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Intramolecular C–H activation and oxidative addition reactions of iridium complexes containing arylamines with bulky substituents on nitrogen; X-ray structures of $[Ir^{I}(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N)(cod)]$ and $[Ir^{III}(C_6H_4CH_2NEt(CHMe)\text{-}2\text{-}C,N,C')I(cod)]$ (cod = cycloocta-1,5-diene)

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Abstract

Square-planar iridium(I) complexes $[Ir(C_6H_4CH_2NRR')(cod)]$ (R = R' = Et; R = Me, R' = t-Bu; cod = cycloocta-1,5-diene) containing C,N-chelating arylamine ligands have been synthesized and characterized by NMR spectroscopy. An X-ray diffraction study of $[Ir(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N)(cod)]$ shows a weak agostic interaction between the d^8 metal center and a methyl H atom of one ethyl group. An oxidative addition reaction of this complex with MeI affords an Ir(III) complex $[Ir(C_6H_4CH_2NEt(CHMe)\text{-}2\text{-}C,N,C')I(cod)]$ which results from an intramolecular methylene C–H activation process. This latter complex has been characterized with 2D NMR techniques and an X-ray diffraction study. The reactivity of the new iridium(I) complexes as well as $[Ir(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(cod)]$, $[Ir(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(cod)]$ and $[Ir(C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2\text{-}C,N)(cod)]$ towards H_2 is reported; the different products obtained are discussed with reference to reaction pathways influenced by the steric bulk on the nitrogen donor atom. Crystals of $[Ir(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N)(cod)]$ are triclinic, space group $P\bar{1}$ with unit-cell dimensions $a = 9.154(1)$, $b = 9.992(1)$, $c = 10.846(1)$ Å, $\alpha = 93.46(1)$, $\beta = 113.03(1)$, $\gamma = 109.84(1)°$, $Z = 2$, final $R = 0.0234$, $wR = 0.0295$ for 3465 reflections with $I > 2.5\sigma(I)$ and 197 parameters. Crystals of $[Ir(C_6H_4CH_2NEt(CHMe)\text{-}2\text{-}C,N,C')I(cod)]$ are triclinic, space group $P\bar{1}$ with dimensions $a = 7.591(1)$, $b = 11.406(1)$, $c = 13.511(1)$ Å, $\alpha = 65.63(1)$, $\beta = 88.34(1)$, $\gamma = 83.29(1)°$, $Z = 2$, final $R = 0.0319$, $wR = 0.0402$ for 4236 reflections with $I > 2.5\sigma(I)$ and 228 parameters.

Keywords: Crystal structures; Iridium complexes; Arylamine complexes ; Oxidative addition

1. Introduction

The intramolecular and intermolecular activation of C–H bonds by transition metal complexes is a topic of current interest [1], and it is particularly interesting in those instances where it leads to the generation of functionalized hydrocarbon products [2]. Whereas intramolecular C–H activation, i.e. cyclometallation, has received considerable attention during the last two decades [1c,3] the study of intermolecular C–H activation has gained more importance in recent years due to the possible role it can play in catalytic reactions [1a,b,4].

Computational studies of intermolecular C–H activation indicated that steric rather than electronic effects are important for C–H bond activation [5a,b], though a recent study has shown that C–H bond cleavage of alkanes can be promoted by metal species with spectator ligands having correct σ-donating properties [5c]. It has also been suggested that intramolecular C–H activation may be promoted by steric hindrance [6,7], and with coordinatively unsaturated d^8 metal species this often results in five-membered chelate rings [1c,3].

In many of our studies we use arylamine ligands where properties of the nitrogen donor unit such as cone angle and basicity are of particular interest since they may influence metal reactivity in various critical reaction steps. For example, nitrogen coordination/decoordination may precede C–H

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activation [6], and the Lewis basicity of the N-donor unit as a non-coordinated group may assist proton stabilization in a later phase of an electrophilic substitution process [3e,8].

Recently, we reported that oxidative addition of MeI to both [Ir($C_6H_4CH_2NMe_2$-2-*C,N*)(cod)] and [Ir(1-$C_{10}H_6$-NMe_2-8-*C,N*)(cod)] (cod = cycloocta-1,5-diene) proceeds via an initial S_N2 type process [9], and that the subsequent stereoselective isomerization of the initial Ir(III) product is influenced by flexibility and steric requirements of the C,N chelate. In an extension of this study, we have now synthesized the new Ir(I) complexes [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] and [Ir($C_6H_4CH_2NMe$(t-Bu)-2-*C,N*)(cod)] in which steric requirements (i.e. nitrogen cone angle) as well as nitrogen basicity are greatly different. Some comparative oxidation reactions of these species with MeI and H_2 show that steric bulk in a coordinatively saturated d^6 Ir(III) species can induce an intramolecular C–H activation process that affords (with methane elimination) a complex containing a three-membered metallacyclic ring.

2. Results

2.1. Synthesis of [Ir($C_6H_4CH_2NRR'$-2-C,N)(cod)] (R = R' = Et (5); R = Me, R' = t-Bu (6))

Reaction of exactly one equivalent of n-BuLi with the *ortho*-bromobenzylamines $BrC_6H_4CH_2NEt_2$-2 (**1**) and $BrC_6H_4CH_2NMe$(t-Bu)-2 (**2**) affords the respective lithium complexes [Li($C_6H_4CH_2NEt_2$-2-*C,N*)] (**3**) and [Li(C_6H_4-CH_2NMe(*t*-Bu)-2-*C,N*)] (**4**) in a halide–lithium exchange reaction. Species **3** and **4** may also be obtained by a direct *ortho*-lithiation reaction of the corresponding non-brominated benzylamines ($C_6H_5CH_2NEt_2$ and $C_6H_5CH_2NMe$-(t-Bu), respectively) with one equivalent of t-BuLi, but this procedure due to its much longer reaction time (3–7 days instead of 12–24 h) and lower yields, is less suitable.

The aryllithium complexes **3** and **4** are air- and moisture-sensitive white solids which are readily soluble in diethyl ether and only slightly soluble in benzene. Their ^1H NMR data (see Section 5) show them to be pure *ortho*-lithiated complexes with a characteristic low-field chemical shift for one aromatic proton and resonance patterns, including the AB pattern for the benzylic moiety, that are similar to that of *ortho*-lithiated [Li($C_6H_4CH_2NMe_2$-2-*C,N*)] [10].

Reaction of two equivalents of **3** and **4** with one equivalent of dimeric $[IrCl(cod)]_2$, Eq. (1), affords the aryliridium(I) complexes [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] (**5**) and [Ir($C_6H_4CH_2NMe$(t-Bu)-2-*C,N*)(cod)] (**6**), respectively, which can be isolated in high yield.

$$[IrCl(cod)]_2 + 2[Li(C_6H_4CH_2NRR'\text{-}2)] \rightarrow 2[Ir(C_6H_4CH_2NRR'\text{-}2)(cod)] + 2LiCl \quad (1)$$

5: R = R' = Et; **6**: R = Me, R' = t-Bu

This synthesis is similar to that described for the related complexes [M($C_6H_4CH_2NMe_2$-2-*C,N*)(cod)] (M = Ir [6a], Rh [11]).

Complexes **5** and **6** are red, air- and moisture-sensitive, materials which have good solubility in benzene, toluene and dichloromethane and low solubility in pentane, hexane and diethyl ether. These complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and elemental microanalysis and for **5** also by an X-ray crystallographic study.

2.2. Structure of complexes 5 and 6 in solution

The ^1H NMR spectrum of [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] (**5**), see Table 1, shows two broad resonances for both the olefinic and the aliphatic protons of the cod ligand, one low-field shifted doublet at 7.58 ppm for an aryl proton *ortho* to the iridium center, one singlet for the benzylic protons and one triplet for the $-NCH_2-CH_3$ group. The two multiplet resonances at 2.48 and 2.57 ppm for the diastereoscopic methylene protons of the NEt groups reflect the Ir–N coordination, i.e. the bidentate bonding mode of the C ~ N ligand [12,13]. The ^{13}C NMR spectral data of **5** (see Table 2) include one resonance for the benzylic carbon, one for the $-N-CH_2-CH_3$ carbons, one for the $-NCH_2-CH_3$ carbons but two for both the sp^2 and sp^3 carbons of the cod ligand. The resonance position for C_{ipso} at 167.1 ppm is in agreement with a formal oxidation state of the Ir center that is 1+ [6a]. The ^1H and ^{13}C NMR data are consistent with a square-planar Ir(I) structure, with the arylamine and cod ligands both present as bidentates, as shown in Fig. 1; the coordination plane (which contains the aryl ring) is the only plane of symmetry present.

In the ^1H NMR spectrum of [Ir($C_6H_4CH_2NMe$(t-Bu)-2-*C,N*)(cod)] (**6**), the benzylic protons are diastereotopic (AB pattern) and this is direct evidence of N-coordination of the nitrogen atom which thereby becomes a stereogenic center. This bidentate bonding mode of the aryldiamine ligand establishes the solution structure for **6** as one in in which the square coordination plane is no longer a plane of symmetry (Fig. 1). Similarly, the four olefinic protons of the cod ligand provide four non-equivalent resonances that also reflect the C,N-bidentate bonding of the arylamine ligand. Consistently, in the ^{13}C NMR spectrum of **6** all carbon atoms afford non-equivalent resonances for this species which has no molecular symmetry plane.

