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# A kinetic investigation of the oxidative addition reactions of the dimeric $Bu_4N$ [ $Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2$ ] complex with iodomethane

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#### ABSTRACT

The IR and UV/visible kinetic results of the oxidative addition of iodomethane to  $Bu_4N[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  (Dcbp = 3,5-dicarboxylatepyrazolate anion) showed three time separable reactions. The first, very fast reaction corresponds to the a Ir(1)–Ir(III) alkyl species formation within  $10^{-3}$  s. The second, relative fast reaction corresponds to Ir(III)–Ir(III) alkyl formation with a rate constant of  $3.25(4) \times 10^{-2} M^{-1} s^{-1}$  while the third and slowest reaction corresponds to Ir(III)–Ir(III) alkyl formation with a rate constant of  $3.25(4) \times 10^{-2} M^{-1} s^{-1}$  while the third and slowest reaction corresponds to Ir(III)–Ir(III) acyl formation with a rate constant of  $1.42 \times 10^{-5} s^{-1}$ . The IR data clearly show the existence of a number of equilibria with the formation of an Ir (I)–Ir(III) alkyl product which then react to form the Ir(III)–Ir(III) which then slowly react to form the Ir(III)–Ir(III) acyl product. A solvent study indicated increased oxidative addition activity in the presence of polar solvents, which is indicative of a polar transition state. The large negative entropy of activation for the Ir(III)–Ir(III) alkyl formation step ( $k_2$ ) of  $-178(23) JK^{-1} mol^{-1}$  is indicative of an associative process. DFT calculations successfully identified the stereochemistry of the starting complex,  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^{-1}$  as well as that of the Ir-alkyl and acyl isomers. A reaction pathway, using the IR data and DFT calculations, is proposed for the reaction.

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#### 1. Introduction

The importance of iridium complexes as catalysts was underlined in 2000 when the  $[Ir(CO)_2(I)_2]^-$  complex (Cativa) replaced the rhodium analogue (Monsanto) for the first time as catalyst in a BP plant in Malaysia for the carbonylation of methanol to produce acetic acid [1]. In addition to cheaper iridium prices, benefits such as increased throughput due to faster reaction rates, milder reaction conditions needed for acetic acid production and the robustness of the catalyst under a wide variety of experimental conditions were achieved from this change in catalyst. Iridium complexes are also used in a number of other industrial processes. [Ir(cod)(PCy<sub>3</sub>) py]<sup>+</sup> is used in the reduction of steroids and the hydrogenation of alkenes and alkynes while the [Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>] complex is used in the conversion of higher alcohols and diols to carboxylic acids as well as the polymerisation of styrene [2]. World consumption of acetic acid was about 6 million metric tons in 2000, which was mainly used as raw material in the production of key petrochemical products and intermediates such as vinyl acetate monomer, acetate esters, cellulose acetate, monochloroacetic acid, etc. The majority of the acetic acid production (65%) was synthesized by methanol carbonylation technology. One of the key steps in the carbonylation of methanol to produce acetic acid involves the oxidative addition of methyl iodide to the metal complex, which was approximately 150 times faster for the Ir complex compared to the rhodium complex [3]. With the change in metal centres the rate determining step changed to the insertion of CO into the Ir–CH<sub>3</sub> bond to from the subsequent acyl intermediate. Reductive elimination of the CH<sub>3</sub>COI group with the subsequent reaction with water completed the acetic acid formation [1].

From these results it should be clear that the metal centre plays an important role in the rate of the catalytic process and possibly as well as to the selectivity of the products that are formed in this process. Research done by Garcia et al. [4–7] indicated an increase in catalytic activity when the monomeric complex is replaced by dimeric metal complexes. It was found for instance that the catalytic hydrogenation of cyclohexene by  $[H(CO)(PPh_3)_2Ru(\mu-bim)M(cod)]$  (bim = 2,2' bi-imidazolate, M = Rh, Ir) is higher than the corresponding monomeric complex. In the case of the production of acetic acid from methanol the

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Fig. 1. General chemical presentation of the di-nuclear  $[Ir_2(\mu\text{-}Dcbp)(CO)_2(PCy_3)_2]^-$  complex.

presence of two metal ions open the possibility of different oxidative addition patterns such as reversible and irreversible oxidative addition and addition on only one or both metal ions [8]. Another new exciting possibility in these type of reactions is the possibility of co-operative effects that may take place between the different metal ions which can lead to metal-metal bond formation and/or the migration of the added fragments between the two metal ions [9-12]. Oxidative addition on one metal ion in some cases can lead to the deactivation of the second metal ion to the same reaction. This type of deactivation is attributed to the electron donation from the metal ion in the lower oxidation state to the metal ion in the higher oxidation state which may result in the activation of the one metal ion towards oxidative addition while the other metal centre may then be activated for reductive elimination which can be very useful in the design of catalysts [13]. Two recent studies [14,15] on di-nuclear rhodium complexes containing flexible trans-chelating diphosphines clearly demonstrated the increased reactivity of di-nuclear complexes towards oxidative addition reactions. The current study is an extension of the kinetic investigation that was recently completed on the Ir-Dcbp cod dimeric complex [16], Dcbp = 3,5-dicarboxylatepyrazolate anion.

#### Table 1

DFT molecular energies (eV) of the possible stereo isomers of  $[Ir_2(\mu$ -Dcbp) (CO)<sub>2</sub>(PX<sub>3</sub>)<sub>2</sub>]<sup>-</sup> (X = Cy or H) relative to the lowest energy isomer as zero.



