

# Substitution of chloride in $[PtCl_2(PEt_3)_2]$ by the chiral anionic ligand $[Mo(CO)_5(PPhH)]^-$ to give mixed platinum-molybdenum compounds and a <sup>31</sup>P{<sup>1</sup>H} NMR analysis of their fluxionality. X-ray crystal structure of $[PtCl(PEt_3)_2$ ( $\mu$ -PPhH){Mo(CO)<sub>5</sub>}] and trans-[Pt(PEt\_3)\_2 ( $\mu$ -PPH)<sub>2</sub>{Mo(CO)<sub>5</sub>}\_2]

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Abstract—Deprotonation of the primary phosphine complex  $[Mo(CO)_5(PPhH_2)]$  generated  $[Mo(C-PhH_2)]$  $O_{5}(PPhH)^{-}$ , a chiral anionic ligand which reacted readily with *cis*- or *trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>5</sub>] via facile nucleophilic substitution of one or both chloride ligands to afford *trans*-[PtCl(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH){Mo(CO)<sub>5</sub>] (1) and *cis*- and *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>]<sub>2</sub>] (2), respectively. These are rare examples of heterometallic complexes containing primary phosphido bridges. Compound 1 can be described either as the square-planar Pt<sup>II</sup> complex with the anionic ligand PPhH{Mo(CO)<sub>5</sub>}<sup>-</sup> or as the Pt-Mo phosphido-bridged dimer trans- $[PtCl(PEt_3)_2(\mu-PPhH) \{Mo(CO)_3\}]$ . As a phosphido-bridged heterobimetallic 1 possesses an exceptionally large Pt—P—Mo angle [120.9(1)<sup>o</sup>] reflecting the long Pt—Mo nonbonding interaction (4.5 Å). Compound 2 can correspondingly be described either as a phosphido-bridged PtMo2 trimer or a square-planar arrangement of two neutral PEt<sub>3</sub> and two anionic PPhH {Mo(CO)<sub>5</sub>} ligands at Pt. The low-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 1 showed several ABXY spin systems together with their associated ABXYM ( $M = {}^{195}$ Pt) counterparts and variable-temperature studies revealed the dynamic interconversion of several rotametric isomers arising from restricted rotation about the Pt—P $\mu$  bond. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of *trans*-2 shows its two possible RR/SS and meso diastereoisomers, the latter existing in clearly identifiable rotameric forms which interconvert slowly at  $-75^{\circ}$ C. We note very different values between  ${}^{2}J(P-P)$  and  ${}^{1}J({}^{195}Pt-P)$  for the anionic ligands  $[PPhH\{Mo(CO)_5\}]^-$  and PEt<sub>3</sub>, unattributable to bond length variation but which must reflect reduced s-orbital contribution to the Pt—P bond of the anionic phosphines PPhH{Mo(CO)<sub>5</sub>}. (C) 1997 Elsevier Science Ltd. All rights reserved.

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There has been an explosive growth in the synthesis, characterization and reactivity of heterometallic complexes, many of which comprise metals with very different electronic and coordinative properties [1]. Stephan's review article in 1989 highlighted the large number of heterobimetallics supported by a variety of different bridging ligands [2]. The desire to develop these early-late heterobimetallics has been driven by the belief that they should react with substrates in a cooperative manner [3]. Although there are few examples of successful cooperativity between electron-poor early transition metals and electron-rich transition metal centres, there have been several noteworthy approaches towards achieving this goal. Recent reports by Bergman [4] and Braunstein [5] serve to highlight the value of designed synthesis to achieve participation from each metal. Bergman's elegant syn-

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thesis and reactivity studies with an imido-bridged zirconium-iridium heterometallic clearly demonstrates a cooperativity in its reactions with both polar and non-polar X—H bonds. In contrast, Braunstein and co-workers have shown that the reactivity of iron-platinum heterometallics depends markedly on the nature of the bridging ligand. Following a recent highlight by Herberhold and Jin [6] focusing on heterometallics with polar metal-metal bonds, Chisholm *et al.* [7] suggested that the reactivity anticipated for such early-late heterometallics could be achieved by asymmetric homometallic complexes with polar W—W bonds (W<sup>VI</sup>—W<sup>II</sup>) with the metals in vastly different coordination environments.

Although heterobimetallics with various bridging ligands [8] have been prepared the predominant use of the phosphido ligand  $(PR_2)$  [9] can be attributed to: (i) the ease of synthesis via the bridge-assisted method [10], (ii) stabilization of the metal-atom framework during chemical transformation [11] and (iii) the presence of a <sup>31</sup>P nucleus which is useful for probing solution-state structures and fluxionality [12]. However, several recently reported transformations involving phosphido ligands set limits on their use for framework-stabilizing since they do not invariably behave as innocent bridging ligands [13]. Of the many phosphido-bridged heterometallic complexes reported, most contain two bridging ligands and Baker et al. [14] recently surveyed the area of diphosphido-bridged ELHB compounds up to 1990. However, current efforts have focused on the preparation of singly-bridged  $\mu$ -phosphido binuclear complexes without metal-metal bonds [15] with large M-P-M' angles. Particularly noteworthy are  $[Cp_2M(H)(\mu - PR_2)M'(CO)_5]$  (M = Mo, W; M' = Cr, Mo. W) and  $[CpFe(CO)_2(\mu - PR_2)W(CO)_4L]$  $(L = PMe_3, CH_3CN)$  prepared by the groups of Kubicki [15a] and Shyu, respectively [15c].

The synthesis of  $\mu$ -PR<sub>2</sub> Pt—M (M = Mo, W) heterometallics continues to be of considerable scientific interest despite their limited applications. Geoffroy and co-workers have reported a number of such complexes dominated by M—M' bonding interactions [16] and later Powell demonstrated that oxidative addition of the P—H bond of secondary phosphine complexes to zero-valent platinum centres is an efficient route to heterobimetallics, including [(CO)<sub>4</sub>M( $\mu$ -PR<sub>2</sub>)( $\mu$ -H)Pt(PPh<sub>3</sub>)<sub>2</sub>] [M = Mo, W] [17]. The catalytic activity of diphenylphosphido-bridged heterometallics have been evaluated by Mathieu [18] and there have been studies on metal-assisted substitutions *via* M—M bond formation [19].

This report follows our discovery of some unusual structural and spectroscopic characteristics of chiral MoPt heterometallics bridged by the primary phosphido ligand PPhH. We have recently reported [20] that nucleophilic substitution of chloride in [PtCl<sub>2</sub>(dppe)] by the chiral anionic ligand [Mo (CO)<sub>5</sub>(PPhH)]<sup>-</sup> affords the phosphido-bridged Mo<sub>2</sub>Pt trimer [Pt( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub><sub>2</sub>(dppe)] (3).

The <sup>31</sup>P<sup>1</sup>H NMR spectra of **3** are quite remarkable, highlighting this technique in elucidation of structure and of solution-state fluxional processes. We report the synthesis, spectroscopic and structural characterization of the heterometallic complexes *trans*-[PtCl(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH){Mo(CO)<sub>5</sub>}] (1) and *cis*- and *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}] (2), each containing chiral primary phosphido bridges.

