Complete transligation of $(AcO)_4Rh_2$ applied onto γ-Al_2O_3 with 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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Complete transligation of $(AcO)_4Rh_2$ with 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane was conducted in the solid phase on γ-Al_2O_3. The reduction of Rh^{II} to Rh^{I} on γ-Al_2O_3 at 130 °C under the action of the above-mentioned bicyclic phosphite is accompanied by the oxidation of the acetate anion to the acetoxyl radical. The oxidation products were detected by IR and ESR spectroscopy. 2,6-Di-*tert*-butyl-4-methylphenol was used as a "spin trap" to identify stable secondary radical cations.

Key words: transligation, bicyclic phosphite, dirhodium(II) tetraacetate, ESR.

Bicyclic phosphite, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ($P(OCH_2)_3CEt$) (**1**), which, unlike PPh_3 и $P(OPh)_3$, is characterized by a low steric parameter and the high electron-withdrawing properties,[1] can bring about profound transligation of dirhodium tetraacetate(II)[2] $(AcO)_4Rh_2$ in organic solvents at elevated temperature to give a cationic rhodium(I) complex $Rh[P(OCH_2)_3CEt]_5^+$ (see Ref. 3). It is assumed that the cleavage of the metal—metal bond and the reduction of Rh^{II} to Rh^{I} under the action of $P(OCH_2)_3CEt$ is accompanied by the oxidation of the acetate anion to the acetoxyl radical. However, the experimental data confirming this assumption are missing.[3]

To clarify the peculiarities of complete transligation of $(AcO)_4Rh_2$ with bicyclic phosphite **1**, we carried out a heterophase reaction between these reagents in the absence of any background organic solvent that would prevent such a study.

Results and Discussion

Heating of bicyclic phosphite **1** and $(AcO)_4Rh_2$ (ratio P : Rh $\geq$ 5), applied onto γ-Al_2O_3, at 130 °C results in complete replacement of the acyl ligands in the rhodium complex. This process is accompanied by the cleavage of the metal—metal bond and the reduction of Rh^{II} to Rh^{I}, as in the case for the reaction of $P(OCH_2)_3CEt$ with $(AcO)_4Rh_2$ in toluene[3] at 100 °C, which yielded a homoligand pentasubstituted complex $[Rh(P(OCH_2)_3CEt)_5]AcO$ (**2**). The product of the heterophase reaction can be easily eluted from the support with dichloromethane, and its physicochemical constants are virtually identical with those of pentasubstituted rhodium(I) complex **2** obtained earlier.[3]

Complete transligation of $(AcO)_4Rh_2$ with bicyclic phosphite **1** can be represented by the following scheme:

$$(AcO)_4Rh_2 + 10\ P(OCH_2)_3CEt \longrightarrow$$

$$\longrightarrow 2\ Rh[P(OCH_2)_3CEt]_5AcO + 2\ CO_2 + C_2H_6,$$

$$[Rh_2]^{4+} + 2\ \bar{e} \longrightarrow 2\ Rh^+,$$

$$2\ AcO^- - 2\ \bar{e} \longrightarrow 2\ AcO^\cdot \longrightarrow 2\ CO_2 + C_2H_6.$$

This assumption[3] was based only on the identification of the rhodium(I) complex, the only phosphorus-containing reaction product, using mostly low-temperature ^{31}P NMR spectroscopy.

Here, ESR was used to check whether two different types of species, namely, paramagnetic rhodium ions and radical hydrocarbon fragments, can be generated in the $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$—γ-Al_2O_3 system and can undergo further transformations.

The ESR spectra of specimens prior to (I) and after (II) heating exhibited no signals for the paramagnetic Rh^{2+} ions (the Rh^0 atoms are also paramagnetic, whereas the Rh^+ and Rh^{3+} ions do not contain unpaired electrons). Thus, the initial specimen I contains only binuclear Rh_2^{4+} complexes with paired electrons, which do not appear in the ESR spectra, and subsequent high-temperature transformations of specimen I do not yield appreciable amounts of isolated Rh^{2+} cations and Rh^0 atoms.

