Competitive Cyclocarbonylation of 5c and 3c. A mixture consisting of 0.022 g (0.122 mmol) of $PdCl_2$, 0.024 g (0.128 mmol) of anhydrous $SnCl_2$, 0.065 g (0.246 mmol) of $(C_6H_5)_3P$, and 0.138 g (1.08 mmol) of naphthalene internal standard in 15 mL of acetonitrile was stirred 1.5 h at 65 °C under 70 psi of CO. To this was added 0.117 g (1.06 mmol) of **5c** and 0.165 g (1.50 mmol) of **3c**, and the CO pressure was restored. Aliquots were periodically analyzed by GLC (column C). Relative rates $k_{obsd}(cis)/k_{obsd}(trans)$ were obtained from

$$\frac{k_{obsd}(cis)}{k_{obsd}(trans)} = \frac{\Delta 5c/[5c]_{t=0}}{\Delta 3c/[3c]_{t=0}} = \frac{(\%\text{ yield of trans})\Delta 6c/[5c]_{t=0}}{(\%\text{ yield of cis})\Delta 4c/[3c]_{t=0}}$$

over four time intervals within the first 3 h of reaction; $k_{obsd}(cis)/k_{obsd}(trans) = 1.01 \pm 0.10$ from eight determinations. After 5 h the yield of *cis*-**6c** was 63% and that of *trans*-**4c** 32%.

Acknowledgment. We thank Hoffmann-LaRoche for Microanalytical services and Johnson Matthey, Inc., for a generous loan of $PdCl_2$. We are grateful to Professor J. Schwartz for the use of his liquid chromatography apparatus, to Professor A. I. Meyers for valuable advice on the epimerization of configuration of *trans*-2-ethynylcyclopentyl tosylate, and to J. C. Wojak for her work on the confirmation of the structure of the 4-methylene-2-oxabicyclo[3.3.0]octan-3-ones. This investigation was supported (at Princeton) by Grant No. CA 18546 and by training grants (T.M. and V.V.) awarded by the National Cancer Institute, HEW, and (at Colorado State) by NSF Grant No. CHE 79-20373 and by the Colorado State University Regional NMR Center, funded by NSF Grant No. CHE 78-18581.

Anionic Metal Hydride Catalysts. 1. Synthesis of Potassium Hydrido(phosphine)ruthenate Complexes

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Abstract: The potassium hydrido(phosphine)ruthenate complexes $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (**1**) and $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3$ (**2**) were prepared for study as possible homogeneous catalysts for the catalytic hydrogenation of polar organic substrates. Complex **1** was prepared by reaction of $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$ (1 mol) with potassium naphthalene (2 mol) at −80 to −111 °C in tetrahydrofuran (THF). It was isolated as a yellow crystalline solid from solutions in diethyl ether and in the presence of excess naphthalene ($C_{10}H_8$). The complex was characterized by a combination of chemical and spectral techniques and single-crystal X-ray crystallography. The complex crystallizes in space group $P\bar{1}$ with $a = 15.603$ (6) Å, $b = 15.974$ (4) Å, $c = 23.774$ (8) Å, $\alpha = 90.69$ (2)°, $\beta = 102.96$ (3)°, $\gamma = 106.51$ (3)°, and contains four formula units of **1** in the unit cell. In the asymmetric unit there are two different molecules of **1**: consisting of two $[(Ph_3P)_2Ph_2\overline{PC_6H_4}RuH_2]^-$, ruthenate anions, associated potassium (counterions), and also diethyl ether and naphthalene as molecules of crystallization. In the ruthenate anions there is a distorted octahedral arrangement of two triphenylphosphine and one ortho-metalated triphenylphosphine ligands around ruthenium. Two hydride atoms (not located by the crystallography) are assumed to occupy the remaining pseudooctahedral positions. The presence of the hydride atoms was shown by infrared spectra ($\nu_{Ru-H} = 1735, 1825\ cm^{-1}$), ^1H NMR spectra ($\delta_{(CH_3)_4Si} = -7, -11$), and the reactions of **1** with HCl and CH_3I to give respectively H_2 (2.0 mol/mol of **1**) and CH_4 (2.4 mol/mol of **1**)). The second hydrido(phosphine)ruthenate complex **2** was prepared by the analogous potassium naphthalene reduction of $[(Ph_3P)_2RuHCl]_2\cdot 2$toluene. The composition of **2** as obtained by crystallization from toluene/diglyme ($C_6H_{14}O_3$) was established from ^1H and ^{31}P NMR spectra and its chemical reactivity with HCl to yield H_2 (~2 mol/mol of Ru) and a tris(triphenylphosphine)(diphenylphosphine)diruthenium chloride complex.

In recent years a wide variety of homogeneous catalysts have been developed for the hydrogenation of organic substrates.[1c] The transition-metal phosphine complexes, for example, $(Ph_3P)_3RhCl$, $(Ph_3P)_3RuHCl$,[2] $[Ir(COD)(PMePh_2)_2]PF_6$[3] are highly effective catalysts for the hydrogenation of olefins to alkanes. In contrast there are relatively few homogeneous catalysts for the hydrogenation of polar unsaturated compounds such as aldehydes, ketones, and nitriles.[4]

In this work we sought to prepare a class of soluble metal catalysts which would be widely applicable to the hydrogenation of polar organic functional groups. Main-group metal hydrides (e.g., $LiAlH_4$ and various borohydrides) are widely used for the stoichiometric reduction of ketones, nitriles, etc.[5] We felt that certain formally analogous, anionic transition-metal hydride complexes of formula $A^+[L_nM-H_x]^-$ might be prepared which could act as catalytic hydride-transfer agents, the overall reduction being effected by hydrogen gas in equilibrium with the complex. To this end we attempted the synthesis of several such hydridometalate complexes wherein A^+ is an alkali-metal cation, M is a group 8 metal, and L a tertiary phosphine ligand.

Transition-metal hydride complexes can range from predominantly acidic ($L_nM^{\delta-}-H^{\delta+}$) to hydridic ($L_nM^{\delta+}-H^{\delta-}$) in character, depending on the nature of the metal atom and the charge-transfer characteristics of the complementary ligands.[6] The anionic

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(6) (a) Metal carbonyl hydrides, e.g., $HCo(CO)_4$ and $H_2Fe(CO)_4$, behave as acids in aqueous solution. Hydridic behavior (e.g., liberation of H_2 from alcohols) is most commonly seen in early transition-metal hydrides, e.g., $C_5(CH_3)_5ZrH_2$. See: (a) Schunn, R. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed; Marcel Dekker: New York, 1971; pp 203–269 and references cited therein. (b) Labinger, J. A.; Kawadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25–C28.

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formulation was chosen here in order to achieve the maximum hydridic character and nucleophilicity of the hydride ligand atoms. Ruthenium and rhodium were considered as the preferred central metal atoms because of the inherent capacity of their complexes to reversibly interact with polar organic substrates.[7] Tertiary phosphines which have minimal electron-withdrawing properties (in comparison to, e.g., carbonyls[8]) were used, as ligands.

