

Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine: Di- and tri-substituted triruthenium and phosphido-bridged diruthenium complexes

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Abstract

Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine, $\text{P}(\text{C}_4\text{H}_3\text{O})_3$, at 40 °C in the presence of a catalytic amount of $\text{Na}[\text{Ph}_2\text{CO}]$ furnishes two triruthenium complexes $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_2]$ (**1**) and $[\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_3]$ (**2**) with the ligand coordinated through the phosphorus atom. Treatment of **1** and **2** with Me_3NO at 40 °C affords the dinuclear phosphido-bridged complexes $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]$ (**3**) and $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]$ (**4**), respectively, that are formed *via* phosphorus–carbon bond cleavage of a coordinated phosphine followed by coordination of the dissociated furyl moiety to the diruthenium center in a σ, π -alkenyl mode. Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine in refluxing benzene gives, in addition to **3** and **4**, low yields of the cyclometallated complex $[\text{Ru}_3(\text{CO})_9\{\mu\text{-}\eta^1, \eta^1\text{-P}(\text{C}_4\text{H}_3\text{O})_2(\text{C}_4\text{H}_2\text{O})\}_2]$ (**5**). Treatment of **3** with EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) at room temperature yields the monosubstituted derivatives $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\text{EPh}_3)]$ ($\text{E} = \text{P}$, **8**; $\text{E} = \text{As}$, **9**; $\text{E} = \text{Sb}$, **10**). Similar reactions of **3** with $\text{P}(\text{C}_4\text{H}_3\text{O})_3$, $\text{P}(\text{OMe})_3$ and Bu^tNC yield **4**, $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{OMe})_3\}]$ (**11**) and $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\text{NCBu}^t)]$ (**12**), respectively. The molecular structures of complexes **3**, **4** and **8** have been elucidated by single crystal X-ray diffraction studies. Each complex contains a bridging σ, π -alkenyl group and while in **4** the phosphine is bound to the σ -coordinated metal atom, in **8** it is at the π -bound atom. Protonation of **3** and **4** gives the hydride complexes $[(\mu\text{-H})\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]^+$ (**6**) and $[(\mu\text{-H})\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]^+$ (**7**), respectively, while heating **3** with dimethylacetylenedicarboxylate (DMAD) in refluxing toluene gives the cyclotrimerization product, $\text{C}_6(\text{CO}_2\text{Me})_6$.

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1. Introduction

The chemistry of $[\text{Ru}_3(\text{CO})_{12}]$ with simple alkyl-, aryl- and alkoxy-substituted tertiary phosphines is well-established [1–7] with derivatives containing one, two and three phos-

phorus ligands being accessible. More recently, the reactivity of group 8 metal carbonyls with functionalized phosphines such as diphenyl(2-thienyl)phosphine [8–11], di(2-thienyl)phenylphosphine [12], diphenyl(benzothienyl)phosphine [12], tri(2-thienyl)phosphine [13–15], diphenyl(2-pyridyl)phosphine [16–21] and 2-indolyl phosphine [22] have attracted considerable attention since the presence of a second coordinating atom provides a diversity of coordination modes. It is well-documented that heterodifunctional

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ligands exhibit very interesting properties, such as selective binding to metal ions of different types, dynamic behavior *via* reversible dissociation of the weaker metal–ligand bond and stereoelectronic control of the coordination sphere of the metal [23]. Deeming and co-workers have reported that the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with diphenyl(2-thienyl)phosphine gives, in addition to the phosphine derivatives of the trinuclear cluster, the carbon–hydrogen activated products $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-Ph}_2\text{PC}_4\text{H}_2\text{S})(\mu\text{-H})]$ and $[\text{Ru}_3(\text{CO})_8(\text{Ph}_2\text{PC}_4\text{H}_3\text{S})(\mu_3\text{-Ph}_2\text{PC}_4\text{H}_2\text{S})(\mu\text{-H})]$, the former reacting further with $[\text{Ru}_3(\text{CO})_{12}]$ to yield the thiophyne cluster $[\text{Ru}_4(\text{CO})_{11}(\mu_3\text{-Ph}_2\text{PC}_4\text{H}_2\text{S})(\mu_4\text{-PPh})(\mu_4\text{-C}_4\text{H}_2\text{S})(\mu\text{-H})]$ resulting from phosphorus–carbon bond cleavage [8]. The CO substitution reaction of $[\text{Ru}_3(\text{CO})_{12}]$ by tertiary phosphines occurs favorably *via* electron-transfer catalysis conditions using sodium diphenylketyl [22,24]. Recently, we have investigated the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-thienyl)phosphine *via* electron-transfer catalysis conditions and have obtained the mono-, di- and tri-substituted phosphine derivatives together with carbon–hydrogen and phosphorus–carbon bond cleavage products [25].

In contrast to the extensive chemistry of the pyridyl- and thienylphosphines, there are a few examples of the reactions of tri(2-furyl)phosphine with metal carbonyl clusters [26] although it has become an important ligand in transition metal catalysis [27]. Recently, Wong et al. reported the formation of dinuclear $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]$ from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with $\text{P}(\text{C}_4\text{H}_3\text{O})_3$ at 67 °C. This results from phosphorus–carbon bond cleavage and coordination of the dissociated heteroaromatic group to the bimetallic framework in a σ, π -alkenyl fashion, and they went on to investigate reactions with alkynes [26a] and diphosphines [26b]. Wong and Ting also investigated the reaction of tri(2-furyl)phosphine with $[\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}]$ obtaining a series of tetra ruthenium compounds containing furyl, furyne, phosphido- and phosphinidene ligands [26c]. We were interested in preparing a new family of triruthenium compounds containing furyl phosphines from the $\text{Na}[\text{Ph}_2\text{CO}]$ catalyzed reaction between $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine in order to study the carbon–hydrogen and phosphorus–carbon bond cleavage of these compounds under mild conditions and in a controlled, stepwise manner. Here we describe the isolation of the di- and tri-substituted clusters, $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_2]$ (**1**) and $[\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_3]$ (**2**), and their subsequent transformation under mild conditions to the dinuclear complexes $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]$ (**3**) and $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]$ (**4**), respectively. We have also investigated the reactivity of **3** towards a series of two-electron donor ligands as well as the activated alkyne, dimethylacetylenedicarboxylate (DMAD), the latter leading to cyclotrimerization.

2. Experimental

All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried using standard

procedures and were freshly distilled prior to use. Ruthenium carbonyl and $\text{Bu}'\text{NC}$ were purchased from Strem and tri(2-furyl)phosphine, PPh_3 , Ph_3Sb , Ph_3As and DMAD from Acros and used as received. Infrared spectra were recorded on Nicolet Avatar and Shimadzu FTIR 8101 spectrometers. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Varian Unity Plus 500 and Bruker DPX 400 instruments. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and to external 85% H_3PO_4 for ^{31}P chemical shifts. Elemental analyses were performed by the Microanalytical Laboratories, University College London. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Preparative thin layer chromatography (TLC) was performed on commercial plates (20 × 20 cm), precoated with 0.5 mm silica gel, or with plates prepared at Jahangirnagar University.

2.1. Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine in the presence of $\text{Na}[\text{Ph}_2\text{CO}]$

A dry nitrogen flushed 100 mL three necked flask was charged with $[\text{Ru}_3(\text{CO})_{12}]$ (200 mg, 0.312 mmol), tri(2-furyl)phosphine (146 mg, 0.628 mmol) and 40 mL of freshly distilled THF and the mixture was warmed to 40 °C to dissolve the $[\text{Ru}_3(\text{CO})_{12}]$. $\text{Na}[\text{Ph}_2\text{CO}]$ in THF (five drops) was then added *via* a syringe. Carbon monoxide was evolved, the solution readily darkened and consumption of $[\text{Ru}_3(\text{CO})_{12}]$ was confirmed by TLC. The solvent was then removed *in vacuo*, and the resultant residue was subjected to TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed two bands. The faster moving band afforded the previously reported [25a] disubstituted compound $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_2]$ (**1**) (160 mg, 48%) as red crystals after recrystallization from hexane/ CH_2Cl_2 at –4 °C. The slower moving band gave $[\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_3]$ (**2**) (40 mg, 10%) as red crystals after recrystallization from hexane/ CH_2Cl_2 at +4 °C. Anal. Calc. for $\text{C}_{45}\text{H}_{27}\text{O}_{18}\text{P}_3\text{Ru}_3$: C, 43.18; H, 2.17. Found: C, 43.35; H, 2.30%; IR ($\nu(\text{CO})$, CH_2Cl_2): 2062 m, 2002 vs, 1989 vs, 1962 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.64 (m, 9H), 6.61 (m, 9H), 6.42 (m, 9H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ –16.1 (s); MS (FAB): m/z 1253 $[\text{M}]^+$.

