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Cp*Ir(dab) (dab = 1,4-Bis(2,6-dimethylphenyl)-1,4-diazabutadiene): A Coordinatively Unsaturated Six-π-Electron Metallaheteroaromatic Compound?

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1,4-Bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene (dab) forms the structurally characterized iridium(III) complex [Cp*IrCl(dab)](PF$_6$): $C_{28}H_{35}ClF_6IrN_2P$, orthorhombic, space group *Pnma*, $a = 16.187(2)$ Å, $b = 15.823(2)$ Å, $c = 11.677(1)$ Å, $V = 2990.8(6)$ Å^3, $Z = 4$, and $R = 0.0588$. On reaction with NaBH$_3$CN this compound does not form an iridium(III) hydride but the coordinatively unsaturated reduced product Cp*Ir(dab): $C_{28}H_{35}IrN_2$, monoclinic, space group $P2_1/n$, $a = 8.484(2)$ Å, $b = 14.535(3)$ Å, $c = 20.956(4)$ Å, $\beta = 98.88(3)°$, $V = 2553.2(9)$ Å^3, $Z = 4$, and $R = 0.0586$. The inverted relation d_{CC} (=1.334(15) Å) < d_{CN} (=1.379(13) and 1.366(14) Å) in the dab ligand of Cp*Ir(dab) suggests that the reduction has occurred primarily at that ligand to form an ene-1,2-diamido/iridium(III) moiety or, alternatively, a six-π-electron metallaheteroaromatic system. *Ab initio* pseudopotential calculations of model complexes [CpIr(HNCHCHNH)]$^{0/2+}$ support this description of the bonding.

Introduction

Coordinatively unsaturated complexes Cp*M(α-diimine) are crucial intermediates[1−3] in catalyzed hydride transfer reactions[1−4] which require a two-electron reduction of [Cp*MCl(α-diimine)]$^+$ precursors (M = Rh, Ir; α-diimine = 2,2′-bipyridine or derivatives) prior to protonation. However, the propensity of the electron-rich intermediates Cp*M(α-diimine) for oxidative addition of electrophiles has rendered their investigation and isolation difficult. On the basis of electrochemical and spectroscopic data, we have formulated[2a,b,f] the effective oxidation state distribution Cp*M^{II}(α-diimine^{-I}) with strong spin−spin pairing for the most frequently used[1,2d,3a,b,4] combination M = Rh and α-diimine = 2,2′-bipyridine. In order to drive the apparent intramolecular metal-to-ligand electron transfer still further, we became interested in combining the 14-electron fragment Cp*Ir,[5] an extremely strong π donor,[2d] with the better[6a] π-accepting 1,4-diaza-1,3-butadiene α-diimine ligands.[6]

Considering the coordinative unsaturation of the critical intermediates Cp*M(α-diimine), we employed the sterically protecting 1,4-bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene (dab) as an α-diimine ligand. Previous electrochemical studies of corresponding (pentamethylcyclopentadienyl)rhodium complexes have indicated the ability of that ligand to slow down the (chemical) addition step after (electrochemical) electron transfer.[2e] 2,6-Dimethyl- or 2,4,6-trimethyl-substituted aryl

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Table 1. Crystallographic Data

	[Cp*IrCl(dab)](PF$_6$)	Cp*Ir(dab)
chem formula	$C_{28}H_{35}ClF_6IrN_2P$	$C_{28}H_{35}IrN_2$
fw	772.20	591.78
space group	*Pnma* (No. 62)	$P2_1/n$ (No. 14)
a (Å)	16.187(2)	8.484(2)
b (Å)	15.823(2)	14.535(3)
c (Å)	11.677(1)	20.956(4)
β(deg)		98.88(3)
V (Å^3)	2990.8(6)	2553.2(9)
Z	4	4
ρ_{calc} (g cm^{-3})	1.715	1.540
μ (mm^{-1})	4.665	5.246
λ (Å)	0.710 73	0.710 73
T (°C)	−100	−100
R indices ($I > 2\sigma(I)$)^{a,b}	$R = 0.0588$, $R_w = 0.1454$	$R = 0.0586$, $R_w = 0.1479$

^{a} $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

groups are well-known to protect axial sites such as singly occupied boron p$_z$[7] or platinum d$_{z^2}$ orbitals.[8]

Both the precursor [Cp*IrCl(dab)](PF$_6$) and the coordinatively unsaturated Cp*Ir(dab), obtained unexpectedly from the reaction with cyanoborohydride, could be crystallized and characterized spectroscopically; their electronic structures were studied with the help of *ab initio* pseudopotential[9] calculations.

