

spectral data for (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and its oxidation and reduction products are summarized in Table IX.

The second oxidation of (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (process 1) occurs at the same half-wave potential as for oxidation of (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)ClO<sub>4</sub>. In addition, bulk electrolysis of (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> at +1.2 V in PhCN containing 0.1 M TBAP leads to a species that is ESR inactive. Further electrolysis at +1.6 V generates a solution whose ESR signal is detected at low temperature. The spectrum is singlet and symmetrical with a *g* value of 2.006. This is close to the free spin value, and the absorbance band width of 4.9 G is typical of a porphyrin cation radical which is assigned as [(OEP)Ge(C<sub>6</sub>H<sub>5</sub>)ClO<sub>4</sub>]<sup>+</sup>. Other (P)Ge(R)<sub>2</sub> undergo similar mechanisms.

In conclusion, the photochemistry, electrochemistry, and spectroelectrochemistry of (P)Ge(R)<sub>2</sub> are consistent with a

(30) Kadish, K. M.; Xu, Q. Y.; Barbe, J.-M.; Anderson, J. E.; Wang, E.; Guillard, R., submitted to *Inorg. Chem.*

mechanism involving cleavage of the germanium-carbon bond. This cleavage is either by irradiation with visible light or by electrooxidation of the complex. The low germanium-carbon bond energy of (P)Ge(R)<sub>2</sub> provides the feasibility of generating a very reactive alkyl or aryl radical. Thus, mono-alkyl or aryl monochlorogermanium(IV) porphyrins that cannot be synthesized with standard Grignard reactions are easily formed through photo-reactions involving dialkyl or diaryl germanium(IV) porphyrins in CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>.

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**Registry No.** (OEP)GeCl<sub>2</sub>, 31713-45-8; (TPP)GeCl<sub>2</sub>, 41043-38-3; (OEP)Ge(CH<sub>3</sub>)<sub>2</sub>, 110718-62-2; (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 110718-63-3; (OEP)Ge(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 110718-64-4; (TPP)Ge(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 110718-65-5; (TPP)Ge(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 74344-37-9; (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)Cl, 110718-66-6; (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)OH, 110718-67-7; (OEP)Ge(C<sub>6</sub>H<sub>5</sub>)ClO<sub>4</sub>, 110718-68-8.

## Hydroformylation of Fluoro Olefins, R<sub>f</sub>CH=CH<sub>2</sub>, Catalyzed by Group VIII Transition-Metal Catalysts. Crucial Factors for Extremely High Regioselectivity

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**Abstract:** Hydroformylations of fluoro olefins, trifluoroprop-1-ene (TFP), pentafluorobut-1-ene (PFB), heptafluoropent-1-ene (HPFP), heptadecafluorodec-1-ene (HPDFD), vinyl fluoride (VF), pentafluorostyrene (PFS), and allylpentafluorobenzene (4a), promoted by transition-metal catalysts were studied. Remarkable dependency of the regioselectivity of the reaction on the catalyst metal species (Co, Pt, Ru, and Rh) was found in the reactions of TFP and PFS; e.g., *n*-aldehyde was obtained with >93% selectivity by a cobalt catalyst whereas iso-aldehyde was obtained with >96% selectivity by a rhodium catalyst for the reaction of TFP. On the contrary, the reaction of VF gave 2-fluoropropanal (2-FPA) exclusively, regardless of the metal catalyst species. The effects of temperature and carbon monoxide pressure on the regioselectivity were investigated. Possible mechanisms for the uniquely regioselective hydroformylations are discussed on the basis of the results obtained, and a mechanism that involves an initial formation of isoalkyl-metal species followed by isomerization to *n*-alkyl-metal species and/or followed by carbon monoxide insertion to form isoacyl-metal intermediate was proposed to be the one operating in these reactions.

Hydroformylation of alkenes is an important reaction for the practical synthesis of aldehydes, and detailed studies on the mechanism of the reaction as well as applications to organic syntheses have been extensively studied.<sup>1,2</sup> However, little had been known about the reactions of alkenes bearing perfluoroalkyl or perfluoroaryl substituents when we started the research on this subject.<sup>3</sup> It has been shown that the introduction of trifluoromethyl or fluoro aromatic group into organic compounds often brings about unique chemical and biological properties.<sup>4</sup> Thus, the development of new synthetic methods that enable us to introduce these fluoro groups effectively and selectively to the desired molecules from readily available materials is of significant synthetic importance. With this respect, commercially available fluoro olefins such as 3,3,3-trifluoropropene (TFP), vinyl fluoride (VF), and pentafluorostyrene (PFS) are important starting materials.

Previously we studied the hydroformylation of TFP and PFS as one of our approaches to the functionalizations of these building blocks by means of transition-metal catalysts and briefly reported

unusually high regioselectivities and remarkable dependency of the regioselectivities of the reaction on the catalyst metal species, which is very unique in comparison with the hydroformylation of ordinary alkenes.<sup>5,6</sup> We describe here a full account of our

(1) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, pp 43-231.

(2) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer: Berlin, 1980; pp 1-225.

(3) Hydroformylation of hexafluoropropene was reported to give a mixture of hexafluoropropane (50%), alcohols (40%), and aldehydes (5-8%). See: Rudkovskii, D. M.; Imyanitov, N. S.; Gankin, V. Yu. *Tr., Vses. Nauchno-Issled. Inst. Neftekhim. Protsesov* 1960, 121; *Chem. Abstr.* 1962, 57, 10989. A patent claimed the reaction of heptadecafluorodecene, CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>CH=CH<sub>2</sub>, catalyzed by Co<sub>2</sub>(CO)<sub>8</sub>, which gave the corresponding alcohols or aldehydes. See: Roehrscheid, F. (Hoechst A.G.) *Ger. Offen.* 2 163 752, 1973; *Chem. Abstr.* 1973, 79, 78110m.

(4) (a) Filler, R., Ed. *Biochemistry Involving Carbon-Fluorine Bonds*; ACS Symposium Series 28; American Chemical Society: Washington, DC, 1976. (b) Smith, F. A. CHEMTECH 1973, 422. (c) Filler, R. CHEMTECH 1973, 752. (d) Filler, R.; Kobayashi, Y., Eds.; *Biomedical Aspects of Fluorine Chemistry*; Elsevier Biomedical: Amsterdam, 1982.

(5) Fuchikami, T.; Ojima, I. *J. Am. Chem. Soc.* 1982, 104, 3527.

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Table I. Hydroformylation of 3,3,3-Trifluoropropene (TFP)<sup>a</sup>

catalyst	TFP <sup>b</sup> cat.	pressure, atm <sup>c</sup> (CO/H <sub>2</sub> = 1)	temp °C	time, h	aldehydes <sup>d</sup>		alkane, <sup>d</sup> %
					%	iso/n	
Co <sub>2</sub> (CO) <sub>8</sub>	50	130	100	20	95	7/93	0
Co <sub>2</sub> (CO) <sub>8</sub> /PPh <sub>3</sub>	50	130	100	41	3	9/91	1
PtCl <sub>2</sub> (diop)/SnCl <sub>2</sub>	100	130	100	4	75	29/71	25
Ru <sub>3</sub> (CO) <sub>12</sub>	33	130	100	16	62	85/15	38
Ru <sub>3</sub> (CO) <sub>12</sub> /PPh <sub>3</sub>	33	130	100	39	25	92/8	1
Rh <sub>6</sub> (CO) <sub>16</sub>	1200	110	80	5	98	96/4	2
Rh <sub>6</sub> (CO) <sub>16</sub> /PPh <sub>3</sub>	1200	110	80	22	93	97/3	7
Rh <sub>4</sub> (CO) <sub>12</sub>	1200	110	80	6	97	97/3	3
Rh-C/P(OPh) <sub>3</sub>	1200	110	80	5	98	96/4	2
Rh-C	1200	110	80	5	96	96/4	4
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	1200	110	80	5	95	95/5	5
Rh-C/PPh <sub>3</sub>	1200	110	80	15	90	95/5	10
RhCl(dppb)	1200	110	80	22	42	97/3	<4
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	1200	110	80	22	30	96/4	<3
RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	1200	110	80	22	23	95/5	<2
RhCl <sub>3</sub> ·3H <sub>2</sub> O/PPh <sub>3</sub>	1200	110	80	22	17	96/4	<2

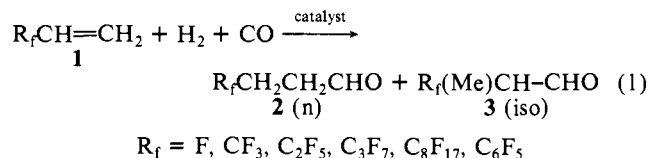
<sup>a</sup>All experiments were run with 130 mmol of TFP and 20 mL of toluene in a 200-mL stainless steel autoclave. <sup>b</sup>In mole TFP/mole metal. <sup>c</sup>Initial pressure at room temperature. <sup>d</sup>Determined by GLC.

