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## COMMUNICATION

Syntheses and Electronic Structures of  $\mu$ -Nitrido Bridged Pyridine, Diimine Iridium Complexes

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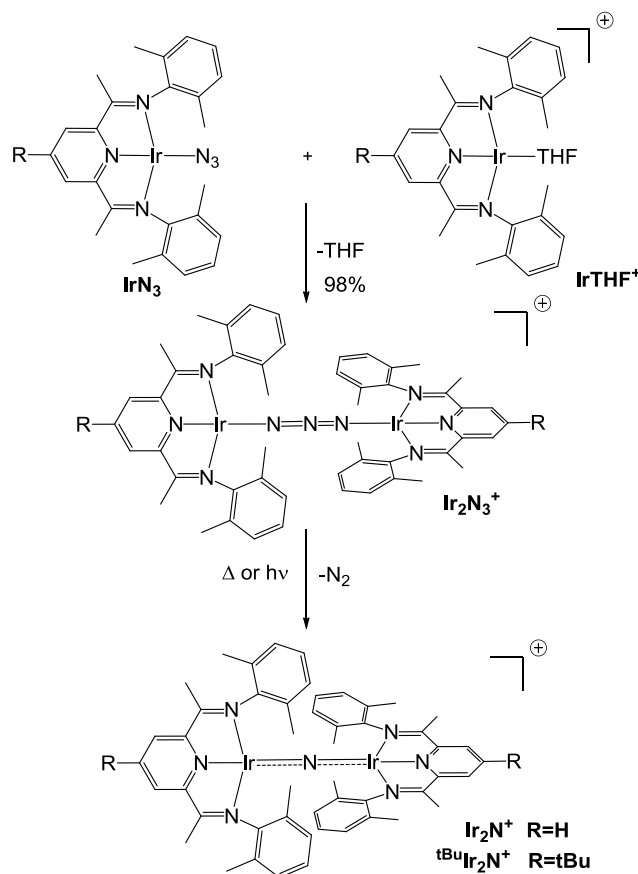
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The syntheses and X-ray crystal structures of dinuclear  $\mu$ -azido and  $\mu$ -nitrido bridged iridium complexes bearing the pyridine, diimine ligand (PDI) are reported. Their electronic structures and formal oxidation states of the metal centers are analyzed by theoretical and experimental methods, revealing the non-innocence of the PDI and nitrido ligands.

Recently, new members beyond group 8 were added to the yet small family of electron rich late transition metal nitrido complexes with a terminal  $M\equiv N$  unit.<sup>1-4</sup> Their unprecedented reactivity was first elucidated by our group in the hydrogenation of a formal  $d^6$ -configured sq.-pl. pyridine, diimine iridium(III) nitrido complex, (PDI)Ir $\equiv$ N, (IrN) to the amido congener.<sup>3</sup> The electronic structure of IrN was analyzed in experimental, theoretical and reactivity studies<sup>3-7</sup> and provided evidence for the non-innocence of the PDI ligand, which is well established in the literature.<sup>8</sup> Our recent study on the Si-H activation in silanes by the nitrido complex IrN revealed an ambiphilic propensity of the iridium nitrido moiety relating to both, a nucleophilic ( $N^{3-}$ ) and electrophilic ( $N^+$ ) center.<sup>7</sup> This corresponds to a formal change of the oxidation state by 4 units in the (PDI)Ir $\equiv$ N system. Therefore a non-innocent propensity can be ascribed also to the nitrido ligand. Herein, we analyze the oxidation state of the nitrido system by the theoretical localized orbital bonding analysis (LOBA), which was introduced by Thom et. al.<sup>9</sup> We will also apply it to a related dinuclear  $\mu$ -N-bridged iridium system,  $[(PDI)Ir_2\mu-N]^{+1,0,-1}$ , which displays variable electron configurations depending on its charge.

