Inorganica Chimica Acta, 25 (1977) L97–L99

Reactions of Pentacarbonylrhenium Bromide with α- and β-Alanines

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Received October 3, 1977

The study of aminoacid complexes of transition metals as models for understanding the many biocatalytic processes requiring metal atoms is most interesting [1]. However, very little attention has been paid to the preparation of organometallic compounds with aminoacids as ligands; there were reported only some π-organic complexes of molybdenum [2] and tungsten [3, 4]. No complexes have been described containing both aminoacid and carbonyl ligands attached to the transition metal atom.

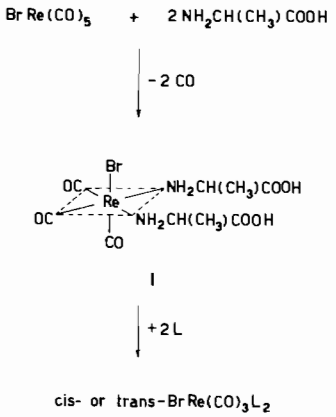
Herein we describe the reactions of pentacarbonylrhenium bromide, $BrRe(CO)_5$, with α- and β-alanines and some properties of the products.

Results and Discussion

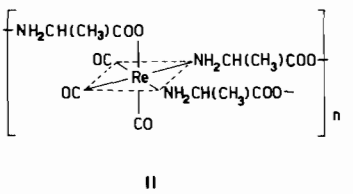
The reaction of $BrRe(CO)_5$ with α-alanine in boiling dioxane gives a yellow halogen-containing oil (I), soluble in water, alcohols, dioxane and tetrahydrofuran (THF) and insoluble in aliphatic hydrocarbons and diethyl ether. Its IR spectrum in THF shows three ν(C=O) bands at 2021s, 1909vs and 1890vs cm^{-1} and ν(COO) bands at 1620m and 1400w cm^{-1}. Compound (I) contains non-stoichiometric amounts of the solvent molecules, which could not be removed under prolonged heating at 100–150 °C *in vacuo*.

The reactions of (I) with such nucleophilic reagents as triphenylphosphine, triphenylphosphite and pyridine in dioxane occur very easily and lead to the abstraction of a free aminoacid and formation of well-known [5] disubstituted tricarbonylrhenium bromides, $BrRe(CO)_3L_2$. The nature of the final products was confirmed by elemental analyses and comparison of their IR spectra with those recorded previously [6]. Whereas pyridine and triphenylphosphine give *cis*-substituted complexes, the reaction with $P(OPh)_3$ gives *trans*-$BrRe(CO)_3[P(OPh)_3]_2$.

The resulting data suggest that in the reaction between $BrRe(CO)_5$ and α-alanine, the latter substitutes the carbon monoxide molecules by coordination with the metal atom through its nitrogen atom. The ν(C≡O) pattern in the IR spectrum of (I) indicates that the aminoacid ligands are in *cis*-configuration:

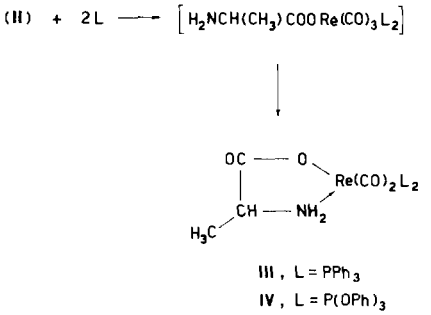


Both the treatment of (I) with methanolic KOH and the reaction between $BrRe(CO)_5$ and potassium salt of α-alanine lead to the precipitation of KBr and preparation of the polymeric product of the formula $[Re(CO)_3(NH_2CH(CH_3)COO)_2]_n$, (II), as an amorphous light-yellow compound, softening at 70–100 °C, well soluble in water, alcohols, dioxane and THF and insoluble in aliphatic hydrocarbons, benzene and diethyl ether. Its IR spectrum shows the ν(C≡O) bands at 2025s, 1905vs cm^{-1} (in THF) and ν(COO) bands at 1655s,br and 1390w cm^{-1} (KBr pellets). We suppose the possible structure for (II) consists of $Re(CO)_3$ fragments bridging aminoacid ligands bound with rhenium atoms through both its NH_2- and COO-groups:



