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Stereoselective Isomerization in Organoiridium(III) Complexes Induced by the Presence of Rigid C,N Chelating Ligands

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The oxidative addition reactions of MeI and MeOTf to the square planar d^8 complexes Ir(L-*C,N*)(cod) (L = 1-$C_{10}H_6NMe_2$-8 or $C_6H_4CH_2NMe_2$-2, cod = cycloocta-1,5-diene) are described, and the stereochemistry of the resulting Ir(III) products is determined by 2D NMR techniques. In the reaction with MeI it is possible to isolate the kinetically preferred *trans*-added product, before rearrangement to the thermodynamic *cis*-isomer takes place. Both the oxidative addition of MeI and the following isomerization proceed through a cationic intermediate, providing strong evidence for an S_N2 type of mechanism for the former and a dissociative type of mechanism for the latter.

Introduction

Over the last two decades, there has been a continuously growing interest in the use of monoanionic chelating ligands in organometallic chemistry.[1] These ligands enhance the reactivity of the metal center, stabilize a variety of metal oxidation states, control the metal stereochemistry, and do not readily dissociate from the metal as this would require the breaking of a σ metal–carbon bond. Metal complexes based on such ligands are now becoming more and more important in homogeneous catalysis.[2]

In our laboratory, much work has been done on organometallic complexes based on the potentially terdentate, monoanionic chelating ligand system $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (abbreviated as NCN); see Figure 1a.[1i,3] This ligand, when terdentate *N,C,N* bonded to a metal, hinders rearrangements due to its rigidity and enhances the nucleophilicity of the metal center due to the presence of two hard N donor atoms and a hard, anionic C atom. Furthermore, complexes of bidentate C,N ligands related to the NCN ligand, see Figure 1b–f, have shown some special reactivity patterns or metal–reagent interactions, particularly when ligands with a fixed C,N chelate orientation, Figure 1b, are used. The increasing steric hindrance present on the N atom in the series Figure 1c < 1d < 1e, *i.e.* increasing ligand cone angle,[4] is of importance, because it weakens the M–N bond. However, steric hindrance on positions that at first sight seem not so important, Figure 1f, also can have surprising effects. The characteristics of the various ligand systems became very clear in several reactions of their organometallic complexes. The reaction of $[Pt(NCN)(H_2O)]BF_4$ with MeI gave, possibly after oxidative addition affording a Pt(IV) intermediate, a 1,2-methyl shift from the metal to the aryl ligand resulting in the new type of arenonium–metal complex $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}N,C,N)]BF_4$.[5] From the reaction of PtI(NCN) with I_2 was isolated the complex PtI(NCN)(η^1-I_2), which can be seen as an intermediate in oxidative addition reactions of dihalogens to d^8 metal complexes.[6] The complex *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$, containing the naphthylamine ligand (Figure 1b) with a rigid five-membered chelate ring, reacts with X_2 (X = Br, Cl) in a stereoselective oxidative addition to provide the corresponding Pt(IV) products.[7] In addition to the influence of the rigidity of the ligands in Figure 1a,b, steric hindrance present on the N atom (*vida infra*) as well as on *ortho* positions of the aryl ring also showed important effects. In the reaction of H_2 with the sterically hindered Ir complexes Ir($C_6H_3CH_2NMe_2$-2-R-6-*C,N*)(cod) (R = CH_2NMe_2, Me, H; cod = cycloocta-1,5-diene) oxidative addition to the Ir(III) dihydride complexes initially took place.[8] However, this is followed by an interesting reactivity pattern, including loss of N-coordination and C–H activation, that results in an isomerized ligand system. This particular reactivity is induced by steric hindrance of the substituent on the 6 position of the ligand aryl ring; only when the ligands shown in Figure 1a,f are present does isomerization take place. The influence of steric bulk present on the N atom can be reflected in the M–N coordination strength,

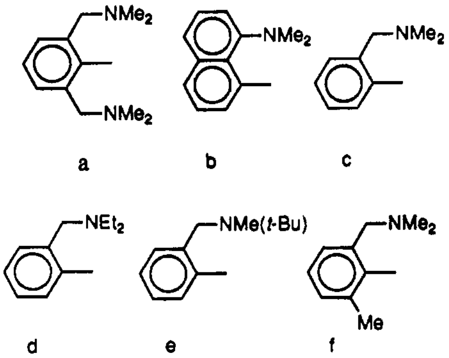

Figure 1. Examples of the (N),C,N ligand systems.

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as was shown for the complexes $MX(C_6H_3(CH_2NRR')_2\text{-}2,6\text{-}$*N,C,N'*) (M = Ni, Pt; X = halide; R, R' = Me, Et, *i*-Pr, *t*-Bu, Ph).[9] For both Ni and Pt complexes, the NMe_2 group is more strongly coordinated to the central metal atom than the NEt_2 group. Recently, we found that the reaction of $Ir(C_6H_4CH_2NEt_2\text{-}2\text{-}$*C,N*)(cod) with MeI first gives oxidative addition, which is followed by C–H activation and methane elimination.[10] In this case we propose that this reactivity is also a consequence of the larger steric hindrance of the NEt_2 than of the NMe_2 group and consequently easier Ir–N bond dissociation.

To check this latter proposal, we have now studied the reaction of MeI with the iridium complexes Ir(L-*C,N*)(cod) (L = $1\text{-}C_{10}H_6NMe_2\text{-}8$ (Figure 1b); L = $C_6H_4CH_2NMe_2\text{-}2$ (Figure 1c)). The ligand $[1\text{-}C_{10}H_6NMe_2\text{-}8]^-$ is included in this investigation because it is far more rigid than $[C_6H_4CH_2NMe_2\text{-}2]^-$. This rigid skeleton keeps the nitrogen in the coordination sphere of the metal center and should, thereby, hinder possible reactivity patterns which would lead to a straightforward stereoselective isomerization process. Furthermore, differences in Lewis basicities of these two amine ligands may also play a role in the reactivity patterns.[4,9]

Experimental Section

General Methods. Syntheses were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. $Li(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}$*C,N*)$(OEt_2)$[11] and $Ir(C_6H_4CH_2NMe_2\text{-}2\text{-}$*C,N*)(cod) (**2**)[12] were prepared by literature methods. ^1H, ^{13}C, and 2D NMR spectra were recorded on a Bruker AC 200 spectrometer, using standard pulse sequences for COSY and NOESY measurements.[13] Mixing times of 1 s were used for the NOESY measurements. Conductivity measurements were carried out by using a Philips PW 9512/00 microcell with a Consort K720 conductometer. Elemental analyses were obtained from the Section Elemental Analyses of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

Synthesis of $[IrCl(cod)]_2$. $[IrCl(cod)]_2$ was prepared by a slightly modified procedure of that reported by Osborn *et al.*[14] $IrCl_3{\cdot}3H_2O$ (6.4 g; 18.2 mmol) was first dissolved at 45 °C in 90 mL of a mixture of $EtOH/H_2O$ (2:1). Then 0.41 equiv (0.83 g) of solid hydroquinone and cod (7.5 g; 69.3 mmol) was added to the dark red solution. During reflux a gentle stream of nitrogen was passed over the reaction mixture in order to remove the evolving HCl. After the standard workup procedure,[14] $[IrCl(cod)]_2$ was obtained as a red powder (5.2 g; 85% yield).

Synthesis of Ir($1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}$*C,N*)(cod) (1). To a red solution of $[IrCl(cod)]_2$ (1.4 g; 2.09 mmol) in C_6H_6 (25 mL) was added at room temperature in 30 min a yellow solution of $Li(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}$*C,N*)$(OEt_2)$ (0.97 g; 3.9 mmol) in C_6H_6 (25 mL). The red suspension was stirred for 1 h and then filtered. The solid was extracted with two portions of C_6H_6 (10 mL each). The combined benzene layers (filtrate and washings) were evaporated to dryness. The residue was washed twice with pentane (10 mL) and dried *in vacuo* to afford **1** as a red powder (1.79 g; 91% yield).

Anal. Calcd for $C_{20}H_{24}IrN$: C, 51.04; H, 5.14; N, 2.98. Found: C, 51.26; H, 4.96; N, 2.97.

Synthesis of *trans*-IrI(Me)(L-*C,N*)(cod) (L = $1\text{-}C_{10}H_6NMe_2\text{-}8$ (3a); L = $C_6H_4CH_2NMe_2\text{-}2$ (4a)). To a red solution of Ir(L-*C,N*)(cod) (**1**, L = $1\text{-}C_{10}H_6NMe_2\text{-}8$ (0.44 g; 0.93 mmol); **2**, L = $C_6H_4CH_2NMe_2\text{-}2$ (0.36 g; 0.8 mmol) in toluene (10 mL) was added 1 equiv (58 and 52 μL, respectively) of freshly distilled MeI. A solid began to precipitate after 30 min of stirring. The yellow suspension was stirred for another 2 h and then filtered. The solid was washed with pentane (5 mL) and dried in air to afford **3a** (**4a**) as an off-white powder (**3a**, 0.46 g (81% yield); **4a**, 0.42 g (91% yield)). The addition of MeI has been carried out both at –70 °C and at room temperature, providing the same result.

