New tertiary phosphine derivatives of Os$_3$(CO)$_{12}$: X-ray structures of 1,2-[Os$_3$(CO)$_{10}$]$_2$[PhP(o-Tol)$_2$]$_2$, 1,2,3-[Os$_3$(CO)$_9$]{(4-FC$_6$H$_4$)$_3$P}$_3$, 1,2,3-[Os$_3$(CO)$_9$]{PhP(Cy)$_2$}]$_3$ and [Os$_3$(µ-OH)$_2$(CO)$_8$]{(4-FC$_6$H$_4$)$_3$P}$_2$

Abdur R Miah$^a$, Subas Rajbangshi$^a$, Ahibur Rahaman$^a$, Kamal Hossain$^a$, Tasneem A Siddiquee$^b$ & Shariff E Kabir$^a$ *

$^a$Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh
$^b$Department of Chemistry, Tennessee State University, 3500 John A Merritt Blvd, Nashville, TN 37209, USA

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Reactions of 1,2-[Os$_3$(CO)$_{10}$](NCMe)$_2$] (1) with tertiary phosphines such as tris(4-fluorophenyl)phosphine (4-FC$_6$H$_4$)$_3$P, bis(o-tolyl)(phenyl)phosphine PhP(o-Tol)$_2$, and dicyclohexyl(phenyl)phosphine PhP(Cy)$_2$ have been examined at room temperature and found to yield the di- and tri-substituted products 1,2-[Os$_3$(CO)$_{10}$]([PR$_3$])$_2$ [(2), PR$_3$ = (4-FC$_6$H$_4$)$_3$P]; (3), PR$_3$ = PhP(o-Tol)$_2$; (4), PR$_3$ = PhP(Cy)$_2$] and 1,2,3-[Os$_3$(CO)$_9$]([PR$_3$])$_3$ [(5), PR$_3$ = (4-FC$_6$H$_4$)$_3$P]; (6), PR$_3$ = PhP(o-Tol)$_2$; (7), PR$_3$ = PhP(Cy)$_2$] as the major products, in addition to the dihydroxy-bridged complexes 1,2-[Os$_3$(CO)$_9$][µ-OH]$_2$[(µ-OH)]$_2$ [(8), PR$_3$ = (4-FC$_6$H$_4$)$_3$P]; (9), PR$_3$ = PhP(o-Tol)$_2$; (10), PR$_3$ = PhP(Cy)$_2$] in trace amounts. Compounds (2)-(10) have been characterized by a combination of elemental analyses, infrared, NMR and mass spectral data together with single crystal X-ray diffraction studies for (3), (5), (7) and (8).

Keywords: Coordination chemistry, Osmium, Cluster compounds, Tertiary phosphines, X-ray structures

Tertiary phosphines, PR$_3$, are well-known to be valuable ligands in inorganic and organometallic chemistry because they constitute one of the few series of ligands in which the steric and electronic properties of the ligands can be altered in a periodic and systematic fashion by varying the nature of the R-group. The chemistry of tertiary phosphine substituted derivatives of triosmium dodecacarbonyl has been fairly extensively studied$^1$$^5$. One interesting aspect of these complexes is the almost exclusive tendency of the phosphine ligands to occupy an equatorial site with respect to the triosmium plane.$^5$$^6$. Electronically, axial substitution is favoured because this leaves a stable fac tricarbonyl unit. The axial CO ligands in Os$_3$(CO)$_{12}$ are more weakly coordinated and would therefore be expected to be more readily substituted than the equatorial ligands. However, the axial sites are more crowded. Steric effects dominate in most cases and only the smallest ligands prefer axial position, while bulky ligands such as tertiary phosphines occupy equatorial position.$^6$. Nine products were shown to be formed in the reaction of Os$_3$(CO)$_{12}$ with PPh$_3$, three of which are simple substituted derivatives of the type [Os$_3$(CO)$_{12}$,x(PPh$_3$)$_3$] (x = 1, 2, or 3). We reported that the reactions of [Os$_3$(CO)$_{10}$]$_2$(η$^4$-s-cis-C$_6$H$_4$)$_2$] and [Os$_3$(CO)$_{10}$ (µ-s-trans-C$_6$H$_6$)] with P(OMe)$_3$ gives 1,1- and 1,2-isomers of [Os$_3$(CO)$_{10}$][P(OMe)$_3$]$_2$.$^7$, whereas [Os$_3$(CO)$_{10}$](MeCN)[PEt$_3$]$^8$ is obtained by the reaction of [Os$_3$(CO)$_{10}$]PEt$_3$] with Me$_2$NO/MeCN. Poe et al.$^9$ studied the kinetics of the stepwise reactions of Os$_3$(CO)$_{12}$ with PBu$_3$. The activated cluster compound [Os$_3$(CO)$_{10}$](NCMe)$_2$] (1) is a useful intermediate in the preparation of a wide variety of derivatives of the inert parent carbonyl cluster Os$_3$(CO)$_{12}$$^{10,14}$. Tachikawa and Shapley$^{11}$ made a series decacarbonyl compounds of the type of 1,2-[Os$_3$(CO)$_{10}$][µ-$L_2$] (L = PPh$_3$, PMe$_2$Ph, P(OMe)$_3$, PMePh$_2$) from the reactions of 1 and the requisite phosphine. Deeming et al.$^{15}$ reported the isomers of [Os$_3$(CO)$_{10}$]PM$_2$Ph$_3$] from the reaction of [Os$_3$(CO)$_{10}$](η$^4$-s-cis-C$_6$H$_4$)$_2$] with PM$_2$Ph at room temperature. Mixtures of all three derivatives [Os$_3$(CO)$_{12}$-x-$L_3$(x = 1-3, L = PM$_2$Ph$_2$, PEt$_2$Ph and PEt$_3$) were obtained by direct reactions of the decacarbonyl with the phosphines.$^{16}$. The reactivity study of tertiary phosphate ligands with mixed substituents has received less attention than that of phosphine ligands with only one kind of substituents. There are some studies of transition metal complexes with ligands
such as (2-hydroxophenyl)diphenyolphosphine\textsuperscript{17} and (2-aminophenyl) diphenyolphosphine\textsuperscript{18,20}. Arce et al.\textsuperscript{21} reported that the reaction of (2-aminophenyl) phosphine P(2-NH$_2$C$_6$H$_5$)$_2$H with [Os$_3$(CO)$_{10}$MeCN]$_2$ gives the compounds[Os$_3$(CO)$_{11}${P(2-NH$_2$C$_6$H$_5$)$_2$}], 1,2-[Os$_3$(CO)$_{10}$P(2-NH$_2$C$_6$H$_5$)$_2$H]$_2$ and [Os$_6$($\mu$-H)(CO)$_{10}$-$\mu$-P(2-NH$_2$C$_6$H$_5$)$_2$H)]. We have now initiated similar investigations on the reactions of [Os$_3$(CO)$_{10}$NCMe]$_2$ with tris(4-fluorophenyl)phosphine, bis(4-tolyl)(phenyl) phosphine and dicyclohexyl(phenyl)phosphine and the results are described herein.

