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Ir≡N Hydrogenation

Isolation and Hydrogenation of a Complex with a Terminal Iridium–Nitrido Bond[**]

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Dedicated to Robert G. Bergman on the occasion of his birthday

Electron-rich late-transition-metal complexes with terminal metal–nitrogen multiple bonds (M=N, M≡N) were considered unstable until only a few years ago. Owing to their postulated existence as transient intermediates in catalytic C−N and H−N bond-formation processes, their synthesis and study remains a highly desirable and challenging target. In this realm, the Haber–Bosch process, for which terminal ruthenium and iron nitrido units are considered active catalytic species, is of special interest.[1] These M≡N structures are formed by cleavage of dinitrogen at elevated temperatures and undergo hydrogenation to ammonia at a later stage. The direct observation by Cummins and Laplaza of dinitrogen cleavage at ambient temperature in d^3 Group 6 compounds to yield the corresponding d^0 metal complexes with metal nitrido triple bonds M≡N (M = Mo, W) was therefore a major achievement.[2] In contrast to these very stable nitrido compounds, terminal oxido and nitrido complexes of late transition metals are still very rare. In fact, only recently the groups of Hill and Milstein reported on d^6 palladium, platinum, and gold complexes with terminal M=O units,[3–6] extending an earlier study of an iridium(V) oxido system.[7]

The presence of vacant metal π-acceptor orbitals has been identified as key to the reactivity and stability of metal–ligand multiple bonding with π-donor oxido or nitrido ligands. For most coordination geometries only d^n electron configurations with $n < 6$ are compatible with this requirement.[8,9] Complexes with a d^4 electron configuration are borderline and include the recently isolated rare examples of Group 8 metals (Fe and Ru) with terminal nitrido ligands.[10–14] Examples for d^6 complexes with metal–nitrogen triple bonds have been reported for imido complexes.[15–18]

Herein, we report the synthesis, characterization, and reactivity of a square planar iridium complex (**1**, Scheme 1), which contains a terminal metal nitrido triple bond (M≡N). Complex **1** undergoes hydrogenation by molecular hydrogen to the corresponding amido complex **3**, which could have bearing on ongoing studies toward alternative Haber–Bosch catalysts.

A straightforward route to the iridium nitrido complex **1** entailed thermolysis of the corresponding green azido complex **2** in the solid state at 40 °C in vacuo (Scheme 1). Compound **2** is obtained in excellent yield by metathesis of the corresponding methoxido compound with trimethylsilylazide.[19]

The nitrido complex **1** was obtained in essentially quantitative yield as a violet, analytically pure sample. The sharp signals in the ^1H and ^{13}C NMR spectra and the observation of a resonance in the ^{15}N NMR spectrum at $\delta = 1117$ ppm (referenced to NH_3) for the nitrido ligand imply that complex **1** is diamagnetic.[20] The $\nu(\text{Ir}-\text{N}_{\text{nitrido}})$ vibrational band in the infrared spectrum as well as the Raman shift were observed at 958 cm^{-1} and confirmed by ^{15}N isotopic labeling in **1**-^{15}N, which displayed a $\nu(\text{Ir}-\text{N}_{\text{nitrido}})$ band at 929 cm^{-1}, giving an isotopic shift in the typical range of 30 cm^{-1}. This $\nu(\text{Ir}-\text{N}_{\text{nitrido}})$ band can be compared with $\nu(\text{Ir}-\text{N}_{\text{nitrido}}) = 1126\ \text{cm}^{-1}$ for the ligand-free diatomic compound Ir≡N generated in the gas phase, which displays an Ir−N bond length of 1.609 Å,[21] and with a $\nu(\text{Ru}-\text{N}_{\text{nitrido}}) = 1030\ \text{cm}^{-1}$ for a structurally related four-coordinate d^4 PNP Ru nitrido complex.[13]

