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A high-yield synthetic approach to *trans*-[Ir(ER₃)₂(CO)X] (ER₃=PMe₃, PEt₃, PPhMe₂, PPh₂Me, P(OMe)₃, AsMe₃, AsEt₃, AsPh₃, SbPh₃; X=Cl, Br)

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Abstract

The complex $[Ir(CO)_2X_2][NBu_4]$ (X=Cl, Br) forms Vaska-type complexes, *trans*- $[Ir(ER_3)_2(CO)X]$, when treated with two equivalents of aryl- or alkyl-phosphines, arsines, or stibines under a CO atmosphere. The synthesis is general for a wide range of phosphines, arsines, or stibines irrespective of the cone angle. For small cone-angle ligands, the initial addition of ligand to $[Ir(CO)_2X_2][NBu_4]$ is performed at low temperature. The synthesis and characterisation of three new Vaska-type complexes *trans*- $[Ir(P(OMe)_3)_2(CO)Cl]$, *trans*- $[Ir(AsMe_3)_2(CO)Cl]$, and *trans*- $[Ir(AsEt_3)_2(CO)Cl]$ is also reported. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One of the most widely studied classes of iridium(I) complexes is that represented by Vaska's complex *trans*- $[Ir(PPh_3)_2(CO)C1]$ [1–10] and its analogues. The interest in these complexes results from the importance of the oxidative-addition reactions that were originally discovered in this series [1–10].

A convenient synthesis of Vaska-type complexes from $[Ir(cod)Cl]_2$ and a wide range of phosphines was reported by Crabtree et al. [11,12]. However, this approach has two significant drawbacks: (i) the synthesis of the precursor complex $[Ir(cod)Cl]_2$ is achieved in highly variable yield; and (ii) the method requires modification for small cone angle phosphines, such as PMe₃ [11,12].

Here we report a synthesis of iridium(I) complexes of the general formula *trans*-[Ir(ER₃)₂(CO)X] (ER₃=PMe₃, PEt₃, PPhMe₂, PPh₂Me, P(OMe)₃, AsMe₃, AsEt₃, AsPh₃, SbPh₃; X=Cl, Br), from [Ir(CO)₂X₂][NBu₄], which is general for all phosphines, arsines, and stibines. The route is based upon the procedure employed by Fisher and Eisenberg [13] for the synthesis of the *cis*-coordinated phosphine complexes [Ir(dppe)(CO)X] (dppe=1,2-*bis*-(diphenylphosphino)ethane; X=Cl, Br).

2. Experimental section

The manipulation and synthesis of air-sensitive phosphines, arsines, stibines, and metal complexes was performed under an atmosphere of nitrogen or carbon monoxide using standard Schlenk or vacuum line techniques.

Tetrahydrofuran (THF) and diethyl ether were obtained from BDH and were dried over sodium wire before distillation from sodium/benzophenone. Ethanol was distilled from diethoxymagnesium. Trimethylphosphine, dimethylphenylphosphine, diphenylmethylphosphine, triethylphosphine, and trimethylphosphite were obtained from Aldrich Co. and used without further purification. Triphenylarsine, triethylarsine, trimethylarsine, and triphenylstibine were obtained from Strem Chemicals Inc. and were used without further purification. Iridium trichloride trihydrate was obtained from Johnson Matthey Co. All compressed gases were obtained from B.O.C. Gases. Nitrogen (>99.5%) and carbon monoxide (>99.0%) were used as received without further purification.

Air-sensitive NMR samples were prepared in a nitrogen

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filled dry-box, with the solvent vacuum transferred into an NMR tube fitted with a concentric teflon valve. ¹H, ³¹P, and ¹³C NMR spectra were recorded on a Bruker DRX400 spectrometer at 400.13, 161.98, and 100.62 MHz, respectively.

Mass spectra were recorded using chemical ionisation (CI) on a Finnigan MAT TSQ-46 equipped with a desorption probe with a source temperature of 140° C and an electron energy of 100 eV. The ionisation gas was methane. In all cases, M represents the molecular ion and L represents the ligand ER₃.

Melting points of air-sensitive samples were determined in a sealed capillary using a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 1600 Series FTIR spectrometer, the samples being run as Nujol mulls with NaCl plates.

The syntheses of $[Ir(CO)_2Cl_2][NBu_4]$ and $[Ir(CO)_2Br_2][NBu_4]$ were based upon the method described by Fisher and Eisenberg [13].

2.1. General preparation of trans- $[Ir(ER_3)_2(CO)X]$ ($ER_3 = PPh_2Me$, $PPhMe_2$, PMe_3 , PEt_3 , $P(OMe)_3$, $AsPh_3$, $AsEt_3$, $AsMe_3$, $SbPh_3$; X = Cl, Br)

A solution of the appropriate ligand $\text{ER}_3(0.530 \text{ mmol})$ in THF (5 ml) was added to a solution of $[\text{Ir}(\text{CO})_2\text{X}_2][\text{NBu}_4]$ (0.265 mmol) in THF (20 ml) under a CO atmosphere with vigorous stirring. In the case of the small cone angle ligands, the $[\text{Ir}(\text{CO})_2\text{X}_2][\text{NBu}_4]$ solution was cooled to -78° C, a chilled solution of the ligand was added dropwise and the reaction mixture was stirred for 1 h at this temperature. After addition was complete the reaction mixture was stirred at room temperature for 1 h.