Anal. Calcd for $C_{21}H_{27}IIrN$ (**3a**): C, 41.18; H, 4.44; N, 2.29; I, 20.72. Found: C, 41.28; H, 4.56; N, 2.34; I, 20.55. Calcd for $C_{18}H_{27}IIrN$ (**4a**): C, 37.50; H, 4.72; N, 2.43; I, 22.01. Found: C, 37.44; H, 4.78; N, 2.39; I, 21.92.

Conversion of 3a (4a) to *cis*-IrI(Me)(L-*C,N*)(cod) (L = $1\text{-}C_{10}H_6NMe_2\text{-}8$ (3b); L = $C_6H_4CH_2NMe_2\text{-}2$ (4b)). Complex **3a** (**4a**) (**3a**, 0.07 g (0.11 mmol); **4a**, 0.06 g (0.1 mmol)) was dissolved in CH_2Cl_2 (5 mL). After 45 min of stirring at 35 °C the yellow solution was evaporated *in vacuo* to dryness, affording **3b** (**4b**) quantitatively as a yellow powder (**3b**, 0.07 g; **4b**, 0.06 g).

Synthesis of [Ir(Me)($1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}$*C,N*)(cod)][OTf] (5). Method a. Freshly distilled MeOTf (24 μL; 0.21 mmol) was added at –50 °C to a red solution of **1** (0.1 g; 0.21 mmol) in toluene (25 mL). The temperature of the solution was raised in 4 h to room temperature during which time the solution became yellow. The solvent was removed *in vacuo*. The yellow residue was washed with pentane (2 × 5 mL) and dried in air to afford **5** as an off-white powder (0.1 g; 79% yield).

Anal. Calcd for $C_{22}H_{27}F_3IrNO_3S$: C, 41.63; H, 4.29; N, 2.21. Found: C, 40.26; H, 4.16; N, 2.09.

Method b. To a yellow solution of **3a** (0.061 g; 0.1 mmol) in THF (20 mL) was slowly added at room temperature a solution of AgOTf (0.026 g; 0.1 mmol) in THF (5 mL). After 10 min of stirring, the resulting yellow suspension was filtered and the yellow filtrate evaporated to dryness. The brownish residue was washed with Et_2O (2 × 5 mL) and dried in air to afford **5** as an off-white powder (0.038 g; 60% yield).

Reaction of 1 with 4-Tolyl Iodide. To a red solution of **1** (0.055 g; 0.12 mmol) in toluene (5 mL) was added a solution of 4-tolyl iodide (0.026 g; 0.12 mmol) in toluene (3 mL) at –50 °C. After being stirred for 1 night at –20 °C, the red solution was evaporated *in vacuo* to dryness to afford a red powder. ^1H NMR in C_6D_6 showed this powder to be an unreacted 1:1 mixture of **1** and 4-tolyl iodide.

Reaction of 1 with MeI in MeCN. To a suspension of **1** (0.30 g; 0.64 mmol) in MeCN (30 mL) was added freshly distilled MeI (40 μL; 0.64 mmol) at –10 °C. After stirring of this mixture for 3 h, during which time the temperature was raised to 25 °C, the resulting yellow solution was evaporated to dryness *in vacuo*. The yellow solid was washed once with pentane (10 mL) and dried *in vacuo* to afford 0.35 g of an off-white powder. ^1H NMR in $CDCl_3$ at room temperature showed this powder to be a 1:1 mixture of **3a,b**.

Reaction of 3a with Bu_4NBr. A solution of Bu_4NBr (0.75 g; 2.3 mmol) in CH_2Cl_2 (15 mL) was added to **3a** (0.35 g; 0.6 mmol). After being stirred for 1 night, this solution was evaporated *in vacuo* to afford a sticky residue. Upon addition of pentane (25 mL), a white solid precipitated. This was filtered off and the yellow filtrate was evaporated *in vacuo* to give a pale yellow powder. ^1H NMR showed this product to be a 1:1.7 mixture of **3b** (*cis*-MeI) and *cis*-IrBr(Me)($1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}$*C,N*)(cod) (**3c**). ^1H NMR for **3c** ($CDCl_3$): δ 7.7–7.1 (m, 6, $C_{10}H_6$), 5.28 (q, 1, $=CH$), 4.4–4.0 (m, 3, $=CH$), 3.51 (s, 3, $N(CH_3)$), 3.11 (s, 3, $N(CH_3)$), 0.67 (s, 3, $Ir(CH_3)$), aliphatic cod-*H* from 3.5 to 1.

NMR Experiments. In a typical experiment, a solution of one of the iridium complexes (10–15 mg) was made in *ca.* 0.5 mL of the requisite solvent. Depending on the type of experiment, an equimolar amount or an excess of the reagent was added to this solution. For the low-temperature experiments, the tube and solution were cooled to –60 °C prior to adding the reagent.

Quantitative Kinetic Experiments. The ^1H NMR spectra of solutions of complexes **3a** or **4a** in CD_2Cl_2 were studied as a function of time at 5 °C. Initial concentrations of **3a** and **4a** vary from 7.3×10^{-4} to 2.9×10^{-1} M. Integration showed that the decrease of the Ir–Me resonance of **3a** and **4a** corresponded with the increase of the Ir–Me resonance of

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Table I. ^{1}H NMR Data for Complexes **1–5**[a]

complex	aryl H	–NMe_2	=CH(cod)[b]	–CH_2–(cod)	Ir–R
Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (**1**)[c]	7.22 (d), 7.38 (m), 7.50 (d), 7.58 (dd)	3.19 (s)	3.78 (s), 3.87 (s)	1.53–1.96 (m), 2.05–2.43 (m)	
Ir($C_6H_4CH_2NMe_2$-2-*C,N*)(cod) (**2**)[c,d]	6.95 (d), 6.99 (t), 7.16 (d), 7.24 (d)	2.68 (s)	3.75 (s), 3.79 (s)		
IrI(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (**3a**)[c,e]	6.65 (d), 7.21 (t), 7.3–7.45 (m), 7.59 (dd)	3.09 (s), 3.86 (s)	4.06 (t), 4.74 (q), 5.05 (t), 5.6 (dt)	1.7–1.93 (m), 2.27–2.57 (m), 2.77 (q), 3.03 (m), 3.51 (m)	1.4 (s)
[Ir(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(CD_3CN)(cod)][I] (**3a′**)[c,e]	6.77 (d), 7.23 (t), 7.41 (t), 7.49 (m), 7.57 (d)	3.18 (s), 3.28 (s)	4.39 (t), 5.11 (m), 5.4 (t)	1.739 (m), 2.28–3.03 (m)	0.91 (s)
IrI(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (**3b**)	7.19 (t), 7.39 (m) 7.54 (m), 7.66 (d)	3.36 (s) 3.76 (s)	3.95 (t), 4.04 (dt) 4.69 (t), 5.51 (q)	1.2–1.94 (m), 2.5 (m) 3.28 (m), 3.72 (m)	1.13 (s)
IrI(Me)($C_6H_4CH_2NMe_2$-2-*C,N*)(cod) (**4a**)[c,e,f]	6.49 (d), 6.81 (t), 6.93 (t), 7.08 (d)	2.26 (s), 3.27 (s)	4.24 (m), 4.37 (t), 5.15 (m)	1.55 (m), 1.83 (m), 2.2–2.27 (m), 3.1 (t), 3.45 (m)	1.43 (s)
IrI(Me)($C_6H_4CH_2NMe_2$-2-*C,N*)(cod) (**4b**)[g]	6.99 (d), 7.1–7.45 (m)	2.74 (s), 3.29 (s)	3.79 (dt), 4.56 (t), 4.78 (t), 5.46 (q)	1.73 (m), 2.06 (m), 2.45 (m), 2.86 (m), 3.41 (m)	0.95 (s)
[IrMe(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)][OTf] (**5a**)	7.12 (d), 7.23 (m), 7.43 (m), 7.67 (dd)	3.22 (s), 3.45 (s)	4.7 (m), 5.18 (m), 5.43 (q)	1.68–2.82 (m), 3.18 (m)	0.99 (s)
[Ir(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(CD_3CN)(cod)][OTf] (**5a′**)[c]	7.32–7.64 (m), 7.72 (d)	3.11 (s), 3.52 (s)	4.46 (m), 5.63 (q)	1.39 (m), 1.79 (m), 2.1 (m), 2.48–2.9 (m)	0.58 (s)
Ir(OTf)(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (**5b**)	6.99 (br), 7.28 (m), 7.47 (m), 7.7 (dd)	3.09 (s), 3.38 (s)	4.52 (m), 4.63 (tr), 4.74 (m), 5.55 (q)	1.4 (m), 1.7–2.8 (m), 2.97 (m)	0.69 (s)

[a] Recorded in $CDCl_3$ at room temperature unless otherwise stated; δ in ppm relative to external TMS. [b] Broad resonances. [c] Recorded in CD_2Cl_2. [d] From ref 12; –CH_2–NMe_2 resonance δ = 4.02 ppm. [e] Recorded at 233 K. [f] –CH_2–NMe_2 resonance δ = 3.76 (d) and 5.14 (d) ppm, diastereotopic protons, $^2J(^1H,^1H)$ = 14.0 Hz. [g] –CH_2–NMe_2 resonance δ = 3.54 (d) and 4.34 (d) ppm, diastereotopic protons, $^2J(^1H,^1H)$ = 14.6 Hz.