2.3. Description of the solid state structure of 5

The X-ray structure of [Ir($C_6H_4CH_2NEt_2$-2-C,N)(cod)] (**5**) and the adopted numbering scheme is shown in Fig. 2. The bond lengths and angles are listed in Table 3.

The iridium(I) center in **5** is four-coordinate with a coordination geometry that is supplied by a bidentate monoanionic C,N-coordinating ligand (through C(1) of the aryl ring and N of the amine substituent) and two olefinic bonds of the cod ligand (C(12)=C(13) with midpoint m(1) and

Table 1
Relevant ^{1}H NMR data of complexes 5–8″ and the hydride complexes [a]

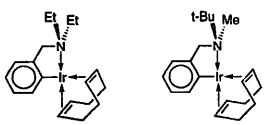
Complex	*ortho* H	$ArCH_2N$	NR, NR′	=CH(cod)	$-CH_2-$(cod)	Ir–H
$[Ir(C_6H_4CH_2NEt_2\text{-}2)(cod)]$ (5) [b]	7.58 (d)	3.62 (s)	2.48 (m) [c], 2.57 (m) [c] 0.84 (t) [e]	3.53 [d], 4.16 [d]	1.75 (m), 2.25 (m)	
$[Ir(C_6H_4CH_2NMe(t\text{-}Bu)\text{-}2)(cod)]$ (6) [b]	7.52 (d)	3.45 (d) [f] 3.90 (d) [f]	2.23 (s), 0.92 (s)	3.75 (dt), 4.01 (m) [g] 4.33 (dt)	1.3–2.4 (m)	
$[Ir(C_6H_4CH_2NEt_2\text{-}2)I(Me)(cod)]$ (7) [b,h]	6.79 (d)	3.13 (d) [f] 3.46 (d) [f]	0.42 (t) [e], 1.07 (t) [e] 2.04 (m) [c], 2.5 (m) [c] 2.84 (m) [c], 4.81 (m) [c]	3.4 [i], 4.42 (t) [d] 4.69 (t) [d], 5.28 (dt)	1.1 (m), 2.15 (m) 2.85 (m)	
$[Ir(C_6H_4CH_2NEt(CHMe)\text{-}2)I(cod)]$ (8′) [b]	6.58 (d)	3.52 (d) [f] 4.19 (d) [f] 3.62 (q) [i]	0.55 (br d), 0.63 (t) [e] 1.84 (m) [c], 3.33 (m) [c]	2.59 (q), 3.25 3.99 (dt), 5.48 (t) [d]	1.32 (m), 1.58 (m) 2.12 (m), 2.93 (m)	
$[Ir(C_6H_4CH_2NEt(CHMe)\text{-}2)I(cod)]$ (8″) [k]	6.65 (d)	4.31 (d) [f]	0.59 (t) [e], 0.81 (d) [j]	4.05 (dt), 5.17 (t)	3.1 (m)	
$[Ir(H)_2(C_6H_4CH_2NEt_2\text{-}2)(cod)]$ [l]	8.11 (d)	[m]	[m]	3.09, 3.75 4.66, 4.99	[m]	−7.25, −16.97
$[Ir(H)_2(1\text{-}C_{10}H_6NMe_2\text{-}8)(cod)]$ [n]	7.55 (dd)		3.50, 3.55	3.10, 4.02 4.42, 4.95	1.4-2.5 (m)	−7.98, −17.79
$[Ir(H)_2(C_6H_4CH_2N(Me)(CH_2)_2NMe_2\text{-}2)(cod)]$ [o]	8.06 (d)	[o]	2.02 [d] 2.33 [d]	3.65, 4.03 4.98 [p]	[o]	−7.99, −17.24 −8.06, −17.58

[a] δ in ppm relative to TMS. Other aromatic resonances present as multiplets in the region of 7.2 ppm.
[b] Recorded in C_6D_6 at r.t.
[c] $^2J(^1H,^1H) = 14$ Hz, $^3J(^1H,^1H) = 7$ Hz.
[d] Broad.
[e] $^3J(^1H,^1H) = 7$ Hz.
[f] AB pattern, $^2J(^1H,^1H) = 13.0$–15.0 Hz.
[g] Double intensity.
[h] Ir–Me resonance at $\delta = 1.4$ ppm.
[i] Shoulder on benzylic proton.
[j] Broad, $^3J(^1H,^1H) = 6$ Hz.
[k] Data obtained from a mixture of 8′ and 8″ by selection based on relative peak intensities; some resonances are obscured by those of 8′.
[l] Recorded in toluene-d_8 at −60°C.
[m] Assignment not carried out in a poorly resolved spectrum with overlapping resonances.
[n] Recorded in CD_2Cl_2 at −60°C.
[o] 3:1 mixture of isomers affords broadened CH_2 resonance patterns that were not assigned. See text for full description of hydride resonances.
[p] Intensity of 2H.

Table 2
^{13}C NMR data of complexes **5**, **6** and **8'** [a]

Complex	Aryl			$-CH_2-N$	–NR, –NR'	cod	
	C(1) C(2)	C(3) C(4)	C(5) C(6)			=CH	$-CH_2-$
[Ir($C_6H_4CH_2NEt_2$-2)(cod)] (**5**)	167.1 152.2	125.2 121.1	125.1 134.1	68.9	11.4, 53.0	56.0, 74.9	31.2, 31.9
[Ir($C_6H_4CH_2NMe$(*t*-Bu)-2)(cod)] (**6**)	165.9 154.1	125.2 120.2	124.9 133.3	55.4	27.9, 42.9 54.0	63.9, 68.9 72.2, 77.4	30.1, 30.3 32.4, 32.8
[Ir($C_6H_4CH_2NEt$(CHMe)-2)I(cod)] (**8'**) [b]	146.5 140.6	125.5 120.1	123.5 129.0	59.6	14.6 [c], 49.4 [d] 57.2	60.3, 61.2 107.6, 112.5	24.8, 29.4 34.5, 39.5

[a] Recorded in C_6D_6 at r.t. unless otherwise stated; δ in ppm relative to TMS.
[b] Recorded in CD_2Cl_2.
[c] Double intensity.
[d] (N)IrCH(Me) resonance.



5 **6**

Fig. 1. Square-planar structures for complexes **5** and **6**.

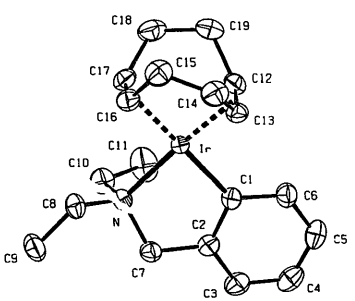


Fig. 2. ORTEP drawing of the molecular structure of [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] (**5**) (drawn at 50% probability level) with the adopted atom labeling. Hydrogen atoms omitted for clarity.

C(16)=C(17) with midpoint m(2)). The interligand angles are close to 90°, i.e. C(1)–Ir–N = 80.98(18), N–Ir–m(2) = 97.53(19), m(1)–Ir–m(2) = 86.9(2) and m(1)–Ir–C(1) = 94.6(2), and the complex is thus best described as having an irregular square-planar geometry. The iridium atom lies only 0.031(9) Å out of the imperfect plane defined by C(1), N, m(1) and m(2). All bond lengths to the iridium center lie in the expected ranges [6a,14,15]. The distances of the midpoints of the double bonds from the iridium center reflect *trans* ligand influences: the bond length Ir–m(2) (2.070(5) Å) is longer than Ir–m(1) (1.978(6) Å), due to the greater *trans* influence of carbon compared to nitrogen, and is in agreement with earlier findings on square-planar Ir(I) and Rh(I) complexes [6a,11].

Table 3
Selected interatomic distances (Å) and interbond angles (°) for **5** [a]

Distances (Å)			
Ir–N	2.201(4)	Ir–C(16)	2.197(5)
Ir–C(1)	2.044(5)	Ir–C(17)	2.170(5)
Ir–C(12)	2.101(5)	Ir–m(1)	1.978(6)
Ir–C(13)	2.097(6)	Ir–m(2)	2.070(5)
Angles (°)			
C(1)–Ir–N	80.98(18)	N–Ir–m(1)	175.41(17)
C(1)–Ir–m(1)	94.6(2)	N–Ir–m(2)	97.53(19)
C(1)–Ir–m(2)	177.3(2)	m(1)–Ir–m(2)	86.9(2)

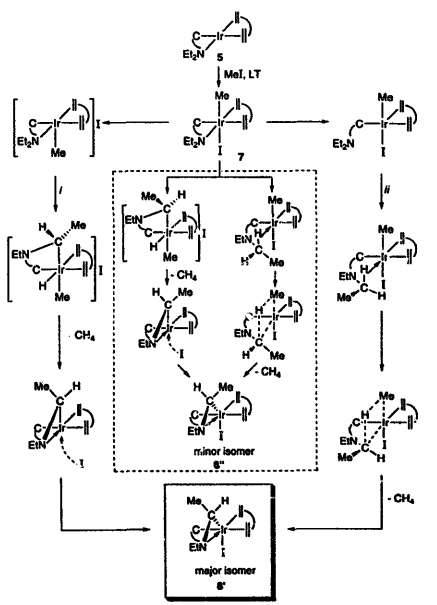
[a] m(1) is the midpoint of C(12)–C(13); m(2) is the midpoint of C(16)–C(17).

