

# Reactivity of $[\text{Ru}_2(\text{CO})_6(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$ (Fu = furyl) Towards Tri(2-furyl)phosphine

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**Abstract:** Reaction of  $[\text{Ru}_2(\text{CO})_6(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  (Fu = furyl) **1** with tri(2-furyl)phosphine under thermal conditions produces simple mono- and disubstitution products  $[\text{Ru}_2(\text{CO})_5(\text{PFu}_3)(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  **2a** and  $[\text{Ru}_2(\text{CO})_4(\text{PFu}_3)_2(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  **2b**. Both complexes were fully characterized by spectroscopic and analytical methods and the molecular structures of **2a** and **2b** were established by X-ray crystallography. The Ru–Ru edge bridged by the  $\mu\text{-}\eta^1, \eta^2$ -bound  $\text{PFu}_2$  fragment remains intact after the substitution reaction. The product yields of both complexes depend on the stoichiometry of the reactants. All of these new diruthenium complexes are electron precise with 34 cluster valence electrons.

## INTRODUCTION

In recent years, the search for catalysts which exhibit higher reactivity or greater efficiency towards transition-metal-mediated organic processes has become an extremely active area of chemical research. It was shown that judicious choice of auxiliary ligands in the coordination sphere of a metal can affect the steric, electronic, and physical properties of a coordinated species, thereby effecting the catalytic activity of the system concerned. Among these, tertiary phosphines are one of the most important ligands in this context. The steric and electronic properties of a tertiary phosphine can markedly influence the reactivity of a metal center and lead to significant changes in chemical reactivity and catalytic behavior [1]. For instance, as the steric bulk of the R groups in  $\text{PR}_3$  is increased, it is expected that the intervalence angles about the phosphorus atom will increase. Such a structural change would reduce the  $\sigma$ -character of the phosphorus lone pair orbital, making the ligand more Lewis basic. While the chemistry and reactivities of triphenylphosphine ( $\text{PPh}_3$ ) and tri(2-thienyl)phosphine ( $\text{PTh}_3$ ) with transition metal clusters have been well established, knowledge pertaining to the use of tri(2-furyl)phosphine ( $\text{PFu}_3$ ) is, however, very limited in the literature (Chart 1). As would be expected from the size of a 2-furyl group relative to a phenyl substituent, the cone angle of  $133^\circ$  measured for  $\text{PFu}_3$  is slightly smaller than that for  $\text{PPh}_3$  ( $145^\circ$ ) [2, 3]. Since heteroaryl groups such as the 2-furyl and 2-thienyl moieties are electron withdrawing relative to the phenyl substituent, 2-furyl and 2-thienyl phosphines are poorer  $\sigma$ -donor ligands. In the absence of synergic bonding, these ligands would dissociate from a metal center more easily. However, the  $\sigma$  withdrawal of electrons away from the phosphorus atom by the heteroaryl groups causes the system to compensate by transferring electron density from the filled metal d orbitals into the  $\pi^*$ -antibonding orbitals of the ligand. In other words, 2-furyl and 2-thienyl phosphines can act as a  $\pi$ -acid [3]. This effect would be more pronounced for late transi-

tion metals in low oxidation states [4]. The pioneering work by Farina and co-workers showed the use of  $\text{PFu}_3$ -derived palladium catalysts to be highly advantageous in the Stille cross-coupling reaction with significant rate accelerations being observed over traditional  $\text{PPh}_3$ -based catalysts, presumably by virtue of its low electron-donating ability toward Pd(II) center [5]. Since then, numerous researchers have sought to evaluate the performance of  $\text{PFu}_3$  in a wide variety of metal-catalyzed processes for the preparation of small molecules, complex natural products as well as polymers [3]. In many cases, Stille coupling with the  $\text{PFu}_3$  ligand allows for milder reaction conditions and hence the attenuation of unwanted side reactions. However, accurate prediction of whether this poor  $\sigma$ -donating  $\text{PFu}_3$  ligand will lead to beneficial effects for a given process still remains elusive.

