

Reaction of a bulky phosphite with $[\text{Ru}_3(\text{CO})_{12}]$: The molecular structure of one of the decomposition products

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Abstract

Mono- and bis-substituted phosphite complexes $[\text{Ru}_3(\text{CO})_{12-x}\text{L}_x]$ (L = tris(2,4-di-*tert*-butylphenyl) phosphite; $x = 1, 2$) were synthesized by simple substitution reactions, and were characterized by spectroscopic methods. The monosubstituted ruthenium complex disproportionates in acetone producing a mononuclear ruthenium complex as one of the decomposition products. Single crystal X-ray diffraction analysis established the molecular structure of this new compound.

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1. Introduction

Transition metal carbonyl cluster compounds have been widely investigated in the past decades [1]. These complexes provide interesting scaffolds for organic substrates to adopt multi-center bonding that could be crucial for their subsequent reactivity. Diverse geometries with varying number of electron counts in these cluster complexes provide good platforms for a number of interesting transformations that may not be possible in mononuclear complexes. It is conceivable that the diverse transformations that are possible on metal cluster complexes make them good candidates as catalysts [2]. Apart from their potential application in homogeneous as well as heterogeneous catalysis, transition metal carbonyl clusters have generated interest in diverse areas such as materials science, etc. [3].

Substitution chemistry of the triangular metal complexes $[\text{M}_3(\text{CO})_{12}]$ (M = Fe, Ru, Os) have been studied in detail [4], and numerous phosphine substituted complexes of for-

mula $[\text{M}_3(\text{CO})_{12-x}\text{L}_x]$ ($x = 1-3$) have been synthesized and characterized [5]. Many of these phosphine substituted metal carbonyl complexes have been shown to display catalytic properties [6]. Although a large number of phosphine derivatives have been synthesized and their properties studied in detail, similar phosphite complexes are scarce.

Ligand modification is known to bring about interesting features in the resulting compounds [7], and the bulkiness of ligands, for example has been shown to direct the reaction pathways in many instances. We focused our interest first to investigate the reactivity of tris(2,4-di-*tert*-butylphenyl) phosphite (**1**) towards CO substitution in the triangular complexes $[\text{M}_3(\text{CO})_{12}]$ (M = Ru, Os). Herein, we report the synthesis and characterization of the above phosphite substituted complexes of triruthenium dodecacarbonyl complex.

2. Experimental

2.1. Reagents and general procedures

All syntheses of air and moisture sensitive compounds were performed using standard Schlenk techniques under

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prepurified N₂ [8]. Dichloromethane was pre-dried by passage over alumina (neutral, Brockmann grade I) and subsequently distilled over CaH₂ [9]. [Ru₃(CO)₁₂] (Strem), tris(2,4-di-*tert*-butylphenyl) phosphite (Aldrich), were used as received. Me₃NO (Aldrich) was sublimed prior to use.

NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer (¹H: 300 MHz, ¹³C: 75.5 MHz, ³¹P: 121.46 MHz) at ambient temperature, and were referenced relative to TMS (¹H and ¹³C) or 85% H₃PO₄ (³¹P), using the residual protonated impurities in the solvent (¹H NMR: CDCl₃: δ 7.27) or external 85% H₃PO₄ (³¹P). Infrared spectra were recorded in solution cells of sodium chloride windows (optical pathlength 0.1 mm) on a Perkin-Elmer 2000 FTIR spectrometer. Mass spectrometric analyses were carried out on a Finnigan LCQ Deca spectrometer. Elemental analyses were performed on a Vario Elemental Analyzer.

