

SOME ALLYL, ALKYL AND OLEFIN COMPLEXES OF TUNGSTEN

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Recent work describes the preparation and properties of allyl, alkyl, and olefin complexes of iron^{1, 2} and molybdenum³. We now report similar studies on some tungsten complexes. In particular, we were interested to find whether the tungsten analogue of the π -allyl-molybdenum complex $C_5H_5Mo(CO)_2-\pi-C_3H_5$ (ref. 3) showed a similarly anomalous proton magnetic spectrum, and also to find the products of the reduction with sodium borohydride of the propene-tungsten analogue of the iron cation $[C_5H_5Fe(CO)_2CH_3-CH=CH_2]^+$ (ref. 1).

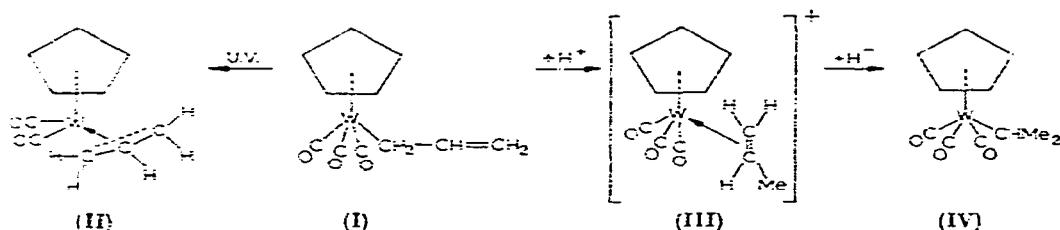
PREPARATION AND PROPERTIES

The σ - and π -allyl complexes, $C_5H_5W(CO)_3-\sigma-C_3H_5$, (I), and $C_5H_5W(CO)_2-\pi-C_3H_5$, (II), were prepared in the manner described for the molybdenum analogues³. They are air-sensitive, volatile compounds, soluble in the common organic solvents. The infrared and proton magnetic resonance spectra are given in the experimental section and Table I, respectively, together with some assignments.

The spectra are very similar to those of the molybdenum analogues. The proton magnetic resonance spectra of the π -allyl complex shows a marked broadening of the doublet assigned to the 3-H protons of the π -allyl group, as does the spectrum of the molybdenum analogue³.

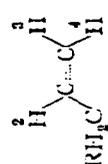
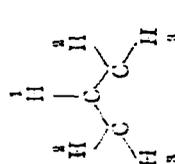
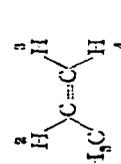
PROTONATION OF THE σ -ALLYL COMPLEX

As shown for the σ -allyl complexes of iron¹, and molybdenum³, the σ -allyl complex (I) reacts readily with hydrogen chloride forming the propene cation



$[C_5H_5W(CO)_3CH_3-CH=CH_2]^+$, (III). The cation (III) hexafluorophosphate was isolated and characterised by analysis and the infrared and proton magnetic resonance spectra. The properties of the cation (III) hexafluorophosphate are given in the experimental section.

TABLE I
NUCLEAR MAGNETIC RESONANCE DATA

Compound	Band pos. (τ) ^b	Rel. intensity ^c	Multiplicity	Sept. of components (τ, J, etc.) ^d	Assignment
R-σ-C ₃ H ₅ in cyclohexane 	7.08	2	2 main bands and some very weak bands ^e	app. J(CH ₂ , 2-H) 8.4	CH ₂ split by 2-H
C ₆ H ₆ W(CO) ₃ ·π-C ₃ H ₃ in benzene 	Centre 5.47 4.75 (Centre ~ 4 8.88	2 5 1 2	Complex band, Centres at 5.71, 5.47, 5.26 Broad doublet, Peaks at 8.76, 8.99		3-H and 4-H C ₆ H ₆ 2-H 3-H protons split by 1-H
[R-C ₃ H ₃] ⁺ PF ₆ ⁻ 	Centre 6.75 5.37 7.78	1 5 3	Complex band (11)	app. J(2,1) 6.8 app. J(CH ₂ , 2) 6.3	2-H protons split by 1-H 1-H split by 2-H and 3-H protons C ₆ H ₆ CH ₂ split by 2-H
R-CHMe ₂ in benzene	Centre 6.71 Centre 5.64 4.01 8.45 7.22 5.41	2 1 5 6 1 5	Complex band (7) Complex band (11) Complex band (9)	app. J(Me ₂ , CH) 6.4	3-H and 4-H 2-H C ₆ H ₆ Me ₂ split by CH CH split by Me ₂ ^o C ₆ H ₆

a R = C₆H₅W(CO)₃.

