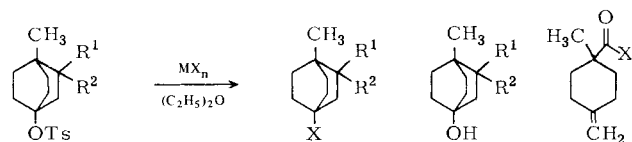
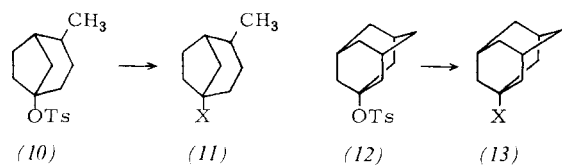


treatment with anhydrous metal halides in diethyl ether. No reaction occurs in more strongly solvating solvents such as THF, dioxane, glyme, or HMPT. In order to prepare the 1-chloro compounds the tosylates are reacted with FeCl<sub>3</sub> or TiCl<sub>4</sub> in boiling diethyl ether, the 1-bromo and 1-iodo compounds being obtained with MgBr<sub>2</sub> and MgI<sub>2</sub> respectively.



(1), R<sup>1</sup> = R<sup>2</sup> = H (2) — —  
 (3), R<sup>1</sup> = H, R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub> (4) + (5) — —  
 (6), R<sup>1</sup>, R<sup>2</sup> = O (7) + (8) + (9)



(a), X = Cl; (b), X = Br; (c), X = I

Table 1. Reaction of the bridgehead tosylates (1), (3), (6), (10), and (12) with anhydrous metal halides MX<sub>n</sub> in refluxing diethyl ether.

Tosylate	MX <sub>n</sub>	MX <sub>n</sub> :Tosylate	Reaction time [h]	Products		
				Yield [%]	M. p. [°C]	B. p. [°C/torr]
(1)	FeCl <sub>3</sub>	4:1	8	(2a)	70	75–75.5
(1)	TiCl <sub>4</sub>	4:1	5	(2a)	74	
(1)	MgBr <sub>2</sub>	1.3:1	1	(2b)	83	90.5
(1)	MgI <sub>2</sub>	1.3:1	1	(2c)	74	71–71.5
(3)	FeCl <sub>3</sub>	4:1	3	(4a)	90	94/0.2
				(5)	2	
(3)	TiCl <sub>4</sub>	4:1	1	(4a)	91	
				(5)	6	
(3)	MgBr <sub>2</sub>	1.3:1	1	(4b)	91	124–127/0.5
				(5)	7	
(3)	MgI <sub>2</sub>	1.3:1	1	(4c)	69	59
				(5)	5	
(6)	TiCl <sub>4</sub>	8:1	60	(7a)	80	63.5–64
				(8)	18	
				(9a)	trace	[a]
(6)	MgBr <sub>2</sub>	2.6:1	8	(7b)	82	75–75.5
				(8)	3	
				(9b)	15	[a]
(6)	MgI <sub>2</sub>	2.6:1	8	(7c)	79	68.5
				(8)	3	
				(9c)	18	[a]
(10)	TiCl <sub>4</sub>	6:1	3	(11a)	92	68–70/11
(10)	MgBr <sub>2</sub>	6:1	3	(11b)	90	82–83/11
(10)	MgI <sub>2</sub>	6:1	3	(11c)	81	45/0.25
(12)	TiCl <sub>4</sub>	1.3:1	0.25	(13a)	95	163–164
(12)	MgBr <sub>2</sub>	1.3:1	0.25	(13b)	90	119
(12)	MgI <sub>2</sub>	1.3:1	0.25	(13c)	89	151–152

[a] Identified as carboxylic acid.

In contrast to previously described syntheses of 1-halodicyclo[2.2.2]octanes<sup>[1]</sup> this method can also be applied to systems containing functional groups (see Table 1).

Tosylates (3) and (6), which contain substituents having a negative inductive effect attached to C-3, also give small amounts of the parent alcohols (5) and (8), respectively. It may therefore be assumed that the reactions proceed *via* bridgehead cations formed according to a S<sub>N</sub>1 mechanism<sup>[2]</sup>.

#### Procedure:

The tosylate (5.4 mmol) is dissolved in anhydrous ether (40 ml) and treated with the amount of TiCl<sub>4</sub> or FeCl<sub>3</sub> given

in Table 1; the bromides and iodides are prepared by adding the tosylate to a freshly prepared solution of MgBr<sub>2</sub><sup>[3]</sup> or MgI<sub>2</sub><sup>[4]</sup>, respectively, in ether. The mixture is refluxed with exclusion of moisture, cooled, and poured into ice-water. After separation of the ethereal phase the aqueous phase is extracted twice with ether. The combined ethereal phases are washed with water and dried over sodium sulfate. After the ether has been distilled off the residue is chromatographed over silica gel with pentane, and with pentane/ether (0–50%) in the case of ketones.

