

Crystal Structure Characterization and Catalytic Application of Novel Route Prepared Ru₃(CO)₉ DPAM (Diphenyl Arsino Methane)-tri Phenyl Phosphine Derivatives

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Triruthenium dodecacarbonyl-Ru₃(CO)₁₂ based diphenylarsino methane-triphenyl phosphine derivatives, such as Ru₃(CO)₉-dpam-tris (methyl phenyl) phosphine (1), Ru₃(CO)₉dpam-tris (methoxy phenyl) phosphine (2), and Ru₃(CO)₉-dpamtris (fluro phenyl) phosphine (3) are synthesized by two step modified method. The catalytic hydrogenation of cyclohexene, styrene, and phenyl acetylene, on above mentioned Ru-based organometallic catalysts, has been studied under high pressure hydrogen atmosphere. The high pressure hydrogenation of cyclohexene and phenyl acetylene on Complex (1–3), showed good catalytic activity under pressurized condition. Hydrogenation of cyclohexene on Complex (3) showed better (50–65%) conversion in the presence of toluene than hexane solvent. The effect of temperature, role of solvent, and pressure conditions have also been studied.

Keywords catalytic hydrogenation, cyclohexene, Ru₃(CO)₁₂, styrene

INTRODUCTION

Triruthenium dodecacarbonyl (Ru₃(CO)₁₂) is a cluster compound that has an equilateral triangle of Ru atom with 12 terminal carbonyl groups, and it is a air-stable orange solid which is soluble in most of the organic solvents.^[1–3] The reactivity of Ru₃(CO)₁₂ has been recognized for a long time by its reaction towards halogens, thiols, phosphines, dienes, etc.^[4] The product of such a reaction with a ligand L is usually of the formula Ru₃(CO)₉L₃.^[3] The tri-substituted complex is unreactive towards small molecules because of steric factor. The mixed-ligand cluster carbonyls with group 15 donor ligands are unique because of their catalytic activity.^[5] The structure of Ru₃(C₂₆H₂₄AsP)(CO)₁₀ was synthesized using Ru₃(CO)₁₂ with Ph₂P(CH₂)₂AsPh₂ ligand, which is similar to $Ru_3(CO)_{10}[Ph_2P(CH_2)_2PPh_2]$.^[6] The previous study about mixed ligands was already conducted by using Rh complexes of (diphenyl arsino diphenyl phosphino) methane.^[7]

According to Sappa et al. (1972), the mono substituted trinuclear compounds of Ru₃(CO)₉ μ_{3-x} [where X = C₂(t-Bu) and $C_2(Ph)$] show that the cluster is stable due to the presence of phenyl acetylene and tert-butyl group which has a strong inductive effect.^[8] Homo- and hetero-metallic rutheniumcontaining carbonyl clusters are proved as an efficient catalyst for hydrogenation of alkynes^[9] and of cyclic dienes.^[10] The structure-reactivity relationships have been studied and reaction intermediates/by-products are isolated and characterized.^[11] In some instances, reaction mechanisms based on the nature of the above derivatives have been proposed.^[12] Ruthenium cluster compounds have been used as catalyst precursors in several catalytic reactions for example, carbonylation of alcohols, isomerization, hydrogenation of olefins,^[13-18] water gas shift reaction,^[19] and hydroformylation,^[20] especially in homogeneous catalysis. Reactivity tests under conditions, where cluster compounds might be expected to display catalytic activity, would provide useful information of their structure and reactivity after the catalytic reactions. Usually under carbon monoxide atmosphere, the simple metal carbonyl clusters tend to fragmentation to lower nuclearity carbonyl compound and in case of hydrogen atmosphere causes the cluster formation. The behavior is more complicated in the case of both fragmentation and formations of new hydride derivatives formation in presence of tri-metalic carbonyl complexes.^[21] Hydrogenation of phenyl acetylene and 3-phenylpropyne using Rh (diene) complexes under homogeneous and heterogeneous condition was reported.[22]

The present study deals with the structure and catalytic activity of newly synthesized *tri*-Ru-dpam derivatives. Hydrogenation of alkene (cyclohexene, styrene) and alkyene (phenyl acetylene), under high pressure conditions, on the synthesized complexes have been studied. The following three organometallic complexes (1)–(3) are characterized by single crystal XRD, and their catalytic properties were studied under high pressure hydrogenation conditions.

