

Synthesis & Reactions of a New Isomer of $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$

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The isomeric butadiene compounds $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}i\text{-}C_4H_6)]$ react with $\text{P}(\text{OMe})_3$ at room temperature to give 1,1- and 1,2-isomers of $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$, whereas PPh_3 reacts with the butadiene compounds to give only the known 1,2-isomer, 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$, which has been characterised by infrared, ^{31}P and ^{13}C NMR data, reacts with trifluoroacetic acid to give the singly protonated cation 1,1- $[\text{Os}_3\text{H}(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]^+$ isolated in good yield as the hexafluorophosphate salt.

The direct reaction of tertiary phosphines (L) with $[\text{Os}_3(\text{CO})_{12}]$ in refluxing toluene is reported¹ to give $[\text{Os}_3(\text{CO})_{11}(\text{L})]$, $[\text{Os}_3(\text{CO})_{10}(\text{L})_2]$ and $[\text{Os}_3(\text{CO})_9(\text{L})_3]$. The mono- and di-substituted derivatives can be obtained in good yields by substitution² of MeCN from $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ and $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$. The desired derivatives can also be obtained in good yields by the addition of catalytic amounts of $[\text{Ph}_2\text{CO}]^+$ to a mixture containing $[\text{Os}_3(\text{CO})_{12}]$ and L in stoichiometric amounts in THF at ambient temperature³. Deeming *et al.*⁴ have recently prepared a new isomer of $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ by displacing butadiene from $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$. This new 1,1-isomer, in which both the phosphines are coordinated to the same metal atom, reacts with trifluoroacetic acid to give the singly protonated cation 1,1- $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]^+$ (ref. 5). Herein is reported the preparation of the corresponding 1,1-isomers of $\text{P}(\text{OMe})_3$ and PPh_3 to establish the generality of this synthetic route.

Materials and Methods

PMR spectra were recorded on a Varian XL 200 instrument, IR spectra on a Perkin-Elmer PE 983 spectrophotometer and ^{13}C NMR spectra at natural abundance for solutions containing ~ 0.05 mol dm^{-3} $[\text{Cr}(\text{acac})_3]$ as a shiftless relaxation reagent. Phosphorus-31 NMR spectra were recorded in CDCl_3 and referenced to $\text{P}(\text{OMe})_3$.

The starting materials $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}i\text{-}C_4H_6)]$ were prepared by published methods⁶.

Reaction of $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}i\text{-}C_4H_6)]$ with trimethyl phosphite

A solution of $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$ (0.3 g) and $\text{P}(\text{OMe})_3$ (0.124 g, 3 mol/mol Os_3) in dichloromethane (50 ml) was allowed to stand at room tem-

perature in the dark under N_2 for 10 days. Removal of solvent *in vacuo* and TLC of the residue over silica gel employing light petrol (b.p. 30-40°)-ether (10:2, v/v) afforded 1,2- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (0.01 g, 3%), characterised by comparison of its spectra with those reported⁷, and 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (0.268 g, 73%) (Found: C, 17.55; H, 1.55; P, 5.6. $\text{C}_{16}\text{H}_{18}\text{O}_{16}\text{Os}_3\text{P}_2$ requires C, 17.5; H, 1.7; P, 5.6%); IR (cyclohexane): ν_{CO} at 2097m, 2045s, 2016(sh), 2010vs, 1995(sh), 1991m, 1980m, 1966m, 1937w cm^{-1} ; PMR (CDCl_3): δ 3.62 (d, OMe, $J = 11.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -38.96; $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_3\text{C}_6\text{D}_5/\text{CH}_3\text{C}_6\text{H}_5$): δ 196.6 [t , $^2J(^{13}\text{C}^{31}\text{P}) = 9.3$ Hz], 186.1(s), 176.5(s) and 170.9(s).

A similar treatment of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}i\text{-}C_4H_6)]$ (0.05 g) with $\text{P}(\text{OMe})_3$ (0.021 g, 3 mol/mol Os_3) for 72 hr gave 1,2- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (0.025 g, 41%) and 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (0.008 g, 13%).

Reaction of $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}i\text{-}C_4H_6)]$ with triphenylphosphine

The reaction between $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}i\text{-}C_4H_6)]$ (0.350 g) and PPh_3 (0.306 g, 3 mol/mol Os_3) in dichloromethane (60 ml) as above for 10 days followed by similar work-up gave 1,2- $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ (0.210 g, 39%) and 1,2,3- $[\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3]$ (0.031 g, 5%) characterised by comparison of their spectra with those reported^{3,8}.

