Letters to the Editor

The first example of coordination of a tricyclic hydrophosphorane with platinum(II)

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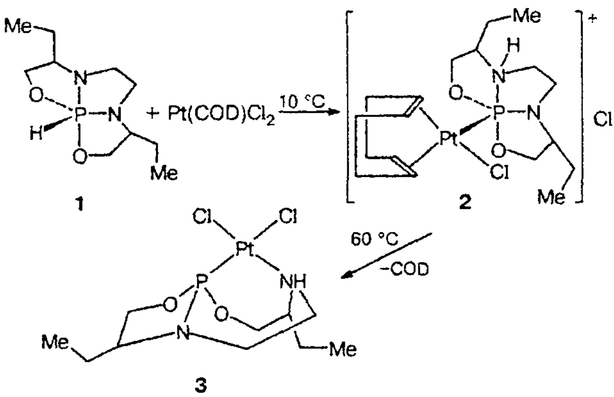
Coordination chemistry of tricyclic hydrophosphoranes is practically unknown at present.[1] This work describes studies on complexing $Pt(COD)Cl_2$ (COD is 1,5-cyclooctadiene) with the previously obtained[2] tricyclic hydrophosphorane(**1**).

We found that the reaction of **1** with an equimolar amount of $Pt(COD)Cl_2$ in $CDCl_3$ at 10 °C yielded the metallated phosphorane (**2**) (Scheme 1). Direct coordination of the phosphoranide center with platinum was confirmed by the ^{31}P NMR data: $\delta P = -12.8$ ppm, $^1J_{P,Pt} = 5105$ Hz. The presence of a 1,5-cyclooctadiene ligand in the coordination sphere of **2** is corroborated by ^{13}C NMR data ($CDCl_3$, δ, ppm, J/Hz): 123.3 ($^2J_{C,P} = 19.8$) and 119.8 ($^2J_{C,P} = 21.6$, $^1J_{C,Pt} \approx 40$) (C=C, in the *trans* position relative to phosphorus); 92.3 ($^1J_{C,Pt} = 184.9$) and 89.6 ($^1J_{C,Pt} = 192.1$) (C=C, in the *trans* position relative to chlorine); 34.8 ($^3J_{C,P} = 5.4$), 30.1, 29.7, 25.4 (CH_2(COD)); 69.7 (OCH_2, $^2J_{C,P} = 9.0$) and 65.5 (OCH_2, $^2J_{C,P} = 5.1$); 57.3 (NCH, $^2J_{C,P} = 12.6$) and 55.8 (NCH, $^2J_{C,P} = 3.6$); 39.7 (NCH_2, $^2J_{C,P} = 5.4$) and 36.1 (NCH_2, $^2J_{C,P} = 7.2$); 24.6 (CH_2, $^3J_{C,P} = 5.4$) and 21.1 (CH_2); 10.7 and 8.7 (CH_3).

Increasing temperature to 60 °C leads to ring opening in the phosphorane structure and the formation of complex **3**.

Scheme 1



Compounds **2** and **3** were isolated and characterized by ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR and IR spectroscopy

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as well as by plasma desorption mass spectrometry and elemental analysis.

Compound 2, m.p. 122—124 °C (decomp.). Found (%): C, 35.39; H, 5.31; Cl, 11.84; N, 4.80. $C_{18}H_{33}Cl_2N_2O_2PPt$. Calculated (%): C, 35.65; H, 5.48; Cl, 11.69; N, 4.62. IR spectrum ($CHCl_3$), ν/cm^{-1}: 320 (Pt—Cl). Mass spectrum (plasma desorption), m/z (I_{rel},%)): 570 $[M]^+$ (100).

Compound 3, m.p. 186—188 °C (decomp.). Found (%): C, 24.32; H, 4.03; Cl, 14.35; N, 5.77. $C_{10}H_{21}Cl_2N_2O_2PPt$. Calculated (%): C, 24.11; H, 4.25; Cl, 14.23; N, 5.62. IR spectrum ($CHCl_3$), ν/cm^{-1}: 336 and 294 (Pt—Cl).

