ChemComm

COMMUNICATION

View Article Online
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Classical and non-classical redox reactions of Pd(II) complexes containing redox-active ligands†

Cite this: *Chem. Commun.*, 2014, **50**, 11676

Received 26th June 2014,
Accepted 6th August 2014

DOI: 10.1039/c4cc04863f

www.rsc.org/chemcomm

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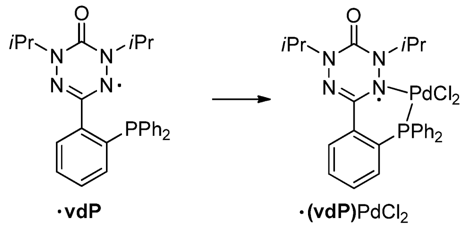
Reactivity studies of a Pd(II)–verdazyl complex reveal novel ligand-centred reduction processes which trigger pseudo-reductive elimination at Pd. Reaction of the complex with water induces a ligand-centred redox disproportionation. The reduced verdazyl ligands can also be reversibly protonated.

The recent resurgence of interest in redox-active ligand (RAL) complexes stems in part from the possibility of discovering and developing new stoichiometric and catalytic reactions.[1] A major motivation for exploring this paradigm is to enable multi-electron chemistry at base metals.[2] Accordingly, much of the activity in this field has focused on RAL complexes of first row transition metals; studies involving heavier metals are far less common.[3]

Palladium complexes are employed as catalysts in a huge range of reactions. Some of these reactions incorporate auxiliary redox reagents, *e.g.*, copper for the Wacker oxidation and Sonogashira reaction. Benzoquinone[4] and TEMPO[5] have also been explored in this context, and Pd–benzoquinone or Pd–TEMPO complexes may well be (labile) intermediates in the catalytic reactions they enable. These and other studies[6] are suggestive of a potentially rich chemistry associated with Pd–RAL complexes, but this concept is an under-explored one. We have recently reported on the *electrochemical* properties of Pd complexes containing verdazyls,[7] a new class of RAL.[8,9] Herein we present preliminary investigations of the *chemical* redox properties of related complexes based on a new phosphine/verdazyl ligand. These studies constitute the first explorations of chemical reactivity *of any type* of a metal complex of a verdazyl radical, and herein we demonstrate that ligand-centered redox processes trigger unexpected and unique metal-centered reactivity.

The phosphine verdazyl ligand •**vdP** was prepared using standard procedures for the synthesis of 1,5-diisopropyl-6-oxoverdazyl radicals (see ESI†).[10,11] Reaction of •**vdP** with $PdCl_2(MeCN)_2$ afforded the complex (•**vdP**)$PdCl_2$, analogously to our previously reported syntheses of related verdazyl–$PdCl_2$ complexes (Scheme 1).[7,12] The electronic structure of the radical ligand, as probed by EPR and UV-vis spectroscopy, is entirely representative of *N*,*N*′-diisopropyl-6-oxoverdazyl derivatives; a the EPR hyperfine coupling to the phosphorus nucleus (9.3 G) indicates only a very small amount of spin density at P. Analogously, the electronic spectrum (Fig. S6, ESI†) and EPR spectrum (Fig. S9, ESI†) of (•**vdP**)$PdCl_2$ are qualitatively consistent with the corresponding data for other verdazyl–palladium complexes,[12] the spin is largely confined to the tetrazine ring of the verdazyl.

The molecular structures of radical •**vdP** and Pd complex (•**vdP**)$PdCl_2$ are shown in Fig. 1. The structural metrics associated with the free ligand are normal for 6-oxoverdazyls.[11,13] The changes in tetrazine ring bond lengths upon coordination to Pd are minor, consistent with related verdazyl–Pd complexes.[12] The larger chelate ring size of the •**vdP** ligand forces a non-coplanar arrangement of the palladium ion's square plane with that of the NCCCP chelate ring. The two Pd–Cl bond lengths are markedly different: the Pd–Cl bond *trans* to the phosphine is 2.38 Å whereas the Pd–Cl *trans* to N is only 2.27 Å. This observation can be ascribed to the *trans* influence of the phosphine ligand.



