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### Metal-only Lewis pairs featuring unsupported $Pt \rightarrow M$ (M = Zn or Cd) dative bonds<sup>†</sup>

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Reactions of  $[Pt(PCy_3)_2]$  (Cy = cyclohexyl) with group 12 metal dihalides have afforded the novel metal only Lewis pair (MOLP) complexes,  $[(Cy_3P)_2Pt \rightarrow MX_2]$  (M = Zn or Cd, X = Br or I), or the oxidative addition product, *trans*-[(Cy\_3P)\_2(I)PtHgI]. The zinc complex represents the first MOLP to contain an unsupported Pt  $\rightarrow$  Zn linkage.

The chemistry of heterobimetallic complexes featuring metalmetal bonds is of considerable importance, both for fundamental reasons, and because such systems have found a variety of applications in synthesis, catalysis, materials chemistry etc.<sup>1</sup> While the majority of such compounds are stabilised by ligands that bridge their metal-metal bonds, compounds with unsupported metal-metal bonds are generally considered as being more reactive species.<sup>1,2</sup> There are a variety of methodologies available for the construction of metal-metal bonded complexes, though the formation of heteronuclear  $M \rightarrow M'$  dative linkages from Lewis basic and Lewis acidic metal fragments is increasingly employed in this field.<sup>3</sup> The popularity of this synthetic approach is derived from its simplicity, but also from the wide array of supported and unsupported  $M \rightarrow M'$  combinations that it offers the synthetic chemist. Compounds bearing such bonds have been termed metal-only Lewis pairs, or MOLPs.<sup>3a</sup>

One of the more important metal donor Lewis bases that have been examined in recent years is the linear platinum(0) complex,  $[Pt(PCy_3)_2]$  (Cy = cyclohexyl). This has been employed to great effect, largely by Braunschweig and co-workers, in the formation of novel complexes with unsupported dative bonds between platinum and an array of s-,<sup>4</sup> p-<sup>5</sup> and d-block<sup>6</sup> metal fragments.<sup>5b,7</sup> Structural and computational studies of several of these adducts have indicated that  $[Pt(PCy_3)_2]$  can act as a relatively strong Lewis base. Moreover, the oxidative addition of metal and non-metal halide bonds to its  $Pt^0$  centre has been demonstrated in some instances.<sup>5b,7</sup> It is surprising that there have been no reports of adducts between  $[Pt(PCy_3)_2]$  and group 12 metal halides, and to the best of our knowledge, unsupported  $Pt \rightarrow Zn$  MOLPs of any kind are unknown. Here we report the preparation of the thermally stable complexes,  $[(Cy_3P)_2Pt \rightarrow MX_2]$  (M = Zn or Cd; X = Br or I), and show that related mercury halide adducts are not easily accessible.

Treatment of toluene solutions of  $[Pt(PCy_3)_2]$  with either ZnBr<sub>2</sub> or CdI<sub>2</sub> led to high isolated yields of the yellow-orange crystalline products, 1 and 2, upon work-up (Scheme 1). Both compounds are thermally robust and show no tendency to convert to oxidative addition products,  $[(Cy_3P)_2(X)PtMX_2]$ , in solution or the solid state at ambient temperature. In contrast, treatment of  $[Pt(PCy_3)_2]$  with HgI<sub>2</sub> afforded a high yield of the yellow addition product, trans-[(Cy<sub>3</sub>P)<sub>2</sub>(I)PtHgI] 3, with no evidence of adduct formation (though the reaction likely proceeds *via*  $[(Cy_3P)_2Pt \rightarrow HgI_2]$ ). Similar oxidative addition processes have been previously described for reactions of  $[Pt(PCy_3)_2]$  with, for example,  $GaX_3$  (X = Br or I), BiCl<sub>3</sub> and group 11 metal halides.<sup>5b,7</sup> However, the outcome of these reactions can be dependent on the nature of the halide as much as the metal, as evidenced by the fact that GaCl<sub>3</sub> forms a stable adduct with the Pt<sup>0</sup> Lewis base.<sup>5b</sup> As a result, we investigated the reaction of  $HgCl_2$  with  $[Pt(PCy_3)_2]$ , and found that this led to deposition of mercury metal and the formation of the known complex, *trans*-[PtCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>],<sup>8</sup> in addition to small amounts of trans-[(Cy3P)2(Cl)PtHgCl] (see ESI<sup>+</sup>). It is



Scheme 1 Reagents and conditions: i, ZnBr<sub>2</sub> or Cdl<sub>2</sub>; ii, Hgl<sub>2</sub> (Cy = cyclohexyl).

