# trans-4-STILBENECARBOXYLATOALKYLPENTAAMMINECOBALT(III) PERCHLORATES: SYNTHESIS AND INTRAMOLECULAR ENERGY TRANSFER\*

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Dedicated to Professor Vaclav Horak.

Three homologs of *trans*-4-stilbenecarboxylic acid, viz., *trans*-4-stilbeneacetic acid (**18**),  $\beta$ -(*trans*-4-stilbene)propionic acid (**19**), and  $\gamma$ -(*trans*-4-stilbene)butyric acid (**20**) were synthesized and, together with the parent *trans*-4-stilbenecarboxylic acid, used to obtain the corresponding  $[\omega$ -(*trans*-4-stilbene)carboxylatoal-kylpentaamminecobalt(III) complexes,  $[(PhCH=CHC_6H_4(CH_2)_nCOO)Co(NH_3)_5]^{2+}$  (**1**–**4**), where n = 0, 1, 2, or 3. Fluorescence studies suggest that an intramolecular excitation energy transfer occurs from the first excited singlet state of the ligand to the metal giving rise to a charge-transfer triplet-excited state of the complex, based on the analogy with previous work on complex **1**. The efficiency of the energy transfer seems to decrease with increasing number of the methylene groups in the ligand.

**Key words:** *trans*-4-Stilbenecarboxylatoalkylpentaamminecobalt(III) complexes; Energy transfer; Electronic spectra; Fluorescence; LMCT.

The existence of intramolecular energy transfer and its importance in photochemistry have been clearly documented in the chemical literature and the examples include or-

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ganic, organometallic, and inorganic coordination compounds<sup>1-9</sup>. A typical example is a molecule consisting of two aromatic or heteroaromatic groups,  $Ar^1$  and  $Ar^2$ , separated from each other by a flexible or a rigid chain, X, i.e.,  $Ar^1-X-Ar^2$ . In such compounds, the two groups  $Ar^1$  and  $Ar^2$  can be excited separately by choosing the appropriate excitation wavelengths. The possible intramolecular energy transfer between the two units  $Ar^1$  and  $Ar^2$  manifests itself in changes of the intensities of emission (fluorescence or phosphorescence) that are characteristic of  $Ar^1$  and  $Ar^2$  (refs<sup>10–17</sup>). The flexibility or rigidity of the connecting chain X plays an important role as it determines the effective distance between the two units and the efficiency of the transfer depends on their mutual distance.

It is well known that electronic excitation energy can be transferred over distances of the order of 30 Å or more<sup>18,19</sup>. According to Förster, the transfer takes place via a dipole–dipole resonance interaction between the energy donor and acceptor chromophores<sup>20,21</sup>. If one considers an excitation energy transfer between two similar molecules in a solution, the critical distance between molecules at which the transfer still occurs can be evaluated from the absorption and emission spectra and the lifetimes of excited states of the respective compounds. Förster has shown that, in the case of weak coupling, the transfer rate constant is proportional to the inverse sixth power of the distance between the groups,  $r^{-6}$  (refs<sup>20,21</sup>). The rate of energy transfer is a function of the respective orientation of the groups, the refractive index of the solvent, and the overlap of the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor.

An instructive example is a study of a series of peptides carried out by Stryer and Haugland<sup>23</sup>. The compounds under study were the oligomers of poly-(*S*)-proline (n = 1 to 12) as spacers of defined length separating the energy donor and acceptor by fixed distances from 12 to 46 Å. The energy donor used was an  $\alpha$ -naphthyl group at the carboxyl end of the peptide and the energy acceptor was a dansyl (1-dimethylamino-5-naphthalenesulfonyl) group at the imino end. The dependence of the efficiency of energy transfer on the distance was in an excellent agreement with Förster's  $r^{-6}$  relationship.

Another similar example involves compounds of the type  $C_{10}H_7(CH_2)_nC_{14}H_9$  ( $C_{10}H_7 =$  naphthyl;  $C_{14}H_9 =$  anthryl)<sup>10</sup>. The irradiation of the naphthyl group present in these compounds leads to a fluorescent emission characteristic of the anthracene moiety. A number of other similar cases are known<sup>11–17</sup>.