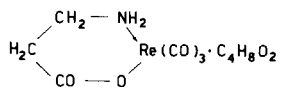
The action of triphenylphosphine and triphenylphosphite on (II) produces the dicarbonyl aminoacid derivatives of the formulae $NH_2CH(CH_3)COORe(CO)_2L_2$, (III), L = PPh_3, m.p. 274–276 °C, ν(C≡O) 1940s and 1860s cm^{-1}, ν(COO) 1640s and 1380w cm^{-1} (in $CHCl_3$); (IV), L = $P(OPh)_3$, m.p. 170–172 °C, ν(C≡O) 1980s and 1900s cm^{-1}, ν(COO) 1640s and 1400w cm^{-1} (in $CHCl_3$). These compounds are soluble in chloroform, dioxane and THF, and insoluble in alcohols, acetone and water. Apparently, the action of the nucleophilic molecules on (II) causes the breaking of the Re–N bonds and forma-

tion in the first stage of tricarbonyl aminocarboxylate intermediates, which then convert under reaction conditions into the stable dicarbonyl chelate complexes by intramolecular displacement of CO-group by NH_2-group of the aminocarboxylate fragment:



III, L = PPh_3
IV, L = $P(OPh)_3$

The reaction of $BrRe(CO)_5$ with β-alanine occurs in two directions. The main product is the yellow intractable oil, similar to (I): ν(C≡O) 2038s, 1910vs cm^{-1}, ν(COO) 1620m, br., 1395w cm^{-1} (in THF), which reacts with PPh_3 to give *cis*-$BrRe(CO)_3(PPh_3)_2$. The second product is the white crystalline chelate complex (V), isolated as an adduct with one molecule of dioxane with 20% yield.



V

Complex (V) may be prepared in quantitative yield when $BrRe(CO)_5$ reacts with the salt of β-alanine in dioxane. It is insoluble in most common solvents and does not melt below 300 °C. Its IR spectrum in CH_3CN shows the bands of ν(C≡O) at 2036s, 1915s and 1895s cm^{-1} and ν(COO) at 1585m and 1400w cm^{-1}.

Experimental

In this work the commercial aminoacids (Reanal, Budapest, Hungary) were used. The solvents were dried and distilled before use. IR spectra were recorded on a UR-20 (Zeiss, Jena) spectrometer.

Reactions with α-Alanine

a) $BrRe(CO)_5$ (0.406 g, 1.0 mmol) and *d,l*-α-alanine (0.200 g, 2.25 mmol) were refluxed in 20 ml of dioxane for 4 h. The reaction was followed by IR spectroscopy. The resulting red–orange solution was filtered, concentrated to *ca.* 5 ml and 15 ml of n-hexane were added. The yellow oil (I) was separated. The attempts to prepare (I) in analytically pure grade were unsuccessful. According to the analytical data the Re/N ratio was 1:2.

b) To the solution of (I), obtained as described in *a*, PPh_3 (0.524 g, 2.0 mmol) was added. After refluxing for 2 h, the solvent was removed *in vacuo*, and the residue was crystallized from chloroform–n-hexane mixture. The yield of *cis*-$BrRe(CO)_3(PPh_3)_2$ was 0.75 g (86%), m.p. 286–288 °C (dec.), ν(C≡O) (in $CHCl_3$) 2043s, 1962s, 1910s cm^{-1}. Found: C 53.78, H 3.81, P 6.83, Br 8.82, Re 20.55%. $C_{39}H_{30}P_2O_3BrRe$ calcd.: C 53.55, H 3.45, P 7.08, Br 9.13, Re 21.28%.

c) To the solution of (I), prepared as described in *a*, $P(OPh)_3$ (0.62 g, 2.0 mmol) was added. After 2 h of refluxing from the reaction mixture was isolated 0.78 g (80%) of *trans*-$BrRe(CO)_3[P(OPh)_3]_2$, m.p. 174–176 °C, ν(C≡O) (in $CHCl_3$) 2090w, 2003vs and 1947s cm^{-1}. Found: C 48.08, H 3.30, P 6.62, Br 8.62, Re 18.70%. $C_{39}H_{30}P_2O_9BrRe$ calcd.: C 48.25, H 3.11, P 6.39, Br 8.23, Re 19.28%.

