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Reversible heterolytic C–H cleavage by intramolecular C–H activation at diazabutadiene ligands at iridium

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Abstract

Reactions between $[Cp^*IrCl_2]_2$ and diaryl-substituted diazabutadienes (dab) ArN=CR′–CR′=NAr (R′ = H: Ar = 4-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$; R′ = Me: Ar = 4-MeC_6H_4) proceed straightforwardly to give the dab complexes $Cp^*Ir(dab)Cl^+Cl^-$. Sterically more encumbered dab ligands (R′ = Me: Ar = 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2,4,6-$Me_2C_6H_3$) instead give products $Cp^*\overline{IrClCH_2C(=NHAr)CMe=N}(Ar)^+Cl^-$ in which the dab ligand has undergone C–H activation at one of methyl groups of the dab bridge. The C–H cleavage reaction is reversible in the sense that thermally, the cyclometalated Ir complex decomposes to regenerate the free ligand.

Keywords: C–H activation; Iridium; Diimine; Metallacycle; Heterolytic cleavage

1. Introduction

Cationic group 10 metal complexes supported by diimine ligands have been demonstrated to be potentially highly active catalysts for alkene polymerization [1–3] and alkene/CO copolymerization [4] chemistry. The diimine moiety has also been recently proven to be a useful supporting ligand in C–H activation reactions of methane, benzene, and other aromatic systems mediated by cationic Pt species [5–9]. It is crucial that the supporting ligands resist C–H activation in order for successful C–H activation to occur. This requirement has been met by some of the diimine systems. We are aware of only one instance of reported C–H activations at diimine ligand systems: Brookhart and coworkers [3] have found that cationic Pd complexes (ArN=CR–CR=NAr)Pd(CH_3)(OEt_2)$^+$ (Ar = 2,6-$^iPr_2C_6H_3$, 2-$^tBuC_6H_4$) undergo C–H activation at the ^iPr and ^tBu substituents of the diimine N-bonded aryl groups to yield six-membered palladacycles with concomitant loss of methane.[1]

Cationic Ir(III) complexes bearing the Cp* ancillary ligand[2] represent the most active systems hitherto reported for methane C–H activation by isolable metal complexes [11–14], but C–H activation at Ir has not been seen in conjunction with diimine ligands. Cyclopentadienylmetal diimine complexes of Rh and Ir have, however, been thoroughly investigated because of their involvement in proton photoreduction [15–28], CO_2 reduction [29], photocatalysis of the water–gas shift reaction [23–38], and NADPH/NADP

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[1] Similar reactivity has been observed, but yet not reported, in certain (diimine)Pt complexes [10].

[2] Abbreviations, bpy: 2,2′-bipyridine; phen: 9,10-phenanthroline; Cp*: η^5-C_5Me_5; dab: non-cyclic diimine RN=CR′CR′=NR.

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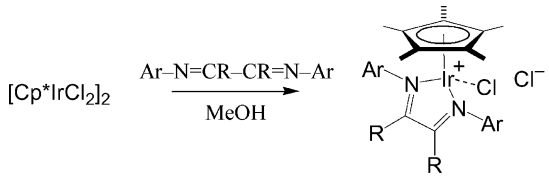


	R =	Ar =
1	H	4-MeC_6H_4
2	H	2,6-$Me_2C_6H_3$
3	H	2,6-$^{i}Pr_2C_6H_3$
4	Me	4-MeC_6H_4

Scheme 1.

redox chemistry [30–35]. The majority of the group 9 species reported in these contexts are supported by substituted bpy or phen ligands in conjunction with the Cp*M moiety. Reactions between the readily available dimers $[Cp^*MCl_2]_2$ and the appropriate diimine ligands have been established as a fairly general route to the $Cp^*M(diimine)Cl^+Cl^-$ compounds that have been used as the entry point to most of this chemistry. Chemical or electrochemical reduction of $Cp^*M(diimine)Cl^+$ gives access to the crucial electroactive Cp*M(diimine) species. It appears that only on one occasion [26], the $Cp^*Ir(bpy)H^+$ species that are believed to be crucial intermediates in many of these processes have been spectroscopically observed and characterized.

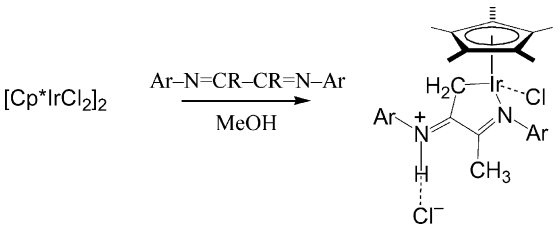
Analogous complexes based on *non-cyclic* diimines, the diazabutadiene (dab) ligands RN=CR′–CR′=NR (see footnote 2), have not been as extensively studied. For example, the synthesis of $Cp^*Ir(dab)H^+$ species apparently has never been reported. In this contribution, we describe the synthesis and complete characterization of some novel Cp*Ir(dab) complexes, including unexpected products arising from heterolytic C–H activation at chelate ring substituents (rather than N-bonded substituents) of the dab ligands under mild conditions.

