

The First Side-on-bound Metal Complex of Diazene, HN=NH

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Supporting Information

Experimental

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in nitrogen or argon filled glove boxes. Solvents were dried and distilled under nitrogen or argon from sodium/benzophenone (tetrahydrofuran and hexane), dimethoxymagnesium (methanol) and diethoxymagnesium (ethanol). Tetrahydrofuran (inhibitor-free) was also dried and deoxygenated using a Pure Solv 400-4-MD (Innovative Technology) solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Tetrahydrofuran-*d*₈ was dried over and distilled from sodium/benzophenone. Acetone-*d*₆ was dried over and distilled from calcium sulfate and stored over activated molecular sieves. Methanol-*d*₄ was dried over, distilled from and stored over activated molecular sieves.

Hydrazine (1M in tetrahydrofuran) were purchased from Aldrich and deoxygenated before use. Hydrazine-¹⁵N₂ was prepared by Soxhlet extraction of ¹⁵N₂H₄·H₂SO₄ with liquid ammonia.¹ Azobenzene-¹⁵N₂ was prepared by oxidation of aniline-¹⁵N with MnO₂.² The complex *trans*-[FeCl₂(dmpe)₂] was prepared using literature methods.³

Air-sensitive NMR samples were prepared in argon or nitrogen filled glove boxes or on a high vacuum line by vacuum transfer of solvent into an NMR tube fitted with a concentric teflon valve. ¹H, ³¹P, ¹⁵N and two-dimensional NMR spectra were recorded on Bruker DMX600, DMX500, DRX400, DPX300 NMR spectrometers. ¹H NMR spectra were referenced to residual solvent resonances whilst ³¹P spectra were referenced to external neat trimethyl phosphite at δ 140.85 ppm. ¹⁵N NMR spectra were reference to external neat nitromethane at δ 0.00 ppm. Infrared spectra were recorded on a Shimadzu 8400 series FTIR spectrometer as nujol mulls or KBr discs. Electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer (USyd) or carried out at the Bioanalytical Mass Spectrometry Facility (UNSW). High resolution mass spectra were recorded on a Bruker Bio Apex II FTICR/MS 7T spectrometer with an Analytica source.

Preparation of cis-[Fe(N₂H₄)(dmpe)₂]²⁺XY

where X=Y=BPh₄

trans-[FeCl₂(dmpe)₂] (0.30 g, 0.70 mmol) was dissolved in a hydrazine solution (1M in tetrahydrofuran, 4.0 mL, 4.0 mmol) under nitrogen to give an emerald green solution.

After several minutes, an orange precipitate started to form. The reaction mixture was stirred at room temperature overnight. The orange solid (0.38 g) was collected by filtration, washed with tetrahydrofuran and dried. The orange solid was suspended in methanol (7 mL) and filtered to remove an insoluble off-white solid (ν (KBr): 3286s, 3231m, 1605m, 1570m, 1385w, 1340w, 1306w, 1153s, 1144m, 964w, 721w, 604w, 552w cm^{-1}) identified as $\text{FeCl}_2(\text{N}_2\text{H}_4)_2$ by comparison with literature data.⁴ A solution of NaBPh_4 (0.53 g, 1.5 mmol in 2 mL methanol) was added to the red-orange filtrate. The yellow-orange precipitate formed was collected by filtration, washed with methanol and dried to give the title compound (0.41 g, 57% yield). $\text{C}_{60}\text{H}_{76}\text{B}_2\text{FeN}_2\text{P}_4\text{H}_2\text{O}$ (1044.7) requires C, 68.98; H, 7.53; N, 2.68; found C, 68.6; H, 7.5; N, 2.6%.

^1H NMR (acetone- d_6 , 400 MHz): δ 7.34 (m, 16H, *o*-Ph), 6.92 (m, 16H, *m*-Ph), 6.78 (m, 8H, *p*-Ph), 5.39 (b, 2H, NHH), 4.69 (b, 2H, NHH), 1.85 (s, 6H, CH_3), 1.65 (s, 6H, CH_3), 1.59 (d, $^2J_{\text{HP}}$ 6.4 Hz, 6H, CH_3), 1.42 (d, $^2J_{\text{HP}}$ 5.8 Hz, 6H, CH_3). CH_2 signals were obscured by the acetone- d_6 residual.

$^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 162 MHz): δ 68.9 (app. t, splitting 39.6 Hz, 2P), 58.3 (app. t, 2P).

$^{15}\text{N}\{^1\text{H}\}$ NMR (acetone- d_6 , 41 MHz, from HN-HSQC): δ -387.9 (corr with ^1H δ 5.39 and 4.69, Fe- NH_2).

