Activation of H_2 by a highly distorted Rh^{II} complex with a new C_3-symmetric tripodal tetraphosphine ligand†

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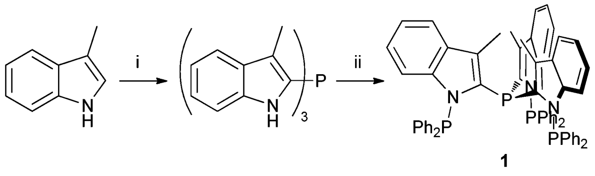
Facile oxidation of a sterically encumbered Rh^{I} complex generates a stable Rh^{II} metalloradical species; the latter is able to activate H_2 under formation of the corresponding Rh^{III} complex.

Activation of dihydrogen provides a basic and often crucial elementary step in many important transition-metal catalyzed processes, such as hydrogenation and hydroformylation. This activation is most commonly achieved by oxidative addition within the coordination sphere of a transition metal.[1,2] Alternatively, dihydrogen activation may be achieved by heterolytic cleavage of the H–H bond, *e.g.* aided by a strong base as observed in some Ru hydrogenation catalysts.[3] However, activation of dihydrogen by metal-centered radical complexes has only been scarcely explored to date. Such a reaction would be the starting point for hydrogen atom-transfer (HAT) reactions,[4] using molecular hydrogen as the hydrogen atom donor. The latter type of activation requires a metal–ligand combination, which is able to stabilize reactive open-shell metalloradical intermediates. Confined metal geometries are therefore a prerequisite for selective transformations of this kind.[5] Multipodal and in particular C_3-symmetric tripodal skeletons are attractive frameworks for this purpose.[6,7] The main advantage of these ligands is the effective shielding of the metal center, preventing side reactions that could lead to decomposition or loss of selectivity. Secondly, a higher number of coordinating atoms is advantageous in stabilizing higher oxidation states, by efficient donation of electron-density to the transition metal. In particular tetradentate architectures that feature an all-phosphorus coordination sphere would be ideally suited.[8] Herein we report a new, sterically demanding, C_3-symmetric tripodal tetraphosphine ligand **1** based on 3-methylindole as a building block, its Rh-complex **2** as well as unusual subsequent reactivity of the related paramagnetic species [**2**]PF_6 to activate dihydrogen.

The 3-methylindole scaffold seemed a very suitable building block for a tripodal tetraphosphine ligand, since it is very rigid and thus minimizes conformational ambiguity.[9] Moreover, we developed the necessary synthetic methods to introduce phosphorus substituents on the nitrogen as well as on the C2 position of the indole ring previously in the synthesis of chiral hybrid bidentate ligand IndolPhos and close analogues thereof.[10]

We set out to construct PP_3 ligand **1**, which features a central bridgehead phosphorus atom that is connected to three 3-methylindole fragments at the 2-position (Scheme 1). Capping of PCl_3 with 3 equiv. 2-lithioindole, employing *in situ* protection of the nitrogen using CO_2,[11] followed by phosphorylation of the nitrogen atom gave the desired product **1** in good yield.† The pivotal P-atom showed up as a quartet at δ −75.1 ppm, whilst a doublet was observed at δ 37.3 ppm for the peripheral PPh_2 units, with a large coupling constant J_{P-P} of 159 Hz. These large coupling constants indicate a high degree of rigidity and suggest a conformation with an overall C_3-symmetry in solution.

In addition to stringent requirements for the ligand, we believe that also the choice of the transition metal is pivotal in order to achieve stable metalloradicals for hydrogen activation. Rhodium was selected as the privileged metal as it is known to form stable odd-electron species, using tetradentate nitrogen donor ligands.[12,13] Complexation with Rh was achieved by reaction of stoichiometric amounts of the ligand with $[Rh(cod)(\mu\text{-}Cl)]_2$.† The ^{31}P NMR spectrum for **2** consists of a doublet-of-quartets at δ 43.5 ppm ($\Delta\delta$ is 80.8 ppm) for the central P-atom, and the peripheral phosphorus-units are present as a doublet-of-doublets at δ 74.0 ppm, suggesting a C_3-symmetric trigonal bipyramidal geometry. The latter was corroborated by single crystal X-ray analysis, see Fig. 1 (left) for the molecular structure.‡ The structure displays a slightly distorted trigonal bipyramidal geometry (τ-value: 0.93).[14] From the structure, it is apparent that ligand **1** is indeed able to fully



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Scheme 1 Straightforward synthesis of tripodal, tetradentate ligand **1**. Conditions: (i) *n*-BuLi, THF, −78 °C; CO_2; *t*-BuLi; PCl_3. (ii) *n*-BuLi, THF, −78 °C; $ClPPh_2$.

