



Article

P-Fluorous Phosphines as Electron-Poor/Fluorous Hybrid Functional Ligands for Precious Metal Catalysts: Synthesis of Rh(I), Ir(I), Pt(II), and Au(I) Complexes Bearing *P*-Fluorous Phosphine Ligands

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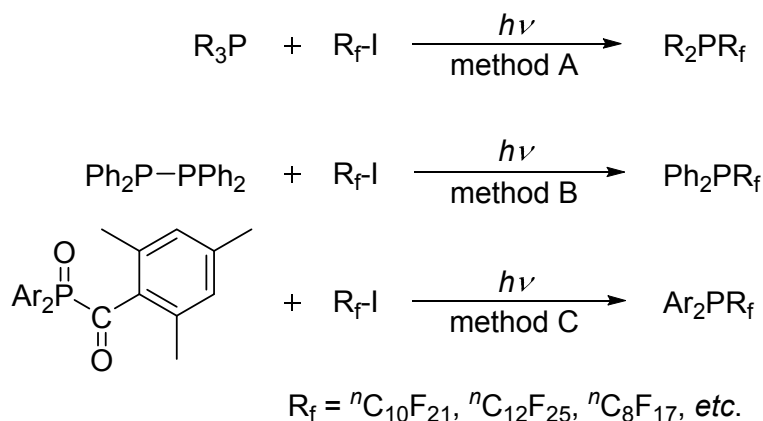
Abstract: *P*-Fluorous phosphine (R_2PR_f), in which the perfluoroalkyl group is directly bonded to the phosphorus atom, is a promising ligand because it has a hybrid functionality, i.e., electron-poor and fluorous ligands. However, examples of *P*-fluorous phosphine–metal complexes are still rare, most probably because the *P*-fluorous group is believed to decrease the coordination ability of the phosphines dramatically. In contrast, however, we have succeeded in synthesizing a series of *P*-fluorous phosphine–coordinated metal complexes such as rhodium, iridium, platinum, and gold. Furthermore, the electronic properties of $R_2P^nC_{10}F_{21}$ are investigated by X-ray analysis of $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ and the infrared CO stretching frequency of $RhCl(CO)(R_2P^nC_{10}F_{21})_2$. $IrCl(CO)(Ph_2P^nC_{10}F_{21})_2$ - and $AuCl(R_2P^nC_{10}F_{21})_2$ -catalyzed reactions are also demonstrated.

Keywords: phosphine-metal complex; fluorous; electron-poor phosphine ligand; precious metal complex

1. Introduction

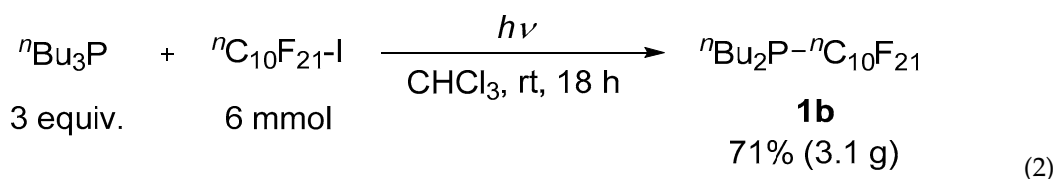
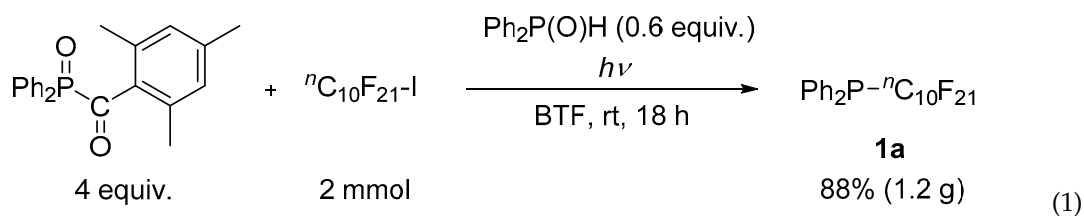
P-Fluorous phosphine (R_2PR_f), in which the perfluoroalkyl group is directly bonded to the phosphorus atom, is a hybrid functional phosphine ligand having both “electron-poor” [1] and “fluorous” [2–8] characteristics. Since strongly electron-withdrawing ligands are known to promote reductive elimination steps in catalytic reactions, the former property may be exploited, not only to optimize known reactions, but also to develop new catalytic reactions [9–12]. As to the latter property, the use of a fluorous biphasic system (FBS) may make it possible to recover catalysts and ligands easily and to reuse them for catalytic reactions. We recently developed a catalytic reaction using *P*-fluorous phosphines as ligands, i.e., a palladium-catalyzed cross-coupling reaction between acid chlorides and terminal alkynes, and have demonstrated the recyclability of the catalyst and the ligand [13]. Namely, the poor electron density of the *P*-fluorous phosphine ligands induced the palladium-catalyzed cross-coupling reaction, even under copper-free conditions, and the fluorous affinity of *P*-fluorous phosphines enabled the reuse of their Pd-complexes by using an FBS.

