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Synthesis of $[Ru_3(CO)_9(\mu\text{-dppf})\{P(C_4H_3E)_3\}]$ (E = O, S) and thermally induced cyclometalation to form $[(\mu\text{-H})Ru_3(CO)_7(\mu\text{-dppf})\{\mu_3\text{-}(C_4H_3E)_2P(C_4H_2E)\}]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene)

Md. Kamal Hossain [a,b], Subas Rajbangshi [b], Ahibur Rahaman [a,b],
Md. Arshad H. Chowdhury [b], Tasneem A. Siddiquee [c], Shishir Ghosh [b,d],
Michael G. Richmond [e], Ebbe Nordlander [a], Graeme Hogarth [d,*], Shariff E. Kabir [b,*]

[a] *Inorganic Chemistry Research Group, Chemical Physics, Center for Chemistry and Chemical Engineering, Lund University, Box 124, SE-221 00 Lund, Sweden*
[b] *Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh*
[c] *Department of Chemistry, Tennessee State University, 3500 John A. Merritt Blvd., Nashville, TN 37209, USA*
[d] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, UK*
[e] *Department of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, TX 76203, USA*

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ABSTRACT

The new clusters $[Ru_3(CO)_9(\mu\text{-dppf})\{P(C_4H_3E)_3\}]$ (**1**, E = O; **2**, E = S) have been prepared from the Me_3NO-induced decarbonylation of $[Ru_3(CO)_{10}(\mu\text{-dppf})]$ in the presence of PFu_3 (E = O) and PTh_3 (E = S), respectively. Upon thermolysis in benzene, the major products are the cyclometalated clusters $[(\mu\text{-H})Ru_3(CO)_7(\mu\text{-dppf})\{\mu_3\text{-}(C_4H_3E)_2P(C_4H_2E)\}]$ (**3**, E = O; **4**, E = S). This thermolytic behavior is in marked contrast to that previously noted for the analogous bis(diphenylphosphino)methane (dppm) complexes $[Ru_3(CO)_9(\mu\text{-dppm})\{P(C_4H_3E)_3\}]$, in which both carbon–hydrogen and carbon–phosphorus bond activation yields furyne- and thiophyne-capped clusters. The crystal structures of **1**, **3** and **4** are presented and reveal that phosphine migration has occurred during the transformation of **1**,**2** into **3**,**4**, respectively. The possible relation of the observed reactivity to the relative flexibilities of the diphosphine ligands is discussed. Density functional calculations have been performed on the model cluster $[Ru_3(CO)_9(\mu\text{-}Me_4\text{-dppf})\{P(C_4H_3O)_3\}]$, and these data are discussed relative to the ground-state energy differences extant between the different isomeric forms of this cluster. The dynamic NMR behavior displayed by the metalated thienyl ring in cluster **4** has also been investigated by computational methods, and the free energy of activation for the “windshield wiper” motion of the activated thienyl moiety determined.

1. Introduction

In recent work we have studied the coordination chemistry of trifurylphosphine (PFu_3) and trithienylphosphine (PTh_3) [1] since they are potential alternatives to triphenylphosphine in a range of stoichiometric and catalytic transformations [2], and may also function as a source of novel alkynyl derivatives based on furyne (C_4H_2O) and thiophyne (C_4H_2S) platforms, which are generated as a result of both carbon–phosphorus and carbon–hydrogen bond activation [3,4]. Thus, we have found that the triruthenium bis(diphenylphosphino)methane (dppm) complexes $[Ru_3(CO)_9(\mu\text{-dppm})\{P(C_4H_3E)_3\}]$ convert cleanly upon mild heating to afford the furyne and thiophyne clusters $[(\mu\text{-H})Ru_3(CO)_7(\mu\text{-dppm})(\mu_3\text{-}C_4H_2E)\{\mu\text{-}P(C_4H_3E)_2\}]$ (Scheme 1) in good yields [3], thus allowing their chemistry to be explored [5]. In seeking to further access these novel metal-bound alkynes, we have attempted to exchange the relatively rigid diphosphine, dppm, for the more flexible 1,1′-bis(diphenylphosphino)ferrocene (dppf) ligand. We herein report that while the new clusters $[Ru_3(CO)_9(\mu\text{-dppf})\{P(C_4H_3E)_3\}]$ (**1**, E = O; **2**, E = S) are readily prepared, their thermal behavior is very different to that observed for the dppm-derivatives, with ring cyclometalation being the major reaction pathway even under forcing conditions.

2. Experimental

2.1. General remarks

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents

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* Corresponding authors.
E-mail address: g.hogarth@ucl.ac.uk (G. Hogarth).

