Ligand–Metal Hydrogen-Transfer Reactions in Triphenyl Phosphite and Triphenylphosphine Complexes[1]

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Abstract: Ligand–metal hydrogen-transfer reactions have been observed with $[(C_6H_5O)_3P]_4CoH$, $[(C_6H_5O)_3P]_4RhH$, $[(C_6H_5O)_3P]_4RuHCl$, $[(C_6H_5)_3P]_3RuHCl$, $[(C_6H_5)_3P]_3Ru(N_2)H_2$, and $[(C_6H_5)_3P]_3Co(N_2)H$. The *o*-phenyl C–H bond has been clearly defined by deuterium exchange and proton nmr studies as the active ligand site in these complexes. A facile equilibrium between $[(C_6H_5O)_3P]_4RuHCl$, hydrogen, and an isolable *o*-phenyl-bonded species, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$, has been found which is consistent with a mechanism proposed for the hydrogen-transfer reactions. $[(C_6H_5)_3P]_3RuHCl$ is an effective catalyst for the selective *ortho* deuteration of triphenylphosphine.

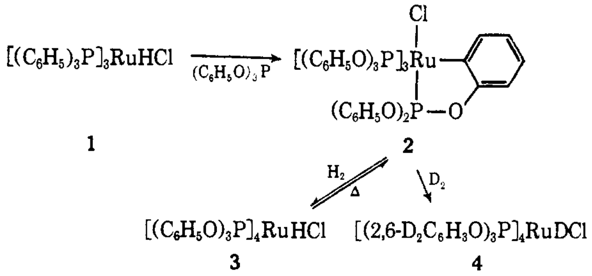
Although several transition metal complexes of tertiary phosphines display an interaction between the central metal atom and C–H bonds of the alkyl or aryl groups of the ligand,[2-9] no such interaction has been reported for phosphite complexes. Additionally, in only a few cases has the active C–H bond in the phosphine complexes been clearly defined. Deuteration studies[2] of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2Ru$ have established the CH_3 groups as the active ligand sites. Activity of an *ortho*-phenyl hydrogen was inferred from an infrared study of the hydride obtained upon heating $[(C_6H_5)_3P]_3IrCl$.[3] The *ortho*-phenyl C–H bonds have also been implicated in other phosphine systems[4-7] although definitive proof of stereochemistry has not been presented.

We wish to report ligand-metal hydrogen-transfer reactions of several triphenyl phosphite and -phosphine complexes and deuteration studies which establish the *ortho*-phenyl C–H bonds as the active ligand sites. The reaction of a metal complex with deuterium gas often provides a convenient means of detecting the phenomenon of ligand-metal hydrogen transfer. The amount of hydrogen in the product gas indicates the extent of hydrogen transfer. The deuteration site, and thus the active C–H bond, may be determined by proton nmr analysis of the recovered complex or ligand.

Results

The deuterated complex, $[(2,6\text{-}D_2C_6H_3O)_3P]_4CoD$, was obtained by the treatment of $[(C_6H_5O)_3P]_4CoH$[10] with three successive portions of deuterium in toluene solution at 100° under pressure. The presence of C–D bonds was established by the observation of ν_{C-D} at 2283 cm^{-1} in the infrared spectrum. *ortho* deuteration of the phenyl rings was established by an analysis of the 220-MHz proton nmr spectrum (Figure 1). The doublet observed at τ 2.90 for the normal complex is clearly assignable to the *ortho* protons and is nearly gone in the deuterated complex. In addition, the shapes of the signals at τ 3.08 and 3.22 due to the *meta* and *para* protons, respectively, have changed upon deuteration in accord with the replacement of the *ortho* protons with deuterium. The relative areas indicate that about 80% of the *ortho* protons have been replaced. The exchange process is completely suppressed by addition of free triphenyl phosphite in toluene at 100° at a deuterium pressure of 1 atm.

The reaction of triphenyl phosphite with chlorohydridotris(triphenylphosphine)ruthenium[11,12] (**1**) gives the new *ortho*-bonded complex **2**. Reaction with hydrogen converts **2** to the "normal" chlorohydridotetrakis(triphenyl phosphite)ruthenium (**3**) which readily reverts to **2** on heating.



The proton nmr spectrum of **2** does not include a metal–hydrogen resonance. The aromatic protons are displayed as two multiplets in a 4.1:1 ratio. The smaller multiplet represents the *ortho* protons of two of the phosphite groups; the resonance due to the remaining *ortho* protons is included in the larger multiplet as shown by deuteration studies. The proton nmr spectrum of **3** exhibits a hydride signal which is split by both *cis* and *trans* ^{31}P nuclei, indicating an octahedral structure in which the hydrogen and chlo-

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(1) (a) Parts of this work have appeared in preliminary form: (a) R. A. Schunn, presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; (b) G. W. Parshall, *J. Am. Chem. Soc.*, 90, 1669 (1968); (c) W. H. Knoth, *ibid*, 90, 7172 (1968); (d) W. H. Knoth and R. A. Schunn, *ibid.*, 91, 2400 (1969).

(2) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(3) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).

(4) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, 2, 127 (1968).

(5) W. Keim, *J. Organometal. Chem.*, 14, 179 (1968).

(6) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

(7) G. Hata, H. Kondo, and A. Miyaki, *J. Am. Chem. Soc.*, 90, 2278 (1968).

(8) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968).

(9) L. Vaska, *J. Am. Chem. Soc.*, 86, 1943 (1964).

