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COMMUNICATION

Formation of organorhodium complexes *via* C–H bond activation of 1,3-di(phenylazo)benzene†

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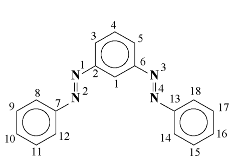
Reaction of a potential NCN-pincer ligand, *viz.* 1,3-di(phenylazo)benzene (L), with [Rh(PPh$_3$)$_3$Cl] affords, *via* a C–H bond activation, an interesting dinuclear Rh(II) complex (1), and with RhCl$_3$·3H$_2$O affords a mononuclear Rh(III) complex (2) containing a catalytically useful Rh-OH$_2$ fragment.

Transition metal mediated C–H bond activation of organic molecules has been of significant current interest, particularly with reference to bringing about catalytic organic transformations,[1] and the present work has originated from our continued interest in this area.[2] Herein, we have chosen a potential NCN-pincer ligand, *viz*. 1,3-di(phenylazo)benzene (**L**), and to interact with it rhodium has been selected as the metal centre. A glance at this ligand **L** indicates that if the N2 and N4 azo-nitrogen atoms coordinate to a metal centre, the central C1–H bond cannot remain indifferent and will be forced to interact with the same metal centre. Thus, an NCN-mode of coordination (**I**) *via* the expected C–H bond activation seems a possibility. It may be relevant to mention here that transition metal complexes of various pincer ligands have been studied extensively,[3] and particularly notable is the contribution of Milstein *et al.*[4] In recent years, NCN pincer complexes, specially those of the platinum group metals, are receiving much attention, mainly because these complexes display remarkable catalytic efficiency in a wide variety of important organic transformations.[5] Though a report on the synthesis of the selected azo-ligand (**L**) is available in the literature,[6] and its spectroscopic properties have also been studied,[7] its coordination chemistry appears to have remained unexplored. We have synthesized this azo-ligand (**L**) by an entirely new method, where 1,3-phenylenediamine was allowed to react with nitrobenzene in the presence of strong alkali to yield **L**. Reaction of 1,3-di(phenylazo)benzene was first carried out with [Rh(PPh$_3$)$_3$Cl], taken as the rhodium starting material, in refluxing toluene under a dinitrogen atmosphere, which afforded an olive-green complex **1** (yield 30%). Structure determination of complex **1** by X-ray crystallography‡ revealed that instead of simple coordination of the ligand **L** to rhodium in the expected fashion (**I**), an unexpected reaction has taken place during formation of this complex (Scheme S1, see ESI).† The structure (Fig. 1) shows that complex **1** is actually a dirhodium species containing two azo-ligands and two chlorides, where each azo-ligand has indeed undergone the anticipated C–H bond activation. However, the observed mode of its coordination is



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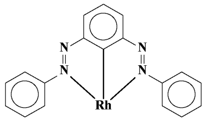

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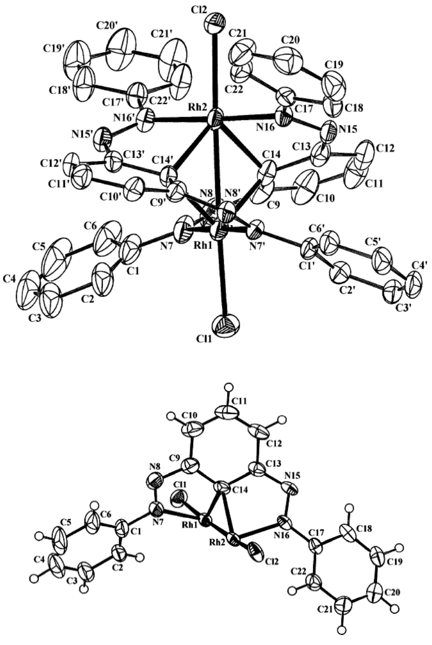

Fig. 1 Molecular structure of complex **1** (hydrogen atoms bound to carbon atoms are omitted for clarity) (top) and partial view of complex **1** (bottom). Selected bond lengths (Å) and angles (°): Rh1–Rh2, 2.6789(5); Rh1–C14, 2.065(4); Rh2–C14, 2.080(3); N7–N8, 1.279(5); N15–N16, 1.279(4); Rh1–C14–Rh2, 80.52(12); Rh1–C14′–Rh2, 79.95(11).

