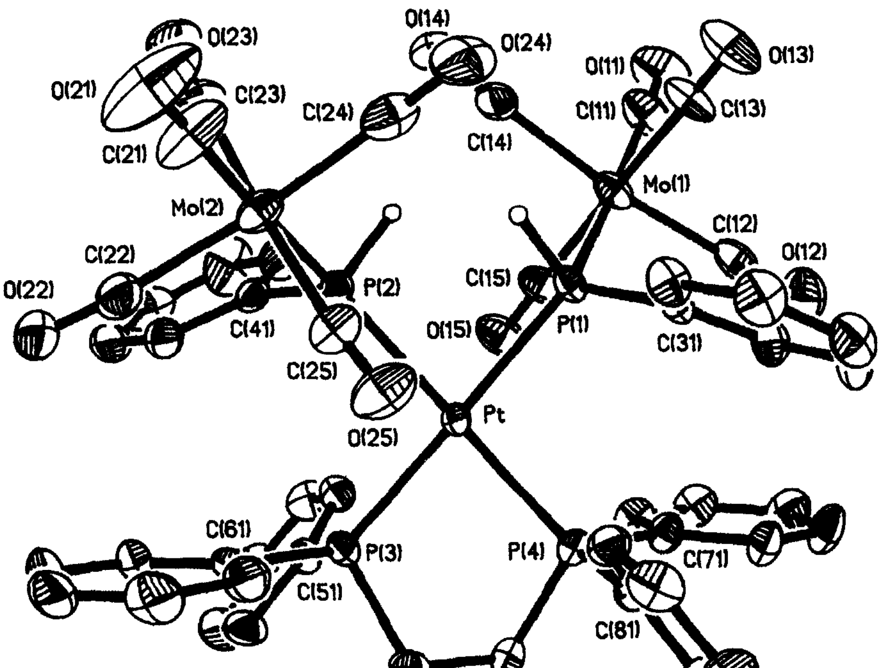


Fig. 2. A plan view ORTEP of [Pt(μ-PPhH)$_2${Mo(CO)$_5$}$_2$(dppe)] (**2**), illustrating the PtP$_4$ planar arrangement and the anti-conformation of the Mo(CO)$_5$ substituents. The P—H atoms were not located, but are shown in idealized positions.

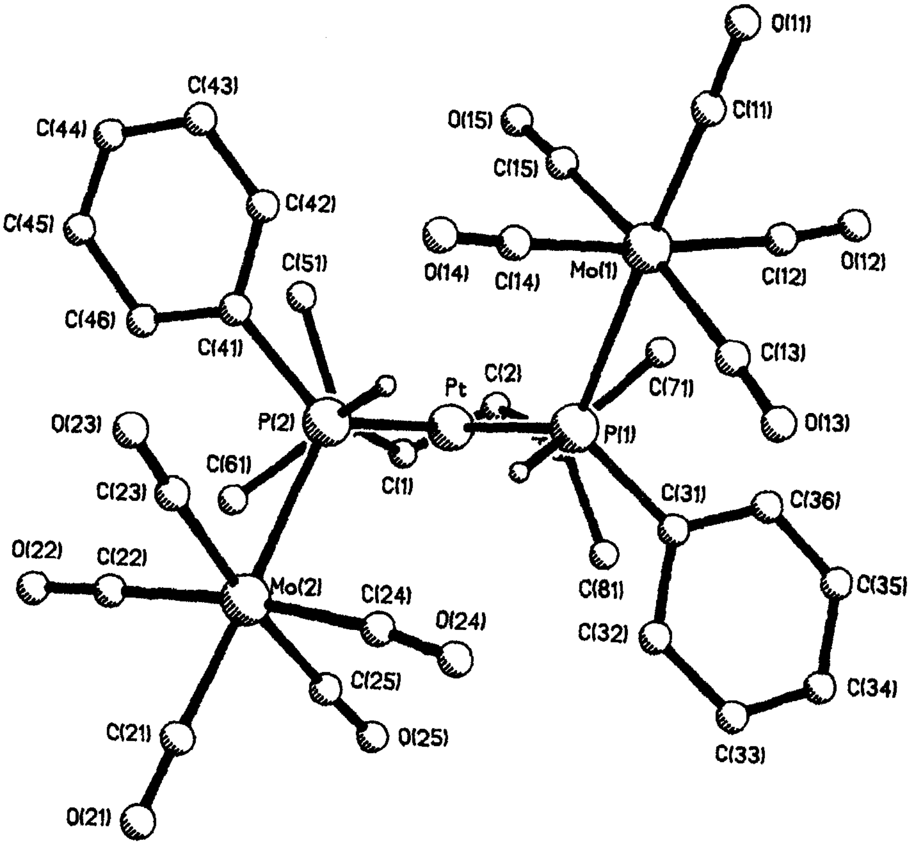
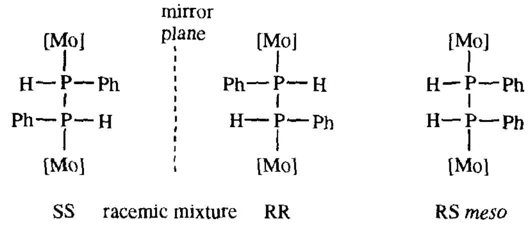


Fig. 3. A view of [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dppe)] (**2**) through the PtP$_4$ plane showing the disposition of substituents at phosphorus with respect to this plane.

Complex **2** is the first example of a monophosphido-bridged heterometallic complex with four unique substituents attached to the phosphido ligands, Ph, H, Pt and Mo, thus, with two equivalent optically active centres, *meso* and racemic forms are expected. The crystal contains the stereoisomer *SS*-[Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dppe)] and its enantiomeric counterpart, *RR*-[Pt(μ-PPhH)$_2$ \{Mo(CO)\}$_2$(dppe)[. The other possible stereoisomer is the achiral *RS-meso* form and was not crystallized. The relationship between these stereoisomers is clearly illustrated by the Fischer projections in Fig. 4.

