

INTERMEDIATES IN A SYNTHESIS OF *trans*-CHLOROBIS(TRIPHENYLPHOSPHINE)(THIOCARBONYL)IRIDIUM(I)

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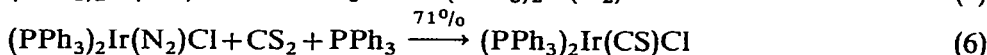
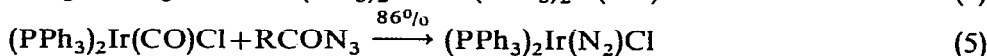
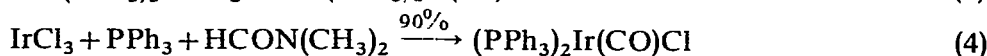
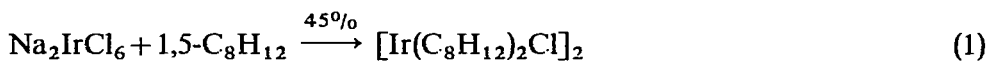
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SUMMARY

The reaction of *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I) and carbon disulfide leads to formation of $\text{IrCl}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{C}_2\text{S}_5$ (II). Reaction of (II) with triphenylphosphine in the presence of methanol gives *trans*-chlorobis(triphenylphosphine)(thiocarbonyl)iridium(I). Treatment of (II) with triphenylphosphine in dichloromethane gives $(\text{PPh}_3)_2\text{Cl}(\text{CS})\text{Ir}(\text{CS}_3)$ (IV) a product, which can be converted to $(\text{PPh}_3)_2\text{Ir}(\text{CS})\text{Cl}$. Thermal decomposition of (II) and (IV) gives another (thiocarbonyl)iridium(III) product (V) which cannot be readily converted to $(\text{PPh}_3)_2\text{Ir}(\text{CS})\text{Cl}$. The carbonylation of $(\text{PPh}_3)_2\text{IrClC}_2\text{S}_5$ is described.

INTRODUCTION

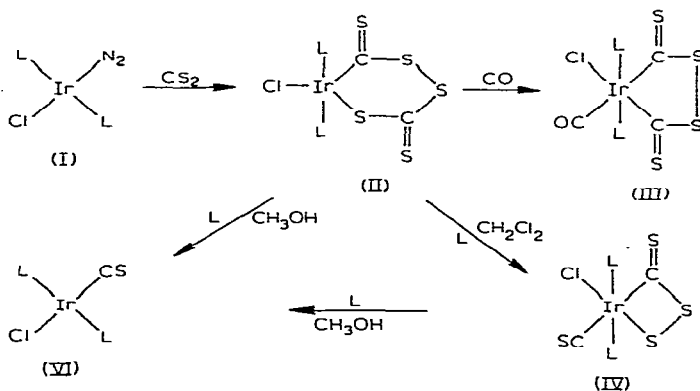
Experimental difficulties and low yields in the synthesis of *trans*-chlorobis(triphenylphosphine)(thiocarbonyl)iridium(I), $(\text{PPh}_3)_2\text{Ir}(\text{CS})\text{Cl}$, (VI), have limited investigation of its reactions mainly to a spectroscopic survey¹. Addition of chloroform to the unstable products $(\text{PPh}_3)_x\text{IrCl}(\text{CS}_2)_y$, where $x=2-3$ and $y=1-3$, which were obtained from the reaction of chlorotris(triphenylphosphine)iridium(I) and carbon disulfide gave small amounts of (VI) and an unidentified (thiocarbonyl)iridium(III) product¹. Compared to the sequence of reactions (1)², (2)³ and (3)¹, previously employed to prepare *trans*- $(\text{PPh}_3)_2\text{Ir}(\text{CS})\text{Cl}$, the reactions (4)⁴, (5)⁵ and (6) utilized in this study gave appreciable enhancement of yields.