Materials and Methods

All reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. [Os$_3$(CO)$_{10}$NCMe]$_2$ (1) was prepared according to the published procedure\textsuperscript{22}. Tris(4-fluorophenyl)-phosphine, bis(4-tolyl)(phenyl)phosphine and dicyclohexyl(phenyl)phosphine were purchased from Acros and used as received. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Unity Plus 500 instrument. The chemical shifts were referenced to residual solvent resonances or external 85% H$_3$PO$_4$ in $^1$H and $^3$P spectra respectively. Elemental analyses were performed by the Microanalytical Laboratories of the Wazed Miah Science Research Centre at Jahangirnagar University. Preparative thin layer chromatography was carried out on 1 mm plates prepared from silica gel GF254 (type 60, E. Merck) at Jahangirnagar University.

Reaction of [Os$_3$(CO)$_{10}$NCMe]$_2$ with tris(4-fluorophenyl)-phosphine

A dichloromethane solution (30 mL) of [Os$_3$(CO)$_{10}$NCMe]$_2$ (1) (40 mg, 0.043 mmol) and tris(4-fluorophenyl)phosphine (27 mg, 0.086 mmol) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH$_2$Cl$_2$ (9:1, v/v) developed five bands. The first band afforded 1,2-[Os$_3$(CO)$_{10}${(4-$\mu$FC$_6$H$_5$)$_3$}P]$_2$ (2) (18 mg, 30%) as yellow crystals, the second band gave 1,2,3-[Os$_3$(CO)$_{10}${(4-$\mu$FC$_6$H$_5$)$_2$}P]$_3$ (5) (15 mg, 20%) as red crystals and the fifth band furnished 1,2-[Os$_3$(CO)$_{10}${(4-$\mu$FC$_6$H$_5$)$_2$}P]$_2$($\mu$-OH)$_2$ (8) (8 mg, 13%) as yellow crystals from hexane/CH$_2$Cl$_2$ at 4 °C. The contents of the third and fourth bands were too small for characterization.

1,2-[Os$_3$(CO)$_{10}${(4-$\mu$FC$_6$H$_5$)$_3$}P]$_2$ (2): Anal. (%): Calcd. for C$_{16}$H$_{24}$F$_6$O$_{16}$P$_2$: C 37.25; H 1.63; Found: C 37.45; H 1.87. IR (v$_{CO}$, CH$_2$Cl$_2$): 2087 m, 2032 s, 2008 sh, 1999 vs, 1972 m, 1955 w cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.38 (m, 12H), 7.12 (m, 12H). $^3$P($^1$H) NMR (CDCl$_3$): $\delta$ 2.81 (br s). FAB MS: m/z 1483.

1,2,3-[Os$_3$(CO)$_{10}${(4-$\mu$FC$_6$H$_5$)$_2$}P]$_3$ (5): Anal. (%): Calcd. for C$_{32}$H$_{18}$F$_6$O$_{18}$P$_3$: C 42.71; H 2.05; Found: C, 42.95; H, 2.25. IR (v$_{CO}$, CH$_2$Cl$_2$): 2054 w, 2000 sh, 1988 sh, 1974 s, 1943 m cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.33 (m, 18H), 7.03 (m, 18H). $^3$P($^1$H) NMR (CDCl$_3$): $\delta$ 5.4 (s). FAB MS: m/z 1771.

