

## Metal-Only Lewis Pairs Featuring Unsupported Pt→M (M = Zn or Cd) Dative Bonds

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### SUPPLEMENTARY INFORMATION

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#### 1. Syntheses

**General considerations.** All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene, hexane and benzene were distilled over molten potassium metal. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on either Bruker DXP300 or AvanceIII 400 spectrometers and were referenced to the residual solvent resonances.  $^{31}\text{P}\{^1\text{H}\}$  and  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectra were recorded on either Bruker DXP300 or AvanceIII 400 spectrometers and were referenced to external 85%  $\text{H}_3\text{PO}_4$  and  $\text{Na}_2[\text{PtCl}_6]$  respectively. Microanalyses were carried out by the Science Centre, London Metropolitan University.  $[\text{Pt}(\text{PCy}_3)_2]^1$  and  $\text{IPr}^2$  were prepared by literature procedures. All other reagents were used as received.

See main text for the syntheses of  $[(\text{Cy}_3\text{P})_2\text{Pt}\rightarrow\text{ZnBr}_2]$  (**1**),  $[(\text{Cy}_3\text{P})_2\text{Pt}\rightarrow\text{CdI}_2]$  (**2**) and *trans*- $[(\text{Cy}_3\text{P})_2(\text{I})\text{PtHgI}]$  (**3**). N.B. An attempt to prepare the complex  $[(\text{Cy}_3\text{P})_2\text{Pt}\rightarrow\text{HgCl}_2]$  from the reaction of  $[\text{Pt}(\text{PCy}_3)_2]$  with  $\text{HgCl}_2$  led to the formation of *trans*- $[\text{PtCl}_2(\text{PCy}_3)_2]$  as the major product. A small amount of  $[(\text{Cy}_3\text{P})_2(\text{Cl})\text{PtHgCl}]$  was also identified by the similarity of its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $^{31}\text{P}\{^1\text{H}\}$ :  $\delta = 35.1$  ppm,  $^1J_{\text{PtP}} = 2452$  Hz,  $^2J_{\text{HgP}} = 338$  Hz) to that of **3**.

**Preparation of  $[\{(\text{IPr})\text{ZnBr}(\mu\text{-Br})\}_2]$ .** Toluene (50 cm<sup>3</sup>) was added to a mixture of IPr (0.489 g, 1.26 mmol) and  $\text{ZnBr}_2$  (0.285 g, 1.27 mmol) and the resultant suspension stirred overnight at 20 °C, during which time the title compound deposited as a colourless crystalline solid. This was isolated by filtration and the mother liquor concentrated *in vacuo* to ca. 10 cm<sup>3</sup> and placed at -30 °C overnight to give a further crop of  $[\{(\text{IPr})\text{ZnBr}(\mu\text{-Br})\}_2]$  as a colourless crystalline solid (0.680 g, 88%). N.B. Crystals for the X-ray experiment were grown from benzene. M.p.: 311-316 °C.  $^1\text{H}$

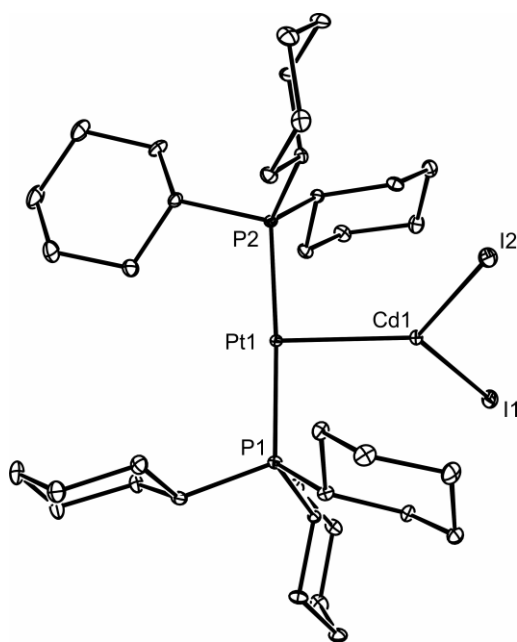
NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.96 (d, 12H,  $^3J_{\text{HH}} = 7.2$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.55 (d, 12H,  $^3J_{\text{HH}} = 7.2$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.87 (sept, 4H,  $^3J_{\text{HH}} = 7.2$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.44 (s, 2H, CH), 7.11 (m, 4H, Ar-CH), 7.20 (m, 2H, Ar-CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, 298K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  26.4 (CH<sub>3</sub>), 26.9 (CH<sub>3</sub>), 29.0 (C(CH<sub>3</sub>)<sub>2</sub>), 121.3 (*im*CH), 126.6, 126.8, 141.2, 148.7 (Ar-C), NCN resonance not observed; IR (Nujol)  $\nu$  (cm<sup>-1</sup>): 1651w, 1589w, 1097s, 1069m, 1018m, 799s, 754m; MS (EI/70eV)  $m/z$  (%): 533.1 (M-Br<sup>+</sup>, correct isotope pattern, 100).

