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Rhodium(I) and Iridium(I) Phosphaferrocene Complexes

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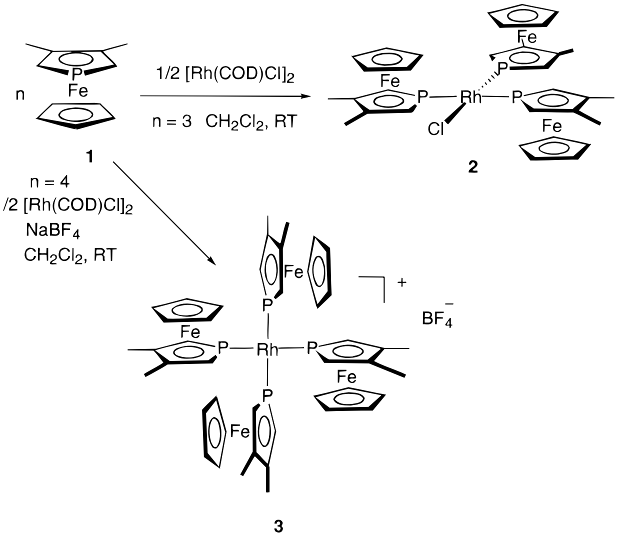
*Summary: The synthesis of 3,4-dimethylphosphaferrocene (**1**) complexes of rhodium ([Rh(**1**)$_3$Cl], **2**, and [Rh(**1**)$_4$][BF$_4$], **3**) and iridium ([Ir(**1**)$_3$(COD)][BF$_4$], **4**) are reported. An X-ray crystal structure analysis of the homoleptic derivative **3** reveals that ligands arrange around the rhodium center without apparent steric congestion. Complex **4**, which was also structurally characterized, adopts a trigonal bipyramid geometry in the solid state. The reaction of **4** with H$_2$ under pressure yields the [Ir(**1**)$_4$H$_2$]$^+$ complex.*

Introduction

Many reports concerning the synthesis and the derivatization of phosphaferrocenes[1] have appeared over the past few years. This renewed interest mainly results from research on planar-chiral ligands. In this respect, phosphaferrocenes can be regarded as molecules associating the electronic properties of a phosphine to the chiral properties brought by a ferrocene-type structure.[2] This concept, which can be enlarged to other π-bounded heterocycles, has recently been exploited by Ganter[2b−e] and Fu[2f−h] in two metal-catalyzed processes of importance: the asymmetric allylic substitution (Pd catalyzed)[2e] and the enantioselective hydrogenation of dehydroamino acids (Rh catalyzed).[2h] Indeed, the strong π-acceptor properties generally encountered in dicoordinate phosphorus centers make phosphaferrocenes attractive ligands for catalytic processes involving soft transition metals. The coordination chemistry of monophosphaferrocene derivatives, unlike that of di- and triphosphaferrocenes, remains largely unexplored. In the case of group 8 metals, although some complexes of 1,2,4-triphosphaferrocene [Fe(η^5-C$_5$Me$_5$)(η^5-P$_3$C$_2$tBu$_2$)] with the tetrairidium undecacarbonyl cluster[3a,b] and with the [Rh(η^5-C$_5$Me$_5$)(CO)] fragment[3c] have been described, complexes of monophosphaferrocenes are unknown. In view of the major role played by Rh and Ir catalysts, we decided to investigate the synthesis of their homoleptic phosphaferrocene complexes. The results of these investigations are reported herein.

Scheme 1



Results and Discussion

To avoid problems due to the planar chirality of phosphaferrocene, all of our experiments were carried out with the symmetrical 3,4-dimethyl derivative **1**, which was prepared according to a reported procedure.[4] Treatment of 6 equiv of **1** with the [Rh(COD)Cl]$_2$ dimer in dichloromethane at room temperature quantitatively yields the corresponding [Rh(1)$_3$Cl] complex **2**, which was characterized in ^{31}P NMR as a broad singlet at δ (CH$_2$Cl$_2$) = −4.0 ppm (see Scheme 1). Apparently a rapid ligand exchange, on the NMR time scale, takes place at room temperature. This phenomenon is not totally unprecedented for Rh(I) complexes, and [Rh(PMe$_3$)$_3$][PF$_6$] undergoes a similar exchange at 25 °C.[5] Variable-temperature measurements were performed in order to extract coupling constants. At −10 °C, the initial singlet splits into two other broad singlets which are totally defined when the temperature reaches −20 °C. As expected, complex **1** appears as a AB$_2$X pattern (see Experimental Part), thus proving the proposed geometry.