#### 2. Experimental

#### 2.1. General considerations

All the preparations were performed under a dry nitrogen atmosphere and unless otherwise stated all the chemicals were reagent grade and used without further purification. IR spectra were recorded with a Hitachi 270-50 spectrophotometer while the NMR spectra were obtained at 293 K on a Bruker 300 and 600 MHz spectrometer. The chemical analyses were performed at Mikroanalytisches Labor Pascher in Remagen-Bandorf, Germany.

### 2.2. Synthesis of tetrabutylammonium μ-3,5-dicarboxylatopyrazolatocarbonyl- tricyclohexylphosphine iridate(I)], (Bu<sub>4</sub>N) [Ir<sub>2</sub>(μ-Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>]

(Bu<sub>4</sub>N)[Ir<sub>2</sub>(µ-Dcbp)(cod)<sub>2</sub>][13](0.1 g, 0.14 mmol) was dissolved in 35 ml acetone. Carbon monoxide was bubbled for 10 min through the solution, while stirring and maintaining a nitrogen atmosphere over the solution. The bright yellow solution changed to light yellow during this process. The formation of the  $(Bu_4N)[Ir_2(\mu-Dcbp)(CO)_4]$ complex was confirmed with liquid IR spectra ( $\nu$ (CO) = 2077 and 1987 cm<sup>-1</sup> [17]). Tricyclohexylphosphine (PCy<sub>3</sub>) (0.22 g, 0.8 mmol) was added slowly to the first solution while stirring and maintaining a nitrogen atmosphere. A light vellow precipitate formed after 45 min. The solution was stirred for another 2 h after which the volume of the solution was reduced to half of its original volume using a flow of nitrogen gas. The precipitate was centrifuged, washed with ether and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> for 8 h. Yield: 63%, IR data (KBr):  $\nu_{(OCO)} = 1617 \text{ m}^{-1}$ ,  $\nu_{(CO)} = 1932 \text{ cm}^{-1}$ , Elemental analysis: (calculated values in brackets): C, 49.6 (50.95); H, 7.10 (7.03); N, 2.35 (3.01), O, 8.25 (6.87), P, 3.75 (4.43), Ir, 27.01 (27.59)%. <sup>1</sup>H NMR (CDCl<sub>3</sub>), Dcbp, δ6.75 ppm (1H, s), NBu<sub>4</sub>, 3.25 (8H, s), 2.58 (8H, s), 0.95 (12H, t), PCy<sub>3</sub>, NBu<sub>4</sub>, 2.20–1.10, (38H, m),<sup>13</sup>C NMR (CDCl<sub>3</sub>, 77.01 MHz) & 206.6 (CO), 172.4 (Dcbp), 65.8 (NBu<sub>4</sub>), 33.6 (PCy), 30.9 (NBu<sub>4</sub>), 30.0 (Dcbp), 27.7 (PCy<sub>3</sub>), 27.6 (PCy<sub>3</sub>), 26.3 (PCy<sub>3</sub>), 19.7 (NBu<sub>4</sub>), 15.2 (NBu<sub>4</sub>), <sup>31</sup>P NMR (CDCl<sub>3</sub>, 36.44 MHz) δ 30.51.

(s = singlet, t = triplet and m = multiplet).

#### 2.3. Kinetics

The solvents used during the kinetic study were purified and dried prior to use by standard procedures [18]. The kinetic measurements were performed at atmospheric pressure on a GBC (Model 916) and a Varian (Cary 50) UV/vis spectrophotometer equipped with a thermostatted 6 cell changer (0.1 °C) while the IR spectra and kinetic runs were performed on a Hitachi 270-50 spectrophotometer using acetone as solvent (2200–1850 cm<sup>-1</sup>) and KBr -disks (4000–251 cm<sup>-1</sup>).

The oxidative addition reactions with CH<sub>3</sub>I were followed on UV/vis at 425.0 nm with the exception of acetonitrile and dichloromethane, which were followed at 420.0 nm. Typical experimental conditions were [Ir<sub>2</sub>-complex] =  $0.5-5.5 \times 10^{-4}$  M and [CH<sub>3</sub>I] varied between  $1.0 \times 10^{-2}$  and 0.2 M thus ensuring good pseudo first order kinetics. The observed first order rate constants where calculated according to  $A_t = A_{\infty} + (A_0 - A_{\infty})e^{(-k_{obs}t)}$  with  $A_t$ ,  $A_{\infty}$  and  $A_0$  the absorbance of the indicated species at time t,  $\infty$  and 0 respectively, using a non-linear least-square program [19]. The experimentally determined pseudo first order rate constants were converted to second order rate constants,  $k_2$ , by determining the slope of the linear plots of  $k_{obs}$  against the concentration of the incoming iodomethane ligand. The metal complex solutions were freshly prepared before each experiment to minimise the extent of the solvolysis reaction.



**Fig. 2.** The OLYP/TZP optimized geometry of  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$ . Selected bond lengths (Å) and angles (°) are shown. The Ir–N–N–Ir dihedral angle is 41.8°. d(Ir–Ir) = 4.44 Å. At the top is a front and side view of the molecule to illustrate the spatial orientation of the ligands attached to Ir(I). H atoms have been omitted for clarity.



