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## Rhodium(I) and iridium(I) complexes with 1,2-bis(dicyclohexylphosphino)ethane ligands, and their reactions with carbon monoxide

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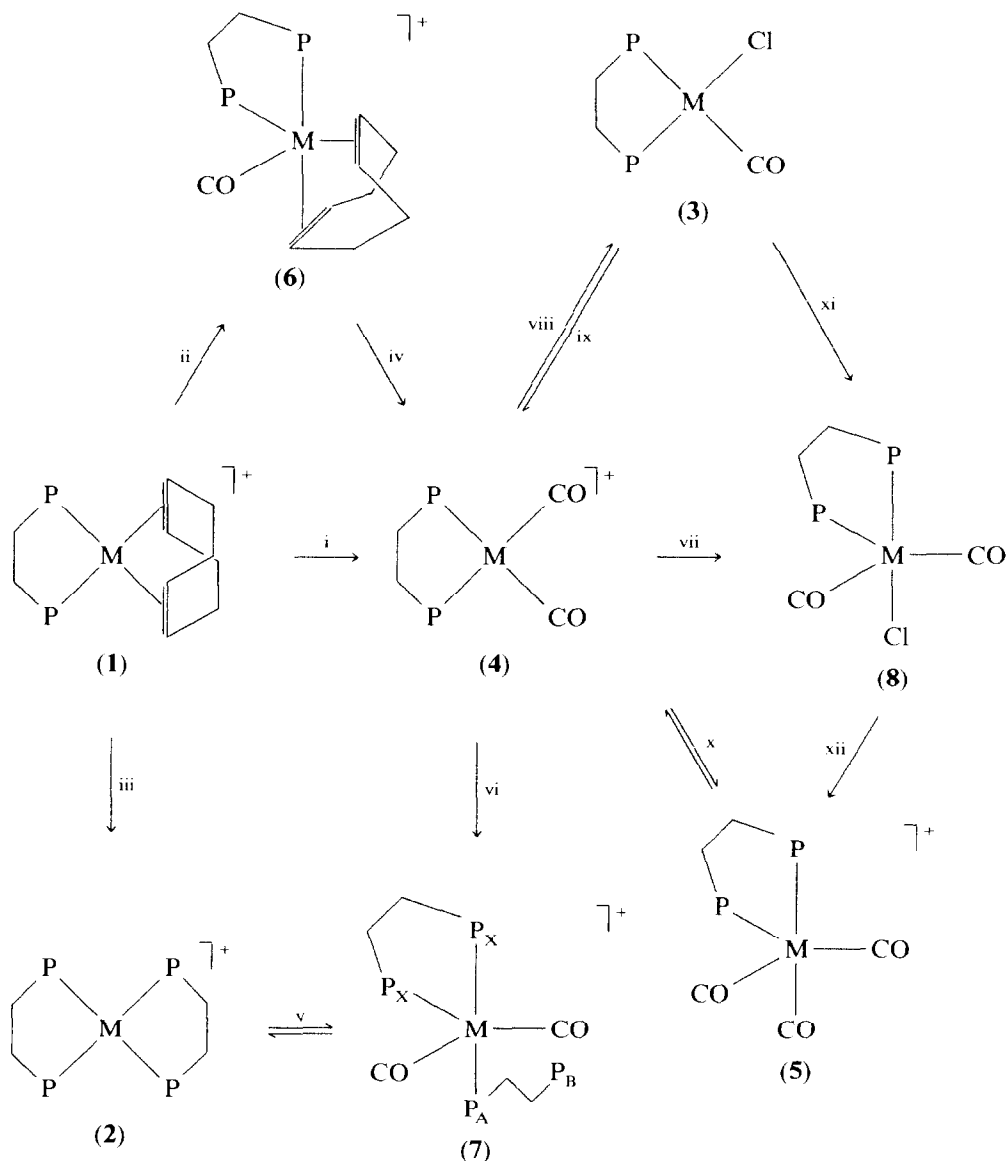
### Abstract

The ditertiary-phosphine 1,2-bis(dicyclohexylphosphino)ethane (dcpe) has been shown to form the mononuclear, square-planar rhodium(I) and iridium(I) complexes  $[M(\text{COD})(\text{dcpe})]\text{BPh}_4$  (COD = 1,5-cyclooctadiene),  $[M(\text{dcpe})_2]\text{BPh}_4$ , and  $[M\text{Cl}(\text{CO})(\text{dcpe})]$ , which have been characterized by elemental analyses, infrared, and  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Their behaviour toward carbon monoxide in dichloromethane solution at different temperatures was examined, and the nature of the products formed established by IR and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Some of the products, including  $[M(\text{CO})_2(\text{dcpe})]\text{BPh}_4$  and  $[\text{Ir}(\text{COD})(\text{CO})(\text{dcpe})]\text{BPh}_4$ , were isolated in the solid state and fully characterized. The catalytic activity of the rhodium derivatives in the decarbonylation of benzaldehyde has been studied, and compared with that of the analogous complexes containing phenyl-substituted diphosphines.

