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Thermally induced dual P–C bond cleavage routes from the imido-capped cluster Ru₃(CO)₇(μ_3 -CO)(μ_3 -NPh)(bpcd): synthesis, spectroscopic properties, and X-ray diffraction structures of Ru₃(CO)₇(μ_3 -CO)(μ_3 -NPh)(bpcd), Ru₃(CO)₅(μ_2 -CO)₂(μ_3 -NPh) (μ_2 -PPh₂)[μ , η^1 , η^1 -C=C(PPh₂)C(O)CH₂C(O)], Ru₃(CO)₆(μ_2 -CO) (μ_3 -NPh)(μ -PhCO)[μ_2 , η^2 , η^1 -PPhC=C(PPh₂)C(O)CH₂C(O)], and Ru₃(CO)₉(μ_3 -NPh)(μ_3 -PPh)

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Abstract

The imido-capped cluster $Ru_3(CO)_9(\mu_3-CO)(\mu_3-NPh)$ (1) reacts with the diphosphine ligand 4,5-bis(diphenylphosphine)-4-cyclopenten-1,3-dione (bpcd) to furnish both $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ (2) and $Ru_3(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ (3) as the major and minor products, respectively, under thermal and Me₃NO activation. The thermolysis of cluster 2 affords the new triruthenium compounds $Ru_3(CO)_5(\mu_2-CO)_2(\mu_3-NPh)(\mu_2-PPh_2)[\mu,\eta^1,\eta^1-C=C(PPh_2)C(O)CH_2C(O)]$ (4), $Ru_3(CO)_6(\mu_2-CO)(\mu_3-NPh)(\mu_2-PPh_2)[\mu,\eta^1,\eta^1-C=C(PPh_2)C(O)CH_2C(O)]$ (4), $Ru_3(CO)_6(\mu_2-CO)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-NPh)(\mu_3-$ NPh)(μ -PhCO)[μ_2, η^2, η^1 -PPhC=C(PPh₂)C(O)CH₂C(O)] (5), and Ru₃(CO)₉(μ_3 -NPh)(μ_3 -PPh) (6). Compounds 2–6 have been fully characterized in solution, and the molecular structures of 2, and 4-6 have been determined. Cluster 2 exhibits a *nido*-NRu₃ core with a face-capping µ₃-CO and a chelating bpcd ligand that occupies an equatorial and axial site. VT ³¹P NMR data indicate that the bpcd ligand in 2 undergoes a rocking motion between the equatorial and axial sites at the attached ruthenium center at elevated temperatures. Cluster 4 possesses a similar nido polyhedral core that is tethered by a bridging phosphido group and the 3e-donor moiety μ_2, η^2, η^1 -C=C(PPh_2)C(O)CH_2C(O). The structure of **5** reveals a *hypho* architecture containing a single Ru–Ru bond and where the three ruthenium centers are bridged by imido and benzoyl moieties and the seven-electron donor ligand μ_2, η^2, η^1 -PPhC=C(PPh₂)C(O)CH₂C(O), which results from the cleavage of one the P-Ph bonds of the original bpcd ligand. The 50e cluster **6** exhibits a *nido* polyhedral core consisting of three Ru(CO)₃ groups that are capped by a μ_3 -imido and μ_3 -phosphinidine unit. Cluster 6 represents the first structurally characterized example of a mixed PhN/PhP capped cluster belonging to the family of $nido-Ru_3(CO)_9(\mu_3-EPh)_2$ clusters. The pertinent structural highlights associated with these clusters are discussed, and the lack of reactivity of the capping imido group with the bpcd ligand in $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ during thermolysis is contrasted with the related benzylidyne-capped cluster $PhCCo_3(CO)_7(bpcd)$. © 2004 Elsevier B.V. All rights reserved.

Keywords: Metal clusters; P-C bond activation; Electrochemistry; Imido-capped clusters; Diphosphine ligand; Redox chemistry

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1. Introduction

The chemistry of imido-capped clusters has been extensively explored over the last several years due to their manifold importance in organometallic transformations and substrate functionalization reactions [1]. For example, unequivocal evidence from myriad studies involving the reductive carbonylation of aryl nitro compounds in the presence of $M_3(CO)_{12}$ (where M = Fe, Ru) reveals that the formation of imido-capped clusters $M_3(CO)_{10}(\mu_3-NR)$ are a prerequisite for productive catalysis [2]. The imido groups in such systems serve as a crucial platform for the ultimate release of carbamates, isocyanates, amides, and oximes, in addition to complex heterocycles depending upon the reaction conditions [3]. Several excellent mechanistic studies have greatly contributed to our overall understanding involving the initial reduction of the nitro group to an imido moiety at a polynuclear cluster [c,4]. These studies have also substantiated the acceleratory effect that halide and alkoxide additives have had on the reduction of the nitro group in organic compounds, along with the importance of single-electron transfer in the activation of the nitro moiety by the anionic cluster $[Fe_3(CO)_{11}]^{2-}$.

The chemistry of the μ_3 -imido ligand in Ru₃ (CO)₁₀(μ_3 -NPh) has also been studied with respect to alkyne insertion and coupling reactivity, with binuclear metallapyrrolidone compounds having been isolated and structurally characterized [5]. The same cluster also functions as a building block for the construction of higher-nuclearity mixed-metal clusters via face capping and polyhedral expansion sequences [6].

Our interest in $Ru_3(CO)_{10}(\mu_3-NPh)$ has focused on the molecular dynamics associated with ligand fluxionality and bonding considerations between the Ru₃ frame and the ancillary ligands [7], in addition to the ligand substitution behavior exhibited by $Ru_3(CO)_{10}(\mu_3-NPh)$ in the presence of PPh₃ under thermal, reagent assisted, and ETC activation [8]. Prior to our latter report, the only other published work with a phosphine-substituted derivative of $Ru_3(CO)_{10}(\mu_3-NPh)$ involved Ru_3 $(CO)_8(\mu_3-NPh)(dppm)$. Here the synthesis and fragmentation of $Ru_3(CO)_8(dppm)(\mu_3-NPh)$ in the presence of alkynes were investigated [9]. Given this dearth of ligand substitution chemistry in $Ru_3(CO)_{10}(\mu_3-NPh)$, coupled with our desire to further our studies with other ligand-capped tetrahedral clusters with the redox-active diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) [10,11], we have investigated the reaction between $Ru_3(CO)_{10}(\mu_3-NPh)$ and bpcd. The propensity of this ligand to undergo facile P–C bond cleavage in the alkylidyne-capped clusters $RCCo_3(CO)_7(bpcd)$ has been unequivocally demonstrated by us, as depicted in Eq. (1). However, given that the majority of our research has relied on clusters that possessed a capping alkylidyne ligand, we wished to

