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# Alkyne or alkene binding versus hydrogenation in reactions with $[Ir_2H(CO)_2(\mu-H)_2(Ph_2PCH_2PPh_2)_2][BF_4]$ . Structure of $[Ir_2(C_2H_4)(CO)_2(\mu-H)(Ph_2PCH_2PPh_2)_2][BF_4]$

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## Abstract

The reactions of  $[Ir_2H(CO)_2(\mu-H)_2(dppm)_2][BF_4]$  (1)  $(dppm = Ph_2PCH_2PPh_2)$  with the alkynes, dimethyl acetylenedicarboxylate, hexafluoro-2-butyne or acetylene yield the respective products  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-RCCR)(dppm)_2][BF_4]$  (R =  $CO_2Me$ , CF<sub>3</sub>, H) in which the alkyne bridges the metals, bound in a parallel orientation. With tetrafluoroethylene the analogous olefn-bridged product  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-CCR)(dppm)_2][BF_4]$  is obtained. The reactions of 1 with diphenylacetylene or ethylene result in hydrogenation, to yield *cis*-stilbene and ethane, respectively, with subsequent reaction of the resulting unsaturated intermediate with additional substrate to give  $[Ir_2(CO)_2(\mu-H)(\mu-CPH)(dppm)_2][BF_4]$  is obtained. The reactions of 1 with diphenylacetylene or ethylene result in hydrogenation, to yield *cis*-stilbene and ethane, respectively, with subsequent reaction of the resulting unsaturated intermediate with additional substrate to is give  $[Ir_2(CO)_2(\mu-H)(\mu-CPH)(dppm)_2][BF_4]$  or  $[Ir_2(C_2H_4)(CO)_2(\mu-H)(dppm)_2][BF_4]$ . In the diphenylacetylene adduct this group is bound in a parallel position bridging the metals whereas the ethylene ligand binds to one metal in a terminal position opposite the It-Ir bond. The structure of this ethylene adduct has been determined by X-ray crystallography. This compound crystallizes in the monoclinic space group  $P_2I_1/n$ , having a = 13.6872(7), b = 15.459(2), c = 23.813(2),  $\dot{A}_1 \beta = 97.870(5)^\circ$  and Z=4. The carbonyl and ethylene ligands are disordered, but their positions have been adequately resolved and the structure has refined (on  $F^2$ ) to  $R_1(F_0) = 0.0344$  (observed data) for 8609 unique reflections (6638 observations) and 653 parameters varied.

Keywords: Crystal structures; Hydrogenation; Iridium complexes; Alkene complexes; Alkyne complexes; Hydrido-bridged complexes

# 1. Introduction

The ability of transition-metal complexes to facilitate numerous transformations of unsaturated substrates, including hydrogenation, hydroformylation, oligomerization and polymerization reactions, has provoked much interest in complexes containing coordinated alkynes and alkenes [1,2]. Among the most studied reactions of these substrates are hydrogenation [3] and related [4] reactions in which metalhydride complexes are involved. Although a large number of reactions of olefins and alkynes with mononuclear metalhydrides have been studied [1,3,4], substantially fewer involving multinuclear complexes have been investigated [5]. Interest in this latter group of species has centered around the possible cooperative interactions of the adjacent metals in the hydrogen-transfer process.

In an earlier study [5f] we had shown that the binuclear hydride species,  $[Ir_2(H)_2(CO)_2(\mu-Cl)(dppm)_2][BF_4]$ (I), reacted with phenylacetylene and dimethyl acetylenedicarboxylate (DMAD) to give the compounds,  $[Ir_2-(RC=C(H)R')_2(CO)_2(\mu-Cl)(dppm)_2][BF_4] (R=H, R' = Ph (IIa) and R=R'=CO_2Me (IID), respectively), in which alkyne insertion into each of the Ir-H bonds of the precursor had occurred. Subsequent reaction of IIa with H_2 gave styrene and two isomers of the tetrahydride, <math>[Ir_2(H)_4Cl(CO)_2(dppm)_2][BF_4]$ , the latter species resulting from the reaction of I with H\_2. The two hydrido groups of I and the vinylic moieties of II were found to be terminally bound to different metals, with an intervening, bridging chloro ligand, effectively isolating the two metal centers. It appeared that in this environment the metals had little opportunity to display cooperative behavior, and instead migratory insertion and alkyne hydrogenation appeared to occur at isolated single-metal sites.

In an attempt to involve both metals in substrate hydrogenation, we turned to the related trihydride species,  $[Ir_2H(CO)_2(\mu-H)_2(dppm)_2][BF_4]$  (1) [6], in which the chloro ligand in I is replaced by a hydride. It was anticipated that this replacement would render the complex more amenable to hydrogenation chemistry, possibly allowing sub-

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strate insertion into one Ir-H bond followed by hydride transfer from the adjacent metal leading to reductive elimination and completion of the hydrogenation sequence. In this paper we describe the reactions of 1 and related species with a number of alkynes and olefins in an effort to elucidate some of the factors influencing hydrogen transfer to unsaturated substrates in the presence of adjacent metal centers.

# 2. Experimental

All solvents were dried and distilled immediately before use. Deuterated solvents used for NMR experiments were degassed and stored under argon over molecular sieves. All reactions were carried out at room temperature by using standard Schlenk procedures, and compounds, which were isolated as solids, were purified by recrystallization. A flow rate of  $\sim 0.1$  ml s<sup>-1</sup> was employed for all reactions which involved purging a solution with a gas. Prepurified argon, ethylene and hydrogen were purchased from Linde, carbon monoxide was purchased from Matheson, hexafluoro-2butyne (HFB) and tetrafluoroethylene from PCR Inc. and diphenylacetylene and dimethyl acetylenedicarboxylate (DMAD) from Aldrich. 13CO (99%) was supplied by Isotec Inc. All gases were used as received. Hydrated iridium(III) chloride was purchased from Engelhard Scientific and bis-(diphenylphosphino)methane (dppm) was obtained from Aldrich. The compounds  $[Ir_2(H)(CO)_2(\mu-H)_2(dppm)_2]$ - $[BF_4]$  (1) [6] and  $[Ir_2(CO)_3(dppm)_2]$  (2) [7] were prepared as previously reported.

The NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.1 MHz for <sup>1</sup>H, at 161.9 MHz for <sup>31</sup>P{<sup>1</sup>H} and at 100.6 MHz for <sup>13</sup>C{<sup>1</sup>H} spectra. The <sup>13</sup>C{<sup>1</sup>H} <sup>31</sup>P} NMR spectra were obtained on a Bruker WH-200 spectrometer operating at 50.32 MHz. All <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained using <sup>13</sup>CO-enriched samples unless otherwise stated. Infrared spectra were obtained on a Nicolet 7199 Fourier transform or a Perkin Elmer 883 IR spectrometer, either as Nujol mulls on KBr plates, or as solutions in KCl cells with 0.5 mm path-length windows. Spectroscopic parameters for the compounds prepared are found in Table 1.

## 2.1. Preparation of compounds

2.1.1.  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-DMAD)(dppm)_2][BF_4](3)$ 

To the compound  $[Ir_2(H)(CO)_2(\mu-H)_2(dppm)_2][BF_4]$ (1) (60 mg, 0.043 mmol) dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub>, was added 1 equiv. (5.3 µl, 0.043 mmol) of DMAD. The solution was stirred for 3 h, after which time the volume of the solvent was reduced to about 2 ml under vacuum. The product was then precipitated by the addition of Et<sub>2</sub>O, filtered and washed with Et<sub>2</sub>O, and the resulting yellow solid dried under an argon stream. After recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, the product was dried again under an argon stream, and then in vacuo (60% yield). The product was obtained as the CH<sub>2</sub>Cl<sub>2</sub> hemi solvate, as shown by NMR and elemental analysis. Anal. Calc. for  $Ir_2CIP_4F_4O_6C_{58.5}BH_{54}$ : C, 47.36; H, 3.67. Found: C, 47.37; H, 3.79%.

# 2.1.2. $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-HFB)(dppm)_2][BF_4](4)$

Hexafluoro-2-butyne was passed through a solution of compound 1 (60 mg, 0.043 mmol) dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> for 2 min. The solution was then stirred under a static atmosphere of the gas for 1 h. The product was isolated (containing ~1/4 equiv. of CH<sub>2</sub>Cl<sub>2</sub>, as confirmed by <sup>1</sup>H NMR) in a manner similar to that used for compound **3** (70% yield). Anal. Calc. for Ir<sub>2</sub>Cl<sub>0.3</sub>P<sub>4</sub>F<sub>10</sub>O<sub>2</sub>C<sub>56.25</sub>H<sub>47.5</sub>B: C, 45.58; H, 3.23; Cl, 1.10. Found: C, 45.11; H, 3.07; Cl, 0.80%.