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis and characterization details. CCDC 997842–997845. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc04863f

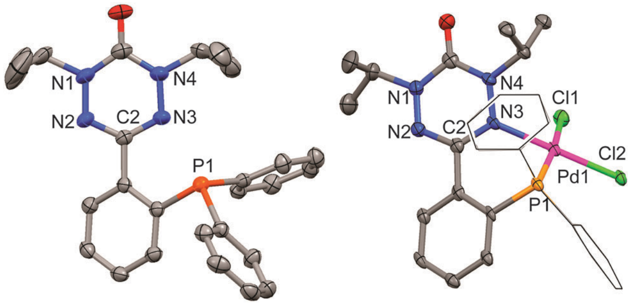

Fig. 1 Structures of •**vdP** (left) and (•**vdP**)PdCl$_2$ (right). Thermal ellipsoids represented at 50%. Hydrogen atoms removed for clarity. Selected bond lengths for •**vdP** (Å): N1–N2 1.360(2), N3–N4 1.368(2), N2–C2 1.331(3), N3–C21.326(3). Selected bond lengths for (•**vdP**)PdCl$_2$ (Å): N1–N2 1.350(6), N3–N4 1.372(6), N2–C2 1.318(7), N3–C2 1.341(7), N3–Pd1 2.065(4), P1–Pd1 2.2243(16), Cl1–Pd1 2.3822(17), Cl2–Pd1 2.2678(16).

The electrochemical properties of (•**vdP**)PdCl$_2$ differ from those of related palladium complexes containing verdazyl ligands.[7] Whereas the latter generally possess reversible one-electron reduction processes, reduction of the former is at best quasi-reversible (Fig. S7, ESI†). This result was somewhat surprising in light of the qualitative similarities of the electronic structures of the radical palladium complexes (see above). In order to understand possible reasons for these differences in electrochemistry, we explored chemical reductions of (•**vdP**)PdCl$_2$. Reaction with decamethylferrocene leads not to the anionic species [(**vdP**)PdCl$_2$] – but instead to an air-stable, binuclear species (**vdP**)$_2$Pd$_2$Cl$_2$ whose structure is shown in Fig. 2 (see also eqn (1)). The structure consists of two square planar Pd ions linked by bridging chlorides. The (μ-Cl)$_2$Pd$_2$ core is a fairly common structural motif in Pd(II) chemistry but is normally accessed by either chloride abstraction from (LL)PdCl$_2$ (where LL is a neutral bidentate ligand)[14] or direct synthesis from a monoanionic ligand LX and a PdCl$_2$ source;[15] in the present system it is the conversion of an LL type ligand (•**vdP**) to an LX ligand *via* ligand reduction that leads to binuclear complex formation. The N–N bonds in the tetrazine ring are significantly longer than in the radical complex (•**vdP**)PdCl$_2$, indicating electron addition has occurred to the (π*, N–N antibonding) ligand SOMO[8] and the Pd ions remain in their +2 oxidation state. The reduction is fully reversible: treatment of (**vdP**)$_2$Pd$_2$Cl$_2$ with PhICl$_2$ regenerates the monopalladium radical complex (eqn (2)). The chloride loss/addition accompanying reduction/oxidation renders these processes non-classical versions of reductive elimination/oxidative addition, in which the ligand has been reduced/oxidized concomitant with ligand loss/addition at the metal. Such processes have been noted in RAL complexes of other metals[16] but not for palladium.

$$2(^{\bullet}\mathbf{vdP})\mathrm{PdCl_2} + 2\mathrm{Fc}^{*} \rightarrow (\mathbf{vdP})_2\mathrm{Pd_2Cl_2} + 2\mathrm{Fc}^{*} + \mathrm{Cl}^{-} \qquad (1)$$

$$(\mathbf{vdP})_2\mathrm{Pd_2Cl_2} + \mathrm{PhICl_2} \rightarrow 2(^{\bullet}\mathbf{vdP})\mathrm{PdCl_2} + \mathrm{PhI} \qquad (2)$$

