

Iron–carbene functionalities supported by a macrocyclic ligand: iron–carbon double bond stabilized by tetramethyldibenzotetraazaannulene

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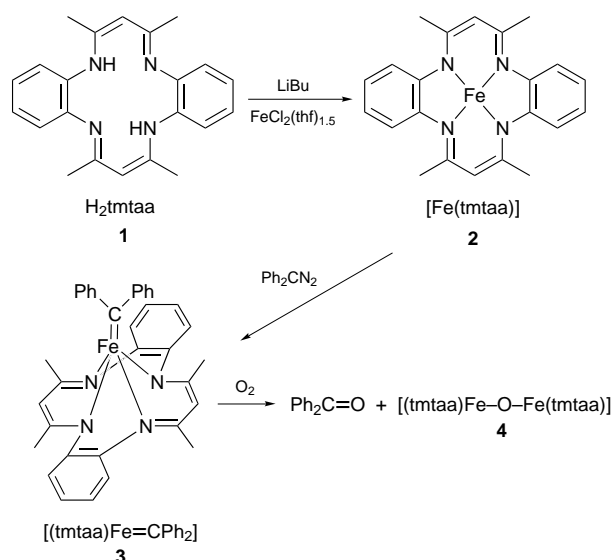
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We report an unprecedented entry to the chemistry of the iron–carbene functionality supported by an easily available macrocycle.

The metal–carbene unit is a key functionality both in organometallic and organic chemistry.¹ It is usually bonded to conventional ancillary ligands, with a few remarkable exceptions in metal–porphyrin chemistry,^{2–6} and particularly in the case of iron² and ruthenium.^{2b,3,5} Despite of considerable effort in this field, owing to the relevance of metal–porphyrin carbene derivatives in chemistry and biology,^{2,3} some facts are particularly surprising: (i) there is an absence of any modeling approach in macrocycle chemistry, *i.e.* the use of readily available macrocycles; (ii) the potential of the metal–carbene bonded to a macrocyclic structure is still to be explored; (iii) very few (three, at present) metal–porphyrin carbenes have been structurally characterized.^{2a,6}

Here, we report a straightforward synthesis of iron–carbenes stabilized by the easily accessible tetramethyldibenzotetraazaannulene ligand (H₂tmtaa)⁷ along with their structural characterization in solution and in the solid state. The availability of tetramethyldibenzotetraazaannulene encourages the use of [Fe(tmtaa)] for developing iron–carbene chemistry based on this and other macrocycles. The synthesis was performed by reacting **2**^{8a} with the corresponding diazoalkane (Scheme 1).

The reaction of **2** with Ph₂CN₂ in THF at –30 °C, and then at room temperature, gave high yields of **3** as a green crystalline solid.[†] Complex **2** showed a very high thermal stability and resistance to hydrolysis. The reaction of **3** with dioxygen gave, almost quantitatively, benzophenone and the well known μ -oxo dimer **4**.^{7a} The stability and the nature of the final compound



Scheme 1

derived from the reaction of **2** with diazoalkanes is strongly dependent on the substituents at the carbene carbon. In the case of PhCHN₂, the carbene derivative forms only at low temperature. It decomposes at room temperature leading to the starting material and *trans*-stilbene (81%) and *cis*-stilbene (19%), while in the presence of dioxygen it forms PhCHO and complex **4**. Owing to its diamagnetism, **3** has been readily characterized by ¹H and ¹³C NMR spectroscopies and structural details have been revealed by X-ray analysis[‡] (see Fig. 1). The coordination environment of iron is a distorted tetragonal pyramid, unlike iron–prophyrin^{2a} or osmium–prophyrin^{6b} examples, where the metal is always six-coordinate. The metal is displaced by 0.335(1) Å from the N₄ average plane. The Fe–C(23) vector is perpendicular to the N₄ core, the dihedral angle with the normal to the N₄ plane being 1.0(1)°. The carbene plane C(23)C(31)C(41) is almost parallel to the N(2)–N(4) vector, the torsion angles C(31)–C(23)–Fe–N(4) and C(41)–C(23)–Fe–N(2) being –15.5(3) and –15.2(3)°, respectively. The Fe–C(23) bond distance [1.794(3) Å] is particularly short compared to the only available iron–porphyrin [Fe=CCL₂ 1.83(3) Å]^{2a} or organometallic derivatives of iron, where it ranges from 1.978(3) to 1.85(3) Å.⁹ The question whether the oxidation state of iron in **3** is +2 or +4 can be reasonably answered, in the absence of Mössbauer measurements, by considering the Fe distance from the N₄ plane. A correlation in tmtaa complexes has been established between the out of plane distance of the metal and its dⁿ configuration.^{7b} The value found in the present case [0.335(1) Å] is expected for low-spin d⁶ five-coordinate iron(II), *e.g.* 0.29 Å in [Fe(tmtaa)(CO)].^{8c} Much longer distances would be found for a d⁴ configuration. The extended

