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Synthesis, characterization, and reactivity of a novel ruthenium carbonyl cluster containing tri-*O*-benzyl-D-glucal as a chiral carbohydrate ligand ☆

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Abstract

A chiral carbohydrate ligand 3,4,6-tri-*O*-benzyl-D-glucal (L) reacts with the cluster triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ giving a novel chiral cluster $Ru_3(\mu\text{-}H)_2(CO)_9$(L-2H) (**I**) that shows fluxional behavior at room temperature. The reaction of $Ru_3(\mu\text{-}H)_2(CO)_9$(L-2H) (**I**) with triphenylphosphine and diphenylphosphinoethane (dppe) gives two new clusters $Ru_3(\mu\text{-}H)_2(CO)_7$(L-2H)$(PPh_3)_2$ (**II**) and $Ru_3(\mu\text{-}H)_2(CO)_7$(L-2H)(dppe) (**III**). The new compounds **I**, **II** and **III** have been characterized by a combination of elemental analysis, mass spectrometry, infrared and variable temperature NMR spectroscopy.

Keywords: Tribenzyl glucal; Triruthenium dodecacarbonyl; Chiral ligand; Triphenylphosphine; Diphenylphosphinoethane; Variable temperature; NMR spectra

1. Introduction

Ruthenium carbonyl clusters have been used in several catalytic reactions. Considerable interest generated in the synthesis of ruthenium clusters [1] containing chiral ligands because of their potential use in asymmetric reactions [2]. This paper describes the synthesis, characterization, and reactivity of a novel triruthenium carbonyl cluster $Ru_3(\mu\text{-}H)_2(CO)_9$(L-2H) (**I**) obtained from the reaction of 3,4,6-tri-*O*-benzyl-D-glucal (tribenzyl glucal) with $Ru_3(CO)_{12}$. Compounds **II** and **III** were prepared from the reaction of compound **I** with triphenylphosphine and diphenylphosphinoethane. Compounds **I**, **II** and **III** will be explored in the synthesis of glycosylated amino acids. The rapidly developing area of glycoproteins is currently under intense study by glycobiologists [3]. As a result, synthetic organic chemistry is required for the synthesis of glycosylated amino acids and peptides.

2. Results and discussion

The reaction of tribenzyl glucal with $Ru_3(CO)_{12}$ in benzene at reflux temperature yields a yellow syrupy compound which could be separated on a silica gel flash column with hexane/dichloromethane (2:1) as well as by preparative thin layer chromatography with hexane/dichloromethane (1:1). It is not been possible to obtain X-ray quality crystals due to the fact that compound **I** is a syrupy liquid. Compound **I** has been characterized by FT-IR and NMR spectroscopy, mass spectrometry, and by elemental analysis. The FT-IR spectrum in dichloromethane exhibits stretching vibrations in the carbonyl region between 1900 and 2100 cm^{-1} indicating that all carbonyl groups are terminal: 2107(m), 2080(vs), 2054(vs), 2041(s, sh), 2012(s, br) cm^{-1}.

^1H NMR spectrum of **I** in $CDCl_3$ in the organic region shows signals corresponding to all of the hydrogens of

☆ Dedicated with admiration and appreciation to Prof. Richard Franck at Hunter College/CUNY on the occasion of his 69th birthday.

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tribenzyl glucal except two, each on C-1 and C-2 carbons. However, these two hydrogens were found in the hydride region of the ^{1}H NMR spectrum as a broad resonance at δ −18.33 due to the rapid exchange of the two bridging hydride ligands on the NMR time scale at room temperature. This is the first example in which C-1 and C-2 carbons of the 3,4,6-tri-*O*-benzyl-D-glucal are bonded to two ruthenium atoms of $Ru_3(CO)_9$ framework. It is well documented in the literature that the reaction of $Ru_3(CO)_{12}$ with olefins (L) gives $H_2Ru_3(CO)_9$(L-2H) [1]. ^{1}H–^{1}H COSY spectrum (Fig. 1) of **I** shows two cross-peaks that reveal the coupling between H-5 (quartet, centered at 4.48 ppm) and both H-4 (triplet, centered at 3.92 ppm), and to H-6 (AB quartet, centered at 3.89–3.81 ppm). ^{1}H NMR shows 15 hydrogens due to three phenyl rings, 6 hydrogens due to benzylic hydrogens in three benzyl groups, and 5 hydrogens of carbohydrate moiety. No coupling between H-1 and H-2 is observed. Apparently, they have been transferred to ruthenium skeleton. ^{13}C NMR spectrum in $CDCl_3$ shows peaks for both aliphatic and aromatic carbons of the carbohydrate portion of the cluster, and four peaks at 206.5, 197.6, 192.8, and 192.1 due to terminal CO groups. ^{13}C APT spectrum in CD_3COCD_3 shows four peaks at 207.1, 198.5, 193.9 and 192.3 due to four carbonyl carbons of ruthenium, three peaks at 138.9, 138.5 and 138.2 due to three quaternary carbons of phenyl groups of benzyl groups in tribenzyl glucal, and four peaks due to benzylic CH_2 carbons as positive peaks; CH carbons of the six-membered carbohydrate ring and CH carbons of phenyl groups as negative peaks. Additional characterization of **I** was performed using variable temperature (VT) ^{1}H NMR and ^{13}C NMR spectroscopic measurements. The variable-temperature ^{1}H NMR spectra in the hydride region are shown in Fig. 2. The ^{1}H NMR spectrum at +20 °C exhibits a broad resonance at δ −18.33, which can be assigned to the two bridging hydride ligands migrating over all three edges of the ruthenium framework in a rapid fluxional process [4,7] as shown in Scheme 1. Upon cooling to −50 °C, the broad resonance becomes two sharp singlets at δ −16.27 and δ −20.41 with the integrated ratio 1:1 similar to the compound $[Ru_4(CO)_{13}(\mu\text{-H})_2(\mu_4\text{-AsCF}_3)]$ [4]. ^{1}H NMR suggests that there are two inequivalent hydrides. The singlet at δ −20.41 may be associated with the bridging hydride ligand between the two-ruthenium atoms that are sigma bonded to the tribenzyl glucal. The singlet at δ −16.27 may be due to the bridging hydride between the ruthenium atom bonded to the double bond and the other ruthenium atom sigma bonded to the tribenzyl glucal. At −8 °C, the two singlets become featureless (slow to fast exchange rate at $T_c = \sim -8$ °C is 3681/s.); above −8 °C, two peaks coalesces to a broad peak. The fluxional process at room temperature can be rationalized in terms of two hydride ligands migrating over all three edges of the triruthenium skeleton producing a broad peak. Variable temperature ^{13}C NMR of **I** in $CDCl_3$ at −50 °C shows expected three peaks at 206.5, 198.1, and 186.4 due to three

