Synthesis and Chemistry of *trans*-[$RhX(CO)L_2$] (X = Anionic Ligand, L = Tertiary Phosphine)†

Yuji Ohgomori,* Shin-ichi Yoshida, and Yoshihisa Watanabe
Central Research Laboratory, Mitsubishi Petrochemical Co. Ltd., 8-3 Chu-ou, Ami, Ibaraki 300-03, Japan

The novel preparation of a wide variety of *trans*-[$RhX(CO)L_2$] complexes (X = anionic ligand, L = tertiary phosphine) from [$Rh_4(CO)_{12}$], phosphine (L), and acid (HX) is described. A plausible formation pathway is proposed. The electron density on the phosphorus atom in *trans*-[$RhX(CO)L_2$] decreases and the length of the Rh–P bond increases with an increase in the electronegativity of the anionic ligand, X, in a *cis* position to the phosphine ligand. The rhodium complexes (X = arylcarboxylate) are reduced to afford rhodate anions such as [$Rh(CO)_3L]^-$ and [$Rh(CO)_4]^-$ in hexamethylphosphoramide solution under CO–H_2. The rate of reduction increases with a decrease in the electron-withdrawing effect of the arylcarboxylate ligand.

The direct conversion of synthesis gas ($CO{:}H_2 = 1{:}1$) to ethylene glycol is known to be effectively catalysed by the rhodium–phosphine system.[1] The rhodium complexes, of the type *trans*-[$RhX(CO)L_2$] (X = anionic ligand, L = tertiary phosphine), are thought to be one of the important catalyst precursors for practical application, because of their stability in air. It is already known that this compound type is an effective catalyst precursor for the hydroformylation of olefins,[2] or formaldehyde.[3,4] A simple method of preparing [$RhX(CO)L_2$] would be useful in order to study the catalytic activity. A number of syntheses for the rhodium complexes have been summarized.[5] Among recent synthetic methods, the most useful has been reported by Vaska and Peone[6] as represented by equations (1) and (2) (R = aryl, X = various anionic ligands). This method is not applicable to the synthesis of the complexes where X is an enolate ligand.

$$2[RhCl(CO)(PR_3)_2] + Ag_2CO_3 + 2NH_4F \longrightarrow 2[RhF(CO)(PR_3)_2] + 2AgCl + CO_2 + 2NH_3 + H_2O \quad (1)$$

$$[RhF(CO)(PR_3)_2] + MX \longrightarrow [RhX(CO)(PR_3)_2] + MF \quad (2)$$

Since dodecacarbonyltetrarhodium is easily prepared by the reduction of $K_3[RhCl_6]$ with carbon monoxide,[7] it is a useful starting material for the preparation of the complexes [$RhX(CO)L_2$].

It is known that $[Rh(CO)_3(PPh_3)]^-$ is the immediate precursor of the catalysts in the hydroformylation of formaldehyde,[4] and it has been shown that $[Rh(CO)_4]^-$ plays an important role in ethylene glycol formation from synthesis gas.[8] The former anion is known to be formed by the reduction of [$RhCl(CO)(PPh_3)_2$] with Na–Hg amalgam under a CO atmosphere.[9] The formation of the anion $[Rh(CO)_4]^-$ has been found in the reduction of [$Rh(CO)_2(acac)$] (acac = acetylacetonate) under a high pressure of synthesis gas.[8,9] The ease of formation of such anions is important for the catalytic activity. Formation of these rhodium anions under atmospheric pressure of synthesis gas has not been reported.

We describe here: (*i*) a novel and convenient synthesis of the complexes *trans*-[$RhX(CO)L_2$] including several new compounds, and a postulation of the reaction pathway; (*ii*) a correlation between spectral data of the complexes and the electronic properties of X and L; (*iii*) a reduction of the complexes under synthesis gas affording anionic species such as $[Rh(CO)_3L]^-$ or $[Rh(CO)_4]^-$.

Results and Discussion

Synthesis of trans-[$RhX(CO)L_2$] (*X = Anionic Ligand,* L = *Tertiary Phosphine*).—The complexes *trans*-[$RhX(CO)L_2$] are obtained by the reaction of stoicheiometric amounts of dodecacarbonyltetrarhodium, tertiary phosphine, L, and acid, HX, in 1,3-dimethylimidazolidin-2-one (dmi), 1,1,3,3-tetramethylurea (tmu), or diethyl ether as the solvent under a nitrogen atmosphere at room temperature. Twenty one compounds, of the type [$RhX(CO)L_2$], have been synthesized by this method and the analytical and physical data are summarized in Table 1. Gas-burette measurements and gas chromatographic analysis indicate that two moles of carbon monoxide and half a mole of hydrogen are evolved per rhodium during the reaction. The reaction is expressed in equation (3).

$$\tfrac{1}{4}[Rh_4(CO)_{12}] + 2L + HX \longrightarrow [RhX(CO)L_2] + 2CO + \tfrac{1}{2}H_2 \quad (3)$$

The configuration of [$Rh(O_2CC_6H_4F\text{-}3)(CO)\{P(C_6H_{11})_3\}_2$] (**3**; C_6H_{11} = cyclohexyl) and the oxidation number of the rhodium were determined by the following analyses. A doublet with *J*(Rh–P) 125 Hz was observed in the ^{31}P n.m.r. spectrum. A binding energy of 307.8 eV for the rhodium was observed by ESCA (electron spectroscopy for chemical analysis) {*cf.* 307.6 eV for [$RhCl(CO)(PPh_3)_2$]; 306.8 eV for [$Rh_4(CO)_{12}$]}. These results indicate that the configuration of (**3**) is *trans* and the oxidation number is one.