extend our studies to a structurally similar bpcd-substituted cluster containing a different organic capping ligand. Here the coordination of bpcd to $Ru_3(CO)_{10}(\mu_3$ -NPh) was expected to afford the new cluster Ru_3 (CO)₈(μ_3 -NPh)(bpcd), from which we could explore the reactivity of (1) the diphosphine ligand at a non-cobalt containing cluster and (2) the propensity of the imido ligand to participate in a reductive coupling reaction with the transient Ru–C(dione) moiety, should P–C bond cleavage be observed in a manner analogous to that of the tricobalt cluster $RCCo_3(CO)_7(bpcd)$.



Herein we report our results on the reaction between $Ru_3(CO)_{10}(\mu_3$ -NPh) and bpcd to furnish the new cluster compounds **2–6**. The solution spectroscopic data and structural features of these products are discussed.

2. Experimental

2.1. General methods

Nitrosobenzene and Me₃NO · 2H₂O were purchased from Aldrich Chemical Co., with the former chemical used as received while the latter was dried by azeotropic distillation from benzene. The bpcd ligand used in these studies was synthesized from 4,5-dichloro-4-cyclopenten-1,3-dione and Ph₂PTMS according to the known procedure [12], while the $Ru_3(CO)_{12}$ used in the preparation of Ru₃(CO)₉(µ₃-CO)(µ₃-NPh) [13] was prepared from hydrated RuCl₃ using the carbonylation procedure of Bruce [14]. All reaction, NMR, and electrochemistry solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels [15]. The tetra-*n*-butylammonium perchlorate electrolyte (TBAP) was purchased from Johnson Matthey Electronics and recrystallized from ethyl acetate/hexane (1:1), followed by drying for at least 48 h under high vacuum. All C and H analyses were performed by Altantic Microlab, Norcross, GA.

The reported infrared data were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells, using PC control and OMNIC software. The ¹H NMR spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer, and the ³¹P NMR spectra were recorded at 121 MHz on a Varian 300-VXR spectrometer. The reported ³¹P chemical shifts are referenced to external H₃PO₄ (85%), taken to have $\delta = 0.0$. Here positive chemical shifts are to low field of the external standard. The cyclic voltammetry studies were carried out on a PAR Model 273 potentiostat/glavanostat under argon in airtight cells, as previously described [16].

2.2. Synthesis of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ (2) and $Ru_3(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ (3)

2.2.1. Me₃NO activation

To 0.30 g (0.45 mmol) of Ru₃(CO)₉(µ₃-CO)(µ₃-NPh) and 0.21 g (0.45 mmol) of bpcd in 50 mL of CH_2Cl_2 in a Schlenk tube was added 67 mg (0.90 mmol) of Me₃NO. The solution was stirred for 2.0 h at room temperature and examined by TLC analysis, which revealed the presence of a small amount of unreacted 1, along with two slower moving spots that corresponded to clusters 2 and 3. $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ was subsequently isolated by column chromatography over silica gel using CH₂Cl₂/petroleum ether (1:1), with Ru₃ $(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ being eluted from the column upon changing the solvent system to CH₂Cl₂. Both products were recrystallized from CH2Cl2/hexane (1:1) to afford the analytical sample of each product and single crystals of Ru₃(CO)₇(µ₃-CO)(µ₃-NPh)(bpcd) suitable for X-ray diffraction analysis. Yield of brown 2: 0.35 g (72%). IR (CH₂Cl₂): v(CO) 2074 (s), 2048 (vs), 2003 (vs), 1944 (m), 1749 (w, symm dione carbonyl), 1718 (m, antisymm dione carbonyl), 1674 (m, br, μ_3 -CO) cm⁻¹. ³¹P NMR (CDCl₃, 222 K): δ 57.84 (s), 44.92 (s). ¹H NMR (CDCl₃): δ 6.67–7.60 (m, 25 H, aryl), 3.28 (s, 2H, CH₂). Anal. Calc. (found) for C₄₃H₂₇NO₁₀₋ P₂Ru₃: C, 47.70 (47.51); H, 2.51 (2.64). Yield of green 3: 42 mg (6%). IR (CH₂Cl₂): v(CO) 2034 (w), 2015 (vs), 1959 (vs), 1746 (m, symm dione carbonyl), 1715 (m, antisymm dione carbonyl), 1639 (m, br, μ_3 -CO) cm⁻¹. ³¹P NMR (CDCl₃, 212 K): δ 50.49 (d, $J_{P-P} = 14$ Hz), 49.18 (dd, $J_{P-P} = 52$, 14 Hz), 16.62 (d, $J_{P-P} = 52$ Hz), 0.89 (t, $J_{P-P} = 52$ Hz). ¹H NMR (CDCl₃): δ 6.53–8.15 (m, 45 H, aryl), 3.22 (AB quartet, 2H, CH₂), 3.16 (AB quartet, 2H, CH₂). Anal. Calc. (found) for $C_{70}H_{49}O_{10}NP_4Ru_3$ · hexane: C, 57.82 (58.47); H, 3.99 (4.31)%.

2.2.2. Thermal activation

Heating 0.30 g (0.45 mmol) of $Ru_3(CO)_9(\mu_3-CO)(\mu_3-NPh)$ and 0.21 g (0.45 mmol) of bpcd together in 50 mL of 1,2-dichloroethane at ca. 75–80 °C in a Schlenk tube over a 0.5–1.0 h period initially produces clusters **2** and **3** as the major and minor products, respectively. However, all thermolysis reactions were accompanied by the formation of clusters **4–6** (vide infra), even at early reaction times, with clusters **4–6** becoming the predominant products as heating was continued. Given the significant band overlap of all five product clusters on silica gel, this thermolysis reaction was

not extensively investigated as a preparative route to cluster 2.

