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Qualitatively Different Reactivities of Hydride Reagents toward [(α-diimine)(η^5-C_5Me_5)ClIr]$^+$ Cations: Substitution, Electron Transfer (Reduction), or Stepwise Hydrogenation

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Summary: Whereas complex cations [(α-diimine)(η^5-C_5Me_5)ClIr]$^+$ with 2,2′-bipyridine and related aromatic ligands show only the expected Cl/H exchange on reaction with borohydrides, the systems [(RN═CHCH═NR)(η^5-C_5Me_5)ClIr]$^+$ undergo reduction to the enediamido(2−)−iridium(III) species [(RNCH═CHNR)(η^5-C_5Me_5)Ir], even in protic media, if R is an axially shielding 2,6-dialkylphenyl group. In protic media the complex ion with R = cyclohexyl undergoes Cl/H exchange and stepwise hydrogenation of the α-diimine ligand via [(RHNCH$_2$CH═NR)(η^5-C_5Me_5)HIr](PF$_6$) to the structurally characterized compound [(RHNCH$_2$CH$_2$NHR)(η^5-C_5Me_5)HIr][BH$_3$(CN)].

Introduction

The halide/hydride exchange using hydridoborate reagents is a standard reaction in synthesizing metal hydride compounds.[1] For instance, systems such as [(α-diimine)(η^5-C_5Me_5)ClIr]$^+$ with aromatic α-diimine ligands were found to undergo clean chloride/hydride substitution (eq 1) on reaction with Na[BH$_3$(CN)],[2d] yielding models for intermediates in hydride transfer catalysis schemes.[2]

substitution:

$$[(\alpha\text{-diimine})(\eta^5\text{-C}_5\text{Me}_5)\text{ClIr}]^+ + [\text{H}^-] \rightarrow [(\alpha\text{-diimine})(\eta^5\text{-C}_5\text{Me}_5)\text{HIr}]^+ + \text{Cl}^- \quad (1)$$

α-diimine = 2,2′-bipyridines, 1,10-phenanthrolines

However, the EPR spectroscopically established electron-transfer reactivity of many main-group-element hydride reagents[3] may also result in reductive elimination of the halide from the substrate, especially in those cases where a lowered coordination number is favored, e.g., for steric reasons. Examples for this reduction (eq 2) have been described for compounds [(α-diimine)(η^5-C_5Me_5)ClIr](PF$_6$), where the α-diimine is the 1,4-disubstituted 1,4-diaza-1,3-butadiene RN═CHCH═NR with R = 2,6-dialkylphenyl.[4] These systems yield the enediamido(2−) complexes [(RNCH═CHNR)(η^5-C_5Me_5)Ir] with 16-valence-electron iridium(III) centers. The oxidation state assignments for the chelate ligand and, by implication, for the metal were based on structural analyses in combination with ab initio calculations.[4a] This unusual reaction was attributed to strong axial shielding by the 2,6-dialkylphenyl substituents in the reduced species, which disfavors the presence of another ligand even as small as a hydride;[4a] [(RNCH═CHNR)(η^5-C_5Me_5)Ir] (R = 2,6-dimethylphenyl), as already formed in an aqueous environment,[4a] was found not to react with protons, and similar results were obtained with R = 2,6-diisopropylphenyl.[4b] We shall describe in this article that corresponding compounds can be obtained also from complexes with less shielding substituents R, however, only under careful exclusion of protons.

reduction:

$$[(\text{RN}{=}\text{CHCH}{=}\text{NR})(\eta^5\text{-C}_5\text{Me}_5)\text{ClIr}]^+ + [\text{H}^-] \rightarrow [(\text{RNCH}{=}\text{CHNR})(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}] + \text{Cl}^- + \text{H}^+ \quad (2)$$

R = aryl, alkyl (in aprotic media);
R = 2,6-dialkylphenyl (in protic environment)

