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Alkyl, aryl and ethynyl group exchange on organocobalt(III)porphyrins. Characterization of anionic bis(ethynyl)cobalt(III)porphyrins[†]

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Summary — Reaction of organolithium compounds with organocobalt(III)porphyrins leads to rapid substitution or equilibrated exchange of the organic fragment depending on the nature of this fragment (aryl, alkyl, styryl, alkynyl). The postulated intermediate anionic complexes could be observed (NMR, UV-visible) on reaction of alkynylcobalt(III)porphyrins with alkynyllithium reagents.

porphyrin / cobalt / organolithium compound / anionic complex

Résumé — **Echange de groupements alkyl-, aryl- et éthynyl- sur des organocobalt(III)porphyrines. Caractérisation de bis(éthynyl)cobalt porphyrines anioniques.** *La réaction d'organolithiens avec des organocobalt(III)porphyrines conduit, suivant la nature du réactif (aryl-, alkyl-, styryl- ou alkynyllithium), à une substitution rapide ou à un échange équilibré des restes organiques. Les intermédiaires anioniques proposés ont pu être observés (RMN, UV-visible) par réaction d'alkynylcobalt(III)porphyrines avec des alkynyllithiens.*

porphyrin / cobalt / organolithien / complexe anionique

Introduction

Organocobalt(III)porphyrins have been the subject of numerous studies [1–3] mostly related to the mechanism of the action of vitamin B_{12} and various other catalytic processes. They have also been used as models of the corresponding, and less stable, organoiron(III)porphyrins. Organocobalt(III)porphyrins are of variable stability; aryl-substituted Co-C bonds are by far the most resistant to heat and light. However, under oxidative conditions they undergo a rearrangement leading to the alkyl or aryl group being attached to a pyrrolic nitrogen [4–6]. While studying reactions of substituted arylcobalt(III)porphyrins with organometallics we found that the substitution on cobalt is a preferential reaction pathway and that, under appropriate conditions, an anionic intermediate could be characterized.

Results and discussion

Metallation (*n*-BuLi; −78 °C) of *p*-bromophenylcobalt(III)-*meso*-tetraphenylporphyrin **1** (*p*-BrC_6H_4Co TPP; TPP = dianion of *meso*-tetraphenylporphyrin), followed by quenching with water, did not produce the lithiophenyl derivative **2** but *n*-BuCoTPP **3**, which was prepared independently by reaction of $[Co(I)TPP]^-$ with butyl bromide [7]. The reaction is rapid (less than 5 min at −78 °C) and the yield quantitative. This led to the conclusion that the attack by a strong nucleophile followed by cleavage of the Co-C bond is a highly favorable process and incited us to investigate the scope of this reaction.

Cobalt porphyrins **1** and **3**–**7** (fig 1) were treated with organolithium or organomagnesium compounds at −78 °C for 10 min, and then quenched with methanol and analyzed (see table I). The results presented in table I demonstrate that the reaction is very fast, even at −78 °C, and that the displacement of the organic fragment attached to cobalt is quantitative, provided it is a better leaving group than the attacking nucleophile. This is illustrated by entries (1), (2), and (5). Reaction of a nucleophile similar to the group already present in the starting material led to an equilibrium illustrated by the competition between aryl fragments as in entries (3) and (4). The result of the reaction of phenyllithium with *n*-BuCoTPP (entry (6)) may produce some *n*-BuLi. Subsequent reaction of *n*-BuLi with the solvent [8] may then explain the formation of **4** in a significant amount, although this may seem unexpected

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[†] Dedicated to Prof Raymond Weiss.

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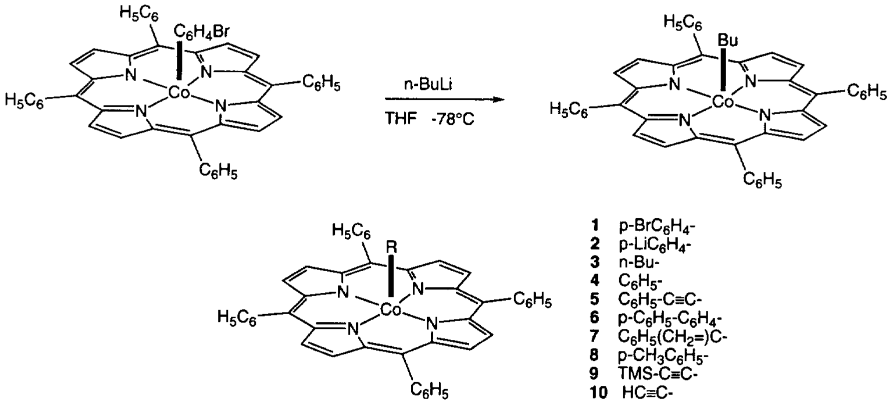

Fig 1

Table I.