3b and **4b**, respectively. Isomerization progress was followed by the decrease of the former resonance.

Interpretation of Figure 5: The slopes of the lines are equal to $\partial\%[A]/\partial t = \partial(100[A]/[A]_0)/\partial t = (100/[A]_0)\partial[A]/\partial t$ (A is *trans*-added MeI complex; $[A]_0$ is the concentration of A when $t = 0$). Because the conversions are not large (the largest conversion in Figure 5 is that of **3a** (7.3×10^{-4} mol dm^{-3}), from 75% to 35%), to a first approximation the slopes of the lines can be taken to represent the initial rates. For **4a** (considered as starting material A) the slopes and their derived rates are as follows:

[A], mol dm^{-3}	$\partial\%[A]/\partial t$, s^{-1}	$\partial[A]/\partial t = (\partial\%[A]/\partial t)([A]_0/100)$, mol dm^{-3} s^{-1}
290×10^{-3}	0.0044	12.76×10^{-6}
10×10^{-3}	0.0148	1.48×10^{6}
7.4×10^{-3}	0.0305	2.22×10^{-6}

Assuming that the rate of the reaction is given by the equation

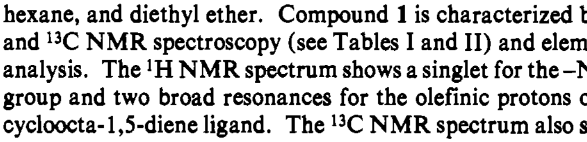
$$\partial[A]/\partial t = k[A]^n \quad (k \text{ is the rate constant})$$

then the slope of the line of $\log(\partial[A]/\partial t)$ against $\log [A]$ affords n. Using the above data, $n = 0.54$, *i.e* experimentally the isomerization is of half-order in A. Using this equation and the data of the three concentrations gives an average value of k of 21×10^{-6} mol$^{0.5}$ dm$^{-1.5}$ s^{-1}. Similar calculations for the concentrations of **3a** give a value of 8×10^{-6} mol$^{0.5}$ dm$^{-1.5}$ s^{-1} for k.

Conductivity Experiments. In a typical experiment, the conductivity was measured on colorless solutions (*ca.* 1×10^{-3} M) of **3** and **5** in CH_2Cl_2 (either with or without MeCN), either at room temperature or at –40 (±5) °C. For comparison [N(CH_2Ph)Et_3][Cl] was measured in the same system and this gave a molar conductivity value, Λ_M, of 17.2 cm^2 Ω^{-1} mol^{-1}.

Results

A. Synthesis and Structure of Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (1). The complex Ir(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod), **1**, is obtained as a red powder in 91% yield from the reaction of 2 equiv of Li(1-$C_{10}H_6NMe_2$-8-*C,N*)(OEt_2) with [IrCl(cod)]$_2$; see eq 1.



1

(1)

Although solid **1** has some air stability, its solutions are very air-sensitive and they change color from red to blue-green on exposure to air.[15] Compound **1** is soluble in benzene, toluene, and dichloromethane but is only slightly soluble in pentane, hexane, and diethyl ether. Compound **1** is characterized by ^{1}H and ^{13}C NMR spectroscopy (see Tables I and II) and elemental analysis. The ^{1}H NMR spectrum shows a singlet for the –NMe_2 group and two broad resonances for the olefinic protons of the cycloocta-1,5-diene ligand. The ^{13}C NMR spectrum also shows one resonance for the –NMe_2 group and two resonances for the olefinic carbon atoms of the cycloocta-1,5-diene ligand. These data are consistent with a square planar Ir(I) structure, in which the 1-naphthyl system and the cycloocta-1,5-diene are present as bidentate ligands as shown in eq 1; this arrangement has also been reported for the compounds Ir($C_6H_3CH_2NMe_2$-2-R-6-*C,N*)(cod) (R = H, CH_3, CH_2NMe_2).[12]

B. Reactions of 1 with RX. Oxidative addition reactions of electrophiles RX to square-planar d^8 organometallic complexes

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(17) In a similar way as for MeI, oxidative addition reactions of **1** and **2** with benzyl bromide and α-bromo-*m*-xylene were carried out affording off-white or yellow powders in *ca.* 90% yield, which were according to ^{1}H and ^{13}C NMR the products *cis*-IrBr(CH_2Ph)(L-*C,N*)(cod) (L = 1-$C_{10}H_6$-NMe_2-8 (**6**) and $C_6H_4CH_2NMe_2$-2 (**7**)) and *cis*-IrBr($CH_2C_6H_4$Me-3)-(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (**8**). Data for **6** are as follows. ^{1}H NMR ($CDCl_3$) (δ): aryl-H, 7.73 (t), 7.63 (d), 7.47 (m), 7.24 (d), 7.09 (d); –NMe_2, 3.56 (s), 3.23 (s); =CH(cod), 5.46 (q), 4.49 (t), 4.14 (t), 3.61; –CH_2–(cod), 3.55, 2.65–2.25 (m), 1.87 (m), 1.6 (m); Ir–CH_2–, 3.99 (d, ^2J(H,H) = 8.5 Hz), 2.58 (d, ^2J(H,H) = 8.5 Hz). ^{13}C NMR ($CDCl_3$) (δ): aryl-C, 155.5, 147.7, 138.7, 137.5, 135.3, 130.6, 128.7, 128.0, 127.4, 127.2, 125.0, 123.7, 122.3, 116.5; –NMe_2, 56.1, 53.2; =CH(cod), 104.5, 100.7, 86.5, 77.3; –CH_2–(cod), 37.2, 30.3, 27.4, 26.2; Ir–CH_2–, 22.4. Data for **7** are as follows. ^{1}H NMR ($CDCl_3$) (δ): aryl-H, 7.65 (d), 7.35 (m), 7.26 (t), 7.06 (br s); –NMe_2, 3.07 (s), 2.63 (s); ar–CH_2–N, 4.31 (d, ^2J(H,H) = 14.6 Hz), 3.64 (d, ^2J(H,H) = 14.6 Hz); =CH(cod), 5.45 (q), 4.84 (t), 4.24 (t), 3.63; –CH_2–(cod), 3.26 (m), 2.6–2.15 (m), 2.0 (t), 1.9–1.4 (m); Ir–CH_2–, 3.98 (d, ^2J(H,H) = 8.5 Hz), 2.34 (d, ^2J(H,H) = 8.5 Hz). ^{13}C NMR ($CDCl_3$) (δ): aryl-C, 148.1, 143.0, 138.2, 134.0, 128.7, 127.6, 127.2, 123.8, 123.2, 122.7; –NMe_2, 54.5, 51.2; ar–CH_2–N, 75.5; =CH(cod), 102.9, 97.3, 84.8, 76.1; –CH_2–(cod), 35.4, 30.5, 28.0, 26.9; Ir–CH_2–, 23.8. Data for **8** are as follows. ^{1}H NMR ($CDCl_3$) (δ): aryl-H, 7.74 (dd), 7.66 (t), 7.46 (m), 7.23 (d), 7.0 (br s), 6.88 (s); –NMe_2, 3.55 (s), 3.24 (s); =CH(cod), 5.46 (q), 4.55 (t), 4.14 (t), 3.6; –CH_2–(cod), 2.6–2.1 (m), 1.86 (m), 1.58 (m), 1.5–1.1 (m); Ir–CH_2–, 3.95 (d, ^2J(H,H) = 8.5 Hz), 2.55 (d, ^2J(H,H) = 8.5 Hz). During the oxidative addition reactions of the benzyl bromides to the Ir(I) complexes no *trans*-added products were detected. We are currently carrying out quantitative mechanistic investigations into these reactions.

