eq 10 and thus shift the mechanism back to an overall third-order process for k_{-1}.

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Registry No. $[Hg_3CO(ClO_4)]_n$, 100485-14-1; HOI, 14332-21-9; I_2, 7553-56-2.

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A Convenient General Synthesis of *trans*-$[IrCl(CO)(PR_3)_2]$

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$[IrCl(cod)]_2$ is treated at room temperature with 4 mol equiv of PR_3 (R = Ph, C_6H_{11}, *o*-MeC_6H_4) and then CO to give the title complexes. In the case of PMe_3, $[IrCl(cod)]_2$ was converted to the new complex $[IrCl(cod)(PMe_3)_2]$, which on treatment with CO gave $[IrCl(CO)_2(PMe_3)_2]$. This readily loses CO in vacuo at 25 °C and in the solid state to give the title complex, which is a reversible CO carrier.

Vaska's complex[1] and its analogues have a special place in inorganic chemistry because of the importance of the oxidative-addition reactions that were discovered in this series. Surprisingly, the syntheses of these complexes[2–7] have almost always been carried out by reduction of Ir(III) or Ir(IV) precursors, often with a refluxing high-boiling solvent. In other cases, substitution reactions involving $[IrCl(CO)(PPh_3)_2]$ or $[Ir(CO)_3Cl]$ were used.[2,5,7a] For some recent investigations in alkane activation chemistry, we required a range of these complexes with different phosphines. We therefore investigated routes starting from the readily available Ir(I) species $[IrCl(cod)]_2$.

Two successful routes are described below, one for PMe_3 and the other for larger cone angle phosphines. A report by Labinger and Osborn[7b] describes a synthesis for the Vaska analogue containing PMe_2Ph, a case in which conventional syntheses fail. This synthesis, although unsuitable as a general method because of the alcohol solvents used, is similar to the route described here. The PMe_3 complex has also been prepared by the same authors[7a] from $[Ir(CO)(PMe_3)_4]Cl$ by repeated sublimations to drive off two of the PMe_3 ligands. Our methods involve only room-temperature, ambient-pressure reactions and are high-yield, rapid, and convenient. In each case the starting material is the commercially available $[IrCl(cod)]_2$.[8]

Results and Discussion

Equation 1 shows the general method for the synthesis of $[IrCl(CO)L_2]$ derivatives. We have not yet found a case where this method does not work, apart from that of PMe_3, for which we also report a second, closely related method. We find that the use of hexanes is essential to both methods because it prevents, or at least minimizes, the expulsion of the chloride ion from the coordination sphere of the metal to give ionic byproducts. This occurs particularly easily with the smaller, more basic phosphines. In contrast to previous methods,[2–7] all the steps involve only room-temperature reactions. In a nonionizing solvent, the larger tertiary phosphines are known[9,10] only to break the chloro bridge of $[IrCl(cod)]_2$ (**1**) to give the monomeric species **2**. The value of *n* in **2** can be 1 or 2 according to the size of the phosphine and whether the material has been recrystallized or not. Only when CO is added, is cod displaced. Complexes of type **3** are formed in quantitative yield over 1 h and can be crystallized to give the isolated materials in 85–95% yield, depending on the solubility of the product.

$$\underset{\mathbf{1}}{[\mathrm{Ir(cod)Cl}]_2} \xrightarrow{\mathrm{PR_3}} \underset{\mathbf{2}}{[\mathrm{IrCl(cod)(PR_3)}_n]} \xrightarrow{\mathrm{CO}} \underset{\mathbf{3}}{[\mathrm{IrCl(CO)(PR_3)_2}]} \tag{1}$$

This method is not applicable to the case of PMe_3, and so we were forced to consider alternatives. The best method requires isolating the intermediate of type **2** and is shown in eq 2 and 3.