2.2. Reaction of [Ru₃(CO)₁₂] with P(O-2,4-*t*Bu₂C₆H₃)₃

A mixture of [Ru₃(CO)₁₂] (0.104 g, 0.162 mmol) and P(O-2,4-*t*Bu₂C₆H₃)₃ (**1**, 0.409 g, 0.632 mmol) was heated under reflux in dichloromethane (100 cm³) for 3 h. The color of the reaction mixture changed from light yellow to dark red during this time. After cooling, the mixture was left stirring overnight. The volatiles were removed *in vacuo* and the residue dissolved in minimum amount of hexane. A short silica gel column (1.5 cm × 10 cm) was used to separate the products formed. The major red fraction, which followed unreacted [Ru₃(CO)₁₂] and the phosphite ligand, was eluted using hexane and was identified as the monosubstituted product (**2**) using spectroscopic methods. After evaporation of the solvent, **2** was obtained as a dark red solid (0.110 g; 54%); ν_{CO}/cm⁻¹: 2084 (w), 2035 (s), 2013 (s), 2004 (s), 1989 (sh), 1948 (w), 1942 (w), 1813 (w); δ_H(CDCl₃, 300 MHz): 7.49 (d), 7.36 (d), 6.97 (dd), 1.54 (s), 1.26 (s); δ_C(H₁)(CDCl₃, 75.5 MHz): 204.4 (–CO), 148.1, 146.3, 138.1, 124.7, 123.3, 119.5 (Ar), 35.1 (–CMe₃), 34.1 (–CMe₃), 31.3 (–CMe₃), 30.5 (–CMe₃); δ_P(H₁)(CDCl₃, 121.46 MHz): 128; *m/z*(ES): 1260 (M⁺), (at least 6 clear peaks corresponding to CO losses were also observed).

The second, yellow band was eluted using 5% dichloromethane in hexane and was identified as the bis-substituted product (**3**). After evaporation of the solvent, **3** was obtained as a yellow powder (0.039 g, 13%); Ru₃C₉₄O₁₆P₂H₁₂₆ requires: C, 60.15; H, 6.77. Found: C, 60.28; H, 6.57%. ν_{CO}/cm⁻¹: 2084 (w), 2030 (m), 2017 (s), 1983 (w), 1948 (w), 1942 (w), 1813 (br, w); δ_H(CDCl₃, 300 MHz): number of overlapping signals observed between 7.93 and 7.00, 1.59, 1.57, 1.44, 1.28, 1.26, 1.19 (the signals observed between 1.59 and 1.19 are due to the methyl protons); δ_C(H₁)(CDCl₃, 75.5 MHz): aromatic signals observed between 170 and 110 ppm, the aliphatic signals were observed between 29 and 36 ppm; δ_P(H₁)(CDCl₃, 121.46 MHz): 148 (d), 126 (d); *m/z*(ES): 1877 (M⁺), (10 peaks corresponding to subsequent CO losses observed in the mass spectrum).

2.3. Reaction of **2** with acetone

In an attempt to recrystallize **2** from acetone, a large amount of black precipitate was formed, as well as well-shaped colourless needles. Single crystal X-ray diffraction of the compound revealed **4**.

Counter intuitively, recrystallisation of **3** from acetone did not result in the formation of **4**.

2.4. Structure determination

Crystals of [Ru(CO){P(O-2,4-*t*Bu₂C₆H₃)(O-2,4-*t*Bu₂C₆H₃)₂}(OH₂)(OC(CH₃)₂)]₂[O₂P(O-2,4-*t*Bu₂C₆H₃)₂] (**4**), were grown from acetone as described above. X-ray diffraction data for **4** were collected on a Bruker X8 APEX II diffractometer using Mo Kα (0.71073 Å) radiation with φ and ω-scans at 100(2) K. All reflections were merged and integrated using SAINT [10] and were corrected for Lorentz, polarization and absorption effects using SADABS [10]. The structures were solved by the direct method using SIR97 [11] and refined through full-matrix least-squares cycles using

Table 1
Crystal data and structural refinement for **4**

	4
Empirical formula	C ₇₇ H ₁₁₈ O ₁₁ P ₂ Ru
Formula weight	1382.72
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> 1
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	15.855(5)
<i>b</i> (Å)	16.153(5)
<i>c</i> (Å)	16.688(5)
<i>α</i> (°)	110.129(5)
<i>β</i> (°)	99.882(5)
<i>γ</i> (°)	94.148(5)
Volume (Å ³)	3913(2)
<i>Z</i>	2
<i>D</i> _{calc} (Mg/m ³)	1.173
Absorption coefficient (mm ⁻¹)	0.295
<i>F</i> (000)	1484
Crystal size (mm ³)	0.28 × 0.09 × 0.09
<i>θ</i> Range for data collection (°)	1.32–28.32
<i>Index ranges</i>	
	–21 ≤ <i>h</i> ≤ 21, –21 ≤ <i>k</i> ≤ 21, –22 ≤ <i>l</i> ≤ 22
Reflections collected	58442
Independent reflections [<i>R</i> _{int}]	19421 [0.0542]
Completeness to <i>θ</i> = 28.32°	99.7%
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.9739 and 0.9219
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	19421/14/900
Goodness-of-fit on <i>F</i> ²	1.080
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0452, <i>wR</i> ₂ = 0.1073
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0710, <i>wR</i> ₂ = 0.1271
Largest difference in peak and hole (e Å ⁻³)	0.887 and –0.555

