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Preliminary communication

REACTION OF DIPHENYLTUNGSTACARBENE WITH CYCLIC ENOL ETHERS; STRUCTURE OF THE INSERTION PRODUCT

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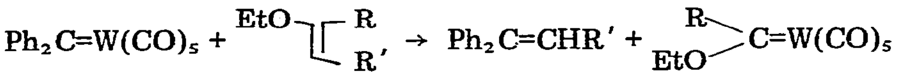
Summary

Reaction of $(CO)_5W{=}CPh_2$ with 2-ethoxynorbornene gives a new tungstacarbene which has been characterized by crystal structure analysis. There is no interaction between the unsaturated moiety and the tungsten atom.

The structure of diphenylcarbenopentacarbonyltungsten has been determined by X-ray analysis [2] but does not give much information about the Casey reaction [3]:



$$Ph_2C{=}W(CO)_5 + (EtO)(R)C{=}C(R') \rightarrow Ph_2C{=}CHR' + (R)(EtO)C{=}W(CO)_5$$

We showed in an earlier paper [1] that cyclic enol ethers could also be used in this reaction, and gave carbenotungsten containing an additional double bond, i.e. I + II → III. It was therefore of interest to prepare a compound related to III (which unfortunately is a liquid) and suitable for X-ray analysis, in order to study the spatial relationship between the metal and the C=C double bond. We report the preparation of such a compound (V), prepared from I and 2-ethoxynorbornene (IV).

Reaction of I with an excess of 2-ethoxynorbornene (IV) in hexane, at 60°C, followed by silica gel chromatography gave V as yellow crystals, m.p. 138—139°C, in 35% yield. Infrared (1950, 1985 and 2073 cm^{-1}) and ^1H and ^{13}C NMR data (Table 1) are in agreement with structure V, and closely parallel those described for III [1]. Structure V was confirmed by X-ray crystallography.

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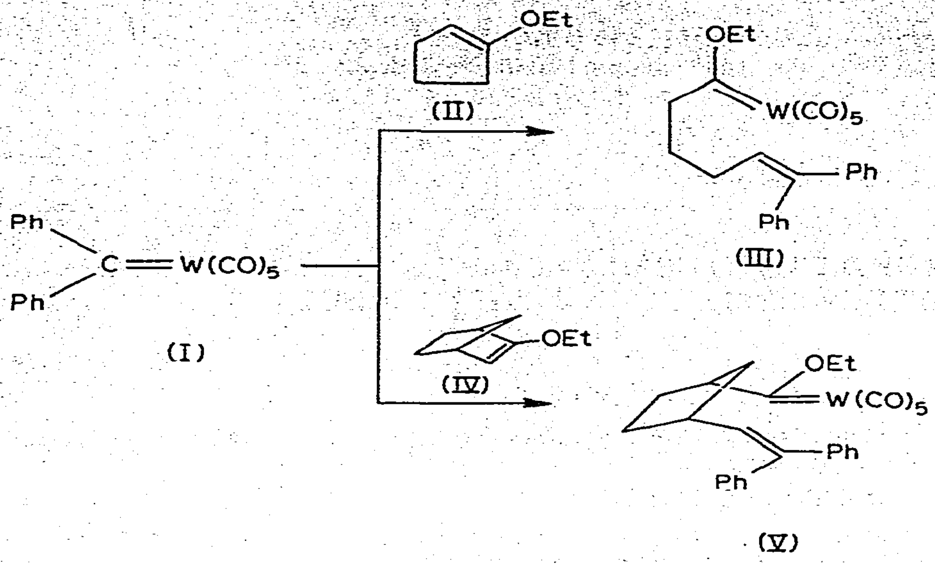


