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

Stefan Greulich, Wolfgang Kaim,* and Andreas F. Stange

Institut für Anorganische Chemie der Universität, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

Hermann Stoll

Institut für Theoretische Chemie der Universität, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

Jan Fiedler and Stanislav Záliš

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

Received November 17, 1995[⊗]

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 $NaBH_3CN$ 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

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1996.

(1) (a) Kölle, U.; Grätzel, M. *Angew. Chem.*, **1987**, *99*, 572; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 568. (b) Kölle, U.; Kang, B.-S.; Infelta, P.; Compte, P.; Grätzel, M. *Chem. Ber.* **1989**, *122*, 1869. (c) Kölle, U. *New J. Chem.* **1992**, *16*, 157.

(2) (a) Ladwig, M.; Kaim, W. *J. Organomet. Chem.* **1991**, *419*, 233. (b) Ladwig, M.; Kaim, W. *J. Organomet. Chem.* **1992**, *439*, 79. (c) Bruns, W.; Kaim, W.; Ladwig, M.; Olbrich-Deussner, B.; Roth, T.; Schwederski, B. In *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., McCleverty, J., Eds.; Kluwer: Dordrecht, The Netherlands, 1993; p 255. (d) Reinhardt, R.; Fees, J.; Klein, A.; Sieger, M.; Kaim, W. In *Wasserstoff als Energieträger*; VDI-Verlag: Düsseldorf, Germany, 1994; p 133. (e) Reinhardt, R.; Kaim, W. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1998. (f) For related examples see: Kaim, W.; Reinhardt, R.; Sieger, M. *Inorg. Chem.* **1994**, *33*, 4453.

(3) (a) Cosnier, S.; Deronzier, A.; Vlachopoulos, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1259. (b) Chardon-Noblat, S.; Cosnier, S.; Deronzier, A.; Vlachopoulos, N. *J. Electroanal. Chem.* **1993**, *352*, 213. (c) Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1988**, 16. (d) Youinou, M.-T.; Ziessel, R. *J. Organomet. Chem.* **1989**, *363*, 197. (e) Ziessel, R. *Angew. Chem.* **1991**, *103*, 863; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 844. (f) Ziessel, R. *J. Am. Chem. Soc.* **1993**, *115*, 118. (g) Ziessel, R.; Chardon-Noblat, S.; Deronzier, A.; Matt, D.; Toupet, L.; Balgroune, F.; Grandjean, D. *Acta Crystallogr.* **1993**, *B49*, 515. (h) Watson, K. J.; Ziessel, R. *Inorg. Chim. Acta* **1992**, *197*, 125. (i) Craix, C.; Chardon-Noblat, S.; Deronzier, A.; Ziessel, R. *J. Electroanal. Chem.* **1993**, *362*, 301.

(4) (a) Ruppert, R.; Herrmann, S.; Steckhan, E. *J. Chem. Soc., Chem. Commun.* **1988**, 1150. (b) Steckhan, E.; Herrmann, S.; Ruppert, R.; Dietz, E.; Frede, M.; Spika, E. *Organometallics* **1991**, *10*, 1568. (c) Westerhausen, D.; Herrmann, S.; Hummel, W.; Steckhan, E. *Angew. Chem.* **1992**, *104*, 1496; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1529. (d) Steckhan, E.; Herrmann, S.; Ruppert, R.; Thömmes, J.; Wandrey, C. *Angew. Chem.* **1990**, *102*, 445; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 388.

(5) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. (c) Grotjahn, D. B.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 6969.

(6) (a) tom Dieck, H.; Franz, K.-D.; Hohmann, F. *Chem. Ber.* **1975**, *108*, 163. (b) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151. (c) tom Dieck, H.; Svoboda, M.; Greiser, T. *Z. Naturforsch.* **1981**, *36B*, 823. (d) Hasenzahl, S.; Hausen, H.-D.; Kaim, W. *Chem. Eur. J.* **1995**, *1*, 95.

(7) (a) Kaim, W.; Schulz, A. *Angew. Chem.* **1984**, *96*, 611; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 615. (b) Schulz, A.; Kaim, W. *Chem. Ber.* **1989**, *122*, 1863. (d) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 4235. (e) Fiedler, J.; Zalis, S.; Klein, A.; Hornung, F.; Kaim, W. *Inorg. Chem.*, in press.

