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Benzo[*h*]quinolin-10-yl-*N* Iridium(III) Complexes

Matsuo NONOYAMA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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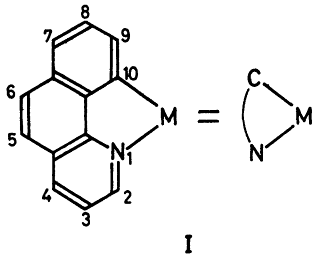
Synopsis. Benzo[*h*]quinoline(bhqH) is metallated with iridium(III) to give $[Ir(bhq)_2Cl]_2$ in which bhq is coordinated at 1-N and 10-C atoms. This complex reacts with a ligand(L) such as tri-*n*-butylphosphine and diethylsulfide to yield $[Ir(bhq)_2ClL]$.

The metallation reactions of organic nitrogen compounds with palladium(II) and platinum(II) to form a metal-carbon σ-bond have been studied widely, but the same reactions with other platinum metals have scarcely been investigated at all. A nitrogen heterocyclic base, benzo[*h*]quinoline(abbreviated as bhqH), has been reported[1] to form a π-complex with chromium hexacarbonyl, $Cr(CO)_3(bhqH)$. A different type of a benzo[*h*]quinoline complex has been prepared with palladium(II),[2,3] platinum(II),[3] and rhodium(III)[4] halides. In these complexes, the ligand loses one proton and coordinates to a metal ion through the carbon (10-C) and nitrogen (1-N) atoms, thus forming a five-membered chelate ring containing a metal-carbon σ-bond (Formula I). As a part of our studies of the metallation reactions of this ligand, the reaction of bhqH with $Na_3[IrCl_6]$ will be reported here.



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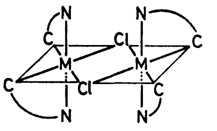

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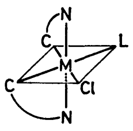

III

Experimental

The Reaction of bhqH with $Na_3[IrCl_6]$. To a solution of 0.5 g of $Na_3[IrCl_6]$ in 2-methoxyethanol (30 ml), we added 0.6 g of bhqH. The mixture was stirred for 8 hr at room temperature and then refluxed for 24 hr. A brownish-yellow precipitate was obtained. The crude product was washed with ethanol and extracted three times with 100 ml of chloroform. The extract was then concentrated to a small volume to give a yellowish-orange powder (0.3 g), $[Ir(bhq)_2Cl]_2\cdot 2/3CHCl_3$, which decomposed above 305 °C.

Found: C, 50.80; H, 2.70; N, 4.54; Cl, 11.12%. Calcd for $Ir_2C_{52}H_{32}N_4Cl_2\cdot 2/3CHCl_3$: C, 50.70; H, 2.64; N, 4.49; Cl, 11.37%.

When this chloroform adduct was recrystallized from benzene, an unsolvated complex, $[Ir(bhq)_2Cl]_2$, was obtained.

Found: C, 53.55; H, 2.92; N, 4.52%. Calcd for $Ir_2C_{52}H_{32}N_4Cl_2$: C, 53.47; H, 2.76; N, 4.80%.

In a similar manner, $Na_3[IrBr_6]$ gave yellowish-orange $[Ir(bhq)_2Br]_2\cdot 1/2CHCl_3$.

Found: C, 47.80; H, 2.37; N, 4.31%. Calcd for $Ir_2C_{52}H_{32}N_4Br_2\cdot 1/2CHCl_3$: C, 47.89; H, 2.49; N, 4.25%.

*The Reactions of $[Ir(bhq)_2Cl]_2$ with Tri-*n*-butylphosphine and Diethylsulfide.* To a chloroform suspension (20 ml) of 0.3 g of $[Ir(bhq)_2Cl]_2$, we added 0.1 g of tri-*n*-butylphosphine (PBu_3). The suspension became transparent, and upon the addition of *n*-hexane, a yellow powder, $[Ir(bhq)_2Cl(PBu_3)]$, was precipitated. It melted at 214—217 °C.

Found: C, 57.51; H, 5.29; N, 3.49; P, 3.44%. Calcd for $IrC_{38}H_{43}N_2PCl$: C, 58.04; H, 5.51; N, 3.56; P, 3.94%.

A similar reaction of $[Ir(bhq)_2Cl]_2$ with diethylsulfide (SEt_2) in benzene gave a yellow powder, $[Ir(bhq)_2Cl(SEt_2)]$, which decomposed above 300 °C.

Found: C, 53.18; H, 3.83; N, 4.11; S, 4.82%. Calcd for $IrC_{30}H_{26}N_2SCl$: C, 53.44; H, 3.89; N, 4.15; S, 4.76%.