This paper describes the synthesis characterization and basic chemical properties of the potassium hydrido(phosphine)ruthenate complexes $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (**1**) and $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3$ (**2**). The application of these and related complexes to the hydrogenation of polar organic compounds is discussed in the following paper.[9] The application of **1** to the selective hydrogenation of polynuclear aromatics (which appears to be unrelated to its anionic character) has been published elsewhere.[10] Preliminary accounts of some of this work have appeared.[11,12]

Results and Discussion

Preparation of Hydridometalate Complexes. Hydridometalates containing strongly π-acid ligands, e.g., sodium hydridotetracarbonylferrate, $Na^+[HFe(CO)_4]^-$,[6a] and sodium hydridopentacyanocobaltate, $Na_3^+[HCo(CN)_5]^{3-}$,[13] are well-known. The electronegative ligands tend to stabilize the complex anion species; hydridometalates containing only weakly π-acceptor ligands are relatively rare. Octahydro(tertiary phosphine)rhenates, for example, $Et_4N^+[ReH_8(Ph_3P)]^-$, have been prepared and studied by Ginsberg.[14] The ternary hydrides K_2TcH_9,[15] K_2ReH_9,[16] Li_4RhH_4, Sr_2RuH_6, Sr_2RhH_5, etc.,[17] containing hydrogen as the only electronegative ligand, are known. Lithium-transition-metal complexes $[(\eta\text{-}C_5H_5)_2Mo(H)Li]_4$,[18] $(\eta\text{-}C_5H_5)(C_5H_5)Ti(H)Li$,[19] $(COD)_{1.5}NiLi_2H_2(THF)_x$,[20] and $RuH(Me)(PPh_3)_2(MeLiOEt_2)_2$,[21] which could chemically react as anionic hydrides, are known. In the reduction of $(Ph_3P)_3CoH(N_2)$ with sodium naphthalene, the formation of a hydridodinitrogencobaltate species is indicated.[22] Chatt and Davidson[23] reported that the reaction of *trans*-[Ru(PP)$_2$HBr] (PP = 1,2-bis(dimethylphosphino)ethane) with 2 equiv of sodium naphthalene gives the sodium hydridobis(1,2-bis(dimethylphosphino)ethane)ruthenate(1−) salt, $Na^+[Ru(PP)_2H]^-$, identified (apparently in situ) by its reaction with D_2O to yield *cis*-[Ru(PP)$_2$DH]. No other chemical properties or further characterization data for $Na^+[Ru(PP)_2H]^-$ were given.

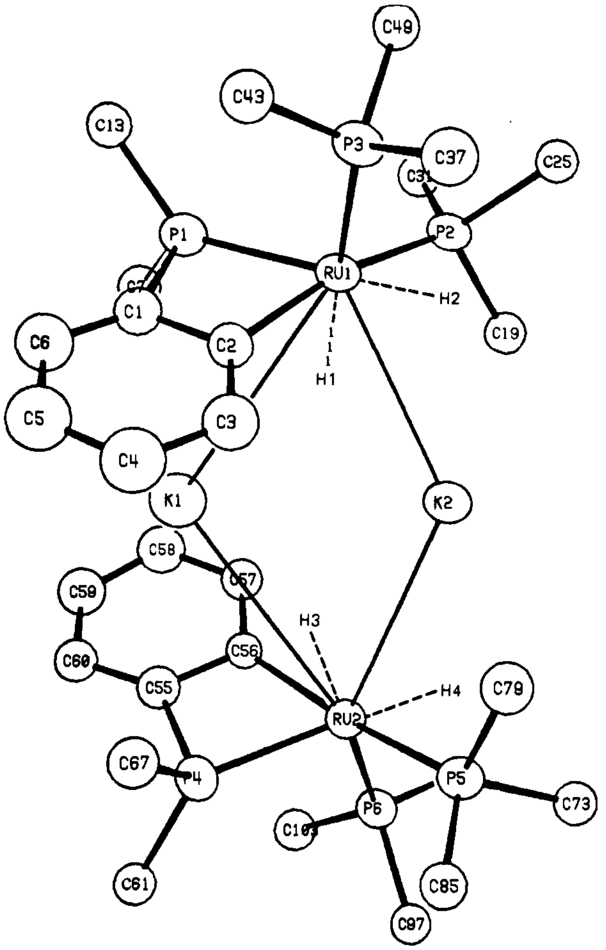

Figure 1. Structure of the two, $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-$, potassium hydridoruthenate molecules in the asymmetric unit of 1. For clarity, the phenyl (C_6H_5) rings of the triphenylphosphine ligands are not shown. The hydrogen atoms H1 and H2 were not located by the X-ray work (see text).

This report by Chatt and Davidson suggested that hydrido(phosphine)ruthenates could indeed by prepared, but since we were primarily interested in obtaining highly catalytically active compounds, we felt it important to synthesize hydrido(phosphine)ruthenates having less than four phosphorus ligand atoms per ruthenium. We accordingly attempted the syntheses of tris(triphenylphosphine) and bis(triphenylphosphine) hydridoruthenates by the reduction of $(Ph_3P)_3RuHCl$[2,24] and $[(Ph_3P)_2RuHCl]_2$,[25a] respectively.

Preparation of $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (1). The title complex was prepared by the slow addition of a solution of potassium naphthalene to a suspension of $(Ph_3P)_3RuHCl$ in tetrahydrofuran (THF) cooled to from −80 to −111 °C (see eq 1). The product **1** was isolated after suitable

$$(Ph_3P)_3RuHCl + 2K^+C_{10}H_8^- \xrightarrow{THF,\ Et_2O} 1 + KCl \qquad (1)$$

workup, as a bright yellow powder. This material is sufficiently pure for most purposes; however, crystalline samples of **1** were prepared by slow evaporation of solutions in diethyl ether in the presence of excess naphthalene. The composition of **1** was established from elemental analyses and chemical reactivity studies, ^{31}P and ^{1}H NMR spectra, and single-crystal X-ray crystallography.[25b]

Crystal and Molecular Structure of 1. The complex was isolated from solutions in diethyl ether, as bright yellow prisms. The

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[7] As shown, for example, by their reported catalytic activity in reactions involving ketones, aldehydes, etc.,[9] in contrast to the behavior of early transition-metal systems (e.g., Ti, Zr, metallocenes) which react irreversibly with such substrates to yield alkoxides.[6b]

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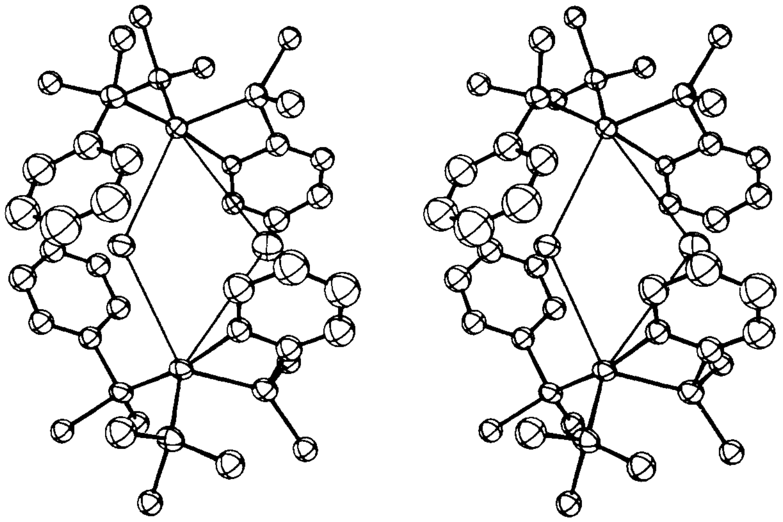

Figure 2. Stereoscopic view of the two $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-$ molecules in the asymmetric unit of 1. For clarity, only the phenyl and phenylene rings close to the potassium atoms are shown.

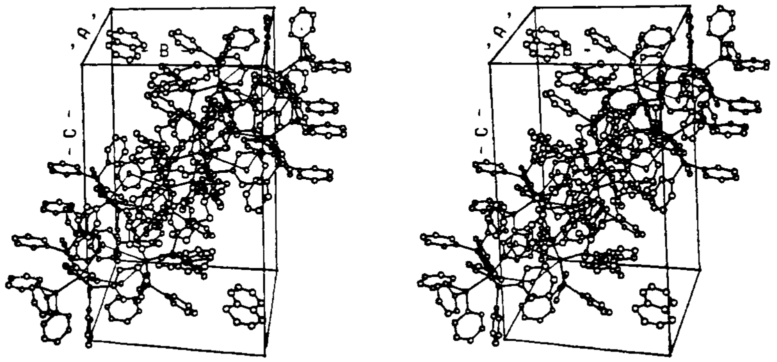

Figure 3. Stereoscopic view showing the full unit cell, containing four molecules of $K^+[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (**1**).

crystals were found to be triclinic of space group $P\bar{1}$ and containing four molecules of $C_{68}H_{64}OP_3RuK$ (**1**) per unit cell.