2. Results and discussion

Reactions between $[Cp^*IrCl_2]_2$ and a number of aryl-substituted dab ArN=CR–CR=NAr proceed in the anticipated fashion to yield the $Cp^*Ir(dab)Cl^+Cl^-$ species (**1**–**4**) in good yields when R = H, and for R = Me if Ar is not substituted in the 2 and 6 positions, as depicted in Scheme 1.[3] These products have been fully characterized by spectroscopic methods and elemental analyses (see Section 4 for full details). In particular, the ^1H NMR spectra are uncomplicated and in accord with species containing a κ^2-bonded dab ligand. An overall C_s symmetry is indicated for **1**–**4** by the presence of only one set of signals for the R substituents at the dab chelate ring. Rotation around the N–Ar bonds in **2** and **3** appears to be hindered, presumably because of considerable steric interactions between the Ar-alkyl substituents and the bulky Cp* ligand: the ^1H NMR spectrum of **2** shows two well-separated Ar–Me resonances, whereas that of **3** shows two separate sets of signals arising from the Ar–^{i}Pr groups. On the other hand, rotation around the N–Ar bonds in **1** and **4** appears to be relatively unrestricted since a similar symmetry breaking of the signals arising from their Ar–H(2,6) and Ar–H(3,5) protons is not observed.

Surprisingly, attempts at preparing similar complexes for diazabutadiene ligands with R = Me and bearing 2,6-dialkylsubstituted aryl groups do not furnish the anticipated products analogous to **1**–**4**. The bright red color of the new products gave a first indication of radically different chemistry—the dab complexes **1**–**4** were strongly, dark green- or brown-colored species, indicative of the characteristic d(metal) → π*(diimine) charge transfer bands that are commonly encountered in (diimine)metal complexes [37]. The ^1H NMR spectroscopic data of these species indicate that not only has the C_s symmetry of the ligand been broken, but the spectra also suggest that ligand C–H activation of a methyl group at the dab ligand must have occurred (products **5**–**7**, Scheme 2). For example, the ^1H NMR spectrum (CD_2Cl_2) of **5**, the product of the reaction between $[Cp^*IrCl_2]_2$ and (2,6-$Me_2C_6H_3$)N=CMe–CMe=N(2,6-$Me_2C_6H_3$) exhibits five methyl singlets of equal intensities at δ 1.95–2.63. In addition, two mutually coupled doublets (1 H each) were observed at δ 2.54 and 4.01 (J = 9.9 Hz). These data suggest that one of the methyl

[3] Compound **2** has been previously reported [36].



	R =	Ar =
5	Me	2,6-$Me_2C_6H_3$
6	Me	2,6-$^i Pr_2C_6H_3$
7	Me	2,4,6-$Me_3C_6H_2$

Scheme 2.

groups of the ligand has undergone C–H activation to furnish a methylene group with diastereotopic protons. The third proton originating from this methyl group presumably gives rise to the broadened resonance observed at δ 14.77. As for **2** and **3**, the spectra indicate that rotation around both N–Ar bonds must be restricted.

More elaborate NMR techniques were utilized in order to determine whether the C–H bond activation had occurred at an aryl methyl or at a dab chelate-bonded methyl group in **5**. A $^1H^1H$ COSY NMR spectrum of **5** confirmed the coupling between the two methylene doublets. A gs-HSQC[4] spectrum reaffirmed the presence of a methylene group with cross correlations at δ 29 in the ^{13}C direction for the methylene protons at δ 2.54 and 4.01 in the ^1H direction. This large difference in chemical shift of these geminal protons indicate a considerable difference in shielding of the two nuclei. Possible sources of the shielding are ring current effects from the neighboring Cp* and aryl groups as well as metal anisotropy effects. The X-ray structure of **5** (Fig. 1, vide infra) indicates that the position of these hydrogens might be different enough relative to the two rings to effect this. The $^2J_{HH}$ coupling constant of ca. 9 Hz is consistent with geminal protons (methane $^2J = -12.4$ Hz, cyclopropane $^2J = -4.5$ Hz [38]). Finally, a gs-HMBC (see footnote 4) experiment allowed the observation of correlation signals that confirmed the presence of a CH_2–C–C–CH_3 fragment of the C–H activated dab moiety. This should not be observed if C–H activation had occurred at an aryl methyl group. Similar spectroscopic features were observed for **7**.