Table II. Hydroformylation of Pentafluorostyrene (PFS)<sup>a</sup>

catalyst	PFS <sup>b</sup> cat.	pressure, atm <sup>c</sup> (CO/H <sub>2</sub> = 1)	temp, °C	time, h	conv, <sup>d</sup> %	aldehydes <sup>d</sup>		alkane, <sup>d</sup> %
						%	iso/n	
Co <sub>2</sub> (CO) <sub>8</sub>	21	80	90	12	67	54	21/79	9
	20	54 <sup>e</sup>	120	16	81	59	10/90	22
PtCl <sub>2</sub> (diop)/(SnCl) <sub>2</sub>	100	80	90	4	100	76	49/51	20
Ru <sub>3</sub> (CO) <sub>12</sub>	33	80	90	17	49	22	74/26	25
Rh <sub>6</sub> (CO) <sub>16</sub>	5000	80	90	3	100	100	97/3	0
Rh <sub>4</sub> (CO) <sub>12</sub>	5000	82 <sup>e</sup>	100	2	100	100	98/2	0
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	5000	80	90	8	100	100	98/2	0
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	333	90	90	20	100	100	97/3	0

<sup>a</sup>Reactions were run with 30–100 mmol of PFS and 15–30 mL of benzene in a 200-mL stainless steel autoclave. <sup>b</sup>In mole PFS/mole metal. <sup>c</sup>Initial pressure at room temperature. <sup>d</sup>Determined by GLC. <sup>e</sup>Pressure at the given temperature.

research on the hydroformylation of fluoro olefins, R<sub>f</sub>CH=CH<sub>2</sub> (R<sub>f</sub> = F, perfluoroalkyl, perfluorophenyl), catalyzed by group VIII transition-metal catalysts including a possible mechanism that can accommodate all the results obtained (eq 1).



## Results and Discussion

**Observation of Remarkable Dependency of Regioselectivity on the Catalyst Metal Species.** The hydroformylation of TFP was carried out with Co<sub>2</sub>(CO)<sub>8</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, Rh<sub>6</sub>(CO)<sub>16</sub>, and PtCl<sub>2</sub>(diop)/SnCl<sub>2</sub>, which are typical hydroformylation catalysts, at 100 °C (100 atm) (CO/H<sub>2</sub> = 1) for the Co, Pt, and Ru catalysts and at 80 °C (130 atm) (CO/H<sub>2</sub> = 1) for the Rh catalysts. Although the conditions employed were rather mild for the cobalt catalyst and rather drastic for the rhodium catalyst, we chose these conditions for fair comparison purpose. Results are listed in Table I.

As Table I shows, the reaction of TFP catalyzed by Co<sub>2</sub>(CO)<sub>8</sub> gave (trifluoromethyl)propanals (TFMPA) in 95% yield where a "normal" aldehyde, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO (3-TFMPA), was formed with high regioselectivity (93%). In sharp contrast with Co<sub>2</sub>(CO)<sub>8</sub>, the rhodium carbonyl cluster Rh<sub>6</sub>(CO)<sub>16</sub> exhibited extremely high catalytic activity and regioselectivity (96%) to give "iso" aldehyde, CF<sub>3</sub>(CH<sub>3</sub>)CHCHO (2-TFMPA). The platinum catalyst, PtCl<sub>2</sub>(diop)/SnCl<sub>2</sub>, favored the formation of *n*-aldehyde (n/iso = 71/29), while Ru<sub>3</sub>(CO)<sub>12</sub> gave iso-aldehyde as main product (n/iso = 15/85), and in both cases, substantial amounts of hydrogenated product, CF<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, were formed (25–38%). Addition of triphenylphosphine to the Co, Ru, and Rh catalysts

considerably decreased the catalytic activities but somewhat increased the iso-aldehyde selectivity. The result forms a contrast to the cases of ordinary olefins where the addition of triphenylphosphine increases *n*-aldehyde selectivity.

Since Rh<sub>6</sub>(CO)<sub>16</sub> gave excellent regioselectivity in the formation of 2-TFMPA, several other rhodium catalysts were employed to examine their catalytic activities as well as regioselectivities. Results are also listed in Table I. The results clearly indicate that the rhodium(I) complexes having chlorine as ligand, such as RhCl(PPh<sub>3</sub>)<sub>3</sub>, are less active than HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, Rh-C, Rh<sub>4</sub>(CO)<sub>12</sub>, and Rh<sub>6</sub>(CO)<sub>16</sub>, but the regioselectivity is virtually the same in all cases examined.

Consequently, it is disclosed that the nature of the central metal of the catalyst plays a key role in determining the regioselectivity of the reaction. Moreover, it should be noted that the metal species dependency of regioselectivity in the present reaction is extremely remarkable compared with that reported for propene.<sup>7</sup>

In a similar manner, the hydroformylation of PFS was carried out at 90 °C (80 atm) with the use of cobalt, platinum, ruthenium, and rhodium catalysts. The results are as shown in Table II.

As Table II shows, rhodium catalysts exhibited high catalytic activity to give iso-aldehyde, C<sub>6</sub>F<sub>5</sub>(CH<sub>3</sub>)CHCHO (2-PFPPA), with excellent regioselectivity (97–98%) and quantitative yield, while Co<sub>2</sub>(CO)<sub>8</sub> gave *n*-aldehyde (3-PFPPA) as the major product, where the regioselectivity was not so high as that observed in the

(7) The reported regioselectivities in the formation of butanal with cobalt, platinum, ruthenium, and rhodium catalysts are as follows: Co<sub>2</sub>(CO)<sub>8</sub><sup>8</sup> [150 atm; CO/H<sub>2</sub> = 1; 110 °C] 94%, iso/n = 20/80; PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/SnCl<sub>2</sub><sup>9</sup> [89 atm; CO/H<sub>2</sub> = 1; 66 °C] 90%, iso/n = 13/87; Ru<sub>3</sub>(CO)<sub>12</sub><sup>8</sup> [150 atm; CO/H<sub>2</sub> = 1; 110 °C] 40%, iso/n = 26/74; Rh<sub>6</sub>(CO)<sub>16</sub><sup>10</sup> [120 atm; CO/H<sub>2</sub> = 1; 70 °C] 51%, iso/n = 49/51.

(8) Pino, P.; Piacenti, F.; Bianchi, M.; Lazzaroni, R. *Chim. Ind. (Milan)* **1968**, *50*, 106.

(9) Shwager, I.; Knifton, J. F. (Texaco Development Co.) *Ger. Offen.* 2 322 751, 1973; *Chem. Abstr.* **1974**, *80*, 70327m.

(10) Booth, B. L.; Else, M. J.; Fields, R.; Haszeldine, R. N. *J. Organomet. Chem.* **1971**, *27*, 119.

(6) Ojima, I.; Fuchikami, T. U.S. Patent 4 370 504, 1983.

