

OXIDATIVE ADDITION OF ARYL HALIDES TO IRIDIUM(I) COMPLEXES. A NEW ARYLATION REAGENT

JOCHANAN BLUM *, MOSHE WEITZBERG

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel)
and ROLAND J. MUREINIK *

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel)

(Received June 9th, 1976)

Summary

Oxidative addition of aryl halides, ArX, to chlorocarbonylbis(triphenylphosphine)iridium(I) yields iridium(III) aryl complexes, $\text{IrCl(X)(Ar)(CO)(PPh}_3)_2$. The reactivity of the aryl halide decreases in the order $\text{I} > \text{Br} > \text{Cl}$, and electron-withdrawing substituents in the aryl ring accelerate the reaction. The Ir^{III} compounds may be utilised as arylating agents.

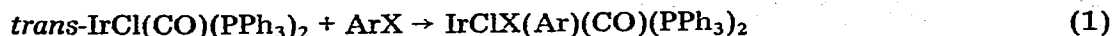
Introduction

A considerable variety of molecules of the type A–B are known to undergo oxidative addition to transition metal d^8 complexes yielding octahedral d^6 species, in which both A and B are directly bound to the metal [1,2]. Although the oxidative addition reaction of organic molecules such as alkyl and acyl halides has been extensively investigated, the reaction of aryl halides with Ir^{I} complexes does not appear to have been reported. Aryl complexes of Ir^{III} can in fact be prepared by indirect routes in which the key step is the oxidative addition of derivatives such as arylsulphonyl chlorides [3,4] or aroyl halides [5,6] to Ir^{I} complexes of the Vaska type. Aryl halides undergo oxidative addition to d^{10} complexes of the nickel triad [7], and preliminary work in this laboratory [8] revealed the possibility of the oxidative addition of iodo- and bromo-benzene to $\text{IrCl(CO)(PPh}_3)_2$. In this paper we describe the general, facile synthesis of Ir^{III} aryl complexes, and present preliminary data on the potential use of these compounds as arylating agents.

* To whom correspondence should be addressed.

Results and discussion

Aryl halides undergo direct reaction with Vaska's compound I yielding aryl Ir^{III} complexes (reaction 1). The Ir^{III} species are stable in air, but since I is



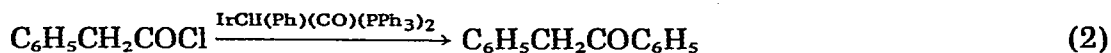
(I)

(II)

sensitive to oxidation it is better to carry out reaction 1 in a pressure tube under nitrogen. Reaction is complete in times ranging from minutes to several hours at temperatures between 140–180°C, depending on the nature of the halide X, and on the substituents present in the aryl group. For Ar = *p*-tolyl, X = I, Br, Cl, reaction 1 was found to be first order in I for over 50% of the reaction. Initial first-order rate constants of 6×10^{-2} , 8×10^{-3} and $8 \times 10^{-4} \text{ sec}^{-1}$ at 150°C were obtained for *p*-tolyl iodide, bromide and chloride, respectively. The reactivity order I > Br > Cl has also been observed for the reaction of I with methyl halides [9], as well as for the oxidative addition of aryl halides to Ni⁰ complexes [7]. Preliminary observations indicate that electron-withdrawing substituents tend to increase the reaction rate, contrary to the trend noted [7] for the reaction of aryl halides with Ni(PPh₃)₃. The kinetics and mechanism of reaction 1 are currently being investigated.

In the proton NMR spectrum of IrCl(*p*-tolyl)(CO)(CH₃PPh₂)₂ (III), derived from addition of *p*-tolyl iodide to IrCl(CO)(CH₃PPh₂)₂, the phosphine methyl protons are observed as a triplet (δ 2.043 ppm; *J* 3 Hz), indicating that the *trans* disposition of the two phosphines is maintained in the Ir^{III} species [10]. The far infrared spectrum of III shows weak bands at 315 cm⁻¹ and 350 cm⁻¹ in the spectral region characteristic of the stretching frequency $\nu(\text{Ir}-\text{Cl})$ *trans* to a carbonyl group [11], suggesting that the overall addition reaction (1) is *trans*, in keeping with the stereochemical path followed in the majority of cases [1,2].

Aryl Ir^{III} complexes, II, can function as arylating agents. The reaction of chlorobenzene with I clearly yields an Ir^{III} product, as shown by appearance of a carbonyl stretching frequency at 2050 cm⁻¹, but the adduct could not be isolated in pure form. However, on prolonged heating of the reaction mixture above 200°C (for two days), biphenyl was obtained. The reaction of II (Ar = Ph; X = I) with α -phenylacetylchloride afforded desoxybenzoin in reasonable yield



on brief heating on 220°C (eq. 2).

We are currently investigating the use of II as arylating agents in other systems.