An interesting feature in **5** is the close approach between the iridium center and a hydrogen atom (and carbon center) of the CH_3 group of one of the N–Et units; note that hydrogen atoms are placed at calculated positions with C–H = 0.98 Å. The resulting distances Ir···H(112) of 2.765(8) Å and Ir···C(11) of 3.307(8) Å are both less than the sum of the corresponding van der Waals radii (3.32 and 3.82 Å, respectively). Although these short distances represent the right conditions to be an intramolecular interaction, it has been shown that such distances in isolation are not the right criteria to distinguish whether one is dealing with an (agostic) interaction or not [16]. Instead, one needs to use the effective covalent radius r_{bp} (i.e. the distance between the metal and the bonding pair of electrons of the C–H bond, corrected for the size of the metal) and *H* (the M–H–C angle). For complex **5** the value of r_{bp} is calculated to be 1.35 Å (with an *H* value of 113.7°) and this value is in the range for identified agostic interactions (~0.4–1.5 Å) [16]; bearing in mind that H(112) is located at a calculated position, this probably represents a weak agostic interaction. For closely related

[Ir($C_6H_3(CH_2NMe_2)_2$-2,4-*C,N*)(cod)] the calculated r_{bp} value of 1.67 Å for the N–Me CH_3 group is consistent with only van der Waals interactions.

2.4. Reaction of Ir(I) complex 5 with MeI; formation of Ir(III) complexes 7, 8′ and 8″

In the temperature range of −65 to −20°C complex **5** reacts with methyl iodide to afford *trans*-[Ir($C_6H_4CH_2NEt_2$-2-*C,N*)I(Me)(cod)] (**7**) which was isolated in poor yield, Scheme 1. Methyl iodide has to be used in a non-stoichiometric amount (less than one equivalent) to prevent several further reactions of methyl iodide with complex **7**, resulting in mixtures of unidentified products. The structure of **7** has been established with ^{1}H NMR spectroscopy (Table 1). Firstly, the four signals found for the olefinic protons of the cod ligand indicate the absence of symmetry in this complex. This asymmetry is also clear from the AB pattern for the benzylic moiety and the diastereotopic ethyl groups (four separate signals for the CH_2 protons and two signals for the CH_3 protons). These data show that the nitrogen atom is a stereogenic center, i.e. it coordinates to the metal center, and the ligand thus coordinates as a C,N-bidentate. Importantly, there is a signal at $\delta = 1.4$ ppm that can be assigned to an Ir–Me moiety. These combined data show that the complex has most likely an octahedral structure, and this means that it is an oxidative addition Ir(III) product in which the sixth position is occupied by the iodide. An alternative five-coordinate structure arising from monodentate MeI coordination, i.e. [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)(η^1-IMe)], is also theoretically possible but unlikely. Although such an Ir(η^1-IMe) moiety has been found earlier, in cationic Ir(III) complexes [17], with starting material **5** we are dealing with a neutral Ir(I) complex that has, by comparison, a much lower Lewis acidity and a much lower tendency to bind MeI in this way.



Scheme 1. Proposed mechanisms for C–H activation: (i) electrophilic C–H activation; (ii) multi-centred, homolytic C–H activation; LT = low temperature.

For octahedral complexes like **7**, ten stereoisomers consisting of five pairs of enantiomers are possible [9,18]. Four of these pairs contain the methyl and iodide group in a *cis* arrangement. Complex **7** is, however, not likely to have such a *cis* arrangement; in its ^{1}H NMR spectrum the very pronounced low-field shift of one of the $-CH_2-$ protons of the ethyl substituents at 4.8 ppm is explicable if it is near to and thus influenced by the iodide atom and its anisotropic effects [19,20]. This is only possible in the structure with the methyl group and iodide atom in mutually *trans* positions. Moreover, the ^{1}H NMR spectrum of **7** is fairly similar to that of *trans* MeI addition complexes [Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)I(Me)(cod)] *trans*-[Ir($C_6H_4CH_2NMe_2$-2-*C,N*)I(Me)(cod)] [18]. All the evidence thus points to complex **7** having an octahedral structure with the methyl and the iodide ligands in mutually *trans* positions as depicted in Scheme 1.

When the reaction of [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] with methyl iodide was carried out at room temperature (instead of in the temperature range of −65 to −20°C) then, instead of complex **7**, [IrI($C_6H_4CH_2NEt$(CHMe)-2-*C,N,C′*)(cod)] (**8**) was isolated in 95% yield, see Scheme 1. This product consists, according to ^{1}H NMR data, of two diastereoisomers **8′** and **8″** in a ratio of 4:1. The same mixture is also obtained when a ^{1}H NMR sample of pure **7** in benzene-d_6 is kept for 24 h or more at room temperature. In this transformation of **7** to **8**, the production of methane has been established by gas chromatography and ^{1}H NMR spectroscopy (see Section 5).

Pure **8′** can be obtained by recrystallization of **8** upon cooling a toluene solution. The ^{1}H NMR spectrum of **8′** resembles in complexity very much that of **7**, although the chemical shifts are different, and there is a total lack of molecular symmetry. There are two distinctive aspects in this spectrum of **8′** which distinguish it from that of **7**: (i) the singlet resonance of the Ir–Me group in **7** is now lacking; (ii) there is a resonance at 0.54 ppm that shows an unexpected doublet multiplicity instead of the triplet pattern found for the methyls of the –NEt groups in **7**. This doublet is consistent with an –N(R)$CHCH_3$ moiety and one finds the corresponding quartet resonance for the –N(R)CH–CH_3 proton at $\delta = 3.62$ ppm; homonuclear irradiation of the doublet resonance was used to confirm this structural feature. The other ethyl group on the N atom is intact and the aryl and cyclooctadiene parts of the molecule all afford normal resonance patterns. From these ^{1}H NMR data it can be concluded that C–H activation of one

methylene moiety of an $-NCH_2CH_3$ unit in **7** has occurred and that in **8′** the originally methylenic carbon has now become bonded to the iridium center. Accordingly, this carbon atom is stereogenic and a priori exists in either the *R* or *S* configuration. Since this configuration can combine with several possibilities for the stereochemistry of the iridium center in **8′** some further NMR measurements were made to aid elucidation of the molecular structure.

In the ^{13}C NMR spectrum of **8′** the most important aspect is the $-N(R)CH-CH_3$ atom resonance at $\delta = 49.44$ ppm (cf. the $-N-CH_2-CH_3$ signal in **8′** at 57.2 ppm and in **5** at 53.0 ppm); this upfield shift is in accord with an iridium-bonded carbon atom [19]. Extra identification of this resonance came from an APT (attached proton test) NMR experiment that showed it to be a tertiary carbon atom peak. In the ^{13}C NMR spectrum of **8′** one also finds, compared with olefinic carbon resonance positions for most d^6 metal cod complexes, that two olefinic carbon atoms have resonances at very low field; this we believe to be due to anisotropic effects of a neighboring iodide [19,20].

A full assignment and interpretation of both ^1H and ^{13}C NMR spectra is possible when these data are combined with those of two-dimensional NMR techniques: $^1H,^{13}C$ and $^1H,^1H$ COSY (correlation spectroscopy) and ^1H NOESY (nuclear Overhauser effect spectroscopy). The most important results from these spectra are the assignment of all olefinic and aliphatic hydrogen and carbon atoms of the cod ligand and some structural information. In NOESY spectra there are strong interactions of the aryl *ortho* H atom with both protons of the same olefinic moiety, i.e. one olefinic unit is perpendicular to the aryl plane, and an NOE between two protons on opposite sides of the cod ring that indicates that the normal boat conformation of the cod ligand is strongly distorted [21]. Based on all these spectroscopic data, the structure of **8′** in solution is proposed to be as shown in Scheme 1. Although there is less information available to determine the structure of **8″** we propose, on the basis of the most important ^1H NMR data (such as a doublet Me group resonance), see Table 1, that it is a diastereoisomer of **8′** with the inverse configuration of the chiral carbon atom as depicted in Scheme 1. For confirmation of our stereochemical assignments of **8′**, a single crystal X-ray diffraction study has been carried out.

