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The 1,8-Substituted Anthracenes as a New Type of Binucleating ligand.
I. A Preliminary Report

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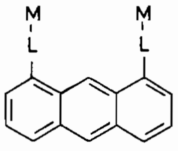
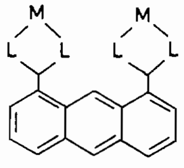
A typical target of the studies concerning polynuclear complexes is a bimetallic compound able to promote the reaction between two substrates, through their simultaneous activation on the two metal centers [1]. The consequent interest for binucleating ligands prompted us to investigate the 1,8-derivatives of anthracene with coordinating atoms in the substituent groups [2]. These systems appear to be a class of versatile ligands, since they may offer a variety of coordination modes depending on the nature of the substituents.

The expected binuclear complex (**I**–M_2) deriving from one of these types of anthracene derivatives (**I**, where L is a monodentate ligand group) is schematically represented below. We have prepared two type **I** ligands, anthracene 1,8-dicarboxaldehyde-bis(t-butylimine) (**Ia**) and anthracene 1,8-dicarboxaldehyde-bis-(N,N-dimethylhydrazone) (**Ib**), from commercial 1,8-dichloroanthraquinone (DCAQ). The anthracene-1,8 dicarboxylic acid was obtained from DCAQ in three steps according to Golden and Stock [3], and transformed by three-step procedure of Akiyama *et al.* [4] in the 1,8-dialdehyde, which was finally condensed with $(CH_3)_3CNH_2$ or $(CH_3)_2NNH_2$.

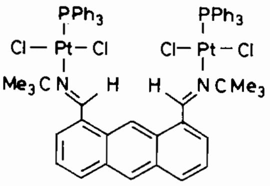


I - M_2

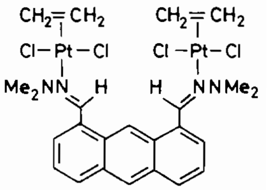


II - M_2

Both **Ia** and **Ib** can easily bind two metal centers. For instance, a binuclear Pt(II) complex (**Ia**–Pt_2) is obtained when **Ia** is reacted with $[Pt(PPh_3)Cl_2]_2$. Another Pt(II) complex (**Ib**–Pt_2) can be prepared by reaction of **Ib** with $[Pt(C_2H_4)Cl_2]_2$. The proposed structure of **Ia**–Pt_2 and **Ib**–Pt_2 are given.

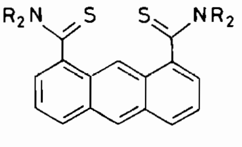


Ia - Pt_2



Ib - Pt_2

The 1,8-disubstituted anthracenes with two L groups in both substituents are another type of conceivable ligand system. If the nature of the L groups is such that two four-membered rings can be formed upon coordination, such ligands (type **II**) could afford complexes of the **II**–Me_2 type. Type **II** systems appear to be reasonably promising* for the synthesis of bimetallic catalysts. We prepared two type **II** ligands, the dithioamides **IIa** and **IIb**. The corresponding diamides were obtained by adapting the procedure described for the unsubstituted diamide [5]. The diamides were converted to the thiodiamides by utilizing the Lawesson reagent [6]. Our preliminary results concerning the coordination properties of **IIa**, **b** indicate that binuclear complexes can be easily obtained from these ligands. The reaction of **IIa** and **IIb** with $Pd(PhCN)_2Cl_2$ in 1:2 ratio afforded the complexes **IIa**–Pd_2 and **IIb**–Pd_2 respectively, with high yield. Analyses and spectral properties of both products are consistent with the N, S coordination of the dithioamides to two $PdCl_2$ fragments. It is also found that the coordination ability of the L group in **II** can be markedly different from that observed in a simple phenyl derivative PhL. For instance, no reaction between **IIb** and $CoCl_2$ was observed in the conditions described for the synthesis of $Co(PhC[=S]NEt_2)Cl_2$ [7].



II (a, R = Me; b, R = Et)

Current studies investigate the ligand properties of several 1,8-substituted anthracenes and probe the catalytic activity of their complexes.

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*A simplifying approach to the design of bimetallic homogeneous catalysts could be to assume that the two substrates are coordinated through the atoms (say, A and B) which are to be activated. Although this approach can be inadequate, it is appealing to investigate those binucleating systems which accordingly are able to hold the metal atoms M and M', so that the A···B distance could be suitable for interaction. Thus, a 'correct' M···M' distance should be comprised in the range from one bond distance to the sum of the M–A, M'–B and A––B bond distances. The molecular models show that a type II ligand can easily fulfill this requirement.

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Experimental*

All reactions were carried out in nitrogen atmosphere. The ^{1}H NMR spectra were recorded on a Bruker 270 MHz. The analytical data are consistent with the assigned formulas.

