

Preliminary communication

Coordination behavior of monoalkynylphosphines with metal carbonyls: X-ray crystal structure of $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2$

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The reaction of $\text{Co}_2(\text{CO})_8$ with alkynes yields a fascinating array of organometallic compounds in which the alkyne may or may not polymerize¹. In comparison, the reaction of $\text{Co}_2(\text{CO})_8$ with tertiary phosphines² or phosphites³ yields relatively simple products in which usually two CO groups are displaced by the phosphorus ligands. However, the reactions of $\text{Co}_2(\text{CO})_8$ with alkynylphosphines or -arsines have not previously been extensively studied. Furthermore, in the only two reactions reported, a simple monosubstituted product $[\text{Co}_2(\text{CO})_7]_2\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ ($\text{Ph} = \text{C}_6\text{H}_5$) without coordination of the acetylene is formed in one case,⁴ while in the other example $[\text{Co}_2(\text{CO})_6\text{HC}\equiv\text{C}]_3\text{As}$, the acetylene is coordinated but not the arsenic atom⁵. We have synthesized a variety of phosphinoacetylenes⁶ in order to investigate the reactions of these ligands with metal carbonyls in more detail. We report here the preparation and characterization of complexes of the type $\text{Co}_4(\text{CO})_{10}[\text{Ph}_2\text{MC}\equiv\text{CR}]_2$ ($\text{M} = \text{P}$, $\text{R} = \text{H}$, CH_3 , $\text{C}(\text{CH}_3)_3$, CF_3 and $\text{M} = \text{As}$, $\text{R} = \text{CF}_3$). An X-ray structure analysis of $\text{Co}_4(\text{CO})_{10}[\text{Ph}_2\text{PC}\equiv\text{CCF}_3]_2$ has confirmed that this is the first example in which a phosphino- or arsinoacetylene combines the coordinating powers of an acetylene with those of a phosphine or arsine.

Reaction of resublimed $\text{Co}_2(\text{CO})_8$ with $\text{Ph}_2\text{MC}\equiv\text{CR}$ in benzene at room temperature followed by careful chromatography on alumina yielded dark red crystals analyzing as $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{MC}\equiv\text{CR})_2$. Infrared spectra indicated coordination of the acetylenic moiety and similar structures for all the above compounds. Spectra for $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{PC}\equiv\text{CR})_2$ ($\text{R} = \text{CF}_3$, CH_3) are typical [$\nu(\text{CO})$, CHCl_3 ; ($\text{R} = \text{CF}_3$), 2075 s, 2040 s, 2034 (sh), 2020 (sh), 1999 m cm^{-1} ; ($\text{R} = \text{CH}_3$) 2059 s, 2019 s, 2012 (sh), 1995 s cm^{-1} ; $\nu(\text{C}\equiv\text{C})$, ($\text{R} = \text{CF}_3$), 1535 cm^{-1} ; ($\text{R} = \text{CH}_3$), 1530 cm^{-1} ; cf. $\nu(\text{C}\equiv\text{C})$ in $\text{Ph}_2\text{PC}\equiv\text{CCF}_3$ 2200 cm^{-1} ; $\text{Ph}_2\text{PC}\equiv\text{CCH}_3$, 2195 cm^{-1}]. The absence of a strong $\nu(\text{CO})$ band at 2100 cm^{-1} , typical of the simple acetylene derivatives $(\text{RC}\equiv\text{CR})\text{Co}_2(\text{CO})_6$ ¹, is strong evidence against a structure involving uncoordinated phosphorus atoms.

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The phosphites $(\text{CH}_3\text{O})_3\text{P}$ and $(\text{C}_6\text{H}_5\text{O})_3\text{P}$ displace two molecules of CO from the $\text{Co}_4(\text{CO})_{10}[\text{Ph}_2\text{M}\equiv\text{CR}]_2$ complexes on refluxing in benzene, giving the crystalline disubstituted derivatives $\text{Co}_4(\text{CO})_{10}[\text{Ph}_2\text{MCCR}]_2\text{L}_2$, where $\text{L} = (\text{CH}_3\text{O})_3\text{P}$ or $(\text{C}_6\text{H}_5\text{O})_3\text{P}$. The fact that two CO groups in $\text{RC}\equiv\text{CR Co}_2(\text{CO})_6$ complexes are readily displaced by phosphines or phosphites¹, suggested that only two $\text{Co}(\text{CO})_3$ groups were present in the $\text{Co}_4(\text{CO})_{10}[\text{Ph}_2\text{MCCR}]_2$ complexes. Furthermore, since polymerization of acetylenes by $\text{Co}_2(\text{CO})_8$ does not generally occur below 50° , we concluded that these complexes contained both coordinated phosphines and acetylenes. An X-ray crystal structure study was undertaken to confirm these conclusions.