Usually, it is difficult to obtain direct experimental evidence in favor of the radical mechanism of transfor-

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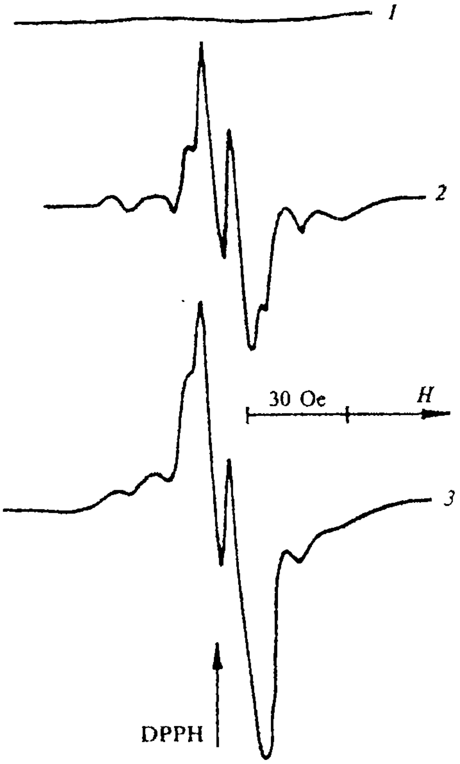

Fig. 1. ESR spectra of Rh systems applied onto γ-Al_2O_3 after heating at 130 °C in a flow of N_2: (*1*) $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$ (specimen II), T_{rec} = 20 °C; (*2*) $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$—ionol (specimen III), T_{rec} = 20 °C; (*3*) specimen III, T_{rec} = −196 °C.

mations, because the current concentration of radicals is so low that they cannot be detected by ESR. In our case too, no significant ESR signal was observed at g = 2.002 upon heating of the $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$—γ-Al_2O_3 system (Fig. 1, spectrum *1*). A well-known experimental procedure, where a "spin trap" is introduced into a system, favors accumulation of stable secondary radical cations[6] and considerable enhancement of the sensitivity of the method. We used 2,6-di-*tert*-butyl-4-methylphenol (ionol) as a "spin trap." Heating of the $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$—ionol—γ-Al_2O_3 system in an atmosphere of nitrogen (specimen III) yields a characteristic violet color, and the ESR spectra of the specimen exhibit intense signals (see Fig. 1, spectra *2* and *3*). When the sample was frozen to −196 °C, the signals of an eight-component ESR spectrum became more intense with splitting 8—11 Oe and g = 2.004 (see Fig. 1, spectrum *2*), but the shape of the spectrum changes only slightly, *e.g.*, moderate broadening of the components is observed (see Fig. 1, spectrum *2*). The signals observed are characteristic of organic radical cations devoid of rotational freedoms, which is typical of ionol molecules firmly chemisorbed onto alumina surface.

When Al_2O_3 is used as a support, it should be taken into account that Lewis centers may occur on its surface, whose concentration depends on the conditions of preliminary calcination. These centers can generate radical cations from molecules with a low ionization potential, such as ionol. For comparison, the γ-Al_2O_3—ionol (specimen V) and $P(OCH_2)_3CEt$—ionol—γ-Al_2O_3 (specimen IV) systems heated in an atmosphere of nitrogen under the conditions of treatment of specimen III were studied. In contrast to specimen III, the latter two specimens remain white colored upon heating. At −196 °C, specimen V exhibits an ESR signal (see Fig. 2, spectrum *2*), which is, however, one order of magnitude less intense than that for specimen III (see Fig. 2, spectrum *1*). Therefore, the formation of ionol radicals on the Lewis centers of γ-Al_2O_3 makes a minor contribution. Moreover, the presence on the surface of phosphite, which blocks effectively the Lewis centers, decreases this contribution by an additional order of magnitude (see Fig. 2, spectrum *3*), making it negligible compared to the main route of radical accumulation according to the scheme

