

Reactivity of $[\text{Ru}_2(\text{CO})_6(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$ ($\text{Fu} = 2\text{-furyl}$) towards Diphosphanes – Substitution, Polymerisation, Cyclometallation and Elimination Reactions

Wai-Yeung Wong,^{*,[a]} Fai-Lung Ting,^[a] and Wai-Lim Lam^[a]

Keywords: Ruthenium / Phosphane ligands / Phosphido complexes

Thermal reaction of $[\text{Ru}_2(\text{CO})_6(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$ ($\text{Fu} = 2\text{-furyl}$) (**1**) with bis(diphenylphosphanyl)methane (dppm), bis(diphenylphosphanyl)amine (dppam), or bis(diphenylphosphanyl)methylamine (dppma), produces the substitution products $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-L})]$ [**2** ($\text{L} = \text{dppm}$), **3** ($\text{L} = \text{dppam}$), **4** ($\text{L} = \text{dppma}$)] in good yields. The Ru–Ru edge is bridged by the diphosphane in each case, while the $\mu\text{-}\eta^1, \eta^2\text{-bound}$ furyl fragment remains intact. When the reactions were carried out using bis(diphenylphosphanyl)ethane (dppe) or bis(diphenylphosphanyl)propane (dppp), the compounds $[\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_n\text{PPh}_2)]$ [**5** ($n = 2$), **6** ($n = 3$)] were isolated as the thermodynamic products in which both P atoms chelate to one Ru centre to afford five- (for **5**) and six-membered (for **6**) ruthenacycles, accompanied by orthometallation of one of the phenyl rings of the phosphane ligand. Interestingly, elimination of the coordinated furyl moiety occurs during the formation of **5** and **6**. Upon reaction with bis(diphenylphosphanyl)butane (dppb), bis(diphenylphosphanyl)pentane (dpppe), or bis(diphenylphosphanyl)ferrocene (dppf), cyclometallation is not favoured in each case. Instead, $[\{\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})\}_2(\text{L})]$ [**7a** ($\text{L} = \text{dppb}$), **8a** ($\text{L} = \text{dpppe}$), **9a** ($\text{L} = \text{dppf}$)] and polymeric $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\text{L})]_n$ [**7b** ($\text{L} = \text{dppb}$), **8b** ($\text{L} = \text{dpppe}$), **9b** ($\text{L} = \text{dppf}$)] were obtained with the product yield depending on the stoichiometry of the reactants. All these new diruthenium complexes are electron-precise with 34 cluster valence electrons.

phane ligand. Interestingly, elimination of the coordinated furyl moiety occurs during the formation of **5** and **6**. Upon reaction with bis(diphenylphosphanyl)butane (dppb), bis(diphenylphosphanyl)pentane (dpppe), or bis(diphenylphosphanyl)ferrocene (dppf), cyclometallation is not favoured in each case. Instead, $[\{\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})\}_2(\text{L})]$ [**7a** ($\text{L} = \text{dppb}$), **8a** ($\text{L} = \text{dpppe}$), **9a** ($\text{L} = \text{dppf}$)] and polymeric $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\text{L})]_n$ [**7b** ($\text{L} = \text{dppb}$), **8b** ($\text{L} = \text{dpppe}$), **9b** ($\text{L} = \text{dppf}$)] were obtained with the product yield depending on the stoichiometry of the reactants. All these new diruthenium complexes are electron-precise with 34 cluster valence electrons.

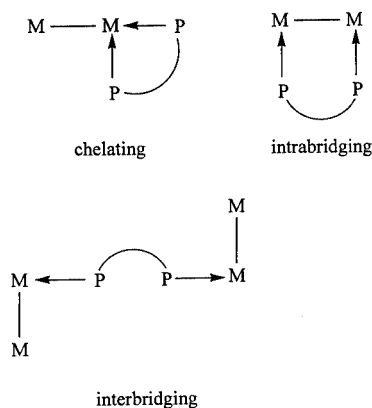
(© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

There is a continuing interest in the synthesis and chemistry of phosphido-bridged di- and polynuclear complexes.^[1–7] Several recent developments provide a wealth of unexpected and intriguing reactivity of some dinuclear allenyl complexes of the type $[\text{M}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-}\eta^1, \eta^1_{\alpha, \beta}\text{-C}_\alpha(\text{R})=\text{C}_\beta=\text{CR}_2)]$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{R} = \text{H}, \text{Ph}$) towards mono- and bidentate phosphanes.^[8–12] In these studies, the nature of the phosphane plays a significant role in governing the reaction pathways involved and the final products isolated.^[8–12]

We are interested in the use of tris(2-furyl)phosphane (PFu_3) as a ligand in organometallic syntheses.^[13,14] 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 in the synthesis of a new class of complexes with different ligand environments.^[13] In order to explore the synthetic potential of this system, we have now initiated a comprehensive study of the reactions of **1** with some diphosphane ligands. Herein, we describe results on reactions of **1** with various diphosphanes $\text{PPh}_2\text{EPPH}_2$ [$\text{E} = (\text{CH}_2)_n$, $n = 1\text{--}5$; $\text{N}(\text{H})$; $\text{N}(\text{Me})$; or $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$], which lead to the formation and

characterisation of a range of novel carbonyl(μ -phosphido)-diruthenium complexes. These products are formed by different reaction pathways embracing (i) simple phosphane substitution with displacement of carbonyl ligands, (ii) polymerization, and (iii) phosphane coordination accompanied by cyclometallation. Another noteworthy feature of these phosphane-containing compounds is the various modes of coordination towards metal atoms which the ligands exhibit^[15–18]. Three binding modes have been observed for the diphosphanes used in our studies, namely chelating, intrabridging, and interbridging (Scheme 1).



Scheme 1

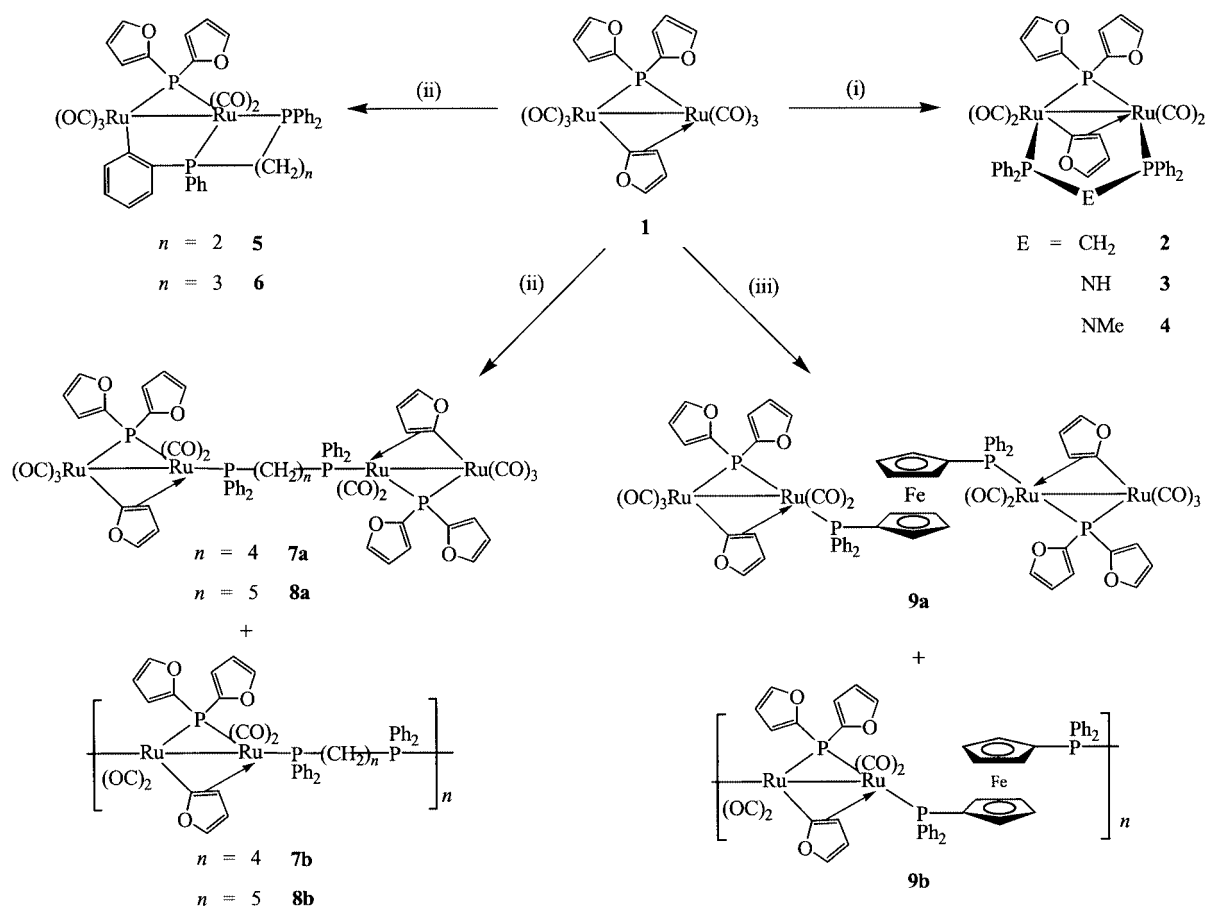
^[a] Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China
E-mail: rwywong@hkbu.edu.hk