#### 2.1.3. $[Ir_2(CO)_2(\mu-H)(\mu-PhC_2Ph)(dppm)_2][BF_4](6)$

Compound 1 (60 mg, 0.043 mmol) was dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub>. 2 equiv. (15.5 mg, 0.087 mmol) of diphenylacetylene, dissolved in 2 ml of CH<sub>2</sub>Cl<sub>2</sub>, were then added. The mixture was stirred for 24 h, after which time the product was isolated in a similar manner to that used for compound 3 (60% yield). *Anal.* Calc. for  $fr_2P_4F_4O_2C_{66}H_{53}B$ : C, 53.73; H, 3.76. Found: C, 53.14; H, 3.68%.

# 2.1.4. $[Ir_2(H)(CO)_3(\mu-DMAD)(dppm)_2][BF_4](8)$

l equiv. (7.0 μL, 0.048 mmul) of HBF<sub>4</sub>·OEt<sub>2</sub> was added to a solution of  $[Ir_2(CO)_3(dppm)_2]$  (2) (60 mg, 0.048 mmol) in 3 ml of THF, resulting in an immediate color change from orange to dark reddish-purple. I equiv. (6.0 μl, 0.048 mmol) of DMAD was then added to the solution, giving rise to an immediate change in color to red. The red product was precipitated immediately with hexane, collected, and after washing with hexane, it was dried under an argon stream and then under vacuo. Anal. Calc. for  $Ir_2P_4F_4$ -0.3<sub>C57</sub>H<sub>51</sub>B: C, 48.20; H, 3.50. Found: C, 48.36; H, 3.68%.

### 2.1.5. $[Ir_2(C_2H_4)(CO)_2(\mu-H)(dppm)_2][BF_4](9)$

Ethylene was passed through a solution of compound 1 (60 mg, 0.043 mmol) in 6 ml of CH<sub>2</sub>Cl<sub>2</sub> for 1 min. The mixture was then stirred under a static atmosphere of the gas for 4 h, during which time the color changed from orange to red. The red product was precipitated by addition of Et<sub>2</sub>O, washed with Et<sub>2</sub>O, and dried under a stream of argon. After recrystallizing from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, the product was dried again under a stream of argon and then under vacuum (70% yield). Anal. Calc. for 1r<sub>2</sub>Pa<sub>4</sub>O<sub>2</sub>BC<sub>3</sub>H<sub>4</sub>O<sub>2</sub>C, 48.94; H, 3.73. Found: C, 48.04; H, 3.79%. The poor results for the carbon analysis is presumably due to the formation of iridium carbides since many attempts on crystalline material, suitable for X-ray analysis, gave consistently low results for carbon. No solvent was detected by <sup>1</sup>H NMR spectroscopy.

#### 2.2. Reaction of compound 1 with acetylene

The procedure was the same as that used for preparing compound 4, except that acetylene was used in this case instead of hexafluoro-2-butyne, and the mixture was stirred for 24 h instead of 1 h. This reaction never proceeded

Table 1 Spectroscopic data for the compounds <sup>a</sup>				
Compound	IR be (cm <sup>-1</sup> )	NMR		
		p ({H <sub>1</sub> }d <sub>1€</sub> )g	y-, (H <sub>1</sub> )8	¢ (اH <sub>1</sub> ) در الله ال
[Ir <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (μ-H)(μ-DMAD)(dppm) <sub>2</sub>  [BF₄] (3)	2057(vs), 1970(st), 1685(m) <sup>s</sup> , 1575(w) <sup>1</sup>	– 13.7 (s)	4.72 (m, 2H), 4.44 (m, 2H), 3.15 (s, 6H), -11.30 (m, 2H), -17.81 (q, 1H)	
[Ir <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (μ-H)(μ-HFB)(dppm) <sub>2</sub> ][BF4] (4)	2052(vs), 1976(med), 1579(w) <sup>h</sup>	– 14.7 (s)	4.52 (q, 4H), – 11.69 (b, 2H), – 17.28 (q, 1H)	
[Ir <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (μ·H)(μ·C <sub>2</sub> H <sub>2</sub> )(dppm) <sub>2</sub> ][BF <sub>4</sub> ] (5)		– 14.6 (s)	4.85 (m, 2H), 4.36 (m, 2H), – 10.90 (m, 2H), – 17.59 (q, 1H)	102.7 (s,C <sub>2</sub> H <sub>2</sub> )
[Ir <sub>2</sub> (CO) <sub>2</sub> (μ-H)(μ-Ph <sub>2</sub> C <sub>2</sub> )(dppm) <sub>2</sub> ][BF4] (6)	1995(vs), 1940(sh), 1590(w) <sup>h</sup>	1.5 (s)	3.27 (m, 2H), 2.55 (m, 2H), – 14.08 (q, 1H)	
[IF <sub>2</sub> (H)(CO) <sub>3</sub> (μ-DMAD)(dpm) <sub>2</sub> ][BF <sub>4</sub> ](8)	2064(s), 2022(vs), 1965(s), 1691(s) <sup>s</sup> , 1555(med) <sup>h</sup>	– 14.2 (m), –29.8 (m)	4.88 (m, 2H), 4.73 (m, 2H), 3.83 (s, 3H), 2.28 (s, 3H), - 12.03 (t, <sup>2</sup> J(P–H) = 16.0 Hz, 1H)	176.8 (t, <sup>2</sup> /(P-C) = 5.4 Hz, IC), 164.2 (dt, <sup>2</sup> /(P-C) = 9.0 Hz, <sup>3</sup> /(C-C) = 10.6 Hz, IC), 152.5 (dt, <sup>3</sup> /(P-C) = 11.0 Hz, <sup>3</sup> /(C-C) = 10.6 Hz, IC)
[Ir <sub>2</sub> (C <sub>2</sub> H4,)(CO) <sub>2</sub> (µ-H)(dppm) <sub>2</sub> ][BF4] (9) <sup>1</sup>	1977(vs)	12.1 (m), 6.8 (m) <sup>1</sup>	4.25 (m, 2H), 3.68 (m, 2H), 0.90 (b, 2H), 0.62 (b, 2H), – 9.93 (m, 1H) <sup>1</sup>	181.9 (b, IC), 177.6(t, <sup>2</sup> J(P-C) = 13.3 Hz, IC) <sup>4</sup>
[lr <sub>2</sub> (H) <sub>2</sub> (CO) <sub>2</sub> (μ·H)(μ·C <sub>2</sub> F₄)(dppm) <sub>2</sub> ][BF₄] (10)		-8.5 (s)	4.86 (m, 2H), 4.66 (m, 2H), - 10.76 (m, 2H), - 18.02 (q, 1H)	
[Ir <sub>2</sub> (CO) <sub>2</sub> (μ-H)(μ-SO <sub>2</sub> )(dppm) <sub>2</sub> ][BΓ ] (11)	1993(vs)	3.9 (s)	4.22 (m, 2H), 3.95 (m, 2H), – 10.33 (q, 1H)	
l1 <sub>2</sub> H(CO) <sub>2</sub> (PMe <sub>3</sub> )(dppm) <sub>2</sub> ][BF4] (12)	1948(b)	0.04 (m), - 14.3 (m), - 56.0 (t)	5.21 (b, 4H), 0.67 (d, 9H, <sup>2</sup> /(H-P) = 9.6 H2), - 10.1 (dt, 1H, <sup>2</sup> /(H-P) = 24, 12 Hz)	186.7 (b, IC), 172.4 (dt, <sup>2</sup> /(P–C) = 16.1, 10.1 Hz, IC)
				- F. F

Abbreviations used: med = medium, st = strong, vs = very strong, w = veak, sh = shoulder, s = singlet, t = triplet, q = quintet, m = multiplet, dm = doublet of multiplets, b = broad.
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to completion, always yielding  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-C_2H_2)(dppm)_2][BF_4]$  (5) together with starting material in close to 1:1 proportions. In addition, a number of minor unidentified products were also observed spectroscopically. Compound 5 was only characterized in solution, by spectral techniques, owing to the lability of the acetylene group which resulted in regeneration.

# 2.3. Reaction of compound 1 with tetrafluoroethylene

Tetrafluoroethylene was passed through a solution of compound 1 (60 mg, 0.043 mmol) in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> for 1 min. The solution was then stirred under a static atmosphere of the gas for 48 h. The <sup>31</sup>P<sup>1</sup>H] NMR spectrum showed the presence of a mixture of compound 1 and [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -H)( $\mu$ -C<sub>2</sub>F<sub>4</sub>)(dppm)<sub>2</sub>][BF<sub>4</sub>] (12). To obtain <sup>1</sup>H NMR spectra the reaction was carried out in CD<sub>2</sub>Cl<sub>2</sub> solution. Compound 12 could not be isolated as a solid owing to facile loss of C<sub>2</sub>F<sub>4</sub> and reversion to 1.

