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SYNTHESIS OF DERIVATIVES OF PENTACARBONYLRHENIUM BROMIDE WITH *o*-SUBSTITUTED AZOBENZENES. THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(*o*-PHENYLAZOPHENOLATORHENIUM-(I) TRICARBONYL)

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Summary

New dimeric complexes of general formula $[Re(CO)_3C_6H_4(E)N{=}NPh]_2$ with E = O (I) and S (II) has been synthesized. The structure of I has been established by an X-ray study.

Results and discussion

The reaction of $BrRe(CO)_5$ with potassium salts of *o*-phenylazophenol, o-$C_6H_4(OH)N{=}NPh$, and *o*-phenylazophenylthiocyan, o-$C_6H_4(SCN)N{=}NPh$, in boiling dioxane leads to precipitation of KBr and formation of dimeric products of the general formula $[Re(CO)_3C_6H_4(E)N{=}NPh]_2$ with E = O (I) and S (II).

These products are crystalline orange-red solids, readily soluble in tetrahydrofuran (THF), chloroform, alcohols and insoluble in aliphatic hydrocarbons and diethyl ether. Absorption bands of $\nu(C{\equiv}O)$ stretches of terminal carbonyl groups in the IR spectra of both compounds correspond to a local C_{3v} symmetry of the $M(CO)_3$ fragment with a *fac*-configuration of CO groups at an octahedrally coordinated metal atom.

To determine the manner of *o*-phenylazophenol coordination by the Re atom we carried out an X-ray structural study of $[Re(CO)_3C_6H_4(O)N{=}NPh]_2$. A binuclear molecule of I is situated in the centre of symmetry and consists of two $Re(CO)_3C_6H_4(O)N{=}NPh$ fragments bonded with bridging oxygen atoms of chelating *o*-phenylazophenol ligands (Fig. 1). Each such ligand is tridentate being coordinated with Re atoms through O(4) and N(1) and forming a six-membered metallocycle. The O(4) atom is also symmetrically bonded to the second Re atom of the dimeric molecule. Bond lengths Re—O(4) and Re′—O(4) are 2.148(8) and 2.159(8) Å, respectively, i.e. they are close to the Re—N(1) bond length of 2.14(1) Å. Coordination of Re atoms is completed to distorted octahedral by