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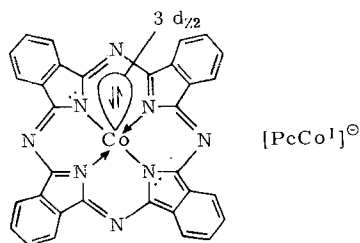
## Phthalocyaninecobalt(I) Salts, "Supernucleophilic" Vitamin B<sub>12</sub> Models Stable in Neutral Medium<sup>[\*\*]</sup>

By Heiner Eckert and Ivar Ugi<sup>[\*]</sup>

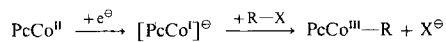
Salts of the phthalocyaninemetall anion [PcM]<sup>⊖</sup> such as Li<sub>2</sub>[PcFe]·5.5 THF<sup>[1]</sup> and Li[PcCo]·4.5 THF, with a central

[\*] Dipl.-Chem. H. Eckert and Prof. Dr. I. Ugi  
 Laboratorium für Organische Chemie der Technischen Universität  
 8 München 2, Arcisstrasse 21 (Germany)

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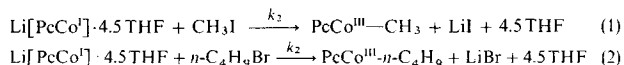
atom in low oxidation state and having  $d^8$  configuration with  $2a_{1g}$  orbital formed predominantly from a  $3d_{z^2}$  orbital, undergo substitution reactions with alkyl halides in THF to give stable organometalphthalocyanines<sup>[2]</sup>



We have recently found that  $\text{Li}[\text{PcCo}]\cdot 4.5$  THF, which is very sensitive toward oxygen and water, yet completely stable in their absence, forms stable neutral solutions in alcohols (ethanol, methanol) and has "supernucleophilic" properties therein which had not been observed in previous investigations in THF.

Anionic complexes with formal negative charges, strongly nucleophilic transition metal central atoms, and high relative nucleophilicities ( $n_{\text{CH}_3\text{I}} > ca. 10$ ; cf. Table 2) are referred to as "supernucleophiles"<sup>[3]</sup>. The relative nucleophilicity is calculated from the rate constant  $k_2$  of the methylation reaction (Tables 1 and 2).

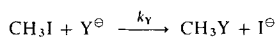
Table 1. Conductometrically determined kinetic data of the following 2nd order reactions:



in methanol at 25°C.

		Reaction with	
		CH <sub>3</sub> I	n-C <sub>4</sub> H <sub>9</sub> Br
Rate constant	at 0°C	0.37	—
$k_2$ [l mol <sup>-1</sup> s <sup>-1</sup> ]	at 25°C	7.4	$2.9 \times 10^{-3}$
Activation enthalpy $\Delta H^\ddagger$ [kcal/mol]		18.7	—
Activation entropy $\Delta S^\ddagger$ [cal K <sup>-1</sup> mol <sup>-1</sup> ]		7.0	—

Table 2. Relative nucleophilicity  $n_{\text{CH}_3\text{I}}$  (according to Pearson [4]) for reactions of the type



$n_{\text{CH}_3\text{I}}$  is defined as  $\log(k_Y/k_{\text{CH}_3\text{OH}})$ .  $k_Y$  is the 2nd order rate constant for the methylation of nucleophile Y with CH<sub>3</sub>I in CH<sub>3</sub>OH at 25°C (for [PcCo]<sup>⊖</sup>,  $k_Y = k_2$ );  $k_{\text{CH}_3\text{OH}}$ , the corresponding constant for the solvolysis of CH<sub>3</sub>I in CH<sub>3</sub>OH, is  $1.3 \times 10^{-10}$  l mol<sup>-1</sup> s<sup>-1</sup>.

Nucleophile	$n_{\text{CH}_3\text{I}}$	Ref.
CH <sub>3</sub> OH	0.00	[4]
Cl <sup>⊖</sup>	4.37	[4]
Br <sup>⊖</sup>	5.79	[4]
CN <sup>⊖</sup>	6.70	[4]
I <sup>⊖</sup>	7.42	[4]
S <sub>2</sub> O <sub>3</sub> <sup>⊖</sup>	8.95	[4]
C <sub>6</sub> H <sub>5</sub> S <sup>⊖</sup>	9.92	[4]
[PcCo] <sup>⊖</sup> [a]	10.8	
Cobaloximes, [a]	10.5—14.3 [b]	[3, 5]
Vitamin B <sub>12a</sub> [a]	14.4 [b]	[3]

[a] Contains Co<sup>I</sup>.