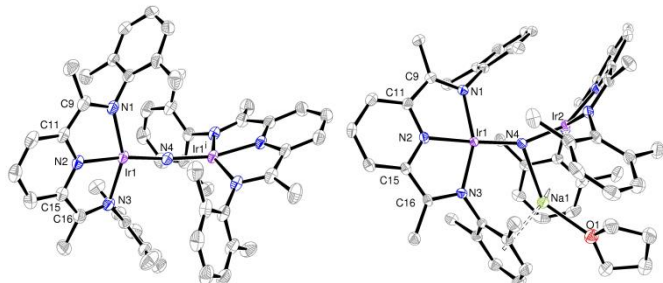
The syntheses of the previously unknown cationic  $\mu$ -azido and  $\mu$ -nitrido bridged dinuclear complexes are summarized in Scheme 1. The reaction of the terminal azido compound IrN<sub>3</sub> with the THF complex IrTHF<sup>+</sup> leads to the diamagnetic  $\mu$ -azido bridged product Ir<sub>2</sub>N<sub>3</sub><sup>+</sup>. The presence of the azido ligand was evidenced by an  $\nu(N_3)$  IR band at 2143 cm<sup>-1</sup>, its dinuclear structure was established by ESI mass spectrometry. The <sup>1</sup>H NMR spectrum of Ir<sub>2</sub>N<sub>3</sub><sup>+</sup> revealed a highly symmetrical environment consistent with either D<sub>2d</sub>- or D<sub>2h</sub>-symmetry. X-ray crystallography of Ir<sub>2</sub>N<sub>3</sub><sup>+</sup> (see ESI) revealed a perpendicular arrangement of the individual sq.-pl. ligand frameworks (D<sub>2d</sub>).



**Scheme 1.** Synthetic access to  $\mu$ -nitrido bridged compounds.

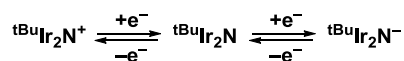
Both, photolysis or thermolysis of Ir<sub>2</sub>N<sub>3</sub><sup>+</sup> induce loss of dinitrogen and lead to the corresponding symmetrically  $\mu$ -nitrido bridged complex Ir<sub>2</sub>N<sup>+</sup>. The structural assignment of the dinuclear paramagnetic compound Ir<sub>2</sub>N<sup>+</sup> was assisted by X-ray crystallography (Fig. 1). The bridging  $\mu$ -nitrido unit is slightly bent and

displays an Ir1-N4-Ir1<sup>i</sup> angle of 167.3(2)° and an Ir-1N4 distance of 1.8067(3) Å. Related  $\mu$ -nitrido bridged systems were previously reported for Ru, Os and Ir complexes and display M-N <sub>$\mu$ -nitrido</sub> bond lengths in the range of 1.68–1.87 Å.<sup>10</sup> The value for **Ir<sub>2</sub>N<sup>+</sup>** is ca. 0.15 Å longer than the related Ir≡N bond (1.646 Å) in the terminal nitrido complex **IrN** and 0.15 Å shorter than the Ir-N<sub>azido</sub> bond in **Ir<sub>2</sub>N<sub>3</sub><sup>+</sup>** suggesting a bond order between 1–3. This is tentatively supported by the recorded  $\nu$ (Ir-N) vibrational stretch of 852 cm<sup>-1</sup>, which is red-shifted from the terminal  $\nu$ (Ir≡N) IR band at 958 cm<sup>-1</sup> observed in the mononuclear nitrido complex **IrN**.

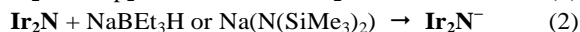
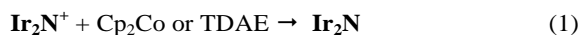


**Fig. 1.** Ortep representation of the  $\mu$ -nitrido bridged complexes **Ir<sub>2</sub>N<sup>+</sup>** (left) **Ir<sub>2</sub>N<sup>-</sup>** (right, 50% probability level). The triflate counterion of **Ir<sub>2</sub>N<sup>+</sup>**, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond distances in [Å] and angles in [°]: **Ir<sub>2</sub>N<sup>+</sup>**: Ir1-N4 1.8067(3); Ir1-N4-Ir1<sup>i</sup> 167.3(2). **IrN**: Ir1-N4 1.845(2); Ir2-N4 1.838(2); Ir1-N4-Ir2 156.3(1).

