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Dissociation of Dichlorotris(triphenylphosphine)ruthenium(II) in Benzene and in *N,N*-Dimethylacetamide Solution

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Spectrophotometric methods have been used to estimate thermodynamic parameters for the dissociation equilibria involving loss of a phosphine molecule from dichlorotris(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$, in benzene and in DMA (K_1 equilibria) and loss of a chloride ion from the bis(phosphine) complex $RuCl_2(PPh_3)_2$ in DMA (K_2). K_1 values at 25° are 2.7×10^{-3} *M* (benzene) and 4.6×10^{-2} *M* (DMA); K_2 at 25° is 7.3×10^{-5} *M*. $\Delta H°$ and $\Delta S°$ values for these equilibria are also reported.

Introduction

Extensive dissociation of the dichlorotris(triphenylphosphine)ruthenium(II) complex, $RuCl_2(PPh_3)_3$, with loss of a coordinated triphenylphosphine molecule has been considered to occur in solution, based on molecular weight measure-

$$\underset{\text{I}}{RuCl_2(PPh_3)_3} \overset{K_1}{\rightleftharpoons} \underset{\text{II}}{RuCl_2(PPh_3)_2} + PPh_3 \qquad (1)$$

ments in benzene.[1] However, analogous molecular weight data obtained[2] on solutions of the related rhodium complex $RhCl(PPh_3)_3$ were later refuted; similar measurements performed under strictly anaerobic conditions[3] indicated that the degree of dissociation of the rhodium complex in solution was much smaller than previously concluded. Nmr data obtained by other workers[4,5] support this conclusion. In the course of some work on the hydrogenolysis of $RuCl_2(PPh_3)_3$ in *N,N*-dimethylacetamide (DMA) solution,[6,7] a spectrophotometric study was undertaken to determine unambiguously the extent of phosphine dissociation by this complex in solution. Such information is important for a more detailed understanding of the homogeneous catalytic properties of such complexes.[8,9]

Experimental Section

Materials. The complex $RuCl_2(PPh_3)_3$ was prepared according to the method of Stephenson and Wilkinson.[1] Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) was obtained on loan from Johnson Matthey Ltd. Reagent grade triphenylphosphine (Strem Chemicals) was recrystallized from benzene–ethanol before use. Certified *N,N*-dimethylacetamide (Fisher Scientific Co.) was purified by distillation from calcium hydride under nitrogen and was stored on Linde 4A molecular sieve under a nitrogen atmosphere. Spectranalyzed grade benzene (Fisher) was used without further purification.

Methods. Because of the extreme air sensitivity of the $RuCl_2(PPh_3)_3$ complex in solution, solvents were carefully degassed by repeated freezing and pumping before the addition of the ruthenium compound. DMA solutions of LiCl were prepared by dilution of a freshly prepared standard solution. Visible spectra were recorded using a Perkin-Elmer 202 spectrophotometer equipped with a constant-temperature compartment, the solutions being contained under vacuum in 10-mm anaerobic cells.

Conductivity measurements on DMA solutions of $RuCl_2(PPh_3)_3$ were recorded at 25° using a Thomas Serfass conductivity bridge and dip-type conductivity cell. A stream of inert gas (purified nitrogen or argon) was used to remove the oxygen present in the solvent contained in an enclosed solution compartment. The ruthenium compound was then added from a suspended glass bucket. The gas stream was continued until measurements were completed.

Results

Preliminary conductivity studies on $RuCl_2(PPh_3)_3$ in DMA solution indicated that partial ionization of the complex was occurring in this solvent (see below). The complex was therefore examined first in benzene solution, where the nonpolar nature of the solvent would preclude the formation of charged species.