Our group recently developed three types of convenient synthetic methods of *P*-fluorous phosphine ligands (R_2PR_f) (see, Scheme 1): method A, the photoinduced direct displacement of R_3P with R_fI under radical conditions [13]; method B, the photoinduced S_H2 reaction of $(Ph_2P)_2$ with R_fI [14]; method C, the reductive substitution reaction of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO, known as a representative radical initiator for polymerization) with R_fI under light [15].



Scheme 1. Synthetic methods of *P*-fluorous phosphines.

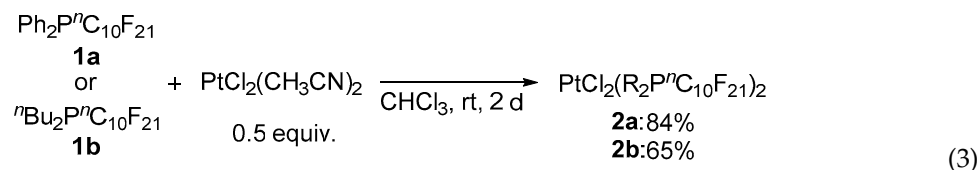
To synthesize a diphenyl-substituted *P*-fluorous phosphine ligand ($Ph_2P^{}nC_{10}F_{21}$ **1a**), method C is the best because method C can be applied to the gram-scale synthesis of **1a** (Equation (1)) [15]. In the case of the synthesis of the dialkyl-substituted *P*-fluorous phosphine ligand (${}^nBu_2P^{}nC_{10}F_{21}$ **1b**), method A is the most suitable because the gram scale of **1b** can be obtained by this method (Equation (2)).



Our recent success in palladium-catalyzed cross-coupling using *P*-fluorous phosphines [13] and the establishment of their synthetic methods [13–15] strongly suggest their promising usability as functional ligands in many transition metal-catalyzed reactions. However, examples of *P*-fluorous phosphine–metal complexes are still rare in the literature [16–20], and are limited to metal- R_2PR_f complexes bearing a short-chain perfluoroalkyl (light fluorine) group, which cannot be separated by a FBS due to the low content of fluorine atoms. To encourage the use of *P*-fluorous phosphine ligands in various catalytic reactions, we investigated their reactions with representative transition metal catalysts to prepare the corresponding *P*-fluorous phosphine-coordinated metal catalysts. In this paper, we report the synthesis of *P*-fluorous phosphine-coordinated rhodium, iridium, platinum, and gold complexes, and also describe their electronic properties, structural features, and catalytic activities.

2. Results and Discussion

First, we investigated the coordination of R_2PR_f to Pt. When a mixture of $Ph_2P^nC_{10}F_{21}$ (**1a**) and $PtCl_2(CH_3CN)_2$ was stirred in $CHCl_3$ for two days, the *P*-perfluoroalkylated phosphine–platinum complex, $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ (**2a**), was obtained successfully (Equation (3)). The ^{31}P NMR spectrum showed a triplet with satellites ($J_{P-F} = 55.8$ Hz, $J_{P-Pt} = 3878$ Hz). This indicated the successful complexation between the *P*-fluorous phosphine–platinum complex. When $^nBu_2P^nC_{10}F_{21}$ (**1b**) was used, instead of **1a**, for complexation with platinum under similar conditions, the *P*-perfluoroalkylated phosphine–platinum complex *trans*- $PtCl_2(^nBu_2P^nC_{10}F_{21})_2$ (**2b**) was also obtained in good yield (Equation (3)).



We fortunately obtained a single crystal of complex **2a** by recrystallization from $CHCl_3$, which was suitable for X-ray analysis. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) representation of **2a** is shown in Figure 1. The P–Pt–P bond angle is 178.66° . This indicates that the platinum complex $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ has the structure of the *trans* form. The Pt–P bond lengths in *trans*- $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ are 2.3027(6) and 2.3039(6) Å. These are shorter than the corresponding bond lengths in *trans*- $PtCl_2(PPh_3)_2$ (2.319(3) and 2.316(3) Å) [21]. The P–CF₂ bond lengths in *trans*- $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ are 1.913(3) and 1.909(3). They are longer than the P–CF₂ bond length in $Ph_2PC_2F_5$ (1.891(3) Å) [18]. The four P–C(*ipso*) lengths in *trans*- $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ are 1.810(4), 1.813(3), 1.810(4), and 1.815(3) Å. These are shorter than the P–C(*ipso*) bond lengths in $Ph_2PC_2F_5$ (1.832(3) and 1.835(3) Å) [22]. On the other hand, the average Pt–P–C(*ipso*) angle in *trans*- $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ is 115.3° . It is similar to the average Pt–P–C(*ipso*) angle in *trans*- $PtCl_2(PPh_3)_2$ (113.8°). The ORTEP representation also shows two perfluoroalkyl chains aligned in a parallel direction. The nearest distance between the two F atoms of each perfluoroalkyl chain is 2.734 Å, which is slightly shorter than the sum of the van der Waals radii of two F atoms (2.94 Å). Moreover, the packing diagram of *trans*- $PtCl_2(Ph_2P^nC_{10}F_{21})_2$ shows that the long perfluoroalkyl chains are assembled into a fluorous layer (Figure 2) [23–25]. In the case of the reported light fluorous phosphine–metal complexes, such a parallel direction of the fluorous group was not observed [18,19].