Experimental Section

Materials and Procedures. 1,4-Bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene (dab) and [Cp*IrCl(μ-Cl)]$_2$ were prepared according to published procedures.[6a,10]

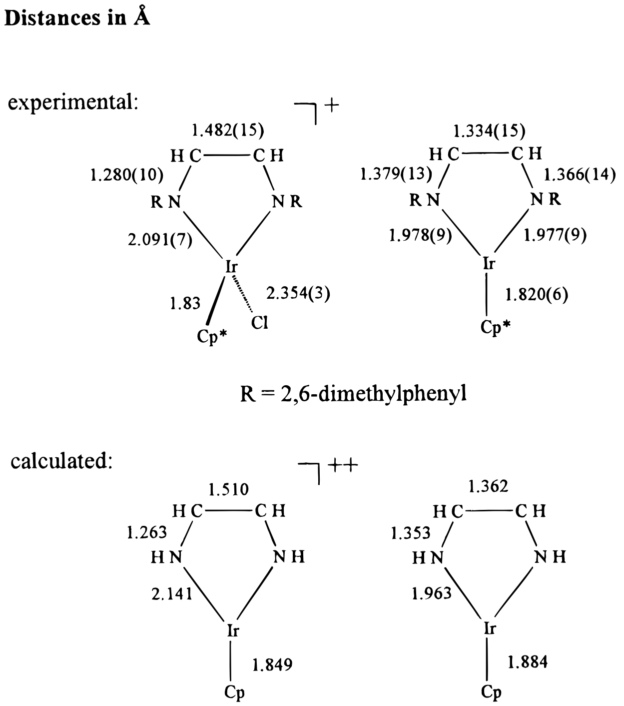
[Cp*IrCl(dab)](PF$_6$). A 202 mg (0.253 mmol) amount of [Cp*IrCl(μ-Cl)]$_2$ was reacted with 167 mg (0.632 mmol) of dab for 4 h in methanol (30 cm^3). Precipitation of the green hexafluorophosphate by addition of 390 mg (1 mmol) of Bu$_4$NPF$_6$ was almost quantitative (95%). Anal. Calcd for $C_{28}H_{35}ClF_6IrN_2P$: C, 43.55; H, 4.57; N, 3.63. Found: C, 43.51; H, 4.50; N, 3.65. UV/vis (acetone, λ_{max} in nm): 580, 425.

Cp*Ir(dab). A suspension of 77.2 mg (0.10 mmol) of [Cp*IrCl(dab)](PF$_6$) in a mixture of 20 cm^3 of ethanol and 5 cm^3 of water was reacted with 31.5 mg (0.50 mmol) of sodium cyanoborohydride under argon. After the mixture was stirred for 5 h at ambient temperature, the air-sensitive yellow-orange precipitate was filtered off, washed with water, and dried under vacuum. Yield: 42 mg (71%). Anal. Calcd for $C_{28}H_{35}IrN_2$: C, 56.83; H, 5.96; N, 4.73. Found: C, 56.61; H, 5.90; N, 4.72. UV/vis (toluene): $\lambda_{max} = 431$ nm (log $\epsilon = 4.00$).

[Cp*Ir(CH$_3$CN)(dab)](PF$_6$)$_2$. About 20 mg (0.061 mmol) of solid [Cp$_2$Fe](PF$_6$) was added to a solution of 18 mg (0.0304 mmol) of Cp*Ir(dab) in 10 cm^3 of acetonitrile. After the mixture was stirred for 1 h, the unreacted ferrocenium hexafluorophosphate was filtered off and the solvent removed from the reddish brown filtrate. Extraction of the solid residue with *n*-hexane to remove ferrocene and brief drying under vacuum produced 20 mg (71%) of a reddish brown material which was immediately dissolved in CD$_3$CN for NMR spectroscopy (Table 2).

