

Ligand degradation and phosphorus scavenging in the reaction between 1,2-bis(diphenylphosphino)benzene (dppbz) and $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$: Synthesis and X-ray structure of the edge-bridged square-pyramidal cluster $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$

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Abstract

Thermolysis or Me_3NO activation of the hexaruthenium cluster $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ in the presence of the diphosphine ligand 1,2-bis(diphenylphosphino)benzene (dppbz) does not furnish the expected dppbz-substituted cluster $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\text{dppbz})$ but rather $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$, whose edge-bridged square-pyramidal structure has been established by X-ray crystallography. Accompanying the opening of the original *closo* Ru_6 polyhedron is the dephosphination of a second dppbz ligand through three rapid P–C bond cleavages, leading to the capture of the phosphorus atom as a face-capping phosphido ligand. This unprecedented reactivity between $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and the dppbz ligand is discussed relative to other diphosphine ligands.

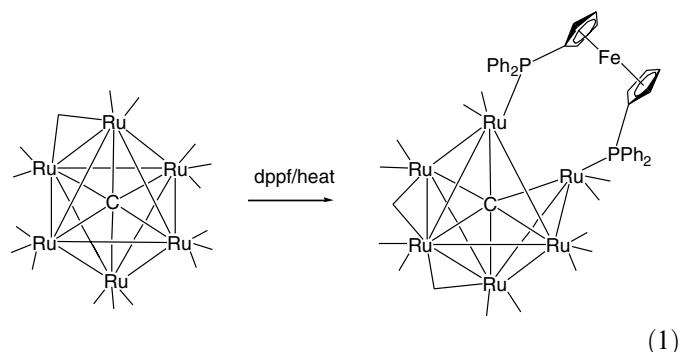
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1. Introduction

The replacement of two CO groups in the octahedral cluster $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ by the ligands dppm, dppe, and dppp proceeds readily under mild conditions and without complications to afford the corresponding diphosphine-bridged clusters $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\mu\text{-P-P})$ [1]. The substitution reaction between $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and dppf follows a similar path inasmuch as the dppf ligand serves to bridge adjacent ruthenium centers in the product $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\mu\text{-dppf})$. However, unlike the octahedral Ru_6 structures exhibited by the aforementioned $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\mu\text{-P-P})$ derivatives, the dppf ligand promotes a partial expansion of the *closo* Ru_6 core to a “hinged” or edge-bridged square-pyramid Ru_6 polyhedral motif, as shown in Eq. (1) [2]. A full or more

developed opening of the wing-tip ruthenium center relative to the square-pyramidal base is arrested due to dppf coordination of the wing-tip and one of the non-hinged ruthenium atoms within the square base of the molecular polyhedron.



The dppf-induced polyhedral opening attendant in the formation of $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\mu\text{-dppf})$ suggests that other diphosphine ligands have the potential to function similarly, which could in turn expose reactive ruthenium sites

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within an intact molecular cluster capable of participation in unusual catalytic cycles. Given the general paucity of reactions involving $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and diphosphine ligands [1–3], we have initiated substitution studies between the parent Ru_6 cluster and the unsaturated diphosphine ligands 4,6-bis(diphenylphosphinomethyl)-*m*-xylene (dppx), 1,2-bis(diphenylphosphino)benzene (dppbz), and (*Z*)-1,2-bis(diphenylphosphino)ethylene (dppen). Our interest in such ligands stems, in part, from the coordinative flexibility exhibited by these and related diphosphines at metal cluster compounds in terms of nondissociative isomerization behavior [4]. In comparison to the extensive literature examples that exist for dppm-, dppe-, and dppf-substituted polynuclear compounds, metal clusters containing a dppx or dppbz ligand are essentially nonexistent. The synthesis and structural characterization of the double homometallic cluster $[\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{16}]_2(\text{dppx})$ and its thermal conversion to the pincer-bridged cluster $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\text{dppx})$ have recently been reported by us [5]. Herein we present our data on the reaction between $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and the diphosphine ligand dppbz to give $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$. The chelation of one dppbz ligand to a single ruthenium atom and the facile decomposition of an additional dppbz ligand to furnish the observed capping phosphido moiety in the product are discussed.

