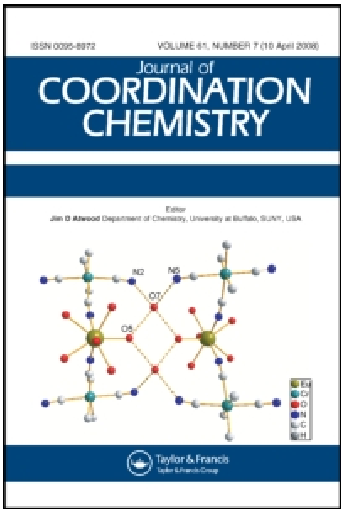

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Synthesis and characterization of the substituted products from the reaction of a bulky phosphite with $[Os_3(CO)_{12}]$

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Synthesis and characterization of the substituted products from the reaction of a bulky phosphite with [$Os_3(CO)_{12}$]

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Reaction of (acetonitrile)-undeca(carbonyl)-tri-osmium and *tris*(2,4-di-*tert*-butylphenyl) phosphite yielded the phosphite clusters [$Os_3(CO)_{11}L$] (**4**) and [$Os_3(CO)_{10}L_2$] (**5**) [$L = P(O\text{-}2,4\text{-}^tBu_2C_6H_3)_3$]. These compounds were characterized spectroscopically and the molecular structure of **5** was determined by single crystal X-ray diffraction, the first reported structural analysis of a tri-osmium cluster containing aromatic phosphite ligands. Compound **5** crystallized in the triclinic space group $P\bar{1}$, and revealed an equatorial *trans–trans* position of the bulky phosphite ligands.

Keywords: Osmium; Cluster; Phosphite; Substitution

1. Introduction

The extensive ligand chemistry reported on the tri-osmium cluster [$Os_3(CO)_{12}$] can be attributed to the robustness of the osmium compounds that are formed [1]. Several review articles demonstrate the versatility of osmium clusters to facilitate various organic transformations on the metal framework [2]. These features make osmium clusters ideal candidates for catalytic exploration [3].

Although many phosphine substituted triosmium compounds have been reported, similar phosphite substituted complexes are scarce [4]. Recently we reported the synthesis and characterization of ruthenium derivatives of *tris*(2,4-di-*tert*-butylphenyl) phosphite (**1**) and one of its decomposition products [5]. As an extension of that work, we synthesized corresponding osmium compounds and herein report the synthesis and characterization of the mono- and *bis*-substituted tri-osmium derivatives of the same ligand, **1**.

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2. Experimental

2.1. *Reagents and general procedures*

All syntheses of air and moisture sensitive compounds were performed using standard Schlenk techniques under prepurified N_2 [6]. Dichloromethane was pre-dried by passage over alumina (neutral, Brockmann grade I) and subsequently distilled from CaH_2 [7]. [$Os_3(CO)_{12}$] (Johnson-Matthey) and *tris*(2,4-di-*tert*-butylphenyl) phosphite (Aldrich) were used as received. Me_3NO (Aldrich) was sublimed prior to use.

NMR spectra were recorded on an Avance Bruker 300 MHz spectrometer (^{1}H: 300 MHz, ^{13}C: 75.5 MHz, ^{31}P: 121.46 MHz) at ambient temperature, and were referenced relative to TMS (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P), using one of the following: the residual protonated solvent (^{1}H NMR: $CDCl_3$: δ 7.27) or external 85% H_3PO_4 (^{31}P). 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.

2.2. *Reaction of [$Os_3(CO)_{12}$] with $P(O\text{-}2,4\text{-}^tBu_2C_6H_3)_3$*