Our attempts to separate isomers of **2** by fractional crystallization were only partially successful, but did provide sufficient sample to confirm, by ^{31}P\{^{1}H\} NMR, that the major diastereoisomer was that for which the crystal structure was determined. However, this procedure was not satisfactory for the isolation of a pure sample of *meso*-[Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dppe)], although pure samples of both stereoisomers were eventually obtained using preparative HPLC with a 30% ethyl-acetate/70% n-hexane eluant and the ^{31}P\{^{1}H\} NMR spectra of these separated samples are shown in Figs 1(b)–(c).

Few monophosphido-bridged heterobimetallic complexes without metal–metal bonds have been isolated from the *in situ* lithiation of a secondary phosphine complex and subsequent metathesis with a metal halide. Such reactions often lead to undesirable products, for instance, the Pt—W bonded dimer [(CO)$_5$W(μ-PPh$_2$)Pt(PPh$_3$)] was isolated from the reaction of [W(CO)$_5$(PPh$_2$)]$^-$ with



[Mo] = Mo(CO)$_5$

Fig. 4. Stereoisomers of [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$ (dppe)] (**2**).

[$PtCl_2(PPh_3)_2$], while the reaction of [$Mo(CO)_5(PBu^t_2)$]$^-$ with [$CoCl(PMe_3)_3$] generated [$Mo(CO)_4(PMe_3)_2$], not the expected heterobimetallic bridged MoCo dimer. Among successfully generated non-bonded heterobimetallics are the W(μ-PPh_2)Re and W(μ-PPh_2)Mo species prepared by Geoffroy[22(b)] and Shyu,[16(c)] respectively.

$^{31}P\{^1H\}$ *NMR studies of* [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dppe)] (**2**) *and an analysis of its fluxionality*

Initially we were tempted to assign the line broadening in the $^{31}P\{^1H\}$ NMR spectrum of [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dppe)] to restricted conformational exchange of the dppe backbone. However, an analysis of the isomeric distribution expected at the slow exchange limit was sufficient to eliminate this possibility. The *SS/RR* enantiomers would generate non-equivalent rotameric forms containing equivalent phosphido bridges and give rise to two sets of A_2X_2-type resonances in the low-temperature limiting spectrum, while the *meso* diastereoisomer would generate a single rotamer comprised of an ABXY spin system (Fig. 5). The low-temperature $^{31}P\{^1H\}$ NMR spectra of the separated diastereoisomers showed a single set of resonances for the major (RR/SS) isomer, while the *meso* stereoisomer appeared as two sets of signals, an observation only consistent with a low barrier to dppe conformational exchange.

We have also shown that the $^{31}P\{^1H\}$ NMR spectrum of [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dpae)] (**3**) (dpae = bisdiphenylarsinoethane) contains a similar set of exchange broadened signals. Compound **3** was prepared from [$Mo(CO)_5(PPhH)$]$^-$ and [$PtCl_2$(dpae)] in order to eliminate the complicated non-first-order coupling in the $^{31}P\{^1H\}$ NMR spectrum of **2**, while retaining similar solution-state structural and fluxional characteristics. Indeed, the $^{31}P\{^1H\}$ NMR spectrum of **3** was shown to contain two singlet phosphido resonances at δ −30.1 (major) and δ −43.1 ppm (minor). By analogy with **2** we have assigned the major stereoisomer to the sterically most favourable *SS/RR* configuration. The low-temperature $^{31}P\{^1H\}$ NMR spectrum of **3** supported our interpretation of the behaviour of [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$(dppe)] (**2**) with two of the three resonances originating from the minor stereoisomer, whilst the major isomer gave rise to a single resonance. Finally, we argued that the nature of any conformational change originating from the backbone of the chelating ligand should depend markedly on its structural characteristics. Thus, [Pt(μ-PPhH)$_2$\{Mo(CO)$_5$\}$_2$($Ph_2PCH{=\!=}CHPPh_2$)] (**4**) was prepared in the belief that a rigid ethylenic spacer would eliminate this conformational exchange. The $^{31}P\{^1H\}$ NMR of **4** is shown in Fig. 1(d) and serves to highlight its close similarity with the exchange broadened characteristics of **2** and **3**. These experiments reinforce our assignments and confirm that the observed line broadening cannot arise from a conformational exchange of the dppe backbone.

The fluxionality is better understood by considering compounds **2**–**4** as square-planar Pt^{II} coordinated to four phosphines. Some time ago we described some quite remarkable $^{31}P\{^1H\}$ variable-temperature NMR studies of the tetrakisphosphine complex [$IrCl_2(PMe_2Ph)_4$][ClO_4], which exists in three clearly identifiable rotameric forms which interconvert slowly at −50°C.[25] In a subsequent paper we described a similar behaviour for the sterically less crowded system [$IrCl_2(PMe_3)_3L$][ClO_4] (L = PMe_2Ph, $PMePh_2$).[26] It appeared that a general requirement for the occurrence of these rotamers was the presence of four coplanar phosphines

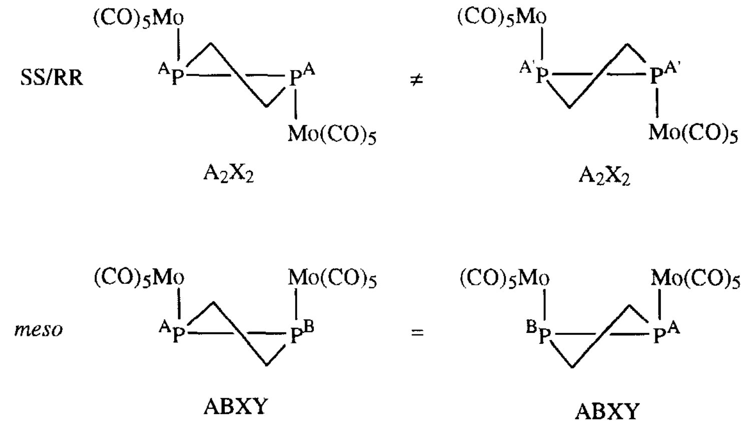


Fig. 5. Conformations arising from restricted inversion of the dppe backbone for the *SS/RR* and *SR* diastereoisomers of **2**.

and that pairs of *trans*-phosphines have to be eclipsed. The crystal structure of **2** (Figs 2 and 3) reveals a similar alternating two above one below the PtP_4 plane arrangement of substituents and can therefore exist as interconverting rotational isomers. The similarity between the structures of $[IrCl_2(PMe_2Ph)_4][ClO_4]$ and $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ shown in Fig. 6 suggests that the latter may also exist in several rotameric forms, arising from a restricted rotation about the Pt—Pμ bonds. Restricted rotation would account for the observed line broadening with the sterically least demanding rotamers being the most populated. To test this hypothesis we prepared $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**), a compound containing two chelating ligands designed to prevent access to rotational isomers.

