Notes

High-Yield General Synthesis of *trans*-Ir(PR$_3$)$_2$(CO)Cl (PR$_3$ = PPh$_3$, PPh$_2$Me, PPhMe$_2$, PEt$_3$, PMe$_3$)

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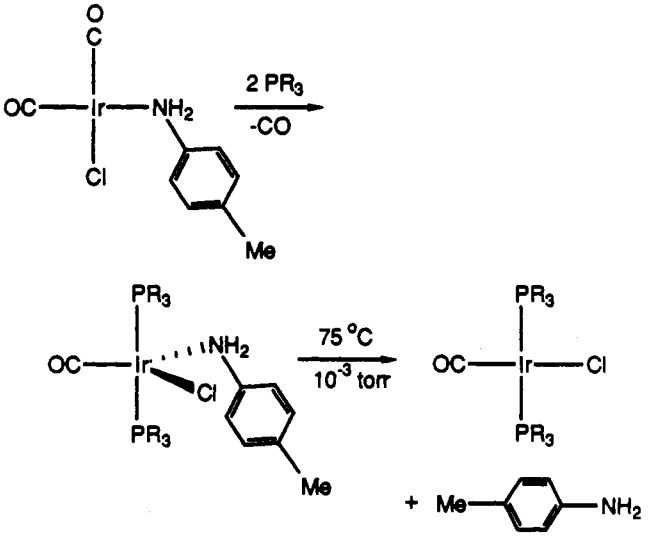
The square-planar Ir(I) complex *trans*-Ir(PPh$_3$)$_2$(CO)Cl, commonly referred to as "Vaska's complex",[1] has played an important role in inorganic and organometallic chemistry since its discovery. The most widely used synthetic procedure for its preparation involves refluxing IrCl$_3$ and PPh$_3$ in *N*,*N*-dimethylformamide.[2] The preparation of "Vaska-analogs", i.e. *trans*-Ir(PR$_3$)$_2$(CO)Cl complexes where PR$_3$ is a phosphine other than PPh$_3$, however, cannot be accomplished by this method. Although a number of methods have been reported in the literature, most suffer from drawbacks: low yield; too many steps to get to the final product; the lack of a single starting material for use with different phosphines; and, perhaps more seriously, erratic and unreliable results. For example, the PPh$_2$Me analog has been synthesized from Ir(PPh$_3$)$_2$(CO)Cl by ligand exchange;[3] however, the same procedure for the synthesis of the PPhMe$_2$ analog is very sensitive to the purity of the starting material, sometimes giving low or no yield at all.[4] The addition of PMe$_3$ to Vaska's complex produces [Ir(PMe$_3$)$_4$(CO)]Cl, which converts to *trans*-Ir(PMe$_3$)$_2$(CO)Cl when sublimed at 130 °C.[5] This method is unsatisfactory due to the need for repeated sublimation to purify the product, thus giving a low overall yield. Burk and Crabtree[6] have developed a synthesis of the PMe$_3$ complex from [IrCl(1,5-cyclooctadiene)]$_2$ in ~50% yield. If one takes into account that [IrCl(1,5-cyclooctadiene)]$_2$ is obtained from IrCl$_3$ in ~70% yield,[7] the overall yield in the above case becomes even lower. The methods known for the synthesis of *trans*-Ir(PEt$_3$)$_2$(CO)Cl involve several steps and give poor product yield.[8]

In our studies of square-planar Ir(I)-amido complexes,[9] we developed the need for a simple, reliable, and high-yield method for the preparation of "Vaska-analogs" containing PPh$_2$Me, PPhMe$_2$, PEt$_3$, and PMe$_3$. We discovered that these analogs, including the original complex, can be directly synthesized in high yields from *cis*-Ir(CO)$_2$Cl[NH$_2$(*p*-C$_6$H$_4$Me)],[10] for which a high-yield, "one-pot" synthesis employing IrCl$_3$·*x*H$_2$O is available.[11]

Results and Discussion

As shown in the following equation, the general method is applicable to all the phosphines that we have tested (PPh$_3$, PPh$_2$Me, PPhMe$_2$, PEt$_3$ and PMe$_3$). [*Warning note: Most alkylphosphines are very toxic volatile materials. All manipulations must be carried out in a well-ventilated hood using extreme care.*]



PR$_3$ = PPh$_3$, PPh$_2$Me, PPhMe$_2$, PEt$_3$ and PMe$_3$

In each case, the phosphine is added slowly as a solution in toluene to *cis*-Ir(CO)$_2$Cl[NH$_2$(*p*-C$_6$H$_4$Me)], also dissolved in toluene. Since Ir(PPh$_3$)$_2$(CO)Cl is rather insoluble in toluene, it readily precipitates from the reaction mixture and can be removed by filtration. The crude products after phosphine addition show the presence of NH$_2$(*p*-C$_6$H$_4$Me) as a coordinated ligand, which can be easily driven off by heating the solids at 75 °C under reduced pressure (10^{-3} Torr). All the reactions proceed in high yields and are insensitive to the presence of impurities in the starting material. We view the method of Collman *et al.*[2] to be a preferred one for the synthesis of *trans*-Ir(PPh$_3$)$_2$(CO)Cl; for synthesizing its analogs, our method is superior to those previously reported.