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EXPERIMENTAL

Single Crystal X-ray Diffraction Study

Determination of cell constants and data collection were carried out at 100.0(1) K, using the Oxford Cryosystem Cobra low-temperature attachment with Mo Ka radiation (k = 0.71073 Å) on a Bruker SMART APEX2 CCD area-detector diffractometer equipped with a graphite monochromator. The structure was solved by direct methods and refined against F2 by full-matrix least-squares, using SHELXTL.^[23] Hydrogen atoms were placed in calculated positions.

Synthesis of Complex 1

All manipulations were performed under a dry oxygenfree dinitrogen atmosphere using standard Schlenk techniques; all solvents were dried over sodium and distilled from sodium benzophenone ketyl under nitrogen. Tris (4-methylphenyl) phosphine was used as ligand and μ -bis (diphenylarsino) methane decacarbonyl triruthenium(0) (Bruce et al., 1982) was prepared by two step route.^[6] The title compound was obtained by refluxing equimolar quantities of Ru₃(CO)₁₀(μ -Ph₂AsCH2AsPh₂) (105.5 mg, 0.1 mmol) and tris (4-methylphenyl) phosphine (30.4 mg, 0.1 mmol) in hexane under a nitrogen atmosphere. Crystals suitable for X-ray diffraction were grown by slow solvent/solvent diffusion of CH₃OH into CH₂Cl₂.

Synthesis of Complex 2

All manipulations were performed under a dry oxygen-free dinitrogen atmosphere using standard Schlenk techniques, under nitrogen atmosphere. Tris (4-methylphenyl) phosphine was used as ligand, and μ -bis (diphenylarsino) methane decaarbonyl triruthenium(0) was prepared by two step route.^[25] The title compound was obtained by refluxing equimolar quantities of Ru₃(CO)₁₀(μ -Ph₂AsCH2AsPh₂) (105.5 mg, 0.1 mmol) and tris (4-methoxyphenyl) phosphine (32.23 mg, 0.1 mmol) in hexane under a nitrogen atmosphere. Crystals suitable for X-ray diffraction were grown by slow solvent/solvent diffusion of CH₃OH into CH₂Cl₂.

Synthesis of Complex 3

Tris (4-flurophenyl) phosphine and bis (diphenylarsino) methane (Strem chemicals) are used as received. $Ru_3(CO)_{10}(\mu$ -Ph₂AsCH₂AsPh₂) (105.5 mg, 0.1 mmol) and tris (4-flurophenyl) phosphine (31.62 mg, 0.1 mmol) were refluxed for 15 minutes in hexane (25 ml) under nitrogen atmosphere. Once the reaction mixture turned into intense red colour, the solvent was removed under vacuum. The reaction mixture was separated by TLC (dichloromethane: hexane, 30:70). Two bands are appeared. The major band (red) Rf = 0.56, yielded the title compound which was crystallized from CH₂Cl₂—CH₃OH.

Catalytic Activity Test

The stainless steel autoclave with inserted glass tube was used as pressurized vessel to study the catalytic activity. The



FIG. 1a. ORTEP diagram of Complex (1).

hydrogen pressure maintained between 20–60 bar for different conditions, temperature is fixed at 313 K for all reactions, solvent effect (pentane and toluene) studied at fixed reaction time of 5 hours. Conversion of the respective substrate was analyzed by gas chromatography, using SPB non-polar capillary column.

RESULTS AND DISCUSSION

Single Crystal X-ray Diffraction Study of Complex (1)–(3) Complex 1:

In the title triangulo-triruthenium compound, $[Ru_3(C_{25}H_{22} As_2)(C_{21}H21_P)(CO)_9]$, the bis (diphenylarsino) methane ligand bridges a Ru—Ru bond and the monodentate phosphine ligand bonds to the third Ru atom. Both the phosphine and arsine ligands are equatorial with respect to the Ru3 triangle. Additionally, each Ru atom carries one equatorial and two axial terminal carbonyl ligands. The three phenyl rings of the phosphine make



FIG. 1b. Crystal packing structure diagram of Complex (1).

dihedral angles of 86.89 (19)°, 82.1 (2)°, and 63.0 (2)° with each other. The dihedral angles between the two phenyl rings are 73.8 (2)° and 82.2 (3)°, for the two diphenylarsino groups (Fig. 1a). An intramolecular C–H–O hydrogen bond stabilizes the molecular structure. In the crystal packing, molecules are linked into chains down the *b*-axis via intermolecular C–H–O hydrogen bonds.