[b] Determined at 30°C.

[PcCo<sup>I</sup>]<sup>⊖</sup> is prepared by reduction of PcCo<sup>II</sup> with benzo-phenonedilithium or naphthalenesodium in THF at 20°C<sup>[2]</sup>. The blue PcCo<sup>II</sup> is practically insoluble in all common solvents, while Li[PcCo<sup>I</sup>] and Na[PcCo<sup>I</sup>] are readily soluble in methanol, ethanol, isopropanol, acetonitrile, DMSO, DMF, and dioxane. In cold THF and cold dioxane they are only sparingly soluble and can be recrystallized from these solvents.

In contrast to the cobaloxime<sub>s</sub> derivatives and vitamin B<sub>12a</sub>, which contain Co<sup>I</sup> and are only stable in alkaline medium, the [PcCo<sup>I</sup>] ion is also stable in neutral, protonic solution.

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CAS Registry numbers:

Li[PcCo<sup>I</sup>], 14516-90-6; CH<sub>3</sub>I, 74-88-4; n-C<sub>4</sub>H<sub>9</sub>Br, 109-65-9;

PcCo<sup>III</sup>-n-C<sub>4</sub>H<sub>9</sub>, 54774-62-8

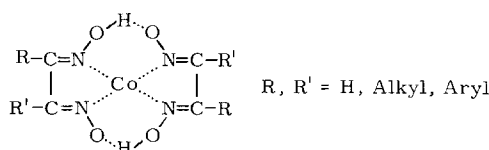
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[5] The cobalt(II) complexes of the type

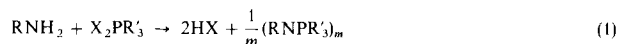


were named cobaloximes by Schrauzer [3]. The relative nucleophilicity of the cobaloximes with Co<sup>I</sup> (also referred to as cobaloximes<sub>s</sub>) is strongly dependent on the type of substituents R and R', particularly on their inductive effect. Thus  $n_{\text{CH}_3\text{I}}$  for bis(glyoxaldioximato)cobalt(I) is 10.5 and for bis(butanedionedioximato)cobalt(I) 13.3 (both complexes have tri-n-butylphosphane as axial ligands).

## Formation of Cyclopolyposphazenes in an "Anomalous Kirsanov Reaction"

By Christopher Glidewell<sup>[\*]</sup>

The Kirsanov reaction<sup>[1]</sup> between primary amines and dihalophosphoranes generally produces either imidophosphoranes ( $m = 1$ ) or 1,3,2λ<sup>5</sup>,4λ<sup>5</sup>-diazadiphosphetidines ( $m = 2$ ):



For X = R' = Cl, the reaction is generally carried out either by refluxing PCl<sub>5</sub> with the amine or its hydrochloride in an inert solvent, or by heating PCl<sub>5</sub> with the amine (if solid) or its hydrochloride in the absence of a solvent.

Thus when R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, treatment of PCl<sub>5</sub> with either benzylamine or benzylammonium chloride in refluxing carbon tetrachloride yields (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NPCl<sub>2</sub>)<sub>2</sub> (1), identified by its mass spectrum and its NMR spectra [<sup>1</sup>H-NMR (from TMS): δ = 7.18 (C<sub>6</sub>H<sub>5</sub>), 4.58 (t, CH<sub>2</sub>) ppm, <sup>3</sup>J(HCNP) = 30 Hz; <sup>31</sup>P-NMR (from 85% H<sub>3</sub>PO<sub>4</sub>): δ = +75.04 ppm]. However, when [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>3</sub>]Cl and PCl<sub>5</sub> are heated alone at ca. 150°C, no diazadiphosphetidine (1) is produced: instead the sole products are now benzyl chloride and the cyclopolyp-λ<sup>5</sup>-phosphazenes (NPCl<sub>2</sub>)<sub>3</sub> (2) and (NPCl<sub>2</sub>)<sub>4</sub> (3), characterized by their mass<sup>[2]</sup> and NMR spectra [(2): δ<sub>p</sub> = -19.78 (-19 ± 1<sup>[3]</sup>) ppm; (3): δ<sub>p</sub> = +3.04 (+4.6 → +7.0<sup>[3]</sup>) ppm]:

[\*] Dr. C. Glidewell

Chemistry Department, University of St. Andrews  
St. Andrews KY 16 9ST (Great Britain)