RESULTS AND DISCUSSION

The addition of carbon disulfide to $(\text{Ph}_3\text{P})_2\text{Ir}(\text{N}_2)\text{Cl}$ (I) leads to quantitative evolution of nitrogen and formation of black crystals with empirical formula, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{IrClC}_2\text{S}_5$, (II). This compound can be recrystallized unchanged from dichloromethane/methanol, but its solutions in benzene, chloroform or dichloromethane are unstable when heated at reflux temperature for several hours. Gradual decomposition of the compound was noted in preliminary attempts to obtain single crystal diffraction data. The IR spectrum of (II) is similar in many respects to that observed¹ for $(\text{PPh}_3)_2\text{IrCl}(\text{CS}_2)_3$. The IrC_2S_5 compound (II), however, does not have bands in the 1510 cm^{-1} region characteristic of sulfur coordinated CS_2 . Absence of absorption in the $1100\text{--}1200\text{ cm}^{-1}$ region other than weak bands due to the triphenylphosphine ligand rule out the $\pi\text{-CS}_2$ bonding⁶ mode. Yagupsky and Wilkinson¹ interpreted IR absorption at $1050, 900$ and 838 cm^{-1} as diagnostic of bonding of the type Ir-S-C(S)-Ir . The observed molecular weight of (II) in chloroform, however, is consistent with the existence of a monomeric species. Since the IR spectrum of $(\text{PPh}_3)_2\text{IrClC}_2\text{S}_5$ (II) in chloroform has bands at $1045, 900$ and 837 cm^{-1} , it is likely that the same type of structure persists in the solid state and in solution. As the IR frequencies of (II) closely resemble the pattern of absorption observed in complexes of d^8 metals with the perthiocarbonato ligand⁷, we propose an analogous -S-S-C(S)-S- linkage for bonding in $(\text{Ph}_3\text{P})_2\text{IrClC}_2\text{S}_5$, and thus a structure shown in Scheme 1 is tentatively proposed.

SCHEME 1

Tentatively proposed structures, $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$ 

Formulation of the IrC_2S_5 complex (II) as a five-coordinated complex is supported by the facile carbonylation reaction leading to formation of $(\text{PPh}_3)_2\text{IrCl}(\text{CO})\text{C}_2\text{S}_4$ (III). The Ir-C-O stretching frequency observed for this compound at 2081 cm^{-1} is diagnostic of CO bonded to iridium(III). Since this compound has IR bands at $1042, 992$ and 800 cm^{-1} , a similar -S-S-C(S)- linkage is tentatively proposed. The six-coordinated d^6 complex (IV) could not be carbonylated under similar conditions.

When $(\text{Ph}_3\text{P})_2\text{IrClC}_2\text{S}_5$ (II) is refluxed with triphenylphosphine in chloroform/methanol, the color of the reaction mixture changes from black to orange, and orange crystals of *trans*- $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CS})\text{Cl}$ (VI) are precipitated in good yield. Addition of

methanol or ether to the reaction mixture upon change of the color from black to orange, but before crystals are precipitated, leads to precipitation of *trans*-(Ph₃P)₂-Ir(CS)Cl, as well as a product (Ph₃P)₂IrCl(CS)(CS₃) (IV). When (Ph₃P)₂IrClC₂S₅ is refluxed with triphenylphosphine in chloroform in the absence of methanol, the sole product obtained is (Ph₃P)₂IrCl(CS)CS₃ (IV). This product refluxed with triphenylphosphine in chloroform/methanol leads to formation of *trans*-(Ph₃P)₂Ir(CS)Cl. The 1360 cm⁻¹ peak of (PPh₃)₂IrCl(CS)CS₃ which is due to Ir^{III}C-S stretching may be compared to the (r^IC-S frequency at 1332 cm⁻¹ observed for *trans*-(PPh₃)₂Ir(CS)Cl. This shift of ν(CS) to higher energy is analogous to similar shifts of ν(CO) in metal carbonyl complexes. A structure containing the -S-S-C(S)-ligand as a chelate is tentatively proposed for (PPh₃)₂IrCl(CS)CS₃ as shown in Scheme 1. The basis for this proposal resides primarily in the observation of absorption at 1050 and 868 cm⁻¹, which is the general pattern of absorption previously mentioned for the IrC₂S₅ complex (II) and the Ir(CO)C₂S₄ complex (III).