Results and Discussion

Synthesis and Spectroscopic Characterisation

Complex **1** reacts with an equimolar amount of the bidentate phosphane, namely bis(diphenylphosphanyl)methane (dppm), bis(diphenylphosphanyl)amine (dppam), or bis(diphenylphosphanyl)methylamine (dppma), in refluxing toluene to afford three new diruthenium compounds $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-dppm})]$ (**2**), $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-dppam})]$ (**3**), and $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-dppma})]$ (**4**) as the sole products after TLC purification on silica, all in reasonable yield (Scheme 2). They were isolated as bright yellow crystalline solids and are soluble in common organic solvents. These compounds display almost identical IR $\nu(\text{CO})$ absorption patterns, suggesting a great resemblance of their structures. Each of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** and **4** consists of two separated sets of resonance signals. The resonance due to the phosphido-P atom shows equal coupling to the two coincidentally equivalent P atoms of the chelating diphosphanes, thus appearing as a pseudo-triplet ($^2J_{\text{P-P}} = 172$ for **2** and 169 Hz for **4**). For **3**, a doublet of doublets appears around $\delta = 94.0$ ppm, attributable to the $\mu\text{-PFu}_2$ entity and two interpenetrating sets of doublets in close proximity centred at $\delta = 87.16$ and 87.18 ppm were also observed for the coordinated dppam ligand.

In order to further investigate, how the separation between the P donor atoms in $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ (i.e. the value of n) might affect the chemistry of such classes of complexes, we have examined the reactions that take place with the related bidentate phosphanes containing more methylene groups, namely bis(diphenylphosphanyl)ethane (dppe), bis(diphenylphosphanyl)propane (dppp), bis(diphenylphosphanyl)butane (dppb), or bis(diphenylphosphanyl)pentane (dpppe). To our surprise, two novel 34-electron phosphido-stabilised diruthenium complexes $[\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPhCH}_2\text{CH}_2\text{PPh}_2)]$ (**5**) and $[\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPhCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$ (**6**) were obtained as the thermodynamically stable products, upon reaction of **1** with dppe or dppp at elevated temperatures. In both structures, the two P atoms chelate to one Ru atom to result in five- (for **5**) and six-membered (for **6**) ruthenacycles, followed by orthometallation of one of the phenyl rings of $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ ($n = 2, 3$).^[18] No sign of the formation of polymeric species in these reactions was observed under our experimental conditions. The transformation of these two products is illustrated in Scheme 2. Most interestingly, in marked contrast with **2–4**, the $\mu\text{-}\eta^1, \eta^2$ -bonded furyl group was found to be detached during the formation of **5** and **6** so as to stabilize the products to retain 34 cluster valence electrons (CVE). However, the mechanism for this reaction is not yet ascertained. The IR spectral features of **5** and **6**



Scheme 2. (i) $\text{PPh}_2\text{EPPH}_2$; (ii) $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$; (iii) dppf

are almost identical, indicative that they have similar structures. They exhibit different patterns from the dppm analogue. Their $\nu(\text{CO})$ bands absorb at lower energies than those of **1**, in agreement with chelation of the strongly electron-donating phosphane ligands. They display three distinct sets of resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and afford a typical AMX spectrum in each case. Compound **5** gives a characteristic doublet of doublets at $\delta = 99.08$ ppm ($^2J_{\text{P-P}} = 25$ and 146 Hz) due to the $\mu\text{-PFu}_2$ group and another doublet of doublets at $\delta = 68.36$ ppm ($^2J_{\text{P-P}} = 25$ and 146 Hz) for the orthometallated PPh moiety. We note that the resonance peak at $\delta = 65.67$ ppm due to the PPh₂ group shows equal coupling to the other two *cis*-phosphorus atoms ($^2J_{\text{P-P}} = 25$ Hz), thereby appearing as a virtual triplet. A similar coupling phenomenon has been observed in $[\text{CpW}_2(\text{CO})_5(\mu\text{-PPh}_2)(\eta^2\text{-dppe})]$.^[19] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** reveals three sets of doublets of doublets at $\delta = 84.27$, 21.82, and 20.60 ppm with the most downfield signal corresponding to the phosphido group.

As a continuation of our effort in the study of the effect of the methylene chain length on the identity of products formed, similar reactions with dppb or dppe were also carried out and in none of the cases was the product analogous to other PPh₂(CH)_{*n*}PPh₂-bridged species (*n* = 1–3) obtained. Complex **1** undergoes a rapid ligand substitution reaction with a 0.5 equiv. of dppb or dppe in refluxing toluene for 1 h to give $[\{\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})\}_2(\text{dppb})]$ (**7a**) (70%) and $[\{\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})\}_2(\text{dppe})]$ (**8a**) (65%) as yellow solids (Scheme 2). Their structures were firmly supported by spectroscopic data. There is also no indication of the formation of dppb- or dppe-bridged analogues of **2–4**. Apparently, the long methylene bridge separating two bulky PPh₂ groups would favour the isolation of **7a** and **8a**. Although it is commonly found that the dppe and dppb can form stable five- and six-membered chelating rings with the metal centre without imposing strong steric interactions between the two PPh₂ groups,^[12,19–22] chelation at the Ru atom by the dppb or dppe is inhibited since the formation of 7- or 8-membered rings is generally not feasible. Moreover, the formation of a sterically unfavourable four-membered metallacycle for dppm would disfavour coordination via a chelating mode.

When the experiment was conducted with an equimolar amount of **1** and dppb or dppe for 1 h, polymerisation occurred producing yellow polymers $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\text{L})]_n$ [**7b** (L = dppb) or **8b** (L = dppe)] in high yields and purity, which could not be isolated by TLC or column chromatography. Purification of the polymers was accomplished by extraction of the yellow residues with several portions of hot hexane, followed by repeated precipitation from their toluene solutions with methanol. Both polymers were characterized by Gel Permeation Chromatography (GPC) as low-molecular-weight substances. A prolonged heating of the reaction mixture was found to increase the extent of polymerisation, and we observed that polymer **7b** shows 23 repeating units ($M_w = 24500$, $M_n = 22700$) in the main chain when the reaction is carried out for 10 h. They are both air-stable and soluble in common

organic solvents. By virtue of symmetry, they both present almost equivalent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and each shows two ^{31}P resonances at $\delta \approx 34.0$ and 39.0 ppm. However, no attempts have been made to fully assign these signals. The rather upfield resonances observed for the μ -phosphido atom in **7** and **8** were found to be in line with that for the disubstituted product $[\text{Ru}_2(\text{CO})_4(\text{PFu}_3)_2(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$ which gave a pseudo AX₂ $^{31}\text{P}\{^1\text{H}\}$ spectrum with a triplet at $\delta = 48.00$ ppm and a doublet at $\delta = -12.28$ ppm ($^2J_{\text{P-P}} = 23$ Hz) for the $\mu\text{-PFu}_2$ and PFu₃ groups, respectively, in an intensity ratio of 1:2.^[23]