2.5. Description of the solid state structure of 8′

Fig. 3 shows the X-ray molecular structure of [Ir(C_6H_4-CH_2NEt(CHMe)-2-*C,N,C′*)I(cod)] (**8′**) together with the adopted numbering scheme. The bond lengths and angles are listed in Table 4. The geometry of the iridium center that is supplied by two coordinating double bonds of the cod ligand, a tridentate dianionic C,N,C′ ligand (C(1), N and C(10)) and an iodide can be described as distorted octahedral. An almost linear axial arrangement is formed by the C_{ipso} atom of the aryl ligand (C(1)) and the midpoint (m(2)) of the double bond C(16)=C(17); ∠C(1)–Ir–m(2) = 177.0(2)°. The meridional plane is formed by C(10)

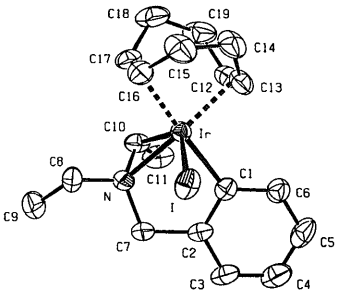


Fig. 3. ORTEP drawing of the molecular structure of [Ir(C_6H_4-CH_2NEt(CHMe)-2-*C,N,C′*)I(cod)] (**8′**) (drawn at 50% probability level) with the adopted atom labeling. Hydrogen atoms omitted for clarity.

Table 4
Selected interatomic distances (Å) and interbond angles (°) for **8′** [a]

Distances (Å)			
Ir–C(1)	2.044(7)	Ir–C(16)	2.363(7)
Ir–N	2.122(4)	Ir–C(17)	2.375(7)
Ir–C(10)	2.096(6)	Ir–m(1)	2.002(6)
Ir–I	2.7726(6)	Ir–m(2)	2.267(7)
Ir–C(12)	2.116(6)	Ir–m(3)	1.983(6)
Ir–C(13)	2.134(6)	C(10)–N	1.437(7)
Angles (°)			
C(1)–Ir–I	83.3(2)	C(10)–Ir–I	132.3(2)
C(1)–Ir–m(1)	94.0(3)	C(10)–Ir–m(1)	113.7(3)
C(1)–Ir–m(2)	177.0(2)	C(10)–Ir–m(2)	95.5(2)
C(1)–Ir–m(3)	83.0(2)	I–Ir–m(1)	113.4(2)
N–Ir–C(1)	80.6(2)	I–Ir–m(2)	97.2(2)
N–Ir–I	92.51(12)	I–Ir–m(3)	112.3(2)
N–Ir–m(1)	152.8(2)	m(1)–Ir–m(2)	83.1(3)
N–Ir–m(2)	102.3(2)	m(1)–Ir–m(3)	133.5(3)
C(10)–Ir–N	39.8(2)	m(2)–Ir–m(3)	99.5(2)
C(10)–Ir–C(1)	86.3(2)		

[a] m(1) is the midpoint of C(12)–C(13); m(2) is the midpoint of C(16)–C(17); m(3) is the midpoint of C(10)–N.

and N of the –NCH(Me) unit of the aryl ligand, the iodide atom and m(1) (midpoint of the double bond C(12)=C(13)). The distortion of the octahedral geometry is clearly shown in the meridional interligand angles which differ significantly from the expected 90°: N–Ir–I = 92.51(12)°, C(10)–Ir–N = 39.8(2)°, C(10)–Ir–m(1) = 113.7(3)° and I–Ir–m(1) = 113.4(2)°.

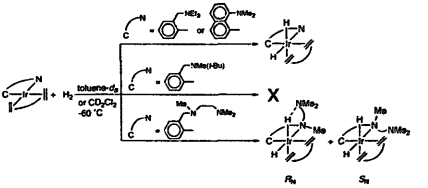
For this complex it is worthwhile examining an alternative structure description, since one sees that the angle N–Ir–C(10) of 39.8(2)° closely resembles that made by one cod double bond with the iridium center (i.e. C(12)–Ir–C(13) = 39.0(3)°) and one might, therefore, consider the C(10)–N bond as being side-on coordinated to iridium, i.e. in a three-center four-electron interaction. Taking this view and m(3) as the midpoint of C(10)–N, then the geometry around the iridium center is a slightly distorted trigonal bipyramid (24.0% distortion in the direction of a square-

pyramidal geometry along the Berry pseudo rotation path). The equatorial interligand angles are now, I–Ir–m(3) = 112.3(2)°, m(1)–Ir–m(3) = 133.5(3)° and I–Ir–m(1) = 113.4(2)°. In favor of this trigonal bipyramidal description is the geometry around the C(10)–N bond that does show features of a C=N bond but its length of 1.437(7) Å, although too short for a C–N single bond, is probably too long for a coordinated imine bond. However, the major objection to a trigonal bipyramidal description is the implication that **8′** is a 16-electron complex which should be reactive towards several reagents [22]. Since this complex shows no reactivity towards H_2 or CO, see Section 5, we prefer the former description of **8′** as a distorted octahedral Ir(III) complex, wherein an iridaazacyclopropane moiety is present; we found Ta–C–N units in [$TaCl_2$\{C_6H_4(CH(Me)N(Me)CH_2)-2-*C,N,C′*\}-(CH_2Ph)(THF)] and [TaCl\{C_6H_3(CH_2N(Me)CH_2)-2-(CH_2NMe_2)-6-*C,N,C′,N′*)(=CH-t-Bu)] that are similar [23].

In **8′** most of the bond distances involving iridium are in the normal range for related iridium complexes [6a,20b]. However, the distance from iridium to the axial double bond m(2) is much longer than that to m(1) and this may be due to a large *trans* influence of the anionic (aryl) C_{ipso} donor atom C(1). An interesting consequence of the large angle between the cod moiety C(12)=C(13) and the C(10)–N bond (m(1)–Ir–m(3) = 133.5(3)°) is the presence of an empty space on one side of the iridium center. In the crystal structure this space allows the next molecule of **8′** to approach with its iodide positioned towards H(1) in the NCHMe unit and (with C(10,2)–H(1,2) = 1.08 Å) this results in a fairly short intermolecular distance I(1,1)···H(1,2) of 2.762(6) Å, see Fig. 4, that is 0.418 Å shorter than the sum of the van der Waals radii (3.18 Å). Since the I(1,1)–C(10,2) distance of 3.815(6) Å is only a little longer than the sum of their van der Waals radii (3.68 Å) and the C–H···I angle is 164.9(5)° we consider this to be a hydrogen bond donor–acceptor interaction (see Section 3.2).

2.6. *Reactions of Ir(I) complexes [Ir(L-C,N)(cod)] with H_2*

When H_2 is bubbled through a solution of [Ir(L-*C,N*)(cod)] (L = $C_6H_4CH_2NEt_2$-2 or 1-$C_{10}H_6NMe_2$-8) at −60°C, the Ir(III) dihydride complexes [$Ir(H)_2$(L-*C,N*)(cod)] are formed quantitatively. When L is $C_6H_4CH_2NMe$(t-Bu)-2 no reaction occurs, whereas when L is $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2 two isomeric dihydrides in a 3:1 ratio are formed, see Scheme 2.



Scheme 2. Reactions (in situ) of [Ir(L-*C,N*)(cod)] with H_2.

All these Ir(III) dihydrides are stable in solution in the temperature range −60 to −30(±5)°C, but at higher temperatures they start to reductively eliminate H_2 resulting in the reformation of the starting Ir(I) complex. This process is accompanied by hydrogenation of the cod ligand, as well as formation of LH and metallic iridium for ~10–50%. Even when the reaction is carried out in a closed high-pressure NMR tube and a pressure of 20 bar of H_2 is applied, reductive elimination still takes place below 0°C. Due to the instability of these Ir(III) dihydrides at higher temperatures, no attempts were made to isolate them, and they have only been characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra, see Table 1, of these hydride complexes are very characteristic. For [$Ir(H)_2$(L-*C,N*)(cod)] (L = $C_6H_4CH_2NEt_2$-2 or 1-$C_{10}H_6NMe_2$-8), the signals in the 10–0 ppm region are indicative for an asymmetric structure, as reflected by four olefinic signals and two different resonance patterns for the substituents of the NR_2 groups. For this asymmetric structure, two isomers are possible as shown in Fig. 5. The two hydridic resonances are found widely separated at high field at ~ −8 and ~ −17 ppm. These positions were also found for the hydride atoms in [$Ir(H)_2$(L-*C,N*)(cod)] (L = $C_6H_4CH_2NMe_2$-2, $C_6H_4(CH_2NMe_2)_2$-2,6 and $C_6H_4CH_2NMe_2$-2-Me-6) [24], which have been proposed to have asymmetric structure **a** (Fig. 5), with one H atom *trans* to the olefinic moiety of the cod ligand and the other *trans* to the N atom. Based on the ^{1}H NMR similarities with these complexes, the new complexes [$Ir(H)_2$(L-*C,N*)(cod)] (L = $C_6H_4CH_2NEt_2$-2 or 1-$C_{10}H_6NMe_2$-8) are also proposed to have structure **a**.