2.2. Thermolysis of **1** in the presence of Me_3NO

To a CH_2Cl_2 solution (30 mL) of **1** (50 mg, 0.048 mmol) was added Me_3NO (4.3 mg, 0.057 mmol) and heated to reflux for 2 h during which time the color changed from red to yellow. Work-up and chromatographic separation as above afforded the known compound $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]$ (**3**) (20 mg, 69%) [26a].

2.3. Thermolysis of **2** in the presence of Me_3NO

Thermolysis of a CH_2Cl_2 solution (30 mL) of **2** (70 mg, 0.056 mmol) and Me_3NO (4.9 mg, 0.065 mmol) for 12 h

followed by chromatographic separation afforded $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]$ (**4**) (40 mg, 88%) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at $+4^\circ\text{C}$. Anal. Calc. for $\text{C}_{29}\text{H}_{18}\text{O}_{11}\text{P}_2\text{Ru}_2$: C, 43.19; H, 2.25. Found: C, 43.28; H, 2.39%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2064 vs, 2018 vs, 2000 vs, 1978 vs cm^{-1} ; ^1H NMR (CDCl_3): δ 7.64 (s, 1H), 7.55 (m, 3H), 7.45 (s, 2H), 6.60 (m, 3H), 6.41 (m, 3H), 6.38 (m, 1H), 6.34 (s, 1H), 6.26 (s, 1H), 6.22 (s, 1H), 5.50 (m, 1H), 4.09 (m, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 53.7 (d, J 20.2 Hz), -11.0 (d, J 20.2 Hz); MS (FAB): m/z 808 $[\text{M}]^+$.

2.4. Protonation of **3** and **4**

To a CD_2Cl_2 solution (0.75 mL) of **3** (10 mg, 0.016 mmol) in an NMR tube was added CF_3COOH (one drop from a Pasteur pipette). The ^1H and ^{31}P NMR spectra indicated formation of the cation $[(\mu\text{-H})\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]^+$ (**6**). IR ($\nu(\text{CO})$, CH_2Cl_2): 2137 s, 2122 vs, 2085 vs, 2065 vs cm^{-1} ; ^1H NMR (CDCl_3): δ 8.27 (m, 1H), 8.01 (s, 1H), 7.82 (m, 1H), 7.38 (m, 1H), 6.83 (m, 1H), 6.61 (m, 1H), 6.58 (m, 1H), 6.52 (m, 1H), 6.24 (m, 1H), -12.25 (d, $J = 24.8$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 58.6 (s). A similar protonation to that above of **4** gave $[(\mu\text{-H})\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]^+$ (**7**). IR ($\nu(\text{CO})$, CH_2Cl_2): 2121 vs, 2088 s, 2071 s, 2051 s cm^{-1} ; ^1H NMR (CDCl_3): δ 7.77 (s, 2H), 7.66 (s, 1H), 7.60 (s, 3H), 6.64 (m, 3H), 6.55 (m, 6H), 6.50 (m, 1H), 5.49 (m, 2H), -11.91 (dd, J 23.6, 24.0 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 48.4 (d, J 22.4 Hz), -5.81 (d, J 22.4 Hz). Attempts to isolate **6–7** as PF_6 salts upon addition of an aqueous solution of $[\text{NH}_4][\text{PF}_6]$ resulted only in complete deprotonation to give **3–4**, respectively.

2.5. Thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine

A benzene solution (40 mL) of $[\text{Ru}_3(\text{CO})_{12}]$ (200 mg, 0.313 mmol) and $\text{P}(\text{C}_4\text{H}_3\text{O})_3$ (146 mg, 0.628 mmol) was refluxed for 15 min during which time the color changed from orange to pale yellow. The solvent was removed under reduced pressure and the resultant residue was subjected to TLC on silica gel. Elution with hexane/ CH_2Cl_2 (9:1, v/v) gave three bands. The first band gave **3** (140 mg, 74%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at $+4^\circ\text{C}$. The second moving band afforded $[\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{O})_2(\text{C}_4\text{H}_2\text{O})\}_2]$ (**5**) (20 mg, 6%). Anal. Calc. for $\text{C}_{33}\text{H}_{16}\text{O}_{15}\text{P}_2\text{Ru}_3$: C, 38.95; H, 1.58. Found: C, 39.15; H, 1.78%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2087 w, 2077 m, 2057 w, 2032 vs, 2015 s, 1968 s cm^{-1} ; ^1H NMR (CDCl_3): δ 7.61 (s, 2H), 7.56 (s, 2H), 6.99 (s, 2H), 6.95 (d, J 3.2 Hz, 2H), 6.55 (d, J 3.2 Hz, 2H), 6.39 (m, 2H), 6.10 (m, 2H), 5.92 (s, 2H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 90.0 (s); MS (FAB): m/z 1019 $[\text{M}]^+$. The slowest moving band gave **4** (25 mg, 10%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at $+4^\circ\text{C}$.

2.6. Reactions of **3** with Ph_3E ($\text{E} = \text{P}, \text{As}, \text{Sb}$)

A CH_2Cl_2 solution (20 mL) of **3** (30 mg, 0.049 mmol) and one equivalent of Ph_3E ($\text{E} = \text{P}, \text{As}, \text{Sb}$) was stirred at room temperature ($\text{E} = \text{P}$, 2 h; $\text{E} = \text{As}$, 6 h; $\text{E} = \text{Sb}$, 12 h). The color changed from pale yellow to dark yellow. The solvent was removed by rotary evaporation and the resultant residue was subjected to TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed only one band which afforded $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\text{Ph}_3\text{E})]$ (**8**, $\text{E} = \text{P}$, 33 mg, 79%; **9**, $\text{E} = \text{As}$, 34 mg, 77%; **10**, $\text{E} = \text{Sb}$, 36 mg, 78%) as yellow crystals after recrystallization from CH_2Cl_2 /hexane at $+4^\circ\text{C}$. Spectroscopic data for **8**: IR ($\nu(\text{CO})$, CH_2Cl_2): 2061 vs, 2009 vs, 1978 s, 1960 s cm^{-1} ; ^1H NMR (CDCl_3): δ 7.51 (s, 1H), 7.42–7.27 (m, 17H), 6.40 (s, 1H), 6.28 (s, 1H), 6.12 (s, 1H), 5.82 (s, 1H), 5.44 (s, 1H), 3.58 (s, 1H); ^1H NMR (CD_2Cl_2 , 273 K): δ 7.72 (dt, J 2.0, 1.0 Hz, 1H), 7.46 (quintet, J 0.7 Hz, 1H), 7.45 (dd, J 2.0, 0.9 Hz, 1H), 7.41–7.28 (m, 15H), 6.45 (ddd, J 3.4, 1.8, 0.5 Hz, 1H), 6.27 (ddd, J 3.3, 1.5, 0.7 Hz, 1H), 6.15 (ddd, J 3.3, 1.8, 1.0 Hz, 1H), 5.77 (dd, J 2.6, 1.7 Hz, 1H), 5.42 (dd, J 2.5, 2.4 Hz, 1H), 3.75 (ddd, J 6.3, 3.7, 2.8 Hz, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 48.3 (d, J 15.3 Hz), 45.7 (d, J 15.3 Hz); MS (FAB): m/z 838 $[\text{M}]^+$. Anal. Calc. for $\text{C}_{35}\text{H}_{24}\text{O}_8\text{P}_2\text{Ru}_2$: C, 50.25; H, 2.89. Found: C, 50.39; H, 3.07%. Spectroscopic data for **9**: IR ($\nu(\text{CO})$, CH_2Cl_2): 2064 vs, 2007 vs, 1978 s, 1956 m cm^{-1} ; ^1H NMR (CDCl_3): δ 7.68 (s, 1H), 7.43 (s, 1H), 7.36 (m, 10H), 7.29 (m, 6H), 6.40 (s, 1H), 6.24 (s, 1H), 6.19 (s, 1H), 6.16 (s, 1H), 5.23 (m, 1H), 3.84 (m, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 50.1 (s); MS (FAB): m/z 882 $[\text{M}]^+$. Anal. Calc. for $\text{C}_{35}\text{H}_{24}\text{O}_8\text{PAsRu}_2$: C, 47.74; H, 2.75. Found: C, 47.95; H, 2.90%. Spectroscopic data for **10**: IR ($\nu(\text{CO})$, CH_2Cl_2): 2065 vs, 2008 vs, 1978 s, 1958 s cm^{-1} ; ^1H NMR (CDCl_3): δ 7.66 (s, 1H), 7.39 (m, 10H), 7.32 (m, 6H), 7.18 (s, 1H), 6.45 (s, 1H), 6.40 (s, 1H), 6.26 (s, 1H), 6.18 (m, 1H), 5.48 (m, 1H), 3.87 (m, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 53.6 (s); MS (FAB): m/z 92 $[\text{M}]^+$. Anal. Calc. for $\text{C}_{35}\text{H}_{24}\text{O}_8\text{PSbRu}_2$: C, 45.33; H, 2.61. Found: C, 45.55; H, 2.75%.