1,2-[Os$_3$(CO)$_{10}${(4-FC$_6$H$_5$)$_2$}P]$_2$($\mu$-OH)$_2$ (8): Anal. (%): Calcd. for C$_{44}$H$_{28}$F$_6$O$_{16}$P$_2$: C, 36.17; H, 1.79; Found: C, 36.43; H, 1.98. IR (v$_{CO}$, CH$_2$Cl$_2$): 2062 s, 2005 vs, 1988 m, 1965 s, 1926 m. (KBr): 3448 br cm$^{-1}$. $^1$H NMR (DMSO-d$_6$): $\delta$ 7.80 (m, 2H), 7.60 (m, 2H), 7.41 (m, 6H), 7.23 (m, 8H), 7.12 (m, 6H), 0.06 (t, 2H, J = 3.4 Hz). $^3$P($^1$H) NMR (DMSO-d$_6$): $\delta$ 3.9 (s). FAB MS: m/z 1461.

Reaction of [Os$_3$(CO)$_{10}$NCMe]$_2$ with bis(4-tolyl)(phenyl)-phosphine, PhP($\mu$-To$_2$)

A similar reaction between [Os$_3$(CO)$_{10}$NCMe]$_2$ (40 mg, 0.043 mmol) and PhP($\mu$-To$_2$) (25 mg, 0.086 mmol) for 19 h followed by similar chromatographic separation afforded 1,2-[Os$_3$(CO)$_{10}$PhP($\mu$-To$_2$)]$_2$ (3), 1,2,3-[Os$_3$(CO)$_{10}$PhP($\mu$-To$_2$)]$_3$ (6) and 1,2-[Os$_3$(CO)$_{10}$PhP($\mu$-To$_2$)]$_2$($\mu$-OH)$_2$ (9).

1,2-[Os$_3$(CO)$_{10}$PhP($\mu$-To$_2$)]$_2$ (3): Yield (15 mg, 24%). Anal. (%): Calcd. for C$_{50}$H$_{42}$O$_{10}$P$_2$: C, 41.95; H, 2.68; Found: C, 42.15; H, 2.71. IR (v$_{CO}$, CH$_2$Cl$_2$): 2084 m, 2029 s, 1998 vs, 1968 w, 1953 sh cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.87 (m, 4H), 7.49 (m, 4H), 7.26 (m, 14H), 7.09 (m, 4H), 1.83 (s, 12H). $^3$P($^1$H) NMR (CDCl$_3$): $\delta$ -14.3 (br s). FAB MS: m/z 1431.

1,2,3-[Os$_3$(CO)$_{10}$PhP($\mu$-To$_2$)]$_3$ (6): Yield (12 mg, 16%). Anal. (%): Calcd. for C$_{90}$H$_{86}$O$_{30}$P$_3$: C, 48.93; H, 3.39; Found: C, 48.97; H, 3.43. IR (v$_{CO}$, CH$_2$Cl$_2$): 1986 s, 1972 vs, 1927 s, 1923 sh cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 8.19-7.63 (m, 39H), 2.27 (s, 18H). $^3$P($^1$H) NMR (CDCl$_3$): $\delta$ 35.1 (s). FAB MS: m/z 1693.

1,2-[Os$_3$(CO)$_{10}$PhP($\mu$-To$_2$)]$_2$($\mu$-OH)$_2$ (9): Yield (6 mg, 10%). Anal. (%): Calcd. for C$_{40}$H$_{30}$O$_{10}$P$_2$: C, 40.90; H, 2.86; Found: C, 40.96; H, 2.90. IR (v$_{CO}$, CH$_2$Cl$_2$): 2062 s, 2000 vs, 1982 s, 1962 sh, 1922 cm$^{-1}$. (KBr): 3452 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.26 (m, 26H), 1.20 (s, 12H), 0.07 (t, 2H, J = 3.5 Hz). $^3$P($^1$H) NMR (CDCl$_3$): $\delta$ 34.9 (s). FAB MS: m/z 1409.
Reaction of [Os₃(CO)₁₀(NCMe)₂] with dicyclohexylphosphine, Ph₂P(Cy)

A reaction similar to that above using [Os₃(CO)₁₀-(NCMe)₂] (40 mg, 0.043 mmol) and Ph₂P(Cy)₂ (24 mg, 0.086 mmol) for 3 h followed by similar chromatographic separation afforded 1,2,3-[Os₃(CO)₉(Ph₂P(Cy)₂)] (4), 1,2,3-[Os₃(CO)₉(Ph₂P(Cy)₂)] (7) and 1,2-2-[Os₃(CO)₉-(Ph₂P(Cy)₂)] (10).

1,2-[Os₃(CO)₁₀(Ph₂P(Cy)₂)] (4): Yield: (15 mg, 25%). Anal. (%): Calcd. for C₄₈H₆₀O₁₀Os₂P₂: C, 39.48; H, 3.89; Found: C, 39.73; H, 4.13. IR (vCO): 2082 m, 2024 s, 1959 vs, 1961 w, 1442 vv, 1396 sh cm⁻¹. ¹H NMR (CDCl₃): δ 7.85 (m, 10H), 1.85 (m, 14H), 1.62 (m, 6H), 1.44 (m, 14H). ³¹P [¹H] NMR (CDCl₃): δ -10.3 (br s). FAB MS: m/z 1399.