### Introduction

Several complexes of rhodium(I) and iridium(I) with diphosphine ligands have been reported and extensively studied [1,2], particularly in respect of their use in the activation of small molecules and their relevance in homogeneous catalysis [3]. Most work has been done with the bis(tertiary-phosphine) ligand system  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$ , dppm;  $n = 2$ , dppe;  $n = 3$ , dppp;  $n = 4$ , dppb) which forms complexes in which the ligand either chelates a single metal center or bridges two metal atoms. Monomeric chelate complexes are commonly formed when  $n = 2$ , while when  $n = 1, 3, 4$  dimeric derivatives are also obtained [4–8]. Apparently the geometry and the reactivity of these species depend on the chelate ring strain, flexibility, and electronic properties of the diphosphine. In order to gain a better understanding of the factors affecting the behaviour of these compounds, we have investigated the rhodium and iridium complexes containing the diphosphine 1,2-bis(dicyclohexylphosphino)ethane (dcpe). This ligand is attractive because it provides both increased basicity and increased crowding at the metal centre. It was expected that the bulkiness of the substituents at the phosphorus atom might facilitate the dissociation of the  $-\text{PCy}_2$  groups to give coordinatively unsaturated species; it is

known that in complexes of this type the inter-ligand repulsions cause lengthening of the M–P bonds and significant distortion from the expected geometry [4b,9]. Moreover, the dcpe complexes are expected to be more electron-rich than their  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  analogues. This should facilitate oxidative addition, a key step in



Scheme 1. P–P = dcpe, M = Rh or Ir. (i) CO in  $\text{CH}_2\text{Cl}_2$  at room temperature, M = Rh, Ir; (ii) CO in  $\text{CH}_2\text{Cl}_2$  at  $T < -10^\circ\text{C}$ , M = Ir; (iii) P–P in  $\text{CH}_2\text{Cl}_2$ , M = Rh; (iv) CO in  $\text{CH}_2\text{Cl}_2$ , M = Ir; (v) CO in  $\text{CH}_2\text{Cl}_2$ , M = Ir; (vi) P–P in  $\text{CH}_2\text{Cl}_2$ , M = Ir; (vii)  $\text{NBu}_4\text{Cl}$  in acetone, M = Ir; (viii)  $\text{NBu}_4\text{Cl}$  in acetone, M = Rh; (ix) CO in ethanol, M = Rh; (x) CO in  $\text{CH}_2\text{Cl}_2$ , M = Ir; (xi) CO in  $\text{CH}_2\text{Cl}_2$  at low temperature, M = Ir; (xii) CO in  $\text{CH}_2\text{Cl}_2$  at room temperature, M = Ir.

many homogeneously catalyzed reactions, such as hydrogenation, hydroformylation, and decarbonylation [3].

We report here the synthesis and characterization of the novel rhodium and iridium complexes  $[M(\text{COD})(\text{dcpe})]\text{BPh}_4$  (**1**) (COD = 1,5-cyclooctadiene),  $[M(\text{dcpe})_2]\text{BPh}_4$  (**2**),  $[\text{MCl}(\text{CO})(\text{dcpe})]$  (**3**), and  $[M(\text{CO})_2(\text{dcpe})]\text{BPh}_4$  (**4**). The reactions of these complexes with carbon monoxide at various temperatures were studied by IR and NMR spectroscopy (Scheme 1). The catalytic activity of the rhodium derivatives in the decarbonylation of benzaldehyde has also been briefly investigated, and compared with that of the analogous complexes containing phenyl-substituted diphosphines [10].

## Results and discussion

### Synthesis and characterization

The complexes **1–3** were made by procedures similar to those previously reported. Treatment of dichloromethane solutions of the dimeric complexes  $[\text{MCl}(\text{COD})]_2$  with one equivalent of dcpe gives orange or red solutions from which the compounds  $[M(\text{COD})(\text{dcpe})]\text{BPh}_4$  ( $M = \text{Rh}$ , **1a**;  $M = \text{Ir}$ , **1b**) are isolated after addition of sodium tetraphenylborate. When an excess of dcpe is used, a further reaction occurs in the case of rhodium, involving displacement of the diene and formation of the bis(diphosphino) derivative  $[\text{Rh}(\text{dcpe})_2]\text{BPh}_4$  (**2a**). However, the latter complex is more conveniently prepared from  $[\text{RhCl}(\text{CO})_2]_2$ . By contrast, dcpe is ineffective at displacing the coordinated COD molecule from the iridium derivative **1b** but the complex  $[\text{Ir}(\text{dcpe})_2]\text{BPh}_4$  (**2b**) was obtained in nearly quantitative yield by the room-temperature reaction of *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  with two equivalents of dcpe in dichloromethane/ethanol in the presence of  $\text{NaBPh}_4$ . The neutral compound  $[\text{RhCl}(\text{CO})(\text{dcpe})]$  (**3a**) can be obtained by reaction in benzene solution between dcpe and  $[\text{RhCl}(\text{CO})_2]_2$  in 1 : 1 ratio, though the yield is poor owing to the competing formation of the bis(chelate) complex  $[\text{Rh}(\text{dcpe})_2]\text{Cl}$ . The analogous derivative  $[\text{IrCl}(\text{CO})(\text{dcpe})]$  (**3b**) separates as yellow crystals when Vaska's compound *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  is stirred with an equimolar amount of dcpe in benzene solution. It is noteworthy that, when the same reaction is carried out with dppe, the bis(chelate)  $[\text{Ir}(\text{dppe})_2]^+$  is the only product [7e].

