Estimating Effective Steric and Electronic Impacts of a Ferrocenyl Group in Organophosphines

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ABSTRACT: A series of monodentate ferrocenylphosphines, Fc_3P (**1a**), Fc_2PhP (**1b**), and Fc_2ArP (**1c**; Fc = ferrocenyl, Ar = 3,4-methylenedioxyphenyl), were prepared, and their electronic and steric properties were quantitatively determined. By the IR measurements of their respective $Ni(CO)_3$(phosphine) complexes, the electronic properties of the ferrocenyl group in organophosphines were estimated to be similar to those of primary alkyl groups. The ferrocenyl group is a better electron donor than a methyl group and a poorer donor than an ethyl group. The gold(I) chloride complexes of **1a−c** were prepared and their X-ray crystal structures were determined. The $\%V_{bur}$ parameters for **1a−c** were calculated using the X-ray structural data, and their "Tolman cone angles" were estimated. The steric influence of the ferrocenyl group in organophosphines was clarified to be larger than those of cyclohexyl, *tert*-butyl, and *o*-tolyl groups and is comparable to that of a mesityl group.

Fc- : (Fe)
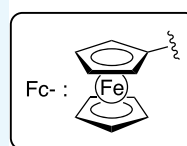
steric properties
Ph ≪ *t*Bu < *o*-tolyl < Fc ≤ mesityl
smaller ← → larger

electronic properties
Ph ≪ Me < Fc < Et
poorer donor ← → better donor

INTRODUCTION

Bis(cyclopentadienyl)iron(II), commonly known as ferrocene, is a stable 18-electron organometallic compound. While cyclopentadienyl anion fulfills the Hückel's rule with six π-electrons, ferrocene also shows aromatic character. Hence, the ferrocenyl group (Fc) can be classified as an aryl substituent.[1]

Recently, we reported a novel chiral bisphosphine ligand, Fc-Segphos **A**, in which the conventional diphenylphosphino-donor moieties in parent Segphos **B** were replaced with the diferrocenylphosphino-groups (Figure 1, center).[2] Fc-Segphos

Fc- : (Fe)

Ar = Fc; (*R*)-Fc-Segphos (**A**)
Ph; (*R*)-Segphos (**B**)

Ar = Fc; (*S,S*)-Fc-tfb* (**C**)
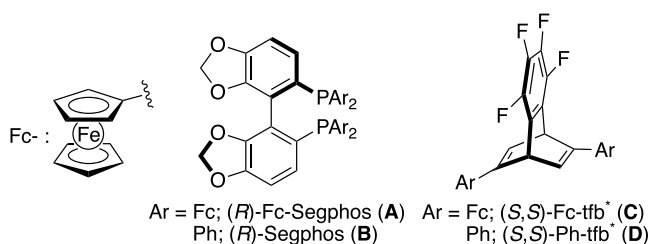Ph; (*S,S*)-Ph-tfb* (**D**)

Figure 1. Structures of the ferrocenyl group, (*R*)-Segphos derivatives **A** and **B**, and chiral diene ligands **C** and **D**.

was applied in the palladium-catalyzed asymmetric synthesis of axially chiral allenes achieving higher enantioselectivity than **B**. Ferrocenyl substituents were also utilized as effective "chiral-defining" substituents in chiral diene ligand (*S,S*)-Fc-tfb* **C** (Figure 1, right), and the ferrocenyl derivative showed better performances than the corresponding phenyl analogue, (*S,S*)-Ph-tfb* **D**, in various rhodium-catalyzed asymmetric reactions.[3]

The unique properties of chiral ligands **A** and **C** can be attributed to the peculiar steric and electronic characteristics of

ferrocenyl substituents, which are significantly different from those of classical benzenoid aryl substituents. While benzenoid aromatics are planar, ferrocene is cylindrical. Ferrocene is an electron-rich molecule showing the high reactivity in electrophilic aromatic substitution reactions such as the Friedel−Crafts acylation. Consequently, a ferrocenyl group is highly electron-donating compared to other aromatic substituents.[4] In this article, we have estimated the steric and the electronic impacts of the ferrocenyl group in a series of organophosphine compounds. The two steric models, namely, the Tolman cone angle (TCA)[5] and the percent buried volume ($\%V_{bur}$),[6] were utilized to quantify the steric effects of Fc-substituents (Figure 2). The electronic effects were determined by the Tolman electronic parameters (TEPs).[5b,7]

Various ferrocenylphosphine derivatives have played integral roles in organophosphorus chemistry;[8−10] however, the quantitative evaluation of the steric and the electronic properties of ferrocenylphosphines has been limited (and some results have been contradictory). The TCA values of $FcPh_2P$ (**E**) were evaluated in various transition-metal complexes. The values, ranging from 144° to 180°, were found to be sensitive to the orientation of the ferrocenyl moieties in the complexes.[11] The TCA parameters of Fc_2PhP (**1b**) were also determined to be 190−191° based on the X-ray crystal structures of its
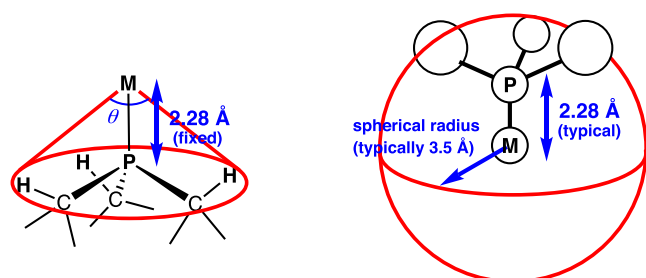
Figure 2. Concepts of the Tolman cone angle (TCA; left)[5] and percent buried volume (%V_{bur}; right).[6]

