X-Ray Structure of $[(\eta^5\text{-}C_5H_5)W(CO)_2C_{15}H_{15}]$: a Compound Containing Three Unusually Bonded Five-membered Rings

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Summary The X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)W(CO)_2C_{15}H_{15}]$ has revealed a unique arrangement of three five-membered rings in the $C_{15}H_{15}$ ligand.

In the reaction of $[C_5H_5M(CO)_2Cl_3]$ (M = Mo, W)[1] with NaC_5H_5 in tetrahydrofuran the yellow sublimable compounds $[C_{20}H_{20}M(CO)_2]$ are formed.[2] Addition of $NaBH_4$ increases the yield for M = Mo to 35% and for M = W to 40%. From the ^1H n.m.r. spectrum one of the C_5H_5 rings in $[C_{20}H_{20}M(CO)_2]$ is π-bonded. The other 3 five-membered rings, which formally replace the 3 Cl substituents, give rise to a very complicated ^1H n.m.r. pattern. Raising the temperature does not cause marked changes in the ^1H n.m.r. spectrum which would be expected for an increased rate of ring rotation in the monohapto C_5H_5–M groups[3] in $[(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^1\text{-}C_5H_5)_3]$. Therefore structures with other arrangements of the five-membered rings must be considered. To determine which of these possibilities is present a single crystal X-ray structure determination of $C_{20}H_{20}W(CO)_2$ was undertaken.

Crystal data: M, 500·2, monoclinic, $a = 13{\cdot}578(8)$, $b = 20{\cdot}967(9)$, $c = 13{\cdot}831(8)$ Å, $\beta = 109{\cdot}72(6)^\circ$, $U = 3706{\cdot}8$ Å^3, $Z = 8$, $D_c = 1{\cdot}79$ g cm^{-3}, μ (Mo-K_α) = 65·9 cm^{-1}, space group $P2_1/c$. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the ω—2θ scan technique. All reflections in one independent quadrant out to $2\theta = 50^\circ$ were measured; 2661 reflections were considered observed $[I > 3\sigma(I)]$. The structure was solved by Patterson and difference Fourier techniques, and refined to a conventional R value of 0·088. There are two molecules in the asymmetric unit; the tungsten atoms were refined with anisotropic thermal parameters, while those of carbon and oxygen were treated isotropically. The two crystallographically different molecules are chemically equivalent, and the molecular arrangement of one is shown in the Figure.†

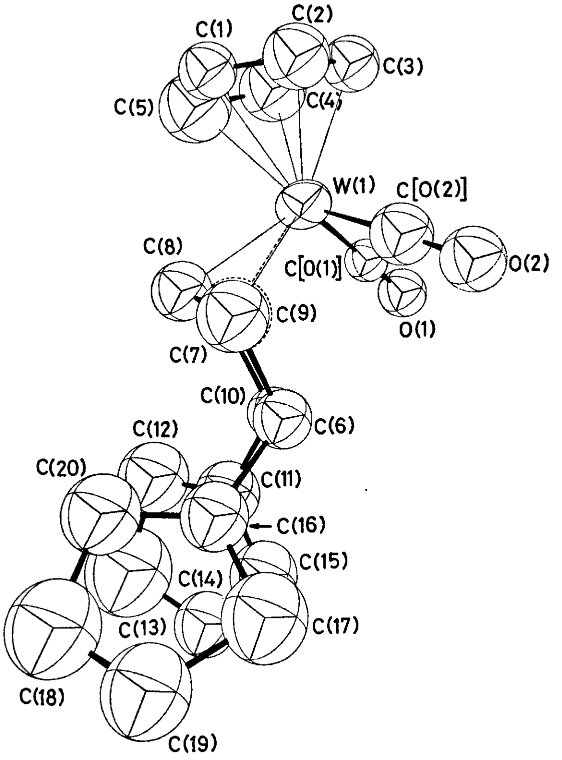
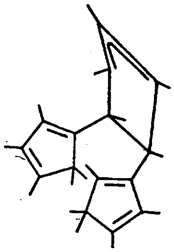


Figure. *X*-Ray crystal structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{C}_{15}\text{H}_{15})]$. (One atom of the η^3-allyl system is obscured).

Thus, $\text{C}_{20}\text{H}_{20}\text{W(CO)}_2$ containing an η^3-allyl system[4] is a derivative of the cyclopentadienyl-cyclopentenyl-dicarbonyl compounds of the 6th triad.[5] The five-membered ring bonded in an allylic fashion to the tungsten atoms is decidedly nonplanar. The plane of the η^3-group makes an angle of 30° with the plane formed by the exclusion of the unique carbon atom. The $\text{C}_{15}\text{H}_{15}$ ligand may therefore be best viewed as (I). In the related compound $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\eta^3\text{-C}_5\text{H}_5)]$[6] the $\eta^3\text{-C}_5\text{H}_5$ ligand is also bent, the angle between the allylic system and the olefinic system being 20°.



(I)

The W–C(η^5) bond lengths range from 2·23 to 2·44 Å, and average 2·34 Å compared to 2·31—2·47 Å, average 2·37 Å, for $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\eta^3\text{-C}_5\text{H}_5)]$[6] and 2·34 Å for $[\text{C}_5\text{H}_5\text{W(CO)}_3]_2$.[7] The W–C($\eta^3$) bonds show a significantly internal variation: the unique W–C bond lengths average 2·19 Å, and the remaining ones 2·37 Å. For $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\eta^3\text{-C}_5\text{H}_5)]$ the corresponding values are 2·30 and 2·42 Å, respectively.[6] The 2·19 Å value is close to that found for W–C(σ) compounds such as $[\text{WMe}_2(\text{NEt}_2)_4]$ (2·17 Å) and $[\text{W}_2(\text{CH}_2\text{SiMe}_3)_6]$ (2·14 Å).[8]

The five-membered ring bonded to the W atom by the allylic system contains two tetrahedral carbon atoms, each of which carries one C_5H_5 group and one hydrogen atom. The structure determination shows that the two C_5H_5 rings are in a *cis*-arrangement, both being oriented away from the tungsten atom. Interestingly, in (I) the two C_5H_5 substituents on the allylic five-membered ring differ in the location of the double bonds. Whereas in one C_5H_5 ring the tetrahedral centre is in the 2 position, in the other it is in the 3 position. The *cis*-arrangement allows the possibility of further bonding of the C_5H_5 rings to an Fe atom or a TiCl_2 group.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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