**Preparation of [(IPr)CdI( $\mu$ -I)]<sub>2</sub>.** The title compound was prepared by a similar procedure to that used for the synthesis of [(IPr)ZnBr( $\mu$ -Br)]<sub>2</sub> (yield 73%). M.p.: 240-247 °C. (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.92 (d, 12H,  $^3J_{\text{HH}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.60 (d, 12H,  $^3J_{\text{HH}} = 7.2$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.78 (sept, 4H,  $^3J_{\text{HH}} = 7.2$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.43 (s, 2H, CH), 7.07 (m, 4H, Ar-CH), 7.20 (m, 2H, Ar-CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, 298K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.7 (CH<sub>3</sub>), 28.9 (CH<sub>3</sub>), 29.8 (C(CH<sub>3</sub>)<sub>2</sub>), 124.9 (*im*CH), 127.6, 128.8, 143.3, 147.7 (Ar-C), NCN resonance not observed; IR (Nujol)  $\nu$  (cm<sup>-1</sup>): 1621w, 1589w, 1059m, 1017m, 802s, 759m; MS (EI/70eV)  $m/z$  (%): 629.1 (M-I<sup>+</sup>, correct isotope pattern, 100).

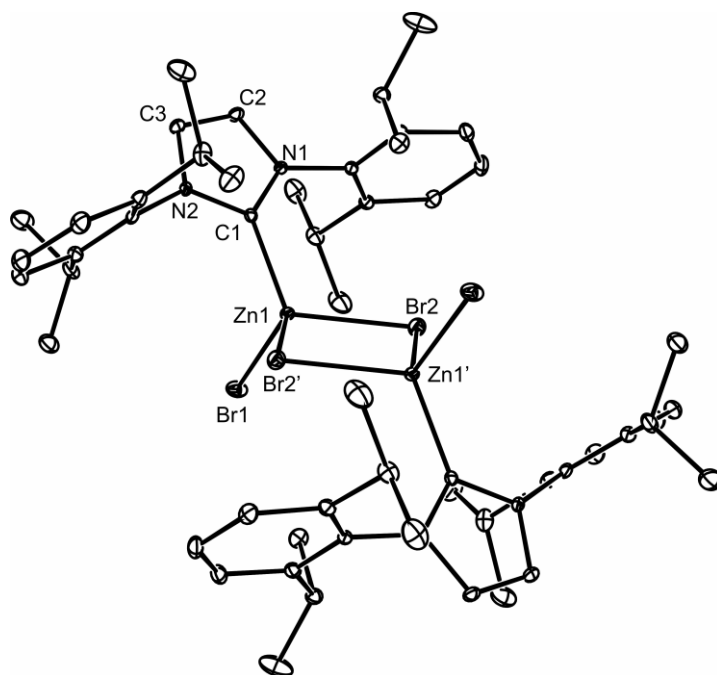
## 2. X-Ray Crystallography

Crystals of **1-3**, [(IPr)ZnBr( $\mu$ -Br)]<sub>2</sub> and [(IPr)CdI( $\mu$ -I)]<sub>2</sub> suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either Oxford Gemini Ultra or Nonius Kappa CCD diffractometers using a graphite monochromator with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). All structures were solved by direct methods and refined on F<sup>2</sup> by full matrix least squares (SHELX97)<sup>3</sup> using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Crystal data for **1-3** can be found in the main text.