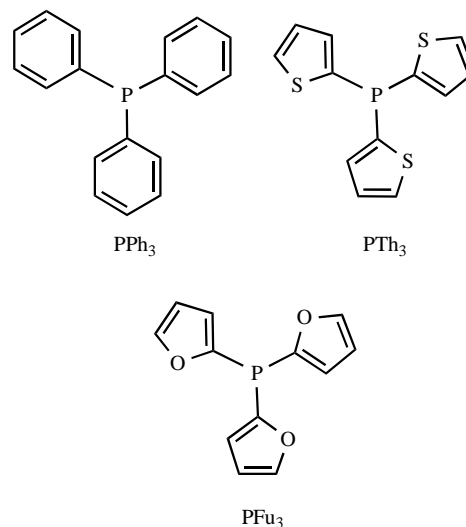
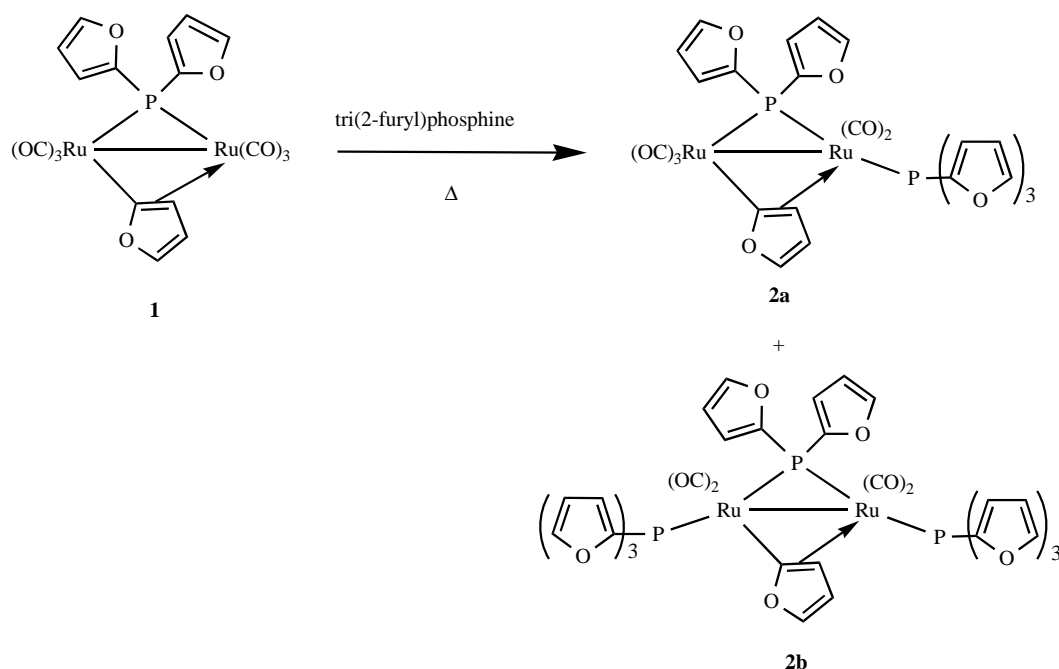


Chart 1.

Reactions of triruthenium carbonyl clusters with alkyl-, aryl- and alkoxy-substituted phosphines L have been widely studied in the past few decades, affording a series of substitution products  $[\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n]$  ( $n = 1\text{--}4$ ) [6]. More recently, much effort was devoted to the reactivity

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**Scheme 1.** Synthesis of **2a** and **2b**.

studies of phosphine ligands bearing additional donor sites towards  $[\text{Ru}_3(\text{CO})_{12}]$  and other cluster derivatives [7–10], and trinuclear ruthenium carbonyl clusters with functionalized phosphine ligands such as  $\text{PPh}_2(\text{C}_5\text{H}_4\text{N})$  [8],  $\text{PPh}_2(\text{CH}_2\text{COPh})$  [9] or  $\text{PPh}_2(\text{C}_6\text{H}_4\text{X}-2)$  ( $\text{X} = \text{CHO}, \text{NH}_2, \text{NCHPh}$ ) [10] can be isolated. Phosphine ligands containing sulfur donor substituents were also used in this context, with particular attention to phosphines with the 2-thienyl group [11].