# 2.4. Reaction of compound 9 with H<sub>2</sub>

Compound 9 (30 mg, 0.024 mmol) was dissolved in 0.6 ml of  $CD_2Cl_2$  in an NMR tube which was then capped with a rubber septum. Hydrogen was then passed through the solution for 1 min. The NMR spectra of the solution showed the presence of compound 1 and ethylene as the only products.

### 2.5. Reaction of compound 9 with CO

Carbon monoxide was passed over a solution of compound 9 (20 mg, 0.015 mmol) in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> for 1 min, iollowed by stirring under a static atmosphere of the gas for 1 h. The solution volume was reduced to ~2 ml and a dark red product was precipitated by the addition of Et<sub>2</sub>O. NMR spectra identified the product as the previously reported [Ir<sub>2</sub>(CO)<sub>2</sub>-( $\mu$ -H)( $\mu$ -CO)(dppm)<sub>2</sub>][BF<sub>4</sub>] [7].

# 2.6. Reaction of compound 9 with SO2

The procedure used was exactly as described for the reaction with CO except that the  $PF_6^-$  salt of 9 was used. A dark blue solid,  $[Ir_2(CO)_2(\mu-H)(\mu-SO_2)(dppm)_2][PF_6](10)$ , was isolated in 72% yield. Anal. Calc. for  $Ir_2SP_3F_6O_4C_{52}H_{45}$ : C. (44.00; H, 3.20; S, 2.26. Found: C, 43.98; H, 3.13; S, 2.64%.

# 2.7. Reaction of compound 9 with PMe3

30 mg (0.023 mmol) of compound 9 were dissolved in 0.5 ml of  $CD_2Cl_2$  in an NMR tube. To this were added 2.3  $\mu$ l (0.023 mmol) of PMe<sub>3</sub> by syringe, causing an immediate

color change from dark red to bright yellow. Characterization of  $[Ir_2H(CO)_2(PMe_3)(dppm)_2][BF_4]$  (11) was only by spectroscopy, since attempts to isolate a solid product gave only decomposition products.

#### 2.8. X-ray data collection

Orange crystals of  $[Ir_2(C_2H_4)(CO)_2(\mu-H)(dppm)_2]$ -[BF<sub>4</sub>] (9) were obtained by slow diffusion of diethyl ether into a conc. CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Several suitable crystals were mounted and flame sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K\alpha radiation <sup>1</sup>. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range  $20.0 \le 2\theta \le 24.0^\circ$ . The monoclinic diffraction symmetry and the systematic absences (hOl, h+l=odt; 0k0, k=odd) were consistent with the space group  $P_2/n$ .

Intensity data were collected at 22°C using the  $\theta/2\theta$  scan technique to a maximum  $2\theta = 50.0^\circ$ , collecting reflections with indices of the form  $\pm h + k + l$ . Backgrounds were scanned for 25% of the peak width on either side of the peak scan. Three reflections were chosen as intensity standards, being remeasured at 120 min intervals of X-ray exposure time. There was no significant systematic decrease in the intensities of these standards thus no decomposition correction was applied. A total of 8924 unique reflections was measured of which 6638 were considered to be observed ( $F_o^2 \ge 2\sigma (F_o^2)$ ). Absorption corrections were applied to the data using the method of Walker and Stuart [8]. See Table 2 for crystal data and more information on X-ray data collection.

## 2.9. Structure solution and refinement

The structure was solved in the space group  $P2_1/n$  using standard Patterson and Fourier techniques. Although location of all atoms was straightforward, initial refinements <sup>2</sup> [9] resulted in unusually high thermal parameters for the atoms of the carbonyl groups and the ethylene carbon atoms. A difference Fourier calculation at this stage showed the presence of superimposed carbonyl and ethylene carbon atoms. This led to the model in which 9 is disordered in two orientations, represented as A and B in the diagram below (the

<sup>&</sup>lt;sup>1</sup> Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius.

<sup>&</sup>lt;sup>2</sup> Refinement on  $F_o^2$  for all reflections except for 1 having  $F_o^2 < -3\sigma(F_o^2)$ . Weighted R-factors  $wR_a$  and all goodnesses of fit S are based on  $F_o^2$ ; onwerthough R-factors R are based on  $F_o^2$ ; onwerthough R-factors R, are based on  $F_o^2$ , the observed criterion of  $F_o^2 > 2\sigma(F_o^2)$  is used only for calculating R, and is not relevant to the choice of reflections for refinement. R-factors based on  $F_o^2$  are statistically about twice as large as those based on  $F_o$  and R-factors based on all data will be even larger.

Table 2 Crystallographic data for  $[Ir_2(CO)_2(\eta^2-C_2H_4)(\mu-H)(dppm)_2][BF_4]$  (9)

Formula	C54H49BF4Ir2O2P4
Formula weight	1325.02
Crystal shape	monoclinic prism
Crystal dimensions (mm)	0.60×0.42×0.38
Crystal system	monoclinic
Space group	$P2_1/n$ (a non-standard setting of $P2_1/c$
	(No. 14))
Unit cell parameters	
a (Å)	13.6872(7)
b (Å)	15.459(2)
c (Å)	23.8127(15)
β(°)	97.870(5)
V (Å <sup>3</sup> )	4991.0(7)
z	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.763
$\mu$ (mm <sup>-1</sup> )	5.512
Diffractometer	Enraf-Nonius CAD4
Radiation ( $\lambda$ (Å))	graphite-monochromated Mo Kα (0.71073)
Temperature (°C)	22
Scan type	θ_2 <i>θ</i>
Data collection $2\theta$ limit (°)	50.0
Total data collected	$8924(-16 \le h \le 16, 0 \le k \le 18)$
	0 <28)</td
Independent reflections	8699
Number observations (NQ)	$6638(F^2 > 2\sigma(F^2))$
Range absorption correction	1,189-0,894
factors	
No. narameters varied	653
Goodness-of-fit (S) *	$1044(F^2 > -3\sigma(F^2))$
Final R indices b	1.000 (18 2 30(18))
$R_{1}$ w $R_{2}$ $(F_{2}^{2} > 2\sigma(F_{2}^{2}))$	0.0344_0.0699
$R_1, wR_2$ (all data)	0.0635, 0.0778
Largest difference peak, hole	0.792 0.861
(e Å <sup>-3</sup> )	

<sup>a</sup>  $S = [\Sigma w(F_o^2 - F_c^2)^{2/}(n-p)]^{1/2}$  (*n* = number of data; *p* = number of parameters varied; *w* = [ $\sigma^2(F_o^2) + (0.0310P)^2 + 9.7379P]^{-1}$  where *P* = [max.( $F_o^2$ , 0) + 2 $F_c^2$ ]/3). <sup>b</sup>  $R_i = \Sigma [|F_0| - |F_i|]/S [|F_0|; wR_2 = [\Sigma w(F_c^2 - F_c^2)^2 [\Sigma w(F_c^4)]^{1/2}$ .

dppm ligands are omitted for clarity), in an approximately 50:50 ratio (determined from the relative peak intensities of the ordered and disordered atoms). The resulting model in which the **A** and **B** orientations are superimposed is



diagrammed in C, in which the solid lines connect atoms of one disordered molecule, having unprimed atom labels, and the dashed lines show the other one, having primed atoms



labels. There is no apparent disorder involving the phosphine groups, which are well behaved. Although an alternate structure, having one CO ligand on one metal and the second one on the other metal (represented as A' and B' in the diagram below), could not be ruled out by the X-ray study, that shown in A and B is favored for reasons that will be outlined in the discussion of the NMR spectroscopic data. Rotational disorder of this type is not uncommon in these dppm-bridged binuclear systems [10].



All non-hydrogen atoms of the complex cation and anion as well as the hydride ligand were located. Atomic scattering factors [11,12] and anomalous dispersion terms [13] were taken from the usual tabulations. The hydride ligand H(1) was located and refined with the Ir(1)-H(1) and Ir(2)-H(1) distances constrained to be equal within 0.01 Å. The other hydrogen atoms were included as fixed contributions and not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms, using a C-H bond length of 0.95 Å, and they were assigned thermal parameters 20% greater than the  $U_{eq}$  of their attached carbon atoms.