Attempts have also been made to study the interaction between **1** and the organometallic diphosphane ligand $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ (dppf) in view of the considerable research attention on the use of the latter in the syntheses of di- or polymetallic complexes.^[24] Instead of producing a chelating complex as in **2–4**, thermal reaction of **1** with dppf in a 2:1 molar ratio for a short period of time (ca. 1 h) afforded the complex $[\{\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})\}_2(\text{dppf})]$ (**9a**) in fairly good yield in which two phosphido-bridged diruthenium fragments are linked by a bridging bis(diphenylphosphanyl)ferrocene moiety (Scheme 2). The two PPh₂ groups in dppf are separated by a large ferrocenyl moiety and are free to form bidentate complex **9a**. On the contrary, the relatively short bridging length between both PPh₂ groups in PPh₂EPPH₂ [E = CH₂, N(H), N(Me)] appears to hinder the adoption of such an interbridging mode. Spectroscopic and MS data of **9a** are consistent with the formula of the product having a 2:1 stoichiometry (Ru₂/dppf) with the loss of two CO ligands. The IR spectrum of **9a** shows a rather different $\nu(\text{CO})$ pattern from those of **2–4**, indicating that an intrabridging interaction probably did not happen in this case. Like the spectrum of $[\{\text{CpW}_2(\text{CO})_6(\mu\text{-PPh}_2)\}_2(\text{dppf})]$,^[19] two phosphorus doublets were clearly shown in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, in agreement with the structure shown. An attempt to generate a polymeric complex was also carried out via the reaction of **1** with dppf in a 1:1 stoichiometric ratio. Only a

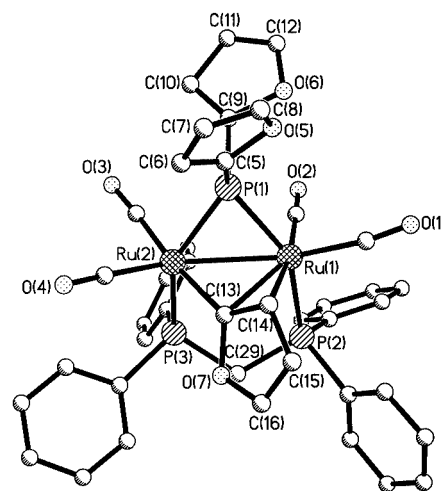


Figure 1. A perspective drawing of compound **2**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atoms

trace quantity of **9a** was detected in this reaction and its yield was reduced as the time of reflux was increased. An air-stable polymeric substance $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\text{dppf})]_n$ (**9b**) was obtained as the major product following similar purification procedures as for **7b** and **8b**. An analytically pure sample of **9b** was collected as an orange solid in 64% yield which is soluble in chlorinated solvents such as CH_2Cl_2 and CHCl_3 . Analysis of **9b** by GPC revealed a low-molecular-weight polymer ($M_w = 11400$, $M_n = 8550$, average degree of polymerization = 8). Compound **9b** displays NMR spectroscopic data that is very similar to that of the model complex **9a**, except that its resonance peaks are rather broad in appearance.

Crystal Structure Analyses

Perspective drawings of the structures of **2** (Figure 1, Table 1), **3** (Figure 2, Table 1), **4** (Figure 3, Table 1), **5** (Figure 4, Table 2), **6** (Figure 5, Table 3), **8a** (Figure 6, Table 4), and **9a** (Figure 7, Table 5) are shown together with the atomic numbering schemes used and selected bond lengths and angles are given. The general structural features of **2–4** are very similar. Each of them possesses a difurylphosphido-bridged diruthenium skeleton and the Ru–Ru edge is spanned by a bridging $\text{PPh}_2\text{EPPH}_2$ [**2** ($\text{E} = \text{CH}_2$), **3** ($\text{E} = \text{N(H)}$), **4** ($\text{E} = \text{N(Me)}$)] ligand. In each case, the C- or N(R)-bridged ($\text{R} = \text{H, Me}$) diphosphane forms a non-planar, five-membered metallacyclic ring. While the Ru–Ru distances in **2–4** are relatively insensitive to the nature of the bridging unit between both of the PPh_2 end groups, they are shorter than those in **1** and other related dialkyne-bridged Ru_2 complexes reported recently [ca. $2.7735(3)–2.8006(6)$ Å].^[13] For **2–4**, the P(1) atom is asym-

metrically bonded to Ru(1) and Ru(2). The furyl unit is σ -bonded to Ru(2) and π -bonded to Ru(1). These compounds display only slight chelate ring twisting about the Ru–Ru axis for the diphosphane ligands and the torsion angles defined by P(2)–Ru(1)–Ru(2)–P(3) are 7.3, 8.9, and 4.5° for **2–4**, respectively. Within the five-membered ruthenacycle in **2**, the structural parameters of the coordinated dppm are very similar to those found in other Ru_2 complexes bridged by dppm, such as in $[\text{Ru}_2(\text{CO})_4(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1, \eta^2_{\alpha, \beta}\text{-C(Ph)=C=CPPH}_2\}(\mu\text{-dppm})]$ [$2.367(1)$ Å and $113.6(2)^\circ$],^[12] $[\text{Ru}_2(\text{CO})_3(\text{MeCN})(\mu\text{-O}_2\text{CMe})(\mu\text{-dppm})_2]^+$ [$2.37(1)$ Å and $113(2)^\circ$],^[25] and $[\text{Ru}_2(\text{CO})_2(\text{PPh}_3)(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-CH}_2\text{PPh}_2)(\mu\text{-dppm})]^+$ [$2.405(3)$ Å and $110.0(4)^\circ$].^[25] The P–N–P angle for **3** is $126.0(4)^\circ$, in common with other dinuclear compounds with bridging dppam in the literature.^[26–31] The corresponding angle is $121.59(15)^\circ$ for **4**. These angles are slightly larger than $118.9(2)$ and $114.6(1)^\circ$ in free dppam and dppma,^[32] respectively. To date, relatively few structural data are available for metal complexes containing dppma as a bridging ligand.^[32,33]

The structural characterisations of **5** and **6** provide unequivocal proof of the identity of both molecules in the solid state. Basically, both structures contain a difurylphosphido-substituted diruthenium framework with the $(\text{CH}_2)_n$ -bridged diphosphane ligands ($n = 2, 3$) interacting with both metal atoms in an η^1 -bonding mode. The furyl moiety that is originally present in **1** has been eliminated. The two P atoms chelate to Ru(1) to afford a sterically favourable five- and six-membered ruthenacycle for **5** and **6**, respectively, accompanied by orthometallation of one of the phenyl rings on the P(3) atom. The coordination around the Ru(1) and Ru(2) atoms is completed by two and three

Table 1. Selected bond lengths [Å] and angles [$^\circ$] for complexes **2**, **3**·0.5MeOH, and **4**·2 CH_2Cl_2

	2	3 ·0.5MeOH	4 ·2 CH_2Cl_2
Ru(1)–Ru(2)	2.7443(6)	2.7292(11)	2.7339(4)
Ru(1)–P(1)	2.325(2)	2.356(3)	2.3370(9)
Ru(1)–P(2)	2.376(2)	2.348(2)	2.3728(9)
Ru(2)–P(1)	2.299(2)	2.318(3)	2.2951(9)
Ru(2)–P(3)	2.357(2)	2.327(3)	2.3416(9)
Ru(1)–C(13)	2.363(6)	2.365(9)	2.358(3)
Ru(1)–C(14)	2.504(5)	2.501(9)	2.558(3)
Ru(2)–C(13)	2.093(6)	2.090(9)	2.120(3)
C(13)–C(14)	1.390(10)	1.388(12)	1.390(5)
P(2)–X	1.843(6) [X = C(29)]	1.682(7) [X = N(1)]	1.717(3) [X = N(1)]
P(3)–X	1.869(6) [X = C(29)]	1.704(7) [X = N(1)]	1.717(3) [X = N(1)]
Ru(1)–P(1)–Ru(2)	72.80(6)	71.46(7)	72.34(3)
Ru(2)–Ru(1)–P(1)	53.16(5)	53.62(7)	53.12(2)
P(2)–Ru(1)–Ru(2)	97.17(5)	94.55(7)	92.47(2)
P(3)–Ru(2)–Ru(1)	91.45(4)	91.96(7)	93.79(2)
Ru(1)–C(14)–C(13)	67.9(3)	68.1(5)	65.81(18)
Ru(1)–C(13)–Ru(2)	75.76(19)	75.3(3)	75.05(10)
Ru(2)–Ru(1)–C(13)	47.65(15)	47.8(2)	48.51(8)
Ru(2)–Ru(1)–C(14)	75.61(13)	75.9(2)	75.31(8)
Ru(1)–C(13)–C(14)	79.1(3)	78.9(6)	81.7(2)
C(13)–Ru(1)–C(14)	33.0(2)	33.0(3)	32.54(11)
Ru(2)–C(13)–C(14)	134.5(6)	134.6(7)	133.3(2)
P(2)–X–P(3)	114.3(4) [X = C(29)]	126.0(4) [X = N(1)]	121.59(15) [X = N(1)]