Compounds (**6**), (**7**), and (**8**) are prepared by the reaction with phthalic acids. These compounds have not been reported previously. A signal assigned to the carboxylic proton of compound (**8**) is observed at a very low magnetic field (δ 18.5 p.p.m.). It is understood that the electron-withdrawing effect of Rh^I, or the hydrogen bonding between the carboxylic proton and Rh^I, causes the decrease of electron density on the hydrogen atom in the carboxyl group.

Compound (**20**), [$Rh\{OC(Me){=}CHCO_2Me\}(CO)(PPr^i_3)_2$], is formed by the reaction of [$Rh_4(CO)_{12}$], methyl acetoacetate, and PPr^i_3 in the presence of triethylamine. This is a first example of an enolate complex of the type of [$RhX(CO)L_2$]. A similar enolate complex [$Pd\{OC(Me){=}CHCO_2Et\}\{P(C_6H_{11})_3\}(\eta^3\text{-}C_8H_{13})$] has been found in a thf (tetrahydrofuran) solution at low temperature (−50 °C).[10] However, complex (**20**) is stable in air at room temperature. The ^{13}C n.m.r. spectrum of the enolate moiety is similar to that of the palladium complex and is shown in Figure 1. Attempts to prepare this type of complex having a PPh_3 ligand instead of PPr^i_3 were unsuccessful. The product is stable only under a CO atmosphere and decomposes under a nitrogen atmosphere. Chemical shifts

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† *Non-S.I. unit employed:* eV = 1.602×10^{-19} J.

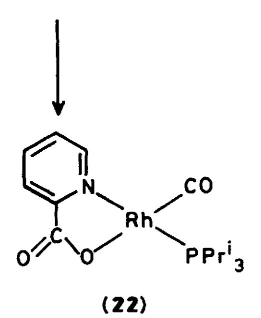
Table 1. Analytical[a] and physical data for *trans*-[RhX(CO)L$_2$]

				Analysis (%)				
Compound	X	L	M^+	C	H	N	P	Rh
(1)	O_2CPh	$P(C_6H_{11})_3$	812	65.3 (65.0)	9.0 (8.8)		7.3 (7.6)	12.7 (12.7)
(2)	$O_2CC_6H_4F$-3	PPr^i_3	590	52.9 (52.9)	7.7 (7.9)		10.6 (10.5)	17.6 (17.4)
(3)	$O_2CC_6H_4F$-3	$P(C_6H_{11})_3$	830	64.1 (63.6)	8.4 (8.5)		7.5 (7.5)	12.4 (12.4)
(4)	$O_2CC_6H_4F$-3	PPh_3	794	66.4 (66.5)	4.4 (4.3)		7.7 (7.8)	12.9 (13.0)
(5)	$O_2CC_6H_4NO_2$-4	$P(C_6H_{11})_3$	858[b]	61.6 (61.6)	8.2 (8.2)	1.5 (1.6)	7.3 (7.2)	12.1 (12.0)
(6)[c]	$O_2CC_6H_4CO_2H$-4	$P(C_6H_{11})_3$	*d*	61.6 (61.8)	8.7 (8.4)	2.9 (2.9)	6.4 (6.4)	10.6 (10.6)
(7)	$O_2CC_6H_4CO_2H$-3	$P(C_6H_{11})_3$	856	65.5 (63.1)	8.9 (8.4)		7.6 (7.2)	12.8 (12.0)
(8)	$O_2CC_6H_4CO_2H$-2	$P(C_6H_{11})_3$	857[b]	63.1 (63.1)	8.8 (8.4)		7.4 (7.2)	11.7 (12.0)
(9)	O_2CMe	PPr^i_3	510	49.8 (49.4)	9.0 (8.9)		12.1 (12.1)	19.7 (20.2)
(10)	O_2CMe	$P(C_6H_{11})_3$	750	62.5 (62.4)	9.4 (9.3)		8.2 (8.3)	13.8 (13.7)
(11)	OPh	PPr^i_3	544	55.1 (55.2)	8.8 (8.7)		11.4 (11.4)	18.9 (18.9)
(12)	OC_6F_5	$P(C_6H_{11})_3$	874	59.2 (59.0)	7.5 (7.6)		7.1 (7.1)	11.4 (11.8)
(13)	$O_3SC_6H_4Me$-4	PPr^i_3	622	49.8 (50.2)	7.9 (7.9)		10.0 (10.0)	16.3 (16.5)
(14)	$O_3SC_6H_4Me$-4	$P(C_6H_{11})_3$	862	61.8 (61.2)	8.5 (8.5)		7.2 (7.2)	12.0 (11.9)
(15)	ClO_4	$P(C_6H_{11})_3$	790	56.0 (56.2)	8.3 (8.4)		7.7 (7.8)	12.8 (13.0)
(16)	Cl	$P(C_6H_{11})_3$	726	61.2 (61.1)	9.1 (9.2)		8.5 (8.5)	14.0 (14.2)
(17)	Cl	PBu^n_3	570	51.4 (52.6)	9.5 (9.5)		10.8 (10.9)	17.7 (18.0)
(18)	Cl	PPh_3	690	64.3 (64.3)	4.4 (4.4)		9.3 (9.0)	15.0 (14.9)
(19)	I	$P(C_6H_{11})_3$	817	54.5 (54.3)	7.9 (8.1)		7.7 (7.6)	12.8 (12.6)
(20)	$MeO_2CCH{=}C(Me)O$	PPr^i_3	566	51.0 (50.9)	9.0 (8.7)		11.5 (10.9)	18.4 (18.2)
(21)	$NC_5H_4CO_2$-4	PPr^i_3	573	52.1 (52.4)	7.8 (8.1)	2.5 (2.4)	10.6 (10.8)	17.6 (17.9)