The complexes **1–3** were characterized by elemental analyses, and IR,  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (Table 1); species **1** and **2** were found to be 1 : 1 electrolytes in nitromethane. Their formulation as monomeric complexes containing chelating dcpe ligands is consistent with the large downfield  $^{31}\text{P}$  coordination chemical shifts  $[\delta(^{31}\text{P}_{\text{coord}}) - \delta(^{31}\text{P}_{\text{free ligand}})]$ , which are typical of five-membered chelate rings [11]. No binuclear species containing bridging diphosphines are observed. Like the analogous ligand dppe, dcpe shows a strong preference for acting as a chelating ligand, probably owing to the high stability of the five-membered chelate ring.

The  $^{31}\text{P}\{^1\text{H}\}$  spectra of the rhodium(I) derivatives **1a** and **2a** show a doublet at 67.7 [ $J(\text{Rh}-\text{P}) = 145.2$  Hz] and 66.0 ppm [ $J(\text{Rh}-\text{P}) = 129.4$  Hz], respectively, while those of the iridium analogues **1b** and **2b** show a singlet at ca. 57 ppm. Both patterns are indicative of equivalent phosphorus atoms. The presence of a chelating 1,5-cyclooctadiene ligand in complexes **1** is supported by the  $^1\text{H}$  NMR spectra, which show two broad resonances, integrating in a 2 : 1 ratio, centred at 2.29 and 5.26 ppm

Table 1  
 IR and  $^{31}\text{P}$  NMR data

Complex	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) <sup>a</sup>	$\delta$ (ppm) <sup>b</sup>	$J(\text{Rh}-\text{P})$ (Hz)	$J(\text{P}-\text{P}')$ (Hz)
[Rh(COD)(dcpe)]BPh <sub>4</sub> ( <b>1a</b> )		67.7 (d)	145.2	
[Ir(COD)(dcpe)]BPh <sub>4</sub> ( <b>1b</b> )		57.1 (s)		
[Rh(dcpe) <sub>2</sub> ]BPh <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub> ( <b>2a</b> )		66.0 (d)	129.4	
[Ir(dcpe) <sub>2</sub> ]BPh <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub> ( <b>2b</b> )		56.9 (s)		
[RhCl(CO)(dcpe)] ( <b>3a</b> )	1977, 1966; 1992 <sup>c</sup>	69.4 (dd), 93.2 (dd)	124.5, 156.2	25.6
[IrCl(CO)(dcpe)]·C <sub>6</sub> H <sub>6</sub> ( <b>3b</b> )	1966, 1955, 1982 <sup>c</sup>	62.2 (d), 64.4 (d)		8.8
[Rh(CO) <sub>2</sub> (dcpe)]BPh <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub> ( <b>4a</b> )	2086, 2027	85.2 (d)	116.2	
[Ir(CO) <sub>2</sub> (dcpe)]BPh <sub>4</sub> ( <b>4b</b> )	2076, 2014	73.1 (s)		
[Ir(CO) <sub>3</sub> (dcpe)]BPh <sub>4</sub> ( <b>5b</b> )	2091, 2027, 2006 <sup>c</sup>	57.4 (s)		
[Ir(CO)(COD)(dcpe)]BPh <sub>4</sub> ( <b>6b</b> )	1988	32.7 (s)		
[Ir(CO) <sub>2</sub> (dcpe) <sub>2</sub> ]BPh <sub>4</sub> ( <b>7b</b> )	2002, 1947 <sup>c</sup>	1.3(m), 4.8(m), 33.8(m) <sup>d</sup>		<sup>e</sup>
[IrCl(CO) <sub>2</sub> (dcpe)] ( <b>8b</b> )	2021, 1963 <sup>c</sup>	55.5 (s) <sup>f</sup>		