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**Fig. 1** Molecular structure of **1** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **1**: Pt(1)–P(1) 2.2760(6), Pt(1)–Zn(1) 2.4040(6), Br(1)–Zn(1) 2.3305(5), P(1)'–Pt(1)–P(1) 176.28(3), Br(1)–Zn(1)–Br(1)' 118.75(3), Br(1)–Zn(1)–Pt(1) 120.626(15), Br(1)'–Zn(1)–Pt(1) 120.626(15); symmetry operation: '-x + 1, y, -z + 1/2. Selected bond lengths (Å) and angles (°) for **2** (see ESI+ for ORTEP diagram): Pt(1)–P(1) 2.2799(13), Pt(1)–P(2) 2.2920(13), Pt(1)–Cd(1) 2.5867(6), I(1)–Cd(1) 2.6974(8), I(2)–Cd(1) 2.6997(8), P(1)–Pt(1)–P(2) 176.92(3), Pt(1)–Cd(1)–I(1) 122.176(19), Pt(1)–Cd(1)–I(2) 117.531(19), I(1)–Cd(1)–I(2) 120.21(2).

noteworthy that a similar result was obtained from the reaction of  $Hg_2Cl_2$  with  $[Pt(PCy_3)_2]$ .

The NMR spectroscopic data for 1 and 2 are similar and suggest both retain their solid state structures in solution.§ Their <sup>31</sup>P{<sup>1</sup>H} NMR spectra display singlet resonances at  $\delta$  = 53.0 and 51.6 ppm respectively, each of which exhibits <sup>195</sup>Pt satellites ( ${}^{1}J_{PtP}$  = 2982 Hz 1; 2978 Hz 2). These values are comparable to those for the isostructural adduct,  $[(Cy_3P)_2Pt \rightarrow$ BeCl<sub>2</sub>] ( $\delta$  = 53.6 ppm, <sup>1</sup>*J*<sub>PtP</sub> = 3240 Hz),<sup>4</sup> but lower in magnitude than the values for the precursor complex,  $[Pt(PCy_3)_2]$  $(\delta = 62.2 \text{ ppm}, {}^{1}J_{\text{PtP}} = 4155 \text{ Hz}).^{7a}$  Furthermore,  ${}^{111/113}\text{Cd}$ satellites  $(^{2}J_{CdP} = 36 \text{ Hz})$  flank the signal for 2. Triplet resonances were observed in the 195Pt{1H} NMR spectra of the compounds (1:  $\delta = -5425$  ppm, 2:  $\delta = -5260$  ppm), which are significantly downfield of that for  $[Pt(PCy_3)_2]$  ( $\delta =$ -6505 ppm).<sup>7a</sup> The NMR spectroscopic data for the insertion product 3 ( ${}^{31}P{}^{1}H{}$ ;  $\delta = 31.0$  ppm,  ${}^{1}J_{PtP} = 2448$  Hz,  ${}^{2}J_{HgP} = 299$  Hz; <sup>195</sup>Pt{<sup>1</sup>H}:  $\delta = -5052$  ppm) compare well with data for similar compounds, *e.g. trans*-[(Cy<sub>3</sub>P)<sub>2</sub>(I)PtGaI<sub>2</sub>] (<sup>31</sup>P{<sup>1</sup>H}:  $\delta$  = 23.1 ppm,  ${}^{1}J_{\text{PtP}} = 2281 \text{ Hz}$ .

X-ray crystallographic studies determined **1** and **2** to be monomeric and isostructural in the solid state. Therefore only the molecular structure of **1** is depicted in Fig. **1** (see ESI<sup>†</sup> for an ORTEP diagram of **2**).¶ Both compounds are also broadly isostructural with  $[(Cy_3P)_2Pt \rightarrow BeCl_2]$  in that their Lewis acidic metal centres all possess trigonal planar geometries, while their Pt centres have T-shaped coordination environments with close to linear P–Pt–P fragments. In fact, this unit in **1** and **2** is more obtuse than in any other metal adduct of  $[Pt(PCy_3)_2]$ . The PtMX<sub>2</sub> and P<sub>2</sub>PtM least squares planes of **1** and **2** bisect each other at angles of 71.8° **1** and 69.7° **2** (*cf.* 71.8° in  $[(Cy_3P)_2Pt \rightarrow BeCl_2]^4$ ). With regard to the Pt–M distances in the compounds, that in **1** (2.4040(6) Å) is at the short end of the known range (2.343– 3.003 Å),<sup>9</sup> with only covalently bonded two-coordinate zinc compounds, *e.g.*  $[Cp*Pt(ZnCp*)_3]$ ,<sup>10</sup> having shorter Pt–Zn bonds.



