Enhanced Dihydrogen Activation by Mononuclear Iridium(II) Compounds: A Mechanistic Study

N. Hidalgo, J. J. Moreno, I. García-Rubio, J. Campos*
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1. Synthesis and characterization of compounds

**General considerations.** All preparations and manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 3 Å molecular sieves, and degassed prior to use. Toluene (C$_7$H$_8$) and $n$-pentane (C$_5$H$_{12}$) were distilled under nitrogen over sodium. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen over sodium/benzophenone. [D$_6$]Benzene was dried over molecular sieves (3 Å) and fluorobenzene over CaH$_2$ and distilled under argon. Compound $^{t}$Bu$_4$POCOPIrHCl was prepared as described previously.$^1$ Other chemicals were commercially available and used as received. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe$_4$ ($\delta$: 0 ppm) using the residual proton solvent peaks as internal standards ($^1$H NMR experiments) or the characteristic resonances of the solvent nuclei ($^{13}$C NMR experiments), while $^{31}$P was referenced to H$_3$PO$_4$ and $^{19}$F to CFCl$_3$. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. The magnetic moment was determined at room temperature by a modification of the Evans method using the shift of the residual solvent proton resonance (C$_6$D$_6$) versus the signal in a sealed capillary and corrected for diamagnetic contribution.$^2$ Infrared spectra were recorded on a Bruker Vector 22 spectrometer and sampling preparation was made in Nujol. For elemental analyses, a LECO TruSpec CHN elementary analyzer was utilized. EPR samples were dissolved in trifluorobenzene under argon atmosphere and transferred to quartz tubes that were subsequently sealed. EPR experiments were performed with a Bruker Elexsys spectrometer working in X-Band (~ 9.47 GHz) equipped with a helium gas-flow cryostat. Continuous-wave experiments were carried out at different temperatures ranging from room temperature to 10K. For every temperature, the used microwave power was selected making sure no power-saturation effects were taking place. Spectral simulations were made using EasySpin, a specialized toolbox for Matlab.$^3$ Cyclic voltammetry experiments were carried out in a Metrohm Autolab PGSTAT204 potentiostat. Glassy carbon working ($\varnothing = 3$ mm) and non-aqueous silver/silver chloride pseudoreference electrodes were obtained from CH Instruments. The counter electrode was a glassy carbon rod ($\varnothing = 3$ mm) from ALS. CV experiments were performed in a 20 mL cell with custom-made ports for all electrodes.
Tetrabutylammonium hexafluorophosphate was purified by recrystallization from ethanol and dried under vacuum before being stored in a desiccator. All data were referenced to an internal ferrocene standard.

**Compound 1.** $\text{^{tBu}POCOPIrHCl}$, previously reported,\(^1\) (500 mg, 0.799 mmol) and NaO'Bu (84 mg, 0.878 mmol) were placed in an ampoule, dissolved in toluene (15 mL) and stirred at room temperature overnight under N\(_2\) atmosphere. The orange solution was filtered and the volatiles were removed in vacuo. The solid was extracted with pentane (5 x 15 mL) and dried to yield complex 1 as an orange powder, (420 mg, 85 %). It can be recrystallized by slow evaporation of pentane solution.

**Anal. Calcd.** for C\(_{22}\)H\(_{39}\)IrN\(_2\)O\(_2\)P\(_2\): C, 42.8; H, 6.4; N, 4.5. **Found:** C, 42.8; H, 6.4; N, 4.6.

\(^1\text{H NMR}\) (400 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\), ppm: 6.87-6.76 (m, 3 H, H\(_a\), H\(_b\)), 1.33 (t, 36 H, \(^3\)J\(_{\text{HP}}\) = 7 Hz, \(^\text{tBu}\)).

\(^{13}\text{C}\{^1\text{H}\}\text{NMR}\) (100 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\), ppm: 170.1 (t, \(^2\)J\(_{\text{CP}}\) = 6 Hz, C\(_2\)), 127.4 (brs, C\(_1\)), 126.9 (CH\(_b\)), 104.3 (t, \(^3\)J\(_{\text{CP}}\) = 6 Hz, CH\(_a\)), 41.2 (t, \(^1\)J\(_{\text{CP}}\) = 12 Hz, C(CH\(_3\))\(_3\)), 28.3 (t, \(^2\)J\(_{\text{CP}}\) = 3 Hz, C(CH\(_3\))\(_3\)).