While there are numerous studies available on intramolecular energy transfer in organic photochemistry, intramolecular electronic excitation energy transfer in coordination compounds has been studied to a lesser extent. If, within a complex system containing a transition metal ion, one part of the molecule acts as a donor and another part as an acceptor, an intramolecular transfer of excitation energy can occur. For instance, an excitation energy transfer can take place between an organic ligand and a central transition metal ion. 344

Some transition metal chelates and metal carbonyls have been reported as quenchers of organic triplet excited states; however, at least in some cases this effect may be due to the catalysis of the radiationless return of the energy donor to its ground state. A very interesting example of intramolecular energy transfer has been reported in the case of certain rare earth chelates<sup>23,24</sup> where excitation in the region of ligand absorption results in emission from rare earth ion levels. Some evidence supporting energy transfer in the opposite direction has also been found<sup>25</sup>.

In the solid complex  $[Cr(urea)_6][Cr(CN)_6]$ , the low-temperature irradiation of the cation absorption band leads to emission which is characteristic of the anion<sup>26</sup>. At low temperatures, but not in the rigid media, organic donors were found to sensitize the characteristic phosphorescence of  $[Cr(NCS)_6]^{3-}$  (benzil was one of the reported sensitizers)<sup>27</sup>.

In principle, excitation energy transfer can lead not only to spectroscopic situations in which the transfer results in emission of radiation but to chemical reactions as well. This latter possibility represents an extremely valuable approach in studies of photochemical reactions of coordination compounds. A few typical examples of photochemical reactions occurring as a result of an intermolecular or intramolecular excitation energy transfer will be given.

It has been determined that organic senzitizers induce the photoaquation of aqueous Reinecke sals, trans-[Cr(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>4</sub>]<sup>-</sup>, and [Cr(NH<sub>3</sub>)<sub>5</sub>(NCS)]<sup>2+</sup> (ref.<sup>28</sup>). Intermolecular energy transfer has been shown to occur in redox photodecomposition of cobalt(III) ammines with organic compounds known to have relatively stable triplet excited states (benzil, *trans*-4-stilbenecarboxylic acid, benzophenone, biacetyl)<sup>29</sup>. It is assumed that an energy transfer takes place between the lowest triplet state of the donor and a charge transfer triplet state of the complex. Similar results were obtained by two other groups of workers<sup>30,31</sup>.

Also, the biacetyl-sensitized  $[Cr(CN)_6]^{3-}$  photoaquation was studied<sup>32</sup> as well as the naphthalene-sensitized redox photodecomposition of  $[Co(NH_3)_6]^{3+}$  (ref.<sup>33</sup>). Other examples are available. In all the above-mentioned cases an *intermolecular* excitation energy transfer occurs. Even more interesting are, of course, situations where an *intra-molecular* excitation energy transfer leads to a photochemical reaction. Such an intra-molecular excitation energy transfer was observed in aqueous solutions of the (*trans*-4-stilbene)carboxylatopentaamminecobalt(III) ion,  $[Co(NH_3)_5(TSC)]^{2+}$  (where TSC = *trans*-4-stilbenecarboxylate) (**1**; ref.<sup>34</sup>).

It is likely that the energy transfer generates a charge-transfer triplet-excited state of the complex which subsequently undergoes redox decomposition. The suggested process is intersystem crossing from the first excited singlet state of the organic ligand.

The goal of the present study was to synthesize a series of homologs of the above complex 1 studied by Adamson, Vogler, and Lantzke<sup>34</sup> (with a varying number of methylene groups between the stilbene unit and the carboxylate group, 2-4), and to

explore intramolecular energy transfer in these complex salts, as a function of distance of the stilbene unit from the cobalt ion.



The geometry of the complexes is shown below (1-4, R = an organic group constituting the remainder of the respective carboxylic acid).



