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The Interaction of Transition Metal Hydride Complexes with Deuterium, Ethylene-d_4, and 1-Butene[1]

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The reactions of a series of transition metal hydride complexes with D_2, C_2D_4, and 1-butene were studied by mass spectroscopic and gas chromatographic techniques. Exchange of D_2 and C_2D_4 with the metal–hydrogen bond was observed and the degree of exchange varied with the nature of the complex. The activity of the complexes in the isomerization of 1-butene generally paralleled the activity toward exchange with C_2D_4 except in the cases of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2RhH$ and $[(C_6H_5)_3P]_3Ir(CO)H$. Ligand–metal hydrogen transfer was observed in the D_2 and C_2D_4 exchange studies of $[(C_6H_5O)_3P]_4CoH$, $[(C_6H_5O)_3P]_3Co(CO)H$, $[(C_6H_5)_3P]_3Co(N_2)H$, $[(C_6H_5)_3P]_3RuHCl(CO)$, and $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$. The synthesis and properties of the new metal–hydride complexes $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$, $[(C_6H_5O)_3P]_3Co(CO)H$, and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$ are described.

Introduction

The significant role of transition metal to hydrogen bonds in catalytic processes has become increasingly apparent.[2–5] The reversible reaction of a metal hydride with an unsaturated hydrocarbon to give a metal–alkyl intermediate has been proposed as a step in the hydrogenation,[6] isomerization,[7] hydroformylation[8], hydrosilation,[9] and dimerization[10] of unsaturated hydrocarbons.

Studies which have demonstrated the reversible addition of a metal–hydrogen bond to a simple olefin include the reactions of ethylene with $[(C_6H_5)_3P]_2RhHCl_2$,[11] $[(C_6H_5)_3P]_3RuHCl$,[12] $[(C_6H_5)_3P]_3RuH(OCOCF_3)$,[13] and $[(C_2H_5)_3P]_2PtHCl$,[14] the thermal decomposition of $[(C_2H_5)_3P]_2Pt(CD_2CH_3)Br$,[15a] and the deuteration of C_2H_4 in the presence of $[(C_6H_5)_3P]_2Ir(CO)Cl$.[15b] However, thermal decomposition of π-$C_5H_5Mo(CO)_3C_2H_5$[16] and $C_2H_5Mn(CO)_5$[17] produced $[\pi$-$C_5H_4C_2H_5Mo(CO)_3]_2$ and $Mn_2(CO)_{10}$ + n-C_4H_{10}, respectively. The reaction of $HMn(CO)_5$ with ethylene has been reported[17] to give $Mn_2(CO)_{10}$ and C_2H_6. The isomerization of 1-butene has been shown to involve the reversible addition of a metal–hydrogen bond to the olefin.[7,18]

The catalytic activation of hydrogen by transition metal complexes[19] is basic to the hydrogenation of unsaturated hydrocarbons but few examples of hydrogen activation by metal hydride complexes have been reported. For example, $[(C_6H_5)_3P]_3Ir(CO)H$,[20] $[(C_6H_5)_3P]_3RuHCl(CO)$,[20] $[(C_6H_5)_3P]_3OsHCl(CO)$,[20] $[(C_6H_5)_3P]_3RuHCl$,[12] and $[(C_6H_5)_3P]_3Rh(CO)H$[21] have been shown to exchange the metal–hydrogen bond with deuterium gas. It has been proposed[20] that the exchange occurs through an MHD_2 intermediate formed by the oxidative addition[22,23] of D_2 to the metal.

In this paper the results of a study of the interaction of a series of transition metal hydride complexes with deuterium, ethylene-d_4, and 1-butene under comparable conditions are presented. These studies were undertaken in an effort to define more closely the relative reactivity of various metal hydrides in these catalytically important reactions. In addition, several new transition metal hydride complexes were synthesized.

Experimental Section

The following hydride complexes were prepared by procedures similar to those described in the literature: $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2CoH$,[24] $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2RhH$,[24] $[(C_2H_5O)_3P]_4CoH$,[25,26] $[(C_6H_5O)_3P]_4CoH$,[27,28] $[(C_6H_5)_3P]_3Co(N_2)H$,[29] $[(C_6H_5)_3P]_3Rh(CO)H$,[30,31] $[(C_6H_5)_3P]_3Ir(CO)H$,[31] $[(C_6H_5)_3P]_2Ir(CO)Cl_2H$,[32] $[(C_2H_5)_2C_6H_5P]_3RuHBr(CO)$,[33] $[(C_6H_5)_3P]_3Ru(CO)ClH$,[34] $[(C_6H_5)_3P]_3RuClH \cdot C_6H_5CH_3$,[12] $[(C_2H_5)_3P]_2PtClH$,[14]

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," American Elsevier, New York, N. Y., 1968.

[3] M. L. H. Green in "Organometallic Compounds," Vol. II, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen, London, 1968.

[4] R. F. Heck, *Accounts Chem. Res.*, **2**, 10 (1969).

[5] R. Cramer, *ibid.*, **1**, 186 (1968).

[6] J. Halpern, J. F. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **88**, 5150 (1966).

[7] R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966).

[8] R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4023 (1961).

[9] J. F. Harrod and J. F. Chalk, *ibid.*, **87**, 1133 (1965).

[10] R. Cramer, *ibid.*, **87**, 4717 (1965).

[11] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967).

[12] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *ibid.*, *A*, 3143 (1968).

[13] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *ibid.*, *A*, 2610 (1969).

[14] J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).