To a methylene chloride (30 mL) solution of [$Os_3(CO)_{12}$] (0.050 g, 0.055 mmol) was added Me_3NO (0.006 g, 0.080 mmol) in acetonitrile (5 mL). The reaction mixture was monitored by IR to confirm formation of the acetonitrile complex, [$Os_3(CO)_{11}(NCMe)$]. (The bis-substituted product, [$Os_3(CO)_{10}(NCMe)_2$], also formed as indicated by IR spectroscopy). A fresh batch of CH_2Cl_2 (30 mL) was added after removing the solvent from the reaction mixture. Subsequently, the phosphite ligand $P(O\text{-}2,4\text{-}^tBu_2C_6H_3)_3$ (0.075 g, 0.115 mmol) was added and the reaction mixture heated under reflux for 3 h. The volatiles were removed *in vacuo* and the residue dissolved in minimum hexane. A short silica gel column (1.5 cm × 10 cm) was used to separate the products formed. The two fractions isolated were purified by preparative TLC. The first yellow fraction (minor) was eluted using hexane and was identified as the mono-substituted product **4** using spectroscopic methods. After evaporation of the solvent, **4** was obtained as a yellow solid (0.019 g; 23%); $Os_3C_{59}O_{14}PH_{77}$ ($Os_3(CO)_{11}L \cdot C_6H_{14}$) requires: C, 43.96; H, 4.81. Found: C, 44.33; H, 4.43%; ν_{CO}/cm^{-1}: 2112(m), 2058(vs), 2041(s), 2025(vs), 2005(m), 1996(s), 1986(s), 1977(m), 1953(vw), 1941(vw); δ_H($CDCl_3$, 300 MHz): 7.55(d), 7.38(m), 7.02(dd), 1.57(s), 1.27(s); $\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz): 148.0(d), 146.7, 138.1(d), 125.1, 123.4, 119.3(d), 35.2, 34.5, 31.4, 30.6; $\delta_{P\{H\}}$($CDCl_3$, 121.46 MHz): 78.9; *m/z* (ES): 1527 (M^+) (peaks corresponding to CO losses were also observed, 1499 [$M^+ - CO$], 1471 [$M^+ - 2$ CO] etc.).

The second, orange-yellow band was eluted using 5% dichloromethane in hexane and was identified as the *bis*-substituted product **5**. After evaporation of the solvent, **5** was obtained as a dark yellow powder (0.048 g, 41%); $Os_3C_{94}O_{16}P_2H_{126}$ requires: C, 52.64; H, 5.92. Found: C, 53.13; H, 6.05%. ν_{CO}/cm^{-1}: 2097(w), 2040(s), 2027(m), 2015(vs), 1988(m), 1980(m); δ_H($CDCl_3$, 300 MHz): 7.53(d), 7.33(d), 6.96(dd), 1.50(s), 1.25(s); $\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz): 148.4(t), 146.3, 138.0, 124.8, 123.4, 119.4, 35.2, 34.4, 31.4, 30.6; $\delta_{P\{H\}}$($CDCl_3$, 121.46 MHz): 78.0, 74.9.

2.3. *Structure determination*

Crystals of $[Os_3(CO)_{10}(P(O\text{-}2,4\text{-}^tBu_2C_6H_3)_3)_2]$ (**5**), were grown from hexane at −4°C. Single crystal X-ray diffraction data for **5** were collected on a Bruker X8 Apex II 4K Kappa CCD diffractometer using Mo-Kα (0.71073 Å) radiation with φ and ω-scans at 100(2) K. The initial unit cell and data collection were achieved by the Apex2 [8] software utilizing COSMO [9] for optimum collection of more than a hemisphere of reciprocal space. 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 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 = 0.95 Å for aromatic and 0.98 Å for Me) 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 deepest residual electron-density hole ($-2.962\ e\ Å^{-3}$) is located 0.42 Å from C1, and the highest peak ($4.431\ e\ Å^{-3}$) 1.02 Å from H53. The disorders on the 4-^{t}Bu groups were refined as a 53.7 : 46.3 disorder on ring 1; 60.4 : 39.6 on ring 3; 51.4 : 48.6 on ring 4 and 67.9 : 32.1 on ring 5.