(10) J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1405 (1968); these authors subsequently prepared complexes 1 and 2 and characterized them by infrared and nmr spectroscopy. (Presented at the annual meeting of The Chemical Society, Nottingham, England, April 1969.)

(11) P. S. Hallman, D. F. Evans, J. A. Osborn, and G. Wilkinson, *ibid.*, 305 (1968).

(12) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc., A*, 3143 (1968).

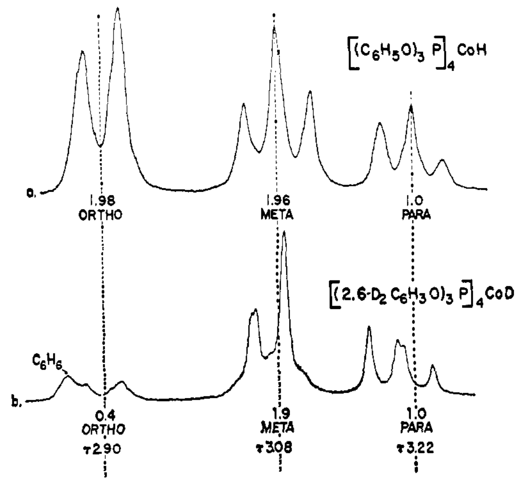

Figure 1. Proton nmr spectra of $[(C_6H_5O)_3P]_4CoH$ (a) and $[(2,6\text{-}D_2C_6H_3O)_3P]_4CoD$ (b) at 220 MHz in C_6D_6 solution with $(CH_3)_4Si$ as an internal standard. Assignments and observed relative intensities are shown under the respective resonances.

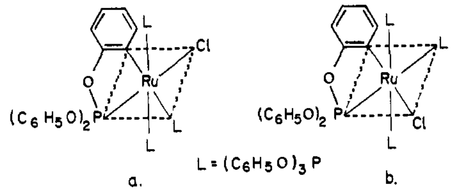

Figure 2. Possible structure of $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$ (**2**).

rine atoms are *cis*. The phosphorus nmr spectrum of **2** consists of two pairs of triplets and one pair of doublets with relative intensities 1:1:2. This pattern is consistent with both structures shown in Figure 2. We prefer **2a** to **2b** for the following reasons. Structure **2a** is consistent with that proposed for **3**, whereas structure **2b** requires a rearrangement during the hydrogenation–dehydrogenation equilibrium. The ^{31}P nmr resonances of the two unique phosphorus atoms in **2** are at −152 and −121 ppm. Such a substantial difference would not be expected for structure **2b**, in which the unique phosphorus atoms have very nearly the same environment, but can readily be reconciled with structure **2a**, in which the two unique phosphorus atoms have different *trans* groups. Finally, all the observable P–P couplings are in the same range (~40–60 cps) which suggests that all interactions are similar (*i.e.*, *cis*) as in **2a**. A greater range of P–P couplings would be expected if both *cis* and *trans* relationships between nonequivalent phosphorus atoms were present, as in **2b**.

Reaction of **2** with deuterium gives **4**, the *ortho*- and metal-deuterated analog of **3**. Recrystallization from hot methylcyclohexane converts **4** to *ortho*-deuterated **2**. In the ^1H nmr spectrum of the latter, the absolute intensities of both the large and small doublets have decreased by very nearly equivalent amounts, the decrease in the smaller multiplet being 80% of the undeuterated intensity. This is consistent with 80% *ortho* deuteration and with part of the *ortho* resonance being included in the larger multiplet. The deuteration is assumed to be *ortho* by analogy with the deuteration of $[(C_6H_5O_3)P]_4CoH$. The ^1H nmr spectra of the ruthenium complexes **2** and **3** are not sufficiently well resolved even at 220 MHz to permit an independent assignment.

The deuteration of **2** is facile; equilibrium is attained within 2 days at ambient temperature and less than 1 atm of deuterium. The addition of excess triphenyl phosphite slows but does not stop the deuteration. Complexes **2** and **3** can be handled in air both as solids and in solution. They catalyze the *ortho* deuteration of phenol, presumably by exchange of phenoxy groups with complexed or dissociated phosphite.

We observe that the infrared spectra of $[(C_6H_5O)_3P]_4RuHCl$ and $[(C_6H_5O)_3P]_4RhH$ are nearly identical and that recrystallization of the latter from boiling heptane gives a compound which has an infrared spectrum very similar to that of complex **2**. It has been reported[10] that reaction of $[(C_6H_5)_3P]_3Rh(CO)H$ with triphenyl phosphite in refluxing ethanol gives $[(C_6H_5O)_3P]_4RhH$, while the same reaction in refluxing *n*-alkanes gives "$\{[(C_6H_5O)_3P]_4Rh\}_2$."[13] The only evidence for the dimeric nature of the latter is the observed diamagnetism of the complex and the lack of a hydride ligand. On the basis of the observed equilibrium between complexes **2** and **3**, and the similarities between the infrared spectra of **2** and the compound obtained by recrystallizing $[(C_6H_5O)_3P]_4RhH$ from boiling heptane, we suggest that the supposed $\{[(C_6H_5O)_3P]_4Rh\}_2$ is actually

$$[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Rh}$$

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an *ortho*-phenyl-bonded complex analogous to **2**. Similarly,[11] "$\{[(C_6H_5O)_3P]_4Ir\}_2$" (**6**)[13] may also be an *ortho*-phenyl-bonded species.

Reaction of $[(C_6H_5O)_3P]_4RhH$ with deuterium at 100° and 65 psig in toluene resulted in extensive *ortho*-phenyl deuteration, thus supporting the new assignment of "$\{[(C_6H_5O)_3P]_4Rh\}_2$" as an *ortho*-phenyl-bonded species.