**Fig. 3.** The first (black arrows) and second (blue arrows) steps in the oxidative addition step between CH<sub>3</sub>I (0.0113 M) and  $(Bu_4N)[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  (4.9 × 10<sup>-4</sup> M) with the formation of the Ir(III)-alkyl complex in dichloromethane, T = 25.0 °C, with 2 min intervals. Inset: The absorbance-time data measured at the indicated wavelengths for the second step. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



**Fig. 4.** Ir(III)-acyl formation (red arrow) as the third step in the oxidative addition reaction between CH<sub>3</sub>I (0.176 M) and (Bu<sub>4</sub>N)[Ir<sub>2</sub>( $\mu$ -Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] (0.024 M), = 25.0 °C and time intervals of 60 min. Inset: The absorbance-time data measured at 1714 cm<sup>-1</sup> for the third step. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



**Fig. 5.** Spectral changes during the reaction between Bu<sub>4</sub>N[ $Ir_2(\mu$ -Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] (4.9 × 10<sup>-4</sup> M) and CH<sub>3</sub>I (0.390 M) in dichloromethane (2 min intervals, 25.0 °C).

#### 2.4. Computational study

Density Functional Theory (DFT) calculations were carried out using the Amsterdam Density Functional 2007 (ADF) program system [20] with the OLYP [21,22] generalized gradient approximation (GGA). The ZORA/TZP [23] (Triple  $\zeta$  polarized) all electron basis set, a fine mesh for numerical integration (5.5 for geometry optimizations and 6.0 for frequency calculations), a spin-restricted (gas-phase) formalism and full geometry optimization with tight convergence criteria as implemented in the ADF 2007 program, were used. Optimized structures were verified as a minimum through frequency calculations. No symmetry limitations were imposed on the calculations.

### 3. Results and discussion

#### 3.1. Synthesis of complexes

The novel dimeric  $(Bu_4N)[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  was obtained by the substitution reaction of CO for PCy<sub>3</sub> in  $(Bu_4N)[Ir_2(\mu-Dcbp)$  $(CO)_4]$ . Since the nitrogen atom of the heterocyclic ring has a larger *trans* influence than the oxygen atom [24], a structure with the PCy<sub>3</sub> group *trans* to N is expected as illustrated in Fig. 1. Symmetric substitution of one CO on each iridium(I) centre is compatible with the single absorption observed at 1932 cm<sup>-1</sup> in the CO region of its infrared spectrum. The results obtained from the chemical analysis

#### Table 2

Kinetic results and activation parameters (forward and reverse) for the oxidative addition reaction between  $CH_3I$  and  $(Bu_4N)[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  at different temperatures in dichloromethane.

Temperature (°C)	$(10^2) k_2 (M^{-1} s^{-1})$	$(10^3) k_{-2} (s^{-1})$	$K_2^{a} (M^{-1})$
15.1	2.46(3)	1.40(3)	17.6(4)
25.0	3.25(4)	2.30(5)	14.1(3)
34.9	5.61(5)	2.50(5)	22.4(5)
$\Delta H^{\neq} (kJ mol^{-1})$ $\Delta S^{\neq} (J K^{-1} mol^{-1})$	28(7) -178(23)	17(9) -238(30)	
	-( - )		

 $\neq$  = Activation.

<sup>a</sup>  $K_2 = k_2/k_{-2}$ .

of the starting complex indicate that a fair presentation of the expected formula has been made. <sup>1</sup>H, spectra also verified the presence of the Dcbp anion through its weak methine signal ( $\delta 6.75$  ppm) whilst the multiplet signals of the phosphine and NBu<sup>4</sup> species dominated the NMR spectrum. <sup>13</sup>C and <sup>31</sup>P NMR are also consistent with the expected formulation of the starting complex.

In order to continue with the identification of the stereochemistry of the di-nuclear  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  complex, a computational study by means of density functional theory has been performed on the three possible isomers of  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$ . The isomer with the PCy<sub>3</sub> groups *trans* to N, as expected from *trans* influence considerations, is the most stable, see Table 1. The most unstable isomer is the isomer with the PCv<sub>3</sub> groups adjacent to each other and *trans* to O, while the most stable isomer has the PCv<sub>3</sub> groups in the sterically unhindered position on the "outside" of the molecule. To further investigation of the sterical effect of the PC<sub>v3</sub> groups, calculations on a simplified version,  $[Ir_2(\mu-Dcbp)]$  $(CO)_2(PH_3)_2$  were performed which led to the same results, suggesting that the trans influence also plays an important role (as opposed to the sterical effect of PCy<sub>3</sub>) in the substitution of the specific CO by a phosphine group in  $[Ir_2(\mu-Dcbp)(CO)_4]^-$ . Structural highlights of  $[Ir_2(\mu-Dcbp)(CO)_2(PX_3)_2]^-$  are presented in Fig. 2. The most significant feature of the structure of the complex is the distortion from planar geometry. The  $\mu$ -Dcbp backbone is still flat as in the uncoordinated µ-Dcbp ligand [25], while the iridium atoms are located slightly above and below the plane of the ligand with an Ir–N–N–Ir dihedral angle of 41.8°. Similar distortion from planar geometry is observed in the crystal structure of [Rh<sub>2</sub>(µ-Dcbp)(CO)<sub>4</sub>]<sup>-</sup> [17], with a dihedral angle of 30.3°. The geometry around the two iridium atoms is square-planar, with iridium located within 0.09 Å from the plane defined by  $P-C_{CO}-N_{Dcbp}-O_{Dcbp}$ , similar as the distance between Rh and the  $C_{CO}-C_{CO}-\dot{N}_{Dcbp}-\dot{O}_{Dcbp}$  plane in



**Fig. 6.**  $k_{obs}$  vs [CH<sub>3</sub>I] for the oxidative addition reaction (alkyl formation) between CH<sub>3</sub>I and (Bu<sub>4</sub>N)[Ir<sub>2</sub>(µ-Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] in dichloromethane (380.0 nm).