The bond lengths and angles of title compound (Fig. 1a) are comparable to those in related structures (Shawkataly et al.2006, 2009a).^[24-26] The bis (diphenylarsino) methane ligand bridges the Ru1-Ru2 bond and the monodentate phosphine ligand bonds to the Ru3 atom. Both the phosphine and arsine ligands are equatorial with respect to the Ru3 triangle. Additionally, each Ru atom carries one equatorial and two axial terminal carbonyl ligands. The three phosphine substituted phenyl rings make dihedral angles (C26-C31/C32-C37, C26-C31/C38-C43, and C32–C37/C38–C43) of 86.89 (19)°, 82.1 (2)°, and 63.0 (2)° with each other respectively. The dihedral angles between the two phenvl rings (C1-C6/C7-C12 and C14-C19/C20-C25) are $73.8(2)^{\circ}$ and $82.2(3)^{\circ}$ for the two diphenylarsino groups respectively. An intramolecular C27-H27A····O9 hydrogen bond stabilizes the molecular structure. In the crystal packing (Fig. 1b), the molecules are linked together into chains via intermolecular C54—H54A···O2 hydrogen bonds along the *b*-axis (Fig. 1b).

Complex 2:

The asymmetric unit of the title triangulo-triruthenium compound, $Ru_3(C_{25}H_{22}As_2)(C_{20}H_{19}O_2P)(CO)_9]$ 0.15CH₂Cl₂, contains one molecule of the triangulo-triruthenium complex and one partially occupied dichloromethane solvent molecule. The dichloromethane solvent lies across a crystallographic inversion center, leading to the molecule being disordered over two positions of equal occupancy. The bis (diphenylarsino) methane ligand bridges an Ru—Ru bond, and the monodentate arsine ligand bonds to the third Ru atom. Both the arsine ligands are equatorial with respect to the Ru3 triangle. In addition, each Ru atom carries one equatorial and two axial terminal carbonyl ligands. The three phosphorus bound benzene rings make dihedral angles of 72.7 (3)°, 80.9 (3)°, and 70.8 (2)° with each other. The dihedral angles between the two benzene rings are 79.9 (3)° and 81.5 (2)° for the two diphenyl arsino groups (Fig. 2a).

The asymmetric unit consists of one molecule of the *triangulo*-triruthenium complex and a 15% partially occupied molecule of dichloromethyl solvent (Fig. 2a). The dichloromethyl solvent lies across a crystallographic inversion center, leading to the molecule being disordered over two positions of equal occupancy. The bond lengths and angles of title compound are comparable to those found in related structure (Shawkataly et al., 2009a).^[24–26] The bis (diphenylarsino) methane ligand bridges the Ru1—Ru2 bond and the monodentate arsine ligand bonds to the Ru3 atom. Both the arsine ligands are equatorial with respect to the Ru3 triangle. Additionally, each Ru atom carries one equatorial and two axial terminal carbonyl ligands. The three phosphine-substituted



FIG. 2a. ORTEP diagram of Complex (2).

benzene rings make dihedral angles (C26–C31/C32–C37, C26–C31/C38–C43, and C32–C37/C38–C43) of 72.7 (3)°, 80.9 (3)°, and 70.8 (2)° with each other respectively. The dihedral angles between the two benzene rings (C1–C6/C7–C12 and C14–C19/C20–C25) are 79.9 (3)° and 81.5 (2)° for the two diphenylarsino groups respectively. In the crystal structure, the molecules are stacked along the *b*-axis (Fig. 2b).



FIG. 2b. Crystal packing structure diagram of Complex (2).



FIG. 3a. ORTEP diagram of Complex (3).

Complex 3

In the title triangulo-triruthenium compound, $[Ru_3(C_{25}H_{22}-(As_2)(C_{18}H_{12}F_3P)(CO)_9]$, the bis(diphenylarsino) methane ligand bridges an Ru—Ru bond and the monodentate phosphine ligand bonds to the third Ru atom. Both the phosphine and arsine ligands are equatorial with respect to the Ru3 triangle. Additionally, each Ru atom carries one equatorial and two axial terminal carbonyl ligands. The three phosphine-substituted rings make dihedral angles of 87.76 (13)°, 57.43 (13)°, and 73.81 (12)° with each other. The dihedral angles between the pairs of rings are 69.78 (14)° and 83.38 (16)° for the two diphenylarsino groups (Fig. 3a). In the crystal packing, molecules are linked by intermolecular C—H—F and C—H—O hydrogen bonds, forming two-dimensional planes parallel to the *ab* plane. These planes are also linked by intermolecular C—H—O hydrogen bonds



FIG. 3b. Crystal packing structure diagram of Complex (3).

into a three dimensional framework. Intermolecular C—H interactions further stabilize the crystal structure.