Entry		*Starting material* *RCoTPP (R =)*	*Reagent* *R'M (equiv)*	*Recovered starting material*[c] *and product (relative %)* *RCoTPP*		*R' CoTPP*		*Total yield*
					(%)		(%)	(%)
(1)[a]	**4**	C_6H_5	*n*-BuLi (6)	**4**	0	**3**	100	70
(2)[a]	**5**	C_6H_5-C≡C	C_6H_5Li (5)	**5**	0	**4**	100	72
(3)[a]	**1**	*p*-BrC_6H_4	C_6H_5Li (5)	**1**	15	**4**	85	87
(4)[a]	**6**	*p*-biphenyl	C_6H_5Li (5)	**6**	33	**4**	67	83
(5)[a]	**7**	$(CH_2=)$(*p*-MeC_6H_4-)C	C_6H_5Li (5)	**7**	0	**4**	100	79
(6)[a]	**3**	*n*-Bu	C_6H_5Li (5)	**3**	63	**4**	37	55
(7)[b]	**1**	*p*-BrC_6H_4	C_6H_5MgBr (20)	**1**	89	**4**	11	>99
(8)[b]	**4**	C_6H_5	*p*-$CH_3C_6H_5MgBr$ (20)	**4**	89	**8**	11	64

[a] Reaction run at −78 °C for 10 min; [b] +20 °C for 10 min; [c] % measured by NMR.

in view of the relative reactivity. The corresponding Grignard reagents can also cleave the cobalt-carbon bond of RCoTPP, but the reaction is much slower, even at room temperature, as shown by entries (7) and (8).

These results suggest the initial *trans* addition of the attacking nucleophile to the 16e cobalt center. It is known that various ligands bind to cobalt of organocobalt(III)porphyrins. However, due to the strong *trans* effect of the organic ligand, the stability of the resulting products is generally low, compared to the corresponding products obtained from halogenocobalt(III)porphyrins [1–3, 9]. The anionic 'ate' complex resulting from the addition of the lithium compound may then loose one of its axial ligands, according to the relative stabilization of the formed organolithium compound [10]. Under the conditions of entries (1) to (8) there was no visual evidence for a long-lived intermediate, which we expected to show a significantly different visible spectrum, as compared to both starting material or product. The ease of the reaction, even at low temperature, is in agreement with the relative weakness of the cobalt-carbon bonds in organocobalt complexes, even if one takes into account that cobalt-aryl bonds are among the strongest [11]. This is in contrast with the reactivity of rhodium(III)porphyrins: addition of an excess aryllithium to a methylrhodium(III)octaethylporphyrin produced a solution suspected to be an anionic complex, which slowly transformed into a *meso* substituted porphyrin, via a non-aromatic phlorin [12].

However, when we reacted phenylethynyl-CoTPP **5** with phenylethynyllithium, or simply added an excess of the same reagent to ClCoTPP, a bright green color developed which proved to be stable for long periods at 20 °C under anhydrous conditions. The electronic absorption of this green solution is typical for a porphyrin, however, with a pronounced bathochromic shift (Soret band 464 nm compared with 428 nm for **5**). On hydrolysis of this green solution **5** was recovered quantitatively.

The stoichiometry of the reaction was deduced from the NMR spectrum in THF which showed an integral for two equivalent phenylethynyl fragments, as well as the signals expected for a porphyrin possessing a symmetry axis perpendicular to the macrocycle. Similar solutions of the green anions $[(R\text{-}C{\equiv}C)_2CoTPP]^-$ (fig 2) were obtained from XCoTPP complexes (X = halogen or R-C≡C) when R = $(CH_3)_3Si$ or H. The UV-visible and NMR data of these anions are collected in table II.