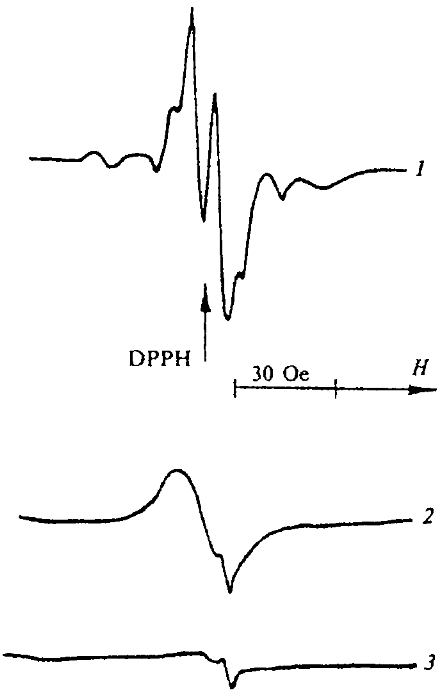

Fig. 2. ESR spectra of system applied onto γ-Al_2O_3 after heating at 130 °C in a flow of N_2: (*1*) $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$ (specimen II), T_{rec} = 20 °C; (*2*) ionol (specimen V), T_{rec} = 20 °C; (*3*) $P(OCH_2)_3CEt$—ionol (specimen IV), T_{rec} = 20 °C.

$$Bu^t_2MeC_6H_2OH - \bar{e} \xrightarrow[-H^+]{} Bu^t_2MeC_6H_2O^{\cdot},$$

$$AcO^{\cdot} + \bar{e} \xrightarrow{+H^+} AcOH.$$

Acetic acid resulting from the reaction of ionol with the acetoxyl radical was detected in the gaseous phase by

IR spectroscopy (ν(CO)/cm^{-1}: 1735, 1785) and can be isolated preparatively. It should also be noted that the formation of CO_2, a possible product of decomposition of the intermediate acetoxyl radical, was detected in the synthesis of specimen II in the absence of ionol (IR, ν/cm^{-1}: 2300 (C=O)).[5]

Thus, the data obtained can be considered as evidence in favor of the radical mechanism of high-temperature reaction of extensive transligation in the $(AcO)_4Rh_2$—$P(OCH_2)_3CEt$ system.

Experimental

^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer (32.4 MHz) at 30 °C with 85% H_3PO_4 as the external standard. IR spectra were recorded on a Specord 75 IR instrument using a 100-mL gas cell or for a solution in CH_2Cl_2 (KBr). ESR spectra were obtained with a reflector-type spectrometer in the X range (λ = 3.2 cm) at 20 and −196 °C. Samples (~40 mg) were placed in an ESR cell ~4 mm in diameter and sealed. ESR spectra were recorded in the magnetic field strength range 0—4500 and 3200—3500 Oe for more precise measurements of narrow signals for radical species. UHF power was varied to check the absence of saturation effect. ESR spectra were characterized by the hyperfine structure (HFS) constant and *g* factor values determined with respect to diphenylpicrylhydrazine (DPPH) as the standard.