the SHELXL 97 [12] software package with $\Sigma(|F_o| - |F_c|)^2$ being minimized. All non-H atoms were refined with anisotropic displacement parameters. Aromatic and methyl H atoms were placed in geometrically idealized positions (C–H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and $1.5U_{eq}(C)$ for methyl H atoms. The protons of the coordinated aqua moiety were located and refined from the Fourier difference map. The deepest residual electron-density hole ($-0.555 \text{ e } \text{Å}^{-3}$) is located 0.29 Å from H3A, and the highest peak ($0.887 \text{ e } \text{Å}^{-3}$) 1.39 Å from C77A. The acetone solvate molecule was modelled disordered over two positions with a 69.7/30.3% occupancy. The solvate molecule was restrained to keep the refinement stable.

The DIAMOND [13] Visual Crystal Structure Information System software was used for the graphics. Crystal data and details of data collection and refinement are given in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopy

Reaction of an excess of phosphite (**1**) with $[\text{Ru}_3(\text{CO})_{12}]$ in dichloromethane under reflux produced mono and bis substituted products (Scheme 1).

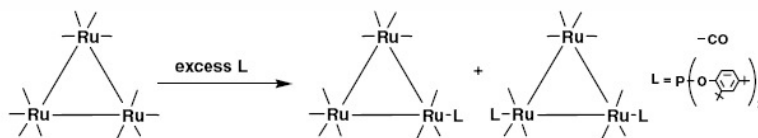
The two fractions collected were characterized by spectroscopic methods as well as by elemental analyses. IR spectroscopy of the first, red band, which is presumed to be the mono-substituted compound $[\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{OR})_3\}]$ (**2**) (R = 2,4-di-*tert*-butylphenyl) showed bands in the infrared spectrum that can be assigned as absorption due to terminal CO groups. The second, yellow, product (**3**) showed a simpler IR $\nu(\text{CO})$ spectrum.

The ^1H NMR spectrum of **2** consists of two sets of resonances due to the aromatic and aliphatic protons. As expected, three sets of resonances are observed for the three aromatic protons, which show a very small shift upon coordination of the phosphite ligand to the metal. However, the methyl signals from the *tert*-butyl groups experience significant change in their chemical shift compared to that of the free ligand. The two signals for the methyl groups in the coordinated ligand (in **2**) are observed at δ 1.54 and 1.26 ppm, as opposed to δ 1.40 and 1.31 ppm for the free ligand. A single resonance at δ 128 ppm in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum and the expected number of resonances in the $^{13}\text{C}\{\text{H}\}$ NMR spectrum (six signals for the aromatic carbons and four signals for the *tert*-butyl carbons apart

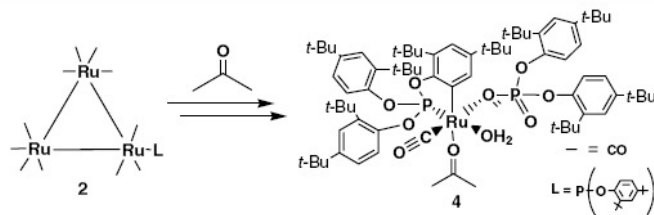
from the resonance for the CO carbons) adequately support the formation of the mono-substituted product **2**. Electrospray mass spectrometry carried out on the red fraction confirmed the suggested molecular formula of **2** as $[\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{OR})_3\}]$ (R = 2,4-di-*tert*-butylphenyl). A molecular ion peak around 1260 with subsequent peaks corresponding to CO losses establishes the molecular formula suggested for this fraction. Our attempts to obtain meaningful elemental analyses were unfortunately not successful. Spectroscopic evidence suggests the formation of other species upon standing and meaningful elemental analysis could not be carried out as it was difficult to obtain a sample with adequate purity. Formation of other species upon standing also prevented the growth of good single crystals for X-ray analysis of **2**.

