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Journal of Organometallic Chemistry 691 (2006) 224–228
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Ruthenium carbonyl clusters derived from pyrazolyl substituted diphosphazanes: Crystal and molecular structure of a triruthenium cluster featuring a triply bridging μ_3-η^1:η^1:η^1 coordination mode of pyrazolate moiety ☆

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Received 14 February 2005; accepted 28 June 2005
Available online 4 October 2005

Abstract

The radical initiated reactions of $Ru_3(CO)_{12}$ with pyrazolyl substituted diphosphazanes $Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5) [R = (*S*)-*CHMePh (**1**) or $CHMe_2$ (**2**)] proceed via P–N(pyrazole) bond rupture resulting in the formation of phosphido clusters, $[Ru_3(CO)_5(\mu_{sb}$-$CO)_2(\mu_3$-N,N′-η^1:η^1:η^1-$N_2C_3HMe_2$-3,5){μ-P,P′-$Ph_2PN(R)PPh$}] [R = (*S*)-*CHMePh (**3**) or $CHMe_2$ (**4**)]. The pyrazolate moiety adopts an unusual triply bridging μ_3-η^1:η^1:η^1-mode of coordination in these clusters.

Keywords: Ruthenium carbonyl clusters; P–N ligands; Phosphane–phosphido clusters, Chirality; μ_3-η^1:η^1:η^1-Pyrazolyl coordination

1. Introduction

There has been an increasing interest in the area of metal clusters in recent years for a variety of reasons, especially the use of metal clusters in catalysis [1]. Homogeneous catalysis by metal clusters holds great promise as it has the advantage of cooperative effects of several metal atoms held in close proximity to each other. The reactivity and selectivity of the cluster catalysts can be altered by appropriate ligand design. The synthesis of a large number of metal carbonyl clusters bearing a variety of ligands and the use of some of these clusters in homogeneous catalysis are well documented [1–3]. A major impediment in the reactions of metal carbonyl clusters with various ligands is cluster degradation; use of bidentate ligands of the type L–X–L (where L carries a group 14, 15 or 16 donor atom and X is C, N or O) can obviate this difficulty to a large extent [1].

Recently, we have reported the synthesis and characterization of ruthenium carbonyl clusters of diphosphazanes bearing axially chiral 1,1′-binaphthylene-2,2′-dioxy moiety [4], and found that the cluster nuclearity is preserved by diphosphazanes containing a strong π-acceptor phosphorus and also bearing sterically bulky substituents. We have also reported the chalcogen bridged ruthenium carbonyl clusters derived from diphosphazane mono- and dichalcogenides [5]. In an attempt to prepare chiral clusters bearing a stereogenic phosphorus centre, and in continuation of our research program on the organometallic chemistry of diphosphazane ligands [6], we report here the reactions of pyrazolyl substituted diphosphazanes $Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5) [R = (*S*)-*CHMePh (S_CR_P)-(**1**) or $CHMe_2$ (**2**)] with $Ru_3(CO)_{12}$.

☆ Part 24 of the series "Organometallic chemistry of diphosphazanes"; for Part 23, see [5b].

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doi:10.1016/j.jorganchem.2005.06.047

2. Experimental

2.1. General

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen prior to use. The NMR spectra (^{1}H, ^{31}P{^{1}H}) were recorded in $CDCl_3$ at 298 K using Bruker Avance-400 MHz spectrometers. IR spectra were recorded using a Bruker FT-IR spectrometer as a thin film on a KBr disk. Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyser. Melting points were recorded in a Buchi B-540 melting point apparatus and were uncorrected. The ligands (S_CR_P)-**1** [7] and **2** [8] were prepared by previously reported procedures. Me_3NO (Aldrich) and $Ru_3(CO)_{12}$ (Strem Chemicals) were used as received.

