

PCP pincer ligands based on metallocenes. Crystal structure of the rhodium complex *cis*-RhCl₂(CO)[{2,5-(Prⁱ₂PCH₂)₂C₅H₂}Fe(C₅H₅)]

A. A. Koridze,^{a,b*} A. M. Sheloumov,^a S. A. Kuklin,^a V. Yu. Lagunova,^a I. I. Petukhova,^a
F. M. Dolgushin,^a M. G. Ezernitskaya,^a P. V. Petrovskii,^a A. A. Macharashvili,^b and R. V. Chedia^b

^aA. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.

Fax: +7 (095) 135 5085. E-mail: koridze@ineos.ac.ru

^bI. Javakhishvili Tbilisi State University, Chemical Department,
1 av. Chavchavadze, 380028 Tbilisi, Georgia.

Fax: (995 32) 22 5107

The anionic pincer tridentate ligands [2,6-(R₂PCH₂)₂C₆H₃][−] find wide use in the organometallic synthesis and catalysis.^{1–3} Recently, it has been demonstrated⁴ that the rhodium and iridium hydride complexes with such ligands, viz., MH₂{2,6-(R₂PCH₂)₂C₆H₃} (M = Rh or Ir; R = Prⁱ or Bu^t), catalyze dehydrogenation of alkanes to form H₂ and olefins.

We believed that the PCP pincer ligands based on ferrocene could possess electronic and steric features, which distinguish them from their benzene analogs and are attractive from the viewpoint of their use in catalysis. It is known that the ferrocenyl group has a stronger electron-donating ability than the phenyl group, which can be favorable for the oxidative addition of the C–H bonds of alkanes to the activation center, viz., rhodium or iridium. The sandwich nature of the metallocenyl unit can help in tuning the steric environment about the rhodium or iridium atoms. This property can prevent isomerization of α -olefins (which are initially generated by dehydrogenation of alkanes) into less desirable internal olefins. Finally, the iron atom in ferrocene can rapidly and reversibly enter into redox reactions thus providing the electronic effect on the nearby catalytic center.

Due to the geometric characteristics, the P donor atoms in 1,3-bis(dialkylphosphinomethyl)metallocenes are more remote from each other than those in the corresponding benzene derivatives. Hence, the possibility of the formation of pincer complexes based on metallocenes was not evident. One would expect that the formation of these complexes will be accompanied by a decrease in the bond angles at the C(1) and C(3) atoms compared to the standard value (126°).

We synthesized 1,3-disubstituted metallocenes according to a procedure based on the use of the appropriately substituted fulvenes.⁵ Thus, the reaction of [(C₅H₅)Fe(1,4-Me₂C₆H₄)]PF₆ (**1**) with 6-dimethylamino-3-(ethoxycarbonyl)fulvene (**2**) gave rise to 3-ethoxycarbonyl-1-formylferrocene whose subsequent

reduction with LiAlH₄ (ether, 22°C, 2 h) produced diol {1,3-(HOCH₂)₂C₅H₃}Fe(C₅H₅) (**3**). The ruthenocene analog {1,3-(HOCH₂)₂C₅H₃}Ru(C₅H₅) (**4**) was synthesized analogously starting from [(C₅H₅)Ru(MeCN)₃]PF₆ and fulvene **2**.

Heating of diols **3** and **4** with secondary phosphines HPR₂ (R = Prⁱ or Bu^t) in acetic acid at 80 °C afforded the corresponding diphosphine derivatives of metallocenes {1,3-(R₂PCH₂)₂C₅H₃}M(C₅H₅) (M = Fe, R = Prⁱ, **5a**; M = Fe, R = Bu^t (**5b**); M = Ru, R = Prⁱ (**6a**); M = Ru, R = Bu^t (**6b**)).

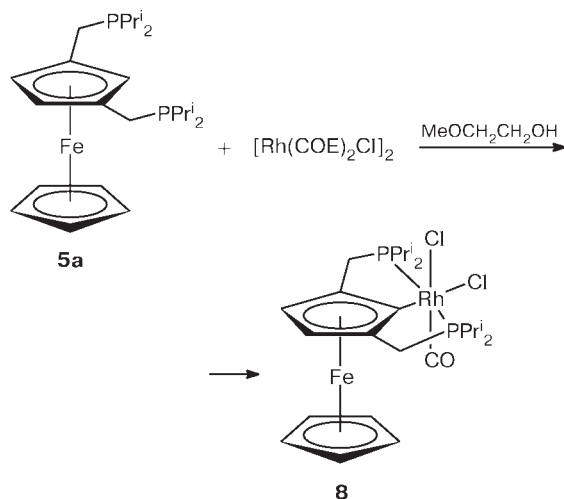
The reaction of complex **1** with 6,6-bis(dimethylamino)-3-(ethoxycarbonyl)fulvene yielded {1-(EtOOC)-3-(Me₂NCO)C₅H₃}Fe(C₅H₅). Reduction of the latter with LiAlH₄ in THF gave rise to 3-dimethylaminomethyl-1-(hydroxymethyl)ferrocene. Heating of this amino alcohol with HPPH₂ in AcOH afforded aminophosphine {1-(Ph₂PCH₂)-3-(Me₂NCH₂)C₅H₃}Fe(C₅H₅) (**7**).