#### EXPERIMENTAL

#### General consideration

Standard double manifold vacuum-line techniques were used for all chemical manipulations and all reactions were performed under dry nitrogen. All solvents were dried prior to use, hexane and tetrahydrofuran over sodium/benzophenone and dichloromethane over  $P_2O_5$ . Reactions were monitored by IR spectroscopy and TLC (Baker flex, silica gel 1B-F). Products were purified by column chromatography  $(330 \times 30 \text{ mm})$  with silica gel (70–230 mesh) or TLC on silica gel plates ( $20 \times 20$  cm, Merck, TLC grade, Aldrich Chemical Co.). Solution IR spectra were recorded on a Perkin-Elmer 983 spectrometer using calcium fluoride cells. <sup>1</sup>H NMR spectra were recorded on Varian VXR400 or XL200 spectrometers and all <sup>31</sup>P NMR spectra were recorded on a Varian VXR400 instrument at 162.0 MHz and referenced to external 85% H<sub>3</sub>PO<sub>4</sub>. Elemental analysis were carried out in the Analytical Laboratory at University College London. All chemicals except where stated were used as obtained from commercial sources and the starting materials [PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] [21] and [Mo(CO)<sub>5</sub>(PPhH<sub>2</sub>)] [22] were prepared as reported.

Reaction of  $[Mo(CO)_5(PPhH)]^-$  with cis- $[PtCl_2 (PEt_3)_2]$ 

A solution of  $[Mo(CO)_5(PPhH_2)]$  (0.1264 g, 0.4 mmol) in dry THF (50 cm<sup>3</sup>) was treated with the base DBU (0.160 cm<sup>3</sup>, 1.1 mmol). The reaction mixture was stirred for 10 min and a solution of  $[PtCl_2(PEt_3)_2]$ (0.090 g, 0.18 mmol) in THF  $(5 \text{ cm}^3)$  was added dropwise. After stirring for a further 20 min, the solvent was removed under reduced pressure to leave a brown-orange oil, which was dissolved in a minimum of dichloromethane and chromatographed on silica gel plates. Elution with dichloromethane/n-hexane (2/3, v/v) afforded three well-separated bands. The gave trans- $[Pt(PEt_3)_2(\mu-PPhH)_2]$ fastest band  ${Mo(CO)_{5}_{2}}$  (2), which was crystallized from dichloromethane/ethanol and vacuum-dried to afford colourless crystal of 2 (0.025 g, 24%). IR [v(CO),  $cm^{-1}$ ,  $C_6H_{14}$ ]: 2061 (w), 1938 (s), 1924 (sh). Found: C, 33.6; H, 4.3; P, 11.8. Calc. for  $C_{34}H_{42}Mo_2O_{10}P_4Pt$ (mol.wt = 1121.61): C, 36.3; H, 3.7; P, 11.1%. The second minor bad was identified spectroscopically as cis-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub>] (2) and crys-

| Compound  | $\delta^a$ | Assignment       | J(PP) <sup>trans</sup><br>(Hz) | J(PP) <sup>cis</sup><br>(Hz) | J( <sup>195</sup> Pt—P)<br>(Hz) |
|---|------------|------------------|--------------------------------|------------------------------|---------------------------------|
| $PtCl(PEt_3)_2(\mu-PPhH)\{Mo(CO)_5\}$             | +10.5      | PEt <sub>3</sub> |                                |                              | 2465.2                          |
| Room temperature                                  | -66.4      | PPhH             |                                | 25.5                         | 2078.0                          |
| $[PtCl(PEt_3)_2(\mu-PPhH)\{Mo(CO)_5\}]^h$         | +9.0       | $PEt_3$          | 366.0                          | 17.3                         | 2526.4                          |
| Major rotamer A <sup>1</sup> B <sup>1</sup> X     | +14.1      | PEt <sub>3</sub> | 366.0                          | 9.6                          | 2413.0                          |
|   | -66.5      | <b>PPhH</b>      |                                | 17.3, 9.6                    | 2135.0                          |
| $[PtCl(PEt_3)_2(\mu-PPhH) \{Mo(CO)_5\}]^b$        | +8.6       | PEt <sub>3</sub> | 376.0                          | 15.0                         | _                               |
| Minor rotamer A <sup>2</sup> B <sup>2</sup> X     | +13.7      | PEt <sub>3</sub> | 376.0                          | 9.0                          |                                 |
|   | -67.0      | <b>PPhH</b>      |                                | 15.0, 9.0                    | 2179.6                          |
| $[PtCl(PEt_3)_2(\mu-PPhH)\{Mo(CO)_5\}]^b$         | +8.4       | $PEt_3$          | 376.0                          | 15.4                         | _                               |
| Minor rotamer A <sup>3</sup> B <sup>3</sup> X     | +13.6      | PEt,             | 376.0                          | 9.6                          |                                 |
|   | -67.2      | PPhH             | _                              | 15.0, 9.6                    |                                 |
| $[PtCl(PEt_3)_2(\mu-PPhH)_2\{Mo(CO)_5\}_2]$       | +44.7      | PEt <sub>3</sub> | 200.0                          | -15.0                        | 2277.7                          |
| <i>cis</i> isomer                                 | +5.7       | <b>PPhH</b>      | 200.0                          | -15.0                        | 1400.6                          |
| $[PtCl(PEt_3), (\mu-PPhH), \{Mo(CO), \}]$         | +0.7       | PEt <sub>3</sub> |                                | 13.6                         | 2512.0                          |
| <i>trans</i> minor diastereoisomer $A^{\prime 3}$ | -71.4      | <b>PPhH</b>      | _                              | 13.6                         | 1110.0                          |
| $[PtCl(PEt_3)_2(\mu - PPhH)_2 \{Mo(CO)_3\}_3]^c$  | +1.2       | PEt <sub>3</sub> |                                | _                            | 2512.0                          |
| trans major diastereoisomer                       | -68.5      | <b>PPhH</b>      |                                | 12.7                         | 1146.0                          |
| $[PtCl(PEt_3)_2(\mu-PPhH)_2\{Mo(CO)_5\}_2]^b$     | +1.8       | PEt,             |                                | 14.8                         | 2459.0                          |
| Major diastereoisomer rotamer $A^2$               | -67.8      | <b>PPhH</b>      | _                              | 16.4                         | 1127.0                          |
| $[PtCl(PEt_3)_2(\mu-PPhH)_2\{Mo(CO)_5\}_2]^h$     | +5.8       | PEt <sub>3</sub> | 340.0                          | 16.6                         | 2401.0                          |
| Major diastereoisomer rotamer                     | -2.4       | PEt <sub>3</sub> | 340.0                          | 8.8                          | 2592.0                          |
| $A^{T}$ and $B^{T}$                               | -72.0      | PPhH             | _                              | 12.8                         | 1136.0                          |

Table 1. <sup>31</sup>P<sup>1</sup>H NMR data for the phosphido-bridged heterometallic complexes [PtCl(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH){Mo(CO)<sub>5</sub>}] (1) and trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}] (2)

"Recorded in CDCl<sub>3</sub> at 162 MHz with chemical shifts referenced to external 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>*b*</sup> Recorded  $CD_2Cl_2$  at  $-80^{\circ}C$ .