We are interested in the use of tri(2-furyl)phosphine ( $\text{PFu}_3$ ) as a ligand in organometallic cluster syntheses [12]. The recent preparation of  $[\text{Ru}_2(\text{CO})_6(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  **1** and its reactivity with 1-alkynes sparked our interest for the synthesis of a new class of complexes with different ligand environments [12a]. To explore the synthetic potential of this system, we have now initiated a comprehensive study of the reactions of **1** with some mono- and diphosphine ligands. In this connection, efforts have been directed to the synthesis, spectroscopic and structural characterization of dinuclear ruthenium carbonyl clusters derived from  $\text{PFu}_3$ .

## RESULTS AND DISCUSSION

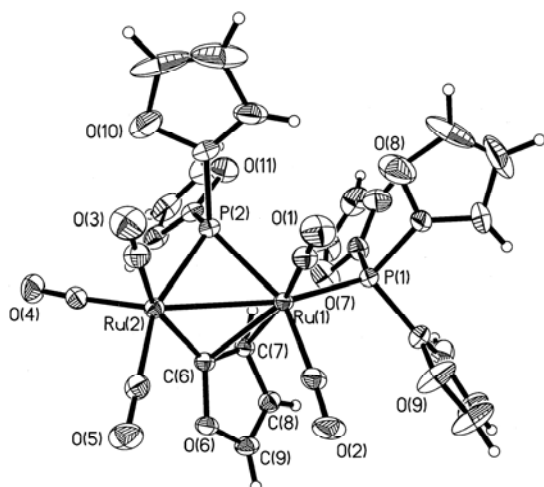
### Reaction of **1** with Tri(2-furyl)phosphine

Treating  $[\text{Ru}_2(\text{CO})_6(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  **1** with  $\text{PFu}_3$  in refluxing toluene for 3 h generates a separable mixture of two substitution products identified as  $[\text{Ru}_2(\text{CO})_5(\text{PFu}_3)(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  **2a** and  $[\text{Ru}_2(\text{CO})_4(\text{PFu}_3)_2(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$  **2b** (Scheme 1). They can be purified by preparative TLC on silica and isolated as yellow solids. Their yields vary with the mole ratio of starting reagents used and an increased amount of **2b** was obtained at the expense of **2a** when two molar equivalents or more of  $\text{PFu}_3$  was added to react with **1**. Both compounds were characterized by spectroscopic and crystallographic methods.