The UV-visible spectra of anions **11–13** show a bathochromic shift as observed earlier on addition of anionic ligands (thiolate and thiocyanate) to cobalt(III)porphyrins [13, 14]. The significant difference

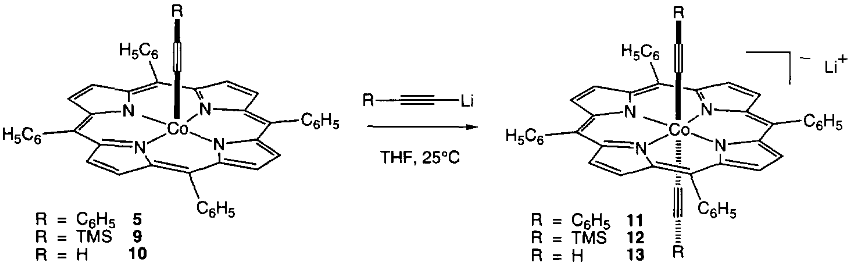

Fig 2

Table II.

	UV-vis data (nm, (log ε), in THF)			NMR data (δ, in THF) Pyrrole	5,10,15,20-Phenyl	R
5	428 (5.14)	548 (4.17)		8.93 (8 H)	8.19 (o), 7.78 (m + p) (8 + 12 H)	6.29 (m + p), 5.08 (o) (3 + 2 H)
11	464 (5.01)	610 (3.46)	664 (4.04)	8.59 (8 H)	8.16 (o), 7.63 (m + p) (8 + 12 H)	6.19 (m + p), 5.20 (o) (6 + 4 H)
9	430 (5.14)	546 (4.14)		8.90 (8 H)	8.19 (o), 7.78 (m + p) (8 + 12 H)	−1.43 (9 H)
12[a]	460 (5.04)	606 (3.86)	658 (4.15)	8.50 (8 H)	8.10 (o), 7.57 (m + p) (8 + 12 H)	−1.48 (18 H)
10	428 (5.21)	544 (4.20)		8.90 (8 H)	8.17 (o), 7.78 (m + p) (8 + 12 H)	−2.26 (1 H)
13[b]	438 (5.29)	560 (4.28)	602 (4.08)	8.49 (8 H)	8.02 (o), 7.58 (m + p) (8 + 12 H)	−2.22 (2 H)

Composition of the solution: [a] 94% **12**, 6% **9**; [b] 85% **13**, 15% **10**.

between the UV-visible data for **11** and **12** vs **13** suggests that the cation–anion interaction is different, possibly in connection with the steric hindrance introduced by the larger phenylethynyl and TMS-ethynyl groups. The NMR data for **11**–**13** confirm the modification of the electron density on the porphyrin macrocycle as shown by the shielding of the pyrrole protons.

Various σ-ethynylmetallomacrocycles (metal = Ga, In, Fe, Si, Sn, Ge; macrocycles = porphyrins or related compounds) have been prepared [15], as well as several ethynylcobalt(III) complexes of Schiff bases and glyoximes [16]. It has often been observed that the *trans* effect of the ethynyl ligand is lower than that of other organoligands, closer to that of a halogeno ligand, the ethynyl ligand being more ionic in character. The lowering of the *trans* effect allows the right balance for the observation of the intermediate in the TPP series. On the other hand, addition of ca 100 equiv lithium acetylide ethylene diamine complex to **4**, whose phenyl group should disfavor the formation of an anionic complex, did not produce a significant spectral change. On addition of a larger excess (> 10^4 equiv) a splitting of the Soret band as well as the appearance of a low intensity band at long wavelength revealed the formation of some corresponding anionic complex.

Various attempts were made to obtain single crystals of an anionic complex suitable for X-ray analysis. Although **13** (counterion lithium or [K ⊂ 2.2.2]) could be crystallized in THF/hexane the crystals were either too small (Li) or too unstable (K ⊂ 2.2.2) for recording intensity data.

Experimental section

NMR spectra were obtained on Bruker WP-200 SY and ARX 500 spectrometers. The solvent were $CDCl_3$ and d_8-THF (reference spectra, see below) or undeuterated anhydrous THF (anionic solutions, see table II). Chemical shifts (δ) are expressed in ppm from TMS. UV-visible spectra were obtained with a Hewlett-Packard 8452A spectrometer in CH_2Cl_2 or anhydrous THF. Elemental analyses were performed by the Service de microanalyse de l'Institut de chimie de Strasbourg. Chromatographic separations were obtained using Merck 60 silica-gel column. Reactions were run under argon. THF was distilled from sodium-benzophenone ketyl under argon. Organic phases were routinely dried over anhydrous Na_2SO_4 before being evaporated under vacuum (rotary evaporator). Organolithium compounds were purchased from Fluka (2 M phenyllithium in 70:30 cyclohexane/diethyl ether, and lithium acetylide ethylene diamine complex in oil), or Aldrich (1.6 M *n*-butyllithium in hexane).