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10.1021/om980838j CCC: $18.00

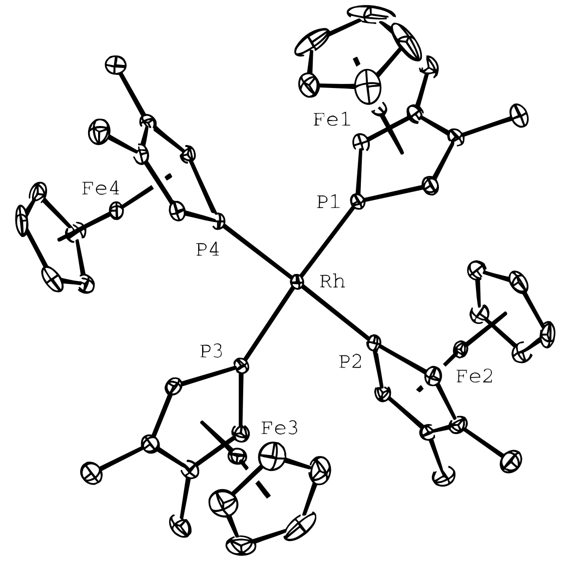

Figure 1. ORTEP diagram of complex **3**. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for the assignment of the ^{13}C spectra. Selected bond distances (Å) and angles (deg): Rh−P(1), 2.2645(9); P(1)−C(1), 1.744(4); Rh−P(2), 2.271(1); P(1)−C(4), 1.751(4); Rh−P(3), 2.2532(9); C(2)−C(3), 1.427(5); Rh−P(4), 2.270(1); C(3)−C(4), 1.492(5); P(1)−Rh−P(2), 90.25(3); P(2)−Rh−P(4), 177.18(3); P(1)−Rh−P(3), 176.46(4); P(3)−Rh−P(4), 91.95(3); P(1)−Rh−P(4), 91.03(3); C(1)−P(1)−C(4), 91.1(2).

Table 1. Summary of Crystallographic Data for 3 and 4

	compound	
	3	**4**
empirical formula	$C_{44}H_{52}BF_4P4Fe_4Rh$	$C_{41}H_{51}BF_4P_3Fe_3Ir$
fw	1117.9	1083.3
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*21/*c*
a, Å	21.360(2)	12.632(1)
b,Å	13.766(1)	14.986(1)
c, Å	29.647(3)	21.189(2)
β, deg	91.73(2)	90.00(2)
volume, Å^3	8713	4011
Z	8	4
ρ (calc), g cm^{-3}	1.70	
radiation	MoKα (λ = 0.710 73 Å)	
2θ range, deg	5.00−56.08	5.00−60.02
rflns collected	10 552	11 723
indep rflns	8299 ($F_o^2 > 3.0\sigma(F_o^2)$)	8775 ($F_o^2 > 3.0\sigma(F_o^2)$)
R(*F*), %^{a}	3.70	3.20
R(*wF*), %^{b}	6.30	4.20
Δ/σ (max)	0.01	0.04
$\Delta(\rho)$, e Å^{-3}	1.83/−0.18	2.13/-0.22
GOF^c	1.30	1.07

^{a} $R_F = \Sigma(F_o - F_c)/\Sigma(F_o)$. ^{b} $R_w = [\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o^2)]^{1/2}$. ^{c} GOF $= [\Sigma(w(F_o - F_c)^2)/((\text{no. of rflns}) - (\text{no. of params}))]^{1/2}$.