The cationic complex **Ir<sub>2</sub>N<sup>+</sup>** is paramagnetic and displays broad <sup>1</sup>H NMR resonances with a chemical shift range of +120 to -90 ppm at 298 K. The <sup>1</sup>H NMR data were consistent with a time averaged D<sub>2d</sub>-symmetrical structure with a linear  $\mu$ -nitrido bridge. The cyclic voltammogram of the *t*-butyl substituted derivative **tBuIr<sub>2</sub>N<sup>+</sup>** in THF revealed two reduction waves at -300 and -800 mV vs the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> redox couple. This corresponds to the electrochemical scheme shown below,



and sparked the idea to synthesize the singly and doubly reduced neutral and anionic complexes **Ir<sub>2</sub>N** and **Ir<sub>2</sub>N<sup>-</sup>**. The reaction of **Ir<sub>2</sub>N<sup>+</sup>** with either TDAE, ((NMe<sub>2</sub>)<sub>2</sub>C=C(NMe<sub>2</sub>)<sub>2</sub>) or cobaltocene provided indeed the neutral complex **Ir<sub>2</sub>N** in good yields (eq. 1).

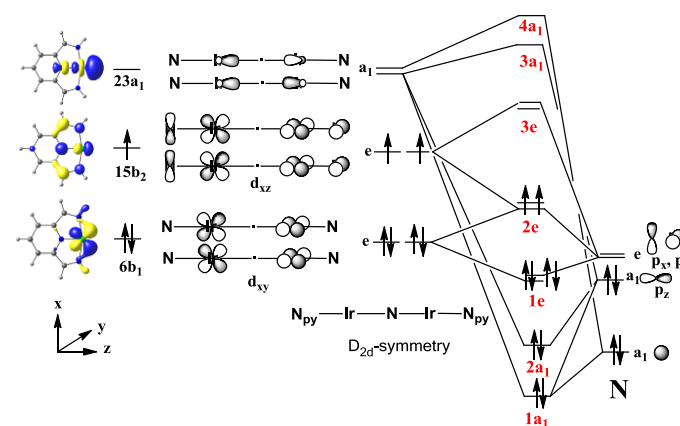


Further reduction of **Ir<sub>2</sub>N** with Na(N(SiMe<sub>3</sub>)<sub>2</sub>) or NaBEt<sub>3</sub>H as unconventional reducing agents led to the anionic  $\mu$ -nitrido bridged complex **Ir<sub>2</sub>N<sup>-</sup>** in 79–98 % yield (eq. 2). The neutral complex **Ir<sub>2</sub>N** can also be obtained in the comproportionation reaction of complexes **Ir<sub>2</sub>N<sup>+</sup>** and **Ir<sub>2</sub>N<sup>-</sup>** according to eq. (3). From the separation of the two redox waves  $\Delta\Delta E = 500$  mV in the cyclovoltammogram a comproportionation constant of  $K_c = 6.5 \cdot 10^8$  can be estimated from the previously established relation<sup>11</sup>  $K = 10^{(\Delta\Delta E/59\text{mV})}$  for the equilibrium according to eq. (3).

Due to the lack of single crystals for the open-shell, paramagnetic complex **Ir<sub>2</sub>N**, its structural assignment had to be based on X-band ESR-, NMR- and IR-spectroscopic, ESI-mass spectrometric and elemental analysis, which were fully consistent with our proposal. Besides the electrochemical and mass spectrometric

data further indirect support for a dinuclear structure was obtained from the X-ray analysis of the anionic congener **Ir<sub>2</sub>N<sup>-</sup>** (Fig. 1), as the  $\mu$ -nitrido bridged dinuclear structure is maintained in the anionic complex **Ir<sub>2</sub>N<sup>-</sup>**. In comparison with the cationic congener **Ir<sub>2</sub>N<sup>+</sup>** the bonds of the iridium centers to the central nitrido nitrogen atom are slightly elongated by 0.04 Å. The **Ir- $\mu$ N-Ir** bridging unit is slightly more bent than in the cationic complex **Ir<sub>2</sub>N<sup>+</sup>** (167.3°) and displays an angle of 156.3(1)°. This might be caused by the sodium counterion, which is weakly coordinated to the nitrido nitrogen atom N4. The coordination sphere of the sodium ion is completed by a THF ligand and two aryl rings of the ketimine unit, which bind in a  $\eta^6$ -fashion.