A similar treatment of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}i\text{-}C_4H_6)]$ (0.05 g) and PPh_3 (0.044 g, 3 mol/mol Os_3) for 72 hr gave 1,2- $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ (0.038 g, 50%) and 1,2,3- $[\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3]$ (0.07 g, 8%).

Protonation of 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$

A solution of $\text{CF}_3\text{CO}_2\text{H}$ (0.016 ml, 5 mol/mol Os_3) and 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (0.046 g) in

CDCl_3 (0.5 ml) when monitored by PMR spectroscopy indicated that complete protonation had occurred. The solvent was removed *in vacuo* and the residue dissolved in methanol (5 ml). To this was added a methanolic solution of $[\text{NH}_4][\text{PF}_6]$ (0.011 g) followed by a few drops of water to give a yellow precipitate, which was filtered off. Recrystallisation from CH_2Cl_2 -ether gave 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]\text{PF}_6$ (0.044 g, 71%) (Found: C, 15.3; H, 1.4; P, 7.35. $\text{C}_{16}\text{H}_{19}\text{F}_6\text{O}_{16}\text{Os}_3\text{P}_3$ requires C, 15.45; H, 1.55; P, 7.45%; IR (CH_2Cl_2): ν CO at 2139m, 2089s, 2065s, 2055vs, 2038m, 2010m, 2000(sh), 1970w cm^{-1} ; PMR (CDCl_3): δ 3.79 (d, OMe, $J(\text{PH})=7.2$ Hz), 3.85 (d, $J(\text{PH})=7.2$ Hz) and -20.61 dd, OsH, $J(\text{PH})=26.2$ Hz (*trans*), 9.5 Hz (*cis*).

Results and Discussion

In $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-}s\text{-}cis\text{-}\text{C}_4\text{H}_6)]$ (compound-I), the *s-cis*-diene is coordinated to the same metal atom at axial and equatorial sites. In $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}s\text{-}trans\text{-}\text{C}_4\text{H}_6)]$ (compound-II), the diene is coordinated to two metal atoms. Both the compounds I and II react with trimethyl phosphite to afford 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (compound-III) as the major product in the case of I (73% yield) along with 1,2-isomer as the minor product (3%) and in the case of II 1,2-isomer as the major product (39%) along with 1,1-isomer (III) as the minor product. This indicates that when diene is attached to one metal atom, it is displaced by $\text{P}(\text{OMe})_3$ to give the 1,1-isomer as the major product but when diene acts as a bridge between two metal atoms it is displaced to give 1,2-isomer as the major product. We have recently observed that the 1,2-isomer exists in solution as two

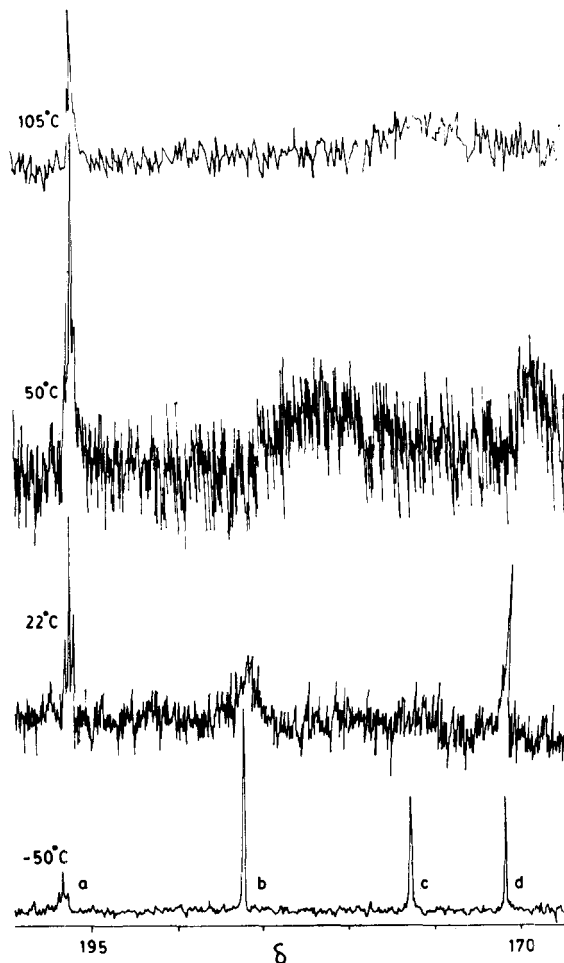
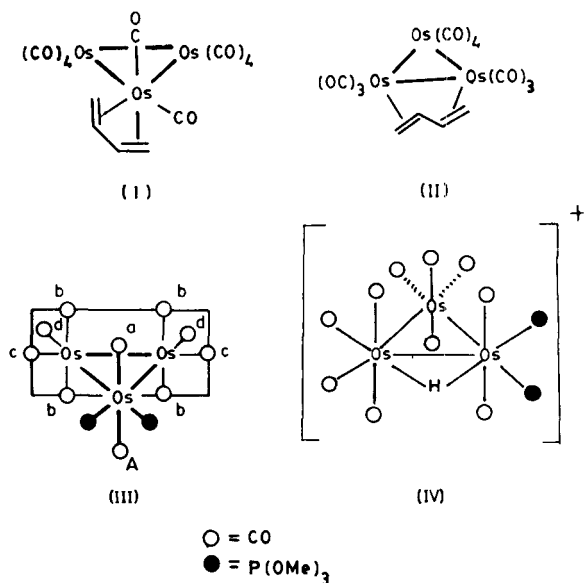