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interestingly different than that expected (**I**). The two terminal nitrogen atoms are bonded to two different rhodium centres, and the central carbon is linked with both of these metal centres. Thus the azo-ligand is acting as a NCN-donor as well as a bridging ligand (see Fig. 1 bottom), and the Rh–C–Rh bridge is describable in terms of a three-centred two-electron bond formation by the central carbon. Such a bridging mode of phenyl-carbon, involving several 3d, 4d and 5d metal centres, is well precedent in the literature (Ref. R, see ESI).† However, we could locate only one example involving rhodium, that too as one of the two metal centres, the other metal centre being titanium.[8] Thus, the observed coordination mode of ligand **L** in complex **1**, where an anionic phenyl-carbon is bridging two rhodium centres, seems to be unprecedented. The structure also reveals the existence of a metal-metal bond between the two rhodium centres. The Rh–Rh distance in this complex is found to be significantly longer than the commonly observed Rh(II)–Rh(II) distances.[9] The sixth coordination positions on the two metal centres are satisfied with chloride ions. The Rh–C, Rh–N, Rh–Cl bond distances are all quite normal, and so are the bond distances within the coordinated azo-ligands. Though formal oxidation state of each rhodium in complex **1** is +2 (d^7), the complex is diamagnetic as a whole, and the observed diamagnetism is attributable to strong antiferromagnetic interaction between the two proximal metal centres. It is relevant to mention here that dimeric complexes of rhodium(II) have significant importance in various catalytic organic transformations.[10]

The unexpected binding mode of the azo-ligand (**L**) observed in complex **1** seems to have resulted primarily from the initial oxidative insertion of rhodium into the central C1–H bond of the azo-ligand, though the entire mechanism of the reaction remains unresolved. This hypothesis, if it holds, indicates that if the reaction of the same azo-ligand is carried out with a rhodium centre that is already in its trivalent state, probably the expected NCN-mode of binding (**I**) can be achieved. In order to verify this hypothesis, reaction of the azo-ligand (**L**) was carried out with a rhodium(III) starting material, *viz*. $RhCl_3{\cdot}3H_2O$, in refluxing ethanol. This reaction yielded an orange complex (complex **2**) (yield 60%) and its structure determination by X-ray crystallography‡ (Fig. 2) shows that the azo-ligand is indeed coordinated to the metal centre in the expected NCN-mode (**I**), along with two chlorides and a water molecule.

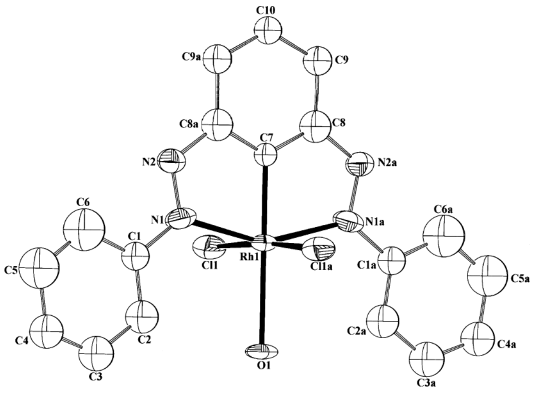

Fig. 2 Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°): Rh1–Cl1, 2.319(10); Rh1–N1, 2.13(3); Rh1–C7, 1.92(4); Rh1–O1, 2.36(2); N1–N2, 1.28(3); Cl1–Rh1–Cl1a, 174.4(3); N1–Rh1–N1a, 153.1(9); C7–Rh1–O1, 179.98(4); N1–Rh1–C7, 76.6(7).