**Fig. 2** Molecular structure of **3** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Hg(1)–Pt(1) 2.5250(2), Hg(1)–I(2) 2.6764(16), Pt(1)–P(1) 2.3304(10), Pt(1)–P(2) 2.3403(10), Pt(1)–I(1) 2.6542(3), Pt(1)–Hg(1)–I(2) 173.05(3), P(1)–Pt(1)–P(2) 168.10(4), Hg(1)–Pt(1)–I(1) 178.850(11), P(1)–Pt(1)–Hg(1) 85.99(2), P(2)–Pt(1)–Hg(1) 87.17(3).

Furthermore, the Pt–Cd bond in 2 (2.5867(6) Å) is shorter than all of the more than 50 other reported examples of such interactions (range: 2.606–3.129 Å).<sup>9</sup> This, combined with the fact that **1** and **2** possess very rare examples of terminal  $MX_2$  fragments, could indicate that  $[Pt(PCy_3)_2]$  acts as a strong nucleophile to those fragments.<sup>11</sup>

The molecular structure of **3** (Fig. 2) confirms it to be an oxidative addition product. The compound is monomeric and its Pt center has a square planar coordination environment, with the two phosphine ligands *trans*- to each other. The Pt–Hg bond length is at the low end of the reported range for unsupported interactions of this nature (2.509–2.808 Å),<sup>9</sup> while the terminal Hg–I and Pt–I distances are unexceptional. It is of note that several reports have detailed the oxidative addition of mercury( $\pi$ ) dihalides to platinum( $\pi$ ) centres,<sup>12</sup> though we are not aware of any prior structurally authenticated examples of such additions to platinum(0) complexes.

In conclusion, the first examples of adducts between the widely used metal donor Lewis base,  $[Pt(PCy_3)_2]$ , and group 12 metal fragments have been prepared and structurally characterised. One synthesised complex,  $[(Cy_3P)_2Pt \rightarrow ZnBr_2]$ , represents the first MOLP containing an unsupported  $Pt \rightarrow Zn$  linkage, while attempts to prepare a related  $Pt \rightarrow Hg$  adduct, instead lead to an oxidative addition reaction. We are currently exploring the controlled reduction of 1–3 and related compounds with the aim of forming well defined, low valent bimetallic cluster compounds. Our results in this direction will be reported in due course.

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#### Notes and references

§  $[(Cy_3P)_2Pt \rightarrow ZnBr_2]$  (1):  $ZnBr_2$  (0.039 g, 0.173 mmol) was added to a solution of  $[Pt(PCy_3)_2]$  (0.131 g, 0.173 mmol) in toluene (80 cm<sup>3</sup>) at -70 °C. The mixture was warmed to room temperature overnight, then concentrated to *ca.* 25 cm<sup>3</sup> *in vacuo.* Yellow-orange crystals of **1** 

