Square-Planar Iridium(III)

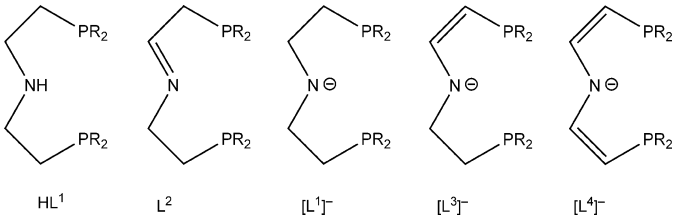
DOI: 10.1002/anie.201102795

Square-Planar Iridium(II) and Iridium(III) Amido Complexes Stabilized by a PNP Pincer Ligand**

Jenni Meiners, Markus G. Scheibel, Marie-Hélène Lemée-Cailleau, Sax A. Mason, M. Bele Boeddinghaus, Thomas F. Fässler, Eberhardt Herdtweck, Marat M. Khusniyarov, and Sven Schneider**

Coordination compounds of the precious metals are of enormous importance in homogeneous catalysis. Generally, their electronic structures favor closed-shell states, thus explaining the typical preference of two-electron (oxidative addition/reductive elimination) over one-electron redox reactions.[1] However, the importance of the latter was more recently emphasized for platinum metal complexes, for example in radical H_2, C–H, and C–C activation reactions or catalytic oxidations.[2–5] Nevertheless, fully characterized metalloradical complexes of these metals remain scarce.[6] Alternatively, radical complexes with the spin density mainly located on redox non-innocent ligands have been described, such as strongly N-centered radical complexes resulting from oxidation of Rh^I and Ir^I dialkylamides.[5b,7] However, in contrast to rhodium, these iridium aminyl radicals were described as being transient intermediates. In analogy, upon oxidation of the Pd^{II} amide $[PdPh(L^1)]$ (with R = *i*Pr), only the follow-up products $[PdPh(HL^1)]^+$ and $[PdPh(L^2)]^+$ (R = *i*Pr) were obtained (Scheme 1).[8]

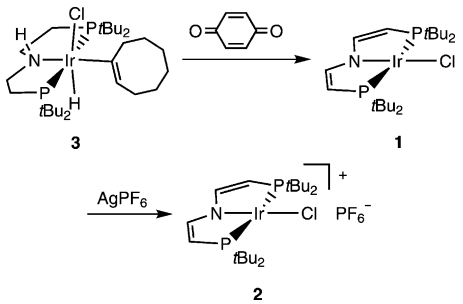
Similarly, complexes of the platinum metals with an even number of valence electrons in high-spin configuration are extremely rare owing to the generally larger ligand field splitting of the 4d/5d metal ions compared to their 3d homologues. An exception is provided by the square-planar d^6 disilylamido complexes $[MX(L^5)]$ (M = Ru, Os; X = F, Cl, I, trifluoromethanesulfonate (OTf); $L^5 = N(SiMe_2CH_2P\textit{t}Bu_2)_2$), which exhibit an electronic intermediate-spin configuration, in analogy to iron(II).[9,10] However, the stronger N→M π donation in the related dialkylamido complex $[RuCl(L^1)]$ (R = *t*Bu) results in a low-spin ground state.[11]



Scheme 1. PNP chelating ligands derived from $HN(CH_2CH_2PR_2)_2$.

These examples demonstrate the importance to rationalize the parameters that control the electronic structure and therefore the reactivity of such radical complexes and coordinatively strongly unsaturated complexes of the platinum metals. Regarding the PNP pincer ligands used in our group (Scheme 1), the dehydrogenation of one of the chelate backbone ethylene bridges to ligand L^3 allows the donor properties to be fine-tuned.[12] Herein, we present the versatile ligand functionalization towards the novel diene-amido ligand $(L^4)^-$ (R = *t*Bu; Scheme 1), which afforded the isolation of iridium(II) amido complex $[IrCl(L^4)]$ (**1**; R = *t*Bu). Oxidation of **1** gives diamagnetic $[IrCl(L^4)]PF_6$ (**2**; R = *t*Bu), the first example of a square-planar iridium(III) complex.