$$\underset{\mathbf{1}}{[\mathrm{IrCl(cod)}]_2} \xrightarrow{\mathrm{PMe_3}} \underset{\mathbf{2}}{[\mathrm{IrCl(PMe_3)_2(cod)}]} \tag{2}$$

$$\underset{\mathbf{2}}{[\mathrm{IrCl(PMe_3)_2(cod)}]} \xrightarrow{\mathrm{CO}} \underset{\mathbf{4}}{[\mathrm{IrCl(PMe_3)_2(CO)_2}]} \tag{3}$$

$$\underset{\mathbf{4}}{[\mathrm{IrCl(PMe_3)_2(CO)_2}]} \xrightarrow[\text{in vacuo}]{-\mathrm{CO}} \underset{\mathbf{3}}{[\mathrm{IrCl(CO)(PMe_3)_2}]} \tag{4}$$

Again, the first two steps are carried out in hexanes. Non-alkane solvents appeared to react with **2** to give uncharacterized materials and so were unsuitable. In the first step, some $[Ir(cod)(PMe_3)_3]Cl$ was also formed as a white precipitate but could be removed by filtration. Either the new complex **2** can be isolated at this stage, or, more conveniently, the solution can be treated with CO directly without isolation. The second step forms the dicarbonyl complex **4**. This is particularly convenient to isolate because, unlike **3**, it is relatively insoluble in hexanes. This complex (**4**) appears to be a classical 5-coordinate species and is fluxional on the NMR time scale down to −70 °C. It shows two bands in the IR spectrum at 1909 and 1970 cm^{-1} corresponding to the asym and sym stretching vibrations, with an intensity ratio appropriate to a ca. 120° interligand angle (calculated angle from IR data 123°). The

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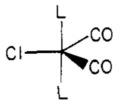
^1H NMR shows a virtually coupled triplet for the PMe_3 groups, suggesting that these groups are trans. We therefore propose the structure shown for **4**. Vaska[1] proposed a similar structure for the much less stable PPh_3 analogue. In the third and final stage the isolated complex **4** is exposed to a high vacuum (≤1 torr) in the solid state at ambient temperature. This leads to loss of the second CO ligand and formation of $IrCl(CO)(PMe_3)_2$ in analytically pure form. It is convenient to run this last step in the solid state because the very soluble product **3** does not then need to be isolated from solution at the end of the reaction.



4

The PMe_3 analogue of Vaska's complex is a reversible CO carrier in solution, and so the manipulations in stage 2 (eq 3) were carried out by maintaining a CO atmosphere over the reaction mixture and isolated products. Alternatively, the second and third stages may be combined by pumping on the solution containing **4** to give **3** directly.

$[IrCl(CO)(PMe_3)_2]$ is best recrystallized by conversion to the insoluble dicarbonyl and then removing the extra CO by exposing the isolated dicarbonyl to a dynamic vacuum. This is a superior method to the repeated sublimations previously described.

Experimental Section

Reagents and solvents were obtained from Aldrich Co., and all manipulations were carried out in the absence of O_2. IR spectra were obtained on a Nicolet 7000 instrument, and NMR spectra, on an FY-90Q.

General Preparation of *trans*-$[IrCl(CO)(PR_3)_2]$ (R = C_6H_{11}, C_6H_5, and *o*-MeC_6H_4). A solution of $[IrCl(cod)]_2$ (100 mg, 0.15 mmol) and PR_3 (0.6 mmol) in hexanes/CH_2Cl_2 (50:50 v/v, 20 mL) is stirred under N_2 for 10 min. The N_2 atmosphere is then removed and CO (1 atm) introduced. Stirring is continued for 1 h, during which time a light yellow precipitate forms. After this time, the volume of the solution is halved in vacuo and the resulting suspension filtered to give the product, which is washed with hexanes (3 × 5 mL) and dried in vacuo. In each case the products are spectroscopically identical with the authentic materials.[2-7] L = PCy_3:[2,5] yield 85%; ^1H NMR (C_6D_6) [reported as position in δ (multiplicity, assignment)] 1.7–2.66 (complex, C_6H_{11}); IR (CH_2Cl_2) $\nu(CO)$ = 1922 cm^{-1}. L = PPh_3:[1-4] yield 95%; ^1H NMR ($CDCl_3$) 7.34–7.48 7.70 (complex, C_6H_5); IR ($CHCl_3$) $\nu(CO)$ = 1957 cm^{-1}. L = *o*-MeC_6H_4:[2,10] yield 90%; ^1H NMR (CD_2Cl_2) 7.27 (complex), 7.83 (broad, Ar), 2.26 (CH_3).