Whereas in the monoanionic ligands $C_6H_4CH_2NEt_2$-2 and 1-$C_{10}H_6NMe_2$-8 the coordinated nitrogen atom is achiral, in the ligand $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2 we deal with two N atoms which on coordination are either achiral

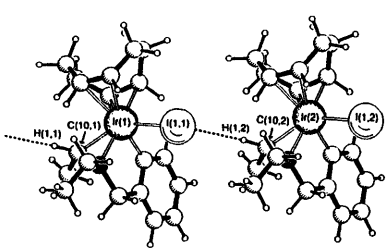


Fig. 4. The interaction between I(1,1) and H(1,2).

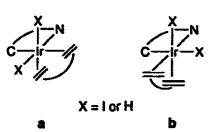


Fig. 5. Proposed isomers for an asymmetric Ir(III) structure.

(–NMe_2) or stereogenic (–NMe) [25]. In the square-planar Ir(I) complex [Ir($C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N*)(cod)] only the N(Me) atom is coordinating to the Ir center and the other is non-coordinating (in solution) [25a]. When this complex is treated with H_2, two isomeric dihydrides are formed; this is clear from the hydride region of the ^1H NMR spectrum which shows four hydride resonances at −7.99, −8.06, −17.24 and −17.58 ppm. The resonances are pairwise present (−7.99/−17.24 and −8.05/−17.58) in a 3:1 ratio; the former pair are somewhat broader than the latter. Based on the position of these hydride resonances (around −8 and −17 ppm), the same structure **a** as for the other dihydrides is proposed. In contrast to the hydride data, the signals of the two species in the region 10–0 ppm overlap (thereby affording an apparently single set of broadened resonances) and, for example, the *ortho* protons provide only one broadened signal (200 MHz) with the same intensity as the 3:1 hydride resonances together, i.e. there is great similarity between the two isomers. Therefore, the two isomers are proposed to have the diastereoisomeric structures depicted in Scheme 2; the difference between these isomers is in the position of the $–CH_2CH_2NMe_2$ substituent, i.e. in the configuration of the stereogenic N(Me) atom. It is interesting to note that in the diastereoisomer with the *R* configuration at N(Me) there is in principle an interaction possible between the Lewis basic nitrogen atom and a hydride atom. Upon warming the solution of this mixture of isomers of [Ir(H)$_2$($C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2-*C,N*)(cod)] to 0°C, the ratio between the two does not change, though the broader hydride resonances do become somewhat sharper. Finally, at room temperature the starting Ir(I) complex is formed for 50% together with $C_6H_5CH_2N(Me)CH_2$-CH_2NMe_2, cyclooctane and metallic iridium.

3. Discussion

3.1. Synthesis and properties of 5 and 6

In the high yield transmetallation route to the cyclometallated complexes **5** and **6** N-alkyl steric bulk (NMe(t-Bu) > NEt_2 > NMe_2) does not affect the synthesis efficacy. However, geometric parameters do show the influence of this bulk and the Ir–N distance in [Ir($C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] (**5**) is 0.04 Å longer than that in analogous [Ir($C_6H_3(CH_2NMe_2)_2$-2,4-*C,N*)(cod)] [6a]. This difference is in line with the expectations based on the cone angle concept [13,26], i.e. when a coordinating N-donor atom carries more steric bulk a longer M–N distance with decreased N-coordination strength results. This effect was also shown for the complexes [MX($C_6H_3(CH_2NRR')_2$-2,6-*N,C,N'*)] (M = Ni, Pt; X = halide; R = R' = Me, Et; R = Me, R' = i-Pr, t-Bu or Ph) [13], where for both Ni(II) and Pt(II) the –NMe_2 group is more strongly coordinating than the –NEt_2 group. We anticipate, based on known Ir–C and Ir–N distances, that the coordination ability order of the –NRR' groups to iridium is $NMe_2 \approx$ NMe(t-Bu) > NEt_2.

3.2. Agostic interactions in 5 and intermolecular interaction in 8'

In the solid state structure of [Ir($C_6H_3CH_2NEt_2$-2-*C,N*)(cod)] (**5**) it is the space-filling steric properties of the ethyl group that can be seen as the reason why there is a weak agostic interaction between the CH_3 group of one N–Et unit and the iridium center **5** (r_{bp} = 1.35 Å). Since the ^1H and $^{13}C\{^1H\}$ NMR data of **5** show no features that might indicate retention of this weak interaction in solution more detailed NMR studies were not carried out; a highfield shifted ^1H resonance and a lower than normal value for $^1J(C,H)$ can be evidence for strong agostic C–H interactions [27].

There is significant interest in intermolecular interactions in the solid state structures of organometallic species, and interactions X–H···M (X = C, O, N, S) where the metal atom acts as the hydrogen bond acceptor have recently been reviewed [28]. In the structure of **8'** the interaction C–H···I–Ir is one where a metal bound halide is the hydrogen bond acceptor and a related example from the literature shows that a three-center hydrogen bond, i.e. N–H···Cl_2Ir, is also possible [29]. The potential of this type of intermolecular donor–acceptor interaction for molecular recognition has very recently been exploited by us to generate in the solid state organometallic polymeric chains with both –C≡C–H···Cl–Pt and O–H···Cl–Pt motifs [30].

3.3. Reactivity of Ir(I) complexes towards MeI

Steric bulk on the N-donor atom does not influence the outcome of oxidative addition reactions of MeI with **5** and the less sterically hindered complexes [Ir($C_6H_4CH_2NMe_2$-2-*C,N*)(cod)] and [Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)]; in all cases the product [Ir(L-*C,N*)I(Me)(cod)] has *trans* positioning of the Me and I groups [9]. This *trans* stereochemistry is indicative for an S_N2 type of mechanism that is normally found for oxidative addition reactions of electrophiles like MeI to d^8 metal complexes [9,31]. However, steric bulk on the N-donor atom does influence the further destiny of the *trans*-added product.

As previously reported, the –NMe_2 substituted complexes *trans*-[Ir(L-*C,N*)I(Me)(cod)] (L = $C_6H_4CH_2NMe_2$-2 or 1-$C_{10}H_6NMe_2$-8) isomerize stereoselectively to *cis*-[Ir(L-*C,N*)I(Me)(cod)] [9], whereas we have now shown that the –NEt_2 substituted complex **7** reacts further in a C–H activation reaction to afford [Ir($C_6H_4CH_2NEt(CHMe)$-2-*C,N,C'*)I(cod)] (**8**). Note that this is an α C–H bond activation of the NCH_2Me unit and not of the methyl C–H bond which participates in the weak agostic C–H–Ir interaction in the solid state structure of **5**. This activation of a C–H bond of an N-alkyl group as realized in the transformation of **7** to **8** is by no means unique; recent results from other groups include examples from ruthenium cyclopentadienyl chemis-

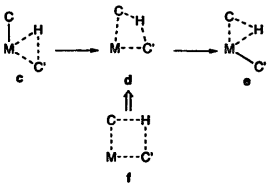
try [27] and from vanadium(III) amide chemistry [32]. Preliminary results of the reaction of MeI with the even more sterically hindered complex [Ir($C_6H_4CH_2NMe$(t-Bu)-2-*C,N*)(cod)] (**6**) also point to the formation of a C–H activated product analogous to **8** (see Section 5). The probable way in which the steric bulk on the N-donor atom induces the observed reactivity is that it destabilizes, through steric interactions with the Me and I ligands, the octahedral species *trans*-[Ir(L-*C,N*)I(Me)(cod)]. This then promotes Ir–N bond dissociation that affords a free site for further reaction, i.e. C–H activation.

3.4. Mechanism of the C–H activation reaction

The C–H bond is much stronger than the M–C bond and the thermodynamic barrier for C–H activation is high [33]. In general an intramolecular C–H process is favored by both entropy (the chelate effect) and the thermodynamic stability of the resulting cyclo-adduct and much detailed information about this process has been obtained. It has been found, for instance, that sp^2 C–H bonds are more easily activated than sp^3 C–H bonds, and this is proposed to be a result of initial η^2 coordination of the unsaturated molecule [2,34]. Several mechanisms have been proposed for metal complex promoted C–H activation reactions [1]. The most relevant mechanisms are those based on: (i) electrophilic displacement or heterolytic cleavage; (ii) a nucleophilic pathway or oxidative addition; (iii) the multicentered pathway. The first mechanism is known in cyclopalladation chemistry [35] and the second mechanism is mostly observed for coordinatively unsaturated d^8 metal species, obtained from square-planar d^8 metal complexes by ligand dissociation or from octahedral d^6 metal complexes by reductive elimination [6,24,36]. Examples of oxidative addition of intramolecular C–H bonds to coordinatively saturated systems, i.e. without predissociation of a ligand, are rare [37]. The third mechanism features mainly for high-valent, early transition metal complexes [23,38], although it may sometimes account for results in late transition metal chemistry [7c,d,39].

Based on earlier proposals [40], the C–H activation process in **7**, that affords **8**, could follow two mechanistic pathways, both of which can explain the formation of the two diastereoisomers, see Scheme 1. One of these is based on an oxidative addition and there are two reasons why we consider this mechanism to be less likely. Firstly, complex **7** is an octahedral, coordinatively saturated d^6 metal complex, unlikely to undergo oxidative addition. Secondly, although coordinative unsaturation could be achieved by dissociation of the iodide, which has been recognized before [9,41], and/or dissociation of the amine function [6,24], oxidative addition to **7** would then involve the improbable involvement of a six- or seven-coordinated Ir(V) intermediate [42]. Finally, no Ir–H species were observed by ^1H NMR spectroscopy during the C–H activation process.