Additional experiments carried out at −20 °C with excess ligand (4−5 equiv) showed the presence of a second complex **3**, which was characterized as a doublet (δ (CD$_2$Cl$_2$) = −16.0 ppm, ^1J(Rh−P) = 149.80 Hz). Suspecting that this compound could be the homoleptic [Rh(**1**)$_4$][Cl] complex, resulting from the substitution of the chloride ion, we investigated the reaction of **1** with the [Rh(COD)$_2$][BF$_4$] precursor. Indeed, substitution of the COD ligands readily occurs at room temperature in dichloromethane, yielding **3**, which appears, like **2**, as a broad singlet at −16.0 ppm (see Scheme 1).

Crystals, suitable for X-ray diffraction studies were obtained by a slow diffusion of pentane into a dichloromethane solution of **3**. An ORTEP drawing of **3** is presented in Figure 1 along with the more relevant bond distances and angles. Crystallographic data are listed in Table 1. In the solid state, **3** adopts a perfectly square planar geometry, all *cis*-P−Rh−P bond angles ranging from 90.25(3)° to 91.95(2)° and *trans*-P−Rh−P angles being nearly equivalent at 176.46(4)° and 177.18(3)°. The most interesting feature resides in the fact that, despite the bulkiness of phosphaferrocene units, the four ligands arrange without apparent steric crowding around the rhodium center. Whereas ligands P(1), P(2), and P(4) are significantly twisted (Θ = 57°, 73°, and 60°, repectively, where Θ is the dihedral angle between the plane defined by the four P atoms and Rh, and that defined by each phospholide unit), ligand P(3) presents a less pronounced twist (Θ = 30°). We believe that this specific orientation results more from packing forces in the crystal than from a steric congestion. Apart from this observation, the structure of **3** reveals no special features, and Rh−P bond distances appear to be significantly shorter than those recorded for the [Rh(PMe$_3$)$_4$][Cl],[5] as expected for complexes bearing phosphorus sp^2-hybridized ligands.

This result prompted us to investigate the preparation of the homoleptic iridium analogue of **3**. So far, to the best of our knowledge, no mononuclear iridium complexes of phosphaferrocenes have been described. The reaction of 4 equiv of **1** with [Ir(COD)$_2$][BF$_4$] in dichloromethane at room temperature yielded complex **4**, which was characterized in ^{31}P NMR spectroscopy as a well-resolved singlet at δ (CH$_2$Cl$_2$) = −16.0 ppm. Surprisingly, ^{31}P NMR monitoring of the reaction showed that 1 equiv of ligand remained uncomplexed. This indicated that only one COD ligand had been displaced. As in other [Ir(COD)(PR$_3$)$_3$] cationic complexes[6a] we noted that addition of free ligand to the NMR solution did not induce a broadening or a shift of the singlet observed in ^{31}P NMR, thus showing that complex **4** undergoes a rapid Berry-type pseudorotation.[6b] Further experiments aimed at synthesizing the [Ir(P)$_4$]$^+$ complex under more strenuous conditions only resulted in partial destruction of **4**. Additionally, we found that another approach using the reaction of **1** with [Ir(COD)Cl]$_2$ in the presence of NaBF$_4$ gave **4** in better yields.

The formulation of **4** could be unambiguously established on the basis of ^{1}H and ^{13}C NMR data and elemental analysis. Definitive evidence was given by a crystal structure analysis of **4**. An ORTEP drawing of **4** is presented in Figure 2 along with the more relevant bond distances and angles.

The complex adopts a slightly distorted trigonal bipyramid geometry (see P−Ir−P bond angles) as found for all five-coordinate Ir d^8 complexes with phosphorus ligands,[7] but one, [Ir(PMe$_3$)$_3$(COD)]$^+$.[8] The two ligands P(2) and P(3) occupy two equatorial sites, whereas P(1)

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(8) The [Ir(PMe$_3$)$_3$(COD)] complex adopts a square pyramidal-type structure; see: Frazier, J. F.; Merola, J. S. *Polyhedron* **1992**, *11*, 2917.