(18) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393.

Table II. ^{13}C NMR Data for Complexes **1**–**5**[a]

complex	aryl C(1), C(2)	aryl C(3), C(4)	aryl C(5), C(6)	aryl C(7), C(8)	aryl C(9), C(10)	–NMe$_2$	=CH(cod)	–CH$_2$–(cod)	Ir–R
Ir(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)(cod) (**1**)	165.5, 131.4	124.0, 127.8	126.8, 124.5	112.8, 159.1	144.5, 134.9	51.6	56.9, 76.0	31.3, 31.9	
Ir(C$_6$H$_4$CH$_2$NMe$_2$-2-*C,N*)(cod) (**2**)[b]	166.8, 151.5	125.2, 128.9	121.4, 133.9			50.2	57.2, 74.5	30.9, 32.0	
IrI(Me)(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)(cod) (**3a**)[c]	156.5, 126.5	122.1, 128.1	127.2, 125.6	117.0, 147.5	142.0, 134.9	52.8, 68.4	77.4, 81.9, 96.6, 101.6	26.4, 30.4, 33.3, 33.9	9.0
IrI(Me)(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)(cod) (**3b**)	155.5, 129.6	128.0, 127.7	122.2, 125.5	116.5, 141.6	138.3, 135.3	54.4, 60.3	76.1, 80.6, 99.9, 100.1	27.0, 27.3, 30.2, 42.4	–2.8
IrI(Me)(C$_6$H$_4$CH$_2$NMe$_2$-2-*C,N*)(cod) (**4b**)[d]	n.o., 143.7	123.2, 127.9	122.6, 133.5			53.9, 56.9	75.1, 78.9, 96.2, 98.7	27.9, 28.9, 30.2, 39.5	–0.2
Ir(OTf)(Me)(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)(cod) (**5b**)	153.7, 129.3	128.2, 126.9	122.5, 125.2	115.9, 134.9	138.1, 134.9	53.3,[e] 56.0[e]	82.6, 88.1,[e] 108.6[e]	24.9, 27.9, 31.0, 33.9	2.4[e]

[a] Recorded in CD$_2$Cl$_2$ at room temperature unless otherwise stated; δ in ppm relative to TMS. [b] From ref 13; –*C*H$_2$–NMe$_2$ resonance δ = 75.7 ppm. [c] Recorded at 233 K. [d] –*C*H$_2$–NMe$_2$ resonance δ = 75.2 ppm. [e] Broad resonance.

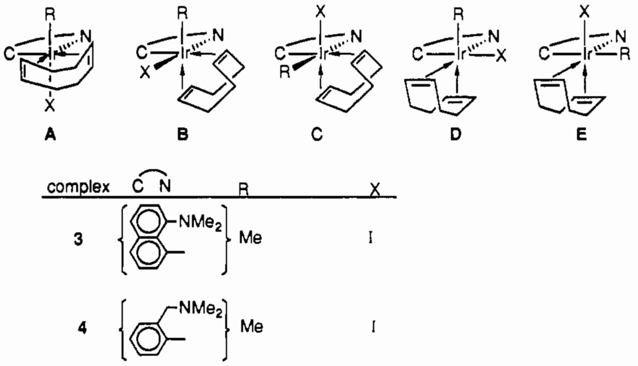
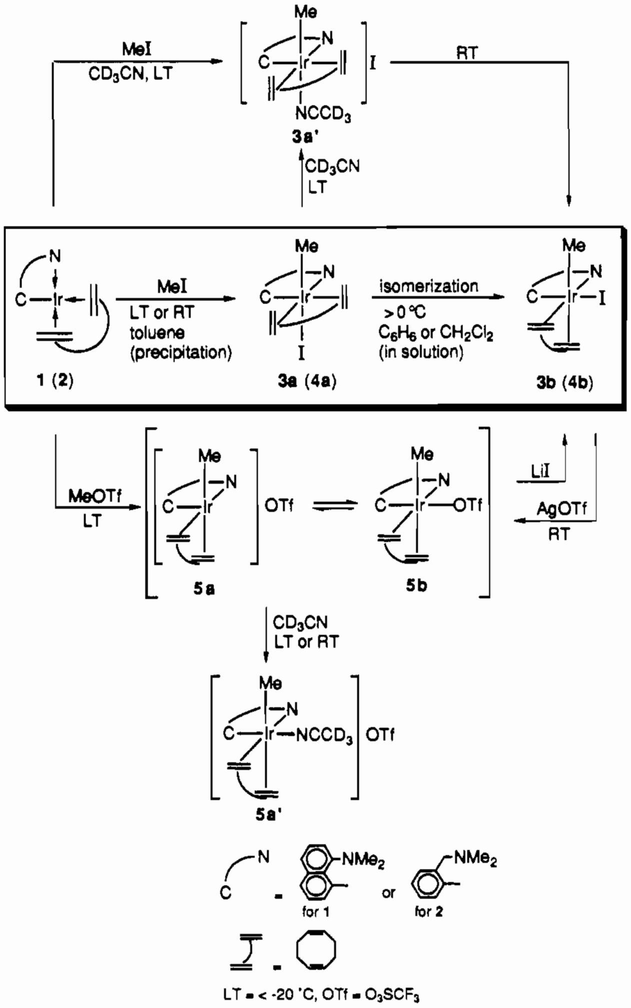


Figure 2. The five possible diastereoisomeric structures A–E for complexes IrX(R)(L-*C,N*)(cod).

often result in the formation of octahedral complexes. In general, an octahedral complex M(a)(b)(c)(d)(e)(f) has a total of 30 stereoisomers,[16] and this number of possible isomers can complicate structural assignment(s). In **1** as well as in Ir(C$_6$H$_4$-CH$_2$NMe$_2$-2-*C,N*)(cod) (**2**) two rigid bidentate ligands are present, and consequently for the octahedral oxidative addition products, IrX(R)(L-*C,N*)(cod), the number of possible stereoisomers is restricted to 10, consisting of 5 pairs of enantiomers. In Figure 2 is given, for each of these pairs, the possible structure of one enantiomer. Since all five structures A–E are asymmetric, all the prochiral groupings are diastereotopic and, consequently, afford nonisochronous ^{1}H NMR resonances.

Oxidative Addition Reactions of RI (R = Me, C$_6$H$_4$Me-4) to 1 and 2.[17] The reaction of complex **1** or **2** with methyl iodide in toluene, either at –70 °C or at room temperature, affords an off-white, air-stable product *trans*-IrI(Me)(L-*C,N*)(cod) (L = 1-C$_{10}$H$_6$NMe$_2$-8 (**3a**), 81% yield; L = C$_6$H$_4$CH$_2$NMe$_2$-2 (**4a**), 91% yield); see Scheme I. Both **3a** and **4a** are soluble in dichloromethane and chloroform and slightly soluble in toluene and benzene; in these solvents quantitative isomerization to another off-white compound *cis*-IrI(Me)(L-*C,N*)(cod) (L = 1-C$_{10}$H$_6$NMe$_2$-8 (**3b**) and L = C$_6$H$_4$CH$_2$NMe$_2$-2 (**4b**), respectively) took place (Scheme I). The four complexes are identified by a combination of ^{1}H, ^{13}C (see Tables I and II), and 2D NMR spectroscopy and elemental analysis. The products **3a,b** were shown to be neutral complexes by conductivity measurements (measured molar conductivity value in CH$_2$Cl$_2$ at –25 °C; for **3a** 0.08 cm^2 Ω^{-1} mol^{-1} and for **3b** 0.007 cm^2 Ω^{-1} mol^{-1}). Furthermore, **3a** gave no reaction with sodium tetraphenylborate, which is a known reagent for the direct titration of univalent inorganic or organic cations.[18]

Scheme I. Reaction Sequences and Conditions for the Oxidative Addition Reactions, Intermediate Detection, and Isomerization Processes



The ^{1}H NMR spectra of **3a** and **4a**, acquired at low temperature to prevent further reaction, are very similar to each other. The ^{1}H NMR spectrum of **3a** is easier to interpret because of the absence of benzylic protons and will be explained in detail. This spectrum of **3a** shows two singlets for the –NMe$_2$ group at 3.86 and 3.09 ppm, four resonances for the olefinic cod protons at 5.6, 5.05, 4.74, and 4.06 ppm, several multiplets for the aliphatic cod protons, a singlet for the Ir–Me group at 1.4 ppm, and three well-separated aromatic resonances at 7.59, 7.21, and 6.65 ppm together with multiplets for the other aromatic protons. The chemical shift values indicate respectively that (a) the –NMe$_2$ group is coordinating to the metal center (a noncoordinating–NMe$_2$ group shows a singlet resonance at 2.5 ppm),[11] (b) both olefinic moieties of the cod ligand are coordinating to the metal center, and (c) the Me group is bonded to the metal center (free MeI shows a resonance at 2.1 ppm). The nonequivalence of the –NMe$_2$ methyl groups and cod olefinic protons shows these groups and protons to be diastereotopic, which is further evidence for the chelate binding mode of the ligands. These data point to an