1,2,3-[Os₃(CO)₉(Ph₂P(Cy)₂)] (7): Yield: (12 mg, 17%). Anal. (%): Calcd. for C₄₆H₅₈O₁₀Os₂P₂: C, 45.97; H, 4.96; Found: C, 46.28; H, 5.25. IR (vCO): 1982 s, 1964 vs, 1928 cm⁻¹. ¹H NMR (CDCl₃): δ 7.49 (m, 5H), 7.26 (m, 10H), 1.86 (m, 6H), 1.78 (m, 6H), 1.69 (m, 12H), 1.55 (m, 6H), 1.15 (m, 36H). ³¹P [¹H] NMR (CDCl₃): δ -2.9 (s). FAB MS: m/z 1645.

[Os₃(CO)₉(Ph₂P(Cy)₂)] (10): Yield: (8 mg, 13%). Anal. (%): Calcd. for C₄₄H₅₆O₁₀Os₂P₂: C, 38.36; H, 4.10; Found: C, 38.42; H, 4.14. IR (vCO): 2054 s, 1994 vs, 1978 sh, 1954 s, 1912 cm⁻¹ (KBr): 3438 br cm⁻¹. ¹H NMR (CDCl₃): δ 7.33 (m, 6H), 7.18 (m, 4H), 2.03 (m, 4H), 1.62 (m, 20H), 1.21 (m, 6H), 1.06 (m, 14H), -0.95 (t, 2H, J = 3.5 Hz). ³¹P [¹H] NMR (CDCl₃): δ 18.1 (s). FAB MS: m/z 1377.

X-ray crystallography

Single crystals of (3), (5), (7) and (8) suitable for X-ray diffraction were obtained by recrystallization from hexane/CH₂Cl₂ at 4 °C and mounted on a MiteGen loop with Apiezen grease at 293 K (for 3) and 277 K (for 5, 7 and 8). Diffraction studies were carried out on a Rigaku XtaLab mini bench-top instrument. Data collection and data reduction was done with the “Crystal Clear” software of the instrument. The radiation source was Mo-Kα (λ = 0.71075Å) radiation. All data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3 frame widths. The final cell parameters were determined from least-squares refinement on 13556, 10479, 10125 and 16467 reflections, respectively, for (3), (5), (7) and (8). The structures were solved using direct methods and difference Fourier techniques (SHELXL-97). Hydrogen atoms were placed in their expected chemical position using the HFIX command and were included in the final cycles of least squares with isotropic Uij’s related to the atoms ridden on. All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from International Tables for X-ray Crystallography Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXL-97, ORTEP-3 for windows as incorporated in WinGX program suite. Additional details of data collection and structure refinement are given in Table 1.

Results and Discussion

Reactions of [Os₃(CO)₁₀(NCMe)₂] with two equivalents of (4-FC₆H₄)₃P, Ph₂P(o-Tol)₂ and Ph₂P(Cy)₂ at room temperature afforded, after separation by thin layer chromatography, the di- and tri-substituted compounds [Os₃(CO)₁₀(PR₃)₂] (2, PR₃ = (4-FC₆H₄)₃P, 30%; 3, PR₃ = Ph₂P(o-Tol)₂, 24%; 4, PR₃ = Ph₂P(Cy)₂, 25%) and [Os₃(CO)₉(PR₃)₃] (5, PR₃ = (4-FC₆H₄)₃P, 20%; 6, PR₃ = Ph₂P(o-Tol)₂, 16%; 7, PR₃ = Ph₂P(Cy)₂, 17%) respectively as well as the dihydroxyl-bridged complexes 1,2-[Os₃(CO)₉(PR₃)₂(µ-OH)₂] (8, PR₃ = (4-FC₆H₄)₃P, 13%; 9, PR₃ = Ph₂P(o-Tol)₂, 10%; 10, PR₃ = Ph₂P(Cy)₂, 13%) (Scheme 1).

Compounds (2)-(4) have been characterized by a combination of elemental analyses, infrared, NMR and mass spectrometry and by single crystal X-ray diffraction analysis in the case of (3). The infrared spectra of (2)-(4) in the carbonyl stretching region are similar to those of the related disubstituted decacarbonyl compounds [Os₃(CO)₉L₂] [L = PPh₃, PH₂PPh₂, PMe₃, PEt₃, PEt₃Ph, PMePh₂]. The FAB mass spectra of (2)-(4) show a parent molecular ion peak [m/z 1483 for (2), m/z 1431 for (3) and m/z 1399 for (4)] together with fragmentation peaks due to the sequential loss of ten carbonyl ligands. The ¹H NMR spectrum of (2) exhibits two multiplets centered at δ 7.38 and 7.12 (each integrated to 12 H) attributed to the phenyl ring protons of (4-FC₆H₄)₃P moiety. The aromatic region of the ¹H NMR spectrum of (3) contains four multiplets centered at δ 7.87, 7.49, 7.09 (each integrated to 4H) and 7.26 (integrated to 4H) while the aliphatic region shows a singlet at δ 1.83 (integrated to 12H) for the methyl protons of the tolyl group. In addition to usual phenyl proton resonances, the ¹H NMR spectrum of (4) displays a series of multiplets centered at δ 1.85, 1.70, 1.62 and
Table 1—Crystallographic data and structure refinement for (3), (5), (7) and (8)

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<td>P - 1</td>
<td>P - 1</td>
<td>P 1 2₁/c 1</td>
</tr>
</tbody>
</table>

