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## Lewis acid-base interactions between platinum(II) diaryl complexes and bis(perfluorophenyl)zinc: strongly accelerated reductive elimination induced by a Z-type ligand<sup>+</sup>

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Z-type interactions between bis(perfluorophenyl)zinc and platinum(II) diaryl complexes supported by 1,10-phenanthroline (phen), 2,2'-bipyridine (bpy), and bis(dimethylphosphino)ethane (dmpe) ligands are reported. In the solid state, the nature of the Pt–Zn interaction depends on the bidentate ligand; the phen-supported complex exhibits an unsupported Pt–Zn bond, while the dmpe derivative features additional bridging aryl interactions. A strongly accelerated rate of reductive elimination is observed for phen- and bpy-supported complexes, while aryl exchange between Pt and Zn is observed for the dmpe complex.

Understanding the interactions of a transition metal with its surrounding ligands is a central focus of organometallic chemistry. Many  $\sigma$ -donor ligands are Lewis bases that interact with metal centers by the donation of electron density. In fewer cases, Lewis basic transition metals donate electron density to Lewis acids (denoted Z-type ligands) to form retro-dative  $\sigma$ -bonding interactions.<sup>1</sup> Often, the Lewis acidic component is incorporated into a multi-dentate ligand to favor coordination.<sup>2</sup> Relatively few examples of unsupported Z-type interactions exist, particularly those featuring metal-metal bonds, termed metal-only Lewis pairs.<sup>3</sup>

Although Group 13 elements (B, Al, Ga) feature prominently in reports of Z-type ligands,<sup>3</sup> interactions of this type with Group 12 elements (Zn, Cd, Hg) remain rare.<sup>4</sup> The recently reported [(Cy<sub>3</sub>P)<sub>2</sub>Pt–ZnBr<sub>2</sub>] complex contains the first unsupported  $M \rightarrow Zn$  interaction,<sup>5</sup> and to our knowledge, there are no reported examples of Z-type bonds featuring organozinc components. However, these heterobimetallic interactions may be present during reactions between transition metal complexes and organozinc reagents. For example, transient Pd–Zn bonds have been invoked to account for the low energy barrier for transmetalation from

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organozinc reagents to palladium(II) complexes during the Negishi coupling reaction.<sup>6</sup> These heterobimetallic intermediates have also been proposed to lead to *cis/trans* isomerization of  $L_2PdR^1R^2$  complexes ( $R^1$ , $R^2$  = alkyl or aryl) and undesirable secondary transmetalation events that form homocoupling products under Negishi cross-coupling conditions.<sup>7</sup> Understanding the binding motifs and reactivity of organozinc complexes with Group 10 organometallic complexes could provide insight into the behavior of these proposed intermediates and inspire improved catalysts and conditions.

We have previously reported the ligand-based binding of bis(perfluorophenyl)zinc,  $ZnAr^{F_2}$ , to a 2,2'-bipyrimidyl–platinum(n) complex, which leads to dramatically enhanced rates of reductive elimination.<sup>8</sup> In the current work, we have demonstrated that if remote binding sites are omitted,  $ZnAr^{F_2}$  can directly bind to a platinum(n) center. Addition of  $ZnAr^{F_2}(\eta^2$ -toluene)<sup>9</sup> to a solution of (phen)PtAr<sub>2</sub> (1, Ar = 4-*tert*-butylphenyl) led to rapid formation of the heterobimetallic complex (phen)PtAr<sub>2</sub>( $ZnAr^{F_2}$ ) (2, eqn (1)). Yellow crystals of 2 were formed by vapor diffusion of pentane into a toluene solution at -35 °C (56% isolated yield). Treatment of (bpy)PtAr<sub>2</sub> (3, Ar = 4-*tert*-butylphenyl) with  $ZnAr^{F_2}(\eta^2$ -toluene) afforded an analogous (bpy)PtAr<sub>2</sub>( $ZnAr^{F_2}$ ) adduct (4) (64% isolated yield).