S0020-1669(95)01481-9 CCC: $12.00

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

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_4NPF_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.

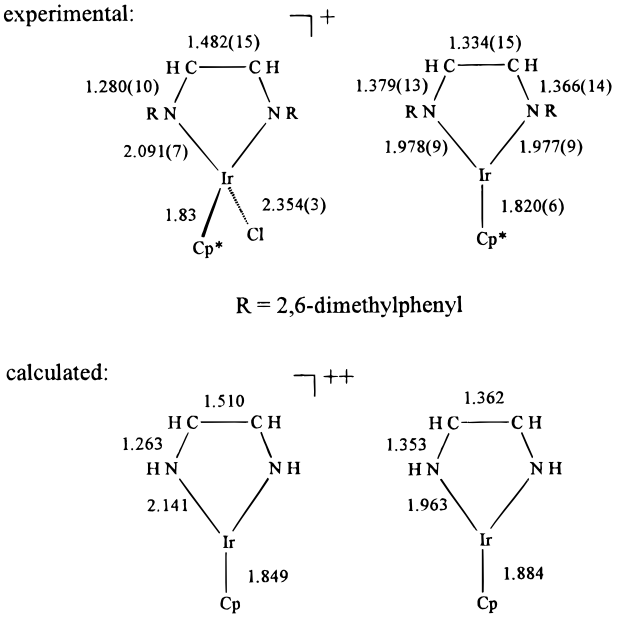
Cp*Ir(dab). A suspension of 77.2 mg (0.10 mmol) of [Cp*IrCl(dab)](PF_6) in a mixture of 20 cm^3 of ethanol and 5 cm^3 of water was reacted with 31.5 mg (0.50 mmol) of sodium cyanoborohydride under argon. After the mixture was stirred for 5 h at ambient temperature, the air-sensitive yellow-orange precipitate 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_2Fe](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_3CN 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_4NPF_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

Distances in Å



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_5H_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

(8) (a) Kaim, W.; Klein, A. *Organometallics* **1995**, *14*, 1176. (b) Klein, A.; Kaim, W.; Waldhör, E.; Hausen, H.-D. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2121.
(9) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
(10) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.
(11) Krejcik, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *317*, 179.
(12) Sheldrick, G. M. SHELXTL-PLUS: An Integrated System for Solving, Refining and Displaying Structures from Diffaction Data; Siemens Analytical X-Ray Instruments Inc., 1989.
(13) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Determination; Universität Göttingen, Göttingen, Germany, 1993.
(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(15) (a) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1976; Chapter 1. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson; B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefaonov, B. B.; Nanayakkara, A.; Challacome, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94; Gaussian Inc., Pittsburgh, PA, 1995.

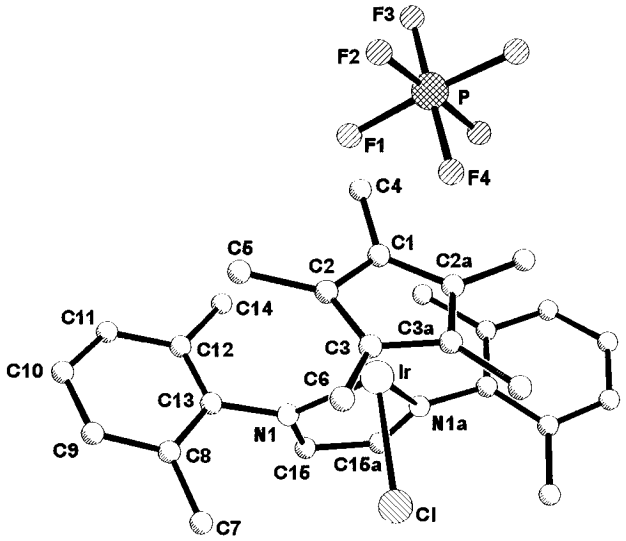


Figure 1. Molecular structure of [Cp*IrCl(dab)](PF_6) in the crystal ("staggered" configuration of Cp*). Selected bond lengths (Å) and angles (deg): Ir−Cl = 2.354(3), Ir−N1 = 2.091(7), N1−C15 = 1.280(10), C15−C15a = 1.482(15), N1−C13 = 1.450(10), Ir−C1 = 2.215(21), Ir−C2 = 2.198(14), Ir−C3 = 2.196(15); 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°.