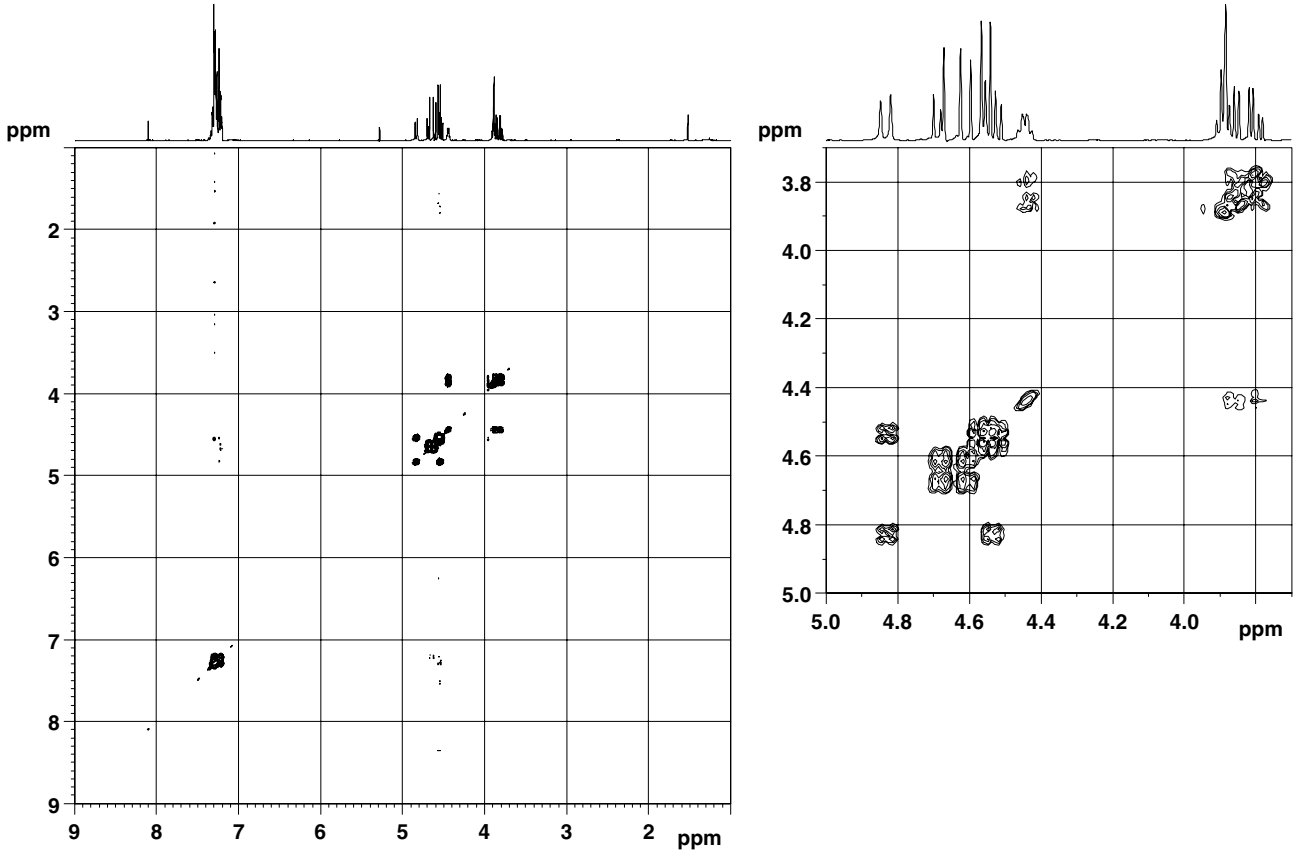


Fig. 1. ^{1}H–^{1}H COSY spectrum of compound **I** in $CDCl_3$.