\(^{31}\text{P}\{^1\text{H}\}\text{NMR}\) (160 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\), ppm: 184.7.

**IR** (Nujol): \(\nu\) (N\(_2\)) 2094 cm\(^{-1}\).

**UV-vis** (Tol) \(\lambda_{\text{max}}\) (\(\varepsilon\) [cm\(^{-1}\) M\(^{-1}\)]): 392 nm (2360)
Compound 2. Compound 1 (100 mg, 0.162 mmol) was placed in an ampoule and dissolved in toluene (15 mL), then AgOTf (42 mg, 0.162 mmol) was added. The orange solution was stirred at room temperature for 3 hours, time after which a grey precipitate appeared, and the solution turned green. After filtration, the volatiles were removed in vacuo to yield complex 2 as green powder (111 mg, 93 %). Compound 2 can be recrystallized by slow diffusion of pentane into a toluene solution at -30 °C (2:1 by vol.).

Anal. Calcd. for C_{23}H_{39}F_{3}IrO_{5}P_{2}S: C, 37.4; H, 5.3; S, 4.3. Found: C, 37.4; H, 5.4; S, 4.1.

Effective magnetic moment. (Evans method, C_{6}D_{6}) \(\mu_{\text{eff}} = 1.56 \mu_{B}\)

UV-vis (Tol) \(\lambda_{\text{max}} (\varepsilon [\text{cm}^{-1} \text{ M}^{-1}]): 490 \text{ nm (1760)}\)

Compound 3. Compound 1 (30 mg, 0.049 mmol) was placed in an ampoule and dissolved in fluorobenzene (8 mL), then AgBARF_{4} (48 mg, 0.049 mmol) was added and the solution stirred at room temperature for 2 hours under N_{2} atmosphere. After this time the orange solution turned brown and a grey precipitate appeared. After filtration, the volatiles were removed in vacuo to yield complex 3, as a brown powder, (62 mg, 86 %). Compound 3 can be recrystallized by slow evaporation from a fluorobenzene solution.
Anal. Calcd. for C\textsubscript{54}H\textsubscript{51}BF\textsubscript{24}IrN\textsubscript{2}O\textsubscript{2}P\textsubscript{2}: C, 43.8; H, 3.5; N, 1.9. **Found:** C, 43.9; H, 4.0; N, 0.6. The reduced amount of nitrogen is attributed to partial N\textsubscript{2} loss during work-up.

\textsuperscript{11}B\textsuperscript{[1\textsubscript{H}]} NMR (76.8 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) δ, ppm: 6.0.

**Effective magnetic moment.** (Evans method, C\textsubscript{6}H\textsubscript{5}F) $\mu\text{eff} = 1.75 \mu_B$

IR (Nujol): ν(N\textsubscript{2}) 2007 cm\textsuperscript{-1}.

**UV-vis** (C\textsubscript{6}H\textsubscript{5}F) $\lambda_{\text{max}}$ (ε [cm\textsuperscript{-1} M\textsuperscript{-1}]): 328 nm (1730)

**Compound 4.** Compound 2 (50 mg, 0.067 mmol) was placed in an ampoule, dissolved in toluene (8 mL) and stirred at room temperature for 7 hours under H\textsubscript{2} atmosphere (1 bar). The green solution became orange and it was filtered. The volatiles were removed in vacuo to yield complex 4 as an orange powder (45 mg, 91 %). It can be recrystallized by slow diffusion at −30 °C of pentane into a toluene solution (2:1 by vol.).

Anal. Calcd. for C\textsubscript{23}H\textsubscript{40}F\textsubscript{3}IrO\textsubscript{5}P\textsubscript{2}S: C, 37.3; H, 5.4; S, 4.3. **Found:** C, 37.4; H, 5.1; S, 4.0.

\textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) δ, ppm: 6.66 (t, 1 H, $^3J_{HH} = 7.7$ Hz, H\textsubscript{b}), 6.55 (d, 2 H, $^3J_{HH} = 7.7$ Hz, H\textsubscript{a}), 1.19 (m, 36 H, tBu), -42.88 (t, 1 H, $^2J_{HP} = 13.0$ Hz, Ir-H).

