Photosubstitution Reactions of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$: † Some Evidence for an α-Elimination Mechanism

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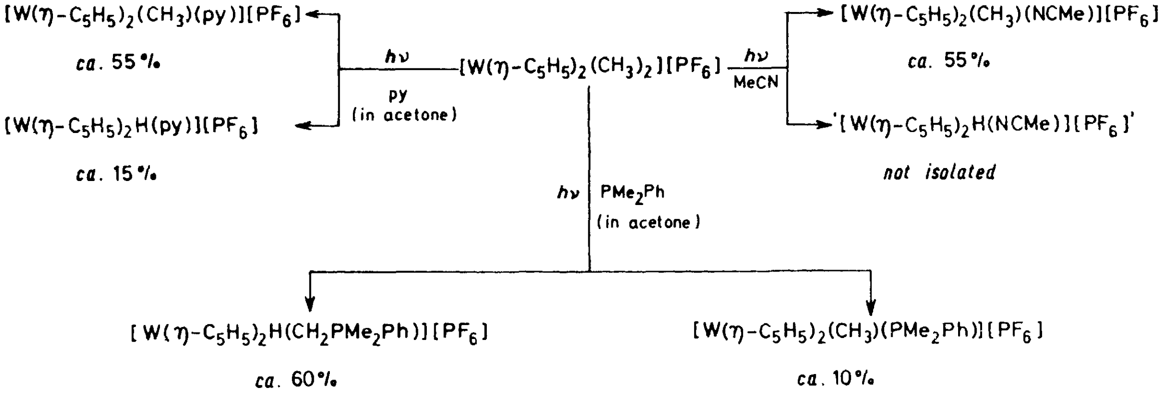
Irradiation of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ in the presence of L [L = pyridine (py), acetonitrile, or dimethylphenylphosphine] led to the isolation of the following products: $[W(\eta\text{-}C_5H_5)_2(CH_3)L][PF_6]$, $[W(\eta\text{-}C_5H_5)_2H(CH_2L)][PF_6]$ (when L = PMe_2Ph), and $[W(\eta\text{-}C_5H_5)_2HL][PF_6]$, $[W(\eta\text{-}C_5H_5)_2(CH_3)L][PF_6]$ (when L = py or MeCN). An α-elimination mechanism is proposed for these reactions. In a study of the related thermal reactions the products were the same as in the photochemical reactions for L = PMe_2Ph; for L = py the sole product isolated was $[W(\eta\text{-}C_5H_5)_2(CH_3)L][PF_6]$; and no reaction was observed with L = MeCN.

THE photochemistry of bent metallocene derivatives has recently received some attention.[1] In a recent paper[2] we described some photosubstitution reactions on di-η^5-cyclopentadienyl-molybdenum and -tungsten complexes; it was reported that the complex $[Mo(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$, when irradiated at $\lambda > 310$ nm in pyridine, yields the monosubstituted derivative and when irradiated in acetonitrile yields both the monosubstituted and the disubstituted derivatives. In this note we describe the results of the photosubstitution studies on the analogous compound $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ where the products obtained can best be explained in terms of an α-elimination mechanism; the comparison of these results with those of thermal reactions is also reported.



SCHEME 1 Photochemical reactions ($h\nu > 310$ nm)

RESULTS AND DISCUSSION

The photochemical and thermal reactions of the complex $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ (1) are presented in Schemes 1 and 2.

With pyridine and acetonitrile the thermal behaviour of (1) is analogous to that reported for the molybdenum complex $[Mo(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ (2)[2] but in the reaction of (2) with dimethylphenylphosphine only the starting materials were recovered[3] while with (1) the phosphine gave the same results both thermally and photochemically. The photochemical behaviour of complexes (1) and (2) differs markedly: while in the latter case substitution reactions were observed with both pyridine and acetonitrile[2] (an intractable oil being obtained from the reaction with dimethylphenylphosphine[3]), the products obtained from the reactions of complex (1) imply a different type of mechanism. As in the case of the molybdenum analogue the first step seems to be the homolytic dissociation of one methyl group, equation (1).