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer. UV/vis absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in acetonitrile/0.1 M Bu$_4$NPF$_6$ using a three-electrode configuration (glassy-carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273A potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell.[11]

Chart 1



Crystallography. Data were collected on a Syntex P2$_1$ diffractometer. An empirical absorption correction (ψ scans) was applied. The structures were solved by the Patterson method using the SHELXTL-PLUS program.[12] Refinement was achieved with SHELXL-93[13] employing full-matrix least-squares methods.

[Cp*IrCl(dab)]PF$_6$. Dark green crystals were obtained by slow diffusion of diethyl ether into a methanol solution at room temperature. The Cp* ring showed disorder in terms of a "staggered" (55%, Figure 1) or "eclipsed" orientation (45%, designated as A) of the Ir−Cl bond relative to Cp* methyl groups. All non-hydrogen atoms apart from those of the disordered Cp* ring were refined anisotropically. Hydrogen atoms were placed in their ideal positions and were allowed to ride on the corresponding carbon atoms.

[Cp*Ir(dab)]. Dark orange crystals suitable for X-ray diffraction were obtained by slow cooling of an ethanol/water mixture (4/1, v/v). The DIFABS absorption correction[14] was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their ideal positions and were allowed to ride on the corresponding carbon atoms.

Calculations. *Ab initio* calculations were performed for (η^5-C$_5$H$_5$)Ir(HNCHCHNH) using Dunning's valence double-ζ basis with polarization functions for H, C, and N[15a] and quasirelativistic effective core pseudopotentials and corresponding basis functions for the iridium

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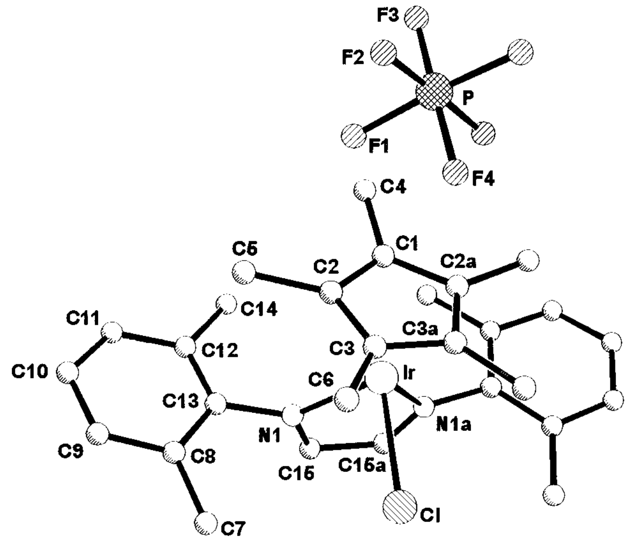


Figure 1. Molecular structure of [Cp*IrCl(dab)](PF$_6$) in the crystal ("staggered" configuration of Cp*). Selected bond lengths (Å) and angles (deg): Ir−Cl = 2.354(3), Ir−N1 = 2.091(7), N1−C15 = 1.280(10), C15−C15a = 1.482(15), N1−C13 = 1.450(10), Ir−C1 = 2.215(21), Ir−C2 = 2.198(14), Ir−C3 = 2.196(15); N1−Ir−N1a = 76.0(4), Ir−N1−C15 = 115.3(5), N1−C15−C15a = 115.3(4). Dihedral angles (deg) between rings: IrNCCN/Cp* = 74.7(6), IrNCCN/R = 81.7(3) (R = 2,6-dimethylphenyl); angle IrCNNC/IrCl = 78.2°.