The assignment of the oxidation states, respectively the study of the non-innocence of the PDI and nitrido ligands was our central focus and was addressed through a combined analysis of the electronic, magnetic and structural properties of the  $\mu$ -nitrido bridged systems **Ir<sub>2</sub>N<sup>+</sup>**, **Ir<sub>2</sub>N**, **Ir<sub>2</sub>N<sup>-</sup>**. The most important results are summarized in Table 1, further details can be found in the ESI. The anionic  $\mu$ -nitrido bridged complex **Ir<sub>2</sub>N<sup>-</sup>** is diamagnetic, both of its neutral and cationic congeners **Ir<sub>2</sub>N<sup>+</sup>** and **Ir<sub>2</sub>N** are paramagnetic. For the open-shell system **Ir<sub>2</sub>N**, the X-band EPR signal at  $g = 1.95$  and the Curie-Weiss behaviour of the  $\nu T$  <sup>1</sup>H NMR shifts were consistent with a  $S = 1/2$  ground state.<sup>12</sup> The comproportionation constant  $K_c = 6.5 \cdot 10^8$  for eq. (3) corroborated a strongly electronically delocalized structure according to a Robin-Day class III system for **IrN**.<sup>13</sup> The paramagnetism of the even-electron complex **Ir<sub>2</sub>N<sup>+</sup>** on the other hand came as surprise. It manifested itself through a magnetic moment of  $\mu_{\text{eff}} = 3.23 \mu_B$  in THF solution, an X-band EPR-signal at  $g = 1.92$  and the large dispersion and temperature dependence of the <sup>1</sup>H NMR shifts. The  $\nu T$  <sup>1</sup>H NMR data for **Ir<sub>2</sub>N<sup>+</sup>** can be fitted to the Van-Vleck equation<sup>14</sup> for a  $S=0 \rightleftharpoons S=1$  spin equilibrium with a preference of ca. 4 kJ/mol for an open shell singlet ground state (vide infra). It was supported by broken symmetry DFT calculations for the unsubstituted D<sub>2d</sub>-symmetrical model system, which revealed an essentially energetically degenerate situation for the  $S=0$  and  $S=1$  states. The bonding scheme and magnetic properties in the  $\mu$ -nitrido bridged systems can be explained with aid of the MO diagram shown in Fig. 2.



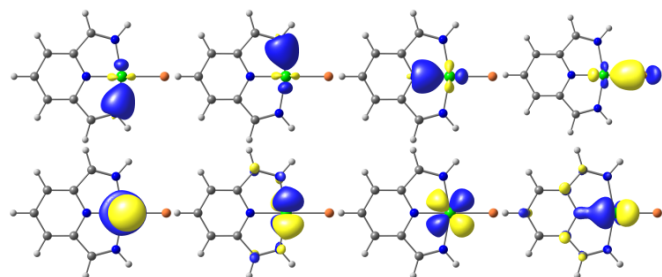
**Fig. 2.** Frontier orbitals of the open shell radical (PDI)Ir and qualitative bonding scheme in **Ir<sub>2</sub>N<sup>+1,0,-1</sup>** (diagram for **Ir<sub>2</sub>N<sup>+</sup>**)

The  $\mu$ -nitrido bridged system in Fig. 2 is assembled from the central nitrido nitrogen atom and two open-shell [(PDI)Ir] model fragments. For the latter a doublet ground state with a  $\pi$ -symmetrical SHOMO (15b<sub>2</sub>) was previously reported by us.<sup>3,4</sup>