$[Ir(H)Cl(C_8H_{13})(HL^1)]$ (**3**; R = *t*Bu)[13] can be oxidized in situ with benzoquinone (2.5 equiv) to give turquoise complex **1** in yields of isolated product of up to 60% (Scheme 2).[14] A ^{31}P NMR spectrum of **1** exhibits no signals. The three broad signals in the ^1H NMR spectrum are strongly paramagnetically shifted and can be assigned to the *t*Bu substituents ($\delta = 10.5$ ppm) and two sets of ligand backbone



Scheme 2. Synthesis of iridium complexes **1** and **2**.

[*] J. Meiners, M. G. Scheibel, Dr. M. M. Khusniyarov, Prof. Dr. S. Schneider
Department Chemie und Pharmazie
Friedrich-Alexander-Universität
Egerlandstrasse 1, 91058 Erlangen (Germany)
E-mail: sven.schneider@chemie.uni-erlangen.de
Dr. M.-H. Lemée-Cailleau, Dr. S. A. Mason
Institut Laue Langevin (ILL), 6 Rue Jules Horowitz, BP 156
38042 Grenoble (France)
M. B. Boeddinghaus, Prof. Dr. T. F. Fässler, Dr. E. Herdtweck
Department Chemie, Technische Universität München
Lichtenbergstrasse 4, 85748 Garching (Germany)

[**] This work was supported by the Emmy-Noether program of the Deutsche Forschungsgemeinschaft (SCHN950/2-1). J.M. thanks the international graduate school NANOCAT and the TUM Graduate School. M.M.K. thanks the Fonds der Chemischen Industrie for a Liebig stipend.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102795.

C–H protons ($\delta = -6.8, -138.2$ ppm), respectively, indicating C_{2v} symmetry on the NMR spectroscopy timescale.

The potential redox non-innocence of amido ligands has attracted considerable interest in recent years.[5b,7,15,16] For example, radical complexes with related, chelating amido ligands, such as [(cod)Ir{N(CHC_5H_5N)($CH_2C_5H_5N$)}] (cod = 1,5-cyclooctadiene) or $[NiCl\{N(C_6MeH_3PiPr_2)_2\}]^+$, were reported to exhibit strongly ligand-centered spin densities.[16c,d] Thus, resonance structures which describe **1** in terms of an iridium(II) amido or iridium(I) aminyl complex provide conceivable alternatives. Mononuclear iridium(II) complexes were frequently postulated as transient reaction intermediates. However, fully characterized examples are considerably more rare than those of rhodium(II).[6,17] The rhombic EPR spectrum of **1** indicates a large anisotropy of the *g* tensor, suggesting a metal-centered radical (Figure 1). Hyperfine coupling with iridium is not resolved (86 K). Similar EPR parameters were reported for other iridium(II) complexes.[17e,g] The spectroscopic results are supported by DFT calculations, suggesting 67% of the spin density to be located at the metal center. The magnetic moment in the solid state (Supporting Information, Figure S1) confirms the doublet ground state of **1** ($\mu_{eff} = 2.2\ \mu_B$; $g = 2.5$) and is in agreement with the EPR spectrum ($g_{av} = ((g_1^2 + g_2^2 + g_3^2)/3)^{1/2} = 2.41$).

Single-crystal X-ray diffraction of **1** confirms a C_{2v}-symmetric molecular structure (Figure 2a). The metal center has a square-planar coordination geometry with an ideally linear N1-Ir1-Cl1 axis. The Ir1–N1 distance (1.985(2) Å) of **1** compares well with the iridium(I) amido complex [Ir(C_2H_4)(L^1)] (R = *i*Pr; **4**; 1.99(2) Å) and is slightly shorter than in [Ir(CO)(L^1)] (R = *i*Pr; **5**; 2.035(4) Å).[18] The planar nitrogen atom (sum of angles 360.0°) and the short C2–C3 (1.342(3) Å; **4** 1.50(3)/1.56(3) Å; **5** 1.521(9)/1.528(9) Å) and N1–C2 distances (1.387(2) Å; **4** 1.43(3)/1.48(3) Å; **5** 1.438(7)/1.464(8) Å) are in agreement with the dehydrogenation of both pincer backbone ethylene bridges and formation of the novel $(L^4)^-$ dieneamido ligand with considerable C=C und C=N double bonding contributions.