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

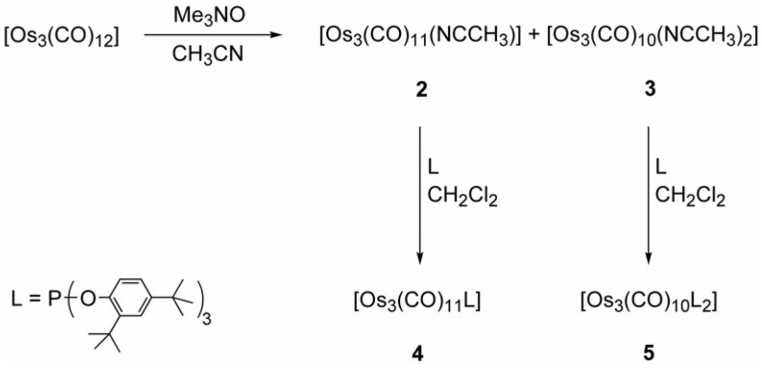
3.1. *Synthesis and spectroscopy*

Substitution on the tri-osmium complex $[Os_3(CO)_{12}]$ can easily be achieved by initially removing one or two of the carbonyl groups using trimethylamineoxide [14]. Numerous substituted tri-osmium complexes have been synthesized using this facile method [15]. Though mono- and *bis*-substituted ruthenium complexes of the phosphite ligand **1** can easily be synthesized by heating $[Ru_3(CO)_{12}]$ with the ligand, similar reaction of $[Os_3(CO)_{12}]$ with **1** did not yield the desired substituted products. However, substituted derivatives of $[Os_3(CO)_{12}]$ can be synthesized by reacting **1** with $[Os_3(CO)_{11}(NCMe)]$ (**2**) or $[Os_3(CO)_{10}(NCMe)_2]$ (**3**). Thus, $[Os_3(CO)_{11}L]$ (**4**) and $[Os_3(CO)_{10}L_2]$ (**5**) (L = *tris*(2,4-di-*tert*-butylphenyl) phosphite) were synthesized by reaction of **1** with **2** and **3** in dichloromethane, while heating under reflux (scheme 1).

Compounds **4** and **5** were isolated using preparative TLC and were characterized by spectroscopic methods. Infrared spectra of the two isolated fractions showed characteristic bands in the CO stretching range. The first yellow band (minor fraction) and the second orange band (major fraction) displayed CO stretching bands that can be assigned as terminal carbonyl ligands. The patterns displayed in the spectra are comparable with those observed for the ruthenium counterparts. Also, the IR absorption pattern matches very well with other mono-substituted phosphine [16] and substituted phosphine [17] tri-osmium compounds, further confirming formation of the monosubstitution product. Similarly, IR spectrum of the second band shows good

Table 1. Crystal data and structural refinement for **5**.

Empirical formula	$C_{94}H_{126}O_{16}Os_3P_2$
Formula weight	2144.49
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	11.9983(5)
b	18.9119(8)
c	24.0734(10)
α	77.418(2)
β	78.629(2)
γ	71.742(2)
Volume (Å^3)	5013.7(4)
Z	2
D_{Calcd} (Mg m^{-3})	1.421
Absorption coefficient (mm^{-1})	3.881
$F(000)$	2152
Crystal size (mm^3)	0.25 × 0.12 × 0.10
θ range for data collection (°)	0.88–28.35
Index ranges	$-16 \leq h \leq 15$, $-25 \leq k \leq 25$, $-30 \leq l \leq 32$
Reflections collected	75620
Independent reflections [R_{int}]	24884 [0.0358]
Completeness to $\theta = 28.35°$	99.4%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.6976 and 0.4437
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	24884/108/1001
Goodness-of-fit on F^2	1.196
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.1155$
R indices (all data)	$R_1 = 0.0656$, $wR_2 = 0.1310$
Largest difference peak and hole (e Å^{-3})	4.431 and −2.962



Scheme 1. Synthesis of [$Os_3(CO)_{11}L$] (**4**) and [$Os_3(CO)_{10}L_2$] (**5**) ($L = P(O\text{-}2,4\text{-}{}^{t}Bu_2C_6H_3)_3$).

correspondence with *bis*-substituted phosphine tri-osmium compounds. In addition to the expected pattern for [$Os_3(CO)_{10}L_2$], some additional absorptions are observed in the IR spectrum measured in hexane, attributed to the presence of isomers in solution. Similar IR absorption bands were reported for the phosphine tri-osmium complex

$[Os_3(CO)_{10}(PMe_2Ph)_2]$ and were corroborated by variable temperature NMR studies [18].