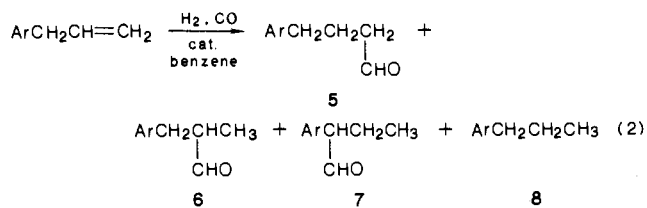
reaction of TFP. The ruthenium catalyst,  $Ru_3(CO)_{12}$ , showed rather low catalytic activity, giving iso-aldehyde as the major isomer, and a substantial amount of hydrogenated product,  $C_6F_5CH_2CH_3$ , was formed. The platinum catalyst,  $PtCl_2(\text{diop})/SnCl_2$ , showed a high catalytic activity, but virtually no regioselectivity was observed; the hydrogenation of PFS took place as a severe side reaction. As a whole, the metal species dependency of regioselectivity is similar to that for TFP, and it is also remarkable compared with that reported for styrene.<sup>11</sup>

A kinetic study was performed for the  $Rh_4(CO)_{12}$ - and  $Co_2(CO)_8$ -catalyzed reactions of PFS. At 100 °C (82 atm) ( $CO/H_2 = 1$ ) with  $1.0 \times 10^{-5}$  M catalyst concentration, the rhodium-catalyzed reaction is first order to the PFS concentration and the apparent rate constant for  $Rh_4(CO)_{12}$  is calculated to be  $6.2 \times 10^{-4} s^{-1}$ ; i.e., the turnover number is estimated to be  $55\,800 h^{-1}$  per rhodium metal. The cobalt-catalyzed reaction with  $1.0 \times 10^{-2}$  M catalyst concentration at 100 °C (82 atm) ( $CO/H_2 = 1$ ) is also first order to the PFS concentration, and the apparent rate constant is calculated to be  $1.6 \times 10^{-5} s^{-1}$ ; i.e., the turnover number per cobalt metal is  $2.88 h^{-1}$ . Namely, the rhodium catalyst is ca. 20 000 times more active than the cobalt catalyst per metal, provided that all metal species participate in the catalysis.<sup>15</sup>

Judging from the fact that the addition or the introduction of tertiary phosphines to the catalyst brings about only a slight change of regioselectivity, in sharp contrast with the hydroformylation of propene or styrene with the same catalysts, both TFP and PFS may well have a large binding constant with catalyst metal species, and thus they should act as an important ligand that stabilizes the catalysts during the reaction.

In order to examine the effects of perfluoroalkyl substituents longer than the trifluoromethyl group on the regioselectivity, we carried out the hydroformylation of other fluoro olefins of the type  $R_fCH=CH_2$  where  $R_f$  is  $C_2F_5$  (PFB),  $C_3F_7$  (HPFP), and  $C_8F_{17}$  (HPDFD). As shown in Table III, the reactions gave much lower regioselectivities than that for TFP under standard conditions, i.e., at 80 °C (110 atm) ( $CO/H_2 = 1$ ).

Next, we carried out the hydroformylation of allylpentafluorobenzene with rhodium catalysts (eq 2). The reaction gave the iso/n ratio of 3/2-2/1, and the difference in the regioselectivity between allylpentafluorobenzene and allylbenzene was not as remarkable as that for PFS and styrene (Table IV).



The cobalt-catalyzed reactions of allylpentafluorobenzene and allylbenzene gave rather complicated results because of the occurrence of severe isomerization especially for allylbenzene, which led to the formation of the other branched aldehyde 7 through the hydroformylation of propen-1-ylbenzene generated in situ by the isomerization (Table IV). It should also be noted that only

(11) The reported regioselectivities in the formation of phenylpropanal under typical conditions are as follows:  $Co_2(CO)_8$  [80 atm;  $CO/H_2 = 1$ ; 120 °C] 46%, iso/n = 59/41;  $PtCl_2(\text{diop})/SnCl_2$  [250 atm;  $CO/H_2 = 1$ ; 100 °C] 60%, iso/n = 57/43;  $Rh_2Cl_2(CO)_4$  [62 atm;  $CO/H_2 = 1$ ; 130 °C] 93%, iso/n = 43/57;  $Rh_2Cl_2(CO)_4/PPh_3$  [62 atm;  $CO/H_2 = 1$ ; 130 °C] 98%, iso/n = 72/28.

(12) Botteghi, C.; Consiglio, G.; Pino, P. *Chimia* 1972, 26, 141.

(13) Kawabata, Y.; Suzuki, T.; Ogata, I. *Chem. Lett.* 1978, 361.

(14) Ogata, I.; Ikeda, Y.; Asakawa, T. *Kogyo Kagaku Zasshi* 1971, 74, 1839.

(15) Under the reaction conditions employed (82 atm;  $CO/H_2 = 1$ ; 100 °C), all of  $Rh_4(CO)_{12}$  and  $Co_2(CO)_8$  is not necessarily converted to the corresponding "real active catalyst species", e.g.,  $HRh(CO)_4$  and  $HCo(CO)_4$ . Thus, those values do not directly reflect the relative activity of real active catalyst species.

Table III. Regioselectivities in the Hydroformylation of  $R_fCH=CH_2$  Catalyzed by  $Rh_4(CO)_{12}$ <sup>a</sup>

$R_fCH=CH_2$	pressure, <sup>b</sup> atm ( $CO/H_2 = 1$ )	temp, <sup>c</sup> °C	time, h	aldehydes <sup>c</sup> (iso/n)
$FCH=CH_2$	110	80	6	100/0
$CF_3CH=CH_2$	110	80	6	96.6/3.4
$C_2F_5CH=CH_2$	110	80	6	83.1/16.9
	110	60	6	94.7/5.3
$C_3F_7CH=CH_2$	110	80	6	74.3/25.7
	110	60	6	91.0/9.0
$C_8F_{17}CH=CH_2$	110	80	6	72.8/27.2
	110	60	6	92.2/7.8

<sup>a</sup> Reactions were run with 0.12–0.77 mmol of substrate and  $5.0 \times 10^{-4}$  mmol of  $Rh_4(CO)_{12}$  in 0.5 mL of toluene. <sup>b</sup> Initial pressure at the given temperature. <sup>c</sup> Determined by GLC.

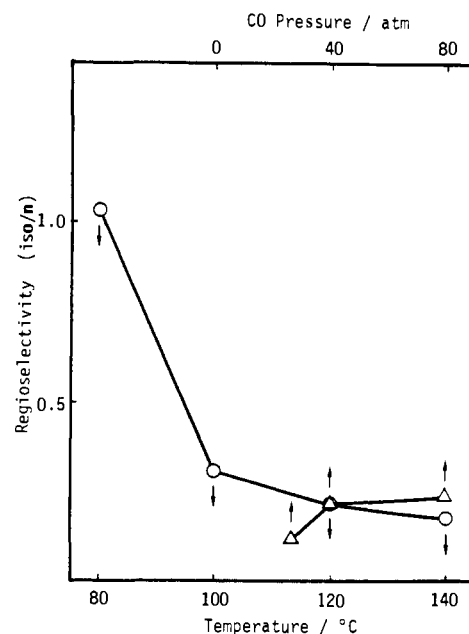


Figure 1. Effects of reaction temperature (O) and carbon monoxide pressure (Δ) on the regioselectivity of the hydroformylation of PFS catalyzed by  $Co_2(CO)_8$ . All reactions were run with 1.0 mM PFS and 0.05 mM  $Co_2(CO)_8$  in benzene for 16 h.

a negligible amount (1–2%) of isomerization was observed in the rhodium-catalyzed reactions of allylbenzene and no isomerization was detected for allylpentafluorobenzene.