With an intention of examining the possible utilization of the Rh-OH_2 fragment in complex **2** towards displacement by neutral monodentate ligands leading to formation of new complexes, complex **2** was first treated with acetonitrile at room temperature, which yielded the expected acetonitrile-coordinated complex (complex **3**). The structure of complex **3** (Fig. S1, ESI)† is found to be mostly similar to that of complex **2**. On our attempt to isolate an analogous benzonitrile-coordinated complex by treatment of complex **2** with benzonitrile, an interesting complex **4** was obtained. Structure determination has revealed that instead of coordinated benzonitrile, complex **4** contains a coordinated benzamide (Fig. 3). We believe that formation of the benzamide-coordinated complex **4** proceeds *via* formation of the targeted benzonitrile-coordinated complex as an active intermediate **5** (see Scheme S2, ESI).† The long reaction time needed for removal of solvent (benzonitrile) in the isolation of **4** is thought to be adequate enough for intermediate **5** to undergo interaction with moisture present in the solvent and afford **4** as the end product. In order to trap the intermediate **5**, by reducing its exposure time to water, a similar reaction was carried out using very little benzonitrile diluted in acetone (main solvent). This strategy indeed worked nicely allowing isolation of complex **5** followed by its structural characterization (Fig. 4). Isolation of both the benzamide complex **4** as well as its benzonitrile precursor **5** testifies the feasible hydrolysis of rhodium-bound benzonitrile to benzamide. It is relevant to mention here that metal-mediated, as well as metal-catalysed, transformation of nitrile to amide is of considerable current interest.[11] The potential of the aquo complex **2** as a

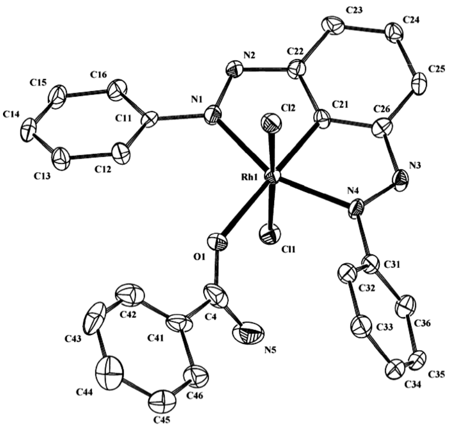

Fig. 3 Molecular structure of complex **4**.

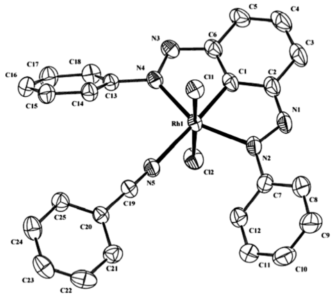

Fig. 4 Molecular structure of complex **5**.

mediator for useful transformations, and also as a synthon towards preparation of new complexes is currently under exploration.

The present study shows that 1,3-di(phenylazo)benzene (**L**) can undergo facile rhodium-assisted C1–H bond activation and, depending on the nature of rhodium starting compound, binds to the metal centre either as an NCN-pincer ligand (**I**), or as an NCN-donor with the central carbon bridging two different rhodium centres (see Fig. 1 bottom). While catalytic potential of the dirhodium complex **1** is yet to be explored, this study already demonstrated the promise of the aquo complex **2** as a synthon as well as a mediator for nitrile hydrolysis.

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Notes and references

‡ Selected crystallographic data: for complex **1**: $C_{36}H_{26}Cl_2N_8Rh_2\cdot 1.5CH_3CN$, M_r = 908.95, monoclinic, space group $P2_1/c$, a = 15.3407(15) Å, b = 13.3922(13) Å, c = 19.0850(19) Å, β = 103.245(2)°, V = 3816.6(6) Å^3, Z = 4, μ = 1.047 mm^{-1}, T = 150 K, λ = 0.71073 Å, R_1 = 0.0363, wR_2 = 0.0819, GOF = 0.84. For complex **2**: $C_{18}H_{13}Cl_2N_4ORh$, M_r = 475.13, monoclinic, space group $C2/c$, a = 19.488(5) Å, b = 12.271(2) Å, c = 7.9630(16) Å, β = 106.575(16), V = 1825.1(7) Å^3, Z = 4, μ = 1.243, T = 273 K, λ = 0.71073 Å, R_1 = 0.1050, wR_2 = 0.3086, GOF = 1.31.