In addition, we report a further reaction alternative for this class of compounds, viz., the successive hydrogenation (eqs 3 and 4) of the unsaturated α-diimine chelate ligand in a protic environment. The changed

hydrogenation (and substitution):

$$[(\text{RN}{=}\text{CHCH}{=}\text{NR})(\eta^5\text{-C}_5\text{Me}_5)\text{ClIr}]^+ + 2[\text{H}^-] + \text{H}^+ \rightarrow [(\text{RHNCH}_2\text{CH}{=}\text{NR})(\eta^5\text{-C}_5\text{Me}_5)\text{HIr}]^+ + \text{Cl}^- \quad (3)$$

$$[(\text{RHNCH}_2\text{CH}{=}\text{NR})(\eta^5\text{-C}_5\text{Me}_5)\text{HIr}]^+ + [\text{H}^-] + \text{H}^+ \rightarrow [(\text{RHNCH}_2\text{CH}_2\text{NHR})(\eta^5\text{-C}_5\text{Me}_5)\text{HIr}]^+ \quad (4)$$

R = cyclohexyl (in protic medium)

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pattern of reactivity was obtained by making just minor modifications, working in a protic solvent and using saturated cyclohexyl substituents at the 1,4-positions of the 1,4-diaza-1,3-butadiene ligand.

Not only have the noninnocent 1,4-diaza-1,3-butadiene ligands been used in complexes $[(\alpha\text{-diimine})(\eta^5\text{-}C_5Me_5)ClM]^+$ (M = Rh, Ir), which are related to hydride transfer catalytic schemes[2,5] but they are also increasingly popular as components of efficient polymerization catalysts.[6] Their reactivity as coordinated ligands of catalytic species is therefore of some relevance.

In the following we report results from the reactions of compounds $[(RN{=}CHCH{=}NR)(\eta^5\text{-}C_5Me_5)ClIr](PF_6)$ (**1**) with hydride reagents. Since these results are compared with observations made previously for systems with R = 2,6-dialkylphenyl,[4] we chose as starting compounds complex **1a**, with the nonaromatic and moderately bulky substituent R = cyclohexyl, and the structurally characterized complex **1b**, with the 2-alkylphenyl substituent R = 2-methylphenyl = *o*-tolyl.

Experimental Section

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker AC 250 spectrometer, and infrared spectra were obtained using a Perkin-Elmer PE 684 spectrometer. Absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at a 100 mV/s standard scan rate in CH_3CN/0.1 M Bu_4NPF_6 using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

$[(RN{=}CHCH{=}NR)(\eta^5\text{-}C_5Me_5)ClIr](PF_6)$ (R = Cyclohexyl; 1a). A suspension of 254 mg (0.318 mmol) of $[Ir(C_5Me_5)Cl_2]_2$[7] was obtained in 30 mL of methanol with the help of an ultrasonic bath. Adding 175 mg (0.80 mmol) of 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene and stirring for 3 h at room temperature produced a clear red solution which was reduced to about 10 mL volume. An excess of a methanolic solution of Bu_4NPF_6 was added to yield a red precipitate, which was collected, washed with methanol and diethyl ether, and dried under vacuum. Yield: 393 mg (85%). Anal. Calcd for $C_{24}H_{39}ClF_6IrN_2P$ (mol wt 726.2): C, 39.58; H, 5.40; N, 3.85. Found: C, 39.08; H, 5.53; N, 3.85. ^{1}H NMR (CD_3CN): δ 1.17−2.45 (m, 20H, CH(R)), 1.70 (s, 15H, $CH(C_5Me_5)$), 4.16 (m, 2H, NCH(R)), 8.75 (s, 2H, CH(imine)) ppm. ^{13}C NMR (CD_3CN): δ 9.2 ($CH_3(C_5Me_5)$), 25.9, 26.5, 34.1, 35.4, 49.9, 72.9 (*C*H(R)), 93.3 ($CCH_3(C_5Me_5)$), 166.0 (*C*H(imine)) ppm. UV/vis (CH_3CN): λ_{max} (ϵ) 515 (290), 388 (3920), 277 (5650) nm.