Definitive proof that the C–H activation had occurred at a methyl group bonded at the dab chelate ring, rather than at an N-aryl methyl substituent, was obtained by an X-ray crystal structure determination of **5**. Selected bond distances and angles are provided

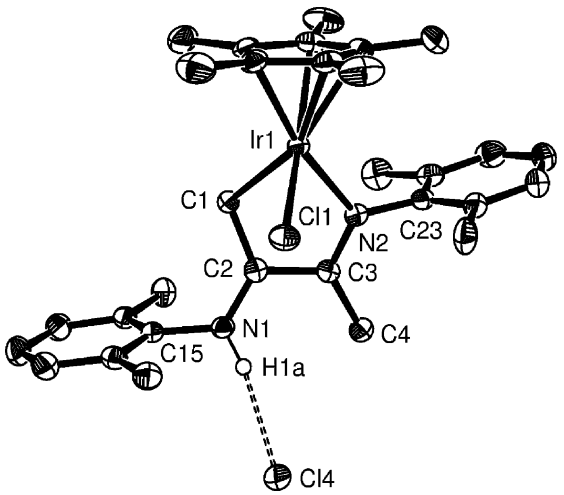


Fig. 1. ORTEP plot of **5** at the 50% probability level. Hydrogen atoms have been omitted for clarity.

[4] gs-HSQC (gradient selected heteronuclear single-quantum correlation) is a proton observed heteronuclear experiment for the observation of ^1H–^{13}C correlations. The experiment is based on the INEPT method for sensitivity enhancement of insensitive nuclei. An INEPT sequence transfers polarization from a sensitive (^1H) to an insensitive (^{13}C) nucleus, and thus amplifies the magnetization of the insensitive nucleus. In the reverse two-dimensional experiment this polarization is transferred back by a reverse INEPT sequence, and the spectrum now recorded for the sensitive nucleus contains the information of the ^1H–^{13}C correlations. One special feature of this experiment is that it selects only single-quantum transitions, and only $^1J_{HC}$ couplings are observed. The gradient selection further enhances sensitivity, removes the peaks from protons attached to ^{12}C, etc. The technique is very useful when there is very little sample available (only a proton sample is needed). A good ^1H–^{13}C two-dimensional spectrum can be obtained in only 5 min. The HMBC experiment has the same basic features as HSQC, but is a technique specifically designed for observation of couplings over greater distances (2–3 bonds) [38–41].

Table 1
Selected interatomic distances and angles in **5** and **8**

	Distances (Å)			Angles (°)	
	Compound **5**	Compound **8**		Compound **5**	Compound **8**
Ir1–C1	2.165(3)	2.117(2)	Ir1–C1–C2	102.4(2)	107.52(15)
C1–C2	1.454(4)	1.499(3)	C1–C2–C3	113.5(3)	112.46(19)
C2–C3	1.488(5)	1.488(3)	C2–C3–N2	112.6(3)	114.0(2)
N2–C3	1.296(4)	1.297(3)	C3–N2–Ir1	116.5(2)	117.83(16)
Ir1–N2	2.073(3)	2.081(2)	C1–Ir1–N2	76.20(12)	76.94(8)
N1–C2	1.305(4)	1.285(3)	C1–Ir1–Cl1	88.18(9)	85.97(7)
C15–N1	1.442(4)	1.422(3)	N2–Ir1–Cl1	88.08(8)	86.21(6)
C23–N2	1.441(4)	1.438(3)	Cl1–Ir1–Ctr	123.0	123.7
C3–C4	1.491(5)	1.499(3)	N2–Ir1–Ctr	136.9	136.4
N1–H1a	0.886	n.a.	C1–Ir1–Ctr	128.1	130.2
Ir1–Cl1	2.4103(8)	2.4421(10)	N1–H1a–Cl4	172.3	n.a.
H1a–Cl4	2.27	n.a.			
Ir–Ctr[a]	1.817	1.826			

[a] Cp* centroid.

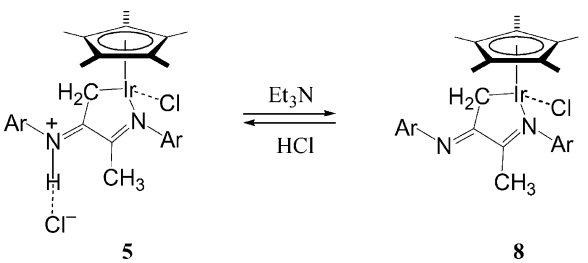
Table 2
X-ray crystallographic data for **5** and **8**