Similar to the pattern seen for the ligand, three sets of signals arising from phenyl protons and two signals due to methyl protons are seen in the proton NMR spectrum of **4**. Very little perturbation for the phenyl resonance compared to that of the free ligand is observed upon coordination. Significant changes in the chemical shift for the methyl signals from free ligand are seen. Similar changes were observed for the ruthenium analogue of **4**. The expected six resonances for the phenyl carbons and four signals for the *tert*-butyl group constitute the ^{13}C NMR spectrum of **4**.

Three of the phenyl carbon signals appear as doublets due to phosphorus coupling. Coupling values for two of the resonances around 6.9 Hz can be attributed to three bond coupling, whereas the magnitude of the other coupling (8.6 Hz) can be attributed to two bond coupling. A single resonance at δ 78.9 in the ^{31}P NMR adds support to formulation of **4** as the mono-substituted product. Osmium satellites (^{187}Os, $I = ½$ 1.6% nat. abund.) are observed in this spectrum with a coupling constant of 374 Hz, comparable to those previously reported for phosphite complexes [19]. The mass spectrum of **4** confirms the molecular formula suggested for **4**. A molecular ion peak around $m/z = 1527$ along with 11 peaks corresponding to carbonyl losses provides support for **4** as the mono-substituted product. Satisfactory elemental analysis was obtained for this compound with one molecule of hexane associated with **4**.

NMR spectra of **5** are indicative of the *bis*-substituted product. The proton NMR spectrum is very similar to that of the free ligand as well as that of the mono-substituted product. Except for the methyl signals, little perturbations were observed in the chemical shifts. One notable feature of the ^{13}C NMR spectrum, which consists of six resonances due to the phenyl carbons and 4 resonances from the *tert*-butyl carbons, is the triplet seen at δ 148.4. The triplet can be explained in terms of virtual coupling experienced by the carbon atom (directly attached to the oxygen in the ligand). The bis-substituted product in the ruthenium reaction gives rise to a number of possible isomers which are very evident in its proton as well as carbon NMR spectra [5]. However, both proton as well as carbon NMR spectra of the osmium complex are indicative of a single isomer.

As one would anticipate, very little difference is noted in the proton as well as carbon NMR of both the mono- and *bis*-substituted compounds. The chemical shifts are also very similar to the ruthenium analogues. However, there is substantial difference in the phosphorus chemical shifts (**4**: δ 78.9; **5**: δ 78.0 and 74.9) as compared to the ruthenium counterparts ($[Ru_3(CO)_{11}L]$: δ 121.5; ($[Ru_3(CO)_{10}L_2]$: δ 148.0 and 126.0 [5]). The greater upfield shifts observed for **4** and **5** are nothing unusual. However, the two signals (one sharp and the other relatively broad) seen for **5** are interesting. In the case of the ruthenium analogue, various isomers are formed and can be easily identified in the ^{1}H and ^{31}C NMR spectra. These isomers are not visible in the room temperature ^{1}H or ^{13}C NMR of **5**, but the two signals seen in the ^{31}P NMR are indicative of dynamic behavior in solution. The smaller (broader) peak gradually broadens further upon heating and almost disappears at 50°C.

Two signals in the ^{31}P NMR spectrum of **5** are in accordance with literature. A rapid equilibrium between the *trans*,*trans*- and the *cis*,*trans*-isomers, relative to the phosphorus substituted osmium of $[Os_3(CO)_{10}P_2]$ complexes, was observed previously [20]. The isomerization mechanism in these systems has been fairly well studied and