Addition of excess triphenylphosphine to an orange-brown solution of $RuCl_2(PPh_3)_3$ resulted in a distinct change in the visible spectrum (Figure 1), indicating that the equilibrium shown in eq 1 was being shifted to the left. Spectra recorded at intermediate concentrations of added phosphine showed isosbestic points at 440 and ~560 nm. A limiting spectrum for the tris(phosphine) complex was observed at the higher phosphine concentrations; absorbance measurements were recorded at 480 and 750 nm. The absorbance of a solution containing species I and II in a 10-mm optical cell is given by $\epsilon_I[I] + \epsilon_{II}[II]$, where ϵ_I and ϵ_{II} are the molar extinction coefficients at the given wavelength. Since the total ruthenium equals [I] + [II], and the total triphenylphosphine concentration $[PPh_3]_t = [II] + [PPh_3]_a$, where the subscript a refers to the phosphine added, the estimation of K_1 ($=[II][PPh_3]_t[I]^{-1}$) is a simple matter once the ϵ_I and ϵ_{II} values are known. ϵ_I is readily determined from the limiting spectrum at higher phosphine concentration; an approximate ϵ_{II} value was estimated from spectrum A for the solution with no added phosphine, by assuming that I is completely dissociated at the ruthenium concentration used. Using ϵ_I and the approximate ϵ_{II} values, K_1 was calculated for each of the intermediate phosphine concentrations used. Using the median of these K_1 values, the concentrations of I and II were then calculated for the solution having spectrum A; this allows a more accurate estimation of ϵ_{II} and a second computation of K_1 values. This successive approximation procedure led to self-consistent extinction coefficients (M^{-1} cm^{-1}) for the two wavelengths corresponding to the absorption maxima of $RuCl_2(PPh_3)_3$: ϵ_I 1350 (480 nm), 515 (750 nm); ϵ_{II} 370 (480 nm), 0 (750 nm).

From the slope of a plot of $[II][I]^{-1}$ *vs.* $[PPh_3]_t^{-1}$ for data at 480 and 750 nm (Figure 2), the value of K_1 was estimated to be $(2.7 \pm 0.5) \times 10^{-3}$ *M* at 25°. A 10^{-3} *M* benzene solu-

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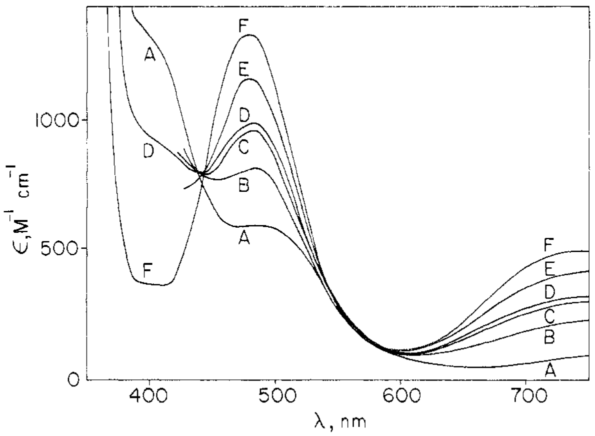

Figure 1. Spectrophotometric study of phosphine dissociation from $RuCl_2(PPh_3)_3$ in benzene at 25°; [Ru] = 1.04×10^{-3} *M*. $[PPh_3]_a \times 10^2$ *M*: (A) 0.0, (B) 0.14, (C) 0.38, (D) 0.52, (E) 0.76, (F) 9.24.

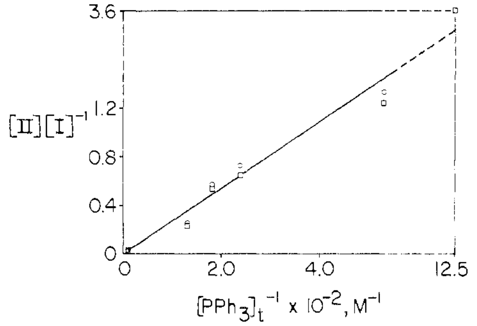

Figure 2. Plot of $[RuCl_2(PPh_3)_2][RuCl_2(PPh_3)_3]^{-1}$ *vs.* $[PPh_3]_t^{-1}$ in benzene (data from Figure 1): (○) 750 nm; (□) 480 nm.

tion of $RuCl_2(PPh_3)_3$ is thus about 80% dissociated at 25° in the absence of added phosphine.