chlorogold(I) complex[12a] or of unligated **1b**.[13] The TCA value of 211° was reported for Fc$_3$P (**1a**), which was calculated using the X-ray structure of the corresponding phosphine oxide Fc$_3$P=O.[14] The preparation of Ni(**E**)(CO)$_3$ was reported in 2010, and its IR analysis determined the TEP of phosphine **E** to be 2066 cm^{-1}.[11d] The TEP of **E** was also estimated by the indirect method. Using the experimental correlation between the ν_{CO} values in the Vaska-type complex *trans*-RhCl(CO)-(phosphine)$_2$ and the ν_{CO}(A$_1$) frequencies in Ni(phosphine)-(CO)$_3$, the TEP of **E** was determined to be 2065.5 cm^{-1} from the ν_{CO} frequency in *trans*-RhCl(CO)(**E**)$_2$.[11c] The TEP values of **E** indicated that **E** was a better electron donor than triphenylphosphine. On the other hand, the comparison of the $^1J_{P-Se}$ spin–spin coupling constants for Ph$_3$P=Se and for FcPh$_2$P=Se insisted that the ferrocenyl substituent made FcPh$_2$P slightly more electron-withdrawing than Ph$_3$P.[15] Apparently, this statement is against the conclusions drawn from the IR measurements of the metal–phosphine/carbonyl complexes. A series of phosphine/carbonyl complexes of (phosphine)M(CO)$_5$ (M = Cr, Mo, W), (phosphine)Fe(CO)$_4$, and (phosphine)Mn$_2$(CO)$_9$, where "phosphine" is **1a**, **1b**, **E**, or PPh$_3$, were prepared, and the comparison of their IR spectra showed that the σ-donor ability of the phosphine increases as the number of ferrocenyl groups is increased.[16] The electrochemistry of ferrocenylphosphines Fc$_n$Ph$_{3-n}$P (n = 1–3) was reported as well.[17] With these precedented reports in mind, here we have intended to quantify the electronic and the steric properties of the ferrocenyl group in organophosphines in a reliable way.

■ RESULTS AND DISCUSSION

Ferrocenylphosphines for Consideration. Four monodentate triarylphosphines **1a–d** were chosen for this study and were prepared as in Scheme 1 (see Experimental Section for details). Phosphines **1a** and **1b** are known compounds and were originally prepared from ferrocene and PCl$_3$[18] or PhPCl$_2$[19] under Friedel–Crafts conditions. The synthetic method we employed was reactions of nucleophilic ferrocenyllithium with an appropriate electrophilic chlorophosphine, which gave the

Scheme 1. Monodentate Triarylphosphines 1a–d Used in This Study
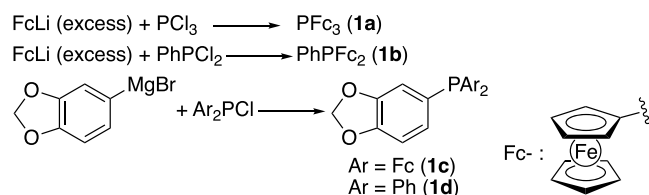
desired ferrocenylphosphines cleanly. Preparation of **1a** with a similar method was described recently.[20]

Phosphine **1c** has a structure similar to the half portion of bisphosphine Fc-Segphos **A**. Likewise, **1d** mimics the bisected structure of Segphos **B**. The electronic properties of **1c** and **1d** are expected to be comparable to those of **A** and **B**, respectively. Although phosphine **1d** has no ferrocenyl substituents, it was used in this study for comparison.

Determination of the Tolman Electronic Parameters for Ferrocenylphosphines. In the 1970s, Tolman demonstrated that the IR frequency of the A$_1$ stretch in Ni(CO)$_3$L, where L was a monodentate phosphorus donor ligand of interest, was a useful probe to quantify the electron-donating ability of the ligand L.[5b,7] The ν_{CO}(A$_1$) values are known as the Tolman electronic parameters (TEPs), and more recently, the method was applied to the determination of the electronic properties of various NHC donors as well.[21]

Tricarbonyl(phosphine)nickel(0) complexes **2a–d**, Ni-(CO)$_3$(phosphine), were prepared starting with Ni(cod)$_2$ and **1a–d** using the procedure of Kündig (Scheme 2).[22] The complexes were obtained as dichloromethane solutions and directly used for the IR measurements without isolation.

Scheme 2. In Situ Preparation of Ni(CO)$_3$(phosphine) Complexes 2a–d
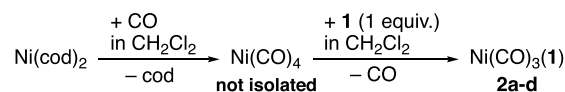
The carbonyl A$_1$ stretching frequencies of complexes **2a–d** are listed in Table 1 together with that of the triphenylphosphine

Table 1. IR ν_{CO}(A$_1$) Frequencies of Ni(CO)$_3$L in CH$_2$Cl$_2$[a]

entry	ligand L	complex	ν_{CO}(A$_1$) (cm^{-1})
1	PPh$_3$	Ni(CO)$_3$(PPh$_3$)	2068.9[a]
2	**1a** (PFc$_3$)	**2a**	2062.7
3	**1b** (PFc$_2$Ph)	**2b**	2064.7
4	**1c**	**2c**	2064.7
5	**1d**	**2d**	2068.5

[a]The same number was reported in ref 7.

complex. In Figure 3, phosphines **1a–d** were arranged on the TEP scale together with some representative phosphines with their TEP values.[7] The homoleptic phosphines (PR$_3$) and the
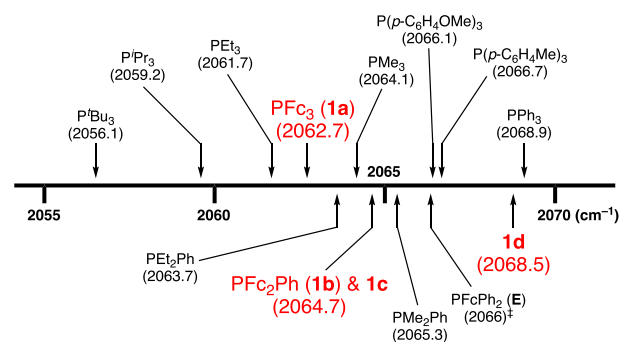
‡ recorded with KBr pellet (ref. 11d).

Figure 3. Comparison of TEPs of **1a–d** with those of other phosphines (taken from refs 7 and 11d).

heteroleptic phosphines (PR_2R') were placed above and below the horizontal scale, respectively. The TEP value for Ni-$(CO)_3(PPh_3)$ obtained in our laboratory (Table 1, entry 1) showed a good agreement with that in the Tolman's original article,[7] indicating validity of our measurements.