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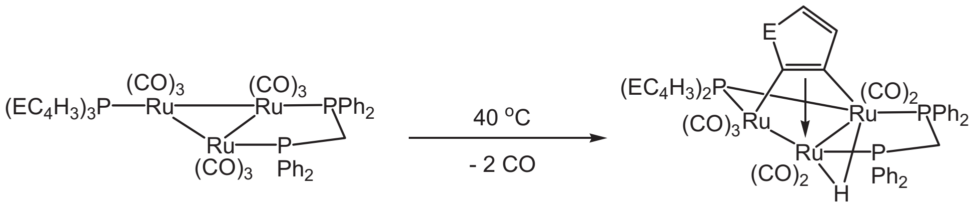

Scheme 1.

were dried and distilled prior to use by standard methods. All phosphines were purchased from Acros Chemicals Inc. and used without further purification. The cluster $[Ru_3(CO)_{10}(\mu\text{-dppf})]$ was prepared according to a published procedure [6]. IR spectra were obtained on a Shimadzu FTIR-8101 spectrophotometer and ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker VNMRS 400 MHz spectrometer. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for protons and to external H_3PO_4 for ^{31}P chemical shifts. Elemental analyses were performed by the Microanalytical laboratory of Wazed Miah Science Research Centre at Jahangirnagar University.

2.2. Synthesis of $[Ru_3(CO)_9(\mu\text{-dppf})(PFu_3)]$ (**1**)

A dichloromethane solution (15 mL) of Me_3NO (14 mg, 0.19 mmol) was added dropwise to a mixture of $[Ru_3(CO)_{10}(\mu\text{-dppf})]$ (0.20 g, 0.18 mmol) and PFu_3 (41 mg, 0.18 mmol) in dichloromethane (25 mL) and after stirring at room temperature for 3 h the color became deep red. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed a single band which afforded $[Ru_3(CO)_9(\mu\text{-dppf})(PFu_3)]$ (**1**) (0.17 g, 70%), as red crystals after recrystallization from hexane/CH_2Cl_2 at -4 °C. Anal. Calcd. for $C_{55}H_{37}FeO_{12}P_3Ru_3$: C, 49.22; H, 2.76. Found: C, 49.61; H, 2.98%. IR (ν_{CO}, CH_2Cl_2): 2053 w, 1993 s br, 1982 s br cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.63 (s, 3H), 7.54–7.36 (br m, 20H), 6.66 (brs, 3H), 6.44 (br, 3H), 4.51 (vbr, 4H), 4.27 (d, *J* 7.0, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 22.9 (s, 1P), 22.8 (d, *J* 20.2, >1P), −14.7(d, *J* 20.2, 1P). FAB-MS: *m/z* 1341 (M^+), 1313 ($M^+ - CO$), 787 ($M^+ -$ dppf).

2.3. Synthesis of $[Ru_3(CO)_9(\mu\text{-dppf})(PTh_3)]$ (**2**)

To a dichloromethane solution (40 mL) of $[Ru_3(CO)_{10}(\mu\text{-dppf})]$ (0.20 g, 0.18 mmol) and PTh_3 (49 mg, 0.176 mmol) was added dropwise a dichloromethane solution (15 mL) of Me_3NO (16 mg, 0.20 mmol), and the reaction mixture was stirred at room temperature for 2 h during which time the color changed from orange to red. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) afforded $[Ru_3(CO)_9(\mu\text{-dppf})(PTh_3)]$ (**2**) (0.17 g, 68%) as red crystals after recrystallization from CH_2Cl_2/hexane at -4 °C. Anal. Calcd. for $C_{55}H_{37}FeO_9P_3Ru_3S_3$: C, 47.40; H, 2.66. Found: C, 49.11; H, 2.83%. IR (ν_{CO}, CH_2Cl_2): 2051 w, 1990 vs, 1977 br cm^{-1}; ^1H NMR ($CDCl_3$) 298 K: δ 7.56 (t, *J* 8.0, 3H), 7.55 (m, 3H), 7.52 and 7.40 (brs, 20H), 7.15 (dt, *J* 8.0, 1.5, 3H), 4.54 (vbr, 4H), 4.36 (s, 4H); 243 K: δ 7.80–7.32 (br, 26H), 7.19 (m, 3H), 5.21 (brs, 1H), 5.14 (brs, 1H), 4.47 (brs, 4H), 3.98 (br,s 1H), 3.88 (brs, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 298 K: δ 25.5 (brs, 1P), 22.8 (brs, 1P), 1.5 (m, 1P). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 243 K: δ 27.1 (s, 1P), 23.8 (d, *J* 14.6, 1P), 1.0 (d, *J* 14.6, 1P).