2.7. Reaction of **3** with $\text{P}(\text{OMe})_3$

Using the same procedure as above, $\text{P}(\text{OMe})_3$ (10 mg, 0.09 mmol) was reacted with **3** (50 mg, 0.083 mmol) to yield $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{OMe})_3\}]$ (**11**) (40 mg, 69%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at $+4^\circ\text{C}$. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{O}_{11}\text{P}_2\text{Ru}_2$: C, 34.39; H, 2.60; Found: C, 34.52; H, 2.78%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2063 vs, 2019 vs, 1996 vs, 1980 vs cm^{-1} ; ^1H NMR (CDCl_3): δ 7.64 (s, 1H), 7.59 (s, 1H), 7.50 (s, 1H), 6.64 (s, 1H), 6.35 (m, 3H), 6.03 (s, 1H), 3.96 (s, 1H), 3.53 (d, J 12.46 Hz, 9H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.9 (d, J 18.2 Hz), 49.1 (d, J 18.2 Hz); MS (FAB): m/z 700 $[\text{M}]^+$.

2.8. Reaction of **3** with tri(2-furyl)phosphine

A similar reaction to that above of **3** (30 mg, 0.049 mmol) and $P(C_4H_3O)_3$ (26 mg, 0.11 mmol) for 24 h at 25 °C followed by similar chromatographic separation gave **4** (35 mg, 87%).

2.9. Reaction of **3** with Bu^tNC

A CH_2Cl_2 solution (5 mL) of Bu^tNC (4 mg, 0.048 mmol) was added dropwise to a CH_2Cl_2 solution (20 mL) of **3** (30 mg, 0.049 mmol) at 0 °C and stirred for 6 h. The color of the solution turned from pale yellow to yellow. Work-up and chromatographic separation as above developed two bands. The minor band gave unreacted **3** (7 mg) and the major band gave $[Ru_2(CO)_5(\mu-\eta^1, \eta^2-C_4H_3O)\{\mu-P(C_4H_3O)_2\}(Bu^tNC)]$ (**12**) (18 mg, 55%) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at +4 °C. Anal. Calc. for $C_{22}H_{18}O_8P_1N_1Ru_2$: C, 40.19; H, 2.76; Found: C, 40.22; H, 2.80%. IR ($\nu(CO)$, CH_2Cl_2): 2058 vs, 2013 vs, 1994 vs, 1978 vs cm^{-1} ; IR ($\nu(NC)$, CH_2Cl_2): 2174 vs cm^{-1} ; 1H NMR ($CDCl_3$): δ 7.64 (s, 1H), 7.59 (s, 1H), 7.50 (s, 1H), 6.65 (s, 1H), 6.36 (m, 3H),

6.04 (s, 1H), 4.13 (m, 1H), 1.40 (s, 9H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.4 (s); MS (FAB): m/z 659 $[M]^+$.

2.10. Reaction of **3** with dimethylacetylenedicarboxylate (DMAD)

A toluene solution (20 mL) of **3** (40 mg, 0.066 mmol) and DMAD (200 mg, 1.41 mmol) was refluxed for 6 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (1:1, v/v) developed two bands. The faster moving band afforded unreacted **3** (10 mg) and the slower moving band afforded $C_6(CO_2CH_3)_6$ (**13**) (50 mg, 25%) as colorless crystals after recrystallization from hexane/ CH_2Cl_2 at +4 °C. Anal. Calc. for $C_{18}H_{18}O_{12}$: C, 50.71; H, 4.26; Found: C, 50.92; H, 4.40%; 1H NMR ($CDCl_3$): δ 3.87 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.2 (s), 133.9 (s), 53.5(s).

2.11. X-ray structure determination of compounds **3**, **4** and **8**

Single crystals of **3**, **4**, and **8** suitable for X-ray diffraction were grown by slow diffusion of hexane into a

Table 1
Crystallographic data and structure refinement^a for **3**, **4** and **8**

| | 3 | 4 | 8 |
|--|---|---|---|
| Empirical formula | $C_{18}H_9O_9PRu_2$ | $C_{29}H_{18}O_{11}P_2Ru_2$ | $C_{35}H_{24}O_8P_2Ru_2$ |
| Formula weight | 602.36 | 806.51 | 836.62 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| <i>a</i> (Å) | 9.2384(12) | 21.3397(14) | 11.2573(6) |
| <i>b</i> (Å) | 12.4863(17) | 16.4859(11) | 11.8204(7) |
| <i>c</i> (Å) | 17.673(2) | 18.4174(12) | 13.1742(7) |
| α (°) | 90 | 90 | 86.1070(10) |
| β (°) | 97.521(2) | 110.0880(10) | 69.6650(10) |
| γ (°) | 90 | 90 | 85.0590(10) |
| Volume (Å ³) | 2021.1(5) | 6085.2(7) | 1636.32(16) |
| <i>Z</i> | 4 | 8 | 2 |
| <i>D</i> _{calc} (Mg/m ³) | 1.980 | 1.761 | 1.698 |
| μ (Mo K α) (mm ⁻¹) | 1.622 | 1.157 | 1.073 |
| <i>F</i> (000) | 1168 | 3184 | 832 |
| Crystal size (mm ³) | 0.25 × 0.24 × 0.10 | 0.21 × 0.18 × 0.05 | 0.35 × 0.16 × 0.16 |
| θ Range (°) | 2.00–28.31° | 1.60–28.28 | 1.65–28.27 |
| Index ranges | –12 ≤ <i>h</i> ≤ 12 –16 ≤ <i>k</i> ≤ 16 –23 ≤ <i>l</i> ≤ 23 | –27 ≤ <i>h</i> ≤ 28 –21 ≤ <i>k</i> ≤ 21 –24 ≤ <i>l</i> ≤ 24 | –14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 17 |
| Reflections collected | 17331 | 52663 | 14416 |
| Independent reflections | 4822 [<i>R</i> _{int} = 0.0198] | 14503 [<i>R</i> _{int} = 0.0286] | 7507 [<i>R</i> _{int} = 0.0135] |
| Reflections with <i>F</i> ² > 2 σ | 4504 | 12147 | 6920 |
| Maximum and minimum transmission | 0.6873 and 0.8546 | 0.7931 and 0.9444 | 0.7052 and 0.8471 |
| Weighting parameters <i>a</i> , <i>b</i> | 0.0315, 1.8788 | 0.0283, 2.0349 | 0.0241, 0.6295 |
| Data/restraints/parameters | 4822/0/272 | 14503/0/818 | 7507/0/436 |
| Goodness-of-fit on <i>F</i> ² | 0.976 | 1.021 | 1.028 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0212 <i>wR</i> ₂ = 0.0555 | <i>R</i> ₁ = 0.0268 <i>wR</i> ₂ = 0.0603 | <i>R</i> ₁ = 0.0203 <i>wR</i> ₂ = 0.0486 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0234 <i>wR</i> ₂ = 0.0566 | <i>R</i> ₁ = 0.0352 <i>wR</i> ₂ = 0.0635 | <i>R</i> ₁ = 0.0228 <i>wR</i> ₂ = 0.0496 |
| Largest difference in peak and hole, e Å ⁻³ | 0.815 and –0.449 | 0.600 and –0.413 | 0.446 and –0.477 |