2.3. Thermolysis of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$

To 0.35 g (0.32 mmol) of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-CO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-\mu_3-LO)(\mu_3-\mu_3-\mu_3-\mu_3-\mu_3-\mu_3-$ NPh)(bpcd) in a large Schlenk tube was added 50 mL of 1,2-dichloroethane. The vessel was sealed and then heated for 5.0 h at ca. 70 °C. At this point TLC analysis of the reaction solution using CH₂Cl₂ revealed the complete consumption of the starting cluster and the presence of three new products, in addition to a tiny amount of material that remained at the origin. Column chromatography over neutral alumina using petroleum ether as the eluent gave a yellow band that corresponded to $Ru_3(CO)_9(\mu_3-NPh)(\mu_3-PPh)$ (6). Changing the eluent to CH₂Cl₂/petroleum ether (1:1) next afforded the brown-colored cluster $Ru_{3}(CO)_{5}(\mu_{2}-CO)_{2}(\mu_{3}-NPh)$ $(\mu_2 - PPh_2)[\mu, \eta^1, \eta^1 - C = C(PPh_2)C(O)CH_2C(O)],$ while pure CH₂Cl₂ finally furnished a red band belonging to $\operatorname{Ru}_3(\operatorname{CO})_6(\mu_2-\operatorname{CO})(\mu_3-\operatorname{NPh})(\mu-\operatorname{PhCO})[\mu_2,\eta^2,\eta^1-\operatorname{PPhC}=$ $C(PPh_2)C(O)CH_2C(O)$]. Recrystallization of Ru₃ $(CO)_9(\mu_3-NPh)(\mu_3-PPh)$ from hexane at -5 °C gave single crystals suitable for X-ray crystallography and analytical pure $Ru_3(CO)_9(\mu_3-NPh)(\mu_3-PPh)$. The analytical sample and crystals for X-ray diffraction analysis of clusters 4 and 5 were obtained from CH₂ Cl₂/methanol (1:1) at -10 °C. Yield of 4: 95 mg (28%). IR (CH₂Cl₂): v(CO) 2063 (s), 2043 (s), 2005 (vs), 1939 (w), 1865 (w), 1725 (w, symm dione carbonyl), 1694 (m, antisymm dione carbonyl) cm⁻¹. ³¹P NMR (CDCl₃, 298 K): δ 165.92 (d, J_{P-} $_{\rm P}$ = 87 Hz), 0.80 (d, $J_{\rm P-P}$ = 87 Hz). ¹H NMR (CDCl₃): δ 6.46–7.50 (m, 25 H, aryl), 2.78 (b, 2H, CH₂). Anal. Calc. (found) for C₄₂H₂₇NO₉P₂Ru₃: C, 47.82 (48.39); H, 2.58 (2.86). Yield of 5: 0.17 g (48%). IR (CH₂Cl₂): v(CO) 2063 (sh), 2051 (vs), 2036 (s), 1996 (s), 1914 (w), 1715 (w, symm dione carbonyl), 1668 (m, antisymm dione carbonyl) cm⁻¹. ³¹P NMR (CDCl₃, 298 K): δ 66.82 (d, $J_{P-P} = 17$ Hz), -4.19 (d, $J_{P-P} = 17$ Hz). ¹H NMR (CDCl₃): δ 6.47-8.27 (m, 25 H, aryl), 3.14 (AB quartet, 2H, CH₂). Anal. Calc. (found) for C₄₃H₂₇NO₁₀₋ P₂Ru₃: C, 47.40 (48.34); H, 2.51 (3.04). Yield of **6**: 38 mg (16%). IR (hexane): v(CO) 2091 (w), 2070 (vs), 2045 (vs), 2022 (vs), 1999 (vs) cm⁻¹. ³¹P NMR (CDCl₃): δ 269.66. ¹H NMR (CDCl₃): δ 6.70–7.60 (m, 10 H, aryl). Anal. Calc. (found) for C₂₁H₁₀NO₉PRu₃: C, 33.43 (34.65); H, 1.34 (1.82)%.

2.4. X-ray crystallography

Table 1 contains the X-ray data and processing parameters for the compounds 2 and 4–6. Selected crystals of 2 and 4–6 suitable for X-ray diffraction analysis were grown as described above and were each sealed inside a Lindemann capillary, followed by mounting on an Enraf-Nonius CAD-4 diffractometer. After the cell

Table 1 X-ray crystallographic data and processing parameters for the triruthenium compounds **2** and **4–6**

Compound	2	4	5	6
CCDC entry no	23990	239901	239902	239720
Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, P1
a (Å)	19.909(2)	11.9071(8)	9.6690(7)	10.0505(5)
b (Å)	11.847(1)	16.5367(9)	36.247(4)	10.1915(8)
c (Å)	20.547(3)	20.920(1)	11.560(1)	12.4045(9)
α (°)				86.156(6)
β (°)	113.47(1)	100.496(5)	92.808(7)	87.520(5)
γ (°)				81.429(5)
$V(Å^3)$	4445.3(9)	4050.3(4)	4046.6(6)	1252.9(2)
Mol. formula	$C_{43}H_{27}NO_{10}P_2Ru_3$	$C_{42}H_{27}NO_9P_2Ru_3$	$C_{43}H_{27}NO_{10}P_2 Ru_3$	$C_{21}H_{10}NO_9PRu_3$
fw	1082.85	1054.84	1082.85	754.50
Formula units per cell (Z)	4	4	4	2
D_{calc} (g/cm ³)	1.618	1.730	1.777	2.000
λ (Mo Ka) (Å)	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (cm^{-1})	11.11	12.16	12.21	19.0
R _{merge}	0.037	0.023	0.031	
Abs. corr. factor	0.76-1.25	0.91-1.12	0.88-1.09	0.86-1.25
Total reflections	5661	5457	2858	3056
Independent reflections	3680	2869	1377	2780
Data/res/parameters	3680/0/412	2869/0/304	1377/0/252	2780/0/316
R	0.0458	0.0370	0.0423	0.0249
R_w	0.0534	0.0403	0.0479	0.0285
GOF	1.16	0.67	0.53	1.41
Weights	$[0.04F^2 + (\sigma F)^2]^{-1}$			