Synthesis and $^{31}P\{^1H\}$ *NMR investigation of* $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**)

We postulate that $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**), a compound possessing one neutral chelate (dppe) and one dianionic metallo-chelate, $[Mo(CO)_4(PPhH)_2]^{2-}$, would exist as a mixture of two diastereoisomers with only a single accessible rotameric form and that the $^{31}P\{^1H\}$ NMR spectrum should therefore contain two sets of sharp resonances for the two rigid diastereoisomers.

The synthesis of **5** from $[Li]_2[Mo(CO)_4(PPhH)_2]$ and $[PtCl_2(dppe)]$ is illustrated in Scheme 1. $[Mo(CO)_4(PPhH_2)_2]$ was isolated from the reaction of $[Mo(CO)_4(piperidene)_2]$[29] and phenyl phosphine under mild conditions to prevent its undesirable *cis–trans* isomerization. $[Li]_2[Mo(CO)_4(PPhH)_2]$ was generated *in situ* by treating a THF solution of $[Mo(CO)_4(PPhH_2)_2]$ with MeLi at −40°C.[29] Solutions of $[Li]_2[Mo(CO)_4(PPhH)_2]$ reacted rapidly with $[PtCl_2(dppe)]$ to afford **5** in a reasonable yield. The IR spectrum of **5** in the CO region is strikingly similar to those of several related $M(CO)_4$-containing compounds including $[(CO)_4W(\mu\text{-}PPh_2)_2M(PPh_3)]$ (M = Ni, Pd, Pt),[22(a)] $[(CO)_4Mo(\mu\text{-}PPhSiMe_3)_2MCp_2]$ (M = Ti, Zr)[30] and $[Cp_2Zr(\mu\text{-}PEt_2)_2M(CO)_4]$ (M = Mo, W),[12(e)] unequivocally confirming the presence of a disubstituted $Mo(CO)_4$ fragment.

Figure 7 shows the $^{31}P\{^1H\}$ NMR spectra of **5** in the dppe and phosphido region. Although these spectra appear rather complicated, they are rich with information and have been successfully analysed (Figs 7 and 8). The sharpness of the individual resonances indicates that the dynamic process giving rise to the exchange-broadened $^{31}P\{^1H\}$ NMR spectra in Figs 1(a)–(d) is inoperative in this PtP_4 complex, which contains two chelating ligands. This lends credibility to our hypothesis that the broad spectral characteristics of **2** are due to the presence of interconverting rotameric forms. The signals in Fig. 7 assigned to the phosphido bridges of **5** (δ −134.5 and −141.8 ppm) are shifted to

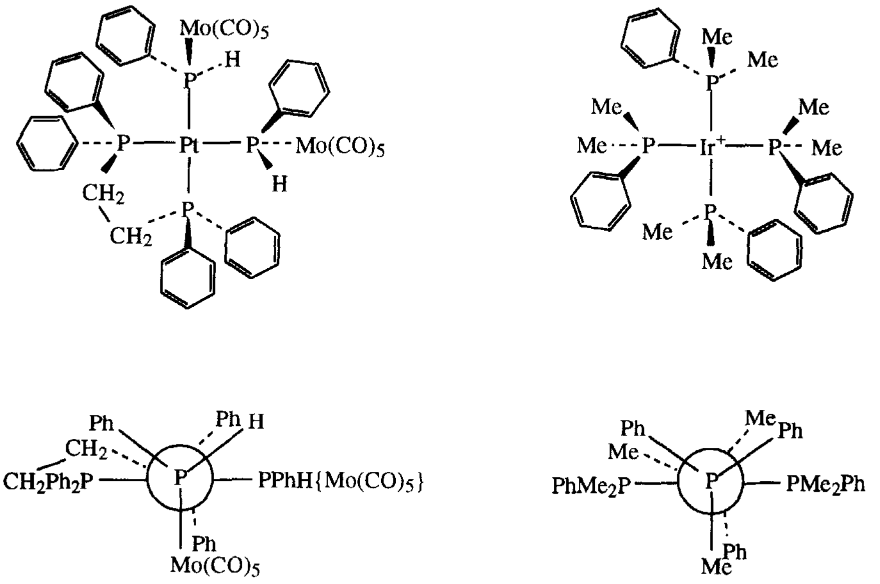
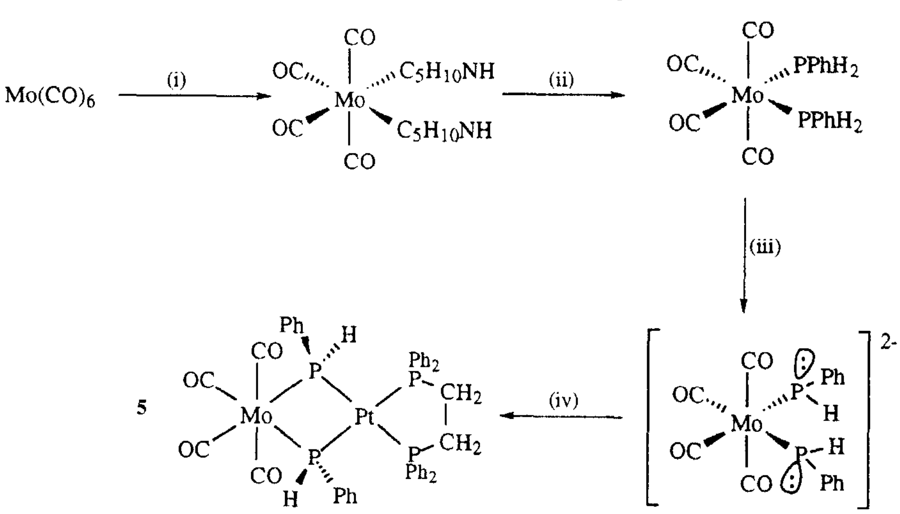