Compound	**5**	**8**
Chemical formula	$C_{31}H_{41}Cl_4IrN_2$	$C_{30}H_{38}ClIrN_2$
FW	775.66	654.27
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/*n*	P1
Z	4	2
a (Å)	16.6632(11)	8.514(2)
b (Å)	9.1112(6)	12.137(5)
c (Å)	21.0120(14)	13.282(5)
α (°)	90	78.66(2)
β (°)	90.051(3)	85.59(3)
γ (°)	90	86.04(3)
Volume (Å^3)	3190.1(4)	1339.8(8)
ρ_{calc} (g cm^{-3})	1.615	1.622
Crystal dimensions (mm)	0.25 × 0.15 × 0.07	0.3 × 0.3 × 0.1
Temperature (K)	150(2)	150(2)
Diffractometer	Siemens SMART CCD	Siemens SMART CCD
Radiation	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
2θ range (°)	3.12–61.08	5.08–60
Number of data collected	53317	18198
Number of unique data	9742	7655
Number of observed data ($I > 2\sigma(I)$)	9742	7283
Agreement between equivalent data (R_{int})	0.081	0.030
Number of parameters varied	507	317
μ (mm^{-1})	4.54	5.1
Absorption correction	Multi-scan (SADABS) Sheldrick, 1996	Multi-scan (SADABS) Sheldrick, 1996
R1(F_0), wR2(F_0^2) ($I > 2\sigma$)	0.0337, 0.0595	0.0199, 0.0507

in Table 1. Crystallographic data are listed in Table 2. The complex 5 cocrystallized with a CH_2Cl_2 molecule which has been omitted from the ORTEP plot which is displayed in Fig. 1. The molecule is chiral at Ir, and both enantiomers are found in the crystallographic unit cell. The structure of **5** in Fig. 1 depicts a typical three-legged piano stool structure which has a pseudo-octahedral ligand arrangement about the metal center. A five-membered metallacycle has been produced in the C–H activation reaction. The bond distance data clearly show C3–N2 to be a double bond, whereas C1–C2 and C2–C3 are rather typical of single bonds. The Ir–C1 bond length of 2.165 Å in **5** is in the range of Ir–C bond lengths reported for variously ligated Cp*Ir(III) complexes (typically 2.0–2.2 Å) [11,12,42–45]. For example, the Ir–C1 bond in complex **5** is slightly longer than the one in Bergman's $Cp^*Ir(PMe_3)(CH_3)(ClCH_2Cl)^+$ (2.105 Å) [11]. The aromatic rings in **5** are tilted approximately 90° with respect to the dab-derived chelate ring, thus alleviating steric repulsions. This tilting is quite typical for N-aryl substituted diimine complexes. The N atom of the uncomplexed C2–N1 imine group is protonated (N1–H1a distance 0.886 Å); the proton H1a is hydrogen bonded to a chloride counterion at a distance of 2.27 Å through a nearly linear Cl4–H1a–N1 alignment (Cl–H–N angle 172.3°). The C–H activation is clearly the product of a heterolytic bond cleavage reaction, resulting in a proton and a formally anionic metal-bonded alkyl group.

2.1. Reversible deprotonation of 5

Treatment of **5** with triethylamine served to remove HCl. The neutral compound **8** was isolated in 58% yield (Scheme 3) but the reaction was essentially quantitative by ^{1}H NMR. This reaction could be readily reversed: addition of ethereal HCl to an ether solution of **8** resulted in protonation at the free imine to regenerate complex **5**. An X-ray crystal structure determination was also performed on **8**, which (like **5**) crystallized with both enantiomers contained in the unit cell. The bond distances and angles (Table 1) show that there are only a few significant differences in the metrical data of the cation **5** and the neutral complex **8**, and so the two structures are very similar in their overall geometries. The most pronounced change takes place in the Ir–C1 bond length. In the cation this distance is 0.048 Å longer than in the more electron-rich neutral compound. The two other bonds that display significant differences are C1–C2 and Ir–Cl1. These bonds become 0.045 and 0.032 Å longer, respectively, in the neutral **8**. The differences in the presumably somewhat polar Ir–Cl bond may be a consequence of a higher positive charge at Ir in **5** than in **8**. The shortening of the bond in **5** relative to **8** would then be an example of the combined effect of reduced ionic radius of Ir and increased electrostatic attraction between Ir and Cl [46–49].

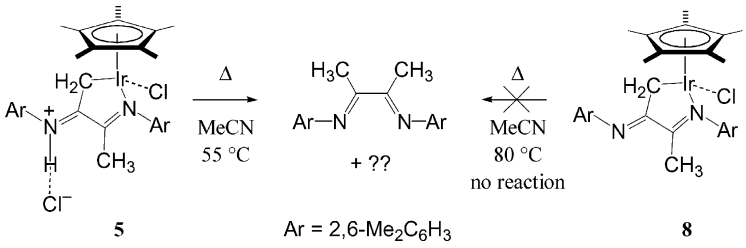


5 **8**

Scheme 3.

