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Preliminary communication

A NOVEL CLASS OF ARYLDIAZENE COMPLEXES: $[(PPh_3)_2(CO)IrCl(HN{=}NC_6H_4R\text{-}p)(C{\equiv}CPh)](BF_4)$ ($R = NO_2$, CN, $COCH_3$)

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Summary

In the reaction with phenylacetylene leading to $[(PPh_3)_2(CO)IrCl(HN{=}NC_6H_4R\text{-}p)(C{\equiv}CPh)](BF_4)$ ($R = NO_2$, CN, $COCH_3$), the vacant coordination site in $[(PPh_3)_2(CO)IrCl(N_2C_6H_4R\text{-}p)](BF_4)$ plays a key role in the activation of the acetylenic C—H bond.

Recently it was reported that $(PPh_3)_2Pt(HC{\equiv}CPh)$ reacts with the diazonium salt $(p\text{-}FC_6H_4N_2)(BF_4)$ to yield the aryldiazenephenylacetylideplatinum(II) complex *trans*-$[(PPh_3)_2(HN{=}NC_6H_4F\text{-}p)Pt(C{\equiv}CPh)](BF_4)$ [1]. It was proposed that the formation of this complex occurs via the intermediate "$Pt(BF_4)(N_2Ar)(PPh_3)_2$" [2] which possesses a readily available coordination site capable of promoting the formation of the M—acetylide bond [1].

We have now found that the five-coordinate aryldiazenatoiridium(III) complex $[(PPh_3)_2(CO)IrCl(N_2C_6H_4R)](BF_4)$ [3] reacts readily with phenylacetylene yielding a new class of aryldiazenephenylacetylide complexes of iridium(III), according to the scheme:

$$\underset{\text{(A)}}{[(PPh_3)_2(CO)IrCl(N_2C_6H_4R\text{-}p)](BF_4)} + HC{\equiv}CPh \xrightarrow[C_6H_6\text{/acetone}]{\text{ethanol or}}$$

$$[(PPh_3)_2(CO)IrCl(HN{=}NC_6H_4R\text{-}p)(C{\equiv}CPh)](BF_4)$$

(I)

$$\text{(I)} \underset{HBF_4}{\overset{NEt_3}{\rightleftharpoons}} (PPh_3)_2(CO)IrCl(N_2C_6H_4R\text{-}p)(C{\equiv}CPh)$$

(II)

$R = NO_2$, CN, $COCH_3$

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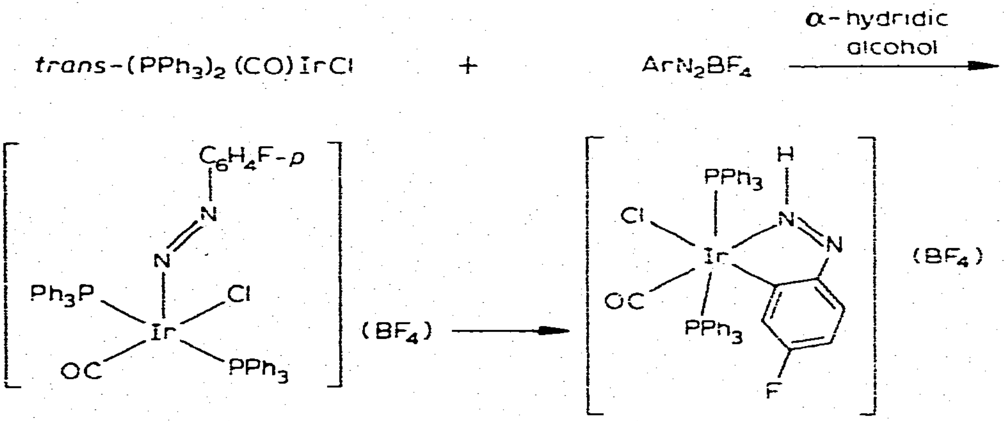
I can be reversily deprotonated to the corresponding aryldiazenatophenylacetylide complex II.

Complexes I and II present $\nu(C\equiv C)$ and $\nu(C\equiv O)$ at ca. 2130 and 2070 cm^{-1}, respectively. The latter value is close to that of the starting complex A [3]. Thus I and II can be considered to be iridium(III) complexes of the ArN=NH or $ArN=N^-$ species. There are several bands in the 1600—1400 cm^{-1} region, where $\nu(N=N)$ usually occurs [4], but the exact assignment by ^{15}N-substitution has not been carried out. The ^1H NMR spectrum in $CDCl_3$ shows the nitrogen-bonded proton at ca. τ —3 to —2 ppm where aryldiazene complexes usually show the signal for the proton bonded to the nitrogen atom coordinating the metal [1,5].

The formation of I may be related to that of the cationic iridium(III) *ortho*-metallated diazene complex III, which seems to occur via a coordinatively unsaturated complex of type A [6].



(III)

However, it is interesting to note that in this case activation of the C—H bond *ortho* to the coordinated nitrogen atom seems to occur only in the presence of α-hydridic alcohols such as ethanol or propan-2-ol [7]. Since (i) the acetylenic C—H activation leading to I occurs even in the absence of such α-hydridic agents, and (ii) no Ir—acetylide bond formation occurs with the coordinatively saturated six-coordinate complex $(PPh_3)_2(CO)IrCl_2(N_2Ar)$ [3], it seems that the vacant coordination site in complex A plays a key role in the formation of I.

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