[15] (a) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *ibid.*, *A*, 190 (1968); (b) G. G. Eberhardt and L. Vaska, *J. Catal.*, **8**, 183 (1967).

[16] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4096 (1963).

[17] W. Hieber and G. Wagner, *Justis Liebigs Ann. Chem.*, **618**, 24 (1958).

[18] R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966).

[19] J. Halpern, *Proc. Int. Congr. Catal., 3rd, 1964*, 146 (1965).

[20] L. Vaska, *Proc. Int. Conf. Coord. Chem., 8th, 1964*, 99 (1964).

[21] D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).

[22] J. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[23] L. Vaska, *ibid.*, **1**, 335 (1968).

[24] A. Sacco and R. Ugo, *J. Chem. Soc.*, 3274 (1964).

[25] L. G. Cannell, U. S. Patent 3,102,899 (1963).

[26] W. Kruse and R. H. Atalla, *Chem. Commun.*, 921 (1968).

[27] J. J. Levison and S. D. Robinson, *J. Chem. Soc. A.*, 96 (1970).

[28] This complex was also prepared independently in these laboratories: M. O. Unger and R. A. Schunn, unpublished results.

[29] B. R. Davis, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, **8**, 2719 (1969), and references therein.

[30] D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).

[31] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, **85**, 3500 (1963). $NaBH_4$ was used in place of hydrazine hydrate.

[32] L. Vaska and J. W. Diluzio, *ibid.*, **83**, 2784 (1961).

[33] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

[34] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc*, **83**, 1262 (1961).

$C_5H_5Mo(CO)_3H$,[35] and $(CO)_5MnH$.[36] Procedures for the preparation of the new hydride complexes are described below. The reagents used were as follows: deuterium, Matheson Co. CP grade; C_2D_4, Merck Sharp and Dohme of Canada, dried and degassed over P_2O_5 before using; 1-butene, Phillips Petroleum, dried and degassed over P_2O_5 before using; benzene, reagent grade, dried on molecular sieves and deoxygenated by several freeze–thaw cycles under vacuum; tetrahydrofuran, distilled from $LiAlH_4$. Proton nmr spectra were obtained at 60 MHz on a Varian Associates A-60 or HR60 spectrometer using $(CH_3)_4Si$ as an internal reference. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer. Mass spectra were obtained using a CEC 21-103C mass spectrometer.

Preparation of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$ Using H_2O.—The entire procedure was performed in a dry nitrogen atmosphere. A mixture of 6.2 g (0.048 mol) of naphthalene and 2.7 g (0.12 g-atom) of sodium chips in 75 ml of tetrahydrofuran was stirred at 25° for 2.5 hr to give a dark green solution of sodium naphthalenide. This solution was added in portions to a suspension of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoBr_2$ which had been prepared *in situ* from 3.1 g (0.014 mol) of $CoBr_2$ and 4.7 g (0.031 mol) of $(CH_3)_2PCH_2CH_2P(CH_3)_2$[37] in 100 ml of tetrahydrofuran. The green color of the sodium naphthalenide solution was rapidly discharged to give a dark red solution containing a brown solid. After the mixture was stirred for 15 min, 0.31 g (0.017 mol) of H_2O was added and the mixture rapidly became brownish yellow. The mixture was stirred at 40° for 0.5 hr, the solvent was removed under vacuum, and the residue was extracted with a total of 300 ml of *n*-hexane. The filtered extracts were evaporated under vacuum and naphthalene was removed from the orange residue by sublimation at 30° (0.5 μ). The remaining residue was sublimed at 90° (0.6 μ) to give 3.7 g (64%) of yellow $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$, mp 99–101°. An analytical sample was prepared by recrystallization from *n*-hexane at −78° followed by two additional sublimations and melted at 101–103°. *Anal.* Calcd for $C_{12}H_{33}CoP_4$: C, 40.0; H, 9.2; Co, 16.4; P, 34.4. Found: C, 39.6; H, 9.4; Co, 15.9; P, 34.5.

The product is a yellow, pyrophoric solid which inflames when crushed in air; it is also decomposed by water. The infrared spectrum of a Nujol mull showed ν_{Co-H} at 1855 cm^{-1}. The use of D_2O in the preparation gave the corresponding deuteride (mp 101–103°) which showed ν_{Co-D} at 1337 cm^{-1}. The ^1H nmr spectrum of the hydride complex showed a quintet Co–H resonance at τ 17.8 in tetrahydrofuran and τ 23.4 in benzene with $J_{PH} = 25$ Hz.

Preparation of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$ Using H_2.—A solution was prepared as above from 4.2 g (0.0280 mol) of $(CH_3)_2PCH_2CH_2P(CH_3)_2$, 3.0 g (0.0137 mol) of $CoBr_2$, 5.4 g (0.0422 mol) of naphthalene, and 1.8 g (0.0782 g-atom) of sodium in a total of 200 ml of tetrahydrofuran. Hydrogen gas was passed through the solution at a rate of *ca.* 80 ml/min for 7.0 hr at 25°. During this time, the solution changed from red-brown to orange and a brown solid formed. After solvent removal under vacuum, the residue was extracted with petroleum ether (bp 30–60°), the brown extracts were evaporated, and the naphthalene was removed at 40° (0.1 mm). Sublimation of the brown residue at 80–90° (3 μ) gave 3.0 g (75%) of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$ which was identified by its infrared spectrum.