Phosphine Complexes

Equilibration of $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$ in toluene with several successive portions of deuterium at less than 1 atm pressure and 50° over a 13-day period gave (after crystallization from benzene–heptane) $[(2,6\text{-}D_2C_6H_3)_3P]_3RuDCl \cdot 1.5C_6H_6$ in 71% yield.[14] The infrared spectrum showed ν_{C-D} at 2247 cm^{-1} and ν_{Ru-D} at 1456 cm^{-1}. The proton nmr spectrum (Figure 3) indicates that 80% of the *ortho*-phenyl positions were deuterated.

Selective catalytic *ortho* deuteration of $(C_6H_5)_3P$ was achieved by treatment of a toluene solution of $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$ and $(C_6H_5)_3P$ (mole ratio = 1:20) with a stream of D_2 at 100° for 30 hr. The deuterated ruthenium complex was recovered in 70% yield and $(2,6\text{-}D_2C_6H_3)_3P$ was isolated in 83% yield (>95% *ortho* deuterated, Figure 4). The infrared spectra of normal and *ortho*-deuterated $(C_6H_5)_3P$ are compared in Figure 5.

The proton nmr spectra of deuterated and normal $(C_6H_5)_3P$ (Figure 4) show that the complex resonance at τ 2.64 due to the *ortho* hydrogens in the normal compound virtually disappears on deuteration and only the resonance due to the *meta* + *para* protons at τ 2.97 remains. The mass spectrum showed only traces of

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(13) S. D. Robinson, *Chem. Commun.*, 521 (1968).

(14) Ligand deuteration of $[(C_6H_5)_3P]_3RuHCl$ was recently discovered independently.[12]

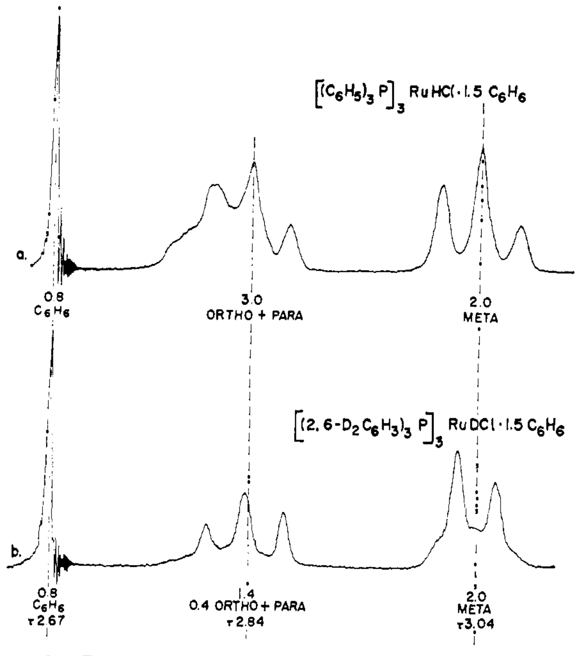


Figure 3. Proton nmr spectra of $[(C_6H_5)_3P]_3RuHCl \cdot 1.5C_6H_6$ (a) and $[(2,6\text{-}D_2C_6H_3)_3P)_3RuDCl \cdot 1.5C_6H_6$ (b) at 220 MHz in CD_2Cl_2 solution with $(CH_3)_4Si$ as an internal standard. Assignments and observed relative intensities are shown under the respective resonances.

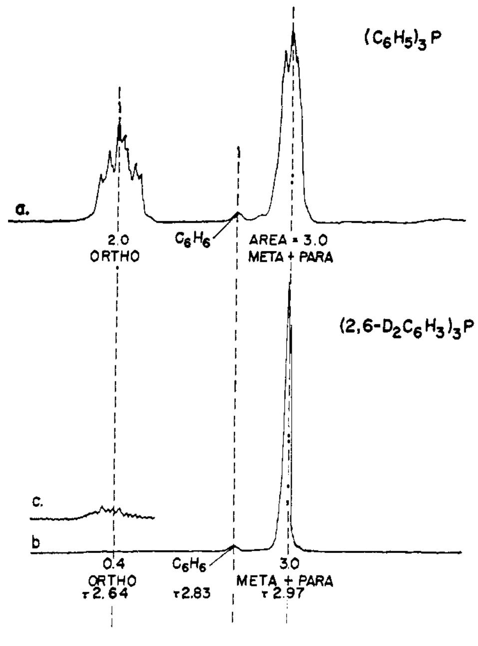


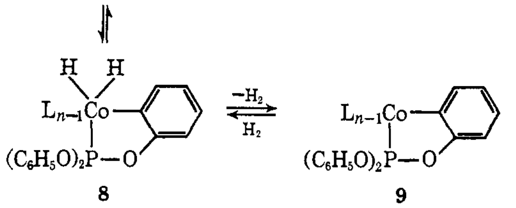
Figure 4. Proton nmr spectra of $(C_6H_5)_3P$ (a) and $(2,6\text{-}D_2C_6H_3)_3P$ (b) at 220 MHz in C_6D_6 solution with $(CH_3)_4Si$ as an internal standard. The *ortho*-phenyl region of $(2,6\text{-}D_2C_6H_3)_3P$ is shown at increased intensity in (c). Assignments and observed relative intensities are shown under the respective resonances.

species other than $(C_6H_3D_2)_3P$ to be present. The ^1H nmr spectrum of the phosphonium derivative, $(2,6\text{-}D_2C_6H_3)_3PCH_3{}^+I^-$, showed that exchange occurred exclusively at the *ortho* positions; the ratio of aromatic (*meta* + *para*) protons to CH_3 protons was 3.0/1.0 in agreement with the absence of *ortho* protons only.