Unit cell dimensions

\[
\begin{align*}
a (Å) & = 16.1(3) \quad 14.602(7) \quad 13.885(6) \quad 16.750(14) \\
b (Å) & = 16.5(3) \quad 15.340(7) \quad 13.994(7) \quad 13.259(11) \\
c (Å) & = 19.2(3) \quad 17.256(9) \quad 21.445(10) \quad 20.949(17) \\
\alpha (°) & = 90 \quad 112.764(5) \quad 88.272(15) \quad 90 \\
\beta (°) & = 113.7(3) \quad 100.03 \quad 72.495(15) \quad 103.613(10) \\
\gamma (°) & = 90 \quad 109.097(3) \quad 73.706(13) \quad 90 \\
\end{align*}
\]

Volume (Å³) | 4661(14) | 3161(3) | 3808(3) | 4522(6) |

\[
\begin{align*}
Z & = 4 \quad 2 \quad 2 \quad 4 \\
Density (calc.) (mg/m³) & = 2.003 \quad 1.861 \quad 1.435 \quad 2.143 \\
Abs. coeff. (mm⁻¹) & = 8.283 \quad 6.717 \quad 5.100 \quad 8.561 \\
F(000) & = 2648 \quad 1680 \quad 1608 \quad 2720 \\
\end{align*}
\]

Crystal size (mm³) | 0.20 x 0.10 x 0.08 | 0.20 x 0.18 x 0.09 | 0.16 x 0.14 x 0.10 | 0.20 x 0.16 x 0.04 |

θ range for data collection (°) | 1.69 to 27.48 | 1.57 to 27.50 | 1.77 to 27.53 | 1.83 to 27.66 |

Index ranges | -16 ≤ h ≤ 20, -18 ≤ k ≤ 18, -19 ≤ l ≤ 22 | -16 ≤ h ≤ 18, -17 ≤ k ≤ 17, -22 ≤ l ≤ 27 | -16 ≤ h ≤ 21, -18 ≤ k ≤ 19, -22 ≤ l ≤ 27 | -21 ≤ h ≤ 21, -17 ≤ k ≤ 17, -22 ≤ l ≤ 27 |

Reflections collected | 16284 | 17307 | 21199 | 35523 |

Independent reflections (Rint) | 10125(0.1018) | 13556(0.0348) | 16467(0.0485) | 10479(0.1294) |

Completeness to θ = 27.50° | 94.8 % | 93.4 % | 93.9 % | 99.4 % |

Max. and min. transmission | 1.000 and 0.558 | 0.6066 and 0.3716 | 0.6295 and 0.4958 | 0.7258 and 0.2793 |

Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |

Data/restraints/parameters | 10125 / 0 / 336 | 13556 / 10 / 784 | 16467 / 0 / 703 | 10479 / 0 / 589 |

Goodness of fit on F² | 1.027 | 1.146 | 1.123 | 1.071 |

Final R indices [I > 2σ(I)] | R1 = 0.0973, wR2 = 0.1990 | R1 = 0.0544, wR2 = 0.1073 | R1 = 0.0751, wR2 = 0.1875 | R1 = 0.0764, wR2 = 0.1382 |

R indices (all data) | R1 = 0.213, wR2 = 0.2774 | R1 = 0.0872, wR2 = 0.1273 | R1 = 0.1372, wR2 = 0.2325 | R1 = 0.1282, wR2 = 0.1691 |

Largest difference inpeak and hole (eÅ⁻³) | 7.743 and −3.153 | 1.527 and −2.615 | 2.176 and −1.377 | 3.067 and −2.817 |

1.44 with a relative intensity of 14:10:6:14 assigned to the cyclohexyl protons. ³¹P[¹H] NMR spectra of (2)-(4) exhibit a broad singlet (δ) −2.1 for (2), −14.3 for (3) and −10.3 for (4). The broad signals of ³¹P[¹H] NMR for (2)-(4) are indicative of flucutional behavior, which has also been observed for the analogous disubstituted clusters 1,2-[Os₅(CO)₁₀(PMe₂Ph₂)]¹⁵ and 1,2-[Os₅(CO)₁₀(P₃Ph₃(C₆H₅S))₂]²⁰. It has been reported that these 1,2- compounds exist in solution as a mixture of trans-trans and cis-trans isomers, which are in rapid equilibrium at room temperature. As the three species (2)-(4) exhibit similar behavior in solution, the VT ³¹P[¹H]NMR of (2) will be discussed in detail. The ³¹P[¹H]NMR spectrum of (2) at −30 °C (Fig.1) reveals that the predominant form is the cis-trans isomer with non-equivalent phosphorus nuclei, represented by two singlets at δ −5.5 and −8.2, while the third singlet at δ −5.4 is attributed to the trans-trans isomer.

In general, the trans-trans isomers crystallize and their structures are well established. The structures of the trans-trans isomer of [Os₅(CO)₁₀(P₃Ph₃)]⁴,
Reactions of \([\text{Os}_3(\text{CO})_{10}]\) with (4-FC₆H₄)₃P, PhP(o-Tol)₂ and PhP(Cy)₂

