1854 *Organometallics* **2006,** *25,* 1854−1856

Unusual Transformation of $[Fe\{\eta^5\text{-}C_5H_4P(OEt)_2\}_2Pd(H_2O)_2](OTf)_2$ to a Hexanuclear Cyclopentadienylpalladium Complex

A. M. Kalsin, P. V. Petrovsky, K. A. Lyssenko, and O. V. Gusev*

A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences,
Vavilov St. 28, 119991 Moscow, Russia

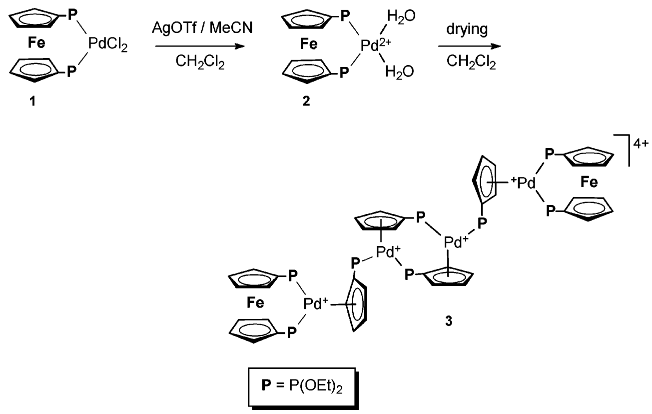
Received September 19, 2005

Summary: Transfer of a functionalized cyclopentadienyl ring under mild conditions is achieved. Treating a palladium dichloride complex with 1,1′-bis(diethylphosphonito)ferrocene, $[Fe\{\eta^5\text{-}C_5H_4P(OEt)_2\}_2PdCl_2]$ *(**1**), with silver triflate gives the dicationic complex* $[Fe\{\eta^5\text{-}C_5H_4P(OEt)_2\}_2Pd(H_2O)_2](OTf)_2$ *(**2**). Unexpectedly, crystals grown from **2** in anhydrous* CH_2Cl_2/Et_2O *appear to be the hexanuclear complex* $[Fe\{\eta^5{:}\kappa^2\text{-}C_5H_4P(OEt)_2\}_2Pd\{\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4P(OEt)_2\}Pd\{\mu\text{-}\eta^5{:}\kappa^1\text{-}(EtO)_2PC_5H_4\}]_2(OTf)_4$ *(**3**), a product of cyclopentadienyl transfer from iron to palladium. The mechanism of the rearrangement is discussed.*

Cyclopentadienyl ring transfer reactions from one transition metal to another have been known for a long time and described in reviews.[1] However, substitution of cyclopentadienyl rings in ferrocene is rather difficult, and a few examples reported of this reaction required high temperatures. Thermal substitution of the Cp ligand with arenes in the presence of $AlCl_3$ and Al is the most investigated example.[1] The cyclopentadienyl ligands of ferrocene can also be transferred to other metals. Heating of ferrocene with anhydrous $RuCl_3$ at 250 °C for several days yielded ruthenocene.[2] Double cyclopentadienyl ring transfer has been also observed for rhenium and technetium when ferrocene and metal carbonyls were heated with MO_4^- salts (M = Tc, Re) under reductive conditions.[3] Thus, employing $BrMn(CO)_5$ as the starting carbonyl substrate and TcO_4^- salt gave a mixture of two complexes, $[M(\eta^5\text{-}C_5H_4R)(CO)_3]$ (M = Mn, Tc).[4] Generally Cp ring transfer reactions occur under severe conditions and have been used so far only for nonfunctionalized Cp ligands. Here we report a facile transfer of Cp rings from the 1,1′-bis(diethylphosphonito)ferrocene moiety to palladium, which occurs under mild conditions, at room temperature, and in a noncoordinating solvent.

The dicationic palladium complex **2** is prepared by treatment of the corresponding palladium dichloride diphosphane complex **1**[5] with silver triflate in the presence of acetonitrile (Scheme 1).[6]

Scheme 1



Interestingly, when dried, **2** does not contain acetonitrile ligands, in contrast to the analogous cationic palladium complexes with 1,1′-bis(diarylphosphino)ferrocenes;[7] instead, according to elemental analysis palladium coordinates two molecules of water. Perhaps acetonitrile ligands initially form a weakly bound complex with palladium and decoordinate upon drying under vacuum, and subsequent exposure to air gives the diaqua complex.