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 $Na[BH_3CN]$ 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

$$[Cp^*IrH(dab)](PF_6) \xleftarrow{\text{"H}^-\text{"}} \not\rightarrow [Cp^*IrCl(dab)](PF_6) \xrightarrow{\text{"H}^-\text{"}} Cp^*IrCl(dab) \quad (1)$$

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

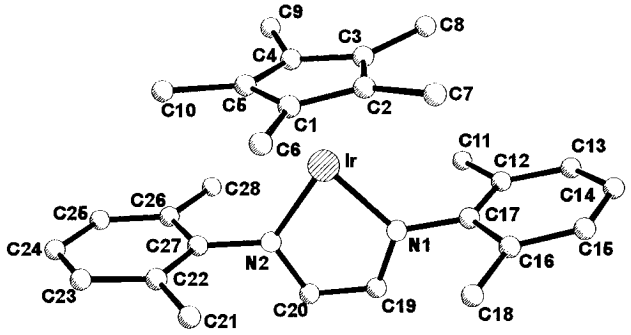
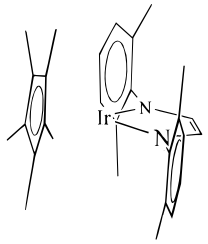


Figure 2. Molecular structure of Cp*Ir(dab) in the crystal. Selected bond lengths (Å) and angles (deg): Ir−N1 = 1.977(9), Ir−N2 = 1.978(9), N1−C19 = 1.366(14), C19−C20 = 1.334(15), N2−C20 = 1.379(13), N1−C17 = 1.419(14), N2−C27 = 1.432(14), Ir−C1 = 2.175(12), Ir−C2 = 2.199(12), Ir−C3 = 2.199(12), Ir−C4 = 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).

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

(16) (a) Richter, B.; Scholz, J.; Neumüller, B.; Weimann, R.; Schumann, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 365. (b) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

(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.

(18) (a) Zambrano, C. H.; Sharp, P. R.; Barnes, C. L. *Organometallics* **1995**, *14*, 3607 and literature cited therein. (b) Ghedini, M.; Longeri, M.; Neve, F.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1217. (c) Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* **1972**, *11*, 2827.

(19) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Rieger, D.; Lotz, S. D.; Kernbach, U.; André, C.; Bertran-Nadal, J.; Fehlhammer, W. P. *J. Organomet. Chem.* **1995**, *491*, 135. (c) Kuhn, N.; Kratz, T.; Bläser, D.; Boese, R. *Chem. Ber.* **1995**, *128*, 245. (d) Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, *501*, C1.

(20) (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (b) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

(21) (a) Geoffrey, F.; Cloke, F. G. N.; Dalby, C. I.; Henderson, M. J.; Hitchcock, P. B.; Kennard, C. H. L.; Lamb, R. N.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1394. (b) Geoffrey, F.; Cloke, F. G. N.; Hanson, G. R.; Henderson, M. J.; Hitchcock, P. B.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1002. Kaim, W.; Matheis, W. *J. Chem. Soc., Chem. Commun.* **1991**, 597. (c) Weidenbruch, M.; Lesch, A. *J. Organomet. Chem.* **1991**, *407*, 31. (d) Rijnberg, E.; Boersma, J.; Jastrzebski, J. T. B. H.; Lakin, M. T.; Spek. A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1839.

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 ϵ = 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.

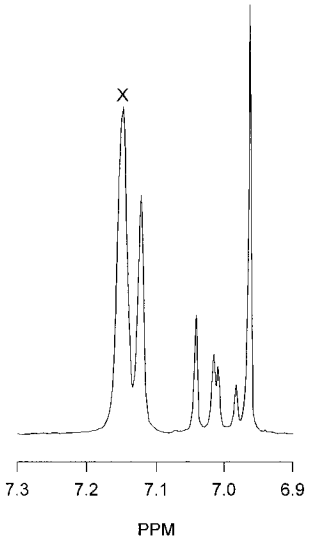


Figure 3. ^{1}H NMR spectrum (low-field section) of Cp*Ir(dab) in C$_6$D$_6$, illustrating the nonsymmetry of the CH(aryl) protons (X denotes the resonance of C$_6$H$_x$D$_{6-x}$, which obscures one part of the signal from the protons H^{3,5}.

