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Structural diversity and solution behavior of low-valent iridium complexes bearing 1,4-diazabutadiene ligands

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ABSTRACT

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Keywords: Iridium Diazabutadiene ligand Non-innocent ligand Crystal structure Three types of 1,4-diazabutadiene stabilized low-valent iridium complexes, namely [IrCl(cod)(MesDAB)] (1), [IrCl(coe)(MesDAB)] (2) and [IrCl(MesDAB)₂] (3), have been prepared from 1,4-bis(2,4,6-trimethylphenyl)-1,4-diaza-1,3-butadiene (MesDAB) and [IrCl(cod)]₂ or [IrCl(coe)₂]₂, respectively. The complexes have been investigated by NMR spectroscopy and X-ray diffraction experiments. While tetra-coordinated 2 and penta-coordinated 3 maintain their solid state structure in solution, penta-coordinated 1 shows fluxional behavior. The crystal structures determined indicate strong π -backbonding towards the MesDAB ligand in all cases. © 2011 Elsevier B.V. All rights reserved.

1,4-diaza-1,3-butadiene (DABs) are an important and widely studied class of 1,2-diimine ligands. Complexes with nearly every metal across the periodic table in different oxidation states, and various coordination modes of these ligands are known [1]. Some of the complexes, like DAB rhenium compounds, have received considerable interest due to their photophysical properties and the related photochemistry [2]. Others were found to be active catalysts in numerous transformations, e. g. the nickel or palladium catalyzed polymerisation of olefins as reported by Brookhart and co-workers [3]. Additionally, the non-innocent nature of DAB ligands in redox reactions was also a subject of interest [4]. In light of their simple preparation and broad range of possible applications, it is surprising that little is known about DAB complexes of iridium, especially in the formal oxidation state +1. In principle, the combination of an iridium (I) center with a neutral 1,4-diazabutadiene ligand should lead to complexes, in which the resonance structures A-C, shown in Chart 1, contribute differently to the overall structure, depending on the coligands present.

Kaim and co-workers found, that the reduction of the iridium(III) complex [IrCl(Cp*)(dab)]PF₆ (dab = 1,4-Bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene) by sodium cyanoborohydride took place at the ligand, not at the metal center leading to [Ir(Cp*)(dab)] which is best described by resonance structure C (see Chart 1) [5]. Garralda and co-workers synthesized a series of complexes of the general formula [IrX(cod)(DAB)] (X=Cl, SnCl₃), which were successfully applied as catalysts in the transfer hydrogenation of ketones [6]. Recently, cationic iridium(I) complexes of the type [Ir(cod)(DAB)]⁺BF₄⁻ were

used as precursors for the synthesis of iridium(III) difluoro complexes [7]. However, structurally characterized examples of such compounds are very rare [8].

In order to gain insight into the behavior in solution and the solid state structures of iridium(I) complexes containing DAB ligands, the most widely used iridium(I) precursors, [IrCl(cod)]₂ and [IrCl(coe)₂]₂ (cod = 1,5-cyclooctadiene; coe = cyclooctene), were reacted with a representative DAB ligand, namely 1,4-bis(2,4,6-trimethylphenyl)-1,4-diaza-1,3-butadiene (MesDAB) [9] (Scheme 1). When [IrCl(cod)]₂ was allowed to react with two equivalents of the ligand in toluene, the solution turned rapidly to a bluish black. A solvent change to diethyl ether induced crystallization of the iridium(I) complex [IrCl(cod) (MesDAB)] (1) [10]. In solid state, the compound exhibits a distorted square pyramidal geometry around the iridium center, with the nitrogen donors of the DAB ligand and the olefinic bonds of cyclooctadiene in basal positions (see Fig. 1) [11]. The observed bond lengths and angles are similar to related complexes containing other chelating 1,2-diimine ligands (see Table 1).



Chart 1. Resonance structures A-C.