The proposed C_{2v}-symmetrical geometry was confirmed by X-ray crystal structure analysis of complex **1** (Scheme 1).[22] The very short $\text{Ir}-\text{N}_{\text{nitrido}}$ (Ir1−N4) bond of 1.646(9) Å and the sum of angles around Ir of exactly 360°, which indicates a planar geometry, are the most prominent features of the molecular structure. The $\text{Ir}-\text{N}_{\text{pyridine}}$ bond (Ir1−N1, 2.007(6) Å) *trans* to the nitrido ligand is 0.1 Å longer than the average value for bonds of this type in related Rh and Ir chlorido complexes, which suggests a substantial *trans* influence of the nitrido group. In an otherwise unchanged geometry, this bond elongation is accompanied by a decrease of the angle between the diimine N donors and the Ir center to 150.6(3)° (N2-Ir1-N3). This type of deviation from perfect square-planar geometry has previously been observed and analyzed by our group.[23,24] It contributes to the enhanced π-acceptor properties of the iridium pyridine diimine frag-

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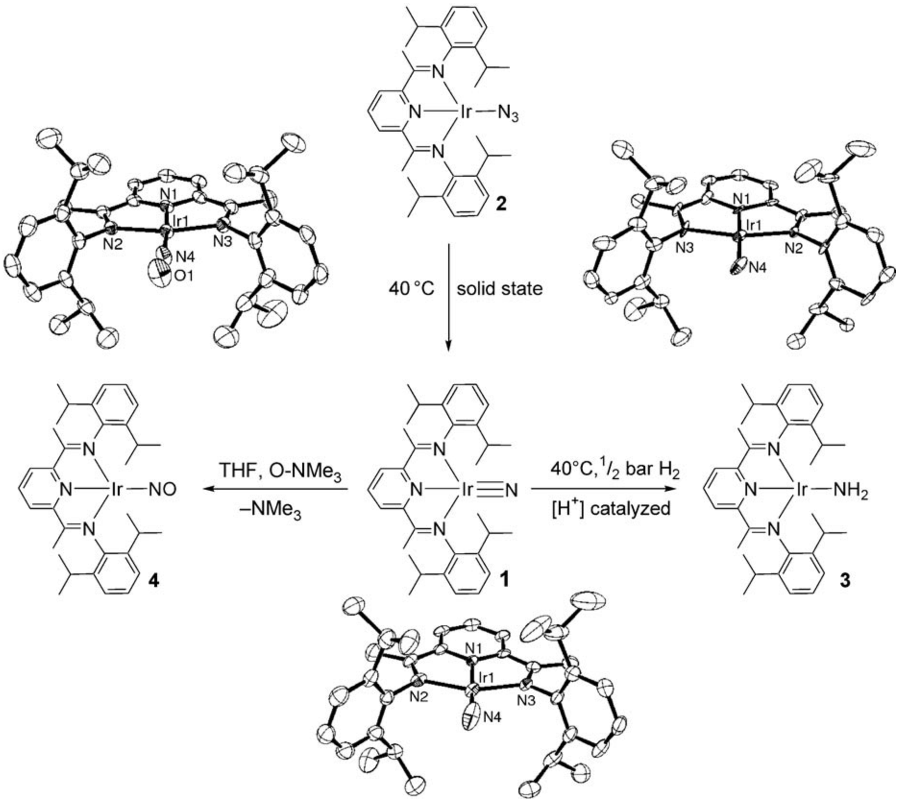

Scheme 1. Synthesis and reactivity of the iridium nitrido complex **1** and molecular structures of **1**, **3**, and **4** (thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted).

ment N_3Ir, thus increasing its tendency to host the strong nitrido π-donor ligand.

This view is corroborated by the results of density functional theory (DFT) calculations for the C_{2v}-symmetrical model complex **1**-H, which bears hydrogen atoms rather than aryl substituents at the pendant ligand nitrogen atoms. The calculations revealed a Mayer bond order of 2.3 for the Ir–$N_{nitrido}$ bond. Further support was gained from the partitioning of the Mayer bond order according to symmetry contributions. Values of 0.86 for the σ bond (a_1) and of 0.6 and 0.84 for the out-of-plane (b_1) and in-plane (b_2) π bonds, respectively, clearly document Ir–$N_{nitrido}$ multiple bonding. For the bond ellipticity according to the atoms-in-molecule (AIM) theory, a value of 0.05 is calculated at the Ir–$N_{nitrido}$ bond-critical point. This result is consistent with a rotationally symmetric electron density distribution and is in the same range as the triple bond in acetylene at the DFT level of theory.[25] Furthermore, the natural bond orbital (NBO) population analysis for **1**-H clearly revealed a triple Ir–N bond with sp hybridization of the terminal nitrogen atom, that is, with one lone pair located at the $N_{nitrido}$ donor.