2. Experimental

2.1. General methods

The $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ cluster used in these studies was synthesized from $\text{Ru}_3(\text{CO})_{12}$ and ethylene using a 450 mL Parr Series 4560 bench-top mini reactor [6], while the latter cluster was prepared from hydrated RuCl_3 and CO using a 11 Parr Series 4000 rocking autoclave [7]. The chemicals dppbz and $\text{Me}_3\text{NO} \cdot n\text{H}_2\text{O}$ were purchased from Aldrich Chemical Co. The $\text{Me}_3\text{NO} \cdot n\text{H}_2\text{O}$ was dried by azeotropic distillation from benzene and the anhydrous Me_3NO was stored in a Schlenk tube under argon. All reaction, IR, and NMR solvents were of reagent grade and were distilled from a suitable drying agent and stored in Schlenk vessels equipped with Teflon stopcocks [8]. The combustion analysis was performed by Atlantic Microlab, Norcross, GA.

The reported infrared spectral data were recorded on a Nicolet 20 SXB FT-IR spectrometer in a 0.1 mm NaCl cell, using PC control and OMNIC software. The ^1H (200 MHz) and $^{31}\text{P}\{^1\text{H}\}$ (162 MHz) spectra were recorded on Varian Gemini-200 and Bruker AVANCE DRX-400 spectrometers, respectively.

2.2. Me_3NO activation of $\text{Ru}_6(\mu_6\text{C})(\text{CO})_{17}$ in the presence of dppbz

To a 250 mL Schlenk flask under argon was added 0.10 g (0.091 mmol) of $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$, 43 mg (0.096 mmol) of dppbz, and 14 mg (0.19 mmol) of Me_3NO , followed by 20 mL of CH_2Cl_2 via syringe. The solution was stirred at

room temperature for 1 h and then examined by TLC using $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) as the eluent. A small, fast moving spot belonging to the starting cluster ($R_f = 0.90$; estimated at ca. 20%) and one large spot ($R_f = 0.50$) corresponding to $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ were observed, in addition to some black material that remained irreversibly bound at the origin of the plate. The solvent was concentrated and the desired product separated by column chromatography over silica gel using the aforementioned mobile phase. The crude sample was recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to afford X-ray quality crystals of $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ in 40% yield (55 mg). An acceptable combustion sample was obtained from a sample of $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ that was recrystallized from $\text{C}_6\text{H}_6/\text{hexane}$. IR (CH_2Cl_2): $\nu(\text{CO})$ 2079 (s), 2044 (vs), 2018 (s) cm^{-1} . ^1H NMR (C_6D_6): δ 6.60–7.50 (m, 24H), –21.55 (s, bridging hydride). ^{31}P NMR (CD_2Cl_2): δ 76.51 (s, 2P, dppbz), 68.30 (s, $\mu_3\text{-P}$ moiety). Anal. Calc. (found) for $\text{C}_{45}\text{H}_{25}\text{O}_{14}\text{P}_3\text{Ru}_6 \cdot \text{C}_6\text{H}_6$: C, 39.09 (39.02); H, 1.99 (2.27).

2.3. Thermolysis of $\text{Ru}_6(\mu_6\text{C})(\text{CO})_{17}$ in the presence of dppbz

This reaction was carried out in a Schlenk tube employing 50 mg (0.045 mmol) of $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$, 23 mg (0.052 mmol) of dppbz, and 20 mL of 1,2-dichloroethane (DCE). The solution was heated at 45 °C overnight and then checked by TLC analysis, which revealed the presence

Table 1
Crystal data and structure refinement details for $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$

CCDC entry no.	622,560
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.334(2)
b (Å)	17.446(2)
c (Å)	21.050(2)
β °	94.026(2)
V (Å ³)	4884.7(9)
Molecular formula	$\text{C}_{45}\text{H}_{25}\text{P}_3\text{O}_{14}\text{Ru}_6$
f_w	1487.97
Formula units per cell (Z)	4
D_{calcd} (Mg/m^3)	2.023
λ (Mo K α) (Å)	0.71073
Absorption coefficient (mm^{-1})	1.970
R_{merge}	0.1064
Absorption correction	SADABS
Absorption correction factor	0.8481/0.6499
Total reflections	41940
Independent reflections	11594
Data/res/parameters	11594/0/614
R_1^a [$I \geq 2\sigma(I)$]	0.0552
wR_2^b (all data)	0.0965
GOF on F^2	0.884
$\Delta\rho(\text{max}), \Delta\rho(\text{min})$ ($\text{e}/\text{Å}^3$)	0.996, –0.786