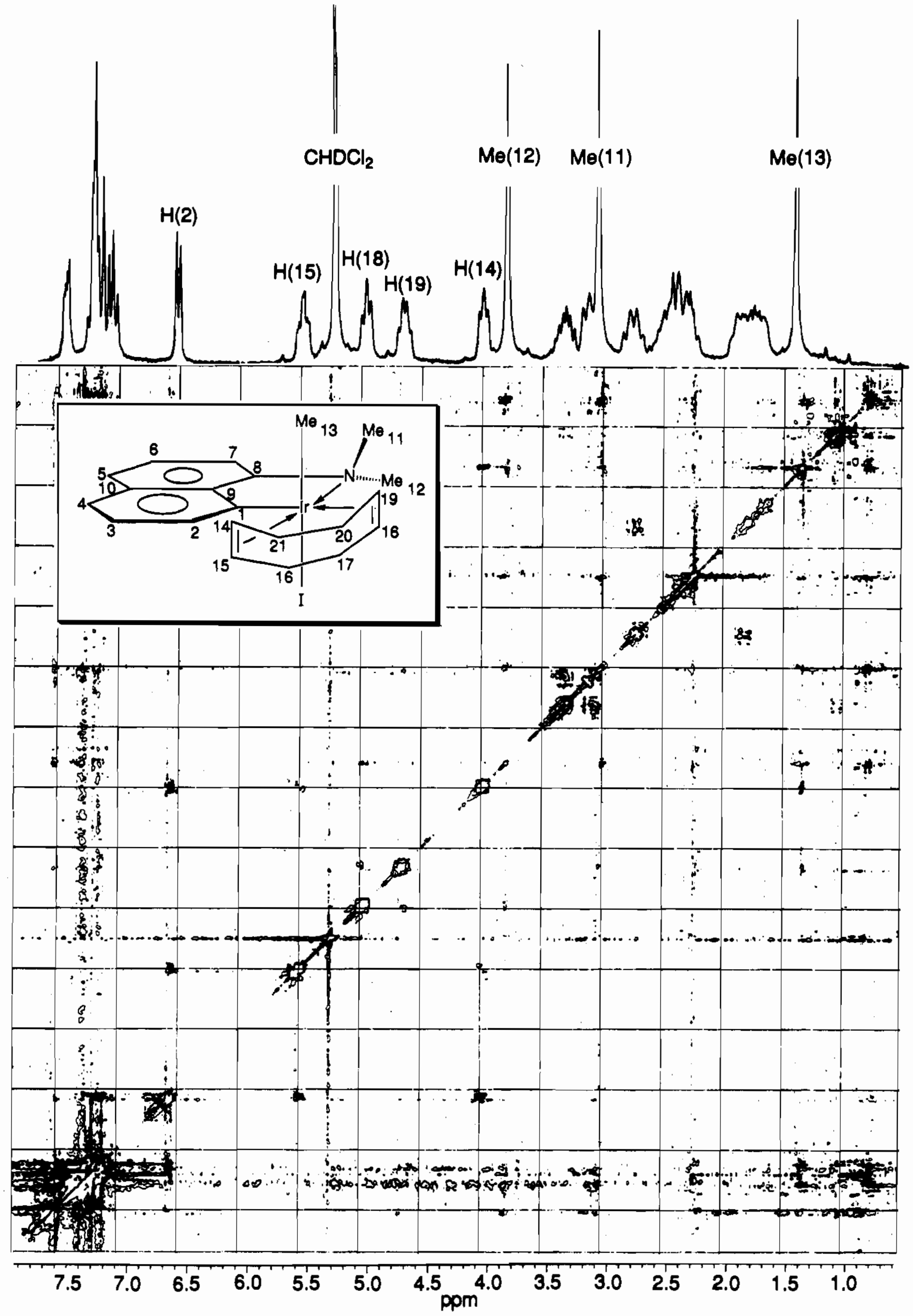


Figure 3. 2D NOESY spectrum and the structure together with the adopted numbering scheme of **3a**.

octahedral structure IrI(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) for complex **3a**. Further support for this proposal for **3a** being a d^6 Ir(III) oxidative addition product comes from the ^{13}C NMR spectrum which shows C_{ipso} is at 156.5 ppm (in the starting Ir(I) complex **1**, C_{ipso} is at 165.5 ppm), the Ir–Me resonance is at 9 ppm (free MeI has a resonance at −18 ppm), and all the other ^{13}C resonances are inequivalent and in the expected regions.

The ^1H and ^{13}C NMR data show the reactions of both **1** and **2** with MeI to be stereoselective; only one species is observed in solution whereas 5 isomers (A–E; *vide supra*) could be expected. However, on the basis of the 1D NMR data, it is not possible with certainty to identify which of the structures A–E has been formed. To help elucidate the structure of **3a** in solution, 2D NOESY (nuclear Overhauser enhancement spectroscopy) NMR experiments, which are facilitated by the rigidity of the octahedral complexes, have been carried out. For **3a** several nOe's may be expected of which the most significant ones are likely to be those between the aromatic *ortho* protons and the olefinic cod protons. Therefore, we first deduced with COSY (correlation spectroscopy) experiments that the aromatic resonance at 6.65 ppm belongs to the *ortho* proton. The 2D ^1H NOESY spectrum of **3a** is shown in Figure 3, together with the adopted numbering scheme. The aromatic *ortho* proton H(2) (6.65 ppm) shows two cross peaks for the interactions with the olefinic protons H(14) and H(15), which, on the basis of decoupling experiments, are bound to the same olefinic unit of the cod ligand. These two nOe interactions are indicative for a structural moiety in which at least one olefinic unit is perpendicular to the plane of the naphthyl ligand, and this immediately rules out structures **C**–**E**. One can also rule out structure **B**, because a downfield shift for the aromatic *ortho* proton, due to anisotropic effects of the iodide,[7,19] is expected in