We consider the most likely route for the C–H activation process in **7** to be a multicentered, σ-bond metathesis pathway that, although rare in late transition metal chemistry, has recently received some attention [1c,43]. This pathway may be described as an electrophilic one which is nucleophilically assisted, that is to say, the metal center is the electrophile assisted by the metal-bonded organic group that acts as a 'base'. In our case the Ir(III) center acts as an electrophile that is assisted by the 'basic' Me ligand to afford **8** and methane. In this mechanism only the amine unit has to dissociate from the iridium center and this could be induced by the steric hindrance between the NEt_2 group and the Me and I ligands. After the C–H activation process the N-donor atom then recoordinates. This 'arm-off'/'arm-on' process has recently been reported in reactions such as hydrogenation with complexes containing tripodal phosphine ligands [44], and in the unprecedented rearrangement of [Ir(C_6H_3(CH_2-NMe_2)-2-R-6-*C,N*)(cod)] to [Ir(C_6H_3(CH_2NMe_2)-2-R-4-*C,N*)(cod)] (R = Me, CH_2NMe_2) [6a].



Scheme 3. Schematic representation of the transition states of oxidative addition (**c**), reductive elimination (**e**) and the multicentered pathway (**f**).

For the formation of **8** one can ask whether it is really possible to distinguish between the proposed one-step process of the multicentered pathway and the two-step process of oxidative addition/reductive elimination. The transition states of these processes are schematically represented in Scheme 3, wherein transition states **c** and **e** represent oxidative addition and reductive elimination, respectively, and **f** represents the transition state for the multicentered pathway. It is important to note that theoretical calculations on a four-center geometry in a $(CO)_3CoC(O)Me(\eta^2\text{-}H_2)$ system reveal this geometry not to be flat, as in **f**, but distorted, as in **d**, so that the agostic H atom is brought closer to the metal center [43b]. From these pictures it is clear that one can consider the multicentered transition state as a concerted intermediate in the oxidative addition/reductive elimination process; the total process now represents a transfer of the H atom via the metal center.

3.5. (Oxidative) addition reactions of H_2

The oxidative addition of H_2 to square-planar late transition metal complexes has been intensively studied and it is generally accepted that a concerted process is the operative mechanism [45]. The *cis* position of the hydride ligands in the Ir(III) products of the reactions of H_2 with **5** and [Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)] points to such a concerted process here also. The reversibility of this type of H_2 addition has

been reported earlier for the reaction of [Ir($C_6H_4CH_2NMe_2$-2-*C,N*)(cod)] with H_2 [24].

Steric influences on reactions with H_2 are known [46], but in our system are not noticed for either the bulky Et groups or the rigid naphthyl skeleton of the iridium complexes **5** and [Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)], respectively. However, steric influences do become clear in the behavior of [Ir($C_6H_4CH_2NMe$(t-Bu)-2-*C,N*)(cod)] (**6**) which does not react with H_2. Apparently, side-on coordination of H_2 to the iridium center is hindered at one side of the square coordination plane by the presence of the t-Bu group, and at the other, more open, side by the bending pack of two *trans* ligands [45] which are also hindered by the bulky t-Bu group.

The complex [Ir($C_6H_4CH_2N$(Me)$CH_2CH_2NMe_2$-2-*C,N*)(cod)] has been included in the present study, because an extra potentially ligating N-donor atom might give rise to different reactivity patterns [25]. Although the $-CH_2CH_2-NMe_2$ moiety in this complex is coordinated to the metal center in the solid state, the complex in solution shows the same reactivity behavior towards H_2 as **5**, [Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)] and [Ir($C_6H_4CH_2NMe_2$-2-*C,N*)(cod)], i.e. a concerted addition affords an Ir(III) species. Nevertheless, the coordination of the –N(Me)– unit makes this nitrogen atom stereogenic and the reaction affords two diastereoisomeric dihydrides. In one of these the hydride resonances are broadened and a possible explanation is an interaction with the $-CH_2CH_2NMe_2$ substituent that is only possible in one isomer, see Scheme 2. Although an M–H···N interaction is only possible with one of the hydride ligands, the observation that *both* resonances are broadened points to a possible hydride exchange process within the complex, but this has not been investigated. Combined interactions between metal centers, hydrogen atoms and nitrogen centers have recently been recognized [8,28,47], but it is interesting that we are here dealing with an interaction between two relatively electron rich units, i.e. a metal hydride system (M–H) and a tertiary amine.

4. Conclusions

This study clearly shows that variation of the steric (and electronic) properties of intramolecularly positioned amine donor atoms in complexes of the type [Ir[1](arylamine-*C,N*)(cod)] can affect the reactivity of the iridium center and it is shown that the influence can be so large that the course of a reaction can be completely altered. These large effects can be primarily associated with either different steric constraints of these iridium arylamine complexes in the initial reaction step with reactants or to the different steric bulk of the N-donor atom that results in a change of the metal–nitrogen coordination strength. Increased steric bulk weakens the metal–nitrogen coordination and it is in the arm-off situation that the observed C–H bond activation pathway occurs.

5. Experimental

5.1. General

Syntheses were carried out using standard Schlenk techniques in an atmosphere of purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. The complexes $[IrCl(cod)]_2$ [9], [Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)] [9] and [Ir($C_6H_4CH_2N$(Me)$CH_2CH_2NMe_2$-2-*C,N*)(cod)] [13a] were prepared by literature methods. ^1H, ^{13}C NMR and 2D NMR spectra were recorded on Bruker AC 200 and AC 300 and Varian 300 MHz spectrometers. Standard pulse sequences were used for COSY and NOESY measurements [48]. The time data for both COSY and NOESY experiments (200 MHz) (typically 512×1024 points in t_1 and t_2, respectively) acquired with 32 scans (2 dummy) per increment, were processed with a shifted sine bell window function. Mixing times of 1 s were used for the NOESY measurements. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer. Elemental analyses were obtained from the section Elemental Analyses of the Institute for Applied Chemistry TNO, Zeist, Netherlands.

5.2. Synthesis of $BrC_6H_4CH_2NEt_2$-2 (1)

To a solution of $HNEt_2$ (26.1 ml, 0.25 mol) in C_6H_6 (20 ml) was added slowly at 5°C a solution of 2-bromobenzyl bromide (20 g, 0.08 mol) in C_6H_6 (20 ml). After 10 min a white solid precipitated and after stirring this mixture for 1 h, the solid was filtered off and washed once with C_6H_6 (10 ml). The combined filtrate and C_6H_6 washings were evaporated to dryness and the yellow residue was extracted with pentane (3×10 ml). Evaporation of the combined pentane extracts gave a yellow oil. This was distilled (b.p. 77°C; 1 mmHg) to afford a pale yellow oil (20.4 g; 84% yield). NMR ($CDCl_3$) δ: ^1H 7.65–6.85 (m, 4, Ar–*H*), 3.55 (s, 2, Ar–CH_2–N), 2.53 (q, 4, N–CH_2–CH_3, $^3J(H,H) = 7$ Hz), 0.98 (t, 6, N–CH_2–CH_3, $^3J(H,H) = 7$ Hz) ppm.

5.3. Synthesis of $BrC_6H_4CH_2NMe$(t-Bu)-2 (2)

Starting from t-butylamine (41.5 ml, 0.4 mol) and 2-bromobenzyl bromide (25 g, 0.1 mol) the synthesis is analogous to that of **1**. After evaporation of the pentane extracts the yellow oil was used for further reaction without any purification. The methylation was carried out via the Eschweiler–Clark method [49] affording after distillation (b.p. 83°C, 0.2 mmHg) a colorless oil (21 g; 82% overall yield). NMR ($CDCl_3$) δ: ^1H 7.77 (d, 1, Ar–*H*, $^3J(H,H) = 7.8$ Hz), 7.60 (d, 1, Ar–*H*, $^3J(H,H) = 7.8$ Hz), 7.37 (t, 1, Ar–*H*, $^3J(H,H) = 7.8$ Hz), 7.14 (t, 1, Ar–*H*, $^3J(H,H) = 7.8$ Hz), 3.75 (s, 2, Ar–CH_2–N), 2.28 (s, 3, NCH_3), 1.28 (s, 9, $NC(CH_3)_3$) ppm. ^{13}C: 140.5 (Ar–*C*(2)), 132.2 (Ar–*C*(6)), 131.4 (Ar–*C*(3)), 127.9 (Ar–*C*(4)), 127.1 (Ar–*C*(5)), 124.2 (Ar–*C*(1)), 55.0 (Ar–CH_2–N), 54.3 ($NC(CH_3)_3$), 35.5 (NCH_3), 26.2 ($NC(CH_3)_3$) ppm.