Scheme 1

In order to confirm whether compounds (2)-(4) crystallizes in the trans-trans or cis-trans form, single crystal X-ray analysis of (3) was undertaken. The structure of (3) is shown in Fig. 2; the selected bond distances and angles are given in the caption. The overall structure of (3) is similar to that of trans-trans isomer of \([\text{Os}_3(\text{CO})_{10}]\) \(\text{PPh}_3\) \(^{1,4,26,31,32}\). The molecule consists of a triangular metal core of osmium atoms with ten terminal carbonyl ligands and two PhP(o-Tol)₂ ligands. The Os(1) and Os(3) atoms each
carry three terminal carbonyl ligands and the Os(2) atom possesses four carbonyl ligands. The metal-metal bond distances \([\text{Os}(1)-\text{Os}(2) = 2.91(5), \text{Os}(1)-\text{Os}(3) = 2.90(6)\) and \(\text{Os}(2)-\text{Os}(3) = 2.91(4)\) Å] are longer than the average osmium-osmium distances of 2.877(3) Å in \(\text{Os}_3(\text{CO})_{12}\), but comparable to the Os-Os distances in both isomers of \([\text{Os}_5(\text{CO})_{10}(\text{PPh}_3)_2]\) and \(\text{trans},\text{trans}-[\text{Os}_5(\text{CO})_{10}][\text{P}(\text{C}_6\text{H}_5\text{S}_2)_2]\). Two \(\text{PhP}(\alpha-\text{Tol})_2\) ligands occupy equatorial coordination sites on adjacent osmium atoms and each of them is \textit{trans} to the phosphine-substituted Os-Os edge. The Os-P bond distances \([\text{Os}(1)-\text{P}(1) = 2.40(5), \text{Os}(3)-\text{P}(2) = 2.38(4)\) Å] are normal but somewhat longer than those reported for both isomers of \([\text{Os}_5(\text{CO})_{10}(\text{PPh}_3)_2]\) \([2.351(2)\) and 2.361(2) Å] for the \textit{cis},\textit{trans} isomer and 2.3607(12) and 2.3478(13) Å for the \textit{trans},\textit{trans} isomer \([26]\).

Compounds (5)-(7) have been characterized by a combination of IR, \(\text{H}^1\) and \(\text{31P}^1\) NMR, FAB mass spectrometry and single crystal X-ray diffraction studies for (5) and (7). The pattern of the infrared spectrum of (5)-(7) is very similar to that of the related tertiary phosphine-substituted trismium nonacarbonyl compounds \([15,28,29,34-36]\). The \(\text{H}^1\) NMR spectrum of 5 exhibits two multiplets centered at \(\delta 7.33\) and 7.03 (each integrated for 18H) due to the methyl protons of the tolyl groups. The \(\text{H}^1\) NMR spectrum of (6) shows a complex multiplets at \(\delta 8.19-7.63\) (integrated to 39H) assigned to the ring protons and a singlet at \(\delta 2.27\) (integrated to 18H) due to the methyl protons of the tolyl groups. The \(\text{H}^1\) NMR spectrum of (7) displays two multiplets at \(\delta 7.49, 7.26\) (integrated to 5H and 10H, respectively) for the phenyl protons and five multiplets at \(\delta 1.86, 1.78, 1.55\) (each integrated to 6H), 1.69 (integrated for 12H) and 1.15 (integrated to 36H) due to the cyclohexyl ring protons. The \(\text{31P}^1\) NMR spectra show a singlet \(\delta -5.4\) for (5), 35.1 for (6) and \(-2.9\) for (7)] indicating that the phosphorus atoms of the phosphine ligands are in equivalent environment. The mass spectra of (5)-(7) exhibit the parent molecular ion peak \([\text{m/z} 1771\) for (5), \text{m/z} 1693 for (6) and \text{m/z} 1645 for (7)] as well as peaks due to stepwise loss of nine carbonyls.

The molecular structures of (5) and (7) are depicted in Figs 3 and 4, respectively with selected bond lengths and angles in the captions. The structures of (5) and (7) are based on a triangular arrangement of the three osmium atoms with nine terminal CO ligands. Three \(\text{Pr}_3\) \([\text{R} = \text{P}(4-\text{FC}_6\text{H}_4), \text{Ph}(\text{Cy})_2]\) ligands bonded one to each metal atom in equatorial sites, such that one is as far away from the other two as possible. The dispositions of the phosphines substituent are such that one lies below the plane, while the other two lie above it (see Figs 3 and 4).

So each osmium contains one equatorial and two axial CO ligands. The Os-Os distances \([\text{Os}(1)-\text{Os}(2) = 2.9143(12), \text{Os}(1)-\text{Os}(3) = 2.9105(15), \text{Os}(2)-\text{Os}(3) = 2.9096(12)\) Å] for (5); \(\text{Os}(1)-\text{Os}(2) = 2.9516(13), \text{Os}(1)-\text{Os}(3) = 2.9494(16)\) and \(\text{Os}(2)-\text{Os}(3) = 2.9531(15)\) Å] for (7)] are longer than the Os-Os distances in \(\text{Os}_3(\text{CO})_{12}\) but are comparable to those in \([\text{Os}_5(\text{CO})_{10}(\text{PPh}_3)_2]\) \([37]\). The Os-P distances in (5) lie in the normal range \([\text{Os}(1)-\text{P}(1) = 2.341(3), \text{Os}(2)-\text{P}(2) = 2.348(3), \text{Os}(3)-\text{P}(3) = 2.351(3)\) Å] and comparable to those in \([\text{Os}_5(\text{CO})_{10}(\text{PPh}_3)_2]\) \([37]\), whereas the Os-P distances in (7) \([\text{Os}(1)-\text{P}(1) = 2.391(4), \text{Os}(2)-\text{P}(2) = 2.382(4), \text{Os}(3)-\text{P}(3) = 2.379(4)\) Å] are longer than those in (5) and \([\text{Os}_5(\text{CO})_{10}(\text{PPh}_3)_2]\) \([37]\).