Crystals of **1** contain in the asymmetric unit two separate molecules of the potassium hydrido(phosphine)ruthenate complex, $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-$ (see Figures 1 and 2). The asymmetric unit in **1** contains, in addition, two molecules of naphthalene and two molecules of diethyl ether. These are not directly bonded to any atoms of the ruthenate complex and may essentially be regarded as molecules of crystallization. Their spatial relationship to the metal complex is seen in the stereoscopic projection of the full unit cell shown in Figure 3. Selected bond lengths and bond angles data for **1** are listed in Tables I and II.

The ruthenate anion, $[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-$, consists of a central, formally divalent ruthenium coordinated by two triphenylphosphine and one ortho-metalated triphenylphosphine ligands. The two hydrides were not located by the X-ray work but are most likely trans to P1 and P3 (and P4 and P6) (vide infra). With the hydride atoms in these positions, the overall coordination may be described as that of a distorted octahedral arrangement of phosphorus, phenyl carbon, and hydride ligand atoms around ruthenium. The Ru–P bond lengths in **1** range from 2.302 (3) to 2.351 (3) Å; the shorter lengths (2.302 (3) and 2.320 (3) Å) are of the Ru–P linkages, approximately trans to the phenyl–ruthenium bonds. These distances are intermediate between Ru–P lengths found in $(Ph_3P)_3RuCl_2$ (2.230 (8), 2.374 (6), 2.412 Å),[26] $(Ph_3P)_3RuHCl$ (2.206 (4), 2.329, 2.361 Å),[27] and $(Ph_3P)_2Ru(styrene)_2$ (2.216 (4), 2.411 (9) Å).[28]

Table I. Selected Bond Distances (Å) for 1

K1	K2	3.857 (4)	Ru2	P4	2.339 (3)
K1	Ru1	4.034 (3)	Ru2	P5	2.320 (3)
K1	Ru2	4.078 (3)	Ru2	P6	2.350 (3)
K2	Ru1	3.617 (3)	Ru2	C56	2.069 (10)
K2	Ru2	3.673 (3)	P4	C55	1.837 (11)
Ru1	P1	2.347 (3)	P4	C61	1.848 (11)
Ru1	P2	2.302 (3)	P4	C67	1.848 (12)
Ru1	P3	2.351 (3)	P5	C73	1.852 (12)
Ru1	C2	2.098 (11)	P5	C79	1.904 (13)
P1	C1	1.810 (12)	P5	C85	1.843 (12)
P1	C7	1.851 (11)	P6	C91	1.839 (12)
P1	C13	1.858 (11)	P6	C97	1.843 (11)
P2	C19	1.850 (11)	P6	C103	1.874 (11)
P2	C25	1.896 (11)	C55	C56	1.405 (14)
P2	C31	1.863 (11)	C55	C60	1.401 (15)
P3	C37	1.844 (13)	C56	C57	1.423 (14)
P3	C43	1.860 (12)	C57	C58	1.430 (15)
P3	C49	1.847 (12)	C58	C59	1.41 (2)
C1	C2	1.425 (15)	C59	C60	1.385 (15)
C1	C6	1.40 (2)	mean C_6H_5 (C–C) C61 to C108		1.405 ± 0.019
C2	C3	1.413 (15)			
C3	C4	1.43 (2)			
C4	C5	1.43 (2)			
C5	C6	1.40 (2)			
mean C_6H_5 (C–C) C7 to C54		1.407 ± 0.018			

In the ruthenate anion, the ortho-metalation is of particular interest since although the phenomenon is of wide occurrence, few complexes containing cyclometalated phosphines have been studied by X-ray crystallography. The ortho-metalated phenyl ring systems in **1** involving Ru1, P1, C1, C2 and Ru2, P4, C55, C56 in the two separate ruthenate anions are essentially planar. Equations describing the weighted least-squares planes for the

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Table II. Selected Bond Angles (Deg) for 1

K2	K1	Ru1	54.51 (6)	K1	Ru2	K2	59.41 (6)
K2	K1	Ru2	55.07 (6)	K1	Ru2	P4	71.96 (9)
Ru1	K1	Ru2	109.47 (7)	K1	Ru2	P5	122.16 (9)
K1	K2	Ru1	65.24 (6)	K1	Ru2	P6	139.83 (9)
K1	K2	Ru2	65.52 (6)	K1	Ru2	C56	45.3 (3)
Ru1	K2	Ru2	130.61 (8)	K2	Ru2	P4	125.44 (9)
K1	Ru1	K2	60.25 (6)	K2	Ru2	P5	78.03 (9)
K1	Ru1	P1	67.01 (9)	K2	Ru2	P6	134.36 (9)
K1	Ru1	P2	119.93 (9)	K2	Ru2	C56	92.0 (3)
K1	Ru1	P3	140.4 (1)	P4	Ru2	P5	112.2 (1)
K1	Ru1	C2	47.1 (3)	P4	Ru2	P6	98.5 (1)
K2	Ru1	P1	125.41 (9)	P4	Ru2	C56	67.4 (3)
K2	Ru1	P2	82.98 (9)	P5	Ru2	P6	97.8 (1)
K2	Ru1	P3	131.99 (9)	P5	Ru2	C56	167.4 (3)
K2	Ru1	C2	85.8 (3)	P6	Ru2	C56	94.7 (3)
P1	Ru1	P2	113.5 (1)	Ru2	P4	C55	85.6 (4)
P1	Ru1	P3	97.7 (1)	Ru2	P4	C61	133.0 (4)
P1	Ru1	C2	67.6 (3)	Ru2	P4	C67	121.7 (4)
P2	Ru1	P3	99.7 (1)	C55	P4	C61	105.6 (5)
P2	Ru1	C2	166.4 (3)	C55	P4	C67	107.5 (5)
P3	Ru1	C2	93.4 (3)	C61	P4	C67	98.6 (5)
Ru1	P1	C1	85.9 (4)	Ru2	P5	C73	119.0 (4)
Ru1	P1	C7	120.9 (4)	Ru2	P5	C79	114.0 (4)
Ru1	P1	C13	135.1 (4)	Ru2	P5	C85	122.9 (4)
C1	P1	C7	104.9 (5)	C73	P5	C79	97.0 (5)
C1	P1	C13	109.0 (5)	C73	P5	C85	101.2 (5)
C7	P1	C13	96.6 (5)	C79	P5	C85	97.9 (5)
Ru1	P2	C19	110.7 (4)	Ru2	P6	C91	119.9 (4)
Ru1	P2	C25	121.0 (4)	Ru2	P6	C97	114.8 (4)
Ru1	P2	C31	123.0 (4)	Ru2	P6	C103	122.5 (4)
C19	P2	C25	98.8 (5)	C91	P6	C97	102.2 (5)
C19	P2	C31	99.6 (5)	C91	P6	C103	93.7 (5)
C25	P2	C31	99.3 (5)	C97	P6	C103	99.6 (5)
Ru1	P3	C37	120.1 (4)	P4	C55	C56	97.7 (8)
Ru1	P3	C43	120.1 (4)	P4	C55	C60	136.0 (9)
Ru1	P3	C49	114.4 (4)	C56	C55	C60	126 (1)
C37	P3	C43	95.6 (6)	Ru2	C56	C55	109.4 (8)
C37	P3	C49	103.2 (6)	Ru2	C56	C57	135.8 (8)
C43	P3	C49	99.8 (5)	C55	C56	C57	115 (1)
P1	C1	C2	99.5 (8)	C56	C57	C58	121 (1)
P1	C1	C6	138 (1)	C57	C58	C59	119 (1)
C2	C1	C6	123 (1)	C58	C59	C60	122 (1)
Ru1	C2	C1	107.0 (8)	C55	C60	C59	116 (1)
Ru1	C2	C3	134.2 (9)	P4	C61	C62	118.4 (9)
C1	C2	C3	119 (1)	P4	C61	C66	120.8 (9)
C2	C3	C4	118 (1)	P4	C67	C68	117 (1)
C3	C4	C5	123 (1)	P4	C67	C72	124 (1)
C4	C5	C6	119 (1)	P5	C73	C74	115.9 (9)
C1	C6	C5	119 (1)	P5	C73	C78	125.3 (9)
P1	C7	C8	121.8 (9)	P5	C79	C80	121 (1)
P1	C7	C12	116.5 (9)	P5	C79	C84	114 (1)
P1	C13	C14	117.8 (9)	P5	C85	C86	122.6 (9)
P1	C13	C18	119.9 (9)	P5	C85	C90	117.2 (9)
P2	C19	C20	123.5 (9)	P6	C91	C92	122.3 (9)
P2	C19	C24	117.9 (8)	P6	C91	C96	118.4 (9)
P2	C25	C26	114.6 (9)	P6	C97	C98	118.7 (9)
P2	C25	C30	123.4 (9)	P6	C97	C102	120.6 (9)
P2	C31	C32	121.8 (9)	P6	C103	C104	118.1 (9)
P2	C31	C36	116.9 (9)	P6	C103	C108	121.3 (9)
P3	C37	C38	120 (1)	mean C_6H_5 (C–C–C) C61 to C108			120 ± 1
P3	C37	C42	119 (1)				
P3	C43	C44	125 (1)				
P3	C43	C48	117.2 (9)				
P3	C49	C50	116.1 (9)				
P3	C49	C54	124.2 (9)				
mean C_6H_5 (C–C–C) C7 to C54			120 ± 1				