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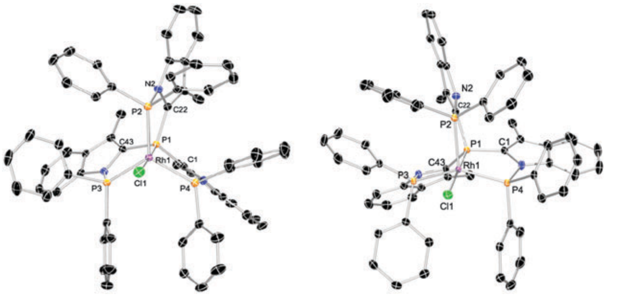


Fig. 1 Displacement ellipsoid plots (50% probability level) of species **2** (left) and [**2**]PF_6. H-atoms and counter ion are omitted for clarity. Selected bond lengths (Å) and angles (°), for **2**: Rh_1–P_1 2.1592(7), Rh_1–P_2 2.2882(8), Rh_1–P_3 2.2980(7), Rh_1–P_4 2.3012(8), Rh_1–Cl_1 2.4402(7), P_1–C_1 1.803(3); P_2–N_2 1.738(2); P_1–Rh_1–Cl_1 177.60(3), P_1–Rh_1–P_3 86.16(3), P_2–Rh_1–P_3 121.79(3), P_2–Rh_1–P_4 120.74(3), P_3–Rh_1–P_4 115.95(3), P_3–Rh_1–Cl_1 94.30(2). For [**2**]PF_6: Rh_1–P_1 2.2040(5), Rh_1–P_2 2.3110(5), Rh_1–P_3 2.3482(6), Rh_1–P_4 2.3094(6), Rh_1–Cl_1 2.3949(5), P_1–C_1 1.801(2); P_2–N_2 1.7128(17); P_1–Rh_1–Cl_1 177.21(2), P_1–Rh_1–P_3 83.83(2), P_2–Rh_1–P_4 107.93(2), P_2–Rh_1–P_3 105.33(2), P_3–Rh_1–P_4 144.21(2), P_3–Rh_1–Cl_1 94.94(2).

embrace the Rh metal center from the top, whereas the other side is protected by a strongly coordinating chloride ligand.

The chloride co-ligand was stable in the presence of Ag-salts, as no abstraction to form AgCl was observed. Instead, an instantaneous colour change from burgundy-red to dark-purple with formation of a Ag^0-mirror indicated redox-based reactivity resulting in the formation of the corresponding $(PP_3)Rh^{II}Cl$ complex [**2**]PF_6. Disproportionation of $(PP_3)Rh^{II}Cl$ is likely hindered by the strained (ligand) geometries of the hypothetical (trigonal pyramidal) $(PP_3)Rh^I$ and (constrained octahedral) $(PP_3)Rh^{III}Cl$ products. In line with this, cyclic voltammetry for complex **2** showed a fully reversible Rh^I/Rh^{II} oxidation wave at −0.4 V, referenced *vs.* Fc/Fc^+.† The relatively low potential indicates facile oxidation, likely due to the coordination of four strongly electron-donating phosphines. Rh^{II} complex [**2**]PF_6 was independently prepared by one-electron oxidation of **2** with ferrocenium hexafluorophosphate. Solution-state RT magnetization measurements by Evans' method are consistent with the formulation of complex [**2**]PF_6 as a radical species, with a μ_{eff} value of 2.29(1) μ_B.[15] This value is somewhat larger than the spin-only value (1.73 μ_B), indicating spin–orbit influences.[16] Species [**2**]PF_6 is a bench-stable solid and no appreciable decomposition is observed in common solvents, indicating highly effective shielding of the Rh^{II} center by the ligand sphere. The proposed formulation of [**2**]PF_6 was confirmed by X-ray crystallography (Fig. 1, right).‡

The molecular structure features a distorted trigonal bipyramidal geometry around the Rh-center, with a τ-value of 0.55. Clearly, the geometric constraints in ligand framework **1** dictate and govern the unusual structural characteristics of the corresponding metalloradical complex. The Rh^{II}-ion is largely shielded and protected by the rigid ligand scaffold.†