The spin density is essentially located on the non-innocent PDI ligand with the electronic structure being best described as  $d^8$ -configured  $(\text{PDI})\text{Ir}^+(\text{I})$ . There are two further relevant orbitals in the frontier orbital region, the occupied  $d_{xy}$ -orbital ( $6b_1$ ) and the vacant metal centered  $\sigma$ -acceptor orbital  $23a_1$ . These orbitals are combined to three sets of symmetry adapted orbitals of  $e$  and  $a_1$  symmetry on the left hand side of Fig. 2 and are essential for binding to the nitrido ligand. Inspection of Fig. 2 immediately reveals that stable electronic situations can be obtained up to a total of 12 electrons. This holds for all the nitrido systems  $\text{Ir}_2\text{N}^+$ ,  $\text{Ir}_2\text{N}$ ,  $\text{Ir}_2\text{N}^-$ , which have 10, 11, and 12 electrons according to this scheme. The open-shell character of the cationic complex  $\text{Ir}_2\text{N}^+$  becomes immediately apparent since the degenerate  $2e$  orbital set is filled with  $2e^-$ .

The MO diagram presented in Fig. 2 also explains the observed diamagnetism of the anionic complex, in which the degenerate  $2e$  orbital set is fully occupied with 4 electrons. The interesting question remains, how many electrons can be assigned to the nitrido ligand, 4, 6, or 8? This will be addressed in our localized bond analysis (LOBA) below and will provide answers to both the oxidation state of the iridium center and the electronic configuration of the nitrido ligand, i.e.  $\text{N}^+$ ,  $\text{N}^-$  or  $\text{N}^{3-}$ .

The LOBA was introduced for the theory assisted assignment of oxidation states of metal centers in coordination compounds.<sup>9</sup> The procedure is straightforward for purely dative bonds with typical ligand contributions of  $> 70\%$ , the situation is complicated for covalent bonds, which approach a population of 50% for both bond partners. The latter situation is observed for the Ir-N<sub>nitrido</sub> bonding in our iridium nitrido systems (vide infra). As a benchmark for the LOBA the  $d^8$ -configured chlorido model complex  $(\text{PDI})\text{Ir}-\text{Cl}$  ( $\text{IrCl}$ ) was chosen. From a DFT calculation four distinct Pipek-Mezey localized molecular orbitals (LMOs) were identified (Fig. 3 top), which could be safely assigned to the ligands. There is also a set of 4 LMOs corresponding to the  $d_{z^2}$ ,  $d_{yz}$ ,  $d_{xy}$ ,  $d_{xz}$  orbitals as anticipated for a  $d^8$ -configured sq.-pl. system (Fig. 3 bottom). In the LOBA for the terminal nitrido complex  $\text{IrN}$  the same set of four ligand based orbitals was derived (see ESI). The situation for the metal centered orbitals is different, however. While the  $d_{z^2}$  and  $d_{yz}$  orbitals can be unambiguously assigned to the metal center summing up to 4 electrons, the situation for the  $d_{xy}$  and  $d_{xz}$  orbitals is severely more complicated. The values of 62% and 57% for the Mulliken population analysis (MPA) of the LMOs suggests a highly covalent character of the Ir-N<sub>nitrido</sub>  $\pi$ -bonds.



**Fig. 3.** LMOs (Pipek-Mezey) used in the LOBA of the  $\text{IrCl}$  model complex. Top: ligand based; bottom: metal centered LMOs (MPA:  $d_{z^2}$ (98%),  $d_{yz}$ (80%),  $d_{xy}$ (98%),  $d_{xz}$ (67%) left to right).