$[(RN{=}CHCH{=}NR)(\eta^5\text{-}C_5Me_5)ClIr](PF_6)$ (R = *o*-Tolyl; 1b). A suspension of 208 mg (0.26 mmol) of $[Ir(C_5Me_5)Cl_2]_2$ was generated in 30 mL of methanol in an ultrasonic bath. Addition of 154 mg (0.65 mmol) of 1,4-bis(*o*-tolyl)-1,4-diaza-1,3-butadiene and stirring for 3 h at room temperature produced a clear green solution which was reduced to about a 10 mL volume. An excess of a methanolic solution of Bu_4NPF_6 was added to yield a green precipitate, which was collected, washed with methanol and diethyl ether, and dried under vacuum. Yieldd: 346 mg (90%). Anal. Calcd for $C_{26}H_{31}ClF_6IrN_2P$ (mol wt 744.2): C, 41.96; H, 4.20; N, 3.77. Found: C, 42.21; H, 4.28; N, 3.81. ^{1}H NMR (CD_3CN): δ 1.18 (s, 15H, $CH_3(C_5Me_5)$), 2.34 (s, 6H, CH_3(R)), 7.36−7.49 (m, 6H, CH(R)), 7.70 (dd, ^3J = 7.5 Hz, 2H, CH(R)), 8.96 (s, 2H, CH(imine)) ppm. ^{13}C NMR (CD_3CN): δ 8.44 ($CH_3(C_5Me_5)$), 18.21 (CH_3(R)), 95.39 ($CCH_3(C_5Me_5)$), 123.07, 128.04, 130.45, 132.30 (*C*H(R)), 148.50 (*C*N(R)), 170.57 (*C*H(imine)) ppm. UV/vis (CH_3CN): λ_{max} (ϵ) 590 (460), 408 (sh) (4260), 360 (4950), 292 (5030) nm.

$[(RNCH{=}CHNR)(\eta^5\text{-}C_5Me_5)Ir]$ (R = Cyclohexyl; 2a). A solution of 73 mg (0.10 mmol) **1a** in 20 mL of cold (−15 °C) acetone was treated with 136 mg (0.53 mmol) Bu_4NBH_4. After a rapid color change from red to orange, the volume was reduced to about 5 mL, and 3 mL of degassed H_2O was added. The air-sensitive orange precipitate was collected, washed with water, and dried under vacuum. Yield: 36 mg (65%). Anal. Calcd for $C_{24}H_{39}IrN_2$ (mol wt 547.8): C, 52.62; H, 7.18; N, 5.11. Found: C, 53.26; H, 7.18; N, 5.25. ^{1}H NMR (C_6D_6): δ 1.00−2.20 (m, 20H, CH_2(R)), 1.86 (s, 15H, $CH_3(C_5Me_5)$), 4.34 (m, 2H, CHN(R)), 7.33. (s, 2H, CH(imine)) ppm. ^{13}C NMR (C_6D_6): δ 10.10 ($CH_3(C_5Me_5)$), 26.40, 27.10, 35.50, (CH_2(R)), 72.20 (*C*HN(R)), 82.50 ($CCH_3(C_5Me_5)$), 129.00 (CH(imine)) ppm. UV/vis (CH_3CN): λ_{max} (ϵ) 424 (15 400), 234 (sh) nm.

$[(RNCH{=}CHNR)(\eta^5\text{-}C_5Me_5)Ir]$ (R = *o*-Tolyl; 2b). A solution of 53.5 mg (0.072 mmol) of **1b** in 10 mL of cold (−15 °C) acetonitrile was treated with 37 mg (0.144 mmol) of Bu_4NBH_4. After 1 h of stirring the solvent was removed from the dark yellow solution and the residue extracted with *n*-hexane. Removal of *n*-hexane produced 14 mg (35%) of a very sensitive yellow-orange solid; an elemental analysis could not be obtained. Reaction of **1b** with $Na[BH_3(CN)]$ also yielded **2b**. ^{1}H NMR (C_6D_6): δ 1.27 (s, 15H, $CH_3(C_5Me_5)$), 2.05 (s, 6H, CH_3(R)), 7.02 (dt, ^3J = 7.4 Hz, ^5J = 1.5 Hz, 2H, H(R)), 7.1, 7.2 (d, ^3J = 7.7 Hz, 4H, H(R)), 7.12 (s, 2H, H(imine)), 7.35 (d, ^3J = 7.4 Hz, 2H, H(R)) ppm. ^{13}C NMR (C_6D_6): δ 8.90 ($CH_3(C_5Me_5)$), 16.50 (CH_3(R)), 83.00 ($CCH_3(C_5Me_5)$), 125.20, 125.50, 125.70, 129.80, 132.60 (*C*H(R)), 132.80 (CN(R)), 157.40 (*C*HN(imine)) ppm. UV/vis (toluene): λ_{max} (ϵ) 430, 285 (sh), 230 (sh) nm.