Reaction of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$ with Potassium.—In a nitrogen atmosphere, a mixture of 0.64 g (0.00178 mol) of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$, 0.2 g (0.00512 g-atom) of potassium chips, and 100 ml of tetrahydrofuran was refluxed for 1.0 hr. After cooling, the solution was filtered and the solvent was removed under vacuum. The yellow, pyrophoric residue had an infrared spectrum identical with that of the starting compound.

Preparation of $[(C_6H_5O)_3P]_3Co(CO)H$.—A 110-ml stainless steel autoclave containing a solution of 2.2 g (0.00169 mol) of $[(C_6H_5O)_3P]_4CoH$ in 50 ml of toluene was pressured to 150 psig with carbon monoxide and the mixture was heated to 100° for 1 hr. The resulting pale yellow solution was filtered in air and the solvent was removed from the filtrate under vacuum. Addition of ethanol to the residual yellow oil gave an off-white solid which was recrystallized from *n*-hexane (300 ml) to give 0.7 g (41%) of $[(C_6H_5O)_3P]_3Co(CO)H$, mp 126–128°. *Anal.* Calcd for $C_{55}H_{46}CoO_{10}P_3$: C, 65.8; H, 4.5; Co, 5.8; P, 9.1. Found: C, 66.2; H, 4.8; Co, 5.4; P, 9.2.

The complex is an off-white solid which only slowly decomposes in air. It is soluble in benzene, acetone, tetrahydrofuran, and dichloromethane, slightly soluble in hexane, and insoluble in ethanol and water. An aqueous slurry showed no detectable pH change at 25 or 80°. The infrared spectrum of a Nujol mull showed ν_{CO} at 2004 cm^{-1} (s); weak bands at 1949, 1938, and 1919 cm^{-1} probably arise from the phosphite ligands and ν_{Co-H} could not be assigned. The ^1H nmr spectrum in benzene solution showed a quartet Co–H resonance at τ 22.3 with $J_{PH} = 41$ Hz.

When $[(C_6H_5O)_3P]_4CoH$ and CO were allowed to react in toluene solution at 860 atm and 100° for 12 hr or at 11 atm and 100° for 12 hr, $[(C_6H_5O)_3PCo(CO)_3]_2$ was isolated in 50% yield and identified by comparison of its infrared spectrum with that of an authentic sample. No reaction occurred at 900 atm and 25° for 12 hr or at 1 atm and 110° for 16 hr.

Preparation of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$.—In a nitrogen atmosphere, a mixture of 8.0 g (7.3 mmol) of $[(C_6H_5)_3P]_3Ir(CO)H \cdot C_3H_5CH_3$ and 8.5 g (21.4 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ in 175 ml of toluene was refluxed for 10 hr. The initially yellow solution became orange and then red; a gas was slowly evolved. The clear, red solution was concentrated under vacuum to *ca.* 75 ml and the orange-red, crystalline solid which formed was collected and washed with toluene. The crude product was crystallized from 300 ml of toluene to give 2.7 g of red, crystalline solid; an additional 1.8 g was obtained on concentration of the filtrate to *ca.* 75 ml. These two fractions were combined and recrystallized from 120 ml of toluene to give 3.3 g (46%) of orange-red, crystalline $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$, mp 265–270°. *Anal.* Calcd for $C_{52}H_{49}IrP_4$: C, 63.1; H, 5.0; P, 12.5. Found: C, 63.2; H, 5.1; P, 12.4.

The solid complex decomposes after a few minutes of exposure to air and with more rapidity in solution. It has slight to moderate solubility in toluene, tetrahydrofuran, dichloromethane, and acetone and is insoluble in water, hexane, and ethanol.

The infrared spectrum of a Nujol mull showed ν_{Ir-H} at 2016 cm^{-1} (m) in addition to bands characteristic of the phosphine ligand. The ^1H nmr spectrum of a CD_2Cl_2 solution showed the Ir–H resonance as a broad, weak, structureless line at τ 23.0.

The reaction of C_2H_5MgBr with $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrCl$[38,39] in diethyl ether–tetrahydrofuran gave $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$ as the only isolable product. $NaBH_4$ and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrCl$ in ethanol also gave the iridium hydride (from infrared spectrum) but the product was difficult to purify.

Exchange Studies of the Metal Hydride Complexes with D_2.—Round-bottom single-necked glass flasks were calibrated to contain 15 ml when sealed on the 10-mm neck. The flasks were charged in a nitrogen atmosphere with 2.0×10^{-4} mol of the metal hydride complex, 5.0 ml of dry, deoxygenated benzene, and a micro stirring bar. The flasks were cooled in liquid nitrogen and evacuated and then were filled with deuterium to a pressure of 370 mm (*ca.* 2.0×10^{-4} mol). The flasks were sealed and warmed and were either tumbled slowly end over end for 5 days at room temperature or stirred in an oil bath at 100° for 24 hr. The flasks were then stored in Dry Ice until they were opened for analysis.

After the tubes were immersed in liquid nitrogen, the 10-mm necks were inserted in a tube opener and the tubes were opened into an evacuated system. The gases thus obtained were analyzed by mass spectrometry, and infrared spectra were obtained of the residues remaining after solvent removal. The results of these experiments are given in Table I. The results given are

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(35) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 107 (1963).

(36) R. B. King, *Organometal. Syn.*, **1**, 158 (1965).

(37) G. W. Parshall, *J. Inorg. Nucl. Chem.*, **14**, 291 (1960).

(38) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966).

