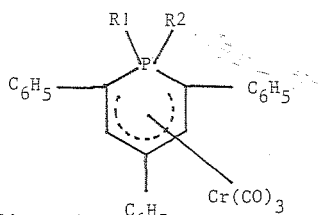


09.3-03 THE CRYSTAL STRUCTURE OF THREE (1,1-DISUBSTITUTED-2,4,6-TRIPHENYL- λ^5 -PHOSPHORIN)TRICARBONYL-CHROMIUM COMPLEXES. By T. Debaerdemaeker, Sektion für Röntgen- und Elektronenbeugung, University of Ulm, D-7900 Ulm, W.Germany.

In order to find out the effect of different substituents on π -complexed λ^5 -phosphorus rings, the present structure analysis was undertaken.

The substituents which were used in this work are given in the caption on the schematic drawing. The crystals were kindly supplied by Prof. K. Dimroth (University of Marburg).

The three structures are isomorphous with the already solved crystal structure of tricarbonyl(1,1-dimethoxy-2,4,6-triphenyl- λ^5 -phosphorin)-chrom(I) (T. Debaerdemaeker, Acta Cryst. (1979) B35, 1686-1689).



	R1	R2
a)	-CH ₃	-C ₂ H ₅
b)	-CH ₃	-OCH ₃
c)	-F	-OCH ₃

The configuration of the three molecules is, as expected, similar to that found for I. The phosphorus atom is located at one side of the C2-C3-C4-C5-C6 plane and the chromium atom on the other side. The planes containing the substituents are not perpendicular to the C2-P-C6 plane except for (c). The orientation of the tricarbonylchromium group is such that one of the carbonyl groups is located above the phosphorus atom. In all three molecules, the smallest substituent is on the side of the tricarbonylchromium group.

09.3-06 THE CRYSTAL STRUCTURES OF TWO CYCLO-PENTADIENYL IRON CARBONYL SULFIDES. By A. Aruffo, E. C. Lingafelter, B. D. Santarsiero, and V. Schomaker, Department of Chemistry, University of Washington, Seattle, WA 98195 USA

Two compounds of apparent composition $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]_2\text{S}_3$, iron sulfanes of possible considerable catalytic and biological import, have been prepared (M. Hinnawi and D. R. McAlister, to be published) by reacting $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ with SCl_2 . With distinct nmr and ir spectra, the one called I from its position in TLC is converted into the one called II rather rapidly in solution at only slightly elevated temperatures.

II readily forms equant crystals: monoclinic with a 6.646, b 12.113, c 10.753 Å, β 91.86°, Z 2, and space group P2₁. Preliminary data (1257 reflections) gave the structure by way of a Patterson map (the iron atoms) and a series of difference-density maps. Least-squares with the final data (2841 reflections) converged at R .065 and GOF 1.61. The two iron atoms in the molecule both coordinate a Cp ring and two carbonyl groups and are joined by a chain of three sulfur atoms. The more important distance and angle averages are Fe-C(Cp) 2.12, Fe-C(CO) 1.77, C-C 1.42, C-O 1.18, Fe-S 2.29, S-S 2.043 Å, C(CO)-Fe-S 91.2, Fe-S-S & S-S-S 111.5, and Fe-S-S-S 77.5. The molecule has rough non-crystallographic symmetry C₂.

I is much more difficult to crystallize, but has been obtained as monoclinic plates, a 22.7, b 11.5, c 7.1 Å, β 99°, Z 4, and space group Ic.

09.3-04 CRYSTALLOGRAPHIC STUDIES OF MOLYBDENUM TO CARBON MULTIPLE BONDS. By N.C. Norman, A.G. Orpen, and I.D. Williams, Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, England.

The crystal structure analyses of a variety of η^5 -cyclopentadienyl-bis and trisphosphite complexes are reported showing molybdenum carbon bonds of order between one and three. The Mo-C bond lengths in these compounds vary between 1.8 and 2.3 Å and a wide variety of Mo-C-C angles are observed (between 176° and 85°). Difference electron density maps illustrate the areas of principle Mo-C orbital overlap in the characterised molybdenum carbyne, carbene, σ -vinyl and metallacyclopentene (see Figure below) complexes studied. Among the complexes whose structures are reported are $\text{Mo}(\text{cp})(\text{P}(\text{OMe})_3)_2 \equiv \text{CCH}_2^t\text{Bu}$, $\text{Mo}(\text{cp})(\text{P}(\text{OMe})_3)_2 \text{HC}=\text{CH}^t\text{Bu}$, $\text{Mo}(\text{cp})_2(\text{P}(\text{OMe})_3)_2 \text{:C}(\text{Ph})_2\text{CHPh}$, illustrating modes I, III and IV below.

