Journal of Organometallic Chemistry, 76 (1974) 49—52

ALKYL—OLEFIN DERIVATIVES OF MOLYBDENUM AND TUNGSTEN

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(Received February 25th, 1974)

Summary

The neutral ethylene complexes $(\pi\text{-}C_5H_5)_2M(C_2H_4)$(M = Mo or W) react with alkyl halides RX, where RX = MeI or $PhCH_2Br$ (M = W only) forming the alkyl—ethylene cations $[(\pi\text{-}C_5H_5)_2M(C_2H_4)R]^+$. The compounds $[(\pi\text{-}C_5H_5)_2\text{-}MMe(PPh_3)]^+PF_6^-$ are also described.

Introduction

We have shown that the olefin derivatives $(\pi\text{-}C_5H_5)_2M(CH_2{=}CH_2)$ (I:M = Mo or W) and $(\pi\text{-}C_5H_5)_2W(CH_2{=}CHMe)$ are very readily protonated, even by weak acids such as water, giving the olefin hydrides $[(\pi\text{-}C_5H_5)_2\text{-}M(CH_2{=}CHR)H]^+PF_6^-$ (R = H or Me) [1]. This observation suggested that the complexes might be sufficiently basic to cause nucleophilic attack on alkyl halides, and our studies of this reaction are described below.

Results and Discussion

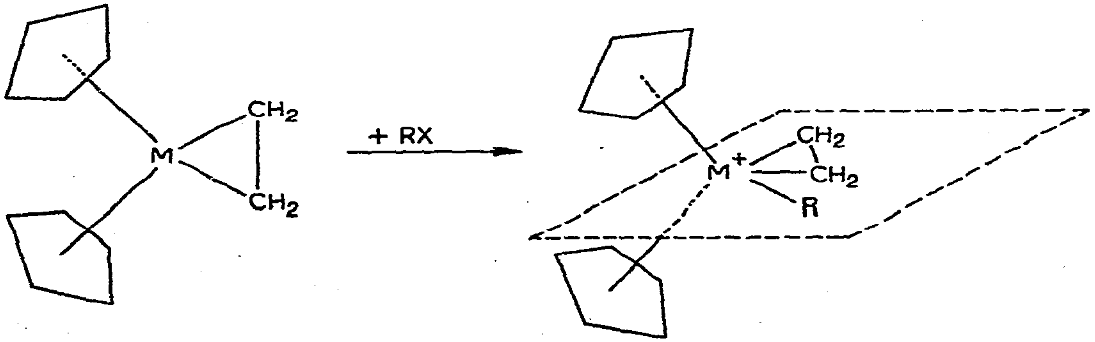
The ethylene compound I(M = W) in benzene was treated with iodomethane. A rapid reaction ensued giving a water-soluble yellow precipitate. Addition of ammonium hexafluorophosphate to aqueous solutions precipitated a pale yellow compound. The data given below show this to be the ethylenemethyl derivative $[(\pi\text{-}C_5H_5)_2W(CH_2{=}CH_2)Me]^+PF_6^-$ (II). The initially formed yellow precipitate is the iodide salt of the same cation.

Compound II is soluble in polar solvents such as acetone, slightly soluble in water and insoluble in diethyl ether and petroleum ether. Solutions are rapidly decomposed on exposure to air ($T_{\frac{1}{2}}$ ca. 30 min.). Compound I (M = Mo) reacts with iodomethane in a similar manner to the tungsten analogue and the resulting compound $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)Me]^+PF_6^-$ (III) has essentially similar properties to compound II. Treatment of compound I(M = W) with benzyl bromide causes a smooth reaction and, following the addition of ammonium hexafluorophosphate, the silvery-white compound $[(\pi\text{-}C_5H_5)_2\text{-}W(CH_2{=}CH_2)CH_2Ph]^+PF_6^-$(IV) is isolated. These reactions are shown in Scheme 1, and demonstrate that the ethylene cations are strong nucleophiles.