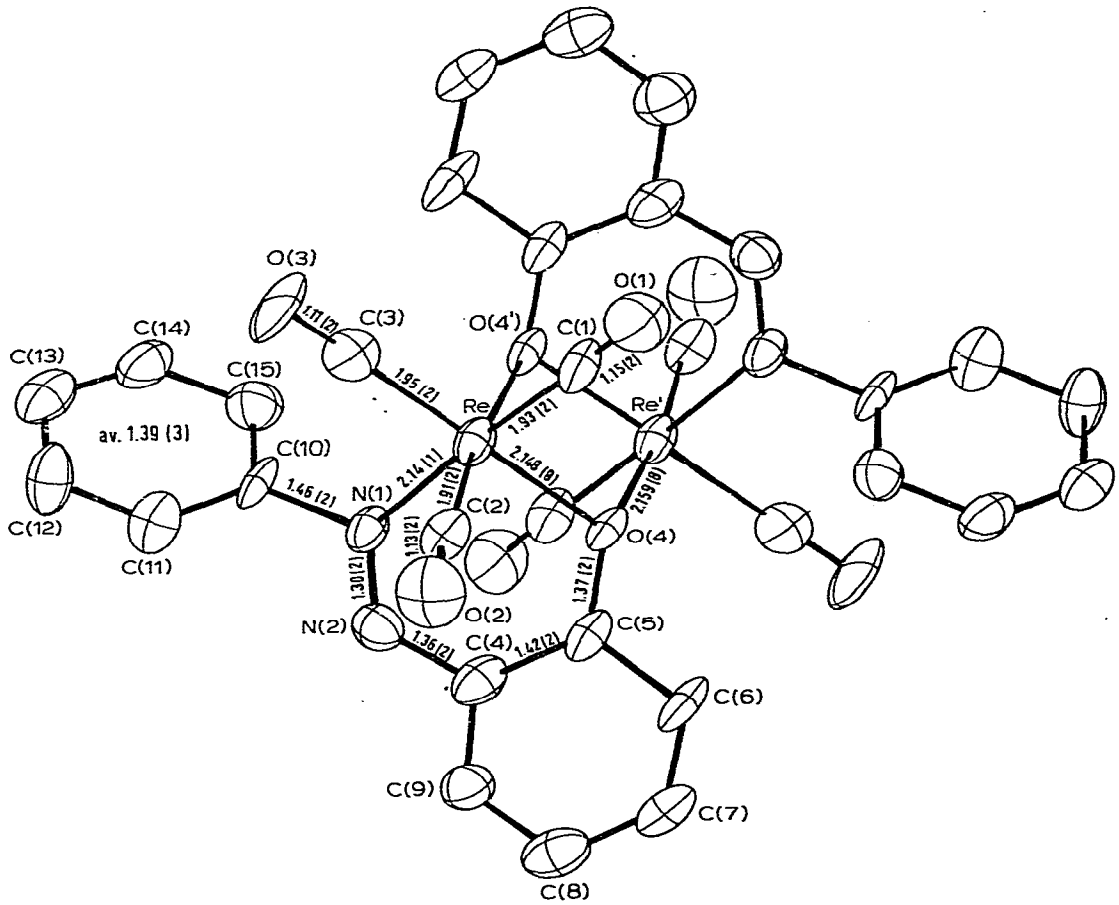

Fig. 1. ORTEP drawing of the molecule I with atom numbering and main bond lengths.

TABLE 1

BOND ANGLES

Angle	ω(°)	Angle	ω(°)	Angle	ω(°)
O(4')ReO(4)	73.3(3)	N(1)ReC(3)	94.7(5)	ReN(1)C(10)	118.3(8)
O(4')ReN(1)	86.2(4)	C(1)ReC(2)	89.2(6)	C(10)N(1)N(2)	113(1)
O(4')ReC(1)	92.9(5)	C(1)ReC(3)	88.3(6)	O(4)C(5)C(4)	123(1)
O(4')ReC(2)	171.7(7)	C(2)ReC(3)	88.8(6)	C(5)C(4)N(2)	126(1)
O(4')ReC(3)	99.3(5)	ReO(4)Re'	106.7(3)	C(4)N(2)N(1)	121(1)
O(4)ReN(1)	79.8(4)	Re'O(4)C(5)	119.3(7)	O(4)C(5)C(6)	119(1)
O(4)ReC(1)	97.1(5)	ReO(4)C(5)	117.8(7)	C(4)C(5)C(6)	118(1)
O(4)ReC(2)	98.4(5)	ReC(1)O(1)	175(1)	C(5)C(4)C(9)	120(1)
O(4)ReC(3)	171.0(5)	ReC(2)O(2)	177(1)	C(9)C(4)N(2)	114(1)
N(1)ReC(1)	176.9(5)	ReC(3)O(3)	178(1)	Average CCC(Ph)	120(1)
N(1)ReC(2)	91.3(5)	ReN(1)N(2)	128.6(8)		