X-ray crystallographic studies confirmed the presence of an unsupported platinum–zinc interaction in 2 (Fig. 1), with the zinc center occupying the apical site of a square pyramidal platinum complex. The platinum–zinc distance of 2.5526(5) Å in 2 is longer than the distance in  $[(Cy_3P)_2Pt-ZnBr_2]$  (2.4040(6) Å)<sup>5</sup>

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Fig. 1 ORTEP diagram of 2, with  $p^{-t}$ Bu groups and hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50%.

but is on the shorter end of the range for previously reported platinum–zinc interactions (~2.34–3.00 Å).<sup>10</sup> The zinc-bound perfluorophenyl ligands of **2** are significantly bent away from the platinum center, with a C–Zn–C angle of 134.8° (compared to ZnAr<sup>F</sup><sub>2</sub> (172.6°)<sup>11</sup> or ZnAr<sup>F</sup><sub>2</sub>(\eta<sup>2</sup>-toluene) (162.4°)<sup>12</sup>).

NMR studies confirmed that the platinum–zinc interaction persists in benzene- $d_6$  solution at 25 °C. The <sup>1</sup>H NMR signal for the *ortho*-aryl protons is shifted upfield and the <sup>3</sup>J(<sup>195</sup>Pt–<sup>1</sup>H) coupling constant is decreased upon zinc binding (8.19 ppm,  $J_{PtH} = 69$  Hz for 1; 7.67 ppm,  $J_{PtH} = 50$  Hz for 2). Similar trends were previously observed upon copper(I) and silver(I) triflate binding to platinum(II) complexes.<sup>13</sup> There is also a small change in the <sup>195</sup>Pt NMR chemical shift upon ZnArF<sub>2</sub> binding ( $\delta = -3355$  ppm for 1 and -3167 ppm for 2).<sup>14</sup> The zinccoordinated bpy derivative 4 exhibited similar chemical shift and coupling constant perturbations compared to those of 3 (see ESI†).

To probe the effect of the platinum-bound chelating ancillary ligand on zinc coordination, the dmpe analogue was selected for comparison. Treatment of a toluene solution of (dmpe)PtAr<sub>2</sub> (**5**, Ar = 4-*tert*-butylphenyl) with ZnAr<sup>F</sup><sub>2</sub> generated the zinc adduct (dmpe)Pt( $\mu$ -Ar)<sub>2</sub>(ZnAr<sup>F</sup><sub>2</sub>) (**6**, eqn (2)). Colorless crystals of **6** were isolated in 68% yield by vapor diffusion of pentane into a toluene solution at -35 °C.



X-ray crystallographic studies revealed a different binding mode of zinc in **6** compared with that of **2** (Fig. 2). Rather than occupying an apical position above the Pt square plane, the zinc atom adopts a position near the *ipso* carbon atoms of the 4-*tert*butylphenyl ligands and is 0.895 Å above the least-squares



Fig. 2 ORTEP diagram of **6**, with  $p^{-t}$ Bu groups and hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50%.

platinum square plane.<sup>15</sup> The platinum–zinc distance of 2.7368(4) Å in **6** is significantly longer than the corresponding bond length for **2** (2.5526(5) Å). The 4-*tert*-butylphenyl groups unsymmetrically bridge the platinum and zinc centers, as evidenced by close contacts between zinc and the *ipso* carbon atoms (2.307(4) and 2.367(4) Å), and the tilt of the aryl rings (average Pt–C<sub>*ipso*</sub>–C<sub>*para*</sub> angles of ~ 163°).

The platinum–zinc interaction of complex **6** remains intact in benzene- $d_6$  solution at 25 °C. The <sup>1</sup>H NMR signal attributable to the *ortho*-aryl position is shifted downfield upon zinc coordination, from 7.85 ppm in 5 to 8.03 ppm for **6**, and the <sup>3</sup>J(<sup>195</sup>Pt–<sup>1</sup>H) coupling constant decreases from 57 Hz to 42 Hz. The <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift is relatively insensitive to zinc binding ( $\delta = 21.2$  and 29.4 ppm for **5** and **6**, respectively); however, the J(<sup>195</sup>Pt–<sup>31</sup>P) coupling constant increases significantly upon zinc coordination ( $J_{PtP} = 1630$  Hz for **5** and 2142 Hz for **6**). This increase in <sup>195</sup>Pt–<sup>31</sup>P coupling constant is consistent with a weaker *trans* influence of the aryl ligands resulting from interaction with zinc.<sup>16</sup> The <sup>195</sup>Pt chemical shifts of **5** and **6** are similar ( $\delta = -4506$  and -4544 ppm, respectively).