2.2. Thermal decomposition of C–H activation products

Complexes **1**–**7** are all thermally stable as solids, except for **6** which slowly decomposes at ambient temperature. The C–H activated complexes **5**–**7** undergo decomposition on the time scale of minutes to hours in solution, in particular in polar solvents such as acetone and acetonitrile. The rate of this decomposition appears to correlate with the size of the 2,6-alkyl groups on the N-aryl rings—greater substituents leading to greater thermal sensitivity. For example, complex **5** is stable for hours or days in solution depending on the solvent used, whereas complex **6** is so labile in solution that obtaining a well-resolved standard ^{1}H NMR spectrum is possible only if special care is taken to ensure rapid handling at sub-ambient temperatures. This affects the possibility of obtaining a pure sample by recrystallization, and it also makes a reliable check of the sample purity difficult. The ^{i}Pr group is also suspected to destabilize the non-CH-activated complex **3**. Contrary to compounds **1**, **2**, and **4**, complex **3** exhibits a pronounced tendency to decompose in solution. There were also qualitative indications of considerably greater thermal stability of **8** relative



Scheme 4.

to **5** in dichloromethane and acetonitrile solutions. Controlled heating of some complexes was conducted in order to provide more insight into the factors that govern the thermal stabilities of these species.

The C–H activated complexes **5** and **7** were heated in dry acetonitrile under an atmosphere of N_2. At a temperature of 55 °C, rapid decomposition (<1 h) occurred. Free dab ligand was the only identifiable product of these reactions (Scheme 4). This was also demonstrated in an experiment on **5** which was performed in acetonitrile-d_3 to which was added 1,4-$(CF_3)_2C_6H_4$ as internal standard in a sealed NMR tube. Heating at 55 °C for 1 h led to the quantitative formation of the dab ligand (2,6-$Me_2C_6H_3$)N=CMeCMe=N(2,6-$Me_2C_6H_3$). Contrasting these results, solutions of the neutral complex **8** were stable on this time scale even at 80 °C.

In addition signals arising from the free diimines, the ^{1}H NMR spectra of the decomposition of **5** and **7** led to several minor singlets suspected to arise from Cp*Ir containing species. Their identities remain unknown, but comparisons with authentic samples reveal that these are not $Cp^*Ir(NCMe)_3^{2+}$ or $Cp^*Ir(NCMe)_2Cl^+$ which might at first appear to be likely candidates.

3. Concluding remarks

In this contribution, we have described the C–H activation of methyl groups that are directly bonded at the diimine backbone of would be diimine chelating ligands. This appears to be a novel reaction type for diimine ligands and demonstrates a possible complication in the use of diimine ligands designed for use in C–H activation reactions. As mentioned in the introduction, ortho alkyl substituents at the N-aryl group have been previously seen to occasionally undergo similar reactions. A related reaction has been seen by Herrmann and coworkers, who reported C–H activation to occur at a cyclohexyl substituent of the *N*,*N*-heterocyclic carbene 1,3-dicyclohexylimidazolin-2-ylidene upon acidification of the $Cp^*Ir(carbene)Me_2$ precursor [43].

The formation of the C–H activation products **5**–**7** represents clear-cut cases of heterolytic C–H activation processes in which the formally negatively charged alkyl group remains bonded at the metal center and the hydrogen is liberated as a proton, possibly by the intermediacy of an acidic, cationic Ir(V) hydride intermediate [50][5] that transfers the hydride in the form of a proton to a basic, pendant imine nitrogen. The mechanistic details of the reaction are not clear, but we suspect that the C–H activation occurs at a mononuclear Ir species resulting from fragmentation of the dimeric $[Cp^*IrCl_2]_2$ precursor. The observation of the same process starting from monomeric $Cp^*Ir(dmso)Cl_2$ supports this hypothesis.

The thermal decomposition of the C–H activated species to regenerate the free diimine ligand is aided by the presence of acid (cationic **5** versus neutral **8**) and it is therefore likely that the reforming of the C–H bond is also an example of a heterolytic process. The overall reaction sequence involving the diimine C–H activation and the C–H bond formation therefore constitutes a case of reversible, heterolytic, intramolecular C–H activation at an alkyl group. Heterolytic processes have been recognized as being of crucial importance in many aspects of metal-mediated C–H activation and functionalization chemistry [51].

[5] For a discussion of the involvement of Ir(V) species in C–H activation at cationic Ir(III) complexes, see [50].

4. Experimental

4.1. General procedures

All reactions were performed under an N_2 atmosphere. Dichloromethane was distilled from CaH_2. For use in the drybox, THF and pentane were dried by distillation from sodium/benzophenone and degassed by repeated pump-thaw cycles. $[Cp^*IrCl_2]_2$ [52] and the diimines ArN=CHCH=NAr [53] and ArN=CMeCMe=NAr [54] were synthesized according to reported procedures.

^1H and ^{13}C NMR spectra were recorded on Bruker Avance DXP 200, 300, and 500 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standard. Elemental analyses were performed by Ilse Beetz Microanalytisches Laboratorium, Kronach, Germany. UV–Visible spectra were recorded on a Shimadzu UV-260 spectrophotometer and are reported as λ_{max} (nm), $\varepsilon \times 10^{-3}$ ($M^{-1}\,cm^{-1}$). Mass spectroscopic analysis was performed on a Fisons VG ProSpec-Q mass spectrometer.