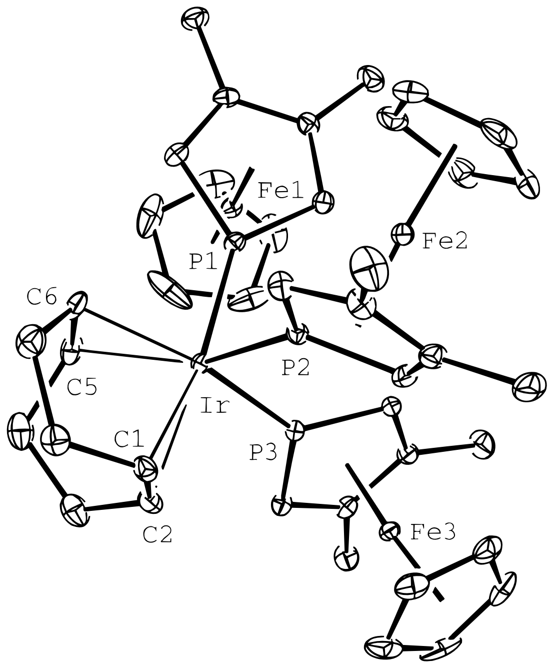
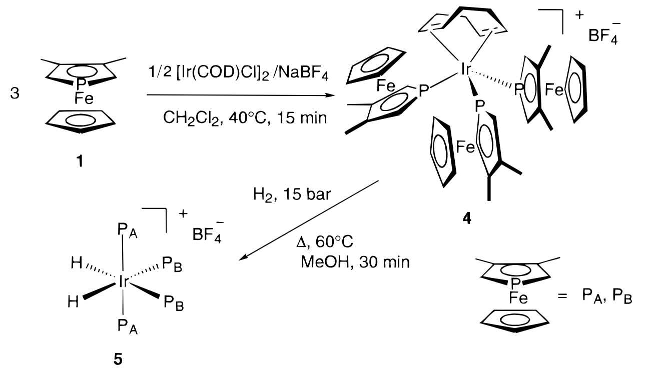


Figure 2. ORTEP diagram of complex **4**. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for the assignment of the ^{13}C spectra. Selected bond distances (Å) and angles (deg): Ir−P(1), 2.261(1); Ir−P(2), 2.317(1); Ir−P(3), 2.315(1); Ir−C(1), 2.250(4); Ir−C(2), 2.254(4); Ir−centroid of C(1)C(2), 2.143; Ir−centroid of C(5)C(6), 2.036; Ir−C(5), 2.165(4); Ir−C(6), 2.153(4); P(1)−C(9), 1.740(4); P(1)−C(12), 1.752(4); C(9)−C(10), 1.429(6); C(10)−C(11), 1.429(6); C(11)−C(12), 1.419(6); P(1)−Ir−P(2), 92.32(3); P(1)−Ir−P(3), 87.85(3); P(2)−Ir−P(3), 97.85(3); C(9)−P(1)−C(12), 92.1(2).

is located in an axial position *trans* to the C(1)−C(2) double bond of the COD ligand. As observed for other [IrP$_3$(COD)] cationic complexes,[8] the phosphorus-to-metal bond length P(1)−Ir appears to be significantly shorter than those of equatorial bonds, concomitant with weaker π-back-bonding to the double bond C(1)−C(2). If one accepts this feature, the structure of **4** deserves no special comments. In view of the importance of [IrP$_3$(COD)]$^+$ complexes for the preparation of Ir(III) derivatives,[9] the hydrogenation of complex **4** was studied. The reaction proceeded cleanly in methanol under H$_2$ pressure (15 bar) at 60 °C to produce **5**, which was identified as the [Ir(P)$_4$H$_2$]$^+$ complex. Better yields were obtained when the reaction was carried out in the presence of excess ligand. This observation is fully rational if we note that one-fourth of the metal is consumed in the redistribution of ligands. On the basis of NMR data, we propose that **5** adopts an octahedral geometry like other known *cis*-[Ir(P)$_4$H$_2$]$^+$ complexes.[10] In fact, the ^{31}P NMR (C$_3$D$_6$O) spectrum exhibits two triplets at −74.3 and −45.8 ppm (A$_2$B$_2$ system, $^2J(\mathrm{P_A{-}P_B}) = 35$ Hz), respectively assigned to P$_A$ and P$_B$ ligands (see Scheme 2). On the other hand, the presence of the two hydrides was confirmed in the ^{1}H NMR spectrum, which shows a characteristic doublet of triplets at −9.89 ppm ($^2J(\mathrm{H{-}P_{B-trans}}) = 155$ Hz, $^2J(\mathrm{H{-}P_{B-cis}}) = 0$ Hz, and $^2J(\mathrm{H{-}P_{A-cis}}) = 35$ Hz).