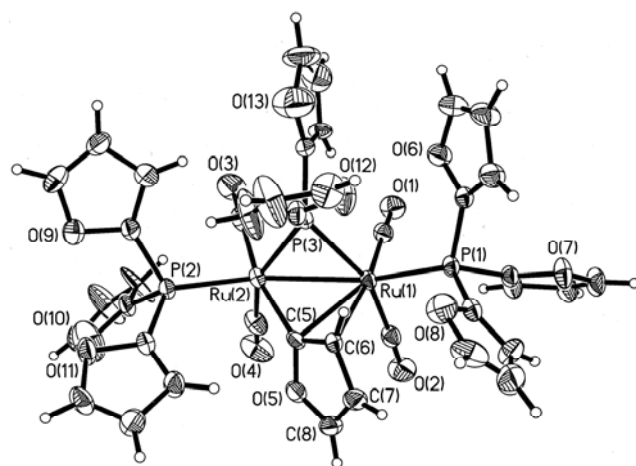
The spectroscopic properties of **2a** and **2b** are fully consistent with their formulations. The formulae of both complexes were initially confirmed by FAB mass spectrometry, the spectra of which revealed the presence of their molecular ion peaks at  $m/z$  807 (**2a**) and 1011 (**2b**). The IR spectral data of **2a** and **2b** in the CO region are shifted to the lower energy compared with that of the precursor complex **1**, in line with the stronger  $\sigma$ -donor and weaker  $\pi$ -acceptor ability of  $\text{PFu}_3$  relative to CO. Complex **2a** gives two doublets at  $\delta$  53.38 and  $-11.52$  with  $^2J_{\text{P-P}} = 21$  Hz in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum while **2b** gives a pseudo  $\text{AX}_2$   $^{31}\text{P}\{-^1\text{H}\}$  spectrum with a triplet at  $\delta$  48.00 and a doublet at  $-12.28$  ( $^2J_{\text{P-P}} = 23$  Hz). The low-field signals for **2a** and **2b** are assigned to the phosphido-P atom (c.f.  $\delta$  58.5 for **1**) [12a] and the other signals in the negative  $\delta$  region are due to the coordinated  $\text{PFu}_3$  group(s). It is apparent that Ru–Ru bond is retained in these complexes since they exhibit similar phosphido resonances as the parent compound **1**. The furyl rings in **2a** and **2b** are expected to give rise to a total of 18 and 27 proton resonances which, from the integral trace of each spectrum, appear to be the case. With reference to the spectral assignment of **1**, we were able to identify the three protons of the  $\mu\text{-}\eta^1, \eta^2\text{-Fu}$  moiety in **2a** and **2b** and examination of the relative intensities of 1:1:1 supported our assignment (see Experimental section).

### Crystal Structures of **2a** and **2b**

The structures of **2a** and **2b** were determined by single-crystal X-ray diffraction and (Figs. 1 and 2) depict their structures, respectively. Selected bond lengths and angles are given in Tables 1 and 2. Although there are numerous structurally characterized examples of ruthenium carbonyl clusters with terminally coordinated  $\text{PPh}_3$  ligands, structures containing  $\text{PFu}_3$  are very rare. The crystal lattice of **2a** contains two independent but structurally similar mole-



**Fig. (1).** X-ray structure of **2a**. Thermal ellipsoids are shown at the 25% probability levels. The carbon labels on carbonyl groups and furyl rings are omitted for clarity.



**Fig. (2).** X-ray structure of **2b**. Thermal ellipsoids are shown at the 25% probability levels. The carbon labels on carbonyl groups and furyl rings are omitted for clarity.

cules per asymmetric unit, the geometry of one molecule being quoted as representative. The basic geometry of both

compounds corresponds closely to that of **1** in which a difurylphosphido group and a furyl moiety bridge the Ru–Ru edge with Ru(1)–Ru(2) distances of 2.7693(4) and 2.7737(8) Å in **2a** and **2b**, respectively. The phosphido bridge is bonded to Ru(1) and Ru(2) nearly symmetrically in both cases [Ru(1)–P(2) 2.3549(8), Ru(2)–P(2) 2.3366(8) Å **2a**; Ru(1)–P(3) 2.364(2), Ru(2)–P(3) 2.349(2) Å **2b**]. Analogous to the structure of **1** [12a], the structures of **2a** and **2b** revealed that the dissociated furyl group is bonded to the Ru<sub>2</sub> unit in a μ-η<sup>1</sup>,η<sup>2</sup> fashion, formally *via* a σ and a π bond. The furyl fragment forms a σ bond to Ru(2) [Ru–C 2.078(7)–2.083(3) Å] and a π bond to Ru(1) [Ru–C 2.349(3)–2.399(6) Å] in **2a** and **2b**. For **2a**, one of the CO groups is replaced by a PFu<sub>3</sub> ligand at Ru(1) whereas substitution of one CO group at each Ru center by two monodentate phosphine ligands occurs for **2b** in a position such that steric repulsion between the bulky phosphines can be minimized. The Ru–PFu<sub>3</sub> distances in **2a** and **2b** are rather similar and span the narrow range 2.299(2)–2.321(2) Å. While each of the phosphido Ru<sub>2</sub>P and μ-η<sup>1</sup>,η<sup>2</sup>-furyl ligands acts as a three-electron donor, **2a** and **2b** are electron precise with 34 cluster valence electrons (CVE), in accordance with the effective atomic number (EAN) rule. Table 3 compares the Ru–Ru and Ru–P(Fu) bond lengths for **2a** and **2b** with some relevant Ru<sub>2</sub> cores in the literature [12a, 13].