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

(22) Görls, H.; Neumüller, B.; Scholz, A.; Scholz, J. *Angew. Chem.* **1995**, *107*, 732; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 673.
(23) Herrmann, W. A.; Denk, M.; Scherer, W.; Klingan, F.-R. *J. Organomet. Chem.* **1993**, *444*, C21.
(24) (a) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1995**, *34*, 4676. (b) For a report on related Cp*Rh(cat) species see: Espinet, P.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1542.
(25) tom Dieck, H.; Haarich, M. *J. Organomet. Chem.* **1985**, *291*, 71.
(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.

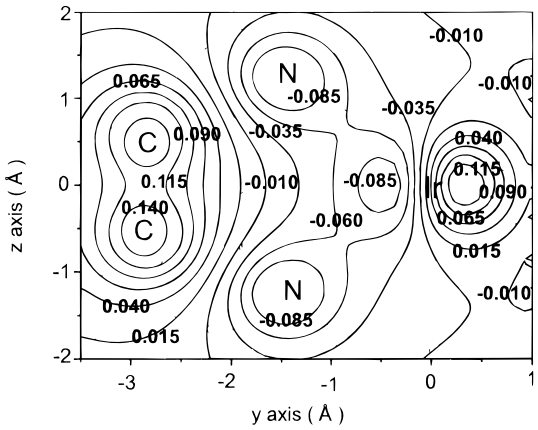
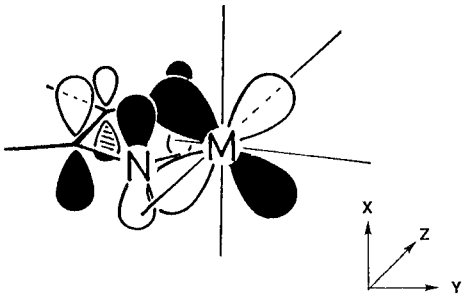


Figure 4. Ab initio/pseudopotential-calculated contour map of the redox orbital (HOMO) of CpIr(HNCHCHNH), 0.5 Å above the IrNCCN plane.

Chart 2

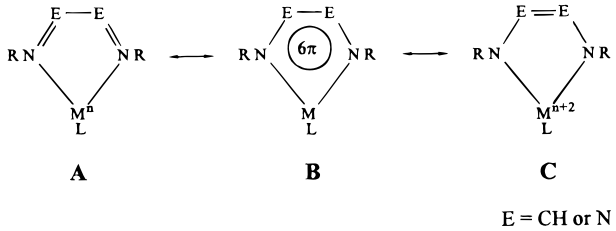


replacement of the two π-accepting N-aryl substituents in the dab ligand and of the five electron-donating methyl groups in the cyclopentadienide ligand by H appears to equilibrate the C−N and C−C distances in CpIr(HNCHCHNH); in the actual structure of Cp*Ir(dab) with a more electron-rich metal and stronger 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 $[Cp^*Ir(dab)Cl]^+$ lowers the Ir−N distance relative to the calculated value for $[CpIr(HNCHCHNH)]^{2+}$ and attenuates the differences of the intra-diazabutadiene distances ($d_{CN} < d_{CC}$).

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 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 $Ir(CO)(PPh_3)_2$ 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



E = CH or N

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.

Acknowledgment. This work has been supported by grants from the Deutsche Forschungsgemeinschaft (DFG), the Volkswagenstiftung, the Fonds der Chemischen Industrie, and an Exchange Program between DFG and the Academy of Sciences of the Czech Republic.

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 $[Cp^*IrCl(dab)](PF_6)$ and Cp*Ir(dab) (16 pages). Ordering information is given on any current masthead page.

IC9514814

(27) (a) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271. (b) Bleeke, J. R.; Bass, L. A.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213. (c) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Clayton, T. W., Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093. (d) See also: Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. T. *J. Am. Chem. Soc.* **1995**, *117*, 9776.

(28) Chen, J.; Young, V. G., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 6362.

(29) (a) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144. (b) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *Organometallics* **1982**, *1*, 732. (c) Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* **1981**, *209*, 407.

(30) Overbosch, P.; van Koten, G.; Spek, A. L.; Roelofsen, G.; Duisenberg, A. J. M. *Inorg. Chem.* **1982**, *21*, 3908.

(31) Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* **1972**, *11*, 2827.

(32) Werner, H. *Angew. Chem.* **1983**, *95*, 932; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.