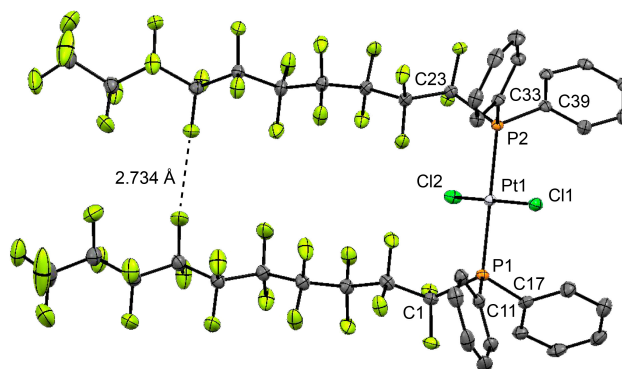


Figure 1. ORTEP representation (thermal ellipsoids at 50%) of $PtCl_2(Ph_2P^nC_{10}F_{21})_2$. Space group: *P*-1 (#2), *Z* = 2, $R_1 = 0.0312$, $wR_2 = 0.0886$, selected bond lengths (Å) and angles ($^\circ$): Pt(1)–Cl(1) = 2.332(10), Pt(1)–P(1) = 2.303(6), P(1)–C(1) = 1.913(3), P(1)–C(11) = 1.810(4), Cl(1)–Pt(1)–Cl(2) = 172.79(3), Cl(1)–Pt(1)–P(1) = 89.10(3), P(1)–Pt(1)–P(2) = 178.66(4), Pt(1)–P(1)–C(1) = 117.15(8), Pt(1)–P(1)–C(11) = 116.41(9), Pt(1)–P(1)–C(17) = 116.41(9), C(1)–P(1)–C(11) = 98.16(14).

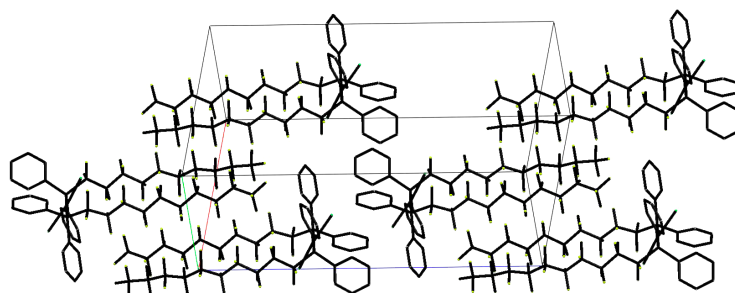
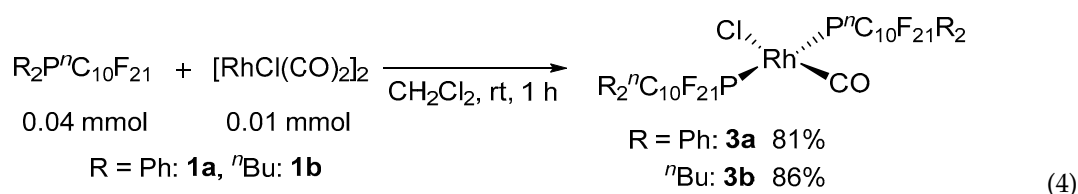


Figure 2. Packing diagram of $\text{PtCl}_2(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$.

The infrared CO stretching frequency ($\nu_{(\text{CO})}$) of the $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ complex provides information on the electronic properties of the phosphines [26]. Therefore, we investigated the reaction of a *P*-perfluoroalkylated phosphine with $[\text{RhCl}(\text{CO})_2]_2$ for the synthesis of $\text{RhCl}(\text{CO})(\text{R}_2\text{PR}_f)_2$. When the reaction of **1a** or **1b** with $[\text{RhCl}(\text{CO})_2]_2$ was examined according to a reported method [9], $\text{RhCl}(\text{CO})(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ (**3a**) and $\text{RhCl}(\text{CO})(^n\text{Bu}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ (**3b**) were obtained in good yields, respectively (Equation (4)). Coupling in the ^{31}P NMR spectrum was assigned to the interaction between ^{31}P and ^{103}Rh ($J_{\text{P-Rh}} = 143.8$ Hz), confirming complexation between the *P*-perfluoroalkylated phosphine and rhodium. Additionally, the symmetry of the ^{31}P NMR spectrum indicates that the steric configuration is *trans*.