The X-band EPR spectrum of [**2**]PF_6 is shown in Fig. 2. Identical data were obtained for stored (one-month old) and *in situ* generated samples, indicative of a highly stable radical species. Simulation of the experimental EPR spectrum of [**2**]PF_6 at 20 K reveals a rhombic g-tensor with moderate g-anisotropy and resolved superhyperfine couplings with mainly three P atoms; large coupling with P_2 and smaller couplings with P_3 and P_4.† The fourth P-atom (pivotal P_1) shows no resolved coupling. A distorted geometry in-between a trigonal bipyramid (tbp) and a square pyramid (sqpy) is revealed. This is remarkable, because 5-coordinate Rh^{II}-complexes generally adopt a square pyramidal geometry (Jahn–Teller effect).[17]

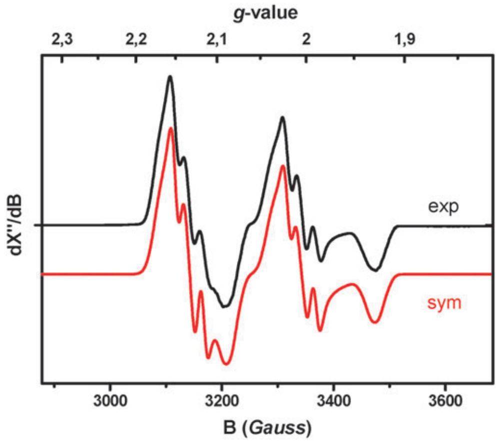
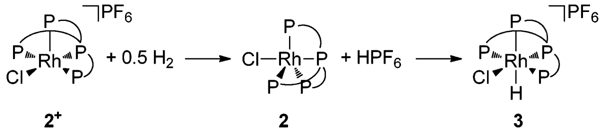


Fig. 2 Experimental (black) and simulated (red) X-band EPR spectrum of [**2**]PF_6. Experimental details: 20 K, frequency 9.3794 GHz, microwave power 0.2 mW, modulation amplitude 4 Gauss. TBAH (~0.1 M) was added to obtain a better glass. DFT calculations and data in ESI.†

DFT calculations show that about 51% of the spin density of $\mathbf{2}^+$ resides on Rh and about 24% on the "apical" P_2-donor.† The species is thus best described as a strongly covalent radical. It has substantial metalloradical character, but with a strong contribution of the square pyramidal 'axial' P_2 donor. Despite the long-term stability of solid samples of metalloradical complex $\mathbf{2}^+$ and the small accessible molecular surface, we wondered if this species would exhibit reactivity towards molecular hydrogen. When [**2**]PF_6 was exposed to molecular hydrogen for 12 hours (5 bar, CD_2Cl_2), Rh^{III}–H species **3** was formed quantitatively. In the ^1H NMR spectrum, a complex doublet-of-doublet-of-doublet-of-triplets was observed at δ −6.52 ppm, with a large $^2J_{P-H}$ coupling of 174.8 Hz (*trans*-disposition with phosphorus).† This strongly suggests the presence of a hydride ligand coupled to three inequivalent P-atoms. In the corresponding ^{31}P NMR spectrum an AM_2X spin pattern could be discerned.† This led us to assign this species as the hydrido complex **3**, formulated as [Rh(Cl)(H)(**1**)]PF_6 (Scheme 2), with the hydrido ligand *trans* to one of the side-arm P-atoms and the chloro ligand *trans* to the pivotal P donor. Independent synthesis of this complex (as the analogous triflate salt) was carried out by protonation of **2** with HOTf. Furthermore, when D_2 instead of H_2 was reacted with [**2**]PF_6, deuterido complex **3-D**, [Rh(Cl)(D)(**1**)]PF_6, was obtained, unambiguously proving that the hydride stems from molecular hydrogen. The NMR spectrum of **3-D** shows only traces of the hydride caused by the presence of H_2 and HD in the D_2 gas.†

The formation of **3** is proposed to proceed *via* an *outer*-sphere redox process, in which the Rh^{II} complex is reduced to Rh^I complex **2** by dihydrogen ($H_2 \rightarrow 2H^+ + 2e$), with subsequent or concerted protonation of Rh^I to Rh^{III}–H. The mechanism of net hydrogen transfer from H_2 to the sterically



Scheme 2 Activation of H_2 by complex [**2**]PF_6, resulting in the formation of Rh^{III} complex **3** *via* intermediacy of species **2**.