<sup>c</sup>Recorded in CDCl<sub>3</sub> at room temperature.

tallization form dichloromethane/ethanol gave colourless crystals of *cis*-**2** (0.010 g, 9.7%). IR [ $\nu$ (CO), cm<sup>-1</sup>, C<sub>6</sub>H<sub>14</sub>]: 2063 (w), 1935 (s), 1929 (sh). The final band to elute was identified as *trans*-[PtCl(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH){Mo(CO)<sub>5</sub>}] (1). Crystallization from dichloromethane/ethanol drying *in vacuo* afforded colourless crystalline 1 (0.017 g, 16.5%). IR [ $\nu$ (CO), cm<sup>-1</sup>, C<sub>6</sub>H<sub>14</sub>]: 2057 (w), 1928 (s), 1901 (sh). Found: C, 34.0; H, 4.4; Cl, 5.2. Calc. C<sub>23</sub>H<sub>36</sub>ClMoO<sub>5</sub>P<sub>3</sub>Pt (mol.wt = 811.98): C, 33.7; H, 3.9; Cl, 4.4%.

#### X-ray structure analysis of 1 and trans-2

Colourless crystals of 1 and *trans*-2 were grown from dichloromethane/ethanol at room temperature. A suitable crystal of each was glued to a glass fibre using epoxy resin and mounted on a goniometer head. Unit-cell parameters were obtained from least-squares refinement of 30 orientation reflections in the range  $10 < 2\theta < 30^{\circ}$  for 1 and 26 orientation reflections in the range  $6 < 2\theta < 27^{\circ}$  for 2, selected from a rotation photograph.

Collection and reduction of intensity data. Details of the intensity data collection parameters for 1 and *trans*-2 are presented in Table 2. The intensity data for both 1 and 2 were collected at 294 K on a Nicolet R3v/m automatic four-circle diffractometer using graphite monochromated Mo- $K_{\alpha}$  ( $\lambda = 0.71073$  Å) radiation with the diffractometer operating in the  $\omega$ -2 $\theta$  scan mode. Three standard reflections monitored every 100 measurements showed no significant deviations during the data collection. Empirical absorption corrections for 1 and *trans*-2 were made by the  $\Psi$ scan method (maximum and minimum transmission factors were 0.950 and 0.511 for 1 and 0.966 and 0.636 for *trans*-2). Reflections were considered observed when  $I_0 > 3\sigma(I_0)$ .

Solution and refinement of the intensity data. The structures were solved by direct methods, followed by full-matrix least-squares refinement of positional and thermal parameters and subsequent conversion to anisotropic coefficients for all non-hydrogen atoms. All hydrogen atoms except those bonded directly to P were included in idealized positions and allowed to ride on carbon atoms with C-H distances fixed at 0.86 Å and isotropic thermal parameters at 0.08 Å<sup>2</sup>. The function minimized in the least-squares calculations was  $\Sigma w(|F_o| - |F_c|)^2$ . The weighted R value is defined as  $Rw = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w |F_0|^2]^{1/2}$ . All calculations were performed on a MicroVax II computer running SHELXTL PLUS (G. M. Sheldrick, Package for crystal structure determination, University of Göttingen, 1986). Further details are available as supplementary material (atomic coordinates, bond distances, bond angles, anisotropic thermal parameters and hydrogen atom positions) deposited at

|                                       | 1  | trans-2                           |
|---------------------------------------|--|-----------------------------------|
| Formula                               | C <sub>23</sub> H <sub>36</sub> ClMoO <sub>5</sub> P <sub>3</sub> Pt | $C_{34}H_{42}Mo_{2}O_{10}P_{4}Pt$ |
| fw                                    | 811.98   | 1121.61                           |
| Crystal size (mm)                     | $0.16 \times 0.20 \times 0.30$                                       | $0.34 \times 0.15 \times 0.08$    |
| Space group                           | $P2_1/n$   | $P_{21}/a$                        |
| a (Å)                                 | 11.159(4)  | 20.027(9)                         |
| b (Å)                                 | 24.57(1)   | 10.465(4)                         |
| c (Å)                                 | 11.897(4)  | 20.774(9)                         |
| $\beta$ ( )                           | 106.61(3)  | 103.00(3)                         |
| $V(\dot{A}^3)$                        | 3125(2)  | 4242(2)                           |
| Z                                     | 4  | 4                                 |
| $D_{\rm calc} ({\rm g}{\rm cm}^{-3})$ | 1.73   | 1.76                              |
| Radiation, $\lambda$ (Å)              | Mo, 0.71073  | Mo, 0.71073                       |
| Temperature (°C)                      | 17   | 18                                |
| $\mu(Mo-K_{x})$ (cm <sup>-1</sup> )   | 51.8   | 40.9                              |
| Total data                            | 5905   | 8086                              |
| Unique data                           | 5459   | 7411                              |
| Reflections used                      | 3575   | 4135                              |
| Parameters                            | 307  | 463                               |
| R <sup>a</sup>                        | 0.0458   | 0.0850                            |
| $R_w^{\ b}$                           | 0.0500   | 0.0679                            |
| Weight w in weighting scheme          | $1/[\sigma^2(F) + 0.00186F^2]$                                       | $1/[\sigma^2(F) + 0.000247F^2]$   |
| Goodness of fit                       | 1.099  | 1.587                             |
| Max shift/e.s.d.                      | 0.006  | 0.005                             |
| Residual density (e Å 3)              | 0.96   | 1.8                               |

Table 2. Crystal and intensity data for  $[PtCl(PEt_3)_2(\mu-PPhH)\{Mo(CO)_5\}]$  (1) and *trans*- $[Pt(PEt_3)_2(\mu-PPhH)_2\{Mo(CO)_5\}_2]$  (2)

 ${}^{a} R = \Sigma[|F_{o}| - |F_{c}|] / \Sigma |F_{o}|.$  ${}^{b} R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2} / \Sigma w |F_{o}|^{2}]^{1/2}.$ 

the Cambridge Crystallographic Data Centre. Observed and calculated structure factors are available from the authors on request. Tables 3 and 4 contain an appropriate selection of bond lengths and angles for these molecules.