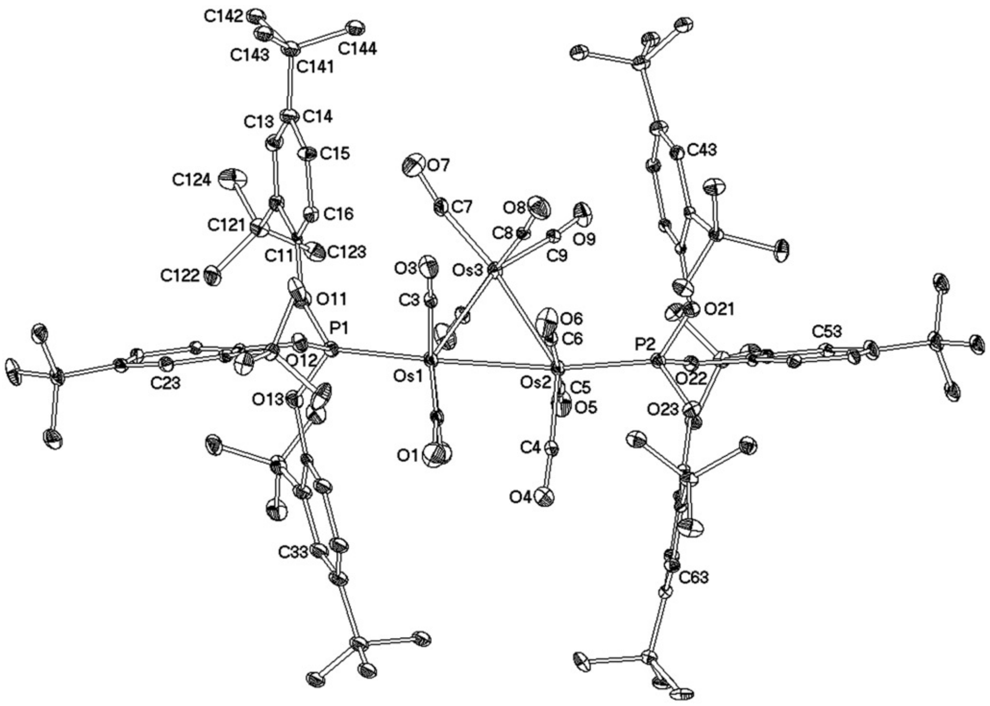


Figure 1. Molecular structure of **5** (50% probability). H atoms, as well as the minor component of the disorders, have been omitted for clarity. For the aromatic rings, the first digit indicates the ring number and the second digit the atom position.

involves restricted turnstile rotation at one of the phosphorus bearing osmiums [18, 21]. Satisfactory elemental analyses were obtained for this compound, which further supports formation of the bis-substituted product.

Our attempts to get good mass spectral analysis of the major fraction were not successful. So we undertook a single crystal X-ray analysis to confirm the molecular structure of this compound. The single crystal X-ray analysis establishes the molecular structure of **5**. To the best of our knowledge, **5** is the first tri-osmium cluster containing two aromatic phosphite ligands that is structurally determined.

3.2. *Solid state structure of 5*

A molecular diagram showing the numbering scheme of $[Os_3(CO)_{10}\{P(O\text{-}2,4\text{-}{}^tBu_2C_6H_3)_3\}_2]$ (**5**), is presented in figure 1, with selected bond lengths, angles and torsion angles in table 2. Comparative bond distances and angles for selected related compounds are given in table 3. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The molecule lies on a general position in the asymmetric unit.

The structure of **5** represents a triangular osmium cluster with the two phosphite ligands in an equatorial *trans–trans* orientation. The almost-exclusive tendency for phosphine ligands to occupy an equatorial site with respect to the tri-osmium plane was noted previously [1, 20, 22–24]. All bond distances and angles are comparative to related Os_3 clusters (see table 3).

Table 2. Selected interatomic bond distances (Å) and angles (°) for **5**.

Distances			
Os(1)–Os(2)	2.9074(3)	Os(1)–P(1)	2.283(2)
Os(1)–Os(3)	2.8858(4)	Os(2)–P(2)	2.284(2)
Os(2)–Os(3)	2.9221(4)		
Angles			
Os(1)–Os(2)–Os(3)	59.345(8)	P(1)–Os(1)–Os(2)	170.10(4)
Os(3)–Os(1)–Os(2)	60.582(9)	P(2)–Os(2)–Os(3)	116.93(4)
Torsion angles			
P(1)–Os(1)–Os(3)–Os(2)	−172.74(4)	Os(3)–Os(1)–Os(2)–P(2)	70.8(2)
P(2)–Os(2)–Os(3)–Os(1)	−169.36(4)		

Table 3. Selected bond distances (Å) for related Os_3 cluster compounds.