Fig. 6. Projections of the conformations of $[IrCl_2(PMe_2Ph)_4][ClO_4]$ and $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**) in the PtP_4 plane (crystal structures). $[IrCl_2(PMe_2Ph)_4][ClO_4]$ exists in three rotameric forms in solution due to restricted rotation about the Ir—P bond. The similarity with **2** suggests a likely explanation for the NMR line broadening effects in its $^{31}P\{^1H\}$ NMR spectrum.



Scheme 1. (i) Piperidine 97°C, 4 h; (ii) $PPhH_2CH_2Cl_2$ reflux 15 min; (iii) THF, MeLi, −40°C; (iv) [$PtCl_2$(dppe)], THF.

high field of the region which characterizes [$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$(dppe)] (**2**). While this region of the $^{31}P\{^1H\}$ NMR spectrum is reserved for μ-PR_2 ligands bridging non-bonded metal atoms, it is surprising that on going from **2** to **5** there is a shift to higher field. This appears to contradict the relationship between the angular parameters at P and the corresponding $\delta^{31}P$ recently reported by Kubicki,[16(a)] if we assume that the formation of **5** is accompanied by a reduction in the M—P—M angle. The effect of a metal–metal bond on δ ^{31}P is clearly illustrated in the reaction of [$PtCl_2(PPh_3)_2$] with $[W(CO)_4(PPh_2)_2]^{2-}$, for which facile PPh_3 dissociation and Pt—W bond formation is associated with a δ $^{31}P\mu$ of 180 ppm.

The two diastereoisomers of **5** are readily ident-

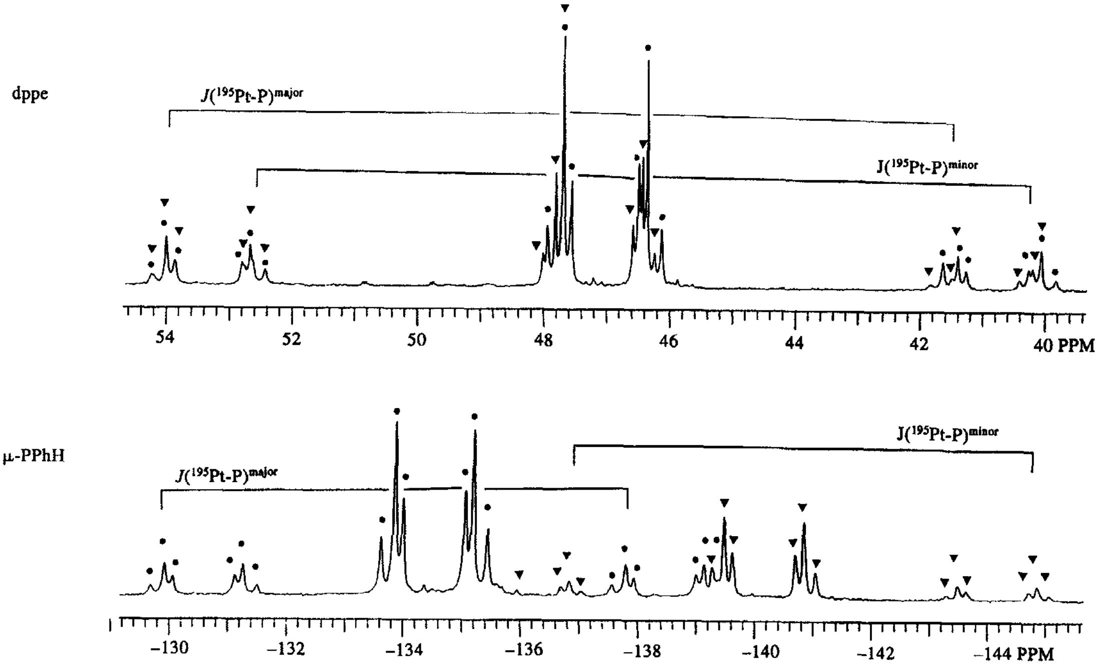
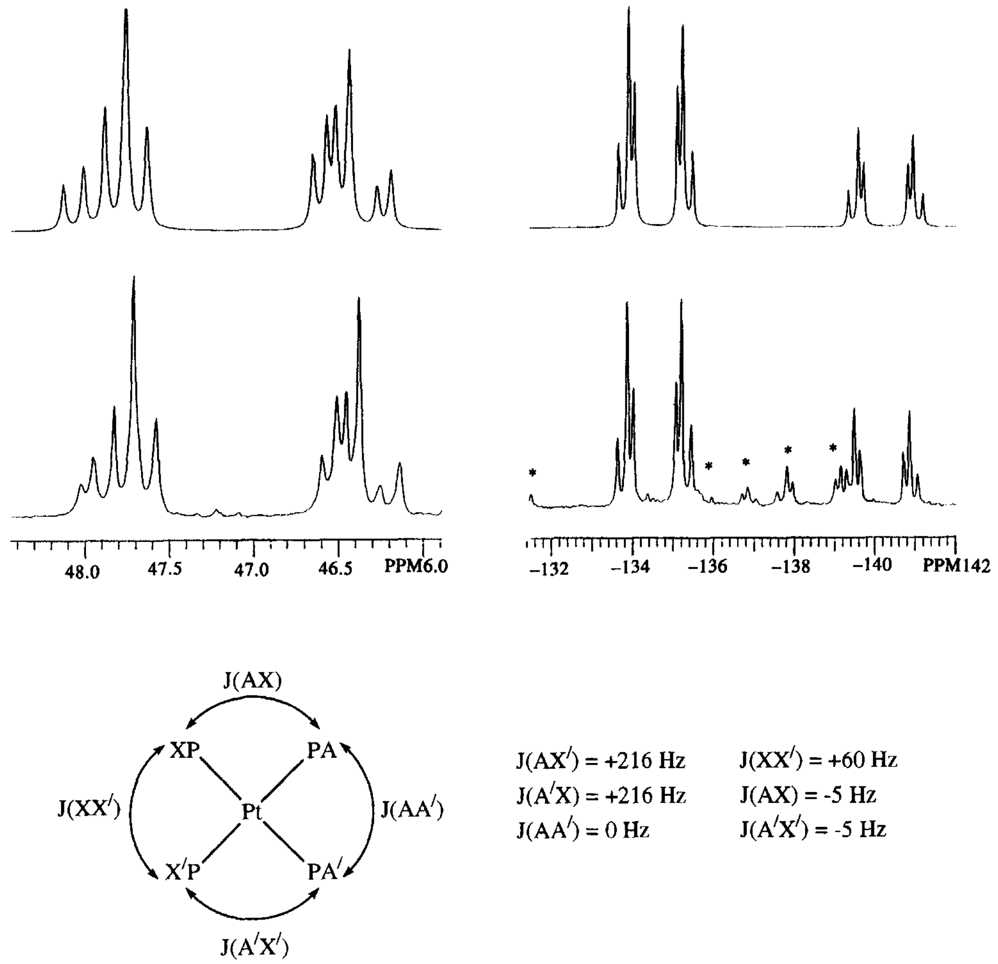


