Synthesis and the fluxional behavior of the 30-electron cationic iron-molybdenum triple-decker complex with a central pentaphospholyl ligand, $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]BF_4$

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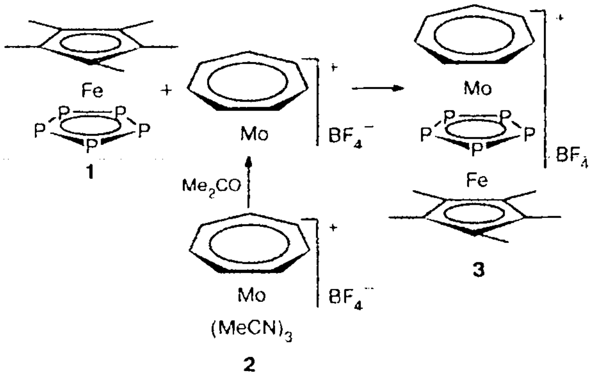
The reaction of $[(\eta\text{-}C_7H_7)Mo(MeCN)_3]BF_4$ with $(\eta\text{-}C_5Me_5)Fe(\eta\text{-}P_5)$ afforded the new 30-electron triple-decker complex $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]BF_4$. Studies of the temperature dependence of the ^1H NMR spectra demonstrated that the resulting compound contains a fluxional cycloheptatrienyl ligand.

Key words: sandwich compounds, triple-decker complexes, pentaphospholyl, iron, molybdenum, fluxionality.

Previously,[1,2] a very simple procedure was developed for the preparation of pentamethylpentaphosphaferrocene (**1**), which appeared to be a suitable starting compound for the synthesis of triple-decker complexes with a central pentaphospholyl ligand. Based on compound **1**, the 30-electron triple-decker complexes $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]^+$ [3] and $(CO)_3M(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)$ (M = Cr, Mo)[4] were prepared.

Recently,[5] we have reported the synthesis of the 30-electron cationic iron- and ruthenium-containing triple-decker complexes with a central pentaphospholyl ligand $[(\eta\text{-}C_5R_5)M(\mu\text{-}\eta{:}\eta\text{-}P_5)Fe(\eta\text{-}C_5Me_5)]^+$ by the stacking reaction of compound **1** with the 12-electron cationic fragments $[(\eta\text{-}C_5R_5)M]^+$ (M = Fe, R = Me; M = Ru, R = H or Me). In some cases, these fragments were generated with the use of the acetonitrile complexes $[(\eta\text{-}C_5R_5)M(MeCN)_3]PF_6$ (M = Fe, R = Me; M = Ru, R = H). With the aim of further extending this procedure for the synthesis of triple-decker compounds, we studied the possibility of the use of the cationic (cycloheptatrienyl)trisacetonitrile molybdenum complex $[(\eta\text{-}C_7H_7)Mo(MeCN)_3]BF_4$ (**2**).



We found that compound **2** actually serves as the source of the cationic 12-electron fragment $[(\eta\text{-}C_7H_7)Mo]^+$ in the reaction with compound **1** in acetone at room temperature to form the new cationic 30-electron iron-molybdenum triple-decker complex **3** with a central pentaphospholyl ligand.

Complex **3** is stable in air during several hours both in the solid state and in a dichloromethane solution.

The structure of complex **3** was proposed based on the data of elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

The ^{31}P NMR spectrum at room temperature has a singlet at δ 27.99.

The ^1H NMR spectrum of this compound in CD_2Cl_2 shows the temperature dependence. At room temperature, the spectrum has two signals of substantially different width at δ ≈ 5.2 (the width of the signal at the half-height is Δν ≈ 520 Hz) and at δ 1.23 (Δν ≤ 1.5 Hz); the ratio of the integrated intensities is 7 : 15. These signals belong to the protons of the C_7H_7 and C_5Me_5 ligands, respectively. When the temperature was decreased to 178 K, the signal of the protons of the C_7H_7 ring was narrowed (δ 5.09, Δν ≈ 63 Hz) and the signal of the protons of the methyl groups of the C_5Me_5 ring was broadened (δ 1.11, Δν ≈ 60 Hz). When the temperature was increased to room temperature, the initial spectral pattern was regained. The temperature dependence of the ^1H NMR spectrum observed indicates that two dynamic processes proceed simultaneously in a solution of complex **3** in CD_2Cl_2. Broadening of the signal of the protons of the methyl groups of the C_5Me_5 ring with