Porphyrins **1** [5], **3** [7], **4** [5], **7** [17], **8** [5] have been described in the literature, while **6** was obtained as a byproduct from the reaction of dilithiobiphenyl with ClCoTPP [18].

Phenylethynylcobalt(III)-m-*tetraphenylporphyrin* **5**

Lithium phenylacetylide (0.26 mmol; from phenylacetylene and *n*-BuLi in THF) was added to a solution of ClCoTPP

(183 mg; 0.26 mmol) in THF (15 mL) at +20 °C. After 1 min methanol (1 mL) was added followed by CH_2Cl_2 (15 mL) and water (30 mL). The organic phase was washed (water, 3 × 30 mL) and dried over Na_2SO_4. Evaporation of the solvent followed by a chromatographic purification (silica gel, CH_2Cl_2/hexane 1:1), and crystallization from methanol gave **5** (166 mg, 83%).

NMR ($CDCl_3$): 8.92 (s, 8H, pyrrole), 8.1 (m, 8H, *meso* Ph *o*-H), 7.7 (m, 12H, *meso* Ph $m+p$-H), 6.40 (m, 3H, axial Ph $m+p$-H), 5.29 (m, 2H, axial Ph *o*-H).

UV-vis (see table II).

Anal calc % for $C_{52}H_{33}N_4Co$: C 80.81; H 4.30; N 7.24. Found: C 80.21; H 4.82; N 7.18.

Trimethylsilylethynylcobalt(III)-m-*tetraphenylporphyrin* **9**

The same procedure as for compound **5**, starting with lithium trimethylsilylacetylide, gave compound **9** (58%).

NMR ($CDCl_3$): 8.90 (s, 8H, pyrrole), 8.1 (m, 8H, *meso* Ph *o*-H), 7.7 (m, 12H, *meso* Ph $m+p$-H), −1.32 (s, 9H, TMS).

UV-vis (see table II).

Anal calc % for $C_{49}H_{37}N_4CoSi$: C 76.56; H 4.85; N 7.29. Found: C 76.07; H 5.09; N 7.33.

Ethynylcobalt(III)-m-*tetraphenylporphyrin* **10**

To a solution of ClCoTPP (150 mg; 0.212 mmol) in THF (5 mL) was added at +20 °C solid lithium acetylide ethylene diamine complex (48 mg; 0.531 mmol). After 5 min the solution turned green. After addition of methanol (1 mL) followed by the usual work-up (see above) the product was crystallized from methanol (126 mg; 86%).

NMR ($CDCl_3$): 8.94 (s, 8H, pyrrole), 8.1 (m, 8H, *meso* Ph *o*-H), 7.7 (m, 12H, *meso* Ph $m+p$-H), −1.72 (s, 1H, ethynyl).

UV-vis (see table II).

Anal calc % for $C_{46}H_{29}N_4Co$: C 79.30; H 4.20; N 8.04. Found: C 78.27; H 4.62; N 7.91 (better analytical data could not be obtained).

p-*Biphen-4-ylcobalt(III)*-m-*tetraphenylporphyrin* **6**

The preparation of this compound will be presented elsewhere.

NMR ($CDCl_3$): 8.85 (s, 8H, pyrrole), 8.1 (m, 8H, *meso* Ph *o*-H), 7.7 (m, 12H, *meso* Ph $m+p$-H), 6.88 (t, 3H, -Ph-*Ph* $m+p$-H), 6.57 (d, 2H, -Ph-*Ph* *o*-H), 5.00 (d, 2H, -*Ph*-Ph *m*-H), 0.39 (d, 2H, -*Ph*-Ph *o*-H).

Anal calc % for $C_{56}H_{37}N_4Co$: C 81.54; H 4.52; N 6.79. Found: C 81.57; H 4.63; N 6.53.

Reaction of organocobalt(III)porphyrins with organometallics

To a solution of the porphyrin in anhydrous THF, under argon at −78 °C, was added RLi. After 10 min the reaction was quenched with excess methanol and the products were filtered through a short silica-gel column (eluent CH_2Cl_2/hexane 1:1), crystallized from CH_2Cl_2/methanol, and analyzed (TLC on crude and crystallized product and NMR). The reactions with Grignard reagents were run under the same conditions except for the temperature (0 or +20 °C; same result).

The NMR data of the anionic complexes were obtained in anhydrous undeuterated THF (2 mg porphyrin in 0.5 mL THF; 3-5 equiv organolithium compound) at 0 °C. Small amounts of starting material were still present in the green solutions from **9** and **10**.

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