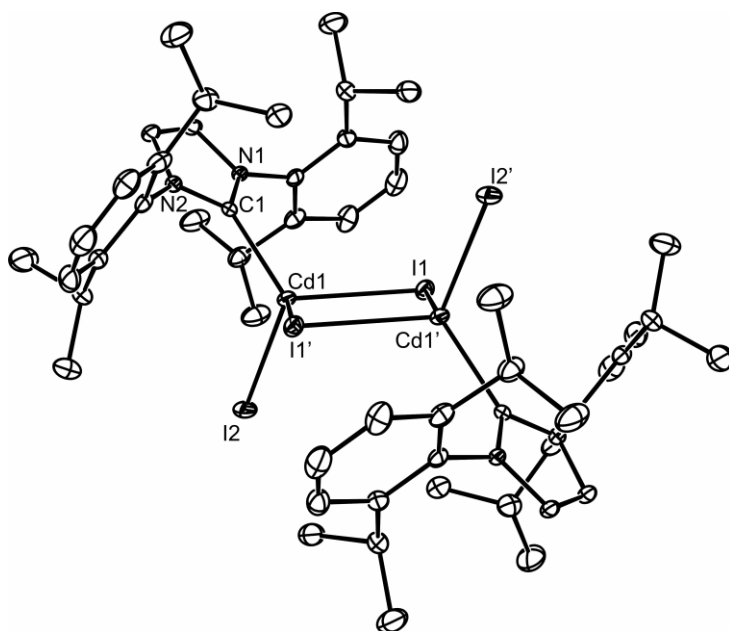
*Crystal data* for [(IPr)ZnBr( $\mu$ -Br)]<sub>2</sub>·(benzene)<sub>4</sub>: C<sub>78</sub>H<sub>96</sub>Br<sub>4</sub>N<sub>4</sub>Zn<sub>2</sub>,  $M = 1539.97$ , triclinic, space group  $P-1$ ,  $a = 10.707(2)$  Å,  $b = 12.313(3)$  Å,  $c = 16.081(3)$  Å,  $\alpha = 70.83(3)^\circ$ ,  $\beta = 88.76(3)^\circ$ ,  $\gamma = 66.98(3)^\circ$ ,  $V = 1829.2(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.398$  gcm<sup>-3</sup>,  $F(000) = 792$ ,  $\mu(\text{Mo-K}\alpha) = 2.884$  mm<sup>-1</sup>, 173(2) K, 14642 collected reflections, 7964 unique reflections [ $R(\text{int})$  0.0375],  $R$  (on  $F$ ) 0.0448 ( $I > 2\sigma I$ ),  $wR$  (on  $F^2$ ) 0.1226 (all data); *Crystal data* for [(IPr)CdI( $\mu$ -I)]<sub>2</sub>·(toluene)<sub>4.5</sub>: C<sub>85.5</sub>H<sub>108</sub>Cd<sub>2</sub>I<sub>4</sub>N<sub>4</sub>,  $M = 1924.16$ , monoclinic, space group  $P2_1/c$ ,  $a = 15.253(3)$  Å,  $b = 19.437(4)$  Å,  $c = 15.846(3)$  Å,  $\beta = 106.39(3)^\circ$ ,  $V = 4507.0(16)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.418$  gcm<sup>-3</sup>,  $F(000) = 1914$ ,  $\mu(\text{Mo-K}\alpha) = 1.882$  mm<sup>-1</sup>, 173(2) K, 18865 collected reflections, 9829 unique reflections [ $R(\text{int})$  0.0329],  $R$  (on  $F$ ) 0.0488 ( $I > 2\sigma I$ ),  $wR$  (on  $F^2$ ) 0.1489 (all data).



**Fig. S1** Molecular structure of  $[(\text{Cy}_3\text{P})_2\text{Pt}\rightarrow\text{CdI}_2]$  (**2**) (25% thermal ellipsoids; hydrogen atoms omitted). See main text for metrical parameters.



**Fig. S2** Molecular structure of  $[(\text{IPr})\text{ZnBr}(\mu\text{-Br})_2]$  (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Br(1)-Zn(1) 2.3642(8), Br(2)-Zn(1)' 2.4658(12), Br(2)-Zn(1) 2.4866(9), Zn(1)-C(1) 2.039(3), Zn(1)′-Br(2)-Zn(1) 86.44(3), C(1)-Zn(1)-Br(1) 108.88(9), C(1)-Zn(1)-Br(2)' 116.35(9), Br(1)-Zn(1)-Br(2) 109.92(3). Symmetry operation: ' -x+1, -y, -z+1.



**Fig. S3** Molecular structure of  $[(\text{IPr})\text{CdI}(\mu\text{-I})_2]$  (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): I(1)-Cd(1) 2.8518(9), I(1)-Cd(1) 2.8565(12), I(2)-Cd(1) 2.7339(7), Cd(1)-C(1) 2.249(5), Cd(1)'-I(1)-Cd(1) 84.35(3), C(1)-Cd(1)-I(2) 113.82(13), C(1)-Cd(1)-I(1)' 115.25(14), I(2)-Cd(1)-I(1)' 107.31(2), C(1)-Cd(1)-I(1) 115.30(12), I(2)-Cd(1)-I(1) 107.79(2), I(1)'-Cd(1)-I(1) 95.65(3). Symmetry operation: '-x+1, -y+1, -z.

N.B.  $[(\text{IPr})\text{CdI}(\mu\text{-I})_2]$  represents the first structurally characterised example of an N-heterocyclic carbene adduct of a cadmium dihalide.

### 3. References

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