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Scheme 1. Synthesis of 1-3

DABs are weaker σ -donor and stronger π -acceptor ligands then e.g. 3,4,7,8-tetramethyl-1,10-phenanthroline which results in slightly shorter Ir-N bonds. Additionally, a shortened distance between the chloride anion and the less electron rich iridium(I) center in 1 was observed when compared to $[IrCl(cod)(Me_4phen)]$ with its stronger donor ligand [12]. The bond distances within the five-membered ring, formed by the coordinated DAB ligand and the iridium center (av. C1 - C2 1.414(5)Å, av. C - N 1.318(4)Å), point towards a certain degree of π -backbonding and hence, partial delocalization of π -electron density in the ring fragment. The values observed come close to those of the one electron reduced DAB ligand for instance in [Gal2(MesDAB)] (C1 – C2 1.408(3)Å, av. C – N 1.338(3)Å) [15]. As expected for a pentacoordinated iridium(I) complex, 1 shows fluctuating behavior in THF solution, most likely related to an inverse Berry pseudo-rotation, and only broad resonances for the protons of cod and the o-methyl groups of the ligand were observed at room temperature. In contrast, at -50 °C two resonances at δ 3.36 and 4.08 for the olefinic protons of coordinated cod and two sharp resonances at δ 2.01 and 2.43 for the o-methyl groups were obtained.

However, the presence of the cod ligand is not desirable in complexes like $\mathbf{1}$ which are to be applied as catalysts in transfer hy-



Fig. 1. Molecular structure of **1** (molecule A of two independent molecules) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir1A–N1A 2.059(3), Ir1A–N2A 2.063(3), Ir1A–C1A 2.4679(9), Ir1A–C21A 2.136(3), Ir1A–C22A 2.144(3), Ir1A–C25A 2.154(3), Ir1A–C26A 2.135(3), N1A–C1A 1.321(4), N2A–C2A 1.316(4) and C1A–C2A 1.414 (5). Selected bond angles (deg): N1A–Ir1A–N2A 76.79(11), N1A–Ir1A–C1A 92.34 (8), N2A–Ir1A–C1A 91.20(8), N1A–Ir1A–C25A 91.63(13), N1A–Ir1A–C26A 99.45 (13), N2A–Ir1A–C21A 101.87(13) and N2A–Ir1A–C22A 89.44(12).

drogenation of ketones. Consequently, cod has to be removed to obtain a catalytically active species [16]. Therefore, complexes containing non-chelating olefin ligands like cyclooctene might be favorable in such applications.

The reaction between $[IrCl(coe)_2]_2$ and MesDAB in an one to two fashion proceeds slowly in THF and allowed monitoring by NMR measurement. As illustrated in Fig. 2, two products were observed. The major component of the mixture was identified as the tetracoordinated complex [IrCl(coe)(MesDAB)] (2) [17], containing a MesDAB ligand coordinated in a non-symmetric fashion as shown by the different chemical shift of the two imine protons (δ 8.93 and 11.75) in the ¹H NMR spectrum (see Fig. 2). Crystals of this compound were obtained from diethyl ether. The molecular structure of 2 (see Fig. 3) [18], determined from these crystals, revealed again a high degree of π -backbonding into the diimine ligand comparable with the situation observed in 1, but more pronounced than in other square planar d⁸ complexes with 16e-configuration containing the MesDAB ligand like [Ni(C₂H₄COO) (MesDAB)] [19]. 2 allowed the study of the different trans influence of coe and the chloride anion on the bonding of the MesDAB ligand. While coe is a competitive π -acceptor, compared to the MesDAB ligand and backbonding to both ligands is observed, the weakened acceptor capacity of the chloride anion facilitates backbonding into the empty π^* -orbital of the imine double bond in *trans* position to it.

Accordingly, the Ir – N1 bond (molecule A: 1.952(4)Å, molecule B: 1.947(4)Å) is shorter by more than 0.1 Å than the Ir – N2 bond (molecule A: 2.061(4)Å, molecule B: 2.073(4)Å), and even slightly shorter than observed in the iridium(III) complex [Ir(Cp*)(dab)] containing a doubly reduced DAB ligand (see Table 2) [5]. Additionally, the N1 – C1 bond (molecule A: 1.339(6)Å, molecule B: 1.331(6)Å) is longer than the N2 – C2 bond (molecule A: 1.306(6)Å, molecule B: 1.290(6)Å). It should be noted, that compound **2** differs from the products commonly observed from the reaction of [IrCl(coe)₂]₂ with most of the bidentate chelating ligands L in this stoichiometry. Chloro bridged dimers of the type [(L)Ir(μ -Cl)]₂ are obtained not only upon use of chelating diphosphane ligands [20] but also if 1,2-diimines like 4,4'-di-t-butyl bipyridine were applied [21]. Similarly, the reaction of the rhodium analog [RhCl(coe)₂]₂ with a related DAB ligand yielded a dimeric chloro bridged product [22].