[a] Calculated values are given in parentheses. [b] $M^+ + 1$. [c] Crystallized with one molecule 1,3-dimethylimidazolidin-2-one. [d] Fragments 576 [Rh($O_2CC_6H_4CO_2H$-4)(CO){$P(C_6H_{11})_3$}] and 280 [$P(C_6H_{11})_3$] were observed.

assigned to PPh_3 are observed in the ^1H n.m.r. spectrum of the product, but no signals assigned to the enolate ligand are observed. This compound is assigned as $[Rh_2(CO)_6(PPh_3)_2]$.[11] The reactivity of methyl acetoacetate with $[Rh_2(CO)_6(PPh_3)_2]$ is considered to be low compared to that with $[Rh_2(CO)_6(PPr^i_3)_2]$ because of the different electronic or steric nature of the phosphine ligand.

Compound **(21)**, $[Rh(NC_5H_4CO_2\text{-}4)(CO)(PPr^i_3)_2]$, is prepared by the reaction of $[Rh_4(CO)_{12}]$, PPr^i_3, and pyridine-4-carboxylic acid. On the other hand only carbonyl(pyridine-2-carboxylato)(tri-isopropylphosphine)rhodium, **(22)**,[12] is formed in the presence of two equivalents of phosphine by the reaction with pyridine-2-carboxylic acid as represented in equation (4). The chelating effect of the anionic ligand may facilitate the formation of **(22)** compared to the formation of carbonyl(pyridine-2-carboxylato)bis(tri-isopropylphosphine)rhodium.



(4)

(22)

Mechanism of $[RhX(CO)L_2]$ *Formation.*—When dmi solutions of $[Rh_4(CO)_{12}]$ and $P(C_6H_{11})_3$ are mixed in a 1:8 molar ratio under a N_2 atmosphere at room temperature, the colour of the solution changes from dark brown to dark red. A single band at 1 943 cm^{-1} is observed after 3 h, and a yellow compound analysing as $[Rh_2(CO)_6\{P(C_6H_{11})_3\}_2]$ **(23)** slowly crystallizes. This compound is stable under a CO atmosphere in the solid state, but deepens to dark brown under a N_2 atmosphere. A similar compound $[Rh(CO)_3(PPr^i_3)_2]$ **(24)**[13] is obtained by the reaction of $[Rh_4(CO)_{12}]$ and PPr^i_3 in diethyl ether solution. Compound **(9)** is obtained by the addition of an equivalent of acetic acid to a solution of **(24)** and PPr^i_3 in a 1:2 molar ratio. Attempts to stop the reaction at an intermediate stage failed. A rhodium–hydride species, in which the hydrogen atom comes from the acid, may be formed as an unstable intermediate.

In order to obtain information about the intermediate stage, the reaction was carried out with bis(triphenylphosphine)iminium acetate $\{[N(PPh_3)_2][O_2CMe]\}$ instead of acetic acid. The dmi solution of **(24)** [$\nu_{max.}$(CO) 1 957 cm^{-1}] is obtained by the reaction of $[Rh_4(CO)_{12}]$ and PPr^i_3 in a 1:8 molar ratio [Figure 2(*a*)]. By the addition of an equivalent of $[N(PPh_3)_2][O_2CMe]$ to the solution, the single band at 1 957 cm^{-1} disappears and bands at 1 917 and 1 841 cm^{-1}, assignable to $[N(PPh_3)_2][Rh(CO)_3(PPr^i_3)]$, arise immediately with a weak band at 1 900 cm^{-1} assignable to $[N(PPh_3)_2][Rh(CO)_4]$, as shown in Figure 2(*b*). A single band at 1 949 cm^{-1} is observed by adding two equivalents of acetic acid to the solution of Figure 2(*b*) [Figure 2(*c*)]. The resultant compound is assigned to **(9)**. These results are summarized in equations (5)—(7), where $L = PPr^i_3$ and $X = O_2CMe$.

$$[Rh_4(CO)_{12}] + 4L \longrightarrow 2[Rh_2(CO)_6L_2] \quad (5)$$

$$[Rh_2(CO)_6L_2] + L + [N(PPh_3)_2]X \longrightarrow [RhX(CO)L_2] + [N(PPh_3)_2][Rh(CO)_3L] + 2CO \quad (6)$$

$$[N(PPh_3)_2][Rh(CO)_3L] + L + 2HX \longrightarrow [RhX(CO)L_2] + [N(PPh_3)_2]X + H_2 + 2CO \quad (7)$$

Based on these results, a possible reaction pathway for $[RhX(CO)L_2]$ formation from $[Rh_2(CO)_6L_2]$, L, and acid is proposed in equations (8) and (9) (L = phosphine, X = various anionic ligands).

$$[Rh_2(CO)_6L_2] + L + HX \longrightarrow [RhX(CO)L_2] + [RhH(CO)_3L] + 2CO \quad (8)$$