IR (KBr): 3302w, 3236w, 3053s, 2999m ν (N-H), 2984m, 2910w, 1601w, 1578m, 1477m, 1423m, 1416m, 1383m, 1267w, 1173w, 1130w, 1036w, 930s, 891m, 835w, 750mw, 735s, 708s, 650w, 611s, 459w cm^{-1} .

The ^{15}N -labelled analogue $[\text{Fe}(^{15}\text{N}_2\text{H}_4)(\text{dmpe})_2]^{2+}[\text{BPh}_4]_2^-$ was prepared in a similar reaction using $^{15}\text{N}_2\text{H}_4$. All ^1H and ^{31}P NMR data were identical to the above except the following:

^1H NMR (acetone- d_6 , 400 MHz): δ 5.41 (bd, $^1J_{\text{HN}}$ 80.5 Hz, ^{15}NHH), 4.70 (bd, $^1J_{\text{HN}}$ 79.6 Hz, ^{15}NHH).

$^{15}\text{N}\{^1\text{H}\}$ NMR (acetone- d_6 , 41 MHz, from HN-HSQC): δ -387.1 (corr with ^1H δ 5.39 and 4.69, Fe- $^{15}\text{NH}_2$).

where $X = \text{PF}_6$, $Y = \text{Cl}$

Hydrazine solution (1M in tetrahydrofuran, 4.0 mL, 4.0 mmol) was added to a solution of *trans*- $[\text{FeCl}_2(\text{dmpe})_2]$ (0.32 g, 0.74 mmol) in tetrahydrofuran (4 mL) under nitrogen. The reaction mixture was stirred for a few minutes then left to stand at room temperature overnight. The orange precipitate (0.27 g) formed was collected by filtration, washed with tetrahydrofuran and dried. The orange solid was then treated with KPF_6 in small batches. Typically, the orange solid (33 mg) was extracted with ethanol (3×0.5 mL) and filtered to remove the insoluble $[\text{FeCl}_2(\text{N}_2\text{H}_4)_2]$ (11 mg, 58 μmol , 64%). The orange-red filtrate was treated with the supernatant liquid of a KPF_6 suspension (80 mg, 0.43 mmol in 0.5 mL boiling ethanol) and left to stand overnight. The title compound was collected in several crops as an orange-red crystalline solid (13 mg, 25% yield).

^1H NMR (methanol- d_4 , 400 MHz): δ 2.17 (m, 2H, CH_2), 2.06-1.91 (m, 6H, CH_2), 1.75 (m, 6H, CH_3), 1.50 (m, 12H, CH_3), 1.34 (m, 6H, CH_3). NH_2 resonances not observed due to exchange with deuterium from methanol- d_4 .

$^{31}\text{P}\{^1\text{H}\}$ NMR (methanol- d_4 , 162 MHz): δ 68.1 (app. t, J 40.1 Hz, 2P), 57.4 (app. t, 2P), -144.2 (sept, $^1J_{\text{PF}}$ 707.8 Hz, 1P, PF_6^-).

ESI (methanol, -ve): m/z 145 [100%, PF_6^-].

ESI (methanol, +ve): m/z 415 [15%], 355 [42, $\text{Fe}(\text{dmpe})_2\text{-H}^+$], 269 [30, $\text{Fe}(\text{N}_2\text{H}_4)(\text{dmpe})(\text{OMe})^+$], 265 [100], 238 [32, $\text{Fe}(\text{N}_2\text{H}_4)(\text{dmpe})^+$], 237 [41, $\text{Fe}(\text{dmpe})(\text{OMe})^+$], 221 [48].

ESI (acetonitrile, +ve): m/z 574 [30%, $\text{Fe}(\text{N}_2\text{H}_4)(\text{dmpe})_2(\text{PF}_6)(\text{CH}_3\text{CN})^+$], 432 [19, $\text{Fe}(\text{dmpe})_2\text{Cl}(\text{CH}_3\text{CN})^+$], 428 [69, $\text{Fe}(\text{N}_2\text{H}_4)(\text{dmpe})_2(\text{CH}_3\text{CN})\text{-H}^+$], 391 [30, $\text{Fe}(\text{dmpe})_2\text{Cl}^+$], 282 [100, $\text{Fe}(\text{dmpe})\text{Cl}(\text{CH}_3\text{CN})^+$], 278 [58, $\text{Fe}(\text{N}_2\text{H}_4)(\text{dmpe})(\text{CH}_3\text{CN})\text{-H}^+$], 273 [37, $\text{Fe}(\text{N}_2\text{H}_4)(\text{dmpe})\text{Cl}^+$].

HRMS (acetonitrile): m/z 428.1339 (calc 428.1366), 391.0456 (calc 391.0493).