According to the NMR spectra the Cp rings in the complex $[Fe\{\eta^5\text{-}C_5H_4P(OEt)_2\}_2Pd(H_2O)_2](OTf)_2$ (**2**) are equivalent: $^{31}P\{^1H\}$ NMR features a singlet at δ 111.39; ^1H NMR shows two signals of pairwise-equivalent Cp protons at δ 4.70 and 5.09, and $^{13}C\{^1H\}$ NMR shows three Cp carbon signals at δ 73.30, 74.04, and 74.76. The ethoxyl groups at the phosphorus atoms give rise in ^1H NMR to a triplet at δ 1.42 and a multiplet at δ 4.31, corresponding to the methyl group and the magnetically inequivalent CH_2 protons, respectively, and in $^{13}C\{^1H\}$ NMR to a singlet at δ 15.77 (Me) and a doublet at δ 66.97 (CH_2).

An attempt to grow crystals of **2** by slow diffusion of diethyl ether into a solution of **2** in CH_2Cl_2 under argon at room temperature yielded the new complex **3** quantitatively, which differs from **2** in its color and solubility (Scheme 1).[8] It is important that the presence of water inhibits the formation of **3**; dissolving **2** in wet CD_2Cl_2 did not show even traces of **3** after several days.

The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of one singlet at δ 142.6 and two doublets at δ 119.0 and 123.2, with integrated intensities of 2:1:1, implying the presence of three different phosphonite ligands. Most likely this corresponds to a structure with two different palladium atoms, where one Pd coordinates to two equivalent phosphorus atoms and another one is bound

---

* To whom correspondence should be addressed. E-mail: gusev@ineos.ac.ru. Tel: 7 (095) 135-9337.

[1] (a) Rubezhov, A. Z.; Gubin, S. P. *Adv. Organomet. Chem.* **1972**, *10*, 347. (b) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639. O'Coonor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

[2] (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1963**, *149*, 615. (b) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, 1725. (c) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1966**, *166*, 607. (d) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 606.

[3] Gauthier, G. J. *J. Chem. Soc., Chem. Commun.* **1969**, 690.

[4] (a) Wenzel, M. *J. Labeled Compd. Radiopharm.* **1992**, *31*, 641. (b) Spradau, T. W.; Katzenellenbogen, J. A. *Organometallics* **1998**, *17*, 2009. (c) Minutolo, F.; Katzenellenbogen, J. A. *Organometallics* **1999**, *18*, 2519. (d) Top, S.; Masi, S.; Jaouen, G. *Eur. J. Inorg. Chem.* **2004**, 2003. (e) Masi, S.; Top, S.; Boubekeur, L.; Jaouen, S.; Mundwiler, S.; Spingler, B.; Alberto, R. *Eur. J. Inorg. Chem.* **2002**, 1848. (f) Wenzel, M. *J. Labeled Compd. Radiopharm.* **1992**, *31*, 641.

[5] Gusev, O. V.; Peganova, T. A.; Kalsin, A. M.; Vologdin, N. V.; Petrovskii, P. V.; Lyssenko, K. A.; Tsvetkov, A. V.; Beletskaya, I. P. Submitted for publication in *Organometallics*.

10.1021/om050808y CCC: $33.50 © 2006 American Chemical Society
Publication on Web 03/15/2006