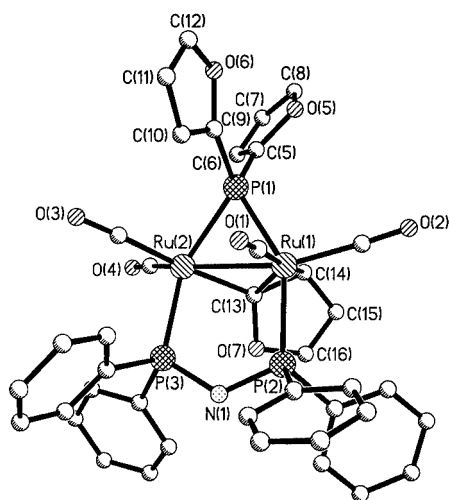


Figure 2. A perspective drawing of compound **3**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atoms

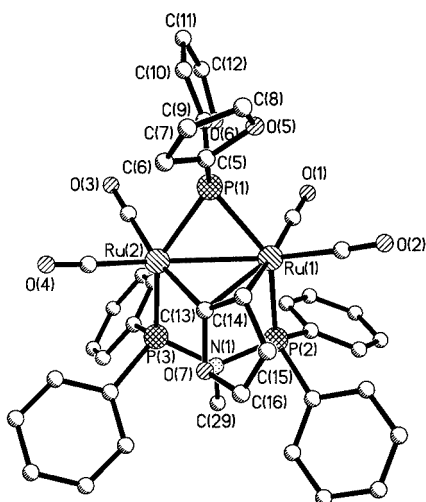


Figure 3. A perspective drawing of compound **4**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atoms

terminal carbonyl ligands, respectively. For **5**, the dppe ligand was shown to coordinate to the Ru centres, being bonded to Ru(1) through both P(2) and P(3) atoms, and to Ru(2) through the C(33) atom of the orthometallated ring. The torsion angle defined by P(2)–C(26)–C(27)–P(3) is 45.5° . A salient structural feature observed in the structure of **6** is the formation of a six-membered ring, which adopts a stable chair conformation. The P(2) and P(3) atoms are bonded to Ru(1) within the metallacycle. The Ru(2)–C(40) distance [$2.174(2) \text{ \AA}$] is typical of a Ru–C bond.^[12,13,34–36] Both compounds have 34 CVE and the EAN rule supports the metal–metal bond formation based on the three- and five-electron contribution from the phosphido and $\text{C}_6\text{H}_4\text{PPh}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2, 3$) units, respectively.

For **8a**, the dppe ligand links two identical $[\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})]$ units such that the two halves of the molecule are symmetrically related by an inversion centre

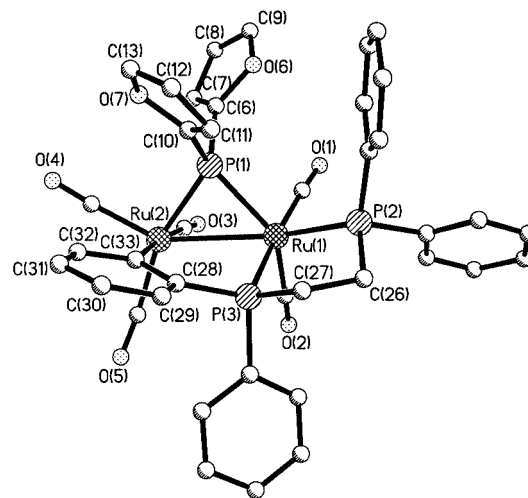


Figure 4. A perspective drawing of compound **5**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atoms

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for complex **5**

Ru(1)–Ru(2)	2.8786(3)	Ru(1)–P(1)	2.3410(7)
Ru(1)–P(2)	2.3302(7)	Ru(1)–P(3)	2.3488(7)
Ru(2)–P(1)	2.3189(8)	Ru(2)–C(33)	2.156(3)
C(28)–C(33)	1.409(5)		
Ru(1)–P(1)–Ru(2)	76.30(2)	Ru(2)–Ru(1)–P(1)	51.50(2)
Ru(2)–Ru(1)–P(2)	154.39(2)	Ru(2)–Ru(1)–P(3)	79.90(2)
Ru(1)–Ru(2)–C(33)	92.74(8)	Ru(1)–P(3)–C(28)	116.20(11)
Ru(2)–C(33)–C(28)	122.4(2)	P(3)–C(28)–C(33)	116.7(2)

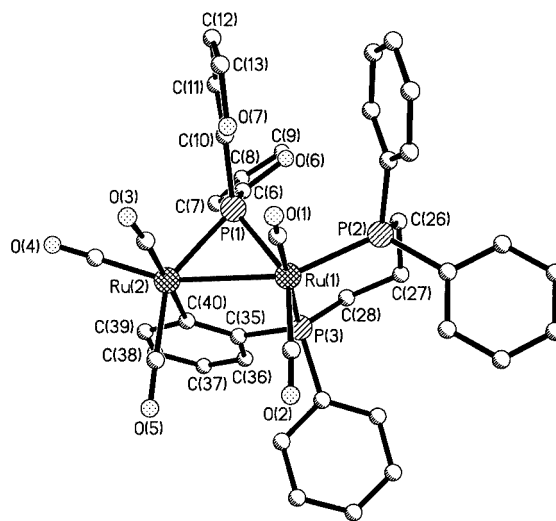
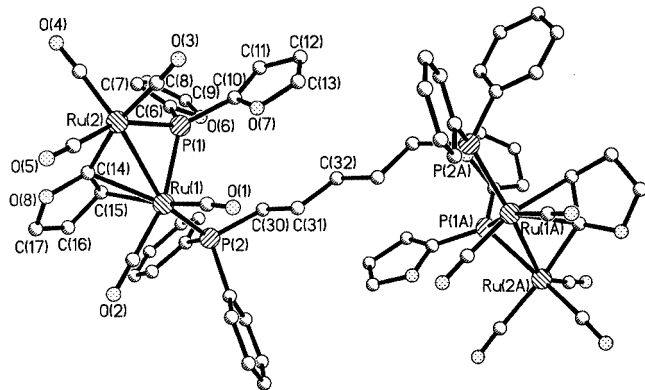


Figure 5. A perspective drawing of compound **6**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atoms

at C(32). The C–C bonds in the aliphatic pentamethylene chain of the molecule are staggered with C–C bond lengths between $1.509(6)$ and $1.511(6) \text{ \AA}$ and C–C–C angles between $111.4(5)$ and $115.4(6)^\circ$. Complex **9a** reveals a symmetrical dppe-bridged structure in which a dppe unit is

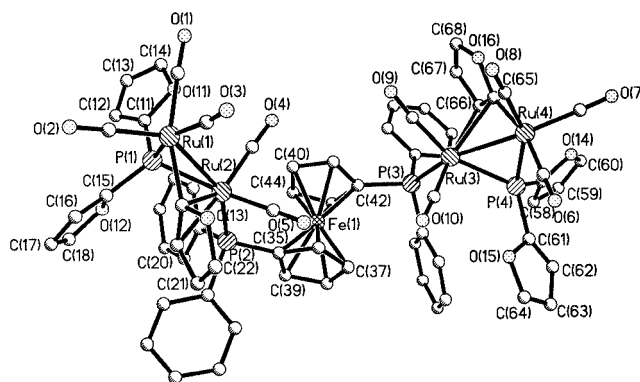
Table 3. Selected bond lengths [Å] and angles [°] for complex **6**·0.5MeOH

Ru(1)–Ru(2)	2.8597(3)	Ru(1)–P(1)	2.3442(6)
Ru(1)–P(2)	2.3339(7)	Ru(1)–P(3)	2.3650(6)
Ru(2)–P(1)	2.3263(7)	Ru(2)–C(40)	2.174(2)
C(35)–C(40)	1.402(3)		
Ru(1)–P(1)–Ru(2)	75.51(2)	Ru(2)–Ru(1)–P(1)	51.961(17)
Ru(2)–Ru(1)–P(2)	152.630(17)	Ru(2)–Ru(1)–P(3)	86.338(16)
Ru(1)–Ru(2)–C(40)	92.06(6)	Ru(1)–P(3)–C(35)	115.16(7)
Ru(2)–C(40)–C(35)	125.70(17)	P(3)–C(35)–C(40)	120.31(17)

Figure 6. A perspective drawing of compound **8a**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atomsTable 4. Selected bond lengths [Å] and angles [°] for complex **8a**·CH₂Cl₂