Table III. Least-Squares Planes

plane no.[a]	A	B	C	D	atoms involved
1	0.3265	0.9265	−0.1870	−0.8648	Ru1, P1, C1, C2
2	0.2414	0.9488	−0.2039	−0.9089	C1 to C6
3	0.3251	0.9102	−0.2566	−7.7603	Ru2, P4, C55, C56
4	0.3283	0.9054	−0.2692	−7.9605	C55 to C60

Deviations of Atoms from Least-Squares Planes (Å × 10^3)

atom	plane no. 1	atom	plane no. 2	atom	plane no. 3	atom	plane no. 4
Ru1	0	C1	−29	Ru2	0	C55	6
P1	−1	C2	19	P4	0	C56	−5
C1	32	C3	3	C55	−5	C57	−2
C2	−27	C4	−30	C56	4	C58	13
		C5	17			C59	−14
		C6	18			C60	3

[a] Equation of plane is of the form $Ax + By + Cz - D = 0$, where x, y, and z are orthogonalized coordinates.

metallocyclic and phenylene ring systems (and a listing of atom deviations) are given in Table III. Planar, four-membered metallocycles are also seen, for example, in the structures of $(CH_3C_6H_4)_2PC_6H_3(CH_3)Mn(CO)_4$ (**3**)[29] and $Ph_2PC_6H_4Ir(PPh_3)L_2$ ($L = C_2H_4$) (**4**) and ($L = CO$) (**5**) but not in the isopropylphosphine complex i-$Pr_2PC_3H_6Ir(i\text{-}Pr_3P)(C_2H_4)_2$[30] where the ring reportedly deviates considerably from planarity. The internal angles of the ortho-metalated rings in **1** are predictably smaller than typical bond angles of the participating atoms. For instance, the mean metallocycle C–Ru–P, Ru–P–C, and C–C–P angles of 67.5 ± 0.3°, 85.7 ± 0.4°, and 98.6 ± 0.4° are considerably distorted from 90°, 109°, and 120°, respectively, expected from the idealized geometries about the respective ruthenium, phosphorus, and carbon atoms. The same trend and indeed very similar internal angles are seen for complexes **3**, **4**, **5**, and $Ph_3P(Ph_2PC_6H_4)_2IrH$ **6**,[31] as shown in Table IV. This distortion of the four-membered metallocycles is very likely indicative of considerable ring strain. In **1** the Ru-phenyl linkage of the metallocycle can be reversibly cleaved by hydrogen, as shown by the occurrence of H/D exchange in the ortho position of the phenyl groups, upon treatment of solutions of the complex and excess triphenylphosphine with deuterium.[9]

The potassium atoms of the two potassium hydrido(phosphine)ruthenate molecules are situated between the two ruthenium centers (see Figures 1 and 2), with Ru–K distances ranging from 3.617 (3) Å to 4.078 (3) Å. Although such distances are too long for potassium to ruthenium bonding,[32] infrared data suggest the presence of potassium to ruthenium hydride interactions (vide infra). There is a relatively close packing of the potassium atoms with some of the aromatic rings of the triphenylphosphine ligands. Atom K1 is clearly "sandwiched" between the two ortho-metalated phenylene rings (see Figure 2), with potassium to carbon distances ranging from 3.07 to 3.61 Å (ring C1–C6) and 2.97 to 3.57 Å (ring C55–C60). Atom K2 is separated by distances ranging from 3.16 to 3.42 Å from the phenyl ring C19–C24 and from 3.10 to 3.59 Å from the phenyl ring C79–C84. This close packing may be the result of potassium to hydrido(phosphine)ruthenate ion-pairing interactions. Significantly, the naphthalene and diethyl ether molecules which might have been expected to solvate the cations are at a distance of at least 4.25 Å from any potassium.

The naphthalene and diethyl ether "solvate" molecules are clearly separated from the ruthenium complex, but unfortunately their structures were not well-defined by the crystallography. Although two naphthalene molecules per asymmetric unit were observed crystallographically, they refined poorly (see Experimental Section). There is in the unit cell a poorly defined ten-membered "chain" that is presumably the two disordered and superposed diethyl ether molecules (see Figure 3). Even though these ethers were not clearly identified by the crystallography,

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[29] McKinney, R. J.; Knobler, C. B.; Huie, B. T.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 2988–2993.

[30] Perego, G.; Del Piero, G.; Cesari, M.; Clerici, M. G.; Perrotti, E. *J. Organomet. Chem.* **1973**, *54*, C51–C52.

[31] Del Piero, G.; Perego, G.; Zazzetta, A.; Cesari, M. *Cryst. Struct. Commun.* **1974**, *3*, 725–729.

[32] Covalent radii: Ru, 1.24 Å; K, 2.025 Å, from "Lange's Handbook of Chemistry", 12th ed.; Dean, J. A., Ed; McGraw-Hill: New York, 1979; Vol. 3, pp 123–124.

Table IV. Comparison of Internal Angles for Metallocycles in Ortho-Metalated Complexes

complex	metallocycle angles, deg C–M–P	M–P–C	C–C–P
$[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^-$ (1) (anion)	67.6 (3), 67.4 (3)	85.9 (4), 85.6 (4)	99.5 (8), 97.7 (8)
$(CH_3C_6H_4)_2PC_6H_3(CH_3)Mn(CO)_4$ (3)	67.5 (3)	85.2 (3)	105.7 (7)
$Ph_2PC_6H_4Ir(PPh_3)(C_2H_4)_2$ (4)		83.7–85.7	101.2
$Ph_2PC_6H_4Ir(PPh_3)(CO)_2$ (5)		83.7–85.7	101.9
$Ph_3P(Ph_2PC_6H_4)_2IrH$ (6)		83.8 (3), 84.1 (2)	100.3 (7), 101.0 (5)

their presence was established from elemental analyses, ^1H NMR spectra, and a direct determination of these molecules by chemical degradation of the complex (see Experimental Section).

Chemical and Spectroscopic Properties of 1. The title complex is obtained from solutions in diethyl ether as a bright yellow, highly air-sensitive solid. Crystals of **1** lose some of their crystallinity upon standing in argon, possibly because of loss of some diethyl ether. The compound is slightly soluble in diethyl ether and aromatic solvents, and consistent with its anionic character, it is extremely soluble in THF, 1,2-dimethoxyethane, and other relatively polar ether solvents. Under an argon atmosphere solid **1** is stable to at least 90 °C (except for possible loss of diethyl ether). Naphthalene, even though it is only present in **1** as a molecule of crystallization, cannot be sublimed from the complex by heating under vacuum to 80 °C. However, slow evaporation of solutions of **1** in toluene gave a crystalline toluene adduct, containing no naphthalene.