# EXPERIMENTAL

Aquapentaamminecobalt(III) chloride was reagent grade and was obtained from Alfa Products, Ward Hill, MA, U.S.A. All other chemicals used in the work were commercial products as well. Aquapentaamminecobalt(III) perchlorate was prepared according to the literature<sup>35</sup>. Benzaldehyde was purified by distillation under nitrogen at reduced pressure. All solvents were purified and/or dried using the standard procedures described in the literature.

Infrared spectra were recorded on a Perkin–Elmer model 710A spectrophotometer in pressed potassium bromide disks ( $\tilde{v}$  in cm<sup>-1</sup>). Electronic absorption spectra were measured on a Beckman DK-25 spectrophotometer in methanol–water (1 : 1, v/v) or ethanol–water (1 : 1, v/v). Fluorescence emission spectra were obtained with an Aminco–Bowman 4-8911 spectrophotofluorometer in the same solvents. Photochemical reactions were carried out in an immersion-well type photochemical reactor (Ace Glass) equipped with a medium-pressure mercury lamp (450 W) and a Rayonet model RPR-208 preparative photochemical reactor, at 300 nm.

Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Elemental microanalyses were performed by the microanalytical laboratory of the Université de Droit, d'Économie et des Sciences d'Aix-Marseille, Saint-Jérôme, Marseille, France.

# Synthesis of p-Chloromethylphenyl Substituted Carboxylic Acids 8-10

*p-Chloromethylphenylacetic acid* (8) (*method A*)<sup>36</sup>. Formalin (40% aqueous formaldehyde, 165 g, 2.2 mol) was added to a mixture of phenylacetic acid (5; 48 g, 0.35 mol) and zinc chloride (18 g, 0.13 mol) and hydrogen gas was passed through the solution at 75–80 °C for 16 h. The usual workup of the reaction mixture and recrystallization of the crude product from chloroform–carbon tetrachloride (1 : 1, v/v) yielded 19.2 g (30%) of *p*-chloromethylphenylacetic acid (8), m.p. 152–153 °C (ref.<sup>36</sup> gives m.p. 152–153 °C).

β-(*p*-*Chloromethylphenyl*)*propionic acid* (9) (*method A*). This compound was prepared from βphenylpropionic acid (6) in the same manner as described for the preparation of 8. Yield 28%; m.p. 117–118 °C (from carbon tetrachloride; ref.<sup>36</sup> gives m.p. 118–119 °C).

 $\gamma$ -(*p*-Chloromethylphenyl)butyric acid (10) (method A). This acid was obtained from  $\gamma$ -phenylbutyric acid (7) in the same fashion as described for 8. Yield 27%; m.p. 118–120 °C (from carbon tetrachloride; ref.<sup>36</sup> gives m.p. 121–122 °C).

The following characteristic frequencies were observed in the infrared spectra of the above acids, **8–10** (KBr disk): 3 050–2 950 (OH stretching), 1 700–1 675 (C=O stretching), 920–895 (OH deformation), 740–720 (C–Cl stretching).

*p-Chloromethylphenylacetic acid* (8) (*method B*)<sup>37</sup>. A mixture of dried phenylacetic acid (5; 1.36 g, 0.01 mol) and chloromethyl methyl ether (11; 2 ml, 2.12 g, 0.026 mol) was added dropwise during 0.5 h to stannic chloride (0.8 ml, 1.78 g, 0.0068 mol) cooled in an ice bath. The reaction mixture was stirred during the addition and then for an additional 1.5 h in an ice bath. The solution was poured into ice water (20 ml) and the white precipitate was filtered off, dried under reduced pressure, and recrystallized from chloroform to give 0.78 g (42%) of *p*-chloromethylphenylacetic acid (8), identical with the product obtained by method A. Additional recrystallization decreased the yield to 35%.

 $\beta$ -(*p*-Chloromethylphenyl)propionic acid (9) (yield 56%) and  $\gamma$ -(*p*-chloromethylphenyl)butyric acid (10) (yield 65%) were obtained by using method *B* with  $\beta$ -phenylpropionic acid (6) and  $\gamma$ -phenylbutyric acid (7), respectively, as the starting materials. After purification, the respective yields of the acids 9 and 10 were 45% and 52%.