Ru(1)–Ru(2)	2.7934(5)	Ru(1)–P(1)	2.3592(12)
Ru(2)–P(1)	2.3243(13)	Ru(1)–P(2)	2.3511(11)
Ru(1)–C(14)	2.347(4)	Ru(1)–C(15)	2.398(4)
Ru(2)–C(14)	2.073(4)	C(14)–C(15)	1.401(6)
Ru(1)–P(1)–Ru(2)	73.23(4)	Ru(2)–Ru(1)–P(1)	52.81(3)
Ru(2)–Ru(1)–P(2)	150.19(3)	Ru(1)–C(15)–C(14)	70.8(3)
Ru(1)–C(14)–Ru(2)	78.12(15)	Ru(2)–C(14)–C(15)	135.1(3)
Ru(2)–Ru(1)–C(14)	46.56(11)	Ru(2)–Ru(1)–C(15)	76.28(10)
C(14)–Ru(1)–C(15)	34.33(15)		

sandwiched by two μ -phosphido Ru₂ moieties to afford a heterometallic complex aggregate. The average Ru–Ru bond length is 2.7982(6) Å. The retention of the dissociated furyl fragment in the structure is highlighted by the formation of a σ and a π bonds between the furyl fragment and the Ru₂ core at both ends, similar to those mentioned before in **2–4**. The two PPh₂ groups are oriented in an *anti* configuration and the two P atoms are displaced from each cyclopentadienyl ring (away from the Fe atom) by 0.2461 Å for P(2) and –0.2649 Å for P(3). The two phosphanylcyclopentadienyl rings are nearly parallel (dihedral angles 4.4°), planar and deviate by 8.1° from the idealised eclipsed conformation.

Figure 7. A perspective drawing of compound **9a**; for clarity, all H atoms and the labels on the phenyl rings are omitted; the labels on the carbonyl C atoms have the same labels as the O atomsTable 5. Selected bond lengths [Å] and angles [°] for complex **9a**·CH₂Cl₂

Ru(1)–Ru(2)	2.8200(6)	Ru(3)–Ru(4)	2.7763(6)
Ru(1)–P(1)	2.3264(17)	Ru(2)–P(1)	2.3545(14)
Ru(2)–P(2)	2.3651(13)	Ru(3)–P(3)	2.3617(13)
Ru(3)–P(4)	2.3671(14)	Ru(4)–P(4)	2.3252(14)
Ru(1)–C(19)	2.063(6)	Ru(2)–C(19)	2.378(5)
Ru(2)–C(20)	2.419(5)	C(19)–C(20)	1.389(8)
Ru(3)–C(65)	2.362(5)	Ru(3)–C(66)	2.419(5)
Ru(4)–C(65)	2.068(6)	C(65)–C(66)	1.395(7)
Ru(1)–P(1)–Ru(2)	74.09(5)	Ru(2)–Ru(1)–P(1)	53.41(4)
Ru(1)–Ru(2)–P(2)	151.81(4)	Ru(1)–C(19)–C(20)	135.7(4)
Ru(2)–C(20)–C(19)	71.6(3)	Ru(1)–C(19)–Ru(2)	78.49(18)
Ru(1)–Ru(2)–C(19)	45.78(13)	Ru(1)–Ru(2)–C(20)	75.05(13)
Ru(2)–C(19)–C(20)	74.8(3)	C(19)–Ru(2)–C(20)	33.65(18)
Ru(3)–P(4)–Ru(4)	72.55(4)	Ru(4)–Ru(3)–P(4)	53.03(4)
Ru(4)–Ru(3)–P(3)	156.10(4)	Ru(3)–C(66)–C(65)	70.8(3)
Ru(3)–C(65)–Ru(4)	77.29(17)	Ru(4)–Ru(3)–C(65)	46.61(14)
Ru(4)–Ru(3)–C(66)	75.91(13)	Ru(3)–C(65)–C(66)	75.3(3)
C(65)–Ru(3)–C(66)	33.91(18)	Ru(4)–C(65)–C(66)	134.8(4)

Concluding Remarks

The work presented here concerns the reaction chemistry of [Ru₂(CO)₆(μ -PFu₂)(μ - η^1 , η^2 -Fu)] (Fu = 2-furyl) (**1**) with various bidentate phosphane ligands. The general reactivity patterns comprise chemical transformations involving (i) substitution of CO ligands by phosphanes via intrabridging or interbridging coordination modes to afford discrete or polymeric molecules, or (ii) cyclometallation reactions accompanied by reductive elimination of the dissociated furyl moiety. In our studies, three bonding types have been encountered for the diphosphanes used: chelating, intrabridging, and interbridging. We have also investigated in detail the factors dictating the preference for a particular coordination geometry and we observe that the mode of coordination is dependent on the nature and the length of the linking chains between the terminal PPh₂ groups. Although the dominant reaction pathway involves replacement of CO li-

gands by phosphido groups to give substitution products in the majority of cases, thermolysis of **1** with dppe or dppp results in orthometallation of the phenyl ring to yield thermodynamically stable 34-electron complexes containing a $\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2, 3$) moiety along with the unprecedented detachment of the original furyl fragment from precursor **1**. Work is in progress to study the reactivity of **1** with other organic and organometallic nucleophilic reagents.

Experimental Section

General Procedures: All reactions were conducted under 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 syntheses of complex **1**^[13] and the ligands dppam^[28,29] and dppma^[32] were carried out as reported previously. IR spectra were recorded as CH_2Cl_2 solutions with a Perkin–Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in CDCl_3 with a JEOL EX270 or a Varian Inova 400 MHz FT NMR spectrometer, with ^1H NMR chemical shifts quoted relative to SiMe_4 and ^{31}P chemical shifts relative to an 85% H_3PO_4 external standard. Fast atom bombardment (FAB) mass spectra were recorded in *m*-nitrobenzyl alcohol matrices with a Finnigan-SSQ 710 spectrometer. Separation of products was accomplished by preparative TLC plates coated with silica (Merck, Kieselgel 60). The molecular weight of each polymer sample was estimated by GPC (HP 1050 series HPLC with visible wavelength and fluorescent detectors) against polystyrene standards.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-dppm})]$ (2**):** A solution of complex **1** (50 mg, 0.083 mmol) in toluene (20 mL) was refluxed with dppm (32 mg, 0.083 mmol) for 4 h. The solution gradually changed from pale yellow to dark orange-yellow. The solvent was then removed in vacuo and the residue taken up in CH_2Cl_2 for TLC separation eluting with hexane/ CH_2Cl_2 (2:1, v/v). The bright yellow band ($R_f = 0.34$) consisting of **2** was obtained and the product was isolated in 84% yield (65 mg). Recrystallisation of the product was achieved by concentration of a hexane/ CH_2Cl_2 solution at room temperature, affording bright yellow block crystals. IR (CH_2Cl_2): $\tilde{\nu} = 2007$ s, 1985 vs, 1942 vs $[\nu(\text{CO})]$ cm^{-1} . ^1H NMR (CDCl_3): $\delta = 3.74$ (t, $^2J_{\text{H-P}} = 10.8$ Hz, 2 H, CH_2), 4.87 (m, 1 H, Fu), 5.63 (m, 1 H, Fu), 6.33–6.46 (m, 4 H, Fu), 6.75 (s, 1 H, Fu), 7.27 (m, 16 H, Ph), 7.54 (s, 1 H, Fu), 7.67 (m, 4 H, Ph), 7.74 (s, 1 H, Fu) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 41.61$ (d, $^2J_{\text{P-P}} = 172$ Hz, PPh_2), 100.46 (t, $^2J_{\text{P-P}} = 172$ Hz, PFu_2) ppm. FAB MS: $m/z = 931$ [M^+]. $\text{C}_{41}\text{H}_{31}\text{O}_7\text{P}_3\text{Ru}_2$ (930.75): calcd. C 52.91, H 3.36; found C 53.14, H 3.30.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-dppam})]$ (3**):** White powdered dppam (32 mg, 0.083 mmol) was added to a toluene solution of **1** (50 mg, 0.083 mmol) and the mixture was stirred under reflux for 3 h to afford a bright yellow solution. The volatile materials were removed in vacuo and subsequent workup by TLC purification with hexane/ CH_2Cl_2 (1:1, v/v) as eluent gave a yellow band ($R_f = 0.60$) which furnished compound **3** as a yellow crystalline solid in 44% (34 mg). IR (CH_2Cl_2): $\tilde{\nu} = 2011$ s, 1989 vs, 1946 vs $[\nu(\text{CO})]$ cm^{-1} . ^1H NMR (CDCl_3): $\delta = 4.42$ (m, 1 H, NH), 4.75 (m, 1 H, Fu), 5.92 (m, 1 H, Fu), 6.31–6.40 (m, 3 H, Fu), 6.73 (s, 1 H, Fu), 7.17 (m, 1 H, Fu), 7.34 (m, 12 H, Ph), 7.48 (m, 5 H, Fu + Ph),