**Fig. 7.**  $k_{obs}$  vs [CH<sub>3</sub>I] for the oxidative addition reactions between CH<sub>3</sub>I and (Bu<sub>4</sub>N) [Ir<sub>2</sub>( $\mu$ -Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] (alkyl formation) in different solvents (25 °C).

#### Table 3

Kinetic results for the oxidative addition reactions between CH<sub>3</sub>I and  $(Bu_4N)[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  (alkyl formation) in different solvents at 25.0 °C.

Solvent	$(10^2) k_2 (M^2)$	$^{-1}$ s <sup>-1</sup> ) (10 <sup>3</sup> ) $k_{-2}$ (s <sup>-1</sup>	$^{-1}) K_2^{a} (M^{-1})$	) $\Delta G^{ob} (kJ mol^{-1})$
Dichloromethane	3.25(4)	2.30(5)	14.1(3)	-6.6(1)
Tetrahydrofuran	1.68(2)	0.29(2)	58(4)	-10.0(7)
Chloroform	1.49(4)	1.12(5)	13.3(7)	-6.4(3)
1,2-Dichlorethan	e 1.26(1)	0.33(1)	38(1)	-9.0(2)
Benzene	0.128(6)	0.292(8)	4.38(1)	-3.6 (1)

 $K = k_2/k_{-2}$ .

<sup>b</sup>  $\Delta G^{o} = -RTlnK.$ 

 $[Rh_2(\mu-Dcbp)(CO)_4]^-$ . The dihedral angles formed by the pyrazole ring and the two coordination mean planes are 26.3° (Ir1) and  $-24.9^{\circ}$  (Ir2) (*ca* 20° (Rh1) and  $-10^{\circ}$  (Rh2) for  $[Rh_2(\mu-Dcbp)(CO)_4]^-$ ). A consequence of this distortion is an Ir1-Ir2 distance equal to 4.44 Å (4.53 Å for  $[Rh_2(\mu-Dcbp)(CO)_4]^-$ , which is somewhat longer than *ca* 3.9 Å that was found in related structures with the flat undistorted anions coordinated to two metals (M = Pd, Cu or Zn) [26].

The UV/visible spectra of the complex that was dissolved in the different solvents used in this study, showed no appreciable absorption change within 120 min, indicating the relative stability of the starting complex in these solvents. Upon addition of  $CH_3I$  to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$ , different product species, in equilibrium with the starting complex, were observed on infrared. This equilibrium between the different products and reactant rendered the isolation of any of the products not possible. However, due to the distinct infrared stretching frequency of CO groups [27,28], it was possible to clearly distinguish between alkyl and acyl products as described in the next section. In addition, the different products is further characterised by means of a computational chemistry study. The possibility of side reactions, as well as the stability of the complex was monitored at the solvent OCO stretching frequency of

1658 cm<sup>-1</sup> for the duration of the reaction. These studies indicated that the OCO peak remains fairly stable for the duration of the study which confirmed the stability of the complex.

#### 3.2. Kinetics

#### 3.2.1. Infrared study

The oxidative addition reaction of CH<sub>3</sub>I to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  was first explored on IR since this technique allow to distinguish between metal-CO bonds in M(I)-carbonyl (resonates at ~ 1900–2000 cm<sup>-1</sup>), M(III)-alkyl (resonates at ~ 2000–2100 cm<sup>-1</sup>) and M(III)-acyl (resonates at ~ 1700–1750 cm<sup>-1</sup>) species, M = metal such as Rh [29] or Ir [30]. Three reactions were observed on the IR. The first and second reactions are illustrated in Fig. 3 and the third reaction in Fig. 4.

The addition of CH<sub>3</sub>I to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  resulted in a very fast first reaction which is observed by an initial fast disappearance of the iridium(I) peak at 1932 cm<sup>-1</sup> with the simultaneous formation of a peak at 2004 cm<sup>-1</sup>. This first reaction was too fast to measure on the timescale of the IR.

A second, slower reaction, resulted in the CO peak formation at 2028 cm<sup>-1</sup> (Ir(III) formation) (Fig. 3) with the simultaneous disappearance of the CO peak at 1932 cm<sup>-1</sup> (Ir(I) disappearance) which appears to be shifted to 1942 cm<sup>-1</sup>. Kinetic results performed on the second reaction showed that the reaction rate measures at 1942 cm<sup>-1</sup> (disappearance of CO) of 2.4(1) × 10<sup>-3</sup> s<sup>-1</sup> is within experimental error the same as that at 2028 cm<sup>-1</sup> (formation of alkyl species),  $2.5(1) \times 10^{-3} s^{-1}$  (dichloromethane at 25 °C with [complex] =  $4.9 \times 10^{-4}$  M and [CH<sub>3</sub>I] = 0.0113 M). A *third, very slow reaction* (Fig. 4) resulted in the decrease of the peak at 2028 cm<sup>-1</sup> and the simultaneous  $\nu$ (CO) peak formation at 1714 cm<sup>-1</sup> with an observed rate constant of  $1.1 \times 10^{-5} s^{-1}$  which is attributed to Ir (III)-acyl formation.

Full experimental system



Fig. 8. Possible products of  $CH_3l$  oxidative addition to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  (top) and a simplified model (bottom).