^a Details in common: X-radiation, Mo K α (λ = 0.71073 Å), temperature (K) 150(2), refinement method: full-matrix least-squares on *F*².

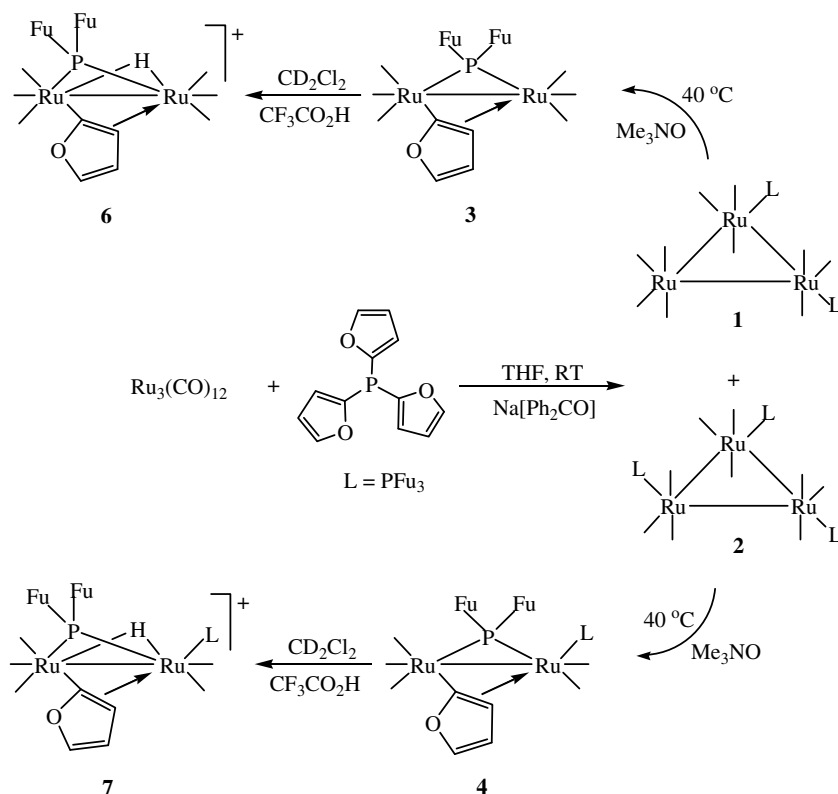
dichloromethane solution at $-4\text{ }^{\circ}\text{C}$. All geometric and crystallographic data of **3**, **4**, and **8** were collected at 150 K on a Bruker SMART APEX CCD diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Data reduction and integration was carried out with SAINT+ and absorption corrections were applied using the program SADABS [28]. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [29]. Final difference maps did not show any residual electron density of stereochemical significance. The details of the data collection and structure refinement are given in Table 1.

3. Results and discussion

3.1. Synthesis of $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_2]$ (**1**) and $[\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_3]$ (**2**)

The electron precise and air stable di- and tri-substituted clusters $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_2]$ (**1**) and $[\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}_3]$ (**2**) (Scheme 1) are obtained in 48% and

10% yields, respectively, by addition of a catalytic amount of $\text{Na}[\text{Ph}_2\text{CO}]$ into a 1:2 solution of $\text{Ru}_3(\text{CO})_{12}$ and tri(2-furyl)phosphine in THF at $40\text{ }^{\circ}\text{C}$. Compound **1** has been previously reported as a minor product (10% yield) from the thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine [26a]. Cluster **1** was characterized by comparison with the previously reported spectroscopic data [26a]. Tri-substituted **2** has been characterized by a combination of IR, ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, mass spectrometry, elemental analysis and single crystal X-ray diffraction studies [30]. The pattern of the IR spectrum in the carbonyl region is similar to that of other previously reported tertiary phosphine substituted derivatives of the type $[\text{Ru}_3(\text{CO})_9(\text{PR}_3)_3]$ [7], indicating that they are isostructural. As expected, the ^1H NMR spectrum shows three multiplets at δ 7.64, 6.61 and 6.42, each integrating for nine hydrogens and the absence of any metal-hydride resonance confirmed that no carbon-hydrogen activation had occurred. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at δ -16.1 assigned to three equivalent terminally coordinated phosphine ligands, the coordination of the tri(2-furyl)phosphine to the ruthenium center resulting in a downfield shift from δ -76.8 in the free ligand [27] to δ -16.1 for the cluster. The FAB mass spectrum exhibits the molecular ion peak at m/z 854 and fragmentation peaks due to the sequential loss of nine carbonyl groups are also observed.



Scheme 1.

3.2. Formation of binuclear phosphido-bridged complexes via phosphorus–carbon bond cleavage

Thermolysis of **1** in the presence of Me_3NO at 40°C gives the known dinuclear complex $[\text{Ru}_2(\text{CO})_6\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})]$ (**3**) (Scheme 1) in 69% yield. Isolation of **3** in this reaction indicates that its previous formation from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine at 68°C proceeded *via* the intermediate formation of **1**. Heating **2** at 40°C in the presence of Me_3NO leads to the formation of dinuclear $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O}\}\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]$ (**4**) in 57% yield (Scheme 1). Both **3** and **4** have been characterized by spectroscopic data and single crystal X-ray diffraction analysis. The X-ray structure of compound **3** is known [26a] but we redetermined this at low temperature [150(2) K]. A determination of the unit cell parameters indicated that the molecule had packed in a different unit cell than that reported by Wong et al. [26a]. The molecular structure of **3** is shown in Fig. 1 and selected bond distances and angles are listed in the caption.

Two crystallographically independent molecules are seen in the asymmetric unit of **4**. The respective bond lengths and angles in the two molecules show only minor variations. The structure of one of these molecules is shown in Fig. 2 and selected bond distances are listed in the caption. Binuclear **4** can be derived from **3** by substitution of one carbonyl group by a $\text{P}(\text{C}_4\text{H}_3\text{O})_3$ ligand. Both consist of a $(\text{OC})_3\text{Ru}\text{-Ru}(\text{CO})_2\text{L}$ [**3**, $\text{L} = \text{CO}$; **4**, $\text{L} = \text{P}(\text{C}_4\text{H}_3\text{O})_3$] skeleton spanned by a difurylphosphido group and a furyl moiety derived by phosphorus–carbon bond cleavage of the coordinated $\text{P}(\text{C}_4\text{H}_3\text{O})_3$ ligand. The $\mu\text{-C}_4\text{H}_3\text{O}$ moiety