Reaction of (**vdP**)$_2$Pd$_2$Cl$_2$ with HCl leads to ligand protonation and generation of a mononuclear Pd complex (**H-vdP**)PdCl$_2$ containing the protonated (reduced) verdazyl (also known as the so-called "leuco" verdazyl[17]). Deprotonation *via* addition of base regenerates the binuclear complex (**vdP**)$_2$Pd$_2$Cl$_2$. The structure of the leuco complex is shown in Fig. 3. The tetrazine bond metrics are consistent with a fully reduced and protonated (at N$_2$) ring. In stark contrast to free leuco verdazyls which are rapidly oxidized to the corresponding radical, this leuco Pd complex is air stable; more powerful oxidants (PhICl$_2$) react with the leuco complex *via* ligand oxidation to give (•**vdP**)PdCl$_2$. The (leuco) verdazyl ligand stability to (de)protonation also contrasts the behaviour of Pd π-complexes of benzoquinone (BQ), in which protonation of formally Pd(0)–BQ induces intramolecular electron transfer, leading to Pd(II) and free 1,4-hydroquinone.[18]

The radical complex (•**vdP**)PdCl$_2$ is unexpectedly – and in contrast to previously reported verdazyl–Pd complexes – very moisture-sensitive; reaction with water produces the reduced binuclear complex described above and one equivalent of uncoordinated radical species in which the phosphine has been converted to its phosphine oxide •**vdP**═O (eqn (3)). The source of the oxygen in the latter was confirmed to be water from H$_2$^{18}O studies (see ESI†). The HCl by-product can be scavenged by added base (NEt$_3$), and a (presumed) equivalent of PdCl$_2$ is also generated. This reaction can also be conducted

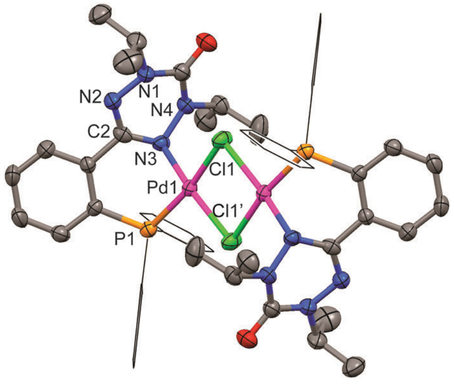

Fig. 2 Structure of (**vdP**)$_2$Pd$_2$Cl$_2$. Thermal ellipsoids represented at 50%. Hydrogen atoms removed for clarity. Selected bond lengths (Å): N1–N2 1.373(4), N3–N4 1.421(4), N2–C2 1.300(5), N3–C2 1.354(5), N3–Pd1 2.054(3), P1–Pd1 2.2273(10), Cl1–Pd1 2.4048(10), Cl1′–Pd1 2.4354(10).

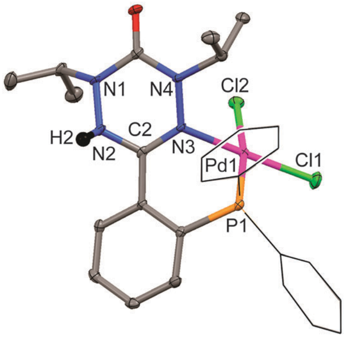

Fig. 3 Structure of (H–**vdP**)PdCl$_2$. Thermal ellipsoids represented at 50%. Hydrogen atoms except H2 removed for clarity. Selected bond lengths (Å): N1–N2 1.417(3), N3–N4 1.417(3), N2–C2 1.368(3), N3–C2 1.292(3), N3–Pd 2.0562(19), P1–Pd 2.2192(6), Cl1–Pd1 2.2791(6), Cl2–Pd1 2.3586(6).

starting from the ${}^{\bullet}\mathbf{vdP}$ ligand, $\mathrm{Pd(MeCN)_2Cl_2}$ and water, which generates the same products without the "extra" $\mathrm{PdCl_2}$ (eqn (4)). In these reactions, water induces a redox disproportionation reaction involving the (coordinated) ${}^{\bullet}\mathbf{vdP}$ ligand: two equivalents are reduced by one electron to their corresponding anions, and the oxidation process involves conversion of the phosphine moiety to its phosphine oxide. This reaction bears some resemblance to the well-known reaction of $\mathrm{Pd(OAc)_2}$ with triphenylphosphine and water, in which Pd(II) is reduced to give a Pd(0) phosphine complex and free phosphine oxide is the oxidation by product.[19]