A cobalt complex of molecular nitrogen, $[(C_6H_5)_3P]_3Co(N_2)H$, readily undergoes hydrogen–deuterium exchange of both the Co–H and *ortho*-phenyl C–H bonds at room temperature in benzene solution. This complex also catalyzes H–D exchange of excess triphenylphosphine in the reaction mixture but is a less satisfactory catalyst than $[(C_6H_5)_3P]_3RuHCl$ because it slowly decomposes under the reaction conditions. The recently reported ruthenium complex of nitrogen,[1c] $[(C_6H_5)_3P]_3Ru(N_2)H_2$, also exchanges both the Ru–H and *ortho*-phenyl C–H bonds on treatment with deuterium.

Discussion

The exchange between deuterium gas and the *ortho*-phenyl hydrogens of the aromatic ligands may be explained by reversible oxidative addition of the *ortho*-phenyl C–H bond to a coordination-deficient metal species as illustrated for the cobalt complex 7. This mechanism is similar to that postulated[1b] for $[(C_6H_5)_3P]_3Co(N_2)H$ and is assumed to be valid for either phosphine or phosphite complexes.



The exchange between D_2 and C–H is proposed to occur in two steps with the metal atom acting as a catalyst. The oxidative addition of deuterium to 7 and 9 generates a Co–D bond in 8 either directly (9 → 8) or indirectly (7 → 10 → 7 → 8). This metal-bonded deuterium atom is then transferred to the *ortho* carbon in the reductive elimination reaction 8 → 7. This second step is directly supported by the isolation of the *ortho*-phenyl-bonded species 2 in the analogous ruthenium system. Indeed, the reaction sequence $7 \rightleftharpoons 8 \rightleftharpoons 9$ is equivalent to the observed transformation

$$L_4RuHCl \rightleftharpoons \mathbf{2} + H_2$$

The oxidative addition process requires that the reactive metal complex be able to increase both its coordination number and its formal oxidation state.[15] With d^8 complexes such as $[(C_6H_5)_3P]_3RhCl$ and $[(C_6H_5)_3P]_2Ir(CO)Cl$, this commonly involves a transition from a four-coordinate d^8 to a six-coordinate d^6 configuration. By analogy we suggest that our cobalt species 7 is four-coordinate, *i.e.*, $n = 3$. This suggestion is supported by the observation that added triphenyl phosphite suppresses the exchange between $[(C_6H_5O)_3P]_4CoH$ and D_2, presumably by suppressing the dissociation: $L_4CoH \rightleftharpoons L + L_3CoH$. In $[(C_6H_5)_3P]_3Co(N_2)H$, the labile N_2 ligand is most likely to dissociate.

Added triphenyl phosphite inhibits deuteration of $[(C_6H_5O)_3P]_4RuHCl$, but triphenylphosphine does not measurably inhibit deuteration of $[(C_6H_5)_3P]_3RuHCl$. This apparent contradiction can be rationalized by assuming that the phosphite complex must dissociate to give a five-coordinate species as a step in the formation of the *ortho*-bonded complex 2 while the triphenylphosphine complex is already in a coordinately unsaturated form.

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(15) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

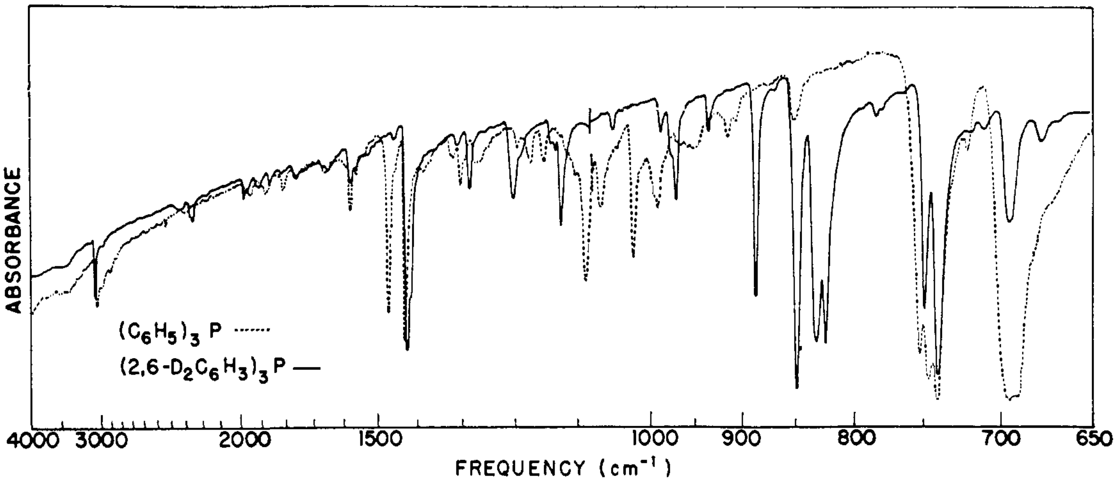

Figure 5. Infrared spectra of $(C_6H_5)_3P$ and $(2,6\text{-}D_2C_6H_3)_3P$ (KBr disks).