Further evidence for the multiple-bond character of the Ir–$N_{nitrido}$ bond was obtained from the calculated bond enthalpy. For the Ir–$N_{nitrido}$ bond energy in complex **1** a value of 149 kcal mol^{-1} was obtained at the DFT level for the dissociation to the ^4S and $^4A_2$ quartet states of the nitrogen atom and the residual metal framework N_3Ir, respectively. Considering, however, that the $^4A_2$ state of the N_3Ir fragment lies 33 kcal mol^{-1} above the $S=1/2$ doublet ground state ($^2B_1$), then an estimate of 116 kcal mol^{-1} for the Ir–$N_{nitrido}$ bond dissociation enthalpy appears more appropriate. This view is fully supported by CASSCF(10,10) and consecutive multireference MCQDPT2 calculations for **1**-Me, a methyl-substituted model of complex **1**, which revealed a weighting of 84% for the leading configuration with an iridium nitrido triple bond (Figure 1). The bond order based on occupations of bonding and antibonding natural orbitals (Figure 1) was found to be 2.8. The preference of the doublet state for the N_3Ir fragment was also confirmed at these levels, with energy differences between the $S=1/2$ and 3/2 states of 31.9 and 44.7 kcal mol^{-1} at the CASSCF(10,10) and MCQDPT2 levels, respectively.

From the multireference calculations, a d-orbital population of 6.49 was obtained for **1**-Me, suggesting a d^6 electron configuration. This view is supported by X-ray photoelectron spectra, which afford an ionization potential of 63.1 eV for the Ir $4f_{7/2}$ component; a value of 62.0 eV was obtained for the corresponding iridium(I) chlorido complex. These results are further consistent with Ir L_1-edge X-ray absorption spectra, which yield a 1.5 eV increase of the position of the L_1 edge for the nitrido complex **1** relative to the lower (Ir^I) oxidation state of the amido complex **3**.[26]

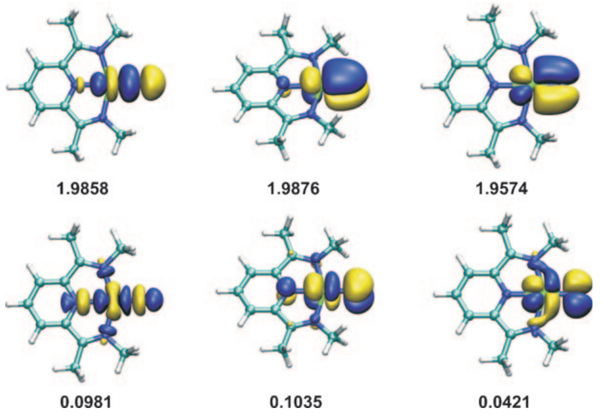

Figure 1. MCQDPT2 natural orbitals with occupation values corresponding to the multiple Ir–$N_{nitrido}$ bond for **1**-Me, in which the aryl substituents at the ligand nitrogen atoms of **1** are replaced with methyl groups (based on the CASSCF(10,10) reference wavefunction). Ir green, N blue, C teal, H white.

The thermal formation of the nitrido complex **1** was monitored by differential scanning calorimetry (DSC) and combined differential thermal gravimetry/mass spectrometry (DTGA/MS) measurements of the azido compound **2** (Figure 2). The moderate exothermic reaction (step 1) sets in at 40 °C and provides a value of $\Delta H = -6$ kcal mol^{-1} for the transformation **2**→**1**.

