References

1. R. F. Heck, *Pure Appl.Chem.*, 1978, **50**, 691.
2. R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146.
3. R. F. Heck, *Organic Reactions,* 1982, **27**, 345.
4. R. F. Heck, in *Palladium Reagents in Organic Chemistry*, Academic Press, London, 1985, 179.
5. N. A. Bumagin, N. P. Andryukhova, and I. P. Beletskaya, Metalloorg. Khim., 1989, 2, 911 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
6. N. A. Bumagin, N. P. Andryukhova, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1990, **313**, 107 [*Dokl. Chem.*, 1990, 313 (Engl. Transl.)].
7. N. A. Bumagin, P. G. More, and I. P. Beletskaya, *J. Organometal. Chem.*, 1989, **371**, 397.
8. N. A. Bumagin, L. I. Sukhomlinova, T. P. Tolstaya, and I. P. Beletskaya, *Dokl. Akad. Nauk,* 1993, **332**, 455 [Dokl. Chem., 1993, 332 (Engl. Transl.)].
9. N. A. Bumagin, V. V. Bykov, L. I. Sukhomlinova, T. P. Tolstaya, and I. P. Beletskaya, *J.Organometal. Chem.*, 1995, **486**, 259.
10. T. J. Jeffery, *Tetrahedron Lett.*, 1994, **35**, 3051.
11. H.-C. Zhang and G. D. Daves, *Organometallics*, 1993, **12**, 1499.
12. A. L. Cazalnuvo and J. C. Calabreze, *J. Am. Chem. Soc.*, 1990, **112**, 4324.
13. T. L. Wallou and B. M. Novak, *J. Am. Chem. Soc.*, 1991, **113**, 7411.
14. P. G. Genet, E. Blart, and M. Savignac, *Synlett*, 1992, 715.
15. N. A. Bumagin, I. G. Bumagina, and I. P. Beletskaya, *Zh. Org. Khim.*, 1984, **20**, 457 [*J. Org. Chem.* USSR, 1984, 20, (Engl. Transl.)].
16. R. F. Heck and J. P. Nolley, *J. Org. Chem.*, 37, 2320.
17. C. Ametore, E. Carre, A. Jutand, M. A. M'Barki, and G. Meyer, *Organometallics*, 1995, **14**, 5605.
18. V. V. Grushin and H. Alper, *Organometallics*, 1993, **12**, 1890.
19. T. Yoahida, T. Okano, and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, 1976, 993.
20. T. A. Stephenson, S. M. Morehouse, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
21. A. O. King and E. Negishi, *J. Org. Chem.*, 1978, **43**, 358.
22. S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 1958, 276.

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Interaction of rhenium hydride (η^5-C_5Me_5)ReH(CO)(NO) with fluorinated alcohols

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The interaction between the fluorinated alcohols R^FOH ($R^F = (CF_3)_2CH$ and $(CF_3)_3C$) and rhenium hydride (η^5-C_5Me_5)ReH(CO)(NO) in hexane and liquid freon was studied in a wide temperature range by IR and ^1H NMR methods, respectively. The formation of hydrogen-bonded complexes of two types, ReH...HOR^F and NO...HOR^F, was established. The hydride signal in the ^1H NMR spectra at 96 K splits into two signals (at $\delta = -7.54$ and -8.87) corresponding to the free ReH and the ReH...HO complex, respectively.

Key words: hydrogen bond, hydrides of transition metals, molecular spectroscopy.

It has been shown that an unusual type of intermolecular hydrogen bond $MH^{\delta-}...H^{\delta+}X$ exists in the interaction of proton donors with tungsten hydrides $WH(CO)_2(NO)L_2$ in solution[1a] and in the interaction of rhenium polyhydride $ReH_5(PR_3)_3$ with indole in the crystal.[1b] In this work, the first results of IR and

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^{1}H NMR studies of the formation of hydrogen bonds by rhenium hydride Cp*ReH(CO)(NO) (Cp* = η^5-C_5Me_5) (**1**) with the fluorinated alcohols $(CF_3)_2CHOH$ and $(CF_3)_3COH$ in hexane (IR) and liquid freon ($CDF_3/CDClF_2$) (^{1}H NMR) in a wide temperature range have been reported. Hydride **1** reacts with strong acids to form a dihydrogen complex, stable at low temperature.[2] Our interest was focussed on the conditions of the formation of the hydrogen bond with the hydride hydrogen.

Experimental

Hydride Cp*Re(CO)(NO)H was synthesized following the procedures[3—5] developed for cyclopentadienyl analogs. IR (hexane), ν/cm^{-1}: 1956 (CO), 1695 (NO), 3375 (2 νNO). ^{1}H NMR (CD_2Cl_2), δ: 2.23 (s, 15 H), −7.59 (s, 1 H).