Proton and carbon NMR spectra of the second (yellow) fraction are indicative of it being the di-substituted product, $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{OR})_3\}_2]$, **3**. Careful examination of both the ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra clearly suggest that this particular product exist in the various possible isomeric forms. Overlap of multiple signals in the aromatic region as well as six methyl signals (three sets) in the ^1H NMR suggests the compound existing in at least three isomers (in approximately 2:1.2:1 ratio). This assumption is further supported by the number of resonances observed in the $^{13}\text{C}\{\text{H}\}$ NMR spectrum. Six resonances each for the quaternary carbon atoms and the methyl carbon atoms of the *tert*-butyl group are due to the various isomers being present. In a monosubstituted complex, preference for the axial or equatorial positions in the trimetal unit would depend largely on the nature of the ligand involved [14]. Additional ligands create the possibility of the various axial–equatorial combinations. A ‘Star-of-David’ disorder has been reported for the known phosphite complex $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ [15]. Two signals, at δ 148 and 126 ppm, in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum provides additional evidence to the bis-substituted complex. These two signals appear as doublets with a coupling constant of 72 Hz. Electrospray mass spectrometric analysis shows the expected molecular ion peak at m/z 1877 along with a number of peaks corresponding to subsequent loss of CO molecules. Elemental analysis confirms the molecular formula deduced from the various spectroscopic data.

The red compound (**2**) initially appeared to decompose in acetone solution over a period of several days. Upon inspection of a sample, colorless needles were observed between the black decomposition product. X-ray diffraction showed these colorless crystals to be compound **4**.



Scheme 1. Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with $\text{P}(\text{O}-2,4\text{-tBu}_2\text{C}_6\text{H}_3)_3$ (L).

Scheme 2. Reaction of 3 with acetone. L = P(O-2,4-*t*Bu₂C₆H₃)₃.

We are currently in the process of exploring ways to synthesize compound **4** independently and will report the details later (see Scheme 2).

3.2. Solid state structure of **4**

A molecular diagram showing the numbering scheme of the title compound [Ru(CO){P(O-2,4-*t*Bu₂C₆H₃)₂(O-2,4-*t*Bu₂C₆H₃)₂}(OH₂){OC(CH₃)₂}[O₂P(O-2,4-*t*Bu₂C₆H₃)₂] (**4**), is presented in Fig. 1, with selected bond lengths, angles and torsion angles in Table 2 and the hydrogen bonding interactions in Table 3. The compound **4**, crystallizes in the triclinic space group *P* $\bar{1}$ with *Z* = 2. The molecule lies on a general position in the asymmetric unit. All angles within the Ru coordination polyhedron show a slightly distorted octahedral environment (Table 2). Intermolecular ring closing of the coordinated phosphite ligand via agnostic intermediates is well known for ruthenium compounds. The Ru–C(39) bond distance of 2.066(3) Å is comparable

to the Ru–C bond distance of 2.12(4) Å, reported previously [16] for a dimeric *ortho*-metallated structure.

Classical intra- and inter-molecular hydrogen bonding is observed between the coordinated aqua (O2) and the P(1) = O(10) oxygen (see Table 3). These interactions cause a pseudo-dimerisation between two molecules situated around the inversion center. The same P(1) = O(10) oxygen shows an intermolecular close contact with the coordinated acetone moiety (Table 3).

The ruthenium atom in **4** is in a formal oxidation state of 2+. Intermolecular ring-closure is observed in the structure of **4**, accounting for one electron. The complete Ru fragment is cationic with the PO₂(OR)₂ moiety functioning as a mono-anionic ligand. Clearly these reactions were necessary in order to stabilize the charge on ruthenium.

Surprisingly no disorder of the *tert*-butyl groups was found in the structure of **4**. Previously, we reported the structures of Co [17] and Rh [18] compounds containing the same phosphite ligand. In solving these structures we

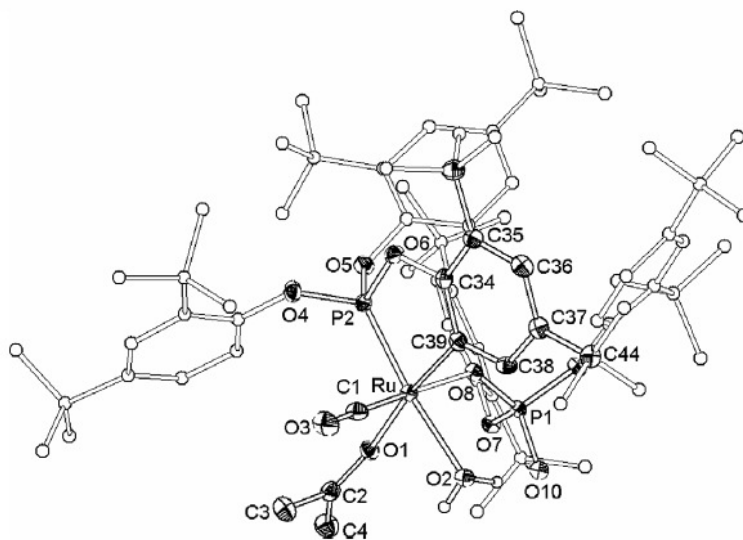
Fig. 1. Molecular structure of **4** (50% probability). H atoms have been omitted for clarity.