$[(RHNCH_2CH{=}NR)(\eta^5\text{-}C_5Me_5)HIr](PF_6)$ (R = Cyclohexyl; 3). A cooled solution (−15 °C) of 54.5 mg (0.075 mmol) of **1a** in a mixture of 10 mL of ethanol and 2.5 mL of water was treated with 23.5 mg (0.375 mmol) of $Na[BH_3(CN)]$. Within 4 h the color changed from red to yellow; then the volume was slowly reduced until a light yellow precipitate began to form. This was collected, washed with degassed H_2O, and dried under vacuum. Yield: 28 mg (55%). Anal. Calcd for $C_{24}H_{42}F_6IrN_2P$ (mol wt 695.8): C, 41.43; H, 6.08; N, 4.03. Found: C, 42.44; H, 6.04; N, 4.32. ^{1}H NMR (CD_3CN): δ −10.80 (s, 1H, Ir−H), 0.99−3.42 (m, 20H, CH_2(R)), 1.80 (s, 15H, $CH_3(C_5Me_5)$), 3.61 (d, 2H, CHN(R)), 5.39 (s, 1H, NH(amine)), 7.81 (s, 1H, NH(imine)) ppm. ^{13}C NMR (CD_3CN): δ 10.22 ($CH_3(C_5Me_5)$), 25.40, 25.70, 25.90, 26.30, 26.40, 26.50, 30.20, 31.80, 33.00, 35.30 (CH_2(R)), 60.38, 66.50, (*C*HN(R)), 72.00 (CH_2(amine)), 88.80 ($CCH_3(C_5Me_5)$), 168.30 (*C*H(imine)) ppm. UV/vis (CH_3CN): λ_{max} (ϵ) 335 (sh) nm. IR (KBr): ν 2069 cm^{-1} (Ir−H).

$[(RHNCH_2CH_2NHR)(\eta^5\text{-}C_5Me_5)HIr][(BH_3(CN)]$ (R = Cyclohexyl; 4). Standing for 2 days and slow cooling of a solution as described above for **3** gave a small amount (ca. 3 mg) of yellowish crystals which were suitable for X-ray diffraction. The presence of an Ir−H bond was confirmed by IR spectroscopy in KBr: ν 2059 cm^{-1}.

Crystallography. Single crystals of **1b** were obtained through slow cooling of a solution in CH_3OH/CH_2Cl_2 (2/1 v/v); single crystals of compound **4** were obtained from the reaction solution. Crystallographic and refinement information is summarized in Table 1; a Siemens P4 diffractometer was used for data collection. The structures were solved using the programs

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Table 1. Crystal Data and Structure Refinement Information for Complex 4

