Unprecedented pentadenticity of the HB(3-Phpz)$_3$ (= Tp^{Ph}) ligand†

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Previously unobserved pentadentate coordination of a tris(pyrazolyl)borate ligand has been ascertained in the compound Ir[κ^5(*N*,*N′*,*N″*,*C*^{Ph},*C*$^{Ph′}$)-Tp^{Ph}](η^2-C$_2$H$_4$) (Tp^{Ph} = hydridotris(3-phenylpyrazolyl)borate] that forms by thermal activation of a mixture of [IrCl(coe)$_2$]$_2$ (coe = cyclooctene) with TlTp^{Ph} and ethene, through the intermediacy of Ir[κ^4(*N*,*N′*,*N″*,*C*^{Ph})-Tp^{Ph}](Et)(η^2-C$_2$H$_4$).

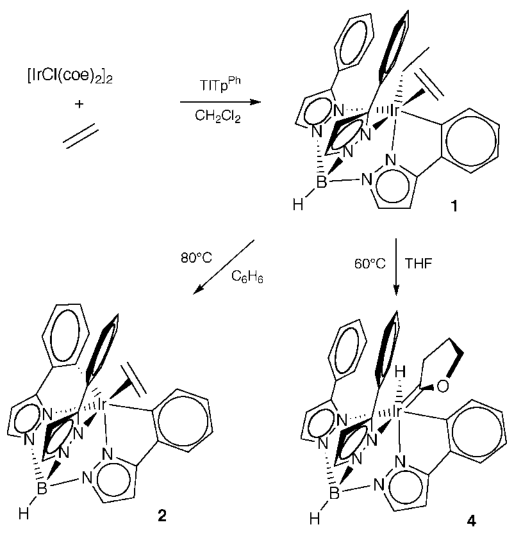
Denticity beyond κ^4 has never been encountered for Tp^R where R contains no heteroatoms. We are reporting herewith the synthesis of the first examples of a Tp^{Ph} ligand acting in an unprecedented pentadentate, as well as tetradentate, fashion in Ir(III) complexes, and the structural characterization of representative compounds.

Homoscorpionate ligands, Tp^R, where R is a 3-substituent on the pyrazolyl ring, have overwhelmingly exhibited a κ^3 coordination mode, usually κ^3-*N*, *N′*,*N″*,[1] and sometimes also κ^3-*N*, *N′*,*H*,[2,3] although lower denticity, such as κ^2-*N*,*N′*, κ^2-*N*,*H*, κ^1-*N*, and even κ^0 (where the Tp^R ligand serves only as an uncoordinated counter ion) has also been encountered.[4] By contrast, expansion of Tp^R denticity beyond κ^3 is rare. On the one hand this can occur by way of the 3-R substituent containing donor atoms, as in the demonstrably hexadentate Tp^{py},[5] or in the potentially hexadentate ligands Tp^{oAn},[6] or Tp$^{2,4(OMe)2Ph}$.[7] On the other hand, tetradenticity has been reported in Tp^R ligands where R contained no donor atoms, either by way of agostic bonding,[8] or through cyclometalation taking place at one of the aliphatic R groups per ligand,[9] or when an oxidative functionalization of one R group per ligand took place, leading to a C–O–M bond.[10,11] An example of reversible oxidative addition of the *ortho*-C–H of the phenyl group in the RhTp^{Ph}(CO)$_2$ complex, thus making the Tp^{Ph} ligand κ^4, has been reported in a dissertation.[12]

The reaction of [IrCl(coe)$_2$]$_2$ (coe = cyclooctene) with ethene and TlTp^{Ph} in CH$_2$Cl$_2$ produced the cyclometalated compound Ir[κ^4(*N*,*N′*,*N″*,*C*^{Ph})-Tp^{Ph}](Et)(η^2-C$_2$H$_4$) **1** (Scheme 1).† This was in sharp contrast to the related reactions of [IrCl(coe)$_2$]$_2$ with ethene and KTp or KTp^{Me2}, which under identical conditions produced the Ir(I) complexes IrTp^{Me2}(η^2-C$_2$H$_4$)$_2$. The propensity of the Ir(I)Tp^R fragments to induce C–H bond activation, enhanced in the present case by the increased steric bulk of the Tp^{Ph} ligand, and coupled with the close proximity of the phenyl rings to the metal, can be used to rationalize the facile activation of one of the phenyl rings, and one of the ethene ligands. The X-ray structure of **1** (see ESI) showed Ir in a distorted octahedral environment,‡ as indicated by the bite angles of the Tp^{Ph} ligand: N(3)–Ir–N(5) 83.3(1)°, N(1)–Ir–N(3) 92.8(2)°, N(1)–Ir–N(5) 76.1(1)°. The difference between the latter two (16.7°) is substantially larger than usual values (< 10°). The metalated phenylpyrazolyl unit showed a strong distortion by which the boron atom and the phenyl ring are considerably displaced from the plane of the pz ring: B by 0.73 Å, Ir by 0.37 Å and C(4) by 0.28 Å. At this stage, it appears appropriate to draw attention on the similarity of the cyclometalation of the phenylpyrazolyl unit of the Tp^{Ph} ligand that leeds to complex **1**, with related transformations that involve donors such as 2-phenylpyridine, 1-phenylpyrazole or bipyridine.[13,14] The metalation of the benzene ring of these compounds attached to the functional group that possesses the donor atom, requires, in general, more forcing conditions[14] than those needed for the generation of **1** but yields related organometallic complexes that incorporate the heterocyclic donor atom.[14]