Note, that this view is consistent with the *ambiphilic* propensity of the nitrido unit observed in H-H, C-H, Si-H bond activation processes.<sup>3,6,7</sup> Two further electrons in  $\text{IrN}$  are stored in the non-inno-

cent PDI ligand. This was previously revealed from a theoretical analysis and experimentally from the relatively short exocyclic  $\text{C}_{\text{py}}-\text{C}_{\text{ini}}$  bond of 1.424 Å between the pyridine ring and the imine unit,<sup>3,5</sup> which was established by a variety of authors as clear diagnostic sign for electron transfer to the *thus* non-innocent PDI ligand.<sup>8</sup> Finally, it deserves a special mention that the LOBA of the nitrido complex  $\text{IrN}$  also gives a clear hint to the non-innocence of the (reduced) PDI ligand. This became aware through a PDI based LMO, which revealed MPA values of 70% for the nitrogen atom of the pyridine group, 24% for iridium and 7% for nitrido nitrogen atom (ESI). Note that this type of LMO is present in all other systems described herein, where the non-innocence of the PDI-ligand comes into play. The electrons of this unique LMO were therefore assigned to the non-innocent, i.e.  $\text{PDI}^{2-}$  ligand. This in full agreement with previous complementary XAS and XPS measurements which supported a  $d^6$ -configured Ir(III) center with an overall “ $(\text{PDI}^{2-})\text{Ir}^{(3+)}(\text{N})$ ” electronic structure.<sup>3,5</sup>

For the  $\mu$ -nitrido bridged systems an analogous analysis was performed. The X-ray photoelectron spectroscopy (XPS) data for  $\text{Ir}_2\text{N}^+$ ,  $\text{Ir}_2\text{N}$ ,  $\text{Ir}_2\text{N}^-$  display ionization energies (IEs) for the iridium  $4f_{7/2}$  component in the narrow range of 61.9 – 62.5 eV, the same holds for the  $4f_{5/2}$  component (Table 1). Although the IE for the cationic system  $\text{Ir}_2\text{N}^+$  is ca. 0.5 eV higher than the identical values for the neutral and anionic and nitrido complexes  $\text{Ir}_2\text{N}^+$  and  $\text{Ir}_2\text{N}^-$ , the data for all nitrido compounds compare well with experimental IEs of the  $d^8$ -configured chlorido and  $\mu$ -bridged azido Ir(I) congeners  $\text{IrCl}^5$  and  $\text{Ir}_2\text{N}_3^+$  (Table 1). For the two  $d^6$ -configured square-planar and octahedral PDI Ir(III) reference compounds significantly higher IEs of 63 eV for the Ir( $4f_{7/2}$ ) components were recorded (Table 1). Considering a typical increase of the IE of ca. 1 eV by the raise of the oxidation state by 1 unit, it can be assumed with some certainty that the oxidation states of the Ir centers in  $\text{Ir}_2\text{N}^+$ ,  $\text{Ir}_2\text{N}$ ,  $\text{Ir}_2\text{N}^-$  are definitely lower than +3. Based on the comparison with the Ir(I) reference compounds  $\text{IrCl}$  and  $\text{Ir}_2\text{N}_3^+$  a  $d^8$ -configuration is therefore suggested for the Ir centers in the dinuclear complexes  $\text{Ir}_2\text{N}^+$ ,  $\text{Ir}_2\text{N}$ ,  $\text{Ir}_2\text{N}^-$ .

**Table 1. Electronic properties of chlorido, azido and nitrido complexes.**

| Parameter                | $\text{IrCl}$ | $\text{IrN}$ | $\text{Ir}_2\text{N}_3^+$ | $\text{Ir}_2\text{N}^+$ | $\text{Ir}_2\text{N}$ | $\text{Ir}_2\text{N}^-$ |
|--------------------------|---------------|--------------|---------------------------|-------------------------|-----------------------|-------------------------|
| ground state             | S=0           | S=0          | S=0                       | S=0 <sup>a</sup>        | S=1/2                 | S=0                     |
| XPS [eV] <sup>b</sup>    |               |              |                           |                         |                       |                         |
| Ir( $4f_{7/2}$ , $5/2$ ) | 62.0          | 63.1         | 62.2                      | 62.5                    | 61.9                  | 61.9                    |
|                          | 65.0          | 66.0         | 65.0                      | 65.3                    | 64.8                  | 64.8                    |
| LOBA / ox.state          | Ir(I)         | Ir(III)      | Ir(I)                     | Ir(I)                   | Ir(I)                 | Ir(I)                   |
| PDI charge               | 0             | -2           | 0                         | -1                      | -1.5                  | -2                      |
| nitrido ligand           | -             | $\text{N}^-$ | -                         | $\text{N}^+$            | $\text{N}^+$          | $\text{N}^+$            |

<sup>a</sup> open shell singlet; <sup>b</sup>XPS of Ir(III) reference compound (see ESI).