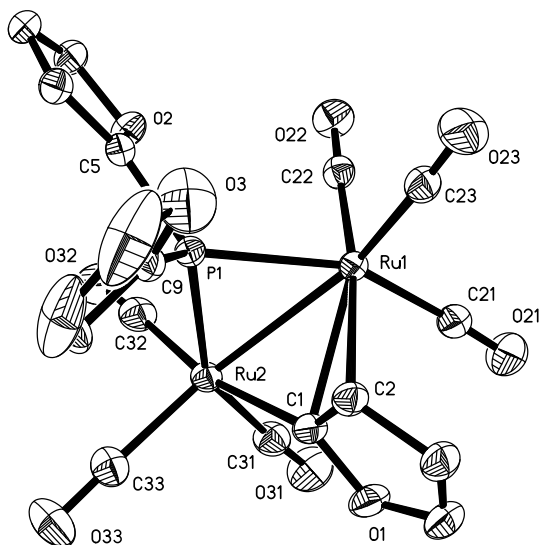


Fig. 1. Molecular structure of $[\text{Ru}_2(\text{CO})_6\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})]$ (**3**) showing 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): $\text{Ru}(1)\text{-Ru}(2) = 2.7695(3)$, $\text{Ru}(1)\text{-P}(1) = 2.3418(6)$, $\text{Ru}(1)\text{-C}(1) = 2.367(2)$, $\text{Ru}(1)\text{-C}(2) = 2.413(2)$, $\text{Ru}(2)\text{-P}(1) = 2.3228(6)$, $\text{Ru}(2)\text{-C}(1) = 2.071(2)$, $\text{P}(1)\text{-Ru}(1)\text{-Ru}(2) = 53.264(13)$, $\text{C}(1)\text{-Ru}(2)\text{-Ru}(1) = 56.36(6)$, $\text{P}(1)\text{-Ru}(2)\text{-Ru}(1) = 53.897(15)$, $\text{Ru}(2)\text{-P}(1)\text{-Ru}(1) = 72.840(17)$.

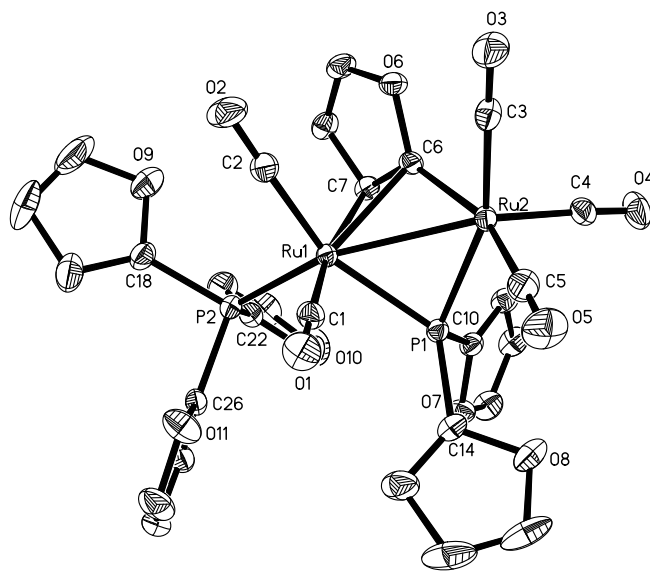


Fig. 2. Molecular structure of one of the two crystallographically independent molecules of $[\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]$ (**4**) showing 50% probability thermal ellipsoids. Selected bond distances (\AA) and angles ($^\circ$): $\text{Ru}(1)\text{-Ru}(2) = 2.7711(3)$, $\text{Ru}(1)\text{-P}(1) = 2.3595(5)$, $\text{Ru}(2)\text{-P}(1) = 2.3304(5)$, $\text{Ru}(1)\text{-P}(2) = 2.3068(6)$, $\text{Ru}(1)\text{-C}(6) = 2.3081(19)$, $\text{Ru}(1)\text{-C}(7) = 2.378(2)$, $\text{Ru}(2)\text{-C}(6) = 2.078(2)$, $\text{P}(2)\text{-Ru}(1)\text{-P}(1) = 104.821(19)$, $\text{C}(6)\text{-Ru}(1)\text{-Ru}(2) = 47.22(5)$, $\text{C}(6)\text{-Ru}(2)\text{-Ru}(1) = 54.61(5)$, $\text{C}(7)\text{-Ru}(1)\text{-Ru}(2) = 77.11(5)$, $\text{P}(2)\text{-Ru}(1)\text{-Ru}(2) = 154.980(15)$, $\text{P}(1)\text{-Ru}(1)\text{-Ru}(2) = 53.298(13)$, $\text{P}(1)\text{-Ru}(2)\text{-Ru}(1) = 54.267(13)$, $\text{Ru}(2)\text{-P}(1)\text{-Ru}(1) = 72.435(16)$.

is bonded through a σ bond between $\text{C}(1)$ and $\text{Ru}(2)$ in **3** [$\text{Ru}(2)\text{-C}(1) = 2.071(2)\text{\AA}$] and $\text{C}(6)$ and $\text{Ru}(2)$ in **4** [$\text{Ru}(2)\text{-C}(6) = 2.078(2)\text{\AA}$] and through an η^2 -interaction between $\text{C}(1)$, $\text{C}(2)$ and $\text{Ru}(1)$ for **3** [$\text{Ru}(1)\text{-C}(1) = 2.367(2)$, $\text{Ru}(1)\text{-C}(2) = 2.413(2)\text{\AA}$] and $\text{C}(6)$, $\text{C}(7)$ and $\text{Ru}(1)$ for **4** [$\text{Ru}(1)\text{-C}(6) = 2.3081(19)$, $\text{Ru}(1)\text{-C}(7) = 2.378(2)\text{\AA}$], thus forming a σ, π -alkenyl bridge between the metal atoms. The $\text{Ru}\text{-C}$ bond distances involving the π -interaction are shorter and more asymmetric in **4** than those of the corresponding distances in **3**. The $\text{Ru}\text{-Ru}$ bond distance of $2.7711(3)\text{\AA}$ in **4** is comparable to that of $2.7695(3)\text{\AA}$ in **3**.

The coordination sphere of the molecules is completed by six terminal carbonyls in **3** and five carbonyls and the tri(2-furyl)phosphine ligand for **4**. The $\text{Ru}\text{-P}$ distances involving the phosphido moiety are more symmetric in **3** [$\text{Ru}(1)\text{-P}(1) = 2.3418(6)$, $\text{Ru}(2)\text{-P}(1) = 2.3228(6)\text{\AA}$] than in **4** [$\text{Ru}(1)\text{-P}(2) = 2.3595(5)$, $\text{Ru}(1)\text{-P}(2) = 2.3068(6)\text{\AA}$] and comparable to those found in related diruthenium complexes. The $\text{Ru}\text{-P}\text{-Ru}$ angle in **4** [$72.43(2)^\circ$] is very similar to the corresponding angle in **3** [$72.80(2)^\circ$]. In **4**, the terminal phosphine is axially coordinated to the ruthenium atom to which the furyl moiety is π -bonded [$\text{P}(2)\text{-Ru}(1)\text{-Ru}(2) = 154.98(2)^\circ$]. Both the $\mu\text{-}\eta^1, \eta^2\text{-furyl}$ and $\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2$ ligands donate three-electrons and thus both **3** and **4** have a 34-valence electron count.

Spectroscopic data for **4** indicate that it retains its solid-state structure in solution. The IR spectrum shows only terminal carbonyl groups and the pattern is consistent with an

$\text{Ru}_2(\text{CO})_5$ moiety. In the ^1H NMR spectrum, in addition to three multiplets at δ 7.55, 6.60 and 6.41, each integrating for three hydrogens, that are assigned to the ring protons of the tri(2-furyl)phosphine ligand, the spectrum contains nine well-separated signals between δ 7.64–4.09, each integrating for one hydrogen, assigned to the $\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2$ and $\mu\text{-C}_4\text{H}_3\text{O}$ ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of two equal intensity doublets at δ -11.0 and 53.7 ($J_{\text{P-P}}$ 20.2 Hz) assigned to the phosphido and phosphine ligands respectively, while the FAB mass spectrum contains a molecular ion peak at m/z 808 and fragmentation peaks due to the sequential loss of five carbonyls.