Table 4DFT molecular energies (eV) of selected stereo isomers of  $[(Ir(II)-Ir(II))(\mu-Dcbp)(CO)_2(PX_3)_2(CH_3)(I)]^-$  and  $[(Ir(I)-Ir(III))(\mu-Dcbp)(CO)_2(PX_3)_2(CH_3)(I)]^-$  (X = Cy or H) relative to the lowest energy isomer as zero.

no	Geometry	Energy/eV	
		X = Cy	X = H
1 Trans	$\begin{bmatrix} 0 \\ C \\ C \\ C \\ T \\ T \\ T \\ T \\ T \\ T \\ T$	_	a
3 Cis	$\begin{bmatrix} 0 & & & & 0 \\ 0 & & & & & 0 \\ 0 & & & &$	_	3.79
4 Cis	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	-	2.84
3 Trans	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	_	b
4 Trans	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\$	-	2.71
1 Cis	$\begin{bmatrix} 0 & & & & 0 \\ 0 & & & & & 0 \\ 0 & & & &$	_	2.36

(continued on next page)

#### Table 4 (continued)

no	Geometry	Energy/eV	
		X = Cy	X = H
2 Cis	$\begin{bmatrix} 0 \\ CH_3 \\ N \\ X_3P \\ OC \\ CO \\ PX_3 \end{bmatrix} =$	_	1.95
2 Trans		1.05	1.48
Ir(I)—Ir(III)			
1	$\begin{bmatrix} 0 \\ C \\ C \\ C \\ T_3P \\ H_3C \end{bmatrix} = \begin{bmatrix} 0 \\ T_1 \\ T_2 \\ T_3P \\ T_4 \\ C \\ T_3P \\ T_4 \\ C \\ T_5 \\ T_7 \\ T_$	0.60	0.46
2		0.33	0.39
3	CH <sub>3</sub> NNN V <sub>1</sub> CH <sub>3</sub> NNNN V <sub>1</sub> CH <sub>3</sub> NNN V <sub>1</sub> CH <sub>3</sub> NNNN V <sub>1</sub> CH <sub>3</sub> NNNN V <sub>1</sub> CH <sub>3</sub> NNNN V <sub>1</sub> CH <sub>3</sub> NNNNN V <sub>1</sub> CH <sub>3</sub> NNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNN	0.00	0.00

a = optimized to 2 *cis*.

b = optimized to 4 cis.

Bold = Isomer with lowest relative energy.

An interesting aspect of the final IR spectra is the stable  $\nu$ (CO) peaks at 2028 and 1942 cm<sup>-1</sup> for the duration of the reaction suggesting equilibria during the reaction sequence.

Results obtained from this IR study can be summarized as follows:

- 1. Alkyl 1 convert into Alkyl 2 through an *unobserved* acyl intermediate. This is possible, but highly unlikely.
- Alkyl 1 is actually an Ir(II)–Ir(II) species with the CH<sub>3</sub> bonded to one iridium metal and I to the other. It is not expected that both Ir(I) centres get oxidized to Ir(II) simultaneously during the

Ir(I)-Ir(I) + CH<sub>3</sub>I (excess) 
$$\begin{array}{c} k_1 \\ \hline k_{-1} \\ 1932 \text{ cm}^{-1} \end{array}$$
 Alkyl 1  $\begin{array}{c} k_2 \\ \hline k_{-2} \\ 1942 \text{ cm}^{-1} \end{array}$  Alkyl 2  $\begin{array}{c} k_3 \\ \hline k_{-2} \\ 1942 \text{ cm}^{-1} \end{array}$  Acyl 1942 cm^{-1} and 2004 cm^{-1} \\ \begin{array}{c} 8low \\ 2028 \text{ cm}^{-1} \end{array} 2028 cm^{-1} 1714 cm^{-1}



Fig. 9. The OLYP/TZP optimized geometry of [Ir(1)-Ir(III)(µ-Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(1)]<sup>-</sup>-alkyl 1. Selected bond lengths (Å) and angles (°) are shown. The Ir–N–N–Ir dihedral angle is 33.2°. d(Ir–Ir) = 4.47 Å. H atoms have been omitted for clarity, except for the methyl H.

first, (fast) reaction, since as soon as the first Ir(I) is oxidized to Ir(II), the second Ir(I) will be more difficult to be oxidized.

3. The two alkyl isomers formed are both in equilibrium with the starting complex, possibly a *cis* and *trans* isomer, and that only one of these isomers undergo CO insertion or methyl migration while an equilibrium is maintained with the starting complex. This does not explain the  $\nu$ (CO) peak at 1942 cm<sup>-1</sup>.



4. Alkyl 1 is a mixed Ir(III)–alkyl–Ir(I) species. This gives a logical explanation for the  $\nu$ (CO) peaks at 2004 and 1942 cm<sup>-1</sup>; the  $\nu$ (CO) peak at 2004 cm<sup>-1</sup> due to the CO bonded to Ir(III) and the  $\nu$ (CO) peak at 1942 cm<sup>-1</sup> due to the CO bonded to Ir(I).