\textsuperscript{13}C\textsuperscript{[1\textsubscript{H}]} NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) δ, ppm: 168.4 (t, $^2J_{CP} = 6$ Hz, C\textsubscript{2}), 128.1 (CH\textsubscript{b}), 119.8 (q, $^1J_{CP} = 320$ Hz, CF\textsubscript{3}), 106.5 (brs, C\textsubscript{1}), 105.4 (t, $^3J_{CP} = 6$ Hz, CH\textsubscript{a}), 43.6 (t, $^1J_{CP} = 13$ Hz, C(CH\textsubscript{3})\textsubscript{3}), 39.8 (t, $^1J_{CP} = 13$ Hz, C(CH\textsubscript{3})\textsubscript{3}), 27.8 (t, $^2J_{CP} = 3$ Hz, C(CH\textsubscript{3})\textsubscript{3}), 27.3 (t, $^2J_{CP} = 3$ Hz, C(CH\textsubscript{3})\textsubscript{3}).
**31P{1H} NMR** (160 MHz, C₆D₆, 25 °C) δ, ppm: 177.0.

**19F{1H} NMR** (376 MHz, C₆D₆, 25 °C) δ, ppm: -76.7.

**IR** (Nujol): v(Ir–H) 1881 cm⁻¹.

**UV-vis** (Tol) λₘₐₓ (ε [cm⁻¹ M⁻¹]): 391 nm (1390).

**Synthesis of AgBAR₄**
AgBAR₄ was prepared according to a published procedure. In 20 mL of diethyl ether NaBAR₄ (493 mg, 1 equiv., 0.556 mmol) was dissolved and vigorously shaken for 5 min with silver nitrate (190 mg, 2 equiv., 1.120 mmol) dissolved in 10 mL of water in a separatory funnel wrapped in aluminium foil. The organic layer was separated and evaporated to give AgBAR₄ as white solid (470 mg, 87 %).
2. Kinetic studies

2.1. Kinetic experiments for the reaction between 2 and H₂

A solution of compound 2 (5 mg, 0.007 mmol) in C₆D₆ (0.5 mL) was placed in a J. Young NMR tube. After two freeze-pump-thaw cycles, the solution was subjected to 2, 3, 4 or 5 bar of H₂ at 298 K. ¹H NMR and ³¹P{¹H} NMR analysis were carried out to monitor the appearance of 4. Each experiment was performed 3 times and hexamethylbenzene and triphenylphosphine oxide were used as internal standards.

Table S1. Observed pseudo-first-order rate constants for reaction of 2 with H₂ at 25 °C varying [H₂] in C₆D₆.

| Initial H₂ pressure (Bar) | k_{obs} (M⁻¹ s⁻¹) | [H₂] (M) |
|---------------------------|-------------------|---------|
| 5                         | 0.0170            | 0.021   |
| 4                         | 0.0122 ± 0.0002   | 0.015   |
| 3                         | 0.0068 ± 0.0003   | 0.008   |
| 2                         | 0.0036 ± 0.0001   | 0.005   |
Figure S1. Plots of $\ln[2]$ against time at several H$_2$ pressures at 298 K.
Figure S2. Plot of $k_{obs}$ against H$_2$ concentration at 298 K.

2.2. Kinetic isotopic effect (KIE)
Kinetic studies were carried out to determine the kinetic isotopic effect (KIE) of dihydrogen activation by compound 2. In a J. Young NMR tube, compound 2 (5 mg, 0.007 mmol) was dissolved in C$_6$D$_6$ (0.5 mL) at room temperature. The nitrogen atmosphere was replaced by either H$_2$ or D$_2$ (1 bar) and the solution was shaken. The progress of the reaction was monitored by $^{31}$P{$^1$H} NMR spectroscopy at 25 °C by means of the appearance of compound 4. Each experiment was performed 3 times using triphenylphosphine oxide as internal standard.
Figure S3. Representative examples of the kinetic profiles for $\text{H}_2/\text{D}_2$ activation by 2.
3. X-Ray structural characterization of new compounds