### Preparation of Phosphonium Salts 12-14

p-(Carboxymethyl)benzyltriphenylphosphonium chloride (12). To a mixture of p-chloromethylphenylacetic acid (8; 26.3 g, 0.142 mol) and triphenylphosphine (37.3 g, 0.142 mol), dry benzene (30 ml) was added and the mixture was heated with stirring at 77–78 °C overnight. The precipitate was washed several times with dry benzene and dried over phosphorus pentoxide under reduced pressure at 90°C; yield 50.5 g (80%), m.p. 245–247 °C.

p-( $\beta$ -Carboxyethyl)benzyltriphenylphosphonium chloride (13). This compound was obtained in the same manner from 9 as the starting material. Yield 99%, m.p. 252–254 °C.

p-( $\gamma$ -Carboxypropyl)benzyltriphenylphosphonium chloride (14). This phosphonium salt was obtained from 10 in the same fashion as described for 12. Yield 75%, m.p. 209–213 °C.

The following characteristic frequencies were observed in the infrared spectra of the above phosphonium salts, **12–14** (KBr disk): 3 000–2 900 (OH stretching), 1 710–1 700 (C=O stretching), 910–860 (OH deformation), 750–740 (P–CH<sub>2</sub>, benzyl, stretching).

Homologs of trans-Stilbenecarboxylic Acid 18, 19 by Wittig Reaction<sup>38-40</sup>

*trans-4-Stilbeneacetic acid* (18). To a well-stirred suspension of 12 (15 g, 0.034 mol) in anhydrous dimethylformamide (34 ml), an excess of sodium methoxide (4 g, 0.077 mol) suspended in anhydrous dimethylformamide (22 ml) was added at 0–5 °C under nitrogen. The phosphorane intermediate (tan to dark orange) formed almost instantaneously. The mixture was stirred for another 30 min and benz-aldehyde (3.4 ml, 3.54 g, 0.033 mol) dissolved in anhydrous dimethylformamide (10 ml) was added dropwise so that the temperature of the reaction mixture did not exceed 30 °C. After a few minutes, the cooling bath was removed and the mixture was stirred for another 4 h at room temperature. Then it was poured into ice water (50 ml), the unreacted benzaldehyde and triphenylphosphine oxide were extracted into ether, and the aqueous layer was acidified with 3 mol/dm<sup>3</sup> HCl, extracted with ether, and the ether solution was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. Recrystallization from carbon tetrachloride and then from ethanol yielded 0.61 g (8%) of 15; m.p. 184–187 °C. This compound was identical in all respects with another sample of 18 prepared by the procedure described below (Wadsworth–Horner reaction).

*trans-4-Stilbenepropionic acid* (19). This compound was obtained in the same manner as above, with 13 as the starting material; yield 6%, m.p. 202-204 °C. An alternate method of preparation used phenyllithium instead of sodium methoxide, with ether as the solvent; the yield was 3%. This acid (19) was identical in all respects with a sample of the acid prepared by the procedure outlined below (Wadsworth–Horner reaction).

Preparation of Phosphonates 15–17 by Wadsworth–Horner Reaction<sup>41–43</sup>

*Diethyl p-(carboxymethyl)benzylphosphonate* (**15**). A mixture of (*p*-chloromethyl)phenylacetic acid (**8**; 2.7 g, 0.015 mol) and triethyl phosphite (2.6 ml, 2.5 g, 0.015 mol) was refluxed at 170–180 °C for 1 h and then cooled. Unreacted triethylphosphite was distilled off at 50 °C/1 333 Pa. The colorless liquid product was **15**; yield 4.18 g (97%),  $n_D^{23}$  1.4921.

Diethyl p-( $\beta$ -carboxyethyl)benzylphosphonate (16). This phosphonate was obtained similarly from 9; yield 96%,  $n_D^{23}$  1.4920.

*Diethyl p-(\gamma-carboxypropyl)benzylphosphonate* (17). This compound was synthesized in the same manner from 10; yield 95%,  $n_{D}^{23}$  1.4952.