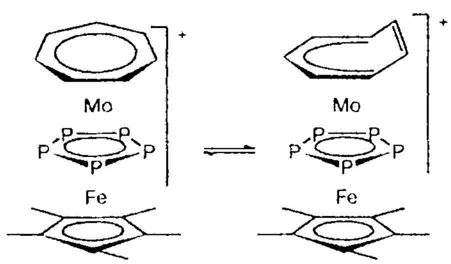
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1374—1376, July, 1999.

1066-5285/99/4807-1362 $22.00 © 1999 Kluwer Academic/Plenum Publishers

decreasing temperature may be associated with hindered rotation both of the five-membered ring and of the methyl groups in this ring. Broadening of the signal of the protons of the cycloheptatrienyl ring is due to fluxional behavior of this ligand.

It should be noted that the fluxional behavior in a solution is typical of η^1-, η^3-, and η^5-cycloheptatrienyl complexes.[6,7] In the ^{1}H NMR spectra of these compounds at room temperature, the signals of the protons of the C_7H_7 ring are observed as a singlet due to their averaging. At low temperature, these protons give a complex pattern typical of an unsymmetrically bound seven-membered ligand. The ^{1}H NMR spectrum of complex **3** at 178 K has the only singlet of the protons of the C_7H_7 ring (δ 5.09), which indicates that the cycloheptatrienyl ligand in this compound is η^7-coordinated. This is confirmed by the $^{13}C\{^1H\}$ NMR spectrum of compound **3** in CD_2Cl_2 at 178 K, which contains the only singlet of the carbon atoms of the C_7H_7 ring at δ 82.48. The spectrum has also two singlets of the C_5Me_5 ligand at δ 88.25 ($\underline{C}_5Me_5$) and 9.12 ($C_5\underline{Me}_5$).

The fluxional behavior of the cycloheptatrienyl ligand in complex **3** is attributable to the equilibrium process which occurs in the solution and is accompanied by a change in the coordination mode of this ligand ($\eta^7 \rightleftharpoons \eta^5$):



3a **3b**

This process is formally associated with a change in the number of valence electrons in the triple-decker complex. Form **3a** with the η^7-C_7H_7 ligand has 30 valence electrons, which corresponds to the 18-electron environment both of the iron and molybdenum atoms. In form **3b**, which contains the η^5-C_7H_7 ligand and possesses 28 valence electrons, the iron atom retains the 18-electron configuration, while the molybdenum atom acquires two less electrons. However, it is probable that the 18-electron environment of the molybdenum atom is retained due to donation of the lone electron pair of the iron atom to form the Fe→Mo donor-acceptor bond. Actually, in the case of large rings, for example, *cyclo*-P_5, *cyclo*-P_6, *etc.*, the metal atoms are at substantially smaller distances from each other than in the cases of C_5H_5 and C_6H_6 carbocycles (as ligands) and the formation of the metal—metal bond becomes possible. These bonds are observed in a number of electron-deficient triple-decker complexes, for example, in the 27-electron chromium compounds $(\eta$-$C_5R_5)Cr(\mu$-η:η-$P_5)Cr(\eta$-$C_5R_5)$ (R = H, Cr—Cr, 2.738 Å[8]; R = Me, Cr—Cr, 2.728 Å[9]) and in the 28-electron molybdenum compound $(\eta$-$C_5Me_5)Mo(\mu$-η:η-$P_6)Mo(\eta$-$C_5Me_5)$ (Mo—Mo 2.648 Å).[10] At the same time, the metal—metal bonds are absent in the 30-electron triple-decker complexes $[(\eta$-$C_5H_5)Fe(\mu$-η:η-$P_5)Fe(\eta$-$C_5Me_4Et)]PF_6$ (Fe...Fe, 3.043 Å)[3] and $(CO)_3Mo(\mu$-η:η-$P_5)Fe(\eta$-$C_5Me_5)$ (Mo...Fe, 3.443 Å).[4] The possibility of formation of the metal—metal bond in triple-decker compounds of this type was theoretically substantiated in Refs. 11 and 12.