Fig. 7. $^{31}P\{^1H\}$ NMR spectrum of [$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}$(dppe)] **5** in $CDCl_3$. Major (●) AA′XX′ and AA′XX′M and minor (▼) $A_1A_1'X_1X_1'$ and $A_1A_1'X_1X_1'M$ (M = ^{195}Pt) diastereoisomers illustrating the disparate values of $^1J(^{195}Pt—P)$ for the phosphido bridge (1450 Hz) and dppe ligands (2323.0 Hz).



J(AX') = +216 Hz
J(A'X) = +216 Hz
J(AA') = 0 Hz
J(XX') = +60 Hz
J(AX) = -5 Hz
J(A'X') = -5 Hz

Fig. 8. $^{31}P\{^1H\}$ NMR spectrum of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**) recorded in CD_2Cl_2 with the computer simulation of the AA'XX' and $A_1A_1'X_1X_1'$ components shown above. Resonances assigned as (*) belong to the AA'XX'M and $A_1A_1'X_1X_1'M$ (M = ^{195}Pt) spin systems.

ified in the high-field region ($\delta = -134.5$ and -141.8 ppm, major and minor, respectively), while accidental coincidence of the dppe resonances makes an assignment of the magnetically non-equivalent stereoisomers more difficult ($\delta = +47.0$ and $+47.1$, major and minor, respectively).

The spectroscopic assignments for **5** together with the associated Pt satellites are shown in Fig. 7. One of its most striking features is the large difference between $^1J(^{195}Pt—P\mu)$ and $^1J(^{195}Pt—Pdppe)$ with the coupling to dppe (2063 and 2066 Hz) being greater than those to the anionic phosphine (1280 and 1304 Hz). These values are similar to those for $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$. The presence of one set of platinum-195 satellites flanking each resonance confirms that only a single platinum centre is bonded to the dppe and the anionic chelating phosphine. Each set of resonances results from the superposition of two spin systems, an AA'XX' corresponding to the isotopomer with no ^{195}Pt and an AA'XX'M for the platinum-195 isotopomer. These two resonance sets are compatible with the two diastereoisomers associated with the two chiral phosphido bridges and are labelled (●) and (▼) for the major and minor diastereoisomers, respectively (Fig. 7). Previous reports[31] of $^{31}P\{^1H\}$ NMR spectra of platinum–phosphine–phosphido containing complexes have highlighted the value of this technique in probing solution-state structure and bonding. Several characteristics of the recently reported phosphido-bridged complex $[(HBu^t_2P)_2Pt(\mu\text{-}H)(\mu\text{-}PBu^t_2)Pt(H)(PBu^t_2H)]$ parallel features of the $^{31}P\{^1H\}$ NMR spectrum of **5** including the reduced values of $^1J(^{195}Pt—P\mu)$ and $^2J(P—P\mu)$ typically in the range 2100–220 Hz, respectively.[31(a)]

Figure 8 shows the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ together with a computer simulation. Successful simulation of the spectrum of **5** requires two overlapping AA'XX' spins systems and was obtained by fixing the *trans* coupling constant at 216 Hz, measured directly from the spectrum, and varying the *cis* coupling constants which finally refined at $J(XX') = 60$, $J(AA') = 0$, $J(AX) = -5$ and $J(A'X') = -5$ Hz (Fig. 8). We[25,26] and others[32] have previously noted the requirement for *cis* and *trans* $^2J(P—P)$ coupling constants of opposite sign in the spin-simulated $^{31}P\{^1H\}$ NMR spectra of complexes containing four coplanar phosphines. A low-temperature $^{31}P\{^1H\}$ NMR spectrum of **5** (CD_2Cl_2, $-75°C$) showed no evidence of line broadening suggesting that the fluxional process observed in the spectra of compounds **2**–**4** is the interconversion of rotational isomers and that conformational changes in the dppe backbone are rapid at this temperature.

Thermolysis of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**)

We noted earlier that a minor amount of $[Mo(CO)_6]$ and an unidentified phosphorus-containing compound were isolated from the reaction of $[Mo(CO)_5(PPhH)]^-$ with $[PtCl_2(dppe)]$. This latter compound was identified spectroscopically as $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**) only after its designed synthesis described above. We examined the purity of the samples of $[Mo(CO)_5(PPhH_2)]$ used for the preparation of **2** to eliminate the possibility that **5** could be formed from a small amount of $[Mo(CO)_4(PPhH_2)_2]$ contaminant, and conclude that $[Mo(CO)_6]$ and $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ were in fact genuine side-products from the reaction of $[Mo(CO)_5(PPhH)]^-$ with $[PtCl_2(dppe)]$.