protected metalloradical species should differ substantially from that proposed by Rauchfuss for H_2 oxidation by an Ir-based ligand-centered radical species.[18] The redox-potential of [**2**]PF_6 *vs.* NHE is 0.28 V, which implies that the overall oxidation of H_2 to $2H^+$ is thermodynamically allowed even without subsequent metal protonation. The process might thus involve the concerted trimolecular two-electron oxidation of H_2 simultaneously by two complexes $\mathbf{2}^+$ (which may proceed over a rather long distance between the species so that steric hindrance plays a minor role). However, we cannot completely exclude other mechanisms, such as two consecutive bimolecular single-electron transfer steps. The formation of high-energy species ($H_2^{\bullet +}$, or $H^{\bullet}$ after immediate proton transfer to Rh^I) in the latter case speaks against such a stepwise process, but this could be possible if tunneling is involved. Direct homolytic splitting of H_2, as observed for Rh^{II}–porphyrin systems,[19] also seems less likely, because this reaction should suffer from extensive steric shielding provided by the ligand protecting the Rh^{II} center (again, unless tunneling is involved). We are currently investigating possibilities to apply the observed activation of dihydrogen by Rh^{II} metalloradicals based on these novel, modular tripodal phosphorus ligands for hydrogen atom-transfer (HAT) reactions.

Summarizing, we have reported the straightforward synthesis of a mononuclear Rh^I complex **2** and the corresponding stable Rh^{II} species $\mathbf{2}^+$, based on a novel tripodal, tetradentate phosphorus ligand **1**. The isolated metalloradical complex $\mathbf{2}^+$ is a rare $Rh^{II}Cl$ compound with an unusual intermediate coordination geometry. Notwithstanding its bench-stable character, $\mathbf{2}^+$ reacts with molecular hydrogen to quantitatively form the corresponding Rh^{III} hydrochloride complex **3**. This is the first example of dihydrogen activation by a metal-centered Rh^{II} metalloradical, which may proceed through complete oxidation of molecular hydrogen followed by protonation of the resulting Rh^I species. This reaction can be considered as a starting point of HAT reactions, using molecular hydrogen as hydrogen atom donor. Further studies aimed at the reactivity of these unusual Rh^{II} metalloradicals are ongoing, including studies derived from the related cationic Rh^I species. Moreover, we are investigating the use of enantiomerically pure C_3-symmetric derivatives of **1** in asymmetric transformations.

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Notes and references

‡ Crystal data. **2**: $C_{63}H_{51}ClN_3P_4Rh\cdot CH_2Cl_2$, FW = 1197.23, 0.10 × 0.14 × 0.27 mm, T = 110 K, triclinic, $P\bar{1}$, a = 11.8086(5), b = 14.6492(4), c = 17.0348(5) Å, α = 83.286(2)°, β = 87.505(2)°, γ = 71.163(2)°, V = 2769.79(17)Å^3, Z = 2, 12 704 reflections, 62 878 unique (R_{int} = 0.062), R = 0.0386, wR_2 = 0.0767 (all data); CCDC 735997. [**2**]PF_6: $C_{63}H_{51}ClN_3P_4Rh\cdot F_6P\cdot 3(CH_2Cl_2)$, FW = 1512.06, 0.26 × 0.31 × 0.32 mm, T = 110 K, triclinic, $P\bar{1}$, a = 13.2110(6)Å, b = 15.3608(8)Å, c = 17.6791(10)Å, α = 93.963(2)°, β = 110.874(2)°, γ = 101.654(3)°, V = 3243.8(3)Å^3, Z = 2, 14 892 reflections, 83 759 unique (R_{int} = 0.024), R = 0.0309, wR_2 = 0.0759 (all data); CCDC 735998.

1 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley-Interscience, New York, 3rd edn, 2001, pp. 152–155.

2 For an overview of H_2 activation by frustrated Lewis pairs, see: D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46.

3 R. Noyori, M. Kitamura and T. Ohkuma, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5356; R. J. Hamilton and S. H. Bergens, *J. Am. Chem. Soc.*, 2008, **130**, 11979.

4 A. Wu, J. Masland, R. D. Swartz, W. Kaminsky and J. M. Mayer, *Inorg. Chem.*, 2007, **46**, 11190, and references therein.