Pentakis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhodium(I) acetate pentahydrate. A solution of bicyclic phosphite **1** (Ref. 4, 0.18 g, 1.1 mmol) in 10 mL of dichloromethane was added to $(AcO)_4Rh_2$ (Ref. 2) (0.05 g, 0.11 mmol). The initial complex gradually dissolved, and the solution turned orange. Calcined γ-Al_2O_3 (1.5 g; neutral, particle size 150 mesh, pore width 58 Å, Brockmann activity I) was added to the resulting solution. Alumina was prepared by calcination at 400—450 °C with complete loss of water. Its activity was judged from R_f of *p*-aminobenzene. The solvent was removed on a rotary evaporator. The dry residue was kept at 30 °C for 0.5 h *in vacuo* (1 Torr) (specimen I) and placed in a flow-type reactor. The sample was heated to 130 °C in a flow of dry oxygen-free nitrogen (gas consumption 4 mL min^{-1}) and kept under these conditions for 1 h. The course of the reaction was monitored by IR spectroscopy of gaseous reaction products. The reactor was then cooled, and the reaction mixture was washed on a filter with 10 mL of dichloromethane. A portion (~30 mg) of the reaction mixture was taken out before washing to study the paramagnetic properties (specimen II). The filtrate was concentrated, and the solid, white rhodium(I) complex was washed on a filter with hexane. Yield 0.048 g (40%), m.p. >185 °C (decomp.). Found (%): C, 36.15; H, 6.40; P, 14.59. $C_{32}H_{68}O_{22}PRh$. Calculated (%): C, 36.39; H, 6.23; P, 14.23. IR (CH_2Cl_2), ν/cm^{-1}: 930, 1015 (POC); 1710 (COO); 3300, 3600 (OH). ^{31}P NMR (CH_2Cl_2, 30 °C), δ: 121.6, $^1J_{P,Rh}$ = 182.5 Hz. The complex is diamagnetic (*cf.* Ref. 3: δP 121.0, $^1J_{P,Rh}$ = 182.5 Hz; Freon 122 : CD_2Cl_2, 3 : 1).

2,6-Di-*tert*-butyl-4-methylphenol (spin trap) was added to the following specimens.

Specimen (III). A solution of bicyclic phosphite **1** (0.18 g, 1.1 mmol) in 10 mL of dichloromethane was added to $(AcO)_4Rh_2$ (0.05 g, 0.11 mmol). Di-*tert*-butyl-4-methylphenol (0.15 g, 0.68 mmol) in 10 mL of CH_2Cl_2 and calcined γ-Al_2O_3 (1.5 g) were added to the reaction mixture. The solvent was removed on a rotary evaporator, and the residue was processed as described above. The reactor was cooled to give violet specimen (III).

Specimen (IV). Di-*tert*-butyl-4-methylphenol (0.15 g, 0.68 mmol) in 10 mL of CH_2Cl_2 and calcined γ-Al_2O_3 (1.5 g) were added to a solution of bicyclic phosphite **1** (0.18 g, 1.1 mmol) in 10 mL of CH_2Cl_2. The solvent was removed on a rotary evaporator, and the residue was worked up as described above. The reactor was cooled to give white specimen (IV).

Specimen (V). Calcined γ-Al_2O_3 (1.5 g) was added to a solution of 2,6-di-*tert*-butyl-4-methylphenol (0.15 g, 0.68 mmol) in 10 mL of CH_2Cl_2. The solvent was removed on a rotary evaporator, and the residue was worked up as described above. The reactor was cooled to give specimen V.

References

1. A. T. Teleshev, N. V. Kolesnichenko, N. A. Markova, E. V. Spivinskii, E. M. Demina, V. I. Kurkin, G. A. Korneeva, S. M. Loktev, and E. E. Nifant'ev, *Neftekhimiya* [*Petroleum Chemistry*], 1991, **31**, 11 (in Russian).
2. G. A. Rempel, P. Legzdins, H. Smith, and G. Wilkinson, *Inorg. Synth.*, 1972, **13**, 90.
3. E. E. Nifantyev, A. T. Teleshev, L. F. Popova, and V. A. Polyakov, *Phosphorus, Sulfur, and Silicon*, 1995, **103**, 253.
4. B. Willam, S. Wadsnorth, J., and W. D. Emmons, *J. Am. Chem. Soc.*, 1962, **84**, 610.
5. D. Nonhebel and J. Walton, *Free-Radical Chemistry: Structure and Mechanism*, Cambridge University Press, Cambridge (UK), 1974.
6. *Organic Electrochemistry*, Eds. M. Baizer and H. Lund, Marcel Dekker, New York, 1985.

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