Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 81 (1) 47–55 (2016) UDC 546.774+546.784+547.636’416:544.433.21
JSCS–4826 *Original Scientific paper*

Coordination studies of 1,2-bis(diphenylphosphino)ethane with di-μ-hydroxo dinuclear complexes of tungsten(IV) and molybdenum(IV)•

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(Received 1 May, revised 28 July, accepted 29 July 2015)

Abstract: New trifluoroethoxido phosphine complexes $[Cp_2M(\eta^1\text{-dppe})(CF_3CH_2O)]^+$ and $[Cp_2(CF_3CH_2O)M(\mu\text{-dppe})MCp_2(CF_3CH_2O)]^{2+}$ (M = Mo or W, Cp = η-C_5H_5 and dppe = $Ph_2PCH_2CH_2PPh_2$) were prepared by reaction of the cationic di-μ-hydroxido dinuclear complex of molybdenocene or tungstenocene $[Cp_2M(\mu\text{-OH})_2MCp_2]^{2+}$ with dppe. From the ^{1}H- and ^{31}P-NMR data, the configurations of the products could be assigned. Furthermore, X-ray crystallography was used to definitively identify one of the products $[Cp_2(CF_3CH_2O)Mo(\mu\text{-dppe})MoCp_2(CF_3CH_2O)]^{2+}$, which crystallizes in the space group $P2_1/c$(#14) with a = 12.230(5) Å, b = 11.149(5) Å, c = 28.966(7) Å, β = 101.07(3)°, V = 3876(2) Å^3 and Z = 2. It was ascertained that the amount of dppe added to the reaction mixture could influence the product distribution. A mechanism involving initial replacement of the hydroxido ligand by the alkoxido group followed by nucleophilic attack of the phosphine is proposed based on the reaction profile.

Keywords: molybdenocene; tungstenocene; dinuclear complexes; dppe.

INTRODUCTION

Previously, it was shown that cationic di-μ-hydroxo dinuclear complexes of molybdenocene and tungstenocene $[Cp_2M(\mu\text{-OH})_2MCp_2]^{2+}$ (Cp = η-C_5H_5; M = = Mo (**1a**) or W (**1b**)) could be conveniently prepared by reactions of Cp_2MH_2 and $Cp_2M(OTs)_2$ (OTs = p-$CH_3C_6H_4SO_3$) in aqueous acetone.[1] These novel dinuclear complexes have attracted much attention due to their ability to catalyze intra- and inter-molecular H/D exchange reactions,[2] and reduction of ketones[3] and nitriles.[4]

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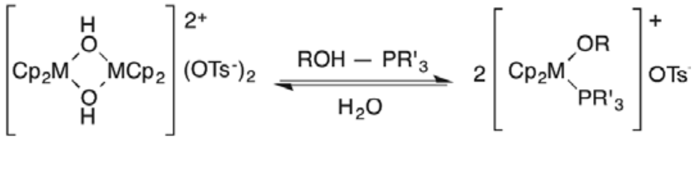
• The authors are pleased to dedicate this paper to Professor Rastko D. Vukicevic in the year of his 65th birthday with continued best wishes for his retirement.

doi: 10.2298/JSC150501066M

The hydroxo groups in complexes **1** were sufficiently labile to undergo displacement by a wide variety of substrates, affording molybdenocene and tungstenocene derivatives and hence, they are useful as precursors of these types of compounds.[1,5,6] It was found that reactions between complexes **1** and monodentate tertiary phosphines always proceeded with the concomitant incorporation of co-existing alcohols to yield novel alkoxido phosphine complexes $[Cp_2M(PR'_3)(RO)]^+(OTs^-)$ (**2**, R′ = Et, Bu^n, and Ph; R = Me, Et, Pr^i, CF_3CH_2 and Ph) (Scheme 1).[1c] It was proven that these reactions occurred spontaneously under mild conditions (20–50 °C). Furthermore, on dissolving in benzene containing a small quantity of water, the resulting complexes **2** readily and quantitatively reverted to the original complexes **1** with liberation of the phosphine ligands, which suggests the reversibility of the reactions.