Significant and reproducible changes in the visible spectra occurred on varying the temperature of the $RuCl_2(PPh_3)_3$-PPh_3 benzene solutions from 25 to 50°. The ϵ_I value of the tris(phosphine) complex (measured at high $[PPh_3]$) at 750 nm was essentially independent of temperature over this range, while ϵ_{II} at this wavelength is zero. Hence, the decreases in absorbance (up to 20%) measured at 750 nm with increasing temperature for mixtures of I and II (at lower $[PPh_3]$) have been analyzed in terms of higher K_1 values. The temperature variation measurements at one particular added phosphine concentration were carried out on the same solution. For example, the K_1 values estimated at 5.2×10^{-3} *M* PPh_3 and 1.0×10^{-3} *M* Ru are given in Table I. Similar sets of K_1 values were obtained at other added phosphine concentrations. Each set of K_1 values gave a good van't Hoff plot and yielded the thermodynamic parameters given in Table II.

DMA solutions of $RuCl_2(PPh_3)_3$ gave molar conductance values of ~10 ohm^{-1} cm^2 at 3×10^{-4} *M* compared to values of 40-60 ohm^{-1} cm^2 for DMA solutions of 1:1 electrolytes in a similar concentration range, suggesting that the complex was partially ionized. However, consistent conductivity results could not be obtained because of the extreme oxygen sensitivity of the dilute ruthenium solutions. Even after the complex had completely dissolved (~30 min), the conductivity of the pale orange solutions continued to increase, and a slow increase was still observed even after many hours. In addition, some of the solutions exhibited a definite green tinge, indicating that some oxidation of the complex was occurring.[1] In contrast, visible absorption spectra recorded on the solutions contained in an anaerobic cell under vacuum remained unchanged from the time the complex was dissolved, confirming that the slow changes in solution color and conductivity were a result of destruction of the complex and not due to a slowly attained equilibrium.

Table I. Temperature Dependence of K_1 and K_2

T, °C	25.0	33.2	40.8	49.0	
10^3K_1,[a] *M*	2.6	3.2	3.8	4.4	
T, °C	25.0	33.0	41.0	48.5	
10^2K_1,[b] *M*	4.4	5.0	5.7	6.4	
T, °C	10.0	20.0	30.0	40.0	50.0
10^5K_2,[c] *M*	5.7	6.7	7.3	8.3	9.4

[a] Benzene solution, 5.2×10^{-3} *M* PPh_3. [b] DMA solution, 2.0×10^{-3} *M* LiCl. [c] DMA solution, no added LiCl.

Table II. Thermodynamic Parameters for Reactions 1 and 2

Reaction	Solvent	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, eu	$\Delta S°$,[a] eu
1	Benzene	4.2 ± 0.3	2.2 ± 1.0	−2.6 ± 1.0
1	DMA	3.1 ± 0.3	4.1 ± 1.0	−0.6 ± 1.0
2	DMA	2.2 ± 0.1	−11.7 ± 0.3	−16.4 ± 0.3

[a] Obtained using K_1 or K_2 values calculated after including one solvent molecule as a reactant.

The addition of LiCl to DMA solutions of $RuCl_2(PPh_3)_3$ resulted in a distinct change in the visible spectrum (Figure 3). The presence of a slight excess of chloride resulted in spectra (Figure 3A) approaching that of the bis(phosphine) complex $RuCl_2(PPh_3)_2$ in benzene (*cf.* Figure 1A); addition of greater than about a twofold excess of LiCl caused no further change in the spectrum. These data indicate the presence of an ionic dissociation

$$\underset{\text{II}}{RuCl_2(PPh_3)_2} \overset{K_2}{\rightleftharpoons} \underset{\text{III}}{RuCl(PPh_3)_2^+} + Cl^- \qquad (2)$$

Addition of PPh_3 to a DMA solution of $RuCl_2(PPh_3)_3$ containing the slight excess of chloride resulted in similar spectral changes (Figure 4) to those which characterized an increase in the I:II ratio in benzene, indicating that the K_1 equilibrium applies to the DMA-LiCl solutions. Such K_1 values were determined by the method described for the benzene solutions. By the successive approximations treatment, ϵ_I was found to be 1370 (480 nm) and 530 (750 nm), and ϵ_{II} was 540 (480 nm) and 40 (750 nm). A K_1 value of $(4.6 \pm 0.5) \times 10^{-2}$ *M* was determined at 25° from the plot of $[II][I]^{-1}$ *vs.* $[PPh_3]_t^{-1}$ (Figure 5, from the data of Figure 4). The greater magnitude of K_1 in DMA than in benzene is evident qualitatively from the much larger concentrations of added PPh_3 required in DMA for an equivalent spectral change; a 10^{-3} *M* solution of $RuCl_2(PPh_3)_3$ in DMA (with a slight excess of chloride) is completely dissociated to the bis(phosphine) complex at 25°. Spectral changes at 750 nm with variation of temperature were measured at one added phosphine concentration to give the data shown in Table I. K_1 increases with temperature, and a good van't Hoff plot yielded the thermodynamic parameters given in Table II.