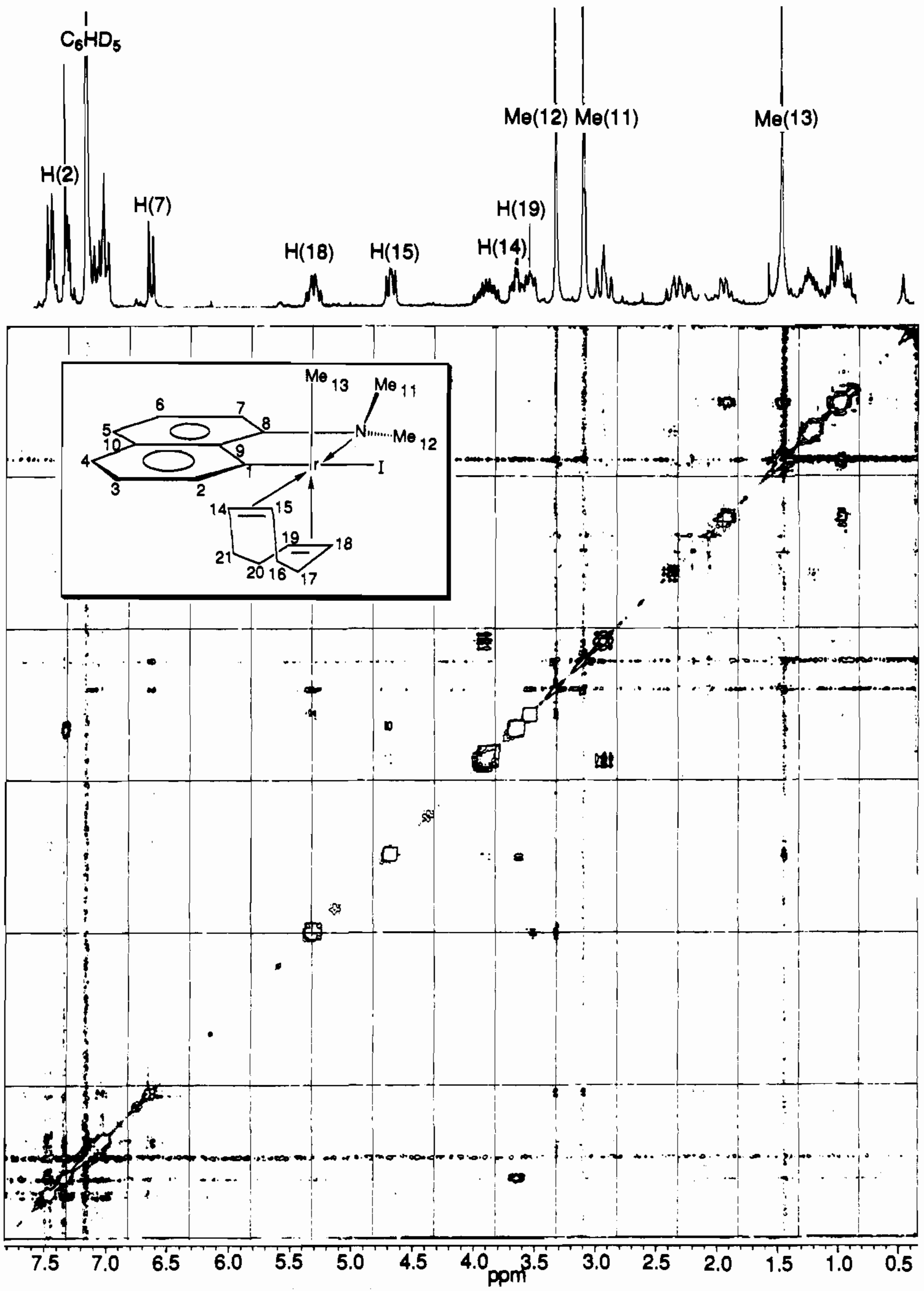


Figure 4. 2D NOESY spectrum and the structure together with the adopted numbering scheme of **3b**.

this case but is not observed for **3a**. Consequently it is structure **A** that complies with all spectroscopic data gathered for this oxidative addition product. This proposal is confirmed by the nOe's between the protons of the other olefinic unit of the cod ligand (H(18) and H(19)) and the $-NMe_2$ unit (Me(11) and Me(12), respectively). On the basis of the great similarity between the ^1H NMR spectra of **3a** and **4a**, structure **A** is also assigned to **4a**.

Complexes **3a** and **4a** are not stable in solution at temperatures higher than −10 °C and isomerize quantitatively to the solution-stable complexes **3b** and **4b**, respectively. The ^1H NMR spectra of **3b** and **4b** not only are very similar to each other but they also resemble the spectra of **3a** and **4a**, respectively. Consequently, the structure of **3b**, the more rigid complex, was determined in the same way as for **3a**. The main difference in the NOESY spectrum of **3b** (see Figure 4) compared to that of **3a** is that only one olefinic proton (H(14)) shows an interaction with the aromatic proton H(2); see Figure 4 for the numbering scheme. This means that in **3b** one olefinic bond lies in the plane of the naphthyl ligand and not in a mutually perpendicular arrangement as in **3a**. Such a structural feature excludes **A**–**C** as possible structures for **3b**, but both isomers **D** and **E** are still possible. From interactions of the olefinic protons H(15) and H(18) with the Me groups H(13) and H(12), respectively, it is possible to exclude structure **E**. Furthermore, the low-field shifts of the olefinic protons H(15) and H(18) (4.69 and 5.51 ppm, respectively), due to anisotropic effects of the iodide, are in agreement with structure **D** for complex **3b**. By analogy structure **D** is also assigned to **4b**.

Complex **1** did not react with 4-tolyl iodide at −20 °C for 18 h.

C. Isomerization of *trans*-IrI(Me)(L-*C,N*)(cod). The isomerization of **3a** to **3b** is a "clean" process during which no other

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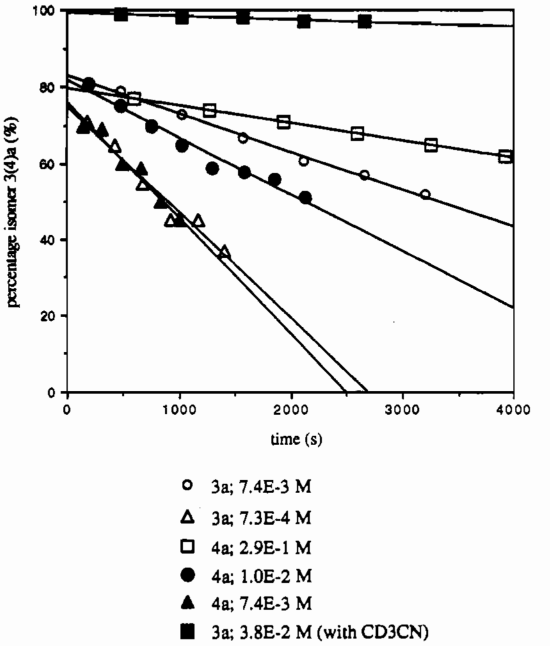

Figure 5. Plot of concentration of **3a** (**4a**) vs time for the isomerization of **3a** (**4a**) to **3b** (**4b**). The concentration of **3a** (**4a**) is represented in percentage such that % **3a** (**4a**) + % **3b** (**4b**) = 100%.

isomers were observed by ^1H NMR spectroscopy. However, the isomerization of **4a** to **4b** (now L is the more flexible $[C_6H_4CH_2NMe_2\text{-}2]^-$ ligand) involves another isomer with similar ^1H NMR resonance patterns. The most striking difference is that instead of two –NMe resonances at *ca.* 3 ppm and one Ir–Me resonance at *ca.* 1 ppm, the new isomer has now two –NMe singlets at 2.65 and 3.3 ppm and one Ir–Me singlet at 2.6 ppm. Unfortunately, a complete characterization of this "intermediate" has not proved possible.

The rate of isomerization of the species with the *trans*-Me–Ir–I geometry (**3a** or **4a**) to the product with the *cis* geometry (**3b** or **4b**) is dependent on several factors. First, concerning the solvent, whereas the isomerization in polar solvents ($CHCl_3$, CH_2Cl_2) takes *ca.* 1–4 h, under similar conditions the isomerization in nonpolar solvents takes 40–60 h. Second, concerning the temperature, no isomerization takes place at temperatures lower than –10 °C. Third, when the isomerizations of **3a** and **4a** are followed at one temperature (5 °C), it is found that both the concentration of the isomers with the *trans* geometry and the type of chelating ligand system influence the rate of the isomerization. For example, as shown in Figure 5, the isomerization of **3a** to **3b** is 2.8 times faster when the concentration of **3a** is a factor of 10 lower. Furthermore, at the same concentration of the starting *trans* isomer the isomerization of **4a** to **4b** is 3.1 times faster than that of **3a** to **3b**. At room temperature the rate of isomerization of **3a** to **3b** can be affected by addition of external reagents. When a solution of $MeBu_3NI$ in $CDCl_3$ is added to a solution of **3a** in $CDCl_3$, the conversion to isomer **3b** within 1 h decreases by 25%. In contrast, addition of a bromide (instead of iodide) salt, *i.e.* Bu_4NBr, decreases the yield within 1 h to 6%. When this latter reaction mixture is measured after 18 h, complex **3a** is still present (for 20%) and, as well as **3b**, there is another product (for 15%) present; this new complex is thought to be the bromide analogue of **3b**, *i.e.* *cis*-IrBr(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod) (**3c**). The latter has also been obtained in a separate experiment (see Experimental Section) where 4 equiv of Bu_4NBr was added to **3a** affording a 1:1.7 mixture of **3b** (*cis*-MeI) and **3c** (*cis*-MeBr).

D. Cationic Complexes. ^1H NMR Detection of the Cationic Complex [Ir(Me)($C_{10}H_6NMe_2$-8-*C,N*)(CD_3CN)(cod)][I] (3a′). Addition of an excess of the coordinating solvent CD_3CN to a solution of **3a** in CD_2Cl_2 at –40 °C affords the cationic complex [Ir(Me)($C_{10}H_6NMe_2$-8-*C,N*)(CD_3CN)(cod)][I] (**3a′**) (see Scheme I), which is easily detected with ^1H NMR. When this experiment is carried out at room temperature, this cationic complex is not detected. The ionic character of complex **3a′** is very clear from conductivity measurements: the molar conductivity value of **3a′** (19.8 $cm^2\ \Omega^{-1}\ mol^{-1}$) is 250 times greater than that of **3a**. In the ^1H NMR spectrum of **3a′**, the Ir–Me resonance at 0.91 ppm is 0.5 ppm upfield of that of **3a** and this difference is in accordance with the *trans* influences of X and CH_3CN.[19] In **3a′** the N–Me resonances are now separated by only 0.1 ppm, whereas in **3a** the separation is 0.77 ppm as a result of the anisotropic effects of the iodide.[7,19]

Addition of less than 1 equiv of CD_3CN to a solution of **3a** in CD_2Cl_2 at –40 °C causes partial (^1H NMR detectable) formation of **3a′**. However, when the temperature was raised (–30, –10, 5 °C), **3a′** is no longer observed. The measured isomerization rate of **3a** to **3b** in presence of added CD_3CN at 5 °C (see Figure 5) shows that conversion is slow.