Experimental Section

Deuteration of $[(C_6H_5O)_3P]_4CoH$. A 500-ml pressure bottle was charged with 2.6 g (0.002 mole) of $[(C_6H_5O)_3P]_4CoH$[10] and 65 ml of toluene. After degassing at −78°, the bottle was pressured to 35 psig with deuterium and stirred at 100° for 24 hr. After degassing at −78°, the mixture was repressured and heated as before. This cycle was performed three times. The resulting yellow solution was filtered in an inert atmosphere, the filtrate was concentrated under vacuum to *ca.* 25 ml, and the product was precipitated with 250 ml of *n*-heptane. Addition of heptane (200 ml) to a toluene extract (100 ml) of the crude product gave a yellow, crystalline solid which was washed with *n*-heptane and dried at 75° (0.1 μ) for 16 hr to give 2.1 g (81%) of $[2,6\text{-}D_2C_6H_3O)_3P]_4CoD$. *Anal.* Calcd for $C_{72}H_{36}D_{25}CoO_{12}P_4$: C, 65.2; H (apparent), 4.9; Co, 4.4; P, 9.3. Found: C, 66.2; H, 5.1; Co, 4.5; P, 9.5.

The ^1H nmr spectrum at 220 MHz of the deuterated complex is shown in Figure 1 along with that of an undeuterated sample. The infrared spectrum shows the C–D stretching frequency at 2283 (m) cm^{-1} (hexachlorobutadiene mull) and characteristic new bands at 978 (m) and 830 (s) cm^{-1} (KBr disk or Nujol mull) when compared with a spectrum of the undeuterated complex.

In an experiment to determine the effect of added ligand, a solution of 2.6 g (0.002 mole) of $[(C_6H_5O)_3P]_4CoH$ and 11.3 g (0.0365 mole) of triphenyl phosphite in 90 ml of toluene was heated to 100°, and deuterium gas was bubbled through the stirred mixture for 18 hr. The mixture was cooled to 25°, solvent was removed under vacuum, and the yellow residue was washed well with *n*-hexane. The insoluble yellow solid was identified as undeuterated $[(C_6H_5O)_3P]_4CoH$ by comparison of infrared spectra. Hexane was removed from the filtrate under vacuum and the residual yellow liquid was identified as undeuterated $(C_6H_5O)_3P$ by comparison of infrared spectra.

Preparation of $[(2,6\text{-}D_2C_6H_3O)_3P]_4RhD$. The rhodium complex $[(C_6H_5O)_3P]_4RhH$ was prepared from $[(C_6H_5)_3P]_3Rh(CO)H$ and triphenyl phosphite.[10] Deuteration was accomplished by a procedure similar to that described above for the cobalt complex except that after each pressure cycle the gases were collected, measured, and analyzed by mass spectrometry. The gas analyses are summarized in Table I. $[(C_6H_5O)_3P]_4RhH$ (2.7 g, 20 mmoles) was used, which provided a total of 50 mg-atoms of exchangeable *ortho*-phenyl and Rh–H hydrogens.

Table I

Time, hr	Gas composition, mole % H_2	HD	D_2	Total H replaced, %
0	0	0	100	0
22	14	45	41	75
44	1	15	84	92
66	0	7	93	99

The initially yellow solution became red after *ca.* 1 hr at 100° and did not change thereafter. After removal of solvent, the red, oily residue was dissolved in 20 ml of C_6H_6, the solution was filtered, and a tan solid was precipitated with 200 ml of CH_3OH. The precipitate was dried at 25° (0.1 mm) for 16 hr to give 1.0 g of $[(2,6\text{-}D_2C_6H_3O)_3P]_4RhD$, which was identified by the close similarity of its infrared spectrum with that of the analogous deuterated cobalt complex.

$[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$ (2). A mixture of the toluene solvate of chlorohydridotris(triphenylphosphine)ruthenium[11,12] (10.0 g, 9.9 mmoles), triphenyl phosphite (20 ml), and benzene (120 ml) was stirred in a nitrogen atmosphere at ambient temperature for 45 min. The mixture was evaporated, leaving a semisolid mass which was extracted with boiling methylcyclohexane (400 ml). Crystalline **2** (6.7 g, 4.9 mmoles, 49%, mp 169–173°) separated from the extracts on cooling. In other runs the yields ranged up to 60%. *Anal.* Calcd for $C_{72}H_{59}ClO_{12}P_4Ru$: C, 62.8; H, 4.3; Cl, 2.6; O, 14.0; P, 9.0. Found: C, 62.8; H, 4.4; Cl, 2.6; O, 13.8; P, 8.8.

The infrared spectrum includes absorption bands at 1100 and 798 cm^{-1} in addition to those found in $[(C_6H_5O)_3P]_4RuHCl$ and is more highly resolved in the 730–690-cm^{-1} region. The Ru–H stretching absorption found in the latter spectrum was absent. It should be noted that in the infrared spectra of all the triphenyl phosphite complexes there are ligand bands in the 1950–1850-cm^{-1} region which can be misinterpreted as Ru–H bands if a direct comparison with the spectrum of triphenyl phosphite is not made. The absence of hydrogen bonded to ruthenium was indicated by the ^1H nmr spectrum which in deuteriochloroform consists only of two multiplets, at τ 2.6 to 3.2 and at τ 3.8 in a 4.1 : 1 ratio. The smaller multiplet therefore represents 11 or 12 protons. No dissociated triphenyl phosphite is apparent in the ^1H nmr spectrum.

The ^{31}P nmr spectrum in methylene chloride at 40.5 MHz (referred to external 85% phosphoric acid) consists of three multiplets in a 1 : 1 : 2 ratio. These consist of two overlapping triplets (δ −152 ppm, J = 62 and 43 cps), two overlapping triplets (δ −121 ppm, J = 50 and 43 cps), and two overlapping doublets (δ −114 ppm, J = 62 and 50 cps).

