Coupling of terminal iridium nitrido complexes†

Josh Abbenseth,a Markus Finger,a Christian Würtele,a Müge Kasanmascheffb and Sven Schneider*a

The oxidative coupling of nitride ligands (N3−) to dinitrogen and its microscopic reverse, N2-splitting to nitrides, are important elementary steps in chemical transformations, such as selective ammonia oxidation or nitrogen fixation. Here an experimental and computational evaluation is provided for the homo- and heterocoupling of our previously reported iridium(IV) and iridium(V) nitrides [IrN(PNP)]n (n = 0, +1; PNP = N(CHCH2PtBu2)) All three formal coupling products [(PNP)IrN2Ir(PNP)]n (n = 0–+2) were structurally characterized. While the three coupling reactions are all thermodynamically feasible, homocoupling of [IrN(PNP)]+ is kinetically hindered. The contributing parameters to relative coupling rates are discussed providing qualitative guidelines for the stability of electron rich transition metal nitrides.

Introduction

The splitting of dinitrogen at ambient temperatures is a highly attractive reaction in the context of nitrogen fixation, yet still represents a challenging goal. Ever since the seminal work of Cummins and co-workers about 20 years ago, several other systems were reported to undergo the splitting of dinitrogen into well-defined nitrido complexes. The first reported and intensively examined example proceeds through diazenido dimer [(ArBuN)3Mo(NN)Mo(ArBuN)3]. Importantly, this linear μ-N2 complex holds 10 π-electrons in the {MNNM}-core (Fig. 1a), finally resulting in the closed-shell nitride [NMo(NArBu)3]. In comparison, the dimers [(ArBuN)3Mo (NN)Mo(NArBu)3]n+ (n = 1–2) exhibit stronger degrees of N2 activation due to depletion of a molecular orbital that is N–N antibonding in character. However, N2-splitting is not observed due to destabilization of the nitrides upon oxidation. Similarly,

![Image of molecular orbitals](image-url)

**Fig. 1** Qualitative molecular orbitals relevant for N2 splitting with Cummins’ complex (a) and schematic transition states that were proposed for N2-splitting/coupling (b–d).

---

*Sven Schneider

†Electronic supplementary information (ESI) available: Spectroscopic, electrochemical, kinetic, and mass spectrometric data and crystallographic and computational details. CCDC 1437698 and 1437699. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5qi00267b
Nishibayashi and co-workers examined the redox series 
\[ ([\text{depf}]_2\text{Cp}^+\text{Mo}(\text{NN})\text{MoCp}^+\text{(depf})_2]^{n+} \]  
\((n = 0 \to 2)\); depf = 1,1’-bis(di-ethyolphosphino)ferrocene), observing \( N_2 \) splitting for the 
10 \( \pi \)-electron system \((n = 0)\) and the reverse, nitride coupling, 
after oxidation of the resulting nitride.\(^3\d\)

A similar picture arises for the reverse reaction, \( i.e. \) the 
coupling of terminal nitrides. Several authors reported the 
fraction of dinitrogen bridged complexes upon reductive coupling 
of octahedral \( M \) nitrides \((M = \text{Fe, Ru, Os})\).\(^6\) These 
transient nitrides are typically formed \( \textit{in situ} \), \( e.g. \) by photolysis of 
\( M^{\text{VII-azides}}, \) reduction of stable \( M^{\text{VI-}} \) nitrides or oxidation of 
low-valent ammine complexes to give divalent \((\{M^{\text{VII}}N_2\} \) or 
\( \{M^{\text{VI}}N_2M^{\text{VI}}\})\) or mixed valent \( \{M^{\text{VII}}N_2M^{\text{VII}}\} \) dinitrogen complexes. 
Except for a few cases, it is not fully clear whether the reaction proceeds via 
\( M^{\text{VII=V}} \) homocoupling or coupling of \( M^{\text{VII=VI}} \) with 
parent \( M^{\text{VII=V}} \). Importantly, within the simplified MO-picture 
(Fig. 1a) the \( M^{\text{VII}} \) and \( M^{\text{VI-VI}} \) dinitrogen bridged complexes 
represent 12 and 11 \( \pi \)-electron \( \{MNNM\} \)-cores, respectively. 
However, some closed-shell nitrides also decay by nitride coupling 
underlining that the electronic configuration is not the only 
predictor for the thermochemistry of \( N_2 \)-splitting/coupling.\(^7\)\(\text{-}^9\)