M = Mo (**1a**), W (**1b**) **2**

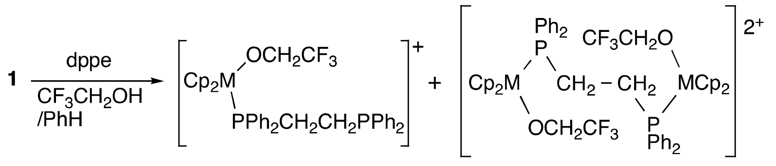
Scheme 1. The reactions between complexes **1** and monodentate tertiary phosphines.

The syntheses of complexes **2** showed the following intriguing trends. In methanol, ethanol, or 2-propanol, only basic phosphines, such as triethylphosphine or tributylphosphine, reacted with **1** and no substitution of the hydroxo bridging groups by triphenylphosphine were observed in these solvents. However, in moderately acidic alcohols, such as trifluoroethanol, or in the presence of phenol, the less reactive triphenylphosphine reacted smoothly to afford **2** in good yields. Therefore, the outcome of the reactions appears to be dependent on the nucleophilicity of the tertiary phosphines and the acidity of the co-existing alcohols. In addition, of particular interest was the fact that no compounds resulting from the incorporation of two phosphine ligands were formed; the labile alkoxido ligand bound to the central metals of **2** was not displaced by a second phosphine ligand even in the presence of excess tertiary phosphine. These results are somewhat puzzling and questions remain regarding a reasonable reaction mechanism.

As a natural extension of this study, the study of the reactions of the dinuclear complexes **1** with a chelating ligand was of interest. The focus of the present paper was the reactions between **1** and dppe (where dppe represents 1,2-bis(diphenylphosphino)ethane), since Green *et al.* reported that the reactions of analogous halogenido complexes $[Cp_2MI_2]$ (M = Mo or W) with dppe resulted in formation of complexes $[Cp_2M(dppe)]^{2+}$ in which the dppe ligand coordinates to the metals in a bidentate mode.[7] Thus, considering the chelate effect of the dppe ligand, the formation of a similar bidentate-type complex could be anticipated in the present case. The results of such experiments are reported herein. In addition, another purpose of this study was to propose a reasonable reaction mechanism pertaining to all reactions between **1** and tertiary phosphines.

RESULTS AND DISCUSSION

The reactions of **1** with dppe were run in CF_3CH_2OH/C_6H_6 at room temperature. The preliminary results demonstrated that the reaction afforded two organometallic species that were assigned as mononuclear complexes **3** containing a monodentate dppe ligand and bridged dimetallic complexes **4** (Scheme 2). The reaction of dppe did not proceed at all in methanol or in ethanol, which is similar to the reaction of triphenylphosphine. It was further ascertained that the amount of dppe added to the reaction mixtures could influence the product distribution. It was then decided to investigate the reaction conditions in order to gain a better understanding of the factors controlling the selectivity of the products. The results are summarized in Table I.



M = Mo (**3a**), W (**3b**) M = Mo (**4a**), W (**4b**)

Scheme 2. The reactions between complexes **1** and dppe to produce mononuclear complexes **3** and bridged dimetallic complexes **4**.

TABLE I. Products obtained from the reactions of **1** with dppe in the presence of CF_3CH_2OH under several conditions

Compound	Complex / mmol	dppe, mmol	CF_3CH_2OH/C_6H_6, mL/mL	Yield, %
3a	**1a** / 0.294	1.300	1.5/5.0	81
3b	**1b** / 0.135	0.880	1.5/5.0	82
4a	**1a** / 0.341	0.339	1.5/1.5	50
4b	**1b** / 0.159	0.158	2.0/2.0	43

As shown in Table I, good yields of complexes **3** could be obtained if a large excess of dppe was added to **1** in solution at room temperature. On the other hand, the reactions of **1** with dppe in a mole ratio of 1:1 gave **4** as the major products. It is worth emphasizing that complexes containing a chelating dppe ligand were not observed in the reactions of complexes **1**. Thus, dppe does not yield the expected chelated complexes.

Complexes **3** are soluble in methanol, ethanol, trifluoroethanol and acetone, while **4** are soluble in the foregoing alcohols and essentially insoluble in acetone. It was found that complexes **3** and **4** were stable to air in the solid state. Complexes **3** and **4** were characterized by standard methods, in particular $^{31}P\{^1H\}$- and ^1H-NMR spectroscopies, as well as by X-ray structural determination of **4a**. In addition, the combustion analyses for **3b** and **4a** were consistent with their spectroscopic properties (see Experimental).[8] Selected NMR data are collected in Table II.