IR spectra were recorded on Specord M80 and Specord M82 spectrophotometers in hexane at concentrations in the 10^{-4}—10^{-2} mol L^{-1} range in CaF_2 cells (d = 0.01—0.12 cm). Hexane was dehydrated and distilled, and the experiments were carried out under an argon atmosphere. A Carl Zeiss Jena cryostat, which allowed working in the temperature range from −190 to +250 °C, was used for the low-temperature measurements of the spectra of the solutions. A liquid nitrogen flow was used for cooling, and the thermostating accuracy was ±1 °C.

^{1}H NMR spectra were recorded on a Bruker AMX 500 spectrometer at a frequency of 500 MHz. The synthesis of the mixture of deuterated freons CDF_3/CDF_2Cl (1 : 1) from $CDCl_3$ and the preparation of the samples *in vacuo* were performed according to known procedures.[6]

Results and Discussion

A decrease in the intensities of the νOH_{free} bands and the appearance of new broad bands of hydroxyl groups bonded by a hydrogen bond is observed in the IR spectrum of **1** in the region of the stretching vibrations of proton donors. These new bands are shifted to the low-frequency region. As in the case of conventional hydrogen bonds, the shift values ($\Delta\nu = \nu OH_{free} - \nu OH_{bond}$) increase as the strength of the proton donor increases and are equal to 211 and 307 cm^{-1} for $(CF_3)_2CHOH$ and $(CF_3)_3COH$, respectively.

To localize the site of the formation of the hydrogen bond, the IR spectra in the region of the stretching vibrations of ligands of complex **1** (2100—1500 cm^{-1}) were investigated in the presence of proton donors in the temperature range from 190 to 290 K. The observed high-frequency shift of the νCO band (νCO_{free} = 1956 cm^{-1}, νCO_{bond} = 1969 cm^{-1}) is evidence for the formation of a hydrogen-bonded complex with no coordination to the oxygen atom of the carbonyl ligand[7] (as in the case of tungsten hydrides[1a]). However, a more complicated spectral picture (Fig. 1) is observed in the region of the stretching vibrations of the NO group. The intensity of the initial νNO_{free} band at 1695 cm^{-1} is decreased and a high-frequency shoulder (νNO(1) = 1710 cm^{-1}) as well as broad νNO(2) bands shifted to the low-frequency region appear at room temperature in the presence of R^{F}OH. The position of the νNO(2) bands depends on the strength of the proton donor and is 1655 and 1644 cm^{-1} in the presence of $(CF_3)_2CHOH$ and $(CF_3)_3COH$, respectively. Such a low-frequency shift is characteristic of the formation of hydrogen-bonded complexes in which the oxygen atom of the nitroso group is the coordination center.[8] The intensities of the initial bands of the CO and NO groups decrease while those of the bands of hydrogen-bonded complexes increase as temperature decreases to 190 K. These results allow us to conclude that hydrogen-bonded complexes of two types are formed in the interaction of **1** with fluorinated alcohols. In the first case, the oxygen atom of the nitroso group is bonded to the hydroxyl hydrogen (ROH...ON—Re), in the second one (as could be expected) the hydride hydrogen atom is bonded to the hydroxyl hydrogen (ROH...H—Re). The value of the high-frequency shift νNO(1) ($\Delta\nu$ = +15 cm^{-1}) is close to that observed in the complex R^{F}OH...HW.[1a]

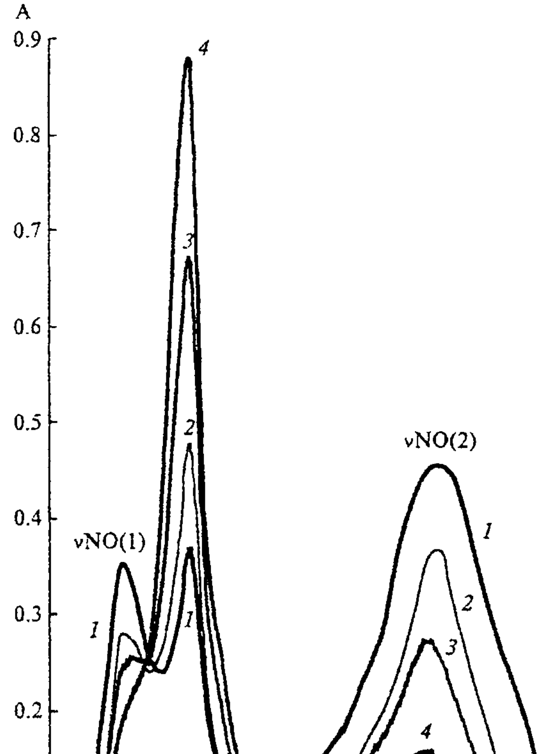

Fig. 1. IR spectra (the νNO region) of hydride Cp*Re(CO)(NO)H (c = 0.003 mol L^{-1}) in the presence of $(CF_3)_3COH$ (c = 0.030 mol L^{-1}) in hexane at temperatures: 220 (*1*), 240 (*2*), 260 (*3*), and 290 K (*4*).