2.2. $Ru_3(CO)_5(\mu_{sb}\text{-}CO)_2\{\mu_3\text{-}N,N'\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_2C_3HMe_2 3,5\}\text{-}\{\mu\text{-}P,P'\text{-}Ph_2PN(R)PPh\}]$ (**3**, **4**)

To a solution of $Ru_3(CO)_{12}$ (0.050 g, 7.82×10^{-5} mol) in THF (6 cm^3) were added a few drops of Bruce catalyst [9] using a syringe until the solution darkened. Immediately the ligand (0.040 g of **1** or 0.035 g of **2**, 7.82×10^{-5} mol) was added. The resulting solution was heated under reflux for 2 h. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture revealed the presence of several products. Solvent was evaporated from the reaction mixture in vacuo to obtain a dark colored residue. The residue was dissolved in dichloromethane (2 cm^3) and subjected to chromatographic separation by thin layer chromatography over silica gel using CH_2Cl_2/petrol (1:1 v/v) as eluant. The red orange band at $R_f = 0.70$ was isolated and the product extracted into dichloromethane. Evaporation of the solvent afforded a dark red residue which was crystallized from dichloromethane–petrol to yield the compounds, [Ru_3-$(CO)_5(\mu_{sb}$-$CO)_2\{\mu_3$-N,N'-η^1:η^1:η^1-$N_2C_3HMe_2$-3,5$\}\{\mu$-P,P'-$Ph_2PN(R)PPh\}$] [R = (*S*)-*CHMePh (**3**) or $CHMe_2$ (**4**)] as dark red orange solids. Efforts to isolate the other product(s) from the reaction mixture were unsuccessful.

2.3. $Ru_3(CO)_5(\mu_{sb}\text{-}CO)_2\{\mu_3\text{-}N,N'\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_2C_3HMe_2 3,5\}\text{-}\{\mu\text{-}P,P'\text{-}Ph_2PN(R)PPh\}]$ (R = (*S*)-*CHMePh)-{(S_CR_P)-(**3a**) and (S_CS_P)-(**3b**)}

Yield: 0.008 g (10%). Anal. Calc. for $C_{38}H_{31}N_3O_7P_2Ru_3$: C, 45.3; H, 3.1; N, 4.2; Found: C, 44.7; H, 3.1; N, 4.0%. M.p. 181–183 °C (d). IR (neat, ν_{CO} cm^{-1}): 2040(w), 2025(m), 1991(vs), 1976(w), 1953(sh), 1930(w), 1892(w, br), 1791(s, br, μ_{sb}-CO). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) for **3a** and **3b**: **3a** (major diastereomer) 5.27 (s, C*H*, $N_2C_3HMe_2$-3,5), 3.90 (m, C*H*, CHMePh), 1.59, 1.46 (s, CH_3, $N_2C_3HMe_2$-3,5), 1.44 (d, ^3J(H,H) = 7.0 Hz, CH_3, CHMePh); **3b** (minor diastereomer) 5.23 (s, C*H*, $N_2C_3HMe_2$-3,5), 4.20 (m, C*H*, CHMePh), 1.38 (s, CH_3, $N_2C_3HMe_2$-3,5), 1.33 (d, ^3J(H,H) = 7.0 Hz, CH_3, CHMePh). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) for **3a** and **3b**: **3a** (major diastereomer) 333.4 (d, ^2J(P,P) = 43.6 Hz, PPh), 76.0 (d, PPh_2); **3b** (minor diastereomer) 333.9 (d, ^2J(P,P) = 43.6 Hz, PPh), 72.7 (d, PPh_2).

2.4. $Ru_3(CO)_5(\mu_{sb}\text{-}CO)_2\{\mu_3\text{-}N,N'\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_2C_3HMe_2 3,5\}\text{-}\{\mu\text{-}P,P'\text{-}Ph_2PN(R)PPh\}]$ (R = $CHMe_2$) (**4**):

Yield: 0.009 g (12%). Anal. Calc. for $C_{33.5}H_{32}N_3O_8P_2Ru_3Cl$: C, 40.0; H, 3.2; N, 4.2; Found: C, 39.2; H, 2.6; N, 4.3%. M.p 186–188 °C (d). IR (neat, ν_{CO} cm^{-1}): 2042(s), 1990(vs), 1976(w, sh), 1957(w, br), 1929(m), 1887(m, br), 1793(s, br, μ_{sb}-CO). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.28 (s, C*H*, $N_2C_3HMe_2$-3,5), 3.30 (m, C*H*, $CHMe_2$), 1.63, 1.43 (s, CH_3, $N_2C_3HMe_2$-3,5), 0.95, 0.80 (d, ^3J(H,H) = 7.0 Hz, CH_3, $CHMe_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): 331.3 (d, ^2J(P,P) = 43.0 Hz, PPh), 69.0 (d, PPh_2).