<sup>a</sup> In Nujol mulls, unless otherwise stated. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution, at 308 K; multiplicity given in parentheses: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>d</sup> For P<sub>A</sub>, P<sub>B</sub>, and P<sub>X</sub>, respectively, see Scheme 1. <sup>e</sup>  $J(\text{P}_A-\text{P}_B)$ ,  $J(\text{P}_A-\text{P}_X)$ , and  $J(\text{P}_B-\text{P}_X)$  are 34.2, 89.0, and 6.1 Hz, respectively. <sup>f</sup> At 193 K.

for **1a**, and 2.09 and 4.89 ppm for **1b**. The  $^{31}\text{P}\{^1\text{H}\}$  spectra of complexes **3** exhibit the pattern expected for two inequivalent phosphorus atoms in a *cis* disposition. The  $^{31}\text{P}$  NMR spectrum of **3a** contains two doublets of doublets centred at 69.4 [ $J(\text{Rh}-\text{P}) = 124.5$  Hz] and 93.2 ppm [ $J(\text{Rh}-\text{P}') = 156.2$  Hz] with a  $J(\text{P}-\text{P}')$  of 25.6 Hz. The signal at 69.4 ppm is assigned to the  $-\text{PCy}_2$  group *trans* to the  $\pi$ -acceptor ligand CO. Similarly the spectrum of **3b** shows two doublets centred at 62.2 and 64.4 ppm [ $J(\text{P}-\text{P}') = 8.8$  Hz]. Similar chemical shift differences between P *trans* to CO and P *trans* to Cl have been reported for the dppe analogues [6b,6f,7e]. The IR spectra in dichloromethane solution show a strong absorption in the CO stretching region at 1992 and 1982  $\text{cm}^{-1}$  for **3a** and **3b**, respectively. In Nujol mull the signal is split, probably due to solid-state effects. The lowering of the  $\nu(\text{CO})$  stretching frequency if compared with that for the dppe complexes reflects the higher basicity of the dcpe ligand.

### Reactions with carbon monoxide

The room temperature reactions of the cyclooctadiene derivatives **1** with carbon monoxide in dichloromethane give the square-planar dicarbonyls  $[\text{M}(\text{CO})_2(\text{dcpe})]\text{BPh}_4$  (M = Rh, **4a**; M = Ir, **4b**), which can be precipitated by addition of 2-propanol. The compounds are air-stable, and their conductivities in nitromethane are those expected for 1 : 1 electrolytes. In keeping with a planar *cis*-geometry, their IR spectra show two strong and sharp  $\nu(\text{CO})$  bands in the range 2010–2090  $\text{cm}^{-1}$  both in solution and in the solid state. The  $^{31}\text{P}$  NMR resonance of the chelating dcpe appears as a doublet at 85.2 ppm [ $J(\text{Rh}-\text{P}) = 116.2$  Hz] for **4a** and as a singlet at 73.1 ppm for **4b**. The reactions between complexes **1** and carbon monoxide were monitored by IR and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. When the cyclooctadiene deriva-

tive **1a** is dissolved in dichloromethane under a carbon monoxide atmosphere, a yellow solution is obtained, with immediate and quantitative conversion into the dicarbonyl derivative **4a**, as indicated by the  $^{31}\text{P}\{^1\text{H}\}$  and IR spectra. In the case of the iridium derivative **1b** the reaction with carbon monoxide gives a colourless solution, whose IR spectrum shows three bands at 2091, 2027, and 2006  $\text{cm}^{-1}$  in the  $\nu(\text{CO})$  stretching region. A single resonance is observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, at 57.4 ppm and this is essentially unchanged on cooling to  $-80^\circ\text{C}$ . If the CO concentration is lowered by purging the solution with argon, the signals typical of the dicarbonyl **4b** appear in the IR and NMR spectra, suggesting the presence of an equilibrium between **4b** and a tricarbonyl derivative of the type  $[\text{Ir}(\text{CO})_3(\text{dcpe})]^+$  (**5b**). Owing to the lability of a carbonyl ligand, we were unable to obtain **5b** pure in the solid state. Like most five-coordinate  $d^8$  metal complexes, the  $[\text{Ir}(\text{CO})_3(\text{dcpe})]^+$  cation probably has a fluxional trigonal-bipyramidal structure, with the dcpe ligand spanning axial and equatorial positions.