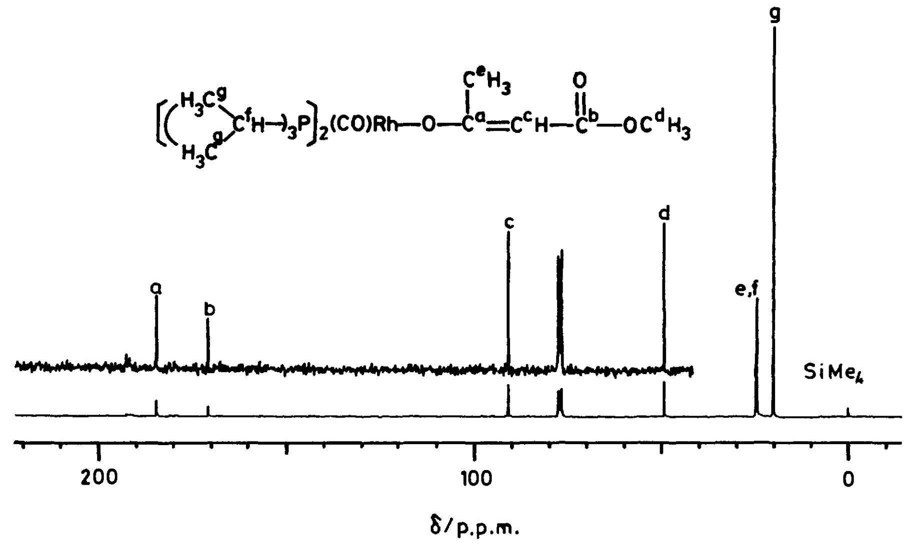


Figure 1. ^{13}C N.m.r spectrum of $[Rh\{OC(Me)=CHCO_2Me\}(CO)(PPr^i_3)_2]$ in $CDCl_3$; standard $SiMe_4$. Signal for the co-ordinated CO was not observed because of weakness. Chemical shifts are as follows, those for $[Pd\{OC(Me)=CHCO_2Et\}(CO)\{P(C_6H_{11})_3\}(\eta^3\text{-}C_8H_{13})]$[10] are given in parentheses: a, 187.57 (185.09); b, 170.84 (169.73); c, 90.90 (89.20); d, 49.35; e, 24.76 (28.21); f, 24.48; g, 20.07 p.p.m.

Table 2. Infrared and ^{31}P n.m.r. data for some $[RhX(CO)L_2]$ complexes

Compound	X	L	pK_a of HX	$\nu_{max.}(CO)^a$/cm^{-1}	$\delta(^{31}P)^b$/p.p.m.	J(Rh–P)/Hz	Δ/p.p.m.
(15)	ClO_4	$P(C_6H_{11})_3$	-14^c	1 969	45.09	99.6	33.57
(14)	$O_3SC_6H_4Me$-4	$P(C_6H_{11})_3$	1.70	1 954	39.00	119.1	27.48
(8)	$O_2CC_6H_4CO_2H$-2	$P(C_6H_{11})_3$	2.95	1 954	38.30	123.1	26.78
(5)	$O_2CC_6H_4NO_2$-4	$P(C_6H_{11})_3$	3.44	1 948	38.01	125.0	26.49
(6)	$O_2CC_6H_4CO_2H$-4	$P(C_6H_{11})_3$	3.54	1 943	38.09	127.0	26.57
(3)	$O_2CC_6H_4F$-3	$P(C_6H_{11})_3$	3.87	1 946	37.95	125.0	26.43
(1)	O_2CPh	$P(C_6H_{11})_3$	4.21	1 944	37.95	125.0	26.43
(7)	$O_2CC_6H_4CO_2H$-3	$P(C_6H_{11})_3$	4.60	1 942	37.74	125.0	26.22
(10)	O_2CMe	$P(C_6H_{11})_3$	4.76	1 943	37.82	127.0	26.30
(12)	OC_6F_5	$P(C_6H_{11})_3$	6.10	1 944	36.10	123.1	24.58
(2)	$O_2CC_6H_4F$-3	PPr^i_3	3.87	1 949	50.09	127.0	28.44
(4)	$O_2CC_6H_4F$-3	PPh_3	3.87	1 972	32.46	136.7	26.56

[a] In dichloromethane. [b] In $CDCl_3$; standard H_3PO_4. [c] Estimated.

$$[RhH(CO)_3L] + L + HX \longrightarrow [RhX(CO)L_2] + H_2 + 2CO \quad (9)$$

Electronic Properties of X *and* L.—Table 2 shows spectral data measured for 12 complexes of the type *trans*-$[RhX(CO)\{P(C_6H_{11})_3\}_2]$ and *trans*-$[Rh(O_2CC_6H_4F\text{-}3)(CO)L_2]$. For the former complexes, the value of the carbonyl absorption, ν(CO), correlates with the value of pK_a for the conjugate acid of X (linear correlation coefficient = −0.916). The co-ordination chemical shift Δ,[14] which is defined in equation (10), also correlates well with the value of pK_a for HX, with a correlation coefficient of −0.990, as shown in Figure 3.

$$\Delta = \delta[RhX(CO)L_2] - \delta(\text{free L}) \quad (10)$$

The value of Δ is considered to depend on the change in the electron density at phosphorus by co-ordination of the rhodium. These results indicate that the electron density on the rhodium decreases with an increase in the electronegativity of X. The coupling constant J(Rh–P) for the $P(C_6H_{11})_3$ complexes decreases with an increase in the value of pK_a for HX. The value of J(Rh–P) for the 3-fluorobenzoate complexes increases in the following order: $P(C_6H_{11})_3 < PPr^i_3 < PPh_3$.

