

Oligonuclear Tricarbonylchromium- and Tricarbonyltungsten Derivatives of Tris(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$, and Related Ligands

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A series of trinuclear carbonylmetal complexes of tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$ (**1**), has been prepared by the reaction of $P(SiMe_3)_3$ with η^7 -tropylium halfsandwich salts, $[(\eta^7-C_7H_7)M(CO)_3]BF_4$, ($M = Cr, Mo, W$). While phosphorus remains uncoordinated in the chromium complex $P[(\eta^6-C_7H_7)Cr(CO)_3]_3$ (**2a**), the molybdenum and tungsten analogues, $P[(\eta^4-C_7H_7)M(CO)_3][(\eta^6-C_7H_7)M(CO)_3]_2$ ($M = Mo$ (**2b**), W (**2c**)), contain a coordinated phosphorus atom together with a η^4 -norcaradienyl substituent. Reaction of **2a** with pentacarbonylmetal fragments, $[M(CO)_5]$, leads to trinuclear products, $P[(\eta^2-C_7H_7)M(CO)_4][(\eta^6-C_7H_7)M(CO)_3]_2$ ($M = Cr$ (**5a**), W (**5c**)), in which phosphorus is coordinated next to an η^2 -cycloheptatrienyl substituent. Several alkyl- and arylphosphanes containing $[(\eta^6-C_7H_7)Cr(CO)_3]$ substituents (X), e. g. $Ph_2P(X)$ (**6a**), $RP(X)_2$ ($R = Me$ (**7a**), CH_2Ph (**8a**), Ph (**9a**)) and $(X)_2P(R')P(X)_2$ ($R' =$ methylene (**10a**) or o -phenylene (**11a**)), have also been synthesized. The chromium complexes **6a** - **11a** contain an uncoordinated phosphorus center, but in contrast to **9a**, the corresponding tungsten compound $PhP[(\eta^4-C_7H_7)W(CO)_3][(\eta^6-C_7H_7)W(CO)_3]_2$ (**9c**) has again a structure similar to **2c**. The arsenic complexes, $As[(\eta^6-C_7H_7)M(CO)_3]_3$ ($M = Cr$ (**12a**), W (**12c**)) both contain an uncoordinated arsenic center, analogous to **2a**. The molecular structures of all new complexes in solution at room temperature were deduced from a consistent set of 1H , ^{13}C and ^{31}P NMR data, and X-ray structure determinations were carried out for **2a** and **5c**.

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