	1b	**4**
formula	$C_{26}H_{31}ClF_6IrN_2P$	$C_{25}H_{47}BIrN_3$
mol wt	744.15	592.70
temp, K	183	183
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	8.0220(8)	13.030(2)
b, Å	10.9726(11)	16.307(2)
c, Å	31.414(4)	12.373(4)
α, deg	90.00	90.00
β, deg	95.625(11)	90.53(3)
γ, deg	90.00	90.00
V, Å^3	2751.8(5)	2628.9(10)
Z	4	4
ρ(calcd), g cm^{-3}	1.796	1.490
abs coeff, mm^{-1}	5.066	5.094
F(000)	1456	1188
cryst size, mm	0.4 × 0.3 × 0.1	0.4 × 0.1 × 0.1
θ range, deg	1.97−28.00	3.52−28.00
index ranges	$-10 \le h \le 10$, $0 \le k \le 14$, $0 \le l \le 41$	$-17 \le h \le 17$, $-21 \le k \le 5$, $-16 \le l \le 16$
no. of rflns measd	6646	6538
no. of indep rflns	6646 (*R*(int) = 0.0378)	6261 (*R*(int) = 0.0636)
abs cor	DIFABS	XABS2
refinement method	full-matrix least squares	full-matrix least squares
no. of data/restraints/ params	6646/0/334	6261/0/276
goodness of fit on F^2	1.046	1.116
final R^a indices ($I > 2\sigma(I)$)	R1 = 0.0345, wR2 = 0.0717	R1 = 0.0587, wR2 = 0.1328
R^a indices (all data)	R1 = 0.0555, wR2 = 0.0792	R1 = 0.0974, wR2 = 0.1479
largest diff peak and hole, e Å^{-3}	0.750 and −0.634	1.521 and −1.394

[a] $R|1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(F_o^4)]\}^{1/2}$.

SHELXTL PLUS and SHELXL 97,[8] and heavy atoms were located via the Patterson procedure. The programs DIFABS[9] and XABS2[10] were used for absorption correction. The $[BH_3(CN)]^-$ anion in **4** was found to be disordered. Non-hydrogen atoms, except for those of the disordered cyanoborohydride in **4**, were refined anisotropically, and hydrogen atoms were introduced at appropriate positions with coupled isotropic temperature factors.

Results and Discussion

Reactivity. The starting compounds [(RN=CHCH=NR)(η^5-C_5Me_5)ClIr](PF_6) (R = cyclohexyl (**1a**), *o*-tolyl (**1b**)) were obtained in the usual manner[4] by reacting the corresponding 1,4-diazabutadiene ligand with [(η^5-C_5Me_5)(μ-Cl)ClIr]$_2$.[7] Related complexes with R = 2,6-dimethylphenyl and 2,6-diisopropylphenyl have been structurally characterized; complex **1b** shows no unusual structure (see below).[4] The compounds **1a**,**b** were reacted with borohydride reagents under different conditions, of which the following experiments gave clean results.

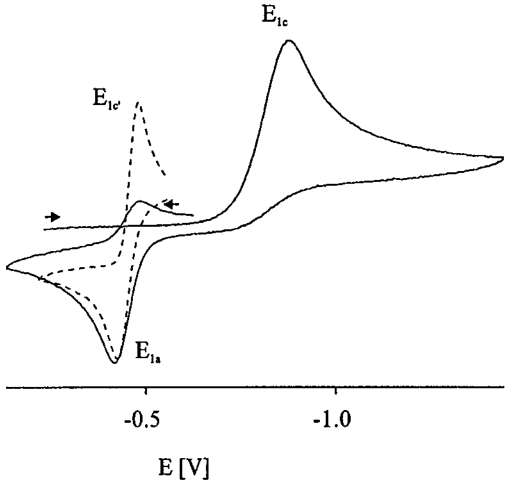

Figure 1. Cyclic voltammograms of complexes **1a** (—) and **2a** (- - -) in CH_3CN/0.1 M Bu_4NPF_6 at 500 mV/s scan rate (potential vs ferrocenium/ferrocene).

(1) Reaction of red **1a** with (Bu_4N)(BH_4) at −15 °C in acetone yields the air-sensitive orange reduction product [(RNCH=CHNR)(η^5-C_5Me_5)Ir] (**2a**), identified by its high-field-shifted NMR signals. The resonances for the enediamido(2−) entity with 7.33 ppm (^{1}H NMR) and 129.0 ppm (^{13}C NMR) are especially indicative.[4] The intense absorption band at 424 nm is also typical for such metal/ligand π-delocalized "metallaheteroaromatic" systems.[4,11] Compound **2a** is also the product of the familiar[5,12] irreversible two-electron reduction of **1a**, as observed by cyclic voltammetry (Figure 1). The peak potentials are $E_{1c} = -0.86$ V for the chloride-dissociative reduction of **1a** to **2a** and $E_{1a} = -0.46$ V for the reoxidation (all values vs ferrocenium/ferrocene). In agreement with E_{1a}, the chemically isolated compound **2a** itself is oxidized reversibly in a two-electron step at $E_{1/2} = -0.50$ V vs ferrocenium/ferrocene. Due to the stronger donor character of alkyl vs aryl substituents this latter value is slightly more negative than the −0.39 V reported for the 1,4-bis(2,6-dimethylphenyl)-1,4-diazabutadiene analogue.[4a]