The mechanism of displacement of diolefin by CO in complexes **1** probably involves formation of a five-coordinate intermediate,  $[\text{M}(\text{CO})(\text{COD})(\text{dcpe})]^+$  (**6**), with subsequent loss of the COD molecule and formation of the final product. The intermediate **6** was isolated in the case of iridium. When crystals of **1b** are stored under a carbon monoxide atmosphere, the red colour slowly fades and a cream solid is formed; this compound, which analyses as  $[\text{Ir}(\text{COD})(\text{CO})(\text{dcpe})]\text{BPh}_4$  (**6b**), does not lose CO under reduced pressure either in the solid state or in solution. The same product can be obtained if the reaction between **1b** and CO is carried out in solution at low temperature ( $< -10^\circ\text{C}$ ). Complex **6b** was characterized by IR and variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. A single CO stretch is present at 1988  $\text{cm}^{-1}$ , and the  $^{31}\text{P}\{^1\text{H}\}$  room-temperature spectrum in dichloromethane solution shows a singlet at 32.7 ppm. When the sample is cooled to  $-90^\circ\text{C}$  only a slight broadening is observed. Like the other five-coordinate complexes containing only one dcpe ligand, complex **6b** appears to be highly fluxional on the NMR time-scale, and we tentatively suggest a trigonal bipyramidal structure with the CO ligand in an equatorial position, in keeping with the theoretical treatment which suggests that stronger  $\pi$ -acid ligands prefer equatorial sites [12]. Complex **6b** reacts rapidly with CO at room temperature in dichloromethane solution to form the tricarbonyl **5b**.

The rhodium derivative **2a** is unreactive toward carbon monoxide under pressures as high as 40 atm in dichloromethane at room temperature. Such behaviour was previously observed for  $[\text{Rh}(\text{dppe})_2]^+$ , but appears anomalous in the light of the behaviour of the series of the four-coordinate bis(diphosphino) complexes  $[\text{M}(\text{L}-\text{L})_2]^+$  ( $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{L}-\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ;  $n = 1, 2, \text{ or } 3$ ), which generally add carbon monoxide yielding the five-coordinate adducts  $[\text{M}(\text{CO})(\text{L}-\text{L})_2]^+$ . The unreactivity of **2a** is probably due to steric factors, as suggested for the dppe analogue [6e,13]. By contrast, the iridium derivative **2b** readily reacts with carbon monoxide in dichloromethane solution. However, instead of a monocarbonyl, the dicarbonyl derivative  $[\text{Ir}(\text{CO})_2(\text{dcpe})_2]^+$  (**7b**) is formed, as shown by the appearance of two  $\nu(\text{CO})$  bands, at 2002 and 1947  $\text{cm}^{-1}$ , in the IR spectrum. A monocarbonyl adduct is not observed even when the reaction between **2b** and carbon monoxide is carried out at  $-80^\circ\text{C}$ , the dicarbonyl **7b** being the only product detected. An interesting feature of this carbonylation reaction is its reversibility; vigorous purging of the solution with argon slowly removes the coordinated CO. Another route to **7b** involves the reaction of dicarbonyl **4b** with a stoichiometric amount of dcpe.

Complex **7b** could not be obtained pure in the solid state, and so it was characterized in solution by IR and variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  spectroscopy. On the basis of the relative intensities of the symmetric and antisymmetric CO stretching vibrations, a value of  $130^\circ$  can be calculated for the OC–Ir–CO angle [14]. The  $^{31}\text{P}\{^1\text{H}\}$  spectrum shows a complex pattern, which can be reproduced by computer simulation on the bases of an  $\text{ABX}_2$  spin system. The low-field signals centred at 33.8 ppm can be attributed to the P atoms of a chelating dcpe, while the high-field ones are assigned to the P atoms of a dangling monodentate diphosphine. These results suggest a trigonal-bipyramidal structure with two equatorial CO ligands in which the chelate dcpe ligand spans axial and equatorial positions. An intramolecular exchange between axial and equatorial phosphorus atoms ( $\text{X}_2$  part of the spin system), which appears to be rapid at room temperature on the NMR time-scale, accounts for the equivalence of the phosphorus atoms of the chelating dcpe, and for the  $J(\text{P}-\text{P}')$  value of 89.0 Hz, which results from the average of  $J(\text{P}_a-\text{P}_e)$  and  $J(\text{P}_a-\text{P}_a)$  values (a = axial, e = equatorial). It should be noted that the coordination chemical shift of the P atom of the dcpe ligand acting as monodentate is, unusually, very close to zero. When the temperature is lowered to  $-50^\circ\text{C}$ , drastic changes are observed, in both the AB and in the  $\text{X}_2$  part of the  $^{31}\text{P}\{^1\text{H}\}$  spectrum, but the slow-exchange spectrum was not obtained even at  $-90^\circ\text{C}$ , the lowest accessible temperature.