We also carried out the hydroformylation of vinyl fluoride (VF) promoted by rhodium, ruthenium, and cobalt catalysts (eq 3). To

#### Scheme I

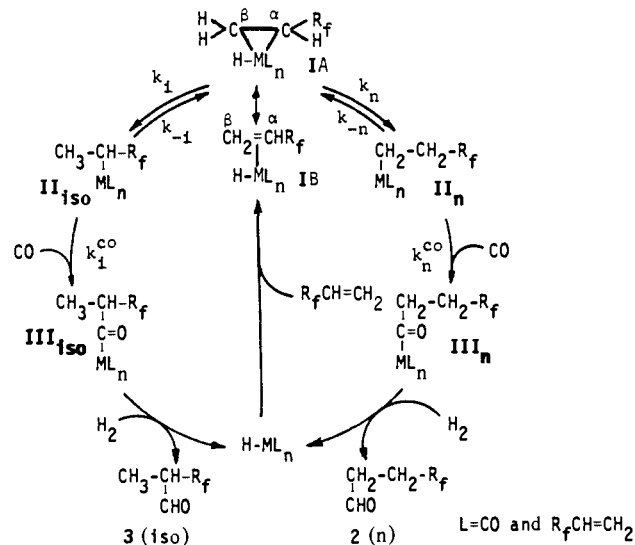


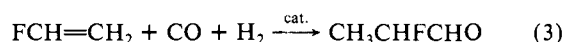
Table IV. Hydroformylation of (Pentafluoroallyl)benzene and Allylbenzene<sup>a</sup>

Ar	catalyst	pressure, <sup>b</sup> atm (CO/H <sub>2</sub> = 1)	temp, °C	time, h	conv, %	yield, <sup>c</sup> %	5/6/7/8
C <sub>6</sub> F <sub>5</sub>	Co <sub>2</sub> (CO) <sub>8</sub>	80	100	16	82	79	53/41/2/4
	Rh <sub>6</sub> (CO) <sub>16</sub>	80	95	13	100	100	41/59/0/0
	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	80	95	3	100	94	39/61/0/0
Ph	Co <sub>2</sub> (CO) <sub>8</sub>	80	100	16	100	45	60/14/26/0
	Rh <sub>6</sub> (CO) <sub>16</sub>	80	95	3	100	76	47/52/1/0
	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	80	95	3	100	78	50/48/2/0

<sup>a</sup> Reactions were run with 0.5 mmol of substrate and 0.001–0.0012 mmol (for rhodium) or 0.05 mmol (for cobalt) of catalyst in 1.0 mL of benzene.

<sup>b</sup> Initial pressure at room temperature. <sup>c</sup> Determined by GLC.

our surprise, the reaction gave 2-fluoropropanal (2-FPA) exclusively, regardless of the catalyst species! (See the Experimental Section.)



cat. = Rh<sub>4</sub>(CO)<sub>12</sub>, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, Co<sub>2</sub>(CO)<sub>8</sub>

**Mechanism of the Highly Regioselective Hydroformylation.** The observed remarkable dependency of regioselectivity on the catalyst metal species may well be accommodated by considering the stability of isoalkyl-metal species, the isomerization ability of isoalkyl-metal species, and the relative rate of the migratory insertion of carbon monoxide into isoalkyl- and *n*-alkyl-metal bonds.<sup>16</sup>

(16) We also considered other possible rationalizations, i–iii, to accommodate the observed unique regioselectivities. However, these possibilities were ruled out as described below. (i) The charge distribution of the hydrogen-metal bond of HM(CO)<sub>n</sub>(R<sub>f</sub>CH=CH<sub>2</sub>)<sub>m</sub>, which is assumed to be an active catalyst species in the reaction, is dependent on the metal, M; e.g., H–Rh species is more hydridic than H–Co species, and thus H–Rh species undergoes a hydride addition to the terminal carbon (C<sup>2</sup>) of R<sub>f</sub>CH=CH<sub>2</sub>, giving a branched alkyl-Rh complex, whereas H–Co species undergoes a Michael-type addition to R<sub>f</sub>CH=CH<sub>2</sub>, giving a straight-chain alkyl-Co complex provided that R<sub>f</sub>CH=CH<sub>2</sub> has negative hyperconjugation. However, this rationalization seems rather unlikely since Vidal and Walker reported<sup>17</sup> that HRh(CO)<sub>4</sub> is a slightly stronger Brønsted acid than HCo(CO)<sub>4</sub>; viz., the charge distribution of the H–Rh bond is hydrogen positive and rhodium negative as in the case of the H–Co bond. Thus, there should not be a substantial difference in the mode of the addition of metal hydride to R<sub>f</sub>CH=CH<sub>2</sub> in these two hydridometal species. However, Norton et al. reported<sup>18</sup> that HCo(CO)<sub>4</sub> is much more acidic than H<sub>2</sub>Ru(CO)<sub>4</sub>, and there have been no data for the acidity of hydridometal complexes of the type, HM(CO)<sub>n</sub>(CH<sub>2</sub>=CHR<sub>f</sub>)<sub>m</sub>. Also, the reactivity of metal hydrides does not necessarily reflect the acidity. Thus, this possibility cannot completely be ruled out, but at least it should not be the major factor. (ii) The rhodium complex has an attractive interaction between the central rhodium metal and fluorine of the R<sub>f</sub> group, which can stabilize either a branched alkyl-Rh complex or a branched acyl-Rh complex while the cobalt complex does not have such Co...F interaction, and the platinum and ruthenium complexes are in between cobalt and rhodium. If this rationalization were true, the hydroformylation of PFB, HPFP, and HPDFD should give similar regioselectivity to that for TFP. However, the reactions of those fluoro olefins gave substantially lower regioselectivities (Table III); viz., the results do not support this rationalization. If the attractive Rh...F interaction were crucial, (a) the regioselectivity attained in the reaction of allylpentafluorostyrene should be as high as that for PFS and (b) the reactions of VF should give 3-fluoropropanal (3-FPA), predominantly. However, any remarkable difference in regioselectivity was observed between allylbenzene and (pentafluoroallyl)benzene as shown in Table IV in the former case and 2-FPA was exclusively formed in the latter case. All these results were unfavorable to this rationalization. Thus, this possibility was eliminated. (iii) As trifluoromethyl and pentafluorophenyl groups are strongly electron-withdrawing substituents, a negative charge on the α-carbon stabilizes the branched alkyl-metal intermediate while a positive charge on the α-carbon destabilizes the branched alkyl-metal intermediate, and thus the straight-chain intermediate becomes preferable. The alkyl-cobalt species may cause a fairly large positive charge on the α-carbon whereas the alkyl rhodium species may generate relatively large negative charge on the α-carbon, and the platinum and ruthenium species can be placed between cobalt and rhodium. However, this rationalization is also unlikely, at least as it is, since alkyl-cobalt complexes usually generate nucleophilic carbons reacting with electrophiles and do not behave as carbenium ion like species. However, it is reasonable to think that there is a substantial difference between rhodium and cobalt in the polarizability of carbon-metal bond. Accordingly, the carbon-rhodium bond of R<sub>f</sub>(Me)CH–Rh(CO)<sub>n</sub>(R<sub>f</sub>CH=CH<sub>2</sub>)<sub>m</sub> is more carbanion-like than the carbon-cobalt bond of R<sub>f</sub>(Me)CH–Co(CO)<sub>n</sub>(R<sub>f</sub>CH=CH<sub>2</sub>)<sub>m</sub>, which may reflect the difference in stability of the isoalkyl metal intermediates and thus the regioselectivity of the reaction.

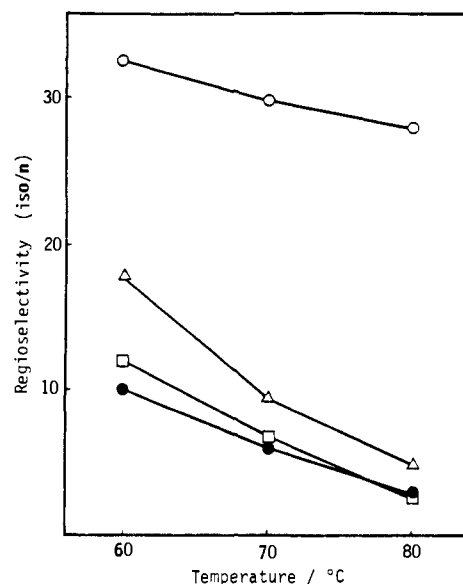


Figure 2. Effects of reaction temperature on the regioselectivity of the hydroformylation of TFP (○), PFB (△), HPFP (●), and HPDFD (□) catalyzed by Rh<sub>4</sub>(CO)<sub>12</sub>. All reactions were run with 0.12–2.5 mM fluoro olefin and 5.0 × 10<sup>-4</sup> mM Rh<sub>4</sub>(CO)<sub>12</sub> in toluene under the pressure of carbon monoxide (55 atm) and hydrogen (55 atm) for 6 h.