7.62 (m, 4 H, Ph), 7.71 (s, 1 H, Fu) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 87.16$ (d, $^2J_{\text{P-P}} = 191$ Hz, PPh_2), 87.18 (d, $^2J_{\text{P-P}} = 162$ Hz, PPh_2), 93.97 (dd, $^2J_{\text{P-P}} = 162$, 191 Hz, PFu_2) ppm. FAB MS: $m/z = 876$ [$(\text{M} - 2\text{CO})^+$]. $\text{C}_{40}\text{H}_{30}\text{NO}_7\text{P}_3\text{Ru}_2$ (931.74): calcd. C 51.56, H 3.25, N 1.50; found C 51.30, H 3.16, N 1.32.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\mu\text{-dppma})]$ (4**):** This compound was prepared similarly as described above for **2** and **3** from **1** (50 mg, 0.083 mmol) and dppma (33 mg, 0.083 mmol). The resulting reddish-orange mixture was subjected to preparative TLC eluting with hexane/ CH_2Cl_2 (3:1, v/v). From the bright yellow band ($R_f = 0.21$), the title compound was obtained in 42% yield (33 mg) as bright yellow block-shaped crystals upon recrystallisation from hexane/ CH_2Cl_2 under ambient conditions. IR (CH_2Cl_2): $\tilde{\nu} = 2007$ s, 1988 vs, 1944 vs $[\nu(\text{CO})]$ cm^{-1} . ^1H NMR (CDCl_3): $\delta = 2.47$ (t, $^3J_{\text{H-P}} = 6.4$ Hz, 3 H, NMe), 5.02 (m, 1 H, Fu), 5.28 (m, 1 H, Fu), 6.34–6.38 (m, 3 H, Fu), 6.49 (m, 1 H, Fu), 6.68 (m, 1 H, Fu), 7.44 (m, 16 H, Ph), 7.66 (s, 1 H, Fu), 7.72 (m, 4 H, Ph), 7.75 (s, 1 H, Fu) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 91.80$ (t, $^2J_{\text{P-P}} = 169$ Hz, PFu_2), 106.92 (d, $^2J_{\text{P-P}} = 169$ Hz, PPh_2) ppm. FAB MS: $m/z = 946$ [M^+]. $\text{C}_{41}\text{H}_{32}\text{NO}_7\text{P}_3\text{Ru}_2$ (945.77): calcd. C 52.07, H 3.41, N 1.48; found C 51.73, H 3.25, N 1.70.

$[\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_2\text{PPh}_2)]$ (5**):** A mixture of compound **1** (50 mg, 0.083 mmol) and dppe (33 mg, 0.083 mmol) in toluene was stirred under reflux for 5 h resulting in a reddish-brown mixture. Removal of the solvent followed by TLC separation on silica eluting with hexane/ CH_2Cl_2 (2:1, v/v) gave a yellow solid of complex **5** (35 mg, 46%) after recrystallisation from a hexane/ CHCl_3 mixture at room temperature. IR (CH_2Cl_2): $\tilde{\nu} = 2046$ vs, 2002 vs, 1980 m, 1961 s $[\nu(\text{CO})]$ cm^{-1} . ^1H NMR (CDCl_3): $\delta = 1.98$ –2.06 (m, 2 H, CH_2), 2.81–2.91 (m, 2 H, CH_2), 5.45 (m, 1 H, Fu), 5.91 (m, 1 H, Fu), 6.01 (m, 1 H, Fu), 6.19 (m, 1 H, Fu), 6.42 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 1 H, Fu), 6.70–7.63 (m, 19 H, aromatic), 8.06 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1 H, Fu) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 65.67$ (t, $^2J_{\text{P-P}} = 25$ Hz, PPh), 68.36 (dd, $^2J_{\text{P-P}} = 25$ and 146 Hz, PPh), 99.08 (dd, $^2J_{\text{P-P}} = 25$ and 146 Hz, PFu_2) ppm. FAB MS: $m/z = 850$ [$(\text{M} - 2\text{CO})^+$]. $\text{C}_{39}\text{H}_{29}\text{O}_7\text{P}_3\text{Ru}_2$ (904.72): calcd. C 51.78, H 3.23; found C 51.42, H 3.16.

$[\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_3\text{PPh}_2)]$ (6**):** In a manner similar to compound **5**, refluxing a toluene solution (20 mL) of **1** (50 mg, 0.083 mmol) and dppp (34 mg, 0.083 mmol) in a 1:1 molar ratio for 5 h produced a dark yellowish-brown solution. The usual workup procedures afforded a colourless TLC band (hexane/ CH_2Cl_2 , 4:1, v/v; $R_f = 0.31$), which became apparent under UV light. The title complex was subsequently isolated as a pale yellow solid in 40% yield (31 mg). IR (CH_2Cl_2): $\tilde{\nu} = 2049$ vs, 2004 s, 1985 s, 1959 s $[\nu(\text{CO})]$ cm^{-1} . ^1H NMR (CDCl_3): $\delta = 2.03$ –2.42 (m, 4 H, CH_2), 2.85–3.06 (m, 2 H, CH_2), 5.57 (m, 1 H, Fu), 5.96 (m, 1 H, Fu), 6.10 (m, 1 H, Fu), 6.22 (m, 1 H, Fu), 6.56 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 1 H, Fu), 6.74–7.91 (m, 19 H, aromatic), 8.22 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1 H, Fu) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 20.60$ (dd, $^2J_{\text{P-P}} = 31$ and 38 Hz, PPh), 21.82 (dd, $^2J_{\text{P-P}} = 4$ and 38 Hz, PPh), 84.27 (dd, $^2J_{\text{P-P}} = 4$ and 31 Hz, PFu_2) ppm. FAB MS: $m/z = 919$ [M^+]. $\text{C}_{40}\text{H}_{31}\text{O}_7\text{P}_3\text{Ru}_2$ (918.74): calcd. C 52.29, H 3.40; found C 52.01, H 3.19.

$[\{\text{Ru}_2(\text{CO})_5(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})\}_2(\text{dppb})]$ (7a**) and $[\text{Ru}_2(\text{CO})_4(\mu\text{-PFu}_2)(\mu\text{-}\eta^1, \eta^2\text{-Fu})(\text{dppb})]_n$ (**7b**):** A toluene solution (20 mL) of **1** (50 mg, 0.083 mmol) was heated at reflux in the presence of a 0.5 equiv. of dppb (18 mg, 0.042 mmol). After 1 h, the solvent was removed and the residue chromatographed. A yellow band, eluted with hexane/ CH_2Cl_2 (1:1, v/v), yielded the linking cluster **7a** (46 mg, 70%) after recrystallisation from the same solvent mixture.

Mixing compound **1** with 1 mol-equiv. of dppb (0.083 mmol) in toluene (20 mL), followed by heating to reflux for 1 h, generated a deep yellow solution. TLC screening essentially revealed the absence of **7a**. The solvent was removed and the crude solid obtained after washing with hot hexane was redissolved in the minimum volume of toluene. Analytically pure sample of **7b** was isolated as a yellow solid (56 mg, 69%) by repeated precipitation from methanol, washing with hexane and drying in vacuo. **7a**: IR (CH₂Cl₂): $\tilde{\nu}$ = 2060 vs, 2006 vs, 1974 m, 1958 sh [v(CO)] cm⁻¹. ¹H NMR (CDCl₃): δ = 2.09–2.57 (m, 6 H, CH₂), 3.50 (m, 2 H, CH₂), 4.83 (m, 2 H, Fu), 6.04–6.44 (m, 10 H, Fu), 7.08–7.57 (m, 26 H, Fu + Ph) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 34.58 (m, PFu₂ or PPh₂), 48.80 (m, PFu₂ or PPh₂) ppm. FAB MS: m/z = 1491 [(M – 3 CO)⁺]. C₆₂H₄₆O₁₆P₄Ru₄ (1575.21): calcd. C 47.28, H 2.94; found C 46.95, H 2.80. **7b**: IR (CH₂Cl₂): $\tilde{\nu}$ = 2014 vs, 1982 m, 1951 s [v(CO)] cm⁻¹. ¹H NMR (CDCl₃): δ = 2.00–2.50 (m, 6 H, CH₂), 3.49 (m, 2 H, CH₂), 4.52 (m, 1 H, Fu), 5.36 (m, 1 H, Fu), 5.85–6.32 (m, 4 H, Fu), 7.05–7.56 (m, 23 H, Fu + Ph) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 34.33 (m, PFu₂ or PPh₂), 38.60 (m, PFu₂ or PPh₂) ppm. GPC (THF as eluent): M_w = 5030, M_n = 4810 (n = 1.05). When the polymerization was performed for 10 h, M_w = 24500, M_n = 22700 (n = 1.08). C₄₄H₃₇O₇P₃Ru₂·0.5C₆H₁₄ (1015.92): calcd. C 55.57, H 4.37; found C 55.79, H 4.34.