In comparison, the relationship of electronic structure and 
kinetics received less attention. Ware and Taube examined the 
thermal decomposition of \([\text{Os}^\text{VII}N\text{Cl}_3(\text{py})_2]\) by nitride coupling to 
\([\text{Os}^\text{VII}N\text{Cl}_2(\text{py})_2]\).\(^7\) They pointed out that donation from a 
nitride lone-pair into an empty \( M \) \( \pi \)-orbital should be 
favored over a collinear approach of the two monomers and 
therefore proposed a semi-bent transition state (Fig. 1b). In 
line with such a polar transition state (TS), Seymour and Brown 
showed that heterocoupling of electrophilic \( \text{Os}^\text{VI-} \) and nucleophilic \( \text{Os}^\text{VII-} \) 
moieties proceeds \( \textit{via} \) a non least-motion pathway 
or in-plane zig-zag TS, which features mutual \( \pi / \sigma \) donor–acceptor interactions of the 
two monomer fragments (Fig. 1c).\(^11\)

Recently, we reported that photolysis of the iridium(\(u\)) azide 
\([\text{Ir}_2N_2]\)(PNP)\(^1\) results in the formation of iridium(\(v\)) nitride \([\text{Ir}^\text{III}(\text{PNP})]\) \(2, \) Scheme 1).\(^1\) Spectroscopic and computational analysis suggested that 2 and 
the analogous rhodium compound are \( \pi \)-radicals with strong de-localization of the unpaired electron over the \( M^{\text{VII=VII}} \) core, \( i.e. \) considerable “nitridyl” character.\(^12,13\) In solution, these transi-

tent nitrides undergo clean coupling, \( e.g. \) to 12-\( \pi \)-electron \( N_2 \)- 
complex \([N_2^\text{Ir}(\text{PNP})]\) \(3\) \( \) in case of 2 (Scheme 1). The 
computed TS for a \( \text{PMe}_2\)-truncated model featured a mutual \( \pi / \pi \) 
MO-interaction as the most favorable pathway with an out of 
plane zig-zag arrangement of the two monomer radicals (Fig. 1d).\(^12\) Alternatively, oxidation of 1 
results in formation of isolable iridium(\(v\)) nitride \([\text{Ir}^\text{III}(\text{PNP})]\) \(4, \) which in turn also 
gives 2 upon reduction (Scheme 1). In this context, we were 
interested whether the enhanced thermal stability of 4 can be 
attributed to thermodynamic or kinetic arguments. Here, we 
present a systematic experimental and computational study 
that addresses the stability of the iridium nitrides with respect 
to oxidative coupling.

**Results and discussion**

**Synthesis of the \([N_2^\text{Ir}(\text{PNP})]\)\(^{n+} \) \((n = 0 \to 2) \) redox series**

In a slightly improved synthetic protocol, the neutral dimer 3 
can be obtained analytically pure in 66\% yield on the 
iridium(\(v\)) nitride reduction route using \( \text{Na/Hg} \) with strict 
 exclusion of light. Complex 3 was characterized by cyclic voltammetry 
(CV, see ESI†). The CV reveals three oxidative redox processes at 
\( E_{1/2} = -0.27, 0.18, 0.35 \) \( V \) \( \text{vs. FeCp}_2/\text{FeCp}_2 ^+ \), respectively. While the 
\( \text{Ir}^{IV^+=IV} \) couple is fully reversible at \( r.t. \), the higher 
oxidations seem pseudo-reversible, as evidenced by the observation 
of small additional peaks upon cyclic back to low potentials. 
Hence, the electrochemical results suggest, that one- and 
two-electron oxidation of 3 could give isolable products.

Chemical oxidation of 3 with one equivalent of \( \text{FeCp}_2\)PF\(_6\) 
in dichloromethane at \( -35 \) °C affords the isolation of \( \text{Ir}^{IV^+=IV} \) 
\( N_2 \)-complex \([N_2^\text{Ir}(\text{PNP})]\)\(^4\) (5) as a temperature, light, and air 
sensitive dark green solid (Scheme 2). The X-band EPR spectrum 
of 5 in frozen solution (4 K) reveals a rhombic signal 
corresponding to an \( S = 1/2 \) system (ESI†). The large anisotropy 
of the \( g \)-tensor (\( g_x = 2.66, g_y = 2.12, g_z = 1.62 \)) without resolved 
 hyperfine coupling was similarly observed for several \( \text{Ir}^{III}(\text{PNP}) \) 
complexes with square-planar geometry.\(^5,14\) From the CV data 
a comproportionation constant \( K_C \) is estimated to be around 
\( 10^4 \). A large \( K_C \) like this is frequently stressed as a simple 
 predictor for electronic delocalization in the mixed valent 
complex indicating stabilization due to resonance exchange.\(^15\) 
Note that \( K_C \) data should be treated with caution and is easily 

---

**Scheme 1** Syntheses of iridium(\(v\)) and iridium(\(v\)) PNP nitrides 2 and 4 
and coupling to iridium(\(l\))/iridium(\(l\)) \( N_2 \)-complex 4.\(^12\)