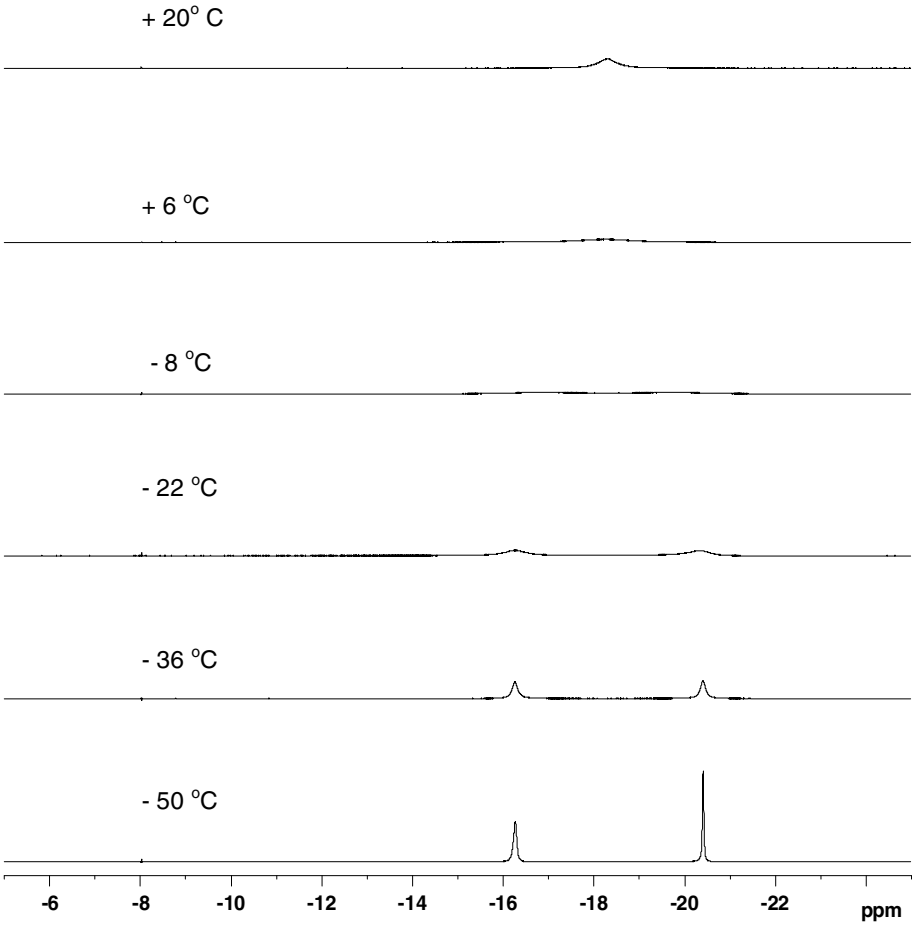
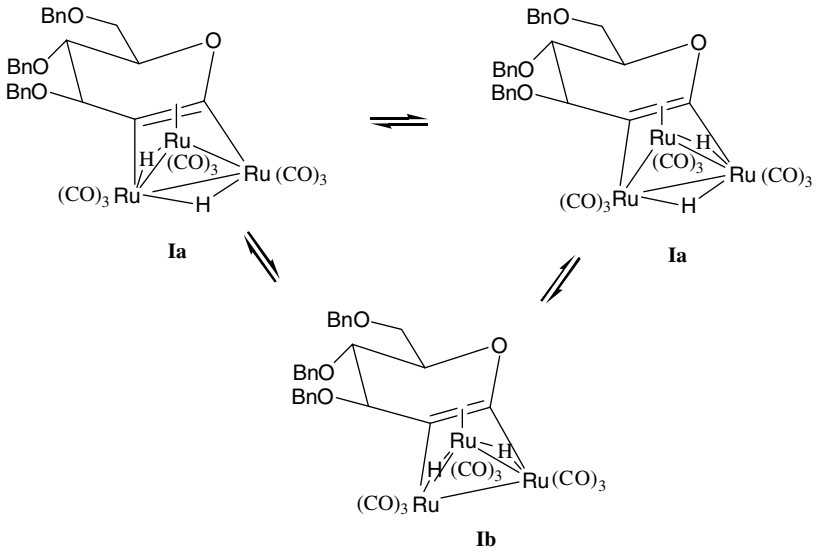


Fig. 2. Variable-temperature ^{1}H NMR spectra of compound **I** in the hydride region.



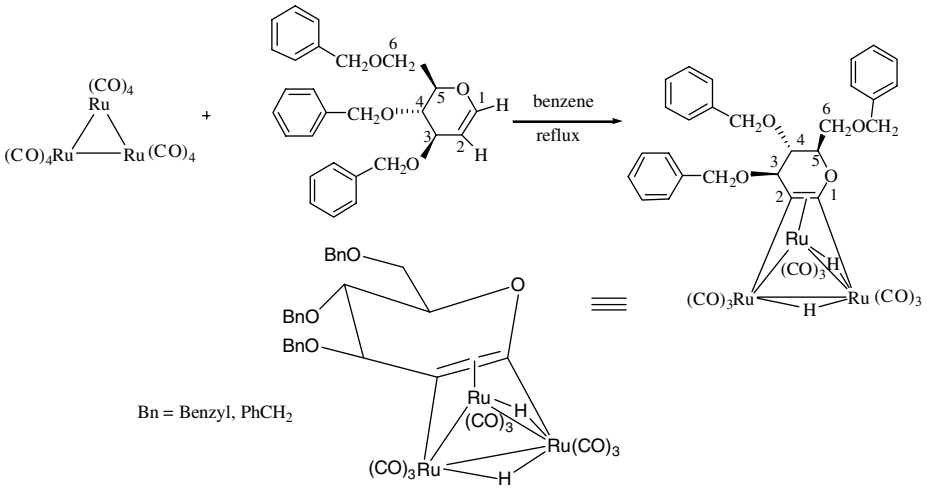
Scheme 1. Rapid fluxional process in compound **I** at room temperature.

CO groups that are dynamic at each ruthenium center. At +20 °C, it shows four peaks at 206.5, 197.6, 192.8, and 192.1 due to exchange of CO groups among the three-ruthenium atoms in the cluster. As the temperature is raised from −50 to +20 °C axial-radial exchange at ruthenium atoms followed by total CO scrambling probably via CO-bridged intermediates as has been noted for many transition metal-carbonyl clusters [5].

