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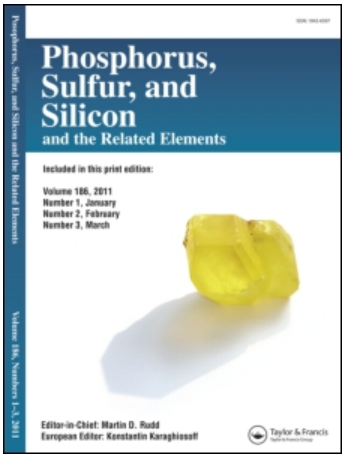

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Metallo Dioxaphospholanes with Metal to Phosphorus Single and Double Bonds

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Metallo Dioxaphospholanes with Metal to Phosphorus Single and Double Bonds

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Metallo dioxaphospholanes $Cp(CO)_3M\text{-}\overline{POCMe_2CMe_2O}$ (M=Cr, Mo, W) **1**, which contain the σ-bound metal ligand in a pseudo axial position at the pyramidally configurated phosphorus, are obtained by a nucleophilic metallation of 1-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane with the anions $Na[M(CO)_3Cp]$ (M=Cr, Mo, W). **1** (M=W) is highly reactive towards quaternisation with MeI and oxidation with elementary sulfur, which reactions yield $[Cp(CO)_3W\text{-}\overline{P(Me)OCMe_2\text{-}CMe_2O}]I$ **2** and $Cp(CO)_3W\text{-}\overline{P(S)OCMe_2CMe_2O}$ **3**, respectively. Exchange of CO against $P(OMe)_3$ affords $Cp(CO)_2[P(OMe)_3]W\text{-}\overline{POCMe_2CMe_2O}$ **4**, which rapidly rearranges to $Cp(CO)_2\text{-}[P(O)(OMe)_2]W\text{-}\overline{P(Me)OCMe_2CMe_2O}$ **5** via an O-P methyl group shift.

The high reactivity of the metallo dioxaphospholanes **1** is also documented in the facile intramolecular decarbonylation to yield the metal to phosphorus doubly bonded species $Cp(CO)_2M{=}\overline{POCMe_2CMe_2O}$ (**6**). According to the structure analysis **6** (M = W) contains a planar phosphorus atom and a rather short W-P distance (2.181 A).

An alternate route to **6** is the dehydrohalogenation of the bifunctional complexes cis/trans $Cp(CO)_2(H)M[\overline{P(Cl)OCMe_2\text{-}CMe_2O}]$, with amines. The double bond in **6** readily adds MeOH, HCl, S_8, and $Fe(CO)_4$.