Compounds **5a,b**, **6a,b**, and **7** were obtained in ~40% total yields. These compounds were characterized by ¹H and ³¹P NMR spectroscopy and mass spectrometry. ³¹P NMR (CDCl₃), δ : 10.91 (**5a**); 23.18 (**5b**); 9.61 (**6a**); 36.83 (**6b**); −15.53 (**7**).

We obtained unambiguous evidence for the formation of the PCP complex based on ferrocene. The complex *cis*-carbonyl[2,5-bis(diisopropylphosphinomethyl)ferrocen-1-yl]dichlororhodium(III), *cis*-RhCl₂(CO)[{2,5-(Prⁱ₂PCH₂)₂C₅H₂}Fe(C₅H₅)] (**8**), was synthesized by the reaction of diphosphine **5a** with [Rh(COE)₂Cl]₂ (COE is cyclooctene) in 2-methoxyethanol (120 °C, 1 h, non-optimized yield was 25%) (Scheme 1). The ³¹P NMR spectrum (CDCl₃) of complex **8** shows a doublet at δ 62.61 (*J*_{Rh,P} = 82.8 Hz). The ¹H NMR spectroscopic data are indicative of *ortho*-metallation of the cyclopentadienyl ring. Thus, this ring gives only a singlet at δ 4.15 (2 H) without evidence for splitting. In addition, the methylene protons of the CH₂PPrⁱ₂ groups are pairwise non-equivalent and are observed as a doublet of virtual trip-

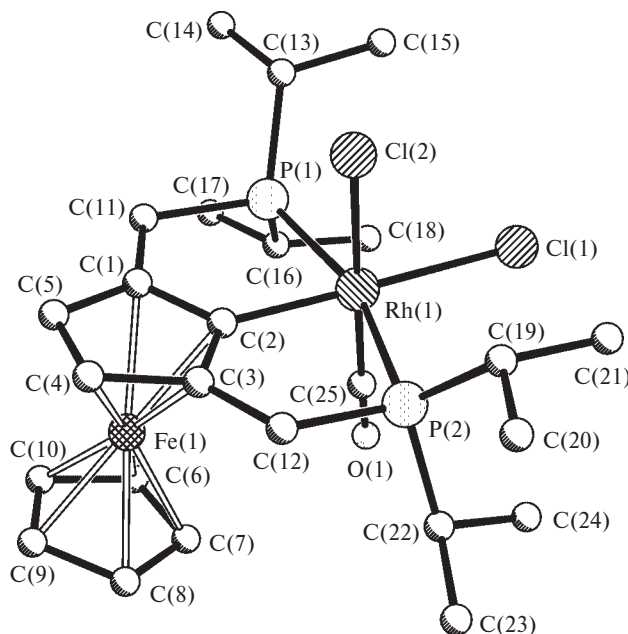
lets at δ 2.99 (2 H, $J_{\text{H,H}} = 16.4$ Hz, $J_{\text{H,P}} = 3.5$ Hz) and 2.82 (2 H, $J_{\text{H,H}} = 16.4$ Hz, $J_{\text{H,P}} = 4.6$ Hz). The IR spectrum bears witness to the presence of the CO ligand ($\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$: 2055 cm^{-1}) generated from 2-methoxyethanol. The mass spectrum shows a peak at 618.0 [$\text{M}^+ - \text{CO}$] (calculated for $\text{C}_{24}\text{H}_{39}\text{Cl}_2\text{FeP}_2\text{Rh}$ 619.18).

Scheme 1



The single-crystal X-ray diffraction study demonstrated* that the Rh atom in complex **8** (Fig. 1) has an octahedral environment with the *cis* arrangement of the chloride ligands and the CO group in the *endo* position. The Rh(1)—C(2) distance is 2.017(4) Å, and the P(1)—Rh(1)—P(2) angle is 161.92(4)°. As expected, the formation of complex **8** led to a noticeable decrease (by 4–5°) in the bond angles at the C(1) and C(3) centers (C(2)—C(1)—C(11), 122.1(4)°; C(2)—C(3)—C(12), 121.5(4)°) as compared to the standard value (126°).

The results of the investigation on the synthesis and the catalytic properties of the rhodium and iridium hydride complexes with the metallocene-derived PCP

Fig. 1. Molecular structure of complex **8**.

ligands as well as the synthesis of the optically active PC(H)P and PC(H)N derivatives of 1,3-disubstituted metallocenes will be published elsewhere. We plan to use the latter compounds for the preparation of metal complexes as catalysts of asymmetric reactions.

Reference

1. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.
2. M. Albrecht and G. van Koten, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 3750.
3. B. Rybtchinsky and D. Milstein, *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 870.
4. C. M. Jensen, *Chem. Commun.* 1999, 2443.
5. P. Bickert, B. Hildebrandt, and K. Hafner, *Organometallics*, 1984, **3**, 653.

* Complete X-ray structural data for compound **8** were deposited with the Cambridge Structural Database.

Received February 14, 2002;
in revised form May 29, 2002