The second product isolated from the reaction of MesDAB and $\frac{1}{2}$ [IrCl(coe)₂]₂, is the penta-coordinated complex [IrCl(MesDAB)₂] (**3**) which is formed in minor extent in THF. The ratio of the products **2** and **3** is solvent dependent and the use of less polar toluene instead

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Comparis	son of 1 and related	1 1,2-diimine iridium	(I) complexes.	
Entry	Compound	[Å] web	(Å) (har) durc(and	d [

Entry	Compound	d _{IrN} [A]	d _{IrC(cod)} [A]	d _{IrX} [A]	Ref.
1	1	2.061(3) ^a	$2.140(3)^{a}$	2.4662(9) ^a	-
2	[IrCl(cod)(Me ₄ phen)] ^b	$2.122(7)^{a}$	2.112(8) ^a	2.589(2)	[12]
3	[IrI(cod)(Me ₄ phen)]	$2.106(14)^{a}$	2.117(18) ^a	$2.878(1)^{a}$	[12]
4	[IrI(cod)(PPEI)] ^c	$2.10(2)^{a}$	$2.14(2)^{a}$	2.839(1)	[13]
5	[IrI(cod)(APPEI)] ^d	$2.084(9)^{a}$	$2.14(2)^{a}$	2.8476(7)	[13]
6	[lr(acac)(cod)(bipy)]	$2.104(4)^{a}$	$2.126(6)^{a}$	2.420(6)	[14]

^a Average value.

 $Me_4phen = 3,4,7,8$ -tetramethyl-1,10-phenanthroline.

^c PPEI = 1-phenyl-N-((pyridin-2-yl)methylene)ethanamine.

^d APPEI = 1-phenyl-N-(1-(pyridin-2-yl)ethylidene)ethanamine.



Fig. 2. Time dependent formation of 2 and 3 from 1/2 [IrCl(coe)₂]₂ and MesDAB(*);(¹H NMR, imine protons).



Fig. 3. Molecular structure of **2** (molecule A of two independent molecules) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir1A–N1A 1.952(4), Ir1A–N2A 2.061(4), Ir1A–C1A 2.2885(12), Ir1A–C21A 2.166(5), Ir1A–C22A 2.169(5), N1A–C1A 1.339(6), N2A–C2A 1.306(6) and C1A–C2A 1.394(7). Selected bond angles (deg): N1A–Ir1A–N2A 78.26 (15), N1A–Ir1A–C1A 169.77(12), N1A–Ir1A–C21A 92.29(17), N1A–Ir1A–C22A 96.92(17), N2A–Ir1A–C1A 150.150(11), N2A–Ir1A–C21A 158.36(17) and N2A–Ir1A–C22A 161.97(18).

of THF favors the formation of **3**. However, when all MesDAB is finally consumed, the product ratio between the two products remains unaltered for days. A redistribution of the ligands between two molecules of **2** to form **3** and $\frac{1}{2}$ [IrCl(coe)₂]₂ was not observed.

Table 2

Selected bond distances within the metallacyclic ring of **1–3** and related compounds.

Compound	d _{CC} [Å]	d _{CN} [Å]	d _{MN} [Å]	Ref.
MesDAB	1.463(2)	1.273(2)	-	[9b]
1	$1.415(5)^{a}$	$1.318(4)^{a}$	2.061(3) ^a	-
2	$1.404(7)^{a}$	$1.316(6)^{a}$	$2.008(4)^{a}$	-
3	1.393(9) ^a	$1.324(8)^{a}$	$2.024(5)^{a}$	-
[IrCl(CNtBu)(L)] ^b	1.447(4)	$1.318(4)^{a}$	$2.010(2)^{a}$	[8]
[Ir(Cp*)(dab)]	1.334(15)	1.372(14) ^a	$1.978(9)^{a}$	[5]
[IrCl(Cp*)(dab)]PF ₆	1.482(15)	1.280(10)	2.091(7)	[5]
[IrCl(Cp [*])(PhBIAN)]BF ₄	1.473(10)	1.299(7)	2.101(4)	[26]
[IrCl(Cp*)(MesBIAN)]BF ₄	1.474(7)	1.276(8)	2.122(5)	[27]
[GaI ₂ (MesDAB)]	1.408(3)	1.338(3) ^a	1.9386(18) ^a	[15]
$[Ni(C_2H_4COO)(MesDAB)]$	1.455(3)	1.284(3) ^a	1.9315(2) ^a	[19]

^a Average value.