d) Pyridine (0.35 g, 2.8 mmol) was added to the solution of (I), prepared as in *a*. After stirring at 20 °C for 0.5 h, the colorless crystals were filtered off, washed with aqueous methanol and ether and dried. The yield of *cis*-$BrRe(CO)_3Py_2$ was 0.5 g (95%), ν(C≡O) (in $CHCl_3$) 2040s, 1935s and 1905s cm^{-1}. Found: C 31.03, H 2.33, N 5.74, Br 15.74, Re 36.66%, $C_{13}H_{10}N_2O_3BrRe$ calcd.: C 30.72, H 1.98, N 5.51, Br 15.72, Re 36.63%.

e) The solution of 0.15 g KOH in 10 ml of methanol was added to the solution of (I), prepared as in *a* from 1.0 g (2.47 mmol) of $BrRe(CO)_5$ and 0.425 g (5.0 mmol) of α-alanine in 20 ml of dioxane. After boiling for 1 h, the precipitate of KBr was formed. The reaction mixture was filtered and the filtrate was evaporated *in vacuo* to yield *ca.* 1 g of amorphous light-yellow (II). Found: C 23.41, H 3.00, N 5.81, Re 41.41%. $C_9H_{12}N_2O_7Re$ calcd.: C 24.22, H 2.72, N 6.29, Re 41.71%.

Reactions with $NH_2CH(CH_3)COOK$

a) The mixture of $BrRe(CO)_5$ (1.0 g, 2.47 mmol) and $NH_2CH(CH_3)COOK$ (0.64 g, 5.0 mmol) was refluxed in 20 ml of dioxane for 4 h. Then the solution was filtered from the precipitate of KBr and evaporated *in vacuo* to give 0.95 g (85%) of (II), identical with that prepared in 1*e*.

b) To a solution of 0.5 g of (II) in 20 ml of dioxane PPh_3 (0.70 g, 2.66 mmol) was added. The mixture was refluxed for 3 h, then evaporated and the residue was crystallized from chloroform–n-hexane mixture to yield 0.4 g (42%) of the colorless crystals of (III). Found: C 57.23, H 4.35, P 7.15, Re 21.68%. $C_{41}H_{36}NP_2O_4Re$ calcd.: C 57.60, H 4.22, P 7.02, Re 21.78%.

c) The reaction of 0.5 g of (II) and $P(OPh)_3$ (0.75 g, 2.42 mmol) under conditions described in *b*, yielded 0.6 g (54%) of the pale crystals of (IV). Found: C 51.62, H 4.11, P 6.87, Re 19.66%. $C_{41}H_{36}NP_2O_{10}Re$ calcd.: C 51.79, H 3.80, P 6.52, Re 19.58%.

Reactions with β-Alanine

a) $BrRe(CO)_5$ (1.0 g, 2.47 mmol) and β-alanine (0.425 g, 5.0 mmol) were refluxed in 20 ml of dioxane for 4 h to give a light-yellow solution and a bright colorless crystalline residue. The crystals were filtered off, washed with aqueous methanol and ether and dried. The yield of (V) was 0.21 g (19%). Found: C 26.53, H 3.19, Re 41.21%. $C_{10}H_{14}NO_7Re$ calcd.: C 26.91, H 3.16, Re 41.71%.

The evaporation of the filtrate gave a light-yellow intractable oil, which could not be obtained in analytically pure grade. This oil was redissolved in 20 ml of dioxane and PPh_3 (1.32 g, 5.0 mmol) was added. Refluxing of this mixture for 2 h gave 1.2 g (54%) of *cis*-$BrRe(CO)_3(PPh_3)_2$, isolated as described above.

b) The reaction of $BrRe(CO)_5$ (0.5 g, 1.23 mmol) and $NH_2CH_2CH_2COOK$ (0.32 g, 2.5 mmol) in 20 ml of boiling dioxane for 3 h gave 0.47 g (90%) of (V).

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