The reactions shown in Scheme 1 can be interpreted in terms of some well known reactivity patterns. The IrC₂S₅ compound (II) may be formed by an oxidative addition reaction of carbon disulfide and *trans*-(PPh₃)₂Ir(N₂)Cl with elimination of nitrogen. Reaction with a second molecule of carbon disulfide leading to formation of a five-coordinated metallocyclic compound is analogous to cyclization reactions of substituted acetylenes with d⁸ complexes⁹. Treatment of (PPh₃)₂IrClC₂S₅ with triphenylphosphine gives triphenylphosphine sulfide^{6,7}, and migration of the CS group to the metal. This latter step is analogous to the conversion of an acetyl ligand to a methyl and a carbonyl ligand. The conversion of (PPh₃)₂IrCl(CS)CS₃ (IV) to *trans*-(PPh₃)₂Ir(CS)Cl is a reductive elimination step. The requirement of methanol in this step is significant, inasmuch as another product (V) is formed in its absence. It is reasonable to propose that methanol facilitates ionization of the chloro ligand¹, so that (PPh₃)₂IrCl(CS)CS₃ may form a species which can interact with triphenylphosphine via an atom transfer step¹⁰, leading to formation of triphenylphosphine sulfide. Sulfur elimination in a disulfide linkage in a metal complex has been previously demonstrated, but sulfur in a trithiocarbonato linkage is not readily eliminated by reaction with triphenylphosphine⁷.

EXPERIMENTAL

Materials and Apparatus

Chlorobis(triphenylphosphine)dinitrogeniridium(I) (I) was prepared as previously described⁵ with the following modifications. Furoyl azide and (PPh₃)₂Ir(CO)Cl were vigorously stirred in chloroform for only 3–5 min and any unreacted chloro-carbonyl complex was removed by filtration. The product was precipitated with methanol and washed with ether. Carbon disulfide was Mallinkrodt spectrophotometric grade solvent. All other chemicals were of reagent grade quality and were used without special treatment. IR spectra were obtained with a Perkin-Elmer 621 spectrophotometer. Spectra were measured in KBr disks or Nujol mulls between sodium chloride, cesium iodide or polyethylene plates. IR peaks recorded herein are only those in addition to peaks due to the triphenylphosphine ligand.

Low temperature study and gas evolution

Carbon disulfide was frozen on a sample of dinitrogeniridium complex (I) in

a vacuum system and the mixture was allowed to thaw. The initial yellow color of (I) changed to an orange-red, followed by a deep green and finally black color. Nitrogen gas [390 mmoles per 384 mmoles of (I)] was measured on a Toepler pump. Removal of carbon disulfide by evaporation left a black powder which had IR bands typical of (II) (below).

Isolation of $(PPh_3)_2IrClC_2S_5$, (II)

The addition of 3 ml of cold carbon disulfide to 300 mg of (I) gave an immediate dark green solution which rapidly turned black. The carbon disulfide was evaporated with a stream of nitrogen. The black solid which was obtained was recrystallized from dichloromethane/methanol. (Found: C, 47.60, 47.47; H, 3.24, 3.23; Cl, 4.10, 4.12; P, 6.54; S, 17.8, 17.0; mol. wt. osmometric in $CHCl_3$, 949. $C_{38}H_{30}ClIrP_2S_5$ calcd.: C, 47.82; H, 3.24; Cl, 3.79; P, 6.61; S, 17.1%; mol. wt., 936.6.) IR: 1050 vs, 900 m, 838 m, 290 w, cm^{-1} .

