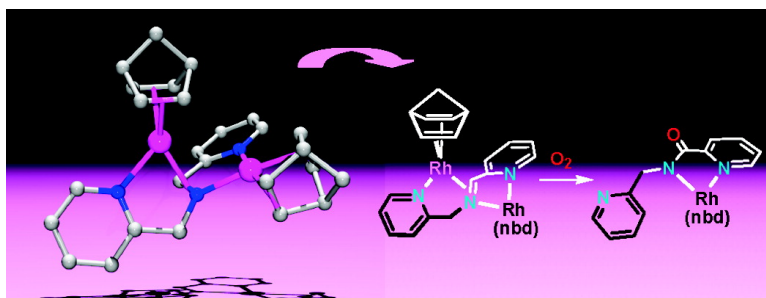


Deprotonation Induced Ligand-to-Metal Electron Transfer: Synthesis of a Mixed-Valence Rh(I,II) Dinuclear Compound and Its Reaction with Dioxygen

Cristina Tejel, Miguel A. Ciriano, M. Pilar del Río, Fieke J. van den Bruele, Dennis G. H. Hetterscheid, Nearchos Tzichlis i Spithas, and Bas de Bruin

J. Am. Chem. Soc., **2008**, 130 (18), 5844-5845 • DOI: 10.1021/ja711495v • Publication Date (Web): 11 April 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Deprotonation Induced Ligand-to-Metal Electron Transfer: Synthesis of a Mixed-Valence Rh(–I,I) Dinuclear Compound and Its Reaction with Dioxygen

Cristina Tejel,^{*,†} Miguel A. Ciriano,[†] M. Pilar del Río,[†] Fieke J. van den Bruele,[†] Dennis G. H. Hetterscheid,[‡] Nearchos Tschlis i Spithas,[‡] and Bas de Bruin^{*,‡}

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, E-50009 Zaragoza, Spain, and Homogeneous and Supramolecular Catalysis, Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received December 31, 2007; E-mail: ctejel@unizar.es; bdebruin@science.uva.nl

For discrete mixed-valence complexes, an interesting chemistry and various practical utilities can be envisaged.¹ Particularly those in which the oxidation states of the metals differ by two-electrons have emerged as promising tools to manage two- and four-electron transformations, such as those involved in hydrogen and oxygen activations.² Two-electron mixed-valence M(I,III) dinuclear rhodium and iridium complexes prepared by oxidative addition reactions at one metal center are well-known.³ Some of them are key intermediates in oxidative addition reactions of halocarbons,⁴ protic acids,⁵ and C–H activation reactions.⁶ Their two-electron-reduced analogues, such as mixed-valence dinuclear M(0,II)⁷ complexes, are also known. They have been synthesized using special ligands, capable of stabilizing redox asymmetric environments, as developed by Nocera et al.,^{8,2b} and show interesting new mechanisms in hydrogenation reactions⁹ and are photoactive in hydrogen production.¹⁰ Relevant to this paper, two-electron mixed-valence species in even further reduced M(–I,I) oxidation states were so far unknown in rhodium chemistry. Herein, we report the synthesis of a unique redox asymmetric dinuclear Rh(–I,I) complex and its reaction with O₂ leading to O atom transfer to a benzylic group of the N ligand.

While [$\{\text{Rh}(\mu\text{-OMe})(\text{nbd})\}_2$] (nbd = norbornadiene) reacts with $[\text{Rh}(\text{bpa})(\text{nbd})]\text{Cl}$ (bpa = bis(2-picoly)amine) to give the amido-bridged dinuclear complex [$\{\text{Rh}(\text{nbd})\}_2(\mu\text{-bpa-H})\text{Cl}$] **[1]Cl**, the reaction of [$\{\text{Rh}(\mu\text{-OMe})(\text{nbd})\}_2$] with free bpa in benzene-*d*₆ gave the unique asymmetric dinuclear complex [$\{\text{Rh}(\text{nbd})\}_2(\mu\text{-bpa-2H})$] (**2**) and methanol (Scheme 1). Complex **2** was isolated as a deep-purple solid in high yield by carrying out the reaction in diethyl ether. Protonation of **2** with NHEt_3Cl generates **[1]Cl**, while the latter reacts with KO^tBu to produce **2**. Thus, complexes **[1]Cl** and **2** are related by acid–base chemistry.