The chloride dissociation (eq 2) was studied by recording the spectra of DMA solutions of 10^{-3} *M* $RuCl_2(PPh_3)_3$, containing in fact bis(phosphine) species, with various concentrations of added chloride (Figure 3); an isosbestic point was observed at 440 nm. The absorbance data at 480 nm, where III exhibited a maximum, were used for determining K_2. Compound III also exhibited an absorption maximum at 670 nm. Although ϵ_{II} [460 (480 nm) and 70 (670 nm)] was readily determined at these wavelengths using solutions containing high chloride, it was more difficult to estimate ϵ_{III} values because the major complex present in solution is the

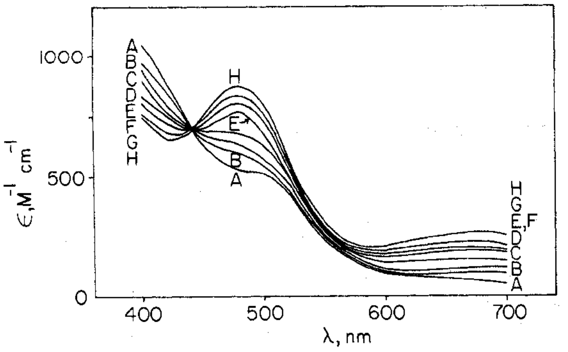

Figure 3. Spectrophotometric study of chloride dissociation from $RuCl_2(PPh_3)_2$ in DMA at 25°; [Ru] = 9.75 × 10^{-4} *M*. [LiCl] × 10^4 *M*: (A) 14.40, (B) 7.20, (C) 5.04, (D) 3.60, (E) 2.16, (F) 1.44, (G) 0.72, (H) 0.0.

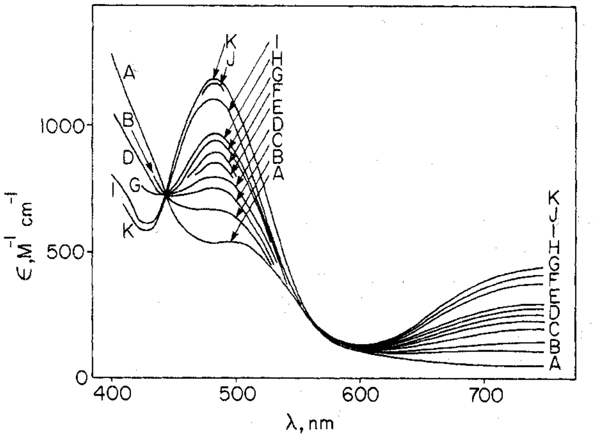

Figure 4. Spectrophotometric study of phosphine dissociation from $RuCl_2(PPh_3)_3$ in DMA at 25°; [Ru] = 1.04 × 10^{-3} *M*, [LiCl] = 2.0 × 10^{-3} *M*. $[PPh_3]_a$ × 10^2 *M*: (A) 0.0, (B) 0.76, (C) 1.22, (D) 1.90, (E) 1.98, (F) 2.82, (G) 3.69, (H) 4.19, (I) 8.56, (J) 14.20, (K) = 18.40.