$$3({}^{\bullet}\mathbf{vdP})\mathrm{PdCl_2} + \mathrm{H_2O} \rightarrow (\mathbf{vdP})_2\mathrm{Pd_2Cl_2} + {}^{\bullet}\mathbf{vdP}{=}\mathrm{O} + 2\mathrm{HCl} + \text{“}\mathrm{PdCl_2}\text{”} \tag{3}$$

$$3{}^{\bullet}\mathbf{vdP} + 2(\mathrm{MeCN})_2\mathrm{PdCl_2} + \mathrm{H_2O} \rightarrow (\mathbf{vdP})_2\mathrm{Pd_2Cl_2} + {}^{\bullet}\mathbf{vdP}{=}\mathrm{O} + 2\mathrm{HCl} + 4\mathrm{MeCN} \tag{4}$$

In summary, we have presented fundamental reactivity studies of a Pd complex containing a redox-active ligand. These studies constitute the very first investigations of the chemical reactivity of metal–verdazyl complexes. Ligand-centred redox activity appears to subsume possible Pd-based reduction, leading to the observation of non-classical versions of oxidative addition and reductive eliminations endemic to palladium. Perhaps most interestingly, the reduced verdazyl ligand can be protonated, a rare finding among redox-active ligand complexes and one which suggests the possibility of multi-channel ligand involvement ("cooperativity") in RAL complex chemistry.[20] As such the fundamental reactivity studies presented herein lay the foundation for possible exploitation of metal–verdazyl complexes in new stoichiometric or catalytic transformations.

Notes and references

1 (*a*) V. Lyaskovskyy and B. de Bruin, *ACS Catal.*, 2012, **2**, 270–279; (*b*) V. K. K. Praneeth, M. R. Ringenberg and T. R. Ward, *Angew. Chem., Int. Ed.*, 2012, **51**, 10228–10234; (*c*) O. R. Luca and R. H. Crabtree, *Chem. Soc. Rev.*, 2013, **42**, 1440–1459.

2 P. J. Chirik and K. Wieghardt, *Science*, 2010, **327**, 794–795.

3 (*a*) M. Konigsmann, N. Donati, D. Stein, H. Schonberg, J. Harmer, A. Sreekanth and H. Grutzmacher, *Angew. Chem., Int. Ed.*, 2007, **46**, 3567–3570; (*b*) M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2008, **130**, 788–789; (*c*) C. A. Lippert, S. A. Arnstein, C. D. Sherrill and J. D. Soper, *J. Am. Chem. Soc.*, 2010, **132**, 3879–3892; (*d*) S. J. Kraft, U. J. Williams, S. R. Daly, E. J. Schelter, S. A. Kozimor, K. S. Boland, J. M. Kikkawa, W. P. Forrest, C. N. Christensen, D. E. Schwarz, P. E. Fanwick, D. L. Clark, S. D. Conradson and S. C. Bart, *Inorg. Chem.*, 2011, **50**, 9838–9848.

4 (*a*) J. E. Backvall, A. K. Awasthi and Z. D. Renko, *J. Am. Chem. Soc.*, 1987, **109**, 4750–4752; (*b*) J. E. Backvall, R. B. Hopkins, H. Grennberg, M. M. Mader and A. K. Awasthi, *J. Am. Chem. Soc.*, 1990, **112**, 5160–5166; (*c*) K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 9651–9653; (*d*) N. Decharin and S. S. Stahl, *J. Am. Chem. Soc.*, 2011, **133**, 5732–5735.

5 (*a*) S. Kirchberg, T. Vogler and A. Studer, *Synlett*, 2008, 2841–2845; (*b*) S. Kirchberg, R. Frohlich and A. Studer, *Angew. Chem., Int. Ed.*, 2009, **48**, 4235–4238.

6 (*a*) S. B. Sembiring, S. B. Colbran and D. C. Craig, *Inorg. Chem.*, 1995, **34**, 761–762; (*b*) S. B. Sembiring, S. B. Colbran, D. C. Craig and M. L. Scudder, *Dalton Trans.*, 1995, 3731–3741; (*c*) A. G. Tennyson, V. M. Lynch and C. W. Bielawski, *J. Am. Chem. Soc.*, 2010, **132**, 9420–9429.