Both the amine and one of the bpa methylene groups are deprotonated in the formation of **2** from bpa, as evidenced by ¹H NMR. Neutral bpa-like ligands are generally quite robust and are widely applied in coordination chemistry,¹¹ enzyme modeling, and catalysis,¹² and the “benzylic” methylene protons of (2-picoly)amine-type ligands are not very acidic.¹³ As such, the formation of **2** was not expected.

The X-ray structure of **2** is shown in Figure 1 (for the X-ray structure of **[1]Cl**, see Supporting Information). The dpa-2H ligand in **2** hosts the two Rh(nbd) fragments in two distinct compartments. In the first compartment, a square planar Rh(1) is bound to nbd and to N(1) and the central amido (N3) atoms, while in the second compartment, an almost tetrahedral Rh(2) center is bound to nbd,

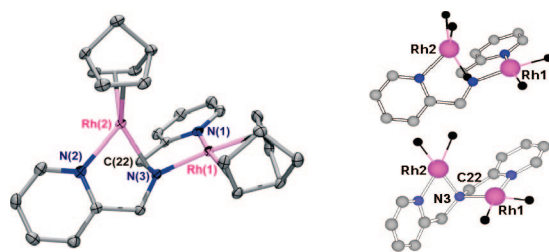
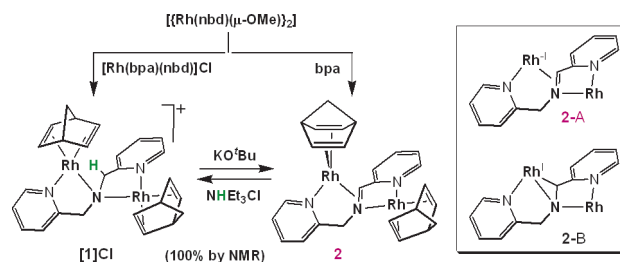


Figure 1. Left: Structure (ORTEP at 50% level) of complex **2** (hydrogen atoms have been omitted for clarity). Right: structural cores of complex **2** (top) and the cation **1**⁺ (bottom).

Scheme 1. Two Extreme Structures for **2** are Shown on the Right



N(2) and is η^2 -coordinated to the C(22)–N(3) bond (see Supporting Information for details).

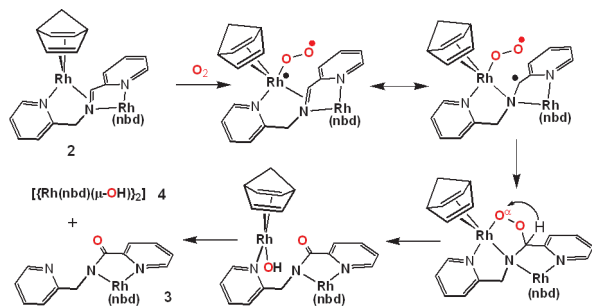
Particularly remarkable are the trigonal geometries of N(3) and C(22), suggesting the formation of a π -coordinating imine C=N fragment. In good agreement, there is a shortening of the C22–N3 distance (1.415(4) Å) when compared to the N–CH₂ distances (mean 1.482(6) Å) in the related complex [$\{\text{Rh}(\text{nbd})\}_2(\mu\text{-bpa-H})\text{Cl}$] **[1]Cl**. Thus, the data strongly suggest that the bpa-2H ligand is transformed into the neutral $\text{PyCH=N-CH}_2\text{Py}$ (bpi) ligand with a π -coordinating imine, by reducing one of the Rh^I(nbd) fragments to a lower valent Rh^{–I}(nbd) fragment. Rhodate(–I) center Rh(2) adopts a tetrahedral coordination geometry, typical for a d¹⁰-ML₄ complex. Therefore, the structure of complex **2** corresponds best with description 2-A in Scheme 1.

Late transition metals interacting with a κ^2 -C–N bond are quite uncommon and are systematically described as metalla-azacyclopropanes (2-B, Scheme 1) in Rh, Ir, and Pd chemistry.¹⁴ For example, the structural parameters of $[\text{Rh}(\text{trop}_2\text{NCH}_2\text{-})\text{PPh}_3]$,^{14a} the sole precedent for rhodium, fit better in the description indicated by 2-B (Scheme 1). The ¹³C{¹H} signal of the rhoda-azacyclopropane carbon of $[\text{Rh}(\text{trop}_2\text{NCH}_2\text{-})\text{PPh}_3]$ was found at 62.4 ppm, while the “imine” carbon of **2** is observed at 76.9 ppm.