4.2. General procedure for preparation of the *Cp*Ir(diimine)Cl$^+$Cl$^-$* complexes **1–4**

The Ir complexes **1**–**4** (Scheme 1) were prepared by adding the appropriate diimine ArN=CRCR=NAr (0.8 mmol) to a suspension of $[Cp^*IrCl_2]_2$ (0.4 mmol, 300 mg) in methanol (20 ml) in a 100 ml round-bottom flask equipped with a magnetic stirrer. Stirring for 2–12 h under an atmosphere of N_2 resulted in a dark solution. The products were isolated by filtration and recrystallization from dichloromethane/pentane.

4.2.1. *Cp*Ir[(4-MeC$_6$H$_4$)NCHCHN(4-MeC$_6$H$_4$)]Cl$^+$Cl$^-$* (**1**)

Yield: 74%. ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 15 H, Cp*), 2.41 (s, 6H, Me), 7.25 (d, $J = 8.3$ Hz, 4 H, Ar*H*), 7.78(d, $J = 8.3$ Hz, 4H, Ar*H*), 8.78 (s, 2H, NC*HCH*N). λ_{max} (CD_2Cl_2) 343 (6.7). Anal. Calcd. for $C_{26}H_{31}Cl_2IrN_2$: C, 49.20; H, 4.92; Cl, 11.17; Ir, 30.29; N, 4.41. Found: C, 45.76; H, 5.12;Cl, 10.73; Ir, 28.89; N, 4.23. EI MS *m/z*: 564.3 (M^+-2Cl, 100%).

4.2.2. *Cp*Ir[(2,6-Me$_2$C$_6$H$_3$)NCHCHN(2,6-Me$_2$C$_6$H$_3$)]Cl$^+$Cl$^-$* (**2**)

Yield: 88%. ^1H NMR (200 MHz, $CDCl_3$) δ 1.13 (s, 15H, Cp*), 2.24 (s, 6H, Me), 2.37 (s, 6H, Me), 7.14 (br s, 6H, Ar*H*), 9.79 (s, 2H, NC*HCH*N). λ_{max} (CD_2Cl_2) 398 (4.1). This complex has been previously reported [36]. EI MS *m/z*: 592.3 (M^+-2Cl, 10.4%).

4.2.3. *Cp*Ir[(2,6-^{i}Pr$_2$C$_6$H$_3$)NCHCHN(2,6-^{i}Pr$_2$C$_6$H$_3$)]Cl$^+$Cl$^-$* (**3**)

Yield: 69%. ^1H NMR (200 MHz, $CDCl_3$) δ 1.10 (d, $J = 6.8$ Hz, 6H, CH*Me*2), 1.15 (s, 15H, Cp*), 1.24 (d, $J = 6.7$ Hz, 6H, CH*Me*$_2$), 1.35 (d, $J = 6.2$ Hz, 6H, CH*Me*$_2$), 1.38 (d, $J = 6.4$ Hz, 6H, CH*Me*$_2$), 2.43 (m, septet, $J = 6.6$ Hz, 2H, CH*Me*$_2$), 3.85 (m, septet, $J = 6.6$ Hz, 2H, CH*Me*$_2$), 7.30 (m, 6H, Ar*H*), 9.88 (s, 2H, NC*HCH*N). λ_{max} (CD_2Cl_2): 427 (3.2). Anal. Calcd. for $C_{36}H_{51}Cl_2IrN_2$: C, 55.80; H, 6.63; N, 3.61; Cl, 9.15. Found: C, 52.92; H, 6.36; N, 3.33; Cl, 10.12. EI MS *m/z*: 704.0 (M^+-2Cl, 9.7%).

4.2.4. *Cp*Ir[(4-MeC$_6$H$_4$)NCMeCMeN(4-MeC$_6$H$_4$)]Cl$^+$Cl$^-$* (**4**)

Yield: 47%. ^1H NMR (200 MHz, $CDCl_3$) δ 1.17 (s, 15H, Cp*), 2.41 (s, 6H, Me), 2.51 (s, 6H, Me), 7.2 (br s, 4H, Ar*H*), 7.4 (br dd, 2H, Ar*H*), 7.6 (br dd, 2H, Ar*H*). λ_{max} (CD_2Cl_2) 326 (4.9). Anal. Calcd. for $C_{28}H_{35}Cl_2IrN_2$: C, 50.75; H, 5.32; N, 4.23; Cl, 10.70. Found: C, 49.74; H, 5.61; N, 4.27; Cl, 8.33.

