Russian Chemical Bulletin, International Edition, Vol. 50, No. 7, pp. 1332—1333, July, 2001

Synthesis of dicationic triple-decker complexes with a central *B*-cyclohexyl-substituted borole ligand

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Stacking reactions of the dicationic fragments $[LM]^{2+}$ (LM = (η-C_6H_6)Ru, (η-$C_6H_3Me_3$)Ru, or (η-C_5Me_5)Rh) with the complex (η-C_5H_5)Co(η-C_4H_4BCy) (Cy = *cyclo*-C_6H_{11}) afforded new dicationic 30-electron triple-decker complexes [(η-C_5H_5)Co(μ-η:η-C_4H_4BCy)ML]$(BF_4)_2$ containing a cyclohexyl-substituted borole ligand in the central position.

Key words: sandwich compounds, triple-decker complexes, borole, cobalt, ruthenium, rhodium.

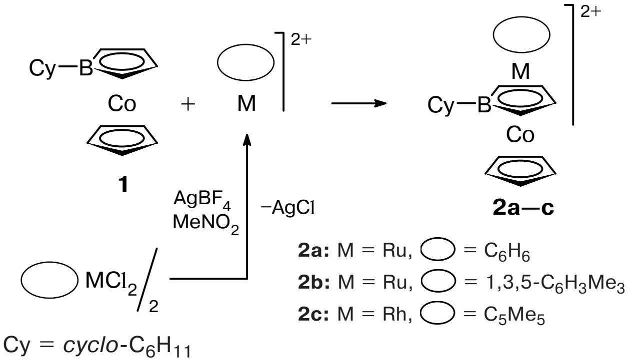
A rather wide range of neutral[1—3] and anionic[3,4] triple-decker complexes based on the borole ligand C_4H_4BR (R = Me or Ph) are known. However, only two cationic triple-decker complexes were described, *viz.*, [(η-C_5H_5)Co(μ-η:η-C_4H_4BPh)ML]$(BF_4)_2$ (LM = (η-C_6Me_6)Ru or (η-C_5Me_5)Ir).[5,6]

As part of our continuing studies on the synthesis of transition metal triple-decker complexes,[7,8] we examined the stacking reactions of the neutral borole complex (η-C_5H_5)Co(η-C_4H_4BCy) (Cy = *cyclo*-C_6H_{11}) (**1**) with the dicationic fragments $[LM]^{2+}$ (LM = (η-C_6H_6)Ru, (η-1,3,5-$C_6H_3Me_3$)Ru, or (η-C_5Me_5)Rh) (Scheme 1).

Results and Discussion

Using these reactions, we prepared new dicationic 30-electron triple-decker complexes **2a—c**, which were isolated as tetrafluoroborates. The fragments $[LM]^{2+}$ were generated *in situ* by the reactions of the chloride complexes $[LMCl_2]_2$ with $AgBF_4$ in nitromethane. The starting complex **1** was synthesized by the reaction of $[(C_4H_4BCy)Co(CO)_2]_2$ with nickelocene analogously to the synthesis of (η-C_5H_5)Co(η-C_4H_4BPh).[9] The compound $[(C_4H_4BCy)Co(CO)_2]_2$, in turn, was prepared by the reaction of 1-cyclohexylborol-3-ene[10] with $Co_2(CO)_8$ analogously to the synthesis of $[(C_4H_4BR)Co(CO)_2]_2$ (R = Me or Ph)[11].

Scheme 1



The structures of compounds **1** and **2a—c** were confirmed by elemental analysis and the data from ^{1}H and ^{11}B NMR spectroscopy (Table 1). As in the case of the related compounds [(η-C_5H_5)Co(μ-η:η-C_4H_4BPh)ML]$(BF_4)_2$ (LM = (η-C_6Me_6)Ru or (η-C_5Me_5)Ir) described previously,[5,6] the signals for the protons of the borole ring in compounds **2a—c** are shifted downfield and the signals for the B atoms are shifted upfield compared to those in the spectra of sandwich complex **1**.

Compounds **2a—c** are bright-colored crystalline substances stable in air both in the solid state and in solutions in $MeNO_2$ for several hours. In stronger coordinating solvents (Me_2CO, MeCN, *etc.*), these compounds gradually decompose.