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$^b R_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

Table 2
Selected bond distances (Å) and angles (°) for $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$

Bond distances			
Ru(1)–P(2)	2.280(2)	Ru(1)–P(1)	2.284(2)
Ru(1)–P(3)	2.300(2)	Ru(1)–Ru(2)	2.8557(9)
Ru(1)–Ru(3)	2.8620(9)	Ru(2)–P(3)	2.349(2)
Ru(2)–Ru(3)	2.6703(9)	Ru(2)–Ru(6)	2.8200(9)
Ru(2)–Ru(5)	2.8540(9)	Ru(3)–P(3)	2.342(2)
Ru(3)–Ru(6)	2.8127(9)	Ru(3)–Ru(4)	2.885(1)
Ru(4)–Ru(6)	2.8096(9)	Ru(4)–Ru(5)	2.902(1)
Ru(5)–Ru(6)	2.8252(9)	C(1)–C(2)	1.39(1)
Bond angles			
P(2)–Ru(1)–P(1)	82.61(7)	C(31)–Ru(1)–P(3)	161.6(2)
P(2)–Ru(1)–P(3)	97.13(7)	P(1)–Ru(1)–P(3)	100.59(7)
C(1)–P(1)–Ru(1)	108.1(3)	C(2)–P(2)–Ru(1)	107.5(2)
Ru(1)–P(3)–Ru(3)	76.12(6)	Ru(1)–P(3)–Ru(2)	75.78(6)
Ru(3)–P(3)–Ru(2)	69.40(6)	O(2)–C(32)–Ru(3)	166.3(7)
O(4)–C(34)–Ru(2)	162.9(7)		

of unreacted $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$. The dppbz-substituted cluster was isolated by column chromatography as described above in 44% yield (30 mg).

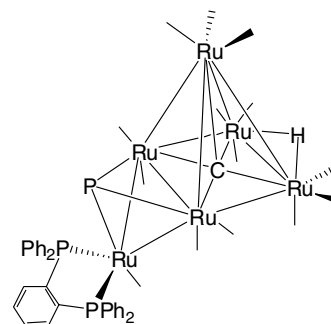
2.4. X-ray structural data

The X-ray data for $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ were collected on a Bruker SMART™ 1000 CCD-based diffractometer at 233 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm [9], and the structure solved and refined using the SHELXTL program package [10]. The molecular structure was checked by using PLATON [11], and all nonhydrogen atoms refined anisotropically. All carbon-bound hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom, unless otherwise noted. The bridging hydride that is assumed to span the Ru(4)–Ru(5) vector was not located during refinement. The refinement for $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ converged at $R = 0.0552$ and $R_w = 0.0965$ for 11,594 independent reflections with $I > 2\sigma(I)$. Tables 1 and 2 summarize the pertinent X-ray data.

3. Results and discussion

Our initial reaction between $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and dppbz was carried out at room temperature. No reaction was observed when equimolar amounts of the reagents were stirred over a 24 h period. The addition of the oxidative-decarbonylation reagent Me_3NO (2 equiv.) to the solution led to the rapid consumption of most of the starting cluster (>70–75%) and formation of the hexaruthenium cluster $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ as the sole mobile product by TLC analysis. The reaction is also accompanied by cluster decomposition based on the presence of an unknown black solid at the origin of the TLC plate, whose in-depth characterization was not pursued due to its irre-

versible binding to the chromatographic support. Doubling of the amount of dppbz relative to the starting cluster and using 2.0 equiv. Me_3NO led only to a modest increase in $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ (ca. 55%), while reactions employing 1 equiv. of Me_3NO and a 1:1 mixture of cluster and ligand gave the title cluster in reduced yields on the order of 25–30%. Thermolysis of $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ and dppbz (1:1) in CH_2Cl_2 , 1,2-dichloroethane, or toluene solvents over the temperature range of 40–55 °C proceeded similarly with only $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ observed by TLC. The product, whose structure is shown below, was isolated by column chromatography over silica gel as a relatively air-stable solid.