b Relative to SiMe₄ as internal standard.

c Estimated to whole numbers by determining areas relative to π-C₆H₆ = 5.

d Where multiplicity occurs which may be described as first order spin-spin couplings the splittings are recorded as the apparent coupling constants (app. J).

e Further structure may arise from the coupling of these hydrogens with the ¹⁸³W nucleus⁶.

REDUCTION OF THE PROPENE CATION (III)

It has been shown that reduction of ethylenic complexes of iron² and molybdenum³ with sodium borohydride affords alkyl complexes. Similarly the reduction of the propene cation (III) under the same conditions affords moderate yields of yellow oil unstable to air. Analysis and the infrared and proton magnetic resonance spectra show it to be the isopropyl complex $C_5H_5W(CO)_3CHMe_2$, (IV).

DISCUSSION

The chemistry of the complexes (I)–(IV) is very similar to that of the comparable complexes of iron^{1,2} and molybdenum³. Possible mechanisms for the protonation of the σ -allyl complex (I) are discussed for the related iron complexes¹.

The strongly anomalous proton magnetic resonance spectrum of the π -allyl complex (II) and of the molybdenum analogue³, namely, the marked broadening and complex nature of the band assigned to the 3-H protons, may be understood if the two 3-H protons have different chemical shifts. In this case, coupling could arise between the two 3-H protons as well as between the 3-H and 1-H protons. If this suggestion is valid then it would be expected that the 1-H proton would show a more complicated spectrum than in normal π -allyl complexes, as is observed. The differentiation between the two 3-H protons could arise from some interaction of the π -allyl ligand with the rest of the molecule.

As in the case of the related iron complex², the reduction of the propene cation (III) gives the isopropyl complex (IV) and no *n*-propyl isomer was found in the reduction products. A mechanism of hydride addition in this reaction and the factors which may influence the hydride ion to add to the 1- or 2-carbon have been discussed for the related iron complexes². The same arguments may be applied to the reduction of the propene cation (III).

EXPERIMENTAL

Microanalyses were done in the Microanalytical Department, Lensfield Road, Cambridge. All preparations, reactions and chromatographic separations were carried out in nitrogen or in a vacuum; solvents were degassed before use. Light petroleum was "AnalaR" material of b.p. 30–40°.

Tricarbonyl- σ -allylcyclopentadienyltungsten

The compound was prepared and purified from the reaction of sodium tricarbonylcyclopentadienyltungsten⁴ (20 g) with allyl chloride (20 ml) in an identical manner to that described for the molybdenum analogue³. Yield 40%. [Found: C, 35.5; H, 2.7; mol. wt. (cryoscopic in benzene), 375. $C_{11}H_{10}O_3W$ calcd.: C, 35.2; H, 2.7%; mol. wt., 374.] The compound forms pale yellow crystals, m.p. 24–6°; solutions in petrol, when kept in air, show decomposition after a few minutes.

Dicarbonyl- π -allylcyclopentadienyltungsten

Pure tricarbonyl- σ -allylcyclopentadienyltungsten (2.0 g) in a quartz flask and under a vacuum was irradiated with intense ultraviolet light for 6 h. The pure π -allyl complex (II) was isolated from the reaction products as described for the molybdenum ana-

logue³. [Found: C, 35.1; H, 3.0; mol. wt., (cryoscopic in benzene), 341. $C_{11}H_{10}O_2W$ calcd.: C, 34.7; H, 2.9%; mol. wt., 346.] The yellow crystals of the pure compound showed decomposition when kept in air after ~ 12 h.

Tricarbonylcyclopentadienyl-propenetungsten hexafluorophosphate

The compound was prepared from tricarbonyl- σ -allylcyclopentadienyltungsten (2.0 g) by the same method described for the molybdenum analogue³. [Found: C, 25.6; H, 2.4. $C_{11}H_{11}O_3W$ calcd.: C, 25.4; H, 2.1%.] The salt is slightly soluble in water and the solutions slowly decompose evolving a gas, presumably propene¹. The salt decomposes slowly when exposed to air and even when kept under nitrogen it darkens when kept in the light.