The carbonyl stretching frequency of complex **2a** is significantly redshifted compared with those of the nickel(0) complexes of other triarylphosphine ligands. This indicates that PFc_3 (**1a**) is strongly donating for a triarylphosphine, and indeed, its TEP value was detected in the region of trialkylphosphines. Judging from the TEP values, PFc_3 (**1a**) is a better donor than PMe_3 and is slightly less donating than PEt_3. The strong basicity of **1a** could be attributed to the electron richness of the ferrocenyl group.[4] In accordance with this assessment, the TEP of PFc_2Ph was detected at 2064.7 cm^{-1}, which was smaller than that of PMe_2Ph (2065.3) and larger than that of PEt_2Ph (2063.7). The methylenedioxyphenyl group was slightly more electron-donating than the phenyl group, but its electronic influences were minimal. The TEPs of **1b** and **1c** were nearly same, and the TEP of **1d** was only 0.4 point smaller than that of triphenylphosphine.

In Tolman's original report about TEP, the substituent contribution parameters $"\chi_i"$ of various substituents were determined from the TEP values of diverse phosphine ligands $PX_1X_2X_3$.[5b,7] Equation 1 shown below was proposed to estimate $\nu_{CO}(A_1)$ frequencies of any $Ni(CO)_3(PX_1X_2X_3)$ complexes from the respective χ_i values of the substituents X_1, X_2, and X_3.

$$\nu_{CO}A_1 = 2056.1 + \sum_{i=1}^{3} \chi_i \, (cm^{-1}) \tag{1}$$

substituent X_i	χ_i (cm^{-1})
Et	1.8
Fc	2.2
Me	2.6
p-C_6H_4OMe	3.4
Ph	4.3

The parameter χ_i represents the electronic nature of the substituents in organophosphines; the smaller χ_i values mean the substituents are better donors. Selected χ_i values are listed above with eq 1 (see ref 7 for the additional data). The χ_i parameter of the ferrocenyl group was determined to be 2.2 from the $\nu_{CO}(A_1)$ frequency of **2a**.[23] Once again, this value is larger than that of the ethyl group and smaller than that of the methyl group. Using this number, the TEPs of PFc_2Ph and $PFcPh_2$ were calculated to be 2064.8 and 2066.9, respectively, and these numbers showed the excellent agreement with the experimental observations (Figure 3).[11d]

In short, the ferrocenyl group is strongly electron-donating for an aryl substituent, and its electronic properties in organophosphines are similar to those of primary alkyl groups. The ferrocenyl group is clarified to be a better donor than the methyl group and a weaker donor than the ethyl group.

Preparation and X-ray Crystal Structure Determination of Gold(I) Chloride Complexes 3a−c. Dissolving an equimolar mixture of monodentate ferrocenylphosphine (**1a**, **1b**, or **1c**) and $(Me_2S)Au(I)Cl$ in dichloromethane showed quantitative conversion to the corresponding (phosphine)Au(I)Cl complex (**3a**, **3b**,[12] or **3c**) within 30 min. These gold(I) complexes were recrystallized by slow diffusion of pentane into the concentrated chloroform solutions at room temperature yielding red-orange prisms, and the X-ray crystallography revealed their three-dimensional structures.

The structure of **3a** is shown in Figure 4 with selected bond lengths and angles. All the three ferrocenyl substituents take
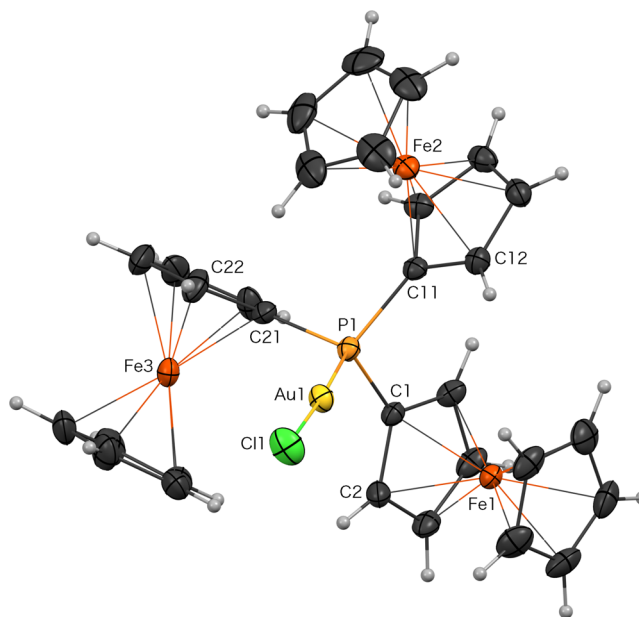

Figure 4. ORTEP drawing of the X-ray structure of $(Fc_3P)AuCl$ (**3a**) with thermal ellipsoids at the 20% probability level. Cocrystallized chloroform molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1−Cl1 = 2.281(2), Au1−P1 = 2.223(1), P1−C1 = 1.787(5), P1−C11 = 1.795(5), P1−C21 = 1.778(6), Cl1−Au1−P1 = 177.18(6), Au1−P1−C1 = 116.0(2), Au1−P1−C11 = 113.6(2), Au1−P1−C21 = 111.5(2), C1−P1−C11 = 103.2(2), C1−P1−C21 = 106.2(2), and C11−P1−C21 = 105.4(2); torsion angles: Au1−P1−C1−C2 = 35.06, Au1−P1−C11−C12 = 34.93, and Au1−P1−C21−C22 = 25.80; dihedral angles between the two Cp planes in a Fc substituent = 3.99 (Fe1), 1.88 (Fe2), and 3.25 (Fe3).

eclipsed conformations. The two cyclopentadienyls in each ferrocenyl substituent are nearly parallel with dihedral angles between the two Cp planes ranging from 1.88° to 3.99°. All the three $(\eta^5$-$C_5H_5)Fe$ moieties in the respective ferrocenyl substituents protrude outward to avoid steric congestion, and all the CpFe fragments are located on the side closer to the gold atom. Hence, the overall geometry of **3a** in the solid state is pseudo-C_3-symmetric.