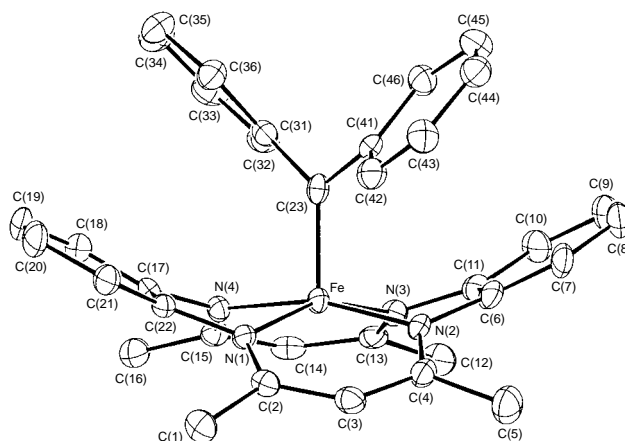


Fig. 1 ORTEP drawing of complex **3** (50% probability ellipsoids). Selected interatomic distances (Å) and angles (°): Fe–N(1) 1.921(3), Fe–N(2) 1.926(2), Fe–N(3) 1.911(3), Fe–N(4) 1.920(2), Fe–C(23) 1.794(3), C(23)–C(31) 1.487(5), C(23)–C(41) 1.472(4); N(3)–Fe–N(4) 94.6(1), N(2)–Fe–N(4) 163.3(1), N(2)–Fe–N(3) 82.7(1), N(1)–Fe–N(4) 82.3(1), N(1)–Fe–N(3) 156.4(1), N(1)–Fe–N(2) 93.6(1), Fe–C(23)–C(41) 122.6(2), Fe–C(23)–C(31) 121.7(2), C(31)–C(23)–C(41) 115.7(3).

Hückel calculations further support the +2 oxidation state for iron in **3** and the use of carbene rather than alkylidene terminology for the present complexes. The tmtaa, which shows the usual saddle shape conformation,⁷ has structural parameters quite close to those reported for the other iron complexes.⁸

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Footnotes and References

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† *Preparation of 3*: To a cooled (−30 °C) THF solution (140 ml) of [Fe(tmtaa)]·thf^{8a} (1.79 g, 3.80 mmol) was added dropwise a THF solution (40 ml) of diphenyldiazomethane (0.78 g, 4.0 mmol). When warmed to room temperature the solution became red. Nitrogen gas was slowly given off. After stirring for 2 d, the green solution was concentrated *in vacuo* (20 ml) and then hexane (15 ml) added. A green crystalline solid was obtained (1.70 g, 75%). Crystals suitable for X-ray analysis were grown in toluene (Found: C, 74.53; H, 5.77; N, 9.91. C₃₅H₃₂FeN₄ requires C, 74.47; H, 5.71; N, 9.92%). ¹H NMR (200 MHz, C₆D₆, 25 °C): δ 6.88–6.76 (m, 8 H), 6.35–6.33 (m, 10 H), 5.13 (s, 2 H), 2.12 (s, 12 H). ¹³C NMR (100.6 MHz, C₆D₆, 25 °C): δ 313.2 (C carbene), 166.6, 157.9, 149.3, 127.1, 124.8, 120.9, 120.5, 119.7, 107.3, 67.8, 25.8, 23.2.

‡ *Crystal data for 3*: C₃₅H₃₂FeN₄·C₇H₈, *M* = 656.7, triclinic, space group *P*1̄, *a* = 11.670(3), *b* = 13.593(4), *c* = 11.234(3) Å, α = 106.72(2), β = 96.21(2), γ = 77.62(2)°, *U* = 1665.0(8) Å³, *Z* = 2, *D*_c = 1.310 g cm^{−3}, *F*(000) = 692, Mo-Kα radiation (λ = 0.7109 Å), μ(Mo-Kα) = 4.87 cm^{−1}; crystal dimensions 0.08 × 0.72 × 0.85 mm. The structure was solved by the heavy atom method and anisotropically refined for all the non-H atoms. All the hydrogen atoms were located from difference Fourier maps and introduced as fixed contributors in the last stage of refinement (*U*_{iso} = 0.05 Å²). For 4428 unique observed reflections [*I* > 2σ(*I*)] collected at *T* = 133 K on a Rigaku AFC6S diffractometer (5 < 2θ < 50°) and corrected for absorption the final *R* is 0.059 (*wR*₂ = 0.163 for the 5293 reflections having *I* > 0 used in the refinement). All calculations were carried out on a QUANSAN Personal Computer equipped with an INTEL PENTIUM processor. CCDC 182/644.

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