The bond lengths and angles of the above compound (Fig. 3a) are comparable to its related structures (Shawkataly et al., 2006; Shawkataly et al., 2009a,b).^[24–26] The bis (diphenylarsino) methane ligand bridges the Ru1—Ru2 bond and

TABLE 1				
Unit cell parameters of as prepared three complexes				

Complex 1 F(000) = 2632[Ru3(C25H22As2) (C21H21P)(CO)9] Mr = 1331.91 $Dx = 1.652 \text{ Mgm}^{-3}$ Monoclinic, P21/c Mo $K\alpha$ radiation, $\lambda =$ 0.71073 Å Hall symbol: -P 2ybc Cell parameters from 9940 reflections $\theta = 2.3 - 26.0^{\circ}$ a = 16.2585 (2) Å b = 16.9247 (2) Å $\mu = 2.15 \text{ mm}^{-1}$ c = 19.6900 (2) ÅT = 296 K $\beta = 98.680 \, (1)^{\circ}$ Plate, red $V = 5356.05 (11) \text{ Å}^3$ $0.21 \times 0.21 \times 0.03$ mm Z = 4Complex 2 [Ru3(C25H22As2)(C20H19O2P) F(000) = 2689(CO)9]·0.15CH2Cl2 Mr = 1362.63 $Dx = 1.594 \text{ Mgm}^{-3}$ Mo $K\alpha$ radiation, $\lambda =$ Monoclinic, P21/c 0.71073 Å Hall symbol: -P 2ybc Cell parameters from 9029 reflections $\theta = 2.5 - 27.7^{\circ}$ a = 13.3723 (4) Å b = 16.9461 (6) Å $\mu = 2.04 \text{ mm}^{-1}$ c = 25.0956 (8) Å T = 296 K $\beta = 93.293 \ (2)^{\circ}$ Block, purple V = 5677.5 (3) Å3 $0.31 \times 0.21 \times 0.16$ mm Z = 4Complex 3 F(000) = 2632[Ru3(C25H22As2) (C18H12F3P)(CO)9] $Dx = 1.748 \text{ Mgm}^{-3}$ Mr = 1343.81Mo $K\alpha$ radiation, $\lambda =$ Monoclinic, P21/c 0.71073 Å Hall symbol: -P 2ybc Cell parameters from 9910 reflections a = 16.3071 (2) Å $\theta = 2.5 - 31.1^{\circ}$ b = 16.8142 (2) Å $\mu = 2.26 \text{ mm}^{-1}$ c = 18.8085 (2) ÅT = 296 K $\beta = 98.105 \ (1)^{\circ}$ Plate, red $V = 5105.6 (1) \text{ Å}^3$ $0.38 \times 0.25 \times 0.14 \text{ mm}$ Z = 4

the monodentate phosphine ligand bonds to the Ru3 atom. Both the phosphine and arsine ligands are equatorial with respect to the Ru3 triangle. Additionally, each Ru atom carries one equatorial and two axial terminal carbonyl ligands. The three phosphine substituted phenyl rings (C26–C31, C32–C37, and C38-C43) make dihedral angles (C26-C31/C32-C37, C26-C31/C38-C43, and C32-C37/C38-C43) of 87.76 (13)°, $57.43 (13)^{\circ}$, and $73.81 (12)^{\circ}$ with each other respectively. The dihedral angles between the two phenyl rings (C1-C6/C7-C12 and C14-C19/C20-C25) are 69.78 (14)° and 83.38 (16)° for the two diphenylarsino groups respectively. In the crystal packing (Fig. 3b), the molecules are linked by intermolecular C23—H23A…F3 and C34—H34A…O3 hydrogen bonds to form two-dimensional planes parallel to ab plane. These planes are further linked by intermolecular C42-H42A...O2 hydrogen bonds into a three-dimensional framework. Intermolecular C—H \cdots π interactions further stabilize the crystal structure. The unit cell parameters of as synthesized three complexes are shown in Table 1.