[{Ru₂(CO)₅(μ-PFu₂)(μ-η¹,η²-Fu)₂(dpppe)] (**8a**) and [Ru₂(CO)₄(μ-PFu₂)(μ-η¹,η²-Fu)(dpppe)]_n (**8b**): A mixture of **1** (50 mg, 0.083 mmol) and dpppe (19 mg, 0.042 mmol) in toluene (20 mL) was heated to reflux for 1 h. Concentration of the resulting yellow solution followed by TLC separation gave a bright yellow band (R_f = 0.55) from which compound **8a** was isolated in 65% yield (43 mg). When a similar reaction was performed using a 1:1 molar ratio of **1** and dpppe (0.083 mmol), the desired polymer **8b** formed after 1 h of reflux, which was worked up in a fashion identical to that for **7b**, to afford a yellow-orange solid (60 mg, 73%). **8a**: IR (CH₂Cl₂): $\tilde{\nu}$ = 2060 vs, 2006 vs, 1973 m, 1957 sh [v(CO)] cm⁻¹. ¹H NMR (CDCl₃): δ = 2.25–2.62 (m, 8 H, CH₂), 3.48 (m, 2 H, CH₂), 4.83 (s, 1 H, Fu), 4.90 (s, 1 H, Fu), 6.21–6.33 (m, 10 H, Fu),

7.20–7.46 (m, 26 H, Fu + Ph), 7.54 (s, 2 H, Fu) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 34.75 (m, PFu₂ or PPh₂), 49.15 (m, PFu₂ or PPh₂) ppm. FAB MS: m/z = 1561 [(M – CO)⁺]. C₆₃H₄₈O₁₆P₄Ru₄ (1589.24): calcd. C 47.61, H 3.04; found C 47.32, H 2.85. **8b**: IR (CH₂Cl₂): $\tilde{\nu}$ = 2014 vs, 1981 m, 1951 s [v(CO)] cm⁻¹. ¹H NMR (CDCl₃): δ = 2.08–2.67 (m, 8 H, CH₂), 3.49 (m, 2 H, CH₂), 4.88 (m, 1 H, Fu), 5.39 (m, 1 H, Fu), 6.12–6.34 (m, 4 H, Fu), 7.10–7.89 (m, 23 H, Fu + Ph) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 34.22 (m, PFu₂ or PPh₂), 38.99 (m, PFu₂ or PPh₂) ppm. GPC (THF as eluent): M_w = 8550, M_n = 7270 (n = 1.18). C₄₅H₃₉O₇P₃Ru₂·0.5C₆H₁₄ (1029.95): calcd. C 55.98, H 4.50; found C 55.97, H 4.27.

[{Ru₂(CO)₅(μ-PFu₂)(μ-η¹,η²-Fu)₂(dppf)] (**9a**) and [Ru₂(CO)₄(μ-PFu₂)(μ-η¹,η²-Fu)(dppf)]_n (**9b**): Compound **1** (50 mg, 0.083 mmol) and dppf (23 mg, 0.042 mmol) in a 2:1 molar ratio were dissolved and mixed in toluene (20 mL). After heating to reflux and stirring for about 1 h, the resulting mixture was purified by chromatography on silica plates using hexane/CH₂Cl₂ (3:1, v/v) as eluent, leading to the isolation of an orange product **9a** (R_f = 0.38, 38 mg, 53%). When an equimolar amount of **1** and dppf (0.083 mmol) was employed in the reaction whilst stirring for 1 h, an orange solution resulted and the solvent was evaporated. The crude product was then washed with several portions of hot hexane (3 × 10 mL) and the resulting solid was reprecipitated thrice from toluene/methanol to produce an orange powder of **9b** in 64% yield (59 mg) after drying in vacuo. **9a**: IR (CH₂Cl₂): $\tilde{\nu}$ = 2061 vs, 2005 vs, 1978 s, 1957 sh [v(CO)] cm⁻¹. ¹H NMR (CDCl₃): δ = 3.78 (m, 4 H, C₅H₄), 4.05 (m, 2 H, C₅H₄), 4.32 (m, 2 H, C₅H₄), 4.52 (s, 2 H, Fu), 5.16 (s, 2 H, Fu), 5.96 (s, 2 H, Fu), 6.18 (m, 4 H, Fu), 6.39 (m, 2 H, Fu), 6.97–7.51 (m, 24 H, Fu + Ph), 7.66 (s, 2 H, Fu) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 36.13 (d, ² J_{P-P} = 20 Hz, PFu₂ or PPh₂), 47.86 (d, ² J_{P-P} = 20 Hz, PFu₂ or PPh₂) ppm. FAB MS: m/z = 1703 [M⁺]. C₆₈H₄₆FeO₁₆P₄Ru₄ (1703.13): calcd. C 47.96, H 2.72; found C 47.52, H 2.40. **9b**: IR (CH₂Cl₂): $\tilde{\nu}$ = 2014 vs, 1981 m, 1953 s [v(CO)] cm⁻¹. ¹H NMR (CDCl₃): δ = 3.48–4.56 (m, br, 9 H, Fu + C₅H₄), 5.20 (m, 1 H, Fu), 5.81–6.02 (m, 3 H, Fu), 6.30 (m, 1 H, Fu), 6.72–7.65 (m, 23 H, Fu + Ph) ppm. ³¹P{¹H} NMR

Table 6. Summary of crystal data

	2	3 ·0.5H ₂ O	4 ·2CH ₂ Cl ₂	5	6 ·0.5MeOH	8a ·CH ₂ Cl ₂	9a ·CH ₂ Cl ₂
Empirical formula	C ₄₁ H ₃₁ O ₇ ·P ₃ Ru ₂	C ₄₀ H ₃₀ NO ₇ ·P ₃ Ru ₂ ·0.5H ₂ O	C ₄₁ H ₃₂ NO ₇ ·P ₃ Ru ₂ ·2CH ₂ Cl ₂	C ₃₉ H ₂₉ O ₇ ·P ₃ Ru ₂	C ₄₀ H ₃₁ O ₇ ·P ₃ Ru ₂ ·0.5MeOH	C ₆₃ H ₄₈ O ₁₆ ·P ₄ Ru ₄ ·CH ₂ Cl ₂	C ₆₈ H ₄₆ FeO ₁₆ ·P ₄ Ru ₄ ·CH ₂ Cl ₂
Formula mass	930.71	940.71	1115.58	904.67	934.72	1674.17	1787.98
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	triclinic	monoclinic	triclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> 2/ <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	21.3556(15)	18.9075(14)	12.2529(13)	9.6249(6)	10.1612(6)	22.0907(14)	11.5260(6)
<i>b</i> [Å]	17.0951(12)	27.521(2)	13.0394(14)	11.2508(7)	11.5813(7)	10.4004(7)	16.4507(9)
<i>c</i> [Å]	10.9896(8)	15.1706(11)	15.4098(16)	18.0515(11)	18.8017(11)	31.980(2)	19.0961(11)
α [°]	90	90	79.028(2)	105.9470(10)	78.5950(10)	90	81.0200(10)
β [°]	90	90.1050(10)	71.699(2)	91.0220(10)	80.1120(10)	98.4900(10)	75.8440(10)
γ [°]	90	90	87.659(2)	95.0250(10)	67.5230(10)	90	85.0760(10)
<i>V</i> [Å ³]	4012.0(5)	7894.1(10)	2294.3(4)	1870.5(2)	1992.8(2)	7266.9(8)	3463.5(3)
<i>Z</i>	4	8	2	2	2	4	2
<i>T</i> [K]	293	293	293	293	293	293	293
<i>F</i> (000)	1864	3768	1116	904	938	3328	1772
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.920	0.938	1.045	0.984	0.927	1.037	1.293
Reflections collected	19431	38989	13482	11086	9946	17500	20763
Unique reflections	6147	13841	9807	8062	6870	6364	15005
<i>R</i> _{int}	0.0389	0.0851	0.0179	0.0154	0.0174	0.0332	0.0274
Observed reflections	6147	13841	9807	8062	6870	6364	15005
GOF on <i>F</i> ²	0.998	0.908	0.841	0.779	0.986	1.031	0.876
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2.0σ(<i>I</i>)] ^[a]	0.0395, 0.1035	0.0582, 0.1317	0.0364, 0.0993	0.0307, 0.0851	0.0355, 0.1095	0.0433, 0.1183	0.0476, 0.1017

[a] $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$; $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^2]^{1/2}$.