Upon addition of excess $\text{CF}_3\text{CO}_2\text{H}$ to a CD_2Cl_2 solution of **3**, the color rapidly changed from pale yellow to yellow, and consistent with the formation of cationic species, the $\nu(\text{CO})$ absorption bands were strongly shifted to higher wave numbers. The cation generated is formulated as $[(\mu\text{-H})\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]^+$ (**6**) and protonation across the Ru–Ru vector is indicated by the appearance of a high-field doublet at δ -12.25 ($J_{\text{P-H}}$ 24.8 Hz). In an analogous manner, addition of $\text{CF}_3\text{CO}_2\text{H}$ to **4** results in formation of cation $[(\mu\text{-H})\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{C}_4\text{H}_3\text{O})_3\}]^+$ (**7**). In support of this, the hydride region of the ^1H NMR of **7** exhibits a doublet of doublets at δ -11.91 ($J_{\text{P-H}}$ 23.6, 24.0 Hz), while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two doublets at δ 48.40 and -5.81 ($J_{\text{P-P}}$ 25.3 Hz).

3.3. Thermolytic reaction of $[\text{Ru}_3(\text{CO})_{12}]$ and tri(2-furyl)phosphine

Heating $[\text{Ru}_3(\text{CO})_{12}]$ and tri(2-furyl)phosphine in benzene affords, together with the dinuclear complexes **3** and **4** in 74% and 10% yields respectively, a third minor (6% yield) product characterized as trinuclear $[\text{Ru}_3(\text{CO})_9\{\mu\text{-}\eta^1, \eta^2\text{-P}(\text{C}_4\text{H}_3\text{O})_2(\text{C}_4\text{H}_3\text{O})\}_2]$ (**5**) (Scheme 2). We were unable to obtain X-ray quality crystals of **5** and therefore characterization is based on elemental analysis, IR, ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR and mass spectral data.

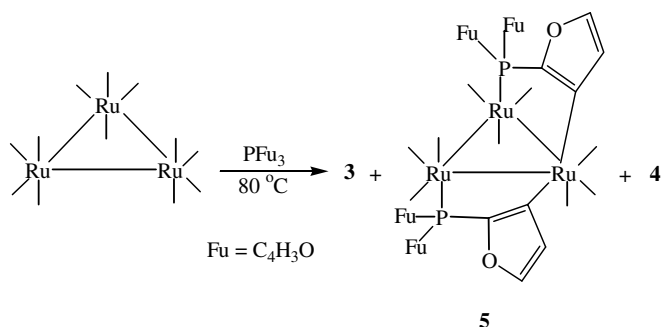
The FAB mass spectrum of **5** shows a molecular ion peak at m/z 1019 and fragmentation peaks due to the sequential loss of nine carbonyl groups suggesting an $\text{Ru}_3(\text{CO})_9$ core while the IR spectrum indicates that all carbonyl groups are terminal. Most informative is the ^1H

NMR spectrum, which displays eight well-separated signals in the region δ 7.61–5.92 (each integrating for two protons), assigned to the protons of the furyl rings. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** contains only a singlet at δ 90.0 showing that the two phosphorus-containing ligands are equivalent. Based on the spectroscopic data, we postulate that **5** is a 48-electron cluster with two bridging orthometallated trifurylphosphine ligands [i.e. $\mu\text{-}\eta^1, \eta^1\text{-P}(\text{C}_4\text{H}_3\text{O})_2(\text{C}_4\text{H}_2\text{O})$] and nine carbonyl groups. The precise relative orientation of the phosphine ligands is unknown. Complex **5** probably forms *via* the intermediate generation of **1** followed by carbon–hydrogen activation of one of the furyl rings of the coordinated ligand and subsequent H_2 elimination. This transformation is accompanied by dissociation of carbonyl in order to keep the closed triruthenium framework. We have recently reported a similar bonding mode of the $\mu\text{-}\eta^1, \eta^1\text{-P}(\text{C}_4\text{H}_3\text{S})_2(\text{C}_4\text{H}_2\text{S})$ ligand in the triosmium cluster $[\text{Os}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_3\text{S})_3\{\mu\text{-P}(\text{C}_4\text{H}_3\text{S})_2\text{-}(\text{C}_4\text{H}_2\text{S})\}\mu\text{-H}\}]$ obtained from the reaction of $\text{Os}_3(\text{CO})_{12}$ with tri(2-thienyl)phosphine at 110°C [13]. To the best of our knowledge, this type of furyl cyclometallation at a trimetallic framework is unprecedented in the literature.

3.4. Facile CO substitution in $\text{Ru}_2(\text{CO})_6\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})$ (**3**)

Previous studies have shown that **3** reacts with a series of diphosphines including $\text{Ph}_2\text{PXPPH}_2$ ($\text{X} = \text{CH}_2, \text{NH}, \text{NMe}$) and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2\text{--}3$) at elevated temperatures (110°C), the products depending critically upon the nature of the backbone. Thus $\text{Ph}_2\text{PXPPH}_2$ produce the substitution products $[\text{Ru}_2(\text{CO})_4(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-Ph}_2\text{PXPPH}_2)]$ in which the diphosphine and the furyl ligands simultaneously bridge the ruthenium–ruthenium vector, whereas $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ give the cyclometallated products $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_n\text{PPh}_2\}\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]$ by elimination of the coordinated furyl moiety [26b]. Following these observations we set out to investigate the reactivity of **3** with a series of two-electron donor ligands to see the effect of the steric bulk of the ligand on the structures of the products. Complex **3** reacts rapidly and smoothly with an equimolar amount of EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) at room temperature to give the substitution products $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\text{EPh}_3)]$ ($\text{E} = \text{P}$, **8**; $\text{E} = \text{As}$, **9**; $\text{E} = \text{Sb}$, **10**) in good yields. Compounds **8–10** have been characterized by a combination of elemental analysis, IR, NMR and mass spectral data together with single crystal X-ray diffraction analysis for **8**.

The molecular structure of **8** is depicted in Fig. 3 and selected bond distances and angles are collected in the caption. The salient features of **8** in the solid-state remain essentially the same as those of **4** except that the phosphine ligand is coordinated to the ruthenium atom [Ru(1)] that is σ -bonded by the bridging $\sigma\text{-}\pi$ alkenyl moiety. The distribution of carbonyl ligands around the diruthenium center is the same as that found in **4** and satisfies the requirement for an electron precise 34 valence electron complex. The



Scheme 2.