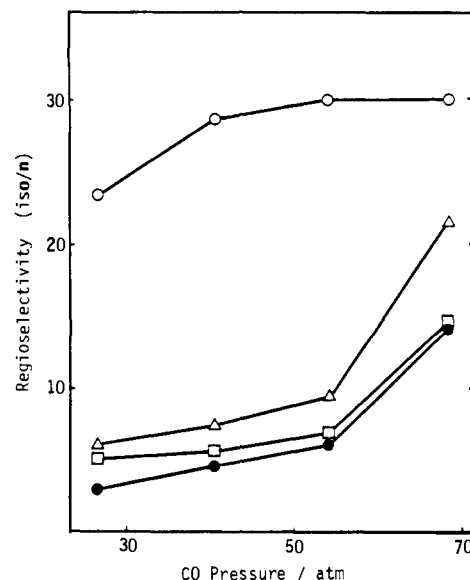


Figure 3. Effects of carbon monoxide pressure on the regioselectivity of the hydroformylation of TFP (○), PFB (△), HPFP (●), and HPDFD (□) catalyzed by Rh<sub>4</sub>(CO)<sub>12</sub>. All reactions were run with 0.12–2.5 mM fluoro olefin and 5.0 × 10<sup>-4</sup> mM Rh<sub>4</sub>(CO)<sub>12</sub> in toluene at 70 °C for 6 h.

As shown in Scheme I, when a substituent possessing a large "group electronegativity"<sup>19</sup> is introduced to an olefin, the metal-C<sup>α</sup>

(17) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* 1981, 20, 249.

bond of a  $\eta^2$ -olefin-metal complex (IA) should be stronger than the metal-C $\beta$  bond because of substantial stabilization of the formal negative charge developing on the C $\alpha$ . Therefore, the formation of isoalkyl-metal species (II<sub>iso</sub>) should be much more favorable than that of *n*-alkyl-metal species (II<sub>n</sub>) regardless of the group VIII transition-metal species. In fact, the results of the hydroformylations of vinyl fluoride (VF) provide strong supporting evidence for this. Namely, regardless of the catalyst species employed, the reaction of VF gave 2-fluoropropanal (2-FPA) exclusively (eq 3).<sup>20</sup>

The iso/*n* ratio of aldehydes should reflect the ratio of the intermediate isoacyl- and *n*-acyl-metal species (III<sub>iso</sub> and III<sub>n</sub>) (Scheme I) under the sufficient pressure of hydrogen; i.e., under such conditions, the hydrogenolysis of the acyl-metal species is not the rate-determining step. Thus, it is deduced that, in the rhodium-catalyzed reaction, the rate constants of carbon monoxide insertion,  $k_{iso}^{CO}$  and  $k_n^{CO}$ , are much larger than those of isomerization,  $k_{-1}$  and  $k_{-n}$  (viz.,  $k_{iso}^{CO} \gg k_{-1}$  and  $k_n^{CO} \gg k_{-n}$ ), and thus the initially formed isoalkyl-Rh species (II<sub>iso</sub>; M = Rh) generates isoacyl-Rh species (III<sub>iso</sub>; M = Rh) and gives the corresponding iso-aldehyde with high regioselectivity. In sharp contrast with this, in the cobalt-catalyzed reaction, the following relations are deduced:  $k_{-n} \gg k_n^{CO}$  and  $k_{-1} \gg k_{iso}^{CO}$ . Accordingly, the alkyl-metal intermediates, II<sub>iso</sub> and II<sub>n</sub> (M = Co), should be in a preequilibrium, which favors sterically less demanding II<sub>n</sub> (M = Co) and then gives the corresponding *n*-aldehyde selectively.<sup>21</sup> The substantial isomerization observed in the cobalt-catalyzed hydroformylation of allylbenzene strongly supports this proposed mechanism (vide supra).

The rhodium- and cobalt-catalyzed reactions are extremely selective cases and the platinum- and ruthenium-catalyzed reactions are in between the two extreme cases.

**Effects of Reaction Temperature and Pressure of Carbon Monoxide on Regioselectivity.** In order to obtain supporting evidence for the proposed mechanism, we looked at the effects of temperature and carbon monoxide pressure on the regioselectivity of the reactions catalyzed by Co<sub>2</sub>(CO)<sub>8</sub> and Rh<sub>4</sub>(CO)<sub>4</sub>. If the proposed mechanism is operative, the iso/*n* ratio of aldehydes should decrease at a high temperature and a low carbon monoxide pressure since a high temperature facilitates the isomerization and a low carbon monoxide pressure slows down the carbon monoxide insertion step, and vice versa.

In fact, the expected effects of temperature and carbon monoxide pressure were observed as shown in Figure 1. Thus, it is apparent that the isoalkyl-metal species (II<sub>iso</sub>; M = Co) is the favorable initial intermediate even in the cobalt-catalyzed reaction.<sup>22</sup>

(18) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(19) For a review of "group electronegativity", see: Wells, P. R. In *Progress in Physical Organic Chemistry*; Streitwieser, A., Jr., Taft, R. W., Eds.; Wiley-Interscience: New York, 1968; Vol. 6, pp 111-145. For a calculation, see: Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271.

(20) Since the F substituent has much stronger electronegativity than any perfluoroalkyl groups, an  $\alpha$ -fluoroethyl-metal species (equivalent to the isoalkyl-metal species in this discussion) should be much more favorable than the corresponding  $\beta$ -fluoroethyl-metal species (equivalent to the *n*-alkyl-metal species in this discussion).

(21) A similar kinetically controlled formation of an isoalkyl-cobalt species was reported in the hydroformylation of styrene catalyzed by HCo(CO)<sub>4</sub>: Ungvary, F.; Marko, L. *Organometallics* **1982**, *1*, 1120.

(22) It should be noted that in the hydroformylations of ordinary 1-alkenes, the *n*/*iso* ratio goes down as the reaction temperature becomes higher to lose the selectivity; i.e., the *n*/*iso* ratio is reaching 1. A remarkable dependence of regioselectivity on the reaction temperature similar to the PFS case was reported in the hydroformylations of methyl methacrylate with Co<sub>2</sub>(CO)<sub>8</sub> by Falbe and Huppel,<sup>2</sup> and ethyl acrylate with Rh<sub>4</sub>(CO)<sub>4</sub> by Takegami et al.<sup>23</sup> In those cases, an inversion of regioselectivity was observed by changing the reaction temperature; viz., the rhodium carbonyl behaved similarly to cobalt carbonyl. The Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed reaction of ethyl acrylate was reported to give *n*-aldehyde with high selectivity and did not show such drastic change in regioselectivity as the rhodium-catalyzed reaction although the tendency was similar, i.e., the lower the temperature, the higher the iso-aldehyde content. A similar dependence of regioselectivity on the reaction temperature was also reported by Botteghi et al.<sup>24</sup>

(23) Takegami, Y.; Watanabe, Y.; Masada, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1459.

Clear effects of the reaction temperature on the regioselectivity were also observed in the Rh<sub>6</sub>(CO)<sub>16</sub>-catalyzed reaction of PFS.<sup>25</sup>

The results with the use of TFP, PFB, HPFP, and HPDFD as substrates and Rh<sub>4</sub>(CO)<sub>12</sub> as the catalyst are shown in Figures 2 and 3.

Besides these kinetic aspects, we should take into account the fundamental difference between each isoalkyl-metal intermediate. For example, we must ask ourselves why rhodium prefers the isoalkyl-metal intermediate much more than cobalt does and why the  $k_i/k_{CO}$  ratio is much larger for cobalt than for rhodium. In order to answer these questions, we should take into account the size of the metal and the polarizability of the metal-carbon bond in each case. Since rhodium is substantially larger than cobalt, rhodium should be less sensitive to steric effects than cobalt and the rhodium-carbon bond should have more polarizability than the cobalt-carbon bond. Consequently, (i) the less sterically demanding *n*-alkyl-metal species is much more favorable in the cobalt case than the rhodium case, and thus cobalt has a much larger  $k_i/k_{CO}$  ratio than rhodium, and (ii) the isoalkyl-rhodium species can obtain much larger stabilization than the isoalkyl-cobalt species because of the larger polarizability of the rhodium-carbon bond. According to this rationalization, the relative stability of II<sub>iso</sub> can be estimated to increase in the order R<sub>f</sub>(Me)CH-CoL<sub>n</sub> < R<sub>f</sub>(Me)CH-PtL<sub>n</sub> < R<sub>f</sub>(Me)CH-RuL<sub>n</sub> < R<sub>f</sub>(Me)CH-RhL<sub>n</sub>.