The reaction of **1** with MeI carried out in CD_3CN at –40 °C also affords the cationic complex **3a′**. Interestingly, if MeI is added to a solution of **1** in CD_3CN, the complex **3a′** can now be detected even at room temperature. The cationic complex **3a′** in solution at room temperature has some stability and after 15 min isomerization to **3b** and some decomposition becomes appreciable. This isomerization is not accelerated by addition of a solution of 40 equiv of LiI in CD_3CN.

Attempts to isolate the cationic complex **3a′** failed; after workup of the reaction of **1** with MeI in CH_3CN, only a mixture of **3a** and **3b** was obtained.

When CD_3CN was added to a solution of **3b** in $CDCl_3$, at temperatures from –40 °C to room temperature, no reaction was observed.

Synthesis of [Ir(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)][OTf] (5). The oxidative addition reaction of methyl trifluoromethanesulfonate (CF_3SO_3Me = MeOTF) to **1** dissolved in toluene affords the white solid [Ir(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)][OTf] (**5**) in 79% yield; see Scheme I. Complex **5** can also be synthesized by the reaction of **3** with silver trifluoromethanesulfonate. This product, which is air-stable and soluble in chloroform and dichloromethane, has been characterized with ^1H and ^{13}C NMR spectroscopy (Tables I and II, respectively) and elemental analysis. Variable-temperature NMR data in solution at room temperature for **5** have shown that this complex exists as two isomers which are in equilibrium. At room temperature broad signals for both isomers **5a,b** (each with two –NMe singlets and one Ir–Me singlet) are present in a 3:2 ratio. Above 30 °C only 1 isomer, **5a**, is present and all lines sharpen. Upon cooling, the ratio of the two isomers **5a,b** changes to 2:3 at –50 °C. A clear saturated solution of **5** in $CDCl_3$ at room temperature shows with ^1H NMR only one isomer **5b**; dilution of this sample with $CDCl_3$ gives a mixture of **5a,b**. Therefore, we propose that **5a** is the five-coordinate ionic complex [Ir(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod)][OTf] and that **5b** is the neutral six-cooordinate octahedral complex Ir(OTf)(Me)(1-$C_{10}H_6NMe_2$-8-*C,N*)(cod). Although the trifluoromethanesulfonate group is a poorly coordinating anion,[20] in a saturated solution of **5** the equilibrium between **5a** and **5b** is shifted completely to the side of **5b** with a coordinated OTf group. Further evidence for the proposed structures of **5a,b** is provided by the observation that a clear dilute sample of **5** in the apolar solvent C_6D_6 shows only the presence of isomer **5b**. The ionic character of the mixture was confirmed with conductivity experiments; the measured molar conductivity value of **5** in CH_2-

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Cl_2 at −25 °C is 4.81 $cm^2\ \Omega^{-1}\ mol^{-1}$, which is between the value of the neutral complex **3a** and the cationic complex **3a′**.

The proposed stereochemistry of the two isomers of **5** is shown in Scheme I. The ^1H NMR spectra of pure **5a,b**, obtained from dilute samples at high temperature and saturated ones at room temperature, respectively, both resemble the spectrum of **3b** as regards the aromatic region and the three methyl signals. This similarity points to a *cis* configuration of the Me ligand and the free coordination site in **5a** and of the Me and OTf groups in **5b** rather than a *trans* arrangement as found for Me and I in **3a**. Upon addition of CD_3CN at room temperature to a solution containing **5a,b**, only one isomer is formed, *i.e.* $[Ir(Me)(1\text{-}C_{10}H_6\text{-}NMe_2\text{-}8\text{-}C,N)(CD_3CN)(cod)][OTf]$ (**5a′**), which is stable in solution for days. Compared to the spectrum of **5b** that of **5a′** shows a small upfield shift of the Ir–Me resonance from 0.69 to 0.58 ppm, though both –NMe resonances at 3.52 and 3.11 ppm and the olefinic cod signals are hardly shifted. The small upfield shift of the Ir–Me resonance points to a *cis* position of the CD_3CN and the Me group and is, thus, further evidence for the proposed structures for **5a,b**. Moreover, the conductivity of the solution containing **5a,b** is enhanced 10 times by addition of acetonitrile, and **5a′** so formed is ionic (measured molar conductivity value of **5a′** in CH_2Cl_2 at −25 °C is 49.7 $cm^2\ \Omega^{-1}\ mol^{-1}$).

Starting from the solution containing **5a,b**, it is also possible to generate the $Ir^{III}(Me)(I)$ complex **3b**; see Scheme I. Addition of a solution of 4 equiv of LiI in methanol-d_4 to a solution containing **5a,b** in methanol-d_4 results in the immediate precipitation of an off-white solid, which is soluble in $CDCl_3$ and has been shown by ^1H NMR to be pure **3b**. This experiment also provides extra evidence for the *cis* configuration of **5a,b**. The possibility that the off-white precipitate is **3a** which then isomerized to **3b** in $CDCl_3$ can be ruled out, because isomerization of pure **3a** to **3b** does not take place either in the solid state or in solution within 5 min.

Discussion

Mechanism of Oxidative Addition Reactions. Alkyl halides are known to react as electrophiles with a metal complex to give an oxidative addition reaction. In general, for an oxidative addition reaction with a square planar d^8 metal complex, three mechanisms have been proposed, the S_N2 type, the concerted addition, and the free radical (chain or nonchain) process.[21] In these reactions, the outcome of the product stereochemistry is indicative for the operative mechanism. For the oxidative addition of alkyl halides the S_N2 type of mechanism is most common, very often resulting in a *trans* positioning of the alkyl and the halide ligands.[22] Further evidence for the operation of the S_N2 type of mechanism comes from the observation of cationic intermediates. Another possible intermediate in the S_N2 type of reaction is a five-coordinate metal complex in which intact RX is coordinated to the metal center. Usually, RX-coordinated complexes are formed from cationic precursor species in which the metal center possesses a high oxidation state for improved acceptor ability.[23] In such RX-coordinated complexes the metal center retains the oxidation state of the precursor complex.

In the reactions of RX with **1** and **2** the precursor material is a neutral Ir(I) complex, which is not very likely to coordinate RX to form five-coordinate Ir(I) products. Here, our evidence points to the reaction of MeI with **1** or **2** to be proceeding by an S_N2 type of mechanism. First, we find that in the initial products **3a** and **4a** the methyl and iodide ligands are *trans*-positioned and, second, the reaction of **1** with MeI in CD_3CN provides the cationic complex **3a′**. It is important to note that although many cationic intermediates are known in the oxidative addition reactions of 18-electron complexes, **3a′** is, in fact, one of the first examples of a cationic intermediate to be detected during an oxidative addition reaction with a 16-electron Ir(I) complex.[24] This common failure to observe cationic species from 16-electron precursors is probably related to the relative rates of oxidative addition and subsequent ligand substitution. The first (oxidative addition) step to form the cation is likely to be much slower than the second step (ligand substitution of the coordinating solvent by the halide).[1d] In our work, the first step in the reaction of **1** with MeI is fast enough to enable detection of the cationic intermediate. Puddephatt *et al.* have shown that the oxidative addition step of the reactions of $PtMe_2L_2$ with RX in coordinating solvents was fast enough to detect a cationic intermediate[1d,20c,25] but only for the most reactive systems, *i.e.* RX = MeI and $PhCH_2Br$ in combination with L_2 = bipy and L = PMe_2Ph.

In our case further indirect evidence for the S_N2 mechanism for the MeI reaction comes from the reaction of **1** with 4-tolyl iodide where no oxidative addition products are found. In the few examples where aryl halide oxidative addition to a square-planar d^8 metal complex does occur, kinetic data have shown that an S_N2 mechanism was not involved.[26]

The reaction of **1** with MeOTf in toluene is in several aspects different from that with MeI in CD_3CN and leads to a product mixture of two isomers **5a,b**, five- and six-coordinate Ir complexes which are in equilibrium with each other (see Results). This formation of a five-coordinate cationic metal species is also indicative for an S_N2 type of mechanism. However, the six-coordinate species is not a product with *trans* geometry. This result can be readily explained by assuming that the initially formed cationic complex (with an apical Me group) first isomerizes by an intramolecular ligand rearrangement to afford the observed five-coordinate species before the OTf^- group coordinates to afford the six-coordinate product. Although the OTf^- group is a weak ligand for the Pt group metals and unlikely to coordinate,[20] precedents for a coordinating OTf^- group have been found in palladium,[27a] cobalt,[27b] ruthenium,[27c,28] and zinc chemistry.[28]

Finally, it is worth emphasising that it is fully consistent that the equilibrium isomer mixture of **5a,b** in toluene when treated with CD_3CN should afford **5a′** with a ligand arrangement different from the MeI oxidative addition product **3a′** realized in CD_3CN solution.