In a similar but smaller scale preparation conducted on a vacuum line, hydrogen evolution (0.7 mole equiv) was detected during the reaction. The crude product contains a small amount of $[(C_6H_5O)_3P]_4RuHCl$ which is dehydrogenated during the crystallization.

$[(C_6H_5O)_3P]_4RuHCl$. A mixture of **2** (2 g) and benzene (50 ml) was charged to a glass pressure bottle and stirred under hydrogen pressure (40 psig) overnight. The benzene was removed *in vacuo* at ambient temperature; the residue was washed with hexane and dried to obtain 1.6 g of $[(C_6H_5O)_3P]_4RuHCl$ (80%) as a white powder which softens about 55° and melts at 166–169°. *Anal.* Calcd for $C_{72}H_{61}ClO_{12}P_4Ru$: C, 62.7; H, 4.5; Cl, 2.6; P, 9.0. Found: C, 62.9; H, 4.4; Cl, 2.6; P, 8.4.

The infrared spectrum exhibited a somewhat broad ruthenium–hydrogen stretching absorption centered at about 1930 cm^{-1}. The other major infrared bands (Nujol mull) are at 1580 (s), 1200 (vs, multiplet), 1070 (m), 1020 (s), 1000 (m), 910 (vs, broad), 830 (w), 760 (s), 720 (s), and 690 (s) cm^{-1}. The proton nmr spectrum in deuteriochloroform has a hydride resonance at τ 16.8 which is split into two multiplets ($J_{H-P_{trans}}$ = 174 cps). Each multiplet consists of a doublet ($J_{H-P_{cis}}$ = 28 cps) which is further split into two overlapping triplets ($J_{H-P_{cis}}$ = 24 cps).

$[(C_6H_3D_2O)_3P]_4RuDCl$. A mixture of **2** (2 g, 1.45 mmoles) and benzene (30 ml) was stirred under deuterium pressure (30 psig) for 3 days. The residue after evaporation of the benzene was rinsed with hexane and dried to obtain 1.8 g (88%) of $[(C_6H_3D_2O)_3P]_4RuDCl$ as a white powder which softens at about 115° and melts at 168–172°.

Anal. Calcd for $C_{72}D_{25}H_{36}ClO_{12}P_4Ru$: C, 61.6; H (apparent), 4.6. Found: C, 62.2; H, 4.7.

The major infrared bands as determined in a Nujol mull are at 1595 (s), 1200 (vs, multiplet), 1100 (m), 1070 (s), 1040 (m), 1020 (m), 970 (ms), 910 (vs, broad), 840 (m), 820 (s), 760 (vs), 720 (s), and 700 (s).

The *ortho* deuteration was about 80% complete as determined by nmr studies on the derived *ortho*-phenyl bonded species, described below.

$[(C_6H_3D_2O)_3P]_3(C_6H_3D_2O)_2\overline{POC_6H_3DRu}Cl$. Recrystallization of $[(C_6H_3D_2O)_3P]_4RuDCl$ (0.7 g) from hot methylcyclohexane gave this product **2a** (0.4 g, 57%), mp 177–179°.

Anal. Calcd for $C_{72}D_{23}H_{36}ClO_{12}P_4Ru$: C, 61.6; H (apparent), 4.5. Found: C, 61.5; H, 4.6.

The infrared spectrum includes a moderately strong band at 790 cm^{-1} in addition to those reported for the spectrum of $[(C_6H_3D_2O)_3P]_4RuDCl$.

The proton nmr spectrum consisted of two multiplets, similar in position to those in the spectrum of the undeuterated analog. The absolute intensities of both multiplets had decreased by equivalent amounts upon deuteration, the decrease in the smaller multiplet being 80% of the original intensity. The equivalent decrease in both multiplets showed that approximately 23 protons were involved in the exchange, in agreement with the results in the following low-pressure deuteration.

A mixture of **2** (0.35 g, 0.26 mmole) and toluene (50 ml) was stirred in a glass reactor (~355 ml) in a deuterium atmosphere (415 mm) for 48 hr. Analysis of the noncondensable gases (6.7 mmoles) revealed a H_2:HD:D_2 ratio of 10.7:41.7:47.6. The calculated percentages for random statistical exchange of 23 hydrogen atoms with 6.96 mmoles of deuterium (6.7 mmoles of gas recovered + 0.26 mmole utilized in cleavage of Ru-C bond) are 9.3% H_2, 42.2% HD, and 48.5% D_2.

In an experiment to determine the effect of added ligand, a mixture of **2** (0.371 g, 0.27 mmole), triphenyl phosphite (7.58 g, 24.4 mmoles), and toluene (50 ml) was stirred in a deuterium atmosphere (626 mm) in a glass reactor (~350 ml volume) for 7 days. Analysis of the noncondensable gases (9.7 mmoles) revealed a H_2:HD:D_2 ratio of 6.4:18.0:75.6. This is a nonstatistical distribution and contains only 65% of the hydrogen that should have been liberated even if none of the excess phosphite exchanged. Comparison of this with the liberation of virtually 100% of the theoretical amount of hydrogen in a much shorter reaction time in the preceding experiment reveals an inhibiting effect of the added phosphite.