The reactions of the chloro-carbonyl derivatives **3** with carbon monoxide also depend on the nature of the metal. IR measurements indicate that complex **3a** does not react with CO in dichloromethane solution under ambient conditions. However, when CO is bubbled through a dichloromethane solution of **3a** the  $^{31}\text{P}\{^1\text{H}\}$  eight-line spectrum collapses into a slightly broadened doublet centred at 82.0 ppm [ $J(\text{Rh}-\text{P}) = 140$  Hz]. These values are very near to the average of those observed for the two non-equivalent phosphorus atoms in the spectrum of **3a**. If CO is removed by purging the solution with argon, the characteristic eight-line pattern of **3a** is restored. When a CO-saturated solution of **3a** in dichloromethane is cooled below  $-30^\circ\text{C}$ , the doublet is broadened and then replaced by four broad humps. Further cooling to  $-80^\circ\text{C}$  gives a static spectrum which shows the eight-line pattern of **3a**. These observations suggest that a fast equilibration of the two P atoms occurs at room temperature on the NMR time-scale, probably via a five-coordinate dicarbonyl adduct of the type  $[\text{MCl}(\text{CO})_2(\text{dcpe})]$  (**8**). Similar fluxional behaviour in the presence of carbon monoxide was reported for the analogous  $[\text{RhCl}(\text{CO})(\text{dppe})]$  [6f]. The equilibrium concentration of the five-coordinate intermediate appears to be very low at room temperature, since it is spectroscopically undetectable. As the temperature is lowered to  $-80^\circ\text{C}$ , the rate of the fluxional process falls and the static spectrum of **3a** is restored. By contrast, if the reaction between **3a** and CO is carried out in a polar solvent such as ethanol, displacement of  $\text{Cl}^-$  occurs and in the presence of  $\text{BPh}_4^-$  ions the dicarbonyl derivative **4a** is readily formed.

The iridium analogue **3b** reacts rapidly with carbon monoxide at ambient pressure in dichloromethane solution with liberation of chloride ion and giving (as it also does at low temperature) the tricarbonyl derivative **5b**. However, a dicarbonyl derivative can be detected if the reaction is carried out at low temperature by bubbling the stoichiometric amount of CO from a syringe through a dichloromethane solution of **3b**. The  $^{31}\text{P}$  NMR spectrum of this sample shows a resonance at ca. 55 ppm, together with the signals due to the presence of small amounts of **5b** and

Table 2  
Decarbonylation of benzaldehyde in the presence of rhodium(I) catalysts <sup>a</sup>

Catalyst	Catalytic activity <sup>b</sup>
[Rh(COD)(dcpe)] <sup>+</sup> ( <b>1a</b> )	69
[Rh(dcpe) <sub>2</sub> ] <sup>+</sup> ( <b>2a</b> )	86
[RhCl(CO)(dcpe)] ( <b>3a</b> )	56
[Rh(CO) <sub>2</sub> (dcpe)] <sup>+</sup> ( <b>4a</b> )	33
[Rh(dppm) <sub>2</sub> ] <sup>+</sup>	74 <sup>c</sup>
[Rh(dppe) <sub>2</sub> ] <sup>+</sup>	210 <sup>c</sup>
[Rh(dppp) <sub>2</sub> ] <sup>+</sup>	1100 <sup>c</sup>

<sup>a</sup> Experimental conditions:  $1.25\text{--}2.5 \times 10^{-5}$  mol of catalyst in 25 ml of freshly distilled benzaldehyde, under argon atmosphere, at 178 °C. <sup>b</sup> Moles of benzene/moles of catalyst per hour. The activities have been averaged over the first 6 h. <sup>c</sup> Ref. 16.

unreacted **3b**. The new signal, which predominates also in the <sup>31</sup>P NMR spectrum of a solution containing **4b** and Cl<sup>-</sup> ion in 1:1 molar ratio, can reasonably be attributed to the five-coordinate species [IrCl(CO)<sub>2</sub>(dcpe)] (**8b**). The formation of a dicarbonyl intermediate is confirmed by the appearance of two bands at 2021 and 1963 cm<sup>-1</sup> in the IR spectrum of the solution. The <sup>31</sup>P NMR resonance of the five-coordinate **8b** broadens when the temperature is lowered, suggesting fluxionality, but unfortunately the slow-limiting spectrum was not reached. Complexes of type **8** with the diphosphine dppe are well known [7f]. In contrast, the tendency of the iridium-dcpe system to give a tricarbonyl species is noteworthy, since in the case of dppe this could be achieved only by removing the halide ligand as its silver salt in the presence of CO [7e].

#### *Rhodium complexes in the decarbonylation of benzaldehyde*

The catalytic decarbonylation of aldehydes with [Rh(L-L)<sub>2</sub>]<sup>+</sup> complexes as catalyst has been thoroughly investigated by Pignolet [15]. The proposed catalytic cycle involves cleavage of the rhodium–phosphorus bond, followed by aldehyde association and oxidative addition to give a hydride-acyl intermediate, which undergoes migratory deinsertion and elimination of the corresponding hydrocarbon. The Rh–P bond rupture was suggested to determine the reaction rate when P–P is dppe or dppp. In order to compare the dcpe derivatives with the analogous complexes with phenyl-substituted diphosphines, the activities of complexes **1a–4a** for the decarbonylation of neat benzaldehyde were measured at 178 °C. The results of these experiments are reported in Table 2 along with the activities of other rhodium diphosphine complexes. As shown in Table 2, all the dcpe complexes react more slowly than the complexes containing the diphosphines Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>. If the mechanism is similar to that proposed for [Rh(dppp)<sub>2</sub>]<sup>+</sup> [15], this low activity may arise from a slower reductive-elimination step and/or from a lower concentration of the CO-free catalytic species. In fact, both the Rh–P rupture and the oxidative addition should be easier in the Rh–dcpe system. However, more detailed kinetic and chemical studies are needed to clarify the mechanism of the reaction.