In the case of the large cone angle ligands (PPhMe₂, PPh₂Me, AsPh₃, SbPh₃) the solvent was removed under vacuum, and ethanol (15 ml) was added. The solvent was reduced under vacuum until precipitation of the metal complex was complete.

In the case of the small cone angle ligands (PMe_3 , PEt_3 , $P(OMe)_3$, $AsMe_3$, $AsEt_3$) the solvent was reduced under vacuum and the residue was extracted with ether. The solvent was removed under vacuum, and the metal complex was purified by sublimation.

2.2. Transbromocarbonylbis(trimethylphosphine)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (86 mg, 72%). IR (Nujol), ν (CO): 1951 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 1.31 (multiplet, splitting=4.0 Hz, CH₃). ³¹P{¹H} NMR (benzene- d_6): δ -18.6 (s) ppm. Infrared and the ³¹P{¹H} NMR were in good agreement with the literature [8].

2.3. Trans-

carbonylchlorobis(trimethylphosphine)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (81 mg, 75%). IR (Nujol), ν (CO): 1943 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 1.26 (m, splitting=3.6 Hz, CH₃) ppm. ³¹P{¹H} NMR (benzene- d_6): δ -19.2 (s) ppm. Infrared, ³¹P{¹H} and ¹H NMR were in good agreement with the literature [14,15].

2.4. Trans-bromocarbonylbis(triethylphosphine)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (85 mg, 60%). IR (Nujol), ν (CO): 1941 (vs) cm⁻¹. ¹H NMR (benzene- d_6): 61.88 (m, 12H, CH₂), 0.98 (m, splitting=8.0 Hz, 18H, CH₃) ppm. ³¹P{¹H} NMR (benzene- d_6): δ 17.3 (s) ppm. Infrared data was in good agreement with that reported in the literature [15].

2.5. Trans-carbonylchlorobis(triethylphosphine)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (102 mg, 78%). IR (Nujol), ν (CO): 1944 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 1.81 (multiplet, 12H, CH₂), 1.00 (m, splitting=8.0 Hz, 18H, CH₃) ppm. ³¹P{¹H} NMR (benzene- d_6): δ 19.7 (s) ppm. Infrared data was in good agreement with that reported in the literature [15].

2.6. Trans-

bromocarbonylbis(dimethylphenylphosphine)iridium(I)

The title complex was obtained as a bright yellow microcrystalline solid (99 mg, 65%) by precipitation from ethanol. IR (Nujol), ν (CO): 1950 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 7.48 (m, 4H, o-H), 7.36 (m, 6H, m-, p-H), 1.64 (m, 12H, splitting=3.9 Hz, CH₃) ppm. ³¹P{¹H} NMR (benzene- d_6): δ -8.4 (s) ppm. Infrared data was in good agreement with that reported in the literature [15].

2.7. Trans-

carbonylchlorobis(dimethylphenylphosphine)iridium(I)

The title complex was obtained as a bright yellow microcrystalline solid (104 mg, 74%) by precipitation from ethanol. IR (Nujol), ν (CO): 1954 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 7.67 (m, 4H, *o*-H), 7.03 (m, 6H, *m*-, *p*-H), 1.65 (m, 12H, splitting=3.4 Hz, CH₃) ppm. ³¹P{¹H} NMR (benzene- d_6): δ -5.6 (s) ppm. Infrared data was in good agreement with that reported in the literature [15].

2.8. Transcarbonylchlorobis(diphenylmethylphosphine)iridium(1)

The title complex was obtained as a bright yellow microcrystalline solid (122 mg, 70%) by precipitation from ethanol. IR (Nujol), ν (CO): 1950 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 7.97 (m, 8H, *o*-H), 7.28 (m, 12H, *m*-, *p*-H), 2.36 (s, 6H, CH₃) ppm. ³¹P{¹H} NMR (benzene- d_6): δ 5.20 (s) ppm. Infrared data was in good agreement with that reported in the literature [16].

2.9. Trans-

carbonylchlorobis(trimethylphosphite)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (101 mg, 65%), m.p. 186–187°C (dec). IR (Nujol), ν (CO): 1988 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 3.55 (m, splitting=5.9 Hz) ppm. ³¹P{¹H} NMR (benzene- d_6): δ 124.4 (s) ppm. ¹³C{³¹P, ¹H} NMR (benzene- d_6): δ 169.8, 52.5 ppm. m/z (CI, CH₄): 505 (MH⁺, 57%), 477 ([IrL₂(CO)]H⁺, 100), 125 (LH⁺, 82). Anal. Calcd. C₇H₁₈ClIrO₇P₂: C, 16.69; H, 3.61. Found: C, 16.9; H, 3.7.