### **RESULTS AND DISCUSSION**

Reaction of the chiral anion  $[Mo(CO)_5(PPPhH)]^$ with *cis*- $[PtCl_2(PEt_3)_2]$  proceeds rapidly at room temperature to afford, after chromatographic work-up, a mixture of  $[PtCl(PEt_3)(\mu-PPhH)\{Mo(CO)_5\}]$  (1) and

Table 3. Selected interatomic bond distances (Å) and angles (<sup>°</sup>) for [PtCl(PEt<sub>3</sub>)<sub>2</sub>(μ-PPhH) {Mo(CO)<sub>5</sub>}] (1)

| Pt - Pt(1) | 2.288(3)     | MoC(1)    | 1.972(16) |
|------------|--------------|-----------|-----------|
| Pt-P(2)    | 2.327(3)     | Mo-C(2)   | 2.052(15) |
| Pt—P(3)    | 2.325(4)     | MoC(3)    | 2.051(12) |
| Pt-Cl      | 2.384(4)     | MoC(4)    | 2.065(17) |
| Mo-P(1)    | 2.601(3)     | Mo—C(5)   | 2.053(11) |
| P(1)PtP    | (2) 95.6(1)  | P(2)PtCl  | 83.3(1)   |
| P(1)-Pt-P  | (3) 93.8(1)  | P(3)-PtCl | 87.4(1)   |
| P(2)-Pt-P  | (3) 169.9(1) | P(1)-PtCl | 177.5(1)  |
| PtP(1)M    | lo 120.9(1)  |           |           |
|            |              |           |           |

Table 4. Selected interatomic bond distances (Å) and angles (<sup>+</sup>) for *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub>] (2)

| Pt(1) - P(1)        | 2.407(5)    | Mo(1)—P(1)         | 2.644(5)        |
|---------------------|-------------|--------------------|-----------------|
| Pt(1) - P(2)        | 2.340(6)    | Mo(2)-P(2)         | 2.648(5)        |
| Pt(2)—P(3)          | 2.397(4)    | Mo(1)-C(20)        | 2.064(22)       |
| Pt(2)—P(4)          | 2.333(6)    | Mo(1)C(21)         | 2.069(24)       |
|                     |             |                    |                 |
| Mo(1)C(22)          | 2.048(23)   | Mo(1)—C(23)        | 2.027(25)       |
| Mo(1)C(24)          | 1.981(23)   | Mo(2)—C(50)        | 2.089(23)       |
| Mo(2)—C(51)         | 2.061(21)   | Mo(2)—C(52)        | 2.040(25)       |
| Mo(2)—C(53)         | 2.077(24)   | Mo(2)—C(54)        | 1.968(20)       |
|                     |             |                    |                 |
| P(1) - P(1) - P(1)  | 2) 87.3(2)  | P(3) - P(2) - P(4) | 4a) 87.4(2)     |
| P(2)-Pt(1)-P(       | la) 92.7(2) | Mo(1) - P(1) - P   | t(1) = 126.1(2) |
| P(3) - Pt(2) - P(4) | 4) 92.6(2)  | Mo(2)P(3)P         | t(2) = 130.0(2) |
|                     |             |                    |                 |

*cis*- and *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub>] (2) complexes containing primary phosphido bridges.

Elemental analytical data for 1 was insufficient to distinguish between  $[PtCl(PEt_3)(\mu-PPhH)\{Mo(CO)_5\}]$  and  $[Pt(PEt_3)_2(\mu-PPhH)_2\{Mo(CO)_5\}_2] \cdot CH_2$  $Cl_2$ . However, <sup>31</sup>P<sup>1</sup>H NMR spectroscopy confirmed its structure as well as giving considerable insight into a fluxional process in solution. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 1 contains two distinct types of resonance. Our assignment of the high-field triplet

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resonance ( $\delta = -66.0$  ppm) to the bridging phosphido ligand was confirmed by its large one-bond phosphorus-hydrogen coupling constant  $[^{I}J(P\mu - H) =$ 287 Hz] consistent with previous observations [22]. Note that a high-field chemical shift ( $\delta$  + 50 to -200 ppm) for a phosphido bridge indicates the presence of a metal-metal bond, while low-field resonances ( $\delta$  + 50 to 300 ppm) imply non-bonded metal atoms [12]. An exchange-broadened low-field resonance [ $\delta = +11.5$  ppm], although uninformative, confirmed the presence of PEt<sub>3</sub> ligands. The roomtemperature triplet phosphido resonance  $[^{2}J(\text{PEt}_{3}$ - $P\mu$ ) = 25.0 Hz] is consistent with the presence of two PEt<sub>3</sub> ligands cis to the anionic phosphine  $[PPhH\{Mo(CO)_5\}]^-$ . The low-temperature  ${}^{31}P^1H$ NMR spectrum of 1 ( $CD_2Cl_2$ ,  $-75^{\circ}C$ ) several rotational isomers in slow exchange (vide infra). Also, the PEt<sub>3</sub> ligands each couple to <sup>195</sup>Pt with different  $^{1}J(^{195}\text{Pt}-\text{PEt}_{3})$  values (2413 and 2526 Hz), although these are in the range expected for mutually trans tertiary phosphines [23].  ${}^{1}J({}^{195}\text{Pt}-\text{P}\mu)$  (2078 Hz) is lower than expected for a phosphorus donor trans to a chloride, based on the value for PEt, trans to chloride in cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] [<sup>1</sup>J(<sup>195</sup>Pt-PEt<sub>3</sub>) = 3500 Hz] [23]. We have previously noted a similar low value for  $^{1}J(^{195}\text{Pt}-\text{P}\mu)$  for coordinated [PPhH{Mo(CO)<sub>5</sub>}]<sup>-</sup>, consistent with lower s-orbital contribution to the Ptphosphido bond compared with Pt-phosphine bonds of similar length. The values of  ${}^{2}J(PEt_{3}-PEt_{3})$  (366) Hz) and  ${}^{1}J({}^{195}Pt-PEt_3)$  (2413 and 2526 Hz) for 1 are close to those expected for complexes containing trans-tertiary phosphines [23,24] indicating that there is, if any, only a weak dependence on the nature of the cis ligand. Note that  ${}^{2}J(P-P)$  values for transphosphines are typically an order of magnitude greater than those of their *cis* counterparts [24].

Two products analysing as  $[Pt(PEt_3)_2(\mu-PPhH)_2]$  ${Mo(CO)_5}_2$  (2) were isolated from the reaction of cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] with [PPhH{Mo(CO)<sub>5</sub>}]<sup>-</sup> and  ${}^{31}P{}^{1}H$  NMR spectroscopy was used to identify these as cis-2 and trans-2. Both isomers are formed from pure *cis* or a mixture of *cis*- and *trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]. One striking characteristic of the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of cis-2 is that  ${}^{2}J(\text{PEt}_{3}-\text{P}\mu)$  (200 Hz) is lower than expected for trans tertiary phosphines [24], but large enough to confirm the presence of a PEt<sub>3</sub> trans to  $[PPhH\{Mo(CO)_5\}]^-$ . We have recently reported [20] similar spectroscopic characteristics for  $[Pt(\mu PPhH_{2}\{Mo(CO)_{5}\}_{2}(dppe)\}$  (3) in which <sup>2</sup>J(Pdppe—  $P\mu$ ) for [PPhH{Mo(CO)<sub>5</sub>}]<sup>-</sup> trans to dppe was 213.0 Hz. The reduced  ${}^{2}J(P-P\mu)$  values in *cis*-2 and in 3 are also paralleled by lower  ${}^{1}J({}^{105}\text{Pt}--\text{P}\mu)$  coupling constants  $[{}^{1}J({}^{195}\text{Pt}-\text{PEt}_{3}) = 2277.7$  Hz and  ${}^{1}J({}^{195}\text{Pt}-P\mu) = 1400.6$  Hz for *cis*-2 and  ${}^{1}J({}^{195}\text{Pt}$ dppe) = 2323.0 Hz and  ${}^{1}J({}^{195}\text{Pt}-P\mu) = 1450.0$  Hz for 3] emphasizing the unusual spectroscopic characteristics associated with the  $[PPhH\{Mo(CO)_5\}]^{-1}$ ligand. The close structural and spectroscopic similarities of cis-2 and 3 are further highlighted by their distinctive non-first-order AA'XX' spin systems. Each