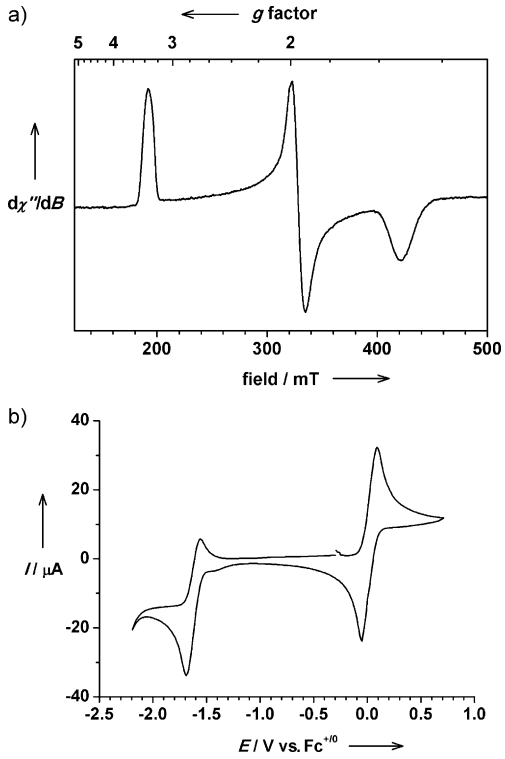


Figure 1. a) X-band EPR spectrum of **1** (Et_2O/Toluene glass, 86 K, frequency 8.9931 GHz, power 0.5 mW, modulation 1 mT/100 kHz). b) Cyclic voltammogram of **1** in CH_2Cl_2 at room temperature (glassy carbon electrode, 0.15 M [N*n*Bu$_4$]PF_6, scan rate 100 mV s^{-1}). Fc = ferrocene.

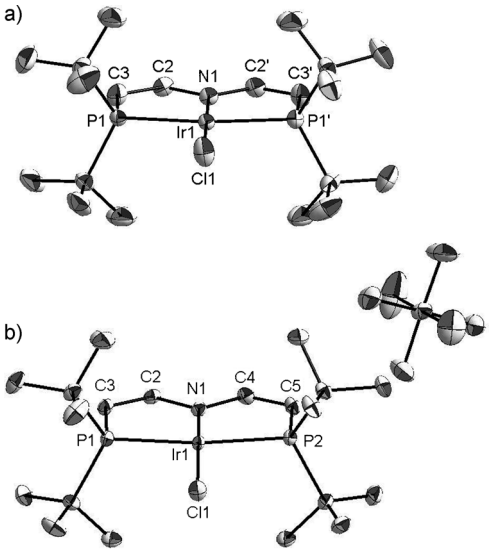


Figure 2. DIAMOND plots of the molecular structures of a) **1** and b) **2** from single crystal X-ray diffraction (ellipsoids set at 50% probability, hydrogen atoms and one THF solvent molecule in of **2** are omitted for clarity). Selected bond lengths [Å] and angles [°]: **1**: Ir1–Cl1 2.3390(7), Ir1–N1 1.985(2), Ir1–P1 2.3190(6), N1–C2 1.387(2), C2–C3 1.342(3); N1-Ir1-Cl1 180.0, P1-Ir1-P1′ 166.22(2). **2**: Ir1–Cl1 2.2966(6), Ir1–N1 1.922(2), Ir1–P1 2.3416(6), Ir1–P2 2.3443(6), N1–C2 1.414(3), N1–C4 1.415(3), C2–C3 1.335(3), C4–C5 1.334(3); N1-Ir1-Cl1 174.93(6), P1-Ir1-P2 167.56(2).

The mass spectrum of **1** provides no indication for further hydrido ligands at the vacant coordination sites. The IR spectrum of **1** shows three very weak absorptions between 1870 und 1960 cm^{-1}. However, although open-shell hydrido complexes are very rare,[19] the presence of a hypothetical iridium(IV) complex [Ir($H)_2$Cl(L^4)] (R = *t*Bu) could not be fully excluded on the basis of these results. Interestingly, the synthesis of iridium(IV) dihydrido complexes [Ir($H)_2$($Cl)_2$-($PR_3)_2$] (R = *i*Pr, cyclohexyl) had been reported earlier, but reevaluation of these results could not confirm their existence.[20,21] Therefore, single crystals of **1** were also characterized by neutron diffraction (Supporting Information, Figure S4).[14,22] The neutron-diffraction results confirm the square-planar geometry around the metal center and the absence of further hydride ligands. Furthermore, the localization of the hydrogen atoms indicates the absence of significant Ir···H–C interactions at the vacant coordination sites.