The final least-squares cycles of refinement were carried out on  $F^2$  using all data. The final model, with 653 parameters refined, converged to values of  $R_1(F_o) = 0.034$  (observed data) and  $wR_2(F_o^2) = 0.078$  (all data). The final difference Fourier map contained no residual features of chemical significance (highest residual peak =  $0.79 \text{ e} \text{ Å}^{-3}$ ). Atomic coordinates and isotropic displacement parameters for selected atoms of the complex are given in Table 3 while selected interatomic distances and angles are given in Tables 4 and 5, respectively.

Atom x y	z	$U_{\rm eq}$ (Å <sup>2</sup> )
r(1) 0.23371(2) 0.13630(2)	-0.022269(10)	0.03204(7) *
Ir(2) 0.39014(2) 0.25191(2)	0.011498(10)	0.03447(8)*
P(1) 0.19100(13) 0.20771(12)	-0.10739(7)	0.0352(4)*
P(2) 0.36185(13) 0.32679(11)	-0.07352(7)	0.0370(4) *
P(3) 0.25191(12) 0.07038(11)	0.06592(7)	0.0330(4)*
P(4) 0.41715(12) 0.19472(11)	0.10241(7)	0.0318(4)*
O(1) <sup>b</sup> 0.5685(10) 0.3562(10)	0.0365(6)	0.070(4)*
O(1') bc 0.0967(14) 0.0009(11)	-0.0672(6)	0.076(4) *
O(2) 0.4439(4) 0.0742(4)	-0.0433(3)	0.071(2)*
C(1) <sup>b</sup> 0.4977(19) 0.3168(13)	0.0272(9)	0.042(5)*
C(1') be 0.1376(38) 0.0502(33)	-0.0487(20)	0.085(19)*
C(2) b 0.4156(13) 0.1386(13)	-0.0257(7)	0.053(4) *
$C(2')^{bc} = 0.3648(12) = 0.1034(13)$	-0.0335(6)	0.048(4) *
$C(3)^{b}$ 0.0834(12) 0.0852(13)	-0.0307(7)	0.056(5)*
$C(3')^{bc} = 0.4779(12) = 0.3581(12)$	0.0451(7)	0.045(4) *
C(4) <sup>b</sup> 0.1519(22) 0.0335(36)	-0.0542(16)	0.059(11)*
$C(4')^{bc} = 0.5426(19) = 0.2977(17)$	0.0245(11)	0.060(8)*
C(5) 0.2940(5) 0.2643(4)	-0.1315(3)	0.042(2)*
C(6) 0.3752(4) 0.0835(4)	0.1049(3)	0.036(2)*
H(1) 0.2616(18) 0.235(2)	0.017(2)	0.040(17)

Table 5				
Atomic coordinates and equivalent isotrop	ic displacement parameter	s for selected atoms of [Ir2(CC	$D_{2}(\eta^{2}-C_{2}H_{4})(\mu-H)(d)$	ppm)2][BF4] (9)

\*Anisotropically-refined atoms. The form of the anisotropic displacement parameter is:  $\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+h^2c^{*2}U_{33}+2klb^*c^*U_{23}+2kla^*c^*U_{13}+2kla^*b^*U_{12})\right]$ .

<sup>b</sup> Refined with an occupancy factor of 0.5.

e Primed atoms are related to unprimed ones via the rotational disorder (see text).

#### 3. Results and compound characterization

# Table 4

# 3.1. Reactions with alkynes

The reaction of  $[Ir_2(H)(CO)_2(\mu-H)_2(dppm)_2][BF_4]$ (1) with dimethyl acetylenedicarboxylate (DMAD) gives  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-DMAD)(dppm)_2][BF_4]$  (3) as outlined in Scheme 1. Although this product was prepared previously [14], it was obtained in a mixture of two products at that time, and had not been fully characterized. The NMR spectroscopic data of compound 3 are the same as were previously reported, with the IR spectrum showing CO stretches at 2057 and 1970 cm<sup>-1</sup>, indicating the presence of two terminal CO ligands, as well as a peak at 1685 cm<sup>-1</sup>, due to the C=O stretch of the coordinated DMAD. A peak at 1575 cm<sup>-1</sup> in this spectrum is assigned to the C=C stretch of the coordinated alkyne. This is within the range of 1530-1642 cm<sup>-1</sup> observed in closely related dppm-bridged binuclear complexes in which the alkyne bridges the two metals parallel to the metal-metal axis [14-21], and is the coordination mode assumed for 3 3. In related binuclear complexes in which the alkyne bridges the two metals perpendicular to the metalmetal axis ( $\mu$ - $\eta^2$ : $\eta^2$ - mode), the C=C stretch usually occurs at lower frequencies. For example, a value of 1425 cm<sup>-1</sup> was observed in  $[Rh_2(CO)_2(\mu-\eta^2:\eta^2-PhC_2H)(dppin)_2]$  and  $[Rh_2(CO)_2(\mu - \eta^2: \eta^2 - PhC_2Ph)(dppm)_2]$  [22]. The <sup>1</sup>H

Bonded			
lr(1)–lr(2)	2.8202(4)	Ir(2)-C(3')	2.12(2)
Ir(1)-P(1)	2.312(2)	lr(2)C(4')	2.18(3)
lr(1)-P(3)	2.317(2)	lr(2)H(1)	1.80(3)
lr(1)-C(1')	1.92(6)	P(1)-C(5)	1.818(7)
lr(1)-C(2)	2.50(2)	P(2)-C(5)	1.831(6)
lr(1)-C(2')	1.92(2)	P(3)-C(6)	1.822(6)
lr(1)-C(3)	2.19(2)	P(4) - C(6)	1.816(6)
Ir(1)-C(4)	2.03(5)	O(1)-C(1)	1.14(3)
Ir(1)-H(1)	1.80(3)	O(1')-C(1')	1.01(6)
Ir(2)-P(2)	2.318(2)	O(2)-C(2)	1.17(2)
lr(2)-P(4)	2.321(2)	O(2)-C(2')	1.22(2)
Ir(2)-C(1)	1.78(2)	C(3)-C(4)	1.40(5)
lr(2)C(2)	2.02(2)	C(3')-C(4')	1.42(3)
lr(2)C(2')	2.54(2)		
Non-bonded			
P(1)…P(2)	2.998(2)	P(3)…P(4)	3.004(2)

Selected distances (Å) in  $[Ir_2(CO)_2(\eta^2 - C_2H_4)(\mu - H)(dppm)_2][BF_4]$  (9)

NMR spectrum clearly identifies 3 as a trihydride, with two highfield resonances in a 2:1 ratio at  $\delta - 11.30$  and - 17.81, respectively. Also consistent with the proposed structure, the six DMAD methyl protons appear as a singlet at  $\delta 3.15$ , and the dppm-methylene protons appear as two resonances indicating a 'front-back' asymmetry in the complex.

The reaction of compound 1 with HFB (hexafluoro-2butyne) gives the analogous product,  $[I_2(H)_2(CO)_2 (\mu-H)(\mu-HFB)(dppm)_2][BF_4]$  (4). The spectroscopic properties of 4 are similar to those of compound 3, showing a singlet at  $\delta - 14.7$  in its <sup>31</sup>P[<sup>1</sup>H] NMR spectrum, and

<sup>&</sup>lt;sup>3</sup> Such binuclear complexes, with an alkyne bridging two metals parallel to the metal-metal axis, are sometimes referred to as dimetalated olefinic compounds in which case reference is made to the C=C stretch of the olefin instead of the C=C stretch of the coordinated alkyne.