1 (*a*) O. Daugulis, H. Q. Do and D. Shabashov, *Acc. Chem. Res.*, 2009, **42**, 1074; (*b*) N. A. Foley, J. P. Lee, Z. Ke, T. B. Gunnoe and T. R. Cundari, *Acc. Chem. Res.*, 2009, **42**, 585; (*c*) B. H. Lipshutz and Y. Yamamoto, *Chem. Rev.*, 2008, **108**, 2793; (*d*) J. C. Lewis, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2008, **41**, 1013; (*e*) Y. J. Park, J. W. Park and C. H. Jun, *Acc. Chem. Res.*, 2008, **41**, 222; (*f*) W. Leis, H. A. Mayer and W. C. Kaska, *Coord. Chem. Rev.*, 2008, **252**, 1787; (*g*) M. Lersch and M. Tilset, *Chem. Rev.*, 2005, **105**, 2471; (*h*) E. Carmona, M. Paneque, L. L. Santos and V. Salazar, *Coord. Chem. Rev.*, 2005, **249**, 1729.

2 (*a*) S. Basu, R. Acharyya, F. Basuli, S. M. Peng, G. H. Lee, G. Mostafa and S. Bhattacharya, *Inorg. Chim. Acta*, 2010, **363** in press; (*b*) S. Nag, J. A. K. Howard, H. A. Sparkes and S. Bhattacharya, *J. Organomet. Chem.*, 2010, **695**, 2068; (*c*) S. Baksi, D. K. Seth, H. Tadesse, A. J. Blake and S. Bhattacharya, *J. Organomet. Chem.*, 2010, **695**, 1111; (*d*) R. Acharyya, S. M. Peng, G. H. Lee and S. Bhattacharya, *J. Chem. Sci.*, 2009, **121**, 387; (*e*) S. Dutta, F. Basuli, A. Castineiras, S. M. Peng, G. H. Lee and S. Bhattacharya, *Eur. J. Inorg. Chem.*, 2008, 4538.

3 (*a*) D. L. M. Suess and J. C. Peters, *Chem. Commun.*, 2010, **46**, 6554; (*b*) K. Kutlescha, T. Irrgang and R. Kempe, *New J. Chem.*, 2010, **34**, 1954; (*c*) Z. Huang, J. Zhuo and J. F. Hartwig, *J. Am. Chem. Soc.*, 2010, **132**, 11458; (*d*) W. Baratta, F. Benedetti, A. Del Zolto, L. Fanfoni, F. Felluga, S. Magnolia, E. Putignano and P. Rigo, *Organometallics*, 2010, **29**, 3563; (*e*) A. E. W. Ledger, A. Moreno, C. E. Ellul, M. F. Mohan, P. S. Pregosin, M. K. Wittlesey and J. M. J. Williams, *Inorg. Chem.*, 2010, **49**, 7244; (*f*) J. Koller and R. G. Bergman, *Organometallics*, 2010, **29**, 3350; (*g*) A. R. Chianese, A. Mo, N. L. Lampland, R. L. Swartz and P. T. Bremer, *Organometallics*, 2010, **29**, 3019; (*h*) J. Kuwabara, G. Mnezawa, K. Okamoto and T. Kanbara, *Dalton Trans.*, 2010, **39**, 6255; (*i*) E. Sola, A. Garcia-Camprubi, J. L. Andres, M. Martin and P. Plou, *J. Am. Chem. Soc.*, 2010, **132**, 9111; (*j*) Y. Zhang, X. Li and S. H. Hong, *Adv. Synth. Catal.*, 2010, **352**, 1779.