^b L- $(2,6-Me_2C_6H_3)N=C(Me)C(Me)=N(2,6-Me_2C_6H_3).$

Pure **3** was obtained by the reaction of $[IrCl(coe)_2]_2$ with four equivalents of MesDAB [23]. Crystals of this product are accessible from THP (tetrahydropyran) (see Fig. 4) [24]. In 3 the iridium atom is chelated by the imine nitrogen atoms of two MesDAB ligands which are arranged in a square planar fashion. The approximately square pyramidal coordination environment is completed by the chloride anion which adopts the apical position. While the NMR data suggests two identical MesDAB ligands in solution and only one signal at δ 8.17 was observed for all four imine protons in the ¹H NMR spectrum, in solid state slight differences were found. Here, the chloride anion is displaced from its ideal position towards one of the MesDAB ligands, forcing the mesityl substituents to bend away from it. Consequently, the ipso carbon atoms of the mesityl groups of this ligand are located 0.434 and 0.513 Å, respectively, above the plane defined by Ir1, N1, N2, C1, and C2 while for the other ligand only displacements of 0.076 and 0.109 Å from the corresponding plane were observed. Additionally, differing C-C bond lengths of 1.411(8)(C1-C2) and 1.375(9)(C21 - C22) were found in the two five-membered metallacycles. Again, differences to related diphosphane complexes of iridium(I) became



Fig. 4. Molecular structure of **3** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and co-crystallized THP are omitted for clarity. Selected bond lengths (Å): Ir1-N1 2.028(5), Ir1-N2 2.030(5), Ir1-N3 2.020(5), Ir1-N4 2.016(5), Ir1-Cl1 2.3818(14), N1-C1 1.323(8), N2-C2 1.320(8), N3-C21 1.322(8), N4-C22 1.329(8), C1-C2 1.411(8) and C21-C22 1.375(9). Selected bond angles (deg): N1-Ir1-N2 77.78(19), N1-Ir1-N3 101.0(2), N1-Ir1-N4 169.4(2), N1-Ir1-Cl1 90.03(14), N2-Ir1-N3 169.67(19), N2-Ir1-N4 101.7(2), N2-Ir1-Cl1 91.63(13), N3-Ir1-N4 77.5(2), N3-Ir1-Cl1 98.64(15) and N4-Ir1-Cl1 100.54(15).

obvious. While those compounds exist predominantly as ionic species of the type $[(L)_2Ir]^+CI^-$ (L = chelating diphosphane) [20,25], the use of the DAB ligands leads to less electron-rich iridium species and therefore to a coordination of the anion.

In conclusion, a series of low-valent MesDAB iridium complexes was prepared, showing an increased contribution of the resonance forms A and especially B to the overall bonding situation. Although the structural data suggests the presence of mono-reduced DAB ligands in **1–3**, an assignment of the oxidation states of the ligand and the iridium center solely based on structural features remains uncertain and will need further investigation. Especially compounds like **3** are of interest for multiple electron reductions, as **3** should be able to store and provide up to six electrons in its fully reduced form.

These easily accessible complexes now permit the development of a rich organometallic, redox and coordination chemistry as well as catalytic applications of such species. Due to the often weaker σ donor and stronger π -acceptor characters of the DAB ligands and their non innocent nature in redox reactions when compared to the extensively used diphosphane ligands, a different reactivity of DAB iridium complexes should be expected.

Appendix A. Supplementary material

CCDC 821234 for **1**, CCDC 821235 for **2**, and CCDC 821236 for **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary materials related to this article can be found online at doi:10.1016/j.inoche.2011.06.022.