deposited from this solution over 1 week (0.14 g, 0.143 mmol, 83%). N.B. Crystals for the X-ray experiment were grown from benzene. M.p. 258–260 °C; <sup>1</sup>H NMR (300 MHz, 303 K,  $C_6D_6$ ):  $\delta$  = 1.29 (br., 18H, Cy-CH2), 1.60-1.73 (m, 30H, Cy-CH2), 2.06-2.12 (m, 12H, Cy-CH2), 2.28 (m, CH<sub>2</sub>), 1.60–1.73 (m, 30H, Cy-CH<sub>2</sub>), 2.00–2.12 (iii, 12H, Cy-CH<sub>2</sub>), 2.20 (iii, 6H, Cy-CH); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 26.4$  (s, C<sup>4</sup>, Cy), 27.6 (virtual triplet,  $J_{PC} = 11$  Hz, C<sup>2,6</sup>, Cy), 31.6 (s, C<sup>3,5</sup>, Cy), 35.7 (virtual t,  $J_{PC} = 27$  Hz, C<sup>1</sup>, Cy); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 53.0$  (s,  $J_{Pt-P} = 2982$  Hz); <sup>195</sup>Pt{<sup>1</sup>H} NMR (85.6 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = -5425$  (s,  $J_{Pt-P} = 2980$  Hz); IR (Nujol)  $\nu$  (cm<sup>-1</sup>): 1601s, 1006s, 889s, 851s, 814s, 7405 Cose: MS ( $\nu \approx CU/CH$ ) m/7 ( $\phi$ ), 981.2 (M<sup>-</sup>-B) 898.0 (M<sup>-</sup>-Br, 1): 748s, 698s; MS (-ve CI/CH<sub>4</sub>) m/z (%): 981.2 (M<sup>-</sup>, 6), 898.0 (M<sup>-</sup>-Br, 1); anal. calcd for C<sub>36</sub>H<sub>66</sub>Br<sub>2</sub>P<sub>2</sub>PtZn: C 44.07%, H 6.78%; found: C 44.10%, H 6.87%.  $[(Cy_3P)_2Pt \rightarrow CdI_2]$  (2): A similar procedure to that used to prepare 1 was employed for the synthesis of 2 (yield: 74%). M.p. 229-231 °C; <sup>1</sup>H NMR (300 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.30 (br., 18H, Cy-CH<sub>2</sub>), 231 C; H NMR (300 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.30$  (b1., 18H, Cy-CH<sub>2</sub>), 1.61–1.74 (m, 30H,  $-CH_2$ ), 2.06 (m, 12H,  $-CH_2$ ), 2.22 (m, 6H,  $-CH_2$ );  ${}^{13}C_1^{[1]}H$  NMR (75.5 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 26.4$  (s, C<sup>4</sup>, Cy), 27.7 (virtual t,  $J_{PC} = 11$  Hz, C<sup>2.6</sup>, Cy), 31.8 (s, C<sup>3.5</sup>, Cy), 36.0 (virtual t,  $J_{PC} = 27$  Hz, C<sup>1</sup>, Cy);  ${}^{31}P_1^{[1]}H$  NMR (121.5 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 51.6$  (s,  ${}^{1}J_{Pt-P} = 2978$  Hz,  ${}^{2}J_{Cd-P} = 36$  Hz);  ${}^{195}Pt_1^{[1]}H$  NMR (85.6 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = -5260$ (s,  ${}^{1}J_{Pt-P} = 2974$  Hz); IR (Nujol)  $\nu$  (cm<sup>-1</sup>): 1494w, 1027s, 914m, 887m, 851m, 7995, 7325, 695m; MS ( $-\nu c$ Cl/CH) M/2 ( $^{10}$  M/2 ( $^{11}$ ) 122 1 (M<sup>-1</sup>), 75.4 851m, 799s, 732s, 695m; MS (-ve CI/CH<sub>4</sub>) m/z (%): 1122.1 (M<sup>-</sup>, 1), 754.3  $(M^{-}-CdI_{2}, 1)$ , 367.6  $(CdI_{2}^{-}, 2)$ ; anal. calcd for  $C_{36}H_{66}CdI_{2}P_{2}Pt$ : C 38.53%, H 5.93%; found: C 38.42%, H 5.90%. trans-[(Cy<sub>3</sub>P)<sub>2</sub>(I)PtHgI] (3): HgI<sub>2</sub> (0.101 g, 0.222 mmol) was added to a solution of  $[Pt(PCy_3)_2]$  (0.167 g, 0.221 mmol) in toluene (20 cm<sup>3</sup>) at -65 °C. The mixture was warmed to room temperature over 2 h, then concentrated to ca. 8 cm<sup>3</sup> in vacuo. Hexane (20 cm<sup>3</sup>) was added to this solution and the mixture allowed to stand in the absence of light for 1 day, yielding yellow crystals of 3 (0.24 g, 0.198 mmol, 90%). M.p. 270-272 °C; <sup>1</sup>H NMR (300 MHz, 303 K,  $C_6D_6$ ):  $\delta = 1.22$  (m, 6H, Cy-CH<sub>2</sub>), 1.37 (m, 12H, Cy-CH<sub>2</sub>), 1.60-1.73 C<sub>6</sub>D<sub>6</sub>J;  $\vartheta = 1.22$  (III, 6rI, Cy-CH<sub>2</sub>), 1.37 (III, 12H, Cy-CH<sub>2</sub>), 1.60<sup>-1</sup>.73 (III, 30H, Cy-CH<sub>2</sub>), 2.14 (d, 12H, Cy-CH<sub>2</sub>), 2.89 (br., 6H, Cy-CH);  ${}^{13}C_1^{[1H]}$ NMR (75.5 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 26.9$  (s, C<sup>4</sup>, Cy), 27.7 (virtual t,  $J_{PC} =$ 11 Hz, C<sup>2,6</sup>, Cy), 31.1 (virtual t,  $J_{PC} = 22$  Hz, C<sup>3,5</sup>, Cy), 39.0 (virtual t,  $J_{PC} = 29$  Hz, C<sup>1</sup>, Cy).  ${}^{31}P_1^{[1H]}$  NMR (121.5 MHz, 303 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 31.0$ (s,  ${}^{1}J_{Pt-P} = 2448$  Hz,  ${}^{2}J_{Hg-P} = 299$  Hz);  ${}^{195}Pt_1^{[1H]}$  NMR (85.6 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = -5052$  (s,  ${}^{1}J_{Pt-P} = 2446$  Hz); IR (Nujol)  $\nu$  (cm<sup>-1</sup>): 1445s, 1050m, 1002s, 015m, 2015, 242s, 216m, 273c; MS (EU7.0 eV),  $m_2^{(2)}$  ( $\psi_2$ ), 1092 1002s, 916m, 891s, 848s, 816m, 733s; MS (EI/70 eV) m/z (%): 1082.3 (M<sup>+</sup>-I, 1), 755.4 (M<sup>+</sup>-HgI<sub>2</sub>, 75); anal. calcd for C<sub>36</sub>H<sub>66</sub>HgI<sub>2</sub>P<sub>2</sub>Pt: C 35.72%, H 5.50%; found: C 35.63%, H 5.38%.