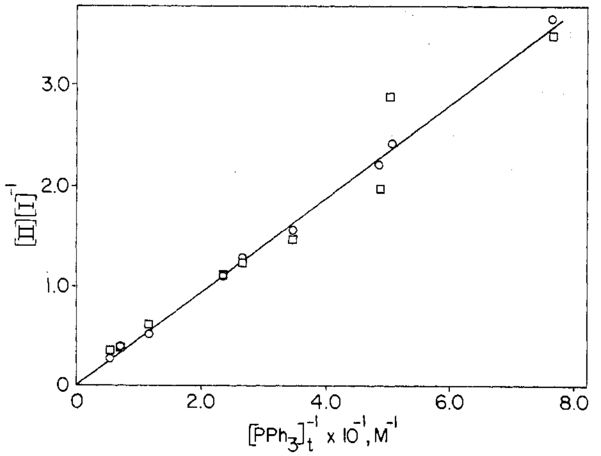

Figure 5. Plot of $[RuCl_2(PPh_3)_2][RuCl_2(PPh_3)_3]^{-1}$ *vs.* $[PPh_3]_t^{-1}$ in DMA (data from Figure 4): (○) 750 nm; (□) 480 nm.

neutral species II, even in the absence of added chloride. However, using the successive approximations treatment, extinction coefficients for species III, $RuCl(PPh_3)_2^+$, at the two maxima were 2360 (480 nm) and 940 (670 nm). The concentrations of II and III were then calculated, and the slope of a plot of $[III][II]^{-1}$ *vs.* $[Cl^-]_t^{-1}$ (Figure 6), where $[Cl^-]_t$ = [LiCl] + [III], yielded a K_2 value of (7.3 ± 0.5) × 10^{-5} *M* at 25°. Such a value indicates 25% ionic dissociation at 10^{-3} *M* Ru at this temperature.

The temperature variation of K_2 (Table I) was determined

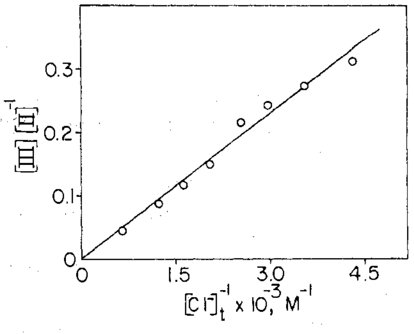

Figure 6. Plot of $[RuCl(PPh_3)_2^+][RuCl_2(PPh_3)_2]^{-1}$ *vs.* $[Cl^-]_t^{-1}$ in DMA (data from Figure 3 at 480 nm).

by using absorbance measurements at 480 nm for a solution containing no added chloride and at a ruthenium concentration (~10^{-3} *M*) where phosphine dissociation from $RuCl_2(PPh_3)_3$ is virtually complete. A van't Hoff plot yielded the thermodynamic parameters given in Table II.

Discussion

It is interesting to note that the visible spectra of the tris(phosphine) complex $RuCl_2(PPh_3)_3$ are essentially identical in benzene and in DMA; this is consistent with the presence of an unsolvated pseudooctahedral complex in which a hydrogen atom of a phenyl ring effectively blocks the sixth coordination site.[10] The corresponding spectra of the bis(phosphine) complex are somewhat different (*cf.* Figures 1A and 4A) and this species is likely solvated. Incorporation of one solvent molecule as a reactant in eq 1 and 2 (to give solvated products) yields unitless equilibrium constants lower by a factor of about 10 than those given in Table I, since neat benzene and DMA have concentrations of 11.3 and 10.8 *M*, respectively; the decreases manifest themselves as a decrease in the entropy of the reactions by about 5 eu (Table II).

The spectrophotometric data confirm that extensive dissociation of phosphine occurs from the complex $RuCl_2(PPh_3)_3$ in solution at concentrations (~10^{-3} *M*) commonly employed in homogeneous catalytic conditions. At 25°, complete dissociation occurs in DMA, while ~80% dissociation occurs in benzene. The $\Delta H°$ values give an indication of the relative coordination strength of the phosphine and solvent molecules. The slightly endothermic $\Delta H°$ values indicate that the third triphenylphosphine molecule coordinates more strongly than either solvent molecule and that DMA forms a stronger coordinate bond than benzene. DMA is known to be a good coordinating solvent and for example has a donor strength comparable to that of water.[11] The order-of-magnitude difference between the K_1 values in DMA and in benzene results from both the enthalpy and entropy factors being more favorable in DMA.

The negative $\Delta S°$ value observed for loss of chloride from the bis(phosphine) complex in DMA is characteristic of a dissociation reaction producing ions in a polar medium and is due to the high degree of solvation of the ionic species.[12] It is not easy to predict enthalpy for such ionization reactions;[12] the system shows a small endothermic $\Delta H°$ value, indicating that the heat of solution of the ions does not quite compensate for the energy required to dissociate the chloride.