The lengthening of the bond distances (Os-Os, Os-P) in (7) compared to (5) and \([\text{Os}_5(\text{CO})_{10}(\text{PPh}_3)_2]\)

**Fig. 3** — Molecular structure of 1,2,3-\([\text{Os}_5(\text{CO})_{10}(\text{4-FC}_6\text{H}_4))\] showing 50% probability thermal ellipsoids. Ring hydrogen atoms are omitted for clarity. [Selected bond distances (Å) and angles (°): \(\text{Os}(1)-\text{Os}(2) = 2.9143(12), \text{Os}(1)-\text{Os}(3) = 2.9105(15), \text{Os}(2)-\text{Os}(3) = 2.9096(12)\) Å; \(\text{Os}(1)-\text{P}(1) = 2.341(3), \text{Os}(2)-\text{P}(2) = 2.348(3), \text{Os}(3)-\text{P}(3) = 2.351(3)\) Å; \(\text{Os}(1)-\text{Os}(2)-\text{Os}(3) = 59.94(4)°\); \(\text{Os}(1)-\text{Os}(2)-\text{Os}(3) = 60.098(17)°\); \(\text{Os}(2)-\text{Os}(1)-\text{Os}(3) = 60.987(17)°\); \(\text{Os}(2)-\text{Os}(1)-\text{Os}(3) = 59.7(3)°\); \(\text{Os}(1)-\text{Os}(2)-\text{Os}(3) = 2.9516(13)°\); \(\text{Os}(1)-\text{Os}(2)-\text{Os}(3) = 2.9494(16)°\); \(\text{Os}(2)-\text{Os}(1)-\text{Os}(3) = 111.00(7)°\); \(\text{Os}(3)-\text{Os}(1)-\text{Os}(2) = 111.42(7)°\); \(\text{Os}(3)-\text{Os}(1)-\text{Os}(2) = 111.52(7)°\).]
Fig. 4 — Molecular structure of \(\text{[OS}_3\text{(CO)}_8\text{][PhP(Cy)}_2\text{]}\) showing 50% probability thermal ellipsoids. Ring hydrogen atoms are omitted for clarity. [Selected bond distances (Å) and angles (°): \(\text{Os}(1)\text{─Os}(2) 2.9516(13), \text{Os}(1)\text{─Os}(3) 2.9494(16), \text{Os}(2)\text{─Os}(3) 2.9531(15), \text{Os}(1)\text{─P}(1) 2.391(4), \text{Os}(2)\text{─P}(2) 2.382(4), \text{Os}(3)\text{─P}(3) 2.379(4); \text{Os}(1)\text{─Os}(2)\text{─Os}(3) 59.93(3)\) and \(\theta\) can be explained from their respective cone angles. The calculated effective cone angles (\(\theta\)) are 145°, 155°, and 163° respectively. Bruce et al. \(\text{37}\) suggested that, the lengthening of the bonds (M-M and M-P) with the introduction of tertiary phosphine in cluster compounds increases with the increasing cone angle of the corresponding ligands. The steric interactions resulting in the introduction of PhP(Cy)\(_2\) are relieved by twisting of the Os(CO)\(_3\) group about the Os─Os vector. The gross structures of (5) and (7) are similar to those of the previously characterized trisubstituted clusters of the general formula \([\text{M}_3\text{(CO)}_9\text{(phosphane)}]_{\text{3}(\text{M} = \text{Os, Ru; phosphane = PMe}_2\text{(CH}_3\text{Ph), PMe}_2\text{Ph, PPh(OMe)}_2, \text{PPh(OEt)}_3, \text{P(OCH}_3\text{CF}_3)_2, \text{PPh}_3)}\). Compounds (8)-(10) have been characterized by elemental analyses, IR, \(\text{H}\), and \(\text{P}^{1\text{H}}\) NMR, FAB mass spectrometry together with single crystal X-ray diffraction studies for (8). The pattern of the infrared spectrum of (8)-(10) is very similar to that of \([\text{Os}_5\text{(CO)}_3\text{(PPh}_3)_2\text{(µ-OH)}_2]^{40}\) indicating that they have similar distribution of the carbonyl ligands. The FAB mass spectra of all three compounds exhibit a parent molecular ion peak \([m/z 1461\text{ for (8), } m/z 1409\text{ for (9) and } m/z 1377\text{ for (10)}]\) and ions due to the sequential loss of eight carbonyl groups consistent with their stoichiometric formulas and microanalytical data are also in complete agreement with the proposed formula. The \(\text{H}\) NMR spectra of compounds (8)-(10) showed the expected spectra in the phenyl and aliphatic regions. The \(\text{P}^{1\text{H}}\) NMR spectra of (8)-(10) show a singlet [\(\delta 3.9\text{ for (8), 34.9 for (9) and 18.1 for (10)}\)], suggesting that the three phosphine ligands are in equivalent environment. In the \(\text{H}\) NMR spectra, the OH protons give a triplet [\(\delta 0.06\text{ (}\text{J}_{\text{PH}} = 3.4\text{ Hz)}\text{ for (8), } \delta 0.07\text{ (}\text{J}_{\text{PH}} = 3.5\text{ Hz)}\text{ for (9) and } \delta 0.95\text{ (}\text{J}_{\text{PH}} = 3.5\text{ Hz)}\). The high-field chemical shift and \(\text{J}_{\text{PH}}\) values for the OH protons in (8-10) are in the range of values found for related structurally characterized OH-bridged trisodium clusters: \([\text{Os}_5\text{(CO)}_3\text{(PPh}_3)_2\text{(µ-OH)}_2]\) [\(\delta -0.18, \text{J}_{\text{PH}} = 3.6\text{ Hz}\) \(40\), \([\text{µ-H]}\text{Os}_5\text{(CO)}_3\text{(µ-dppm)(µ-OH)}_2]\) [\(\delta 0.44, \text{J}_{\text{PH}} = 4.3\text{ Hz}\) \(41\) and \([\text{Os}_5\text{(µ-MeOCO})(\text{CO})_3\text{(PPh}_3)(µ\text{-OH})]\) [\(\delta -1.98, \text{J}_{\text{PH}} = 4.8\text{ Hz}\) \(32\).

