Iron and ruthenium triple-decker complexes with a central pentaphospholyl ligand

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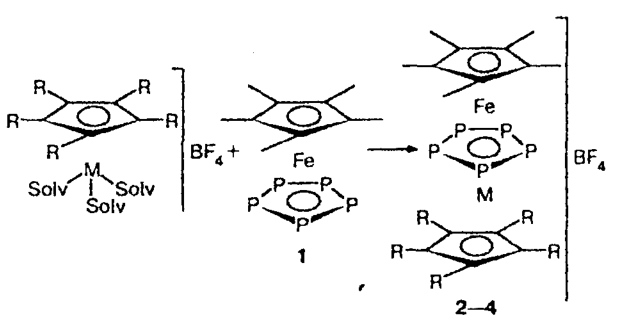
Thirty-electron triple-decker complexes with a central pentaphospholyl ligand $[(\eta\text{-}C_5Me_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)M(\eta\text{-}C_5R_5)]BF_4$ (M = Fe, R = Me or M = Ru, R = H, Me) were synthesized by a stacking reaction of cationic 12-electron fragments $[(\eta\text{-}C_5R_5)M]^+$ with $(\eta\text{-}C_5Me_5)Fe(\eta\text{-}P_5)$.

Key words: triple-decker complexes, pentaphospholyl ligand, iron complexes, ruthenium complexes.

Earlier, we have obtained 30-electron triple-decker complexes of the iron subgroup metals with a central cyclopentadienyl ligand $[(\eta\text{-}C_5R_5)M(\mu\text{-}\eta{:}\eta\text{-}C_5Me_5)M'(\eta\text{-}C_5Me_5)]^+$ by a stacking reaction of coordinatively unsaturated 12-electron fragments $[(\eta\text{-}C_5R_5)M]^+$ (M = Fe, R = H and M = Ru, R = H, Me) with decamethylmetallocenes $M'(\eta\text{-}C_5Me_5)_2$ (M′ = Fe, Ru, Os).[1–3] Based on this method, Scherer *et al.* synthesized[4] a triple-decker complex with a central pentaphospholyl ligand $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]^+$ by the reaction of the $[(\eta\text{-}C_5H_5)Fe]^+$ fragment with pentamethylpentaphosphaferrocene $(\eta\text{-}C_5Me_5)Fe(\eta\text{-}P_5)$ (**1**).

We found that the reaction of a cationic acetonitrile iron complex $[(\eta\text{-}C_5Me_5)Fe(MeCN)_3]BF_4$, which serves as a source of the $[(\eta\text{-}C_5Me_5)Fe]^+$ fragment, with compound **1** (CH_2Cl_2, 20 °C) leads to a symmetrical triple-decker iron complex **2** (Scheme 1).

Scheme 1



2: M = Fe, R = Me
3: M = Ru, R = H
4: M = Ru, R = Me

Analogous reaction with a ruthenium compound $[(\eta\text{-}C_5H_5)Ru(MeCN)_3]BF_4$ under mild conditions (CH_2Cl_2, 20 °C) results in a complex mixture of products, which was demonstrated by ^{31}P NMR spectroscopy. Apparently, along with the formation of an iron—ruthenium triple-decker compound **3**, the coordination of the $[(\eta\text{-}C_5H_5)Ru(MeCN)_3]^+$ complex to the lone electron pairs of the phosphorus atoms in compound **1** takes place. Such compounds as, for example, $(\eta\text{-}C_5Me_5)Fe(\eta\text{-}P_5)[Cr(CO)_5]_2$ and $(\eta\text{-}C_5Me_5)Fe(\eta\text{-}P_5)[Mn(CO)_2Cp]_n$ (*n* = 1—4), are the products of the reactions of this type.[4] We succeeded in performing selective synthesis of a triple-decker complex **3** under more drastic conditions ($MeNO_2$, 100 °C), where the formation of by-products resulting from the interaction with the lone electron pairs of the phosphorus atoms was suppressed.

The sole reaction product of the $[(\eta\text{-}C_5Me_5)Ru]^+$ fragment with compound **1** was triple-decker complex **4**. The $[(\eta\text{-}C_5Me_5)Ru]^+$ fragment was generated from $[(\eta\text{-}C_5Me_5)RuCl_2]_2$ by the reaction with zinc dust and $TlBF_4$ in acetone at room temperature[5] or by refluxing in ethanol.[6]

Compounds **2**—**4** are much more stable than related triple-decker complexes with the central C_5Me_5 ligand obtained by us earlier.[1–3] They are stable in air for several hours (both in solid state and in solution), but gradually decompose on prolonged storage.