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- [10] Synthesis of [IrCl(cod)(MesDAB)] (1):Solid MesDAB (50 mg, 0.17 mmol) was added to a stirred solution of [IrCl(cod)]₂ (56 mg, 0.083 mmol) in toluene (5 mL). The mixture, which rapidly turned to bluish black, was stirred for six hours at room temperature. Afterwards, the solvent was removed in vacuo and the remaining residue was taken up in diethyl ether (6 mL), initiating crystallization. The reaction mixture was allowed to stand at room temperature for 30 min. Then, the formed crystals were isolated by decantation and dried in a vacuum. The mother liquor was stored at -10 °C over night, yielding a second crop of well shaped black crystals. Yield: 62 mg (0.098 mmol, 59%). Elemental analysis (C28H36ClIrN2, 628.283 g/mol): calc.: C 53.53, H 5.78, N 4.46; found: C 53.66, H 5.55, N 4.70. ¹H NMR (200 MHz, 223 K): δ 1.79 (m, 2H, CH₂ cod), 1.9–2.5 (m, 6H, CH₂ cod), 2.01 (s, 6H, o-CH₃ Mes), 2.27 (s, 6H, p-CH₂ Mes), 2.43 (s, 6H, o-CH₃ Mes), 3.36 (m, 2H, CH cod), 4.08 (m, 2H, CH cod), 6.90 (s, 4H, *m*-H Mes), 8.92 (s, 2H, HC=N). ¹³C NMR (50.3 MHz, 223 K): δ 17.8 (2C, o-Me Mes), 20.5 (2C, o-Me Mes), 20.8 (2C, p-Me Mes), 30.9 (2C, CH₂ cod), 35.4 (2C, CH₂ cod), 63.2 (2C, CH cod), 78.0 (2C, CH cod), 128.8 (2C, m-CH Mes), 130.2 (2C, Mes), 130.3 (2C, Mes), 130.5 (2C, Mes), 136.5 (2C, p-C Mes), 148.6 (2C, i-C Mes), 161.9 (2C. C=N).
- [11] The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_{α} radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [28,29].The structures were solved by direct methods (SHELXS [30]) and refined

by full-matrix least squares techniques against Fo² (SHELXL-97 [30]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [30]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystal data for 1: C₂₈H₃₆ClIrN₂, M = 628.24, triclinic, space group P ī, *a* = 12.0458(3) Å, *b* = 12.3221(2) Å, *c* = 17.6943(4) Å, *α* = 97.245(1)°, *β* = 100.044(1)°, *γ* = 99.962 (1)°, *V* = 2513.82(9) Å³, *Z* = 4, *ρ* = 1.660 g cm⁻³, µ= 54.36 mm⁻¹, T = -140(2) °C, measured data 15957, data with I>2σ(I) 10282, unique data (R_{int}) 11157/0.0206, *w*_{*R*</sup> (all data, on F²) = 0.0667, *R*₁ (I>2σ(I)) = 0.0255, *S* = 1.049, Res. dens. = .120/ -1.355 e Å⁻³.}