We have been unable to isolate cationic complexes of the

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type $RuCl(PPh_3)_n^+$ from the DMA solutions; no such cationic phosphine complexes appear to have been isolated. However, Stephenson and Wilkinson[1] reported their probable existence in nitromethane solution, and corresponding trialkyl phosphite complexes have been synthesized by other workers[13,14] using solutions of $[RuCl_2(diene)]_n$ in polar solvents such as methanol or acetonitrile.

Although ligand dissociation from platinum metal-phosphine complexes is an important factor as regards their potential catalytic properties,[15] few quantitative data are available. Some kinetic data[7] on the reaction of HCl with $HRuCl(PPh_3)_3$ in DMA analyze to give an equilibrium constant for reaction 3 of 3×10^{-4} *M* at 23°. Less intramolecular steric strain in the hydridochloride might account for the difference in magnitudes of K_1 (4.4×10^{-2} *M* at 25°) and K_3.

$$HRuCl(PPh_3)_3 \overset{K_3}{\rightleftharpoons} HRuCl(PPh_3)_2 + PPh_3 \quad (3)$$

A spectrophotometric study by Arai and Halpern[16] of the analogous phosphine dissociation from $RhCl(PPh_3)_3$ gave an equilibrium constant of about 1.4×10^{-4} *M* at 25° in benzene. However, the quantitative aspects of the data have been questioned[5] in terms of a possible contribution from the dimerization equilibrium

$$2RhCl(PPh_3)_3 \rightleftharpoons [RhCl(PPh_3)_2]_2 + 2PPh_3 \quad (4)$$

At the dilute concentrations used in the present studies ($\sim 10^{-3}$ *M*), the presence of any dimeric species seemed unlikely, especially in the strongly donating DMA. The spectral data do not analyze satisfactorily for the production of significant amounts of dimers such as $[RuCl_2(PPh_3)_2(solvent)]_2$.

Phosphine dissociation from $HRh(CO)(PPh_3)_3$ has been shown to be endothermic,[17] and although equilibrium constants were not determined, the bis(phosphine) complex was said to predominate at 10^{-3} *M* in benzene at 25° while at 10^{-2} *M* there was considerable reassociation to the tris complex. These data indicate that the equilibrium constant is probably similar to that determined here for the $RuCl_2(PPh_3)_3$ complex in benzene.

A tetrakis(phosphine) complex $RuCl_2(PPh_3)_4$, which has been synthesized by Stephenson and Wilkinson, dissociates extensively in solution.[1] In the present study, no evidence was obtained for the tetrakis complex in solution over the range of phosphine concentration used.

The extreme sensitivity of the $RuCl_2(PPh_3)_3$ solutions to oxygen, accompanied by a rapid color change from orange to green, with the production of triphenylphosphine oxide, has been noted by other workers.[1,9] Cenini, *et al.*,[9] have postulated an intermediate oxygen complex $RuCl_2(PPh_3)_2 \cdot O_2$ on the basis of an oxygen absorption approaching 1 mol of O_2 per mole of complex at ambient temperatures in benzene. Under similar conditions we have observed an initial rapid uptake of 1.5–1.6 mol of O_2 per mole of Ru, consistent with the overall stoichiometry of eq 5 with no direct evidence for formation of a molecular oxygen complex. Khan, *et al.*,[18] however, have isolated the $RuCl_2(AsPh_3)_3O_2$ complex from the corresponding triphenylarsine system. The nature of ruthenium complex present in the green solutions after the initial oxygenation remains uncertain; however, a subsequent much slower oxidation yields brownish solutions and this is likely attributed to oxidation of the ruthenium.

$$RuCl_2(PPh_3)_3 + 1.5O_2 \rightarrow 3Ph_3PO + \text{"}RuCl_2\text{"} \quad (5)$$

The catalytic oxygenation of triphenylphosphine in the presence of excess phosphine is autocatalytic in nature and appears to be due to a shifting of equilibrium 1 to the right as phosphine is consumed; the tris(phosphine) complex is virtually inactive as a catalyst for the reaction.[19]

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Registry No. I, 15529-49-4; II, 34076-51-2; III, 42740-90-9.

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