The value of J(Pt–P) has been shown to increase with a decrease in the Pt–P length,[15] or in the oxidation number of the metal,[16] for the square-planar platinum complexes. The large overlap of *s* orbitals is said to cause large coupling constants.[17] The differences in J(Rh–P) can be explained in the same context because rhodium possesses the same dsp^2 hybrid orbitals and conformation as platinum. The length of the Rh–P bond is considered to increase in the following order: $PPh_3 < PPr^i_3 < P(C_6H_{11})_3$, which is deduced from the order of the J(Rh–P) values. This order is the same for the cone angle of the phosphine.[18] The length of the Co–P bond for the cobalt complex, $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}CO)_2Co(CO)_2L]$ (L = phosphine), is also shown to increase with an increase in the cone angle of the phosphine.[18] The basicity of tertiary phosphines is known to increase in the following order: $PPh_3 < P(C_6H_{11})_3 < PPr^i_3$.[19] Since the $Rh\text{–}P(C_6H_{11})_3$ bond length is longer than $Rh\text{–}PPh_3$, the electron donation of $P(C_6H_{11})_3$ to rhodium may be weaker than that of PPh_3. The order for the value of Δ, $PPh_3 \simeq P(C_6H_{11})_3 < PPr^i_3$, is understood in this respect.

Reduction of the Rhodium Complexes under Synthesis Gas.—The arylcarboxylate complexes are reduced to afford $[Rh(CO)_4]^-$ under atmospheric pressure of synthesis gas

Table 3. Reduction of $[Rh(O_2CC_6H_4R)(CO)L_2]$ under synthesis gas[a]

R	σ of R[b]	L	Additive (mmol)	Rate (h^{-1})	Product
H	0	$P(C_6H_{11})_3$		1.03	$[Rh(CO)_4]^-$
3-F	0.34	$P(C_6H_{11})_3$		0.76	$[Rh(CO)_4]^-$
3-F	0.34	$P(C_6H_{11})_3$	$[N(PPh_3)_2][O_2CMe]$ (0.1)	0.33	$[Rh(CO)_4]^-$, $[Rh(CO)_3L]^-$
3-F	0.34	$P(C_6H_{11})_3$	$[N(PPh_3)_2][O_2CMe]$ (0.1) $P(C_6H_{11})_3$ (1.0)	0.07	$[Rh(CO)_4]^-$, $[Rh(CO)_3L]^-$
3-F	0.34	PPr^i_3		0.48	$[Rh(CO)_4]^-$
3-F	0.34	PPh_3		*c*	$[Rh(CO)_4]^-$, $[RhH(CO)_2L_2]$[d]
$3-CO_2H$	0.45	$P(C_6H_{11})_3$		0.70	$[Rh(CO)_4]^-$
$4-NO_2$	0.78	$P(C_6H_{11})_3$		0.59	$[Rh(CO)_4]^-$

[a] Reaction conditions: complex (0.1 mmol); hmpa (5 cm^3); $CO:H_2$ (1:1), atmospheric pressure; temperature, 20 °C. [b] Substitution constant. [c] Not measured. [d] $\nu_{max.}(Rh\text{–}H)$, 2 039w; $\nu_{max.}(CO)$, 1 989s (sh), 1 942s cm^{-1}; $\delta(Rh\text{–}H)$, −9.5 p.p.m.

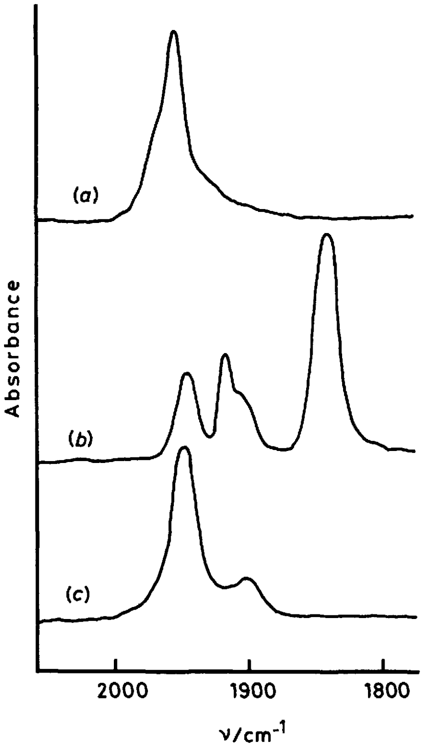


Figure 2. I.r. spectra for the reaction of $[Rh_2(CO)_6(PPr^i_3)_2]$, $[N(PPh_3)_2][O_2CMe]$, and $MeCO_2H$. Conditions: Rh, 0.1 mmol; dmi, 5 cm^3; N_2 atmosphere. (*a*) Reaction solution of $[Rh_4(CO)_{12}]$ and PPr^i_3; (*b*) $[N(PPh_3)_2][O_2CMe]$ (0.1 mmol) added to the solution in (*a*); (*c*) $MeCO_2H$ (0.2 mmol) added to the solution in (*b*)

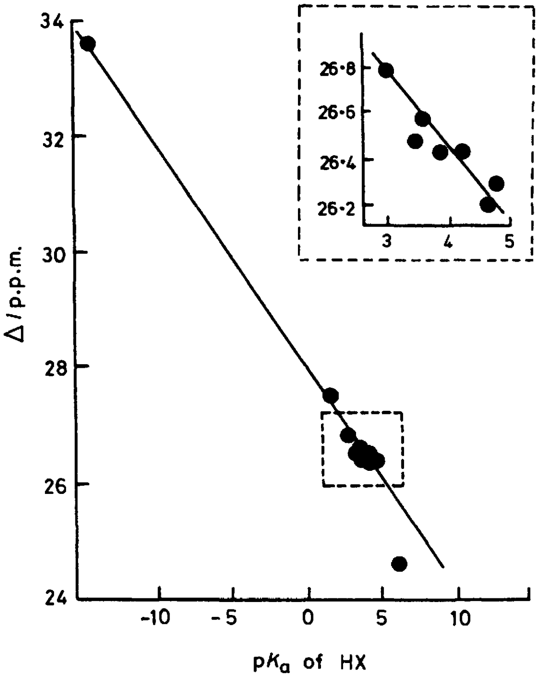


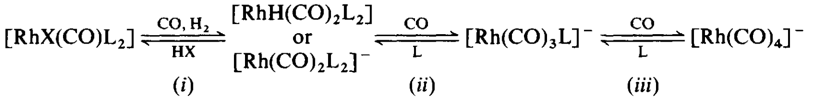
Figure 3. Relationship between co-ordination chemical shift and pK_a of HX