(2) Reaction of green **1b** with Na[BH_3(CN)] or (Bu_4N)(BH_4) at −15 °C in acetonitrile also produces the highly air-sensitive orange reduction product [(RNCH=CHNR)(η^5-C_5Me_5)Ir] (**2b**), characterized through its high-field-shifted NMR signals. The diminished stability of **2b** in comparison to the higher substituted analogues[4] reflects the decrease in axial shielding. Neutral **2b** can also be generated through irreversible two-electron reduction of **1b**; the peak potentials at $E_{1c} = -0.84$ V and $E_{1a} = -0.43$ V are close to those of the **1a/2a** system. Compound **1b** exhibits a reversible $Ir^{III} \rightarrow Ir^{IV}$ oxidation at $E_{ox} = 1.48$ V to **1b**$^+$ and an irreversible reduction of the two-electron-reduced intermediate **2b** at $E_{2a} = -2.73$ V. The latter value is almost 1 V more negative than the peak potential of −1.88 V for the reduction of free 1,4-bis(*o*-tolyl)-1,4-diaza-1,3-butadiene, confirming the extremely strong π-back-donation exerted by the (C_5Me_5)Ir fragment.[13]

(3) Reaction of **1a** with Na[BH_3(CN)] at −15 °C in aqueous ethanol and workup within 4 h produced the light yellow compound [($RHNCH_2CH$=NR)(η^5-C_5Me_5)-

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Scheme 1

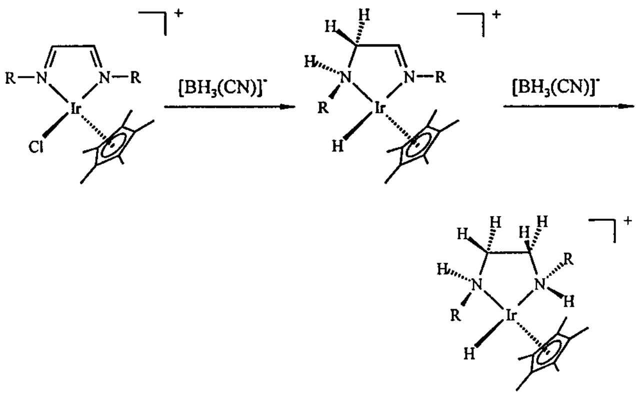

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1b

	Distances		
Ir−Cl	2.380(1)	Ir−C5	2.185(5)
Ir−N1	2.067(4)	N1−C18	1.288(6)
Ir−N2	2.082(4)	N2−C19	1.287(6)
Ir−Cl	2.197(5)	C18−C19	1.446(7)
Ir−C2	2.165(4)	N1−C11	1.448(6)
Ir−C3	2.195(5)	N2−C20	1.444(6)
Ir−C4	2.167(5)		
	Angles		
N1−Ir−N2	75.83(16)	C19−N2−C20	119.5(4)
Ir−N1−C18	117.4(4)	C11−N1−Ir	125.5(3)
Ir−N2−C19	116.0(3)	C20−N2−Ir	124.5(3)
N1−C18−C19	114.6(5)	N1−Ir−Cl	86.97(11)
N2−C19−C18	116.2(5)	N2−Ir−Cl	86.48(11)
C11−N1−C18	117.1(4)		

HIr](PF_6) (**3**). NMR and IR spectroscopy show the presence of a hydride ligand; however, the product has also undergone a partial hydrogenation of one of the imine functions. The sequence of Cl/H exchange and hydrogenation reaction has not been established; it probably depends on the proton availability.