While the hydride atoms were not located in the X-ray work, the hydridic nature of **1** is clearly manifested in its chemical and spectroscopic properties. Solutions of **1** in THF react with dry HCl to yield 2 mol of H_2 per ruthenium, as expected from eq 2.

$$K^+[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^- + 3HCl \xrightarrow{THF} (Ph_3P)_3RuCl_2 + 2H_2 + KCl \quad (2)$$

Reaction with CH_3I gave slightly more than 2 mol of methane/mol of **1**. These results clearly show that **1** is a dihydridoruthenate.

The infrared spectrum of **1**, taken as a suspension in Nujol, shows two intense bands at 1735 and 1825 cm^{-1}. These are assigned to the ν_{Ru-H} stretching frequencies for the two nonequivalent metal hydrides in **1**. The bands disappear after reaction of **1** with HCl in THF (see above). Their intensity rapidly diminishes upon brief exposure of the Nujol suspension to air. (This serves as a useful diagnostic technique for identifying ν_{M-H} absorptions for air-sensitive hydrides.) The ν_{Ru-H} bands for **1** are at significantly lower frequencies than the corresponding frequencies for $[(Ph_3P)_2RuHCl]_2$ (2020 cm^{-1})[25a] and $(Ph_3P)_3Ru(N_2)H_2$ (1917, 1947 cm^{-1}).[33,34] This may be ascribed in part to a $Ru^{\delta+}–H^{\delta-}$ polarization which would be expected to weaken the ruthenium-hydrogen bonds. The ν_{M-H} absorptions of the dihydridoruthenate **1** may also be lowered by ion-pairing interactions with the potassium counterion. Solutions of **1** in THF display only a broad metal hydride related absorption at 1825 cm^{-1} (width at half-height ($W_{1/2} \approx 170$ cm^{-1}). A potassium-crown ether complex prepared by treatment of **1** with 18-crown-6 likewise shows only a single broad infrared band (in the solid state) at 1820 cm^{-1} ($W_{1/2} \approx 75$ cm^{-1}).

In such cases, only a diffuse interaction between the metal hydride and the solvated cation may be expected. However, in the case of the solid complex **1**, the appearance of two distinct bands at 1825 and 1735 cm^{-1} indicates that there are significant nonequivalent interactions of the hydrides with the potassium cation.[35] The lower frequency band is assigned to H1 since, as can be seen from the model shown in Figure 1, it is in a position to interact with two potassium atoms while H2 can only interact with one. In the $RuH(Me)(PPh_3)_2(MeLiOEt_2)_2$ complex,[21] an even lower ν_{Ru-H} frequency of 1610 cm^{-1}, ascribed to a Li···H–Ru interaction, is observed. The infrared spectrum of **1**, aside from the metal hydride features, is similar to that of typical triphenylphosphine complexes. Medium intensity absorptions at ~1410 and 1550 cm^{-1}, regarded at indicative of the presence of ortho-metalated ligands,[21] are observed.

Table V. ^1H (Metal Hydride) and ^{31}P NMR Data for 1

^1H NMR (at 100 MHz)

$\delta_{(CH_3)_4Si}$	hydride atom	J_{P3-H}	J_{P1-H}	J_{P2-H}	J_{H-H}
-7.0^a	H1	81.1	26.5	20.6	6.2
-11.0^b	H2	18.6	80.6	18.6	6.2

^1H-Decoupled ^{31}P NMR (at 80.98 MHz)^d

$\delta_{H_3PO_4}{}^c$	phosphorus atom	coupling constants, Hz
62.9	P2	$J_{P-P} \approx 16$
55.0	P3	$J_{P-P} \approx 16$
−18.3	P1	$J_{P-P} \approx 16$

^{a} Two doublets of doublets with an additional fine splitting of 6.2 Hz. ^{b} A doublet of triplets with an additional doublet fine splitting of 6.2 Hz. ^{c} Positive displacement downfield with respect to external 85% H_3PO_4. ^{d} Signals are apparent triplets with some further splitting (~0.2 Hz) in the middle peaks.

Proton (^1H) NMR spectra of solutions of **1** in THF-d_8 at 60 MHz clearly show the presence of naphthalene and diethyl ether and also signals at $\delta_{(CH_3)_4Si}$ 6.4–7.5 ascribed to the protons of the triphenylphosphine ligands. The $C_{10}H_8$ and Et_2O NMR patterns in the ^1H NMR spectrum of **1** are identical with those of their solutions in THF-d_8.[36] The relatively weak hydride signals for **1** were seen at $\delta_{(CH_3)_4Si}$ −7 and −11 by using a pulsed FT spectrometer operating at 100 MHz. The spectrum shows well-resolved spin-spin coupling from the mutual interaction of ^{31}P and ^1H nuclei. A listing of the spectral assignments and coupling constants is given in Table V. The largest ^1H signal splittings ($J_{P-H} \approx 80$ Hz) arise from interactions with the trans-situated ^{31}P nuclei, P1 and P3. Noise decoupling of the ^{31}P nuclei resulted in the observation of only two structureless hydride signals. The −7-ppm ^1H signal is attributed to H1 since the observed multiplet pattern (in the ^{31}P-coupled spectrum) implies the presence of two distinctly different cis-situated ^{31}P nuclei, i.e., P1 (the ortho-metalated phosphine) and P2. On the other hand, the −11-ppm signal from H2 shows a single coupling (of 18.6 Hz) to the two *cis*-triphenylphosphine ligand atoms, P2 and P3. The fine splittings of ~6 Hz in the hydride multiplets are due to H1–H2 coupling. This was confirmed experimentally by the selective irradiation at each of the hydride frequencies.

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(33) Knoth, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 104–109.

(34) Note, however, that for $(Ph_3P)_2(Ph_2PC_6H_4)RuH(Et_2O)$ and in $(Ph_3P)(Ph_2PC_6H_4)RuH(Et_2O)_2$, $\nu_{Ru-H} = 1773$ cm^{-1} (medium int, v br) and 1790 cm^{-1} (m br), respectively. See: Cole-Hamilton, D. J. et al., ref 21.

(35) With the assumption that *D*(Ru–H) in **1** is 1.65 Å as in $HRuCl(diop)_2$ (Ball, R. G.; James, B. R.; Trotter, J.; Wang, D. K. W.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 460–461) and that H1 is trans to P3 and H2 is trans to P1 (as in Figure 1), then *D*(K2–H1) = 3.44 Å, *D*(K1–H1) = 3.72 Å, and *D*(K2–H2) = 3.51 Å.

(36) Only the four-line, low-field multiplet of the ^1H NMR of $C_{10}H_8$ is clearly separated from the aromatic proton signals of **1**.

Table VI. ^1H (Metal Hydride) and ^{31}P NMR Data for 2

^1H NMR (at 270 MHz)

atom	H1	H2	H3	H4
$\delta_{(CH_3)_4Si}$	−13.0	−13.74	−15.64	−16.75
multiplet	*a*	d[e]	*b*	d[e]
J_{P-H}, Hz		37		42

^1H-Decoupled ^{31}P NMR (at 32.199 MHz)

atom	P1	P2	P3	P4
$\delta_{85\% H_3PO_4}$[d]	110.6	76.4	69.8	69.1
multiplet	d of d[e]	d[e]	d of d[e]	d[e]
J_{P-P},[c] Hz	$J_{P1-P4} = 153$	$J_{P1-P2} = 23$	$J_{P1-P3} = 27$	$J_{P3-P4} = 17$

[a] Complex, seven-line multiplet with strong central peak. [b] Complex, five-line multiplet. [c] Measured first-order coupling constants. [d] Chemical shifts measured at 80.98 MHz: Positive displacement downfield with respect to external 85% H_3PO_4. [e] Abbreviations: d, doublet; d of d, doublet of doublets.