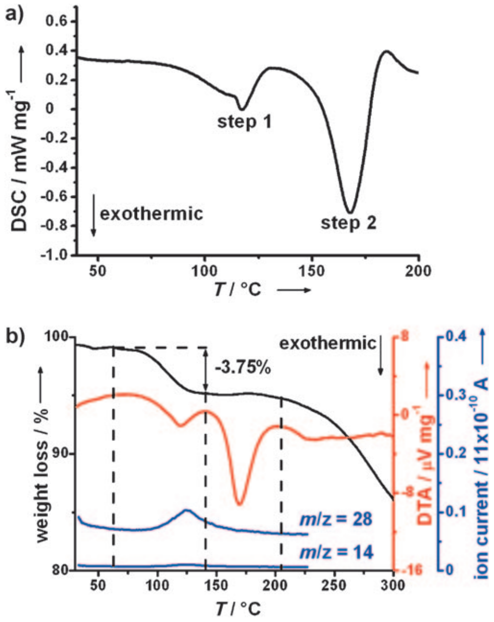

Figure 2. a) DSC and b) DTGA/MS measurements for the transformation **2**→**1**. Black: weight loss; red: DTA signal; blue: MS peaks $m/z = 28$ and 14.

This value is in agreement with the results of DFT calculations, which gave gas-phase reaction energies of −1 and −7 kcal mol^{-1} with the BP86 and B2PLYP DFT functionals. For the corresponding barrier, estimates of $\Delta E = 26$ and 29 kcal mol^{-1}, respectively, were derived at these levels of theory. The observation of a mass loss of $\Delta m = 3.75\,\%$ with concomitant appearance of a peak at $m/z = 28$ in the MS trace of the DTGA/MS experiment provided convincing support for the envisioned N_2 extrusion step, for which a value of $\Delta m = 3.91\,\%$ is expected. Subsequent to step 1, an additional strong exothermic reaction (step 2) with $\Delta H = -21$ kcal mol^{-1} takes places above $T > 168$ °C. The constant mass during step 2 suggests an intramolecular transformation.

Identification of the product formed in step 2 is currently underway, and a tuck-in (i.e. ligand C−H activated) structure is the anticipated product. The DSC measurements revealed that both steps 1 and 2 are irreversible for complex **2**.[19] For the isolated nitrido complex **1**, thermolysis (monitored by DSC) yielded a single irreversible exothermic step, with the same set-in temperature and exothermicity as step 2 of complex **2** ($\Delta H = -21$ kcal mol^{-1}, $T = 168$ °C). These results support the view that steps 1 and 2 have significantly different energy barriers, which explains the clean formation of the nitrido complex **1** by solid-state vacuum thermolysis of the azido compound **2** at 40 °C.

To explore the reactivity of the iridium nitrido moiety, we investigated reactions of **1** with H_2 and the oxygen transfer reagent trimethyl amine *N*-oxide, which resulted in the corresponding products **3** and **4**, respectively (Scheme 1). Prior DFT calculations at the BP86/DFT level predicted substantial exothermicity for these transformations: −60 kcal mol^{-1} for **1**→**3** and −66 kcal mol^{-1} for **1**→**4**. Whereas the formation of the nitrosyl complex **4** was essentially instantaneous at room temperature,[27] the reaction of **1** with H_2 to yield the amido complex **3** required several hours at 40 °C at an H_2 pressure of 500 mbar. Both **3** and **4** were isolated in nearly quantitative yields and were unambiguously identified by the results of single crystal X-ray diffraction experiments (Scheme 1). The linear bonding mode observed for the nitrosyl ligand in **4** is supported by the observation of a ν(NO) IR absorption band at 1759 cm^{-1} and the chemical shift in the ^{15}N NMR spectrum at $\delta = 569$ ppm. In the crystal structure of amido complex **3**, we observed an extension of the terminal Ir−N bond (Ir1−N4) to 1.926(13) Å from 1.646(9) Å in the nitrido complex.