Table 5 Selected angles (°) in  $[l_{12}(CO)_2(\eta^2-C_2H_4)(\mu-H)(dppm)_2][BF_4]$  (9)

Bond angles			
Ir(2) - Ir(1) - P(1)	92.20(4)	P(2)-Ir(2)-C(1)	86.4(7)
lr(2)-lr(1)-P(3)	92.13(4)	P(2)-Ir(2)-C(2)	93.9(5)
lr(2)-lr(1)-C(1')	173.8(16)	P(2)-Ir(2)-C(2')	94.9(3)
Ir(2)-Ir(1)-C(2)	44.0(5)	P(2)-Ir(2)-C(3')	87.8(4)
lr(2)-lr(1)-C(2')	61.3(6)	P(2)-lr(2)-C(4')	90.3(6)
lr(2)-lr(1)-C(3)	157.4(5)	P(2)-lr(2)-H(1)	94.9(18)
lr(2)-lr(1)-C(4)	163.9(12)	P(4)-Ir(2)-C(1)	89.8(7)
lr(2)-lr(1)-H(1)	38.4(10)	P(4)-lr(2)-C(2)	93.7(5)
P(1)-lr(1)-P(3)	171.00(6)	P(4)-Ir(2)-C(2')	92.6(3)
P(1)-lr(1)-C(1')	87.9(11)	P(4)-Ir(2)-C(3')	86.2(4)
P(1)-lr(1)-C(2)	95.6(4)	P(4)-Ir(2)-C(4')	87.9(7)
P(1)-lr(1)-C(2')	97.6(4)	P(4)-Ir(2)-H(1)	84.9(18)
P(1)-lr(1)-C(3)	88.3(4)	C(1)-Ir(2)-C(2)	113.3(10)
P(1)-Ir(1)-C(4)	89.2(10)	C(1)-Ir(2)-H(1)	148.9(12)
P(1)-lr(1)-H(1)	93.4(17)	C(2')-lr(2)-C(3')	153.6(6)
P(3)-lr(1)-C(1')	88.6(11)	C(2')-lr(2)-C(4')	115.2(8)
P(3)-Ir(1)-C(2)	93.0(4)	C(2')-Ir(2)-H(1)	79.6(10)
P(3)-Ir(1)-C(2')	91.4(4)	C(3')-Ir(2)-C(4')	38.4(8)
P(3)-lr(1)-C(3)	84.7(4)	C(3')-lr(2)-H(1)	126.4(11)
P(3)-lr(1)-C(4)	88.9(10)	C(4')-Ir(2)-H(1)	163.9(14)
P(3)-lr(1)-H(1)	85.2(18)	Ir(1)-P(1)-C(5)	113.1(2)
C(1')-lr(1)-C(2')	112.5(17)	Ir(2)-P(2)-C(5)	113.7(2)
C(1')-lr(1)-H(1)	147.8(19)	lr(1)-P(3)-C(6)	112.9(2)
C(2)-lr(1)-C(3)	158.4(7)	lr(2)-P(4)-C(6)	112.4(2)
C(2)-Ir(1)-C(4)	119.9(13)	Ir(2)-C(1)-O(1)	177.7(25)
C(2)-Ir(1)-H(1)	82.2(11)	ľr(1)–C(1')–O(1')	169.1(49)
C(3)-lr(1)-C(4)	38.7(13)	lr(1)-C(2)-lr(2)	76.4(6)
C(3)-lr(1)-H(1)	118.9(11)	lr(1)-C(2)-O(2)	112.4(13)
C(4)-lr(1)-H(1)	157.4(16)	lr(2)-C(2)-O(2)	170.3(15)
lr(1)-lr(2)-P(2)	92.17(4)	lr(1)-C(2')-Ir(2)	77.2(6)
lr(1)-lr(2)-P(4)	92.42(4)	Ir(1)-C(2')-O(2)	172.9(16)
lr(1)-lr(2)-C(1)	172.6(8)	Ir(2)-C(2')-O(2)	109.9(12)
lr(1)-lr(2)-C(2)	59.6(5)	Ir(1)-C(3)-C(4)	64.6(19)
lr(1)-lr(2)-C(2')	41.5(4)	Ir(2)-C(3')-C(4')	73.1(15)
Ir(1)-Ir(2)-C(3')	164.8(5)	Ir(1)-C(4)-C(3)	76.7(26)
lr(1)-lr(2)-C(4')	156.7(7)	Ir(2)-C(4')-C(3')	68.5(13)
lr(1)-lr(2)-H(1)	38.4(10)	P(1)-C(5)-P(2)	110.5(4)
P(2)-Ir(2)-P(4)	172.36(6)	P(3)-C(6)-P(4)	111.3(3)
Torsional angles			
C(3)-lr(1)-lr(2)-P(4)	80.5(11)	P(1)-Ir(1)-Ir(2)-C(3')	86.9(16)
C(4)-Ir(1)-Ir(2)-P(2)	92.0(35)	P(3)-Ir(1)-Ir(2)-C(4')	89.7(17)



hydride resonances at  $\delta - 11.69$  (multiplet) and -17.28 (quintet), corresponding to the two terminal and one bridging hydride ligands, respectively. The IR spectrum of 4 shows

carbonyl stretches at 2052 and 1976 cm<sup>-1</sup>, and the alkyne C=C stretch at 1579 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectrum of 4, the four dppm methylene protons give rise to a quintet at  $\delta$  4.52 even at  $-80^{\circ}$ C. Although the structure proposed for 4 should have two chemically inequivalent methylene resonances, it appears that their chemical shifts are coincidentally equivalent. The <sup>10</sup>F NMR spectrum of compound 4 shows a singlet at  $\delta$  -54.8, similar to that observed in related compounds [20,21].

Compound 1 also reacts with acetylene to give  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-C_2H_2)(dppm)_2][BF_4](5)$ , analogous to 3 and 4, as shown by its very similar <sup>1</sup>H and <sup>31</sup>P[<sup>1</sup>H] NMR spectroscopic parameters to those of 3 and 4 (see Table 1). In the <sup>1</sup>H NMR spectrum of 5, the resonance for the protons of the coordinated acetylene are not observed, presumably being obscured by the phenyl resonances, as is frequently the case [22,23]. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of a sample of 5, obtained from a <sup>13</sup>C-enriched acetylene sample, shows the resonance for the coordinated acetylene as a slightly broadened singlet at  $\delta$  102.7. This chemical shift

is close to those observed for the carbon nuclei of the coordinated acetylene group in  $[Ir_2(I)(CO)_2(\mu-C_2H_2)-(dppm)_2][I]$  [23].

Although the reactions of 1 with DMAD and HFB vielded pure product in each case, that involving acetylene never proceeded to completion, yielding approximately equal proportions of 5 and the precursor 1. In addition, the acetylene reaction yielded a number of minor unidentified products in approximately 15% combined yield. Interestingly, the <sup>13</sup>C<sup>1</sup>H NMR spectrum of a sample prepared from <sup>13</sup>C<sub>2</sub>H<sub>2</sub> suggests that one of the by-products is a vinylidene species, displaying typical <sup>13</sup>C resonances at  $\delta$  224 (doublet of multiplets) and 122 (doublet) with a C-C coupling of 63 Hz. Unfortunately, its low abundance and the presence of several other species in similar amounts precluded its identification. The transformation of a 1-alkyne to a vinylidene moiety in the presence of two adjacent metals would not be surprising [22-24]. Based on the structures proposed for compounds 3-5, it appears that alkyne attack occurs between the two adjacent hydride ligands, on the front face of complex 1 (as it is diagrammed in Scheme 1). Previous studies showed that the two adjacent hydrides in 1 undergo exchange between the terminal and bridging positions, so an intermediate, such as III is possible and this could yield the observed products via alkyne attack at some site between these terminal hydride groups. Alkyne attack presumably occurs at one metal, followed by movement into the bridging position.





In contrast to the reactions described above, reaction of 1 with 2 equiv. of diphenylacetylene results in the formation of the monohydrido, alkyne-bridged product,  $[Ir_2(CO)_2(\mu-$ H)( $\mu$ -PhC<sub>2</sub>Ph)(dppm)<sub>2</sub>][BF<sub>4</sub>] (6). The four phosphorus nuclei of compound 6 are equivalent, as is indicated by a singlet at  $\delta$  1.5 in its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The only hydride resonance, integrating as a single hydrogen, appears as a quintet at  $\delta - 14.08$ , in the <sup>1</sup>H NMR spectrum, displaying coupling to the four phosphorus nuclei. Two CO stretches appear at 1995 and 1940 cm<sup>-1</sup>, in the IR spectrum, while a band at 1590 cm<sup>-1</sup> is assigned to the C≡C stretch of the coordinated alkyne. These data are consistent with the assignment of a bridging hydride ligand, two terminal CO ligands and a bridging alkyne in 6. The high frequency C≡C stretch indicates a parallel alignment of the alkyne with regards to the metals. This monohydrido, alkyne-bridged product can also be obtained from the reaction of diphenylacetylene with the monohydride,  $[Ir_2(CO)_2(\mu-H)(\mu-CO)(dppm)_2][BF_4]$ (7) [7], accompanied by loss of one CO ligand.

The other product in the reaction of 1 with diphenylacetylene is *cis*-stilbene (PhCH=CHPh), identified by the singlet resonance at  $\delta 6.60$  in the <sup>1</sup>H NMR spectrum (by comparison with an authentic sample) of the reaction mixture, when the reaction is carried out in CD<sub>2</sub>Cl<sub>2</sub>. The essentially quantitative formation of *cis*-stilbene, as suggested by integration of the <sup>1</sup>H NMR resonance, also suggests that any of the *trans* isomer that might have been formed must be in trace amounts. Unfortunately, this cannot be confirmed by the <sup>1</sup>H NMR spectrum of the reaction mixture, as the resonances due to any of this isomer that might be present will be masked by the intense signals due to the dppm and coordinated alkyne phenyl protons.