In conclusion, the remarkable dependence of regioselectivity on the catalyst metal species was disclosed by using fluoro olefins as unique substrates. It is also noteworthy that we demonstrated the excellent applicability of homogeneous transition-metal catalysts to the functionalization of fluoro olefins, which has opened a new research area in the interface of organofluorine chemistry and homogeneous catalysis. From a synthetic viewpoint, the hydroformylation products, 3-R<sub>f</sub>-propanal and 2-R<sub>f</sub>-propanal (R<sub>f</sub> = F, perfluoroalkyl, and perfluorophenyl), are versatile building blocks for the synthesis of a variety of fluorine-containing compounds. For instance, 2- and 3-TFMPA and 2- and 3-PFPPA have been successfully converted to the corresponding biologically active fluoro amino acids and related compounds such as trifluorovaline,<sup>26,27</sup> trifluoronorvaline,<sup>26,27</sup> trifluoroisoleucine,<sup>27</sup> trifluoronorleucine,<sup>27</sup> tetrafluorotryptophan,<sup>27-29</sup> tetrafluoroindoleacetic acid,<sup>27,28</sup> tetrafluorotryptamine,<sup>27,28</sup> and tetrafluoroindoles.<sup>27,28</sup> 2-FPA is an excellent precursor of monofluorinated compounds such as 3-fluorohomocysteine, which is known to be a strong enzyme inhibitor of cystathionases.<sup>30</sup>

## Experimental Section

**General Methods.** Boiling points and melting points are uncorrected. The <sup>1</sup>H NMR spectra were measured with a Nicolet NT-300, a Varian XL-100-15A, or a Varian EM 390 spectrometer with Me<sub>4</sub>Si as the internal standard. The <sup>19</sup>F NMR spectra were recorded on a Nicolet NT-300, a Varian XL-100-15A, or a Hitachi R-20B spectrometer with CFC<sub>3</sub> as the internal standard. The IR spectra were recorded on a Perkin-Elmer 1310 or 1430 or a Jasco A-202 spectrophotometer with samples as neat liquid or KBr disks. Analytical gas chromatography was carried out with a Hewlett-Packard 5830A, Perkin-Elmer 3920 with a Hewlett-Packard 3380A integrator, or Shimadzu GC-7A gas chromatograph.

(24) Botteghi, C.; Branca, M.; Marchetti, M.; Saba, A. *J. Organomet. Chem.* **1978**, *161*, 197.

(25) Results obtained by using 80 atm of carbon monoxide and hydrogen (CO/H<sub>2</sub> = 1) are as follows: at 60 °C, iso/*n* = 199; at 70 °C, iso/*n* = 99; at 95 °C, iso/*n* = 49. Although the tendency is the same as the cobalt case, it is apparent that there is a strong bias to the formation of iso-aldehyde in the rhodium case.

(26) Ojima, I.; Hirai, K.; Fujita, M.; Fuchikami, T. *J. Organomet. Chem.* **1985**, *279*, 203.

(27) (a) Ojima, I. *Actual. Chim.* **1987**, 171. (b) Ojima, I. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; Jai: Sherwood Place, 1987; in press.

(28) Fujita, M.; Ojima, I. *Tetrahedron Lett.* **1983**, *24*, 4573.

(29) (a) Knorre, D. G.; Lavrik, O. I.; Petrova, T. D.; Savchenko, T. I.; Yakobson, G. G. *FEBS Lett.* **1971**, *12*, 204. (b) Nevinsku, G. A.; Favorova, O. O.; Lavrik, O. I.; Petrova, T. D.; Kochkina, L. L.; Savchenko, T. I. *Ibid.* **1974**, 135.

(30) Johnston, M.; Marcotte, P.; Donovan, J.; Walsh, C. *Biochemistry* **1979**, *18*, 1729.

graph by using columns packed with Dexsil-300, OV-101, OV-17, SE-30, or DC-550. Preparative gas chromatography was performed with a Varian Aerograph 920 or a 90 P on columns packed with 30% SE-30 or 3% OV-17.

**Materials.** 3,3,3-Trifluoropropene (TFP) was purchased from Japan Halon Co., Ltd., and Halocarbon Co. and used as obtained. Pentafluorostyrene (PFS) was commercially available from SCM Chemicals, Inc., and was used as purchased. Vinyl fluoride (VF) was purchased from Halocarbon Co. and used as received. 3,3,4,4,4-Pentafluorobut-1-ene (PFB), 3,3,4,4,5,5,5-heptafluoropent-1-ene (HPFP), and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodec-1-ene (HPDFD) were commercially available from Japan Halon Co., Ltd., and were used as received. Dicobalt octacarbonyl was purchased from Strem Chemicals, Inc., and recrystallized from *n*-heptane before use under carbon monoxide. Hexarhodium hexadecacarbonyl, triruthenium dodecacarbonyl, triphenylphosphine, and (–)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop) were obtained from Strem Chemicals, Inc., and used as purchased. Tetra-rhodium dodecacarbonyl and (diop)platinum dichloride–stannous chloride were prepared by the literature methods.

**Hydroformylation of TFP Catalyzed by HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>.** A 200-mL autoclave was charged with 91.8 mg ( $1.00 \times 10^{-2}$  mmol) of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> in 20 mL of toluene, and TFP gas (2.688 L, 120 mmol) was introduced at –78 °C. Then, the autoclave was filled with carbon monoxide and hydrogen (25 atm each; initial pressure at 20 °C). The mixture was stirred magnetically at 80 °C for 15 h. After the pressure was released from the autoclave, the reaction mixture was taken out from the autoclave and was submitted to GLC analysis, which showed the formation of 2- and 3-(trifluoromethyl)propanal (2- and 3-TFMPA) in 96% yield (2-TFMPA/3-TFMPA = 96/4). Distillation of the reaction mixture at ambient pressure gave 13.6 g (90%) of 2-TFMPA and 400 mg (2.6%) of 3-TFMPA.

A larger scale experiment with 1.2 mol of TFP and  $2.4 \times 10^{-4}$  mol (TFP/Rh = 1/5000) of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> at 90 °C (80 atm) (CO/H<sub>2</sub> = 1/1) for 6 h gave virtually the same yield (95%) and regioselectivity (iso/*n* = 96/4).

**2-TFMPA:** bp 66 °C (760 mmHg); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.33 (d, *J* = 7.2 Hz, 3 H), 3.10 (qdd, *J* = 9.8, 7.2, 1.1 Hz, 1 H), 9.76 (qd, *J* = 1.8, 1.1 Hz, 1 H); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>/CFCl<sub>3</sub>) δ –68.1 (dd, *J* = 9.8, 1.8 Hz); IR (neat) 1740 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 126 (10, M<sup>+</sup>), 77 (100). Anal. Calcd for C<sub>4</sub>H<sub>3</sub>F<sub>3</sub>O: C, 38.11; H, 4.00. Found: C, 38.25; H, 4.18.

**3-TFMPA:** bp 94–96 °C (760 mmHg) (lit. bp 94–96 °C,<sup>31a</sup> 93–97 °C<sup>31b</sup> (760 mmHg)); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.45 (m, 2 H), 2.77 (t, *J* = 7.5 Hz, 2 H), 9.80 (br s, 1 H); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>/CFCl<sub>3</sub>) δ –66.1 (t, *J* = 11.2 Hz); IR (neat) 1735 (ν<sub>C=O</sub>) cm<sup>–1</sup>.

In a similar manner, the hydroformylation of TFP with other rhodium, cobalt, platinum, and ruthenium catalysts was performed. The results are listed in Table I.

**Hydroformylation of PFS Catalyzed by RhCl(PPh<sub>3</sub>)<sub>3</sub>.** A 200-mL autoclave was charged with 28 mg ( $3.04 \times 10^{-2}$  mmol) of RhCl(PPh<sub>3</sub>)<sub>3</sub>, 5.86 g (30.2 mmol) of PFS, and 20 mL of benzene, and the autoclave was filled with carbon monoxide and hydrogen (40 atm each; initial pressure at 20 °C). The mixture was stirred at 90 °C for 20 h. The adsorption of carbon monoxide and hydrogen stopped, and the reaction was completed. After the pressure was released from the autoclave, the solvent was removed, and the residue was distilled under reduced pressure to give 2-PFPPA (6.43 g, 95% yield). The GLC analysis of the reaction mixture revealed that (pentafluorophenyl)propanals (2- and 3-PFPPA) were produced in quantitative yield (2-PFPPA/3-PFPPA = 97/3).