Oxidative addition of H_2 is a typical reaction of square-planar iridium(I) complexes, but was not observed for

iridium(II) compound **1** over a prolonged period of time. The cyclic voltamogram of **1** (Figure 1; Supporting Information, Figure S2) exhibits a reduction wave at $E_{1/2} = -1.61$ V (vs. $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$) that is quasireversible only at high scan rates ($> 800\ mV\,s^{-1}$). Accordingly, all efforts to isolate the corresponding iridium(I) complex $[IrCl(L^4)]^-$ (R = *t*Bu) were unsuccessful to date. However, reversible oxidation at $E_{1/2} = +0.02$ V ($100\ mV\,s^{-1}$) is observed, even at low scan rates. This result is particularly surprising, as the chemical oxidation of the related complex $[Ir^{II}Cl\{N(SiMe_2CH_2PtBu_2)_2\}]$ resulted in the isolation of subsequent products after P*t*Bu cyclometalation.[17g] In contrast, the reversible electrochemical oxidation of **1** is also observed by chemical redox titration, which can be monitored by ^1H NMR spectroscopy: An equimolar mixture of **1** and $[Fe(C_5H_5)_2]PF_6$ in CD_2Cl_2 exhibits a broad signal at $\delta = 7.4$ ppm, which is assignable to one averaged signal for the *t*Bu substituents of $[IrCl(L^4)]$ (R = *t*Bu; $\delta_{tBu} = 10.7$ ppm) and $[IrCl(L^4)]^+$ ($\delta_{tBu} = 2.3$ ppm; see below), which form a fast redox equilibrium on the NMR timescale (Supporting Information, Figure S3). From this solution, **1** can be recovered without decomposition almost quantitatively. Reaction of **1** with $AgPF_6$ enables the isolation of the primary oxidation product, $[IrCl(L^4)]PF_6$ (**2**) in yields of about 40% (Scheme 2). Compound **2** is thermally labile, and complete decomposition to several products is observed after about 4 h in solution at room temperature. The sharp NMR signals for **2** point towards a diamagnetic, C_{2v}-symmetric cation. The diamagnetism of **2** is unexpected, as square-planar d^6 complexes with a formal 14-valence-electron count typically exhibit an electronic intermediate-spin ($S = 1$) configuration.[11a]

The molecular structure of **2** in the crystalline state confirms the square-planar geometry (Figure 2b). The steric bulk of the *t*Bu substituents or the planarization of the ligand backbone possibly contribute to the stabilization of square-planar instead of saw-horse coordination, which is generally observed for four-coordinate iridium(III).[23] However, DFT calculations predict a square-planar structure for the less sterically encumbered model complex $[IrCl(L^4)]^+$ (R = Me; $\mathbf{2}^{Me}$), as well (see below). The structural parameters of **2** and **1** in the crystalline state are very similar. As the most striking difference, the Ir1–N1 bond shortens considerably upon oxidation (**2** 1.922(2), **1** 1.985(2)). The comparison with the Ir1–Cl1 bond lengths (**2** 2.2966(6), **1** 2.3390(7)) suggests that the Ir–N bond contraction cannot only be attributed to the smaller ionic radius of iridium(III). Furthermore, significant elongation of the pincer backbone N–C bonds and slight contraction of the C–C bonds are also observed (Scheme 3). These structural features indicate stronger weighting of mesomeric structure **A** for **2** compared with structure **B**, which is tantamount to enhanced N→Ir π donation.