4 (*a*) B. Ganaprakasam, J. Zhang and D. Milstein, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 1468; (*b*) M. Feller, E. Ben-Ari, M. A. Iron, Y. Diskin–Posner, G. Leitus, L. J. W. Shimon, L. Konstantinovski and D. Milstein, *Inorg. Chem.*, 2010, **49**, 1615; (*c*) M. Montg, I. Efremenko, R. Cohen, L. J. W. Shimon, G. Leitus, Y. Diskin-Posner, Y. Ben-David, H. Salem, J. M. L. Martin and D. Milstein, *Chem.–Eur. J.*, 2010, **16**, 328; (*d*) M. A. Iron, E. Ben-Ari, R. Cohen and D. Milstein, *Dalton Trans.*, 2009, 9433; (*e*) H. Salem, L. J. W. Shmon, Y. Diskin-Posner, G. Leitus, Y. Ben-David and D. Milstein, *Organometallics*, 2009, **28**, 4791.

5 (*a*) S. Das Adhikary, T. Samanta, G. Roymahapatra, S. Giri, P. K. Chattaraj and J. Dinda, *New J. Chem.*, 2010, **34**, 1974; (*b*) B. Enk, D. Eisenstecken, H. Kopacka, K. Wurst, T. Muller, F. Penvy, R. F. Winter and B. Bildstein, *Organometallics*, 2010, **29**, 3169; (*c*) J. Al Thagfi, S. Dastgir, A. J. Lough and G. G. Lovie, *Organometallics*, 2010, **29**, 3133; (*d*) P. Simon, F. De Proft, R. Jambor, A. Ruzicka and L. Dostal, *Angew. Chem., Int. Ed.*, 2010, **49**, 5468; (*e*) B. M. J. M. Suijkerbuijk, D. J. Schamhart, H. Kooijman, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, *Dalton Trans.*, 2010, 6216; (*f*) J. Martincova, R. Dostalova, L. Dostal, A. Ruzicka and R. Jambor, *Organometallics*, 2009, **28**, 4823; (*g*) M. C. Jahnke, T. Pape and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2009, 1960; (*h*) S. Bonnet, M. Lutz, A. L. Speck, G. van Koten and R. J. M. Klein Gebbink, *Organometallics*, 2008, **27**, 159; (*i*) W. Gao and D. Cui, *J. Am. Chem. Soc.*, 2008, **130**, 4984; (*j*) M. Gagliardo, D. J. M. Snelders, P. A. Chase, R. J. M. Klein Gebbink, G. P. M. van Klink and G. van Koten, *Angew. Chem., Int. Ed.*, 2007, **46**, 8558.

6 P. von Ruggil and W. Wust, *Helv. Chim. Acta*, 1945, **28**, 781.

7 Y. Ito, H. Ito and T. Matsuura, *Tetrahedron Lett.*, 1988, **29**, 563.

8 J. W. Park, L. M. Henling, P. Schaefer and R. H. Grubbs, *Organometallics*, 1991, **10**, 171.

9 (*a*) F. A. Cotton, J-Y. Jin, Z. Li, C. Y. Liu and C. A. Murillo, *Dalton Trans.*, 2007, 2328; (*b*) F. A. Cotton, C. A. Murillo, S.-E. Stiriba, X. Wang and R. Yu, *Inorg. Chem.*, 2005, **44**, 8223; (*c*) F. A. Cotton, C. A. Murillo, X. Wang and R. Yu, *Inorg. Chem.*, 2004, **43**, 8394; (*d*) F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, M. Schmitz and P. J. Stang, *Inorg. Chem.*, 2002, **41**, 2903; (*e*) F. A. Cotton, E. A. Hillard, C. Y. Liu, C. A. Murillo, W. Wang and X. Wang, *Inorg. Chim. Acta*, 2002, **337**, 233; (*f*) F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Angew. Chem., Int. Ed.*, 2000, **39**, 2362; (*g*) H. Hückstädt, C. Bruhn and H. Homborg, *J. Porphyrins Phthalocyanines*, 1997, **1**, 367; (*h*) G. Bruno, G. De Munno, G. Tresoldi, S. Lo Schiavo and P. Piraino, *Inorg. Chem.*, 1992, **31**, 1538; (*i*) J. Halpern, E. Kimura, J. Molin-Case and C. S. Wong, *J. Chem. Soc., Dalton Trans*, 1971, 1207.

10 J. Hansen and H. M. L. Davies, *Coord. Chem. Rev.*, 2008, **252**, 545.

11 V. Y. Kukushkin and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2005, **358**, 21.