It was not possible to unambiguously identify bands assignable to $\nu(C{=}C)$; in the IR spectra of the complexes II and III; very possibly bands at 1510 or 1470 cm^{-1} respectively arise from this mode

Some ^1H and ^{13}C NMR data for the complexes II-IV and the ^{13}C NMR spectrum of the ethylene hydride $[(\pi\text{-}C_5H_5)_2W(CH_2{=}CH_2)H]^+PF_6^-$ are given in the experimental section. All the ^1H NMR spectra show an AA'BB' pattern assignable to a coordinated ethylene ligand in an asymetric environment. The ^{13}C NMR spectra of II show that the two carbon atoms of the ethylene ligand are in different chemical environments. This is most consistent with a structure where the metal atom and the three carbon atoms of the methyl and ethylene groups are coplanar, as shown in Scheme 1. The ^{13}C NMR spectrum shows that the WC_2 system in the ethylene hydride must also be co-planar with the hydride ligand.

SCHEME 1



(I: M = Mo or W)

(II: R = Me, M = W;
III: R = Me, M = Mo;
IV: R = CH_2Ph, M = W)

TABLE 1

ANALYTICAL DATA

Compound	Colour	Analytical data found (calcd.) (%)	
		C	H
$[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)Me]^+PF_6^-$	Lemon-yellow	38.1(37.8)	4.2(4.1)
$[(\pi\text{-}C_5H_5)_2W(C_2H_4)Me]^+I^-$	Pale-yellow	32.1(32.2)	3.5(3.5)
$[(\pi\text{-}C_5H_5)_2W(C_2H_4)Me]^+PF_6^-$	Pale-yellow	31.4(31.1)	3.4(3.4)
$[(\pi\text{-}C_5H_5)_2Mo(PPh_3)Me]^+PF_6^-$	Red-orange	53.7(53.7)	4.3(4.3)
$[(\pi\text{-}C_5H_5)_2W(PPh_3)Me]^+PF_6^-$	Red-orange	47.2(47.3)	3.8(3.9)
$[(\pi\text{-}C_5H_5)_2W(C_2H_4)CH_2Ph]^+PF_6^-$	Silvery	39.8(39.5)	3.6(3.6)

Treatment of the previously described [2] tertiary phosphine complexes $[(\pi\text{-}C_5H_5)_2M(PPh_3)Br]^+PF_6^-$(V:M = Mo or W) with methylmagnesium chloride gives orange compounds which the data show to be the methyl derivatives $[(\pi\text{-}C_5H_5)_2M(PPh_3)Me]^+PF_6^-$ (VI). These are generally similar in their stability and solubility to complexes II-III.

Experimental

All preparations and purifications were carried out in the absence of oxygen. Where required, solvents were dried by refluxing over and distillation from calcium hydride. Light petroleum used was Analar, 30—40°. IR spectra were measured on mulls using a Perkin—Elmer 457 instrument calibrated with polystyrene. The compounds $(\pi\text{-}C_5H_5)_2M(C_2H_4)$ (M = Mo or W) were prepared as previously described [1]. ^{1}H NMR spectra were determined on a Jeol C60 HL or a Perkin—Elmer R14 100 MHz instrument. ^{13}C NMR spectra were determined on a Bruker WH90 instrument.

Methylethylenedi-π-cyclopentadienyltungsten hexafluorophosphate

The complex $(\pi\text{-}C_5H_5)_2W(C_2H_4)$(0.45 g, 1.32 mmol) in benzene (50 ml) was treated with methyl iodide (1.5 mmol). After a few minutes the solution became cloudly and a solid began to precipitate. The colour of the solution was slowly discharged and after 4 h the colourless mother liqour was filtered from the precipitated white solid which was washed with benzene (2 × 5ml) followed by light petroleum (2 × 5ml) and dried in vacuo. The product was extracted with the minimum quantity of hot water (90°) and the solution filtered whilst hot giving a pale-yellow filtrate which deposited pale-yellow crystals on cooling to room temperature. The mother liqour was decanted from the crystals which were washed with cold water (ca. 0°) (2 × 1ml) and dried in vacuo, giving the pure iodide salt; yield, ca. 75%.

The iodide salt was dissolved in hot water and an aqueous solution of ammonium hexafluorophosphate was added to give a pale yellow precipitate. This was crystallised from acetone/water by slow removal of solvent in vacuo giving a further yield of yellow crystals which were collected, washed with water and dried in vacuo; yield, ca. 70%.

The experiment was repeated with the molybdenum analogue $(\pi\text{-}C_5H_5)_2$-$Mo(C_2H_4)$ and the hexafluorophosphate salt $[(\pi\text{-}C_5H_5)_2MoMe(C_2H_4)]^+PF_6^-$ was obtained as lemon-yellow crystals from acetone/water mixtures by slow removal of solvent in vacuo; yield, ca. 70%.