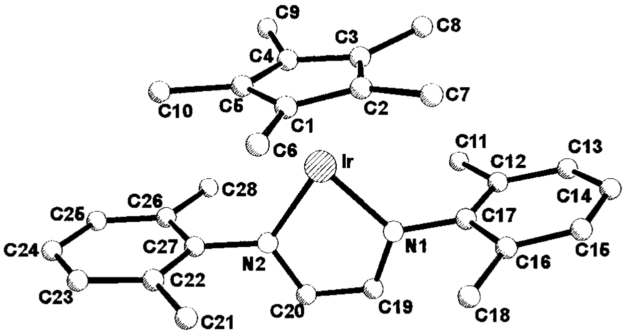


Figure 2. Molecular structure of Cp*Ir(dab) in the crystal. Selected bond lengths (Å) and angles (deg): Ir−N1 = 1.977(9), Ir−N2 = 1.978(9), N1−C19 = 1.366(14), C19−C20 = 1.334(15), N2−C20 = 1.379(13), N1−C17 = 1.419(14), N2−C27 = 1.432(14), Ir−C1 = 2.175(12), Ir−C2 = 2.199(12), Ir−C3 = 2.199(12), Ir−C4 = 2.151(14), Ir−C5 = 2.209(12); N1−Ir−N2 = 76.9(4), Ir−N1−C19 = 118.7(7), Ir−N2−C20 = 116.0(7), N1−C19−C20 = 112.2(10), N2−C20−C19 = 116.1(10). Dihedral angles (deg) between rings: IrNCCN/Cp* = 88.9(4), IrNCCN/R = 89.0(4) (R = 2,6-dimethylphenyl).

atom.[9] Geometry optimizations were performed within C_s constrained symmetry using the GAUSSIAN 94 program package.[15b]

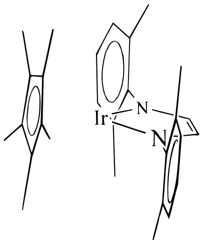
Results and Discussion

When the conventionally synthesized[2b,3d,g] and structurally characterized [Cp*IrCl(dab)](PF$_6$) (dab = 1,4-bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene) was reacted with sodium cyanotrihydridoborate in ethanol/water (4/1, v/v), the result was yellow-orange Cp*Ir(dab), which could also be crystallized and characterized spectroscopically and electrochemically. The reaction of the chloroiridium(III) precursor with Na[BH$_3$CN] did thus not result in the familiar[2b,3] substitution of Cl by H but in a *reduction* of the complex (eq 1). Bearing in mind the

$$[\mathrm{Cp^*IrH(dab)}](\mathrm{PF_6}) \overset{\text{“H}^-\text{”}}{\nleftarrow} [\mathrm{Cp^*IrCl(dab)}](\mathrm{PF_6}) \xrightarrow{\text{“H}^-\text{”}} \mathrm{Cp^*IrCl(dab)} \quad (1)$$

noninnocent nature of dab ligands,[6,16] the product of this reduction was studied by experimental methods and by *ab initio* pseudopotential calculations.

The results of the crystal structure analyses are summarized in Table 1, Chart 1, and Figures 1 and 2. [Cp*IrCl(dab)](PF$_6$) shows the expected[3g] pseudotetrahedral arrangement, the short C═N and long C−C and N−Ir bonds within the chelate ring clearly indicating an Ir^{III}/dab^0 oxidation state situation (Chart 1).[6,16] On the other hand, the neutral compound Cp*Ir(dab) exhibits a metal center in a pseudo-trigonal-planar environment with virtually orthogonal Cp* and IrNCCN(dab) chelate rings. The coordinatively unsaturated metal in that five-membered ring is effectively protected by all three mutually parallel Cp* and 2,6-dimethylphenyl ring systems:



Whereas the α-diimine ligand in a previously reported related compound described as Cp*Ir(bpy-4,4′-COOH) (bpy-4,4′-COOH = 2,2′-bipyridine-4,4′-dicarboxylic acid)[3g] shows no significant structural evidence for ligand reduction, as is evident from the single-bond length of 1.47(1) Å between the pyridine moieties,[3g,17] the C−C, C−N,[6,16] and Ir−N[18] distances in the chelate ring in Cp*Ir(dab) suggest strong contributions from the ene-1,2-diamide structure RN$^-$−CH═CH−NR$^-$ of the dab ligand. This also implies that the reduction producing this compound has effectively occurred at the α-diimine ligand and not at the metal site (which remains Ir^{III}). Similarly short C═C distances and long C−N bond lengths in chelate complexes of 1,4-diaza-1,3-butadienes were previously only known from carbene[19] and silylene[20] compounds, from main-group[21] or

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(17) The compound formulated as Cp*Ir(bpy-4,4′-COOH) has a pseudopyramidal configuration at the metal with a tilt angle of about 75° between the Cp* ring and the heterocyclic plane; two of the carboxylic oxygen atoms show very large thermal motion.[3g] Intramolecular protonation of the *unprotected* Ir^I site by the acidic COOH groups may be considered.