For the conversion of **1** to **3**, the origin of the amido Ir−NH_2 protons in **3** was unambiguously confirmed by reaction of **1** with D_2. The exclusive formation the iridium amido Ir−ND_2 isotopologue (within the detection limits of ^{1}H NMR spectroscopy) clearly established the intermolecular reaction of **1** with D_2 (or H_2). The results of DFT calculations for the reaction pathway indicate direct attack of H_2 at the terminal nitrido unit without prior coordination of H_2 at the Ir center. The calculated activation barrier of 21 kcal mol^{-1} is consistent with the observed reaction time. The low-lying lowest unoccupied molecular orbital (LUMO) centered on the terminal nitrido group is essential for the reaction of **1** with the amine *N*-oxide and with H_2. This reactivity is best viewed through the f_+ Fukui function for the nucleophilic attack of **1**-H, which shows the most electrophilic region of a compound. For **1**-H, this region is located in the square plane at the nitrogen atom (Figure 3).[28]

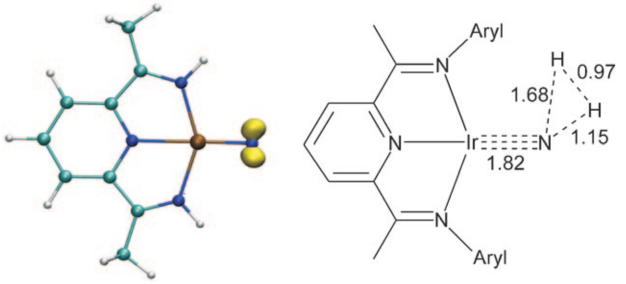

Figure 3. Fukui f_+ function for the model complex **1**-H (left; Ir brown, N blue, C teal, H white) and transition-state geometry for H_2 activation in complex **1** with selected distances [Å] (right).

The DFT-calculated value of 258 kcal mol^{-1} for the proton affinity of complex **1** at the Ir−N moiety surpasses the experimental value of 188 kcal mol^{-1} for acetonitrile significantly and is even higher than the proton affinity of trimethylamine (228 kcal mol^{-1}). This result implies substantial basic character of the iridium nitrido unit, which has yet to be verified experimentally.

For the protonated nitrido complex **1**-H$^+$, on the other hand, a lower barrier of only 8 kcal mol^{-1} (21 kcal mol^{-1} in the absence of protons) is predicted for the activation of H$_2$. This result was confirmed by preliminary experimental studies in the presence of a catalytic amount of acid, which revealed a tenfold increase in rate compared to the uncatalyzed reaction.[19]

We have presented the synthesis of a novel iridium nitrido complex and reported its unprecedented hydrogenation to the amido complex, which was traced by a combination of quantum chemical methods, physical measurements, and additional reactivity studies. Further investigations including the chemistry of the related rhodium congener and experiments related to the mechanism of the hydrogenation step will be reported in due course.

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[20] The calculated ^{15}N NMR shift of $\delta = 1154.2$ ppm at the DFT level of theory for complex **1**-H is in accordance with this value (for details see the Supporting Information). A similar good agreement of experimental and calculated data for nitrido complexes was reported: E. L. Sceats, J. S. Figueroa, C. C. Cummins, N. M. Loening, P. Van der Wel, R. G. Griffin, *Polyhedron* **2004**, *23*, 2751–2768.