The structures of compounds **2**—**4** obtained were confirmed by data from elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy (Table 1). Data for the known related compound $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]PF_6$ are also given in the table for comparison.[6]

Experimental

Reactions were carried out under argon. Reaction products were isolated in air. The initial compounds **1**,[7]

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Table 1. Parameters of the ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **2—4** and $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]PF_6$ [a]

Compound	Solvent	δ		
		^{1}H	^{13}C	^{31}P
2	$(CD_3)_2CO$	1.22 (Me)	8.14 (10 C, Me); 88.47 (10 C, $\underline{C}_5Me_5$)	−23.0
3	$(CD_3)_2CO$	1.32 (15 H, Me); 4.35 (5 H, C_5H_5)	8.20 (5 C, Me); 81.37 (5 C, C_5H_5); 88.26 (5 C, $\underline{C}_5Me_5$)	−37.2
4	CD_2Cl_2	1.27 and 1.30 (Me)	8.77 (5 C, $FeC_5\underline{Me}_5$); 9.14 (5 C, $RuC_5\underline{Me}_5$); 87.98 (5 C, $Fe\underline{C}_5Me_5$); 96.91 (5 C, $Ru\underline{C}_5Me_5$)	−39.2
$[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]PF_6$ [b]	CD_2Cl_2	1.11 (Me); 3.48 (C_5H_5)		−15.8 (P_5); −144.0 (septet, PF_6, $J_{P,F}$ = 710 Hz)

[a] All signals for compounds **2—4** are singlets.

[b] See Ref. 4.

$[(\eta\text{-}C_5Me_5)Fe(MeCN)_3]BF_4$,[8] $[(\eta\text{-}C_5H_5)Ru(MeCN)_3]BF_4$,[9] and $[(\eta\text{-}C_5Me_5)RuCl_2]_2$ [10] were obtained according to known procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX-400 instrument.

$[(\eta\text{-}C_5Me_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]BF_4$ (2). A mixture of complex **1** (115 mg, 0.33 mmol) and $[(\eta\text{-}C_5Me_5)Fe(MeCN)_3]BF_4$ (131 mg, 0.33 mmol) in 5 mL of CH_2Cl_2 or Me_2CO was stirred at −20 °C for 1.5 h. The solvent was removed *in vacuo*. The residue was twice reprecipitated with ether from CH_2Cl_2 to yield a green solid (84 mg, 31%). Found (%): C, 36.2; H, 4.7. $C_{21}H_{32}BCl_2F_4Fe_2P_5$ ($2 \cdot CH_2Cl_2$). Calculated (%): C, 35.8; H, 4.6.

$[(\eta\text{-}C_5Me_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Ru(\eta\text{-}C_5H_5)]BF_4$ (3). A mixture of complex **1** (69 mg, 0.2 mmol) and $[(\eta\text{-}C_5H_5)Ru(MeCN)_3]BF_4$ (79 mg, 0.21 mmol) in 5 mL of $MeNO_2$ was refluxed for 4.5 h. The solvent was removed *in vacuo*. The residue was twice reprecipitated with ether from CH_2Cl_2 to yield a red-brown solid (75 mg, 63%). Found (%): C, 29.5; H, 3.4. $C_{15}H_{20}BF_4FeP_5Ru$. Calculated (%): C, 30.1; H, 3.4.

$[(\eta\text{-}C_5Me_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Ru(\eta\text{-}C_5Me_5)]BF_4$ (4). ***A.*** A mixture of compound **1** (80 mg, 0.23 mmol), $[(\eta\text{-}C_5Me_5)RuCl_2]_2$ (57 mg, 0.09 mmol), $TlBF_4$ (125 mg, 0.43 mmol), and an excess of zinc dust (100 mg) in 5 mL of Me_2CO was stirred at −20 °C for 2 h. The solvent was removed and the residue was twice reprecipitated with ether from CH_2Cl_2 to give complex **4** (104 mg, 84%) as a red-brown solid. Found (%): C, 35.2; H, 4.6. $C_{20}H_{30}BF_4FeP_5Ru$. Calculated (%): C, 35.9; H, 4.5.

B. A solution of complex **1** (87 mg, 0.25 mmol) and $[(\eta\text{-}C_5Me_5)RuCl_2]_2$ (77 mg, 0.125 mmol) in 5 mL of EtOH was refluxed for 1 h. The solvent was removed *in vacuo*. The residue was dissolved in water (5—10 mL) and filtered. An excess of a 48% aqueous HBF_4 (0.2 mL) was added to the filtrate. The precipitate that formed was filtered off, washed with water, dried *in vacuo*, and reprecipitated with ether from CH_2Cl_2. Complex **4** (146 mg, 80%) was obtained as a red-brown solid.

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