2.5. X-ray crystallography

The crystal was mounted on a glass fibre and the intensity data was obtained at room temperature from a Bruker SMART APEX CCD diffractometer equipped with fine focus 1.75 kW sealed tube Mo Kα X-ray source with increasing ω (width of 0.3°/frame) at a scan speed of 5 s/frame. The SMART [10a] software was used for cell-refinement and data acquisition and the SAINT [10b] software was used for data reduction. Lorentzian and polarization corrections were made on the intensity data. An absorption correction was made on the intensity data using the SADABS [10c] program. The structure was solved using SHELXTL [10d] and the WINGX graphical user interface [11]. Least-square refinements were performed by the full-matrix method with SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically and were fixed at idealised positions. The carbon atom C(21) attached to C(19) was disordered over two sites and was modelled with 50:50 occupancy. Hence, the hydrogen atom bound to C(19) was not fixed. The lattice held water and the solvent dichloromethane molecules were refined separately during final refinement cycles. The carbon and chlorine atoms of the solvent dichloromethane were refined isotropically. The hydrogen atoms of the lattice held dichloromethane and water were not located.

3. Results and discussion

In contrast to the reactivity of diphosphazanes reported earlier [4], the unsymmetrical pyrazolyl substituted diphosphazanes $Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5) [R = (*S*)-*CHMePh (S_CR_P)-(**1**), $CHMe_2$ (**2**)] display a different type of reactivity towards $Ru_3(CO)_{12}$. The reaction of $Ru_3(CO)_{12}$ with an equimolar quantity of the diphosphazane **1** or **2** in the presence of benzophenone-ketyl radical in boiling THF results in the formation of several products from

which the phosphido clusters, $[Ru_3(CO)_5(\mu_{sb}\text{-}CO)_2(\mu_3\text{-}N,N'\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_2C_3HMe_2\text{-}3,5)\{\mu\text{-}P,P'\text{-}Ph_2PN(R)PPh\}]$ [R = (*S*)-*CHMePh (**3**) or $CHMe_2$ (**4**)] could be isolated in low yields after chromatographic separation (Scheme 1). These clusters have been characterized by elemental analyses, IR and NMR (^1H and $^{31}P\{^1H\}$) spectroscopic techniques. The molecular structure of **4** has been determined by single crystal X-ray crystallography [13]. Evidently, P–N(pyrazolyl) bond has cleaved to give phosphido and pyrazolate moieties which bind to the Ru centres. The infrared spectrum of the cluster **3** or **4** displays bands in the region 2042–1790 cm^{-1}. The band at 1790 cm^{-1} is assigned to the semi-bridging carbonyl ligand. The $^{31}P\{^1H\}$ NMR spectrum of cluster **4** displays an AX spin system. The "PPh_2" phosphorus appears as a doublet at 69.0 ppm while the "PPh" phosphorus resonates very much downfield at 331.3 ppm. The chemical shift of PPh_2 phosphorus is very much downfield shifted compared to the free ligand. The reaction of the diastereomerically pure diphosphazane (S_CR_P)-Ph_2PN((*S*)-*CHMePh)PPh ($N_2C_3HMe_2$-3,5) (**1**) with $Ru_3(CO)_{12}$ gives a mixture of two diastereomeric clusters, **3a** and **3b**. The formation of two diastereomers arises due to P–N bond rupture, which can lead to either retention (R_P) or inversion (S_P) of configuration at the phosphorus. Tentatively, the major diastereomer **3a** is assigned the S_CR_P configuration and the minor diastereomer **3b** the S_CS_P configuration. The $^{31}P\{^1H\}$ NMR spectrum of the mixture consists of two AX spin systems. The "PPh" phosphorus of the major and minor diastereomers appear at 333.4 and 333.9 ppm, respectively while the resonances at 76.0 and 72.7 ppm are assigned to the "PPh_2" phosphorus of the major and minor diastereomers respectively. The ^1H NMR spectrum displays two sets of resonances corresponding to the two diastereomers. From the relative integrated intensities of the two sets of signals in the ^1H and ^{31}P NMR spectra of the reaction mixture, we can estimate that the two diastereomers are formed in the ratio 1.0:2.2. Attempts to separate the diastereomers were unsuccessful.