7 C. W. Johnston, S. D. J. McKinnon, B. O. Patrick and R. G. Hicks, *Dalton Trans.*, 2013, **42**, 16829–16836.

8 (*a*) S. D. J. McKinnon, B. O. Patrick, A. B. P. Lever and R. G. Hicks, *Chem. Commun.*, 2010, **46**, 773–775; (*b*) S. D. J. McKinnon, B. O. Patrick, A. B. P. Lever and R. G. Hicks, *J. Am. Chem. Soc.*, 2011, **133**, 13587–13603.

9 K. J. Anderson, J. B. Gilroy, B. O. Patrick, R. McDonald, M. J. Ferguson and R. G. Hicks, *Inorg. Chim. Acta*, 2011, **374**, 480–488.

10 E. C. Pare, D. J. R. Brook, A. Brieger, M. Badik and M. Schinke, *Org. Biomol. Chem.*, 2005, **3**, 4258–4261.

11 J. B. Gilroy, B. D. Koivisto, R. McDonald, M. J. Ferguson and R. G. Hicks, *J. Mater. Chem.*, 2006, **16**, 2618–2624.

12 S. D. J. McKinnon, J. B. Gilroy, R. McDonald, B. O. Patrick and R. G. Hicks, *J. Mater. Chem.*, 2011, **21**, 1523–1530.

13 J. B. Gilroy, S. D. J. McKinnon, P. Kennepohl, M. S. Zsombor, M. J. Ferguson, L. K. Thompson and R. G. Hicks, *J. Org. Chem.*, 2007, **72**, 8062–8069.

14 (*a*) R. C. Smith and J. D. Protasiewicz, *Organometallics*, 2004, **23**, 4215–4222; (*b*) C. X. Li, R. Pattacini, R. Graff and P. Braunstein, *Angew. Chem., Int. Ed.*, 2008, **47**, 6856–6859; (*c*) A. R. Shaffer and J. A. R. Schmidt, *Organometallics*, 2009, **28**, 2494–2504; (*d*) C. L. Chen and R. F. Jordan, *J. Am. Chem. Soc.*, 2010, **132**, 10254–10255.

15 (*a*) M. Akita, T. Miyaji, N. Muroga, C. Mock-Knoblauch, W. Adam, S. Hikichi and Y. Moro-oka, *Inorg. Chem.*, 2000, **39**, 2096–2102; (*b*) J. L. Pratihar, B. Shee, P. Pattanayak, D. Patra, A. Bhattacharyya, V. G. Puranik, C. H. Hung and S. Chattopadhyay, *Eur. J. Inorg. Chem.*, 2007, 4272–4281; (*c*) A. Hadzovic and D. Song, *Organometallics*, 2008, **27**, 1290–1298.

16 (*a*) K. J. Blackmore, J. W. Ziller and A. F. Heyduk, *Inorg. Chem.*, 2005, **44**, 5559–5561; (*b*) M. R. Haneline and A. F. Heyduk, *J. Am. Chem. Soc.*, 2006, **128**, 8410–8411; (*c*) C. Stanciu, M. E. Jones, P. E. Fanwick and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2007, **129**, 12400–12401; (*d*) A. L. Smith, K. I. Hardcastle and J. D. Soper, *J. Am. Chem. Soc.*, 2010, **132**, 14358–14360.

17 R. G. Hicks, in *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, ed. R. G. Hicks, Wiley, NY, 2010, pp. 245–280.

18 H. Grennberg, A. Gogoll and J. E. Backvall, *Organometallics*, 1993, **12**, 1790–1793.

19 (*a*) C. Amatore, A. Jutand and M. A. Mbarki, *Organometallics*, 1992, **11**, 3009–3013; (*b*) F. Ozawa, A. Kubo and T. Hayashi, *Chem. Lett.*, 1992, 2177–2180; (*c*) C. Amatore, E. Carre, A. Jutand and M. A. Mbarki, *Organometallics*, 1995, **14**, 1818–1826.

20 (*a*) H. Grutzmacher, *Angew. Chem., Int. Ed.*, 2008, **47**, 1814–1818; (*b*) R. H. Crabtree, *New J. Chem.*, 2011, **35**, 18–23.