set of resonances for 2 results from the superposition of two spin systems, an AA'XX' corresponding to isotopomers with no <sup>195</sup>Pt and an AA'XX'M spin system for the <sup>195</sup>Pt isotopomer. Figure 1 shows the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of *cis*-2 together with an accurate computer simulation of its AA'XX' region. This simulation was obtained by fixing the trans coupling constants at +200 Hz, measured directly from the spectrum, and varying the cis coupling constant which refined at  ${}^{2}J(\text{PEt}_{3}-\text{P}\mu) = -15$  Hz. We [25] and others [26] have previously noted that cis and trans- $^{2}J(P-P)$  coupling constants are of opposite sign in the sign-simulated  ${}^{31}P{}^{1}H$  spectra of complexes containing four coplanar phosphorus donor ligands. The most notable differences between the  ${}^{31}P{}^{1}H{}$  NMR spectra of cis-2 and 3 is the absence of line broadening and the observation of only a single diastereoisomer for cis-2.

The  ${}^{31}P{}^{1}H$  spectral characteristics of *trans*-2 are markedly different to those of cis-2 and consistent with *trans*-PEt<sub>3</sub> ligands. Its room-temperature  ${}^{31}P{}^{1}H{}$ NMR spectrum contains two sets of resonances, signals for PEt<sub>3</sub> ( $\delta = +0.7$ , 1.2 ppm) as well as highfield signals ( $\delta = -71.4, -68.5$  ppm) for a phosphido ligand bridging non-bonded metal atoms [13,17a-c]. The most striking spectral feature of trans-2 is that the PEt<sub>3</sub> resonance of the minor diastereoisomer is a sharp triplet resonances flanked by <sup>195</sup>Pt satellites, while that of the major diastereoisomer appears as a broad featureless resonance. The value of  $^{1}J(^{195}\text{Pt}-\text{PEt}_{3})$  for the minor diastereoisomer (2512) Hz) is similar to that in *trans*- $[PtCl_2(PEt_3)_2]$  [23] and supports a trans arrangement of these ligands. The lower  ${}^{1}J({}^{195}\text{Pt}-P\mu)$  coupling constant (1146.0 Hz) confirms our previous observation of reduced  ${}^{1}J({}^{195}\text{Pt}-P\mu)$  and  ${}^{2}J(P-P\mu)$  values associated the  $[PPhH{Mo(CO)_{5}}^{-}$  ligand. Specifically,  ${}^{1}J({}^{195}Pt-$ P $\mu$ ) is approximately 50% that of <sup>1</sup>J(<sup>195</sup>Pt--PR<sub>3</sub>) in complexes with similar bond lengths. The value of <sup>31</sup>P<sup>1</sup>H NMR spectra in studying Pt-phosphido complexes has been noted [27]. For instance, several characteristics of the recently reported phosphidobridged complex  $[(HBut_2P)_2Pt(\mu-H)(\mu-PBut_2)Pt(H)]$  $(PBut_2H)[BF_4]$  [27a] parallel features of the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of cis- and trans-2 including reduced values of  ${}^{1}J({}^{195}\text{Pt}-P\mu)$  and  ${}^{2}J(P-P\mu)$ .

Finally, *trans*-2 contains two chiral primary phosphido bridges and, as with 3, we assign the two sets of  ${}^{31}P{}^{1}H$  NMR resonances to the *meso* and *racemic* diastereoisomers.

X-ray structures of trans-[PtCl(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH) {Mo(CO)<sub>5</sub>}] (1) and trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub> {Mo(CO)<sub>5</sub>}] (2)

The unusual  ${}^{31}P{{}^{1}H}$  NMR spectroscopic characteristics associated with 1 and 2 together with the presence of rare examples of chiral phosphido bridges has prompted single-crystal X-ray structural studies.



Fig. 1. <sup>31</sup>P{<sup>1</sup>H} NMR spectra of *cis*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub>] (2) in CDCl<sub>3</sub> (a) together with an accurate spin simulation, (b) illustrating the non first-order AA'XX' nature of its spin system.





Fig. 2. Perspective ORTEP view of the molecular structure of *trans*-[PtCl(PEt<sub>3</sub>)<sub>2</sub>(μ-PPhH){Mo(CO)<sub>5</sub>}] (1) showing the square-planar coordination geometry at platinum.

(a) Trans-1. The molecular structure of 1 in Fig. 2 unequivocally identifies it as *trans*-[PtCl(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH){Mo(CO)<sub>5</sub>}] (1), a  $\mu$ -PPhH-bridged Mo—Pt dimer. Selected bond lengths and bond angles in Table 3. An alternative projection (Fig. 3) illustrates the PtP<sub>3</sub>Cl planar arrangement of ligands, which successfully accounts for its unusual <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic characteristics (*vide infra*).

The crystal structure of 1 reveals that only a single has been substituted by chloride ligand [PPhH{Mo(CO)<sub>5</sub>}]<sup>-</sup> resulting in a Pt<sup>II</sup> coordination sphere comprised of one chloride, one  $[PPhH{Mo(CO)_5}]^-$  and two  $PEt_3$  ligands. The geometry about the platinum centre is essentially square planar [Cl-Pt-P(1) = 177.5(1)]and P(1)—Pt— $P(2) = 169.9(1)^{\circ}$ ] with the larger angles of P(1)—Pt—P(2) = 95.6(1) and P(1)—Pt—P(3) = $93.8(1)^{\circ}$  compared with P(2)—Pt—Cl = 83.3(1) and

Fig. 3. View down the P(1)—Pt—Cl axis of  $[PtCl(PEt_3)_2(\mu-PPhH){Mo(CO)_5}]$  (1) showing the conformation about the Pt—PPhHMo(CO)<sub>5</sub> bond.