The structure of **4** has been determined by a single crystal X-ray diffraction study (Fig. 1). The compound crystallises in the space group *C*2/*c*. The molecule has a triangular arrangement of three ruthenium atoms bearing a triply bridging pyrazolate group, two semi-bridging carbonyl ligands and a diphosphorus species in both chelating and bridging mode of coordination. One of the nitrogen atoms of the pyrazolate group is bonded to one ruthenium while the other nitrogen atom is bonded to the other two ruthenium centres. To our knowledge, such a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ mode of coordination of a pyrazolate ligand has been observed previously only in two instances, viz for a thallium complex and a trinuclear rhenium complex [14]. This unusual feature may be contrasted with the common $\mu\text{-}\eta^1\text{:}\eta^1$ and the other less-common ($\mu\text{-}\eta^1\text{:}\eta^2$, $\mu\text{-}\eta^2\text{:}\eta^2$, $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1$, etc.),

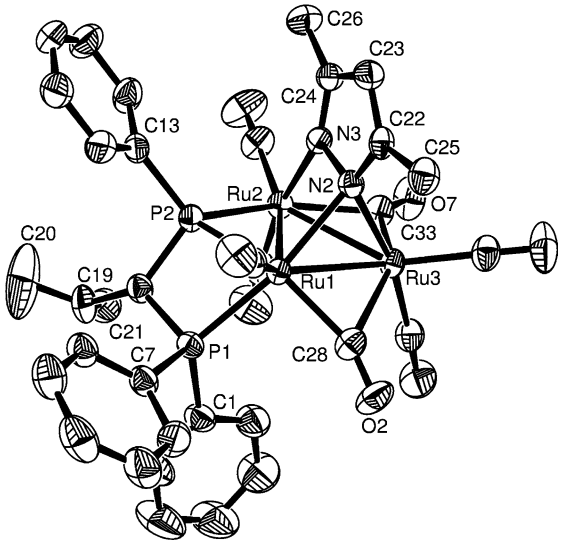
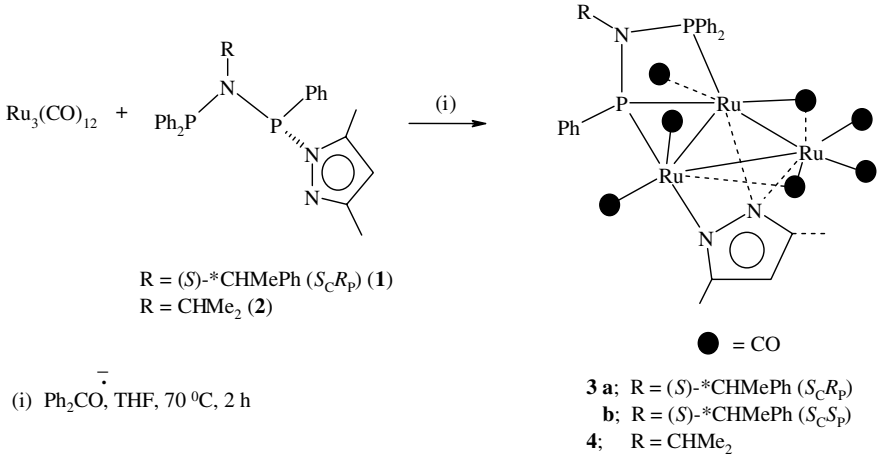


Fig. 1. Molecular structure of $[Ru_3(CO)_5(\mu_{sb}\text{-}CO)_2(\mu_3\text{-}N,N'\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_2C_3HMe_2\text{-}3,5)\{\mu\text{-}P,P'\text{-}Ph_2PN(CHMe_2)PPh\}]\cdot 0.5\ CH_2Cl_2\cdot H_2O$ (**4**). Thermal ellipsoids are shown at 30% probability level. The carbon atom C(21a), lattice held solvent molecules (dichloromethane and water) and the hydrogen atoms are not shown for clarity.