The molecular structure of (8) is shown in Fig. 5 and selected bond distances and angles are collected
in the caption. The structure of (8) consists of an open triangular cluster of three Os atoms with eight terminal CO, two bridging OH and two (4-FC\textsubscript{6}H\textsubscript{4})\textsubscript{3}P ligands. The non-bonded Os(1)----Os(2) distance of 3.112(2) Å in compound (8) is comparable to the non-bonded Os(1)----Os(2) distances of 3.1197(2) Å in [Os\textsubscript{3}(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(μ-OH)]\textsubscript{2}\textsuperscript{40}. Nevertheless the cluster is electron-precise without the Os(1)----Os(2) bond. The Os(1)----Os(3) and Os(2)----Os(3) distances in (8) are also comparable to those in [Os\textsubscript{3}(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(μ-OH)]\textsubscript{2} [Os(1)----Os(3) = 2.8572(2), Os(2)----Os(3) = 2.8585(2)]\textsuperscript{40}. The phosphine ligands occupy equatorial sites and the Os-P distances (Os(1)----P(1) = 2.372(4), and Os(2)----P(2) = 2.357(4) Å) distances are comparable to those in [Os\textsubscript{3}(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(μ-OH)]\textsubscript{2} [Os(1)----P(1) = 2.3682(8), and Os(2)----P(2) = 2.3864(8) Å]\textsuperscript{40}. Both OH groups symmetrically span the open Os(1)----Os(2) edge and the Os-O distances (Os(1)----O(1) = 2.158(9), Os(1)----O(2) = 2.137(8), Os(2)----O(1) = 2.137(8) and Os(2)----O(2) = 2.126(9) Å) are comparable to the Os-O distances in other OH-bridged triosmium clusters\textsuperscript{40,43,44}. We believe that the shortness of the non-bonded Os(1)----Os(2) edge is attributed to the presence of two hydroxylbridges, and in support of this, we note that a similar shortening is found in [Os\textsubscript{3}(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(μ-OH)]\textsubscript{2} [3.1197(2) Å]\textsuperscript{40}. The origin of the hydroxy ligands in (8), (9) and (10) may be dioxygen, or more likely water; there are examples of the formation of OH ligands in triosmium and triruthenium clusters from water or dioxygen\textsuperscript{35,47}.

**Conclusions**

In conclusion, the introduction of tertiary phosphines such as (4-FC\textsubscript{6}H\textsubscript{4})\textsubscript{3}P, PhP(o-Tol)\textsubscript{2} and PhP(Cy)\textsubscript{2} into the coordination sphere of triosmium cluster by substitution of the acetonitrile ligand of 1,2-[Os\textsubscript{3}(CO)\textsubscript{10}(NCMe)\textsubscript{2}] (1) at room temperature is facile. Di- and tri-substituted products 1,2-[Os\textsubscript{3}(CO)\textsubscript{10}(PR\textsubscript{3})\textsubscript{2}] \{2, PR\textsubscript{3} = (4-FC\textsubscript{6}H\textsubscript{4})\textsubscript{3}P; 3, PR\textsubscript{3} = PhP(o-Tol)\textsubscript{2}; 4, PR\textsubscript{3} = PhP(Cy)\textsubscript{2}\} and 1,2,3-[Os\textsubscript{3}(CO)\textsubscript{9}(PR\textsubscript{3})\textsubscript{3}] \{5, PR\textsubscript{3} = (4-FC\textsubscript{6}H\textsubscript{4})\textsubscript{3}P; 6, PR\textsubscript{3} = PhP(o-Tol)\textsubscript{2}; 7, PR\textsubscript{3} = PhP(Cy)\textsubscript{2}\} could be prepared from these reactions. The VT \textsuperscript{31}P\textsuperscript{1}H\textsuperscript{1}NMR spectra of the disubstituted products (2)-(4) demonstrate that a mixture of two isomers, which are in rapid exchange at room temperature is present. The structure of the trans-trans isomer has been determined by X-ray crystallography.

**Supplementary Data**

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data centre. CCDC 1010006, CCDC 1010004, CCDC 1010729 and CCDC 1010005 contain supplementary crystallographic data for compound (3), (5), (7) and (8) respectively. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; Email: depot@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk). Check CIF data are available in the electronic form at http://www.niscair.res.in/ jinfo/jca/IJCA_54A(02)161-169_SupplData.pdf.

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**References**