(39) L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

TABLE I

MASS SPECTROMETRIC ANALYSIS OF THE GASEOUS PRODUCTS FROM THE REACTION OF D_2 WITH METAL HYDRIDE COMPLEXES IN C_6H_6

	—25° for 5 days—			—100° for 1 day—		
Complex[a]	D_2	HD	H_2	D_2	HD	H_2
$[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$	76	22	2	66	30	4
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2CoH$	98[f]	2	0	90	10	0
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2RhH$	76[f]	22	2	73	25	2
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$	69[f]	28	3	74	24	2
$[(C_2H_5O)_3P]_4CoH$	90	10	0	64	32	4
$[(C_6H_5O)_3P]_4CoH$	89	11	0	3	24	73
$[(C_6H_5O)_3P]_3Co(CO)H$	94	6	0	7	38	55
$[(C_6H_5)_3P]_3Co(N_2)H$[c]	8[b]	37	53	d	. . .	. . .
$[(C_6H_5)_3P]_3Rh(CO)H$	74	24	2	75[b]	23	2
$[(C_6H_5)_3P]_3Ir(CO)H$	74	24	2	75	23	2
$[(C_6H_5)_3P]_2Ir(CO)Cl_2H$	96[f]	4	0	82	17	1
$[(C_2H_5)_2C_6H_5P]_3RuBr(CO)H$	76	22	2	72	26	2
$[(C_6H_5)_3P]_3Ru(CO)ClH$	62	33	5	13	44	43
$[(C_6H_5)_3P]_3RuClH \cdot C_6H_5CH_3$	1[f]	17	82	2	22	76
$[(C_2H_5)_3P]_2PtClH$	95	5	0	78	21	1
$C_5H_5Mo(CO)_3H$	98	2	0	91	8	1
$(CO)_5MnH$	99[e]	0	0	92[e]	6	2
Blank	99	1	0	99	1	0
Theory for MnH exchange only	44.5	44.5	11	44.5	44.5	11

[a] The original hydride complex and/or the corresponding deuteride was identified by infrared spectroscopy after the reaction period except in the cases noted. [b] The infrared spectrum of the residue indicated extensive decomposition of the original complex. [c] N_2 (2%) was also observed in the recovered gases. [d] Reproducible results were not obtained under these conditions. [e] The complex was not recovered after the reaction. [f] The solution was saturated with the complex under these conditions.

the average of two or more separate experiments that were reproducible to within ±2%. A binomial distribution of H_2, HD, and D_2 was assumed and the fractions of H_2, HD, and D_2 representing complete exchange were calculated from the expressions $[H_2] = x^2$, $[HD] = 2x(1 - x)$, and $[D_2] = (1 - x)^2$ where x is the atom fraction of hydrogen ($^1/_3$) and $1 - x$ is the atom fraction of deuterium ($^2/_3$). Isotope effects due to differences in M–H and M–D bond strengths were disregarded.

Exchange Studies of Metal Hydride Complexes with C_2D_4.—Flasks similar to those used in the D_2 exchange experiments were charged in a nitrogen atmosphere with 2.0×10^{-4} mol of the metal hydride complex, 5.0 ml of dry, deoxygenated benzene, and a micro stirring bar. The flasks were cooled in liquid nitrogen and evacuated, and 2.0×10^{-4} mol of C_2D_4 was condensed in. The flasks were sealed and the mixtures were tumbled at 25° for 5 days or stirred at 100° for 24 hr. The flasks were then stored in Dry Ice until the contents could be analyzed.

The flasks were immersed in liquid nitrogen and opened into an evacuated system. The mixtures were then distilled at 25°; the volatile gases which passed a −78° trap were collected in liquid nitrogen and submitted for mass spectrometric analysis. The mass spectra were analyzed using American Petroleum Institute reference spectra for the various deuterated ethylene and ethane species.

Infrared spectra of the residues remaining in the reaction flasks were obtained. The results of the C_2D_4 exchange experiments are given in Table II. The results given are the average of two or more separate experiments which were reproducible to within ±2%. A binomial distribution of ethylene species was assumed and the fractions of C_2D_4, C_2D_3H, etc., representing complete exchange were calculated from the expressions $[C_2D_4] = x^4$, $[C_2D_3H] = 4x^3(1 - x)$, $[C_2D_2H_2] = 6x^2(1 - x)^2$, $[C_2DH_3] = 4x(1 - x)^3$, and $[C_2H_4] = (1 - x)^4$, where x is the atom fraction of deuterium ($^4/_5$) and $1 - x$ is the atom fraction of hydrogen ($^1/_5$). Isotope effects due to differences in M–H and M–D or C–H and C–D bonds were disregarded.

Nmr Studies of the Reaction of the Metal Hydride Complexes with C_2H_4.—Saturated solutions of the metal hydride complexes in C_6D_6 were prepared in a nitrogen atmosphere. Each solution (0.5 ml) was charged into each of two standard-wall precision nmr tubes and the solutions were degassed on the vacuum line. One tube was sealed and used as a reference; the other tube was charged with *ca.* 50 mm (310 ml) of C_2H_4 and also sealed. All the nmr tubes were pressure tested at 50° for 8 hr and cooled, and nmr spectra were obtained. The tubes were then heated to 100° for 16 hr and cooled, and the spectra were again obtained. External $(CH_3)_4Si$ was used as a reference.

New resonances characteristic of $M–C_2H_5$ groups were observed only for $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$ (τ 9.82, t, J = 7 Hz; τ 8.73, q, J = 7 Hz) at 50° and for $C_5H_5Mo(CO)_3H$ (τ 9.73, t, J = 7 Hz; τ 8.75, q, J = 7 Hz) after heating to 100°. Heating of the $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3–C_2H_4$ solution destroyed the $Ru–C_2H_5$ resonances. All the other complexes listed in Table II exhibited only minor changes in their nmr spectra in the presence of C_2H_4.