Unfortunately, unlike the νWH band, the νReH band is not detected in the IR spectra of hydride **1**.[1a] The evidence for the formation of a hydrogen bond of the ReH...HOR type was obtained in studying the interaction of **1** with $(CF_3)_3COH$ in liquid freon (CDF_2/CDF_2Cl) by the ^1H NMR method; the high effectiveness of using liquid freon at very low temperatures (down to 96 K) was shown previously in a study of hydrogen bonds with organic bases.[6] A high-field shift (by 0.60—0.82 ppm) of the signal of the hydride hydrogen ($\delta_{\text{init}} = -7.54$) that depended on the temperature and the amount of excess proton donor was observed in the spectra of **1** in the presence of $(CF_3)_3COH$ in the temperature range from 140 to 110 K. At 96 K, we succeeded for the first time in detecting splitting of the hydride signal into two signals (at δ −7.54 and −8.87) corresponding to free ReH and the ReH...HO complex, respectively. This proves that the formation of the hydrogen bond involves the hydride hydrogen. Note that in this case the signal of the OH group is split into three signals (at δ 5.6, 9.8, and 8.2) corresponding to the OH groups of the monomer, the OH...HRe complex, and the OH...ON complex, respectively.

Thus, rhenium hydride **1** forms hydrogen bonds of two types with R^FOH, namely, bonds with the oxygen atom of the NO group (NO...HO) and bonds with the hydride hydrogen (ReH...HO).

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References

1. (a) E. S. Shubina, N. V. Belkova, A. N. Krylov, E. V. Vorontsov, L. M. Epstein, D. G. Gusev, M. Niedermann, and H. Berke, *J. Am. Chem. Soc.*, 1996, **118**, 1105; (b) E. Peris, J. Wessel, B. P. Patel, and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1995, 2175.
2. M. S. Chinn, D. M. Heinekey, N. G. Payne, and C. D. Sofield, *Organometallics*, 1989, **8**, 1824.
3. A. T. Patton, C. E. Strouse, C. B. Knobler, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1984, **105**, 5804
4. N. E. Kolobova, I. A. Lobanova, V. I. Zdanovich, and P. V. Petrovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 935 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 707 (Engl. Transl.)].
5. I. A. Lobanova, V. I. Zdanovich, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 691 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 642 (Engl. Transl.)].
6. (a) N. S. Golubev and G. S. Denisov, *J. Mol. Struct.*, 1992, **270**, 263; (b) N. S. Golubev, S. N. Smirnov, V. A. Gindin, G. S. Denisov, H. Benedict, and H.-H. Limbach, *J. Am. Chem. Soc.*, 1994, **116**, 12055; (c) S. N. Smirnov, N. S. Golubev, G. S. Denisov, H. Benedict, P. Shah-Mohammedi, and H.-H. Limbach, *J. Am. Chem. Soc.*, 1996, **118**, 4094.
7. B. V. Lokshin, S. G. Kazaryan, and A. G. Ginzburg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 562 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37** (Engl. Transl.)].
8. B. V. Lokshin, S. G. Kazaryan, and A. G. Ginzburg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 948 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36** (Engl. Transl.)].

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One-step synthesis of α-hydroxy-α-azinylcyanoacetic esters from α-nitro derivatives of α-azinylcyanoacetic esters

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When boiled in aromatic hydrocarbons, solutions of α-nitro-α-azinylcyanoacetic esters of the pyrimidine, pyrazine, and *s*-triazine series gave the corresponding α-hydroxy derivatives of α-azinylcyanoacetic esters in high yields.

Key words: nitrocyanoacetic esters, hydroxycyanoacetic esters, pyrazine, pyrimidine, *s*-triazine, derivatives.

Previously, we have demonstrated that nitration of dihydroazinylidenecyanoacetic esters of the pyrimidine series, **1a—d**,[1] and of the pyrazine series, **1e**,[2] afforded α-hydroxy derivatives of α-azinylcyanoacetic esters **3a—e** in low yields along with α-nitro derivatives **2a—e**.

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