The title compound, as a mixture of its stereoisomers, was heated at reflux in THF and the progress of the reaction monitored by IR and NMR spectroscopy. The gradual appearance of low-frequency IR absorptions of **5** was used to monitor the transformation. After 45 min at reflux there was no further change in the composition of the reaction mixture, which consisted of a mixture of $[Mo(CO)_6]$, $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ and $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$. Analysis of the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at regular intervals revealed that the *meso* stereoisomer rapidly converted to **5** and $[Mo(CO)_6]$. In contrast, the *SS*/*RR* enantiomeric pair underwent a much slower transformation into unidentified products and not **5**. We believe these observations to be related to the accessibility of conformations of **5** that contain *syn*-$Mo(CO)_5$ substituents and can be understood with reference to the rotameric form that crystallize out for *SS*/*RR*-$[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (Figs 2 and 3). The reluctance of the *SS*/*RR* enantiomeric pair to undergo an intramolecular elimination of $[Mo(CO)_6]$ is due to the *anti*-arrangement of the $Mo(CO)_5$ substituents in its lowest energy rotameric form. In contrast, the *syn*-arrangement in the *meso* configuration is energetically more accessible, favouring the elimination of $[Mo(CO)_6]$ and the formation of **5**. We were unable to isolate any intermediates during this transformation. The isolation of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ from the reaction of $[PtCl_2(dppe)]$ and $[Mo(CO)_5(PPhH)]^-$ and the transformation of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ into $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ confirms that **2** is indeed thermodynamically unstable with respect to $[Mo(CO)_6]$ and $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$.

CONCLUSIONS

These studies have expanded the utility of the bridge-assisted synthetic approach for directing the synthesis of phosphido bridged compounds. Our approach has enabled us to prepare and isolate heterotrimetallic Mo_2Pt and bimetallic MoPt complexes containing the first examples of primary chiral phosphido bridges. The $^{31}P\{^1H\}$ NMR spectrum of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ contains two sets of resonances corresponding to two diastereoisomers which have been successfully separated. The exchange-broadened $^{31}P\{^1H\}$ NMR spectrum of **2** and its related compounds **3**–**4** have been interpreted in terms of the presence of several rotameric forms which interconvert by rotation about the Pt—Pμ bonds. We have investigated, in detail, previously similar processes occurring in $[IrCl_2(PMe_2Ph)_4][ClO_4]$ and $[IrCl_2(PMe_3)_3L][ClO_4]$ ($L = PMe_2Ph$, $PMePh_2$), each of which has a common feature of four coplanar phosphine ligands, suggesting that compounds **2**–**5** should be considered as square-planar PtP_4 complexes rather than phosphido-bridged heterometallics in order to account for their spectroscopic characteristics. $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ was prepared and shown to be conformationally rigid and characterized by a complex but informative $^{31}P\{^1H\}$ NMR spectrum which analysed for two diastereoisomers each consisting of AA′XX′ and AA′XX′M ($M = {}^{195}Pt$) spin systems. The absence of line broadening in this spectrum was attributed to the inaccessibility of alternative rotameric forms in solution. The *meso* stereoisomer of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ was shown to be thermodynamically unstable with respect to $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ and $[Mo(CO)_6]$ while the *SS*/*RR* enantiomers were shown to be more stable, only decomposing at far higher temperatures to unidentified products.

Examination of the $^{31}P\{^1H\}$ spectra of **2**–**5** revealed reduced values of $^2J(P—P)$ for phosphido ligands *trans* to tertiary phosphines [$^2J(P—P\mu) = 220$ Hz] compared with the larger values reported for pairs of *trans* tertiary phosphines [$^2J(PP) = 350$ Hz]. This reduction in $^2J(P—P\mu)$ appears to be accompanied by reduced values of $^1J(^{195}Pt—P\mu)$ in comparison to those reported for neutral tertiary phosphines with similar Pt—P bond lengths. In particular the value of $^1J(^{195}Pt—P\mu)$ is approximately one half that of ^1J(Pt—Ptertiary) for complexes with similar bond lengths. These reduced coupling constants are consistent with a lower *s*-orbital contribution to the platinum-phosphorus bond of the anionic phosphine compared with their more common neutral conterparts.

EXPERIMENTAL

$^{31}P\{^1H\}$ data for the compounds reported here are presented in Table 1.

General considerations

All manipulations were performed using standard Schlenk-line techniques under dry dinitrogen. Solvents were dried and degassed according to standard procedures. ^{1}H NMR were recorded on Varian VXR 400 or XL 200 spectrometers and all ^{31}P NMR spectra were recorded on a Varian VXR 400 instrument at 162.0 MHz and referenced to external 85% H_3PO_4 IR spectra were recorded on a Perkin–Elmer 983 spectrometer and elemental analysis were carried out by the Analytical Laboratory at University College London.

[$PtCl_2$(dppe)],[33] [$PtCl_2$(dpae)][33] and [$Mo(CO)_4(C_5NH_{11})_2$][29] were prepared according to previously reported procedures. Methyl lithium and DBU were purchased from Aldrich and phenyl phosphine ($PPhH_2$) from Strem Chemical Company and used without further purification.