Interaction of Metal Hydride Complexes with 1-Butene.—The round-bottom glass flasks described above were charged in a nitrogen atmosphere with 1.2×10^{-4} mol of the metal hydride complex, 3.0 ml of dry, degassed benzene, and a micro stirring bar. The flasks were cooled in liquid nitrogen and evacuated, and 1.2×10^{-3} mol of 1-butene was added. The flasks were sealed and maintained at 25° for 5 days or 100° for 24 hr as before. The reaction mixtures were then stored in Dry Ice until analyzed.

The flasks were immersed in liquid nitrogen and opened into an evacuated system. The mixture was then distilled at 25°; the volatile gases which passed a −78° trap were collected in liquid nitrogen and analyzed by gas chromatography on a 6-ft, 20% ester amide/60–80 mesh Gas-Chrom RA column maintained at 0° using a helium flow rate of 10 cm³/15.0 min and a detector temperature of 50°.

Infrared spectra were obtained of the residues in the reaction flasks. The results of the 1-butene isomerization experiments are given in Table III. The results given in the table are the average of two or more separate experiments which agreed to within ±2%.

Results and Discussion

Synthesis of New Metal Hydride Complexes.—The cobalt hydride complex, $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$, has been prepared from the reaction of water or hydrogen with the solution obtained by the reduction of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoBr_2$ with excess sodium napthalenide. The hydride complex is a yellow, volatile, pyrophoric solid. The presence of the Co–H bond was confirmed by preparation of the corresponding deuteride, by observation of ν_{Co-H} and ν_{Co-D} in the infrared spectra, and by the presence of a quintet Co–H resonance in the high-field ^1H nmr spectrum. Formation of the hydride complex may be explained by the reaction of a cobalt(0) species with hydrogen which is either supplied directly or formed in the reaction of water with the excess sodium naphthalenide. In several attempts to isolate a product from the reduced solutions before addition of water or hydrogen only low yields of the cobalt hydride complex were obtained.

The reduction of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoCl_2$ with sodium napthalenide has previously been reported[40] to produce a cobalt(0) complex, $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2Co$. However, the reported melting point and color of the proposed cobalt(0) complex are similar to those found for the cobalt hydride. It is likely that the product previously identified as a cobalt(0) complex was actually the cobalt hydride species reported here.

The synthesis of $[(C_6H_5O)_3P]_3Co(CO)H$ from $[(C_6H_5O)_3P]_4CoH$ and carbon monoxide completes the

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(40) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 2545 (1962).

TABLE II

MASS SPECTROMETRIC ANALYSIS OF THE C_2 HYDROCARBONS RESULTING FROM THE REACTION OF C_2D_4 WITH METAL HYDRIDE COMPLEXES IN C_6H_6[a]

	25° for 5 days						100° for 1 day					
Complex[b]	C_2D_4	C_2D_3H	$C_2D_2H_2$	C_2DH_3	C_2H_4	Ethanes[c]	C_2D_4	C_2D_3H	$C_2D_2H_2$	C_2DH_3	C_2H_4	Ethanes[c]
$[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$	99[h]	1	...	...	...	...	85	14	1	...	...	...
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2CoH$	100	...	...	...	...	...	95	5	...	...	...	...
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2RhH$	56[h]	34	9	1	...	...	42	40	15	3	...	2
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$	98	2	...	...	...	...	87	13	...	...	...	...
$[(C_2H_5O)_3P]_4CoH$	97	3	...	...	...	...	62	31	6	1	...	...
$[(C_6H_5O)_3P]_4CoH$	96	4	...	...	...	...	9	22	30	39	...[d]	3–8
$[(C_6H_5O)_3P]_3Co(CO)H$	98	2	...	...	...	...	9	22	29	38	2[d]	3–10
$[(C_6H_5)_3P]_3Co(N_2)H$	13[e]	20	29	23	14	3–10	*f*	...	...	...	...	...
$[(C_6H_5)_3P]_3Rh(CO)H$	53[e]	38	8	1	...	1–4	48[e]	40	9	3	...	3–10
$[(C_6H_5)_3P]_3Ir(CO)H$	48	39	12	1	...	5	39	41	17	3	...	1–3
$[(C_6H_5)_3P]_2Ir(CO)Cl_2H$	100[h]	...	...	...	...	...	98[h]	2	...	...	...	...
$[(C_2H_5)_2C_6H_5P]_3Ru(CO)BrH$	77	21	2	...	...	...	41	40	16	3	...	1
$[(C_6H_5)_3P]_3Ru(CO)ClH$	48	38	12	2	...	...	20	34	26	20	...[d]	5–20
$[(C_6H_5)_3P]_3RuClH \cdot C_6H_5CH_3$	2[h]	3	9	32	54	1–3	7	19	29	45	...[d]	5–20
$[(C_2H_5)_3P]_2PtClH$	100	...	...	...	...	...	98	2	...	...	...	...
$C_5H_5Mo(CO)_3H$	100	...	...	...	...	...	*f*	...	...	...	...	...
$(CO)_5MnH$[g]	100	...	...	...	...	...	53	38	9	...	...	6
Blank	100	...	...	...	...	...	100	...	...	...	...	...
Theory for complete M–H exchange	41	41	15	3	0	0	41	41	15	3	0	0

[a] Reference patterns were obtained both from these laboratories and from the American Petroleum Institute. [b] The original hydride complex and/or the corresponding deuteride was identified by infrared spectroscopy after the reaction period except in the cases noted. [c] These values are less accurate than those for the ethylene species due to overlap of the fragmentation patterns and represent the amount of ethane present relative to the total amount of ethylene; all ethanes except C_2DH_5 and C_2H_6 were detected. [d] These low values for C_2H_4 are best explained by inaccuracies introduced by overlap of the fragmentation patterns of the deuterated ethanes. [e] The infrared spectrum of the residue indicated extensive decomposition of the original complex. [f] Reproducible results were not obtained under these conditions. [g] The complex was not recovered after the reaction. [h] The solution was saturated with the complex under these conditions.