The synthesized phosphonates **15–17** displayed the following characteristic frequencies in their infrared spectra (KBr disk): 3 005–2 995 (OH stretching), 1 730 (C=O stretching), 890–840 (OH deformation), 1 270–1 240 (P=O, free), 1 180–1 160 (P–OEt), 890–840 (OH deformation).

Homologs of trans-Stilbenecarboxylic Acid 18-20

*trans-4-Stilbeneacetic acid* (**18**). A solution of benzaldehyde (1.52 ml, 1.58 g, 0.015 mol) and **15** (4.32 g, 0.015 mol) in anhydrous dimethylformamide (5 ml) was added dropwise to a stirred suspension of sodium methoxide (2.5 g, 0.048 mol) in anhydrous dimethylformamide (10 ml) at 0–5 °C within 10–15 min. The cooling bath was removed and stirring was continued at room temperature for 5 h. A similar work-up of the reaction mixture as in the above-described preparation of **18** gave 0.33 g (9%) of the product; m.p. 187–188 °C (from benzene, refs<sup>44–46</sup> gives m.p. 186–187 °C). IR spectrum (KBr disk): 3 020 (OH stretching), 1 680 (C=O stretching), 1 505–1 395 (Ph), 950 (*trans*-CH=CH), 900 (OH deformation). UV spectrum (50% aq. MeOH),  $\lambda_{max}$  nm (log  $\varepsilon$ ): 228 (4.00), 298 (4.31), 311 (4.32), 323 sh (4.12). For C<sub>16</sub>H<sub>14</sub>O<sub>2</sub> (283.3) calculated: 80.65% C, 5.92% H; found: 80.39% C, 6.04% H.

 $\beta$ -(*trans-4-Stilbene*)propionic acid (19). This compound was obtained in a similar manner as above. Yield 20%, m.p. 209–211 °C (from benzene). IR spectrum (KBr disk): 3 050 (OH stretching), 1 705 (C=O stretching), 1 515–1 420 (Ph), 965 (*trans*-CH=CH), 915 cm<sup>-1</sup> (OH deformation). UV

spectrum (50% MeOH),  $\lambda_{max}$  nm (log  $\epsilon$ ): 228 (4.05), 297 (4.31), 311 (4.33), 322 sh (4.11). For C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> (252.3) calculated: 80.92% C, 6.39% H; found: 81.63% C, 6.60% H.

 $\gamma$ -(*trans-4-Stilbene*)*butyric acid*<sup>47</sup> (**20**). This acid was obtained in the same manner as described above. Yield 22%, m.p. 162–164 °C (from carbon tetrachloride with a small amount of methanol). IR spectrum (KBr disk): 3 030 (OH stretching), 1 690 (C=O stretching), 1 510–1 410 (Ph), 960 (*trans*-CH=CH), 910 (OH deformation). UV spectrum (50% aq. MeOH),  $\lambda_{max}$  nm (log  $\epsilon$ ): 227 (3.99), 297 (4.30), 310 (4.31), 323 sh (4.11). For C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> (266.3) calculated: 81.17% C, 6.81% H; found: 81.12% C, 7.00% H.

### trans-cis Photoisomerization of the Acids

A solution of *trans*-4-stilbeneacetic acid (**18**; 0.028 g, 0.001 mol) in dioxane (10 ml) was irradiated at 300 nm in dioxane (10 ml) for 20 h. Work-up of the reaction mixture and separation of the two isomers in the form of their sodium salts (sodium salt of the *trans*-acid precipitates out in 1 mol/dm<sup>3</sup> aqueous sodium hydroxide, the salt of the *cis*-isomer remains in the solution) gave crude *cis*-4stilbeneacetic acid (**21**) (68%). UV spectrum (50% MeOH),  $\lambda_{max}$  nm (log  $\varepsilon$ ): 223 (4.06), 308 (4.20).