DFT calculations were performed to provide insight into the bonding interactions in 2 and 6. The complementary occupied-virtual pairs (COVPs) method was selected to visualize charge transfer interactions between the platinum and zinc fragments (Fig. 3).<sup>17</sup> Each COVP corresponds to a donation of electron density from an occupied orbital on one fragment to an acceptor orbital of the other fragment.

Unsurprisingly, the platinum-zinc interaction in **2** is dominated by donation from the  $d_z^2$  orbital of platinum to a vacant zinc p orbital. There is a secondary backbonding interaction from a filled Zn d orbital to an orbital with antibonding platinum-ligand character, which weakens the platinum-ligand bonds of **2** (see ESI† for details). In contrast, complex **6** features donations from both the platinum  $d_z^2$  orbital and the aryl ligand  $\pi$ -system into vacant zinc p orbitals. Backbonding from a zinc d orbital to the platinum-bound aryl ligands also strengthens the zinc-aryl interactions of **6** (see ESI†).



Fig. 3 Selected COVPs for **2** and **6**. Donor orbitals are represented by solid intense colors, and complementary acceptor orbitals have mesh isosurfaces. Hydrogen atoms and <sup>t</sup>Bu are omitted for clarity.

To investigate the different geometric preferences of 2 and 6, energy decomposition analysis (EDA) calculations were performed to compare the apical and aryl-bridged isomers of both complexes. The apical isomer of the phen-supported complex 2 is favored by 7.7 kcal mol<sup>-1</sup>, whereas the aryl-bridged isomer of 6 is preferred to a lesser extent (1.1 kcal mol<sup>-1</sup>). These binding differences can be rationalized based on the different donor properties of nitrogenand phosphorus-based ligands. The phen-supported complex 2 has a greater partial charge on platinum (relative to the dmpe complex 6), which favors apical coordination due to greater electrostatic stabilization from the close Pt–Zn contact. In contrast, the platinum complex is more polarizable when ligated by dmpe *versus* phen, making geometric distortion to adopt the aryl-bridged isomer more favorable for 6 than 2.

To assess the effect of zinc binding on reactivity, a solution of **1** with a 10-fold excess of  $ZnAr_{2}^{F}$  was heated to 60 °C in benzene- $d_{67}$ , resulting in quantitative biaryl reductive elimination within 15 minutes, along with formation of Pt(0) and (phen)ZnAr\_{2}^{F} byproducts (eqn (3)).<sup>18</sup> In the absence of added ZnAr\_{2}^{F}, biaryl formation did not proceed from (phen)PtAr<sub>2</sub> (**1**) over 48 hours at 200 °C, demonstrating that the zinc substituent dramatically accelerates reductive elimination.



Quantitative reductive elimination was also observed upon heating (bpy)PtAr<sub>2</sub>(ZnAr<sup>F</sup><sub>2</sub>) (4) for 15 minutes at 60  $^{\circ}$ C in benzene-*d*<sub>6</sub>.

The thermolysis of (bpy)PtAr<sub>2</sub> (3) in the absence of additives at 150 °C has previously been reported to form *tert*-butylbenzene and a platinum–bipyridine polymer.<sup>19</sup> These products are generated by a roll-over cyclometalation reaction, which proceeds by dissociation and rotation of one pyridyl group, followed by C–H activation at the remote C3 pyridyl position.<sup>20</sup> In the current work, addition of ZnAr<sup>F</sup><sub>2</sub> switches the reaction selectivity to elimination of biaryl, rather than intramolecular metalation of a pyridyl group.

In contrast to the reductive elimination observed from phenand bpy-containing complexes 2 and 4, for  $(dmpe)Pt(\mu-Ar)_2$ - $(ZnAr^F_2)$  (6), aryl exchange occurs between platinum and zinc to produce exclusively  $(dmpe)Pt(C_6F_5)_2$  (7) and  $Zn(4^{-t}Bu-Ph)_2$  at 60 °C (eqn (4)). There is no evidence of an interaction between  $(dmpe)Pt(C_6F_5)_2$  and either  $ZnAr^F_2$  or  $Zn(4^{-t}Bu-Ph)_2$  by <sup>1</sup>H or <sup>19</sup>F NMR spectroscopy. DFT calculations are consistent with this result, and EDA data suggest that electrostatic repulsion between zinc and the electron-deficient aryl groups of 7, along with a reduction of the polarizability of 7, disfavors zinc binding.