TABLE III

GAS CHROMATOGRAPHIC ANALYSIS OF THE C_4 HYDROCARBONS RESULTING FROM THE REACTION OF 1-BUTENE WITH METAL HYDRIDE COMPLEXES IN C_6H_6

	25° for 5 days				100° for 1 day			
Complex[a]	*n*-C_4H_{10}	1-C_4H_8	*trans*-2-C_4H_8	*cis*-2-C_4H_8	*n*-C_4H_{10}	1-C_4H_8	*trans*-2-C_4H_8	*cis*-2-C_4H_8
$[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2CoH$	...	99.9+	...	...	0.2	90.8	4.3	4.7
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2CoH$	...[e]	99.7	...	0.3	...	92.2	3.3	4.5
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2RhH$	...[e]	99.8	...	0.2	0.2	87.3	5.6	6.9
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$	...[e]	98.4	1.0	0.6	...	92.9	3.4	3.7
$[(C_2H_5O)_3P]_4CoH$	...	96.2	2.1	1.7	...	29.1	33.5	37.4
$[(C_6H_5O)_3P]_4CoH$	0.1	99.9	...	...	6.2	27.1	32.1	34.6
$[(C_6H_5O)_3P]_3Co(CO)H$	0.1	99.4	0.3	0.2	4.0	45.2	25.2	25.6
$[(C_6H_5)_3P]_3Co(N_2)H$	1.2[b]	2.8	66.9	29.1	*c*	...	...	...
$[(C_6H_5)_3P]_3Rh(CO)H$	0.4[b]	2.8	68.2	28.6	0.2[b]	6.1	60.3	33.4
$[(C_6H_5)_3P]_3Ir(CO)H$	0.7	97.9	0.8	0.6	0.8	9.4	45.4	44.4
$[(C_6H_5)_3P]_2Ir(CO)Cl_2H$	...[e]	99.9+	...	...	...[e]	97.3	1.2	1.5
$[(C_2H_5)_2C_6H_5P]_3Ru(CO)BrH$	...	65.1	16.6	18.3	...	6.0	62.1	31.9
$[(C_6H_5)_3P]_3Ru(CO)ClH$	...	2.9	68.5	28.6	1.9	4.5	62.9	30.7
$[(C_6H_5)_3P]_3RuClH \cdot C_6H_5CH_3$	...[e]	2.8	66.7	30.5	1.8	5.8	61.1	31.3
$[(C_2H_5)_3P]_2PtClH$	...	99.9+	...	...	...	99.8	...	0.2
$C_5H_5Mo(CO)_3H$	...	98.1	1.7	0.2	*c*	...	...	...
$(CO)_5MnH$[d]	...	99.9+	...	...	*c*	...	...	...
Blank	...	99.9+	...	...	...	99.9+	...	...

[a] The original hydride complex and/or the corresponding deuteride was identified by infrared spectroscopy after the reaction period except in the cases noted. [b] The infrared spectrum of the residue indicated extensive decomposition of the original complex. [c] Reproducible results were not obtained under these conditions. [d] The complex was not recovered after the reaction. [e] The solution was saturated with the complex under these conditions.

series of compounds $[(C_6H_5O)_3P]_nCo(CO)_{4-n}H$ (n = 0,[3] 1,[3] 2,[41] 3, 4[27,28]), and its stability and lack of acidity are consistent with the trend previously noted.[3,41] Although ν_{Co-H} was not observed, the appearance of a quartet resonance in the high-field ^1H nmr spectrum confirms the presence of the Co–H bond. The iridium complex $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$ was prepared by the reaction of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with $[(C_6H_5)_3P]_3Ir(CO)H$ and is characterized as a hydride on the basis of its characteristic infrared and ^1H nmr spectra. The complex is similar in stability to the Co and Rh analogs.[24]

Reaction of Metal Hydride Complexes with Deu-

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(41) W. Hieber and H. Duchatsch, *Chem. Ber.*, **98**, 2933 (1965).

terium.—The results of the mass spectrometric analysis of the gaseous products from the reaction of the various metal hydride complexes with deuterium are summarized in Table I. The presence of H_2 and HD in the recovered gases indicates the exchange of the metal–hydrogen bonds with deuterium. Since it was not determined if the data represent equilibrium values, only broad comparisons of relative activities are valid.

Although the extent of exchange varied significantly with the nature of the complex and the conditions, no clear correlations of activity with ligand type or metal are apparent. The degree of exchange more clearly reflects the relative ease of the various metal hydride reactants to undergo oxidative addition[22,23] to give MHD_2 intermediates[20,23] and is not directly related to the reactivity of the original metal–hydrogen bonds.