On the basis of the products obtained, it is proposed that the reaction of 1 with diphenylacetylene proceeds via insertion of the alkyne into one of the Ir-H bonds to yield a dihydrido, diphenylvinyl product in which the vinylic moiety is on one metal with a hydrido ligand occupying an adjacent site on the other metal. Transfer of this hydride to the metal bearing the vinylic group would then be followed by reductive elimination of cis-stilbene and coordination of another equivalent of diphenylacetylene. Unfortunately, attempts to identify such a vinyl hydride intermediate were unsuccessful, even at lower temperatures, although an analogous neutral dichloro species, [Ir<sub>2</sub>Cl<sub>2</sub>H(RC=C(H)R)(CO)<sub>2</sub>(dppm)<sub>2</sub>]  $(R = CO_2Me)$ , has been reported [5d]. Attempts to observe a vinyl hydride species by the addition of only 1 equiv, of diphenylacetylene to 1 yields only 6 and unreacted starting material. This reaction parallels those of [Ru(H)2(CO)2- $(PMe_{2}Ph)_{2}$  [25] and  $[Mo(n^{5}-C_{5}H_{5})_{2}H_{2}]$  [26] with the same alkyne, which resulted in the formation of cisstilbene together with [Ru(CO)<sub>2</sub>(PhC=CPh)(PMe<sub>2</sub>Ph)<sub>2</sub>] and  $[Mo(\eta^5-C_5H_5)_2(PhC \equiv CPh)]$ , respectively.

Compound 1 also reacts with phenylacetylene, yielding styrene and several unidentified products. Although the number of metal-containing products has hampered their characterization, the formation of substantial amounts of styrene indicates that there is hydrogenation of the alkyne at some stage of the reaction, presumably via a pathway similar to that proposed for the reaction of 1 with diphenylacetylene. As was the case for acetylene, the availability of additional reaction pathways for phenylacetylene, possibly via vinylidene species, is not unexpected [22–24], although these are difficult to identify in this study in the absence of doubly-<sup>13</sup>C labelled alkyne.

We had thought that the DMAD analogue of the diphenylacetylene- and hydride-bridged compound 6 could be obtained by protonation of one of the isomers,  $[Ir_2(CO)_2(\mu-\eta^1;\eta^1-DMAD)(dppm)_2]$  or  $[Ir_2(CO)_2(\mu-\eta^2;\eta^2-DMAD)-(dppm)_2]$  [27]. However, other work in our group showed that the first isomer yields  $[Ir_2H(CO)_2(\mu-\eta^1;\eta^1-DMAD)-(dppm)_2]$  [BF4], containing a terminal hydride ligand, whereas the second gives the vinyl-bridged product  $[Ir_2-(CO)_2(\mu-\eta^1:\eta^2-C(R)=C(H)R)(dppm)_2]$  [BF4] ( $R=CO_2-Me$ ) [27]. In addition, attempts to obtain the desired dicarbonyl product by substitution of a carbonyl in 7, by DMAD.



is in the range expected for this alignment. This is supported by a simulation of the <sup>31</sup>P{ <sup>1</sup>H} NMR spectrum, for which the large <sup>2</sup>J(P-P) values (280, 300 Hz) indicate a trans arrangement of diphosphines at both metals [19]. In all previously characterized dppm-bridged binuclear complexes, in which the alkyne binds perpendicular to the metals, a cis arrangement of diphosphines has been observed [22,27,28]. The hydride ligand is shown to be terminal, displaying coupling to only one pair of phosphorus nuclei, and selective <sup>31</sup>P decoupling has established that it is on the same metal as the carbonyl whose resonance is at  $\delta$  164.2, while the other two carbonyls are on the adjacent metal. Furthermore, the large coupling (10.6 Hz) between the carbonyl at  $\delta$  164.2 and one (at  $\delta$  152.5) on the adjacent metal suggests an arrangement in which these carbonyls are trans to the Ir-Ir bond. Large, three-bond coupling through a metal-metal bond has previously been observed when both ligands were opposite this bond [15,18,29]. Attempts to remove a carbonyl from 8 in hopes of generating the DMAD analogue of 6 also failed; in these experiments varying amounts (0-50%) of the vinylbridged product, together with unidentified decomposition products were obtained.

It is an interesting contrast that the alkynes, DMAD, HFB and acetylene yield adducts of the trihydride precursor 1, whereas diphenylacetylene and phenylacetylene are hydrogenated to the corresponding olefins, followed, in the first case, by diphenylacetylene coordination to give an alkynebridged mono-hydride product.

# 3.2. Reactions with alkenes

In light of the above different reactivity patterns exhibited by compound 1 with a few activated and non-activated alkynes, it was also of interest to determine whether similar reactivity differences would result from reaction of 1 with activated alkenes, such as tetrafluoroethylene or non-activated alkenes such as ethylene.

The reaction of compound 1 with ethylene gives a rare mono-hydrido ethylene compound,  $[Ir_2(C_2H_4)(CO)_2 - (\mu-H)(dppm)_2][BF_4]$  (9), as shown in Scheme 2. At temperatures above -40°C the four ethylene protons in 9 appear as one broad resonance at  $\delta$  0.94 in the <sup>1</sup>H NMR



spectrum, but resolve into two broad resonances, at  $\delta 0.90$ and 0.62, at - 80°C, consistent with facile ethylene rotation at higher temperatures. No reason is obvious for the unfield shift of these protons at lower temperatures. At -80°C the hydride resonance appears as a pseudo quintet at  $\delta - 9.93$ , as a result of coupling to the four phosphorus nuclei, indicating that this hydride ligand bridges the two metals. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at the lower temperature shows a broad resonance at  $\delta$  181.9 and a triplet at  $\delta$  177.6, suggesting the presence of two terminally bound CO ligands. Unfortunately, selective <sup>31</sup>P-decoupling NMR experiments could not be carried out to unambiguously establish the connectivity, since the phosphorus resonances are too closely spaced. The <sup>31</sup>P(<sup>1</sup>H) NMR spectrum at -80°C consists of two sharp multiplets at 8 6.8 and 12.1, typical of an AA'BB' spin system, however as the temperature is warmed to around - 40°C the higher-field resonance becomes broad and unresolved. Broadening of only one of the <sup>31</sup>P resonances is consistent with fluxionality of the olefin moiety, which is bound at only one metal.

We suggest that the formation of compound 9 follows a pathway similar to that proposed for compound 6, proceeding via the insertion of ethylene into one of the Ir-H bonds of compound 1, followed by reductive elimination of ethane and coordination of another molecule of ethylene. Evidence for the presence of ethane is given by the singlet that appears at  $\delta$  0.85 in the <sup>1</sup>H NMR spectrum of the reaction mixture. However, attempts to observe the proposed intermediate dihydrido-ethyl complex at low temperatures were unsuccessful.

In addition to the above noted olefin rotation, an additional fluxionality is observed at ambient temperature, as shown by the NMR spectra. This process results in the appearance of only one broad resonance for the dppm methylene protons at ambient temperature and a coalescence of the carbonyl resonances to give a broad featureless signal at  $\delta$  179.2. These data indicate a process which exchanges the ligands on the front and back of the complex and is proposed to occur by the hydride 'tunneling' process [30] diagrammed below (the dppm ligands above and below the plane of the drawing have been omitted for clarity). This tunneling process results from



twisting of the 'IrH(CO)<sub>2</sub>' unit about the P-Ir-P axis, bringing the hydride between the metals and also resulting in exchange of the two carbonyl positions as shown. The observed averaging of the methylene 'H resonances and the '3'CO resonances argues in favor of the ligand arrangement shown above, since a structure having a CO on each metal would give rise to two methylene resonances since hydridetunneling would not equilibrate the methylene protons. However, a more complex fluxional process, as shown below, in which carbonyl transfer from one metal to the other occurs along with hydride tunneling, cannot be ruled out.



Fig. 1. Perspective view of the  $[Ir_2(CO)_2(\eta^2 \cdot C_2H_4)(\mu \cdot H)(dppm)_2]^*$  cation showing the atom labelling scheme. Only one set of the disordered carbonyl and ethylene groups is shown (see text for explanation of the disorder). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the hydride,  $\pi$ -ethylene and dppm methylene groups, and are not shown for the dpm phenyl groups.

Ethylene adducts of dppm-bridged binuclear complexes of Ir are extremely rare. To our knowledge the complexes,  $[MIr(CH_3)(CO)_2(C_2H_4)(dppm)_2][CF_3SO_3] (M=Rh, Ir)$  $[31,32] and [Ir_2(C_2H_4)(CO)(\mu-CO)(\mu-I)(dppm)_2][X]$  $(X=I, BF_4)$  [15] are the only other examples.