Preparation of cis-[Fe(NH=NH)(dmpe)₂]

trans- $[\text{FeCl}_2(\text{dmpe})_2]$ (0.41 g, 0.97 mmol) was dissolved in a hydrazine solution (1M in tetrahydrofuran, 10 mL, 10 mmol) under argon and stirred at room temperature overnight. A suspension of KC_8 (0.31 g, 2.4 mmol, 2.4 equiv) in tetrahydrofuran (10 mL) was added and the reaction mixture stirred at room temperature overnight. The reaction mixture was filtered and the filtrate evaporated to dryness to give a yellow-brown solid. The solid was extracted with pentane, filtered through celite and evaporated to dryness to afford the title compound (0.063 g, 17% yield). The compound is very air-sensitive and has limited stability in the solid state and in solution.

^1H NMR (tetrahydrofuran- d_8 , 300 MHz): δ 2.41-1.80 (br, 4H, **NH** and **CH₂**), 1.66 (m, 2H **CH₂**), 1.50-1.22 (m, 4H, **CH₂**), 1.44 (br s, 6H, **CH₃**), 1.30 (br s, 6H, **CH₃**), 1.02 (br s, 6H, **CH₃**), 0.76 (br s, 6H, **CH₃**).

$^{31}\text{P}\{^1\text{H}\}$ NMR (tetrahydrofuran- d_8 , 122 MHz): δ 67.7 (app. t, splitting 42.3 Hz, 2P), 60.1 (app. t, 2P).

ESI (acetonitrile, +ve): m/z 398 [51%, $\text{Fe}(\text{dmpe})_2(\text{CH}_3\text{CN})\text{-H}^+$], 396 [59, $\text{Fe}(\text{dmpe})_2(\text{CH}_3\text{CN})\text{-H}^+$], 387 [100, $\text{Fe}(\text{N}_2\text{H}_2)(\text{dmpe})_2\text{-H}^+$], 356 [31, $\text{Fe}(\text{dmpe})_2^+$], 355 [43, $\text{Fe}(\text{dmpe})_2\text{-H}^+$].

IR (Nujol): 3188m v(N-H), 1413m, 1289m, 1268m, 1200m, 1162s, 1009m, 1001m, 929s, 900m, 881m, 826m, 712m, 703m, 680m cm^{-1} .

The ^{15}N -labelled analogue $[\text{Fe}(^{15}\text{N}_2\text{H}_2)(\text{dmpe})_2]$ was prepared in a similar reaction using $^{15}\text{N}_2\text{H}_4$. All ^1H and ^{31}P NMR data were identical to the above.

^{15}N NMR (tetrahydrofuran- d_8 , 30 MHz): δ -310.7 (br, **NH**). On standing over a period of several weeks in solution, resonances for $^{15}\text{N}_2$ (-71.9 ppm) and $^{15}\text{NH}_3$ (-388.4 ppm) were observed.

Preparation of cis-[Fe(PhN=NPh)(dmpe)₂]

A suspension of *trans*- $[\text{FeCl}_2(\text{dmpe})_2]$ (75 mg, 0.18 mmol), azobenzene (0.107 g, 0.59 mmol) and KC_8 (60 mg, 0.44 mol) was stirred under nitrogen at room temperature overnight. The reaction mixture was filtered and the filtrate evaporated to dryness to give a red-brown solid. The solid was washed with hexane and dried in vacuo to afford the title compound (0.010 g, 10% yield).

^1H NMR (tetrahydrofuran- d_8 , 300 MHz): δ 7.02 (br s, 2H, **Ph**), 6.75 (br s, 2H, **Ph**), 6.66 (br, s, 2H, **Ph**), 6.15 (t, $^3J_{\text{HH}}$ 8.9 Hz, 2H, **Ph**), 6.12 (br s, 2H, **Ph**), 1.82 (d, $^2J_{\text{HP}}$ 6.5 Hz,

6H, CH₃), 1.79-1.62 (m, 6H, CH₂), 1.38 (m, 2H, CH₂), 1.19 (d, ²J_{HP} 5.8 Hz, 6H, CH₃), 1.08 (br s, 6H, CH₃), 0.74 (br s, 6H, CH₃).

³¹P{¹H} NMR (tetrahydrofuran-*d*₈, 122 MHz): δ 64.3 (app. t, splitting 34.2 Hz, 2P), 57.9 (app. t, 2P) (Lit δ 63.3, 56.0, (splitting 37 Hz) at 25°C in C₆D₆).⁵

The ¹⁵N-labelled analogue [Fe(¹⁵N₂Ph₂)(dmpe)₂] was prepared in a similar reaction using ¹⁵N₂Ph₂. All ¹H and ³¹P NMR data were identical to the above.

¹⁵N NMR (tetrahydrofuran-*d*₈, 30 MHz): δ -269.3 (NPh).

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