at room temperature in hexamethylphosphoramide (hmpa) solution. The initial rate of this reaction for seven of the complexes is shown in Table 3 together with the rates in the presence of $[N(PPh_3)_2][O_2CMe]$ or $P(C_6H_{11})_3$. Formation of arylcarboxylic acid is found from the i.r. spectra of the reaction solutions, in the region 1 720—1 710 cm^{-1}. The reduction is suppressed with addition of excess $P(C_6H_{11})_3$ or an equimolar amount of $[N(PPh_3)_2][O_2CMe]$. In the latter case, small amounts of $[N(PPh_3)_2][Rh(CO)_3\{P(C_6H_{11})_3\}]$ (1 841 cm^{-1}) are detected. This suggests that $[Rh(CO)_3\{P(C_6H_{11})_3\}]^-$, or $[RhH(CO)_3\{P(C_6H_{11})_3\}]$, is a possible intermediate. The decrease in the rate and the observation of the intermediate is considered to be due to stabilization of the intermediate by the large $[N(PPh_3)_2]^+$ cation.

Complex (4) reacts with synthesis gas to afford $[RhH(CO)_2(PPh_3)_2]$[20] and $[Rh(CO)_4]^-$. The former complex is thought to be the other intermediate.[21] No reactions occur in the absence of carbon monoxide. The starting complex is recovered by allowing the resultant solution to stand in a N_2 atmosphere. A possible reaction pathway is illustrated in the Scheme. A linear free energy relationship is found between the relative initial rate (r_R/r_H) of the reduction reaction of $[Rh(O_2CC_6H_4R)(CO)\{P(C_6H_{11})_3\}_2]$ (R = H, F, CO_2H, or NO_2) and the substitution constant, σ, of the substituent R on the arylcarboxylate ligand with a correlation coefficient of −0.985 (ρ = −0.31).

Compound (8) does not react with synthesis gas. This may be due to the high reactivity of the carboxyl group to shift the equilibrium (*i*), in the Scheme, to the left. The *p*-toluenesulphonate, chloro, and iodo complexes do not react with synthesis gas because of the higher electronegativities of the anionic ligands than that of the 4-nitrobenzoate ligand. The reduction rate of $[Rh(O_2CC_6H_4F\text{-}3)(CO)L_2]$ [L = PPr^i_3 or $P(C_6H_{11})_3$] increases with a decrease in the value of Δ. These results indicate that the rate increases with an increase in the electron density on rhodium.

We have found that the direct conversion of synthesis gas to ethylene glycol is more effectively catalysed by these aryl-



$$\underset{(i)}{[RhX(CO)L_2]} \underset{HX}{\overset{CO,\,H_2}{\rightleftharpoons}} \underset{(ii)}{\begin{matrix}[RhH(CO)_2L_2]\\ \text{or}\\ [Rh(CO)_2L_2]^-\end{matrix}} \underset{L}{\overset{CO}{\rightleftharpoons}} \underset{(iii)}{[Rh(CO)_3L]^-} \underset{L}{\overset{CO}{\rightleftharpoons}} [Rh(CO)_4]^-$$

Scheme.

carboxylate complexes than the rhodium–phosphine system.[22] The higher catalytic activities of the complexes may be ascribed to the reactivities with synthesis gas to $[RhH(CO)_2L_2]$ or the anionic rhodium species. The relation between the catalytic activity and the reactivity of the complex with synthesis gas has been discussed separately.[22]

Experimental

Materials.—Dodecacarbonyltetrarhodium was purchased from Nippon Engelhard. Tricyclohexylphosphine, purchased from Strem Chemicals, was dried *in vacuo* over a period of 2 d before use. The other phosphines and acids were purchased and used without further purification. Solvents were dried by standard procedures and distilled under a nitrogen atmosphere before use.

Measurements.—Infrared spectra were recorded on a JASCO A-102 spectrometer with a data processor. Hydrogen-1, ^{13}C, and ^{31}P n.m.r. spectra were recorded on JEOL FX-60SI, JEOL FX-270, and JEOL FX-90 spectrometers respectively. The initial rates of the reduction reaction of $[RhX(CO)L_2]$ under synthesis gas were determined from the decrease in $\nu_{max.}(CO)$ intensities for $[RhX(CO)L_2]$.

Syntheses.—Yields of the products are shown in Table 4, with the solvents employed. All reactions were carried out under a N_2 atmosphere.

(Benzoato)carbonylbis(tricyclohexylphosphine)rhodium, **(1)**. To a solution of $[Rh_4(CO)_{12}]$ (0.561 g, 0.75 mmol) in 1,3-dimethylimidazolidin-2-one (30 cm^3), tricyclohexylphosphine (1.683 g, 6 mmol), and benzoic acid (0.366 g, 3 mmol) were added. After mixing the solution for 5 h at room temperature, yellow crystals were collected, washed with cold diethyl ether (3 × 10 cm^3), and dried *in vacuo*. For further purification, the complex was recrystallized at 0 °C from toluene–hexane solution. A similar method was applied for the preparation of compounds **(3)**, **(5)**, **(6)**, **(7)**, **(8)**, **(12)**, and **(14)**.