Preparation of [$Mo(CO)_5(PPhH_2)$] (**1a**)

A solution of [$Mo(CO)_6$] (1.599 g, 6.0 mmol) and phenylphosphine (0.617 cm^3, 5.6 mmol) in n-octane (200 cm^3) was heated at reflux for 30 min. The solvent was removed under reduced pressure and the residue extracted with n-hexane and the solvent removed to leave an oily residue. This residue was extracted into the minimum quantity of dichloromethane (10–12 cm^3), the solution absorbed on to silica gel, the solvent was removed and the silica placed on a 330 × 30 mm silica gel column and eluted with hexane to afford one major fast moving band. The product from this band was crystallized from n-hexane (−20°C, 4 h) to afford colourless crystals of **1a** in 49% yield (0.900 g). Found: C, 38.3; H, 1.9; P, 8.7; Calc. for $C_{11}H_7MoO_5P$: C, 38.2; H, 2.0; P, 8.9%. IR [ν(CO), cm^{-1}, C_6H_{14}]: 2074 w, 1945 s. ^{1}H NMR (400 MHz, $CDCl_3$, δ):

Table 1. $^{31}P\{^1H\}$ NMR data for the phosphido-bridged heterometallic bridged complexes **2**, **3**, **4** and **5**

Compound	δ^a	Assignment	$J(PP)^{trans}$ (Hz)	$J(PP)^{cis}$ (Hz)	$J(^{195}Pt—P)$ (Hz)
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$(dppe)	+44.8	$Ph_2\underline{P}CH_2$	213.0	—	2323.0
Major diastereoisomer	−33.6	$\underline{P}PhH$	213.0		1450.0
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$(dppe)	+46.0	$Ph_2\underline{P}CH_2$	216.0	—	2187.0
Minor diastereoisomer	−53.0	$\underline{P}PhH$	broad		
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$(dppa)	−30.0	$\underline{P}PhH$	—	—	1730.0
Major diastereoisomer					
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$(dppa)	−43.1	$\underline{P}PhH$	—	—	1730.0
Minor diastereoisomer					
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$	+54.0	$Ph_2\underline{P}CH$	221.0	—	2307.1
($Ph_2PCH{=}CHPPh_2$)	−33.0	$\underline{P}PhH$	221.0		1423.6
Major diastereoisomer					
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2$	+56.5	$Ph_2\underline{P}CH$	206.0	—	2307.0
($Ph_2PCH{=}CHPPh_2$)	−54.0	$\underline{P}PhH$	206.0		—
Minor diastereoisomer					
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}$(dppe)	+47.0	$Ph_2\underline{P}CH_2$	216.0		2063.0
Major diastereoisomer	−134.5	$\underline{P}PhH$	216.0		1280.0
$Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}$(dppe)	+47.1	$Ph_2\underline{P}CH_2$	222.0		2066.0
Minor diastereoisomer	−141.8	$\underline{P}PhH$	222.0		1304.0

[a] In $CDCl_3$ at 162 MHz with chemical shifts referenced to 85% H_3PO_4.

7.56 [ddd, $^3J(PH) = 12.0$ Hz, $^3J(HH) = 7.0$ Hz, $^4J(PH) = 1.2$ Hz, C_6H_5 *ortho*, 2H], 7.40 (m, C_6H_5, 3H), 5.40 [d, $^1J(PH) = 312.0$ Hz, $PPhH_2$, 2H].

Preparation of $[Mo(CO)_4(PPhH_2)_2]$ (**1b**)

Phenylphosphine (0.61 cm^3, 5.5 mmol) was added to a solution of the piperidine complex $[Mo(CO)_4(C_5NH_{11})_2]$ (1.04 g, 2.8 mmol) in dichloromethane (120 cm^3) at ambient temperature. The mixture was refluxed for *ca* 15 min under dinitrogen, after which time the volatile materials were removed under vacuum to leave an oily residue. A chromatographic procedure similar to that used for the purification of $[Mo(CO)_5(PPhH_2)]$ afforded two well separated bands. The first band to elute was characterized spectroscopically as $[Mo(CO)_5(PPhH_2)]$ (0.400 g) and the following fraction was identified as $[Mo(CO)_4(PPhH_2)_2]$ (0.433 g, 40%). The collected fraction was concentrated and left overnight at -20 C to afford colourless crystals. IR [ν(CO), cm^{-1}, C_6H_{14}]: 2026 w, 1916 s, 1896 sh. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50 (m, C_6H_5, 6H), 7.40 [ddd, $^3J(PH) = 12.6$ Hz, $^3J(HH) = 7.3$ Hz, $^4J(HH) = 1.4$ Hz, C_6H_5 *ortho*, 4H], 5.35 [dm, $^1J(PH) = 326.0$ Hz, $PPhH_2$, 4H].

Preparation of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**)

To a solution of $[Mo(CO)_5(PPhH_2)]$ (0.087 g, 0.25 mmol) in THF (50 cm^3) was added an excess of DBU (0.096 cm^3, 0.63 mmol). Reaction was accompanied by the formation of a deep yellow colour and a shift of the carbonyl absorptions to lower frequency. The reaction mixture was stirred under nitrogen for 15 min before the addition of a solution of $[PtCl_2(dppe)]$ (0.085 g, 0.13 mmol) in THF (5 cm^3). After stirring for a further 2 h the solvent was removed under reduced pressure to afford a brown oil. This residue was dissolved in the minimum quantity of dichloromethane and chromatographed on silica gel plates. Elution with dichloromethane/n-hexane (2 : 3, v/v) afforded two bands. The faster moving band was identified spectroscopically as $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (0.015 g) and the slower moving band as **2**. Crystallization from dichloromethane/ethanol and vacuum drying afforded air-stable yellow crystals of **2** in 22% yield (0.037 g). Found: C, 44.7; H, 2.6; P, 9.9. Calc. for $C_{48}H_{36}Mo_2O_{10}P_4Pt$: C, 44.9; H, 2.8;, P, 9.6%. IR [ν(CO), cm^{-1}, C_6H_{14}]: 2058 w, 1953 s, 1906 sh. ^{1}H NMR major diastereoisomer, (400 MHz, $CDCl_3$, δ): 7.5–7.2 (m, C_6H_5, 18H), 6.8 (m, C_6H_5, 12H), 4.80 [dm, $^1J(PH) = 330.0$ Hz, PPh*H*, 2H], 2.2 (m, CH_2, 4H). ^{1}H NMR minor diastereoisomer (400 MHz, $CDCl_3$, δ): 7.0–7.6 (m, C_6H_5, 30 H), 4.81 ($^1J(PH) = 295.0$ Hz, PPh*H*, 2H), 2.1 (m, CH_2, 4H).