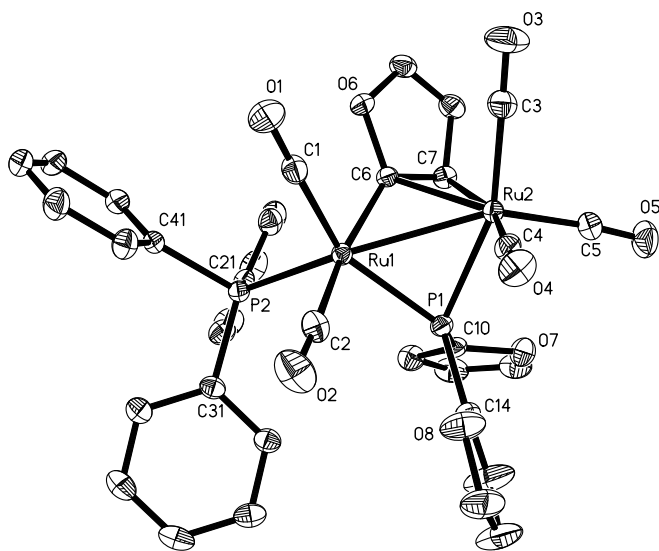


Fig. 3. Molecular structure of $[\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-}\eta^2\text{-C}_4\text{H}_3\text{O})(\text{PPh}_3)]$ (**8**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles ($^\circ$): $\text{Ru}(1)\text{-Ru}(2) = 2.78306(19)$, $\text{Ru}(1)\text{-P}(1) = 2.3322(4)$, $\text{Ru}(1)\text{-P}(2) = 2.3198(4)$, $\text{Ru}(2)\text{-P}(1) = 2.3508(4)$, $\text{Ru}(1)\text{-C}(6) = 2.0693(16)$, $\text{Ru}(2)\text{-C}(6) = 2.3467(15)$, $\text{Ru}(2)\text{-C}(7) = 2.3950(16)$, $\text{C}(6)\text{-Ru}(2)\text{-Ru}(1) = 77.85(5)$, $\text{C}(6)\text{-Ru}(1)\text{-Ru}(2) = 55.52(4)$, $\text{C}(6)\text{-Ru}(2)\text{-C}(7) = 34.65(5)$, $\text{C}(7)\text{-Ru}(2)\text{-Ru}(1) = 76.66(4)$, $\text{P}(2)\text{-Ru}(1)\text{-Ru}(2) = 150.819(12)$, $\text{P}(1)\text{-Ru}(1)\text{-Ru}(2) = 53.846(11)$, $\text{P}(1)\text{-Ru}(2)\text{-Ru}(1) = 53.231(11)$, $\text{C}(6)\text{-Ru}(1)\text{-P}(2) = 103.41(4)$, $\text{P}(2)\text{-Ru}(1)\text{-P}(1) = 108.669(15)$, $\text{Ru}(1)\text{-P}(1)\text{-Ru}(2) = 77.85(5)$.

furyl moiety is σ -bonded to $\text{Ru}(1)$ [$\text{Ru}(1)\text{-C}(6) = 2.069(3)$ Å] and π -bonded to $\text{Ru}(2)$ [$\text{Ru}(2)\text{-C}(6) = 2.3467(15)$, $\text{Ru}(2)\text{-C}(7) = 2.3950(16)$ Å]. These Ru–C distances are comparable to those observed in **3** and **4**. The $\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2$ ligand asymmetrically spans the Ru–Ru edge and the Ru–P distances [$\text{Ru}(2)\text{-P}(1) = 2.3304(5)$, $\text{Ru}(1)\text{-P}(1) = 2.3595(5)$ Å] are comparable to those observed for **3** and **4**. The $\text{Ru}(1)\text{-P}(1)\text{-Ru}(2)$ angle of $108.67(2)^\circ$ is significantly larger compared to the corresponding angles in **3** and **4**. Although bound to a different ruthenium center than that found in **4**, the phosphine still occupies an axial position lying *trans* to the ruthenium–ruthenium bond [$\text{P}(2)\text{-Ru}(1)\text{-Ru}(2) = 150.82(2)^\circ$]. Spectroscopic data for **8–10** are broadly consistent with the solid state structure found in **8**. Their IR spectra in the carbonyl region are virtually indistinguishable, suggesting structural similarity. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** consists of two doublets at δ 45.7 and 48.3 ($J_{\text{P-P}} = 15.3$ Hz) while **9** and **10** exhibit only singlets at δ 50.1 and 53.6, respectively. In addition to the usual phenyl proton resonances, the ^1H NMR spectra of **8–10** display well-separated signals for the bridging $\text{C}_4\text{H}_3\text{O}$ and $\text{P}(\text{C}_4\text{H}_3\text{O})_2$ ligands and FAB mass spectra all show molecular ions at m/z 838, 882 and 928, respectively.

3.5. Stereochemical nonrigidity of the substituted furyl-bridged diruthenium complexes

We were intrigued as to why the phosphine coordination in **4** and **8** differed, as shown by the X-ray structures (Figs.

2 and **3**). The “windshield–wiper” fluxionality [31] of $\sigma\text{-}\pi$ alkenyl ligands is well-documented. In related diiron complexes, it has been established that free energies of activation for this process vary significantly between α - and β -substituted alkenyl ligands [32–35], the barriers for β -substituted complexes being significantly lower than those for isomeric α -alkenyl complexes. Further, disubstituted complexes behave essentially like their β -substituted analogues. For example, the free energies of activation for the isomeric pair $[\text{Fe}_2(\text{CO})_4(\mu\text{-PhC}=\text{CH}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})]$ and $[\text{Fe}_2(\text{CO})_4(\mu\text{-HC}=\text{CHPh})(\mu\text{-PPh}_2)(\mu\text{-dppm})]$ are 63 ± 1 and 45 ± 1 kJ mol^{-1} , respectively [35]. Since all the $\sigma\text{-}\pi$ alkenyl complexes studied here are disubstituted we would expect them to have low free energies of activation for the windshield–wiper fluxionality. The situation in unsymmetrically substituted binuclear centers, such as the $(\text{CO})_3\text{Ru}\text{-Ru}(\text{CO})_2\text{L}$ framework here, is complicated by the inequivalence of the metal atoms in the high temperature regime. Nevertheless, given that both σ - and π -bound phosphine derivatives are accessible (as shown by the solid-state structures of **8** and **4**, respectively) we would not expect a major energy difference between the two. We attempted to probe the fluxionality of **8** by variable temperature NMR. At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** in CD_2Cl_2 consists of two doublets at δ 48.5 and 46.4 ($J_{\text{P-P}} = 16.4$ Hz). Upon cooling to 233 K only small changes are noted, including a slight increase in the separation of the two signals from ca. 2–4 ppm, however, below this temperature the spectrum changes significantly. Thus, at 196 K it consists of a series of very broad resonances spanning nearly 20 ppm. We have not been able to go to lower temperatures but this data clearly shows that the observed room temperature data is a high temperature-limiting spectrum. The extreme broadening observed at 196 K cannot simply be attributed to the $\sigma\text{-}\pi$ alkenyl fluxionality and probably results from a combination of this and fluxionality of the $\text{Ru}(\text{CO})_2(\text{PPh}_3)$ unit *via* the well known trigonal-twist process. If both of these processes are frozen out then a total of six isomeric structures are possible and it may be that at room temperature a number of these are populated. In further support of the facile $\sigma\text{-}\pi$ alkenyl fluxionality in **8** (and presumably other complexes of this type) we note that for the related diphosphine-bridged complexes $[\text{Ru}_2(\text{CO})_4(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-Ph}_2\text{PXPPH}_2)]$ ($\text{X} = \text{CH}_2, \text{NH}$), Wong and co-workers report that the phosphorus nuclei of the diphosphine ligands are equivalent at room temperature [25 b]. They conclude that this is coincidental but we suggest that it is rather due to the facile $\sigma\text{-}\pi$ alkenyl fluxionality of the furyl ligand. They further report that the methylene protons of the dppm ligand in $[\text{Ru}_2(\text{CO})_4(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-dppm})]$ are also equivalent at room temperature – a situation that is only possible if both $\sigma\text{-}\pi$ alkenyl fluxionality and diphosphine fluxionality are facile. We have recently detailed an example of the latter in the somewhat related complex $[\text{Fe}_2(\text{CO})_4(\mu\text{-S}(\text{CH}_2)_3\text{S})\{\mu\text{-dppm}\}]$ [36] and we suggest that a similar concerted dou-