**Scheme 2** Chemical oxidation of iridium(\(l\))/iridium(\(l\)) \( N_2 \)-complex 3.
over-interpreted due to the many other parameters possibly contributing to electrochemical potentials.\(^6\) In fact, the bond parameters in the solid state indicate valence localization in the crystal (see below) and the DFT model of 5 also exhibits localization of the spin density on one of the two Ir(PNP) moieties (ESI\(^\dagger\)). In contrast, the \(^1\)H NMR spectrum of 5 exclusively shows one set of paramagnetically shifted and broadened pincer ligand peaks (ESI\(^\dagger\)), suggesting rapid electron transfer between the N\(_2\)-bridged moieties on the NMR timescale (1–10\(^{-4}\) s). Unfortunately, detailed analysis of the NMR spectrum was hampered by the thermal instability of 5 and dication 6 (see below) and did not allow for a reliable assignment of intercalence charge transfer vs. interconfigurational electronic transitions. However, IR spectroscopy reveals the presence of a relatively intense band assignable to the N\(_2\) stretching vibration both in solution (CH\(_2\)Cl\(_2\): 1959 cm\(^{-1}\)) and in the solid state (nujol: 1960 cm\(^{-1}\)). The assignment was confirmed by DFT computations (ESI\(^\dagger\)) scaled to monomeric complex [Ir(N\(_2\))\(\{\text{PNP}\}\)] (2077 cm\(^{-1}\));\(^1\)\(^2\) The experimental shift \(\Delta\nu\)\(_{N2}\) = 117 cm\(^{-1}\) is well reproduced by DFT (\(\Delta\nu\)\(_{N2}\) = 115 cm\(^{-1}\)). This comparison also excludes the formation of monomeric [Ir(N\(_2\))\(\{\text{PNP}\}\)]\(^\ast\), which should be blue shifted with respect to [Ir(N\(_2\))\(\{\text{PNP}\}\)]. Importantly, the observation of an N\(_2\)-stretch confirms the presence of a permanent dipole, hence valence localization on the IR-timescale (∼10\(^{-14}\) s) also in solution providing an upper limit for the charge transfer rate. Similar properties between localized and delocalized mixed-valence (Class II–III) were found for N\(_2\)-bridged Os\(^{III}\) complexes.\(^1\)\(^7\) Unequivocal assignment of complex 5 requires further investigations.

Confirmation of the molecular structure of 5 is provided by single-crystal X-ray diffraction (Fig. 2 and Table 1). Both Ir ions are in distorted square-planar coordination geometries and bridged by a linear, end-on bound N\(_2\), as in parent 3. The structure features two crystallographically distinctly different Ir(PNP) fragments. For example, the Ir–N\(_{\text{PNP}}\) and Ir–N\(_{\text{N2}}\) distances differ by 0.06 Å and 0.11 Å, respectively. Ir2 exhibits a longer bond to the PNP \(\pi\)-donor ligand and a shorter bond to the \(\pi\)-acceptor N\(_2\) than Ir1. In that respect, Ir2 behaves similar to Ir in 3. Hence, the structural parameters suggest trapped oxidation states in the solid state with Ir1 and Ir2 being associated with the +2 and +1 valence states, respectively. Importantly, the N–N distance (1.136(6) Å) is identical with that in 3 (1.135(4) Å and in [N\(_2\)Ir(\text{PCP})]\(_2\) (1.134(2) Å; PCP = C\(_6\)H\(_{12}\)2,6-\((\text{CH}_2\text{PBu}_{3})_2\))\(^1\)\(^8\) and close to free N\(_2\) (1.097 Å) revealing a weak degree of N\(_2\)-activation upon oxidation.

The reaction of 3 with two equivalents of AgSbF\(_4\) at −70 °C in dichloromethane under the exclusion of light results in the immediate precipitation of metallic silver and formation of a deep red solution (Scheme 2). Monitoring by \(^1\)H NMR spectroscopy reveals the formation of a new paramagnetic compound with one set of signals assignable to a PNP pincer ligand, yet not as clean as in case of 5 (ESI\(^\dagger\)). No signals were found by X-band EPR spectroscopy as expected for a non-Kramers system. Decomposition in solution above −50 °C into several unidentified paramagnetic compounds is indicated by new \(^1\)H NMR signals upon warming. Importantly, the nitride 4 was not found as decomposition product.