Using the same method, a series of $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ complexes were synthesized and their infrared CO stretching frequencies ($\nu_{(\text{CO})}$) were measured to evaluate the electronic properties of R_2PR_f (Table 1). Large $\nu_{(\text{CO})}$ values indicate poor electron-donating abilities of the phosphine ligand. The $\nu_{(\text{CO})}$ of $\text{RhCl}(\text{CO})(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ and $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{F}_5)_3]_2$ are almost the same ($2010, 2008 \text{ cm}^{-1}$), and therefore the electron-donating ability of $\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21}$ is as poor as that of $\text{P}(\text{C}_6\text{F}_5)_3$. The $\nu_{(\text{CO})}$ of $\text{RhCl}(\text{CO})(^n\text{Bu}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ is 1987 cm^{-1} , which is similar to that of $\text{RhCl}(\text{CO})[\text{P}(4\text{-CF}_3\text{C}_6\text{H}_4)_3]_2$ (1990 cm^{-1}). Thus, the electron-donating ability of $^n\text{Bu}_2\text{P}^n\text{C}_{10}\text{F}_{21}$ is similar to that of $\text{P}(4\text{-CF}_3\text{C}_6\text{H}_4)_3$.

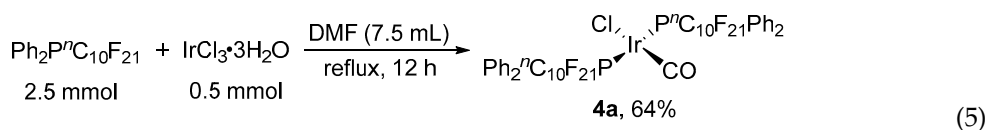
Table 1. The $\nu_{(\text{CO})}$ data of $\text{RhCl}(\text{CO})(\text{PR}_3)_2$.

$$\text{R}_3\text{P} + [\text{RhCl}(\text{CO})_2]_2 \xrightarrow[\text{CH}_2\text{Cl}_2, \text{rt, 1 h}]{} \text{RhCl}(\text{CO})(\text{PR}_3)_2$$

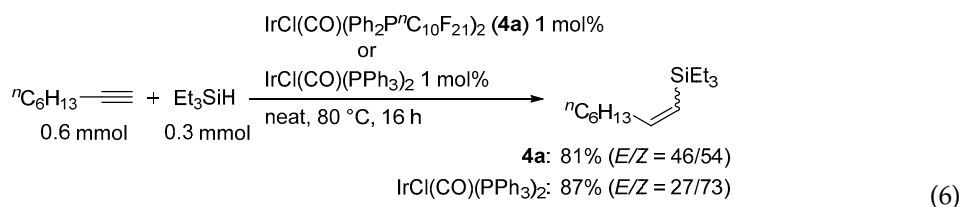
| Entry | $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ | $\nu_{(\text{CO})} (\text{cm}^{-1})$ |
|-------|---|--------------------------------------|
| 1 | $\text{RhCl}(\text{CO})(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ | 2010 |
| 2 | $\text{RhCl}(\text{CO})(^n\text{Bu}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ | 1987 |
| 3 | $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ | 1967 |
| 4 | $\text{RhCl}(\text{CO})[\text{P}(4\text{-CF}_3\text{C}_6\text{H}_4)_3]_2$ | 1990 |
| 5 | $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{F}_5)_3]_2$ | 2008 |

An iridium-phosphine complex (iridium is a congener of rhodium) was also investigated. Vaska-type complexes [27], such as $\text{IrCl}(\text{CO})(\text{PR}_3)_2$, are well-known iridium-phosphine complexes. We examined the preparation of a Vaska-type complex of *P*-perfluoroalkylated phosphine from $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and an excess amount of $\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21}$ via a reduction process [28,29]. As a result, $\text{IrCl}(\text{CO})(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ (**4a**) was successfully obtained (Equation (5)). The $\nu_{(\text{CO})}$ of **4a** was shifted

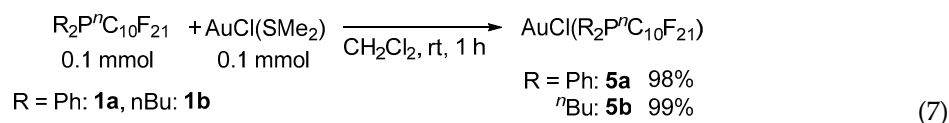
to a higher frequency (1990 cm^{-1}) compared with that of the Vaska complex $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (1944 cm^{-1}) [27], as well as that of the rhodium complex. The symmetry of the ^{31}P NMR spectrum (δ_{P} 45.0 ppm, t, $J_{\text{P-F}} = 34.6\text{ Hz}$) indicates that the steric configuration of **4a** is *trans*.