In a similar manner, the hydroformylation of PFS with other rhodium, cobalt, platinum, and ruthenium catalysts was carried out. Results are summarized in Table II. 2-PFPPA was isolated in its pure state by a preparative GLC separation.

**2-PFPPA:** bp 96 °C (21 mmHg); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.56 (d, *J* = 7.4 Hz, 3 H), 3.93 (q, *J* = 7.4 Hz, 1 H), 9.73 (t, *J* = 2.1 Hz, 1 H); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>/CFCl<sub>3</sub>) δ –142.4 (dd, *J* = 21.4, 7.2 Hz, 2 F), –156.9 (t, *J* = 20.3 Hz, 1 F), –163.4 (ddd, *J* = 21.4, 20.3, 7.2 Hz, 2 F); IR (neat) 1740 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 224 (4, M<sup>+</sup>), 195 (100). Anal. Calcd for C<sub>9</sub>H<sub>5</sub>F<sub>5</sub>O: C, 48.23; H, 2.25. Found: C, 48.00; H, 2.21.

**3-PFPPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.79 (t, *J* = 7.5 Hz, 2 H), 3.02 (t, *J* = 7.5 Hz, 2 H), 9.81 (br s, 1 H); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>/CFCl<sub>3</sub>) δ –144.0 (dd, *J* = 21.9, 7.9 Hz, 2 F), –159.2 (t, *J* = 20.3 Hz, 1 F), –164.3 (ddd, *J* = 21.9, 20.3, 7.9 Hz, 2 F); IR (neat) 1740 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 224 (15, M<sup>+</sup>), 181 (100). Anal. Calcd for C<sub>9</sub>H<sub>5</sub>F<sub>5</sub>O: C, 48.23; H, 2.25. Found: C, 47.91; H, 2.26.

**Kinetic Study of Hydroformylation of PFS.** Kinetic measurements were carried out at 100 °C (82 atm) (CO/H<sub>2</sub> = 1) in a 300-mL auto-

clave with periodical sampling. A mixture of a catalyst and PFS in degassed benzene was transferred to the autoclave, and carbon monoxide was introduced. The mixture was heated to 100 °C, and the pressure of carbon monoxide was adjusted to 41 atm. After the mixture was stirred for 30 min at 100 °C, hydrogen (41 atm) was introduced to the autoclave to start the reaction. For the Rh<sub>4</sub>(CO)<sub>12</sub>-catalyzed reaction,  $5.0 \times 10^{-2}$  M PFS and  $1.0 \times 10^{-5}$  M Rh<sub>4</sub>(CO)<sub>12</sub> in 50 mL of benzene were used. For the Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed reaction, 0.2 M PFS and  $1.0 \times 10^{-2}$  M Co<sub>2</sub>(CO)<sub>8</sub> in 50 mL of benzene were used. Both reactions gave clear first-order plots to the PFS concentration, and some induction periods were observed, which may well be ascribed to the time for saturation of hydrogen in the reaction system and for generation of active catalyst species since hydrogen was separately added at 100 °C to initiate the reaction as mentioned above.

**Hydroformylations of Other (Perfluoroalkyl)ethenes.** The hydroformylations of PFB, HPFP, and HPDFD were carried out in a manner similar to that described for PFS with 0.12–0.77 mmol of (perfluoroalkyl)ethene and Rh<sub>4</sub>(CO)<sub>12</sub> as catalyst in toluene. Results are summarized in Table III. The corresponding aldehydes, (pentafluoroethyl)propanals (2- and 3-PFEPA), (heptafluoropropyl)propanals (2- and 3-HPFPPA), and (heptafluoroheptyl)propanals (2- and 3-HPDFOPA) were isolated by preparative GLC, as colorless liquid.

**2-PFEPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.34 (d, *J* = 7.2 Hz, 3 H), 3.10 (m, 1 H), 9.75 (t, *J* = 0.8 Hz, 1 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>/CFCl<sub>3</sub>) δ –83.0 (br s, 3 F), –117.5 (d, *J* = 15 Hz, 2 F); IR (CCl<sub>4</sub>) 1740 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 176 (6, M<sup>+</sup>), 59 (100). Anal. Calcd for C<sub>7</sub>H<sub>5</sub>F<sub>5</sub>O: C, 34.11; H, 2.86. Found: C, 34.17; H, 2.82.

**3-PFEPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.41 (m, 2 H), 2.81 (t, *J* = 7.6, 2 H), 9.83 (br s, 1 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>/CFCl<sub>3</sub>) δ –85.6 (br s, 3 F), –117.5 (t, *J* = 18 Hz, 2 F); IR (CCl<sub>4</sub>) 1735 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 176 (30, M<sup>+</sup>), 59 (100). Anal. Calcd for C<sub>7</sub>H<sub>5</sub>F<sub>5</sub>O: C, 34.11; H, 2.86. Found: C, 34.06; H, 2.67.

**2-HPFPPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.36 (d, *J* = 7.2 Hz, 3 H), 3.16 (m, 1 H), 9.75 (br s, 1 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>/CFCl<sub>3</sub>) δ –80.3 (t, *J* = 10 Hz, 3 F), –114.5 (m, 2 F), –124.5 (m, 2 F); IR (neat) 1740 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 226 (2, M<sup>+</sup>), 109 (100). Anal. Calcd for C<sub>8</sub>H<sub>5</sub>F<sub>7</sub>O: C, 31.87; H, 2.23. Found: C, 31.64; H, 2.49 (for a mixture of 2- and 3-HPFPPA).

**3-HPFPPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.45 (m, 2 H), 2.83 (t, *J* = 7.5 Hz, 2 H), 9.84 (br s, 1 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>/CFCl<sub>3</sub>) δ –80.7 (t, *J* = 10 Hz, 3 F), –114.5 (m, 2 F), –127.1 (m, 2 F); IR (neat) 1730 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 226 (21, M<sup>+</sup>), 59 (100). Elemental analysis: see 2-HPFPPA.

**2-HPDFOPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.36 (d, *J* = 7.2 Hz, 3 H), 3.17 (m, 1 H), 9.74 (br s, 1 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>/CFCl<sub>3</sub>) δ –80.7 (t, *J* = 10 Hz, 3 F), –113.7 (m, 2 F), –121.1 (m, 2 F), –125.4 (m, 2 F); IR (KBr) 1740 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 476 (0, M<sup>+</sup>), 109 (100). Anal. Calcd for C<sub>11</sub>H<sub>5</sub>F<sub>17</sub>O: C, 27.75; H, 1.06. Found: C, 27.59; H, 0.98 (for a mixture of 2- and 3-HPDFOPA).

**3-HPDFOPA:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.46 (m, 2 H), 2.83 (t, *J* = 7.5 Hz, 2 H), 9.84 (br s, 1 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>/CFCl<sub>3</sub>) δ –80.9 (t, *J* = 10 Hz, 3 F), –113.5 (m, 2 F), –121.5 (m, 10 F), –125.4 (m, 2 F); IR (KBr) 1730 (ν<sub>C=O</sub>) cm<sup>–1</sup>; MS (*m/e*) 476 (1, M<sup>+</sup>), 59 (100). Elemental analysis: see 2-HPDFOPA.

**Study of the Effects of Temperature and Carbon Monoxide Pressure on Regioselectivity.** The reactions were run essentially in the same manner as described above. However, we paid special attention to initiate each reaction exactly at the recorded temperature; viz., to the mixture of substrate and catalyst in a solvent was introduced carbon monoxide only in the beginning, and the autoclave was heated to the reaction temperature and kept at that temperature for 30 min and then hydrogen was introduced. In this way, we obtained consistent data with high reproducibility.

**Hydroformylation of Allylpentafluorobenzene (4a) and Allylbenzene (4b).** The reactions were carried out in a manner similar to that described for PFS with 0.5 mmol of substrate, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (0.0012 mmol, 0.24 mol %), Rh<sub>6</sub>(CO)<sub>16</sub> (0.001 mmol, 0.2 mol %), or Co<sub>2</sub>(CO)<sub>8</sub> (0.05 mmol, 10 mol %) at 90–100 °C (80 atm) (CO/H<sub>2</sub> = 1; initial pressure at 25 °C) in benzene. Results are listed in Table IV.