2.4. Thermolysis of $[Ru_3(CO)_9(\mu\text{-dppf})(PFu_3)]$ (**1**)

A benzene solution (30 mL) of **1** (50 mg, 0.037 mmol) was heated to reflux for 3 h during which time the red color deepened. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (7:3, v/v) developed five bands. The fourth was by far the major band and gave $[(\mu\text{-H})Ru_3(CO)_7(\mu\text{-dppf})\{\mu_3\text{-}Fu_2P(C_4H_2O)\}]$ (**3**) (12 mg, 25%), as pale yellow crystals after recrystallization from CH_2Cl_2/hexane at -4 °C. Anal. Calcd. for $C_{53}H_{37}O_{10}P_3Ru_3Fe$: C, 49.51; H, 2.90. Found: C, 49.70; H, 3.33. IR (νCO, CH_2Cl_2) 2042 vs, 2001 s, 1967 w, 1956 w, 1942 vw cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.75 (m, 3H), 7.63 (d, *J* 1.9, 1H), 7.54–7.22 (m, 16H), 7.14 (t, *J* 6.1, 2H), 6.77 (s, 1H), 6.65 (s, 1H), 6.52 (br, 1H), 6.45 (br, 1H), 5.98 (d, *J* 2.5, 1H), 5.58 (d, *J* 3.1, 1H), 4.88 (s, 1H), 4.37 (s, 1H), 4.34 (s, 1H), 4.05 (s, 1H), 3.95 (s, 1H), 3.65 (s, 1H), 3.50 (s, 1H), 3.08 (s, 1H), − 16.88 (dt, *J* 16.8, 12.0, 1H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.7 (s, 1P), 23.6 (s, 1P), −11.44 (t, *J* 21.4, 1P).

2.5. Thermolysis of $[Ru_3(CO)_9(\mu\text{-dppf})(PTh_3)]$ (**2**)

A benzene solution (30 mL) of **2** (50 mg, 0.036 mmol) was heated to reflux for 3 h during which time the red color deepened. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (7:3, v/v) developed five bands. The fourth band was the major product and gave $[(\mu\text{-H})Ru_3(CO)_7(\mu\text{-dppf})\{\mu_3\text{-}Th_2P(C_4H_2S)\}]$ (**4**) (8 mg, 17%), as pale yellow crystals after recrystallization from CH_2Cl_2/hexane at -4 °C. Anal. Calcd. for $C_{53}H_{37}O_7S_3Ru_3Fe$: C, 47.72; H, 2.80. Found: C, 47.70; H, 3.13%. IR (νCO, CH_2Cl_2) 2040 vs, 1999 s, 1966 sh, 1956 w cm^{-1}; ^1H NMR ($CDCl_3$) 298 K: δ 8.06 (dd, *J* 8.0, 4.0, 1H), 7.76 (m, 2H), 7.66–7.21 (m, 22H), 7.13 (d, *J* 4.0, 1H), 6.60 (t, *J* 4.0, 1H), 5.70 (t, *J* 4.0, 1H), 4.92 (s, 1H), 4.55 (s, 1H), 4.48 (s, 1H), 4.24 (s, 1H), 4.04 (s, 1H), 3.99 (s, 1H), 3.33 (s, 1H), 3.19 (s, 1H), −16.35 (dt, *J* 18.0, 11.6, 1H); 243 K: δ 8.10 (dd, *J* 8.0, 4.0, 1H), 7.80 (d, *J* 4.0, 1H), 7.72 (dd, *J* 8.0, 4.0, 3H), 7.65–7.25 (m, 18H), 7.19 (t, *J* 8.0, 2H), 7.10 (d, *J* 4.0, 1H), 6.62 (t, *J* 4.0, 1H), 5.58 (m, 1H), 4.81 (s, 1H), 4.56 (s, 1H), 4.48 (s, 1H), 4.24 (s, 1H), 4.06 (s, 1H), 3.97 (s, 1H), 3.31 (s, 1H), 3.01 (s, 1H), −16.44 (dt, *J* 18.0, 11.6, 1H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 298 K: δ 31.3 (d, *J* 29.2, 1P), 22.1 (d, *J* 19.4, 1P), 11.55 (dd, *J* 29.2, 19.4, 1P); 243 K $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.0 (d, *J* 27.5, 1P), 22.4 (d, *J* 21.1, 1P), 11.41 (dd, *J* 27.5, 21.1, 1P).

2.6. X-ray structure determinations

Single crystals of **1** were mounted on fibers and diffraction data collected on a Bruker SMART APEX diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Single crystals of **3** and **4** were coated with Paraton N oil, suspended in a small fiber loop, and diffraction data collected on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were measured using a series of combination of φ and ω scans with 5 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART software [7]. Frame integration and final cell refinements were done using SAINT software [8]. SADABS [9] was used to carry out absorption corrections. The structures were solved using the Patterson method and difference Fourier