This qualitative bonding picture was further substantiated by electronic structure calculations using DFT methods for the model complexes $[IrCl(L^4)]$ (R = Me; $\mathbf{1}^{Me}$) and $[IrCl(L^4)]^+$ (R = Me; $\mathbf{2}^{Me}$). The optimized geometries of $\mathbf{1}^{Me}$ (doublet state) and $\mathbf{2}^{Me}$ (singlet state) are in good agreement with the crystallographic results for the respective $\{Ir(L^4)\}^{0/+}$ fragments.[14] $\mathbf{2}^{Me}$ (triplet state) is found at higher energies with respect to the singlet state by around 4.1 kcal mol^{-1} (B3LYP) or 9.3 kcal mol^{-1} (BP). Furthermore, the Ir–N bond length is considerably overestimated in the triplet state ($\Delta d_{Ir\text{-}N} = 0.08$ Å). The structural trends are easily explained by consideration of the frontier orbitals. The SOMO of **1** exhibits considerable N–Ir π* character. Therefore, removal of this electron by oxidation towards **2** in the singlet state effects reinforcement of the N–Ir π bond (Figure 3). Therefore, the

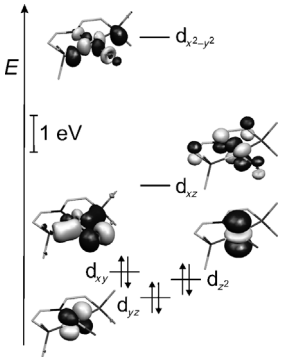
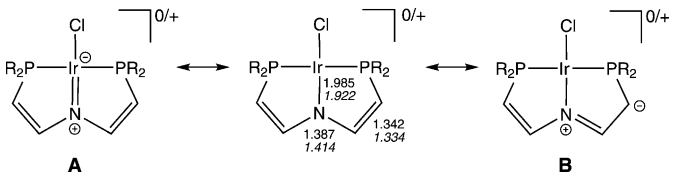


Figure 3. Metal-centered Kohn–Sham frontier orbitals of $\mathbf{2}^{Me}$ in the singlet state from spin-unrestricted ZORA-B3LYP-DFT calculations (the *z* axis is perpendicular to the $\{Ir(L^4)\}$ plane).

unusual electronic low-spin configuration of **2** is attributed to strong N→Ir π donation as in the case of $[RuCl(L^1)]$ (R = *t*Bu).[11] While the π-donor properties of the L^1 ligand should be weakened by dehydrogenation to L^4, this effect is counterbalanced by the cationic charge and the change from a 4d to a 5d metal, which should strengthen M–N bonding.[24]

In conclusion, simple oxidative ligand functionalization of the PNP chelate ligand framework allows for the versatile isolation of unusual square-planar d^7 und d^6 iridium complexes. Surprisingly, the square-planar d^8 complex of the redox series, $[IrCl(L^4)]^-$ (R = *t*Bu), was not stable under the experimental electrochemical and synthetic conditions. Compared to the ethylene-bridged PNP amido ligand, the $(L^4)^-$ pincer is characterized by higher conformational rigidity but electronic flexibility: While the radical complexes from the oxidation of iridium(I) dialkylamides are generally transient species, the metalloradical **1** and the oxidation product **2** are sufficiently stable to be easily isolated.[7,25] Thus the new dieneamido ligand opens up the opportunity to examine an unusual one-electron reactivity of iridium.



Scheme 3. Selected resonance structures and bond lengths (center) for **1** and **2** (italics).

Received: April 21, 2011
Published online: July 8, 2011

Keywords: coordination chemistry · iridium · N ligands · oxidation · pincer ligands

[1] P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794.

[2] a) K. J. Del Rossi, B. B. Wayland, *J. Chem. Soc. Chem. Commun.* **1986**, 1653; b) M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788; c) J. Wassenaar, B. de Bruin, M. A. Siegler, A. L. Spek, J. N. H. Reek, J. I. van der Vlugt, *Chem. Commun.* **2010**, *46*, 1232.

[3] a) R. S. Paonessa, N. C. Thomas, J. Halpern, *J. Am. Chem. Soc.* **1985**, *107*, 4333; b) K. J. del Rossi, B. B. Wayland, *J. Am. Chem. Soc.* **1985**, *107*, 7941; c) B. B. Wayland, S. Ba, A. E. Sherry, *J. Am. Chem. Soc.* **1991**, *113*, 5305; d) K. M. Smith, R. Poli, J. N. Harvey, *Chem. Eur. J.* **2001**, *7*, 1679; e) F. F. Puschmann, H. Grützmacher, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 73.

[4] K. S. Chan, X. Z. Li, W. I. Dzik, B. de Bruin, *J. Am. Chem. Soc.* **2008**, *130*, 2051.