The structure of **3b** is shown in Figure 5 with selected bond lengths and angles. As in the case of **3a**, both ferrocenyl groups in **3b** are eclipsed and the two Cp's in each ferrocenyl group are nearly parallel with their dihedral angles being 4.71° (Fe1) and 1.36° (Fe2), respectively. The ferrocenyl substituents are much bulkier than the phenyl group, and the two Fc groups in **3b** protrude in different directions to minimize steric repulsion. The angles between the Au1−P1 bond and Cp−Fe1−Cp vector or Cp−Fe2−Cp vector are 68.2° and 42.2°, respectively.

Complex **3c** (Figure 6) is almost isostructural to **3b**. The dioxole moiety in **3c** is remote from the gold center and shows very limited influences on the solid-state structure.

Determination of Steric Parameters for Ferrocenyl-phosphines 1a−c. The percent buried volume parameters (% V_{bur}) were determined for ferrocenylphosphines **1a−c** using the X-ray crystallographic data of gold(I) complexes **3a−c**. The calculations were performed using the SambVca 2.1 web application.[6c] The following conditions were used for each
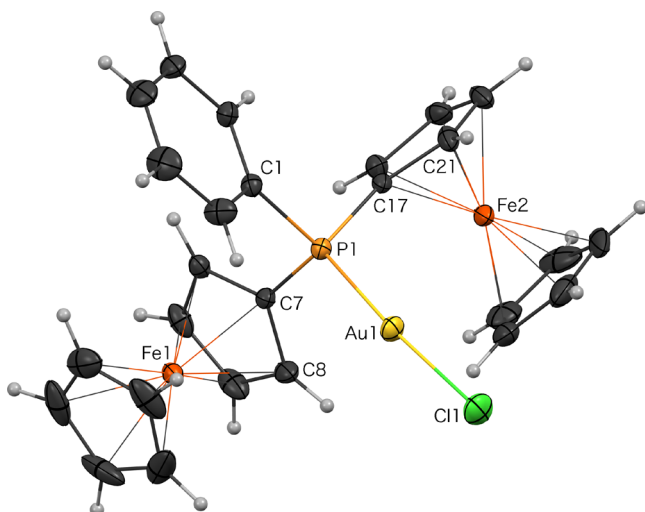
Figure 5. ORTEP drawing of the X-ray structure of (Fc_2PhP)AuCl (**3b**) with thermal ellipsoids at the 20% probability level. Selected bond lengths (Å) and angles (deg): Au1−Cl1 = 2.288(2), Au1−P1 = 2.223(1), P1−C1 = 1.822(6), P1−C7 = 1.795(5), P1−C17 = 1.789(4), Cl1−Au1−P1 = 172.67(6), Au1−P1−C1 = 114.9(2), Au1−P1−C7 = 114.6(1), Au1−P1−C17 = 112.2(1), C1−P1−C7 = 106.5(2), C1−P1−C17 = 105.3(2), and C7-P1-C17 = 102.1(2); torsion angles: Au1−P1−C7−C8 = 27.71 and Au1−P1−C17−C21 = 44.63; dihedral angles between the two Cp planes in a Fc substituent = 4.71 (Fe1) and 1.36 (Fe2).
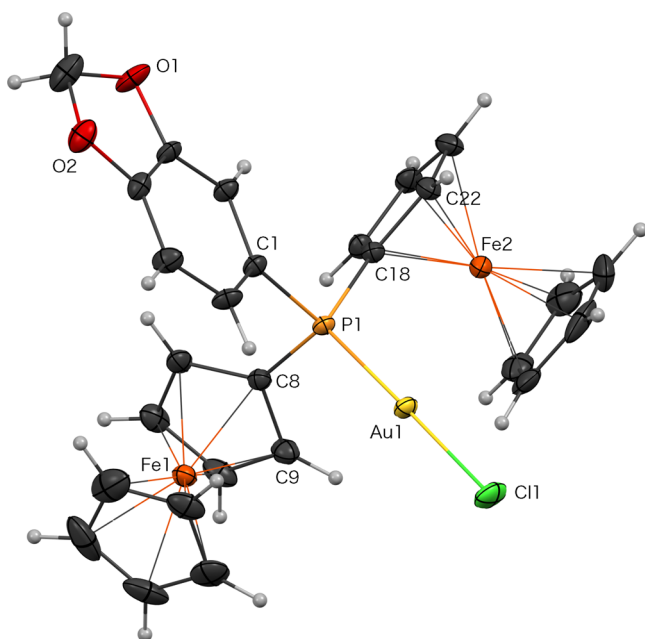

Figure 6. ORTEP drawing of the X-ray structure of [Fc_2(3,4-OCH_2O−C_6H_3)P]AuCl (**3c**) with thermal ellipsoids at the 20% probability level. Selected bond lengths (Å) and angles (deg): Au1−Cl1 = 2.279(2), Au1−P1 = 2.225(2), P1−C1 = 1.808(5), P1−C8 = 1.779(8), P1−C18 = 1.797(6), Cl1−Au1−P1 = 177.53(7), Au1−P1−C1 = 113.9(2), Au1−P1−C8 = 112.7(2), Au1−P1−C18 = 116.2(2), C1−P1−C8 = 105.1(3), C1−P1−C18 = 105.0(3), and C8−P1−C18 = 102.7(3); torsion angles: Au1−P1−C8−C9 = 37.82 and Au1−P1−C17−C21 = 60.94; dihedral angles between the two Cp planes in a Fc substituent = 2.58 (Fe1) and 2.63 (Fe2).

calculation: sphere radius = 3.5 Å, $d_{Au−P}$ = 2.28 Å, H atoms not included, and Bondi radii scaled by 1.17.