Crystallographic details. Low-temperature diffraction data were collected on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a $\mu$S 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of $\omega$ and $\phi$ scans using monochromatic radiation $\lambda(\text{Mo K}\alpha_1) = 0.71073$ Å. The diffraction images collected were processed and scaled using APEX-III software. The structures were solved with SHELXT and was refined against $F^2$ on all data by full-matrix least squares with SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, except for the iridium hydride in structure 4, which was located at the Fourier electron density map and its Ir–H distance restrained to an average value of 1.53Å. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Compound 1 was refined as a structure with two components with a 9:1 ratio. Attempts to model it as a twinned failed, but we could locate the heaviest atoms (Ir1, P1 and P2) as a minor component of the overall integrated data, providing good quality results. The triflate anion in compounds 2 and 4 presented larger adps, as expected for the high libration of this fragment, which was treated using the corresponding restraints. In the case of 4, the fragment was modeled over two positions with a 61:39 ratio. Some of the CF$_3$ groups of the [BARF$_2$] anion in 3 were also modeled over two positions to accommodate the rotation around the C–CF$_3$ bond, with ratios of 0.53:0.47; 0.51:0.49; and 0.67:0.33.

The full numbering scheme of all the reported structures can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information.

Deposition Number(s) 2123397 (for 1), 2123399 (for 2), 2123398 (for 3), 2123400 (for 4), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre (CCDC).
**Figure S4.** ORTEP diagram of compound 1. Hydrogen atoms are excluded for clarity. Thermal ellipsoids are set at 50% probability.

**Figure S5.** ORTEP diagram of compound 4. Hydrogen atoms are excluded for clarity. Thermal ellipsoids are set at 50% probability.
Table S2. Crystal data and structure refinement for compounds 1, 2, 3 and 4.

|       | 1                  | 2                       | 3                  | 4                      |
|-------|--------------------|-------------------------|--------------------|------------------------|
| Formula | C_{22}H_{39}IrN_2P_2 | C_{23}H_{39}F_3IrO_3P_2S | C_{34}H_{51}BF_2IrN_2O_2P_2 | C_{35}H_{51}F_3IrO_3P_2S |
| Fw    | 617.69             | 738.74                  | 1480.92            | 739.75                 |
| cryst.size, mm | 0.17 × 0.11 × 0.04 | 0.20 × 0.18 × 0.16 | 0.19 × 0.12 × 0.06 | 0.27 × 0.20 × 0.06 |
| crystal system | Triclinic          | Triclinic              | Monoclinic         | Monoclinic             |
| space group | P-1               | P-1                    | C2/c               | P21/c                  |
| a, Å  | 8.2571 (5)         | 10.8813 (8)            | 16.9302 (3)        | 17.8274 (8)           |
| b, Å  | 12.1498 (7)        | 11.1583 (8)            | 18.2298 (4)        | 10.8002 (4)           |
| c, Å  | 13.4476 (8)        | 12.6376 (8)            | 40.0759 (9)        | 15.9786 (7)           |
| α, deg | 100.845 (2)       | 94.088 (2)             | 90                 | 90                     |
| β, deg | 95.841 (3)        | 97.739 (2)             | 96.205 (1)         | 109.601 (2)           |
| γ, deg | 104.226 (2)       | 109.652 (3)            | 90                 | 90                     |
| V, Å³ | 1268.75 (13)       | 1420.66 (17)           | 12296.3 (4)        | 2898.2 (2)            |
| T, K  | 193                | 193                    | 193                | 193                    |
| Z     | 2                  | 2                      | 8                  | 4                      |
| ρ_{calc}, g cm⁻³ | 1.617             | 1.727                  | 1.600              | 1.695                  |
| μ, mm⁻¹ (MoKα) | 5.41             | 4.93                   | 2.34               | 4.84                   |
| F(000) | 616              | 734                    | 5864              | 1472                  |
| absorption corrections | multi-scan, 0.59-0.75 | multi-scan, 0.56-0.75 | multi-scan, 0.59-0.75 | multi-scan, 0.53-0.75 |
| θ range, deg | 2.6 – 28.3        | 2.0 – 29.6              | 2.0 – 26.7         | 2.2 – 27.5            |
| no. of rflns measd | 45487          | 63661                  | 48791             | 52634                  |
| R_{int} | 0.044            | 0.042                   | 0.047             | 0.043                  |
| no. of rflns unique | 6280           | 7974                   | 13034             | 6639                   |
| no. of params / restraints | 302 / 0       | 328 / 39                | 871 / 319         | 404 / 139              |
| R₁(I > 2σ(I))° | 0.030            | 0.029                   | 0.052             | 0.028                  |
| wR₂(I > 2σ(I)) | 0.037            | 0.034                   | 0.077             | 0.041                  |
| wR₂ all data | 0.076            | 0.059                   | 0.113             | 0.068                  |
| Diff.Fourier.peaks min/max, eÅ⁻³ | -1.18 / 1.45   | -2.08 / 2.36            | -1.51 / 1.31       | -1.14 / 1.69           |
| CCDC number | 2123397          | 2123399                 | 2123398           | 2123400                |
4. Computational Details.