TABLE II. Selected ^1H-NMR (270 MHz, CD_3OD, 293 K) and ^{31}P-NMR data (202 MHz, CD_3OD, 293 K, J in Hz) for complexes **3** and **4** (δ / ppm)

Compound	^1H-NMR	^{31}P-NMR
3a	7.2–7.6 (20H, *m*, Ar-H), 5.46 (10H, *d*, J_{PH} = 1.83, Cp), 3.20 (2H, *q*, J_{FH} = 9.56, CF_3CH_2O), 2.6–2.9 (2H, *br*, $MoPC\mathbf{H}_2CH_2$), 1.6–1.9 (2H, *br*, $MoPCH_2C\mathbf{H}_2$)	29.9 (*s*), –12.0 (*br*)
3b	7.2–7.6 (20H, *m*, Ar-H), 5.42 (10H, *d*, J_{PH} = 1.22, Cp), 3.45 (2H, *q*, J_{FH} = 9.56, CF_3CH_2O), 2.6–2.8 (2H, *br*, $WPC\mathbf{H}_2CH_2$), 1.7–1.9 (2H, *br*, $WPCH_2C\mathbf{H}_2$)	Not measured
4a	7.2–7.6 (20H, *m*, Ar-H), 5.38 (20H, *d*, J_{PH} = 1.83, Cp), 3.20 (4H, *q*, J_{FH} = 9.56, CF_3CH_2O), 2.2–2.4 (4H, *br*, $MoPCH_2$)	28.0 (s)
4b	7.2–7.6 (20H, *m*, Ar-H), 5.35 (20H, *d*, J_{PH} = 1.22, Cp), 3.40 (4H, *q*, J_{FH} = 9.56, CF_3CH_2O), 2.1–2.3 (4H, *br*, $WPCH_2$)	Not measured

The ^1H-NMR spectra of complexes **3** are similar, showing five different resonances besides the resonances due to the TsO protons, and resemble those of **2** in a previous paper.[1c] As shown in the Table II, resonances for the cyclopentadienyl ring protons of **3a** and **3b** appear at around δ 5.5 ppm as a doublet coupled to phosphorus; this represents significant shielding of these protons compared with the chemical shifts in the parent dinuclear complexes **1** (δ = 6.0 ppm) but are compatible with the observed chemical shifts of **2**. As expected, the spectra of **3** show two separate signals for the CH_2CH_2 fragment of the dppe ligand at δ around 2.7 and 1.8 ppm. The CF_3CH_2O units in **3a** and **3b** show a quartet at δ 3.20 (**3a**, J_{FH} = 9.56 Hz) and 3.45 ppm (**3b**, J_{FH} = 9.56 Hz), respectively.

Assignment of the monodentate coordination mode of the dppe ligand was based on the observation of two discrete equal intensity resonances at δ around 29 and –12 ppm in the $^{31}P\{^1H\}$-NMR spectrum of **3a**. The downfield resonance is assignable to a metal-bonded phosphorus atom, while the high-field resonance can readily be assigned to an uncoordinated phosphorus atom since this chemical shift is very similar to that of free dppe.

In the ^1H-NMR spectrum of complex **4a**, the Cp protons occur at δ = 5.4 ppm as a doublet with a P–H coupling constant of 1.83 Hz, while the CF_3CH_2 protons appear as a quartet with an F–H coupling constant of 9.56 Hz at δ = 3.2 ppm. Unlike complex **3a**, the spectrum of **4a** shows only one multiplet for the

CH_2CH_2 fragment at around δ = 2.3 ppm. Furthermore, the $^{31}P\{^1H\}$-NMR spectrum of **4a** contains only one resonance at around δ 28 ppm, which was assigned to the phosphorus atom on molybdenum. Evidently, these results indicate that **4a** contains the Mo(μ-dppe)Mo group. The spectrum of complex **4b** is almost identical to that of **4a**, supporting a structure analogous to that of **4a**.