Catalytic Deuteration of Phenol. A mixture of **2** (0.327 g, 0.24 mmole), toluene (50 ml), and phenol (0.30 g, 3.18 mmoles) was stirred in a glass reactor (approx 355 ml) in a deuterium atmosphere (509 mm) for 62 hr. Analysis of the noncondensable gases (8.0 mmoles) revealed a H_2:HD:D_2 ratio of 15.3:46.1:38.7. The calculated percentages for statistical exchange of the *ortho* hydrogens if the phenol did *not* participate are 6.4% H_2, 37.8% HD, and 55.6% D_2. The calculated percentages assuming exchange of all *ortho* hydrogens, including those in the phenol, are 17.8% H_2, 48.8% HD, and 33.2% D_2. In a control run in which phenol, triphenyl phosphite, and toluene were stirred in a deuterium atmosphere, no exchange was noted.

Dehydrogenation of $[(C_6H_5O)_3P]_4RhH$. A sample of $[(C_6H_5O)_3P]_4RhH$ was recrystallized from *n*-heptane by allowing the solution to cool after it had been refluxed 5 min in a nitrogen atmosphere. The infrared spectrum of the recovered crystals differed from that of $[(C_6H_5O)_3P]_4RhH$ by having diminished absorption at 1950 cm^{-1} and new bands at 1100 and 790 cm^{-1}. This new species, colorless in the solid state, formed bright yellow benzene solutions. Passing hydrogen through such a solution discharged the color rapidly. Evaporation of the benzene left a residue of $[(C_6H_5O)_3P]_4RhH$.

Deuteration of $(C_6H_5P)_3RuHCl$. A round-bottom flask equipped with a magnetic stirrer and stopcock adapter (volume = 997 ml) was charged with 1.05 g of $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$[11,12] and 50 ml of toluene. The flask was cooled to −78°, evacuated, and then warmed to 25°. The flask was filled with deuterium gas to a total pressure of 543 mm. The mixture was warmed to 50° and stirred vigorously. At intervals as summarized in Table II, the flask was cooled to −78°, the gases were removed and analyzed by mass spectrometry, and fresh deuterium was admitted at 25°. After 328 hr, the mixture was filtered in an inert atmosphere and the purple solid was extracted with hot toluene. Concentration of the extract under vacuum gave 0.8 g of purple, crystalline solid. The toluene solvate was converted to a benzene solvate by extraction with hot benzene (250 ml), addition of *n*-heptane (250 ml) to the filtered extract, and concentration under vacuum. The resulting purple, crystalline solid was dried at 25° (0.5 μ) for 16 hr to give 0.7 g of $[(2,6\text{-}D_2C_6H_3)_3P]_3RuDCl \cdot 1.5C_6H_6$.

Table II

Time, hr	Gas composition, mole % H_2	HD	D_2	Total H replaced, %
0	0	0	100	0
40	2.1	21.3	75.0	32
217	2.5	24.6	72.9	72
328	0.6	14.0	85.4	92

Anal. Calcd for $C_{63}H_{36}D_{19}ClP_3Ru$: C, 71.4; H (apparent), 5.2; Cl, 3.3; P, 8.8. Found: C, 72.3; H, 5.7; Cl, 4.1; P, 9.1.

The ^1H nmr spectra of the deuterated and undeuterated complexes are shown in Figure 3. The infrared spectrum of the deuterated complex (KBr disk) shows major new bands at 2247 (w) (C–D stretch), 1456 (m) (Ru–D stretch), 850 (s), 825 (s), and 770 (s, bd) cm^{-1} when compared with a spectrum of the undeuterated complex.

Tris(2,6-dideuteriophenyl)phosphine. A mixture of 5.2 g (20 mmoles) of triphenylphosphine and 1.02 g (1.0 mmole) of $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$ in 70 ml of toluene was heated to 100°. A slow stream of deuterium gas was bubbled through the stirred solution for 30 hr. The purple solution was cooled to 25°, and the purple crystalline solid was collected in an inert atmosphere. Recrystallization from benzene–heptane gave 0.7 g of $[(2,6\text{-}D_2C_6H_3)_3P]_3RuDCl \cdot 1.5C_6H_6$.

Anal. Calcd for $C_{63}H_{36}D_{19}ClP_3Ru$: C, 71.4; H (apparent), 5.2; Cl, 3.3; P, 8.8. Found: C, 70.5; H, 5.1; Cl, 3.5; P, 9.1.

The ^1H nmr and infrared spectra were similar to those previously obtained.

The filtrate was evaporated to dryness under vacuum, and the residue was twice sublimed at 90–95° (0.1 μ) to give 4.3 g (83%) of white crystalline $(2,6\text{-}D_2C_6H_3)_3P$, mp 79°.

Anal. Calcd for $C_{18}H_9D_6P$: C, 80.6; H (apparent), 5.9; P, 11.5. Found: C, 80.2; H, 5.9; P, 11.3.

The 220-MHz ^1H nmr spectra of deuterated and undeuterated $(C_6H_5)_3P$ are shown in Figure 4 and the infrared spectra in Figure 5. The mass spectrum showed the most abundant ion at *m/e* 268, corresponding to $(C_6H_3D_2)_3P^+$, and gave no evidence for the introduction of more than six deuterium atoms per molecule. Also, very little or no $(C_6H_4D)(C_6H_3D_2)_2P$ or lower deuterated species were observed.

A small portion of $(2,6\text{-}D_2C_6H_3)_3P$ was treated with CH_3I in diethyl ether. The white precipitate of $(2,6\text{-}D_2C_6H_3)_3PCH_3^+I^-$ was purified from $CHCl_3$–heptane. The 60-MHz ^1H nmr spectrum of the deuteriophosphonium salt showed the CH_3 group as a doublet at τ 6.85 (*J* = 14 cps) and the aromatic protons as a complex multiplet at τ 2.25 in the ratio of 3.0:9.1 in agreement with the introduction of six deuterium atoms into the molecule.