We propose that coordination of ZnAr<sup>F</sup><sub>2</sub> favors reductive elimination from 2 and 4 by withdrawing electron density from platinum,<sup>21,22</sup> weakening the platinum–aryl bonds, and increasing steric congestion at the metal center. In the case of the bpy complex 4, zinc binding also prevents roll-over cyclometalation by blocking the intramolecular C–H activation pathway that requires a vacant coordination site.<sup>22</sup> For the dmpe complex 6, there are strong interactions between the zinc center and the platinum-bound aryl groups. If this interaction persists, or even becomes stronger, in the transition state, it could help favor aryl exchange over reductive elimination.

In conclusion, dative, heterobimetallic interactions are observed between platinum(II) diaryl complexes and ZnArF2 in both solution and the solid state. The zinc binding motif is highly sensitive to the nature of the platinum-bound bidentate ligand. The (phen)PtAr2- $(ZnAr_{2}^{F})$  complex 2 features an unsupported Pt–Zn bond, whereas the dmpe analogue 6 features additional interactions between the platinum-bound aryl ligands and zinc. For the dmpe complex, aryl transmetalation between Pt and Zn is exclusively observed, which is reminiscent of the secondary transmetalation pathways that have been proposed for Negishi catalysts.<sup>6</sup> In contrast, the biaryl formation observed from the phen and bpy derivatives 2 and 4 provides a rare example of reductive elimination promoted by a dative, heterobimetallic bond. This result raises the possibility that analogous Pd-Zn interactions may facilitate the reductive elimination step, as well as transmetalation events, of Negishi crosscoupling reactions. Future work is needed to determine whether reductive elimination induced by an organozinc Z-type ligand interaction is a viable mechanism under catalytic conditions.

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## Notes and references

- 1 (a) M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127; (b) A. F. Hill, *Organometallics*, 2006, **25**, 4741; (c) G. Parkin, *Organometallics*, 2006, **25**, 4744.
- 2 A. Amgoune and D. Bourissou, Chem. Commun., 2011, 47, 859.
- 3 (a) A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, Angew. Chem., Int. Ed., 1999, 38, 2759; (b) V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. C. Ulichny and G. Parkin, Inorg. Chem., 2006, 45, 2588; (c) S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, J. Am. Chem. Soc., 2006, 128, 12056; (d) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, J. Am. Chem. Soc., 2008, 130, 16729.
- 4 (a) J. Bauer, H. Braunschweig and R. D. Dewhurst, *Chem. Rev.*, 2012, 112, 4329; (b) M. Kim, T. J. Taylor and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2008, 130, 6332; (c) J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, D. Pascual and T. Lasanta, *Chem. Commun.*, 2011, 47, 6795; (d) T. Lasanta, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and D. Pascual, *Chem. Eur. J.*, 2013, 19, 4754.
- 5 M. Ma, A. Sidiropoulos, L. Ralte, A. Stasch and C. Jones, *Chem. Commun.*, 2013, **49**, 48.
- 6 (a) B. Fuentes, M. García-Melchor, A. Lledós, F. Maseras, J. A. Casares, G. Ujaque and P. Espinet, *Chem. Eur. J.*, 2010, 16, 8596;
  (b) R. Álvarez, A. R. de Lera, J. M. Aurrecoechea and D. Aritz, *Organometallics*, 2007, 26, 2799.
- 7 (a) R. van Asselt and C. J. Elsevier, Organometallics, 1994, 13, 1972;
  (b) J. A. Casares, P. Espinet, B. Fuentes and G. Salas, J. Am. Chem. Soc., 2007, 129, 3508; (c) Q. Liu, Y. Lan, J. Liu, G. Li, Y.-D. Wu and A. Lei, J. Am. Chem. Soc., 2009, 131, 10201; (d) J. delPozo, E. Gioria, J. A. Casares, R. Álvarez and P. Espinet, Organometallics, 2015, 34, 3120.
- 8 A. L. Liberman-Martin, D. S. Levine, W. Liu, R. G. Bergman and T. D. Tilley, *Organometallics*, 2016, **35**, 1064.
- 9 D. A. Walker, T. J. Woodman, D. L. Hughes and M. Bochmann, Organometallics, 2001, 20, 3772.