4.2.5. *Cp*$\overline{\text{IrClCH}_2\text{C(=NH(2, 6-Me}_2\text{C}_6\text{H}_3\text{))CMe=N}}$(2,6-Me$_2C_6H_3$)$^+Cl^-$* (**5**)

The diimine (2,6-$Me_2C_6H_3$)N=Cme–CMe=N(2,6-$Me_2C_6H_3$) (242 mg, 0.828 mmol) was added to a suspension of $[Cp^*IrCl_2]_2$ (297 mg, 0.377 mmol) in methanol (20 ml) in a 100 ml round-bottom flask equipped with a magnetic stir bar. The mixture turned dark red during stirring for 12 h. The product was isolated in 85% yield by filtration and recrystallization from dichloromethane/pentane. An analytically pure sample was prepared by recrystallization and washing with toluene and pentane. Dark red crystals for the X-ray structure determination were obtained by slow evaporation of a saturated dichloromethane solution. ^1H NMR (500 MHz, CD_2Cl_2) δ 1.34 (s, 15H, Cp*), 1.95 (s, 3H, Me), 2.28 (s, 3H, Me), 2.29 (s, 3H, Me), 2.35 (s, 3H, Me), 2.54 (d, $J = 9.9$ Hz, 1H, CH_2), 2.63 (s, 3H, Me), 4.01 (d, $J = 9.9$ Hz,

1H, CH_2), 7.16 (m, 4H, ArH(3,5)), 7.25 (m, 2H, ArH(4)), 14.77 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 187.2, 178.8, 146.1, 136.4, 135.9, 132.6, 132.3, 130.2, 129.5, 129.1, 128.7, 128.4, 127.5, 91.0 (C_5Me_5), 29.3, 22.0, 20.5, 19.1, 18.8, 17.7, 8.4 (C_5Me_5). λ_{max} (CD_2Cl_2) 304 (5.5), 446 (5.3). Anal. Calcd. for $C_{30}H_{39}Cl_2IrN_2{\cdot}CH_2Cl_2$: C, 48.00; H, 5.33; N, 3.61; Cl, 18.28. Found: C, 47.98; H, 5.38; N, 3.95; Cl, 18.26. HRMS (EI) Found: *m/z* 654.2335 ($C_{30}H_{38}ClIrN_2$, M^+-HCl). Calcd. for $C_{30}H_{38}ClIrN_2$: 654.2353.

6 and **7** were made by entirely analogous procedures to that of **5**.

*4.2.6. Cp*IrClCH$_2$C(=NH(2, 6-^{i}Pr$_2$C$_6$H$_3$))CMe=N(2,6-^{i}Pr$_2$C$_6$H$_3$)$^+$Cl$^-$ (**6**)*

Yield, 60%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.09 (4 overlapping d, 12H, CHMe_2), 1.27 (d, 12H, CHMe_2), 1.37 (s, 15H, Cp*), 2.30 (s, 3H, N=CMe), 2.28 (septet, 1H, CHMe_2), 2.60 (d, J = 9.7 Hz, 1H, CH_2), 2.78 (septet, 1H, CHMe_2), 3.45 (septet, 1H, CHMe_2), 3.72 (septet, 1H, CHMe_2), 3.82 (d, J = 9.7 Hz, 1H, CH_2), 7.34 (m, 6H, ArH). λ_{max} (CD_2Cl_2): 335 (3.8). EI MS *m/z*: 765.9 (M^+-HCl–H, 0.4%), 731.1 (M^+-HCl–Cl, 0.4%), 730.1 (M^+-2HCl), 2.4%).

*4.2.7. Cp*IrClCH$_2$C(=NH(2, 4, 6-Me$_3$C$_6$H$_3$))CMe=N(2,4,6-Me$_3$C$_6$H$_3$)$^+$Cl$^-$ (**7**)*

Yield, 83%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (s, 15H, Cp*), 1.87 (s, 3H, Me), 2.23 (s, 6H, 2 Me),2.28 (s, 3H, Me), 2.32 (s, 3H, Me), 2.35 (s, 3H, Me), 2.53 (d, J = 10.3 Hz, 1H, CH_2), 2.60 (s, 3H, Me), 3.85 (d, J = 10.3 Hz, 1H, CH_2), 6.93 (2 br dd, 4H, ArH). λ_{max} (CD_2Cl_2) 294 (5.6), 340 (6.0), 445 (5.6). Anal. Calcd. for $C_{32}H_{43}Cl_2IrN_2$: C, 53.47; H, 6.03; N, 3.90; Cl, 9.86. Found: C, 53.01; H, 5.94; N, 3.85; Cl, 9.90. EI MS *m/z*: 683.1 (M^+-Cl, 5.6%).