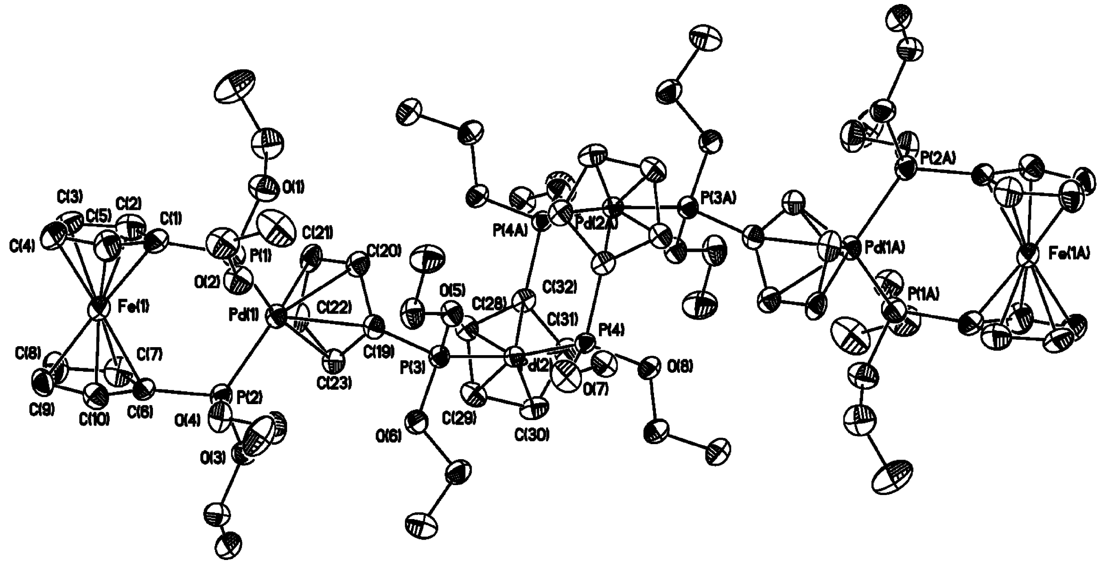


Figure 1. General view of cation **3** with the representation of atoms by the thermal ellipsoids at the 50% probability level. Selected bond lengths (Å): Pd(1)−P(1) = 2.216(1), Pd(1)−P(2) = 2.229(1), Pd(1)−C(23), Pd(1)−C(Cp) = 2.267(5)−2.350(5), Pd(1)−Cp_{cent} = 1.979, Fe(1)−C(Cp) = 2.004(6)−2.048(6), Fe(1)−Cp_{cent} = 1.629−1.633, Pd(2)−P(4) = 2.218(1), Pd(2)−P(3) = 2.219(1), Pd(2)−C(Cp) = 2.287(5)−2.356(5). Selected bond angles (deg): P(1)−Pd(1)−P(2) = 91.21(5), P(4)−Pd(2)−P(3) = 95.55(5).

to two different phosphorus atoms. In the ^{1}H NMR spectrum three different signals from methyl groups of $P(OCH_2CH_3)_2$ arise at δ 1.34, 1.38, and 1.46 with the integrated intensities of 2:1:1, while methylenic protons produce five signals at δ 3.94, 3.99, 4.11, 4.40, and 4.44 with the integrated intensities of 1:2:1:1:1. The two signals at δ 4.46 and 4.78 apparently belong to the Cp protons of the ferrocene moiety, whereas the broadened signals at δ 6.18, 6.30, and 6.53 (integrated intensities of 1:2:1) correspond to the protons of the Cp rings coordinated to palladium. Unfortunately, we were not able to obtain the ^{13}C{^{1}H} NMR spectrum of **3**, due to its low solubility.

Finally, the structure of **3** was determined by X-ray crystallography (Figure 1).[9] Complex **3** is centrosymmetric and consists of four palladium atoms bonded to Cp rings and two ferrocene moieties. Each of the four palladium atoms is coordinated to one cyclopentadienyl group and to two phosphonite groups; two terminal palladium atoms are also capped with bis(phosphonito)ferrocene ligands. The distances Pd−Cp(center) (1.974 and 1.979 Å) and Pd−P (2.216−2.229 Å) are slightly shorter than for other palladium−cyclopentadienyl complexes with alkyl- and aryl-substituted phosphanes $[Pd(\eta^5\text{-}C_5H_5)(PR_3)_2]^+$ (1.986−1.988 and 2.224−2.225 Å, respectively, for Pd−Cp(center) and Pd−P),[10] probably due to the electron-withdrawing character of the $P(OEt)_2$ group. This complex exhibits a rare combination of a small P(1)−Pd(1)−P(2) bite angle (91.21(5) Å) and a staggered conformation of Cp rings in the ferrocene moiety (the dihedral angle P(1)−C(1)−C(6)−P(2) is 2°).[5,7]