Scheme 2



In conclusion, we have shown that despite their forethought bulkiness, phosphaferrocenes can form homoleptic complexes with Rh(I). Investigations are currently under way to enlarge the synthesis of these homoleptic species to other metallic centers, as was recently achieved in the case of phosphinines, another type of phosphorus sp^2-hybridized ligand.[11] Moreover, the preparation of the iridium derivative **4** opens the way to syntheses of other Ir(III) complexes, as attested by the successful preparation of the corresponding dihydride. Further developments will now mainly focus on investigations of catalytic properties of these complexes and on the elaboration of tailor-made polydentate ligands containing, among other things, phosphaferrocenes as binding sites.

Experimental Part

General Considerations. All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry hexane was obtained by distillation from Na/benzophenone and dry CH$_2$Cl$_2$ from P$_2$O$_5$. Methanol was used as received. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H$_3$PO$_4$ (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with a HP 5989 B spectrometer coupled with a HP 5890 chromatograph by the direct inlet method. The following abreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. [Rh(COD)Cl]$_2$,[12] [Rh(COD)$_2$][BF$_4$],[13] and [Ir(COD)Cl]$_2$[14] were prepared according to published procedures.

Chlorotris(3,4-dimethyl-1-phosphaferrocene)rhodium(I) (2). A mixture of phosphaferrocene **1** (100 mg, 0.43

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mmol) and $[Rh(COD)Cl]_2$ (35 mg, 0.07 mmol) was dissolved in dichloromethane (5 mL) at room temperature. After 10 min of stirring, the color had changed to red-brown. Dichloromethane was evaporated and the residue washed with hexanes to extract COD, then dried under vacuum. Yield: 93 mg (80%). ^{31}P NMR ($CDCl_3$, −20 °C): δ 12.0 (dt, $^1J(Rh-P) = 195.2$ Hz, $^2J(P_{cis}-P_{trans}) = 73.8$, P_{trans}), −7.7 (dd, $^1J(Rh-P) = 169.0$, P_{cis}). ^1H NMR ($CDCl_3$): δ 2.20 (s, 18H, Me), 3.70 (br d, 6H, CH), 4.31 (s, 15H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 16.64 (s, Me), 68.76 (br s, CH), 73.73 (s, C_5H_5), 92.28 (br s, C_q of C_6H_8P). Anal. Calcd for $C_{33}H_{39}P_3Fe_3RhCl$: C, 47.50; H, 4.71. Found: C, 47.75; H, 5.06.

[Tetrakis(3,4-dimethyl-1-phosphaferrocene)rhodium(I)]-tetrafluoroborate (3). A mixture of phosphaferrocene **1** (100 mg, 0.43 mmol) and $[Rh(COD)_2][BF_4]$ (41 mg, 0.10 mmol) was dissolved in 5 mL of CH_2Cl_2 and left stirring for 10 min. After evaporation to dryness, the residue was washed with hexanes to extract COD and dried under vacuum. Brown crystals, suitable for X-ray analysis, were obtained by slow diffusion of pentane in a solution of **4** in dichloromethane. Yield: 90 mg (80%). ^{31}P NMR ($CDCl_3$, −20 °C): δ −16.0 (d, $^1J(Rh-P) = 149.80$). ^1H NMR ($CDCl_3$): δ 2.27 (s, 24H, Me), 3.75 (d, 8H, $^2J(P-H) = 33$, CH), 4.28 (s, 20H, C_5H_5). ^{13}C ($CDCl_3$): δ 16.05 (s, Me), 69.47 (s, CH), 74.13 (s, C_5H_5), 93.41 (s, C_q of C_6H_8P). Anal. Calcd for $C_{44}H_{52}BF_4Fe_4P_4Rh$: C, 47.28; H, 4.69. Found: C, 47.08; H, 4.60.