Crystal data: $\text{Co}_4(\text{CO})_{10}[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CCF}_3]_2$, mol.wt., 1072.3 monoclinic crystals; a , 18.13; b , 18.09; c , 19.04 Å; β , 93.26° , space group $P2_1/n$, $Z = 4$, D_c , 1.708 g cm^{-3} , $D_m = 1.716\text{ g cm}^{-3}$.

Intensity data were measured using a Syntex-P1 diffractometer using $\text{Cu-K}\alpha$ radiation. A total of 6865 measurements, including four standard reflections measured after every 96 reflections, were made using the θ - 2θ scan technique. A total of 3148 reflections having $I \geq \sigma(I)$ were used in the analysis and 2533 reflections were considered unobserved. The structure was solved by locating the four cobalt atoms using the Patterson function and the light atoms from successive Fourier syntheses. Refinement by least-squares methods has reduced R ($R = \Sigma |F_o - F_c| / \Sigma F_o$) to 0.135. Measurement of a second set of data using monochromatized molybdenum radiation and further refinement are in progress.

The molecular geometry is illustrated in Fig. 1; a few points are worth noting. The Co-Co distances Co 1-Co3 of 2.482 Å and Co2-Co4 of 2.464 Å are shorter than in the $[(\text{C}_4\text{H}_9)_3\text{PCo}(\text{CO})_3]_2$ complex² but agree well with the distances tabulated recently⁷ for $\text{CCo}_3(\text{CO})_9$ groups which range from 2.457 to 2.498 Å. The C11-C12 distance of 1.377 Å and

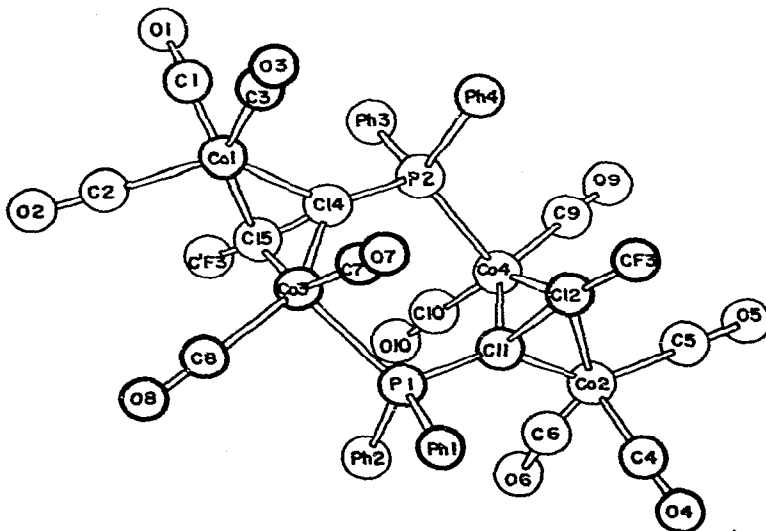


Fig. 1. A view of the $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2$ molecule in an arbitrary direction showing the molecular shape and the atomic numbering. Some pertinent distances Co1-Co3 of 2.482, Co2-Co4 of 2.464, Co3-P1 of 2.236 and Co4-P2 of 2.229 Å.

the C14—C15 distance of 1.320 Å also agree well with the values found in other doubly coordinated acetylenes.⁷ The Co3-P1 distance of 2.236 and Co4-P2 distance of 2.229 Å are slightly shorter than the Co-P distance of 2.253 Å in $\text{CH}_3\text{CCo}_3(\text{CO})_8\text{PPh}_3$ ⁸ but longer than in the $[(\text{C}_4\text{H}_9)_3\text{PCo}(\text{CO})_3]_2$ ² complex of 2.18 Å. Presumably the better donor properties of the trialkylphosphine lead to a shorter Co-P distance with a concomittant increase in the Co-Co bond length. Similarly the Co2-C4 distance of 1.751 Å and the Co1-C1 distance of 1.751 Å are both shorter than the remaining Co-C (of a CO group) distances which average 1.826 Å. The shortening may be related to the location of C1 and C4 *trans* to the Co-Co bond.

The reaction of alkynylphosphines can proceed either through initial reaction of the phosphine followed by reaction with the acetylenic double bond (if steric conditions are favorable) or *vice versa*. The isolation of $[\text{Co}_2(\text{CO})_6\text{HC}\equiv\text{C}]_3\text{As}$ suggests that the reaction with the acetylenic double bond may be the first step in the reaction. Furthermore, we have found that weakly basic phosphines such as $(\text{C}_6\text{F}_5)_2\text{PC}\equiv\text{CR}'$ yield $\text{Co}_2(\text{CO})_6(\text{C}_6\text{F}_5)_2\text{PCCR}'$ complexes. We are currently investigating the copolymerization of coordinated phosphinoacetylenes with other alkynes through routes suggested by the above compounds.

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