Experimental Section

All preparations were carried out under N$_2$. Solvents were purified before use and stored under N$_2$ over 4-Å molecular sieves. Hexanes were distilled from CaH$_2$, and toluene and THF were distilled from Na/K alloy and benzophenone. All the phosphines used in this study were purchased from Strem Chemical Co. and were used without any further purification.

Infrared spectra were obtained on a Nicolet 6000 Series FTIR instrument. ^{1}H and ^{31}P NMR spectra were recorded using a 500-MHz Bruker instrument. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

cis-Ir(CO)$_2$Cl[NH$_2$(*p*-C$_6$H$_4$Me)] was prepared from IrCl$_3$·*x*H$_2$O in 90% yield according to a published method.[11]

***trans*-Ir(PR$_3$)$_2$(CO)Cl.** In all cases, 2-equiv samples of the phosphines, dissolved in 5 mL of toluene, were added via a liquid addition funnel to a solution of *cis*-Ir(CO)$_2$Cl[NH$_2$(*p*-C$_6$H$_4$Me)] (0.40 g, 1.0 mmol), also in toluene (45 mL). Separate workup procedures, as described below, were necessary for the different analogs.

(a) *trans*-Ir(PPh$_3$)$_2$(CO)Cl. The initial dark purple color of the solution containing the iridium complex began to turn yellow as the phosphine solution was added, eventually forming a yellow precipitate. After the addition was complete, the yellow precipitate was removed by filtration, washed with 2 × 5 mL of hexanes, and dried under vacuum. The product was spectroscopically identical to an authentic material. Yield: 85%. ^{1}H

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NMR ($CDCl_3$): δ 7.70, 7.45 (m, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 25.1. IR (CH_2Cl_2, cm^{-1}): 1960.

(b) *trans*-Ir(PPh_2Me)$_2$(CO)Cl. The reaction mixture was allowed to stir at room temperature for 0.5 h, after which the clear yellow solution was filtered and the filtrate was reduced in volume to ~5 mL. Addition of hexane to the toluene solution produced a yellow microcrystalline solid, which was removed by filtration, washed with hexanes (2 × 5 mL), and dried under vacuum. Yield: 0.52 g, 78%. Anal. Calcd: C, 49.42; H, 3.99. Found, C, 48.95; H, 4.32. ^1H NMR (C_6D_6): δ 7.70, 6.95 (m, C_6H_5), 2.11 (t, CH_3). ^{31}P NMR (C_6D_6): δ 10.1. IR (THF, cm^{-1}): 1959.

(c) *trans*-Ir($PPhMe_2$)$_2$(CO)Cl. The reaction mixture was allowed to stir at room temperature for 1 h, after which the clear yellow solution was filtered to remove a small amount of gummy, black residue. After removing the volatiles under reduced pressure, the yellow solid was subjected to high vacuum (10^{-3} Torr) at 75 °C for 48 h to remove the coordinated *p*-toluidine. At the end of this period, recrystallization of the crude product from hexane yielded an analytically pure sample. Yield: 0.38 g, 70%. Anal. Calcd: C, 38.34; H, 4.92. Found: C, 37.98; H, 4.32. ^1H NMR (C_6D_6): δ 7.68, 7.00 (m, C_6H_5), 1.66 (s, CH_3). ^{31}P NMR (C_6D_6): δ −7.5. IR (THF, cm^{-1}): 1950.

(d) *trans*-Ir(PEt_3)$_2$(CO)Cl. After filtration of the reaction mixture and removal of the volatiles, the waxy, yellow solid was transferred to a sublimator equipped with a water-cooled finger. Sublimation at 65 °C and 10^{-3} Torr pressure gave analytically pure product in 80% yield (0.40 g). Anal. Calcd: C, 31.70; H, 6.14. Found: C, 31.03; H, 6.52. ^1H NMR (C_6D_6): δ 1.81 (nine-line multiplet, CH_2), 0.99 (five-line multiplet, CH_3). ^{31}P NMR (C_6D_6): δ 20.4. IR (THF, cm^{-1}): 1940.

(e) *trans*-Ir(PMe_3)$_2$(CO)Cl. During the addition of PMe_3 to *cis*-Ir(CO)$_2$Cl[NH_2(*p*-C_6H_4Me)], a small amount of white precipitate formed, identified as [Ir(PMe_3)$_4$(CO)]Cl, which was removed from the yellow solution by filtration. The formation of the white solid can be minimized by adding the PMe_3 solution at a slow rate (1 mL/5 min). An analytically pure sample of *trans*-Ir(PMe_3)$_2$(CO)Cl was obtained by sublimation of the crude product at 70 °C and 10^{-3} Torr pressure. Yield: 0.29 g, 70%. Anal. Calcd: C, 20.59; H, 4.45. Found: C, 20.02; H, 4.77. ^1H NMR (C_6D_6): δ 1.26 (t, CH_3). ^{31}P NMR (C_6D_6): δ −15.1. IR (THF, cm^{-1}): 1946.

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