5 J. I. van der Vlugt, T. Koblenz, J. Wassenaar and J. N. H. Reek, in *Molecular Encapsulation: Reactions in Constrained Systems*, ed. J.-L. Mieusset and U. H. Brinker, Wiley-VCH, Weinheim, 2009, in press; T. Koblenz, J. Wassenaar and J. N. H. Reek, *Chem. Soc. Rev.*, 2008, **37**, 247; M. Kuil, T. Soltner, P. W. N. M. van Leeuwen and J. N. H. Reek, *J. Am. Chem. Soc.*, 2006, **128**, 11344; K. Drauz and H. Waldmann, *Enzyme Catalysis in Organic Synthesis: A Comprehensive Handbook*, Wiley-VCH, Weinheim, 2nd edn, 2002.

6 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; C. Moberg, *Angew. Chem., Int. Ed.*, 1998, **37**, 248; I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster and F. Breher, *Dalton Trans.*, 2008, 5836.

7 L. Turculet, J. D. Feldman and T. D. Tilley, *Organometallics*, 2004, **23**, 2488; C. Foltz, M. Enders, S. Bellemin-Laponnaz, H. Wadepohl and L. H. Gade, *Chem.–Eur. J.*, 2007, **13**, 5994; C. C. Lu, C. T. Saouma, M. W. Day and J. C. Peters, *J. Am. Chem. Soc.*, 2007, **129**, 4; M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. X. Gu, M. Mercy, C. H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *J. Am. Chem. Soc.*, 2008, **130**, 16729.

8 M. J. Baker and P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, 1993, 314; R. B. King and R. N. Kapoor, *J. Am. Chem. Soc.*, 1969, **91**, 5191; J. W. Dawson and L. M. Venanzi, *J. Am. Chem. Soc.*, 1968, **90**, 7229.

9 M. Ciclosi, J. Lloret, F. Estevan, P. Lahuerta, M. Sanaú and J. Pérez-Prieto, *Angew. Chem., Int. Ed.*, 2006, **45**, 6741; M. Ciclosi, F. Estevan, P. Lahuerta, V. Passarelli, J. Pérez-Prieto and M. Sanaú, *Dalton Trans.*, 2009, 2290.

10 J. Wassenaar and J. N. H. Reek, *Dalton Trans.*, 2007, 3750; J. Wassenaar, M. Kuil and J. N. H. Reek, *Adv. Synth. Catal.*, 2008, **350**, 1610; J. Wassenaar, S. van Zutphen, G. Mora, P. Le Floch, M. Siegler, A. L. Spek and J. N. H. Reek, *Organometallics*, 2009, **28**, 2724; J. Wassenaar and J. N. H. Reek, *J. Org. Chem.*, 2009, **74**, 8403.

11 A. R. Katritzky, K. Akutagawa and R. A. Jones, *Synth. Commun.*, 1988, **18**, 1151; J. O. Yu, C. S. Browning and D. H. Farrar, *Chem. Commun.*, 2008, 1020.

12 B. de Bruin, P. H. M. Budzelaar and A. W. Gal, *Angew. Chem., Int. Ed.*, 2004, **43**, 4142; H. R. L. Davies and J. R. Manning, *Nature*, 2008, **451**, 417; H. R. L. Davies and S. J. Hedley, *Chem. Soc. Rev.*, 2007, **36**, 1109; C. A. Merlic and A. L. Zechman, *Synthesis*, 2003, 1137.

13 W. I. Dzik, J. M. M. Smits, J. N. H. Reek and B. de Bruin, *Organometallics*, 2009, **28**, 1631; W. I. Dzik, J. N. H. Reek and B. de Bruin, *Chem.–Eur. J.*, 2008, **14**, 7594.

14 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

15 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

16 The μ_{eff} value is similar to that of a PNP-based mononuclear Rh^{II} species, see: M. Feller, E. Ben-Ari, T. Gupta, L. J. W. Shimon, G. Leitus, Y. Diskin-Posner, L. Weiner and D. Milstein, *Inorg. Chem.*, 2007, **46**, 10479.

17 D. G. H. Hetterscheid, A. J. J. Koekoek, H. Grützmacher and B. de Bruin, *Prog. Inorg. Chem.*, 2007, **55**, 247.

18 M. R. Ringenberg, S. Latha Kokatam, Z. M. Heiden and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2008, **130**, 788.

19 W. Cui and B. B. Wayland, *J. Am. Chem. Soc.*, 2004, **126**, 8266, and references therein.