2.10. Trans-carbonylchlorobis(trimethylarsine)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (89 mg, 68%), m.p. 186–187°C (dec). IR (Nujol), ν (CO): 1928 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 1.18 (s) ppm. ¹³C{¹H} NMR (benzene- d_6): δ 171.5, 10.5 ppm. m/z (CI, CH₄): 497 (MH⁺, 44%), 461 ([IrL₂(CO)]H⁺, 8), 121 (LH⁺, 100). Anal. Calcd. C₇H_{*8}As₂ClIrO: C, 16.96; H, 3.66. Found: C, 17.2; H, 3.8.

2.11. Trans-carbonylchlorobis(triethylarsine)iridium(I)

The metal complex was purified by sublimation at 60°C (0.06 Torr). The title complex was obtained as a bright yellow microcrystalline solid (128 mg, 83%), m.p. 74–75°C. IR (Nujol), ν (CO): 1939 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 1.78 (q, ³J=7.8 Hz, 12H, CH₂), 1.08 (t, ³J=7.8 Hz, 18H, CH₃) ppm. ¹³C{¹H} NMR (benzene- d_6): δ 170.9, 15.4, 9.6 ppm. m/z (CI, CH₄): 581 (MH⁺, 11%), 545 ([IrL₂(CO)]H⁺, 1), 163 (LH⁺, 100). Anal. Calcd. C₁₃H₃₀As₂CIIrO: C, 26.93; H, 5.21. Found: C, 27.2; H, 5.1.

2.12. Trans-carbonylchlorobis(triphenylarsine)iridium(I)

The title complex was obtained as a yellow microcrystalline solid (159 mg, 69%) by precipitation from ethanol. IR (Nujol), ν (CO): 1940 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 7.87 (s, 12H, *o*-H), 7.01 (bs, 18H, *m*-,

p-H) ppm. Infrared data was in good agreement with that reported in the literature [15].

2.13. Trans-carbonylchlorobis(triphenylstibine)iridium(I)

The title complex was obtained as a yellow microcrystalline solid (168 mg, 66%) by precipitation from ethanol. IR (Nujol), ν (CO): 1953 (vs) cm⁻¹. ¹H NMR (benzene- d_6): δ 7.77 (m, 12H, *o*-H), 7.01 (m, 18H, *m*-, *p*-H) ppm. Infrared data was in good agreement with that reported in the literature [15].

3. Results and discussion

The method for the synthesis for complexes of the formula *trans*-[Ir(ER₃)₂(CO)X] is shown in Eq. (1). This method is general for a large range of Group 15 ligands. The ligands examined here were PPh₂Me, PPhMe₂, PMe₃, PEt₃, P(OMe)₃, AsPh₃, AsEt₃, AsMe₃, and SbPh₃.

$$[Ir(CO)_2X_2][NBu_4] + 2ER_3 \rightarrow [Ir(ER_3)_2(CO)X] + [NBu_4]X + CO \quad (1)$$

The precursor complexes, $[Ir(CO)_2X_2][NBu_4]$, were synthesised in high yield by refluxing $IrCl_3 \cdot 3H_2O$ in formic acid and hydrochloric acid (for X=Cl) or refluxing in a mixture of formic acid, hydrobromic acid, and potassium bromide (for X=Br). $[Ir(CO)_2X_2][NBu_4]$ was precipitated by the addition of tetrabutylammonium chloride and recrystallisation from isopropanol afforded the complexes as moderately air-stable, yellow crystalline solids.

The reaction to produce Vaska-type complexes involves the slow addition of the alkyl- or aryl-phosphine, arsine, or stibine to a THF solution of $[Ir(CO)_2X_2][NBu_4]$ under a CO atmosphere. In the case of the small cone angle ligands (i.e. PMe₃, PEt₃, P(OMe)₃, AsMe₃ and AsEt₃), the reaction mixture was cooled to -78° C then slowly warmed to room temperature upon addition of the ligands. The reaction mixture was stirred for 1 h at room temperature, before the solvent was reduced in vacuo. During the removal of the solvent the original pale yellow solutions darkened in colour to bright yellow, which is the result of the loss of a carbonyl group from the species [Ir(ER₃)₂(CO)₂X] [2].

The isolation of the products was achieved by the addition of dry ethanol followed by reduction of the solvent in vacuo until precipitation of the complexes was complete. In the of complexes case the $[Ir(PMe_3)_2(CO)Cl], [Ir(PEt_3)_2(CO)Cl], [Ir(PEt_3)_2(CO)-$ Br], $[Ir(P(OMe)_3)_2(CO)Cl]$, $[Ir(AsMe_3)_2(CO)Cl]$ and [Ir(AsEt₃)₂(CO)Cl], the solvent was removed under vacuum, the residue was extracted with ether, the ether was removed under vacuum, and the complex purified by sublimation at 60°C (0.06 Torr). Physical and spectroscopic data for known complexes were in good agreement with literature data.

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