Calculations were performed at the DFT level with the Gaussian 09 (Revision E.01) program.\textsuperscript{5} The hybrid functional PBE0\textsuperscript{6} was used throughout the computational study, and dispersion effects were accounted for by using Grimme’s D3 parameter set with Becke–Johnson (BJ) damping\textsuperscript{7}. Geometry optimizations were carried out without geometry constraints, using the 6-31G(d,p)\textsuperscript{8} basis set to represent the C, H, P, O, S, F and N atoms and the Stuttgart/Dresden Effective Core Potential and its associated basis set (SDD)\textsuperscript{9} to describe the Ir atoms. The grid=ultrafine option was used throughout and bulk solvent effects (benzene) were included at the optimization stage with the SMD continuum model.\textsuperscript{10} Energies were refined by means of single-point calculations with the larger 6-311+G(2d,p) basis set. The stationary points and their nature as minima or saddle points (TS) were characterized by vibrational analysis, which also produced zero-point (ZPE), enthalpy (H), entropy (S) and Gibbs energy (G) data at 298.15 K. The minima connected by a given transition state were determined by perturbing the transition states along the TS coordinate and optimizing to the nearest minimum. To take into account the electrostatic interaction in ion pairs, electron transfer reactions were modelled including both complexes in the same calculation, in the triplet (S=1, Ir\textsuperscript{II}-Ir\textsuperscript{II}) or singlet (S=0, Ir\textsuperscript{I}-Ir\textsuperscript{III}) surfaces. Analysis of the electron density was performed within the Atoms In Molecules (AIM) theory of R. F. W. Bader\textsuperscript{11} using the Multiwfn program.\textsuperscript{12}
Figure S6. Plot of the laplacian of the electron density, $\nabla^2 \rho(r)$, of species Ir$^\text{III}$H-HOTf in the Ir-H-H plane calculated with the PBE0 functional. The solid and dashed lines correspond to positive and negative values of $\nabla^2 \rho(r)$, respectively. The optimized geometry and in plane bond critical points (blue dots) and bond paths (brown traces) of the electron density ($\rho(r)$) are superimposed, including those corresponding to the interaction between the hydridic and protic hydrogen atoms. The H–H bond critical point presents an electron density value of 0.044 a.u. (hartree·bohr$^{-3}$), substantially higher than that found for a related gold(I) hydride with [Pt(P$^\text{t}$Bu$_3$)$_2$H]$^+$ (0.020 a.u.).$^{13}$
Figure S7. ZPE profile of the reactivity of complex 2 with H\textsubscript{2} (blue) and D\textsubscript{2} (red).
Figure S8. Free energy profile displaying the oxidative addition of H₂ from the σ-H₂ complex. The minimum corresponding to the Ir(IV) dihydride is a lower-energy conformer of the minimum stemming from TS3.
Figure S9. Lowest-energy (30.9 kcal/mol) transition state corresponding to HAT to from the σ-H₂ complex to benzene. Transition states stemming from the Ir(IV) dihydride were slightly less stable.
**Figure S10.** Overlays of crystallographically determined and calculated molecular geometries, carried out with Mercury (H atoms were omitted). 2 (top): RMSD = 0.2414, Max. D = 0.6161; 3 (middle): RMSD = 0.2429, Max. D = 0.5622; 4 (bottom): RMSD = 0.1134, Max. D = 0.4079.
Table S3. Comparison of crystallographically determined and calculated (in parenthesis) key bond distances (Å) and angles (º).

|          | 2          | 3          | 4          |
|----------|------------|------------|------------|
| d Ir−N   | –          | 2.046 (2.043) | –          |
| d Ir−O   | 2.160 (2.220) | –          | 2.213 (2.194) |
| d Ir−C   | 1.968 (2.004) | 1.979 (2.015) | 1.990 (1.995) |
| d Ir−P (avg.) | 2.301 (2.323) | 2.315 (2.347) | 2.305 (2.312) |
| d Ir−H   | –          | –          | 1.516 (1.523) |
| º C−Ir−N | –          | 179.47 (178.88) | –          |
| º C−Ir−O | 174.86 (173.77) | –          | 167.58 (171.19) |
| º C−Ir−H | –          | –          | 88.76 (89.35) |
| º P−Ir−P | 160.84 (160.71) | 160.26 (159.85) | 160.36 (161.29) |