Complex **4a** was fully characterized by X-ray crystal structure determination. Dark red crystals suitable for the X-ray analysis were obtained by recrystallization from CF_3CH_2OH/Et_2O. The more important bond lengths and bond angles are given in Table III. A summary of the crystallographic data is given in Table IV (see Experimental). As was anticipated from the NMR consideration, the analysis indicated that the molecule has a symmetric structure in the solid state with the formulation $[Cp_2(CF_3CH_2O)Mo(\mu\text{-dppe})Mo(OCH_2CF_3)Cp_2]$-$(OTs)_2 \cdot (CF_3CH_2OH)_2$ in which two molecules of trifluoroethanol are included as a crystallization solvent. An ORTEP drawing of the cation of **4a** is shown in Fig. 1. The TsO molecules were found to be disordered and were omitted for clarity. From this drawing, it is clear that the two molybdenum centers are held together by a dppe ligand. The coordination sphere around the metal center is completed by bridging dppe ligand, CF_3CH_2O group, and two cyclopentadienyl rings, which are arranged in the form of a distorted tetrahedron. The cyclopentadienyl rings are bound to molybdenum in an η^5 fashion and each of the ring carbon atoms are coplanar. Thus, complex **4a** has geometry typical of bent metallocene.

TABLE III. Selected bond distances and angles for **4a**

Bond	Distance, Å	Bond	Distance, Å
Mo1–P1	2.541(4)	Mo1–O1	2.070(10)
Mo1–C1	2.29(2)	Mo1–C2	2.33(2)
Mo1–C3	2.37(3)	Mo1–C4	2.33(2)
Mo1–C5	2.31(3)	Mo1–C6	2.31(2)
Mo1–C7	2.27(2)	Mo1–C8	2.35(2)
Mo1–C9	2.37(2)	Mo1–C10	2.34(2)
O1–C11	1.45(2)	C11–C12	1.37(4)
Bond	**Angle, °**	**Bond**	**Angle, °**
P1–Mo1–O1	75.5(3)	Mo1–P1–C13	113.0(5)
Mo1–P1–C14	111.1(5)	Mo1–P1–C20	116.9(5)
Mo1–O1–C11	119.4(10)	P1–Mo1–C2	132.2(6)

The structure can be compared with that of the related alkoxido phosphine complex $[Cp_2Mo(PBu^n{}_3)(CF_3CH_2O)]^+$ (**2a**).[1c] The Mo–P bond distance (2.541(4) Å) is remarkably similar to that exhibited by **2a** (2.540(4) Å). On the other hand, the Mo–O bond distance of 2.070(10) Å is significantly longer than that found in **2a** (2.019(8) Å). Furthermore, the O–Mo–P angle of 75.5(3)° is slightly greater than the corresponding angle of 74.4(3)° found in **2a**. The most interesting feature of the structure is the observation of the long O–C bond distance of 1.45(2) Å, which is considerably longer than the *ca.* 1.39 Å found in **2a**.

TABLE IV. Summary of the crystal structure data for **4a**•2CF_3CH_2OH

Formula	$C_{68}H_{68}F_{12}P_2O_{10}Mo_2S_2$
M / g mol^{-1}	1591.21
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
a / Å	12.230(5)
b / Å	11.149(5)
c / Å	28.966(7)
β / °	101.07(3)
V / Å^3	3876(2)
Z	2
ρ_c / g cm^{-3}	1.363
μ / cm^{-1}	4.97
R / *wR*	0.102/0.143
GOF	2.28
T / °C	25