Since no other A-frame olefin complexes had been structurally characterized, an X-ray structure determination of 9was undertaken. Unfortunately, due to the 50:50 disorder of the CO and ethylene ligands (vide supra), it is not possible to unambiguously establish whether the carbonyl which is close to a bridging position is  $\sigma$ -bound to Ir(1) or Ir(2), since both orientations are observed in the disordered model.



Nevertheless, the binding mode of the ethylene is clear, and its location adjacent to the bridged hydride ligand is also unequivocal. The perspective view of the cation of 9, shown in Fig. 1, reflects the probable structure based on NMR studies. In Tables 4 and 5 the parameters involving both disordered molecules are shown, with the atoms of one disordered molecule being primed.

Owing to the disorder, there will be some uncertainty in the metal-ligand parameters; nevertheless, most parameters are well determined. The complex has the bridging dppm ligands in a normal *trans* arrangement about the metal centers  $(P(1)-Ir(1)-P(3) = 171.00(6)^{\circ}$  and P(2)-Ir(2)-P(4) = $172.36(6)^{\circ}$ ), and in a *cis* orientation to the other atoms coordinated to the metal nuclei. The Ir(1)-Ir(2) distance of 2.8202(4) Å corresponds to a normal single bond [5d,6,15,19,23,33], and is significantly shorter than the intraligand P-P separations (P(1)-P(2) = 2.998(2) Å, P(3)-P(4) = 3.004(2) Å, indicating substantial attraction

of the adjacent metal centers. The geometry about each metal is different, since one metal has both carbonyls attached whereas the other has the ethylene ligand coordinated. For Ir(2), the geometry is reminiscent of a trigonal bipyramid. having both carbonyls and the hydride ligand in the equatorial plane, and axial phosphine groups, giving this metal an 18electron count. Ir(1) has a geometry best described as square planar, in which the ethylene occupies one site and the Ir(2)-H bond, which can be viewed as forming an agostic bond to Ir(1), occupies the opposite site, with the remaining positions occupied by the mutually trans phosphorus atoms. Donation of the Ir(2)-H electron pair to the cationic Ir(1) center gives this metal the 16-electron configuration that is typical for a  $d^8$ , square planar complex. The Ir(2)-C(2) distance of 2.02(2) Å (1.92(2) Å)<sup>4</sup> is normal for an Ir-CO bond, while the Ir(1)-C(2) distance of 2.50(2) Å (2.54(2) Å) suggests the presence of a weak semibridging interaction. However, the presence of a single CO stretch at 1977 cm<sup>-1</sup> in the IR spectrum of 9, in a region typical of terminally bound carbonyls, suggests that any such interaction between one of the CO ligands and the adjacent metal must be very weak. Although the deviation of the Ir(2)-C(2)-O(2) angle from linearity should give an indication of the strength of the Ir(1)-C(2) interaction, the poorly defined position of O(2), owing to the disorder, casts some doubt on this angle at C(2). The other CO ligand is essentially linear, as indicated by the Ir(2)-C(1)-O(1) angle of  $178(3)^{\circ}$  (169(5)°), and the Ir(2)-C(1) and C(1)-O(1) bond distances of 1.78(2) Å (1.92(6) Å), and 1.14(3) Å (1.01(6) Å), respectively, are normal for a terminally bound carbonyl ligand. The hydride ligand was constrained to bridge the two metals in an approximately symmetrical manner, yielding Ir(1)-H(1) = Ir(2)-H(1) = 1.80(3) Å. The ethylene ligand is coordinated to Ir(1) almost perpendicular to the metal-phosphorus plane with torsion angles of C(3)-Ir(1)-Ir(2)-P(4) = 81(1)°  $(87(2)^{\circ})$  and C(4)-Ir(1)-Ir(2)-P(2) = 92(4)^{\circ} (90(2)^{\circ}). The C(3)-C(4) distance of 1.40(5) Å (1.42(3) Å) is somewhat shorter than that of a C-C single bond, and is close to the C--C distance of the coordinated ethylene ligand in

[PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(NC<sub>7</sub>H<sub>10</sub>)] (1.494(21) Å) [34]. The Ir(1)– C(3) and Ir(1)–C(4) distances of 2.19(2) Å (2.12(2) Å) and 2.03(5) Å (2.18(3) Å), respectively, are within the expected range for Ir–C single bonds. Tetrafluoroethylene reacts with compound 1 to give a mixterrafluoroethylene react with compound 1 to give a mix-

ture of the compound,  $[Ir_2(H)_2(CO)_2(\mu-H)(\mu-C_2F_4)-(dppm)_2][BF_4]$  (10) together with starting material, in a typical ratio of 1:1. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of compound 10 shows a singlet at  $\delta - 8.5$ , indicating the equivalence of all phosphorus nuclei. The high-field region of the <sup>1</sup>H NMR spectrum shows a multiplet at  $\delta - 10.76$ , due to the two terminal hydrides, and a quintet (due to coupling to the

four phosphorus nuclei) at  $\delta = 18.02$ , while the <sup>19</sup>F spectrum shows a broad resonance at  $\delta = 73.9$  due to the  $C_2F_4$  ligand (the intensity of this signal relative to that of the BF<sub>4</sub><sup>-</sup> anion indicates that the former signal is due to four fluorine atoms). All of these NMR data are consistent with the tetrafluoroethylene ligand bridging the two Ir centers in **10**. Binuclear complexes with bridging tetrafluoroethylene ligands are known, and include [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -SMe<sub>2</sub>)<sub>2</sub>( $\mu$ -C<sub>2</sub>F<sub>4</sub>)] [35], [Pt<sub>2</sub>(1,5-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>( $\mu$ -C<sub>2</sub>F<sub>4</sub>)<sub>2</sub>] and [Pd<sub>2</sub>(1,5-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>( $\mu$ -C<sub>2</sub>F<sub>4</sub>)] [36], which are obtained by reacting C<sub>2</sub>F<sub>4</sub> with [Fe<sub>1</sub>(CO)<sub>3</sub>( $\mu$ -SMe<sub>2</sub>)<sub>2</sub>. [Pt<sub>1</sub>(1,5-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>] and [Pd<sub>1</sub>(1,5-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>], respectively. The only other binuclear, dppmbridged complex of Ir having a bridging tetrafluoroethylene ligand is [Ir<sub>2</sub>(CH<sub>3</sub>)(CO)<sub>2</sub>( $\mu$ -C<sub>7</sub>F<sub>4</sub>)(dppm)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>], which has been characterized in this research erroup [37].

The reactions of compound 1 with ethylene and tetrafluoroethylene, once again, follow the trend observed in the reactions with alkynes, in which the unactivated, unsaturated substrates undergo hydrogenation while the activated ones merely coordinate to the metal complex. The extremely slow reaction of 1 with tetrafluoroethylene, compared to that with ethylene, and the incomplete conversion of 1 to 10 is presumably a result of unfavorable interactions between the fluorine substituents and the phenyl groups of the dppm ligands.

## 3.3. Reactions of the ethylene complex 9

Since the olefin ligand and the  $\mu$ -hydrido group in 9 occupy adjacent coordination sites, it was of interest to determine whether this compound would undergo reversible migratory insertion/ $\beta$ -hydride elimination to yield a transient ethyl complex as diagrammed below (dppm groups omitted).



This product would be the ethyl analogue of  $[Ir_2(CH_3)(CO)(\mu_r-CO)(dppm)_2][SO_3CF_3]$ , which has been extensively studied in our group, owing to its ability to undergo facile activation of a methyl C-H bond upon addition of a variety of ligands [38]. If the process shown above were occurring, scrambling of the ethylene hydrogens with the hydrido ligand would be expected. Our failure to detect this scrambling by spin-saturation transfer experiments over the temperature range between -40 and +25°C indicates that it is not occurring on the NMR time scale. However, this process may occur at slower rates as suggested by labeling studies in which reaction of the thydride 1 with C-D\_4 yielded 9 in

<sup>&</sup>lt;sup>4</sup> The parameter quoted in parenthesis throughout this discussion, is for the second disordered molecule of the disordered structure. Therefore, the two equivalent bonds involving Ir and C(2) are Ir(2)-C(2) and Ir(1)-C(2). See the description of the disorder given in Section 2.9.

which <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy showed <sup>1</sup>H/<sup>2</sup>H scrambling over the ethylene and metal-hydride positions. Although this <sup>1</sup>H/<sup>2</sup>H scrambling could have occurred during the initial ethylene hydrogenation step, this does not seem as likely, since one of the hydride ligands in 1, and presumably in the ethyl-dihydride intermediate, is isolated from the other hydrides and is not expected to be readily exchanged with them.