The abstraction of a proton from **1**⁺ is thus accomplished with a strong electronic reorganization, best described as a reduction of

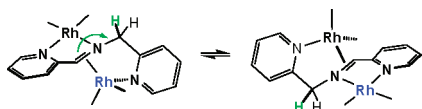
[†] CSIC-Universidad de Zaragoza.

[‡] University of Amsterdam.

Scheme 2. Oxygenation of **2** to the Carboxamido Complex **3**

Rh^I to Rh^{-I} with oxidation of the dianionic bpa-2H ligand to a neutral bpi imine ligand. However, because of the redox ambiguity of imine containing ligands, a singlet diradical structure with a monoanionic ligand and Rh^0, Rh^I centers cannot be excluded. To our best knowledge, the ligand-to-metal electron transfer upon removing a proton from $[1]^+$ to produce the redox asymmetric dinuclear rhodium complex **2** is an unprecedented reaction.

The different nature of the two rhodium centers in **2** is also observed in solution. While the nbd bound to $Rh(1)$ is almost static, the nbd fragment bound to the tetrahedral $Rh(2)$ undergoes a turnstile motion (1H NMR). Interestingly, complex **2** undergoes a slow exchange of one-half of the molecule into the other half, as detected by EXSY spectroscopy ($\Delta H^\ddagger = 19.6 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 8.9 \text{ eu}$). This process involves a 1,3-prototropic shift of one of the methylene protons to the $CH=N$ group. This is associated with a change in the bond order of the C–N bonds and of the coordination geometry of the metals, with the tetrahedral center becoming square planar and vice versa. Combining the 1,3-prototropic shift with π -coordination of the new $CH=N$ fragment, the overall process represents an electronic pump moving electrons from one metal to the other with exchange of their oxidation states



In line with the electron-rich nature of its rhodate($-I$) center, complex **2** is very air-sensitive and it reacts rapidly with O_2 in benzene (Scheme 2). The reaction proceeds with formation of the carboxamido complex $[Rh(nbd)(bpam-H)]$ (**3**) (bpam = *N*-(2-picolyl)picolinamide), along with $[Rh(nbd)(\mu-OH)]_2$ (**4**) in 77% yield (according to 1H NMR integrals against an internal standard). As a reference, neither complex $[1]Cl$ nor **3** react with oxygen under identical conditions. Complexes **3** and **4** were identified by comparison of their spectroscopic data with those of pure samples obtained from straightforward routes (see Supporting Information).

It is quite remarkable that the coordinated diolefins are not oxygenated with formation of metallaoxetanes or metalladioxolanes in this process.¹⁵ Related Cu-mediated oxygenation of picolyl or imine fragments has been reported in only a few exceptional cases.^{12d,16} We propose that the reaction proceeds via initial oxygenation of the most electron-rich Rh center ($Rh(2)$) in Figure 1) to form likely a superoxido ligand, which collapses with the imine carbon atom to form a five-membered ring (Scheme 2). This is comparable to a five-membered 3-rhoda-dioxolane ring, known to decompose via hydrogen transfer to its α -oxygen.^{15b} Similar reactions would explain the formation of the carboxamido fragment. Dissociation of the fragment $[Rh^I(nbd)(OH)]$ from the complex with subsequent formation of $[Rh(nbd)(\mu-OH)]_2$ completes the reaction.

In conclusion, we demonstrated the formation of the unprecedented two-electron mixed-valence $Rh(-I, I)$ complex **2** upon simple deprotonation of the homovalent $Rh(I, I)$ complex 1^+ , which proceeds via an internal ligand-to-metal redox reaction. The thus formed $PyCH_2N=CHPy$ ligand provides two distinct compartments for the stabilization of the valence-separated states, thus preventing comproportionation. Complex **2** reacts with O_2 to form carboxamido- $Rh^I(nbd)$ species **3** via O atom transfer to the $PyCH_2N=CHPy$ ligand. The reported reactions are highly unexpected and raise questions about the chemical innocence of the frequently applied bpa-type ligands. Existing and future reactivity studies of late TM bpa-type complexes may have to be (re)evaluated on the basis of these new insights.

Acknowledgment. The generous financial support from MEC/FEDER (Project CTQ2005-06807), DGA (PIP019 and Research Group E70) (Spain), and The Netherlands Organization for Scientific Research (NWO-CW) is gratefully acknowledged. M.P.R. thanks DGA for a fellowship.