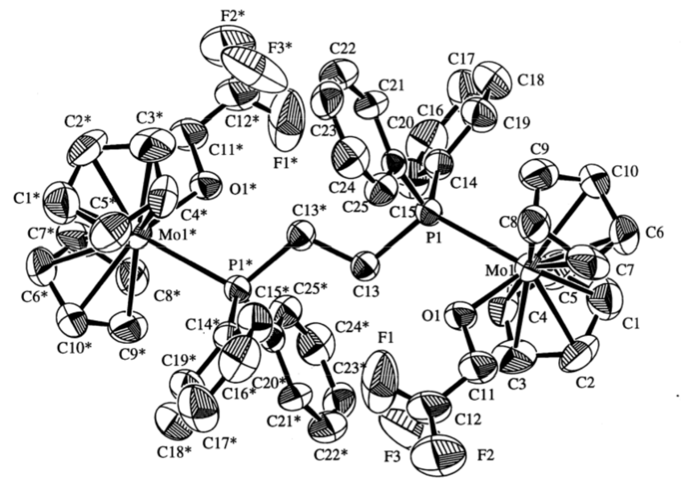
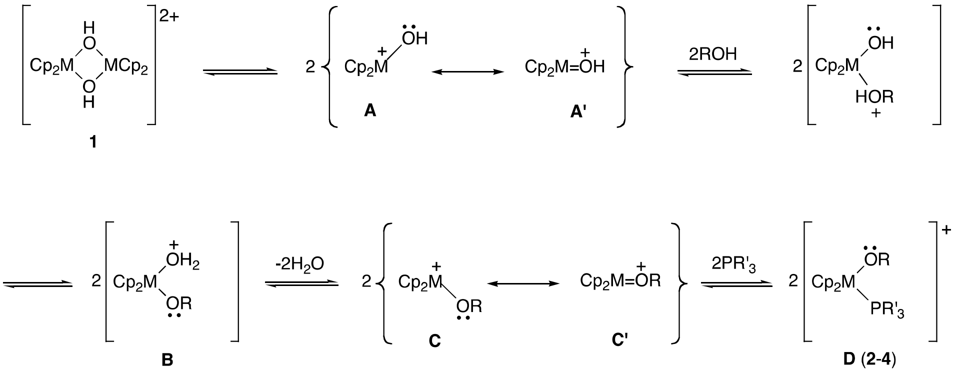


Fig. 1. ORTEP drawing of the cation of complex **4a** with thermal ellipsoid plots (40 % probability). The hydrogen atoms have been omitted for clarity.

A mechanism accounting for the reaction pathways is proposed in Scheme 3 based on literature precedents and the reaction profile. In addition, certain general observations pertained to all reactions between **1** and the tertiary phosphines are included in this study. As mentioned in the Introduction, each step in Scheme 3 is likely to be reversible. It is well known that most 18-electron complexes undergo ligand substitution reactions *via* dissociative pathways.[9] Hence, it is conceivable that the first step in the sequence leading to formation of **2**–**4** (**D**) is dissociation of **1** into the monomeric 16-electron complexes **A**. In this case, it is possible that it is the resonance limiting form **A′**, which may be formally viewed as a protonated oxo-complex.[10] Taking into account the fact that the reaction between **1** and a tertiary phosphine is very susceptible to the co-existing alcohol as noted in the Introduction, it seems likely that the next step consists of nucleophilic attack of an alcohol on the metal center. Then proton transfer to the hydroxy group occurs to give alkoxido complex **B**; this process is quite similar to the reported hydrolysis of **1**.[2] Subsequent elimination of water from **B** produces an unsaturated species **C**. This dehydration step seems to be a facile process since π-donation by an alkoxido ligand is well established toward early transition metals[11] and so the canonical form **C′** would make a greater contribution to the hybrid. Inevitably, the final step in the mechanism is nucleophilic attack of a tertiary phosphine on the central metal to afford the product **D**.



Scheme 3. Possible mechanism for the formation of the complexes **2**–**4**.

EXPERIMENTAL

General procedures

All manipulations were performed under an inert nitrogen or argon atmosphere using standard Schlenk techniques. Commercially available reagent grade chemicals (Wako Chemical) were used as such without any further purification. Solvents were purified according to standard procedures. All NMR spectra were recorded on a JEOL JNMEX-270 spectrometer or a JEOL JNMGX-500 spectrometer. $^{31}P\{^1H\}$-NMR peak positions were referenced to external H_3PO_4. The di-μ-hydroxido dinuclear complexes $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}$ (Cp = η-C_5H_5; M = Mo (**1a**) or W (**1b**)) were prepared by literature procedures.[1c]

Reaction of 1 with excess dppe

A solution containing **1a** (0.244 g, 0.294 mmol) and dppe (0.500 g, 1.260 mmol) in CF_3CH_2OH/C_6H_6 (1.5 mL/5 mL) was stirred at room temperature for 140 h. During this time, the solution changed from green to red. From the resulting solution, the solvent was evaporated to dryness under reduced pressure. The residue was washed successively with hexane and diethyl ether and then extracted with acetone. The extract was reduced to dryness and the residue was washed with hexane and diethyl ether to yield **3a** (0.430 g, 81 %) as an orange–

–red powder. This procedure was also applicable to the synthesis of the tungsten analogue **3b** (yield = 82 %). **3b**: Anal. Calcd. for $C_{45}H_{43}F_3O_4SP_2W$: C, 55.00; H, 4.41 %. Found: C, 54.28; H, 4.53 %.