*Preparation of **Ia***

A solution in benzene (20 ml) of anthracene 1,8-dicarboxaldehyde 3.4 (1.0 mmol) and of $(CH_3)_3CNH_2$ (2.0 ml) was refluxed for 12 h in a flask equipped with a Dean-Stark trap. The solvent was removed *in vacuo* and the residue crystallized from methylene chloride–heptane to give **Ia**, pale-yellow crystals, 0.24 g (71%). ^{1}H NMR ($CDCl_3$, TMS): δ 10.75 (1H, s), 9.12 (2H, s), 8.49 (1H, s), 8.06 (2H, d), 7.95 (2H, d), 7.54 (2H, dd), 1.47 (18 H, s).

*Preparation of **Ib***

The dialdehyde (1.0 mmol) and $(CH_3)_2NNH_2$ (4.0 mmol) were dissolved in 25 ml of benzene, in the presence of A4 molecular sieves. After standing 1 h at 60 °C and 12 h at 20 °C the mixture was filtered and the solvent removed *in vacuo*. The residue was crystallized from methylene chloride–heptane to give **Ib**, yellow crystals, 0.26 g (83%). ^{1}H NMR ($CDCl_3$, TMS): δ 10.24 (1H, s), 8.41 (1H, s), 8.02 (2H, s), 7.88 (2H, d), 7.75 (2H, d), 7.44 (2H, dd), 3.11 (12H, s).

*Preparation of **IIa, b***

Anthracene 1,8-dicarbonylchloride 6 (1.0 mmol) was suspended in 10 ml of diethyl ether and excess R_2NH (**a**, R = Me; **b**, R = Et) was added at 0 °C, with stirring. After 1 h the solvent was removed *in vacuo* and the residue washed with water and dried, affording the crude diamide. A mixture of this material, Lawesson reagent (0.44 g, 1.1 mmol) and toluene (5 ml) was heated under reflux for 4 h. After the solvent was removed *in vacuo* the residue was purified by chromatography on silica gel with methylene chloride to give the dithioamide, which crystallized as yellow crystals from methylene chloride–methanol. **IIa** (0.21 g, 61%); ^{1}H NMR ($CDCl_3$, TMS): δ 8.43 (1H, s), 8.10 (1H, s), 7.96 (4H, m), 3.84 (6H, s), 3.13 (6H, s). **IIb** (0.27 g, 67%); ^{1}H NMR: δ 8.42 (1H, s), 8.27 (1H, s), 7.94 (2H, d), 7.44 (2H, dd), 7.31 (2H, d), 4.42 (2H, dq), 4.10 (2H, dq), 3.30 (4H, m), 1.55 (6H, t), 1.04 (6H, t).

*Preparation of **Ia**–Pt_2*

To a solution of **Ia** (0.5 mmol) in 5 ml of chloroform an equimolar amount of $[Pt(PPh_3)Cl_2]_2$ was added. After two h stirring at 20 °C the solvent was removed *in vacuo* and the residue was crystallized from acetone–methanol to give 0.22 g (31.5%) of **Ia**–Pt_2 as yellow crystals. ^{1}H NMR ($CDCl_3$, TMS): δ 9.50 (2H, d, J_{PH} = 14 Hz), 8.68 (1H, s), 8.57 (2H, d), 8.26 (1H, s), 8.21 (2H, d), 7.63 (2H, dd), 7.1–7.4 (30 H, m), 1.88 (18 H, s).

*Preparation of **Ib**–Pt_2*

A suspension of $[Pt(C_2H_4)Cl_2]_2$ (0.5 mmol) in 3 ml of acetone was added to a solution of **Ib** (0.5 mmol) in the minimum amount of chloroform. The mixture was stirred 10 min at 20 °C. The precipitate was collected by filtration, washed with diethyl ether and dried to give 0.26 g (57%) of **Ib**–Pt_2. ^{1}H NMR (CD_3CN, TMS): δ 10.25 (1H, br), 8.67 (1H, s), 8.31 (2H, br), 8.13 (2H, d), 8.02 (2H, br), 7.66 (6H, dd), 4.89 (8H, br), 3.32 (12 H, s).

*Preparation of **IIa**–Pd_2 and **IIb**–Pd_2*

To a solution of **IIa** or **IIb** (0.25 mmol) in 10 ml of methylene chloride a solution of $Pd(PhCN)_2Cl_2$ (0.5 mmol) in 10 ml of the same solvent was added dropwise with stirring at 20 °C. The brick-red precipitate was collected, washed with diethyl ether and dried. **IIa**–Pd_2 (0.17 g, 97%); ^{1}H NMR (CD_3CN, TMS): δ 8.8–7.6 (8H, m), 3.84 (6H, s), 3.04 (6H, s). **IIb**–Pd_2 (0.18 g, 96%); ^{1}H NMR: δ 8.8–7.6 (8H, m), 4.48 (2H, m), 3.92 (2H, m), 3.53 (2H, m), 3.16 (2H, m), 1.58 (6H, t), 1.00 (6H, t).

Acknowledgements

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References

1 See, for instance, 'The Challenge of Polynuclear Inorganic Compounds', *Inorg. Chim. Acta, 62,* 1(1982), selected plenary lectures from the EUCHEM conference.
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*All manipulations concerning the anthracene derivatives were made by taking into account the carcinogenic potential of these species.