Ligand	Os(1)–Os(2)	Os(1)–Os(3)	Os(2)–Os(3)	Os(1)–P(1)	Os(2)–P(2)	Ref.
$P(O\text{-}2,4\text{-}{}^tBu_2C_6H_3)_3$	2.9074(3)	2.8858(4)	2.9221(4)	2.2832(16)	2.2839(15)	This work
PPh_3	2.9065(4)	2.9095(4)	2.8988(5)	2.351(2)	2.361(2)	[20]
PPh_3[a]	2.909	2.899	2.907	2.362	2.354	[22]
$PPh(OMe)_2$[a]	2.883	2.895	2.892	2.289	2.297	[22]
$P(OMe)_3$[a]	2.869	2.890	2.888	2.280	2.280	[22]
$P({}^tBu)_2F$	2.9244(12)	2.9227(12)	2.9232(11)	2.338(5)	2.336(5)	[23]
$P(CF_3)_3$	2.884(1)	2.892(2)	2.896(1)	2.257(7)	2.236(9)	[24]

[a] Data extracted from the CSD.

A dynamic "Star of David" disorder on the M_3 core was previously observed for $[Ru_3(CO)_{11}(L)]$ and $[Ru_3(CO)_9(L)_3]$ clusters [25]. In addition, a statistical disorder on $[Ru_3(CO)_{10}(L)_2]$ was observed [25, 26]. In systems such as these, the periphery of the molecule is so similar to that of its inversion image that it would be capable of accommodating two different dispositions of the Os_3 core, leading to a situation where the outer sphere of the molecules is independent of the Os_3 core. This solid state behavior is compatible with the known fluxional nature of many of these systems in solution. Here we find, surprisingly, no disorder on the Os_3 core and no "bending" of any CO ligands to accommodate Os_3 disorder (see [25] for a discussion of this phenomenon).

Significant disorder of the 4-*tert*-butyl groups was observed in the structure of **5**. Previously, we reported the structures of Co [27] and Rh [28] compounds containing the same phosphite ligand. In solving these structures, we observed that the 4-*tert*-butyl groups show large thermal motion and were subsequently refined over two disordered positions. In contrast, in the related work on Ru clusters [5] we found no disorder of the *tert*-butyl groups, possibly due to a more restricted packing environment in the latter example. Here we once again observe significant disorder on a few 4-*tert*-butyl groups which were treated in a similar fashion. Additionally, weak hydrogen interactions, mainly involving the 2-*tert*-butyl groups, provides a plausible explanation why no disorders were observed on these groups but rather on the 4-*tert*-butyl groups.

There is also indication of a solvent molecule incorporated in the crystal lattice. However, several attempts to refine its position led to unsatisfactory results and it was subsequently left out, resulting in high residual electron density in the final refinement cycles.

4. Conclusion

Mono- and *bis*-substituted complexes [$Os_3(CO)_{11}L$] and [$Os_3(CO)_{10}L_2$] (L = *tris*(2,4-di-*tert*-butylphenyl) phosphite) were prepared by activating $Os_3(CO)_{12}$ using trimethylamineoxide and subsequently heating it under reflux with the phosphite ligand. Unlike the ruthenium analogue, only one isomer is detected in the room temperature ^{1}H and ^{13}C NMR spectra for the bis-substituted product. However, dynamic behavior of the phosphite ligand is inferred from the ^{31}P NMR. The molecular structure of the [$Os_3(CO)_{10}L_2$] cluster revealed an equatorial *trans*-*trans* position of the bulky phosphite ligands.

Supplementary material

Supplementary material CCDC 676291 contains the supplementary crystallographic data for this article. 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 Email: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found in the online version.

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