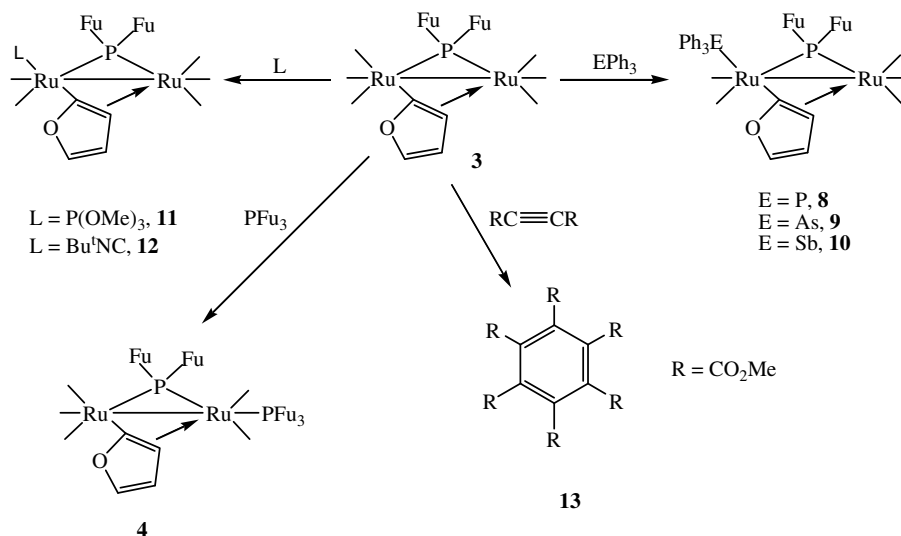
ble trigonal-twist of the diphosphine may be occurring in the above-mentioned dpmm-bridged diruthenium complex. If indeed a diphosphine is able to change coordination sites readily, then this suggests that movement of monodentate ligands in a similar system is likely to be very facile. We are currently investigating the fluxionality of $[\text{Ru}_2(\text{CO})_4(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\mu\text{-Ph}_2\text{PCH}_2\text{-PPh}_2)]$ in order to confirm this. Thus we believe that the room temperature NMR data for **8** (and presumably **9–10** and related complexes discussed below) represent the high temperature-limiting spectra and therefore $\sigma\text{-}\pi$ alkenyl fluxionality and the trigonal-twist of the $\text{Ru}(\text{CO})_2\text{L}$ moieties are both rapid on the NMR time-scale at this temperature. The differences in the observed solid-state structures of **4** and **8** then represent only differences brought about by packing effects and other solid-state interactions. It is clear that positioning of the phosphine *trans* to the ruthenium–ruthenium vector is preferred (since the structures of both **4** and **8** show this) but other conformations must be accessible to permit the suggested fluxional scheme (see Scheme 3).

For comparison, we have also studied the reactions of **3** with $\text{P}(\text{C}_4\text{H}_3\text{O})_3$ and $\text{P}(\text{OMe})_3$. Treatment of **3** with an equimolar amount of $\text{P}(\text{C}_4\text{H}_3\text{O})_3$ and $\text{P}(\text{OMe})_3$ yields **4** and $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}\{\text{P}(\text{OMe})_3\}]$ (**11**) in 87% and 69% yields, respectively. Their IR spectra are very similar, indicating that they are isostructural. The presence of a $\text{P}(\text{OMe})_3$ ligand in **11** is shown in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which consists of equal intensity doublets at δ 157.9 and 49.1 ($J_{\text{P-P}}$ 18.2 Hz), the former being assigned to $\text{P}(\text{OMe})_3$ and latter to $\text{P}(\text{C}_4\text{H}_3\text{O})_2$. The ^1H NMR spectrum of **11** contains six singlets at δ 7.64, 7.59, 7.50, 6.64, 6.03 and 3.96 (each integrating for 1H), a multiplet at δ 6.35 (integrating for 3H), assignable to the protons of the bridging $\text{C}_4\text{H}_3\text{O}$ and $\text{P}(\text{C}_4\text{H}_3\text{O})_2$ ligands and a doublet at δ 3.53 (integrating for 9H) assigned to the $\text{P}(\text{OMe})_3$ ligand.

Isocyanide is isoelectronic with CO and undergoes insertion into M-C bonds, which represents reactions of fundamental importance for stoichiometric organic synthesis and industrial catalysis [37–40]. As part of our investigations into the chemistry of **3**, we set out to investigate its reaction with $\text{Bu}'\text{NC}$ to see whether it inserts into $\text{Ru-C}(\text{furyl})$ bond or displaces CO like the other two-electron donors described above. Reaction of **3** with an equimolar amount of $\text{Bu}'\text{NC}$ at room temperature gives intractable materials. However, dropwise addition of a CH_2Cl_2 solution of $\text{Bu}'\text{NC}$ to a solution of **3** ($\text{3/Bu}'\text{NC}$ molar ratio = 1:1) in the same solvent at 0°C , followed by chromatographic separation, gives $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}(\text{NCBu}'\text{H})]$ (**12**) in 55% yield, instead of the expected insertion product. The IR spectrum of **12** closely resembles that of other monosubstituted derivatives, but **12** is only slightly more electron rich as shown by the shift to lower wave numbers (ca. $2\text{--}6\text{ cm}^{-1}$). The ^1H NMR spectrum contains six singlets at δ 7.64, 7.59, 7.50, 6.65, 6.04, 4.13 (each integrating for 1H) and a multiplet at δ 6.36 (integrating for 3H) assigned to the protons of the bridging $\text{C}_4\text{H}_3\text{O}$ and $\text{P}(\text{C}_4\text{H}_3\text{O})_2$ ligands, with a further singlet at δ 1.40 (9H), assigned to the $\text{Bu}'\text{NC}$ ligand. As expected, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows only a singlet (δ 55.4) and the FAB mass spectrum gives a molecular ion peak at m/z 659.

3.6. Cyclotrimerization of dimethylacetylenedicarboxylate (DMAD)

The synthesis and reactivity of organometallic complexes have attracted considerable attention because of their application to effective organic transformation [41–44]. The reactivity of **3** with a variety of terminal alkynes to give a head-to-tail coupling of a 1-alkyne with the $\mu\text{-}\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O}$ moiety of **3** to form a furyl based four-carbon chain with $\mu\text{-}\eta^1, \eta^1, \eta^2, \eta^3$ -coordination mode to the ruthenium centers has been demonstrated by Wong et al.



Scheme 3.

[26a]. The cyclotrimerization of alkynes to form highly substituted benzenes is an intriguing reaction that has continued to be of interest. Reaction of **3** with excess DMAD in refluxing toluene for 4 h gives a pale yellow solution that, upon separation by TLC, affords $C_6(CO_2Me)_6$ in addition to some unconsumed **3**. The cyclotrimerization product has been characterized by 1H , ^{13}C NMR spectroscopy and elemental analysis, the former corresponding to data reported by Thomas and Darkwa [45].

4. Conclusions

The present work has demonstrated the variable coordination modes of the tri(2-furyl)phosphine ligand. It can serve as monodentate two-electron phosphorus donor in the substitution of $[Ru_3(CO)_{12}]$ with tri(2-furyl)phosphine under mild conditions to afford the di- and tri-substituted complexes $[Ru_3(CO)_{10}\{P(C_4H_3O)_3\}_2]$ (**1**) and $[Ru_3(CO)_9\{P(C_4H_3O)_3\}_3]$ (**2**), respectively. Unlike the triruthenium complexes of related P, S-donor ligands, gentle heating of these clusters in the presence of Me_3NO affords the phosphido-bridged dinuclear compounds $[Ru_2(CO)_6(\mu-\eta^1, \eta^2-C_4H_3O)\{(\mu-P(C_4H_3O)_2)\}]$ (**3**) and $[Ru_2(CO)_5(\mu-\eta^1, \eta^2-C_4H_3O)\{\mu-P(C_4H_3O)_2\}\{P(C_4H_3O)_3\}]$ (**4**), respectively, upon extrusion of a ruthenium atom and concomitant phosphorus-carbon bond cleavage of the coordinated tri(2-furyl)phosphine ligand with the dissociated furyl moiety binding to the diruthenium unit in a σ, π -alkenyl fashion. We have established that the previous formation of **3** from the direct reaction of $[Ru_3(CO)_{12}]$ proceeds *via* the intermediate formation of **2**. Two-electron donor ligands such as EPh_3 ($E = P, As, Sb$), $P(OMe)_3$, Bu^1NC and $P(C_4H_3O)_3$ react smoothly with **3** at room temperature to give substitution products **8–12** and **4**, respectively. In **8**, the substitution takes place at the σ -bonded ruthenium atom, whereas in **4** it is bound to the π -bonded ruthenium atom. We believe that all monosubstituted derivatives are highly fluxional at room temperature; thus, the structures determined by X-ray crystallography are likely to be determined by solid-state interactions (e.g. packing effects) and are not necessarily representative of the (preferred) solution structure(s).

5. Supplementary material

CCDC 655913, 655914, 655915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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