The high lability of the product from double oxidation with respect to ambient temperatures and light hampered a more detailed spectroscopic characterization, so far. However, crystallization at low temperatures afforded red crystals of the dinitrogen bridged Ir\(^{III}\) complex [(N\(_2\))Ir(PNP)]\(_2\)[SbF\(_6\)]\(_2\) (6) that were suitable for X-ray diffraction. In contrast to mixed-valent complex 5, the molecular structure of 6 (Fig. 3 and Table 1)

---

**Table 1** Comparison of selected experimental and computed bond lengths and angles of 3, 5, and 6

<table>
<thead>
<tr>
<th></th>
<th>3(^a)</th>
<th>5(^a)</th>
<th>6(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp</td>
<td>DFT</td>
<td>Exp</td>
</tr>
<tr>
<td>Bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir–N(_2)</td>
<td>1.937(3)/1.933(3)</td>
<td>1.922</td>
<td>1.984(5)/1.878(5)</td>
</tr>
<tr>
<td>Ir–N(_{\text{PNP}})</td>
<td>2.041(3)/2.035(3)</td>
<td>2.055</td>
<td>1.973(4)/2.031(4)</td>
</tr>
<tr>
<td>N–N</td>
<td>1.135(4)</td>
<td>1.136</td>
<td>1.136(6)</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir–N(<em>2)–N(</em>{\text{PNP}})</td>
<td>174.6(2)/172.3(3)</td>
<td>172.8</td>
<td>175.3(4)/174.6(4)</td>
</tr>
<tr>
<td>N–Ir–N(_2)</td>
<td>173.6(2)/171.0(1)</td>
<td>172.0</td>
<td>172.8(2)/173.3(2)</td>
</tr>
</tbody>
</table>

\(^a\)Computed spin ground-states: \(^1\)3, \(^5\)5, \(^6\)6.
features two crystallographically equivalent Ir(PNP) fragments. The Ir–NPNP (1.983(3) Å) and Ir–NN2 (1.954(3) Å) bond lengths are very close to those of Ir1 in 5, supporting the valence state assignments for the structure of 5 and full oxidation of 6 to IrII/II. The N2 bond length (1.138(6) Å) is identical within error compared to the parent IrII (1.135(4) Å) and IrI/II (1.136(6) Å) complexes, indicating that N2 activation is negligible within the [N2{Ir(PNP)}2]n+ (n = 0–2) redox series.

Nitride coupling to [N2{Ir(PNP)}2]n+ (n = 0–2)

The successful preparation of 5 and 6 and the absence of N2 activation upon oxidation of 3 suggest that the iridium(v) nitride 4 is only kinetically stabilized with respect to coupling. We previously reported the kinetics of iridium(IV) nitride coupling (Scheme 3, A): A second order rate-law in 2 was found with a rate constant at room temperature k = 1.1(2) M⁻¹ min⁻¹.

Scheme 3  Nitride coupling reactions examined.

Hence, this reaction is accompanied with a moderate kinetic barrier around ΔG‡298 K = 22 kcal mol⁻¹. In contrast, very slow decay is observed for iridium(v) nitride 4 over several days at elevated temperatures in dichloromethane, into several unidentified products. Furthermore, in contrast to 2, decomposition of 4 follows a rate law that is first-order in 4 (k = 0.474(9) d⁻¹; ESI†). Hence, the nitride coupling rate (Scheme 3, C) could not be directly derived, but the decomposition rate allows for an estimate of a lower limit for the kinetic barrier of nitride coupling (ΔG‡313 K > 25 kcal mol⁻¹).

Coupling of the iridium(IV) and iridium(V) nitrides to mixed-valent 5 was also examined (Scheme 3, B). Spectro-electrochemical reduction of 4 (Ered = −0.86 V) at room temperature results in clean conversion to IrI/II complex 3 (Eox = −0.27 V). The observation of an isosbestic point at 560 nm indicates the absence of long-lived intermediates on the experimental time-scale (ESI†). Moreover, the equimolar addition of 2 to 4 at −70 °C, where both pure nitrides are kinetically stable, results in immediate coupling to 5 (ESI†) confirming much more rapid coupling to 5 than to 3 or 6. Even the addition of a substoichiometric amount of 4 (10 mol%) to 2 at −70 °C results in the immediate formation with dimer 3 as the main product (ESI†). This observation can be rationalized with a redox-catalytic cycle (Scheme 4): Nitrides 2 and 4 undergo rapid coupling. The resulting dimer 5 is then reduced by starting material 2 to restore catalyst 4, which is in line with the potentials of redox couples 2/4 and 3/5, respectively. This mechanism also explains a previously reported observation for the two routes to iridium(IV) nitride 2 (Scheme 1): Unlike the photolysis route, the reduction route also yields considerable amounts of coupling product 3, even at low temperatures where coupling of pure 2 is not observed.