Benzylethylenedi-π-cyclopentadienyltungsten hexafluorophosphate

The ethylene complex $(\pi\text{-}C_5H_5)_2W(C_2H_4)$(0.13 g, 0.38 mmol) in benzene (25 ml) was treated with benzyl bromide (0.3 ml, 1.2 mmol). A creamy precipitate formed within a few min and after 1 h the originally red solution was almost colourless. The solid was collected, washed with light petroleum and then extracted with water. After 1 h the extract was filtered and ammonium hexafluorophosphate was added to the filtrate giving a white precipitate. This was collected, washed with water and then recrystallised from acetone/water by slow removal of the acetone under reduced pressure. The silvery precipitate was washed with water and dried under vacuum giving the pure product; yield, ca. 75%.

Methyltriphenylphosphinedi-π-cyclopentadienylmolybdenum hexafluorophosphate

The compound $[(\pi\text{-}C_5H_5)_2Mo(Ph_3P)Br]^+PF_6^-$ (0.3 g, 0.42 mmol) was suspended in ether (150 ml) and excess methylmagnesium chloride in ether (2 *M*, 2 ml) was added. The mixture was stirred for 2 h at room temperature after which time the initially purple suspension had become light brown. The supernatant liquid was filtered from the suspended solid which was washed with ether (3 × 10ml) to free it from traces of Grignard reagent, then solvent was removed in vacuo. The residue was extracted with acetone and the extract filtered to give a red-orange filtrate. An aqueous solution of ammonium hexafluorophosphate was added and solvent slowly removed in vacuo to give red-orange crystals. These were separated by filtration, washed with water and dried in vacuo. Recrystallisation from liquid sulphur dioxide/ether, or acetone/ether, gave red-orange crystals of the pure compound; yield, ca. 70%.

The tungsten analogue $[(\pi\text{-}C_5H_5)_2WMePPh_3]^+PF_6^-$ was similarly prepared and recrystallised; yield, ca. 60%.

^1H NMR data

Data given as: compound number, chemical shift τ (ppm), rel. intensity, multiplicity (J Hz), assignment; etc.

III: 4.40*; 7.15, 2, three lines, $=CH_2$; 7.72, 2, three lines, $CH_2=$; 9.15, 3, s, Me (In $Me_2CO\text{-}d_6$ or $Me_2SO\text{-}d_6$.)

II: 3.82*; 6.95, 2, three lines, $=CH_2$; 7.75, 2, three lines, $CH_2=$; 8.52, 3, t, $[J(^{183}W,Me)6]$ Me. (In $Me_2SO\text{-}d_6$.)

VI (M = Mo): 2.56, 15, c, Ph_3; 5.67, 10, $d[J(^{31}P,H)1.5]\,(\pi\text{-}C_5H_5)_2$; 9.60, 3, $d[J(^{31}P,Me)7.6]$ Me. (In liquid SO_2.)

VI (M = W): 2.20, 15, c, Ph_3; 4.65, 10, $d[J(^{31}P,H)1.5]\,(\pi\text{-}C_5H_5)_2$; 9.28, 3, $d[J(^{31}P,H)7.5]$ Me. (In liquid SO_2.)

IV: 2.6-3.0, 5, c, Ph; 4.42*; 6.9-8.4, symmetrical, complex pattern with two sets of three main bands typical of C_2H_4 in these systems; 7.64, 2, s, CH_2. (In $Me_2CO\text{-}d_6$ at 60 MHz and 100 MHz and in $Me_2SO\text{-}d_6$ at 100 MHz.)

^{13}C NMR data

Spectra were determined with broad band decoupling of the hydrogen nuclei. Chemical shifts are quoted as δ (ppm) values and the solvent was used as the internal calibrant. The data are presented as; chemical shift (assignment)

II: 96.4($\pi\text{-}C_5H_5$); 28.0,27.7(C_2H_4); —18.5(Me).

$[(\pi\text{-}C_5H_5)_2W(C_2H_4)H]^+PF_6^-$: 88.8($\pi\text{-}C_5H_5$); 15.4, 7.7($C_2H_4$).

Acknowledgements

We wish to thank the Petroleum Research Fund administered by the American Chemical Society for partial support.

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* As 10,s,$(\pi\text{-}C_5H_5)_2$.