Synthesis of triple-decker iron and cobalt complexes with a central tetramethylphospholyl ligand

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30-Electron triple-decker complexes $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_5)]PF_6$ and $[(\eta\text{-}C_4Me_4)Co(\mu\text{-}\eta{:}\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_5)]PF_6$ with a central tetramethylphospholyl ligand were synthesized by stacking reactions of cationic fragments $[(\eta\text{-}C_5H_5)Fe]^+$ and $[(\eta\text{-}C_4Me_4)Co]^+$ with nonamethylphosphaferrocene $(\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_5)$.

Key words: sandwich compounds, triple-decker complexes, phospholyl, iron, cobalt.

Previously,[1] we have synthesized triple-decker complexes with central (bridging) cyclopentadienyl and pentaphospholyl ligands. The syntheses of related iron-ruthenium complexes $[(\eta\text{-}C_5Me_5)Ru(\mu\text{-}\eta{:}\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_4R)]^+$ (R = Me, *cyclo*-$C_6H_{11}CH_2$)[2] with a central phospholyl ligand C_4Me_4P, as well as triple-decker complexes containing a central carborane ligand $Et_2C_2B_3H_3$ and one or two terminal phospholyl ligands,[3] have also been reported.

In this work, we found that the stacking reaction of phosphaferrocene **1** with a cationic fragment $[(\eta\text{-}C_5H_5)Fe]^+$ generated *in situ* upon irradiation of a benzene complex **2** by visible light results in the formation of a 30-electron triple-decker diiron complex **3** with a bridging tetramethylphospholyl ligand (Scheme 1).

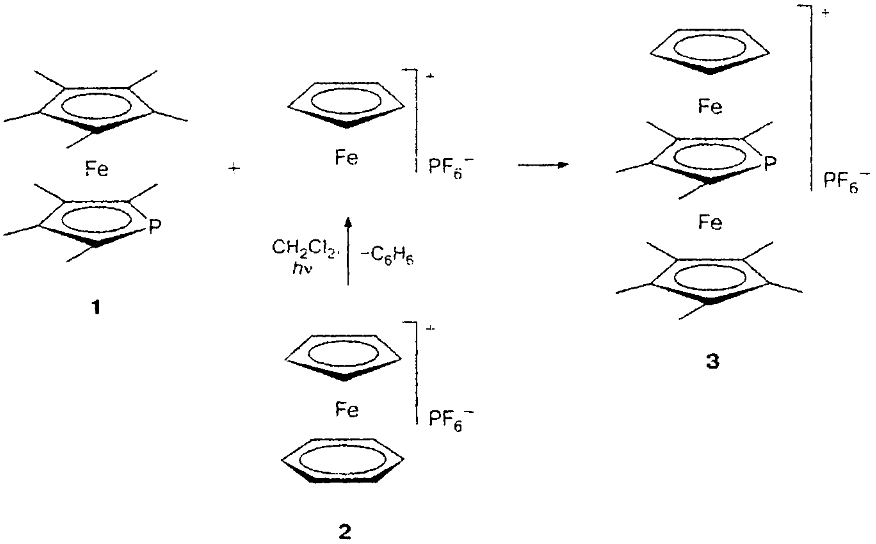
Previously,[4,5] we have used stacking reactions of $[(\eta\text{-}C_5H_5)Fe]^+$ with ferrocene and decamethylmetallocenes $M(C_5Me_5)_2$ (M = Fe, Ru, Os) for the synthesis of triple-decker complexes with central C_5H_5 and C_5Me_5 ligands.

Using a stacking reaction between compound **1** and a cationic fragment $[(\eta\text{-}C_4Me_4)Co]^+$ generated *in situ* upon irradiation of a benzene complex **4** by visible light, in this work we also synthesized a 30-electron triple-decker iron-cobalt complex **5** with a central C_4Me_4P ligand (Scheme 2).

Stacking reactions of cationic fragments $[(\eta\text{-}C_5H_5)Fe]^+$ and $[(\eta\text{-}C_4Me_4)Co]^+$ with phosphaferrocene **1** proceed regioselectively at the C_4Me_4P ring, which is likely due to the higher electron density in this ligand as compared to the C_5Me_5 ring.

The structures of compounds **3** and **5** were confirmed by elemental analysis and by ^1H and ^{31}P NMR spectroscopy (Table 1). For comparison, reference data[2] for the

Scheme 1



Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1647—1649, September, 2000.

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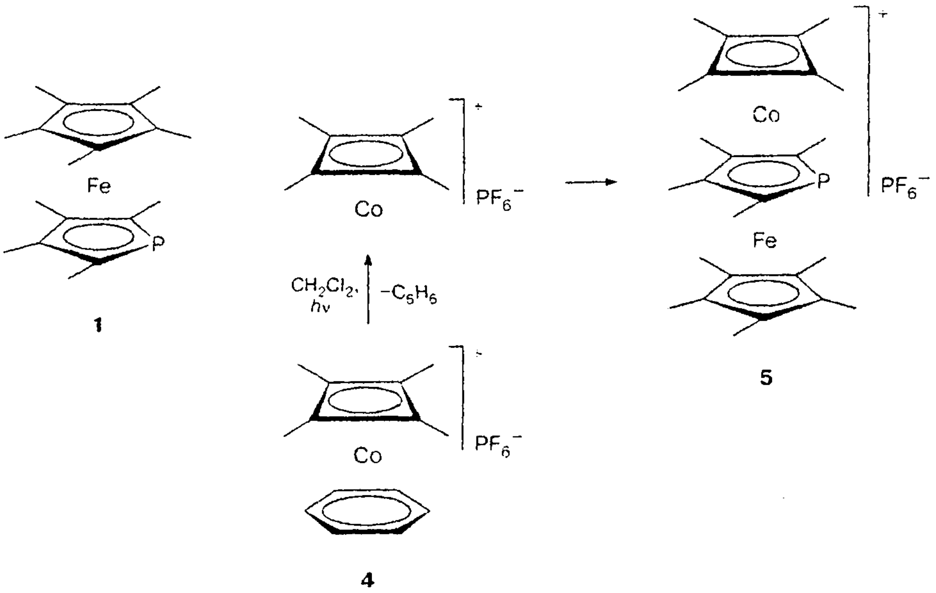
Scheme 2



