Reaction of β-diiodotetraphosphorus trisulfide with dialkyldisulfides

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It has been found that β-diiodotetraphosphorus trisulfide (**1**) reacts with dialkyldisulfides **2a,b** in anhydrous benzene (20°C, 3h) to give trialkyl tetrathiophosphates (**3a,b**).

$$\underset{\mathbf{1}}{\beta\text{-}P_4S_3I_2} + 7\ \underset{\mathbf{2a,b}}{RSSR} \rightarrow 4\ \underset{\mathbf{3a,b}}{(RS)_3P{=}S} + 2\ [RSI]$$

R = Et(**a**), Pr (**b**)

Probably, the reactions also give alkylsulfenyl iodides which could not be isolated due to their instability under the reaction conditions.

Triethyl tetrathiophosphate (3a). Disulfide **2a** (11.9 g, 97.4 mmol) was added dropwise under argon at 20°C to a stirred solution of compound **1** (6 g, 13.9 mmol) in anhydrous benzene (15 mL). The mixture was stirred for 3 h at 20°C. The solvent was distilled off. Distillation of the residue gave 9.0 g (66%) of compound **3a**, b.p. 135—136°C (10 Torr), n_D^{20} 1.6205. ^{31}P NMR (162 MHz, relative to 85% H_3PO_4, C_6H_6), δ: 90.5 (*cf.* Ref. 1: b.p. 124—125°C (1.5 Torr), n_D^{20} 1.6201; ^{31}P NMR, δ: 91.7).

Tripropyl tetrathiophosphate (3b) was obtained in a similar way from compound **1** (5.4 g, 11.4 mmol) and disulfide **2b** (12.0 g, 79.9 mmol). The yield of **3b** was 7.8 g (60%), b.p. 116—118°C (0.02 Torr), n_D^{20} 1.6002. ^{31}P NMR (162 MHz, relative to 85% H_3PO_4, C_6H_6), δ: 92.1 (*cf.* Ref. 1: b.p. 131—132°C (0.5Torr), n_D^{20} 1.5885; ^{31}P NMR, δ: 92.5).

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A novel type of bonding of the metallacyclopentadiene fragment in a trimetallic cluster. Molecular structure and rearrangement of $Os_3\{\mu_3\text{-}2\eta^1\text{-}2\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Ph)\}(CO)_9$

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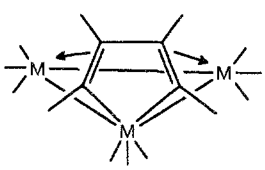
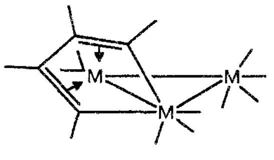
The reactions of carbonyl complexes of iron-subgroup metals with excess alkynes result in $M_3(RC_2R)_2(CO)_9$ clusters. Two structures, **A** and **B**, with a μ_3-2η^1-2η^2- or μ-2η^1-η^4-coordinated organic ligand, respectively, have been considered for these clusters.[1,2] However, no conclusive evidence of the existence of **A**-type complexes containing a diene moiety symmetrically bonded to a metallic "triangle" have been obtained so far. On the other hand, an X-ray diffraction study of $Os_3(PhC_2Ph)_2(CO)_9$ cluster has shown[3] that it has structure **B**. Therefore, similar structures were assigned later on to all related osmium complexes.[4,5]



A



B

In the present work we have unambiguously established for the first time that coupling of alkynes on trimetallic clusters initially gives **A**-type complexes, which further rearrange to **B**-type isomers.

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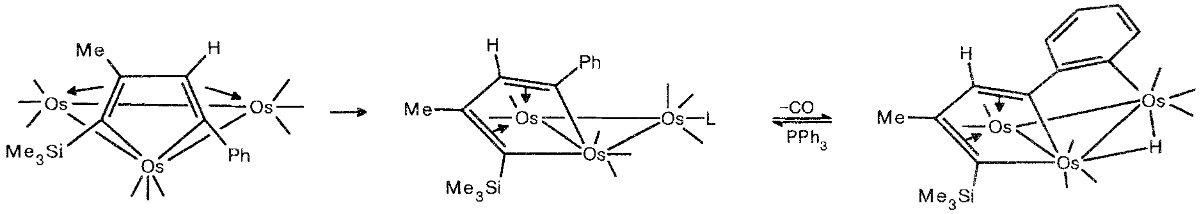
1066-5285/94/4304-0718 $12.50



1 **3a**: L = CO **3b**: L = PPh_3 **2**

We obtained $Os_3\{\mu_3\text{-}2\eta^1\text{-}2\eta^2\text{-}C(SiMe_3)C(Me)C(H)\text{-}C(Ph)\}(CO)_9$ cluster (**1**) during a study of the mechanism of trimethylsilylpropyne dimerization on Ru_3- and Os_3-cluster complexes[6,7] in a reaction of alkyne complex $Os_3(\mu_3\text{-}Me_3SiC_2Me)(\mu\text{-}CO)(CO)_9$ with phenylacetylene in hot hexane. (^1H NMR in C_6D_6, δ: 0.34 (s, 9 H), 2.14 (s, 3 H), 5.69 (s, 1 H), 7.2 (m, 5 H); IR in hexane, ν(CO): 2082, 2044, 2024, 2008, 1994, 1980 cm^{-1}). The structure of compound **1** was unambiguously established by an X-ray single crystal diffraction study (λMo Kα, $P2_1/c$, $Z = 4$, 4359 reflections, $R = 0.0593$). The details of this study will be published in a separate communication.

Heating of compound **1** (85°C, heptane) results in complexes **2** (^1H NMR, C_6D_6, δ: −14,76 (s, 1 H), 0.35 (s, 9 H), 2.34 (s, 3 H), 6.14 (s, 1 H), 6.9—8.0 (m, 4 H) and $Os_2\{\mu\text{-}2\eta^1\text{-}\eta^4\text{-}C(SiMe_3)C(Me)C(H)C(Ph)\}(CO)_6$, evidently, *via* the intermediate formation of compound **3a**. Similarly, complex **3b** (^1H NMR, C_6D_6, δ: 0.65 (s, 9 H), 2.47 (s, 3 H), 6.80 (s, 1 H), 6.99—7.77 (m, 2 OH)) is formed by treatment of complex **2** with triphenylphosphine.

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