Tricarbonylisopropylcyclopentadienyltungsten

Tricarbonylcyclopentadienyl-propenetungsten hexafluorophosphate (4.0 g) in tetrahydrofuran (100 ml), in which it only partially dissolved, was treated with sodium borohydride (4.0 g) in small portions. The mixture was stirred with a stream of nitrogen and, after 30 min, extracted with light petroleum and water. The light petroleum layer was separated, washed twice with water, evaporated to a small volume and placed on an alumina column made up in light petroleum. Elution with light petroleum gave a single yellow band which was collected. The solvent was removed from the eluate and the resulting oil was distilled at $40^\circ/10^{-3}$, to give a dark yellow oil. Yield 17%. [Found: C, 35.5; H, 3.2. $C_{11}H_{13}O_3W$ calcd.: C, 35.2; H, 3.2%.] The infrared and proton magnetic resonance spectra of the pure compound showed that it was the isopropyl isomer (IV). The compound is rapidly decomposed on exposure to air and at temperatures $> 60^\circ$. Amongst the products of thermal decomposition was the binuclear complex $[C_5H_5W(CO)_3]_2^4$. Repeated attempts to prepare the complex (IV) by the reaction of the sodium salt $Na^+[C_5H_5W(CO)_3]^-$ with isopropyl halides were unsuccessful.

Infrared spectra

Measurements were made on a Perkin-Elmer model 21 spectrometer. The spectra and some assignments are given below. Mulls were in Nujol or hexachlorobutadiene; solutions were in carbon disulphide or carbon tetrachloride.

$C_5H_5W(CO)_3-\sigma-C_3H_5$ (film): 3120w^a, 2970vw, 2930vw, 2019vs^b, 1904vs^b, 1609s^c, 1421s, 1401w, 1357w, 1262vw, 1200m, 1109sh, 1078m, 1063m, 1038m, 1011m, 988m, 923w, 881s, 826s, 748m.

$C_5H_5W(CO)_3-\pi-C_3H_5$ (soln.): 3905w, 3875w, 3765w, 3105w^a, 3060m, 2994m, 2925m, 2853w, 2026m, 1960vs^b, 1880vs^b, 1863vs^b, 1733w, 1641w, 1476m, 1461w, 1426m, 1385w, 1260w, 1220w, 1183w, 1110m, 1107s, 942m, 905m, 894m, 810s, 756m.

$[C_5H_5W(CO)_3CH_2-CH=CH_2]^+PF_6^-$ (mulls): 3125w^a, 3045w, 2960w, 2890w, 2855w, 2107s^b, 2053vs^b, 2007vs^b, 1459w, 1463w, 1436m, 1418m, 1400w, 1382w, 1360w, 1223m, 1167w, 1112w, 1070vw, 1040m, 975w, 910m, 880s, 842vs, 825vs, 740m, 720m.

$C_5H_5W(CO)_3CHMe_2$ (soln.): 3100w^a, 2960m, 2900m, 2005vs^b, 1905vs^b, 1465m, 1428m, 1388w, 1375w, 1318w, 1265w, 1187m, 1155w, 1122m, 1085w, 1068m, 1018m, 824s.

a, C-H stretch of $\pi-C_5H_5$; b, $C\equiv O$ stretch; c, Unco-ordinated C=C stretch.

Nuclear magnetic resonance spectra

Measurements were made on a Perkin-Elmer spectrometer at 40 Mc./sec. The data and conditions of measurements are given in Table I.

ACKNOWLEDGEMENTS

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SUMMARY

The preparation and properties of the allyl complexes $C_5H_5W(CO)_3-\sigma-C_3H_5$ and $C_5H_5W(CO)_2-\pi-C_3H_5$ are described. The σ -allyl complex is shown to be protonated with hydrogen chloride forming the propene cation $[C_5H_5W(CO)_3CH_3-CH=CH_2]^+$. Reduction of the propene cation with sodium borohydride affords the isopropyl complex $C_5H_5W(CO)_3CHMe_2$.

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