

Preliminary communication

ARENE SUBSTITUTION BY IRIDIUM COMPLEXES UNDER MILD CONDITIONS

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Summary

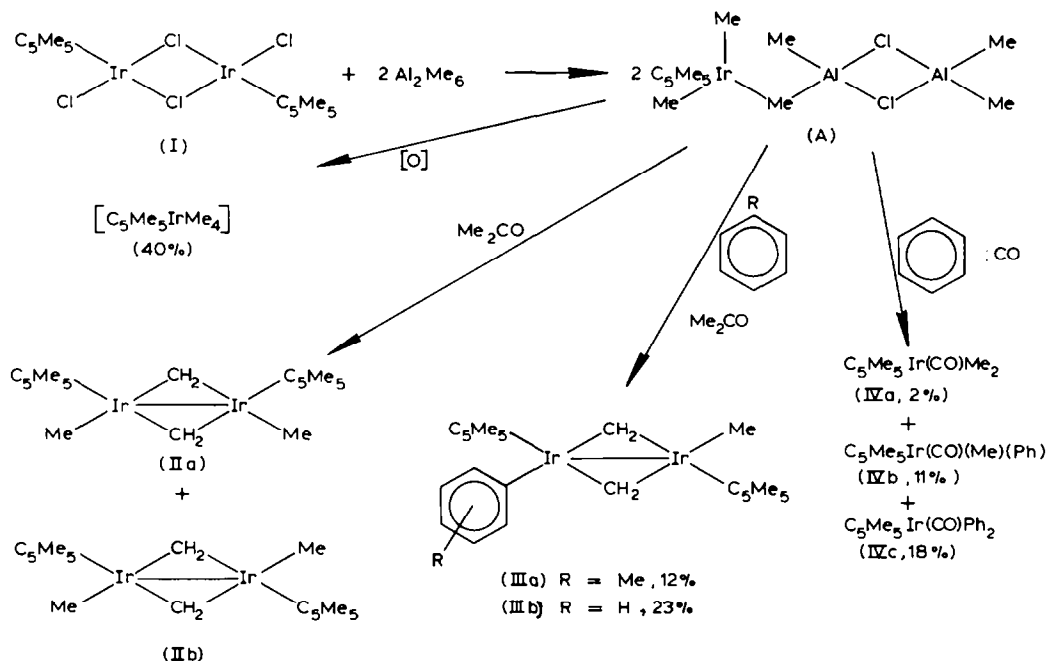
$[(C_5Me_5Ir)_2Cl_4]$ reacts with Al_2Me_6 in saturated hydrocarbons to give $[C_5Me_5IrMe_4]$ or *cis*- and *trans*- $[(C_5Me_5Ir)_2Me_2(\mu-CH_2)_2]$, depending on work-up conditions. In benzene or toluene solution the main product is $[(C_5Me_5Ir)_2Me(Aryl)(\mu-CH_2)_2]$ (aryl = Ph or *m*- plus *p*-tolyl, ratio 2/1); if CO is introduced into the benzene solution the products are $[C_5Me_5Ir(CO)R^1R^2]$ ($R^1 = Me$, $R^2 = Ph$; $R^1 = R^2 = Me$ or Ph).

The recent reports [1] on the oxidative addition of aromatic C—H bonds to pentamethylcyclopentadienyl-rhodium and -iridium species under photolytic conditions prompt us to present some of our results concerning the arylation of pentamethylcyclopentadienyliridium complexes.

Reactions of $[(C_5Me_5Ir)_2Cl_4]$ (I) and Al_2Me_6 in pentane gave a yellow solution (A) which on oxidation gave the iridium(V) complex $[C_5Me_5IrMe_4]$ [2]; by careful working yields of 40% can now consistently be obtained. If the yellow solution A was treated with acetone the *cis*- and *trans*-di- μ -methylene bridged dimethyldiiridium complexes (II) were formed in 33% yield.

