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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*-$[(C_5Me_5Ir)_2Me_2(\mu\text{-}CH_2)_2]$, depending on work-up conditions. In benzene or toluene solution the main product is $[(C_5Me_5Ir)_2Me(Aryl)(\mu\text{-}CH_2)_2]$ (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° C) ^{13}C NMR spectrum of the yellow solution A showed the presence of only a single iridium complex [cyclopentane, —90° 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_2M_6 was made up in toluene-d_8, even at —60° 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° C) a 2/1 mixture of the dimethylene bridged

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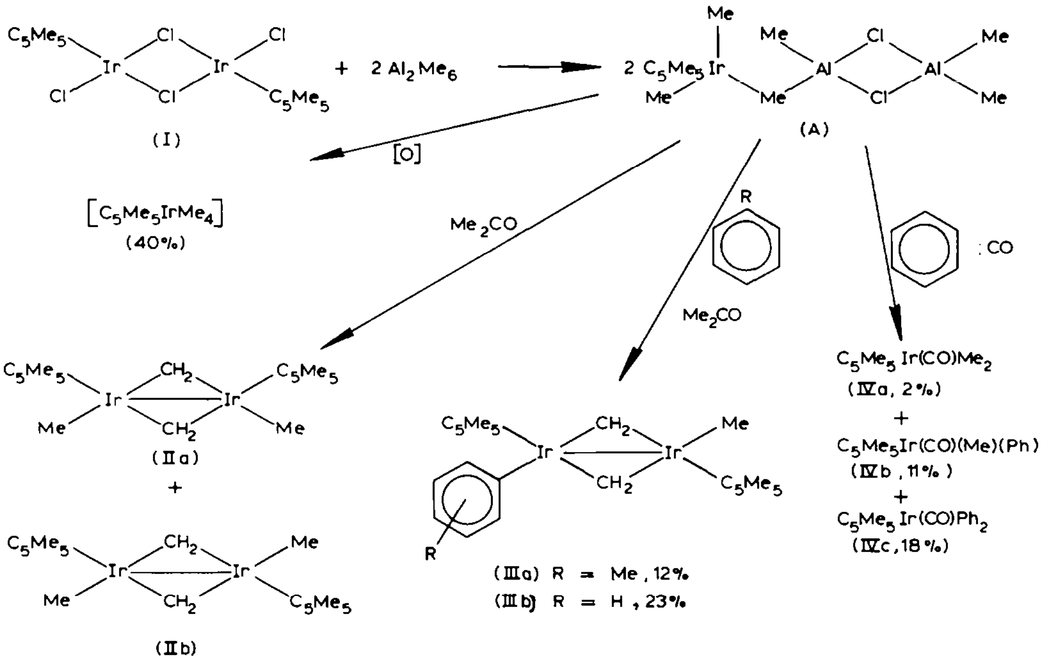

Scheme 1

trans-m- and *-p-*tolyl complexes (IIIa) and (IIIb) was isolated (12%)*. The analogous phenyl complex was obtained (23%) when Al_2Me_6 in benzene was added to complex I.

When a solution of I and Al_2Me_6 in benzene was exposed to carbon monoxide (1 atm, 20° C) the monocarbonyl complexes IVa, IVb and IVc (ν(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 "$C_5Me_5IrPhMe$" and "$C_5Me_5IrPh_2$" rather than by an arylation of a subsequently formed $Ir_2(CH_2)_2$ 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 $C_5Me_5Ir^I$ species. Possible mechanisms include

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* Satisfactory microanalyses were obtained for all new compounds.
^{1}H NMR (400 MHz): *trans*-[$(C_5Me_5Ir)_2(\mu\text{-}CH_2)_2$(Me)(*m*-tolyl)] (IIIa) (CD_2Cl_2) δ —0.512 (Ir—Me), 1.350, 1.589 (2 × C_5Me_5), 2.121 (*Me*C_6H_4), 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 × CH_2).
trans-[$(C_5Me_5Ir)_2(\mu\text{-}CH_2)$(Me)(*p*-tolyl)] ($CD_2Cl_2$) δ —0.516 (Ir—Me), 1.354, 1.585 (2 × C_5Me_5), 2.197 (*Me*C_6H_4), 6.590, 6.698 (2 × d, *J* 8.0 Hz, aromatic H), 7.488, 7.071 (2 × d, *J* 1 Hz, 2 × CH_2).
trans-[$(C_5Me_5Ir)_2(\mu\text{-}CH_2)_2$(Me)(Ph)] (IIIb) ($CDCl_3$) δ —0.5 (Ir—Me), 1.36, 1.59 (2 × C_5Me_5), 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 × CH_2).

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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References

1 A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 104 (1982) 352; J.K. Hoyano and W.A.G. Graham, ibid., 104 (1982) 3723; W.D. Jones and F.J. Feher, ibid., 104 (1982) 4240.
2 K. Isobe, P.M. Bailey and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1981) 808.
3 A. Váquez de Miguel, K. Isobe, B.F. Taylor, A. Nutton and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1982) 758.