Computational results

Our experimental results demonstrate a clear succession in nitride coupling rates (kB > kA > kC). This result was rationalized by means of density functional theory (DFT). The ener-
etics of the three coupling reactions (Scheme 3, A–C) were examined by DFT computations on the D3BJ-PBE0(Cosmo (THF))/def2-TZVP/D3BJ-PBE0/def2-SVP level of theory. The molecular structures of dimers 3, 5 and 6 are well reproduced with singlet (3), doublet (5) and triplet (6) ground states, respectively (Tables 1 and 2 and ESI†). Ferromagnetic coupling ($J = 39 \text{ cm}^{-1}$) of the iridium(u) ions in 6 results in the triplet state being slightly more stable than the open shell singlet state by 0.4 kcal mol$^{-1}$. The computed electronic ground states resemble the simplified picture that arises from symmetry considerations (Fig. 1) for 12 (3, 11 (5) and 10 (6) π-electron configurations, respectively. Accordingly, the geometry of 5 is distorted along the Ir–N–N–Ir axis avoiding uneven occupation of degenerate π-MOs. Similarly, coplanar arrangement of the two Ir(PNP) fragments would also lift π-electron degeneracy due to mixing of the Ir–N–N–Ir π-manifold with PNP nitrogen lone pairs. While such a coplanar conformation is not accessible with bulky PrBu$_3$ groups (see below), the PMe$_2$-truncated model of 5 favors such a conformation, emphasizing the importance of considering the full model.

Computational evaluation of reactions A–C (Scheme 3) fully reproduces our experimental results (Table 2 and ESI†). Nitride coupling is thermodynamically strongly favored for all three reactions. However, the driving force within the redox series 3 ($\Delta G_{298} = -101.5$ kcal mol$^{-1}$), 5 ($\Delta G_{298} = -97.1$ kcal mol$^{-1}$), and 6 ($\Delta G_{298} = -73.9$ kcal mol$^{-1}$) decreases, as expected from the destabilizing population of an Ir–N π*-anti-bonding orbital in 2. For reaction A, a kinetic barrier was computed ($\Delta G^2_{298} = 21.0$ kcal mol$^{-1}$) that is in excellent agreement with experiment (≈ 22 kcal mol$^{-1}$).$^{12}$ It mainly arises from the entropic contribution with only a small electronic fraction. The transition state, $^{1}\text{BS}(1,1)\text{TSA}$ (Fig. 4A), was located on the open shell singlet surface at a rather long N–N distance (2.06 Å). The spin is eventually quenched at significantly smaller N–N distances, leading to the closed shell ground state of dimer 3. The TS structure features the two Ir(PNP) monomer fragments being essentially perpendicular to each other. The two Ir–N groups are offset from collinearity along both relative orientations of the Ir(PNP) planes resulting in an out-of-plane zig-zag transition state. The orthogonalized sets of natural frontier orbitals represent hybrid orbitals from SOMO/LUMO mixing of the nitride monomers. π/π-Orbital overlap between the two monomers is further increased by slightly tilting the two monomer fragments towards each other (Ir–N–Ir dihedral angle: 152°). The previously computed PMe$_2$-truncated model of reaction A also gave a good agreement for the driving force ($\Delta G_{298} = -108.2$ kcal mol$^{-1}$) but underestimation of the reaction barrier ($\Delta G^2_{298} = 13.7$ kcal mol$^{-1}$).$^{11}$ In fact, the smaller model featured a distinctly different conformation for the TS with almost coplanar relative orientation of the two monomers. However, the minute electronic contributions to biradical coupling is almost identical for both models, while the entropic contribution seems underestimated in case of the small model presumably due to steric constraints for vibrational and rotational degrees of freedom of the PrBu$_3$ groups in the TS.

Coupling of $^2$$^2$ to $^2$$^4$, was computed to be essentially electronically barrierless with a free energy of activation $\Delta G^2_{298} = 10.1$ kcal mol$^{-1}$, confirming the experimentally observed rapid coupling reaction B. The transition state $^2\text{TS}_{\text{B}}$ (Fig. 4B) exhibits strong structural similarities with $^{1}\text{BS}(1,1)\text{TSA}$ concerning the N–N distance ($D_{\text{N–N}} = 2.00$ Å) and the out-of-plane zig-zag relative orientation of the two nitride fragments (Ir–N–Ir dihedral angle: 142°). Accordingly, $^2\text{TS}_{\text{B}}$ also features a π/π-interaction between the two monomers, here arising from orbital overlap of the SOMO (2) and LUMO (4) monomer orbitals, respectively. The spin density is equally distributed over

---

**Table 2** Calculated reaction electronic energies ($\Delta E$ including zero point energy) and free energies ($\Delta G$) for the coupling reactions A–C in kcal mol$^{-1}$ and N–N distances in the transition states ($D_{\text{N–N}}$ in Å)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A $^{2+2 \rightarrow 1^3}$</th>
<th>B $^{2+4 \rightarrow 2^5}$</th>
<th>C $^{1^4+1^4 \rightarrow 1^6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>$\Delta G_{298}$</td>
<td>$\Delta E$</td>
<td>$\Delta G_{298}$</td>
</tr>
<tr>
<td>TS</td>
<td>6.9$^{a}$</td>
<td>21.0</td>
<td>1.2$^{a}$</td>
</tr>
<tr>
<td>Product $^{b}$</td>
<td>$-$121.8$^{b}$</td>
<td>$-$101.5</td>
<td>$-$115.6$^{b}$</td>
</tr>
<tr>
<td>$D_{\text{N–N}}$</td>
<td>2.057</td>
<td>2.003</td>
<td>1.841</td>
</tr>
</tbody>
</table>

$^{a}$ With respect to encounter complexes (ESI). $^{b}$ With respect to starting complexes.
the mixed-valent dimer indicating strong electronic coupling and charge delocalization in the TS.