The calculated %V_{bur} parameters for **1a**−**c** are listed in Table 2 together with their estimated Tolman cone angles (vide infra),

Table 2. Cone Angles (C.A.) and %V_{bur} for Ferrocenylphosphines 1a−c and Selected Tertiary Phosphines[a,b,c,d,e,f,g]

entry	ligand L	%V_{bur} in LAuCl[a]	Tolman C.A.	C.A. in LAuCl[b]	P−Au (Å) in LAuCl
1	**1a**	42.3 (**3a**)	204[c]	203	2.224
2	**1b**	39.8 (**3b**)	193[c]	194	2.223
3	**1c**	40.9 (**3c**)	198[c]	196	2.225
4	Ph_3P	29.9[d]	145[e]	153	2.231[24]
5	Cy_3P	33.2[d,f]	170[e]	168	2.242[25]
6	$^tBu_3P$	38.1[d]	182[e]	175[g]	2.253[26]
7	(o-Tol)$_3$P	39.4[d]	194[e]	187	2.239[27]
8	Mes_3P	45.0[d]	212[e]	202	2.263[28]

[a]Calculated using SambVca 2.1 web application with spherical radius = 3.5 Å and P−Au bond length = 2.28 Å. [b]Determined from the X-ray structures. [c]Estimated from the %V_{bur} parameters using eq 2 (ref 6a). [d]Taken from ref 6a. [e]Taken from ref 5b. [f]Recalculated using SambVca 2.1 web application. [g]The hydrogen atom coordinates were not included in the original report (ref 26); the cone angle value was calculated by locating the hydrogen atoms at the idealized positions.

the measured cone angles in gold(I) complexes **3a**−**c**, and the P−Au bond lengths in **3a**−**c** (entries 1−3). These values for the representative bulky phosphines are also compiled in Table 2 for comparison (entries 4−8). The %V_{bur} of **1a** in **3a** is 42.3, which is much larger than those of typical bulky monodentate phosphines in analogous chlorogold(I) complexes (entries 1 vs 5−7). Among the phosphine ligands listed in Table 2, only trimesitylphosphine shows the larger %V_{bur} than **1a** (entry 8). The large %V_{bur} value of **1a** indicates the sterically demanding nature of the ferrocenyl group in organophosphines. The %V_{bur} parameters for **1b** and **1c** are also fairly large (39.8 and 40.9, respectively) due to the presence of the two phosphorus-bound ferrocenyl groups in them.

Clavier and Nolan, who introduced the concept of %V_{bur}, demonstrated the linear correlation between the TCAs of various monodentate phosphines and their %V_{bur} parameters calculated from the (phosphine)Au(I)Cl crystal structures (Figure 7, blue line).[6a] Equation 2 was given for the correlation based on the TCA data of the 15 phosphine ligands and the crystal structures of their chlorogold(I) complexes. The TCA
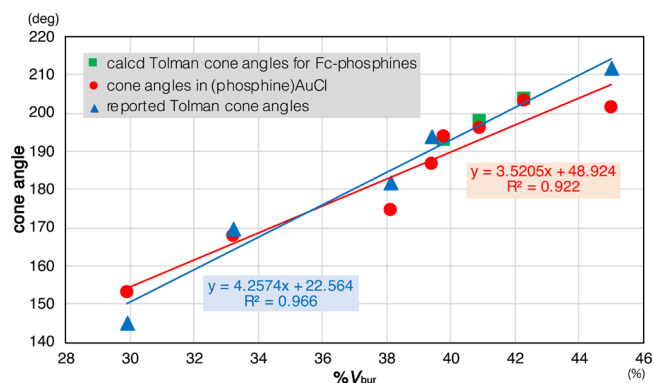

Figure 7. Correlations of the Tolman cone angles and the cone angles in (phosphine)AuCl with the %V_{bur} parameters in the gold complexes.

values of **1a**, **1b**, and **1c** are estimated to be 204°, 193°, and 198°, respectively, using eq 2.[6a]

$$[\mathbf{TCA}] = 4.786[\%V_{\mathbf{bur}}] + 2.037 \quad (R^2 = 0.981) \quad (2)$$

The cone angles of the coordinating phosphines in the Au(I) Cl complexes were determined from their X-ray crystal structures. These cone angles were calculated without adjusting the phosphorus–gold bond lengths (cf., the fixed phosphorus–metal distance of 2.28 Å is used for determining the TCA), and a van der Waals radius of 1.00 Å was used for hydrogen atoms. These cone angle values "in the real systems" also showed an excellent linear correlation with the $\%V_{bur}$ parameters (Figure 7, red line). The cone angle of Mes_3P in the gold complex (202°) is much smaller than its TCA (212°). Among the phosphines in Table 2, Fc_3P (**1a**) showed the largest cone angle in the series of gold complexes.

In brief, the ferrocenyl group is a very bulky substituent. Its steric influence in organophosphines was estimated to be larger than that of cyclohexyl, *tert*-butyl, and *o*-tolyl groups and is comparable to that of a mesityl group.

Consideration of Steric Influence of *P*-Bound Ferrocenyl Groups in Ferrocenylphosphines. A notable steric characteristic of the ferrocenyl group is its cylindrical shape. The two faces of each phosphorus-bound C_5H_4 moiety in **1a**–**c** are heterotopic due to the η^5-coordination of a FeCp fragment onto one side of the planar C_5H_4. Hence, the steric impacts of ferrocenylphosphines are greatly affected by the conformation (orientation) of the ferrocenyl substituents with respect to the Fc–P bond rotation. Figure 8 illustrates the two extreme
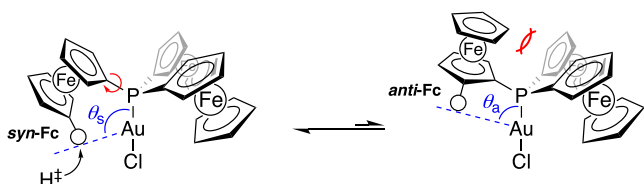

Figure 8. Two extreme conformations of a Fc-substituent in **3a**.

conformations (*syn*-Fc and *anti*-Fc) of a ferrocenyl substituent in **3a**. The participation of the *anti*-Fc conformation must be minimal due to the severe steric repulsion with the other phosphorus-bound substituents. This is indeed the situations observed in the crystal structures of **3a**–**c**. Nevertheless, the cone angles of ferrocenylphosphines (i.e., θ_s in Figure 8, left) are greatly affected by the conformation of the ferrocenyl substituents.