Carbonyl(3-fluorobenzoato)bis(tri-isopropylphosphine)-rhodium, **(2)**. Dodecacarbonyltetrarhodium (0.75 mmol), tri-isopropylphosphine (0.962 g, 6 mmol), and 3-fluorobenzoic acid (0.421 g, 3 mmol) were mixed in diethyl ether (30 cm^3) for 5 h at room temperature. The solvent was evaporated under reduced pressure, and yellow crystals were obtained by recrystallization from hexane. Compounds **(4)**, **(9)**, **(11)**, and **(13)** were prepared by a similar method, but tetramethylurea was used as the solvent for the preparation of compound **(4)**.

Carbonyl(perchlorato)bis(tricyclohexylphosphine)rhodium, **(15)**. To a dmi solution (30 cm^3) of $[Rh_4(CO)_{12}]$ (0.75 mmol) and tricyclohexylphosphine (6 mmol), perchloric acid (60%, 1 cm^3) was added. The solution was mixed for 5 h at room temperature. The resultant solution was poured into water (30 cm^3). The precipitate was washed with diethyl ether (2 × 30 cm^3). Bright yellow crystals were obtained by recrystallization from toluene.

Carbonylchlorobis(tricyclohexylphosphine)rhodium, **(16)**. To a solution of $[Rh_4(CO)_{12}]$ (0.75 mmol) and tricyclohexylphosphine (6 mmol) in tetramethylurea (30 cm^3), hydrochloric acid (36%, 0.5 cm^3) was added, and the solution was mixed for 5 h. After evaporation of the solvent, yellow prisms were recrystallized from toluene. Compounds **(18)** and **(19)** were prepared by the same method.

Table 4. Preparation conditions and product yield (%) for the complexes

Compound	Solvent[a]	Crude product yield[b] (%)	Recrystallisation solvent	Pure product yield[b] (%)
(1)	Dmi	88	Toluene–hexane	79
(2)	Diethyl ether		Hexane	50
(3)	Dmi	75	Toluene–hexane	68
(4)	Tmu		Toluene–hexane	62
(5)	Dmi	87	Toluene–hexane	74
(6)	Dmi	90	Dmi	68
(7)	Dmi	85	Toluene–hexane	77
(8)	Dmi	89	Toluene–hexane	80
(9)	Diethyl ether		Pentane	50
(10)	Dmi	83	Toluene–hexane	71
(11)	Diethyl ether		Hexane	53
(12)	Dmi	65	Toluene–hexane	46
(13)	Diethyl ether		Hexane	65
(14)	Dmi	80	Toluene	75
(15)	Dmi		Toluene	77
(16)	Dmi	90	Toluene	78
(17)	Diethyl ether		Pentane	75
(18)	Tmu		Toluene	80
(19)	Dmi	94	Toluene	75
(20)	Diethyl ether			59
(21)	Diethyl ether			79
(22)	Diethyl ether		Toluene–hexane	93

[a] Dmi = 1,3-dimethylimidazolidin-2-one; tmu = 1,1,3,3-tetramethylurea. [b] Based on rhodium.

Carbonylchlorobis(tri-n-butylphosphine)rhodium, **(17)**. To a solution of $[Rh_4(CO)_{12}]$ (0.75 mmol) and tri-n-butylphosphine (1.213 g, 6 mmol) in diethyl ether (30 cm^3), hydrochloric acid (36%, 0.5 cm^3) was added, and the solution was mixed for 5 h. After the solvent was evaporated under reduced pressure, pentane (10 cm^3) was added to the residue, and the solution was mixed for 5 h. Deep yellow crystals were obtained by allowing the filtrate to stand for 5 h at −78 °C.

Carbonyl(1-methoxycarbonyl-2-propenolato)bis(tri-isopropylphosphine)rhodium, **(20)**. A diethyl ether solution (15 cm^3) of $[Rh_4(CO)_{12}]$ (0.75 mmol), tri-isopropylphosphine (6 mmol), methyl acetoacetate (0.523 g, 4.5 mmol), and triethylamine (1.5 cm^3) was mixed for 3 h at room temperature. The colour of the solution turned to yellow with yellow microcrystals. The crystals were collected, washed with diethyl ether (3 × 5 cm^3) and dried *in vacuo*. This gave satisfactory analysis without further purification. δ_H (270 MHz; solvent $CDCl_3$; standard $SiMe_4$) 4.75 (1 H, s, CH), 3.55 (3 H, s, OMe), 2.22 (6 H, m, 6 $CHMe_2$), 2.12 (3 H, s, Me), 1.34 [36 H, dd, J(CH) 7, J(PH) 14 Hz, 6 $CHMe_2$].

Carbonyl(pyridine-4-carboxylato)bis(tri-isopropylphosphine)-rhodium, **(21)**. Dodecacarbonyltetrarhodium (0.5 mmol), tri-isopropylphosphine (4 mmol), and pyridine-4-carboxylic acid (0.246 g, 2 mmol) were mixed for 24 h in diethyl ether (15 cm^3). The colour of the solution turned to yellow, and yellow crystals were formed slowly. Yellow microcrystals were obtained by allowing the solution to stand for 2 h at −78 °C. δ_H (60 MHz; solvent $CDCl_3$; standard $SiMe_4$) 8.62 (2 H, br d, 2 CH), 7.70 (3 H, d, 3 CH), 2.25 (6 H, m, 6 $CHMe_2$), 1.35 [36 H, dd, J(CH) 7, J(PH) 14 Hz, 6 $CHMe_2$].