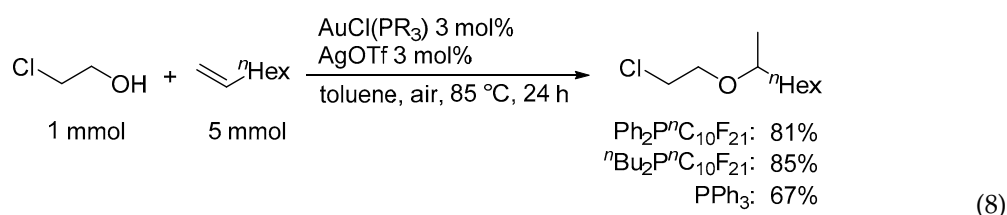
We next investigated the application of **4a** as a catalyst. Several iridium-catalyzed hydrosilylation reactions of alkynes have been reported [30–33]. We therefore attempted alkyne hydrosilylation using **4a** as a catalyst. When a mixture of 1-octyne and triethylsilane was heated in the presence of 1 mol % of **4a**, vinylsilane derivatives as hydrosilylation products were obtained in 81% yield ($E/Z = 46/54$) (Equation (6)). The result clearly indicates that the iridium complex **4a** can catalyze the hydrosilylation of alkynes as well as $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$.



Finally, we investigated a *P*-perfluoroalkylated phosphine–gold(I) complex. $\text{AuCl}(\text{SMe}_2)$ was selected as the starting gold complex [34]. When an equimolar amount of $\text{R}_2\text{P}^n\text{C}_{10}\text{F}_{21}$ (**1a** and **1b**) and $\text{AuCl}(\text{SMe}_2)$ was stirred at room temperature, the desired complexes, $\text{AuCl}(\text{R}_2\text{P}^n\text{C}_{10}\text{F}_{21})$ (**5a** and **5b**), were obtained in quantitative yields, respectively (Equation (7)). The ^{19}F NMR and ^{31}P NMR analyses confirmed the complexation of **1a** with gold(I). The ^{19}F NMR signal of $\text{P-CF}_2\text{-CF}_2\text{-}$ appeared at -107.8 ppm (CDCl_3) as a doublet of triplets ($^2J_{\text{F-P}} = 64.1\text{ Hz}$, $^3J_{\text{F-F}} = 14.2\text{ Hz}$), which was shifted downfield to 0.9 ppm compared with the free $\text{P-CF}_2\text{-CF}_2\text{-}$ of $\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21}$, due to metal complexation. The ^{31}P NMR signal appeared at 40.1 ppm as a triplet of triplets ($^2J_{\text{P-F}} = 65.0\text{ Hz}$, $^3J_{\text{P-F}} = 12.9\text{ Hz}$) in CH_2Cl_2 . HRMS (FAB) analysis further confirmed the complexation: the found value 900.9848 (calculated value for $\text{C}_{22}\text{H}_{10}\text{F}_{21}\text{PAu} [\text{M} - \text{Cl}]^+$: 900.9850) indicated the presence of the $\text{Au}(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})$ moiety.



A catalytic hydroalkoxylation of an alkene was demonstrated using gold complex **5**, according to the literature [35]. In the presence of a catalytic amount of **5a** and AgOTf , the addition reaction of 2-chloroethanol to 1-octene took place to give 2-(2'-chloroethoxy)octane in a good yield (Equation (8)). In the case of $\text{AuCl}(\text{}^n\text{Bu}_2\text{P}^n\text{C}_{10}\text{F}_{21})$, the desired adduct was also obtained in a good yield. The synthesized gold(I) complex, $\text{AuCl}(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})$ and $\text{AuCl}(\text{}^n\text{Bu}_2\text{P}^n\text{C}_{10}\text{F}_{21})$, was found to exhibit more excellent catalytic activity with the ethanol addition to 1-octene compared with AuClPPh_3 .