In contrast, reaction C is associated with a considerably higher computed kinetic barrier ($\Delta G^\ddagger_{298} = 29$ kcal mol$^{-1}$), which is in agreement with the enhanced thermal stability of 4. The transition state $^1$TS$_C$ (Fig. 4C) is located on the singlet surface. At a later stage there is a change to an open shell singlet and eventually the triplet ground state of $^6$ (ESI†). $^1$TS$_C$ exhibits significant differences compared with $^1$ TS$^{(1,1)}$A and $^2$TS$^{(1,1)}$B: The two Ir–N bond vectors are almost parallel (Ir–N–N–Ir dihedral angle: 178°) and the o distances were found and different Ir–N π-orbitals are involved on the two monomers, respectively, due to the perpendicular orientation of the two monomer fragments. Importantly, the N–N distance in $^1$TS$_C$ (1.84 Å) is considerably shorter compared with those in $^1$ TS$^{(1,1)}$A and $^2$TS$^{(1,1)}$B (both >2.00 Å) indicating that a stronger orbital interaction is necessary to overcome the kinetic barrier.

Hence, the computational evaluation confirms the order of relative coupling rates that was found experimentally ($k_B > k_A > k_C$). Albeit partitioning of TS energies into the contributing terms was not done within this study, the TS structures allow for a qualitative rationalization that is in line with the observed order: Coulombic repulsion of the two positively charged nitrides is expected to contribute to the higher barrier of reaction C vs. A. In turn, the TS of reaction B exhibits strong charge delocalization over both monomer moieties, tantamount a stabilizing Coulombic effect. Besides these charge considerations, barrierless coupling of 2 and 4 involves direct overlap of the respective SOMO and LUMO orbitals while diradical coupling reaction A necessitates some electronic rearrangement within $^1$ TS$^{(1,1)}$A with respect to $^2$. However, in all three TSs relatively large N–N distances were found and NBO analysis of $^1$TS$_C$ reflects only a donor–acceptor interaction between electronically weakly perturbed monomers. Hence, these results suggest for the Coulombic interaction to be the main contributor to the computed order of reaction barriers.

Conclusions

We previously reported the coupling of iridium(IV) nitride 2 to the Ir$^{II}$N$_2$-bridged dimer 3. In contrast, iridium(V) nitride 4 does not undergo coupling at room temperature. In the present paper, the other products of formal nitride coupling besides 3, i.e. the N$_2$-bridged Ir$^{II}$ and Ir$^{IV}$ complexes 5 and 6, were synthesized and structurally characterized. None of the dimers reveal structural or spectroscopic features indicative of an appreciable degree of N$_2$-activation. These results suggest that nitride 4 is also inherently thermodynamically unstable with respect to N$_2$-coupling. This notion is supported by DFT computations, though indicating a considerably smaller driving force for homocoupling of 4 vs. 2. Examination of the kinetics of homo- and heterocoupling reactions A–C revealed the order $k_B > k_A > k_C$, also supported by DFT. Analysis of the TS structures indicate that the Coulombic interactions between the nitrides favor this order, leading to stabilization of $^2$TS$_B$ by charge delocalization and repulsion within $^1$TS$_C$. Hence, this work indicates some guidelines for thermodynamic and kinetic stabilization of electron rich transition metal nitrides.

Experimental section

Materials and methods

All experiments were carried out using Schlenk (argon atmosphere) and glove-box (argon atmosphere) techniques. All solvents were dried by passing through columns packed with activated alumina. Deuterated solvents were obtained from Euriso-Top GmbH, dried over Na/K (Toluene-d$_{4}$) or CaH$_2$ (CD$_2$Cl$_2$), distilled by trap-to-trap transfer in vacuo, and degassed by three freeze–pump–thaw cycles, respectively. [FeCp$_2$]PF$_6$ (SigmaAldrich) and AgSbF$_6$ (SigmaAldrich) were used as purchased. Silica gel 60 silanized was purchased from Merck KGAa and heated in vacuo for 5 days prior to use. 1, 4, and Na/Hg were prepared according to published procedures.\textsuperscript{12,19}