Preparation of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dpae)]$ (**3**)

Following the method of **2**, $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dpae)]$ (**4**) was isolated in 19% yield as air-stable pale yellow micro crystals. Found: C, 40.6; H, 2.9; P, 4.6. Calc. for $C_{48}H_{36}As_2Mo_2O_{10}P_2Pt$: C, 42.0; H, 2.6; P, 4.5%. IR [ν(CO), cm^{-1}, C_6H_{14}]: 2062 w, 1935 s, 1908 sh.

Preparation of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe')]$ (**4**)

Following the method for the preparation of **2**, $[Mo(CO)_5(PPhH_2)]$ (0.0747 g, 0.22 mmol), DBU (0.072 cm^3, 0.47 mmol) and $PtCl_2(dppe')$ (0.070 g, 0.11 mmol) gave an orange oily residue after removal of the solvent. A chromatographic procedure similar to that used for the purification of **2** afforded a major band which was crystallized from dichloromethane/ethanol to afford **3** in 25% yield (0.034 g). Found: C, 44.7; H, 2.7. Calc. for $C_{48}H_{34}Mo_2O_{10}P_4Pt$: C, 45.0; H, 2.8%. IR [$\nu$(CO), cm^{-1}, C_6H_{14}]: 2057 2, 1933 s, 1095 sh.

Preparation of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_4\}(dppe)]$ (**5**)

To a THF solution of $[Mo(CO)_4(PPhH_2)_2]$ (0.102 g, 0.24 mmol) was added methyl lithium (0.298 cm^3 of a 1.6 mol dm^{-3} solution in ether, 0.48 mmol) at -40 C. The reaction mixture was allowed to stir under nitrogen for 20 min to generate $[Li]_2[Mo(CO)_4(PPhH)_2]$ *in situ*. A solution of $[PtCl_2(dppe)]$ (0.158 g, 0.23 mmol) in THF (5 cm^3) was added dropwise over a period of 20 min and stirring continued for a further 2 h, after which time the solvent was removed to leave a deep orange oil. This residue was dissolved in the minimum quantity of dichloromethane and chromatographed on silica gel plates. Elution with dichloromethane/n-hexane (2 : 3 v/v) afforded a single major band. Crystallization of the product from dichloromethane/ethanol and vacuum drying afforded **5** as an orange solid in 30% yield (0.075 g). IR [ν(CO), cm^{-1}, C_6H_{14}]: 1996 w, 1875 s, 1852 sh.

Crystal structure determination of **2**

Pale yellow crystals of $[Pt(\mu\text{-}PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (**2**) were grown from dichloromethane–methanol. A platelet selected for study, $0.40 \times 0.50 \times 0.08$ mm^3, was mounted on a glass fibre on the goniometer of a Nicolet R3m/v diffractometer. Details of crystal and intensity data are collected in Table 2. The unit cell was determined from 30 orientation reflections in the range $10 \leqslant 2\theta \leqslant 28°$ selected from a rotation photograph. The structure was solved by direct methods in space group $P2_1/n$ A model using 586 parameters was refined to give R and Rw as in Table 2. All non-hydrogen atoms were refined anisotropically and H atoms of the phenyl rings were included in idealized positions with C—H = 0.96 Å and with thermal parameters 0.08 Å^2. The H atoms bonded to phosphorus were observed in difference maps, but were indistinct and were not included in the final model.

All calculations were carried out on a Micro Vax II computer running SHELXTL-PLUS (G. M. Sheldrick, Package for Crystal Structure Determination, University of Göttenberg, 1986) selected bond distances and angles in Table 3. Further details are available as supplementary material (atomic coordinates, bond distances, bond angles, anisotropic thermal parameters and hydrogen atom positions) deposited at the Cambridge Crystallographic Data Centre. Observed and calculated structure factors are available from the authors upon request.

Table 2. Crystal and intensity collection data for [Pt(μ-PPhH)$_2${Mo(CO)$_5$}$_2$(dppe)] (**2**)

Compound	**2**
Formula	$C_{48}H_{36}Mo_2O_{10}P_4Pt$
Formula weight	1283.69
Space group	$P2_1/n$
a (Å)	14.295(4)
b (Å)	19.439(6)
c (Å)	18.318(5)
β(°)	101.30(2)
V (Å^3)	4991(2)
Z	4
D_{calc}(g cm^{-3})	1.71
μ(Mo-K_α) (cm^{-1})	34.9
Radiation, λ (Å)	Mo, 0.71073
Temperature (°C)	17
Scan mode	ω–2θ
2θ range (°)	$5 \leqslant 2\theta \leqslant 50$
Total data	9472
Unique data	8805
Structure solution	Direct methods
Rejection criteria	$I_0 \leqslant 1.5\sigma(I_0)$
Reflections used	6739
Parameters	586
R^a	0.0568
Rw^a	0.0574
Maximum shift/e.s.d.	0.03
Residual density (e Å^{-3})	1.2

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$; $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + 0.00109F_o^2]$.

Table 3. Selected interatomic distances (Å) and angles (°) for [Pt(μ-PPhH)$_2${Mo(CO)$_5$}$_2$(dppe)] (**2**)

Mo(1)—P(1)	2.574(2)
Mo(2)—P(2)	2.571(2)
Pt—P(1)	2.361(3)
Pt—P(2)	2.363(2)
Pt—P(3)	2.300(3)
Pt—P(4)	2.307(2)
P(1)—Pt—P(2)	82.6(1)
P(1)—Pt—P(3)	177.4(1)
P(2)—Pt—P(4)	96.3(1)
P(1)—Pt—P(4)	96.6(1)
P(2)—Pt—P(4)	178.0(1)
P(3)—Pt—P(4)	84.5(1)
Pt—P(1)—Mo(1)	123.5(1)
Pt—P(2)—Mo(2)	122.1(1)

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