5.4. Synthesis of [Li($C_6H_4CH_2NEt_2$-2-C,N)] (3)

To a solution of **1** (10.9 g, 45.3 mmol) in hexane (30 ml) was added slowly a solution of n-butyllithium in hexane (30.0 ml, 1.5 M, 45 mmol) at r.t. A white solid immediately precipitated and after stirring for 24 h the suspension was centrifuged. The supernatant solution was removed by decantation and the solid washed with hexane (2×20 ml) and dried in vacuo to afford **3** as a white powder (5.82 g; 76% yield). NMR (C_6D_6) δ: ^{1}H 8.50 (d, 1, Ar–*H*(6), ^3J(H,H) = 6 Hz), 7.3–7.1 (m, 3, Ar–*H*), 4.56 (d, 1, Ar–C*H*$_2$–N, ^2J(H,H) = 12 Hz), 3.27 (d, 1, Ar–C*H*$_2$–N, ^2J(H,H) = 12 Hz), 2.31 (m, 2, N–C*H*$_2$–CH$_3$), 1.95 (m, 2, N–C*H*$_2$–CH$_3$), 0.61 (t, 3, N–CH$_2$–C*H*$_3$, ^3J(H,H) = 7.5 Hz), 0.16 (t, 3, N–CH$_2$–C*H*$_3$, ^3J(H,H) = 7.5 Hz) ppm. ^{13}C: 152.5 (Ar–*C*(2)), 140.1 (Ar–*C*(6)), 127.7 (Ar–*C*(4)), 126.8 (Ar–*C*(5)), 125.3 (Ar–*C*(3)), 63.7 (Ar–CH$_2$–N), 46.6 (N–*C*H$_2$–CH$_3$), 43.9 (N–*C*H$_2$–CH$_3$), 9.9 (N–CH$_2$–*C*H$_3$), 7.1 (N–CH$_2$–*C*H$_3$) ppm. C_{ipso} not observed.

5.5. Synthesis of [Li($C_6H_4CH_2NMe$(t-Bu)-2-C,N)] (4)

Starting from **2** (6.39 g, 25 mmol) and 17 ml of n-butyllithium in hexane, the same procedure as described for **3** was followed to afford **4** as a white powder (3.5 g; 77% yield). NMR (C_6D_6) δ: ^{1}H 7.92 (d, 1, Ar–*H*(6), ^3J(H,H) = 6.5 Hz), 7.28–7.02 (m, 3, Ar–*H*), 4.24 (d, 1, Ar–C*H*$_2$–N, ^2J(H,H) = 12 Hz), 2.92 (d, 1, Ar–C*H*$_2$–N, ^2J(H,H) = 12 Hz), 1.80 (s, 3, NC*H*$_3$), 0.79 (s, 9, NC(C*H*$_3$)$_3$) ppm.

5.6. Synthesis of [Ir($C_6H_4CH_2NEt_2$-2-C,N)(cod)] (5)

A solution of **3** (0.26 g, 1.5 mmol) in C_6H_6 (15 ml) was added during 1 h to a solution of [IrCl(cod)]$_2$ (0.53 g, 0.8 mmol) in C_6H_6 (15 ml). After stirring the red suspension for another 1 h, the mixture was centrifuged and the supernatant solution was collected under N_2 by decantation. The lithium chloride was then extracted once with C_6H_6 (10 ml). The combined C_6H_6 supernatant and extract were evaporated in vacuo to afford a red residue. This was washed once with pentane (5 ml) to afford **5** as a red powder (0.64 g; 93% yield). *Anal.* Calc. for $C_{19}H_{28}IrN$: C, 49.33; H, 6.10; N, 3.03. Found: C, 49.22; H, 6.08; N, 3.04%. Crystals of **5**, suitable for a single X-ray diffraction study, were formed within 18 h upon cooling to −20°C a freshly prepared, saturated solution of **5** in toluene.

5.7. Synthesis of [Ir($C_6H_4CH_2NMe$(t-Bu)-2-C,N)(cod)] (6)

The procedure for **6** is analogous to that of **5**. Complex **6** is obtained as a red powder (0.64 g; 91% yield). *Anal.* Calc. for $C_{20}H_{30}IrN$: C, 50.40; H, 6.34; N, 2.94. Found: C, 47.27; H, 6.13; N, 2.63%. The complex appears to be isolated as an adduct with LiCl; *Anal.* Calc. for $C_{20}H_{30}IrN \cdot 0.75LiCl$; C, 47.24; H, 5.95; N, 2.76%.

5.8. Synthesis of [Ir($C_6H_4CH_2NEt_2$-2-C,N)I(Me)(cod)] (7)

To a red solution of **5** (0.46 g, 1 mmol) in toluene (10 ml) at −65°C was added freshly distilled methyl iodide (59.2 μl, 0.95 mmol). After standing for 18 h at −20°C a yellow crystalline solid precipitated. The mixture was filtered and the crystals were washed once with cold pentane (5 ml) and dried in air to afford **7** (0.15 g; 27% yield). The orange filtrate was evaporated to afford a solid residue. ^{1}H NMR showed this solid to be a mixture of **7** and [Ir($C_6H_4CH_2NEt$(CHMe)-2-C,N,C')I(cod)] (**8**). Attempts to purify **7** by recrystallization for elemental microanalysis were unsuccesful.

5.9. Synthesis of [Ir($C_6H_4CH_2NEt$(CHMe)-2-C,N,C')I(cod)] (8)

Freshly distilled methyl iodide (45.0 μl, 0.72 mmol) was added at −65°C to a solution of **5** (0.35, 0.76 mmol) in toluene (10 ml). The temperature was raised slowly to room temperature and after being stirred for 18 h the solution was evaporated to dryness. The red–brown residue was washed once with pentane (5 ml) and then dried in vacuo to afford **8** as a pale brown powder (0.4 g; 95% yield). ^{1}H NMR data showed this solid to be a mixture of two diastereoisomers **8'** and **8''** in a ratio of 4:1. Crystals of **8'**, suitable for a single X-ray diffraction study, were formed from a freshly prepared saturated solution of **8** in benzene-d_6 upon standing for 18 h at r.t.

5.10. Detection of methane from syntheses of 8

(i) The same reaction for the synthesis of **8** as described above was carried out in a vessel closed with a septum. After stirring the mixture for 18 h, a gas sample was taken through the septum. Analysis on a Hewlett-Packard research chromatograph equipped with a Poropack column showed this sample to contain methane.

(ii) A solution of **7** in benzene-d_6 was kept at r.t. for 2 days. The subsequently recorded ^{1}H NMR spectrum showed resonances of **8** and a resonance at δ = 0.15 ppm from methane.

5.11. Reaction of 6 with MeI

A stirred reaction solution of **6** (a solution of 0.26 g (0.54 mmol) in 10 ml of toluene) with freshly distilled MeI (30 μl; 0.5 mmol) was worked up afer 4 days as described under Section 5.9. Recrystallization of the solid from C_6H_6 afforded 0.15 g of an off-white powder. ^{1}H NMR spectrum ($CDCl_3$) δ: 7.05 (d), 6.9 (t), 6.8 (t), 6.55 (d) (Ar–*H*), 4.67 (d), 4.03 (d) (AB pattern, Ar–C*H*$_2$–N), 1.48 (–NC(C*H*$_3$)$_3$), 5.58 (t), 4.99 (q), 4.12 (dt), 3.5 (=C*H*), 3.2 (m), 2.65–2.45 (m), 2.1–1.5 (m) (–C*H*$_2$– (cod)) ppm. Two singlets at 4.49 and 3.07 ppm, both with an intensity of 1H may be the methylenic protons of an Ir–CH$_2$–N(t-Bu)(benzyl) moiety.

5.12. Reactivity of 8 with H_2

Through a solution of **8** (~30 mg) in toluene-d_8 (2.5 ml) was bubbled at −60°C H_2 for 15 min. From the resulting solution, 0.5 ml was transferred to a precooled 5 mm NMR tube and the ^{1}H NMR spectrum was subsequently measured at -60°C. The same procedure was also carried out at room temperature. In all experiments, no evidence for any reaction was found.

5.13. Reactions of [Ir(L-C,N)(cod)] (L = $C_6H_4CH_2NEt_2$-2, $C_6H_4CH_2NMe(t\text{-}Bu)$-2, $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2 and 1-$C_{10}H_6NMe_2$-8) with H_2

(i) A red solution of [Ir(L-*C*,*N*)(cod)] (~0.10 mmol) in dry CD_2Cl_2 or toluene-d_8 (1.5 ml) was cooled to −60°C (±10°C). Hydrogen was bubbled through this solution for ~1–2 min, which resulted for L being $C_6H_4CH_2NEt_2$-2, $C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-2 and 1-$C_{10}H_6NMe_2$-8 in a yellow solution and when L was $C_6H_4CH_2NMe(t\text{-}Bu)$-2 in a red solution. From this solution, 0.5 ml was transferred to a precooled 5 mm NMR tube and the ^{1}H NMR spectra were subsequently recorded at −60°C and then at intervals of 10 or 20°C up to r.t.