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[22] Data collection: Bruker APEX single crystal diffractometer operating at 153(2) K, absorption corrections were carried out empirically with the SADABS program. Structure solution: Direct methods using the SHELX97 program package; refinement against F^2 with SHELX97 (G. M. Sheldrick, SHELXS97 and SHELXL97 programs for crystal structure solution and refinement, Universität Göttingen, Germany). All non-hydrogen atoms were refined anisotropically unless otherwise reported in the Supporting Information; the positions of the hydrogen atoms were calculated in idealized positions and refined using a riding model. Complex **1**: Dark violet needle ($0.31 \times 0.10 \times 0.07$ mm), monoclinic, space group $I2/a$ (No. 15), $Z = 8$, $a = 21.297(3)$, $b = 14.581(2)$, $c = 21.596(5)$ Å, $\beta = 98.844(2)°$ $V = 6627(2)$ Å^3, $\rho_{\text{calcd}} = 1.451$ g cm^{-3}. 37742 reflections collected, thereof 7529 independent; 7529 reflections used for structure solution and refinement. The refinement converged at final R values for reflections with $I > 2\sigma(I)$: $R1 = 0.056$ and $wR2 = 0.101$ for 384 parameters; GOOF, S, 0.97, residual electron density: 2.34, -2.22 e Å^3. Complex **2** (Ortep plot see the Supporting Information): Green rectangular parallelepiped ($0.5 \times 0.31 \times 0.26$ mm), triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $a = 10.0193(4)$, $b = 14.2066(1)$, $c = 15.9325(7)$ Å, $\alpha = 111.742(1)$, $\beta = 93.734(1)$, $\gamma = 104.285(1)°$. $V = 2010.3(2)$ Å^3, $\rho_{\text{calcd}} = 1.421$ g cm^{-3}. 53382 reflections were collected, 13601 independent reflections used for structure solution and refinement. Final R values (488 parameters) for reflections with $I > 2\sigma(I)$: $R1 = 0.026$ and $wR2 = 0.066$; GOOF, S, 1.04, residual electron density: 2.51, -1.97 e Å^3. Complex **3**: The crystals were of low quality; repeated attempts under varied conditions did not provide better single crystals. Green plate ($0.50 \times 0.36 \times 0.07$ mm), triclinic, space group $I2/a$ (No. 15), $Z = 8$, $a = 21.108(2)$, $b = 14.659(2)$, $c = 21.714(4)$ Å, $\beta = 99.003(2)°$. $V = 6636.2(2)$ Å^3, $\rho_{\text{calcd}} = 1.453$ g cm^{-3}. 38755 reflection were collected, thereof 7515 independent reflections used for structure solution and refinement. Final R values (380 parameters) for reflections with $I > 2\sigma(I)$: $R1 = 0.1191$ and $wR2 = 0.2510$. GOOF, S, 1.164, residual electron density: 4.87, -7.52 e Å^3. Complex **4**: Green rectangular parallelepiped ($0.50 \times 0.19 \times 0.14$ mm), monoclinic, space group $C2/c$ (No. 15), $Z = 8$, $a = 27.412(4)$, $b = 14.446(2)$, $c = 20.921(3)$ Å, $\beta = 129.036(2)°$, $V = 6439.9(17)$ Å^3, $\rho_{\text{calcd}} = 1.53$ g cm^{-3}. 37110 reflections collected, thereof 7359 independent; 7359 reflections used for structure solution and refinement. The refinement converged at final R values for reflections with $I > 2\sigma(I)$: $R1 = 0.035$ and $wR2 = 0.078$ for 376 parameters; GOOF, S, 1.034, residual electron density: 2.24, -1.64 e Å^3. CCDC 713135 (**1**), 713139 (**2**), 713136 (**3**), 713137 (**4**) contain the

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[26] Metrical parameters of the pyridine diimine (PDI) ligand for a variety of X-ray crystal structures of square-planar pyridine diimine iridium complexes including **1**–**4** are tabulated in the Supporting Information. On the basis of these data, the PDI ligand in the nitrosyl complex **4** can be described as non-innocent (reduced). For compounds **1**, **2**, and **3** the situation is less clear-cut; Mulliken population analysis of the Piepek–Mezzey localized molecular orbitals suggests a reduced (non-innocent) PDI^{2-} ligand in **1** as well. With this regard, see also: Q. Knijnenburg, S. Gambarotta, P. M. H. Budzelaar, *Dalton Trans.* **2006**, 5442 – 5448; D. Zhu, P. H. M. Budzelaar, *Organometallics* **2008**, *27*, 2699 – 2705. The assignment of the iridium oxidation state in **1** is further complicated by the fact that the iridium nitrido σ bond is polarized toward nitrogen atom while the π bonds are polarized toward the Ir center. We therefore prefer the notation. $\{\mathrm{Ir\text{-}N}\}^4$, which was introduced for electron bookkeeping in metal nitrosyl complexes and also applied by Wieghardt's group for transition-metal nitrido compounds (see J. Bendix, K. Meyer, T. Weyhermüller, E. Bill, N. Metzler-Nolte, K. Wieghardt, *Inorg. Chem.* **1998**, *37*, 1767 – 1775). The number 4 equals the number of d electrons in the $\{\mathrm{Ir\text{-}N}\}^4$ moiety in which the nitrido group is counted as triply charged N^{3-} two-electron donor ligand and with two electrons being donated from the Ir center to the PDI ligand (PDI^{2-}). In the $\{\mathrm{Ir\text{-}N}\}^4$ notation, no assumption is made about the actual distribution of electrons between the iridium center and the nitrido group.

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