Carbonylation of $(PPh_3)_2IrClC_2S_5$, (II)

A solution of 50 mg of (II) in 10 ml of dichloromethane was treated with carbon monoxide at 20 psi resulting in a color change from dark green to orange in 5 min. Orange crystals which were obtained by the addition of methanol were recrystallized from benzene. (Found: C, 49.92; H, 3.29; S, 13.97. $C_{39}H_{30}ClIrOP_2S_4$ calcd.: C, 49.30; H, 3.28; S, 13.90%.) IR: 2081 vs, 1042 vs, 992 m, 800 m, 272 w, cm^{-1} .

trans-Chlorobis(triphenylphosphine)(thiocarbonyl)iridium(I), (VI)

(A). Triphenylphosphine (300 mg) and 134 mg of $(PPh_3)_2IrClC_2S_5$ (II) were placed in 17 ml of chloroform and 7 ml methanol and the solution was refluxed for 1½ h. The solution turned to an orange-brown and finally a deeper orange color and the formation of orange crystals was noted. Diethyl ether (20 ml) was added to precipitate more product. Yield: 88 mg (77%). (Found: C, 54.4, 55.6; H, 3.6, 3.7; S, 3.0. $C_{37}H_{30}ClIrP_2S$ calcd.: C, 55.7; H, 3.28; S, 4.0%.) IR: 1332, 292 cm^{-1} . M.p. 185° decomn.

(B). Chlorobis(triphenylphosphine)dinitrogeniridium(I) (I) (680 mg) was treated with 4 ml of carbon disulfide. The excess carbon disulfide was evaporated with a stream of nitrogen. Triphenylphosphine (2 g), 14 ml of chloroform and 10 ml methanol were added and the mixture was refluxed for 3 h. The orange crystals which were precipitated were collected. Yield: 485 mg (71%). The IR spectrum was identical to that of a sample prepared in (A).

(C). Triphenylphosphine (200 mg) and 100 mg of $(Ph_3P)_2IrCl(CS)CS_3$ (IV) were refluxed for 8 h in 15 ml chloroform and 5 ml methanol. Orange crystals which were isolated from the cooled reaction mixture were found to have IR spectrum identical to that of product obtained in (A).

A thermogram of a sample of (II) obtained with a Perkin-Elmer Differential Calorimeter DSC-1 revealed endothermic transitions commencing at 159° when an orange solid was formed and at 247° when the orange solid decomposed. A mixture of 240 mg of (II) in 25 ml toluene was refluxed for 2 h. The mixture was cooled and 76 mg of orange precipitate, tentatively formulated as $(Ph_2P)_2CS_3Ir(CS)Cl$, (V), was collected. The sample was recrystallized from dichloromethane/ethanol. (Found: C, 41.0, 41.0; H, 2.53; Cl, 5.30; S, 17.9. $C_{26}H_{20}ClIrP_2S_4$ calcd.: C, 41.6; H, 2.57; Cl, 4.73; S, 17.1%.) IR: 1360, 1000, 288 cm^{-1} .

$(PPh_3)_2IrCl(CS)CS_3$ (IV)

Triphenylphosphine (800 mg) and 400 mg of (II) were refluxed in 30 ml dichloromethane for 16 h. Slow addition of hexane gave orange crystals (265 mg) which were dried *in vacuo* at room temperature. The product was recrystallized from dichloromethane/ether and dried at 100° for 2 h. The product begins to decompose at 165°. (Found: C, 50.65; H, 3.32; S, 14.22. $C_{38}H_{30}ClIrP_2S_4$ calcd.: C, 50.48; H, 3.34; S, 14.18 %.) IR: 1360, 1050, 868, 286 cm^{-1} . Complex (IV) was also prepared by the following routes.

(A). Triphenylphosphine (200 mg) and 530 mg of (II) were refluxed in 10 ml chloroform for 70 min. The reaction mixture was cooled and 395 mg of (IV) were isolated.

(B). Triphenylphosphine (1 g) and 440 mg of (II) were refluxed in a mixture of 10 ml chloroform and 8 ml methanol for 1 h. At this point some of the solvent was stripped under reduced pressure and 30 ml of diethyl ether was added to give 222 mg of (IV).

(C). A solution of 144 mg of (II) and 200 mg triphenylphosphine in 20 ml benzene was stirred for 3 days. A pale yellow precipitate identified as (IV) was obtained. In each case, product (IV) was identified by its characteristic IR spectrum.

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