The *cis*-isomers of **19** and **20** were obtained in the same way. UV spectrum (50% aq. MeOH),  $\lambda_{\text{max}}$  nm (log  $\varepsilon$ ):  $\beta$ -(*cis*-4-stilbene)propionic acid (**22**): 223 (4.06), 309 (4.23);  $\gamma$ -(*cis*-4-stilbene)butyric acid (**23**): 221 (4.04), 308 (4.22).

#### Cobalt(III) Complexes 1-4

(*trans-4-Stilbene*)*carboxylatopentaamminecobalt*(*III*) *perchlorate* (1). This compound was obtained from the sodium salt of *trans-4-stilbenecarboxylic* acid and aquapentaamminecobalt(*III*) perchlorate as described in the litarature<sup>34</sup>. An adaptation of this procedure was also used to obtain the three new cobalt(*III*) complexes, **2–4**.

(*trans-4-Stilbene*)acetatopentaamminecobalt(III) perchlorate monohydrate (**2**). A mixture of the sodium salt of **18** (0.119 g, 0.00046 mol) and of aquapentaamminecobalt(III) perchlorate (0.701 g, 0.00016 mol) was dissolved in dimethylacetamide (5 ml) and dimethylformamide (5 ml) and the mixture was heated on a water bath at 80 °C with stirring for 3 h in the absence of light. The mixture was poured into diluted perchloric acid (7%, approximately 30–40 ml), and the precipitated product was recrystallized from hot water with added sodium perchlorate. The solution was filtered, and **2** was washed twice with cold water, once with ethanol, and several times with ethyl ether, and dried in the dark over anhydrous magnesium perchlorate. The entire crystallization procedure was repeated to remove traces of uncomplexed **18**. The yield of **2** was 0.063 g (25%). IR spectrum (KBr disk): 3 250 (bonded NH), 1 560 (COO<sup>-</sup> asym. stretching), 1 390 (COO<sup>-</sup> sym. stretching), 1 305, 1 110, 965 (*trans*-stilbene), 840; UV-VIS spectrum (50% aq. MeOH),  $\lambda_{max}$  nm (log  $\varepsilon$ ): 228 (4.26), 298 (4.37), 311 (4.39), 323 sh (4.23), 500 (1.95). For C<sub>16</sub>H<sub>30</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>11</sub> (598.3) calculated: 32.12% C, 5.05% H; found: 31.98% C, 4.51% H.

β-(*trans-4-Stilbene*)propionatopentaamminecobalt(III) perchlorate (**3**). The perchlorate salt **3** was prepared in the same manner as **2**; yield 26%. IR spectrum (KBr disk): 3 250 (bonded NH), 1 560 (COO<sup>-</sup> asym. stretching), 1 370 (COO<sup>-</sup> sym. stretching), 1 290, 1 070, 945 (*trans*-stilbene), 825 cm<sup>-1</sup>. UV-VIS spectrum (50% aq. MeOH),  $\lambda_{max}$  nm (log ε): 228 (4.29), 297 (4.40), 311 (4.44), 322 sh (4.25), 500 (2.11). For C<sub>17</sub>H<sub>30</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>10</sub> (608.3) calculated: 33.56% C, 4.97% H, 11.51% N; found: 34.14% C, 5.08% H, 12.00% N.

 $\gamma$ -(*trans-4-Stilbene*)*butyratopentaamminecobalt*(*III*) *perchlorate* (**4**). This complex was obtained in the same fashion as **2**; yield 28%. IR spectrum (KBr disk): 3 275 (bonded NH), 1 580 (COO<sup>-</sup> asym. stretching), 1 390 (COO<sup>-</sup> sym. stretching), 1 300, 1 090, 965 (*trans*-stilbene), 830. UV-VIS spectrum (50% aq. MeOH),  $\lambda_{max}$  nm (log  $\varepsilon$ ): 227 (4.41), 297 (4.41), 310 (4.42), 323 sh (4.22), 500 (1.88). For

 $C_{18}H_{32}Cl_2CoN_5O_{10}~(622.4)$  calculated: 34.73% C, 5.18% H, 11.25% N; found: 34.62% C, 5.10% H, 10.51% N.