The ^1H-noise-decoupled, ^{31}P NMR spectrum shows signals at 62.9, 55, and −18.3 (positive displacement downfield) with respect to 85% H_3PO_4.[37] With proton coupling, an ~80 Hz, J_{P-H} splitting of the 55- and −18.3-ppm signals is observed; these resonances are thus assigned to P3 and P1, which are trans to the hydride atoms. The −18.3-ppm signal most likely arises from P1 since ^{31}P resonances of ortho-metalated phosphines and of phosphines trans to hydride ligands are generally seen at higher fields.[21] Details of the observed multiplet structure and coupling constants are given in Table V. A similar degree of spin–spin coupling (~16 Hz) is seen between all the phosphorus atoms. This result is consistent with the solid-state structure of 1 wherein all phosphorus atoms are situated cis to one another (see Figure 1).

Preparation of $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3$ (2). The hydrido(phosphine)ruthenate complex 1 proved to be a good catalyst for the hydrogenation of ketones, aldehydes, activated carboxylic acid esters, etc.; this is discussed in the following paper.[9] We next sought to prepare a more powerful catalyst by the analogous potassium naphthalene reduction of the bis(triphenylphosphine)ruthenium hydridochloride complex, $[(Ph_3P)_2RuHCl]_2\cdot 2C_6H_5CH_3$.[25a] Reaction of the latter with $K^+C_{10}H_8^-$ (2 mol per Ru) at low temperatures in THF gave two major potassium (phosphine)ruthenate products. One of these, a THF-soluble, diethyl ether insoluble material, showed particularly interesting catalytic properties.[9] This complex was subsequently obtained in a purer form as the diglyme adduct 2 (see Experimental Section). The composition of 2 was determined from a combination of elemental analyses, chemical reactivity studies and infrared and NMR spectra.[38]

The proton-noise-decoupled ^{31}P NMR spectrum of 2 (see Table VI) shows the presence of four nonequivalent phosphorus nuclei with coupled spins. Three of the ^{31}P resonances are grouped in the region of $\delta_{H_3PO_4}$ 70, which is fairly typical for (triphenylphosphine)ruthenium complexes.[21,24,39] The fourth ^{31}P resonance is seen at conspicuously lower field strengths (δ 110.6).

In the 270-MHz, ^1H NMR spectrum of 2 (see Table VI), four signals (two doublets and two relatively complex multiplets) are seen in the metal hydride region, the multiplicity arising from spin–spin interactions with the ^{31}P nuclei. Infrared spectra of 2 (taken in hexadecane-d_{34} oil mulls) display a medium intensity absorption from 1700 to 1900 cm^{-1}, partially resolved into a doublet at 1745 and 1775 cm^{-1}, and a somewhat more intense maximum at 1830 cm^{-1}. Reaction of THF solutions of 2 with HCl gives hydrogen (~4 mol of H_2/mol of 2), diglyme (recovered ~1.5 mol/mol of 2) (see Experimental Section) and a red-brown complex 7. Proton-noise-decoupled ^{31}P NMR spectra of solutions of 7 at 80.98 MHz in THF-d_8 show two separated AB spin–spin patterns arising from four nonequivalent phosphorus nuclei: δ_A 54.5, δ_B 55.8 (J = 44 Hz); $\delta_{A'}$ 46.7, $\delta_{B'}$ 48.4 (J = 37 Hz). With ^1H coupling, all the ^{31}P signals are broadened by ~80 Hz as a result of interactions with the aryl protons. However, the lower field signal at δ_B 55.8 is in addition clearly split into a doublet with $J_{P-H} \approx 330$ Hz. This signal must thus originate predominantly from the ^{31}P nucleus of a diphenylphosphine ligand. On the basis of the above data, complex 7 is therefore formulated as $(Ph_3P)_3(Ph_2PH)Ru_2Cl_4$. For comparison, the ^1H-decoupled ^{31}P NMR spectrum of the chloro-bridged dimer $(Ph_3P)_4Ru_2Cl_4$ taken at −70 °C in toluene, reportedly, shows a single AB pattern with δ_A 58.8 and δ_B 53.0 with J_{PP} = 41.5 Hz.[40] The diphenylphosphine in 7 is presumably formed by the protonation of a diphenylphosphido ligand in 2, by reaction of the complex with HCl (see eq 3). The ^{31}P resonance for 2 at 110.6 ppm can now be reasonably assigned to a probably bridging, diphenylphosphido ligand. For a number of iron, ruthenium, and palladium complexes with μ-PPh_2 bridging metal–metal bonds ^{31}P μ-diphenylphosphido resonances are usually seen at relatively low-field strengths (δ 100–200).[41] The μ-PPh_2 ligand in 2 presumably originates from a reductive cleavage[42] of a triphenylphosphine during the potassium naphthalene reduction. Reaction of tris(triphenylphosphine)ruthenium hydridochloride with NaOH in acetone gives a tetranuclear species believed to contain a μ-diphenylphosphido ligand.[43] From the magnitude of the J_{PP} coupling constants for 2 it appears that the μ-PPh_2 ligand is trans to one triphenylphosphine with J_{PP} = 153 Hz and cis to the other two triphenylphosphines with J_{PP} = 23–27 Hz (see Table VI).

$$K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3 \xrightarrow{HCl} (Ph_3P)_3(Ph_2PH)Ru_2Cl_4 + 4H_2 + 2C_6H_{14}O_3 + 2KCl \quad (3)$$

The metal hydride ^1H NMR spectrum of 2 shows doublet signals for H2 and H4 with $J_{P-H} \approx 40$ Hz, indicative of a cis coupling of each hydride with a phosphorus ligand atom. The other hydride multiplets are relatively complex and suggest that H1 and H3 are in central locations in the molecule where they can couple with all four ^{31}P nuclei. In the infrared spectrum of 2 medium to weak absorptions at 1403 and 1550 cm^{-1} are indicative of the presence of ortho-metalation[21] in at least one of the

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(37) The ^{31}P chemical shifts for 1 and 2 given in the preliminary reports (ref 11 and 12) were incorrectly referenced.

(38) The composition of 2 as given in ref 12 (which was based on incomplete NMR data) is incorrect.

(39) (a) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080–4089. (b) Komiya, S.; Yamamoto, A. *J. Mol. Catal.* 1979, *5*, 279–292.

(40) James, B. R.; Thompson, L. K.; Wang, D. K. W. *Inorg. Chim. Acta* **1978**, *29*, L237–L238.

(41) (a) Carty, A. J. "Chemistry of Some Phosphido Bridged Iron Group Clusters", *Adv. Chem. Ser.*, in press. (b) Mott, G. N.; Carty, S. J. *Inorg. Chem.* **1979**, *18*, 2926–2928. (c) Carty, A. J.; McLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27–C32. (d) Petersen, J. L.; Stewart, R. P. *Inorg. Chem.* **1979**, *19*, 186–191. (e) Kreter, P. E., Jr.; Meek, D. W.; Christoph, G. G. *J. Organomet. Chem.* **1980**, *188*, C27–C30. (f) Garrou, P. E. *Chem. Rev.*, in press.

(42) (a) The generation of phosphido bridges from Ph_3P ligands has been noted previously for platinum metal compounds, see, e.g.: Taylor, N. J.; Chieh, P. D.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448–449. (b) See also: Uhlig, E.; Walther, D. *Coord. Chem. Rev.* **1980**, *33*, 31–32 and references therein.

(43) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546–1557.

phosphine ligands. With the present data it is not possible to assign an unambiguous structure for **2**. Elucidation of the detailed molecular structure of the complex will require X-ray crystallographic studies.