#### 3.2.2. UV/visible study

The UV/visible spectra (Fig. 5) of the reaction between (Bu<sub>4</sub>N)  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  and methyl iodide indicated two clearly distinguishable reactions within the first 30 min. A fairly quick spectrum change in Fig. 5 (a to b) resulted after the addition of CH<sub>3</sub>I to the metal complex. A subsequent slower spectrum change (b to c) was observed which also resulted in the formation of isosbestic points at 399 and 414 nm in the UV/visible spectra. The isosbestic point, which was detected for the second slower part of

the oxidative addition reaction, implies that only one product is formed during this reaction. A comparison of the kinetic results obtained from the UV/visible and IR indicated that the second reaction observed in the UV/visible region corresponds to the Ir (III)-alkyl formation ( $\nu$ (CO) at 2028 cm<sup>-1</sup>) with observed rate constants of 2.6 × 10<sup>-3</sup> (UV) and 2.5 × 10<sup>-3</sup> s<sup>-1</sup> (IR) respectively ([CH<sub>3</sub>I] = 0.01 M).

A third, much slower reaction (not shown in Fig. 5) was also observed on UV/visible with an observed rate constant of  $1.42 \times 10^{-5} \, \rm s^{-1}$  ( $t_{1/2} = 13.6$  h), which is of the same order as the Ir (III)-acyl formation reaction observed on IR ( $\nu$ (CO) stretching frequency growth at 1714 cm<sup>-1</sup>) with observed rate constant of  $1.1 \times 10^{-5} \, \rm s^{-1}$  ([CH<sub>3</sub>I] = 0.35 M). The long half-life of this reaction implied that it could not be followed with great accuracy due to, for example, evaporation problems of the solvent. The first (fast) reaction was investigated with a stopped-flow method, but the results were inconclusive.

The second slower reaction, corresponding to the Ir(III)-alkyl 2 formation (2028 cm<sup>-1</sup>) reaction on IR, was followed at three different temperatures on the UV/visible (380 nm) to ascertain the activation parameters for this reaction. Since the second reaction was much slower than the first reaction, and much faster that the third reaction, the kinetic data of the second reaction could be treated in isolation from the other reactions. From the results obtained under pseudo first order conditions, shown in Fig. 6, it is clear that the rate law  $k_{obs} = k_2[CH_3I] + k_{-2}$  (see Equation (2)) gives a fair presentation of the reaction (straight line) and that the substantial intercept is interpreted as the reverse reaction i.e. the dissociation of the CH<sub>3</sub>I from the Ir centre. Results are tabulated in Table 2.

#### 3.2.3. Solvent study

A solvent study was also performed on the second reaction, the alkyl 2 formation reaction, to try and find valuable information on the transition state of the complex. Five different solvents with a wide variety of dielectric constants and donocity properties were selected and the oxidative addition reaction between Bu<sub>4</sub>N

#### Table 5

DFT molecular energies (eV) of the selected alkyl stereo isomers of  $[(Ir(III)-Ir(III))(\mu-Dcbp)(CO)_2(PX_3)_2(CH_3)_2(I)_2]^-$  (X = Cy or H) relative to the lowest energy isomer as zero.



Bold = Isomer with lowest relative energy.

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ČΗ<sub>3</sub>

 $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]$  and CH<sub>3</sub>I were studied at 25 °C. The results are presented in Fig. 7 while the calculated rate constants and activation parameters are given in Table 3.

Results obtained from the solvent variation study (Fig. 7 and Table 3) show the influence of both the polarity and donocity of the different solvents on the oxidative addition reaction. The results clearly show a 25x increase in reaction rate when the reaction is performed in halogenated solvents (polar solvents) compared to that of benzene (non-polar) which is substantially smaller than that observed for the same reaction in the case of  $[Ir(\mu-pz)_2(CO)_4]$ , where an increase of up to a factor of  $10^3$  was observed when more polar solvents were used during the oxidative addition reaction. These relative moderate increases in oxidative addition reaction rate are normally an indication that a concerted three centre transition state was formed during the reaction.

#### 3.2.4. Computational study

Oxidative addition of CH<sub>3</sub>I to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  may lead to different alkyl species. Ignoring the stereochemistry, three possible alkyl products can be envisioned, see Fig. 8. While only 3 isomeric forms of the Ir(I)–Ir(I) reactant complex is possible, 36 isomers of the Ir(II)–Ir(I) complex, 48 isomers of the Ir(I)–Ir(III) complex and 576 isomers (enantiomers included) of the Ir(II)–Ir(III) complex are possible! To calculate the optimized geometry of each of these isomers (the Ir(III)–Ir(III) complex has 132 atoms!) by means of computational chemistry, such as DFT, is thus a senseless project when taking the computational hours needed into account. Therefore we first calculate the relative energies of simplified versions where the PCy<sub>3</sub> group is substituted for PH<sub>3</sub> in the full model (Fig. 8 bottom).

Test calculations on both the full as well as the simplified system indicated that complexes with both the PCy<sub>3</sub> (full model) or PH<sub>3</sub> (simplified model) groups on the "outside" position of the complex, as was found for the Ir(I)–Ir(I) starting complex (Fig. 2) are *ca* 1 eV more stable than isomers having the PCy<sub>3</sub> (full model) or PH<sub>3</sub> (simplified model) groups in other positions. Calculations on all isomers with the PH<sub>3</sub> (simplified model) groups on the "outside"

position of the complex were performed in order to identify the more stable isomers. Calculations on the most stable isomers were repeated for the full experimental system. Results for selected alkyl addition products resulting from one CH<sub>3</sub>I molecule addition are presented in Table 4. From the relative energies given in Table 4 it is clear that all Ir(I)–Ir(III) alkyl products are more stable than the Ir (II)–Ir(II) products. This finding is in agreement with the IR results presented above that Alkyl 1 is a mixed Ir(III)–alkyl–Ir(I) species. The first product of the oxidative addition reaction to [Ir<sub>2</sub>( $\mu$ -Dcbp) (CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, the Alkyl 1 species, is thus a mixed Ir(III)–alkyl–Ir (I) complex. The computational results further indicate that *trans* addition to one of the iridium metal centres occurs. The optimized geometry of the [Ir(1)-Ir(III)( $\mu$ -Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(I)]<sup>-</sup>-alkyl 1 is presented in Fig. 9.