constants were obtained for all four samples, intensity data in the range of $2^{\circ} \leq 2\theta \leq 44^{\circ}$ (clusters 2, 4, and 6) and $2^{\circ} \leq 2\theta \leq ^{\circ}$ (cluster 5) were collected at 298 K and were corrected for Lorentz, polarization, and absorption (DIFABS). Cluster 2 was solved by using Multan, while clusters 4 and 5 were solved by using standard Patterson techniques, which revealed the positions of the ruthenium and phosphorus atoms. The structure of cluster 6 was established by using SIR. In the case of 2, all non-hydrogen atoms were located with difference Fourier maps and full-matrix least-squares refinement and were refined anisotropically with the exception of the phenyl carbon atoms. Except for the carbon atoms in 4, all non-hydrogen atoms in 4 were refined anisotropically, and refinement of cluster 5 followed similar data reduction procedures, with only the ruthenium atoms receiving anisotropic treatment. All non-hydrogen atoms in 6 were refined with anisotropically. Refinement on 2 converged at R = 0.0458 and $R_w = 0.0534$ for 3680 unique reflections with $I > 3\sigma(I)$, while for 4 refinement converged at R = 0.0370 and $R_w = 0.0403$ for 2869 unique reflections with $I > 3\sigma(I)$. The refinement for **5** and **6** afforded convergence values of R = 0.0423 and $R_w = 0.0479$ for 1377 unique reflections with $I > 3\sigma(I)$ and R = 0.0249 and $R_w = 0.0285$ for 2780 unique reflections with $I > 3\sigma(I)$, respectively.

2.5. Extended Hückel MO calculations

The extended Hückel calculations on the Ru_3 (CO)₇(μ_3 -CO)(μ_3 -NPh)(bpcd) and Ru_3 (CO)₅(μ_3 -CO)

 $(\mu_3-NPh)(bpcd)_2$ were carried out with the original program developed by Hoffmann and Lipscomb [17], as modified by Mealli and Proserpio [18], using the program contained weighted H_{ii} 's. The input Z-matrix for the model cluster $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NHh)(H_4-bpcd)$ possessing a chelating diphosphine ligand was constructed from the X-ray fractional coordinates of Ru₃ $(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$. All phenyl groups were replaced by a hydrogen, with the N-H and P-H bond distances assigned lengths of 1.01 and 1.41 Å, respectively [19]. The bridged isomer of Ru₃(CO)₇- $(\mu_3$ -CO) $(\mu_3$ -NH) $(H_4$ -bpcd), which was confined to C_s symmetry, and the bis-ligand substituted cluster Ru₃ $(CO)_5(\mu_3-CO)(\mu_3-NH)(H_4-bpcd)_2$ were both constructed with bond distances and angles appropriate for this genre of cluster.

3. Results and discussion

3.1. Synthesis of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ and $Ru_3(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ and X-ray diffraction structure of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$

Treatment of an equimolar mixture of $Ru_3(CO)_9(\mu_3-CO)(\mu_3-NPh)$ (1) and bpcd in CH₂Cl₂ with two equiv. of Me₃NO at room temperature led to a rapid reaction and the formation of two products, as assessed by TLC analysis. Both of these products were subsequently isolated by chromatography and characterized in solution as $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ (2, major) and

 $Ru_3(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ (3, minor). The room temperature ³¹P NMR spectrum of 2 revealed a single, broad resonance at δ 50.00 indicative of a fluxional bpcd ligand. As the coordination mode of the ancillary phosphine ligand in 2 could not be assigned with certainty under these conditions, we examined the ³¹P NMR spectrum of 2 at 222 K. Dropping the temperature gave a pair of equal intensity ³¹P resonances at δ 44.92 and 57.84, which immediately rules out a bridging bpcd ligand and supports a chelating bpcd ligand that is bound to a ruthenium center via an axial and equatorial site. The fluxional behavior exhibited by the bpcd ligand presumably involves the rocking of the two ³¹P centers between the axial and equatorial positions as shown below in Eq. (2) [20]. The chelation of the bpcd ligand and the overall molecular structure of 2 was established by X-ray crystallography. Fig. 1 shows the ORTEP diagram of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$, with selected bond distances and angles reported in Table 2. The overall structure of 2 is unchanged form the parent cluster 1, insomuch that it contains 48 valence electrons and a *nido*-Ru₃N core [21]. The coordination of the bpcd ligand to the axial and one of the two equatorial sites at Ru(1) is in excellent agreement with the limiting ³¹P NMR data for cluster 2 and stands in contrast to the cluster $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(dppm)$ that contains a bridging dppm ligand. To our knowledge, the latter dppm-substituted cluster and 2 represent the only structurally characterized $Ru_3(CO)_7(\mu_3-CO)$ (μ_3-NPh)(P–P) clusters to date. The mean Ru-Ru and Ru-N bond distances of 2.753 and 2.047 Å, respectively, are unremarkable in comparison to the parent cluster and



Fig. 1. ORTEP drawing of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ (2) showing the thermal ellipsoids at the 50% probability level.

 $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)P_2$ (where $P_2 = dppm$, PPh₃) [8,9a,22], confirming the absence of any significant perturbation on the cluster core by the bpcd ligand.



The minor product from the reaction was assigned to that of the bis-phosphine cluster $Ru_3(CO)_5(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)$ NPh)(bpcd)₂, on the basis of solution IR and NMR data. Our attempts to grow single crystals of 3 suitable for X-ray analysis were not successful. The μ_3 -CO group at 1639 cm^{-1} in 3 has shifted 35 cm^{-1} to lower energy relative to 2 consistent with the introduction of a second bpcd ligand, while the ¹H NMR appearance of two methylene groups as AB quartets at δ 3.16 and 3.22 clearly support the presence of two inequivalent dione moieties in 3. The room temperature ³¹P NMR spectrum of **3** revealed three broad resonances at δ 50, 16, and 0 in ca. a 2:1:1 integral ratio. When the same spectrum was recorded at 212 K four sharp resonances each integrating for one phosphorus were observed at 50.49 (d), 49.18 (dd), 16.62 (d), and 0.89 (t). On the basis of nuclear shielding arguments and the paradigm of cluster 2, the two downfield resonances may be confidently assigned to the chelating bpcd ligand, with the remaining two higher field resonances belonging to the bridging bpcd group [23]. The structure of Ru₃(CO)₅(µ₃-CO)(μ_3 -NPh)(bpcd)₂ that is consistent with the ³¹P assignments is depicted below.