Table 2
Selected interatomic bond distances (Å) and angles (°) for **4**

Distances			
Ru–C(1)	1.817(3)	Ru–P(2)	2.1783(8)
Ru–C(39)	2.066(3)	Ru–O(2)	2.1979(18)
Ru–O(8)	2.1468(17)	Ru–O(1)	2.2175(18)
P(1)–O(7)	1.5880(17)	P(1)–O(8)	1.4940(18)
P(1)–O(9)	1.6005(18)	P(1)–O(10)	1.4950(18)
P(2)–O(4)	1.5997(19)		
Angles			
O(3)–C(1)–Ru	177.0(2)	C(2)–O(1)–Ru	138.53(18)
C(34)–C(39)–Ru	119.70(17)	C(39)–C(34)–O(6)	116.6(2)
O(6)–P(2)–Ru	109.60(7)		
Torsion angles			
C(39)–Ru–P(2)–O(6)	–0.63(10)	O(2)–Ru–P(2)–O(4)	–134.2(4)
O(8)–Ru–P(2)–O(6)	–92.58(9)	O(2)–Ru–P(2)–O(6)	–22.6(4)
O(1)–Ru–P(2)–O(6)	–172.57(9)	O(2)–Ru–P(2)–O(5)	96.5(4)

Table 3
Selected inter- and intra-molecular hydrogen interactions (Å) and angles (°) for **4**

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
O(2)–H(1W)...O(10)	0.97(4)	1.74(4)	2.681(3)	161(3)
O(2)–H(2W)...O(10)#1	0.78(4)	2.00(4)	2.754(3)	162(4)
C(3)–H(3A)...O(10)#1	0.98	2.56	3.156(3)	119.3
C(38)–H(38)...O(2)	0.95	2.59	3.176(3)	120.4

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$.

observed that especially the 4-*tert*-butyl groups tend to disorder over two different positions.

3.3. Possible mechanism for the formation of **4**

Compound **2** in solutions of hexane or methylene chloride undergoes disproportionation forming small amounts of the bis-substituted complex **3** along with small amounts of decomposition products. Cleavage of metal–metal bonds, initiated by solvation of acetone, has been suggested in a number of mechanistic studies [19]. It is conceivable that coordination of an acetone molecule, upon the metal–metal cleavage, caused a complete degradation of the triangular cluster. Free phosphite in the reaction mixture is a logical result of the degradation of the cluster, which then could add to a ruthenium fragment containing

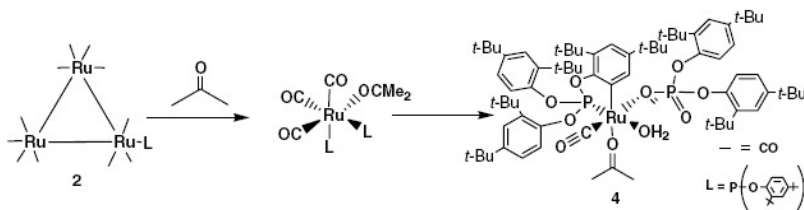
a phosphite ligand, leading to the formation of $[\{P(O-2,4-tBu_2C_6H_3)_3\}_2Ru\{O=C(CH_3)_2\}(CO)_3]$. This intermediate is unstable and intermolecular CH activation with the concomitant loss of one CO starts the oxidation process. Cyclometallation in Ru(II) compounds is fairly common [20]. The Ru(I) intermediate is further oxidised by the triphosphite ligand which is reduced to a diphosphite ligand (see Scheme 3).

4. Conclusions

The reaction of $[Ru_3(CO)_{12}]$ clusters with the bulky phosphite $P(O-2,4-tBu_2C_6H_3)_3$ in dichloromethane under reflux produced the mono-phosphite cluster $[Ru_3(CO)_{11}L]$ and the bis-phosphite cluster $[Ru_3(CO)_{10}L_2]$. The former cluster compound is unstable in acetone solution and decomposes to form metallic ruthenium and a monometallic ruthenium compound. An X-ray crystallographic analysis establishes cyclometallation in this monometallic ruthenium decomposition product.

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Scheme 3. Possible mechanism for the formation of **4**.

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Appendix A. Supplementary material

CCDC 647378 contains the supplementary crystallographic data for this paper. 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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2007.08.008](https://doi.org/10.1016/j.ica.2007.08.008).

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