FAB+ Mass spectrum shows the molecular ion peak at 972 and the successive loss of 9 carbonyl groups. The fragmentation pattern is consistent with the ruthenium carbonyl clusters where ruthenium has many isotopes. Actual isotopic distribution for M^+ ion is in good agreement with the theoretical isotopic distribution. Elemental analysis confirms the molecular formula $C_{36}H_{28}O_{13}Ru_3$. Found: C, 44.75, H, 3.06. Calcd. C, 44.49, H, 2.90%. The spectroscopic data obtained for **I** is consistent with the structure shown in Scheme 1.

The two-ruthenium atoms are bonded to C-1 and C-2 carbons of the tribenzyl glucal and the third ruthenium atom is bonded to the double bond of the tribenzyl glucal as shown in Scheme 2. In terms of the electron counting rules, compound **I** is a 48-electron cluster. Tribenzyl glucal contributing 4 electrons, 9 CO groups contributing 18 electrons, two bridging hydride ligands contributing 2 electrons, and 3 ruthenium atoms contributing $3 \times 8 = 24$ electrons. As per 18-electron rule, compound **I** has $3 \times 18 = 54$ electrons $(54 - 48 = 6$ electrons) containing three Ru–Ru bonds.

Reaction of $Ru_3(\mu\text{-}H)_2(CO)_9(L\text{-}2H)$ (**I**) with triphenylphosphine in methylene chloride gives a yellow new cluster $Ru_3(\mu\text{-}H)_2(CO)_7(L\text{-}2H)(PPh_3)_2$ (**II**) and a previously reported red cluster $Ru_3(CO)_9(PPh_3)_3$ [6]. Compound **II** has been characterized by infrared and NMR spectroscopy, mass spectrometry, and elemental analysis. These compounds were separated by preparative thin layer chromatography with dichloromethane/hexanes (3:2). Several attempts to obtain X-ray quality crystals for compound **II** only resulted in a sticky yellow powder. The FT-IR spectrum in dichloromethane exhibits terminal CO (1900–2100 cm^{-1}) stretching frequencies at 2107(m), 2080(vs), 2054(vs), 2041(s, sh), 2012(s, br) cm^{-1}. ^1H NMR spectrum of **II** in $(CD_3)_2CO$ shows signals corresponding to all of the hydrogens in the organic region as in **I**, hydrogens due to two triphenylphosphine groups, and two hydride ligands coupled to phosphorus atoms in the high field region. The splitting pattern at δ −18.30 indicates the substitution of **I** by triphenylphosphine occurs at a ruthenium atom that is 'sigma' bonded to the tribenzyl glucal [1,7]. The variable-temperature ^1H NMR of **II** in the hydride region is shown in Fig. 3. Two sets of signals are observed in the high field range of ^1H NMR spectrum of compound **II**. The ^1H NMR spectrum −25 °C is much more simplified than at room temperature and coupling constants can be reasonably extracted. The ^1H NMR spectrum at −25 °C shows approximately two equal intensity hydride signals: a virtual doublet of doublets of doublets at δ −15.10 ($^2J_{P-H}$ 7.7 Hz, $^3J_{P-H}$ 2.7, $^2J_{H-H}$ 1.4 Hz, ∼1H), and a virtual triplet of triplets at δ −18.35 ($^2J_{P-H}$ 12.0 Hz, $^2J_{H-H}$ 1.4 Hz, ∼1H) [8,9]. The low value of J_{P-H} 7.7 Hz is being consistent with a structure in which the triphenylphosphine and the hydride have *cis* relationship at ruthenium and high value of J_{P-H} 12.0 Hz is due to *trans* relationship. The splitting pattern at δ −18.30 indicates that the presence of a bridging hydride ligand between the two ruthenium atoms each 'σ' bonded to the tribenzyl glucal and to a triphenylphosphine ligand [10,11]. At −25 °C ^1H NMR shows a virtual triplet of triplets centered at δ −18.35 due to a hydride ligand coupling with the two equivalent triphenylphosphine (**IIb,** Scheme 3) ligands. The splitting pattern at δ −15.10 indicates that the presence of a hydride ligand between a ruthenium atom that is 'σ' bonded to the tribenzyl glucal and a ruthenium atom 'π' bonded to tribenzyl glucal (Scheme 3). The hydride ligand is split by a two-bond phosphorus coupling to give a doublet, this in turn split by a three-bond phosphorus coupling to give a doublet of doublets, this further split by a bridging hydride ligand (between the two ruthenium atoms, each bonded to a triphenylphosphine ligand) to give a virtual doublet of doublets of doublets. The ^1H NMR at low temperature (−25 °C) shows coupling between the two-hydride ligands, indicating that they are coordinated to adjacent Ru–Ru bonds. ^1H NMR suggests that there are two inequivalent hydrides and two inequivalent triphenylphosphine ligands. The cluster **II** exists in solution as a mixture of two isomeric forms **IIa** and **IIb** (Scheme 3).



Scheme 2. Synthesis of compound **I** from $Ru_3(CO)_{12}$ and tribenzyl glucal.