The low temperature ($-90^\circ C$) ^{13}C NMR spectrum of the yellow solution A showed the presence of only a single iridium complex [cyclopentane, $-90^\circ C$, δ -29.9 ($IrMe_2$), -16.6 ($IrMeAl$), -8.9 (Al_2Me_6 , terminal), -4.9 (Al_2Me_6 , bridge), -6.4 (Me_2AlCl), -10.7 ($MeAlCl$), $+7.3$ (C_5Me_5), and $+92.4$ (C_5Me_5)] which because of its similarity to that of the solution from reaction of $[(C_5Me_5Rh)_2Cl_4]$ and Al_2Me_6 in hydrocarbon solvents [3] is assigned the same structure.

If, however, the solution of I and Al_2Me_6 was made up in toluene- d_8 , even at $-60^\circ C$ some new species were immediately formed, as shown by the appearance of extra peaks, for example those due to C_5Me_5Ir at δ 9.2 and 9.9 ppm. After quenching with acetone (at $-10^\circ C$) a 2/1 mixture of the dimethylene bridged



Scheme 1

trans-m- and *p*-tolyl complexes (IIIa) and (IIIb) was isolated (12%)*. The analogous phenyl complex was obtained (23%) when Al₂Me₆ in benzene was added to complex I.

When a solution of I and Al₂Me₆ in benzene was exposed to carbon monoxide (1 atm, 20°C) the monocarbonyl complexes IVa, IVb and IVc ($\nu(\text{CO})$: 1958 (1981sh), 1973 and 1983 cm⁻¹, respectively) were obtained in 2, 11 and 18% yield respectively. Complex IVa was the only product if A made up in pentane was carbonylated.

The formation of IVb and IVc shows that the aryl-Ir bonds arise from A via intermediates of the type "C₅Me₅IrPhMe" and "C₅Me₅IrPh₂" rather than by an arylation of a subsequently formed Ir₂(CH₂)₂ skeleton. The formation of the mixed arylmethyl complexes IVb and III also shows that the reaction does not occur by oxidative of aryl-H to a C₅Me₅Ir^I species. Possible mechanisms include

* Satisfactory microanalyses were obtained for all new compounds.

¹H NMR (400 MHz): *trans*-[(C₅Me₅Ir)₂(μ-CH₂)₂(Me)(*m*-tolyl)] (IIIa) (CD₂Cl₂) δ -0.512 (Ir-Me), 1.350, 1.589 (2 × C₅Me₅), 2.121 (MeC₆H₄), 6.324 (dt, *J* 1.5, 4.5 Hz), 6.622 (d, *J* 4.5 Hz), 6.624 (d, *J* 4.5 Hz), 6.668 (s, br), all aromatic H 7.057, 7.468 (2 × d, *J* 1 Hz, 2 × CH₂).
trans-[(C₅Me₅Ir)₂(μ-CH₂)₂(Me)(*p*-tolyl)] (CD₂Cl₂) δ -0.516 (Ir-Me), 1.354, 1.585 (2 × C₅Me₅), 2.197 (MeC₆H₄), 6.590, 6.698 (2 × d, *J* 8.0 Hz, aromatic H), 7.488, 7.071 (2 × d, *J* 1 Hz, 2 × CH₂).
trans-[(C₅Me₅Ir)₂(μ-CH₂)₂(Me)(Ph)] (IIIb) (CDCl₃) δ -0.5 (Ir-Me), 1.36, 1.59 (2 × C₅Me₅), 6.52 (tt, *J* 1.8, 7.0 Hz, *p*-H), 6.75 (m, *m*-H), 6.83 (m, *o*-H), 7.09 and 7.47 (2 × d, *J* 1.3 Hz, 2 × CH₂).

either an oxidative addition of aryl-H to a $C_5Me_5Ir^{III}Me_2$ species followed by reductive elimination of methane from an Ir^V intermediate or by a type of Friedel—Crafts arylation possibly involving species such as $[C_5Me_5IrMe]^+ [Al_2Me_5Cl_2]^-$.

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