three terminal carbonyl groups. *cis*-Angles around the Re atom vary within the limits 73.3 to 99.4° (Table 1). Average Re—CO and C—O bond lengths are equal to 1.93 and 1.13 Å respectively; the average Re—C—O angle equals to 177°. The six-membered metallocycle is non-planar, the Re and N(1) atoms are displaced from the O(4)C(5)C(4)N(2) plane by 1.274 and 0.325 Å respectively, and this plane forms a dihedral angle of 40.6° with the ReO(4)O(4') plane. The chelate-bridging configuration of *o*-phenylazophenol ligands, resulting in formation of a binuclear system (I), is similar to the configuration of Schiff bases in dimeric complexes of Cu^{II} [1—3] and Ni^{II} [4]. However, if in copper complexes the metal atom has a tetrahedrally distorted square-planar coordination, then in $[Ni\text{-}o\text{-}C_6H_3ClC(Ph)=N(CH_3)(NO_3)(C_2H_5OH)]_2$(III) [4] the Ni atom has a distorted octahedral coordination, i.e. similar to that found for the Re atoms in I. Taking into consideration the difference $\Delta \approx 0.16$ Å between covalent radii of Re (1.51 Å) and Ni (1.35 Å) [5] the bond lengths M—O and M—N in I and III practically coincide (Ni—O and Ni—N distances in III are equal to 2.015 Å).

Experimental

Solvents used were dried and distilled. *o*-Phenylazophenol and *o*-phenylazophenylthiocyan were prepared according to published procedures [6,7]. IR spectra were recorded with an UR-20 spectrometer (Zeiss, Jena).

a) A mixture of $BrRe(CO)_5$ (1.0 g, 2.47 mmol) and $o\text{-}C_6H_4(OK)N=NC_6H_5$ (0.58 g, 2.47 mmol) was refluxed in 20 ml of dioxane for 5 h. The solution was then filtered from a KBr precipitate and evaporated in vacuo. The orange-red

TABLE 2

ATOMIC COORDINATES (X10^3, FOR Re X 10^5) AND PARAMETERS (X10, FOR Re X 10^2) OF AN ANISOTROPIC TEMPERATURE FACTOR IN THE FORM $T = \exp(-1/4(B_{11}h^2a^{*2} + \ldots 2B_{12}hka^*b^* + \ldots))$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	38789(5)	10733(4)	1916(3)	344(3)	172(3)	168(3)	22(1)	52(2)	13(1)
O(1)	536(1)	295(1)	—84(1)	67(6)	31(5)	38(5)	—17(4)	13(5)	9(4)
O(2)	125(1)	194(1)	—93(1)	46(5)	56(7)	53(6)	17(5)	3(5)	10(5)
O(3)	346(1)	272(1)	187(1)	77(7)	43(6)	32(5)	2(5)	15(5)	—22(5)
O(4)	427(1)	—27(1)	—81(1)	30(3)	24(4)	12(3)	1(3)	3(3)	—3(3)
N(1)	282(1)	—26(1)	85(1)	35(5)	20(4)	17(4)	—5(4)	8(3)	0(3)
N(2)	211(1)	—107(1)	40(1)	23(4)	35(6)	30(6)	2(4)	4(4)	1(4)
C(1)	486(2)	222(1)	—46(1)	45(7)	33(6)	21(6)	2(5)	9(5)	—4(5)
C(2)	221(1)	161(1)	—50(1)	42(6)	26(6)	26(6)	12(5)	0(5)	3(5)
C(3)	364(2)	213(1)	127(1)	43(6)	27(6)	31(7)	—1(5)	3(5)	5(5)
C(4)	216(2)	—129(1)	—58(1)	43(6)	19(5)	26(6)	—1(5)	1(5)	—2(5)
C(5)	318(1)	—91(1)	—118(1)	41(6)	22(5)	15(5)	3(4)	5(4)	—2(4)
C(6)	311(2)	—128(1)	—219(1)	67(9)	28(6)	15(6)	0(6)	6(5)	—6(5)
C(7)	202(2)	—191(1)	—257(1)	52(7)	30(6)	22(5)	9(6)	—6(5)	—8(5)
C(8)	99(2)	—228(1)	—196(1)	43(7)	28(6)	39(7)	6(5)	—7(5)	—7(6)
C(9)	114(1)	—199(1)	—99(1)	38(6)	34(7)	34(7)	—2(5)	2(5)	—5(5)
C(10)	269(1)	—22(1)	193(1)	52(7)	18(5)	10(4)	—3(5)	8(4)	—1(4)
C(11)	376(1)	—41(1)	260(1)	33(6)	43(7)	28(6)	—3(5)	6(5)	4(6)
C(12)	359(2)	—33(1)	363(1)	49(7)	38(7)	21(6)	—11(6)	2(5)	—1(5)
C(13)	240(2)	—3(1)	396(1)	56(8)	21(5)	24(6)	—3(5)	4(5)	0(4)
C(14)	127(2)	21(2)	325(1)	60(8)	55(9)	25(6)	9(7)	19(6)	9(6)
C(15)	143(2)	10(1)	224(1)	49(7)	37(7)	26(6)	11(6)	8(5)	2(5)