(CDCl_3): δ = 34.05 (m, PFu_2 or PPh_2), 41.35 (m, PFu_2 or PPh_2) ppm. GPC (THF as eluent): M_w = 11400, M_n = 8550 (n = 1.33). $\text{C}_{50}\text{H}_{37}\text{FeO}_7\text{P}_3\text{Ru}_2$ (1100.75): calcd. C 54.56, H 3.39; found C 54.10, H 3.08.

X-ray Crystallography: Except for compounds **6** and **8a**, good-quality crystals of our compounds suitable for X-ray diffraction studies were grown by slow concentration of their respective solutions in hexane/ CH_2Cl_2 at room temperature. Crystals of **6**-MeOH and **8a**- CH_2Cl_2 were obtained from an MeOH/ CHCl_3 and $\text{C}_6\text{H}_{12}/\text{CH}_2\text{Cl}_2$ mixture, respectively. Geometric and intensity data were collected using graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å) with a Bruker AXS SMART 1000 CCD area-detector diffractometer. The collected frames were processed with proprietary software SAINT^[37] and an absorption correction was applied (SADABS^[38]) to the collected reflections. The space group of each crystal was determined from the systematic absences and confirmed by successful refinement of the structure. The possible alternative *Pbca* for compound **3** was tried but did not give any reasonable solution. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL.^[39] Structure refinements were made on F^2 by the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **2** and **3**, one of the furyl rings was refined isotropically with constrained geometry and the resulting model yielded reasonable bond lengths and angles. 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 6. CCDC-168743 to -168749 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-0333; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

W.-Y. W. thanks the Hong Kong Baptist University (FRG/01-02/I-31) for financial support and F.-L. T. acknowledges the receipt of a studentship administered by the Hong Kong Baptist University.

- [1] P. Blenkiron, G. D. Enright, N. J. Taylor, A. J. Carty, *Organometallics* **1996**, *15*, 2855–2857.
- [2] V. D. Patel, N. J. Taylor, A. J. Carty, *J. Chem. Soc., Chem. Commun.* **1984**, 99–100.
- [3] A. J. Carty, G. Hogarth, G. D. Enright, J. W. Steed, D. Georgianopoulou, *Chem. Commun.* **1999**, 1499–1500.
- [4] A. J. Deeming, S. N. Jayasuriya, A. J. Arce, Y. De Sanctis, *Organometallics* **1996**, *15*, 786–793.
- [5] G. García, M. E. García, S. Melón, V. Riera, M. A. Ruiz, *Organometallics* **1997**, *16*, 624–631.
- [6] Y. Chi, A. J. Carty, P. Blenkiron, E. Delgado, G. D. Enright, W. Wang, S.-M. Peng, G. Lee, *Organometallics* **1996**, *15*, 5269–5271.
- [7] P. Blenkiron, D. Pilette, J. F. Corrigan, N. J. Taylor, A. J. Carty, *J. Chem. Soc., Chem. Commun.* **1995**, 2165–2166.
- [8] S. Doherty, M. R. J. Elsegood, W. Clegg, D. Mampe, N. H. Rees, *Organometallics* **1996**, *15*, 5302–5308.
- [9] S. Doherty, G. Hogarth, M. Waugh, W. Clegg, M. R. J. Elsegood, *Organometallics* **2000**, *19*, 5696–5708.
- [10] S.-M. Hsiao, S.-G. Shyu, *Organometallics* **1998**, *17*, 1151–1154.
- [11] S. Doherty, M. R. J. Elsegood, W. Clegg, T. Scanlan, N. H. Rees, *Chem. Commun.* **1996**, 1545–1546.
- [12] P. Blenkiron, J. F. Corrigan, N. J. Taylor, A. J. Carty, S. Doherty, M. R. J. Elsegood, W. Clegg, *Organometallics* **1997**, *16*, 297–300.
- [13] W.-Y. Wong, F.-L. Ting, W.-L. Lam, *J. Chem. Soc., Dalton Trans.* **2001**, 2981–2988.
- [14] N. G. Andersen, B. A. Keay, *Chem. Rev.* **2001**, *101*, 997–1030.
- [15] J. A. Cabeza, J. M. Fernández-Colinas, *Coord. Chem. Rev.* **1993**, *126*, 319–336.
- [16] J. A. Cabeza, J. M. Fernández-Colinas, V. Riera, M. A. Pellinghelli, A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* **1991**, 371–377.
- [17] J. A. Cabeza, M. A. Martínez-García, V. Riera, D. Ardura, S. García-Granda, J. F. Van der Maelen, *Eur. J. Inorg. Chem.* **1999**, 1133–1139.
- [18] F. Neumann, H. Stoeckli-Evans, G. Süss-Fink, *J. Organomet. Chem.* **1989**, *379*, 151–163.
- [19] W.-Y. Yeh, Y.-J. Cheng, M. Y. Chiang, *Organometallics* **1997**, *16*, 918–925.
- [20] W.-Y. Wong, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1995**, 2831–2836.
- [21] Y.-Y. Choi, W.-Y. Wong, W.-T. Wong, *J. Organomet. Chem.* **1996**, *518*, 227–233.
- [22] F. A. Cotton, E. V. Dikarev, W.-Y. Wong, *Polyhedron* **1997**, *16*, 3893–3898.
- [23] W.-Y. Wong, F.-L. Ting, unpublished work.
- [24] A. J. Deeming, *Adv. Organomet. Chem.* **1986**, *26*, 1–96.
- [25] K.-B. Shiu, S.-W. Jean, H.-J. Wang, S.-L. Wang, F.-L. Liao, J.-C. Wang, L.-S. Liou, *Organometallics* **1997**, *16*, 114–119.
- [26] G. Sánchez-Cabrera, E. V. García-Báez, M. J. Rosales-Hoz, *J. Organomet. Chem.* **2000**, *599*, 313–316.
- [27] F. A. Cotton, F. E. Kühn, *J. Am. Chem. Soc.* **1996**, *118*, 5826–5827.
- [28] D. I. Arnold, F. A. Cotton, F. E. Kühn, *Inorg. Chem.* **1996**, *35*, 4733–4737.
- [29] D. I. Arnold, F. A. Cotton, F. E. Kühn, *Inorg. Chem.* **1996**, *35*, 5764–5769.
- [30] F. A. Cotton, F. E. Kühn, *Inorg. Chim. Acta* **1996**, *252*, 257–264.
- [31] F. A. Cotton, E. V. Dikarev, N. Nawar, W.-Y. Wong, *Inorg. Chim. Acta* **1997**, *262*, 21–32.
- [32] F. A. Cotton, F. E. Kühn, A. Yokochi, *Inorg. Chim. Acta* **1996**, *252*, 251–256.
- [33] C. S. Browning, D. H. Farrar, *J. Chem. Soc., Dalton Trans.* **1995**, 521–530.
- [34] P. Blenkiron, D. Pilette, J. F. Corrigan, N. J. Taylor, A. J. Carty, *J. Chem. Soc., Chem. Commun.* **1995**, 2165–2166.
- [35] M. I. Bruce, P. A. Humphrey, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1997**, 1485–1487.
- [36] E. Delgado, Y. Chi, W. Wang, G. Hogarth, P. J. Low, G. D. Enright, S.-M. Peng, G.-H. Lee, A. J. Carty, *Organometallics* **1998**, *17*, 2936–2938.
- [37] SAINT, Reference manual, Siemens Energy and Automation, Madison, WI, **1994–1996**.
- [38] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Germany, **1997**.
- [39] G. M. Sheldrick, SHELXTLTM, Reference manual, version 5.1, Siemens, Madison, WI, **1997**.

Received November 19, 2001
[1010466]