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Table 2. ^{1}H and ^{13}C NMR Data (δ, ppm) for Iridium/dab Complexes[a]

	[Cp*IrCl(dab)](PF$_6$)	Cp*Ir(dab)		[Cp*Ir(dab)(CH$_3$CN)](PF$_6$)$_2$[b]
	CD$_3$CN	CD$_3$OD	C$_6$D$_6$	CD$_3$CN
		^{1}H Spectra		
CH$_3$(Cp*)	1.13(s)	1.27(s)	1.21(s)	1.18(s)
CH$_3$(R)[d]	2.07(s)/2.41(s)[c]	2.08(s)	2.21(s)	2.12(s)/2.27(s)[c]
CH(R)[d]	7.28(ps)[e]	H^4: 6.97(dd)[f]	7.01(dd)[g]	7.38(ps)[e]
		H^{3,5}: 7.12(d)[h]	7.14(d)[h]	
CH(imine)	9.03(s)	6.81(s)	6.96(s)	9.12(s)
CH$_3$(CH$_3$CN)				1.96(s)
		^{13}C Spectra		
*C*H$_3$(Cp*)	8.40	nd	8.31	nd
*C*H$_3$(R)[d]	19.10/20.05[c]		17.02	
*C*CH$_3$(Cp*)	96.10		82.67	
*C*H(R)[d]	129.50[i]		124.90	
	129.80		129.00	
	130.80		132.24	
	131.16			
	131.35			
*C*N(R)[d]	132.07		132.60	
CH(imine)	174.30		155.50	

[a] dab = 1,4-bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene. [b] From oxidation of Cp*Ir(dab) with ferrocenium hexafluorophosphate. [c] Inequivalent 2- and 6-methyl groups due to restricted rotation. [d] R = 2,6-dimethylphenyl. [e] ps: pseudo-singlet (accidental degeneracy) [f] Different coupling constants: ^{3}J(H^3,H^4) = 6.9 Hz, ^{3}J(H^4,H^5) = 8.0 Hz. [g] Different coupling constants: ^{3}J(H^3,H^4) = 6.5 Hz, ^{3}J(H^4,H^5) = 8.3 Hz. [h] Average coupling constant ^{3}J = 7.4 Hz. [i] Inequivalent 2/6- and 3/5-positions due to restricted rotation.

lanthanoid-element complexes.[22] In the transition-metal series,[6,16,22] only the structure of (η^2-BH$_4$)$_2$Zr(tBuNCHCHNtBu) comes close to that of the organometallic system Cp*Ir(dab) with values of d(CC) = 1.361(5) Å and d(CN) = 1.385(4) and 1.387(4) Å.[23]

Assuming the iridium(III) formulation, the relative stability of a coordinatively unsaturated 5d^6 metal center *despite* the very strong ligand-field preference for close-to-octahedral coordination is not completely without precedent. As in Cp*Ir(dab), the coordinatively unsaturated organotungsten(0) complex dianion [(cat)W(CO)$_3$]$^{2-}$ (cat = catecholate) is stabilized by the extremely strong σ- *and* π-donor effect of a dianionic unsaturated chelate ligand.[24] Similarly, coordinatively unsaturated iridium(III) compounds with 16-electron configurations are stabilized by simultaneously σ- and π-donating ligands;[5b,c] however, Cp*Ir(dab) is an 18-electron species.