Experimental Section

The hydridoruthenate complexes described in this paper are extremely air sensitive and were handled by a combination of argon drybox and high vacuum line techniques, similar to those used for our work with low valent titanium metallocenes.[44] Solvents were purified by distillation after prolonged contact with Na/K alloy (hydrocarbons) or by treatment with $LiAlH_4$, followed by distillation from Na/K alloy, anthracene radical anion solutions (ethers). Infrared spectra were taken as oil mulls or in THF solutions by using a Perkin-Elmer spectrometer. Nujol oil and hexadecane-d_{34} (Merck and Co., Rahway, NJ) (purified by distillation under vacuum from Na/K alloy) were used as mulling agents. ^1H NMR spectra were recorded at 60 MHz (Varian T60), 100 MHz (Varian XL 100), and also at 270 MHz. ^{31}P spectra were recorded by using a Varian CFT 20 spectrometer with a ^{31}P probe and also on an Varian XL-200 multinuclear spectrometer. Elemental analyses were done in this laboratory by Mrs. R. Hogan and by Schwarzkopf Microanalytical Laboratory (Woodside, NY).

Preparation of $K^+[(Ph_3P)_2Ph_2\overline{PC_6HRu}H_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (1). Tris(triphenylphosphine)ruthenium hydridochloride (as the toluene solvate) was prepared by reduction of $(Ph_3P)_3RuCl_2$ (Strem Chemical Co.) suspended in toluene, with hydrogen in the presence of triethylamine, as described by Wilkinson et al.[2,24] For the reduction of $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$ with potassium naphthalene, a special apparatus[44] designed for stirring solutions at low temperatures was used. The upper bulb of the apparatus (500-mL capacity) was loaded (under Ar) with potassium (0.4 g, 10.2 mmol) and naphthalene (1.4 g, 10.9 mmol); the lower bulb (containing the stirring device) was charged with $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$ (5 g, 5.41 mmol). The apparatus was then attached to a vacuum manifold and THF (150 mL) distilled into each of the two bulbs. The mixture in the upper section was stirred until dissolution of potassium (to yield potassium naphthalene) was complete. This solution (cooled from -80 to -20 °C) was then added gradually over ca. 1-2 h to the well-stirred slurry of $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$ in THF cooled from -80 to -111 °C. The resulting reddish yellow solution was stirred at -80 °C (16 h), -35 °C (5 h), and -16 °C (5 h) and then warmed to room temperature. It was evaporated to near dryness by vacuum pumping and octane (50 mL) added.

The mixture was homogenized as much as possible by agitation and freeze-thawing, after which volatiles were removed by vacuum pumping. This treatment with octane was repeated, as required, until a dry yellow-green solid was obtained. The latter was extracted repeatedly with diethyl ether. Evaporation of the combined extracts (collected in the upper bulb), followed by washing with small amounts of diethyl ether, left a bright yellow solid, 1; yield, 3.4 g.

The complex 1 was routinely synthesized by this low-temperature reduction procedure; however, it was also obtained when the reduction was carried out at ~0 °C. This was conveniently done by mixing the reagents in an 80-cm^3, H-shaped apparatus having a filter disk sealed in the horizontal arm. Workup and purification of the complex were done in the same apparatus, as detailed above.

The complex was crystallized from diethyl ether by the following procedure. A H-shaped apparatus of ca. 1-L total capacity, with a fritted disk in the horizontal arm was loaded (under argon) with 1 (3.0 g) and naphthalene (7.7 g). Diethyl ether (390 mL) was added and the mixture, stirred and filtered to yield a clear amber solution. This solution was thermostated to 4 °C, while the other leg of the apparatus was kept at 0 °C. Slow evaporation (3-6 days) to near dryness gave a mass of yellow crystals of 1. Crystals of naphthalene which are also formed can be easily separated mechanically or by judicious washing with small amounts of diethyl ether. The crystals of 1 were dried and collected under argon, without evacuating the apparatus. For the elemental analyses, the NMR characterization, and X-ray work the crystals were handled as much as possible, in an Et_2O-saturated argon atmosphere. Anal. Calcd for $C_{68}H_{64}P_3ORuK$: C, 72.26; H, 5.71; P, 8.22; K, 3.46. Found (mean of duplicate analyses): C, 72.35; H, 5.88; P, 8.55; K, 3.79. To further substantiate the stated composition of 1, $C_{10}H_8$ and $(C_2H_5)_2O$ were directly determined by decomposition of the complex with HCl (vide infra).

Reaction of 1 with HCl and with CH_3I. A 30-mL glass reactor tube was loaded (in an Et_2O/argon atmosphere) with crystals of 1 (108.3 mg, 0.0958 mmol) and toluene (6 mL). The (partial) solution was cooled to -196 °C and pure HCl gas (4 mmol) added. The mixture was allowed to warm slowly to 23 °C where it was stirred for ca. 20 h. Hydrogen (0.192 mmol) was collected with the aid of a Töpler pump. Ratio of **1**:H_2 equals 1:2.00. The condensable volatiles from the reactor tube (warmed to 80 °C) were collected in an in-line U-trap cooled to -196 °C. To the oily residue in the reaction tube was then added octane and the mixture homogenized by freeze-thawing and agitation. The reaction tube was heated to 80 °C, and the volatiles were collected in the U-trap. This procedure was repeated until negligible, incremental quantities of $C_{10}H_8$ were transferred. Volatiles collected in the U-trap were neutralized with KOH pellets and analyzed for naphthalene and diethyl ether by gas chromatography (2-m, 3.2-mm o.d. steel column packed with Carbowax 20M with 2% KOH). Found: naphthalene, 9.58 mg (0.0748 mmol); diethyl ether, 8.2 mg (0.111 mmol). Ratio of 1:$C_{10}H_8$ equals 1:0.78. Ratio of 1:Et_2O equals 1:1.16.

Table VII. Experimental Details for X-ray Structural Determination of 1

A. Crystal Data	
cryst dimens:	0.15 × 0.20 × 0.20 mm
peak width at half-height:	0.40°
Cu Kα radiation:	$\lambda = 1.541\,84$ Å
temp:	-120 ± 1 °C
triclinic space group:	$P\bar{1}$
$a = 15.603$ (6) Å	
$b = 15.974$ (4) Å	
$c = 23.774$ (8) Å	
$\alpha = 90.69$ (2)°	
$\beta = 102.96$ (3)°	
$\gamma = 106.51$ (3)°	
$V = 5518.3$ Å^3	
$Z = 4$	
$\rho = 1.36$ g/cm^3	
$\mu = 42.0$ cm^{-1}	
B. Intensity Measurements	
instrument:	Enraf-Nonius CAD4 diffractometer
monochromator:	graphite crystal, incident beam
attenuator:	Ni foil, factor 27.3
take-off angle:	2.8°
detector aperture:	2.0-3.6 mm horizontal; 2.0 mm vertical
cryst-to-detector dist:	21 cm
scan type:	w-θ
scan rate:	3-20°/min (in ω)
ω-scan width:	$(0.9 + 0.140 \tan\theta)$°
θ-scan width:	(0.667 ω width)°
max 2θ:	115.0°
no. of reflctns measd:	15744 total, 15125 unique
correctns:	Lorentz-polarization; empirical absorption (from 0.88 to 1.00 on I)

In another experiment, crystals of 1 (weighed under argon) were reacted with HCl, in toluene as above, to yield (in duplicate runs) 2.00 and 2.01 mol of H_2/mol of 1. A reddish solid product identified by its infrared spectrum as $(Ph_3P)_3RuCl_2$ was formed.

Crystals of 1 (weighed under argon) (49.66 mg, 0.0439 mmol) were reacted with neat methyl iodide (5 mL), for 16 h at 23 °C. The methane evolved (0.107 mmol) was collected with the aid of a Töpler pump. Ratio of 1:CH_4 equals 1:2.4.

Collection of X-ray Data and Structure Determination of 1.[45] For the X-ray work pale yellow prismatic crystals of 1 were mounted in glass capillaries, under argon. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 diffractometer. Crystal data and experimental details of the diffraction measurements are collected in Table VII.

The structure was solved by using the Patterson method which revealed the positions of the two ruthenium atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$.