Irradiation was carried out with a Lot Oriel Xe-Short arc lamp. Cyclic voltammograms were recorded with a Metrohm Autolab PGSTAT101 using Ag/Ag$^+$ reference-, glassy-carbon working- and Pt-wire counter-electrodes. Pt-net working-electrodes and a spectro-electrochemistry cuvette (0.1 cm optical pathway) were used for UV/Vis-spectroelectrochemical measurements in combination with an Avantes AvaSpec-2048×14 UV/Vis-spectrometer. Otherwise UV/Vis-spectra were recorded with an Agilent Cary 300 UV/Vis-spectrometer at room temperature with a 0.1 mM concentration in quartz cuvettes (1 cm optical pathway). NMR-spectra were recorded on a Bruker Avance 300/400 spectrometer and calibrated to the residual proton resonance of the solvent (CD$_2$Cl$_2$: $\delta_{H} = 5.32$ ppm; $\delta_{C} = 54.00$ ppm; Toluene-d$_{4}$: $\delta_{H} = 7.09$, $\delta_{C} = 137.86$). $^{31}$P-NMR chemical shifts are reported relative to external phosphoric acid ($\delta = 0.00$ ppm). Signal multiplicities are abbreviated as: s (singlet), h (heptet), br (broad). Experimental X-band EPR spectra were recorded on a Bruker ELEXSYS-II E500 CW-EPR. The spectra were simulated by iteration of the anisotropic g-values, (super)hyperfine coupling constants, and line widths using the EPR-simulation program W95EPR developed by Prof. Dr Frank Neese. ESI-MS-experiments employed a micROTOF-Q II instrument (Bruker Daltonik). IR spectra were recorded with a Thermo Scientific Nicolet iZ10 FT/IR spectrometer at r.t. IR spectra in solution were recorded with a thin layer IR cell.

Improved synthesis of [IrCl(PNP)]

To a suspension of [Ir(COE)$_2$Cl]$_2$ (53.8 mg, 60.0 µmol, 1.00 eq.) in THF (50 mL) ($^6$Bu$_3$PCH$_2$CH$_2$)$_2$NH (43.4 mg, 120 µmol, 2.00 eq.) in THF (5 mL) is added. The reaction is stirred for 15 min at room temperature and benzoquinone (32.4 mg, 300 µmol, 5.00 eq.) is added. After stirring for 16 h at room temperature the sus-
pension is extracted with THF (3 × 5 mL), silanized silica is added and the solvent is removed in vacuo under intense stirring. The solid is extracted with pentanes (5 × 5 mL), the solvent removed in vacuo and the remaining residue dissolved in benzene and lyophilized. (Yield: 56 mg, 95.9 µmol, 80%). NMR data were identical with the previously reported synthesis. Anal. Calc. for C_{20}H_{40}IrNP_2 (584.16): C, 41.12; H, 6.90; N, 2.40. Found: C, 41.41; H, 7.05; N, 2.15.

Improved synthesis of [(N_2){Ir(PNP)}_2](SbF_6)_2 (6). Under the exclusion of light, [IrN(PNP)]PF_6 (50.0 mg, 70.7 µmol, 1.00 eq.) is dissolved in DCM (2 mL) at 70 °C. The solution is shaken for 1 min. 1H-NMR: δ = 29.09 (s br, 4H, C−H). The residue is extracted with toluene (3 × 0.8 mL). The product is isolated by column chromatography (2 cm silanized silica gel, 1.5 cm diameter; benzene). (Yield: 27.0 mg, 23.4 µmol, 66%). NMR data were identical with the previously reported synthesis. Anal. Calc. for C_{112}H_{212}IrNP_2 (1125.44): C, 42.69; H, 7.17; N, 4.98. Found: C, 43.34; H, 7.42; N, 2.15.

Synthesis of [(N_2){Ir(PNP)}_2]PF_6 (5). Under the exclusion of light, 3 (5.0 mg, 4.4 µmol, 1.0 eq.) and [Fe(C_5H_5)_2]PF_6 (1.5 mg, 7.6 µmol, 2.0 eq.) are dissolved in DCM (2 mL) at −35 °C and stirred for 5 min. The solvent is removed in vacuo. The residue is exhaustively washed with toluene (−35 °C, 8 × 2 mL) to remove ferrocene, extracted with THF (−35 °C, 4 × 2 mL) and the solvent is removed in vacuo. 1H-NMR: δ = 39.1 (s br, 4H, C−H). 1H-NMR: (300 MHz, CDCl_3, RT): δ = 42.7 (s br, 4H, CH), 5.45 (s br, 72H, PCCCH), −140.1 (s br, 4H, CH). 1H-NMR: (121.49 MHz, CDCl_3, RT): δ = −145.0 (h, 3), 71 Hz, PF_6). ESI-MS (m/z): [M]^+ calc for C_{40}H_{80}NP_2Ir (1124.457; found: 1124.406).