It is assumed that metal- R_2PR_f complexes have fluorophilic affinities because they contain perfluoroalkyl groups. Therefore, the fluorophilic affinities of these metal- $Ph_2P^{n}C_{10}F_{21}$ complexes were investigated; namely, the solubility of **2a–5a** in a fluorophilic solvent (FC-72, perfluorohexane) was measured at 25 °C. The results are as follows: $PtCl_2(Ph_2P^{n}C_{10}F_{21})_2$, 0.32 g/L; $RhCl(CO)(Ph_2P^{n}C_{10}F_{21})_2$, 0.40 g/L; $IrCl(CO)(Ph_2P^{n}C_{10}F_{21})_2$, 0.13 g/L; $AuCl(Ph_2P^{n}C_{10}F_{21})_2$, did not dissolve. Because the fluorine content of $AuCl(Ph_2P^{n}C_{10}F_{21})_2$ is low (42.6%), it did not dissolve in FC-72. These results show that these metal- $Ph_2P^{n}C_{10}F_{21}$ complexes, i.e., $PtCl_2(R_2PR_f)_2$, $RhCl(CO)(R_2PR_f)_2$, and $IrCl(CO)(R_2PR_f)_2$, have fluorophilic affinities, and therefore it is possible to extract them by using a fluorophilic solvent and an appropriate organic solvent.

3. Materials and Methods

3.1. General Comments

$Ph_2P^{n}C_{10}F_{21}$ (**1a**) [15] and $nBu_2P^{n}C_{10}F_{21}$ (**1b**) [13] were synthesized according to the literature. Other materials were obtained from commercial suppliers and used without purification before use.

3.2. Synthesis of P-Perfluoroalkylated Phosphine Complex with Pt(II)

Under inert atmosphere, $Ph_2P^{n}C_{10}F_{21}$ (21.1 mg, 0.03 mmol), $PtCl_2(CH_3CN)_2$ (5.2 mg, 0.015 mmol), and $CHCl_3$ (0.6 mL) were added to a sealed test tube. After standing for two days, white precipitate was formed and filtered. Then enough pure *trans*- $PtCl_2(Ph_2P^{n}C_{10}F_{21})_2$ was obtained in 84% yield.

trans-Dichlorobis((perfluorodecyl)diphenylphosphine)palladium(II) (**2a**): white solid; melting point (mp) 188–190 °C; 1H NMR (396 MHz, CD_2Cl_2): δ 7.52–7.55 (m, 8H), 7.59–7.62 (m, 4H), 7.94 (dd, $J_{H-H} = 7.3$ Hz, $J_{H-P} = 12.7$ Hz, 8H); ^{31}P NMR (160 MHz, CD_2Cl_2): δ 25.8 (t with satellites, $J_{P-F} = 55.8$ Hz, $J_{P-Pt} = 3878$ Hz); ^{19}F NMR (373 MHz, CD_2Cl_2): δ −126.2 (4F), −122.8 (4F), −122.0 (8F), −121.8 (8F), −121.2 (4F), −114.3 (4F), −101.8 (d, $J_{F-P} = 57.0$ Hz, 4F), −81.0 (6F); HRMS (FAB) Calcd. for $C_{44}H_{20}Cl_2F_{42}P_2Pt [M]^+$: 1671.9373, Found: 1671.9396.

Under inert atmosphere, $nBu_2P^{n}C_{10}F_{21}$ (132.8 mg, 0.2 mmol), $PtCl_2(PhCN)_2$ (47.2 mg, 0.1 mmol), and $CHCl_3$ (0.6 mL) were added to a sealed test tube. After standing for two days, white precipitate was formed and then, by filtration, enough pure *trans*- $PtCl_2(nBu_2P^{n}C_{10}F_{21})_2$ was obtained in 65% yield.

trans-Dichlorobis(dibutyl(perfluorodecyl)phosphine)palladium(II) (**2b**): white solid; mp 71–72 °C; 1H NMR (396 MHz, $CDCl_3$): δ 0.97 (t, $J_{H-H} = 7.3$ Hz, 12H), 1.44–1.54 (m, 12H), 1.70–1.83 (m, 4H), 2.18–2.30 (m, 4H), 2.36–2.46 (m, 4H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 24.6 (quint with satellites, $J_{P-F} = 25.8$ Hz, $J_{P-Pt} = 2720$ Hz); ^{19}F NMR (373 MHz, $CDCl_3$): δ −126.2 (4F), −122.8 (4F), −122.0 (4F), −121.8 (12F), −121.5 (4F), −116.4 (4F), −109.1 (dt, $J_{F-P} = 57.0$ Hz, $J = 28.5$ Hz, 4F), −80.9 (t, $J_{F-F} = 11.4$ Hz, 6F); HRMS (FAB) Calcd. for $C_{36}H_{36}Cl_2F_{42}P_2^{194}Pt [M]^+$: 1592.0625, Found: 1592.0603. The copies of 1H NMR, ^{19}F NMR, and ^{31}P NMR spectra of platinum complex (**2a,b**) are shown in Supplementary Materials.