$\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ was initially characterized in solution by spectroscopic methods. The IR spectrum recorded in CH_2Cl_2 revealed only terminal carbonyl bands at 2079 (s), 2044 (vs), and 2018 (s) cm^{-1} , and the ^1H NMR recorded in C_6D_6 exhibited an aromatic multiplet at δ 6.60–7.50 for the dppbz ligand and a high-field bridging hydride at δ –21.55. The chemical shift for the hydride in $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ parallels those ^1H NMR data for the hydride ligands in the pentaruthenium clusters $\text{HRu}_5(\mu_5\text{-C})(\text{CO})_{14}(\text{SiEt}_3)$ and $\text{HRu}_5(\mu_5\text{-C})(\text{CO})_{15}(\text{SiEt}_3)$ [12]. To determine whether the bridging hydride is derived from the dppbz ligand or the reaction solvent, we investigated the reaction between $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$, dppbz, and Me_3NO in CDCl_3 . ^1H NMR analysis of the crude reaction mixture displayed a hydride resonance at δ –18.90 that allows us to rule out solvent participation in the formation of $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$. The presence of different phosphorus groups in $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ was verified by ^{31}P NMR spectroscopy, with the two ^{31}P singlets recorded at δ 76.51 and 68.30 ascribed to a chelating dppbz ligand and a face-capping μ_3 -phosphido moiety, respectively.

The unequivocal identity and the structural composition of $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ were established by X-ray crystallography. Fig. 1 shows the thermal ellipsoid plot of $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$. The title cluster consists of a square-pyramidal Ru_5 core that is edged-bridged by the sixth ruthenium atom and whose polyhedral structure is in keeping with its 88-electron count and structural trends exhibited by other condensed

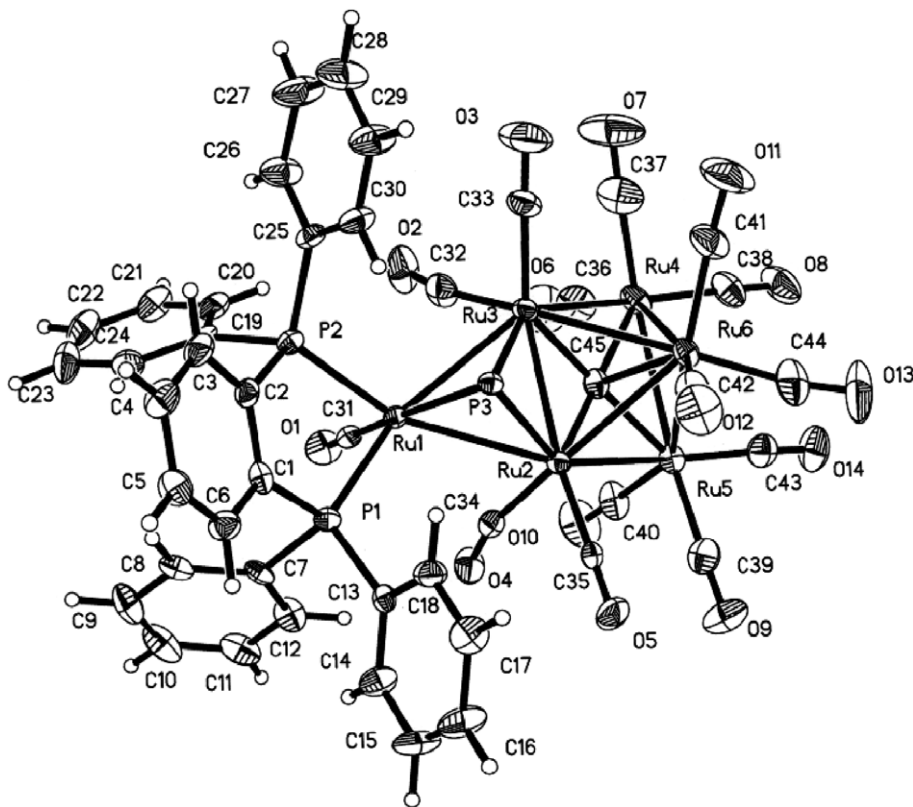
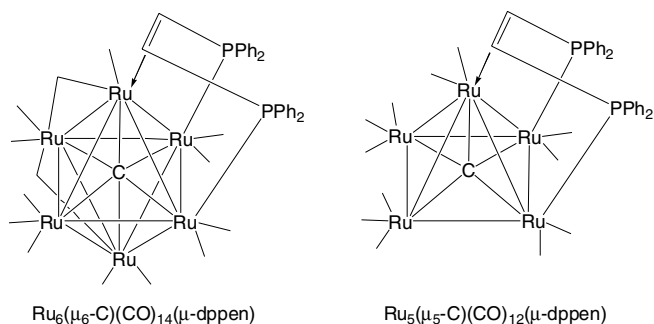