P(3)—Pt— $Cl = 87.4(1)^\circ$ , reflecting a greater steric demand of the anionic phosphine over chloride. The Pt—P(1)—Mo angle of  $120.9(1)^{\circ}$  is comparable to those recently reported for  $[Pt(\mu-PPhH)_2 \{Mo (CO)_{5}_{2}(dppe)$ ] [21] and  $[Cp_{2}W(H)(\mu-PPh_{2})W(CO)_{5}]$ [15], rare examples of singly bridged heterometallics without metal-metal bonds. The Pt-Mo non-bonded distance in 2 [Pt-Mo = 4.255 Å], one of the longest to be reported, is responsible for the high-field shifted <sup>31</sup>P{<sup>1</sup>H} NMR signal of the phosphido ligand [13,17]. The platinum-phosphido bond in 1 is considerably shorter [Pt-P(1) = 2.288(3) Å] than those in 3  $[Pt-P_{av} = 2.362(3) \text{ Å}]$ , which presumably reflects the smaller trans influence of the chloride ligand compared with dppe. However, the value of  ${}^{1}J({}^{195}\text{Pt}--P\mu)$ is too low and the bond too long for  $[PPhH{Mo(CO)_{5}}]^{-}$  to be treated as a "simple" phosphine [for example in trans-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>, Pt-P = 2.258(4) Å]. Finally, the geometry about molybdenum is octahedral with a molybdenum-phosphorus distance [Mo-P(1) = 2.601(3) Å] greater than in  $[Mo(CO)_5(PMe_3)]$  (2.5082 Å) [28], possibly reflecting the greater steric requirements of  $[PPhH{Mo(CO)_5}]^-$ . However, the axial carbonyl bond length [Mo-C(1) = 1.972(1) Å] is characteristic of a Mo-C bond trans to a phosphino donor while the equatorial Mo-C bond lengths are unexceptional. Compound 1 can thus be described either as (i) a square-planar  $Pt^{II}$  with three phosphorus donor ligands and one chloride or (ii) a rare example of a primary phosphido-bridged Mo-Pt heterobimetallic containing an exceptionally large Mo-P-Pt bond angle.

(b) Trans-2. The molecular structure of *trans*-2 is shown in Figs 4 and 5 with a selection of bond lengths and angles in Table 4. trans-2 crystallizes in the monoclinic space group  $P2_1/a$  with two independent molecules in the asymmetric unit and with platinum located on an inversion centre. The projection of trans-2 in Fig. 4 clearly identifies it as a trinuclear phosphido ligand compound, whilst that in Fig. 5 emphasises its alternative description as a squareplanar Pt<sup>II</sup> complex containing two trans-PEt<sub>3</sub> and two *trans*-[PPhH{Mo(CO)<sub>5</sub>}]<sup>-</sup> ligands. Notable features include the exceptionally large Pt-P-Mo angles [Mo(1)-P(1)-Pt(1) = 126.1(2) and  $Mo(2) - P(3) - Pt(2) = 130.0(2)^{\circ}$ , the largest phosphido bridging angles to be reported, as well as long Pt—Mo non-bonded distances [Pt(1)-Mo(1) =4.504(2) and Pt(2)—Mo(2) = 4.573(2) Å]. The asymmetric bridging mode of the phosphido ligand in 2 [Pt(1)-P(1) = 2.407(5), Pt(2)-P(3) = 2.397(4) andMo(1) - P(1) = 2.644(5), Mo(2) - P(3) = 2.648(5)



Fig. 5. A projection down the P(1)—Pt(1)—P(1a) axis of *trans*- $[Pt(PEt_3)_2(\mu$ -PPhH)\_2{Mo(CO)\_5}\_2] (2) showing the staggered nature of the *trans* ligands and the disposition of the substituents at phosphorus with respect to this plane.

Å] is a common feature of heterometallic phosphidobridged complexes. These platinum-phosphido bond lengths are among the longest reported, far greater than that in 1 reflecting the stronger *trans* influence of [PPhH{Mo(CO)<sub>5</sub>}]<sup>-</sup> compared with chloride. As for 1 the axial Mo-CO bonds are substantially longer than their equatorial counterparts supporting the significant *trans* influence associated with the  $\mu$ -PPhH group.

Although 2 contains a  $PtP_4$  planar arrangement of ligands, it adopts a staggered conformation of *trans* 



Fig. 4. Perspective ORTEP view of the molecular structure of one independent molecule of trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>]<sub>2</sub>] (2) showing the square-planar coordination at platinum which lies at a centre of symmetry.



Fig. 6. (a) Variable-temperature <sup>31</sup>P<sup>1</sup>H NMR spectra of  $[PtCl(PEt_3)_2(\mu-PPhH)_2\{Mo(CO)_5\}]$  (1) in the PEt<sub>3</sub> region (AB part of ABX spectrum, plus <sup>195</sup>Pt satellites) showing the broadening and collapse of signals for three rotational isomers. (b) <sup>31</sup>P<sup>1</sup>H NMR spectra of 1 (CD<sub>2</sub>Cl<sub>2</sub>, -75°C), major ABX (A<sup>1</sup>B<sup>1</sup>) and minor (A<sup>2</sup>B<sup>2</sup> and A<sup>3</sup>B<sup>3</sup>) rotational isomers and assignment of the <sup>1</sup>J(<sup>195</sup>Pt—PEt<sub>3</sub>) and <sup>2</sup>J(PA<sup>1</sup>PB<sup>1</sup>) coupling constants for the major isomer. The <sup>195</sup>Pt satellites for the minor isomers were not detected, although the main signals are qualitatively equivalent to those of the major isomer.

ligands with the bulky  $[Mo(CO)_s]$  substituents in an *anti* arrangement, presumably the sterically least demanding conformation. This contrasts with our recent characterization of several square-planar complexes, each of which contains four phosphorus donor ligands with substituents on *trans* ligands eclipsed [29]. Compound **2** is only the second example of a phosphido-bridged heterometallic trimer with the four unique substituents attached to the phosphido ligand, Ph, H, Mo and Pt. Therefore, both *meso* and *racemic* forms are expected, however, the crystal for which the structure was determined was that of the *meso* stereoisomer, *RS*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub>].

## Rotational isomers of trans-1 and trans-2: a variabletemperature ${}^{31}P{}^{1}H{}$ NMR study

Relatively high rotation barriers in octahedral metal complexes containing four coplanar phosphines are common [25,29a]. However, we recently found evidence for rotational isomers of  $[Pt(\mu-PPhH)_2\{Mo(CO)_5\}_2$  (dppe)] (3), a molecule containing two neutral and two

anionic phosphines. Line broadening in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 1 and *trans*-2 prompted us to undertake a variable-temperature study, which also revealed that rotational isomers of these molecules could be observed and that their interconversion is slow at  $-80^{\circ}$ C.

(a) Trans-1. A representative set of  ${}^{31}P^{1}H$  NMR spectra for 1, in the PEt<sub>3</sub> region, is shown in Fig. 6(a) together with our assignment of the low temperature limiting spectrum ( $-75^{\circ}C$ ) in Fig. 6(b).