In a *syn*-Fc substituent of a metal-coordinated ferrocenylphosphine, the atom determining its cone angle is one of the hydrogen atoms in the unsubstituted η^5-C_5H_5 ("H‡" in Figure 8, left). Due to the cylindrical shape of the Fc substituent, the unsubstituted Cp is fairly remote from the metal center. Thus, the Fc groups of ferrocenylphosphines occupy certain space of the coordination spheres especially in the peripheral regions. The $\%V_{bur}$ parameters for the phosphines examined here in the (phosphine)Au(I)Cl complexes were calculated with two additional spherical radii (3.0 and 4.5 Å; see Figure 2, right), and the results are integrated in Table 3 together with those of the standard 3.5 Å spherical radius. In line with the abovementioned "peripheral occupancies of the ferrocenyl substituents", the $\%V_{bur}$ values for three ferrocenylphosphines **1a**–**c** are largest with the spherical radius of 4.5 Å (entries 1–3). On the other hand, the other five "ferrocene-free" phosphines

Table 3. $\%V_{bur}$ for Ferrocenylphosphines 1a–c and Selected Tertiary Phosphines Calculated with Various Spherical Radii[a]

entry	ligand L	spherical radii for $\%V_{bur}$ calculation[a]		
		3.0 Å	3.5 Å	4.5 Å
1	**1a**	38.1	42.3	45.7
2	**1b**	37.1	39.8	40.9
3	**1c**	38.1	40.9	42.1
4	Ph_3P	29.4	29.9[b]	28.9
5	Cy_3P	32.2	33.2[b,c]	32.4
6	$^tBu_3P$	36.4	38.1[b]	37.6
7	$(o\text{-Tol})_3P$	38.3	39.4[b]	37.9
8	Mes_3P	44.4	45.0[b]	42.9

[a]Calculated using SambVca 2.1 web application with indicated spherical radii and P–Au bond length = 2.28 Å. [b]Taken from ref 6a. [c]Recalculated using SambVca 2.1 web application.

showed the largest $\%V_{bur}$ values with the 3.5 Å spherical radius compared to those with spherical radii of 3.0/4.5 Å (entries 4–8).

■ CONCLUSIONS

In this article, we have determined the steric and the electronic impacts of a ferrocenyl group in organophosphines. The three representative ferrocenylphosphines, namely, Fc_3P (**1a**), Fc_2PhP (**1b**), and Fc_2ArP (**1c**; Ar = 3,4-methylenedioxyphenyl), were prepared, and their Tolman electronic parameters (TEPs) were measured by the IR spectroscopy of their respective $Ni(CO)_3$(phosphine) complexes (**2**). In comparison with the TEP values of other phosphines, it was estimated that the electronic properties of the ferrocenyl group in organophosphines were similar to those of primary alkyl groups. A ferrocenyl group is a better donor than a methyl group and is less donating than an ethyl group. The (phosphine)AuCl complexes (**3**) of **1a**–**c** were prepared and their structures were determined by the X-ray crystallography. The $\%V_{bur}$ parameters of **1a**–**c** were calculated using the structural data of **3a**–**c**, and their Tolman cone angles were determined. The steric influence of the ferrocenyl group in organophosphines was estimated to be larger than that of cyclohexyl, *tert*-butyl, and *o*-tolyl groups, and is comparable to that of a mesityl group.

The properties of the ferrocenyl group quantified in this study, very bulky and fairly electron-donating, are unique, and ferrocenylphosphine derivatives should enhance their applicability in transition-metal catalysis, and the data provided in this article will assist the future utilization of ferrocenylphosphines.

■ EXPERIMENTAL SECTION

General Information. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 101 MHz) chemical shifts are reported in parts per million downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran and hexane (homogenized with tetraethylene glycol dimethyl ether) were distilled from benzophenone ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. Chloroform-*d* was distilled from P_2O_5 under vacuum prior to use. Ferrocenyllithium[29] and chlorodiferrocenylphosphine[2] were prepared as reported. All the

other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Triferrocenylphosphine (1a).[17b,18,20] A solution of ferrocenyllithium (1.9 g, 9.9 mmol) in THF (50 mL) was cooled to 0 °C, and to this phosphorus trichloride (0.34 g, 2.5 mmol) was added dropwise by using a syringe. The mixture was warmed to room temperature and stirred for 12 h at this temperature. After quenching the reaction mixture with degassed water (ca. 20 mL), the mixture was extracted with diethyl ether twice (ca. 100 mL each). The combined organic phase was dried over $MgSO_4$, filtered, and then evaporated to dryness. The residue was purified by silica gel chromatography using benzene as an eluent to give the title compound as a yellow solid. Yield: 0.98 g (1.7 mmol, 68%). The spectroscopic data were consistent with those reported previously.[17b20]

Diferrocenylphenylphosphine (1b).[17b,19,30] A solution of ferrocenyllithium (1.0 g, 5.2 mmol) in THF (20 mL) was cooled to 0 °C, and to this was added chlorodiphenylphosphine (0.37 g, 2.1 mmol) dropwise by using a syringe. The mixture was warmed to room temperature and stirred for 12 h at this temperature. After quenching the reaction mixture with degassed water (ca. 10 mL), the mixture was extracted with diethyl ether twice (ca. 50 mL each). The combined organic phase was dried over $MgSO_4$, filtered, and then evaporated to dryness. The residue was purified by silica gel chromatography (with benzene/hexane = 50/50) to give the title compound as an orange solid. Yield: 0.45 g (0.94 mmol, 46%). The spectroscopic data were consistent with those reported previously.[17b,30]