Figure S11. Evolution of molecular geometries of Ir(II)(H)·HOTf and adjacent Ir(II)(OTf) after inducing electron transfer by changing from the S=1 to the S=0 spin manifold. A = initial geometry; B = [Ir(III)(H)]⁺ + HOTf + [Ir(I)(OTf)]⁻; C = [Ir(III)(H)]⁺ + HOTf·[Ir(I)(OTf)]⁻; D = [Ir(III)(H)(HOTf)]⁺·[Ir(I)(OTf)]⁻; E = proton transfer from the cationic to the anionic fragment in D; F = [Ir(III)(H)(OTf)]·[Ir(I)(HOTf)]. The independent optimization of the [Ir(I)(HOTf)] fragment in F gives [Ir(III)(H)(OTf)] (compound 4).
5. NMR spectra of new compounds

Figure S12. $^1$H NMR (400 MHz, C$_6$D$_6$, 25 °C). Compound 1.

Figure S13. $^{13}$C($^1$H) NMR (100 MHz, C$_6$D$_6$, 25 °C). Compound 1.
Figure S14. $^{31}$P{¹H} NMR (160 MHz, C₆D₆, 25 ºC). Compound 1.

Figure S15. $^{11}$B{¹H} NMR (76.8 MHz, C₆D₆, 25 ºC). Compound 3.
Figure S16. $^1$H NMR (400 MHz, C$_6$D$_6$, 25 ºC). Compound 4.

Figure S17. $^{13}$C($^1$H) NMR (100 MHz, C$_6$D$_6$, 25 ºC). Compound 4.
Figure S18. $^{31}$P($^1$H) NMR (160 MHz, C$_6$D$_6$, 25 ºC). Compound 4.
6. EPR spectra of new Ir(II) compounds

**Figure S19.** EPR spectrum of complex 2 in frozen solution of trifluorobenzene. T=20K. The simulation shown in the lower trace was made taking into account an electron spin \( S = \frac{1}{2} \) with g-values 3.95, 1.16 and 0.83. The EPR signals of this complex were detected in a broad range of temperatures from room temperature down to 10K. No signs of hyperfine structure were observed at any of these temperatures.
**Figure S20.** EPR spectrum of complex 3 in frozen solution of trifluorobenzene. T=20K.

The simulation shown in the middle trace is the sum of the two S = ½ species, in about the same amount, shown in the lower trace having g-values: 1) 3.33, 1.92, 1.55 and 2) 3.80, 1.85, 1.50. No hyperfine structure is observed in the spectrum. Additionally, the presence of a small amount of an organic-type radical is evidenced by a g ~ 2 signal labeled with a star in the figure. The EPR signals of this complex were detected in a broad range of temperatures from room temperature down to 10K. We attribute the existence of two sets of very similar signals to the potential equilibrium between dinuclear and mononuclear dinitrogen species, well-known for the diamagnetic version of group-9 pincer-type complexes.\(^{14}\)
7. UV-Vis spectra of new compounds

**Figure S21.** UV-Vis spectrum of compound 1.

**Figure S22.** UV-Vis spectrum of compound 2.
Figure S23. UV-Vis spectrum of compound 3.

Figure S24. UV-Vis spectrum of compound 4.
8. CV of compound 2

**Figure S25.** CV of complex 2 under N\textsubscript{2} saturation conditions, showing an irreversible reduction feature at $E_p = -0.87$ V vs Fc\textsuperscript{+}/Fc. We ascribe the irreversibility to chemical changes following the loss of the triflate anion (eg. N\textsubscript{2} coordination). Conditions: 1.0 mM analyte, 0.1 M TBAPF\textsubscript{6}/1,2-difluorobenzene; glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; 100 mV/s scan rate; referenced to internal ferrocene standard.

**Figure S26.** CVs of 2 at variable scan rates ranging from 100 to 1000 mV/s, obtained under N\textsubscript{2} saturation conditions.
Figure S27. Linear fit of variable scan rate data from Figure S26, demonstrating that 2 shows a diffusion-limited current response.
9. References

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