$$\underset{(1)}{[W(\eta\text{-}C_5H_5)_2(CH_3)_2]^+} \xrightarrow{h\nu} \{[W(\eta\text{-}C_5H_5)_2(CH_3)]^+\} \quad (1)$$

Following a mechanism analogous to the one proposed by Green and co-workers[4] for the thermal reaction of $[W(\eta\text{-}C_5H_5)_2(CH_3)L][PF_6]$ where L = PR_3, the monomethyl species may undergo an α-elimination reaction and the two species in equilibrium may then further

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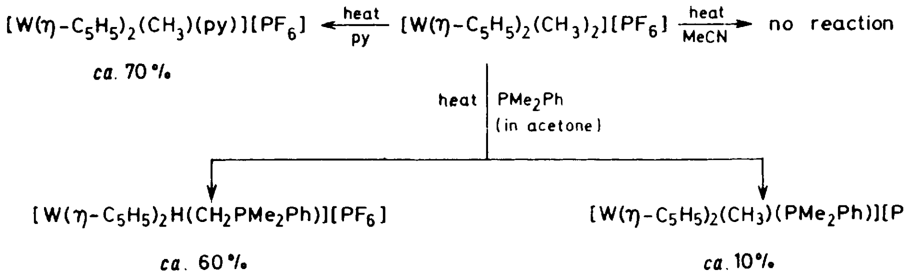
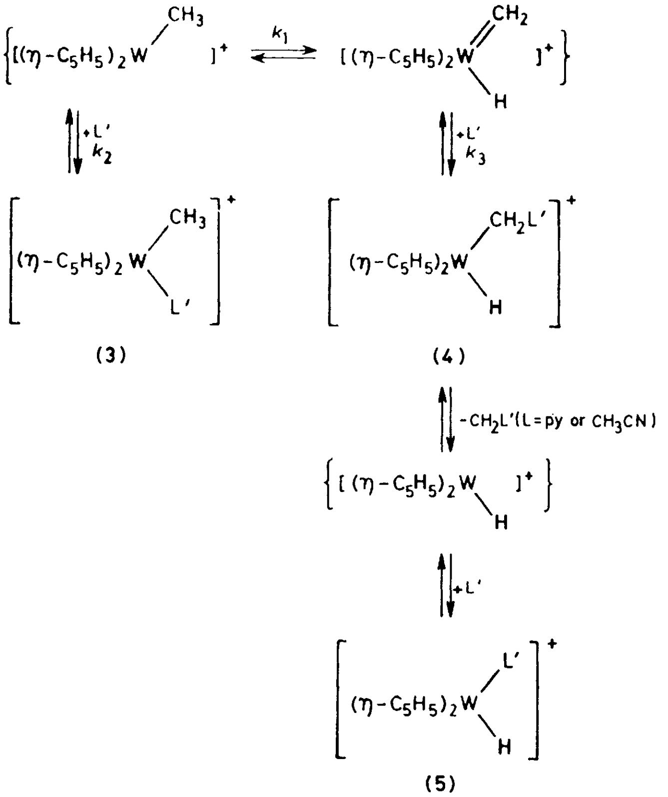
† Bis(cyclopentadienyl)dimethyltungsten hexafluorophosphate.

react with the substrate L′ (L′ = py, CH_3CN, or PMe_2Ph), Scheme 3. The species enclosed in braces are postulated. Complex (5) for L′ = CH_3CN was not isolated but support for its presence in the reaction mixture comes from i.r. and ^1H n.m.r. evidence; attempts to isolate this complex by other routes were unsuccessful.[5]



SCHEME 2 Thermal reactions

The different results obtained in the photosubstitution reactions of molybdenum and tungsten complexes can be explained assuming that for molybdenum $k_2 \gg k_1$ while for tungsten $k_1 \gg k_2$.