Scattering factors were taken from Cromer and Waber.[46] Anomalous dispersion effects were included in F_c;[47] the values for $\Delta f'$ and $\Delta f''$ were

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[44] Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072-8076.

[45] This structure determination was performed by the following crystallographic staff of Molecular Structure Corp. (College Station, TX): Dr. M. W. Extine, Dr. B. A. Frenz, Ms. R. A. Meisner, and Dr. J. M. Troup.

[46] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

[47] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

those of Cromer.[48] Only the 7413 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement (largest parameter shift was 0.4 times its esd) yielded unweighted and weighted agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.089$ and $R_2 = \mathrm{SQRT}\ (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2) = 0.107$. The standard deviation of an observation of unit weight was 1.82. The highest peak in the final difference Fourier had a height of 0.68 e/A^3 with an estimated error based on ΔF[49] of 0.11. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends.

The naphthalene and diethyl ether "solvate" molecules were not well-defined. One of the naphthalene molecules (C201 to C210) refined poorly. The second naphthalene (C301 to C309) yielded only nine "refinable" atoms. Removing the poorly placed atoms, followed by a difference Fourier, showed the presence of ten atoms in a "naphthalene-like" arrangement and suggested that this was in fact a naphthalene. However, only nine of the ten atoms would refine. There is a poorly defined, ten-member "chain" that is presumably the two disordered and superposed diethyl ether molecules (see Figure 3). No attempt was made to assign the chemical type (i.e., carbon vs. oxygen) of these atoms. The chain shows some fairly short end-to-end intermolecular contacts. This suggests that there is a "channel" in the unit cell which contains the disordered diethyl ether molecules.

Preparation of $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3$ (2). The procedure requires the prior synthesis of $(Ph_3P)_2RuCl_3\cdot CH_3OH$ and subsequently $[(Ph_3P)_2RuHCl]_2$, from which **2** is obtained by reaction with potassium naphthalene.

The preparation of $(Ph_3P)_2RuCl_3\cdot CH_3OH$[50] is a modification of the synthesis described by Stephenson and Wilkinson.[51] Their procedure which describes the reaction of $RuCl_3$ hydrate with triphenylphosphine in methanol, to yield a precipitate of $(Ph_3P)_2RuCl_3\cdot CH_3OH$, did not in our hands give any product. However, we found that with use of lithium chloride saturated methanol as the solvent medium the required complex was formed. Ruthenium trichloride hydrate, $RuCl_3\cdot 1\text{-}3H_2O$ (Matthey Bishop Co.) was dissolved in 2400 mL of reagent methanol and lithium chloride (150 g) added. Triphenylphosphine (24 g) was added over 30 min, to the rapidly stirred solution. This solution was then filtered and divided into four, 1-L flasks, and the flasks were put on a mechanical shaker (3 days). A bright green precipitate was collected. Additional Ph_3P (total of 64 g) was added, until after prolonged shaking (7–10 days) no more additional green precipitate collected. The total yield of $(Ph_3P)_2RuCl_3\cdot CH_3OH$ ranged from 25 to 35 g.

The preparation of $[(Ph_3P)_2RuHCl]_2\cdot$toluene is a modification of the synthesis of $[(Ph_3P)_2RuHBr]_2$ briefly described by James et al.[25a]. To $(Ph_3P)_2RuCl_3\cdot CH_3OH$ (19.4 g) (contained in a dumbbell-shaped apparatus with two, 500-mL bulbs separated by a filter tube) was added toluene (500 mL) and dry triethylamine (14 mL). The mixture was stirred under H_2 (~1 atm), at 20–25 °C, until there was no further gas uptake (ca. 20 h). The solvent and other volatiles were then removed by vacuum transfer; and the dark brown mass was washed with 2 × 30 mL of toluene and then dried. It was then extracted repeatedly with dry degassed ethanol until no $Et_3NH^+Cl^-$ (as seen in the infrared spectrum) remained. Finally, the product was washed with toluene (2 × 30 mL) and dried under vacuum. The complex $[(Ph_3P)_2RuHCl]_2\cdot 2C_6H_5CH_3$ (yield, ~10 g) was obtained as a reddish, moderately air-sensitive solid. Its infrared spectrum, taken as a suspension in Nujol, shows a sharp medium intensity absorption at 2020 cm^{-1}. Anal. Calcd for $C_{43}H_{39}RuP_2Cl$: C, 68.48; H, 5.21; Ru, 13.40; P, 8.21; Cl, 4.70. Found: C, 66.88; H, 5.20; Ru, 12.27; P, 8.65; Cl, 4.76.

For the reduction of $[(Ph_3P)_2RuHCl]_2\cdot 2$toluene the same apparatus[44] was used as for the preparation of complex 1. The apparatus was loaded, in the upper bulb with potassium (0.90 g, 23.0 mmol) and naphthalene (3.35 g, 26.2 mmol) and in the lower bulb with $[(Ph_3P)_2RuHCl]_2\cdot 2$-toluene (11.4 mmol of complex, based on analytically determined Cl, i.e., ratio K:Cl equals 2.018:1). Tetrahydrofuran (150 mL) was distilled into each bulb and the $K/C_{10}H_8/THF$ mixture stirred until dissolution of the metal was complete. The resulting solution of potassium naphthalene (cooled to between −80 and −60 °C) was slowly added to the suspension of the hydridochloride complex, cooled from −80 to −111 °C. The mixture was then stirred at −80 °C (1 day), −35 °C (5 h), and −16 °C (5 h) and then warmed to room temperature and filtered. The filtrate was evaporated to a small oily residue and dried under vacuum by a combination of freeze–thawing and agitation with several portions of added octane. The dried filtrate was finally washed by extraction with octane. It is important at this stage to thoroughly dry the solid from any possible adhering THF; yield, 8 g. A portion of this product (3 g) was extracted to exhaustion with diethyl ether. The residue, a reddish solid (1.1 g), was collected as the final (crude) product (**2a**). It was purified as follows. The complex **2a** (600 mg), contained in a H-shaped tube with a filter disk in the horizontal arm, was dissolved in a mixture of toluene (60 mL) and bis(2-methoxyethyl) ether (diglyme) (2.5 mL). A layer of isopentane (180 mL) was distilled over this solution. Slow interdiffusion of the two solvents at 4 °C gave dark orange apparently microcrystalline solid **2**. Calcd for $C_{78}H_{87}P_4Ru_2K_2O_6$ (**2**): C, 61.49; H, 5.75; P, 8.13; K, 5.13. Found: C, 59.88; H, 5.51; P, 8.23; K, 6.05.

Reaction of 2 with HCl. The complex (62.60 mg, 0.041 mmol) was dissolved in THF (1 mL), and dry HCl (1.2 mmol) was then added to the frozen solution at −196 °C. The mixture was stirred at −80 °C (30 min) and then at 0 °C (30 min), resulting in a red-brown solution. This was transferred in vacuum to a U-trap at −196 °C while noncondensables were collected with the aid of a Töpler pump. The solid remaining was treated with octane to dry it and facilitate transfer of the diglyme. Found: H_2 (0.140 mmol). Ratio of **2**:H_2 equals 1:3.4. In another experiment 50.60 mg (0.0332 mmol) of **2** gave 0.132 mmol of H_2. Ratio of **2**:H_2 equals 1:3.98. The contents of the U-trap were analyzed for diglyme by GC methods, recovered 8.23 mg (0.0613 mmol) of diglyme. Ratio of **2**:recovered $C_6H_{14}O_3$ equals 1:1.5.

Acknowledgment. We are grateful to Dr. W. B. Hammond, Mr. G. Babbitt, and Dr. R. Rowan (Univ. of Maryland) for recording the NMR spectra. We thank Mr. R. Crissey for invaluable technical assistance.

Supplementary Material Available: Tables of atom positional coordinates, thermal parameters, and a listing of observed and calculated structure factors are available (39 pages). Ordering information is given on any current masthead page.

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