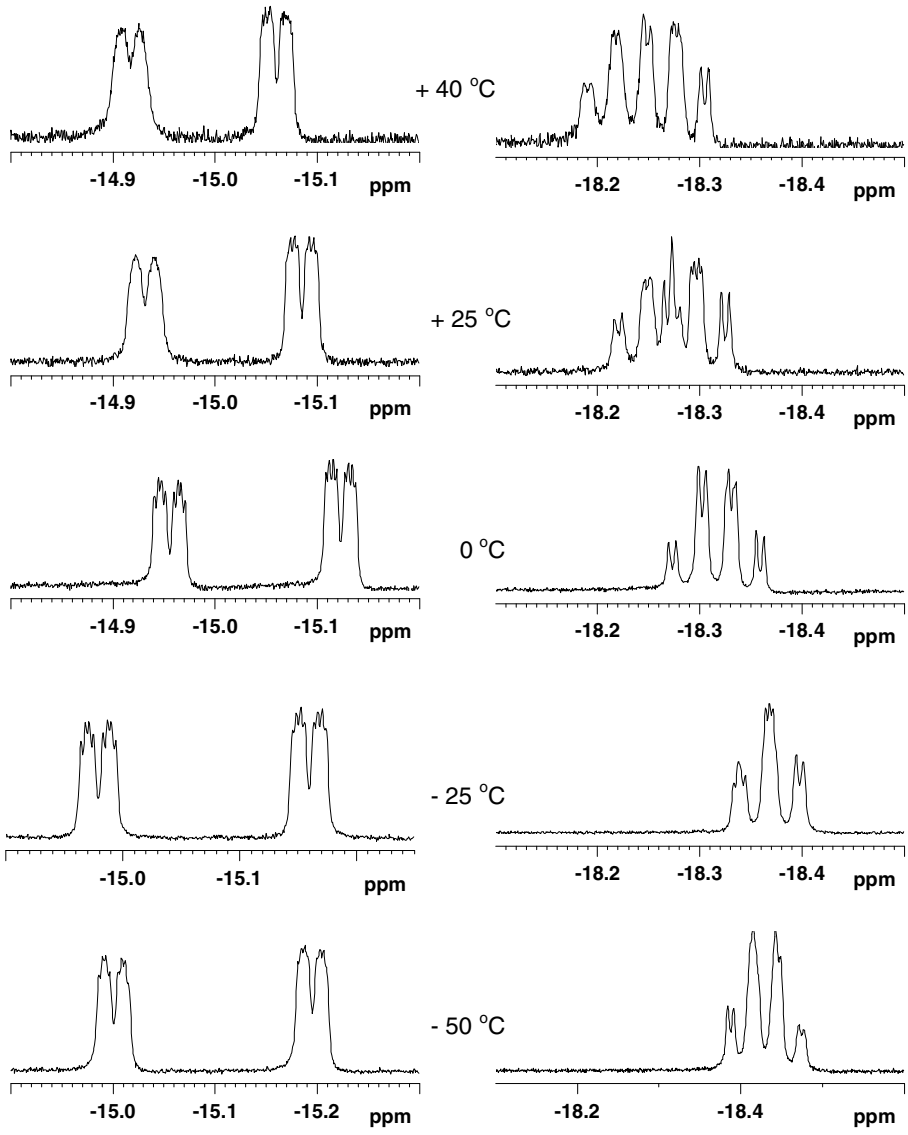
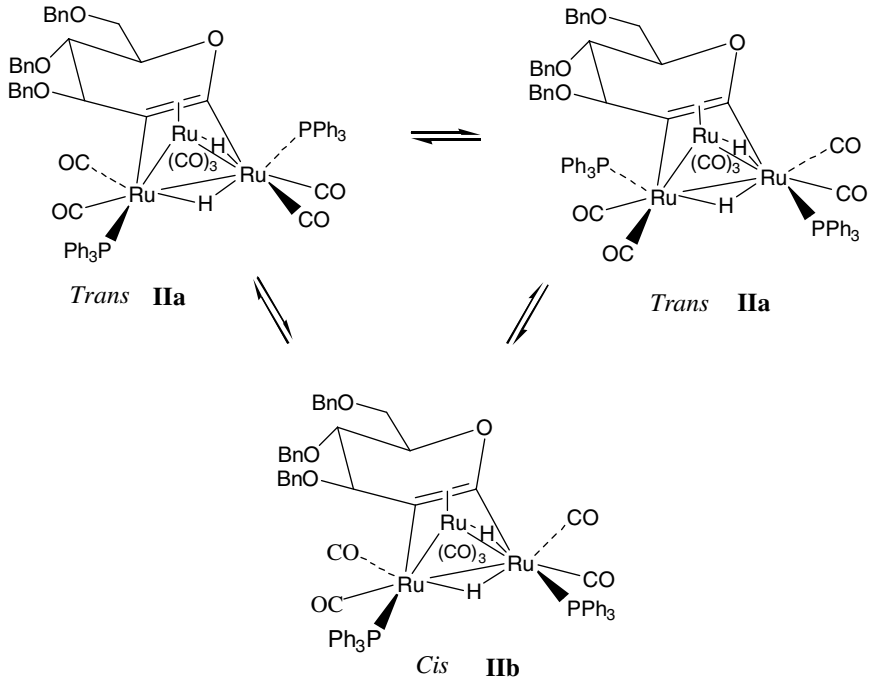


Fig. 3. Variable-temperature ^{1}H NMR spectra of compound **II** in the hydride region.