Supporting Information Available: Full experimental details, selected NMR spectra and discussion on crystallographic information of $[1]Cl$, **2**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) See for example: (a) Kaim, W.; Lahiri, G. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 1778–1796. (b) D'Alessandro, D. M.; Keene, F. R. *Chem. Rev.* **2006**, *106*, 2270–2298. (c) Gatteschi, D.; Sessoli, R. *J. Magn. Magn. Mater.* **2004**, *272–276*, 1030–1036.
- (2) (a) Rosenthal, J.; Nocera, D. G. *Acc. Chem. Res.* **2007**, *40*, 543–553. (b) Rosenthal, J.; Bachman, J.; Dempsey, J. L.; Esswein, A. J.; Gray, T. G.; Hodgkiss, J. M.; Manke, D. R.; Luckett, T. D.; Pistorio, B. J.; Veige, A. S.; Nocera, D. G. *Coord. Chem. Rev.* **2005**, *249*, 1316–1326.
- (3) (a) Molinos, E.; Brayshaw, S. K.; Kociok-Kohn, G.; Weller, A. S. *Dalton Trans.* **2007**, 4829–4844. (b) Pechmann, T.; Brandt, C. D.; Werner, H. *Dalton Trans.* **2004**, 959–966. (c) Polborn, K.; Severin, K. *Eur. J. Inorg. Chem.* **1998**, 1187–1192. (d) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 590–595.
- (4) (a) Tejel, C.; Ciriano, M. A.; López, J. A.; Jiménez, S.; Bordonaba, M.; Oro, L. A. *Chem. Eur. J.* **2007**, *13*, 2044–2053. (b) Tejel, C.; Ciriano, M. A.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2000**, *19*, 4977–4984.
- (5) (a) Tejel, C.; Ciriano, M. A.; Millaruelo, M.; Lopez, J. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2003**, *42*, 4750–4758. (b) Heyduk, A. F.; Nocera, D. G. *J. Am. Chem. Soc.* **2000**, *122*, 9415–9426.
- (6) (a) Tejel, C.; Bravi, R.; Ciriano, M. A.; Oro, L. A.; Bordonaba, M.; Graiff, C.; Tiripicchio, A.; Burini, A. *Organometallics* **2000**, *19*, 3115–3119. (b) Bushnell, G. W.; Fjeldsted, D. O. K.; Stobart, S. R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 580–581.
- (7) Hattori, T.; Matsukawa, S.; Kuwata, S.; Ishii, Y.; Hidai, M. *Chem. Commun.* **2003**, 510–511.
- (8) Gray, T. C.; Nocera, D. G. *Chem. Commun.* **2005**, 1540–1542.
- (9) Veige, A. S.; Gray, T. G.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 17–26.
- (10) (a) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022–4047. (b) Esswein, A. J.; Veige, A. S.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 16641–16651.
- (11) (a) Blackman, A. G. *Polyhedron* **2005**, *24*, 1–39. (b) Hazell, A.; McGinley, J.; Toftlund, H. *Dalton Trans.* **1999**, 1271–1276, and references therein.
- (12) (a) Kim, E.; Chufán, E. E.; Kamaraj, K.; Karlin, K. D. *Chem. Rev.* **2004**, *104*, 1077–1134. (b) Wu, A. J.; Penner-Hahn, J. E.; Pecoraro, V. L. *Chem. Rev.* **2004**, *104*, 903–938. (c) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013–1046. (d) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047–1076. (e) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2004**, *104*, 939–986. (f) Tshuva, E. Y.; Lippard, S. J. *Chem. Rev.* **2004**, *104*, 987–1012, and references therein.
- (13) Cao, L.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2007**, *46*, 1361–1368.
- (14) (a) Marie, P.; Sreekanth, A.; Büttner, T.; Harmer, J.; Gromov, I.; Rügger, H.; Breher, F.; Schweiger, A.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3265–3269. (b) Lu, C. C.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 15818–15832. (c) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 3025–3027. (d) Wehman-Ooyevaar, I. C. M.; Luitwieler, I. F.; Vatter, K.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1996**, *252*, 55–69.
- (15) (a) Tejel, C.; Ciriano, M. A. *Top. Organomet. Chem.* **2007**, *22*, 97–124. (b) de Bruin, B.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 4142–4157.
- (16) (a) Katayev, E. A.; Severin, K.; Scopelliti, R.; Ustynyuk, Y. A. *Inorg. Chem.* **2007**, *46*, 5465–5467. (b) Padhi, S. K.; Manivannan, V. *Inorg. Chem.* **2006**, *45*, 7994–7996. (c) Rowland, J. M.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **2002**, *41*, 2754.

JA711495V