Fig. 1. Thermal ellipsoid plot of $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ at the 50% probability level.

polynuclear clusters [13,14]. The Ru–Ru bond distances range from 2.6703(9) Å [Ru(2)–Ru(3)] to 2.902(1) Å [Ru(4)–Ru(5)] and exhibit a mean distance of 2.830 Å that is in agreement with those Ru–Ru distances found in other carbide-containing Ru_5 and Ru_6 clusters [1,11,15]. Although the bridging hydride was not located during refinement, it has been assigned to the long basal Ru(4)–Ru(5) vector. This hydride location gives rise to a mirror plane of symmetry that bisects the square pyramidal core, the $\mu_3\text{-P}$ moiety, and the dppbz-substituted Ru(1) center of the cluster, leading to a single ^{31}P resonance for the dppbz ligand in agreement with the ^{31}P NMR data. The Ru–P distances associated with the face-capping phosphido moiety reveal an average distance of 2.330 Å that is 0.043 Å longer than the mean distance from the Ru–P bonds from the dppbz ligand. The presence of the $\mu_3\text{-P}$ and chelating diphosphine moieties in $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ is unexampled in carbido-substituted polynuclear ruthenium clusters. A check of the Cambridge Structural Database for dppbz-substituted clusters reveals $\text{Ir}_4(\text{CO})_{10}(\text{dppbz})$ as the only entry. Here the chelating dppbz ligand was formed from an ortho phosphorylation of the PPh_3 ligands in $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$ [16]. The Ru(3)–C(32)–O(2) and Ru(2)–C(34)–O(4) carbonyls are weakly semibridging based on bond angles of 166.3(7)° and 162.9(7)°, respectively, and bent slightly towards the Ru(1) center. Finally, the carbide

C(45) atom is situated in the basal plane of the square pyramid as in $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$ [17]. The remaining distances and angles require no comment.

Documented examples of phosphine ligand activation in clusters derived from $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ are scarce. The phosphine ligands in $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\text{PhPMe}_2)_2$ have been shown to undergo both P–C and C–H bond cleavage on treatment with Me_3NO at room temperature to produce $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{13}(\mu\text{-PMe}_2)(\mu_3\text{-}\eta^3\text{-Me}_2\text{PC}_6\text{H}_4)$ and $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{14}(\text{PhPMe}_2)(\mu\text{-}\eta^2\text{-MePhPCH}_2)(\mu\text{-H})$ [18]. The data from this latter report and our present study support the existence of low-energy manifolds for the deleterious fragmentation of a coordinated phosphine ligand(s) in this genre of cluster. The sequence of events leading to $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ is unknown at this time, and attempts to isolate the presumed intermediate $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{15}(\text{dppbz})$ have not been successful. The facile degradation of the dppbz ligand found here stands in sharp contrast to those results obtained in the reaction of the unsaturated diphosphine ligand dppen with $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ conducted under identical conditions [19]. Here the dppen ligand acts as a face-capping 6e donor through the use of the two phosphine moieties and the alkene π bond to furnish the cluster compounds $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{14}(\mu\text{-dppen})$ and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{12}(\mu\text{-dppen})$ shown below. No evidence for the degradation of the dppen ligand was observed.



4. Conclusions

The coordination and fragmentation of dppbz ligands at $\text{Ru}_6(\mu_6\text{-C})(\text{CO})_{17}$ furnishes the edge-bridged square-pyramidal cluster $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$. The remarkably mild conditions leading to the dephosphination of one of the dppbz ligands and the ensuing formation of the $\mu_3\text{-P}$ moiety are unprecedented in transition-metal cluster chemistry. The substitution chemistry of the dppbz ligand with metal clusters of varying nuclearity is currently being investigated in order to establish the generality of the diphosphine reactivity reported here.

5. Supplementary material

CCDC 260091 contains the supplementary crystallographic data for $\text{HRu}_6(\mu_5\text{-C})(\mu_3\text{-P})(\text{CO})_{14}(\text{dppbz})$ (#622560). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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