[5] a) B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142; b) M. Königsmann, N. Donati, D. Stein, H. Schönberg, J. Harmer, A. Sreekanth, H. Grützmacher, *Angew. Chem.* **2007**, *119*, 3637; *Angew. Chem. Int. Ed.* **2007**, *46*, 3567.

[6] a) K. K. Pandey, *Coord. Chem. Rev.* **1992**, *121*, 1; b) D. G. DeWitt, *Coord. Chem. Rev.* **1996**, *147*, 209; c) R. Poli, *Chem. Rev.* **1996**, *96*, 2135; d) B. de Bruin, D. G. H. Hetterscheid, A. J. J. Koekkoek, H. Grützmacher, *Prog. Inorg. Chem.* **2007**, *55*, 247.

[7] a) T. Büttner, J. Geier, G. Frison, J. Harmer, C. Calle, A. Schweiger, H. Schönberg, H. Grützmacher, *Science* **2005**, *307*, 235; b) P. Maire, M. Königsmann, A. Sreekanth, J. Harmer, A. Schweiger, H. Grützmacher, *J. Am. Chem. Soc.* **2006**, *128*, 6578; c) N. Donati, D. Stein, T. Büttner, H. Schönberg, J. Harmer, S. Anadaram, H. Grützmacher, *Eur. J. Inorg. Chem.* **2008**, 4691.

[8] A. Marziale, E. Herdtweck, J. Eppinger, S. Schneider, *Inorg. Chem.* **2009**, *48*, 3699.

[9] a) L. A. Watson, O. V. Ozerov, M. Pink, K. G. Caulton, *J. Am. Chem. Soc.* **2003**, *125*, 8426; b) A. Walstrom, M. Pink, N. P. Tsvetkov, H. Fan, M. Ingleson, K. G. Caulton, *J. Am. Chem. Soc.* **2005**, *127*, 16780; c) X. Yang, A. Walstrom, N. Tsvetkov, M. Pink, K. G. Caulton, *Inorg. Chem.* **2007**, *46*, 4612; d) N. P. Tsvetkov, M. Pink, J.-H. Lee, K. G. Caulton, *Eur. J. Inorg. Chem.* **2010**, 4790.

[10] a) B. W. Dale, R. J. P. Williams, C. E. Johnson, T. L. Thorp, *J. Chem. Phys.* **1968**, *49*, 3441; b) H. Goff, G. N. La Mar, C. A. Reed, *J. Am. Chem. Soc.* **1977**, *99*, 3641; c) K. Ray, A. Begum, T. Weyhermüller, S. Piligkos, J. van Slageren, F. Neese, K. Wieghardt, *J. Am. Chem. Soc.* **2005**, *127*, 4403; d) E. J. Hawrelak, W. H. Bernskoetter, E. Lobkovsky, G. T. Yee, E. Bill, P. J. Chirik, *Inorg. Chem.* **2005**, *44*, 3103.

[11] a) B. Askevold, M. M. Khusniyarov, E. Herdtweck, K. Meyer, S. Schneider, *Angew. Chem.* **2010**, *122*, 7728; *Angew. Chem. Int. Ed.* **2010**, *49*, 7566; b) B. Askevold, J. T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen, S. Schneider, *Nat. Chem.* **2011**, DOI: 10.1038/nchem.1051.

[12] a) M. Käß, A. Friedrich, M. Drees, S. Schneider, *Angew. Chem.* **2009**, *121*, 922; *Angew. Chem. Int. Ed.* **2009**, *48*, 905; b) A. Friedrich, M. Drees, M. Käß, E. Herdtweck, S. Schneider, *Inorg. Chem.* **2010**, *49*, 5482.

[13] J. Meiners, A. Friedrich, E. Herdtweck, S. Schneider, *Organometallics* **2009**, *28*, 6331.

[14] For experimental, crystallographic and quantum chemical details, see the Supporting Information.

[15] R. G. Hicks, *Angew. Chem.* **2008**, *120*, 7503; *Angew. Chem. Int. Ed.* **2008**, *47*, 7393.