TABLE 3

EQUATIONS $Ax + By + Cz = D$ OF PLANES OF SOME MOLECULAR FRAGMENTS AND ATOMIC DEVIATIONS (Å) FROM THESE PLANES

Plane	Atoms								A	B	C	D
1	Re	O(4)	O(4)						−0.1521	0.6042	−0.7822	0.0000
	0.000	0.000	0.000									
2	O(4)	C(5)	C(4)	N(2)	Re [a]	N(1) [a]			−0.5130	0.8264	−0.2320	−2.2161
	−0.001	0.002	−0.002	0.001	1.274	0.325						
3	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	O(4) [a]	N(2) [a]	−0.5226	0.8138	−0.2544	−2.2170
	0.014	0.021	−0.035	0.014	0.023	−0.037	−0.013	−0.013				
4	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)	N(1) [a]		0.2751	0.9611	−0.0237	0.3566
	−0.009	0.016	−0.007	−0.007	0.014	−0.006	0.048					

[a] Atoms not included in calculation of a corresponding plane equation. Angles between planes: 1/2 = 40.6; 1/3 = 39.6; 1/4 = 56.1; 2/3 = 1.6; 2/4 = 48.6; 3/4 = 49.9°.

crystalline residue was recrystallized from a chloroform/n-hexane mixture. The yield of I was 0.88 g (76%), m.p. 315—317°C (dec.), ν(C≡O) (cm^{-1}, in $CHCl_3$) 2035s, 1938s, 1920s. Anal.: Found: C, 38.25; H, 2.18; N, 6.15; Re, 40.12. $C_{15}H_9N_2O_4Re$ calcd.: C, 38.50; H, 1.94; N, 6.02; Re, 39.84%.

b) The reaction of $BrRe(CO)_5$ (1.0 g, 2.47 mmol) and o-$C_6H_4(SK)N{=}NC_6H_5$ (0.62 g, 2.47 mmol) under conditions described above yielded 0.85 g (71%) of orange-red crystals of II, m.p. 308—309°C (dec.), ν(C≡O) (cm^{-1}, in $CHCl_3$) 2046s, 1940s, 1922s. Anal.: Found: C, 37.16; H, 2.01; N, 5.95; S, 6.80; Re, 38.92. $C_{15}H_9N_2O_3SRe$ calcd.: C, 37.25; H, 1.88; N, 5.82; S, 6.62; Re, 38.50%.

The X-ray study

A diffraction experiment was carried out with a four-circle automatic diffractometer Syntex $P2_1$ (λMo—K_α, graphite monochromator, $2° \leqslant 2\theta \leqslant 60°$, 2700 reflections with $F^2 \geqslant 2\sigma$). The structure was solved by the heavy atom method and refined by full-matrix anisotropic least squares to $R = 0.070$ ($R_w = 0.103$). Crystals of I are monoclinic, a 9.832(1), b 11.960(1), c 13.365(1) Å, β 95.50(1)°, V 1564.5(4) $Å^3$, $D_m = 1.98$, $D_c = 1.99$ g/cm^3 for $Z = 2$, space group $P2_1/c$. Main bond angles are given in Table 1, atomic coordinates and temperature factors in Table 2, and equations of the planes of some molecular fragments in Table 3.

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