3.2. Thermolysis reactivity of $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NPh)(bpcd)$ and X-ray diffraction structures of clusters **4–6**

The thermolysis of $Ru_3(CO)_9(\mu_3-CO)(\mu_3-NPh)$ with bpcd in 1,2-dichloroethane at ca. 75 °C was also investigated and found to furnish cluster **2** as the major product, along with four additional products as judged by TLC analysis, one of which corresponded to cluster **3**. Prolonged reaction times led to the gradual diminution

Table 2

Table 2		
Selected bond distances (Å)	and angles (deg) in the triruthenium	compounds 2, and 4-6 ^a

$Ru_{3}(CO)_{7}(\mu_{3}-CO)(\mu_{3}-NPh)(bpcd)$ (2)			
Bond distances			
Ru(1)–Ru(2)	2.753(1)	Ru(1)-Ru(3)	2.779(1)
Ru(2)–Ru(3)	2.726(1)	Ru(1)–P(1)	2.333(3)
Ru(1) - P(2)	2.334(2)	Ru(1) - N(16)	2.053(9)
Ru(1) - C(2)	2.06(1)	Ru(2) - N(16)	2.040(7)
$R_{11}(2) - C(2)$	2.19(1)	$R_{\rm H}(3) - N(16)$	2.048(8)
Ru(2) = C(2) Ru(2) = C(2)	2.19(1)	C(11) $C(15)$	1.24(2)
$\operatorname{Ku}(3) - \operatorname{C}(2)$	2.24(1)	C(11)-C(13)	1.34(2)
Bond angles			
P(1)-Ru(1)-P(2)	84.6(1)	P(1)-Ru(1)-N(16)	171.0(2)
P(1)-Ru(1)-C(1)	83.5(4)	P(1)-Ru(1)-C(2)	87.2(4)
P(2)-Ru(1)-N(16)	103.6(2)	N(16)-Ru(1)-C(1)	100.1(4)
N(16)-Ru(1)-C(2)	84.0(4)	P(2)-Ru(1)-C(1)	90.2(3)
P(2)-Ru(1)-C(2)	141.0(3)	Ru(1)-N(16)-Ru(2)	84.5(3)
Ru(1)–N(16)–Ru(3)	85.3(3)	Ru(2) - N(16) - Ru(3)	83.7(3)
$Ru_3(CO)_5(\mu_2-CO)_2(\mu_3-NPh)(\mu_2-PPh_2)[\mu_3$	$\eta^{I}, \eta^{I}-C=C(PPh_{2})C(O)CH$	$I_2C(O)](4)$	
Bond distances			
Ru(1)-Ru(2)	2.694(1)	Ru(1)-Ru(3)	2.774(1)
Ru(2)-Ru(3)	2.848(1)	Ru(1)-P(1)	2.358(3)
Ru(1)–P(2)	2.335(3)	Ru(2)–P(2)	2.360(3)
Ru(1)–N(16)	2.109(8)	Ru(2)–N(16)	2.108(7)
Ru(3)–N(16)	2.026(7)	Ru(3)–C(15)	2.032(9)
C(11)-C(15)	1.35(1)	Ru(1)-C(2)	1.90(1)
Ru(3) - C(2)	2.473(9)	Ru(2)-C(4)	1.99(1)
Ru(3)–C(4)	2.458(9)		(-)
Bond angles			
$\mathbf{D}(1) \mathbf{D}_{11}(1) \mathbf{D}(2)$	125 1(1)	$D(1)$ $D_{11}(1)$ $N(16)$	97.0(2)
$\Gamma(1) - \kappa u(1) - \Gamma(2)$ $\Gamma(2) = Ru(1) - \Gamma(2)$	78 4(2)	P(1) = Ru(1) = N(10) P(2) = Pr(2) = N(10)	97.0(2) 77.8(2)
P(2) - Ru(1) - IN(10)	78.4(2)	P(2) = Ku(2) = N(10)	//.8(2)
Ru(3) - Ru(1) - P(1)	89.69(7)	Ru(2)-Ru(3)-C(15)	142.8(3)
Ru(1)-P(2)-Ru(2)	70.03(7)	Ru(1)-C(2)-O(2)	158.0(9)
Ru(2)-C(4)-O(4)	153.5(9)	Ru(3)–C(2)–O(2)	124.2(9)
Ru(3)-C(4)-O(4)	127.4(9)		
$Ru_{3}(CO)_{5}(\mu_{2}-CO)_{2}(\mu_{3}-NPh)(\mu-PhCO)[\mu_{2}]$	$p_{2},\eta^{2},\eta^{1}-PPhC=C(PPh)_{2}C(C)$	$O)CH_2C(O)$] (5)	
Bond distances			
Ru(2)-Ru(3)	2.839(3)	Ru(1) - P(1)	2.301(6)
$R_{1}(1) = P(2)$	2,355(6)	$R_{\rm H}(1) - N(16)$	2.17(1)
$R_{11}(1) = O(23)$	2 16(1)	$R_{\rm H}(1) - C(24)$	2.97(1)
$R_{11}(2) - P(2)$	2.10(1)	Ru(1) = C(21) Ru(2) - N(16)	2.06(1)
$P_{11}(2) C(6)$	2.377(0)	Ru(2) = R(10) Ru(2) = C(24)	1.08(2)
$P_{11}(2) = O(0)$	2.52(5)	$P_{11}(2) - C(24)$	1.96(2)
Ru(3) - N(10) Ru(3) C(11)	2.10(2) 2.26(2)	Ru(3) - C(0) Ru(3) - C(15)	1.93(3)
Ku(3) - C(11)	2.20(2)	$\operatorname{Ku}(5) - \operatorname{C}(15)$	2.21(2)
Bond angles			
P(1)-Ru(1)-P(2)	87.4(2)	P(1)-Ru(1)-O(23)	168.1(4)
P(2)-Ru(1)-N(16)	73.0(4)	P(2)-Ru(1)-O(23)	82.4(4)
N(16)–Ru(1)–O(23)	84.1(5)	Ru(3)–Ru(2)–C(24)	137.6(5)
P(2)-Ru(2)-C(24)	83.3(6)	N(16)–Ru(2)–C(24)	91.9(7)
N(16)-Ru(3)-C(11)	90.0(6)	N(16) - Ru(3) - C(15)	89.1(7)
C(11) = Ru(3) = C(15)	38 5(7)	$R_{11}(1) = P(2) = R_{11}(2)$	87 4(2)
$B_{11}(1) - N(16) - B_{11}(2)$	101.1(6)	$R_{\rm H}(1) - N(16) - R_{\rm H}(3)$	118 2(7)
$P_{u}(2) C(6) P_{u}(3)$	82 0(0)	$R_{11}(1) = R_{11}(10) = R_{11}(0)$	126(2)
Ru(3)-C(6)-O(6)	150(2)	Ru(2) - C(0) - O(0)	120(2)
$Ru_3(CO)_9(\mu_3-NPh)(\mu_3-PPh)$ (6)			
Bona distances	2 7501(6)	D (2) D (2)	0 200200
Ru(1)–Ru(2)	2./591(6)	Ru(2)-Ru(3)	2.7687(6)
Ru(1)–P	2.293(2)	Ru(1)–N	2.129(4)
Ru(2)–P	2.393(2)	Ru(2)–N	2.125(4)
Ru(3)–P	2.302(1)	Ru(3)–N	2.118(4)
			(continued on next page)