Spectroscopic data are in agreement with the proposed oxidation state distribution in Cp*Ir^{III}(dab^{-II}). An intense (log $\epsilon = 4.0$) and relatively[2] high energy absorption at 431 nm points to strong orbital mixing between metal d$_\pi$ and dab π* MOs, creating a $\pi \rightarrow \pi^*$ instead of a charge transfer transition.[25] Cyclic voltammetry and coulometry reveal that a reversible two-electron oxidation occurs at −0.37 V vs Cp$_2$Fe$^{+/0}$.[26] Spectroelectrochemistry in acetonitrile showed a bleaching of the intense 431 nm band and the emergence of low-intensity shoulders at 540, 420, and 345 nm which are typical for the complexes [Cp*M(α-diimine)X]$^{n+}$.[2a,b] Separate chemical oxidation of Cp*Ir(dab) with ferrocenium hexafluorophosphate produced similar spectra, and the ^{1}H NMR spectrum suggests the formation of [Cp*Ir(dab)(CH$_3$CN)]$^{2+}$ with nonlabile acetonitrile as a ligand (Table 2). A comparison of ^{1}H and ^{13}C NMR data between [Cp*Ir(dab)Cl](PF$_6$) and Cp*Ir(dab) reveals particularly large effects for the imine−CH centers, the sizable upfield shifts $\Delta\delta_H > 2$ ppm and $\Delta\delta_C \approx 20$ ppm confirming the predominant dab-centered reduction (Table 2). In complex ions [Cp*M(dab)X]$^{n+}$ the arylmethyl groups in the 2,6-dimethylphenyl substituents are nonequivalent due to restricted rotation.[2e] Remarkably, the H^4 protons of that substituent also show a clear splitting in Cp*Ir(dab) (Figure 3), suggesting a deviation from the symmetric situation found in the solid state; weak axial interactions with one solvent molecule may be responsible for this phenomenon.

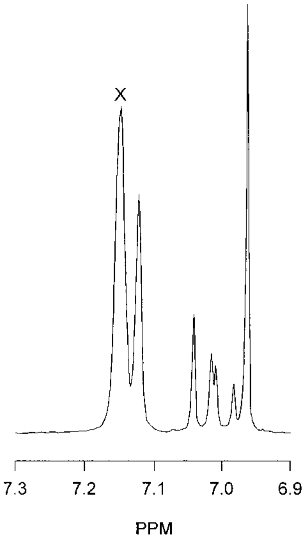

Figure 3. ^{1}H NMR spectrum (low-field section) of Cp*Ir(dab) in C$_6$D$_6$, illustrating the nonsymmetry of the CH(aryl) protons (X denotes the resonance of C$_6$H$_x$D$_{6-x}$, which obscures one part of the signal from the protons H^{3,5}.

Ab initio pseudopotential[9] calculations were performed for the neutral and dicationic complexes, employing *N*-hydrogen substituents instead of the 2,6-dimethylphenyl groups at the 1,4-diaza-1,3-butadiene ligand and Cp instead of Cp* (Chart 1). Considering these changes of substituents, the calculated structures are in good agreement with the experimental data for Cp*Ir(dab) and [Cp*Ir(dab)Cl]$^+$. Not unexpectedly, the

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(26) The peak potential difference of 48 mV and the coulometric peak height of 1.6 charge equiv are also compatible with two very close lying one-electron processes. The oxidized species exhibits no EPR signal down to 4 K.

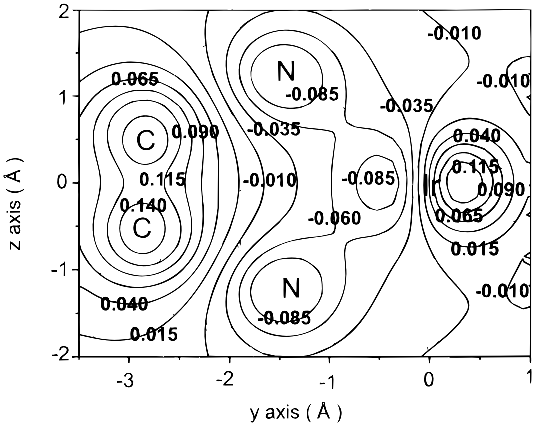
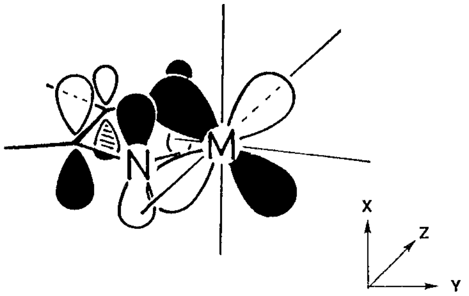


Figure 4. Ab initio/pseudopotential-calculated contour map of the redox orbital (HOMO) of CpIr(HNCHCHNH), 0.5 Å above the IrNCCN plane.