[Tris(3,4-dimethyl-1-phosphaferrocene)cycloocta-dieneiridium(I)]tetrafluoroborate (4). To a solution of phosphaferrocene **1** (100 mg, 0.43 mmol) in dichloromethane was added $[Ir(COD)Cl]_2$ (48 mg, 0.07 mmol) and excess $NaBF_4$. The mixture was kept at 40 °C for 15 min. After filtration of sodium salts, the solution was evaporated to dryness. Yield: 120 mg (80%). ^{31}P NMR ($CDCl_3$): δ −49.0 (s). ^1H NMR ($CDCl_3$): δ 2.26 (s, 18H, Me), 2.63 (br s, 8H, COD), 3.49 (br s, 6H, CH), 4.17 (s, 15H, C_5H_5), 4.43 (br s, 4H, COD). ^{13}C ($CDCl_3$): δ 17.00 (s, Me), 35.11 (s, COD), 65.15 (s, COD), 74.50 (s, C_5H_5), 74.63 (s, CH), 93.52 (s, C_q of C_6H_8P). Anal. Calcd for $C_{41}H_{51}BF_4Fe_3IrP_3$: C, 45.46; H, 4.75. Found: C, 45.80; H, 4.80.

***cis*-[Dihydridotetrakis(3,4-dimethyl-1-phosphaferrocene)iridium(III)]tetrafuoroborate (5).** A mixture of **4** (100 mg, 0.09 mmol) and phosphaferrocene **1** (23 mg, 0.1 mmol) in 5 mL of methanol was stirred under 15 bar of hydrogen, at 50 °C, for 1 h. After evaporation of the solvent, the residue was washed with hexanes and dried under vacuum. Yield: 82 mg (75%). ^{31}P NMR ($CDCl_3$): δ −45.8 (t, 2 × P_{cis}, $^2J(P_{cis}-P_{trans}) = 34.5$), −74.3 (t, 2 × P_{trans}, $^2J(P_{trans}-H) = 154.5$). ^1H NMR ($CDCl_3$): δ −9.90 ("dt", 2H, $^2J(H-P_{cis}) = 22.2$, $Ir-H$), 2.30 (br s, 24H, Me), 3.75 (m, 8H, CH), 4.25 (s, 10H, C_5H_5), 4.35 (s, 10H, C_5H_5). ^{13}C ($CDCl_3$): δ 16.7 (m, Me of C_6H_8P), 67.4 (vtt, $AXX'Y_2$, $J = 3.6$ and $J = 15.4$, CH of C_6H_8P), 68.8 (s, CH of C_6H_8P), 75.2 (s, C_5H_5), 7.1 (s, C_5H_5), 94.1 (vt, $AXX'Y_2$, $\sum|J(C-P)| = 9.4$, 4 × C_q of C_6H_8P), 94.9 (s, 4 × C_q of C_6H_8P). Complex **5** was too sensitive to give satisfactory elemental analysis data.

X-ray Crystallographic Studies of 3 and 4. Crystals of complex **3** and **4** were grown by slow diffusion of hexane into CH_2Cl_2 solutions of the compounds. Data were collected at 123 ± 0.5 K on an Enraf Nonius CAD4 diffractometer using a graphite monochromator. The crystal structures were solved and refined using the Nonius MOLEN package. All structures were solved by direct methods. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. In the case of **4**, all but the Cp hydrogens were located in a difference Fourrier map and refined with isotropic temperature factors. Those of the Cp rings were added as fixed contributions at their calculated positions. All heavier atoms were treated as above. Relevant crystallogaphic details for each compound are summarized in Table 1.

Acknowledgment. The authors thank the CNRS and the Ecole Polytechnique for supporting this work.

Supporting Information Available: Tables of positional parameters and their estimated deviations, tables of refined displacement (β's), tables of bond distances, and tables of bond angles for complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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