## CONCLUDING REMARKS

The work presented here concerns the solution chemistry of [Ru<sub>2</sub>(CO)<sub>6</sub>(μ-PFu<sub>2</sub>)(μ-η<sup>1</sup>,η<sup>2</sup>-Fu)] (Fu = furyl) **1** with a monodentate PFu<sub>3</sub> ligand to afford new 34-electron difurylphosphido-stabilized diruthenium complexes in moderate to good yields. However, it was shown to differ significantly from those reactions for other (CH<sub>2</sub>)-bridged (n = 1, 4, 5) and N(R)-bridged (R = H, Me) diphosphines [13]. Work is in progress to study the reactivity of **1** with other organic and organometallic nucleophilic reagents. Although PFu<sub>3</sub> is similar in size to PPh<sub>3</sub>, they have different electronic properties. The former phosphine is substantially less Lewis basic and should therefore be a poorer σ-donor ligand in transition-metal-mediated organic transformations. Overall, cluster research based on PFu<sub>3</sub> has a great deal to offer in many ways, particularly with regard to synthesizing novel cluster complexes with unusual molecular skeletons and/or unique electronic properties.

**Table 1.** Selected Bond Lengths (Å) and Angles (°) for Complex **2a**

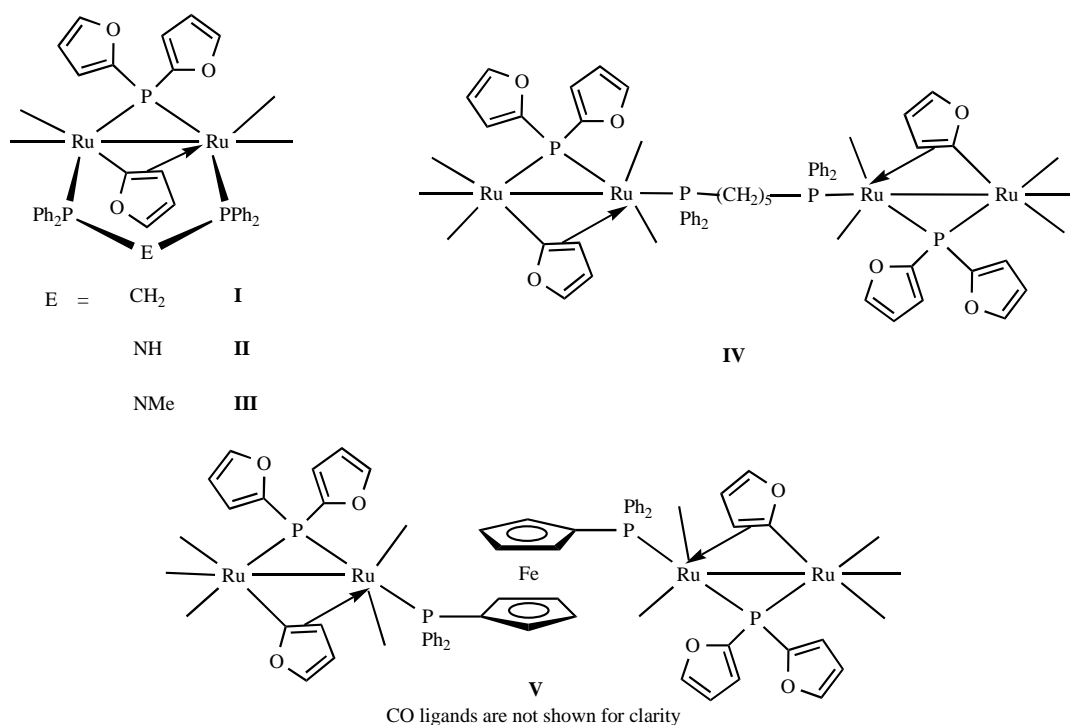
Ru(1)–Ru(2)	2.7693(4)	Ru(1)–P(1)	2.3205(8)
Ru(1)–P(2)	2.3549(8)	Ru(2)–P(2)	2.3366(8)
Ru(1)–C(6)	2.349(3)	Ru(1)–C(7)	2.380(3)
Ru(2)–C(6)	2.083(3)	C(6)–C(7)	1.397(4)
Ru(1)–P(2)–Ru(2)	72.35(2)	Ru(2)–Ru(1)–P(1)	155.58(2)
Ru(2)–Ru(1)–P(2)	53.52(2)	Ru(1)–C(7)–C(6)	71.6(2)
Ru(1)–C(6)–Ru(2)	77.09(9)	Ru(2)–Ru(1)–C(6)	47.15(7)
Ru(2)–Ru(1)–C(7)	76.68(7)	Ru(1)–C(6)–C(7)	74.1(2)
C(6)–Ru(1)–C(7)	34.35(9)	Ru(2)–C(6)–C(7)	133.5(2)