An unusual temperature-dependent ^{31}P NMR behavior of **II** in $(CD_3)_2CO$ at +40 °C shows two doublets at δ 34.5 and δ 40.4, respectively. The doublet at δ 34.5 gradually shifts to 35.3 as the temperature is lowered from +40 to −50 °C where as the other doublet at δ 40.4 remains the same throughout. At +40 °C, ^{31}P NMR shows two doublets centered at δ 34.5 (d, 1P, $^{3}J_{P-P}$ 16.7 Hz) and δ 40.4 (d, 1P, $^{3}J_{P-P}$ 16.9 Hz) with approximately equal intensity due to the *trans* isomer **IIa** (Scheme 3). At +25 °C a doublet at δ 40.4 collapses to a singlet and the other doublet (δ 34.5 at +40 °C) shifts to δ 34.7 ($^{3}J_{P-P}$ 29.1 Hz) with almost 1:1 integrated intensity. An interesting temperature-dependent degeneracy of ^{31}P NMR spectrum generates a singlet where two 'P' atoms are *trans* to two different ligands [14]. At 0 °C, a singlet reemerges to a doublet at δ 40.4 ($^{3}J_{P-P}$ 16.6 Hz) and the other doublet shifts to δ 34.8 ($^{3}J_{P-P}$ 50.7 Hz) with approximately 1:1 integrated intensity. At −25 °C, a doublet remains centered at δ 40.4 ($^{3}J_{P-P}$ 37.5 Hz) and the other doublet shifts to δ 35.1 ($^{3}J_{P-P}$ 76.6 Hz) with almost equal integrated intensity. At −50 °C, a doublet remains at δ 40.4 ($^{3}J_{P-P}$ 48.0 Hz) whereas the other doublet shifts to δ 35.3 ($^{3}J_{P-P}$ 116.6 Hz) with 1:1.3 intensity. The variable-temperature ^{31}P NMR suggests that the two-triphenylphosphine ligands are inequivalent due to their orientation, and the presence of mixture of two geometrical isomers *cis* and *trans* in the solution. Two geometrical isomers [11] are possible, one with two triphenylphosphine ligands in *anti* arrangement and the other with two triphenylphosphine ligands in *syn* arrangement (Scheme 3).

The temperature-dependence of ^{31}P NMR shifts is well documented and indeed has been used for measuring sample temperature in VT work; for example, the δ_p values for PPh_3 and $O=PPh_3$ change linearly with temperature [12]. Further, the temperature-dependence of the δ_p values for the dimetallic mixed-halide $ClPd(\mu\text{-DPPM})_2PdI$ [DPPM = bis(diphenylphosphino)methane] formed in situ varies with solvent, and the A_2B_2 pattern observed in $CDCl_3$ at −20 °C



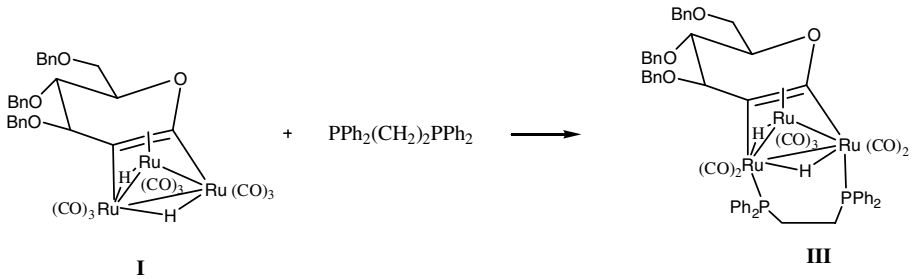
Scheme 3. Possible isomers of compound **II**, $Ru_3(CO)_7(\mu\text{-}H)_2(PPh_3)_2(L\text{-}H_2)$.

collapses to a singlet at 35 °C, and reemerges above 45 °C [13]. Similar behavior was observed for Ru(II)diphosphine/diiminecomplexes [14]. Similarly, in complex **II** (at +40 °C) a doublet centered at δ 40.4 collapses to a singlet at 25 °C and reemerges at 0 °C; the chemical shift of the doublet at +40 °C (δ 34.5) drifts towards the other doublet at δ 40.4 as the temperature is lowered to −50 °C (δ 35.4).

The complex ^1H NMR spectrum of **II** at room temperature in the hydride region is simplified to two-doublet of doublets in phosphorus decoupled $^1H\{^{31}P\}$ NMR spectra. The variable-temperature $^1H\{^{31}P\}$ NMR at +40 °C shows two-doublet of doublets with almost equal intensity centered at δ −15.00 ($^2J_{H-H}$ 2.40, 2.93 Hz) and δ −18.25 ($^2J_{H-H}$ 2.40, 2.93 Hz), indicating the presence of two isomers. One doublet of doublets is due to **IIa** and the other doublet of doublets is due to **IIb** (Scheme 3). At 0 °C the two-doublet of doublets shifts to δ −15.05 ($^2J_{H-H}$ 2.76, 2.76 Hz) and δ −18.30 ($^2J_{H-H}$ 2.79, 2.86 Hz), respectively. At −25 °C, the doublet of doublets shifts to δ −15.07 ($^2J_{H-H}$ 2.74, 2.80 Hz) and the other *doublet of doublets* collapses to a *doublet* at δ −18.35 ($^2J_{H-H}$ 2.64 Hz). At −50 °C, doublet of doublets shifts to δ −15.10 ($^2J_{H-H}$ 2.73, 2.75 Hz) and the other *doublet* reemerges to a *doublet of doublets* at δ −18.35 ($^2J_{H-H}$ 2.77, 2.61 Hz). A gradual shift to higher chemical shift values (+0.1 ppm) of the two-doublet of doublets was observed by lowering the temperature from +40 to −50 °C. The variable-temperature ^1H $\{^{31}P\}$ NMR suggests that the presence of two isomers in the solution (Scheme 3). The temperature-dependent proton coupled ^{31}P NMR spectra at +40 °C shows two broad resonances at δ 40.5 and δ 34.5, respectively. As the temperature is lowered from +40 to −50 °C the two broad peaks at +40 °C split into four broad peaks (−50 °C) suggesting the coupling of two hydrides to the two inequivalent phosphorus atoms.