*Reaction of **1** with 1 equiv. of dppe*

A solution containing **1a** (0.289 g, 0.341 mmol) and dppe (0.135 g, 0.339 mmol) in CF_3CH_2OH/C_6H_6 (1.5 mL/1.5 mL) was stirred at room temperature for 15 h. During this time, the solution changed from green to red. From the resulting solution, the solvent was evaporated to dryness under reduced pressure. The residue was washed successively with hexane, diethyl ether, and acetone, and then extracted with ethanol. The extract was reduced to dryness and the residue was washed with hexane and diethyl ether to yield **4a** (0.237 g, 50%) as an orange–red powder. Purification of the product by recrystallization from $CF_3CH_2OH/$ $/Et_2O$ afforded dark red crystals in the form of flat plates. This procedure was also applicable to the synthesis of the tungsten analogue **4b** (yield = 43 %). **4a**: Anal. Calcd. for $C_{64}H_{62}F_6O_8S_2P_2Mo_2$: C, 55.26; H, 4.49 %. Found: C, 55.03; H, 4.53 %.

*X-Ray crystallographic study of **4a***

A crystal suitable for X-ray crystallography was grown in $CF_3CH_2OH–Et_2O$. The thus obtained dark red crystal was mounted on a glass fiber. Measurement was made on a Rigaku AFC5R diffractometer using Mo K_α radiation (λ = 0.71068 Å) for data collection. The unit-cell parameter was determined by least squares fitting of 25 reflections with a range $21.39 < 2\theta < 25.95°$. The parameters used during the collection of diffraction data are given in Table IV. The structure was solved and refined using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

CONCLUSIONS

New trifluoroethoxido phosphine complexes $[Cp_2M(\eta^1\text{-dppe})(CF_3CH_2O)]^+$ (**3**) and $[Cp_2(CF_3CH_2O)M(\mu\text{-dppe})MCp_2(CF_3CH_2O)]^{2+}$ (**4**) were prepared by reactions of the cationic di-μ-hydroxido dinuclear complex of molybdenocene and tungstenocene $[Cp_2M(\mu\text{-OH})_2MCp_2]^{2+}$ (**1**) with dppe. The products of the reactions were identified using ^{1}H- and ^{31}P-NMR spectroscopy. In addition, X-ray structural data on **4a** clearly established a bridged dimeric structure. It was ascertained that the amount of dppe added to the reaction mixtures could influence the product distribution. Thus, the reaction of **1** with dppe in a molar ratio of 1:1 gives complexes **4** as the major products, while good yields of complexes **3** were obtained if a large excess of dppe was added to **1**.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, as CCDC reference number 605332. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Acknowledgments. We are grateful to Dr. Mikio Yamasaki of the Rigaku Corporation for the X-ray structure analysis. We also thank Dr. Masako Tanaka of the Tokyo Institute of Technology for the elemental analysis.

ИЗВОД

ИСПИТИВАЊЕ КООРДИНАЦИЈЕ 1,2-БИС(ДИФЕНИЛФОСФИНО)ЕТАНА СА ДИ-μ-ХИДРОКСИДО ДИНУКЛЕАРНИМ КОМПЛЕКСИМА ВОЛФРАМА(IV) И МОЛИБДЕНА(IV)

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У реакцији катјонског ди-μ-хидроксидо комплекса молибденоцена или волфрамоцена $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}$ са dppe лигандом синтетисани су нови трифлуороетоксидо-фосфински комплекси, $[Cp_2M(\eta^1\text{-dppe})(CF_3CH_2O)]^+$ и $[Cp_2(CF_3CH_2O)M(\mu\text{-dppe})MCp_2(CF_3CH_2O)]^{2+}$ (M = Mo или W, Cp = η-C_5H_5 и dppe = $Ph_2PCH_2CH_2PPh_2$). Нађено је да дистрибуција реакционих производа зависи од количине додатог dppe лиганда. Дискутован је механизам испитиване реакције који у првој фази укључује супституцију хидроксидо лиганда са алкоксидо групом, а затим у другој фази долази до нуклеофилног напада фосфинског лиганда.

(Примљено 1. маја, ревидирано 28. јула, прихваћено 29. јула 2015)

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