Experimental

All the compounds II were synthesised by the same general method. A mixture of I (0.1 mmol) was placed together with a large excess of the aryl halide (3–5 g), which served as the solvent, in a pressure tube under nitrogen. The

TABLE 1

ANALYTICAL DATA, REACTION CONDITIONS AND PHYSICAL PROPERTIES FOR ARYL-IRIDIUM(III) COMPLEXES

Compounds II IrCl(X)(Ar)(CO)(PPh ₃) ₂	M.p. (°C) (Recrystallised from)	$\nu(\text{CO})^a$ (cm ⁻¹)	Temperature (°C) (Reaction time)	Analysis found (calcd.) (%)		
				C	H	P
C ₄₄ H ₃₇ ClIrOP ₂ (Ar = <i>m</i> -CH ₃ C ₆ H ₄ ; X = I) ^b	241–244 (xylene/ pet. ether)	2040	130 (1 h)	53.2 (53.0)	3.5 (3.7)	
C ₄₄ H ₃₇ ClIrOP ₂ (Ar = <i>p</i> -CH ₃ C ₆ H ₄ ; X = I)	247–249 (benzene)	2040	150 (45 min)	52.9 (53.0)	3.7 (3.7)	6.4 (6.2)
C ₄₃ H ₃₄ Cl ₂ IrOP ₂ (Ar = <i>p</i> -ClC ₆ H ₄ ; X = I)	240–242 (benzene)	2048	150 (35 min)	50.8 (50.7)	3.8 (3.4)	6.3 (6.4)
C ₄₃ H ₃₄ Cl ₂ IrOP ₂ (Ar = <i>m</i> -ClC ₆ H ₄ ; X = I)	251–253 (c)	2043	135 (3 h)	51.2 (50.7)	3.6 (3.4)	
C ₄₃ H ₃₄ BrClIrOP ₂ (Ar = <i>p</i> -BrC ₆ H ₄ ; X = I)	239–241 (xylene/ pet. ether)	2045	150 (40 min)	48.4 (48.6)	3.1 (3.2)	6.1 (5.8)
C ₄₄ H ₃₇ BrClIrOP ₂ (Ar = <i>m</i> -CH ₃ C ₆ H ₄ ; X = Br)	246–247 (c)	2043	175 (3 h)	55.6 (55.6)	4.1 (3.9)	6.2 (6.5)
C ₄₄ H ₃₇ BrClIrOP ₂ (Ar = <i>p</i> -CH ₃ C ₆ H ₄ ; X = Br)	239–243 ^d (xylene)	2050	170 (2.5 h)	55.3 (55.6)	4.3 (3.9)	6.5 (6.5)
C ₄₄ H ₃₇ BrClIrO ₂ F ₂ (Ar = <i>p</i> -CH ₃ OC ₆ H ₄ ; X = Br)	248–250 (benzene)	2040	175 (3.5 h)	54.1 (54.6)	3.9 (3.9)	6.8 (6.4)
C ₄₃ H ₃₄ BrClFIrOP ₂ (Ar = <i>p</i> -FC ₆ H ₄ ; X = Br)	255–259 (c)	2045	175 (40 min)	54.0 (54.1)	3.9 (3.6)	6.7 (6.5)
C ₄₄ H ₃₇ Cl ₂ IrOP ₂ ^e (Ar = <i>p</i> -CH ₃ C ₆ H ₄ ; X = Cl)	281–282 (benzene)	2050 ^f	250 ^g (48 h)	57.9 (58.3)	4.3 (4.1)	6.8 (6.8)

^a Small differences were observed for spectra obtained from Nujol mulls. ^b Found: I = 12.7%; Calcd.: I, 12.7%. ^c Crystallised from the reaction medium. ^d Decomposes. ^e This compound appears to have been prepared by a different route (Ref. 6) but no details are given. ^f In Nujol. ^g A clean product is more conveniently obtained by vigorous heating in a sealed pressure tube over an open flame for about 20 min.

tube was sealed and heated in an oil bath. Reaction times and temperatures, are listed in Table 1, together with the solvent from which the product was recrystallised. Products of the arylation reactions were identified by GLC and comparison with authentic samples. The kinetics of the reaction of I with the *p*-tolyl halides were followed by withdrawing samples from the reaction mixture and quenching by rapid cooling to room temperature. A known volume was then diluted with CH₂Cl₂, and the concentration of I determined from the absorbance at 397 nm.

Acknowledgement

We thank the Israel Commission for Basic Research for financial support.

References

- 1 J.P. Collman and W.R. Roper, *Adv. Organomet. Chem.*, 7 (1968) 53.
- 2 A.J. Deeming, *Reaction Mechanisms in Inorganic Chemistry*, MTP International Review of Science, *Inorganic Chemistry, Series One, Vol. 9*, (1972) p. 117.
- 3 J. Blum and G. Scharf, *J. Org. Chem.*, 35 (1970) 1895.

- 4 M. Kubota and B.M. Loeffler, *Inorg. Chem.*, **11** (1972) 469.
- 5 J. Blum, S. Kraus and Y. Pickholtz, *J. Organometal. Chem.*, **33** (1971) 227.
- 6 M. Kubota and D.M. Blake, *J. Amer. Chem. Soc.*, **93** (1971) 1368.
- 7 M. Foa and L. Cassar, *J. Chem. Soc. Dalton Trans.*, 2572 (1975) and refs. therein.
- 8 J. Blum, Z. Aizenshtat and S. Iflah, *Trans. Metal. Chem.*, **1** (1976) 52.
- 9 F.B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88** (1966) 3511.
- 10 J.P. Collman and C.T. Sears, *Inorg. Chem.*, **7** (1968) 27.
- 11 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc.*, (1965) 6789.