**Table 2.** Selected Bond Lengths (Å) and Angles (°) for Complex **2b**·0.5C<sub>5</sub>H<sub>12</sub>

Ru(1)–Ru(2)	2.7737(8)	Ru(1)–P(1)	2.321(2)
Ru(2)–P(2)	2.299(2)	Ru(1)–P(3)	2.364(2)
Ru(2)–P(3)	2.349(2)	Ru(1)–C(5)	2.364(6)
Ru(1)–C(6)	2.399(6)	Ru(2)–C(5)	2.078(7)
C(5)–C(6)	1.411(9)		
Ru(1)–P(3)–Ru(2)	72.09(5)	Ru(2)–Ru(1)–P(1)	155.22(5)
Ru(2)–Ru(1)–P(3)	53.70(4)	Ru(1)–Ru(2)–P(2)	152.23(5)
Ru(1)–C(6)–C(5)	71.4(4)	Ru(1)–C(5)–Ru(2)	77.0(2)
Ru(2)–Ru(1)–C(5)	46.9(2)	Ru(2)–Ru(1)–C(6)	76.7(2)
Ru(1)–C(5)–C(6)	74.1(4)	C(5)–Ru(1)–C(6)	34.5(2)
Ru(2)–C(5)–C(6)	134.2(5)		

**Table 3.** Comparison of the Ru–Ru and Ru–P Bond Lengths of Some Dinuclear Di(furyl)phosphido-bridged Ruthenium Carbonyl Complexes

Complex	Ru(1)–Ru(2) (Å)	Ru(1)–P(Fu) (Å)	Ru(2)–P(Fu) (Å)	Reference
<b>I</b>	2.7761(3) <sup>a</sup>	2.3409(7) <sup>a</sup>	2.3244(7) <sup>a</sup>	[12a]
<b>2a</b>	2.7693(4)	2.3549(8)	2.3366(8)	This work
<b>2b</b>	2.7737(8)	2.364(2)	2.349(2)	This work
<b>I</b>	2.7443(6)	2.325(2)	2.376(2)	[13]
<b>II</b>	2.729(1)	2.356(3)	2.348(2)	[13]
<b>III</b>	2.7339(4)	2.3370(9)	2.3728(9)	[13]
<b>IV</b>	2.7934(5)	2.359(1)	2.324(1)	[13]
<b>V</b>	2.7982(6) <sup>a</sup>	2.347(2) <sup>a</sup>	2.340(1) <sup>a</sup>	[13]

<sup>a</sup>Average value of the three independent molecules per asymmetric unit of **I**.