Coupling of 2 in the presence of catalytic amounts of 4. [IrN(PNP)]PF_6 (5.0 mg, 7.6 µmol, 1.0 eq.) and [Fe(C_5H_5)_2]PF_6 (1.5 mg, 7.6 µmol, 2.0 eq.) are dissolved in DCM (2 mL) at −70 °C and the solution is shaken for 1 min. 1H-NMR: (400 MHz, CDCl_3, −70 °C): δ = 29.09 (s br, 4H, CH), 21.75 (s br, 72H, PCCCH), −11.25 (s br, 4H, CH).

Thermal stability of 4. 4 (5.3 mg, 7.5 mmol, 1.0 eq.) is dissolved in DCM-d_2 (0.54 mL) and naphthalene (1.9 mg, 15 mmol, 2.0 eq.) is added. The solution is heated to 40 °C for 5 days.

Crystallographic details

Suitable single crystals for X-ray structure determination were selected from the mother liquor under an inert gas atmosphere and transferred in protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold stream on the diffractometer. Intensity data for 5 and 6 were obtained at 100 K on a Bruker D8 three-circle diffractometer, equipped with a PHOTON 100 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (λ = 0.71073 Å). The data obtained were integrated with SAINT and a multi-scan absorption correction with SADABS was applied. Both structures were solved and refined using the Bruker SHELX 2014 software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. All C–H hydrogen atoms were refined isotopically on calculated positions by using a riding model with their U(eq) values constrained to 1.5 U(eq) of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

Crystal structure determination of C_{52}H_{104}F_{12}Ir_{2}N_{4}O_{3}P_{4}Sb_{2} (5): CCDC 1437698, M = 1270.33, orthorhombic, a = 13.1762(5), b = 13.3606(3), c = 28.3330(11) Å, U = 4987.8(3) Å³, T = 100 K, space group P2_12_12_1 (no. 19), Z = 4, 78.343 reflections measured, 12 410 unique (R(int) = 0.0589), which were used in all calculations. The final wR(2F) was 0.0454 (all data). Crystal structure determination of C_{52}H_{104}F_{12}Ir_{2}N_{4}O_{3}P_{4}Sb_{2} (6): CCDC 1437699, M = 1813.17, monoclinic, a = 15.7367(8), b = 15.1562(7), c = 15.2970(8) Å, β = 113.649(2)°, U = 3342.1(3) Å³, T = 100 K, space group P2_1/c (no. 13), Z = 2, 33 855 reflections measured, 8335 unique (R(int) = 0.0446), which were used in all calculations. The final wR(2F) was 0.0600 (all data).

Computational details

DFT calculations were performed with the Turbomole 7.0 package applying the PBE0–22 functional and Grimme’s dispersion correction with Becke–Johnson damping (D3BJ). Ahlrich’s revised basis sets were used (def2-SVP for structure optimization and def2-TZVP for single point energies) with a full basis for all elements but Ir for which a Stuttgart–Dresden 60 electron core potential has been used, replacing the inner shell 1s–4f orbitals. No symmetry restrains were imposed and the optimized structures were defined as minima (no negative eigenvalue) or transition states (one negative eigenvalue) or vibrational analyses at the same level of theory. In case of T_1S_c a small second imaginary mode at −13 cm⁻¹ was observed. Solvent effects were accounted for by applying the COSMO model (ε = 7.6 for THF) in the single point calculations. Final energies were obtained by adding zero point vibrational energies or enthalpies from the optimizations to the SCF energies, in short notified as D3BJ-PBE0(COSMO (THF))/def2-TZVP//D3BJ-PBE0/def2-SVP. The electronic structures of R_{e1}–121S_A and 6 were evaluated by the broken symmetry protocol and the open shell singlet (OSS) structures (BS1,1) were located. The energies of the (multi-determinant) OSS were estimated from the energy ε_0 of the optimized single-determinant broken symmetry solution and the energy ε_1 from a separate unrestricted triplet (m_s = 1) calculation at the same geometry with the same functional and basis set, using the approximate spin correction formula proposed by Yamagushi:26

$$\varepsilon_S \approx \frac{S_1^2 \varepsilon_0 - S_0^2 \varepsilon_1}{S_1^2 - S_0^2}$$
NBO analyses at the D3BJ-PBE0/def2-SV(P) level were performed with Gaussian 09 RevD.01 coupled to NBO6.0 using the structures optimized as described above.

Acknowledgements

The authors thank the European Research Council (Grant Agreement 646747) for generous support, Prof. K. Koszinowski for recording the ESI-MS data, and Prof. M. Bennati for access to EPR facilities and discussion.

References


9 Homocoupling of closed-shell iron[iv] nitride [FeN{PhB-(CH$_2$P$_2$)$_3$}] results in an N$_2$Fe$_{13}$ dimer with high-spin configuration, which therefore represents an 8 π-electron configuration within the {FeNFe}$^+$ core. 8