*4.2.8. Cp*IrClCH$_2$C(=N(2, 6-Me$_2$C$_6$H$_3$))CMe=N(2,6-Me$_2$C$_6$H$_3$) (**8**)*

Triethylamine (20 μl, 0.15 mmol) was added to a solution of 5 (109 mg, 0.16 mmol) in THF (5 ml) in a round-bottom flask. After 10 min of stirring, the solution was filtered and evaporated to dryness. The brown powder was dissolved in dichloromethane and residual triethylamine was extracted with water (5 ml) acidified with a drop of 10% aqueous HCl. Removal of the solvent in vacuo yielded the product **8** (60 mg, 58%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.30 (s, 15H, Cp*), 1.83 (s, 3H, Me), 1.94 (s, 3H, Me), 2.06 (s, 3H, Me), 2.14 (d, J = 13.2 Hz, 1H, CH_2), 2.21 (s, 3H, Me), 2.37 (s, 3H, Me), 3.01 (d, J = 13.2 Hz, 1H, CH_2), 7.05 (m, 6H, ArH). The proposed structure was confirmed by COSY, gs-HSQC and gs-HMBC NMR. λ_{max} (CD_2Cl_2) 334 (4.4). Anal. Calcd. for $C_{30}H_{38}ClIrN_2$: C, 55.07; H, 5.85; N, 4.28; Cl, 5.42. Found: C, 54.80; H, 5.88; N, 4.34; Cl, 3.10. EI MS *m/z*: 654 (M^+, 22.3%).

4.3. Protonation of **8** with HCl to yield **5**

The addition of one equiv of HCl (1.0 M in ether) to a solution of **8** (5 mg in 0.5 ml CD_2Cl_2 in an NMR tube) caused the clear brown solution to turn dark red. The ^{1}H NMR spectrum of the only observed product was identical to the spectrum of **5**, except that the N-bonded proton seen at δ 14.77 in **5** now appeared at δ 14.2. The chemical shift of this proton has been observed to change its position somewhat from sample to sample, an effect that is attributed to the presence of residual water or other impurities capable of interacting with this proton via hydrogen bonding.

4.4. Alternative synthesis of **5** and **8** from Cp*Ir(dmso)Cl$_2$

DMSO (0.085 ml, 1.197 mmol) was added to a solution of $[Cp^*IrCl_2]_2$ (68 mg, 0.085 mmol) in THF (15 ml) [55]. This resulted in an immediate color change from orange to bright yellow. The solution was filtered and the volatiles were removed in vacuo. The intermediate Cp*Ir(dmso)Cl$_2$ (52 mg, 0.11 mmol, 64%) was extracted from the crude mixture by extraction with ether. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (s, 15H, Cp*), 3.21 (s, 6H, Me_2SO). Synthesis of the cyclometalated compound **5** was achieved by treating a solution of Cp*Ir(dmso)Cl$_2$ (52 mg, 0.11 mmol) in methanol (5 ml) with the diimine (2,6-Me$_2$C$_6$H$_3$)N=CMeCMe=N(2,6-Me$_2$C$_6$H$_3$) (35 mg, 0.12 mmol). The reaction mixture was stirred for 21 h during which a dark red color developed. The volume was reduced to 2 ml by vacuum transfer. Analysis of an aliquot by ^{1}H NMR showed that **5** had indeed formed. However, since **5** undergoes facile decomposition at the concentrations of

DMSO that would result after continued removal of the most volatile components, in situ deprotonation was effected by the addition of triethylamine (10 μl) after dilution with dichloromethane (5 ml). The water-soluble constituents of the reaction mixture ($Et_3NH^+Cl^-$, DMSO, and remaining Et_3N) were removed by extraction with water (5 ml). The volatiles were removed in vacuo, and the product was isolated (21 mg, 30% based on $Cp^*Ir(dmso)Cl_2$) by extraction of the crude mixture with pentane followed by evaporation of the solvent. The ^1H NMR spectrum was identical to that of **8**, prepared as described previously.

*4.5. Thermal decomposition of **5** and **7** in acetonitrile*

Acetonitrile solutions of **5** and **7** were slowly heated from 25 to 55 °C during 1 h. This resulted in a change of color of the solution from dark red to yellow. The solvent was removed in vacuo. Extraction with ether gave a bright yellow solution and an orange residue. The extracts contained (^1H NMR) relatively pure diimine ligands and only a very small Cp^* resonance at δ 1.56. ^1H NMR of ether extract of **5** (200 MHz, $CDCl_3$) δ 2.02 (s, 18H, *Me* of free dab ligand), 6.93 (s, 2H, Ar*H* of free dab ligand), 7.02 (s, 4H, Ar*H* of free dab ligand); additional unidentified singlets were present at δ 0.05, 1.77, 1.95 and 2.56. ^1H NMR of ether extract of **7** (200 MHz, $CDCl_3$) δ 1.98 (s, 12H, *Me* of free dab ligand), 2.01 (s, 6H, *Me* of free dab ligand), 2.26 (s, 6H, *Me* of free dab ligand), 6.86 (s, 4H, Ar*H* of free dab ligand). The identity of the diimine ligand from complex **7** (2,4,6-$Me_3C_6H_2$)N=CMeCMe=N(2,4,6-$Me_3C_6H_2$) was supported by mass spectroscopy. EI MS *m*/*z* 320 (M^+, 9.6%).

Heating of an acetonitrile-d_3 solution of **5** at 55 °C for 1 h in the presence of 1,4-$(CF_3)_2C_6H_4$ as an internal standard in a sealed NMR tube established that the diimine forming reaction proceeded quantitatively.

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