Chloro(η^4-1,5-cyclooctadiene)bis(trimethylphosphine)iridium(I). To $[IrCl(cod)]_2$ (700 mg, 1.05 mmol) in hexanes (80 mL) was added PMe_3 (424 mL, 4.2 mmol) dissolved in hexanes (40 mL) slowly over $1^1/_2$ h. The mixture was filtered to remove $[Ir(cod)(PMe_3)_3Cl]$, and the filtrate was concentrated to ca. 10 mL to precipitate a light yellow solid. This is filtered and washed with cold hexanes (−20 °C, 2 × 3 mL): yield 800 mg (80%); ^1H NMR (C_6D_6) 1.18 (d (6.6), PMe_3), 1.9–2.2 (complex, CH_2), 3.19 (complex, CH). Anal. Calcd for $C_{14}H_{30}ClP_2Ir$: C, 34.45; H, 6.20. Found: C, 34.27; H, 6.00.

Chlorobis(carbonyl)bis(trimethylphosphine)iridium(I). $[IrCl(PMe_3)_2(cod)]$ (966 mg, 1.98 mmol) in hexanes (30 mL) or the solution formed in the previous synthesis is treated with CO (1 atm). After 30 min of stirring, the resulting white precipitate is filtered, washed with cold hexanes (3 × 2 mL), and dried in a stream of CO: yield 65%; ^1H NMR (CD_2Cl_2) 1.83 (t (3.8), PMe_3); IR (CD_2Cl_2) $\nu(CO)$ = 1909, 1970 cm^{-1}. The product was not recrystallized because it tends to lose CO.

Chloro(carbonyl)bis(trimethylphosphine)iridium(I). Method A. $[IrCl(CO)_2(PMe_3)_2]$ (100 mg) was subjected to a dynamic vacuum for 1 h at 1 torr or less. This produces the analytically pure product in quantitative yield. The complex is best recrystallized by dissolving the material in a minimal quantity of hexane, preferably by washing the complex through a frit. The solution is treated with CO (1 atm) and $[IrCl(CO)_2(PMe_3)_2]$ precipitates. The product is isolated as described above and converted to **3** in vacuo as also described above. The complex is spectroscopically identical with the authentic material:[7a] ^1H NMR (CD_2Cl_2) 1.62 (t (3.6), PMe_3); IR (CD_2Cl_2) $\nu(CO)$ = 1938 cm^{-1}. Anal. Calcd for $C_7H_{18}OClP_2Ir$: C, 20.61; H, 4.45. Found: C, 20.88; H, 4.2.

Method B. $[IrCl(cod)(PMe_3)_2]$ (700 mg, 1.43 mmol) in hexanes (30 mL) is treated with CO (1 atm). After 30 min of stirring, the solvents are removed in vacuo and the light yellow residue is washed with cold hexanes (2 × 3 mL) and recrystallized as described above: yield 60%. This method gives poorer results than method A.

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Registry No. **1**, 12112-67-3; **2**, 100513-60-8; **3**, 21209-86-9; **4**, 100485-48-1; *trans*-$[IrCl(CO)(P(C_6H_{11})_3)_2]$, 34054-07-4; *trans*-$[IrCl(CO)(P(C_6H_5)_3)_2]$, 15318-31-7; *trans*-$[IrCl(CO)(P(o\text{-}MeC_6H_4)_3)_2]$, 34054-05-2.