Fig. 1—Temperature-dependent $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1,1- $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ in toluene (natural abundance ^{13}C).

inter-converting isomers, the major having non-equivalent ^{31}P nuclei whereas these are equivalent in the minor isomer⁷. In order to examine possible steric effects on isomer distribution, we looked at a bulkier tertiary phosphine. Thus the reaction of PPh_3 with $[\text{Os}_3(\eta^4\text{-}s\text{-}cis\text{-}\text{C}_4\text{H}_6)(\text{CO})_{10}]$ afforded 1,2- $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ (39%) and 1,2,3- $[\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3]$ (5%). The crowding at a single osmium atom necessary to accommodate two bulky triphenylphosphine ligands (cone angle 145°), probably prevents the formation of 1,1-isomer.

The νCO modes of compound-III are higher than those of 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ (ref. 4) and this is expected because $\text{P}(\text{OMe})_3$ is a poor σ -donor and better π -acceptor than PMe_2Ph . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of III exhibits a single resonance at δ -38.96 indicating equivalent ^{31}P nuclei. Compound-III has a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum very similar to that 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ in the carbonyl region. The temperature dependent $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of III are shown in Fig. 1. The low temperature (-50°) spectrum displays a triplet at δ

196.9(a), [$^2J(^{13}\text{C}^{31}\text{P}) = 9.3 \text{ Hz}$] assignable to carbonyls (a) and three singlets at δ 186.1(b), 176.6(c) and 170.9(d) assignable to carbonyls (b), (c) and (d) respectively, the intensity ratio of all the signals being 2 : 4 : 2 : 2. This is consistent with a C_{2v} symmetry in which the $\text{P}(\text{OMe})_3$ ligands are equatorially positioned at the same metal atom. The axial CO ligands (a) are coupled equivalently to the two ^{31}P nuclei and appear as a triplet. As the temperature is increased the signals due to carbonyls (b) and (c) broaden and coalesce at about 40° while that of carbonyls (d) remains distinct. Thus the lowest energy process observed for this cluster involves the two-centre 'merry-go-round' mechanism with a di- μ -CO intermediate involving four axial and two equatorial carbonyls in the plane as shown in structure (III). At higher temperatures (105°) the signals due to carbonyls (d) coalesce with the already coalesced signals for carbonyls (b) and (c). This merging of carbonyl signals is consistent with a *turnstile* mechanism. It should be noted that complete (b)-(c)-(d) scrambling was not observed for $1,1\text{-}[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ (ref. 4) because decarbonylation of the cluster occurs above 100° . Even at 105° the signal for carbonyls (a) is sharp. The only manner in which these carbonyls could exchange with others is by a conical exchange of axial CO ligands leaving the equatorial ligands intact. However, the carrier to such a process appears to be very high.

As expected the compound III reacts with five-fold excess of trifluoroacetic acid at room temperature to give $1,1\text{-}[\text{Os}_3\text{H}(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]^+$ (compound-IV), isolated in good yield (71%) as the hexafluorophosphate salt. The PMR spectrum of IV exhibits two methyl doublets at δ 3.79 and 3.85 [$J(\text{PH}) = 7.2 \text{ Hz}$] and a hydride double doublet at δ

– 20.61 [$J(\text{PH}) = 26.2 \text{ Hz}$] (*trans*) and 9.5 Hz (*cis*) implying that the equivalent $\text{P}(\text{OMe})_3$ ligands in III are not so in the protonated form. This observation is very similar to those for $1,1\text{-}[\text{Os}_3\text{H}(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ (ref. 5) and $1,1\text{-}[\text{Os}_3\text{H}(\text{CO})_{10}(\text{diphosphine})][\text{PF}_6]$ (ref. 9) and so the structure of the cation (IV) may unambiguously be assigned by comparison with the PMe_2Ph analogue, the X-ray structure of which is known⁵.

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