Mechanism of Stereoselective Isomerization. In solution the product with the *trans*-Me–Ir–I geometry **3a** (**4a**) is not stable and isomerizes quantitatively and stereoselectively to the product with the *cis* geometry **3b** (**4b**). *Cis–trans* isomerizations within

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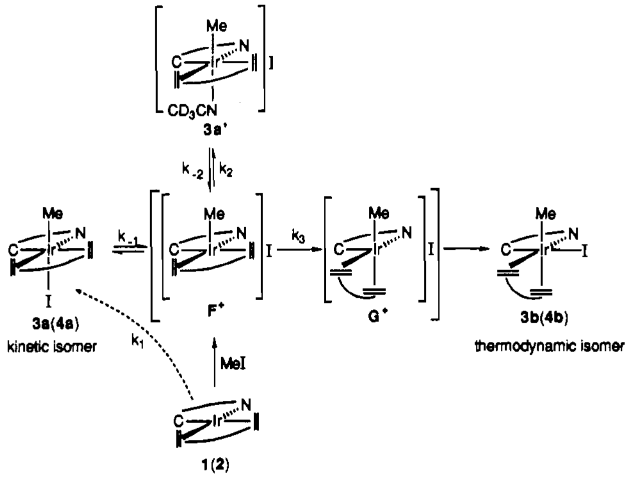
(28) We have very recently found η^1-O bonded OTf^- in the X-ray molecular structures of $MeZn(t\text{-}BuN{=}CHC(H){=}N\text{-}t\text{-}Bu)(OTf)$ (Wissing, E.; Kaupp, M.; Boersma, J.; Spek, A. L.; van Koten, G. Unpublished results) and $Ru\{C_6H_4(CH_2NMe_2)_2\text{-}C,N,N'\}(C_7H_8)(OTf)$ (C_7H_8 = norbornadiene; Sutter, J. P.; van Koten, G.; Spek, A. L.; Veldman, N. Unpublished results).

Scheme II. Proposed Mechanism for the Isomerization Process of the *Trans* to the *Cis* Isomer



octahedral complexes may occur either intra- or intermolecularly and often involve prior dissociation of a ligand to create a free coordination site.[20c,29] The intermolecular process can proceed *via* either a reductive elimination/oxidative addition mechanism (as was found for the iridium hydride complexes $Ir(H)_2(Ph)(CO)(PMe_3)_2$[1e] and $IrX(H)_2(CO)(Ph_2PCH_2CH_2PPh_2)$ (X = Cl, Br, I))[30] or by a dissociative pathway that involves ligand dissociation, rearrangement of the resulting five-coordinate complex and coordination of a free ligand. [We thank the reviewers for correctly pointing out that crossover experiments using CD_3I and isolated species **3a** and **4a** would provide further useful information on possible intermolecular exchange processes. Such experiments will be included in a newly initiated study of oxidative reactions with several chelated transition metal species.] Characteristic for this intermolecular dissociative pathway is that exchange with any free ligand should occur easily. However, there is also an intramolecular process for *cis–trans* isomerizations that can follow a dissociative pathway. In this process, the isomerization rate is much faster than that of the dissociation and consequently the latter becomes the rate-determining step. An example of this process is the first-order isomerization of *cis*-$IrCl_2(R)(CO)(PMePh_2)_2$ to *trans*-$IrCl_2(R)(CO)(PMePh_2)_2$ (R = Me, Et, *n*-Pr) that is proposed to go *via* rate-determining dissociation of Cl^-, rapid rearrangement of the Ir(III) cation, and subsequent reentry of the same Cl^-.[31] The intermediate in this type of reaction may have a trigonal bipyramidal structure, in which an intramolecular Berry pseudorotation takes place.[32] For the cited examples of iridium dihydride[1e,30] and dihalide complexes[31] the isomerizations at room temperature are very slow when no external reagents/ligands are present; the half-lives for isomerization vary from 35 h to 1 week.

Although the complete isomerization of **3a** to **3b** in dry $CDCl_3$ or CD_2Cl_2 (without other reagents present) is relatively fast (1 to 5 h, room temperature, concentrations up to 20 mg/0.5 mL), we still wish to propose that this process follows a dissociative mechanism as given in Scheme II. In this process it is the iodide ligand that dissociates rather than the dimethylamine function in the naphthyl ligand or one of the double bonds of the cyclooctadiene ligand, as occurs in the presence of the coordinating solvent MeCN. First complex **3a** is formed in the oxidative addition reaction of MeI to **1** (k_1), which proceeds through a cationic intermediate represented by the five-coordinate square pyramidal structure F^+. Then, isomerization starts by (reversible) dissociation of the iodide (k_{-1}) from **3a** to recreate cationic F^+. Then isomerization to cation G^+ takes place (k_3). Upon readdition of the iodide to cation G^+, complex **3b** is formed in an irreversible reaction which goes to completion. Whereas **3b** is unaffected by MeCN, **3a** forms with MeCN *via* F^+ (k_2), the MeCN-coordinated cationic complex **3a′**. This dissociation of I^- in **3a** to form F^+ (k_{-1}) is facilitated by the *trans* influence of the methyl group, which makes the I^- anion labile.[33] The formation of **3a′** results in an overal slowing down of the isomerization of **3a** to **3b** when MeCN is present. Although k_{-1} (formation of the cationic intermediate F^+) may be increased by the presence of MeCN (polar solvent), k_3 will be decreased because a concurrent reaction to form **3a′** (k_2) is now also operative. Such a stereoselective oxidative addition to a d^8 metal complex followed by stereoselective isomerization within the d^6 metal complex was earlier reported by Brown *et al.* for the reaction of cationic Ir(I) phosphine complexes with H_2 affording Ir(III) dihydrides.[34]

The proposed mechanism is in accordance with the kinetics described in the Experimental Section and consists of a thermodynamic selectivity of the first step (a pre-equilibrium k_1/k_{-1} (K)) followed by a rate-determining step k_3 and a fast step to give the final product, in summary as follows:

$$\mathrm{A} \overset{K}{\rightleftarrows} \mathrm{F}^+ + \mathrm{I}^- \qquad \text{(fast)}$$

$$\mathrm{F}^+ \xrightarrow{k_3} \mathrm{G}^+ \qquad \text{(slow (rate-determining))}$$

$$\mathrm{G}^+ + \mathrm{I}^- \rightleftarrows \text{product} \qquad \text{(fast)}$$

External R_4NX reagents decrease the reaction rate because they reduce the concentration of F^+ in the pre-equilibrium step. In the isomerization of **3a** to **3b** the fact that Br^- becomes built into the final product when additional R_4NBr is present is also indicative for a rate-determining second step (k_3). As in our system, there are reported examples of external ligands retarding processes in which an equilibrium precedes the rate-determining step, such as in the oxidative addition of aryl iodides to Ir(I) complexes[26a] or in the cyclopalladation of benzylamine systems.[35]

For the isomerization of **4a** to **4b** the same mechanism as described in Scheme II is also likely to be operative. The fact that the isomerization in this case is faster can be explained by electronic rather than steric factors. The amine function of the benzylamine ligand in **4** has more Lewis base character than that of the naphthylamine ligand in **3**. Therefore, with the former the positively charged iridium center in the cation **F** is more stabilized and the species detected during the isomerization of **4a** to **4b** is probably this five-coordinate cation **F**; the low-field shift of the Ir–Me group in the ^1H NMR spectrum is in line with this proposal. When the first step shows thermodynamic selectivity, this preequilibrium shifts to the side of the more stabilized species (**F**) resulting in a higher overall reaction rate for the **4a** → **4b** isomerization than for the **3a** → **3b** isomerization.

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Conclusions

This study has shown that stereoselective oxidative addition of electrophilic reagents to Ir(I) complexes is obtained when using bidentate C,N chelating ligands. With MeI a kinetic isomer could be isolated, which is the result of an S_N2 type of reaction. This kinetic product stereoselectively isomerizes to the thermodynamic isomer, through a cationic intermediate which is detectable when the coordinating solvent MeCN is used. The naphthylamine and benzylamine ligand both give rise to the same stereoselectivity; however, with the less Lewis basic and more rigid naphthylamine ligand the isomerization is slower, allowing an easier study of the total isomerization process. The isomerization involves a pre-equilibrium in which dissociation of the halide takes place.

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