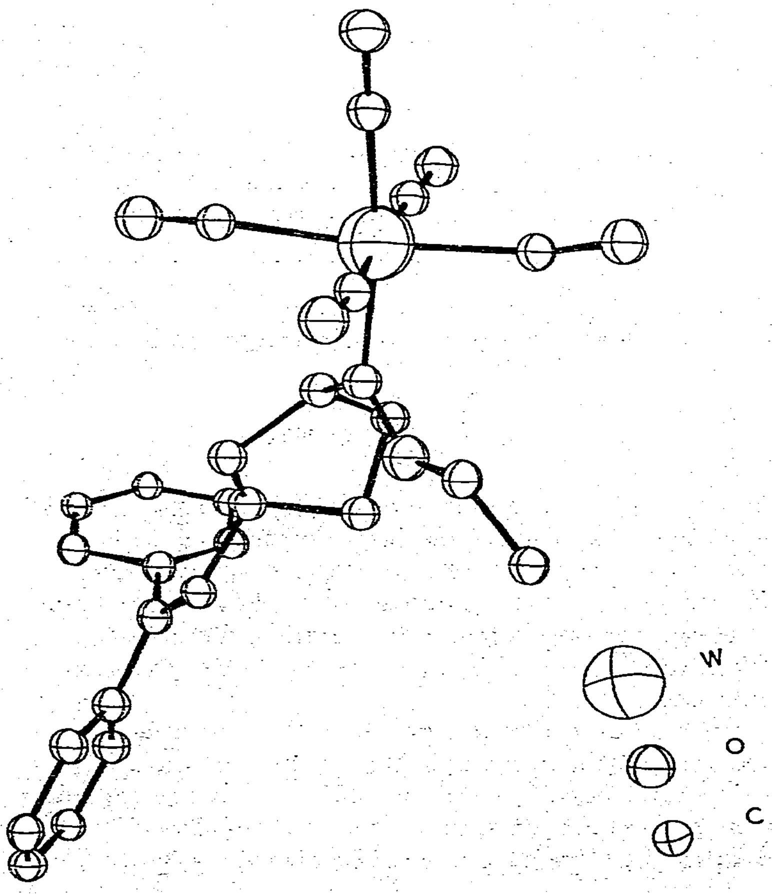
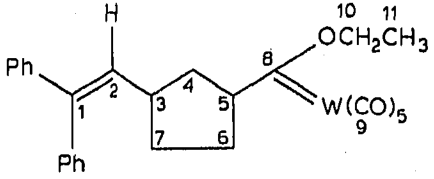


Fig. 1. Perspective drawing of compound V, hydrogen atoms omitted for clarity.

TABLE 1

^{1}H AND ^{13}C NMR DATA (values in ppm, solvent $CDCl_3$)

(s = singlet, t = triplet, m = multiplet, q = quartet; C(Ar) = C aromatic).



Nucleus	C(8)	C(9)	C(1) C(2)	C(Ar)	C(3)	C(4)	C(5)	C(10)	C(11)	C(7)	C(6)
^{13}C	336.0	203.5 197.4	143.7 142.6 141.6 140.2 132.9	131.4 129.8 128.3 127.7 127.2	41.2	39.2	73.2	80.5	14.7	34.0	30.5
			H(Ar)	H(2)		H(3)	H(4)	H(5)	H(10) -	H(11)	H(7,6)
^{1}H			7.16(s) 7.25(s)	5.85(d, J 9 Hz)		2.55(m)	1.7(m)	4.4(m)	4.85(q)	1.6(t)	1.7(m)

Crystal data. Monoclinic, *a* 47.43 (2), *b* 6.440 (3), *c* 16.73 (1); β 89.21° [3]; space group *C*2/*c*, $Z = 8$, D_c 1.63 g cm^{-3}; 3-circle diffractometry data, Cu-K_α radiation, 4339 independent reflections. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares. The conventional agreement index is now 0.096 with isotropic temperature factors for all atoms but W, with anisotropic thermal parameters. The unit cell contains 8 molecules, with the structure shown in Fig. 1. The C=W distance is 2.15 Å, as is also observed in $Ph_2C{=}W(CO)_5$. The molecule is oriented in such a way that phenyl rings point away from the tungsten atom.

Interestingly there is no sign of coordination of the $Ph_2C{=}CHR$ double bond with the tungsten atom: the chemical implications of this result are at present under study.

References

1 J. Levisalles, H. Rudler and D. Villemin, J. Organometal. Chem., 146 (1978) 259.
2 C.P. Casey, T.J. Burkhardt, C.A. Bunnell and J.C. Calabrese, J. Amer. Chem. Soc., 99 (1977) 2127.
3 C.P. Casey and T.J. Burkhardt, J. Amer. Chem. Soc., 96 (1974) 7808.