Refluxing complex **1** in benzene for 17 h produced the bis-metalated species Ir[κ^5(*N*,*N′*,*N″*,*C*^{Ph},*C*$^{Ph′}$)-Tp^{Ph}](η^2-C$_2$H$_4$) **2**, as the only product (NMR monitoring).§ The proposed κ^5 coordination mode was suggested by the presence of four carbon signals in the range δ 123.2–122.5 (this is also the case in compound **3**, *vide infra*). Refluxing **1** in toluene, converted it completely to **2** in 4.5 h. It can be concluded, therefore, that **2** is thermodynamically favored over the *a priori* expected compound Ir[κ^3(*N*,*N′*,*N″*)-Tp^{Ph}](Ph)$_2$(L), where L could be either ethene or dinitrogen, as was in the case with IrTp*(η^2-C$_2$H$_4$)$_2$.[15]

A related compound, which also contained a κ^5-Tp^{Ph} ligand, Ir[κ^5(*N*,*N′*,*N″*,*C*^{Ph},*C*$^{Ph′}$)-Tp^{Ph}](κ^1(*N*^{1})-3-phenylpyrazole) **3**, was formed upon treatment of [IrCl(coe)$_2$]$_2$ with 2,3-dimethylbutadiene and TlTp^{Ph}, the 3-phenylpyrazole resulting from partial ligand degradation. Surprisingly, a direct reaction of **2** with the free pyrazole, Hpz^{Ph}, proceeded only slowly, and yielded other products, in addition to **3**. Spectroscopic data for **3** were in agreement with the proposed structure. While ^{11}B NMR and ν(B–H) data for **3** (as for **1** and **2**) did not indicate the coordination mode of the Tp^{Ph} ligand,[16] the ^{13}C NMR spectrum showed characteristic signals for carbon atoms of the metalated rings at δ 122.9, 122.5, 122.4, and 121.5. By comparison, **1** had only two signals in this region, at δ 122.2 and 121.9. It is



Scheme 1

† Electronic supplementary information (ESI) available: preparation and characterization data for compounds **1**–**4** and ORTEP plot of **1**. See http://www/rsc/org/suppdata/cc/a9/a908478i/

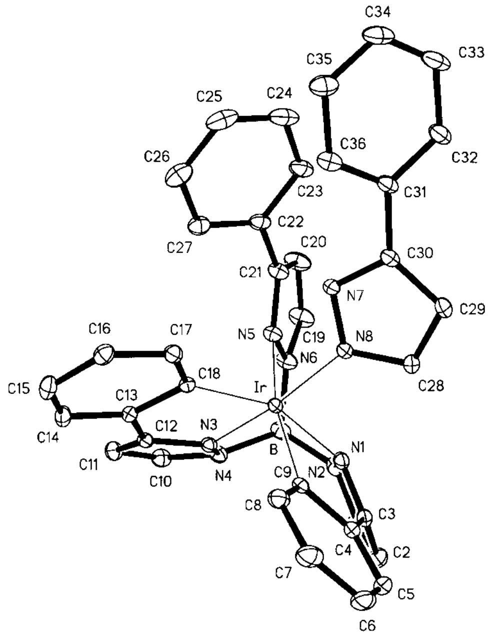


Fig. 1 ORTEP plot of **3** (hydrogen atoms omitted for clarity; thermal ellipsoids are at the 20% probability level). Selected bond lengths (Å) and angles (°): Ir–N(1) 2.114(2), Ir–N(3) 1.989(2), Ir–N(5) 2.219(2), Ir–C(9) 2.053(2), Ir–C(18) 2.051(2), Ir–N(8) 2.059(2), N(3)–Ir–N(1) 84.1(1), N(3)–Ir–N(5) 79.2(1), N(1)–Ir–N(5) 88.7(1), N(3)–Ir–N(8) 172.7(1), N(3)–Ir–C(9) 103.6(1), N(3)–Ir–C(18) 79.3(1), C(9)–Ir–N(1) 77.7(1), C(18)–Ir–C(9) 91.4(1).

noteworthy, that both **2** and **3** contained inequivalent pyrazolyl and phenyl rings. Thus, the diastereoselective cyclometalation of the 3-phenyl group of the pz^{Ph} ring *trans* to the monodentate ligand (in the case of **3**, 3-phenylpyrazole), gave rise to asymmetry of the molecule.