Table 2 (continued)

Bond angles					
P-Ru(2)-N	69.5(1)	P-Ru(3)-N	71.4(1)		
Ru(1)-P-Ru(2)	72.11(5)	Ru(1)-P-Ru(3)	100.59(6)		
Ru(2)-P-Ru(3)	72.24(5)	Ru(1)-N-Ru(2)	80.9(1)		
Ru(1)–N–Ru(3)	112.7(2)	Ru(2)–N–Ru(3)	81.5(2)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

of 2 with the concomitant increase in the three new clusters $Ru_{3}(CO)_{5}(\mu_{2}-CO)_{2}(\mu_{3}-NPh)(\mu_{2}-PPh_{2})[\mu,\eta^{1},\eta^{1} C=C(PPh_2)C(O)CH_2C(O)$] (4), $Ru_3(CO)_6(\mu_2-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_3-CO)(\mu_$ NPh)(μ -PhCO)[μ_2 , η^2 , η^1 -PPhC=C(PPh_2)C(O)CH_2C(O)] (5), and $Ru_3(CO)_9(\mu_3-NPh)(\mu_3-PPh)$ (6), whose structures are depicted below. The source of these new clusters 4-6 was presumed to be that of $Ru_3(CO)_7(\mu_3$ -CO)(μ_3 -NPh)(bpcd), and this fact was easily verified by carrying out control experiments involving cluster 2. Heating pure samples of 2 at ca. 70 °C do indeed produce the clusters 4-6. The thermal chemistry of Ru₃ $(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ was not investigated given the low yields that accompanied the formation of cluster 3. Compounds 4-6 were isolated by careful column chromatography over silica gel and were found to be relatively stable provided that excessive exposure to oxygen was avoided.

quences have precedence and have been demonstrated by us in a variety of dinuclear and polynuclear systems [10,11,24]. The ³¹P NMR spectrum of 4 confirmed the latter bpcd ligand activation possibility since a bridging phosphido moiety was found at δ 165.92, whose downfield location indicates that this phosphido ligand spans a Ru-Ru bond [25]. The remaining phosphorus group still attached to the dione ring appears at δ 0.80. These two resonances are coupled and appear as a pair of doublets having a ${}^{2}J$ value of 87 Hz. While the ${}^{31}P$ NMR data for 4 corroborate the cleavage of one of the two distinctive P-C bonds inherent in the bpcd ligand [i.e., P-Ph vs. P-C(dione)], the unambiguous identity of 4 was ascertained by X-ray crystallography. The ORTEP diagram of 4 is shown in Fig. 2, where the phosphido ligand that bridges the Ru(1)-Ru(2) vector proves the course of bpcd activation as involving that of







Fig. 2. ORTEP drawing of $Ru_3(CO)_5(\mu_2\text{-}CO)_2(\mu_3\text{-}NPh)(\mu_2\text{-}PPh_2)[\mu,\eta^1,\eta^1\text{-}C=C(PPh_2)C(O)CH_2C(O)]$ (4) showing the thermal ellipsoids at the 50% probability level.

P-C(dione) bond cleavage. Cluster 4 is electron precise and contains 48 valence electrons, and the nido polyhedral structure is unchanged from that of $Ru_3(CO)_9(\mu_3$ -CO)(μ_3 -NPh) and cluster 2. The Ru–Ru bond distances range from 2.694(1) A [Ru(1)-Ru(2)] to 2.848(1) A [Ru(2)-Ru(3)] and display a mean distance of 2.772 Å, which agrees with their single-bond designation [26]. The three-electron donor ligand μ_2, η^2, η^1 -C=C(PPh₂) $C(O)CH_2C(O)$ bridges the Ru(1)-Ru(3) bond via a Ru(3)–C(15) σ bond of 2.032(9) A and a Ru(1)–P(1) dative bond of 2.358(3) A. Of the seven CO groups in 4, the Ru(1)-C(2)-O(2) and Ru(2)-C(4)-O(4) linkages are clearly semibridging in nature based on the observed angles of 158.0(9)° and 153.5(9)°, respectively [27]. The presence of these semibridging CO groups in cluster 4 facilitates electron delocalization away from the electron-rich P-substituted ruthenium centers Ru(1) and Ru(2) and towards the Ru(3) center. The carbocyclic portion of the dione ring is nearly coplanar with the three ruthenium atoms based on the ca. 16° dihedral angle found for these groups of atoms.

The P-C bond cleavage that accompanies the formation of cluster 4 is similar to that exhibited by the isolobal tricobalt cluster PhCCo₃(CO)₇(bpcd) [11a,11c], except that the putative σ -bound intermediate PhCCo₃(CO)₆[μ - η^1 , σ -C=C(PPh₂)C(O)CH₂C(O)](μ_2 -PPh₂), which is the first product from P–C(dione) bond scission, undergoes a fast reductive C-C bond coupling of the Co-C(dione) moiety with one of the Co-C(carbyne) bonds to produce $Co_3(CO)_6[\mu_2-\eta^2,\eta^1-C(Ph)C=$ $C(PPh_2) C(O)CH_2C(O)](\mu_2-PPh_2)$. Cluster 4 showed no evidence for the analogous reductive coupling between the Ru-C(dione) and the Ru-N groups, as illustrated in Eq. (3). The negligible coupling reactivity of these latter two bonds in 4 in comparison to the related tricobalt intermediate most likely derives from the greater kinetic stability commonly found for second- and third-row metals versus first-row derivatives.