In previous studies[20] of deuterium exchange with $[(C_6H_5)_3P]_3Ir(CO)H$ and $[(C_6H_5)_3P]_3MHCl(CO)$ (M = Ru, Os), formation of the seven- and eight-coordinate intermediates $[(C_6H_5)_3P]_3Ir(CO)HD_2$ and $[(C_6H_5)_3P]_3M(CO)ClHD_2$, respectively, was postulated. However, ligand dissociation is likely to be an important processs especially at higher temperatures and the higher coordination numbers for the MHD_2 intermediates are not essential. Exchange with the five-coordinate chelated complexes (Table I) is more likely to occur through seven-coordinate $(PP)_2MHD_2$ intermediates. In the series $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2MH$, the degree of deuterium exchange increases in the order M = Co < Rh < Ir which is the order expected for the ease of formation of seven-coordinate intermediates.

The deuterium exchange results (Table I) show that in some cases the amounts of H_2 and HD observed are higher than the theoretical values calculated for complete exchange of the original M–H bond. Complexes which exhibited this behavior are $[(C_6H_5O)_3P]_4CoH$, $[(C_6H_5O)_3P]_3Co(CO)H$, $[(C_6H_5)_3P]_3Co(N_2)H$, $[(C_6H_5)_3P]_3RuHCl(CO)$, and $[(C_6H_5)_3P]_3RuHCl\cdot C_6H_5CH_3$. The excess hydrogen appearing in these systems results from a ligand-to-metal hydrogen-transfer process involving oxidative addition of an ortho-phenyl carbon–hydrogen bond to the metal. Details of the study of the ligand–metal hydrogen-transfer reaction in these and related systems have been described elsewhere.[42–44] The occurrence of ligand–metal hydrogen transfer with the other complexes exhibiting exchange with deuterium and having ligand hydrogen atoms cannot be excluded on the basis of the data obtained. Exchange with the solvent is also possible but has been excluded for $[(C_6H_5O)_3P]_4CoH$ and $[(C_6H_5)_3P]_3RuHCl$ under comparable conditions.[45]

Reaction of Metal Hydride Complexes with C_2D_4 and C_2H_4.—The results of the mass spectroscopic analysis of the C_2 hydrocarbons recovered from the reaction of the various metal hydride complexes with C_2D_4 are summarized in Table II. The appearance of hydrogen-containing ethylene species (C_2D_3H, $C_2D_2H_2$, etc.) indicates the occurrence of a reversible interaction between the M–H bond of the complex and C_2D_4 to give an intermediate metal–ethyl complex.[15]

The exchange studies with C_2D_4 provide a sensitive probe for detecting the interaction of M–H bonds with ethylene and are especially useful for those systems which do not form stable ethyl derivatives under ordinary conditions. For example, the reaction of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrCl$ with C_2H_5MgBr gives the hydride complex $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2IrH$ as the only isolable product. Additionally, ^1H nmr studies of solutions of the hydride complex and C_2H_4 gave no evidence for the formation of an ethyl complex. However, the exchange results of the reaction of the hydride with C_2D_4 show that exchange occurs at 100° and that an unstable iridium–ethyl derivative must be present under these conditions.

The observed lack of exchange with C_2D_4 for some of the complexes (Table II) at 25° may be explained by assuming either no reaction or an *irreversible* reaction giving a stable ethyl derivative. The former postulate seems preferable for those complexes which showed some exchange activity at 100° while the latter may better explain the results for $C_5H_5Mo(CO)_3H$. In this case, ^1H nmr studies of solutions of the hydride complex and C_2H_4 showed the formation of the ethyl complex at 100° while thermal decomposition[16] of $C_5H_5Mo(CO)_3C_2H_5$ did not produce C_2H_4, indicating the irreversibility of the reaction. The C_2D_4 exchange experiments at 100° indicated some exchange but the results were not reproducible, presumably because of thermal decomposition of the molybdenum hydride complex.

For certain hydride complexes, reduction of ethylene to ethane was a competitive but slow process in the C_2D_4 exchange studies, and evidence was obtained (Table II) for the presence of all possible ethanes except C_2DH_5 and C_2H_6. For example, at 100° $[(C_6H_5O)_3P]_4CoH$ produced *ca.* 6% of mixed ethanes. The reaction of $(CO)_5MnH$ and C_2D_4 produced *ca.* 6% ethanes at 100° but extensive MnH–C_2D_4 exchange also occurred; such exchange with $Mn(CO)_5H$ had not been observed in previous studies.[17] The ethane species could arise either from thermal decomposition of the hydride complexes to give H_2 followed by an "ordinary" hydrogenation of ethylene or, in the case of those complexes containing aryl phosphite or arylphosphine ligands, from a ligand–metal hydrogen-transfer process as described below.

Reaction of Metal Hydride Complexes with 1-Butene.—The gas chromatographic analyses of the C_4 hydrocarbons recovered from the reaction of the metal hydride complexes with 1-butene are summarized in Table III. A comparison of these results with those obtained for C_2D_4 exchange (Table II) shows that the activity of the metal hydride complexes toward isomerization of 1-butene generally parallels that of exchange with C_2D_4. Exceptions to this behavior were observed for $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2RhH$ at 25 or 100° and for $[(C_6H_5)_3P]_3Ir(CO)H$ at 25°; both complexes ex-

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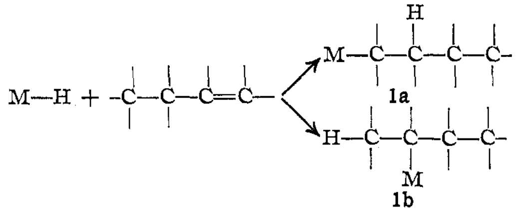
[42] G. W. Parshall, *J. Amer. Chem. Soc.*, **90**, 1669 (1968).