Deuteration of $[(C_6H_5)_3P]_3Co(N_2)H$. A solution of 0.87 g (1.0 mmole) of hydridonitrogentris(triphenylphosphine)cobalt(I)[16–20] in 50 ml of benzene was stirred at room temperature for 6 days with deuterium (21 mmoles) at 1 atm. A gas sample withdrawn at −78° at the end of this period showed 12% H_2, 42.7% HD, and 45.3% D_2. Assuming random exchange of 19 hydrogens per molecule, one would expect 9.7% H_2, 42.9% HD, and 47.3% D_2.

The benzene solution was evaporated and the residue was oxidized with 1.0 ml of 30% hydrogen peroxide in 27 ml of chloroform (25°, 16 hr). The solution was washed with water and filtered. Evaporation of the filtrate and recrystallization of the residue from

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CCl_4 gave white crystals of triphenylphosphine oxide, mp 153.5–154.5°. The proton nmr spectrum (shown in ref 1b) in C_6D_6 solution at 60 MHz showed an intensity ratio of the *meta* + *para* signal at τ 2.9 to the *ortho* signal at τ 2.2 of 9.8, *vs.* a ratio of 1.5 for undeuterated triphenylphosphine oxide. The observed ratio corresponds to 85% deuteration of the *ortho* positions.

Deuteration of $[(C_6H_5)_3P]_3Ru(N_2)H_2$. A solution of 0.50 g of dihydridonitrogentris(triphenylphosphine)ruthenium(II)[1c] in 50 ml of *m*-xylene was stirred and heated at 65° for 24 hr with deuterium (9 mmoles) at 631 mm. Oxidation of the complex with hydrogen peroxide gave triphenylphosphine oxide with 75% deuteration of the *ortho* positions.

Temperature Effects on Charge-Transfer Luminescence Intensity of Some Transition Metal Ion Chelates

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Abstract: The unusually large temperature effect on the luminescence intensity of some imine chelates of d^6 ions of certain group VIII metals can be attributed to the effect on the intersystem crossing rate of a temperature-dependent equilibrium between high- and low-spin states established during the lifetime of the charge-transfer excited state of the chelate. The absence of luminescence from Fe(II)–imine chelates may result from complete crossover to the high-spin state upon excitation.

Most complexes of transition metal ions are paramagnetic by virtue of the partly filled outer d subshell. Because the rate of intersystem crossing in most paramagnetic species is quite rapid, very few of these species are luminescent in fluid solution.[1,2]

Brandt and coworkers reported an intense red-orange luminescence at room temperature upon ultraviolet irradiation of dilute aqueous solutions of several Ru(II)–imine chelates.[3,4] They assigned the luminescence to a radiative ligand-to-metal charge-transfer transition ($\pi^* \rightarrow d$). Recent work[5,6] has confirmed that this luminescence probably originates from a ligand triplet ($^3\pi^*$); thus, it is a phosphorescence.[7] Some imine chelates of Ir(III) and Os(II) also show a charge-transfer luminescence;[8,9] in some cases this radiation is emitted by samples in fluid solution at room temperature.[10,11] These species have several structural characteristics in common: the chelates have octahedral microsymmetry, metal ions with d^6 electron configuration, and ligands which produce strong ligand fields; these species all show charge-transfer excited states at lowest energies, *i.e.*, below ligand field (d^*,d) and ligand (π^*,π) excited states. Also of interest is the very striking temperature dependence of the luminescence intensity in fluid solution near room temperature.[5,11]

However, all transition metal ion chelates that might be expected to show charge-transfer luminescence of the kind just described do not do so. In particular none of the Fe(II)–imines luminesces (even in rigid media); neither does the Ru(II)–ter chelate (ter = 2,2′,2″-terpyridine) at room temperature, although the red-orange phosphorescence characteristic of Ru(II)–imines is seen upon exposure of rigid solutions of $[Ru^{II}(ter)_2]^{2+}$ to near-ultraviolet radiation.[4,7,12] In the present work the unusual temperature effect is studied in more detail, and a simple general explanation for this remarkable phenomenon is proposed. Moreover, the same considerations can also account for the absence of luminescence from these imine chelates of Fe(II) and certain imines formed by Ru(II) and Ir(III).

Results

Absolute ethanol solutions of the chelates shown in Table I were examined at and within *ca.* 50° of room temperature as well as in the form of rigid glasses at *ca.* 80°K (the temperature of liquid nitrogen). Solutions of most of these chelates were prepared by dissolving the solid compounds which were obtained as indicated in Table I. The chelates were also synthesized directly in solution by mixing the metal ion (as ruthenium(III) chloride, iridium(III) chloride, or iron(II) sulfate) and a large amount (5 to 10 molar excess) of the ligand in aqueous solution; solutions containing iridium or ruthenium ions were heated for *ca.* 2 hr at gentle boil and hydroxylamine hydrochloride was also added to the ruthenium solutions. Most of the excess ligand was removed from a nearly neutral aqueous phase (25 ml) by two extractions with 10-ml portions of chloroform. Absolute ethanol was added to the residual aqueous extract after heating to evaporate nearly all of the water (the final solution was at least 95% in ethanol). No differences believed to be of consequence for the present work were detected in the optical properties determined on solutions of the chelates prepared by dissolving the solid or by mixing the metal ion and the ligand. There were small differ-

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