It seemed that it might be possible to observe an ethyl complex if the presumed unsaturated ethyl species, shown above, were trapped by the reaction with other ligands, as was previously demonstrated in a mononuclear iron complex [39]. In addition, an interesting prospect was the possibility that the proposed transient diiridium ethyl species might react as the related methyl complex, with activation of one of the C-H bonds on the  $\alpha$ -carbon to give a bridging ethylidene group. However, with the ligands studied (CO, SO<sub>2</sub>, PMe<sub>3</sub>) no evidence of insertion, to give an ethyl complex, was observed and instead ethylene substitution occurred in each case. With carbon monoxide, the known tricarbonylhydride  $[Ir_2(CO)_2(\mu-H)(\mu-CO)(dppm)_2][BF_4]$  (7) was obtained, whereas with SO2, the analogous SO2-bridged product  $[Ir_2(CO)_2(\mu-H)(\mu-SO_2)(dppm)_2][BF_4]$  (11) resulted. Although spectroscopically it is difficult to distinguish between a terminal and a bridging SO<sub>2</sub> group, the close similarity of the spectral parameters of 7 and 11 suggest related structures, and a symmetrical structure containing only one SO<sub>2</sub> molecule demands that this group be bridging.

The product of the reaction of 9 with PMe<sub>3</sub> is the unstable substitution product  $[Ir_2H(CO)_2(PMe_3)(dppm)_2][BF_4]$ (12) as diagrammed below. The spectral parameters clearly



indicate that one carbonyl and the hydride ligand are terminally bound to the same metal as the PMe<sub>2</sub> ligand, since these groups show substantial coupling to this phosphine and to the adjacent pair of dppm phosphorus nuclei. The exact stereochemistry about this more crowded Ir center is not known, however the structure shown is analogous to the isoelectronic [RhOsH(CO)<sub>3</sub>(dppm)<sub>2</sub>] and [RhRe(CO)<sub>4</sub>(dppm)<sub>2</sub>] [40].

Reaction of 9 with  $H_2$  does not result in ethylene hydrogenation, but instead results in ethylene loss to regenerate compound 1. The signal at  $\delta 5.33$  in the <sup>1</sup>H NMR spectrum of the reaction mixture indicates the presence of free ethylene. The observation that compound 1 reacts with ethylene to give ethane and 9, and that the former complex can be regenerated by reacting 9 with  $H_{23}$  suggests that compound 1 is a potential catalyst for the hydrogenation of ethylene. However no catalytic studies on 1 have been undertaken.

It was anticipated that compound 9 could be obtained directly from  $[Ir_2(CO)_2(\mu-CO)(\mu-H)(dppm)_2][BF_4](7)$ by displacement of one carbonyl by ethylene, much as was observed in the reaction of 7 with PhC<sub>2</sub>Ph to yield  $[Ir_2(CO)_2(\mu-H)(\mu-PhC_2Ph)(dppm)_2][BF_4]$  (6). However 7 did not react with ethylene, over a range of temperatures. Compound 9 can be generated by reaction of 7 with ethylene in the presence of Me<sub>3</sub>NO.

## 4. Discussion

In the chemistry of  $[Ir_2H(CO)_2(\mu-H)_2(dppm)_2][BF_4]$ with unsaturated substrates, the reactions can be separated into two categories depending on whether simple substrate addition occurs, to generate the trihydride products  $[Ir_{2}(H)_{2}(CO)_{2}(\mu-H)(\mu-L)(dppm)_{2}][BF_{4}] (L=DMAD,$ HFB, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>F<sub>4</sub>), or whether substrate hydrogenation followed by coordination of a second equivalent of substrate occurs, to give monohydride products  $[Ir_2(CO)_2(\mu-H) (L)(dppm)_2$  [BF<sub>4</sub>] (L=PhC<sub>2</sub>Ph, C<sub>2</sub>H<sub>4</sub>). With the exception of acetylene, one clear trend emerges, based on the nature of the alkyne or olefin substituents: substrates containing strongly electron withdrawing substituents (the so-called activated substrates) yield the addition products whereas the others proceed by substrate hydrogenation. Clearly the pivotal question that arises from this study is why the two different reactivities occur.

Presumably in each case, the first step is substrate coordination at a single metal. Which of the two routes is subsequently followed, we suggest, depends on the relative tendencies of the substrate to undergo migratory insertion with a hydride ligand, thereby leading to hydrogenation, or to move to the bridging site yielding the simple bridged adduct. Previous studies on the hydrogenation of para-substituted styrenes have shown that the rate of intramolecular migratory insertion of these olefins and a hydride ligand decreases with the electron-withdrawing power of the substituents [41]. Intuitively, this is not surprising, since olefins (and alkynes) having stronger electron-withdrawing groups bind more effectively to low-valent metals, so should be more reluctant to surrender the stability gained through  $\pi$  backdonation by undergoing migratory insertion. Coupled with this is the strong tendency for alkynes, having electronegative substituents, to bind in a bridging mode. In the parallel bridging mode, as observed in this work, the alkyne can be viewed as a dianionic group that binds via two M-C  $\sigma$ -bonds. Electron-withdrawing substituents not only favor the anionic ligand formulation characteristic of this binding mode, but also result in stronger M-C bonds [42]. Once the alkyne is bound in this way, it is our experience [27,43] and that of others [44], that such groups are relatively unreactive. For example, attempts to induce migratory insertion by refluxing these trihydrido, olefin or alkyne adducts either resulted in loss of the unsaturated substrate or no reaction.

In all cases investigated, except for ethylene, the substrate molecule is ultimately bound in a bridging arrangement. For alkynes, such an arrangement is usually the favored one in binuclear complexes [45]. Only in a few cases is the terminal mode observed, and this seems to occur when factors prevent movement of the alkyne to a bridging position [46]. For olefins the bridging mode is much less common [35,36,47]. although it appears to be more favorable for olefins containing electron-withdrawing substituents. While ethylene itself has not yet been observed to bridge in dppm-bridged species, this mode has been seen in a couple of cases in which the steric demands are less [47c,d,l]. Certainly one factor of importance with olefins involves the steric interactions involving the four substituents, which are more severe than those involving two alkyne substituents. For an olefin to bridge in these dppm-bridged complexes under study, the substituents above and below the M2C2 plane of the resulting dimetallacycle will be involved in unfavorable steric repulsions involving the dppm phenyl groups. Even for tetrafluoroethylene, which would be expected to form strong Ir-C  $\sigma$ -bonds in the bridging configuration, the olefin is only weakly bound, with the adduct in equilibrium with the precursor 1, even in the presence of excess olefin. In a related complex [Ru<sub>2</sub>(CO)<sub>4</sub>- $(\mu - \eta^1 : \eta^1 - C_2(H)_2(CO_2CH_3)_2)(dmpm)_2]$ , the structure showed that the bridging dimethylfumarate ligand is skewed substantially owing to steric interactions with the dmpmmethyl groups [47k]. It is to be expected that with the larger phenyl groups in dppm, and with substitution of all four of the small hydrogen substituents on the olefin (as in  $C_2F_4$ ), the steric interactions will be more severe.

The only exception to the reactivity trend noted above is acetylene, which forms a simple adduct,  $[Ir_2(H)_2(CO)_2(\mu -$ H) $(\mu$ -C<sub>2</sub>H<sub>2</sub>)(dppm)<sub>2</sub>][BF<sub>4</sub>], in spite of having no electronegative substituents. We would have expected this alkyne to react by hydrogenation, as observed for diphenylacetylene, phenylacetylene and ethylene. We find no rationalization, based on electronic arguments, for this behavior, in which acetylene resembles the highly activated DMAD and HFB molecules, rather than PhC=CPh. In the absence of such arguments we are forced to conclude that the uniquely small size of acetylene gives rise to substantially fewer steric constraints than with the other substrates studied. It may then be that the absence of substantial steric constraints favors generation of the alkyne-bridged adduct over the combination of migratory-insertion, hydride-migration and reductiveelimination steps.

This study, particularly for the alkynes, presents further evidence that binding of the unsaturated substrate between the late transition metals does not necessarily have a beneficial affect on the reactivity. In the complexes reported herein, the bridged substrate molecules are rather unreactive. In reactions that are promoted by the presence of an adjacent metal center, the promoting influence of the additional metal must be more subtle than to merely offer the possibility of bridged coordination modes.

# 5. Supplementary material

Tables of parameters for the dppm phenyl rings and the  $\mathbb{D}_{4}^{-1}$  anion, anisotropic thermal parameters, calculated hydrogen parameters and all bond lengths and angles (7 pages) are available from the authors upon request.

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