Addition of another CH<sub>3</sub>I molecule to the mixed Ir(III)-alkyl-Ir (I) (Alkyl 1) lead to a Ir(III)–Ir(III)-alkyl product, or the mixed Ir(III)alkyl–Ir(I) could first isomerizes to form an Ir(III)-acyl–Ir(I) species. The possibility of the formation of an Ir(III)-acyl-Ir(I) species is however discarded, since the energy of the optimized Ir(III) $acyl-Ir(I) + CH_3I$  species is much higher than that of the Ir(III)-Ir (III)-alkyl product, see Fig. 11. In Table 5 selected alkyl addition products of two CH<sub>3</sub>I molecules to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$ , as well as their relative energies, are given. The energy of the most stable [Ir(III)-Ir(III)(µ-Dcbp)(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>(I)<sub>2</sub>]<sup>-</sup> isomer, presumable the Alkyl 2 product observed on IR, is slightly higher (0.13 eV) than that of the mixed Ir(III)-alkyl-Ir(I) (Alkyl 1) + CH<sub>3</sub>I (Fig. 11), in agreement with a fast equilibrium between Ir(I)-Ir(I) and the mixed Ir(III)-alkyl-Ir(I) (Alkyl 1) species, leading to the Ir (III)-Ir(III)-alkyl (Alkyl 2) product of oxidative addition. The computational results further indicate that trans addition of CH<sub>3</sub>I to both the iridium metal centres occurs, with the two iodide ions trans to each other. The optimized geometry of [Ir(III)-Ir(III)(µ- $Dcbp)(CO)_2(PCy_3)_2(CH_3)_2(I)_2]^--alkyl 2 is presented in Fig. 10.$ 

CO insertion in  $[Ir(III)-Ir(III)(\mu-Dcbp)(CO)_2(PCy_3)_2(CH_3)_2(I)_2]^{-}$  alkyl 2 leads to an acyl product, as observed on IR. To further identification of the stereochemistry of the acyl product, density functional theory calculations have also been performed on



**Fig. 10.** The OLYP/TZP optimized geometry of  $[Ir(III)-Ir(III)(\mu-Dcbp)(CO)_2(PCy_3)_2(CH_3)_2(I)_2]^-$ -alkyl 2. Selected bond lengths (Å) and angles (°) are shown. The Ir–N–N–Ir dihedral angle is 27.9°. d(Ir–Ir) = 4.53 Å. H atoms have been omitted for clarity, except for the methyl H.



Fig. 11. The calculated reaction pathway for the CH<sub>3</sub>I oxidative addition to  $[Ir_2(\mu$ -Dcbp) (CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>]<sup>-</sup>.

selected Ir(III)—Ir(III) acyl isomers (Table 6). Again it was found that acyl species with the PCy<sub>3</sub> groups on the "outside" position of the complex are more stable than isomers having the PCy<sub>3</sub> groups in other positions by at least 1 eV. The optimized geometry of the lowest energy  $[(Ir(III)-Ir(III))(\mu-Dcbp)(PX_3)_2(COCH_3)_2(I)_2]^-$ -acyl isomer is presented in Fig. 12.

Both the acyl moieties are above the ligand plane with one of the iodide ions in and the other below the ligand plane. The rearrangement of the ligands attached to iridium led to a geometry with the Ir–N–N–Ir dihedral angle reduced to 4.0°. The geometry around the two iridium atoms is square pyramidal. The base of the one pyramid is in the  $\mu$ -Dcbp ligand plane, but the other is perpendicular to it with C<sub>COCH3</sub> and O<sub> $\mu$ -Dcbp</sub> in the apical positions of the two pyramids respectively. Such an arrangement has the least sterical strain in the  $\mu$ -Dcbp backbone and the least sterical interaction between the groups attached to iridium. Results obtained for the most stable [(Ir (III)-Ir(III))( $\mu$ -Dcbp)(PH<sub>3</sub>)<sub>2</sub>(COCH<sub>3</sub>)<sub>2</sub>(I)<sub>2</sub>]<sup>–</sup>-acyl isomer for the simplified system with much less sterical strain, were not in agreement with the results obtained for the full experimental system.

#### 3.2.5. Proposed mechanistic pathway

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The most probable mechanistic pathway for the overall oxidative addition of  $CH_3I$  to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$ , taking into account all the information that was obtained from the IR spectra and DFT calculations and which are presented in Scheme 1, is used to interpret the observed rate constant for the reactions. Using the following observations