Diferrocenyl(3,4-methylenedioxyphenyl)phosphine (1c). To a suspension of activated magnesium [from Mg (0.11 g, 4.5 mmol) and 1,2-dibromoethane (80 mg, 0.43 mmol)] in THF (5 mL), a solution of 4-bromo-1,2-(methylenedioxy)-benzene (0.78 g, 3.9 mmol) in THF (10 mL) was added dropwise via a cannula at room temperature. The mixture was stirred at 40 °C for 5 h; then, the solution of the Grignard reagent was added to a solution of chlorodiferrocenylphosphine (1.1 g, 2.5 mmol) in THF (3.0 mL) at room temperature via a cannula. After stirring the mixture overnight, the reaction mixture was quenched by the addition of a small amount of water (ca. 500 µL). All the volatiles were removed under vacuum, and the residue was purified by silica gel chromatography (with benzene/hexane = 50/50) to give the title compound as a yellow solid. Yield: 0.54 g (1.0 mmol, 41%). ^{1}H NMR (CDCl$_3$, δ): 4.01 (br, 2H, α-C$_5$H$_4$), 4.10 (s, 10H, C$_5$H$_5$), 4.16 (br, 2H, α-C$_5$H$_4$), 4.27−4.28 (m, 2H, β-C$_5$H$_4$), 4.30−4.32 (m, 2H, β-C$_5$H$_4$), 5.96 (s, 2H, −OCH$_2$O−), 6.83 (d, J = 8.0 Hz, 1H, 2-methylenedioxyphenyl), 6.89−6.91 (m, 1H, 5-methylenedioxyphenyl), 7.12−7.17 (m, 1H, 6-methylenedioxyphenyl). ^{13}C NMR (CDCl$_3$, δ): 69.0 (C$_5$H$_5$), 69.9 (d, J_{PC} = 3.5 Hz, β-C$_5$H$_4$), 70.5 (d, J_{PC} = 1.3 Hz, β-C$_5$H$_4$), 71.7 (d, J_{PC} = 12.2 Hz, α-C$_5$H$_4$), 72.5 (d, J_{PC} = 15.8 Hz, α-C$_5$H$_4$), 78.1 (d, J_{PC} = 4.0 Hz, ipso-C$_5$H$_4$), 100.9 (−OCH$_2$O−), 108.0 (d, J_{PC} = 12.2 Hz, 5-methylenedioxyphenyl), 113.1 (d, J_{PC} = 13.7 Hz, 6-methyl-enedioxyphenyl), 128.5 (d, J_{PC} = 33.2 Hz, 2-methylenedioxy-phenyl), 132.2 (d, J_{PC} = 8.8 Hz, 1-methylenedioxyphenyl), 147.3 (d, J_{PC} = 7.0 Hz, 3-methylenedioxyphenyl), 148.3 (4-methylenedioxyphenyl). ^{31}P NMR (CDCl$_3$, δ): −28.4. Anal. Calcd for C$_{27}$H$_{23}$Fe$_2$O$_2$P: C, 62.11; H, 4.44. Found: C, 62.12; H, 4.46. ESI-HRMS Calcd for C$_{27}$H$_{24}$Fe$_2$O$_2$P (M + 1): 523.0213. Found: 523.0219.

(3,4-Methylenedioxyphenyl)diphenylphosphine (1d). To a suspension of activated magnesium [from Mg (0.11 g, 4.5

mmol) and 1,2-dibromoethane (75 mg, 0.40 mmol)] in THF (5 mL), a solution of 4-bromo-1,2-(methylenedioxy)benzene (0.78 g, 3.9 mmol) in THF (10 mL) was added dropwise via a cannula at room temperature. The mixture was stirred at 40 °C for 5 h; then, the solution of the Grignard reagent was added to a solution of chlorodiphenylphosphine (0.57 g, 2.6 mmol) in THF (3.0 mL) at room temperature via a cannula. After stirring the mixture overnight, the reaction mixture was quenched by the addition of a small amount of water (ca. 500 µL). All the volatiles were removed under vacuum, and the residue was purified by silica gel chromatography (with benzene/hexane = 50/50) to give the title compound as a colorless liquid. Yield: 0.48 g (1.6 mmol, 61%). ^{1}H NMR (CDCl$_3$, δ): 5.95 (s, 2H, −OCH$_2$O−), 6.74 (d, J = 6.4 Hz, 1H, 2-methylenedioxyphenyl), 6.81 (d, J = 7.8 Hz, 1H, 5-methylenedioxyphenyl), 6.92 (dd, J = 9.2 and 7.8 Hz, 1H, 6-methylenedioxyphenyl), 7.26−7.35 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$, δ): 101.1 (−OCH$_2$O−), 108.7 (d, J_{PC} = 10.5 Hz, 5-methylenedioxyphenyl), 113.4 (d, J_{PC} = 17.3 Hz, 6-methylenedioxyphenyl), 128.5 (d, J_{PC} = 6.8 Hz, m-Ph), 128.6 (p-Ph), 128.8 (d, J_{PC} = 27.7 Hz, 2-methylenedioxyphenyl), 129.7 (d, J_{PC} = 10.5 Hz, 1-methylenedioxyphenyl), 133.4 (d, J_{PC} = 19.5 Hz, o-Ph), 137.6 (d, J_{PC} = 11.0 Hz, ipso-Ph), 148.0 (d, J_{PC} = 8.3 Hz, 3-methylenedioxyphenyl), 148.5 (4-methylenedioxyphen-yl). ^{31}P NMR (CDCl$_3$, δ): −3.9. Anal. Calcd for C$_{19}$H$_{15}$O$_2$P: C, 74.50; H, 4.94. Found: C, 74.32; H, 5.15. ESI-HRMS Calcd for C$_{19}$H$_{16}$O$_2$P (M + 1): 307.0888. Found: 307.0892.

In Situ Generation of Ni(CO)$_3$(phosphine) Complexes 2a−d and the IR Measurements. Tricarbonyl(phosphine)-nickel(0) complexes **2a−d** were generated in situ starting with Ni(cod)$_2$ and **1a−d** using the procedure of Kündig.[22] The complexes were obtained as dichloromethane solutions and used for the IR measurements without isolation.

A slow stream of carbon monoxide was bubbled through a solution of Ni(cod)$_2$ (28 mg, 0.10 mmol) in dichloromethane (1.0 mL). The initial yellow color of the solution turned colorless in a few minutes. To this was added a solution of monodentate phosphine **1** (0.10 mmol) in dichloromethane (1.0 mL) at 0 °C, and the mixture was stirred for 5 min. The solution was transferred into a nitrogen-purged KBr cell using a syringe, and the IR spectra were measured immediately. Caution! Ni(CO)$_4$, which was generated in situ by the reaction of Ni(cod)$_2$ and carbon monoxide, is highly toxic and volatile. All manipulations need to be carried out in a well-ventilated fume hood. The waste can be decomposed by oxidation with bromine.