Obviously, complex **3** formed as a result of cyclopentadienyl ring transfer from iron to palladium, but surprisingly, it happened under very mild conditions. We suppose that the reaction starts with the relatively easy decoordination of the solvate ligands in $[Fe\{\eta^5\text{-}C_5H_4P(OEt)_2\}_2Pd(H_2O)_2](OTf)_2$ (**2**), resulting in generation of the dicationic 12-electron species $[Fe\{\eta^5\text{-}C_5H_4P(OEt)_2\}_2Pd]^{2+}$ (**4**). Then electrophilic attack of **4** on a Cp ring of the ferrocene moiety of **2** leads to a weakening of the Fe−Cp bond and, further, to transfer of the Cp ligand to the palladium atom (Scheme 2). Finally, the iron(II) atom is eliminated to give **5**, and subsequent slippage of the palladium atom from the phosphorus atom to the Cp ring yields **6**, which undergoes dimerization to produce the hexanuclear complex **3**.

Two notes are in order. (1) The dimerization of **5** is less probable than that of **6**, because it results in a number of side reactions of the cyclopentadienyl anion and some oligomeric products should form, whereas **3** was obtained in nearly quantitative yield even from dilute solutions. (2) A complex

---

(6) Silver triflate (0.24 g, 0.90 mmol) was added with stirring to a solution of **1** (0.25 g, 0.41 mmol) in CH_2Cl_2 (40 mL)/MeCN (0.2 mL) at −78 °C. The mixture was warmed to room temperature and then was stirred overnight. The solvent was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (30 mL). The solution was filtered through Celite, the filtrate was concentrated to 5 mL, and then 40 mL of Et_2O was added, which resulted in a brown precipitate. It was filtered off, washed with Et_2O, and dried under vacuum. Yield of **2**: 0.29 g (82%). The product is hygroscopic. Anal. Calcd for $C_{20}H_{28}F_6FeO_{10}P_2PdS_2 \cdot 2H_2O$: C, 27.71; H, 3.72. Found: C, 27.74; H, 3.47. ^{1}H NMR ($CDCl_3$): δ 1.42 (t, 12H, $^3J_{HH}$ = 7.4 Hz, OCH_2Me); 4.31 (m, 8H, OCH_2Me); 4.73 (t, 4H, C_5H_4, J = 1.7 Hz); 5.09 (s, 4H, C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 111.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.77 (s, OCH_2Me); 66.97 (d, $^2J_{PC}$ = 3.4 Hz, OCH_2-Me); 73.30 (d, $^1J_{PC}$ = 56.1 Hz, *ipso*-Cp); 74.76 (t, $^3J_{PC}$ = 5.3 Hz, β-Cp); 74.04 (t, $^2J_{PC}$ = 7.6 Hz, α-Cp); 121.4 (q, $^1J_{CF}$ = 317.0 Hz, CF_3SO_3).

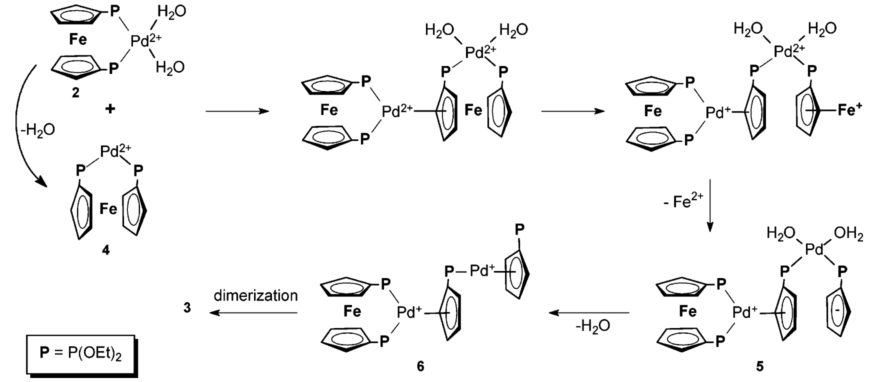
(7) (a) Gusev, O. V.; Kalsin, A. M.; Peterleitner, M. G.; Petrovskii, P. V.; Lyssenko, K. A.; Akhmedov, N. G.; Bianchini, C., Oberhauser, W.; Meli, A. *Organometallics* **2002**, *21*, 3637. (b) Gusev, O. V.; Kalsin, A. M.; Petrovskii, P. V.; Lyssenko, K. A.; Oprunenko, Y. F.; Bianchini, C.; Meli, A.; Oberhauser, W. *Organometallics* **2003**, *22*, 913.