- a) fast oxidative addition step  $(k_1/k_{-1}$  path, the  $\nu$ (CO) at 1942 cm<sup>-1</sup> and shoulder formation at 2004 cm<sup>-1</sup>)
- b) a slower oxidative addition step ( $k_2/k_{-2}$  path,  $\nu$ (CO) formation at 2028 cm<sup>-1</sup>)
- c) a very slow carbonyl insertion/methyl migration reaction ( $k_3$ ) to form the Ir(III)–Ir(III) acyl product ( $\nu$ (CO) formation at 1714 cm<sup>-1</sup>)

the rate of disappearance of the [Ir(I)-Ir(III)] complex can be expressed as follows:

$$\begin{aligned} \text{Rate} &= K_2[\text{Ir}(\text{I}) - \text{Ir}(\text{III})][\text{CH}_3\text{I}] + K_{-1}[\text{Ir}(\text{I}) - \text{Ir}(\text{III})][\text{CH}_3\text{I}] \\ &- K_1[\text{Ir}(\text{I}) - \text{Ir}(\text{I})][\text{CH}_3\text{I}] - K_{-2}[\text{Ir}(\text{III}) - \text{Ir}(\text{III})] \end{aligned} \tag{1}$$

#### Table 6

DFT molecular energies (eV) of the selected acyl stereo isomers of [(Ir(III)-Ir(III))( $\mu$ -Dcbp)(PX<sub>3</sub>)<sub>2</sub>(COCH<sub>3</sub>)<sub>2</sub>(I)<sub>2</sub>]<sup>-</sup> (X = Cy or H) relative to the lowest energy isomer as zero.



a = Optimized to 5 acyl.

b = Optimized to 2 acyl.

Bold = Isomer with lowest relative energy.

The second reaction can be treated in isolation due to the very fast first reaction and the very slow third reaction. Under pseudo-first order conditions,  $[Ir-Ir] < < < [CH_3I]$  and integration, Equation (2) can be obtained

$$k_{\rm obs} = k_2 [{\rm CH}_3 {\rm I}] + k_{-2}$$
 (2)

A graph of  $k_{obs}$  vs [CH<sub>3</sub>I] will yield a straight line with slope =  $k_2$  and intercept  $k_{-2}$  as indicated in Fig. 6 and the results reported in Table 2. It was decided to concentrate on the  $k_2/k_{-2}$  pathway in this study.

The forward rate constant for Ir(III) alkyl 2 formation of 3.25  $(4) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} (25.0 \text{ °C} \text{ in dichloromethane})$  is smaller than the corresponding reaction for the  $(Bu_4N)[Ir_2(\mu-Dcbp)(cod)_2]$  complex



**Fig. 12.** The OLYP/TZP optimized geometry of  $[Ir(III)-Ir(III)(\mu-Dcbp)(PCy_3)_2(COCH_3)_2(I)_2]^-$ -acyl. Selected bond lengths (Å) and angles (°) are shown. The Ir–N–N–Ir dihedral angle is 4.0°. d(Ir–Ir) = 4.18 Å. H atoms have been omitted for clarity, except for the methyl H.

 $(7.0(1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1})$  [16], while the reverse reactions are comparable in magnitude. This decrease in Ir(III)-alkyl 2 formation rate for the title complex are an indication of deactivation by the PCy<sub>3</sub>/CO ligand combination towards the Ir(I) centre compared to the cod ligands in the (Bu<sub>4</sub>N)[Ir<sub>2</sub>(µ-Dcbp)(cod)<sub>2</sub>] complex. The positive activation enthalpy for the  $k_2$  path (see Table 2) of 28 (7) kJ mol<sup>-1</sup> is indicative of an associative mechanism while the negative activation entropy(-178(23) JK<sup>-1</sup> mol<sup>-1</sup>) corresponds to CH<sub>3</sub>–I bond dissociation and which is associated with a polar transition state. These results corresponds favourably with that obtained

by Stobart et al. [31] that was obtained for the oxidative addition reactions between CH<sub>3</sub>I and  $[Ir(\mu-pz)_2(CO)_4]$  (32(2) kJ mol<sup>-1</sup> and -152(8) JK<sup>-1</sup> mol<sup>-1</sup> respectively). The negative activation entropy obtained for the reductive elimination step ( $k_{-2}$  path) is contrary to what is expected due to the fact that both the Ir–CH<sub>3</sub> and Ir–I bonds need to break to from the CH<sub>3</sub>I molecule. A possible explanation for this negative activation entropy is the probable coordination of solvent molecules during the transition state formation.

The rate of acyl formation  $(1.42 \times 10^{-5} \text{ s}^{-1})$  is clearly indicative of a complex which is deactivated towards CO insertion or methyl



Scheme 1. Reaction pathway for the  $CH_3I$  oxidative addition to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  as obtained by an IR and computational study.

migration if compared to reaction rates of complexes such as  $[Rh(acac)(CO)(PPh_3)]$  (1.6 × 10<sup>-3</sup> s<sup>-1</sup>),  $[Rh(hpt)(CO)(PPh_3)]$  (1.0 × 10<sup>-2</sup> s<sup>-1</sup>) [32] (hpt = thiohydroxamate anion) [18] and  $[Rh(tta)(CO)(PPh_3)]$  (1.8 × 10<sup>-3</sup> s<sup>-1</sup>) (tta = 2-thenoyltrifluoroacetonato) [29]. The relative large  $K_2$  values (Table 3) points to a situation where the equilibrium lies to the right and that  $k_{obs} = k_2$ .

#### 4. Conclusions

Combining the results obtained from an IR study for the  $CH_{3I}$  oxidative addition to  $[Ir_2(\mu-Dcbp)(CO)_2(PCy_3)_2]^-$  with the results obtained from a computational chemistry study, led to the reaction scheme which is proposed in Scheme 1.

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#### **Appendix A. Supplementary material**

Optimized Cartesian coordinates for selected systems can be found in the online version, at doi:10.1016/j.jorganchem.2010.10.049.

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