In the ^{31}P NMR spectrum, as the signals of **2** disappear the low-field triplet (δP = 83.2 ppm, $^1J_{P,Pt}$ = 5562.5 Hz) increases. The proposed structure of **3** is also consistent with the ^{13}C NMR data ($CDCl_3$, δ, ppm, J/Hz): 74.2 (OCH_2, $^2J_{C,P}$ = 5.4) and 71.0 (OCH_2); 63.7 and 60.2 (NCH); 52.9 and 41.7 (NCH_2, $^2J_{C,P}$ = 7.3); 23.9 and 23.0 (CH_2); 10.1 and 9.8 (CH_3). The reaction of **1** with Pt(COD)Cl carried out at *ca.* 20 °C yielded a mixture of **2** and **3**.

References

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2. K. N. Gavrilov, D. V. Lechkin, *Koordinats. khimiya*, 1995, **21**, 432 [*Russ. J. Coord. Chem.*, 1995, **21**, 414 (Engl. Transl.)].

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Reactions of $Ru_3(CO)_{12}$ with cinnamic acid amides

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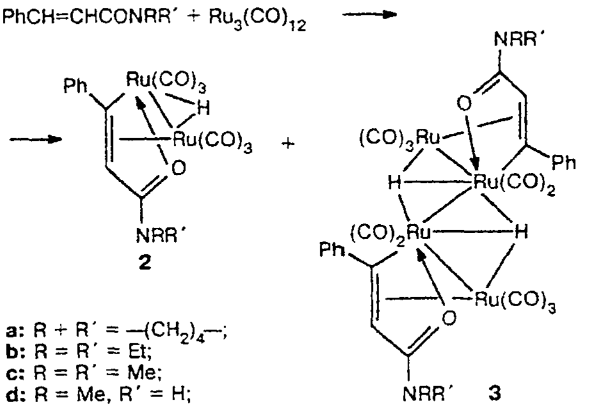
It is known that reactions of $Ru_3(CO)_{12}$ with unsaturated ketones (oxadienes) lead to complexes comprising five-membered oxaruthenacycles as the main structural fragment, with additional η^3-coordination linkages to the other ruthenium atoms.[1,2] In this communication we describe the results obtained in reactions of $Ru_3(CO)_{12}$ with cinnamic acid amides. The latter are oxadienes containing amino substituents known to be potent electron-donating groups. We found that these reactions lead to a new type of tetranuclear complexes (**3**) along with the amino substituted analogs (**2**) of traditional binuclear complexes. Complexes **3** are produced by dimerization of complex **2** with elimination of two CO ligands and the formation of a bond between the oxaruthenacycles. It is interesting to note that the hydride atoms in **3** become unusual μ^3 bridges lying almost in the plane of the three ruthenium atoms. The structures assigned to **2** and **3** are based on preliminary X-ray results* and are consistent with the IR and NMR data. Thus **2a** has the following spectroscopic characteristics: IR spectrum (heptane), ν/cm^{-1}: 2098 m, 2052 vs, 2036 m, 2010 vs, 1990 s, 1974 m (C=O); ^1H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 7.00—7.52 (m, 5 H, Ph); 3.16—3.44 (m, 4 H, CH_2); 2.91 (d, 1 H, J = 1.3); 1.80—2.00 (m, 4 H, CH_2); −12.58 (d, 1 H, J = 1.3, H—M). The IR spectrum of **3a** (tablet with KBr), ν/cm^{-1}: 2055, 2025, 1990, 1970, 1955 (C=O).

Using **2a** and **3a** as an example we studied the interconversion of the complexes. When heated in boiling heptane, complex **2a** is converted into **3a**. The reverse transformation of **3a** into **2a** takes place when **3a** is treated with methylene chloride and leads to partial decomposition of the complex.



a: R + R' = $-(CH_2)_4-$;
b: R = R' = Et;
c: R = R' = Me;
d: R = Me, R' = H;

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* X-ray diffraction analysis was performed by A. I. Yanovsky and F. M. Dolgushin (INEOS, RAS).

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