Carbonyl(pyridine-2-carboxylato)(tri-isopropylphosphine)-

rhodium, (**22**). The reaction was carried out similarly to the method used for (**21**) using pyridine-2-carboxylic acid instead of pyridine-4-carboxylic acid. A yellow solution with small amounts of precipitate was obtained. Yellow crystals were obtained by evaporation of the solvent followed by recrystallization from toluene–hexane solution (Found: C, 46.2; H, 5.9; N, 3.3; P, 8.2; Rh, 24.2. $C_{16}H_{25}NO_3Rh$ requires C, 46.5; H, 6.1; N, 3.4; P, 7.5; Rh, 24.9%). $\nu_{max.}(CH_2Cl_2)$ 1 960 cm^{-1} (CO). δ_H (60 MHz; solvent $CDCl_3$; standard $SiMe_4$) 8.55 [1 H, br d, *J*(CH) 5, CH], 8.08 (1 H, m, CH), 7.93 (1 H, m, CH), 7.43 (1 H, m, CH), 2.33 (3 H, m, 3 C*H*Me$_2$), 1.36 [18 H, dd, *J*(CH) 8, *J*(PH) 12 Hz, 3 C*H*Me$_2$].

Hexacarbonylbis(tricyclohexylphosphine)dirhodium, (**23**). $[Rh_4(CO)_{12}]$ (0.75 mmol) and tricyclohexylphosphine (6 mmol) were mixed in dmi (5 cm^3) for 3 h. Yellow crystals were collected under a CO atmosphere, and washed with diethyl ether (3 × 5 cm^3). The product was dried under carbon monoxide (1.96 g, 70%) (Found: C, 53.3; H, 7.3; Rh, 21.9. $C_{42}H_{66}O_6P_2Rh_2$ requires C, 54.0; H, 7.1; Rh, 22.0%). $\nu_{max.}$ (CH_2Cl_2) 1 943 cm^{-1} (CO).

Hexacarbonylbis(tri-isopropylphosphine)dirhodium, (**24**). $[Rh_4(CO)_{12}]$ (0.75 mmol) and tri-isopropylphosphine (6 mmol) were mixed in diethyl ether (5 cm^3) for 3 h. The solution was cooled (−78 °C, 3 h), and yellow crystals were collected under a carbon monoxide atmosphere, and washed with cold diethyl ether (2 × 5 cm^3). The product was dried under carbon monoxide (1.17 g, 56%) (Found: C, 41.2; H, 6.1; Rh, 29.3. $C_{24}H_{42}O_6P_2Rh_2$ requires C, 41.5; H, 6.1; Rh, 29.6%). $\nu_{max.}$ (CH_2Cl_2) 1 956 cm^{-1} (CO).

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References

1 H. Tanaka, Y. Hara, E. Watanabe, K. Wada, and T. Onoda, *J. Organomet. Chem.*, 1986, **312**, C71; M. Tamura, M. Ishino, T. Deguchi, and S. Nakamura, *ibid.*, p. C75.
2 I. Wender and P. Pino, 'Organic Synthesis via Metal Carbonyls,' John Wiley and Sons, New York, 1977, vol. 2, p. 136.
3 A. Spencer, *J. Organomet. Chem.*, 1980, **194**, 113.
4 A. S. C. Chan, W. E. Carroll, and D. E. Willis, *J. Mol. Catal.*, 1983, **19**, 377.
5 R. P. Hughes, *Compr. Organomet. Chem.*, 1982, **5**, 277.
6 L. Vaska and J. Peone, jun., *Inorg. Synth.*, 1974, **15**, 65.
7 S. Martinengo, P. Chini, and G. Giordano, *J. Organomet. Chem.*, 1971, **27**, 389.
8 E. Watanabe, K. Murayama, Y. Hara, Y. Kobayashi, K. Wada, and T. Onoda, *J. Chem. Soc., Chem. Commun.*, 1986, 227.
9 A. S. C. Chan, H. S. Shieh, and J. R. Hill, *J. Organomet. Chem.*, 1985, **279**, 171.
10 P. W. Jolly, R. Mynott, B. Raspel, and K. P. Schick, *Organometallics*, 1986, **5**, 473.
11 R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1972, 1375.
12 R. Ugo, G. La. Monica, S. Cenini, and F. Bonati, *J. Organomet. Chem.*, 1968, **11**, 159.
13 Y. Tomotake, T. Matsuzaki, K. Murayama, E. Watanabe, K. Wada, and T. Onoda, *J. Organomet. Chem.*, 1987, **320**, 239.
14 B. E. Mann, C. Mesters, and B. L. Shaw, *J. Chem. Soc. A*, 1971, 1104.
15 G. G. Mather, A. Pidcock, and G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.*, 1973, 2095.
16 P. S. Pregosin and L. M. Venanzi, *Chem. Ber.*, 1978, **14**, 276.
17 R. Mason and D. W. Meek, *Angew. Chem.*, 1978, **90**, 195.
18 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 344.
19 W. A. Henderson, jun., and C. A. Streuli, *J. Am. Chem. Soc.*, 1960, **82**, 5791; T. T. Derencsenyi, *Inorg. Chem.*, 1981, **20**, 665.
20 D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 2660.
21 T. Yoshida, T. Okano, and S. Otsuka, *J. Am. Chem. Soc.*, 1980, **102**, 5966.
22 Y. Ohgomori, S. Yoshida, and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1987, 829.

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