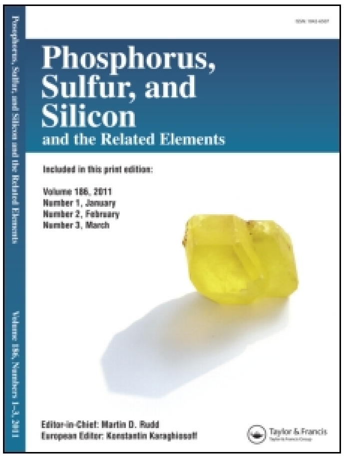

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OXIDATIVE ADDITION OF PHOSPHOLES AND PHOSPHABENZENE INTO TRIOSMIUM AND TRIRUTHENIUM CLUSTERS. RING OPENING VERSUSC-H BOND CLEAVAGE.

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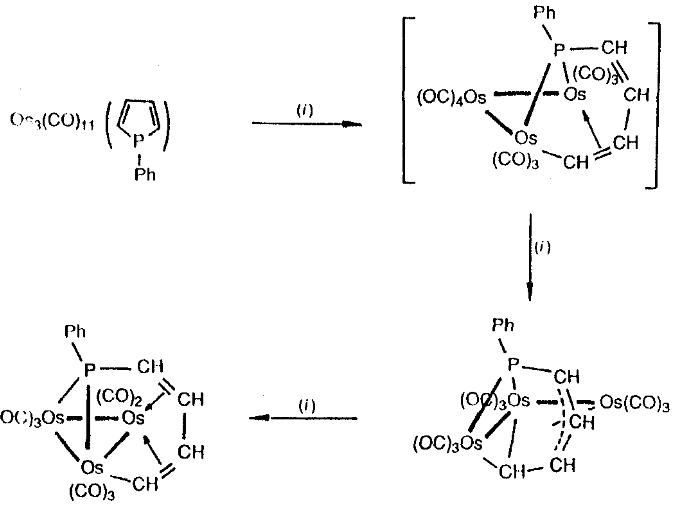
Abstract The five-membered heterocycles compounds 3,4-dimethyl-1-phenylphosphole (PhPCH=CMeCMe=CH) and 1-phenylphosphole (PhPCH=CHCH=CH) react with the clusters $[Os_3(CO)_{11}(MeCN)]$ or $[Os_3(CO)_{10}(MeCN)_2]$ to give the simple substitution products $[Os_3(CO)_{12-x}(phosphole)_x]$ (x= 1 or 2), in which the phospholes are coordinated as tertiary phosphines through the phosphorus atoms. The six membered heterocyclic compounds phosphabenzene and 2-terbutyl-phosphabenzene react with $[Os_3(CO)_{11}(MeCN)]$ or $[Os_3(CO)_{10}(MeCN)_2]$ to give simple substitution products $[Os_3(CO)_{12-x}(phosphabenzene)_x]$ (x=1 or 2). $[Ru_3(CO)_{12}]$ and $[Os_3H_2(CO)_{10}]$ react with 2-terbutyl-phosphabenzene to give the nonacarbonyl species $[HRu_3(CO)_9(P{=}CCH{=}CH{-}CH{=}C\{^tBu\})]$ and $[H_2Os_3(CO)_9(PCHCH{=}CHCH{=}C\{^tBu\})]$ respectively, where a C-H bond cleavage has ocurred and the phosphorus atom is coordinated to a metal center, even though the clusters show different geometries, which are discussed.

1-Phenylphosphole ($PhPC_4H_4$) reacts with $[Os_3(CO)_{11}(MeCN)]$ to give $[Os_3(CO)_{11}(PhPC_4H_4)]$ **1** which thermally decarbonylates to the nonacarbonyl $[Os_3(CO)_9(PhPC_4H_4)]$ **2** and the octacarbonyl $[Os_3(CO)_8(PhPC_4H_4)]$ **3**, which are shown spectroscopically and by X-ray diffraction methods to contain ring-opened ligands. A decacarbonyl intermediate was not observed but is believed to have the structure shown in Scheme 1 on the basis of the known structure of the related compound formed by ring-opening of selenophene[1]. In each decarbonylated product which we isolated, the $PhPC_4H_4$ ligand behaves as an 8-electron donor, but the modes of bonding in the two compounds are very different[2].



SCHEME 1.

Both acetonitrile complexes $[Os_3(CO)_{12-x}(MeCN)_x]$ (x= 1 or 2) react with 3,4-dimethyl-1-phenylphosphole ($PhPC_4H_2Me_2$) to give in different amounts the two complexes $[Os_3(CO)_{12-x}(PhPC_4H_2Me_2)_x]$ **4** and **5** (x=1 or 2 respectively). Thermal decarbonylation of $[Os_3(CO)_{11}(PhPC_4H_2Me_2)]$ **4**, gave purple crystals of the nonacarbonyl $[Os_3(CO)_9(PhPC_4H_2Me_2)]$ **A**, (44% conversion) and two other yellow compounds in less than 2% conversion. One of these was characterised mainly by X-ray diffraction as $[Os_3(\mu\text{-}H)(\mu\text{-}PC_4H_2Me_2)(\mu_3\text{-}C_6H_4)(CO)_9]$ **B**, an isomer of **A**. The other minor yellow product **C** is also an isomer of **A**, but unlike **B**, it is converted readily into **A** on standing. Because of this, **C** was only characterised spectroscopically. We have found that the purple isomer **A** is converted into this other yellow isomer **C** on irradiation with white light from a fluorescent tube. Isomer **C** is converted into a mixture containing predominantly isomer **A** over several hours at room temperature in the dark or under low intensity light conditions. The cluster $[Os_3(CO)_9(PhPC_4H_2Me_2)]$ **A** is not a hydride derivative (^1H nmr evidence) and as well as phenyl resonances in the