(ii) A red solution of [Ir(1-$C_{10}H_6NMe_2$-8-*C*,*N*)(cod)] (0.05 g, 0.1 mmol) in dry CD_2Cl_2 (0.75 ml) was made in a nitrogen atmosphere in a 5 mm high-pressure NMR tube. The NMR tube was cooled to −60°C and a pressure of 20 bar of H_2 was then applied. After 0.5 h the tube was transferred to a 300 MHz spectrometer with the probe precooled at −60°C and the ^{1}H NMR spectrum was recorded at −60°C. The spectrum showed only 50% formation of the dihydride [Ir(H)$_2$(1-$C_{10}H_6NMe_2$-8-*C*,*N*)(cod)]. After 1.5 h (total time) at −60°C the dihydride was quantitatively formed. Further spectra were subsequently recorded at temperatures between −40 and +20°C.

5.14. X-ray data collection, structure determination and refinement of 5 and 8'

Crystal data and numerical details of the structure determinations are given in Table 5. Crystals were transferred to

Table 5
Crystal data and details of the structure determination for **5** and **8'**

	5	**8'**
Crystal data		
Formula	$C_{19}H_{28}IrN$	$C_{19}H_{27}IIrN\cdot 0.5C_6D_6$
Molecular weight	462.66	630.63
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	9.154(1)	7.591(1)
b (Å)	9.992(1)	11.406(1)
c (Å)	10.846(1)	13.511(1)
α (°)	93.46(1)	65.63(1)
β (°)	113.03(1)	88.34(1)
γ (°)	109.84(1)	83.29(1)
V (Å^3)	837.1(2)	1058.1(2)
Z	2	2
D_{calc} (g cm^{-3})	1.836	1.979
F(000), electrons	452	598
μ(Mo Kα) (cm^{-1})	79.4	81.5
Crystal size (mm); color	0.25×0.31×0.45; red	0.30×0.38×0.38; yellow
Data collection and refinement		
θ_{min}, θ_{max} (°)	2.09, 27.50	1.6, 27.5
Radiation (Å)	Mo Kα (Zr-filtered), 0.71073	Mo Kα (Zr-filtered), 0.71073
Scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$(°)	0.60+0.35 tan θ	0.70+0.35 tan θ
Horizontal and vertical aperture (mm)	3.0, 6.0	3.0, 6.0
X-ray exposure time (h)	100	75
Linear decay (%)	1.0	15.5
Reference reflections	1 0 −1, 1 −2 0, 0 1 1	2 0 −3; 3 1 0; 0 4 1
DIFABS correction range	0.880–1.173	0.761–1.287
Data set	h −10:11; k −12:12; l −14:0	h −9:9; k −14:13; l −17:0
Total data	6365	5059
Total unique data	3836 (R_{int} = 0.024)	4853
Observed data	3465 ($I > 2.5\sigma(I)$)	4236 ($I > 2.5\sigma(I)$)
No. refined reflections/parameters	3465, 197	4236, 228
Weighting scheme	$w = 1.0/(\sigma^2(F) + 0.000403F^2)$	$w = 1.6935/(\sigma^2(F) + 0.000070F^2)$
Final R, wR, S	0.0234, 0.0295, 1.04	0.0319, 0.0402, 1.32
(Δ/σ) in final cycle: av., max.	0.0073, 0.0406	0.0439, 0.6132
Min. and max. residual density (e Å^{-3})	−0.89, 0.87	−1.85, 1.36 (near Ir)

Table 6
Final atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for 5 [a]

Atom	x	y	z	U_{eq} [b] (Å²)
Ir	0.91555(2)	0.64509(2)	0.77806(2)	0.0284(1)
N	0.7714(4)	0.6175(4)	0.9028(3)	0.0318(9)
C(1)	0.8127(5)	0.4224(5)	0.7415(5)	0.0359(11)
C(2)	0.7284(5)	0.3629(5)	0.8221(5)	0.0367(11)
C(3)	0.6424(7)	0.2154(6)	0.8048(6)	0.0499(16)
C(4)	0.6346(8)	0.1178(6)	0.7040(7)	0.0583(18)
C(5)	0.7145(8)	0.1701(6)	0.6220(6)	0.0559(17)
C(6)	0.8006(7)	0.3176(5)	0.6400(5)	0.0445(16)
C(7)	0.7449(6)	0.4699(5)	0.9352(5)	0.0381(12)
C(8)	0.8698(6)	0.7312(5)	1.0351(5)	0.0405(12)
C(9)	0.7896(8)	0.7160(7)	1.1354(6)	0.0572(19)
C(10)	0.6006(6)	0.6285(6)	0.8256(5)	0.0467(16)
C(11)	0.4957(8)	0.5398(9)	0.6809(6)	0.071(2)
C(12)	0.9623(6)	0.6542(5)	0.6033(5)	0.0422(14)
C(13)	1.1068(6)	0.6521(5)	0.7150(5)	0.0417(14)
C(14)	1.2758(7)	0.7834(6)	0.7955(7)	0.0536(19)
C(15)	1.2502(7)	0.9162(6)	0.8409(7)	0.0543(19)
C(16)	1.0875(6)	0.8771(5)	0.8623(5)	0.0428(14)
C(17)	0.9287(7)	0.8637(5)	0.7610(5)	0.0433(16)
C(18)	0.8898(9)	0.8773(7)	0.6146(6)	0.060(2)
C(19)	0.9589(9)	0.7906(7)	0.5488(6)	0.058(2)

[a] E.s.d.s of the last significant digits are shown in parentheses.
[b] U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

Table 7
Final atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for 8′ [a]

Atom	x	y	z	U_{eq} [b] (Å²)
Ir	0.31472(3)	0.08421(2)	0.21850(2)	0.0371(1)
I	0.63454(5)	0.08552(5)	0.11381(4)	0.0654(2)
N	0.1853(6)	0.2301(4)	0.0767(3)	0.044(1)
C(1)	0.3909(7)	0.2444(6)	0.2298(5)	0.046(2)
C(2)	0.3534(7)	0.3614(5)	0.1366(5)	0.047(2)
C(3)	0.4005(9)	0.4771(6)	0.1295(6)	0.060(2)
C(4)	0.4873(10)	0.4822(7)	0.2139(6)	0.071(3)
C(5)	0.5250(10)	0.3698(8)	0.3072(6)	0.074(3)
C(6)	0.4788(8)	0.2527(6)	0.3150(5)	0.056(2)
C(7)	0.2594(8)	0.3554(6)	0.0425(5)	0.055(2)
C(8)	0.1516(9)	0.1979(6)	−0.0184(5)	0.059(2)
C(9)	0.0196(11)	0.2959(7)	−0.0995(6)	0.082(3)
C(10)	0.0665(7)	0.1930(5)	0.1664(5)	0.045(2)
C(11)	−0.0204(8)	0.2886(6)	0.2082(6)	0.062(2)
C(12)	0.2470(9)	0.0037(6)	0.3844(5)	0.061(2)
C(13)	0.4207(10)	−0.0503(6)	0.3737(5)	0.061(2)
C(14)	0.4719(12)	−0.1864(6)	0.3871(6)	0.078(3)
C(15)	0.4531(12)	−0.2094(7)	0.2839(6)	0.081(3)
C(16)	0.3209(9)	−0.1154(6)	0.2034(5)	0.057(2)
C(17)	0.1493(9)	−0.0839(6)	0.2269(5)	0.057(2)
C(18)	0.0719(12)	−0.1440(7)	0.3354(7)	0.079(3)
C(19)	0.0878(12)	−0.0676(7)	0.4069(6)	0.079(3)

[a] E.s.d.s of the last significant digits are shown in parentheses.
[b] U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

an Enraf-Nonius CAD4 diffractometer for data collection at 295 K. Unit-cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections and were checked for the presence of higher lattice symmetry [50]. Data for **5** and **8′** were corrected for Lp and for the observed linear decay of the intensity control reflections. The data were also corrected for absorption (DIFABS [51]); redundant data were merged into a unique dataset. The structures were solved with standard Patterson methods (SHELXS86) [52] and a series of subsequent difference Fourier analyses. The unit cell of **8′** contains one perdeuterated benzene molecule disordered around the inversion center at [0, 0.5, 0.5] in a ratio of 0.628(5):0.372(5). Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced in calculated positions (C–H = 0.98 and 1.08 Å for **5** and **8′**, respectively) and included in the refinement riding on their carrier atoms. All non-H atoms (except the disorder atoms in **8′**) were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles and convergence was reached at R = 0.0234 (**5**) and 0.0319 (**8′**). Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 6 and 7 for **5** and **8′**, respectively.

Neutral atom scattering factors were taken from Ref. [53] and corrected for anomalous dispersion [54]. All calculations were performed with SHELX76 [55] and PLATON [56] (geometrical calculations and illustrations) on a MicroVAX-II cluster.

6. Supplementary material

Complete tables of fractional coordinates of all atoms, bond distances and bond angles, anisotropic thermal parameters, and observed and calculated structure factors for **5** and **8′** may be obtained from author A.L.S.

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