SCHEME 3

EXPERIMENTAL

All reactions and manipulations were carried out under nitrogen. All solvents were dried and distilled. Hydrogen-1 n.m.r. spectra were determined using a JEOL JNM 100 PF instrument. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 457 spectrophotometer and were calibrated with polystyrene film. Microanalyses were by the analytical department of this laboratory. The compound $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ was prepared by the reported method,[6] $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ was prepared by the following modification of the reported method.[7]

Preparation of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$.—The compound $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ (1 g, *ca.* 1.8 mmol) was added to a saturated solution of $[NH_4][PF_6]$ in acetone (50 cm^3) and the solution was shaken in air for 5 min. Ethanol was added and the acetone was removed under vacuum giving yellow crystals: yield *ca.* 60%. This method can also be applied, with great advantage over the oxidation with iodine, for the preparation of the analogous molybdenum complex.

Photolysis of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$.—A typical experiment is described. A solution (2×10^{-2} mol dm^{-3}) of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ in acetone (90 cm^3), in the presence of pyridine (10 cm^3), was irradiated for 1 h in a 100-cm^3 reactor with a Pyrex jacket and fitted with a medium-pressure 90-W mercury lamp.

The reaction mixture was taken to dryness under vacuum. The residue was repeatedly washed with diethyl ether and toluene, extracted with acetone, and then chromatographed on an alumina column. Using acetone–diethyl ether (1 : 1) as eluant a red band was collected from which $[W(\eta\text{-}C_5H_5)_2(CH_3)(py)][PF_6]$ was isolated; further elution with acetone yielded an orange band from which $[W(\eta\text{-}C_5H_5)_2H(py)][PF_6]$ was isolated. Both compounds were purified by recrystallisation from acetone–diethyl ether.

Thermal Reactions of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$.—A typical experiment is described. A solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2][PF_6]$ (500 mg) in acetone (45 cm^3), in the presence of pyridine (5 cm^3), was refluxed for 3 h. The reaction mixture was then pumped to dryness, the residue was repeatedly washed with toluene and diethyl ether, and chromatographed on an alumina column. Using acetone as eluant a red band was collected from which $[W(\eta\text{-}C_5H_5)_2(CH_3)(py)][PF_6]$ was isolated and recrystallised from acetone–ethanol. Yield *ca.* 70%.

The complete characterisation of the new compounds described in this note is given in the Table. All the other compounds already described in the literature were identified by comparison of their i.r. and ^1H n.m.r. (or e.s.r.) spectra with those of authentic samples.

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Analytical and spectroscopic data

Compound	Colour	Analysis[a] (%)			^{1}H n.m.r. data[b]	Selected i.r. data[c] (cm^{-1})
		C	H	N		
[W(η-C_5H_5)$_2$(CH_3)($NCCH_3$)][PF_6]	Yellowish brown	30.5 (30.3)	3.15 (3.1)	2.6 (2.7)	4.7, **10**, *s* (η-C_5H_5); 7.2, **3**, *s* (CH_3CN); 9.7, **3**, *s* (M–CH_3)	3 135m,[d] 2 942m,[e] 2 898m,[e] 2 820m,[e] 2 285w,[f] 840s,[g] 560s[g]
[W(η-C_5H_5)$_2$(CH_3)(NC_5H_5)][PF_6]	Red	34.9 (34.7)	3.5 (3.3)	2.6 (2.5)	1.1, **2**, *c* (C_5H_5N); 1.9, **1**, *c* (C_5H_5N); 2.6, **2**, *c* (C_5H_5N); 4.7, **10**, *s* (η-C_5H_5); 9.6, **3**, *s* (M–CH_3)	3 120m,[d] 2 930w,[e] 2 900m,[e] 2 822m,[e] 1 600s,[h] 1 480m,[h] 1 440s,[h] 1 220m,[h] 840s,[g] 560s[g]

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (τ), **relative intensity**, *multiplicity*, and assignment, in (CD_3)CO. [c] KBr pellets. [d] ν(C–H) of η-C_5H_5. [e] ν(C–H) of CH_3. [f] ν(N≡C). [g] PF_6^-. [h] Typical frequencies of *N*-co-ordinated pyridine.

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