The General Procedure for Preparation of Gold(I) Complexes (3). A mixture of (Me$_2$S)AuCl (30 mg, 0.10 mmol) and a ferrocenylphosphine (0.10 mmol) was dissolved in dichloromethane (5.0 mL), and the solution was stirred for 30 min at room temperature. The solution was concentrated to ca. 0.5 mL under vacuum, and to this, hexane (ca. 5 mL) was added dropwise to precipitate the gold complex. The complex was isolated by filtration, washed with hexane, and dried under vacuum. The yields of **3** were nearly quantitative (>90%). Complex **3b** was reported previously,[12] but no ^{13}C NMR data were given. The characterization data for **3a** and **3d** and the NMR data for **3b** are given below.

Chloro(triferrocenylphosphine)gold(I) (3a). ^{1}H NMR (CDCl$_3$, δ): 4.15 (s, 15H, C$_5$H$_5$), 4.39−4.41 (m, 6H, α- or β-C$_5$H$_4$), 4.48−4.49 (m, 6H, β- or α-C$_5$H$_4$). ^{13}C NMR (CDCl$_3$, δ): 70.0 (C$_5$H$_5$), 71.3 (d, J_{PC} = 8.9 Hz, α- or β-C$_5$H$_4$), 72.9 (d, J_{PC} = 14.1 Hz, β- or α-C$_5$H$_4$), 73.6 (d, J_{PC} = 77.0 Hz, ipso-C$_5$H$_4$). ^{31}P NMR (CDCl$_3$, δ): 14.4. Anal. Calcd for C$_{30}$H$_{27}$AuClFe$_3$P: C,

44.02; H, 3.33. Found: C, 43.79; H, 3.31. ESI-HRMS Calcd for $C_{30}H_{27}AuClFe_3P$: 817.9253. Found: 817.9261.

Chloro(diferrocenylphenylphosphine)gold(I) (3b).[12] ^{1}H NMR (CDCl$_3$, δ): 4.19 (s, 10H, C$_5$H$_5$), 4.23−4.25 (m, 2H, C$_5$H$_4$), 4.45−4.48 (m, 4H, C$_5$H$_4$), 4.50−4.52 (m, 2H, C$_5$H$_4$), 7.44−7.53 (m, 3H, *m*- and *p*-Ph), 7.76−7.82 (s, 2H, *o*-Ph). ^{13}C NMR (CDCl$_3$, δ): 70.1 (C$_5$H$_5$), 71.5 (d, J_{PC} = 9.3 Hz, β-C$_5$H$_4$), 71.7 (d, J_{PC} = 74.6 Hz, *ipso*-C$_5$H$_4$), 72.1 (d, J_{PC} = 11.0 Hz, α-C$_5$H$_4$), 72.3 (d, J_{PC} = 6.2 Hz, β-C$_5$H$_4$), 73.4 (d, J_{PC} = 14.5 Hz, α-C$_5$H$_4$), 128.6 (d, J_{PC} = 11.9 Hz, *m*-Ph), 131.6 (d, J_{PC} = 2.3 Hz, *p*-Ph), 131.8 (d, J_{PC} = 65.7 Hz, *ipso*-Ph), 133.7 (d, J_{PC} = 14.4 Hz, *o*-Ph). ^{31}P NMR (CDCl$_3$, δ): 24.0.

Chloro[diferrocenyl(3,4-methylenedioxyphenyl)-phosphine]gold(I) (3c). ^{1}H NMR (CDCl$_3$, δ): 4.22 (s, 10H, C$_5$H$_5$), 4.25 (br, 2H, C$_5$H$_4$), 4.42 (br, 2H, C$_5$H$_4$), 4.48 (br, 2H, C$_5$H$_4$), 4.50 (br, 2H, C$_5$H$_4$), 6.04 (s, 2H, −OCH$_2$O−), 6.91 (d, J = 8.3 Hz, 1H, 5-methylenedioxyphenyl), 7.05 (d, J = 11.9 Hz, 1H, 2-methylenedioxyphenyl), 7.46 (dd, J = 15.1 and 8.3 Hz, 1H, 6-methylenedioxyphenyl). ^{13}C NMR (CDCl$_3$, δ): 70.1 (C$_5$H$_5$), 71.4 (d, J_{PC} = 9.2 Hz, β-C$_5$H$_4$), 72.0 (d, J_{PC} = 13.7 Hz, α-C$_5$H$_4$), 72.1 (d, J_{PC} = 74.6 Hz, *ipso*-C$_5$H$_4$), 72.2 (d, J_{PC} = 8.8 Hz, β-C$_5$H$_4$), 73.2 (d, J_{PC} = 14.7 Hz, α-C$_5$H$_4$), 101.8 (−OCH$_2$O−), 108.5 (d, J_{PC} = 15.9 Hz, 5-methylenedioxyphenyl), 112.4 (d, J_{PC} = 14.7 Hz, 6-methylenedioxyphenyl), 124.4 (d, J_{PC} = 69.4 Hz, 1-methylenedioxyphenyl), 129.4 (J_{PC} = 19.5 Hz, 2-methylene-dioxyphenyl), 147.9 (d, J_{PC} = 16.5 Hz, 3-methylenedioxyphen-yl), 150.5 (d, J_{PC} = 2.0 Hz, 4-methylenedioxyphenyl). ^{31}P NMR (CDCl$_3$, δ): 24.6. Anal. Calcd for $C_{27}H_{23}AuClFe_2O_2P$: C, 42.98; H, 3.07. Found: C, 43.00; H, 3.03. ESI-HRMS Calcd for $C_{27}H_{23}AuClFe_2O_2P$: 753.9489. Found: 753.9494.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00307.

NMR spectra (^{1}H, ^{13}C, and ^{31}P) for all the new compounds and IR spectra of **2a-d** (PDF)
Crystallographic data of 3a (CIF)
Crystallographic data of 3b (CIF)
Crystallographic data of 3c (CIF)

Accession Codes

CCDC 2045424 (**3a**), 2045425 (**3b**), and 2045426 (**3c**) contain the supplementary crystallographic data for this paper.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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