The absence of signals of the η^5-C_7H_7 ligand in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of compound **3** at 178 K indicates that the equilibrium **3a** $\rightleftharpoons$ **3b** is shifted toward the left, which corresponds to the higher stability of 30-electron form **3a** with the η^7-C_7H_7 ligand compared to 28-electron form **3b** with the η^5-C_7H_7 ligand. Apparently, substantial narrowing of the signal of the protons of the C_7H_7 ring observed in the ^{1}H NMR spectrum when the temperature was decreased to 178 K implies that the exchange process essentially slows down. For slow exchange, the rate constant of the exchange $k = \pi\Delta\nu$, where $\Delta\nu$ is the line width (Hz) at the half-height of the signal associated with the exchange process.[6,13] If broadening of the signal of the protons of the C_7H_7 ring at δ 5.09 ($\Delta\nu \approx$ 63 Hz), which is observed for complex **3** at 178 K, is a result only of the equilibrium process **3a** $\rightleftharpoons$ **3b**, the rate constant of this process is 198 s^{-1}, which, according to the Eyring equation, corresponds to the free activation energy $\Delta G^{\neq} \approx 35$ kJ mol^{-1}. This value is somewhat smaller than $\Delta G^{\neq}$ for the η^3- and η^5-cycloheptatrienyl derivatives (40—70 kJ mol^{-1}).[6]

Thus, we obtained the first triple-decker complex with a fluxional cycloheptatrienyl ligand.

Experimental

Compound **3** was synthesized under an argon atmosphere with the use of anhydrous solvents. The product was isolated in air. The initial compounds $(\eta$-$C_5Me_5)Fe(\eta$-$P_5)$ (**1**)[2] and $[(\eta$-$C_7H_7)Mo(MeCN)_3]BF_4$ (**2**)[14] were prepared according to known procedures.

The ^{1}H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra were measured on a Bruker AMX-400 instrument.

(μ-η:η-Pentaphospholyl)[(η-pentamethylcyclopentadienyl)iron][(η-cycloheptatrienyl)molybdenum] tetrafluoroborate, $[(\eta$-$C_7H_7)Mo(\mu$-η:η-$P_5)Fe(\eta$-$C_5Me_5)]BF_4$ (3). Acetone (5 mL) was added to a mixture of $(\eta$-$C_5Me_5)Fe(\eta$-$P_5)$ (87 mg, 0.25 mmol) and $[(\eta$-$C_7H_7)Mo(MeCN)_3]BF_4$ (99 mg, 0.25 mmol). The reaction mixture was stirred for 4 h. The solvent was removed *in vacuo*. The solid residue was washed with ether, dissolved in CH_2Cl_2, and precipitated with ether. A brown solid compound was obtained in a yield of 124 mg (80%). Found (%): C, 31.51; H, 3.70. $C_{17.5}H_{23}BClF_4FeMoP_5$ (**3** · $0.5CH_2Cl_2$). Calculated (%): C, 31.73; H, 3.50. ^{1}H NMR (CD_2Cl_2, 178 K), δ: 5.09 (br.s, 7 H, C_7H_7, $\Delta\nu \approx 63$ Hz); 1.11 (br.s, 15 H, C_5Me_5, $\Delta\nu \approx 60$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 178 K), δ: 88.25 (5 C, $\underline{C}_5Me_5$); 82.48 (7 C, C_7H_7); 9.12 (5 C, $C_5\underline{Me}_5$). ^{31}P NMR (CD_2Cl_2, 20 °C), δ: 27.99 (s).

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Received July 24, 1998;
in revised form March 18, 1999