## EXPERIMENTAL

## General

All reactions were conducted under an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents for preparative work were dried and distilled before use. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The synthesis of complex **1** was carried out as reported previously [12a]. IR spectra were recorded as CH<sub>2</sub>Cl<sub>2</sub> solutions on a Perkin Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in CDCl<sub>3</sub> on a JEOL EX270 or a Varian Inova 400 MHz FT-NMR spectrometer, with <sup>1</sup>H NMR chemical shifts quoted relative to SiMe<sub>4</sub> and <sup>31</sup>P chemical shifts relative to an 85% H<sub>3</sub>PO<sub>4</sub> external standard. Fast atom bombardment (FAB) mass spectra were recorded in *m*-nitrobenzyl alcohol matrices on a Finnigan-SSQ 710 spectrometer. Separation of products was accomplished by preparative TLC plates coated with silica (Merck, Kieselgel 60).

## Syntheses

Compounds **2a** and **2b**. A toluene solution (20 cm<sup>3</sup>) of complex **1** (50 mg, 0.083 mmol) was stirred at reflux with

one molar equivalent of tri(2-furyl)phosphine (20 mg, 0.083 mmol) for 3 h. This generated a bright yellow solution which was evaporated to dryness, the residue redissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on silica plates using hexane-CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) as eluent. Two yellow substitution products were isolated and identified as [Ru<sub>2</sub>(CO)<sub>5</sub>(PFu<sub>3</sub>)(μ-PFu<sub>2</sub>)(μ-η<sup>1</sup>,η<sup>2</sup>-Fu)] **2a** (*R*<sub>f</sub> = 0.69, 44 mg, 65%) and [Ru<sub>2</sub>(CO)<sub>4</sub>(PFu<sub>3</sub>)<sub>2</sub>(μ-PFu<sub>2</sub>)(μ-η<sup>1</sup>,η<sup>2</sup>-Fu)] **2b** (*R*<sub>f</sub> = 0.44, 21 mg, 25%) after recrystallization from a hexane-CH<sub>2</sub>Cl<sub>2</sub> mixture at room temperature. Addition of an excess of the ligand was found to decrease and increase the yields of **2a** and **2b**, respectively. **2a**: IR (CH<sub>2</sub>Cl<sub>2</sub>): 2064vs, 2018vs, 2000s and 1978s cm<sup>-1</sup> (ν<sub>CO</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.66 (s, 1H, Fu), 7.57 (s, 3H, PFu<sub>3</sub>), 7.47 (s, 2H, PFu<sub>2</sub>), 6.61 (m, 3H, PFu<sub>3</sub>), 6.43 (m, 3H, PFu<sub>3</sub>), 6.39 (m, 1H, PFu<sub>2</sub>), 6.34 (s, 1H, PFu<sub>2</sub>), 6.28 (s, 1H, PFu<sub>2</sub>), 6.24 (s, 1H, PFu<sub>2</sub>), 5.49 (s, 1H, Fu) and 4.08 (m, 1H, Fu). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 53.38 (d, <sup>2</sup>*J*<sub>P-P</sub> = 21 Hz, PFu<sub>2</sub>) and -11.52 (d, <sup>2</sup>*J*<sub>P-P</sub> = 21 Hz, PFu<sub>3</sub>). FAB MS: *m/z* 807 (M<sup>+</sup>). Calc. for C<sub>29</sub>H<sub>18</sub>O<sub>11</sub>P<sub>2</sub>Ru<sub>2</sub>: C, 43.19; H, 2.25. Found: C, 42.90; H, 2.18%. **2b**: IR (CH<sub>2</sub>Cl<sub>2</sub>): 2029vs, 1997m and 1969s cm<sup>-1</sup> (ν<sub>CO</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.68 (s, 1H, Fu), 7.55 (s, 6H, PFu<sub>3</sub>), 7.46 (s, 1H, PFu<sub>2</sub>), 7.15 (s, 1H, PFu<sub>2</sub>), 6.60 (s, 6H, PFu<sub>3</sub>), 6.37 (m, 8H, PFu<sub>2</sub> + PFu<sub>3</sub>), 6.27 (s, 1H, PFu<sub>2</sub>), 5.98 (s, 1H, PFu<sub>2</sub>), 5.70 (s, 1H, Fu) and 4.11 (m,