¶ *Crystal data* for 1·(benzene): C<sub>42</sub>H<sub>72</sub>Br<sub>2</sub>P<sub>2</sub>PtZn, *M* = 1059.22, monoclinic, space group *C*2/*c*, *a* = 16.7915(8) Å, *b* = 10.9089(17) Å, *c* = 23.5671(14) Å, *β* = 93.615(5)°, *V* = 4308.4(7) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.633 g cm<sup>-3</sup>, *F*(000) = 2128, μ(Mo·Kα) = 5.757 mm<sup>-1</sup>, 123(2) K, 19036 collected reflections, 6274 unique reflections [*R*<sub>(int)</sub> 0.0240], *R* (on *F*) 0.0251 (*I* > 2*σI*), *wR* (on *F*<sup>2</sup>) 0.0523 (all data); *Crystal data* for 2·(toluene): C<sub>43</sub>H<sub>74</sub>CdI<sub>2</sub>P<sub>2</sub>PtZn, *M* = 1214.25, monoclinic, space group *C*/*c*, *a* = 17.011(3) Å, *b* = 11.399(2) Å, *c* = 23.647(5) Å, *β* = 92.39(3)°, *V* = 4581.2(16) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.761 g cm<sup>-3</sup>, *F*(000) = 2376, μ(Mo·Kα) = 4.959 mm<sup>-1</sup>, 123(2) K, 20129 collected reflections, 8275 unique reflections [*R*<sub>(int)</sub> 0.0253], *R* (on *F*) 0.0192 (*I* > 2*σI*), *wR* 

(on  $F^2$ ) 0.0413 (all data); *Crystal data* for 3: C<sub>36</sub>H<sub>66</sub>HgI<sub>2</sub>P<sub>2</sub>PtZn, M = 1210.31, monoclinic, space group  $P2_1/c$ , a = 13.4975(5) Å, b = 13.4310(3) Å, c = 23.4845(8) Å,  $\beta = 107.180(3)^{\circ}$ , V = 4067.4(2) Å<sup>3</sup>, Z = 4,  $D_c = 1.976$  g cm<sup>-3</sup>, F(000) = 2304,  $\mu$ (Mo-K $\alpha$ ) = 8.825 mm<sup>-1</sup>, 123(2) K, 26 184 collected reflections, 7991 unique reflections [ $R_{(int)}$  0.0245], R (on F) 0.0233 ( $I > 2\sigma I$ ), wR (on  $F^2$ ) 0.0481 (all data).

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