The room-temperature spectrum of 1 contains a sharp high-field triplet resonance  $[\delta - 66.4,$  ${}^{1}J({}^{195}\text{Pt}--\text{P}\mu) = 2078 \text{ Hz}$ ] for the phosphido bridge and an exchange broadened resonance ( $\delta = +10.5$ ppm) corresponding to the PEt<sub>3</sub> ligands. The lowtemperature <sup>31</sup>P<sup>1</sup>H NMR spectrum of 1 unequivocally established the presence of three isomers, a dominant one (94%) characterized by an AB quartet [ $\delta$  $+9.0(B^{1})$ , +14.1 (A<sup>1</sup>)] together with low concentrations of two others ( $A^2B^2$  and  $A^3B^3$ , 5 and 1%, respectively), each with similar spectroscopic features. The diastereotopic PEt<sub>3</sub> ligands couple to the bridging phosphido with different  ${}^{2}J(\text{PEt}_{3}-\text{P}\mu)$  values  $[{}^{2}J(PP) = 17.3 \text{ Hz} (B^{1}) \text{ and } {}^{2}J(PP) = 9.6 \text{ Hz} (A^{1})] \text{ and}$ flanked by <sup>195</sup>Pt satellites also of different magnitude  $[{}^{1}J({}^{195}\text{Pt}-{}^{PA^{\dagger}}) = 2413.0 \text{ Hz and } {}^{1}J({}^{195}\text{Pt}-{}^{PB^{\dagger}}) =$ 2526.4 Hz], although both values are in the range expected for trans-PEt<sub>3</sub> ligands [22]. Figure 6(b) also identifies the two low concentration species, each with a similar AB quartet resonance flanked by <sup>195</sup>Pt satellites  $[\delta + 8.6 (B^2), +13.7 (A^2) \text{ and } +8.4 (B^3), 13.6$ (A<sup>3</sup>)] again with different values of  ${}^{2}J(\text{PEt}_{3}-\text{P}\mu)$  $[{}^{2}J(\mathbf{P}\mu-\mathbf{P}^{\mathbf{A}^{2}}) = 9.0, {}^{2}J(\mathbf{P}\mu-\mathbf{P}^{\mathbf{B}^{1}}) = 15.0,$  ${}^{2}J(P\mu - P^{A^{3}}) = 9.6, {}^{2}J(P\mu - P^{B^{3}}) = 15.4$  Hz]. These three sets of resonances have been assigned to three conformational isomers each with an ABX spin system. We believe that the predominant ABX  $(A_1B_1)$ at low temperature belongs to rotamer (A), the sterically least hindered conformer and that found in the crystal. Rotamers (B) and (C) with the bulky [Mo(CO)<sub>5</sub>] substituents in closer proximity to the PEt<sub>3</sub> are sterically more demanding and much less populated. At higher temperatures rapid rotation about the





Pt—P $\mu$  bond interconverts these rotamers to afford the exchange broadened spectrum illustrated in Fig. 6(a) (+35°C).

(b) Trans-2. The room-temperature  ${}^{31}P{}^{1}H$  NMR spectrum of 2 contains two sets of resonances, each with signals in the phosphido and PEt<sub>3</sub> regions consistent with the two possible non-interconverting diastereoisomeric forms. While the resonances belonging to the minor diastereoisomer are sharp those corresponding to the major stereoisomer are broad and featureless. A representative set of  ${}^{31}P{}^{1}H$  NMR spectra are illustrated in Fig. 7(a) with our assignment of the low-temperature limiting spectrum in the PEt<sub>3</sub>



region, shown in Fig. 7(b). The low-temperature limiting spectrum of trans-2 [Fig. 7(b)] consists of three sets of resonances in significant abundance, two belonging to the major (meso) diastereoisomer [an A triplet of an (AX)<sub>2</sub> spin system at  $\delta$  +1.8 (A<sup>2</sup>) and the AB part of an ABXY pattern at  $\delta$  + 5.8 and -2.4 for  $A^{T}$  and  $B^{T}$ , respectively] and the other, another A triplet of an  $(AX)_2$  system, to the minor (rac) diastereoisomer [ $\delta + 0.7$  (A<sup>3</sup>)]. These isomers have been designated  $A^{T}B^{T}$ ,  $A^{2}$  and  $A^{3}$  to distinguish them from those associated with 1 shown in Fig. 6. Fractional crystallization of trans-2 provided sufficient sample to confirm, by  ${}^{31}P{}^{1}H$  NMR spectroscopy, that the exchange broadened resonance corresponds to the meso stereoisomer, for which the crystal structure was determined. Once separated by crystallization, there is no conversion of the meso into the rac stereoisomer.



Fig. 7. (a) Variable-temperature <sup>31</sup>P<sup>1</sup>H NMR spectra of a diastereomeric mixture of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub>] (2) in the PEt<sub>3</sub> region. (b) <sup>31</sup>P<sup>1</sup>H NMR spectrum of *trans*-2 (CD<sub>2</sub>Cl<sub>2</sub>, -80 °C), major (A<sup>-1</sup>B<sup>-1</sup>) and (A<sup>-2</sup>) and minor (A<sup>-3</sup>) diastereoisomers illustrating their <sup>1</sup>J(<sup>195</sup>Pt--PEt<sub>3</sub>) and <sup>2</sup>J(PEt<sub>3</sub>--P $\mu$ ) coupling constants.

The *meso*-stereoisomer contains pairs of staggered *trans*-phosphines for which there should exist three possible rotamers, (D)–(F). However, only one of these, rotamer (D), contains magnetically equivalent PEt<sub>3</sub> ligands which must therefore correspond to the triplet resonance at  $\delta$  +0.7, while either rotamer (E) or (F) could give rise to the ABXY pattern. Above –80°C these resonances start to broaden and at

+ 35°C rotamers (D), (E) or (F) exchange via rotation about their Pt—P $\mu$  bonds.

In contrast the  ${}^{31}P{}^{1}H$  NMR spectrum of the minor RR/SS diastereoisomer is unchanged over the temperature range +25 to  $-80^{\circ}$ C. The observed A<sub>2</sub>X<sub>2</sub> pattern is not consistent with any one static staggered rotamer since the PEt<sub>3</sub> ligands are necessarily nonequivalent. However, its spectra could be rationalized in terms of one of the eclipsed rotamers (G) or (H). An alternative view is that the lowest energy rotamer is the staggered form (I), which is in rapid equilibrium with its enantiomer (I') by the mechanism shown in Scheme 1, which leads to PEt<sub>3</sub> exchange. However, why should the equilibrium in Scheme 1 be very fast even at  $-80^{\circ}$ C, whereas the equilibria between (D) and (E) or (F) are much slower? Although the projections shown are reminiscent of ethane-type conformations, the dominant steric interactions are between cis ligands and not between the mutually trans-PPhH{Mo(CO)<sub>5</sub>} groups. Thus, the barrier to rotation is a consequence of the movement of the H, Mo(CO)<sub>5</sub> or Ph substituents past the *cis*-PEt<sub>3</sub> ligands. In the equilibria in Scheme 1, the Ph and  $Mo(CO)_5$ groups do not migrate from one side of the Pt coordination plane to the other and only the H substituents are required to migrate past the PEt<sub>3</sub> ligands. Hence, the energy barriers for these rotational equilibria are much lower than for the interconversion of (D) with (E) or (F), which requires the Ph or  $Mo(CO)_5$  substituents to slide past the PEt<sub>3</sub> ligands. On this model, equilibria in Scheme 1 must be fast enough for coalescence temperatures to be well below  $-80^{\circ}$ C. In spite of these arguments we have no experimental evidence to discriminate between (G), (H) and (I).