[43] W. H. Knoth and R. A. Schunn, *ibid.*, **91**, 2400 (1969).

[44] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *ibid.*, **91**, 4990 (1969).

[45] E. K. Barefield, private communication.

hibited extensive exchange with C_2D_4 but were poor isomerization catalysts for 1-butene under these conditions. Assuming that isomerization occurs through an insertion–elimination mechanism,[7] these results imply that under conditions where olefin insertion into the M–H bond is favorable (*cf.* C_2D_4 results), either a preferred addition of the M–H bond to 1-butene to give an *n*-butyl–M intermediate (**1a**) or the preferred abstraction of a primary hydrogen in a *sec*-butyl–M intermediate (**1b**) occurs. Neither of these processes would result in isomerization.[18]

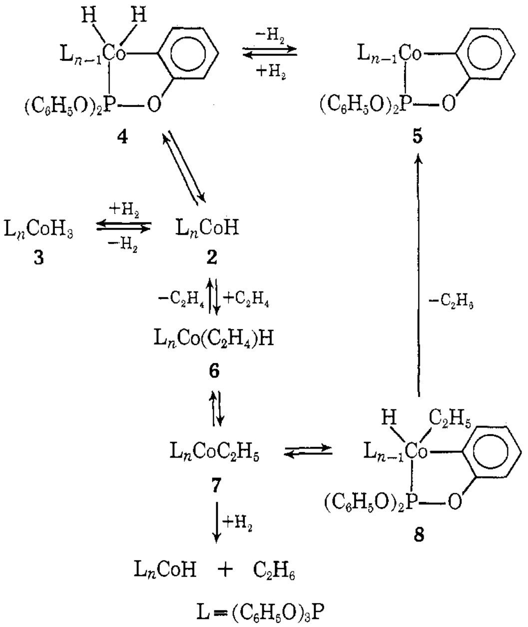


Although the activity of the metal hydride complexes toward isomerization or C_2D_4 exchange varies greatly with the nature of the complex, no clear correlation of activity with ligand type or metal is apparent. The rate-determining step in the exchange or isomerization reactions may be the coordination of the olefin and in some cases this may require prior ligand dissociation. Reduction of the butenes to *n*-butane was also observed and the results generally parallel those obtained in the C_2D_4 exchange experiments.

Ligand–Metal Hydrogen Transfer in the Hydrogenation of Olefins.—The results of the exchange studies with C_2D_4 (Table II) show that the percentages of hydrogen-containing ethylenes (C_2D_3H, $C_2D_2H_2$, C_2DH_3, and C_2H_4) are in some cases much higher than the theoretical values calculated for exchange of the metal–hydrogen bond only. A ligand–metal hydrogen-transfer process similar to that observed in the deuterium exchange studies is very likely also involved in these C_2D_4 exchange reactions. The complexes which exhibited ligand–metal hydrogen transfer in the deuterium and C_2D_4 exchange experiments also catalyze the isomerization of 1-butene and the formation of alkanes.

Scheme I which explains the results reported here for D_2 and C_2D_4 exchange including ligand–metal hydrogen transfer is shown below for $[(C_6H_5O)_3P]_4CoH$. The value of *n*, the number of coordinated phosphite ligands, appears to be less than 4 since the addition of excess triphenyl phosphite inhibits the ligand–metal hydrogen-transfer process with deuterium.[44] The equilibrium **2** → **3** represents the normal, oxidative addition process[20,23] for exchange of a metal–hydrogen bond with hydrogen. The sequence of equilibria **2** ⇄ **4** and **4** ⇄ **5** combined with **2** ⇄ **3** results in exchange of the ortho-phenyl hydrogen atoms of the coordinated phosphite ligands.[44] Combination of the equilibria **2** ⇄ **6** and **6** ⇄ **7** represents the coordination and insertion of the olefin into the metal–hydrogen bond. A combination of the steps **2** ⇄ **6**, **6** ⇄ **7**, and **2** ⇄ **4** is sufficient to account for exchange of the ortho-phenyl hydrogen atoms in the reactions of the metal hydrides with C_2D_4. If some of the metal hydride complex has decomposed to give hydrogen, **7** may react irreversibly to give C_2H_6.

SCHEME I



An alternate process for ligand–metal hydrogen transfer in the C_2D_4 exchange reactions results from the equilibrium **7** ⇄ **8**. The irreversible reaction **8** ⇄ **5** would then account for the formation of ethanes. The two steps **7** → **8** and **8** → **5** have been previously postulated[46] in the conversion of $[(C_6H_5)_3P]_3RhCH_3$ to $[(C_6H_5)_3P]_2(C_6H_5)_2\overline{PC_6H_4Rh}$ and CH_4. An ortho-phenyl-bonded ruthenium phosphite complex analogous to **5**, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$, has also recently been described.[44]

An alternate mechanism for the hydrogenation of olefins which includes ligand–metal hydrogen transfer is thus possible. The sequence of steps **2** → **6** → **7** → **8** → **5** → **4** → **2** represents such a process and cannot *a priori* be eliminated from any hydrogenation process involving aryl phosphite or arylphosphine ligands.

This sequence of steps could also explain the hydrogenation of olefins by phosphine or phosphite complexes in the absence of hydrogen, *e.g.*, methyl linoleate by $[(C_6H_5)_3P]_2NiBr_2$.[47] It seems likely that under conditions in which the ligand–metal hydrogen-transfer process is operative, all the steps shown occur. However, the results of this work do not permit an assignment of the relative rates or equilibrium constants of the various steps.

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[46] W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

[47] H. Itatani and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 1600 (1967).