The IR spectrum of **5** exhibited low-energy dione v(CO) bands at 1715 and 1668 cm⁻¹ analogous to those of cluster **4** and signaled the activation of the ancillary bpcd ligand by the cluster. The ³¹P NMR spectrum of **5** consisted of two doublets at δ 66.82 and -4.19 and provides critical information as to the nature of the two different phosphorus groups. The high-field resonance is assigned to that of the PPh₂(dione) ligand,

while the remaining resonance is ascribed to a phosphido moiety. Besides the ambiguity associated with the aforementioned P-C bond cleavage scenarios, the chemical shift of the phosphido group in 5 presented an additional problem since it is found in a region where this linkage may bridge a Ru-Ru bond as well as span two non-bonded ruthenium centers. The generally recognized trend in ³¹P chemical shifts is that phosphido groups that bridge a metal-metal bond appear over the range of δ 50–300, while the same group, if it spans two non-bonded metals, is found at higher field from δ -300 to 50 [21,28]. Accordingly, the composition and ligand arrangement in 5 was resolved by X-ray analysis. The ORTEP diagram of 5 is shown in Fig. 3, where it is seen that the phosphido moiety derives via the scission of one of the P-Ph groups of the bpcd ligand. The loss of two ruthenium-ruthenium bonds in 5 relative to either the parent cluster 1 or precursor cluster 2 follows from its 52-valence electron count and is understood within the tenets of polyhedral skeletal electron pair (PSEP) theory. Here cluster 5 may by viewed as a four-vertex hypho cluster that possesses 8 SEP and whose polyhedral shape may be traced back to the parent four-vertex nido cluster 1 before the formal association of two additional SEP. The Ru(2)-Ru(3) bond distance of 2.839(3) is similar to the Ru-Ru distances found in clusters 2 and 4, and other polynuclear ruthenium clusters. The $Ru(1) \cdots Ru(2)$ and $Ru(1) \cdots Ru(3)$ distances of 3.269(3) and 3.711(3) A clearly preclude any bonding interactions between these metal centers. μ_2, η^2, η^1 -PPhC=C(PPh₂)C(O)CH₂C(O) ligand The



Fig. 3. ORTEP drawing of $Ru_3(CO)_6(\mu_2$ -CO)(μ_3 -NPh)(μ -PhCO)[μ^2 , η^2 , η^1 -PPhC=C(PPh_2)C(O)CH_2C(O)] (5) showing the thermal ellipsoids at the 50% probability level.

functions as a 7e donor ligand and is attached to the three ruthenium atoms in a fashion analogous to that found by us in the tricobalt cluster $\text{Co}_3(\text{CO})_7[\mu_2,\eta^2,\eta^1-$ PPhC=C(PPh₂)C(O)OC(O)] [11a]. The transient Ru– Ph bond that follows from the P–Ph bond cleavage undergoes rapid carbonylation to furnish the observed benzoyl moiety that tethers the non-bonded Ru(2) and Ru(1) centers. The benzoyl unit is σ -bound through the carbonyl carbon atom C(24) to Ru(2) [1.98(2) Å] and the oxygen atom O(23) to Ru(1) [2.16(1) Å] in a fashion typified by other open triruthenium clusters containing an acyl bridging ligand [29]. The semibridging CO group that spans the Ru(2)–Ru(3) bond is confirmed by the non-linear Ru(2)–C(6)–O(6) and Ru(3)–C(6)– O(6) bond angles of 126(2)° and 150(2)°, respectively.

The mixed phosphinidine-imido capped cluster Ru₃ (CO)₉(μ_3 -NPh)(μ_3 -PPh) was also produced in minor amounts from the thermolysis of **2**. The IR spectrum of **6** exhibited terminal carbonyl stretching bands and no evidence for the presence of the bpcd ligand or a dione-derived moiety. The ³¹P NMR spectrum of **6** exhibited a single resonance at δ 269.66 that is suggestive of a capping-phosphinidine group and agrees closely to the value of δ 239 that has been reported for the Ru₃ (CO)₉(PPh)₂ [30]. The molecular structure of **6**, which is depicted in Fig. 4, consists of a bicapped-Ru₃(CO)₉ cluster that is structurally similar to the well-known bis(imido)- and bis(phosphinidine)-capped family of



Fig. 4. ORTEP drawing of $Ru_3(CO)_9(\mu_3-NPh)(\mu_3-PPh)$ (6) showing the thermal ellipsoids at the 50% probability level.

 $M_3(CO)_9(EPh)_2$ (where M = Fe, Ru, Os; E = N, P) clusters, whose M_3E_2 polyhedra exhibit a *nido* framework given their 50e count. While the mixed phosphinidine-imido cluster $Fe_3(CO)_9(\mu_3-NPh)(\mu_3-PPh)$ has been prepared and structurally characterized [31], the corresponding mixed-capped Ru₃ analogue has not been reported to our knowledge. The three Ru–P and Ru–N bonds display a mean distance of 2.329 and 2.124 Å, respectively, and are not significantly different from the values reported for the homo-capped species Ru₃-(CO)₉(NPh)₂ [32] and related μ_3 -PPh capped clusters [33]. The remaining bond distances and angles are unexceptional and require no comment.