## Experimental

### *General*

All operations were carried out under argon by standard Schlenk techniques. Solvents were distilled, dried, and deoxygenated before use. The ligand dcpe was

made by a published method [16]. The starting complexes  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ,  $[\text{RhCl}(\text{COD})]_2$ , *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ , and  $[\text{IrCl}(\text{COD})]_2$  were prepared by published procedures. IR spectra were recorded on a Jasco DS 702 G spectrophotometer calibrated with polystyrene film as Nujol mulls between CsI plates or as dichloromethane solutions in KBr cells.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded with a Bruker WP 80 SY Fourier transform spectrometer equipped with a variable-temperature probe. Positive chemical shifts are downfield from 85%  $\text{H}_3\text{PO}_4$  as external standard. NMR spectral simulation was performed on an Aspect 2000 computer using PANIC (Bruker Spectrospin). Conductance data were obtained with a Metrohm Herisau E 518 conductivity bridge for  $10^{-3}$  M nitromethane solutions. Elemental analyses were performed in the Microanalytical Laboratory of our Institute. Typical experimental conditions for the measurement of the catalytic activity of rhodium(I) complexes were: catalyst concentration between  $5 \times 10^{-4}$  and  $10^{-3}$  M, neat benzaldehyde (25 ml) as solvent, temperature 178°C. The stirred homogeneous solution was continuously purged with argon and the products collected in a cold trap connected to the end of a condenser. GLC was performed with a DANI 6800 chromatograph equipped with an FI detector and a column filled with Carbowax 20 M (2 m  $\times$  1.5 mm).

#### Syntheses of the complexes

$[\text{Rh}(\text{COD})(\text{dcpe})]\text{BPh}_4$  (**1a**). A solution of  $[\text{RhCl}(\text{COD})]_2$  (0.49 g, 1 mmol) and dcpe (0.84 g, 2 mmol) in dichloromethane (20 ml) was stirred for 1 h and then  $\text{NaBPh}_4$  (1.03 g, 3 mmol) in 2-propanol (30 ml) was added. The orange complex obtained by halving the solution volume *in vacuo* was recrystallized from dichloromethane/2-propanol. Yield: 1.6 g, 84%. Anal. Found: C, 72.97; H, 8.47.  $\text{C}_{38}\text{H}_{80}\text{BP}_2\text{Rh}$  calc.: C, 73.10; H, 8.46%.  $\Lambda_{\text{M}}$ :  $50 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

$[\text{Rh}(\text{dcpe})_2]\text{BPh}_4 \cdot \text{CH}_2\text{Cl}_2$  (**2a**). A solution of  $[\text{RhCl}(\text{CO})_2]_2$  (0.19 g, 0.5 mmol) and dcpe (0.84 g, 2 mmol) in dichloromethane (20 ml) was stirred at room temperature for 1 h.  $\text{NaBPh}_4$  (0.51 g, 1.5 mmol) in 2-propanol (20 ml) was then added and the dichloromethane evaporated. The yellow product was recrystallized from dichloromethane/2-propanol. Yield: 1.2 g, 88%. Anal. Found: C, 68.17; H, 8.81.  $\text{C}_{77}\text{H}_{118}\text{BP}_4\text{Cl}_2\text{Rh}$  calc.: C, 68.39; H, 8.79%.  $\Lambda_{\text{M}}$ :  $49 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

$[\text{RhCl}(\text{CO})(\text{dcpe})]$  (**3a**). A solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (0.19 g, 0.5 mmol) and dcpe (0.42 g, 1 mmol) in benzene (10 ml) was stirred for 3 h, during which a yellow solid separated.  $^{31}\text{P}$  NMR analysis of the crude product indicated the formation of a mixture of the complexes  $[\text{RhCl}(\text{CO})(\text{dcpe})]$  and  $[\text{Rh}(\text{dcpe})_2]\text{Cl}$  (in ca. 1:1 molar ratio). The latter was removed by washing with the minimum amount of methanol. The residual yellow solid was dried *in vacuo* and shown to be pure  $[\text{RhCl}(\text{CO})(\text{dcpe})]$ . Yield: 0.25 g, 42%. Anal. Found: C, 55.21; H, 8.14.  $\text{C}_{27}\text{H}_{48}\text{OP}_2\text{ClRh}$  calc.: C, 55.06; H, 8.21%.