Measurements. All the spectral measurements were carried out by the methods reported previously.[2,4]

Results and Discussion

The reaction of bhqH with iridium(III) halides requires more drastic conditions than that with rhodium(III) halides, which has been reported to proceed in boiling ethanol and to give a similar complex, $[Rh(bhq)_2Cl]_2\cdot 1/4CHCl_3$.[4] This fact is consistent with the general inertness of iridium(III) compared with rhodium(III).

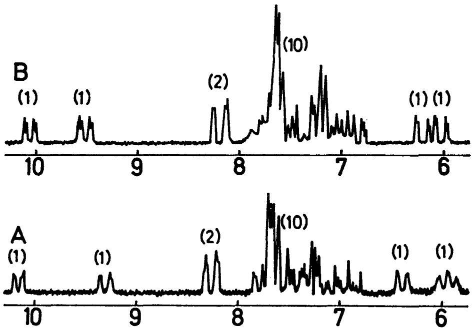

Fig. 1. 60 MHz PMR spectra of (A) $[Ir(bhq)_2Cl(PBu_3)]$ and (B) $[Ir(bhq)_2Cl(SEt_2)]$. Relative intensities of the signals are given in parentheses.

The iridium complex, $[Ir(bhq)_2Cl]_2$, is not sufficiently soluble in common solvents for precise PMR measurements. However, the gross features of the spectrum of its dilute deuterochloroform solution are similar to those of $[Rh(bhq)_2Cl]_2\cdot 1/4CHCl_3$. Three isolated doublet-like signals were observed at δ=*ca.* 9.4, 8.3, and 6.0 ppm, and several overlapped peaks in the 6.7—8.0 ppm region. The former three signals are assigned, respectively, to 2-H, 4-H, and 9-H of the metallated ligand on the basis of the assignments reported for the rhodium analogue.[4] The entire infrared spectrum of $[Ir(bhq)_2Cl]_2$ is very similar to that of the rhodium complex and shows ν_{Ir-Cl} at 219 and 240 cm^{-1}. The structure of the iridium complex seems, therefore, to be similar to that of the rhodium analogue (Formula II).

The PMR spectra of deuterochloroform solutions of $[Ir(bhq)_2Cl(PBu_3)]$ and $[Ir(bhq)_2Cl(SEt_2)]$ are shown in Fig. 1. The spectrum of the phosphine complex is very similar to that of the corresponding $[Rh(bhq)_2Cl(PBu_3)]$. In the spectra of the phosphine and sulfide complexes, the signals due to 2-H and 9-H of $[Ir(bhq)_2Cl]_2$ split into two components, implying that the two bhq moieties are not equivalent, while that of 4-H remains unsplit, probably because 4-H exists in a distant position from the donor atoms. One of the two components of the 9-H of the phosphine complex is a broad doublet at 6.39 ppm (J=6 Hz), and the other is a triplet at 5.95 ppm (J=6 Hz), while both of the sulfide complex are double doublets (at 6.22 and 6.04 ppm (J=6 and 1.5 Hz)). The triplet of the former complex may be due to the coupling of 9-H with the phosphorus atom (I=1/2), which is at the *trans*-position to the metallated carbon atom (10-C) (Formula III, $L=PBu_3$).

The signals due to 2-H are observed at 10.15 and 9.29 ppm for $[Ir(bhq)_2Cl(PBu_3)]$ and at 10.05 and 9.54 ppm for $[Ir(bhq)_2Cl(SEt_2)]$. The large splitting can be explained in terms of the proposed structure III, in which one proton is directed towards the coordinated chlorine atom and the other towards the phosphorus or sulfur atom. The two 2-H protons are, therefore, not equivalent.

The infrared spectrum of the phosphine complex is similar to that of the corresponding $[Rh(bhq)_2Cl(PBu_3)]$, and the band assignable to ν_{Ir-Cl} is observed at 247 cm^{-1}. The corresponding band, ν_{Ir-Cl}, for the sulfide complex is at 245 cm^{-1}. The low frequencies of these bands may be attributed to the fact that the chlorine atom is situated at *trans* position to a carbon atom with a high *trans*-influence (Formula III).[5] A new band observed for the phosphine complex at 397 cm^{-1} is tentatively assigned to δ_{CPC}.

Recently, the octahedral structure of acetatobis(2-(phenylazo)phenyl-*N*)rhodium(III) has been determined by X-rays;[6] the metallated carbon atoms have been found to be located mutually *cis*, and the nitrogen atoms *trans*, to each other. This is consistent with the structures proposed for the rhodium and iridium complexes of benzo[*h*]quinoline, and it is evident that the reaction of bhqH with $Na_3[IrCl_6]$ forms a carbon-iridium bond to give a five-membered metallocycle (Formula I).

References

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