The LOBA unveiled essentially identical situations for the metal centers in all bridging  $\mu$ -nitrido systems. The electrons of the LMOs corresponding to the  $d_{z^2}$ ,  $d_{yz}$ ,  $d_{xy}$  orbitals could be safely assigned to the iridium centers leading to (at least)  $d^6$ -electron configurations. As noted for the terminal nitrido complex  $\text{IrN}$ , the MPAs for the remaining LMOs ( $d_{xz}$ ) also revealed lower values for the Ir centers (62-64%) with contributions of 36-38% from the N<sub>nitrido</sub> atom. This makes an unambiguous assignment of the two bonding electrons to either of the bonding partners difficult. If evenly shared, this would result in  $d^7$ -electron configurations for the Ir centers. The LOBA also revealed the aforementioned PDI ligand based LMOs, elucidating reduced, i.e. non-innocent PDI ligands in the nitrido model systems for  $\text{Ir}_2\text{N}^+$ ,  $\text{IrN}$ ,  $\text{IrN}^-$ . This is consistent with the MO diagram for the open

shell system  $\text{Ir}_2\text{N}^+$  showing that additional electrons enter *PDI based orbitals*, which is also reflected in the experimental and calculated bond distances and orders of the  $\text{C}_{\text{py}}\text{-C}_{\text{imi}}$  and  $\text{C}_{\text{imi}}\text{-N}_{\text{imi}}$  bonds for the model systems of  $\text{Ir}_2\text{N}^+$ ,  $\text{Ir}_2\text{N}$ ,  $\text{Ir}_2\text{N}^-$  (see ESI). This view is further corroborated from inspection of the  $\text{M-N}_{\text{nitrido}}$  bond distances and orders, which display only small changes upon addition of electrons.

Taking the XPS data into account, the following electron configuration is anticipated for the cationic complex  $\text{Ir}_2\text{N}^+$ :

$[\text{((PDI}^{-1})\text{Ir}^+(\text{d}^8))_2\text{-}\mu\text{-N}^+(\text{s}^2\text{p}^2)]$ .

Note, that in this assignment the electrons of the LMO corresponding to the  $\text{d}_{xz}$ -orbital (vide supra) are fully assigned to the iridium centers. For the neutral and anionic congeners the electron configurations shown below are proposed:

$\text{Ir}_2\text{N}: [(\text{PDI}^{-1.5})\text{Ir}^+(\text{d}^8))_2\text{-}\mu\text{-N}^+(\text{s}^2\text{p}^2)]$

$\text{Ir}_2\text{N}^-: [(\text{PDI}^{-2})\text{Ir}^+(\text{d}^8))_2\text{-}\mu\text{-N}^+(\text{s}^2\text{p}^2)]$

The assignment of 1.5 negative charges to both PDI ligands in  $\text{Ir}_2\text{N}$  adheres to the strongly delocalized (Robin-Day class III) electronic structure evidenced from the electrochemical data.

## Conclusions

The nitrido iridium systems display strongly delocalized electronic structures. The LOBA allowed the assignment of the formal oxidation states of the Ir centers and revealed non-innocent PDI ligands,  $\text{N}^+$  nitrido nitrogen atoms and, electron-rich  $\text{d}^8$ -configured Ir(I) centers in the  $\mu$ -nitrido bridged systems. Their reactivity will be reported in due course.

## Notes and references

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Electronic Supplementary Information (ESI) available: [Details of the syntheses and characterization, X-ray-crystallographic data and DFT calculations can be found in the ESI]. See DOI: 10.1039/c000000x/

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