The fluxionality of 1 and 2 is best understood by considering them as square-planar Pt<sup>11</sup> complexes with

 $PtP_3Cl$  and  $PtP_4$  arrangements of ligands. Some time ago we reported detailed variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR studies of the tetrakisphosphine complexes  $[IrCl_2(PMe_2Ph)_3L][ClO_4]$  (L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PMePh<sub>2</sub>) [25,29a] which revealed the existence of rotameric forms that interconvert slowly at  $-50^{\circ}$ C. It appeared that a general requirement for the occurrence of these rotamers was the presence of four coplanar phosphines. More recently we revealed that line broadening effects in the  ${}^{31}P{}^{1}H$  NMR spectrum of  $[Pt(\mu-PPhH)_4 \{Mo(CO)_5\}_2(dppe) (3)$  resulted from restricted rotation about the  $Pt-P\mu$  bond generating rotational isomers. The similarity between  $[Pt(\mu PPhH_2\{Mo(CO)_5\}_2(dppe)\}$  (3) and  $[PtCl(PEt_3)_2(\mu-$ PPhH {Mo(CO)<sub>5</sub>}] (1) and *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ - $PPhH_{2}\{Mo(CO)_{5}\}_{2}\}$  (2) suggests they too may have accessible rotameric forms. For 1 this results in population of the sterically least demanding rotamer (A) with only very low concentrations of less favourable (B) and (C), while restricted rotation at the Pt— $P\mu$ bonds in meso-2 gives rise to rotamers (D) and one of either (E) or (F). In contrast RR/SS-2 is either the conformationally rigid eclipsed rotamer (G) or (H) or the highly dynamic staggered rotamer (I).

### Correlation of <sup>1</sup>J(<sup>195</sup>Pt—P) and Pt—P bond lengths

Correlation between  ${}^{1}J({}^{195}\text{Pt}-P)$  and Pt-P bond lengths in platinum(II) phosphine complexes, a parameter sensitive to the *s*-orbital character of the Pt-P bond, has been the focus of several investigations [17,22]. Powell reports a close correlation between the  ${}^{1}J({}^{195}\text{Pt}-P\mu)$  and platinum phosphorus distances for several heterometallic complexes and our observations for complexes 1-2 support this, provided



Scheme 1.

ligands of the same type are compared, that is we have to distinguish between tertiary and anionic phosphines in order to obtain credible correlations. Powell has also suggested that the decreasing values of  ${}^{1}J({}^{195}Pt-P)$  with increasing bond length reflect a change in s-orbital overlap in the platinum-phosphorus bond [17b,c]. We too have observed a similar trend with  ${}^{1}J({}^{195}\text{Pt}--\text{P}\mu) = 2135 \text{ Hz trans to chloride}$ in 1 [Pt—P = 2.288(3) Å] and  ${}^{1}J({}^{195}\text{Pt}-P\mu) = 1450$ Hz trans in dppe in  $[Pt(\mu-PPhH)_2\{Mo(CO)_5\}_2(dppe)]$ (3) [Pt-P = 2.361(3) Å]. Thus, the values of  $^{1}J(^{195}Pt-P)$  for tertiary phosphines do reflect the Pt—P distances as do those of  ${}^{1}J({}^{195}\text{Pt}-\text{P}\mu)$  for  $[PPhH\{Mo(CO)_5\}]^-$ , which are, in general, considerably lower than their tertiary phosphine counterparts of similar bond length. An examination of the  ${}^{1}J({}^{195}\text{Pt}-\text{P}\mu)$  values in 1 and cis-2 (i.e. 2135 Hz and 1400.6 Hz for 1 and 2, respectively) illustrates the effect of the trans ligand on this parameter, clearly demonstrating that ligands with a strong trans influence lead to reduced  ${}^{1}J({}^{195}Pt-P\mu)$  values and that these are considerably lower than their tertiary phosphine counterparts with similar trans ligands. These reduced  ${}^{1}J({}^{195}\text{Pt}---\text{P}\mu)$  values are illustrated by comparing  $[PtCl(PEt_3)_2(\mu-PPhH)\{Mo(CO)_5\}]$  (1) with cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] for which  ${}^{1}J({}^{195}\text{Pt}-P\mu) = 2135 \text{ Hz}$ and  ${}^{1}J({}^{195}\text{Pt}-\text{PEt}_{3}) = 3500 \text{ Hz in the absence of sig-}$ nificant cis effects.

#### Conclusions

While the synthetic approach described here extends the utility of the bridge-assisted approach for constructing heterometallic complexes, the thrust of our effort has been the structural and spectroscopic characterization of rare examples of heterometallic complexes bridged by chiral primary phosphido bridges. The heterometallic complexes trans- $[PtCl(PEt_3)_2(\mu-PPhH) \{Mo(CO)_5\}]$  (1) and *cis*- and trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>( $\mu$ -PPhH)<sub>2</sub>{Mo(CO)<sub>5</sub>}<sub>2</sub> (**2**) have been prepared by the nucleophilic substitution of chloride in cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] by the chiral anion  $[PPhH{Mo(CO)_{5}}]^{-}$ . Information contained in their <sup>31</sup>P{<sup>1</sup>H} NMR spectra has provided insight into the nature of their accessible rotational isomers. The exchange broadened  ${}^{31}P{}^{1}H$  NMR spectra of 1 and trans-2 have been explained in terms of the presence of several rotameric forms which interconvert by rotation about their  $Pt - P\mu$  bonds, an interpretation supported by similar observations for  $[Pt(\mu PPhH_{2}\{Mo(CO)_{5}\}_{2}(dppe)\}$  (3). cis-2 with  $PEt_{3}$  trans to  $[PPhH{Mo(CO)_5}]^-$  is characterized by reduced values of  ${}^{2}J(PEt_{3}-P\mu)$  (200 Hz) and  ${}^{1}J({}^{195}Pt-P\mu)$ (1400.6 Hz) compared with values reported for mutually trans neutral phosphines for which values close to 300 Hz and 2500 Hz would have been expected. These reduced Pt-P and P-P coupling constants are consistent with a lower s-orbital contribution to the Pt—P bond for the anion  $[PPhH{Mo(CO)_5}]^-$  compared with their tertiary phosphine counterparts. We conclude that the spectroscopic characteristics of 1 and *cis*- and *trans*-2 can most aptly be accounted for by considering them as square-planar Pt<sup>11</sup> complexes containing phosphorus donor ligands rather than  $\mu$ -PPhH bridged heterometallics. Finally, the P—H functionalities of the primary phosphido bridges in 1 and 2 are sites of additional reactivity not available to their  $\mu$ -PR<sub>2</sub> (R = alkyl or aryl) bridged counterparts, thus, complexes of this type allow new developments in heterobimetallic reactivity.

Supplementary material available. Further details for 1 and trans-2 are available as supplementary material (atomic coordinates, anisotropic thermal parameters, bond distances and bond angles, hydrogen-atom coordinates) deposited at the Cambridge Crystallographic Centre. Structure factors are available from the author upon request.

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