Chart 2

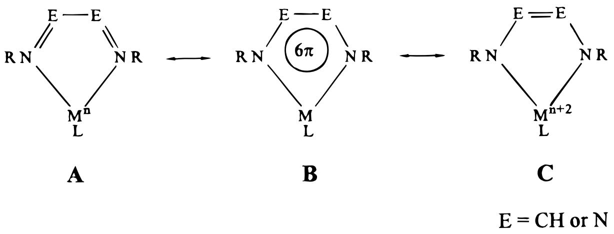


replacement of the two π-accepting N-aryl substituents in the dab ligand and of the five electron-donating methyl groups in the cyclopentadienide ligand by H appears to equilibrate the C−N and C−C distances in CpIr(HNCHCHNH); in the actual structure of Cp*Ir(dab) with a more electron-rich metal and stronger π-accepting dab ligand the ene-1,2-diamide situation with a shorter C−C distance and longer C−N bonds is favored. For the oxidized species, the coordination of negatively charged chloride to the Lewis acidic metal center in $[\mathrm{Cp^*Ir(dab)Cl}]^+$ lowers the Ir−N distance relative to the calculated value for $[\mathrm{CpIr(HNCHCHNH)}]^{2+}$ and attenuates the differences of the intra-diazabutadiene distances ($d_{\mathrm{CN}} < d_{\mathrm{CC}}$).

The highest *occupied* MO of electron-rich Cp*Ir(NHCHCHNH) is shown in Figure 4. It is composed from the lowest unoccupied π MO of 1,4-diaza-1,3-butadiene[6,25] and the distorted d_{xy} orbital of the metal. A side-view representation illustrates this kind of overlap in Chart 2.

While the oxidation state formulation $\mathrm{Ir^{III}/dab^{-II}}$ (Scheme 1; **C**) is thus supported by the calculation, the alternative description **B** (Scheme 1) involves the kind of six-π-electron "metallaaromaticity" that has been reported previously for iridabenzene[27] and iridathiabenzene compounds.[28] Similar, albeit not identical, situations have been reported before in the 3d series between CpCo and diazabutadienes[25] and, on the basis of structural results, between CpCo[29] or CpNi[30] fragments and the extremely strong π-accepting 1,4-diorganotetraaza-1,3-butadiene chelate ligands. Cationic complexes between tetraazabutadienes ("tetrazenes") and $\mathrm{Ir(CO)(PPh_3)_2}$ also bear some resemblance to the species reported here;[31] the crystallographically determined N−N bond length distribution and the Ir−N distances reported for one derivative also supported the formulation **B** or **C** (cf. Scheme 1).

Scheme 1



Employing the established propensity of iridium to engage in efficient d_π/p_π delocalization with light-element π systems[27] and the extreme π-donor capacity of Cp*Ir,[2b,c] we have thus obtained the 1,4-diaza-1,3-butadiene/transition-metal compound Cp*Ir(dab), which comes close to the extreme resonance formulation **C** in Scheme 1. As in the case of carbene[19] and silylene[20] compounds the ene-1,2-diamido chelate ligand system has shown its capacity to stabilize coordinatively unsaturated centers. Although Cp*Ir(dab) contains formally a "basic metal" according to Werner's concept,[32] it remains to be studied whether the unusual structure described here allows for the associated kind of reactivity.

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Supporting Information Available: Tables giving details of X-ray crystal data collection, anisotropic temperature factors, hydrogen atom coordinates, and bond lengths and angles and additional views and stereoviews of $[\mathrm{Cp^*IrCl(dab)}](\mathrm{PF_6})$ and Cp*Ir(dab) (16 pages). Ordering information is given on any current masthead page.

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