- 10 As determined from a survey of the Cambridge Crystallographic Database, March, 2016.
- 11 Y. Sun, W. E. Piers and M. Parvez, Can. J. Chem., 1998, 76, 513.
- 12 A. Guerrero, E. Martin, D. L. Hughes, N. Kaltsoyannis and M. Bochmann, *Organometallics*, 2006, **25**, 3311.
- 13 M.-E. Moret and P. Chen, J. Am. Chem. Soc., 2009, 131, 5675.
- 14 B. M. Still, P. G. A. Kumar, J. R. Aldrich-Wright and W. S. Price, Chem. Soc. Rev., 2007, 36, 665.
- 15 Plane defined to include the phosphorus and platinum atoms. If the plane is defined to also include the *ipso* aryl carbons, the zinc is 1.236 Å above the plane.
- 16 (a) K. M. MacKay, R. A. MacKay and W. Henderson, Introduction to Modern Inorganic Chemistry, Melson Thornes Ltd., London, 6th edn, 2002, p. 174; (b) H. C. Clark and C. R. Milne, Can. J. Chem., 1979, 57, 958.
- 17 R. Z. Khaliullin, A. T. Bell and M. Head-Gordon, J. Chem. Phys., 2008, 128, 184112.
- 18 Reactions were performed with a 10-fold excess of ZnAr<sup>F</sup><sub>2</sub> to ensure that zinc binding was maintained at 60 °C. Several coordinating groups were employed in attempts to trap the platinum(0) product. With 1,5-cyclooctadiene or bis(trimethylsilyl]acetylene as trapping agents, decomposition of ZnAr<sup>F</sup><sub>2</sub> and (phen)PtAr<sub>2</sub> occurred, without clean biaryl formation. In the presence of tri-*tert*-butylphosphine, the bis(phosphine) adduct Pt(P<sup>f</sup>Bu<sub>3</sub>)<sub>2</sub> was cleanly formed; however, there was a substantial decrease in the rate of reductive elimination, increasing the reaction time from 15 minutes to 24 hours at 60 °C. This rate decrease is likely due to phosphine-zinc adduct formation, 'Bu<sub>3</sub>P-ZnAr<sup>F</sup><sub>2</sub>, which decreases the concentration of free ZnAr<sup>F</sup><sub>2</sub> available to interact with platinum.
- 19 A. C. Skapski, V. F. Sutcliffe and G. B. Young, J. Chem. Soc., Chem. Commun., 1985, 609.
- 20 B. Butschke and H. Schwarz, Chem. Sci., 2012, 3, 308.
- 21 J. B. Johnson and T. Rovis, Angew. Chem., Int. Ed., 2008, 47, 840.
- 22 (a) T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 1971,
  93, 3350; (b) S. Komiya, Y. Akai, K. Tanaka, T. Yamamoto and A. Yamamoto, Organometallics, 1985, 4, 1130; (c) A. Gollaszewski and J. Schwartz, Organometallics, 1985, 4, 417; (d) R. Sustmann and J. Lau, Chem. Ber., 1986, 119, 2531; (e) R. Sustmann, J. Lau and M. Zipp, Tetrahedron Lett., 1986, 27, 5207; (f) H. Kurosawa, H. Kijimaru, M.-A. Miyoshi, H. Ohnishi and I. Ikeda, J. Mol. Catal., 1992, 74, 481; (g) B. A. Markies, A. J. Canty, J. Boersma and G. van Koten, Organometallics, 1994, 13, 2053; (h) T. Yamamoto, M. Alba and Y. Murakami, Bull. Chem. Soc. Jpn., 2002, 75, 1997; (i) T. Yamamoto, I. Yamaguchi and M. Alba, J. Organomet. Chem., 2003, 671, 179; (j) A. Yahav, I. Goldberg and A. Vigalok, J. Am. Chem. Soc., 2003, 125, 13634; (k) B. V. Popp and S. S. Stahl, J. Am. Chem. Soc., 2006, 128, 2804; (l) M. P. Lanci, M. S. Remy, W. Kaminsky, J. M. Mayer and M. S. Sanford, J. Am. Chem. Soc., 2009, 131, 15618.