Experimental

The reactions were carried out under an atmosphere of argon. All operations associated with isolation of the products were carried out in air. The ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument relative to the residual protons of the solvent (^{1}H) or $BF_3 \cdot Et_2O$ (the external standard, ^{11}B).

[(η-Benzene)ruthenium]- (2a), [(η-mesitylene)ruthenium]- (2b), and [(η-pentamethylcyclopentadienyl)rhodium](μ-η:η-*B*-cyclohexylborole)[(η-cyclopentadienyl)cobalt] bis(tetrafluoroborate) (2c). $MeNO_2$ (1 mL) was added to a mixture of the complex $[LMCl_2]_2$ (0.147 mg-equiv.) and $AgBF_4$ or

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1267—1268, July, 2001.

Table 1. Parameters of the ^{1}H and ^{11}B NMR spectra of compounds **1** and **2a—c**

Compound	Solvent	δ	
		^{1}H	^{11}B
1	$CDCl_3$	1.05 (m, 1 H, Cy); 1.22 (m, 5 H, Cy); 1.69 (m, 3 H, Cy); 1.83 (m, 2 H, Cy); 3.51 (m, 2 H, α-H, C_4H_4BCy); 4.82 (s, 5 H, C_5H_5); 4.99 (m, 2 H, β-H, C_4H_4BCy)	22.5 (s, C_4H_4BCy)
2a	$(CD_3)_2CO$	1.24 (m, 1 H, Cy); 1.48 (m, 5 H, Cy); 1.79 (m, 3 H, Cy); 2.23 (m, 2 H, Cy); 4.98 (m, 2 H, α-H, C_4H_4BCy); 6.41 (s, 5 H, C_5H_5); 6.56 (m, 2 H, β-H, C_4H_4BCy); 6.60 (s, 6 H, C_6H_6)	19.8 (s, C_4H_4BCy); 0.8 (s, BF_4)
2b	$(CD_3)_2CO$	1.24 (m, 1 H, Cy); 1.48 (m, 5 H, Cy); 1.79 (m, 3 H, Cy); 2.23 (m, 2 H, Cy); 2.32 (s, 9 H, $C_6H_3\underline{Me}_3$); 4.70 (m, 2 H, α-H, C_4H_4BCy); 6.30 (s, 5 H, C_5H_5); 6.41 (s, 3 H, $C_6\underline{H}_3Me_3$); 6.45 (m, 2 H, β-H, C_4H_4BCy)	19.4 (s, C_4H_4BCy); 0.0 (s, BF_4)
2c	$(CD_3)_2CO$	1.29 (m, 1 H, Cy); 1.45 (m, 3 H, Cy); 1.57 (m, 2 H, Cy); 1.79 (m, 3 H, Cy); 2.04 (s, 15 H, C_5Me_5); 2.14 (m, 2 H, Cy); 4.92 (m, 2H, α-H, C_4H_4BCy); 6.25 (s, 5 H, C_5H_5); 6.47 (m, 2 H, β-H, C_4H_4BCy)	19.0 (s, C_4H_4BCy); −0.4 (s, BF_4)

$AgBF_4 \cdot 3C_4H_8O_2$ (0.305 mmol) and the reaction mixture was stirred for ~0.5 h. The precipitate of AgCl that formed was centrifuged off and the resulting solution was added to complex **1** (40 mg, 0.148 mmol). The reaction mixture was stirred for ~2 h and then ether (~10 mL) was added. The bright-colored precipitate was filtered off and reprecipitated with ether from acetone. **Compound 2a**, the yield was 53%, red solid. Found (%): C, 40.59; H, 4.12. $C_{21}H_{26}B_3CoF_8Ru$. Calculated (%): C, 40.49; H, 4.21. **Compound 2b**, the yield was 63%, red solid. Calculated (%): C, 42.53; H, 4.82. $C_{24}H_{32}B_3CoF_8Ru$. Found (%): C, 43.35; H, 4.85. **Compound 2c**, the yield was 75%, orange solid. Found (%): C, 43.71; H, 5.27. $C_{25}H_{35}B_3CoF_8Rh$. Calculated (%): C, 44.04; H, 5.17.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-33106) and by the Federal Target Program "Integration" (Grant AO115).

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Received March 28, 2001