3.3. Cyclic voltammetry and MO data

Due to the ability of an intact bpcd ligand to function as an electron reservoir, we have explored the redox properties of clusters 2 and 3 by cyclic voltammetry at a platinum electrode in CH₂Cl₂ containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) as the supporting electrolyte. We have previously shown that the parent cluster 1 undergoes an irreversible reduction at $E_p^c = -1.47$ V through an ECE path where the rapid loss of CO from the transient radical anion $[Ru_3(CO)_{10}(NPh)]^{-1}$ is followed by a second electron accession to furnish the reactive dianion $[Ru_3(CO)_9(NPh)]^{2-}$ [8]. The CV of 2 (not shown) over the potential range of -1.4 to 1.0 V at a scan rate of 0.1 V/s revealed the expected bpcd-based reduction wave at -0.88 V, along with an irreversible oxidation wave at $E_{\rm p}^{\rm a} = 0.61$ V. Although not examined in detail, the oxidation remained irreversible up to a scan rate of 1.0 V/s. The orbital composition of the $0/1^-$ redox couple was confirmed by carrying out extended Hückel MO calculations on the compound $Ru_3(CO)_7(\mu_3-CO)(\mu_3-NH)(H_4$ bpcd [34].) The LUMO of the model cluster occurs at 10.43 eV and resides on the chelating H₄-bpcd ligand and is best viewed as a ψ_4 -type molecular orbital that is confined to the π system of the cyclopenten-1,3-dione moiety in total agreement with the MO data published on mono- and polynuclear compounds containing either a bpcd or bma ligand [16,24a,35].

The coordination two bpcd ligands to the triruthenium frame of **3** presented us the opportunity to explore the extent, if any, of the electron delocalization between the two ligand reduction sites (chelate and bridge). If the π^* systems of these ancillary diphosphines were extensively coupled, a mixed-valence compound of either Class II or III might result [36]. The CV of **3** exhibits two reversible one-electron reductions at $E_{1/2} = -0.93$ and -1.04 V, as depicted in Fig. 5. Scanning the same sample from 0.0 V out to 1.0 V and back to the resting potential of 0.0 V revealed the presence of an irreversible oxidation wave at $E_{\rm p}^{\rm a} = 0.36$ V. The oxidation wave in **3**



Fig. 5. Cathodic scan cyclic voltammogram of $Ru_3(CO)_5(\mu_3-CO)(\mu_3-NPh)(bpcd)_2$ ca. 10^{-3} M in CH_2Cl_2 containing 0.1 M TBAP at 0.1 V/s at room temperature.

remained irreversible up to a scan rate of 1.0 V/s and was not examined further.

The observation of two reduction waves in 3 gives rise to two likely scenarios, namely two individual one-electron reductions at each bpcd ligand or the sequential reduction of one bpcd ligand to the corresponding dianion. The $\Delta E_{1/2}$ magnitude of 0.11 V for the two reductions leads us to favor the former redox scheme. Our contention is indirectly supported by the CV behavior of free bpcd in CH₂Cl₂ containing 0.1 M TBAP, where the $0/1^{-}$ redox couple is observed at -1.10 V when the sample is scanned from 0.0 V out to -1.5 V [37,38]. Here the absence of an observable reduction of the bpcd radical anion to $[bpcd]^{2-}$ at a potential close to the radical anion (<0.4 V) implies that the second electron transfer to an already reduced bpcd ring is not operative for 3^{-} . When the bpcd ligand does undergo a net 2e⁻ reduction, as it does in the sulfidocapped cluster SFeCo₂(CO)₇(bpcd), the $0/1^{-}$ and $1^{-}/2^{-}$ redox couples are separated by 0.65 V [39]. Accordingly, we assign the two one-electron reduction waves in 3 to the site-localized reduction of each bpcd ligand in 3, as depicted below.



Proof that the first reduction is regioselective and takes place at the bridging diphosphine as opposed to the chelating diphosphine ligand derives from extended Hückel MO calculations on the model cluster compound $Ru_3(CO)_5(\mu_3-CO)(\mu_3-NH)(H_4-bpcd)_2$ that contains both a chelating and bridging H₄-bpcd ligand. Our MO calculations revealed that the LUMO, which occurs at -10.47 eV, in Ru₃(CO)₅(μ_3 -CO)(μ_3 -NH)(H₄bpcd)₂ corresponded to the π^* system associated with the bridging H₄-bpcd ligand, with the analogous ligand-based π^* system of the chelating diphosphine moiety being found only slightly higher in energy at -10.34 eV. While the accuracy of these calculations might lead one to question our conclusion concerning the site of the first electron accession, we note that in the case of the isomeric dicobalt compounds Co₂(- $CO_4(\mu$ -PhCCPh) (bma), the bridged diphosphine was found to undergo reduction at slightly more positive potential than the chelated isomer [40]. Additional examples of compounds containing two different bpcd coordination modes will allow us to validate the generality of bridging versus chelating ligand reduction trends. Since the MO data show no significant orbital overlap between the π^* systems of both ligands, the participation of a mixed-valence intermediate upon the formation of the first radical anion may be eliminated from consideration. That this is correct is further corroborated by the calculated comproportionation constant (K_c) of 72, which clearly places cluster 3 in the Robin– Day scheme of a class I compound ($K_c < 100$). Here the two individual and distinct bpcd reduction sites exhibit minimal electronic communication.

4. Conclusions

CO substitution in $Ru_3(CO)_9(\mu_3-CO)(\mu_3-NPh)$ with the diphosphine ligand bpcd has been studied and found to give initially the mono- and bis-substituted clusters $Ru_3(CO)_{9-x}(\mu_3-CO)(\mu_3-NPh)(bpcd)_n$ (x = 2, n = 1; x = 4, n = 2). The thermal degradation of Ru₃(CO)₇(μ_3 -CO)-(μ_3 -NPh)(bpcd) has been explored and found to proceed via both P-Ph and P-C(dione) bond activation routes. The resulting thermolysis products were isolated and fully characterized in solution and by X-ray crystallography. No evidence for the reductive coupling of the transient Ru-Ph or Ru-C(dione) moieties with the capping imido ligand was observed. The redox properties of $Ru_{3}(CO)_{7}(\mu_{3}-CO)(\mu_{3}-NPh)(bpcd)$ and $Ru_{3}(CO)_{5}(\mu_{3}-CO)$ - $(\mu_3-NPh)(bpcd)_2$ were examined by cyclic voltammetry and MO calculations, which confirm the electron reduction sites being fully localized on the ancillary bpcd ligand(s). In the case of the latter cluster, the addition of the first electron during the reduction is shown to occur exclusively at the bridging bpcd ligand and not the chelating ligand. The calculated comproportionation

constant reveals the both bpcd moieties function as independent and distinct electron sites.

5. Supporting information

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 23990 for **2**; 239901 for **4**; 239902 for **5**; and 239720 for **6**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [fax: +44(1223)336-033; e-mail: deposit@ccdc.ac.uk or http://www:ccdc.cam.ac.uk].

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