Catalytic Activity of Complex (1)–(3) for Hydrogenation of Alkenes and Alkyne Under High Pressure Conditions

The catalytic hydrogenation activity of complexes (1)–(3) is carried out under high pressure hydrogenated conditions. Preliminary test reactions were conducted using cyclohexene as model compound to study their hydrogenation activity by adopting suitable reaction conditions. Table 2 shows the catalytic hydrogenation of cyclohexene, phenyl acetylene, and styrene on complexes (1)–(3) respectively. The complex (3) such as trifluro derivative of ruthenium dodecacorbnyl showed the better (50-65%) activity towards hydrogenation of alkene and alkyne.

The complexes (1) and (2) show different activity toward phenyl acetylene and styrene hydrogenation due to their

 TABLE 2

 Catalytic activity of complex (1)–(3) for high pressure hydrogenation reactions

Catalyst	Substrate conversion (%)		
	Cyclohexene	Phenylacetylene	Styrene
Complex (1)	28	60	22
Complex (2)	45	25	54
Complex (3)	52	65	63

Reaction condition: substrate = 1 mL, solvent = 25 mL, catalyst = 2 mL (0.025g/50 mL toulene); pressure = 40bar; temperature = 313 K; reaction time = 5h

functional methyl and methoxy groups connected to the aromatic ring. Complex (1) showed higher (60%) conversion for phenyl acetylene and less conversion for cyclohexene. Complex (2) showed the effective conversion for alkene substrate (cyclohexene and styrene) for hydrogenation compared to phenyl acetylene conversion (Table 2). The functional group present in the phosphene derivative, attached to the dodeco ruthenium carbonyl, is playing a crucial role via electron transfer mechanism in hydrogenation process of cyclic olefins and phenyl acetylene.^[27] Figure 4 shows the bar diagram of catalytic hydrogenation of phenyl acetylene (PA) and styrene (ST) on complexes (1)–(3) at constant pressure. The trifluro phosphine derivative of tri ruthenium carbonyl complex (3) shows the effective catalytic conversion towards hydrogenation reaction compared to complexes (2) and (3). The electron withdrawing nature of the fluorinated Ph₃P-Ru₃(CO)₉ would weaken the cluster upon hydrogenation and favor the fragment catalysis.^[28] Whereas, complexes (1) and (2) show the vice versa effect on catalytic hydrogenation of PA and ST conversion with respect to the



FIG. 4. Cataytic hydrogeantion of Phenyl acetylene (PA) and Styrene (ST) on complexes (1)-(3) at 40 bar for 5 hour.



FIG. 5. Catalytic hydrogenation of Cyclohexene on complex (3) in different solvent and pressure conditions at fixed reaction time = 5h.

corresponding electron withdrawing and electron donating groups, attached to the tri ruthenium carbonyl complex (Table 2). Electron donating group (methyl) strengthens the ruthenium cluster, and it favors the cluster catalysis, whereas electron withdrawing group weakens the cluster and favors the fragmentation catalysis (methoxy).

Figure 5 shows the solvent effect for hydrogenation of cyclohexene in the presence of complex (3) catalyst, at different pressure condition with constant reaction temperature. The higher hydrogen solubility nature of toluene solvent showed higher conversion for cyclohexene conversion compared to hexane solvent. Increase in hydrogen pressure, increases the catalytic



FIG. 6. Catalytic hydrogenation of Phenyl acetylene and Styrene on complex(3) at different pressure condition and reaction time = 5h.

activity of the cluster *via* increase in more hydrogen consumption capacity. Figure 6 shows the PA and ST hydrogenation activity on complex (**3**), at different pressure conditions. The fluorinated phosphine derivative of tri ruthenium cluster shows the higher catalytic hydrogenation capacity for styrene with complete selectivity towards ethyl benzene formation. The straight forward fragmentation catalysis of complex (**3**) prefers to hydrogenate the C–C double bond in styrene. Whereas, in the case of phenyl acetylene, results in hindering the higher catalytic conversion. Hence, complex (**3**) showed slightly lesser activity for phenyl acetylene conversion compared to styrene (Figure 6).

CONCLUSION

Ru₃(CO)₉-dpam (diphenyl arsino methane) derivatives, such as complexes (1)–(3) are successfully synthesized by two step method. The single crystal X-ray diffraction study confirms their crystal structures. The complex (3) trifluro triphenyl derivative of Ru₃(CO)₉-dpam showed the effective conversion for alkenes and moderate conversion for alkyne, compared to other complexes(1) and (2). Higher hydrogenation activity was observed by tuning the reaction condition such as increasing the hydrogen pressure, adopting suitable toluene solvent in the presence of as prepared Ru-organometallic complexes.

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