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- [17] Synthesis of [IrCl(coe)(MesDAB)] (2):Solid MesDAB (35 mg, 0.12 mmol) was added to a stirred solution of [IrCl(coe)₂]₂ (53 mg, 0.059 mmol) in THF (10 mL). The resulting solution was stirred for 20 hours at room temperature resulting in a color change from orange yellow to dark green. Afterwards, the solvent was removed in vacuo and the remaining residue was taken up in diethyl ether (6 mL) with rapid stirring. The stirring was continued for 30 min and a small amount of a dark precipitate was removed by filtration afterwards. The dark green mother liquor was stored at -20 °C over night. The formed dark green crystals were isolated by decantation and dried in a vacuum. ¹H NMR (400 MHz): δ 1.35–1.60 (m, 10H, CH₂ coe), 1.75-1.9 (m, 2H, CH₂ coe), 1.87 (s, 6H, o-CH₃ Mes), 2.32 (s, 6H, 10 CH₃ Mes), 2.38 (s, 6H, o-CH₃ Mes), 6.77 (m, 2H, *m*-H Mes), 6.84 (m, 2H, CH coe), 6.93 (m, 2H, *m*-CH Mes), 8.93 (d, 1H, $^{3}J_{H,H} = 0.8$ Hz, HC=N), 11.76 (d, 1H, $^{3}J_{H,H} = 0.8$ Hz, HC=N). 1¹C NMR (50.3 MHz): δ 17.1 (2C, o-CH₃ Mes), 19.47 (2C, o-CH3 Mes), 20.9 (1C, p-CH3 Mes), 21.1 (1C, p-CH3 Mes), 27.4 (2C, CH2 coe), 29.1 (2C, CH₂ coe), 31.6 (2C, CH₂ coe), 73.2 (2C, CH coe), 127.4 (2C, o-C Mes), 128.4 (2C, m-CH Mes), 128.7 (2C, o-C Mes), 128.8 (2C, m-CH Mes), 135.7 (1C, p-C Mes), 137.1 (1C, p-C Mes), 150.7 (1C, i-C Mes), 156.4(1C, i-C Mes), 167.5 (1C, C=N), 179.3 (1C, C=N)
- [18] Crystal data for 2: $C_{28}H_{38}$ ClIrN₂, M=630.25, monoclinic, space group P 2₁/n, a=20.7210(4) Å, b=12.2821(2) Å, c=21.2120(4) Å, $\beta=90.769(1)$, V=5397.91 (17) Å³, Z=8, $\rho=1.551$ g cm⁻³, $\mu=50.63$ mm⁻¹, T=-90(2) °C, measured data 31709, data with 1>20(1) 9959, unique data (R_{int}) 12211/0.0660, wR₂ (all data, on F²)=0.0937, R₁ (1>20(1))=0.0393, S=1.004, Res. dens. = 1.239/-1.415 e Å⁻³.
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- [23] Synthesis of [IrCl(MesDAB)₂] (3): Solid MesDAB (60 mg, 0.21 mmol) was added to a stirred solution of [IrCl(coe)₂]₂ (46 mg, 0.051 mmol) in toluene (6 mL). The resulting solution was stirred for 48 hours at room temperature resulting in a color change from orange yellow to dark green. Afterwards, the solvent was removed in vacuo and the remaining residue was taken up in diethyl ether (6 mL) with rapid stirring. The dark precipitate formed was collected by filtration and dried in a vacuum. Yield: 54 mg (0.066 mmol, 65%). Crystals suitable for X-ray diffraction experiments were obtained by recystallization from tetrahydropyran (room temperature to -20 °C). These crystals were used for elemental analysis. Èlemental analysis (C45H58ClIrN4O, 898.659 g/mol): calc.: C 60.14, H 6.51, N 6.23; found: C 59.83, H 5.83, N 5.92. ¹H NMR (200 MHz): & 1.50 (s, 12H, CH₃), 2.25 (s, 12H, CH₃), 2.26 (s, 12H, CH₃), 6.35 (s, 4H, *m*-H Mes), 6.50 (s, 4H, *m*-H Mes), 8.17 (s, 4H, HC=N). ¹³C NMR (50.3 MHz): δ 18.7 (4C, o-Me), 20.9 (4C, Me), 21.2 (4C, Me), 128.3 (4C, m-CH Mes), 129.7 (4C, m-CH Mes), 130.6 (4C, o-C Mes), 132.0 (4C, o-C Mes), 135.2 (4C, p-C Mes), 151.5 (4C, i-C Mes), 160.4 (4C, C=N). MS (DEI, (h, β, β); 812 [2.5] (M⁺), 777 [100] (M⁺ – Cl), 626 [8], 481 [7], 290 [15] (MeSDAB-2H), 289, 290 [18] (MesDAB-3H), 277 [27] (MesDAB-CH₃), 146 [9], 91 [7].
- [24] Crystal data for 3: C40H48ClIrN4·C5H100, M = 898.60, triclinic, space group P $\bar{1}$, a = 9.0621(2) Å, b = 14.6169(5) Å, c = 16.0961(5) Å, $\alpha = 83.827(1)^{\circ}$ $\beta = 73.692$ (2)° $\gamma = 85.220(2)^{\circ}$ V = 2031.28(10) Å³, Z = 2, $\rho = 1.469$ g cm⁻³, $\mu = 33.91$ mm⁻¹, T = -140(2) °C, measured data 12127, data with I>20(I) 8012, unique data (Rint) 8714(0.0331, wR₂ (all data, on F2)=0.1127, R1 (I>20(I))= 0.0457, S = 1.065, Res. dens. = 1.274/-1.233 e Å⁻³.
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