related compound $[(\eta\text{-}C_5Me_5)Ru(\mu\text{-}\eta:\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_5)]CF_3SO_3$ (**6**) with known structure established by X-ray analysis are also listed in Table 1.

Compounds **3** and **5** are brightly colored crystalline substances, which are stable in air over a period of several hours both in the solid state and in CH_2Cl_2 solution. In solvents of higher polarity (Me_2CO, MeCN, *etc.*) they undergo rapid destruction, the decomposition rate for compound **3** being higher than for **5**. Complexes **3** and **5** are more stable to solvolysis than corresponding triple-decker complexes with a central C_5Me_5 ligand, but less stable than compounds with a central P_5 ligand.

Experimental

The reactions were carried out in argon atmosphere. The isolation of reaction products was performed in air. Initial compounds **1**,[6] **2**,[7] and **4**[8] were synthesized following known procedures. Irradiation of complexes was carried in a Schlenk tube of diameter 15 mm using a 400 W high-pressure discharge lamp (a sodium or mercury luminescent lamp). The Schlenk tube and the lamp were placed in an appropriate vessel coated on the inside with aluminum foil and cooled using running water. ^1H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer.

(μ-η:η-Tetramethylphospholyl)[(η-cyclopentadienyl)(η-pentamethylcyclopentadienyl)diiron] hexafluorophosphate, $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta:\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_5)]PF_6$ (3). To a mixture of compounds **1** (49 mg, 0.148 mmol) and **2** (50 mg, 0.145 mmol), 15 mL of CH_2Cl_2 was added, and the reaction mixture was irradiated for ~3 h. After the beginning of irradiation the reaction mixture turned red and then gradually turned green. The solvent was removed *in vacuo*. The residue was reprecipitated twice with ether from CH_2Cl_2 to give **3** as a green solid (56 mg, 65%). Found (%): C, 45.0; H, 5.5. $C_{23}H_{32}F_6Fe_2P_2 \cdot 0.25CH_2Cl_2$. Calculated (%): C, 45.2; H, 5.3.

(μ-η:η-Tetramethylphospholyl)[(η-tetramethylcyclobutadiene)cobalt][(η-pentamethylcyclopentadienyl)iron] hexafluorophosphate, $[(\eta\text{-}C_4Me_4)Co(\mu\text{-}\eta:\eta\text{-}C_4Me_4P)Fe(\eta\text{-}C_5Me_5)]PF_6$

Table 1. Parameters of ^1H and ^{31}P NMR spectra of compounds 3, 5, and $[(\eta\text{-}C_5Me_5)Ru(\mu\text{-}\eta:\eta\text{-}C_4Me_4)Fe(\eta\text{-}C_5Me_5)]CF_3SO_3$ (**6**)

Compound	Solvent	δ, *J*/Hz	
		^1H	^{31}P
3	CD_2Cl_2	1.60 (s, 15 H, C_5Me_5); 2.03 (d, 6 H, α-Me, $^3J_{P,H}$ = 7.8); 2.95 (s, 6 H, β-Me); 4.11 (s, 5 H, C_5H_5)	−45.4 (s, C_4Me_4P); −143.9 (sept, PF_6, $J_{P,F}$ = 722)
5	CD_2Cl_2	1.15 (s, 12 H, C_4Me_4); 1.71 (s, 15 H, C_5Me_5); 1.84 (d, 6 H, α-Me, $^3J_{P,H}$ = 7.4); 2.50 (s, 6 H, β-Me)	−49.8 (s, C_4Me_4P); −142.1 (sept, PF_6, $J_{P,F}$ = 711)
6[2]	$(CD_3)_2CO$	1.67 (s, 15 H, Ru(η-C_5Me_5)); 1.81 (s, 15 H, Fe(η-C_5Me_5)); 1.94 (d, 6 H, α-Me, $^3J_{P,H}$ = 8.3); 2.66 (s, 6 H, β-Me)	−39.5

(5). To a mixture of compounds **1** (41 mg, 0.124 mmol) and **4** (40 mg, 0.103 mmol), 15 mL of CH_2Cl_2 was added, and the reaction mixture was irradiated for 8 h. The solvent was removed *in vacuo*. The residue was reprecipitated twice with ether from CH_2Cl_2 to give **5** as a red solid (50 mg, 76%). Found (%): C, 46.2; H, 6.1. $C_{26}H_{39}CoF_6FeP_2 \cdot 0.5CH_2Cl_2$. Calculated (%): C, 46.5; H, 5.9.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-33106).

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Received March 10, 2000;
in revised form May 18, 2000