(4) Prolonged reaction of **1a** with Na[BH_3(CN)] in aqueous ethanol gave a small amount of yellowish crystals which proved suitable for X-ray diffraction (Scheme 1). The infrared spectrum showed an Ir−H stretching band at 2059 cm^{-1}, slightly shifted in comparison to **3**. This compound was identified by X-ray crystallography as the fully hydrogenated species [($RHNCH_2CH_2NHR$)(C_5Me_5)HIr][BH_3(CN)] (**4**), with the cyanotrihydridoborate anion.

Crystal Structure of 1b. The crystallographic data are summarized in Table 1; Table 2 contains selected bond parameters. Figure 2 shows the molecular structure of **1b**.

The molecular arrangement is rather similar to the structures of analogues with 1,4-bis(2,6-dialkylphenyl) substituents;[4] the C_5Me_5 ligand is coordinated in a η^5 fashion, albeit at a slightly shorter distance. Less steric interference is also responsible for the decreased angle of 61° between the IrNCCN and C_5Me_5 planes; the bis(2,6-dimethylphenyl) analogue has 69° [4a] (the bis(2,6-diisopropylphenyl) derivative exhibits a twisted chelate ring[4b]). The *o*-tolyl substituents are slightly twisted (ca. 14°), with the methyl groups pointing away from the Cl ligand.

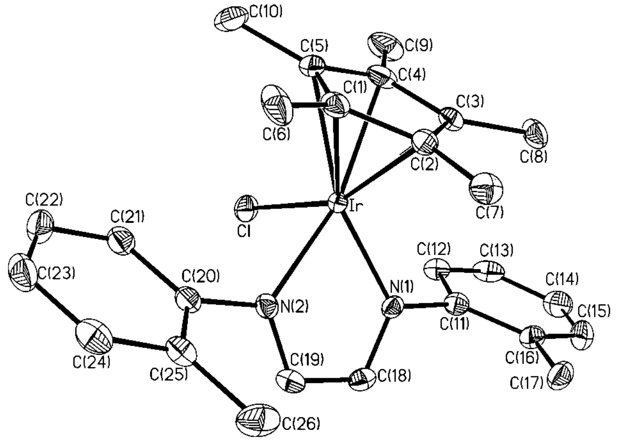

Figure 2. Molecular structure of the cation of complex **1b** in the crystal form.

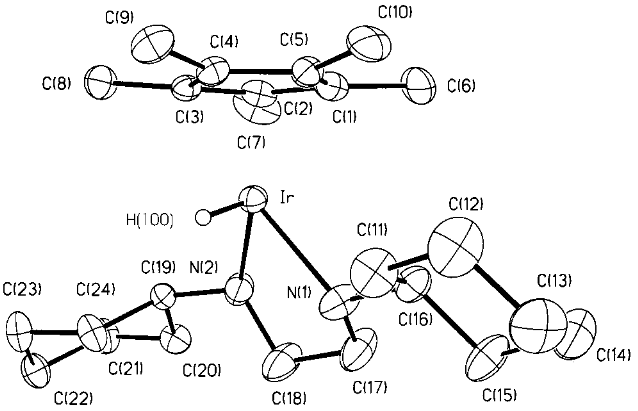

Figure 3. Molecular structure of the cation of complex **4** in the crystal form.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 4

	Distances		
Ir−N1	2.165(8)	Ir−C5	2.214(9)
Ir−N2	2.136(8)	N1−C17	1.428(14)
Ir−C1	2.272(11)	N2−C18	1.404(14)
Ir−C2	2.236(10)	N1−C16	1.477(13)
Ir−C3	2.150(9)	N2−C19	1.494(12)
Ir−C4	2.159(9)	C17−C18	1.488(16)
	Angles		
N1−Ir−N2	78.6(3)	N2−C18−C17	111.3(10)
Ir−N1−C17	107.9(7)	C16−N1−C17	118.9(9)
Ir−N2−C18	112.3(7)	C19−N2−C18	116.5(9)
N1−C17−C18	110.1(10)		

Crystal Structure of 4. The crystallographic data are summarized in Table 1; Table 3 contains selected bond parameters. Figure 3 shows the molecular structure of **4**.