Compound **II** was subjected to a high temperature ^1H, $^1H\{^{31}P\}$, ^{31}P NMR studies in CD_3CN and DMSO-d_6. No appreciable changes in NMR resonances were observed in CD_3CN from +20 to +70 °C and the compound was stable. Similarly, in DMSO-d_6 no appreciable changes were detected from +20 to +100 °C and at +120 °C, the compound decomposed. Efforts to observe broadening and merging of the resonances in the hydride region through high temperature NMR studies were unsuccessful and no resonances were observed at +120 °C.

Reaction of $Ru_3(\mu\text{-}H)_2(CO)_9(L\text{-}2H)$ (**I**) with diphenylphosphinoethane (dppe) at room temperature in methylene chloride produces an oily yellow new cluster $Ru_3(\mu\text{-}H)_2(CO)_7(L\text{-}2H)(dppe)$ (**III**) (Scheme 4). Compound **III** was purified by preparative thin layer chromatography with dichloromethane/hexanes (1:1). Compound **III** has been characterized by a combination of infrared and NMR spectroscopy, mass spectrometry, and elemental analysis. The FT-IR spectrum in dichloromethane exhibits terminal CO (1900–2100 cm^{-1}) stretching frequencies at 2080(w), 2061 (s), 2047(s), 2028(s), 2003(vs), 1982 (m), 1975(m) cm^{-1}. ^1H NMR spectrum of **III** in $CDCl_3$ shows signals corresponding to all of the hydrogens in the organic region as in **I**, the hydrogens due to the dppe ligand, and the two bridging hydride ligands coupled to phosphorus atoms in the high field region. The triplet at δ −20.62 indicates the bridging hydride ligand between the two equivalent phosphorus nuclei and the doublet at δ −16.05 is due to the bridging hydride ligand coupled to a phosphorus atom [7]. FAB+ mass spectrum shows a



I III

Scheme 4. Synthesis of $Ru_3(CO)_7(\mu\text{-}H)_2(dppe)(L\text{-}H)_2$, **III**.

molecular ion peak at 1315. Actual isotopic distribution for M^+ ion is in good agreement with the theoretical isotopic distribution. Elemental analysis confirms the molecular formula $C_{60}H_{52}O_{11}P_2Ru_3$. Found: C, 58.96, H, 4.06. Calcd. C, 58.83, H, 3.99%. The spectroscopic data obtained for **III** is consistent with the structure shown in Scheme 4.

3. Conclusion

In conclusion, three new chiral clusters $Ru_3(\mu\text{-}H)(\mu\text{-}H)(CO)_9(L\text{-}2H)$ (**I**), $Ru_3(\mu\text{-}H)(\mu\text{-}H)(CO)_7(L\text{-}2H)(PPh_3)_2$ (**II**) and $Ru_3(\mu\text{-}H)_2(CO)_7(L\text{-}2H)(dppe)$ (**III**) have been synthesized and characterized. The fluxional process of two-hydride ligands migrating over all three edges of the triruthenium skeleton has been shown by variable-tempe- rature ^1H NMR spectra for compound **I**. Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}H)(CO)_9(L\text{-}2H)$ (**I**) with triphenylphosphine gives a new cluster $Ru_3(\mu\text{-}H)(\mu\text{-}H)(CO)_7(L\text{-}2H)(PPh_3)_2$ (**II**), and a known cluster $Ru_3(CO)_9(PPh_3)_3$. Compound **I** reacts with diphenylphosphinoethane to give $Ru_3(\mu\text{-}H)_2(CO)_7(L\text{-}2H)(dppe)$ (**III**). The solution structures of compound **I**and **II** were studied by NMR spectroscopy.

4. Experimental

4.1. General procedures

All operations were carried out under pure argon or nitrogen with the use of Schlenk techniques, but subsequent work-up was in air. The solvents were purified and distilled under argon or nitrogen atmosphere. Flash column chromatography was performed on silica gel 60 (200–400) using the indicated solvent. Preparative thin layer chromatography was carried out using silica gel plates with plastic backs.

Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer as dichloromethane solution in 0.1 mm path length NaCl cells, ^1H NMR spectra were recorded at 400 MHz, and Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz. NMR Spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ and referenced either to internal TMS or the residual solvent peak. The ^{31}P (162 MHz) chemical shifts reported based on an internal calculation using the solvent lock signal. FAB+ mass spectra and positive electron spray spectra were recorded on a VG analytical ZAB-SE and Q-TOF Mass Spectrometers at University of California, Riverside. The observed isotopic distribution is in good agreement with the calculated ones. Elemental analysis was carried out using a Carlo Erba automatic analyzer from Quantitative Technologies Inc., New Jersey.