3.3. Synthesis of P-Perfluoroalkylated Phosphine Complex with Rh(I)

Rhodium complexes ($RhCl(CO)(PR_3)_2$) were synthesized according to the reported method [9]. Phosphine (0.044 mmol), $[RhCl(CO)_2]_2$ (4.3 mg, 0.011 mmol), and dichloromethane (1.0 mL) were added to a 20 mL two-necked round-bottomed flask under argon. The solution was stirred at room temperature for 1 h. The solution was filtrated, and concentrated under reduced pressure. The resulting solid was purified by recrystallization (solvent: $CHCl_3$).

trans-carbonylchlorobis((perfluorodecyl)diphenylphosphine)rhodium(I) (**3a**): yellow solid; mp 190–192 °C (decomposition); 1H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, $J_{H-H} = 7.3$ Hz, $J_{H-P} = 8.0$ Hz, 8H), 7.52 (t, $J = 7.3$ Hz, 4H), 7.93 (q, $J = 6.3$ Hz, 8H); ^{31}P NMR (162 MHz, $CDCl_3$): δ 52.1 (dq, $J_{P-Rh} = 143.8$ Hz, $J_{P-F} = 33.0$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −125.9 (4F), −122.5 (4F), −121.7 (4F), −121.5 (12F), −121.4 (4F), −113.7 (4F), −104.8 (m, 4F), −80.7 (6F); IR (KBr) 3067, 2010, 1481, 1439, 1373, 1339, 1246, 1207, 1153, 1099, 745, 691, 648 cm^{-1} ; HRMS (ESI) Calcd. for $C_{45}H_{20}ClF_{42}NaOP_2Rh [M + Na]^+$:

1596.8960, Found: 1596.8960; Anal. Calcd. for $C_{45}H_{20}ClF_{42}OP_2Rh$: C, 34.09; H, 1.55%, Found: C, 34.32; H, 1.28%.

trans-carbonylchlorobis(dibutyl(perfluorodecyl)phosphine)rhodium(I) (**3b**): yellow solid; mp 49–50 °C; 1H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, $J_{H-H} = 7.7$ Hz, 12H), 1.48 (sextet, $J_{H-H} = 7.3$ Hz, 8H), 1.61–1.78 (m, 8H), 2.18–2.37 (m, 8H); ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.3 (dq, $J_{P-Rh} = 133.3$ Hz, $J_{P-F} = 30.1$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.3 (4F), −122.9 (4F), −122.0 (4F), −121.8 (12F), −121.5 (4F), −116.5 (4F), −109.0 (m, 4F), −81.0 (t, $J_{F-F} = 11.4$ Hz, 6F); IR (KBr) 2960, 1987, 1372, 1210, 1151, 1111, 973, 852 cm^{-1} ; HRMS (FAB) Calcd. for $C_{37}H_{36}ClF_{42}NaOP_2Rh$ $[M + Na]^+$: 1517.0212, Found: 1517.0245. The copies of 1H NMR, ^{19}F NMR, and ^{31}P NMR spectra of rhodium complex (**3a,b**) are shown in Supplementary Materials.

$RhCl(CO)[P(C_6F_5)_3]_2$ [9], $RhCl(CO)[P(4-CF_3C_6H_4)_3]_2$ [25], and $RhCl(CO)[P(C_6H_5)_3]_2$ [9] were reported in the literature, respectively.

3.4. Synthesis of P-Perfluoroalkylated Phosphine Complex with Ir(I)

$IrCl(CO)(Ph_2P^{n}C_{10}F_{21})_2$ was successfully synthesized according to the reported method [28,29]. Under inert atmosphere, $Ph_2P^{n}C_{10}F_{21}$ (1.76 g, 2.5 mmol), $IrCl_3 \cdot 3H_2O$ (176 mg, 0.5 mmol), and DMF (7.5 mL) were added to a 30 mL two necked flask. The mixture was refluxed for 12 h and the hot solution was filtered. The filtrate was recrystallized from MeOH and *trans*- $IrCl(CO)(Ph_2P^{n}C_{10}F_{21})_2$ was obtained in 64% yield.

trans-carbonylchlorobis((perfluorodecyl)diphenylphosphine)iridium(I) (**4a**): yellow solid; mp 181–183 °C; 1H NMR (400 MHz, $CDCl_3$): δ 7.44–7.56 (m, 12H), 7.93 (dd, $J_{H-H} = 6.4$, $J_{P-H} = 6.4$ Hz, 8H); ^{31}P NMR (162 MHz, $CDCl_3$): δ 45.0 (t, $J_{P-F} = 34.6$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.0 (4F), −122.6 (4F), −121.8 (8F), −121.6 (8F), −121.2 (4F), −113.9 (4F), −104.5 (d, $J_{F-P} = 34.6$ Hz, 4F), −80.7 (6F); IR (KBr) 1990, 1242, 1207, 1153 cm^{-1} ; HRMS (ESI) Calcd. for $C_{45}H_{20}ClF_{42}OP_2Ir$ $[M]^+$: 1663.9636, Found: 1663.9631. The copies of 1H NMR, ^{19}F NMR, and ^{31}P NMR spectra of iridium complex (**4a**) are shown in Supplementary Materials.