The identity of the chelate ligand as an ethylenediamine derivative[14] is clearly evident from the twist conformation of the five-membered chelate ring. The distances inside that ring confirm the single-bond character of N−C and C−C; in addition, the Ir−N bonds are lengthened from about 2.07 Å to ca. 2.15 Å, in agreement with the absence of any π-bonding contribu-

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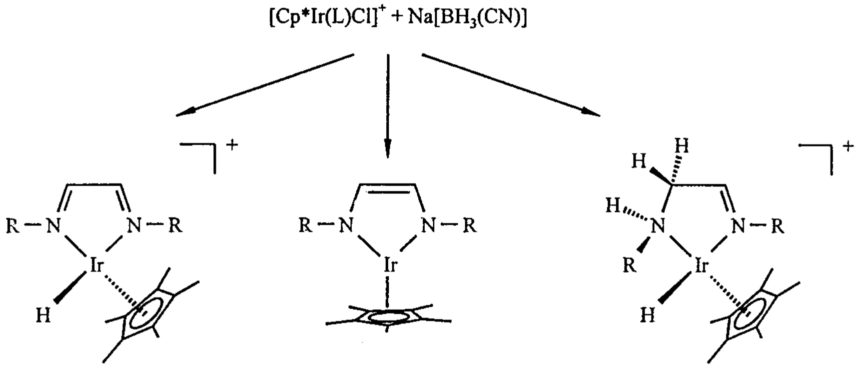
Scheme 2



tions. The general lengthening of intrachelate bonds and the nonplanar chelate ring conformation are accompanied by an increase of the bite angle from about 76° to 78.6(3)°. The presence of the hydride ligand at iridium can be inferred from the interplanar angle of 63.3° between the cyclopentadienide and the N1IrN2 planes. Similar effects occur for the chloro complexes,[4] whereas [(RNCH=CHNR)(η^5-C_5Me_5)Ir] (R = 2,6-dimethylphenyl) exhibits an essentially perpendicular arangement for these planes.[4a] The cyclopentadienide itself adopts a rather unsymmetrical coordination toward the metal with Ir−C distances ranging from 2.150(9) to 2.272(11) Å. Unsymmetrical bonding of C_5Me_5 has also been reported for [(α-diimine)(C_5Me_5)Ir] (α-diimine = 2,2′-bipyridine-4,4′-dicarboxylic acid);[2e] for the iridium(III) complex **4** this deviation from the ideal η^5 coordination probably reflects the σ donor effects from the hydride and the fully saturated ethylenediamine ligand.

Conclusion

The differences in the reactivity of the complexes [(α-diimine)(η^5-C_5Me_5)ClIr]$^+$ vs borohydride reagents as illustrated by Scheme 2 can be attributed to substrate and media variations.

(1) Simple chloride/hydride exchange occurs when the chelate ligand is not easily reduced or hydrogenated: e.g., in the case of aromatic α-diimines.

(2) In the absence of protons the nonaromatic 1,4-diaza-1,3-butadienes can undergo a reduction (electron-transfer reactivity) to enediamido(2−)−iridium(III) complexes [(RNCH=CHNR)(η^5-C_5Me_5)Ir]. With axially shielding substituents R this reaction occurs even in protic media.[4]

(3) With a more normal 1,4-diaza-1,3-butadiene such as the dicyclohexyl derivative presented here the reaction in protic medium yields partially or fully hydrogenated derivatives [(RHNCH$_2$CH=NR)(η^5-C_5Me_5)HIr]$^+$ and [(RHNCH$_2$CH$_2$NHR)(η^5-C_5Me_5)HIr]$^+$. Hydride and protons combine to H_2 equivalents which can apparently attack the nonaromatic imine bonds, perhaps catalyzed by the iridium species present.

Obviously, under such circumstances the 1,4-diaza-1,3-butadiene ligands are “noninnocent”[4a,16] in more senses than one: they are not only capable of changing their effective charge but also sufficiently reactive to undergo hydrogenation. In the context of catalytic hydride generation, activation, and transfer schemes[2,5,17] the latter, irreversible process would be undesired, leading to inactive complexes.

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Supporting Information Available: Tables of X-ray crystallographic data for **1b** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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