# **RESULTS AND DISCUSSION**

In order to obtain the desired series of carboxylatopentaamminecobalt(III) complexes, it was necessary to syntesize the respective homologs of *trans*-4-stilbenecarboxylic acid, viz. *trans*-4-stilbeneacetic acid (18),  $\beta$ -(*trans*-4-stilbene)propionic acid (19), and  $\gamma$ -(*trans*-4-stilbene)butyric acid (20).

Two different methods were employed to obtain the desired homologs of *trans*-4-stilbenecarboxylic acid, with *p*-chloromethyl substituted carboxylic acids used as the starting materials in both cases. These acids, **8–10**, were obtained by direct chloromethylation of the respective phenylalkylcarboxylic acids, i.e., phenylacetic acid (**5**),  $\beta$ -phenylpropionic acid (**6**), and  $\gamma$ -phenylbutyric acid (**7**) which are commercially available. In method *A*, according to Bogdanov<sup>36</sup>, the acids were synthesized by passing gaseous hydrogen chloride through a heated mixture of the respective starting acid and zinc chloride in 40% formalin. The yields of the products were 27–30%. Method *B* involved a reaction of the starting acid with chloromethyl methyl ether (**11**) in the presence of stannic chloride in a cooled bath<sup>37</sup>. The yields in this case were better, 42–52%, and thus method *B* is preferable to method *A*. The two methods are outlined in Scheme 1.

Two different approaches were used to convert the *p*-chloromethylphenylalkylcarboxylic acids into the desired stilbene derivatives. In the first approach, the Wittig reaction involving intermediate phosphonium carbanions (ylides) was employed<sup>38–40</sup>. The chloromethylphenyl acids **8–10** were heated with triphenylphosphine in dry benzene and converted into the corresponding carboxyalkylbenzyltriphenylphosphonium chlorides **12–14** in a 75–99% yield (Scheme 1). Subsequent reaction of the phosphonium salt with benzaldehyde in dimethylformamide in the presence of sodium methoxide or phenyllithium (in diethyl ether) yielded the homologs of *trans*-4-stilbenecarboxylic acid, **18**, **19**, in a low yield (3–8%) (Scheme 1).

The second, preferable approach utilized the Wadsworth–Horner modification of the Wittig reaction, with phosphonates as the intermediates<sup>41–43</sup>. *p*-Chloromethylphenyl-alkylcarboxylic acids **8–10** were converted into the corresponding phosphonates by refluxing with triethyl phosphite in a 95–97% yield. The subsequent reaction of the phosphonates **15–17** with benzaldehyde in dimethylformamide in the presence of sodium methoxide in an ice-cooled bath gave the respective *trans*-4-stilbenealkylcarboxylic acids **18–20** in a 9–22% yield (Scheme 1).

The structures of the resulting acids, **18–20**, as well as of the intermediates in both synthetic sequences were confirmed on the basis of their IR and UV spectra and, where necessary, elemental analyses. The entire synthetic procedure is summarized in Scheme 1.



The red cobalt(III) complexes 1-4 were obtained from the sodium salts of the above acids and aquapentaamminecobalt(III) perchlorate in *N*,*N*-dimethylacetamide<sup>34</sup>.

The electronic absorption spectral data of the homologs of *trans*-4-stilbenecarboxylic acid **18–20** are given in the Experimental. In general, their spectra possess four strong absorption bands (log  $\varepsilon \ge 4.00$ ) at 227–228, 297–298, 310–311, and 322–323 (sh) nm. The spectra are analogous to the spectrum of the parent compound, *trans*-4-stilbenecarboxylic acid, with absorption maxima (in ethanol) at 230 (log  $\varepsilon$  4.16), 310 (sh) (4.53), 319 (4.58), and 327 (sh) nm (4.42) (ref.<sup>48</sup>).