(8) Complex **2** (0.10 g, 0.12 mmol) was dissolved in CH_2Cl_2 (10 mL), and 100 mL of Et_2O was slowly added to form an upper layer. The flask was allowed to stand overnight to produce dark red-brown needles. They were filtered off, washed with Et_2O, and dried under vacuum. Yield of **3**: 0.06 g (80%). Anal. Calcd for $C_{76}H_{112}F_{12}Fe_2O_{28}P_8Pd_4S_4$: C, 34.91; H, 4.32. Found: C, 34.97; H, 4.24. ^{1}H NMR (CD_2Cl_2): δ 1.34 (t, 12H, 4 $^3J_{HH}$ = 6.9 Hz, Me); 1.36 (t, 24H, $^3J_{HH}$ = 6.7 Hz, 8 Me); 1.46 (t, 12H, 4 $^3J_{HH}$ = 6.9 Hz, Me); 3.94 (m, 4H, 2 OCH_2Me); 3.99 (br s, 16H, 8 OCH_2Me); 4.11 (m, 4H, 2 OCH_2Me); 4.40 (m, 4H, 2 OCH_2Me); 4.44 (m, 4H, 2 OCH_2Me); 4.64 (s, 8H, C_5H_4); 4.78 (s, 8H, C_5H_4); 6.18 (br m, 4H, C_5H_4); 6.30 (br m, 4H, C_5H_4); 6.53 (br s, 4H, C_5H_4); 6.53 (br s, 4H, C_5H_4). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 142.63 (s); 123.2 (d, $^2J_{PP}$ = 59.1 Hz); 119.0 (d, $^2J_{PP}$ = 59.1 Hz).

(9) Crystallographic data of **3**: $C_{78}H_{116}Cl_4F_{12}Fe_2O_{28}P_8Pd_4S_4$, M_r = 2784.81, monoclinic, $P2_1/n$, a =12.6930(12) Å, b = 32.431(3) Å, c = 13.2218(12), β = 100.196(2)°, V = 5356.8(9) Å^3, Z (Z') = 2 (0.5), d_{calcd} = 1.727 g cm^{-3}, 9220 unique reflections with $I > 2\sigma(I)$. R (R_w) = 0.0581 (0.133).

(10) (a) Bachechi, F.; Lehmann, R.; Venanzi, L. M. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 721. (b) Manojolovic-Muir, L.; Cross, R. J.; Hoyle, R. W. *Acta Crystallogr., Sect. C* **1993**, *49*, 1603. (c) Cross, R. J.; Hoyle, R. W.; Manojolovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1994**, *468*, 265.

Scheme 2



analogous to an intermediate in the transformation from **5** to **6** (palladium simultaneously coordinated to both the cyclopentadienyl ring and the phosphorus atom in the position α to the Cp ring) has been observed earlier for doubly coordinated phosphines and was structurally confirmed.[11]

In conclusion, the complex [Fe{η^5-$C_5H_4P(OEt)_2$}$_2$Pd](OTf)$_2$ (**2**) undergoes an unusual transformation, involving transfer of a cyclopentadienyl ring, decoordination of an iron atom, and coordination of a palladium atom to the phosphonite groups under mild conditions. This reaction is the first example of facile transfer of a Cp ring bearing a coordinating group; it leads to the formation of a multinuclear complex and may turn out to be a useful tool for the synthesis of supramolecular compounds.

Acknowledgment. Thanks are due to the Russian Foundation for Basic Research (Grant No. 03-03-32471) and the Science Support Foundation of the Russian Federation.

Supporting Information Available: Tables giving crystallographic data for **3**, including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference number 251346 also contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, U.K.; fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

OM050808Y

---

[11] Arif, A. M.; Cowley, A. H.; Nunn, C. H.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1987**, 994.