Table 4. Summary of Crystal Data for the Complexes **2a** and **2b**

	<b>2a</b>	<b>2b·0.5C<sub>5</sub>H<sub>12</sub></b>
Empirical formula	C <sub>29</sub> H <sub>18</sub> O <sub>11</sub> P <sub>2</sub> Ru <sub>2</sub>	C <sub>40</sub> H <sub>27</sub> O <sub>13</sub> P <sub>3</sub> Ru <sub>2</sub> ·0.5C <sub>5</sub> H <sub>12</sub>
Formula weight	806.51	1046.74
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	21.714(2)	18.198(1)
<i>b</i> /Å	16.565(1)	12.762(1)
<i>c</i> /Å	18.571(1)	18.681(2)
<i>β</i> /°	110.440(1)	103.163(2)
<i>U</i> /Å <sup>3</sup>	6259.3(7)	4224.3(6)
<i>Z</i>	8	4
<i>T</i> /K	293	293
<i>F</i> (000)	3184	2100
<i>μ</i> (Mo-K <sub>α</sub> )/mm <sup>-1</sup>	1.125	0.894
Reflections collected	35743	24557
Unique reflections	13947	9519
Observed reflections	8988	4914
GOF on <i>F</i> <sup>2</sup>	0.859	0.894
<i>R</i> <sub>int</sub>	0.0245	0.0661
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2.0σ( <i>I</i> )]	0.0306, 0.0863	0.0570, 0.1399
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0560, 0.1010	0.1256, 0.1761

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)|^2]}{[\sum w|F_o|^2]}^{1/2}$$

1H, Fu).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  48.00 (t,  $^2J_{P-P} = 23$  Hz,  $PFu_2$ ) and  $-12.28$  (d,  $^2J_{P-P} = 23$  Hz,  $PFu_3$ ). FAB MS:  $m/z$  1011 ( $M^+$ ). Calc. for  $C_{40}H_{27}O_{13}P_3Ru_2$ : C, 47.54; H, 2.69. Found: C, 47.20; H, 2.55%.

### X-Ray Crystallography

For compound **2a**, good-quality crystals suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in hexane- $CH_2Cl_2$  at room temperature. Crystals of **2b**· $0.5C_5H_{12}$  were obtained from a pentane- $CH_2Cl_2$  mixture. Geometric and intensity data were collected using graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker Axs SMART 1000 CCD area-detector diffractometer. Cell parameters and orientation matrix for all crystal samples were obtained from the least-squares refinement of reflections measured in three different sets of 15 frames each. The collected frames were processed with proprietary software SAINT [14] and an absorption correction was applied (SADABS [15]) to the collected reflections.

The space groups for all crystals were determined from a combination of Laue symmetry check and their systematic absences, which were then confirmed by successful refinement of the structures. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL [16]. Structure refinements were made on  $F^2$  by the full-matrix least-squares technique. For **2b**, the solvate in the cell lattice was assigned with isotropic displacement parameters and no hydrogen atoms were included to these solvent molecules. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were either generated from Fourier maps or placed in their idealised positions and allowed to ride on the respective carbon atoms. Pertinent crystallographic information is provided in Table 4.

### ACKNOWLEDGEMENTS

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### SUPPORTING INFORMATION AVAILABLE

Complete X-ray crystallographic files in CIF format for the structure determination of the compounds **2a** and **2b**

can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Their deposition numbers are CCDC 168741 (for **2a**) and CCDC 168742 (for **2b**).

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