$[\text{Rh}(\text{CO})_2(\text{dcpe})]\text{BPh}_4 \cdot \text{CH}_2\text{Cl}_2$  (**4a**). A solution of  $[\text{Rh}(\text{COD})(\text{dcpe})]\text{BPh}_4$  (0.48 g, 0.5 mmol) in dichloromethane (20 ml) was saturated with carbon monoxide. Addition of 2-propanol (20 ml) followed by concentration gave a yellow product which was filtered off, washed with hexane, and dried *in vacuo*. Yield: 0.44 g, 89%. Anal. Found: C, 64.82; H, 7.19.  $\text{C}_{53}\text{H}_{70}\text{BO}_2\text{P}_2\text{Cl}_2\text{Rh}$  calc.: C, 64.58; H, 7.16%.  $\Lambda_{\text{M}}$ :  $51 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

$[\text{Ir}(\text{COD})(\text{dcpe})]\text{BPh}_4$  (**1b**). A solution of  $[\text{IrCl}(\text{COD})]_2$  (0.67 g, 1 mmol) and dcpe (0.84 g, 2 mmol) in dichloromethane (20 ml) was stirred for 1 h. A solution of



NaBPh<sub>4</sub> (1.03 g, 3 mmol) in 2-propanol (30 ml) was then added to the deep-red solution. The red-brown complex was isolated by halving the solution volume *in vacuo*, and recrystallized from dichloromethane/2-propanol. Yield: 1.6 g, 76%. Anal. Found: C, 66.70; H, 7.69. C<sub>58</sub>H<sub>80</sub>BP<sub>2</sub>Ir calc.: C, 66.84; H, 7.74%.  $\Lambda_M$ : 51  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

[Ir(dcpe)<sub>2</sub>]BPh<sub>4</sub> · CH<sub>2</sub>Cl<sub>2</sub> (**2b**). A mixture of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (0.78 g, 1 mmol) and dcpe (0.84 g, 2 mmol) in dichloromethane (20 ml) was stirred and the solution was gently warmed for 10 min. Addition of NaBPh<sub>4</sub> (0.51 g, 1.5 mmol) in ethanol (20 ml), followed by concentration of the solution *in vacuo*, gave an orange precipitate, which was recrystallized from dichloromethane/2-propanol. Yield: 1.2 g, 84%. Anal. Found: C, 63.47; H, 8.32. C<sub>77</sub>H<sub>118</sub>BP<sub>4</sub>Cl<sub>2</sub>Ir calc.: C, 64.15; H, 8.25.  $\Lambda_M$ : 49  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

[IrCl(CO)(dcpe)] · C<sub>6</sub>H<sub>6</sub> (**3b**). A mixture of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (0.78 g, 1 mmol) and dcpe (0.42 g, 1 mmol) in benzene (20 ml) was stirred. After ca. 15 min. yellow crystals spontaneously separated, and were filtered off and washed with diethyl ether. A second crop of the product was obtained from the mother-liquor by addition of diethyl ether. Yield: 0.54 g, 72%. Anal. Found: C, 52.01; H, 7.16. C<sub>33</sub>H<sub>54</sub>OP<sub>2</sub>ClIr calc.: C, 52.40; H, 7.20%.

[Ir(CO)<sub>2</sub>(dcpe)]BPh<sub>4</sub> (**4b**). A solution of [Ir(COD)(dcpe)]BPh<sub>4</sub> (0.52 g, 0.5 mmol) in dichloromethane (20 ml) was stirred under a carbon monoxide atmosphere for 10 min. Addition of 2-propanol (20 ml) followed by concentration gave a yellow product, which was filtered off, washed with light petroleum, and dried *in vacuo*. Yield: 0.41 g, 82%. Anal. Found: C, 62.87; H, 6.78. C<sub>52</sub>H<sub>68</sub>BO<sub>2</sub>P<sub>2</sub>Ir calc.: C, 63.08; H, 6.92%.  $\Lambda_M$ : 52  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

[Ir(CO)(COD)(dcpe)]BPh<sub>4</sub> (**6b**). A solution of [Ir(COD)(dcpe)]BPh<sub>4</sub> (0.52 g, 0.5 mmol) in dichloromethane (20 ml) was cooled to -10 °C and saturated with CO. As soon as the solution had become colourless carbon monoxide was pumped off. Addition of 2-propanol (20 ml) followed by concentration of the solution gave a white-cream compound. Yield: 0.51 g, 95%. Anal. Found: C, 65.91; H, 7.48. C<sub>59</sub>H<sub>80</sub>BOP<sub>2</sub>Ir calc.: C, 66.21; H, 7.53%  $\Lambda_M$ : 48  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . This product can be also obtained by keeping solid [Ir(COD)(dcpe)]BPh<sub>4</sub> for at least 12 h under a carbon monoxide atmosphere.

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