The ORTEP diagram of **3**, along with important bond lengths and angles is shown in Fig. 1.‡ The two Ir–C bond lengths are identical within experimental error [2.053(2) Å] and are also identical to the two Ir–C_6H_5 bonds of the somewhat related compound $[IrTp^*(Ph)_2]_2(\mu\text{-}N_2)$ [2.06(2) Å],[15] while Ir–C(9) of **1** is slightly shorter [2.030(4) Å]. Considerable distortion of the pentadentate Tp^{Ph} ligand is evident from Fig. 1. Whereas the d^6 Ir(III), and the bonding implicit in the coordination to the three N atoms of a Tp^R ligand strongly favour octahedral coordination,[17] an unstrained metalation of the two phenyl rings would lead to trigonal prismatic geometry. Reconciling these two desiderata, the dimetalated Tp^{Ph} ligand becomes highly distorted. The degree of distortion of the two Ir–C^{Ph} bonded entities is manifested by the values of the bond angles around iridium [77.7–103.6(1)°, *cisoid*; 157.4–172.7(1)°, *transoid*], and also by the out-of-plane bending of B, Ir and the C atoms C(4) and C(13) of the phenyl substituents with respect to the pz planes. These deviations are 0.763(4), 0.889(4) and 1.101(4) Å for B, Ir and C(4), respectively, referred to the N(1)N(2)C(1)C(2)C(3) ring, and 0.619(4), 0.860(3) and 0.294(3) for B, Ir and C(13), respectively, with respect to the ring containing N(3) and N(4).

In conclusion, we have demonstrated the first instance of κ^5 coordination of a Tp^R ligand. This work also shows that the tendency of Tp^R ligands to strongly favor octahedral geometry at the coordinated metal centers is so pronounced that even severe ligand distortions can be accommodated. The thermodynamic stability of the metalated compounds in refluxing benzene is surprising, in view of the results observed in related systems, and may be due to the chelate effect. The presently reported compounds and related Ir(I) complexes seem to be suitable for various C–H activation reactions. As represented in Scheme 1, compound **1** reacts in THF at 60 °C to yield the Fischer carbene complex **4** as the sole product. Moreover, the phenyl groups could be used as internal probes for C–H activation, as was demonstrated by the incorporation of 1.6 deuterium atoms into only one of the phenyl rings during the reaction of **1** with THF-d_8, producing the appropriate analog of **4**. These, and related, C–H activation reactions are currently being studied.

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Notes and references

‡ *Crystal data*: $C_{31}H_{30}BIrN_6$ **1**: M = 689.62, monoclinic, space group $P2_1/n$ (no. 14), a = 16.399(5), b = 8.691(3), c = 19.809(5) Å, β = 91.77(2)°, U = 2821.9(15) Å^3, T = 295(2) K, Z = 4, μ(Mo-Kα) = 4.763 mm^{-1}, F(000) = 1360, 32 315 reflections measured, 6013 unique (R_{int} = 0.029), R_1 = 0.032 [$I \geq 2\sigma(I)$], R_1 = 0.036 (all data), wR_2 = 0.064 (all data). The structure was solved using direct methods and refined by full-matrix least squares on F^2.

For $C_{36}H_{28}BIrN_8$ **3**: M = 775.67, triclinic, space group $P\bar{1}$ (no. 2), a = 9.543(2), b = 12.043(4), c = 13.941(4) Å, α = 85.35(2), β = 77.78(2),γ = 78.63(2)°, U = 1533.9(7) Å^3, T = 223(2) K, Z = 2, μ(Mo-Kα) = 4.393 cm^{-1}, F(000) = 764, 21 402 reflections measured, 8675 unique (R_{int} = 0.022), R_1 = 0.018 [$I \geq 2\sigma(I)$], R_1 = 0.021 (all data), wR_2 = 0.042 (all data). The structure was solved using direct methods and refined by full-matrix least squares on F^2. CCDC 182/1500. See http://www.rsc.org.suppdata/cc/a9/a908478i/ for crystallographic files in .cif format.

§ Following an NMR-tube reaction (benzene-d_6, 60 °C) an intermediate could be observed, which was not characterized, but was thought to be Ir[κ^4(N,N',N'',C^{Ph})-Tp^{Ph}](Ph)(η^2-C_2H_4). Cyclohexane and hexafluorobenzene as the solvents gave **2**, but a related intermediate was not observed. Using C_6D_6 as the solvent results in perdeuteration of **2** but not of the ethene-ligand.

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