^1H nmr spectrum, four other signals were observed (Me signals at δ 1.07 and 2.30; C-H signals at δ 2.82 and 11.70). Decarbonylation has led to major changes in the bonding of the phosphole ligand, but the product does not correspond spectroscopically at all to the unsubstituted phosphole derivative $[Os_3(CO)_9(PhPC_4H_4)]$ **2.** The molecular structure of **A** is shown in Fig. 1.

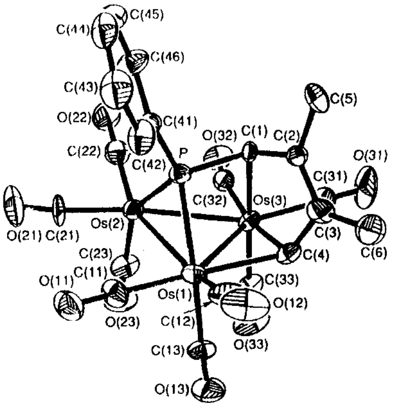
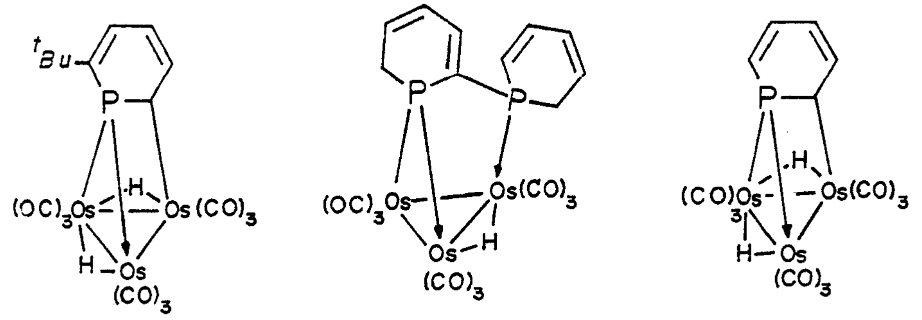


FIGURE. 1. Molecular Structure of $[Os_3(CO)_9(PhPC_4H_2Me_2)]$, cluster **A.**

The cluster $[H_2Os_3(CO)_{10}]$ reacts with phosphabenzene and 2-ter-butyl-phosphabenzene (RC_5H_4P, R=H or ^tBu) in refluxing cyclohexane to give the clusters containing a new type of triply bridging phospabenzene ligand, $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}RC_5H_4P)(CO)_9]$ **6**, and the phosphabenzene coupled product $[Os_3(\mu\text{-}H)(\mu_3\text{-}C_{10}H_{11}P_2)(CO)_9]$ **7**. (Figure 2).



6 7 8

FIGURE 2. Structures of the phosphabenzene-derived triosmium clusters **6, 7** and **8**.

Clusters **6** and **8** have almost identical IR data around 2000 cm^{-1} and hence, directly related structures. The single X-ray crystal structure of cluster **8** has been determined, which shows the phosphabenzene as a μ^3-, 4-electron donor, and the coordinatively saturated phosphorus atom behaves as a 3-electron donating phosphido bridge between two osmium atoms; the *alfa* carbon is *sigma* bonded to the third osmium atom. This leaves the rest of the ring as a diene unit, and the ring is distinctly non-planar as a result of the tetrahedral geometries at the phosphorus and at the *alfa* carbon.

Cluster **7** is derived by coupling of two phosphabenzene ligands, giving a new diphosphine ligand which is bonded to the metal atoms through a phosphido-bridging atom and through a tertiary phosphine atom, and behaves as a 5-electron donor. The mechanism of formation of the diphosphine ligand is unclear and involves various H-atom shifts as well as the formation of the P-C bond.

$[Ru_3(CO)_{12}]$ reacts smoothly with 2-terbutyl-phosphabenzene to give in reasonable yields $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PC_5H_4{}^tBu)]$ **9**, in which C-H bond cleavage occurs. The ligand in this case acts as a five-electron donor, (Fig. 3).

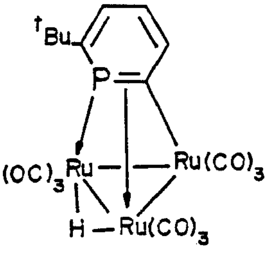


FIGURE 3. Structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PC_5H_4{}^tBu)(CO)_9]$, cluster **9**.

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