Products **5a–8a** were isolated by preparative GLC. The hydroformylation of allylbenzene catalyzed by Co<sub>2</sub>(CO)<sub>8</sub> was reported by Lai and Ucciani; thus, the products were identified by analytical GLC by the comparison with authentically prepared samples.

**4-(Pentafluorophenyl)butanal (5a):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.94 (quintet, *J* = 7.3 Hz, 2 H), 2.52 (t, *J* = 7.3 Hz, 2 H), 2.69 (m, 2 H), 9.78 (t, *J* = 1.2 Hz, 1 H); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>/CFCl<sub>3</sub>) δ –144.7 (dd, *J* = 21.9, 8.1 Hz, 2 F), –159.4 (t, *J* = 20.3 Hz, 1 F), –164.2 (ddd, *J* = 21.9, 20.3, 8.1 Hz, 2 F); IR (neat) 1730 (ν<sub>C=O</sub>) cm<sup>–1</sup>. Anal. Calcd for C<sub>10</sub>H<sub>7</sub>F<sub>5</sub>O: C, 50.43; H, 2.96. Found: C, 50.18; H, 2.79 (for a mixture of **5a**, **6a**, and **7a**).

**3-(Pentafluorophenyl)-2-methylpropanal (6a):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.16 (d, *J* = 6.8 Hz, 3 H), 2.65–2.90 (m, 2 H), 3.10–3.20 (m, 1 H), 9.70

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(br s, 1 H);  $^{19}\text{F}$  NMR (acetone- $d_6$ /CFCl $_3$ )  $\delta$  -143.0 (dd,  $J$  = 21.9, 7.9 Hz, 2 F), -158.6 (t,  $J$  = 20.3 Hz, 1 F), -164.0 (ddd,  $J$  = 21.9, 20.3, 7.9 Hz, 2 F); IR (neat) 1730 ( $\nu_{\text{C=O}}$ )  $\text{cm}^{-1}$ .

**2-(Pentafluorophenyl)butanal (7a):**  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$  0.98 (t,  $J$  = 7.4 Hz, 3 H), 1.85 (m, 1 H), 2.29 (m, 1 H), 3.78 (dd,  $J$  = 9.8, 5.4 Hz, 1 H), 9.75 (t,  $J$  = 2.2 Hz, 1 H);  $^{19}\text{F}$  NMR (acetone- $d_6$ /CFCl $_3$ )  $\delta$  -141.5 (dd,  $J$  = 21.5, 7.0 Hz, 2 F) -156.6 (t,  $J$  = 20.4 Hz, 1 F), -163.4 (ddd,  $J$  = 21.5, 20.4, 7.0 Hz, 2 F); IR (neat) 1730 ( $\nu_{\text{C=O}}$ )  $\text{cm}^{-1}$ .

***n*-Propylpentafluorobenzene (8a):**  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$  0.93 (t,  $J$  = 7.2 Hz, 3 H), 1.60 (sextet,  $J$  = 7.2 Hz, 2 H), 2.65 (m, 2 H);  $^{19}\text{F}$  NMR (acetone- $d_6$ /CFCl $_3$ )  $\delta$  -144.9 (dd,  $J$  = 21.8, 7.4 Hz, 2 F), -159.7 (t,  $J$  = 20.3 Hz, 1 F), -164.4 (ddd,  $J$  = 21.8, 20.3, 7.4 Hz, 2 F); IR (neat) 2980, 2930, 2870, 1515, 1500, 1120, 1105, 1000, 970, 950  $\text{cm}^{-1}$ ; MS 210 (20, M $^+$ ), 181 (100).

**Hydroformylation of Vinyl Fluoride (VF).** Reactions were run in a manner similar to that for TFP with 20 mmol of substrate and Rh $_4$ (C-

O) $_{12}$  (0.01 mmol), HRh(CO)(PPh $_3$ ) $_3$  (0.04 mmol), Ru $_3$ (CO) $_{12}$  (0.2 mmol), and Co $_2$ (CO) $_8$  (0.2 mmol) as catalysts at 80 °C (68 atm) (CO/H $_2$  = 1) for the rhodium and ruthenium catalysts and at 100 °C (110 atm) (CO/H $_2$  = 1) for the cobalt catalyst in toluene for 18 h. The sole product, 2-fluoropropanal (2-FPA), was obtained by distillations as colorless liquid. The yield of 2-FPA was the following: Rh $_4$ (CO) $_{12}$ , 81%; HRh(CO)(PPh $_3$ ) $_3$ , 52%; Ru $_3$ (CO) $_{12}$ , 46%; Co $_2$ (CO) $_8$ , 30%.

**2-Fluoropropanal (2-FPA):** bp 56–56.5 °C;  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$  1.48 (dd,  $J$  = 23.8, 7.0 Hz, 3 H), 4.90 (dq,  $J$  = 48.7, 7.0 Hz, 1 H), 9.78 (d,  $J$  = 5.9 Hz, 1 H);  $^{19}\text{F}$  NMR (CDCl $_3$ /CFCl $_3$ )  $\delta$  -192.87 (dq,  $J$  = 48.7, 23.8, 5.9 Hz); IR (neat) 1724 ( $\nu_{\text{C=O}}$ )  $\text{cm}^{-1}$ .

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## Photochemistry of the Orthometalated *cis*-Bis[2-(2-thienyl)pyridine]platinum(II) Complex in Halocarbon Solvents

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**Abstract:** The photochemical and luminescence behavior of the orthometalated Pt(thpy) $_2$  complex, where thpy $^-$  is the ortho-C-deprotonated form of 2-(2-thienyl)pyridine, has been studied under a variety of experimental conditions, and the mechanisms of the excited-state reactions and of the subsequent thermal processes are discussed. In degassed CH $_3$ CN the complex is not photosensitive and exhibits luminescence from the lowest triplet metal-to-ligand charge-transfer ( $^3\text{MLCT}$ ) excited state with  $\Phi_{\text{em}}$  = 0.26 and  $\tau$  = 2.4  $\mu\text{s}$ . In CH $_2$ Cl $_2$ , CHCl $_3$ , or CH $_3$ CN/CH $_2$ Cl $_2$  solvents, the complex maintains its luminescent properties and undergoes a photooxidative addition reaction with formation of Pt(thpy) $_2$ (Cl)(R) (R = CH $_2$ Cl or CHCl $_2$ ) as the sole observed product. In the mixed solvent, the quantum yield of the photoreaction increases with increasing CH $_2$ Cl $_2$  concentration. In neat CH $_2$ Cl $_2$ , the quantum yield of the photoreaction is 0.30 and 0.10 for 313- and 430-nm excitation, respectively. In CH $_2$ Cl $_2$ , complete quenching of the luminescent  $^3\text{MLCT}$  excited state by anthracene via an energy-transfer mechanism is accompanied by only partial quenching of the photoreaction. By contrast, oxygen is a better quencher for the photoreaction than for the luminescence emission. In both cases the fraction of quenched reaction depends on the excitation wavelength. These and other results are interpreted on the basis of a mechanism involving generation of Pt(thpy) $_2$ Cl and CH $_2$ Cl radicals via (i) a charge transfer to solvent (CTTS) excited state, populated from the intraligand (IL) and metal-to-ligand charge-transfer (MLCT) states obtained by light absorption, and (ii) the thermally relaxed  $^3\text{MLCT}$  luminescent level, through conversion to CTTS or bimolecular reaction with CH $_2$ Cl $_2$ . The primary radicals are then involved in a chain mechanism of the type previously discussed for other oxidative addition reactions, with an average chain length of about 40.

There is currently a growing interest in the study of the photochemical and photophysical behavior of orthometalated transition-metal complexes.<sup>4-11</sup> Such investigations are, on one side, a logical extension of the numerous and detailed studies carried out

in the last decade on transition-metal complexes containing polypyridine-type ligands;<sup>12-15</sup> on another side, they represent one of the expected developments of organometallic chemistry, a field that has so far contributed a relatively small number of studies aimed at the characterization of excited-state reactivity and/or luminescence.<sup>16-18</sup> The main goals of the photochemical and photophysical investigations on organometallic transition-metal complexes are to discover and characterize new molecules that can play the role of light absorption and/or light emission sen-

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