All *trans*-acids undergo facile photoisomerization when irradiated at 300 nm in dioxane, resulting in the formation of the *cis*-isomers, with a shift of the absorption maxima in their electronic absorption spectra ( $\lambda_{max}$  at 221–223 and 308–309 nm; see Experimental). For comparison, the UV spectrum of *cis*-4-stilbenecarboxylic acid has absorption maxima at 233 (log  $\varepsilon$  4.32) and 292 nm (4.13) (refs<sup>48,49</sup>).

When comparing the electronic absorption spectra of the above free ligands with those of the corresponding carboxylatopentaamminecobalt(III) complexes 1–4 (see Experimental), one can see that the spectra in the UV region are practically identical. The difference is in the visible region where the cobalt complexes exhibit an additional absorption band at 500 nm. As an example, the absorption curves of the complexes 2 and 3 are shown in Fig. 1. At 500 nm, the complexes are practically insensitive to light<sup>34</sup>. Also, they are only slightly photosensitive in the ligand excitation region<sup>34</sup>. The first ligand field bands of aqueous cobalt(III) ammine complexes of the type



 $[Co(NH_3)_5X]^{2+}$  correspond to the transition  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  in  $O_h$  symmetry ( $L_1$  and  $L_2$  bands, respectively). However, the complexes are sensitive to light between 340 and 385 nm (internal ligand excitation region)<sup>34</sup>.

While detailed photochemical studies of the complexes were not planned in this work and could be the topic of a subsequent investigation, we have studied emission spectra of the free ligands (also in the form of their sodium salts, i.e., the corresponding anions) and the respective cobalt(III) complexes. The free ligands, their anions, and the cobalt complexes show the expected fluorescent emission which is characteristic of the first excited singlet state of the organic ligand<sup>50</sup>. Stilbenes are not expected to give phosphorescence in solution at room temperature<sup>51</sup>.

The fluorescence measurements were carried out with 312 nm exciting wavelength. The spectra were obtained in 50% aqueous ethanol, for the organic ligands alone (sodium salt), for solutions containing the ligand and a five-fold excess of aquapentaammine-cobalt(III) perchlorate, and, finally, the corresponding carboxylatopentaammine-cobalt(III) perchlorates. A fluorescence emission was observed in each case, with a maximum at 363 nm, characteristic of the first excited singlet state of the ligand. Fluorescence of the free ligand is decreased in the presence of aquapentaamminecobalt(III) perchlorate, however, the intensity of fluorescence is even more diminished in the respective carboxylatopentaamminecobalt(III) complexes. The relative intensities of fluorescence in the case of **19** and its pentaamminecobalt(III) complex are shown in Fig. 2.

A comparison of the quenching effect for the four systems under study indicates that this effect decreases with an increasing number of methylene groups in the organic ligand, i.e., with increasing distance between the presumed energy donor (the stilbene moiety) and the presumed energy acceptor (cobalt). While additional detailed studies of this observation are needed, by analogy with the work of Adamson and co-workers<sup>34</sup> on (*trans*-4-stilbene)carboxylatopentaamminecobalt(III) perchlorate (1), an intramolecular





Fluorescence emission (312 nm exciting wavelength, 50% aqueous ethanol): 1 0.000116 mol/dm<sup>3</sup>  $\beta$ -(*trans*-4-stilbene)propionate ion (19); 2 0.000116 mol/dm<sup>3</sup> 19 + 0.00056 mol/dm<sup>3</sup> [Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>3+</sup>; 3 0.000116 mol/dm<sup>3</sup> [ $\beta$ -(*trans*-4-stilbene)propionato]pentaamminecobalt(III) perchlorate (3)

energy transfer (LMCT, ligand to metal charge transfer) is a distinct possibility. This means that, in such a case, the energy transfer would occur from the first excited singlet state of the organic ligand to the triplet LMCT state of the complex<sup>34</sup>. The number and the accuracy of the data are not sufficient to establish the relationship between the efficiency of energy transfer and the distance at this time.

In conclusion, the results presented here describe a series of cobalt(III) complexes with an aromatic ligand which can be used to study intramolecular energy transfer from the organic ligand to the metal. This work represents a follow-up on the work on the first compound in the series, **1**, as described by Adamson and co-workers<sup>34,52</sup>.

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