Scheme 1. Reaction of pyrazolyl substituted diphosphazanes, $Ph_2PN(R)PPh(N_2C_3HMe_2\text{-}3,5)$ with $Ru_3(CO)_{12}$.

bridging modes of binding observed in pyrazolate coordination chemistry [15,16]. The pyrazolate group in **4** is inclined at an angle of 80.1(2)° to the triruthenium plane and the two nitrogen atoms of this group are at a distance of 1.716(4) and 1.957(4) Å from the Ru_3 plane. The phosphido phosphorus atom of the bidentate diphosphorus ligand occupies the equatorial position and is coordinated to two ruthenium centres. The "PPh_2" phosphorus occupies a pseudo-axial position. The span angle of the "P–N–P" backbone is 99.3(2)° and the bite angle at Ru(1) is 69.03(5)°. The coordination geometry around Ru(2) and Ru(3) ruthenium centres can be regarded as distorted octahedral. All the Ru–Ru bond distances are different. The longest Ru–Ru bond [2.916(2) Å] is the one that bears the bidentate ligand; the phosphido phosphorus is doubly coordinated to these two ruthenium centres. The Ru(1)–P(1) distance is 0.042 Å shorter than Ru(1)–P(2) and Ru(2)–P(2) distances (ave. dist. = 2.326(2) Å). The P(2)–N(1) distance is slightly longer than P(1)–N(1) distance. Two CO ligands adopt a semi-bridging mode of coordination; both of them are located at the two Ru–Ru edges [Ru(1)–Ru(3), Ru(2)–Ru(3)] which are not bridged by the diphosphorus ligand. The individual molecules in the crystal lattice are held together by intermolecular hydrogen bonding involving the hydrogen atoms of the phenyl groups and the oxygen atoms of the carbonyl ligand [the C–H···O non-bonded distances and C–H···O angles lie in the range 2.497(5)–2.883(6) Å and 120.2(4)–174.0(6)°, respectively].

It has been noted earlier that diphosphazane ligands such as $Ph_2PN(R)PPh_2$ (R = $CHMe_2$ or (*S*)-*CHMePh) in which the phosphorus centres have low π-acceptor capability do not stabilize triruthenium clusters [4]. Hence, the retention of the triruthenium cluster core in **4** (and also **3**) may be attributed to the presence of: (i) two π-accepting semi-bridging carbonyls [C(33)–O(7) and C(28)–O(2)] *trans* to the PPh phosphorus [P(2)–Ru(2)–C(33) = 153.7(1)°, P(2)–Ru(1)–C(28) = 153.1(2)°]; and (ii) a triply bridging pyrazolate *trans* to the PPh_2 phosphorus [P(1)–Ru(1)–N(2) = 163.5(2)°].

The cleavage of R_2P–X (X = C, N, S, P) bonds to generate phosphido ligands is well documented in the literature [17]. Particular mention may be made of the recent report by Simón–Manso et al. [17b] on the isolation and characterization of phosphido complexes of nickel by cleavage of the "P–N–P" backbone of the diphosphazane ligand $Ph_2PN(H)PPh_2$. In the present study, we find that the "P–N–P" backbone of the diphosphazane ligand is retained while P–N(pyrazolate) bond is ruptured to form a phosphido moiety bonded to the ruthenium carbonyl cluster framework. The generality of such a reaction with other P–N ligands remains to be investigated [18].

4. Supplementary material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-259131. Copies of the data can be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033); e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Acknowledgments

We thank the Department of Science and Technology, New Delhi, India for financial support and for the data collection using the CCD X-ray facility, IISc, Bangalore set up under IRHPA program.

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$R = 0.0887$, $R_w = 0.1213$; Largest diff. peak and hole, 1.192 and -0.766 e Å^{-3}.

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[18] The reaction of the diphosphazane monosulfide, $Ph_2(S)PN(CHMe_2)$-$PPh(N_2C_3HMe_2$-3,5) [8] with $Ru_3(CO)_{12}$ in the presence of TMNO also gives a phosphido cluster which is formulated as $[Ru_3(CO)_4$-$(\mu$-CO$)(\mu_3$-S$)\{\mu$-*P*,*P*′-$Ph_2PN(R)PPh\}(\mu_3$-*N*,*N*′-η^1:η^1:η^1-$N_2C_3HMe_2$-3,5$)]$ on the basis of IR {2048(s), 1981(vs), 1805(m, br)} and ^{31}P NMR {331.3 (d, ^2J(P,P) = 43.0 Hz, PPh), 69.0 (d, PPh_2)} spectroscopic data; such a cluster is formed as a result of P–N bond cleavage and oxidative sulfur transfer [5].