4.2. Synthesis of *I*: $[Ru_3(CO)_9(C_{27}H_{28}O_4)]$

To a two-necked 50-mL round bottom flask were added $Ru_3(CO)_{12}$ (639.34 mg, 1.0 mmol) and 3,4,6-tribenzyl-D-glucal (416.12 mg, 1.0 mmol) followed by 15 mL of benzene under argon atmosphere, and gently refluxed for 4 days. Benzene was removed in vacuo and the residue subjected to chromatographic work-up on a silica gel TLC plates or by flash column chromatography. Elution (silica gel TLC) with hexanes and dichloromethane (1:1) gave a yellow band. Flash column chromatography was performed by elution with hexanes and dichloromethane (2:1) gave a yellow compound. Yield. 217 mg (22.3%). FT-IR (CH_2Cl_2): 2107(m), 2080(vs), 2054(vs), 2041(s, sh), 2012(s, br) cm^{-1}. ^1H NMR: ($CDCl_3$) δ 7.30(m, 15H), δ 4.83(d, 1H), 4.71–4.51(m, 5H), δ 4.48(q, 1H), 3.91–3.77(m, 4H), −18.33(s, br, 1H); ^{13}C NMR: ($CDCl_3$) δ 206.4, 197.5, 192.7, 192.0, 138.3, 138.0, 137.7, 134.0, 130.0 128.7, 128.6, 128.4, 128.2, 128.1,127.9, 127.8,127.7,121.3, 83.1, 79.5, 73.7, 73.473.3,68.8, 62.9. FAB+ mass spectrum: 972 $[M]^+$, 888 $[M-3CO]^+$, 860 $[M-4CO]^+$, 832 $[M-5CO]^+$, 804 $[M-6CO]^+$, 776 $[M-7CO]^+$, 748 $[M-8CO]^+$, and 720 $[M-9CO]^+$, 718 $[M-(9CO+2H)]^+$, 516 $[M-(9CO+2H+2Ru)]^+$, 415 $[M-(9CO+3Ru)]^+$. Analytical calculated for $C_{36}H_{28}O_{13}Ru_3$, C, 44.49, H, 2.90. Found: C, 44.75, H, 3.06%.

4.3. Synthesis of *II*: $[Ru_3(CO)_7(PPh_3)_2(C_{27}H_{28}O_4)]$

To a two-necked 50-mL round bottom flask were added compound **I** (47.6 mg, 0.049 mmol) and triphenylphosphine (38.56. mg, 0.147 mmol) followed by 2.0 mL of dry methylene chloride under an argon atmosphere, and gently refluxed for 12 h or stirred at room temperature for 4 days. Methylene chloride was removed in vacuo and the residue subjected to chromatographic work-up on a silica gel TLC plates. Elution (silica gel TLC) with hexanes and dichloromethane (2:3) gave a red band 1 and a yellow band 2.

Red band 1: yield = 18.2 mg (25.7% based on **I**), identified as $Ru_3(CO)_9(PPh_3)_3$ by comparison of its IR spectrum ν(CO) [5], ^{1}H NMR, ^{31}P NMR and FAB-MS mass spectrum.

Yellow band: yield = 15 mg (21.2% based on **I**). FT-IR (CH_2Cl_2): 2080(w), 2060(vs), 2047(s), 2032(vs), 2002(vs, sh), 1984 (vs, br), 1944(m) cm^{-1}. ^{1}H NMR: ($CDCl_3$) δ 7.20–7.60(m, 45H), δ 5.10(d, 1H), 4.85–4.50(m, 5H), δ 4.35(q, 1H), δ4.10–3.40(m, 4H), δ −15.0(ddd, 1H), δ −18.30(m, 1H); ^{31}P NMR ($CDCl_3$) at 40 °C: δ 40.46(d), δ 34.50(d), δ 34.53(s); FAB+ mass spectrum: 1440 $[M]^+$, 1412 $[M - CO]^+$, 1356 $[M - 4CO]^+$, 1328 $[M - 5CO]^+$, 1300 $[M - 6CO]^+$, 1038$[M - (6CO + PPh_3)]^+$,1010$[M - (7CO + PPh_3)]^+$, 916$[M - (PPh_3)_2]$, 832 $[M - \{3CO + (PPh_3)_2\}]$, 748$[M - \{7CO + (PPh_3)_2\}]$. Electron Spray: 1440 $[M]^+$. Analytical calculated for $C_{70}H_{58}O_{11}P_2Ru_3$, C, 58.37, H, 4.06. Found: C, 58.11, H, 3.84%.

4.4. Synthesis of *III*: $[Ru_3(CO)_7(dppe)(C_{17}H_{28}O_4)]$

To a two-necked 50-mL round bottom flask were added compound **I** (40.0 mg, 0.041 mmol) and diphenylphosphinoethane (33.60 mg, 0.084 mmol) followed by 1.5 mL of dry methylene chloride under argon atmosphere, and stirred at room temperature for 7 days. The reaction was monitored everyday and methylene chloride was added to maintain the volume 1.5 mL. Methylene chloride was removed in vacuo and the residue subjected to chromatographic work-up on a silica gel TLC plates. Elution (silica gel TLC) with hexanes and dichloromethane (1:1) gave a yellow band. Yield = 24 mg (44.4% based on **I**). FT-IR (CH_2Cl_2): 2080(w), 2061(s), 2047(s), 2028(s), 2003(vs), 1982 (m), 1975(m) cm^{-1}. ^{1}H NMR: ($CDCl_3$) δ 7.01–7.98(m, 35H), 4.80–4.49(m, 4H), δ 4.28–3.15(m, 7H), δ 2.71(m, 2H), δ 2.05(m, 2H), δ −16.05(d, 1H), δ −20.62(t, 1H); ^{31}P NMR ($CDCl_3$): δ 45.70(m), δ 38.05(m); FAB+ mass spectrum: 1315 $[M]^+$, 1201 $[M - 4CO–2H]^+$, 1145 $[M - 6CO]^+$. Analytical calculated for $C_{60}H_{52}O_{11}P_2Ru_3$, C, 58.83, H, 3.99. Found: C, 58.96, H, 4.04%.

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Appendix A. Supplementary data

^{1}H NMR and ^{13}C NMR for compound **I**, Variable-temperature ^{1}H{^{31}P} NMR, ^{31}P NMR, and ^{1}H coupled ^{31}P NMR for compound **II**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.018.

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