3.5. Hydrosilylation Reaction Catalyzed by Iridium Complex (4a)

Under inert atmosphere, **4a** (5.0 mg, 0.003 mmol), Et_3SiH (34.9 mg, 0.3 mmol), and 1-octyne (66.1 mg, 0.6 mmol) were added to a sealed test tube. The solution was heated at 80 °C for 16 h. The production of hydrosilylation adducts [36] was confirmed by 1H NMR using 1,4-dioxane as internal standard.

3.6. Synthesis of P-Perfluoroalkylated Phosphine Complex with Au(I)

Under inert atmosphere, $Ph_2P^{n}C_{10}F_{21}$ (145 mg, 0.2 mmol) or $^{n}Bu_2P^{n}C_{10}F_{21}$ (132.8 mg, 0.2 mmol), $AuCl(SMe_2)$ (59 mg, 0.2 mmol), and CH_2Cl_2 (5 mL) were added to a sealed test tube. The solution was stirred for 1 h. After the solvent was removed in vacuo, solid was obtained as enough pure $AuCl(Ph_2P^{n}C_{10}F_{21})$ in 98% yield or $AuCl(^{n}Bu_2P^{n}C_{10}F_{21})$ in 99% yield.

Chloro((perfluorodecyl)diphenylphosphine)gold(I) (**5a**): white solid; mp 130–131 °C; 1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.62 (m, 4H), 7.66–7.72 (m, 2H), 7.95 (dd, $J_{H-H} = 7.8$, $J_{P-H} = 13.7$ Hz, 4H); ^{31}P NMR (162 MHz, CH_2Cl_2): δ 40.1 (tt, $^2J_{P-F} = 65.0$ Hz, $^3J_{P-F} = 12.9$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.0 (2F), −122.6 (2F), −121.8 (2F), −121.6 (6F), −121.2 (2F), −114.8 (2F), −104.5 (dt, $J_{F-P} = 64.1$ Hz, $J_{F-F} = 14.2$ Hz, 2F), −80.7 (t, $J_{F-F} = 10.1$ Hz, 3F); HRMS (FAB) Calcd. for $C_{22}H_{10}F_{21}PAu$ $[M - Cl]^+$: 900.9850, Found: 900.9848.

Chloro(dibutyl(perfluorodecyl)phosphine)gold(I) (**5b**): reddish purple solid; mp 62–63 °C; 1H NMR (400 MHz, $CDCl_3$): δ 1.52 (sextet, $J_{H-H} = 7.3$ Hz, 4H), 1.59–1.78 (m, 4H), 1.98–2.21 (m, 4H); ^{31}P NMR (162 MHz, CH_2Cl_2): δ 40.1 (t, $J_{P-F} = 65.0$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.0 (2F), −122.6 (2F), −121.7 (2F), −121.5 (6F), −121.1 (2F), −116.5 (2F), −110.9 (dt, $J_{F-P} = 62.6$ Hz, $J_{F-F} = 17.1$ Hz, 2F), −80.6 (3F); HRMS (FAB) Calcd. for $C_{18}H_{18}AuClF_{21}NaP$ $[M + Na]^+$: 919.0063,

Found: 919.0031. The copies of ^1H NMR, ^{19}F NMR, and ^{31}P NMR spectra of gold complex (**5a,b**) are shown in Supplementary Materials.

3.7. Au Complex-Catalyzed Addition Reaction of 2-Chloroethanol to 1-Octene

The addition reaction was conducted according to the reported method [35]. Under inert atmosphere, **5** (0.03 mmol), AgOTf (7.7 mg, 0.03 mmol), 2-chloroethanol (8.0 mg, 1 mmol), 1-octene (561.2 mg, 5 mmol), and toluene (1 mL) were added to a three-necked flask with a condenser. The solution was heated at 85 °C for 24 h.

4. Conclusions

We demonstrated the synthesis of *P*-fluorous phosphine-coordinated metal complexes, $\text{PtCl}_2(\text{R}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$, $\text{RhCl}(\text{CO})(\text{R}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$, $\text{IrCl}(\text{CO})(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$, and $\text{AuCl}(\text{R}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$. The structure of $\text{PtCl}_2(\text{Ph}_2\text{P}^n\text{C}_{10}\text{F}_{21})_2$ was revealed and discussed. The catalytic activities of the iridium and gold complexes for some synthetic reactions were also shown. The promising *P*-fluorous phosphine-transition metal complexes will be used to catalyze novel reactions in future work.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/5/1/5/s1, copies of ^1H NMR, ^{19}F NMR, and ^{31}P NMR spectra of complexes (**2a–5b**). Crystal structure of the complex (**2a**) (CCDC No.:1445325) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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