[16] a) F. N. Penkert, T. Weyhermüller, E. Bill, P. Hildebrandt, S. Lecomte, K. Wieghardt, *J. Am. Chem. Soc.* **2000**, *122*, 9663; b) Y. Miyazato, T. Wada, J. T. Muckerman, E. Fujita, K. Tanaka, Angew. Chem. **2007**, *119, 5830; Angew. Chem. Int. Ed.* **2007**, *46*, 5728; *Angew. Chem. Int. Ed.* **2007**, *46*, 5728; c) D. Adhikari, S. Mossin, F. Basuli, J. C. Huffman, R. K. Szilagyi, K. Meyer, D. J. Mindiola, *J. Am. Chem. Soc.* **2008**, *130*, 3676; d) C. Tejel, M. A. Ciriano, M. P. del Rio, D. G. H. Hetterscheid, N. Tsichlis i Spithas, J. M. M. Smits, B. de Bruin, *Chem. Eur. J.* **2008**, *14*, 10932.

[17] a) M. P. García, M. V. Jimenez, L. A. Oro, F. J. Lahoz, P. J. Alonso, *Angew. Chem.* **1992**, *104*, 1512; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1527; b) A. B. Danopoulos, G. Wilkinson, B. Hussain-Bates, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1992**, 3165; c) H. Zhai, A. Bunn, B. Wayland, *Chem. Commun.* **2001**, 1294; d) B. de Bruin, T. P. J. Peters, S. Thewissen, A. N. J. Blok, J. B. M. Wilting, R. de Gelder, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2002**, *114*, 2239; *Angew. Chem. Int. Ed.* **2002**, *41*, 2135; e) A. S. Ionkin, W. J. Marshall, *Organometallics* **2004**, *23*, 6031; f) D. G. H. Hetterscheid, J. Kaiser, E. Reijerse, T. P. J. Peters, S. Thewissen, A. N. J. Blok, J. M. M. Smits, R. de Gelder, B. de Bruin, *J. Am. Chem. Soc.* **2005**, *127*, 1895; g) N. P. Tsvetkov, M. F. Laird, H. Fan, M. Pink, K. G. Caulton, *Chem. Commun.* **2009**, 4578.

[18] A. Friedrich, R. Ghosh, R. Kolb, E. Herdtweck, S. Schneider, *Organometallics* **2009**, *28*, 708.

[19] R. Poli in *Recent Advances in Hydride Chemistry* (Hrsg.: M. Peruzzini, R. Poli), Elsevier, Amsterdam, **2001**, S. 139.

[20] a) P. Mura, *J. Am. Chem. Soc.* **1986**, *108*, 351; b) P. Mura, A. Segre, *Angew. Chem.* **1986**, *98*, 453; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 460.

[21] a) A. Albinati, V. I. Bakhmutov, K. G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D. G. Gusev, V. V. Grushin, B. E. Hauger, W. T. Klooster, T. F. Koetzle, R. K. McMullan, T. J. O'Loughlin, M. Pelissier, J. S. Ricci, M. P. Sigalas, A. B. Vymenits, *J. Am. Chem. Soc.* **1993**, *115*, 7300; b) D. Capitani, P. Mura, *Inorg. Chim. Acta* **1997**, *258*, 169.

[22] Owing to the small crystal size ($1 \times 1 \times 0.5\ mm^3$), the neutron-diffraction investigation was carried out on VIVALDI, the thermal-neutron Laue diffractometer at the ILL: a) C. Wilkinson, J. A. Cowan, D. A. A. Myles, F. Cipriani, G. J. McIntyre, *Neutron News* **2002**, *13*, 37; b) G. J. McIntyre, M.-H. Lemée-Cailleau, C. Wilkinson, *Phys. B* **2006**, *385–386*, 1055.

[23] G. Ujaque, A. C. Cooper, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1998**, *120*, 361.

[24] The valence-tautomeric description of diamagnetic **2** resulting from ligand centered oxidation of **1** and antiferromagnetic coupling of the ligand with the metal centre ($(L^4)^{\bullet}/Ir^{II}$) cannot be fully excluded. However, a broken-symmetry solution was not found by DFT, and the present experimental results (for example, the Ir–N bond lengths) do not point towards such an electronic structure. Thus, we prefer the more simple description $(L^4)^{-}/Ir^{III}$ (see also: M. Gallagher, N. L. Wieder, V. K. Dioumaev, P. J. Carroll, D. H. Berry, *Organometallics* **2010**, *29*, 591).

[25] B. Askevold, A. Friedrich, E. Herdtweck, A. Filippou, S. Schneider, unpublished results.

