1565 diffraction data (Synthex-P3), $2 \leq 2Q \leq 42°$, ω-scan, λ-$Mo_{K\alpha} = 71.069$ pm, graphite monochromator, $\mu = 11.7$ cm^{-1}; solution: direct methods (Shel-XTL) refinement (Syntex-EXTL): full matrix, $R_1 = 0.046$. The cation $(3)^{2+}$ has crystallographic inversion symmetry; the best planes through the C_5Me_5-ring and the C_4B_2-ring are, within the limits of the accuracy of the determination, parallel. The PF_6 ions are disordered.

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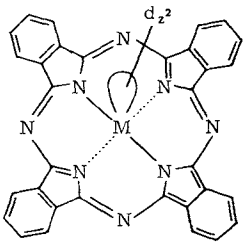
Stable Metal-Phthalocyanines as Poison-Resistant Catalysts in Homogeneous Catalysis: Reduction of Organic Compounds with $NaBH_4$[**]

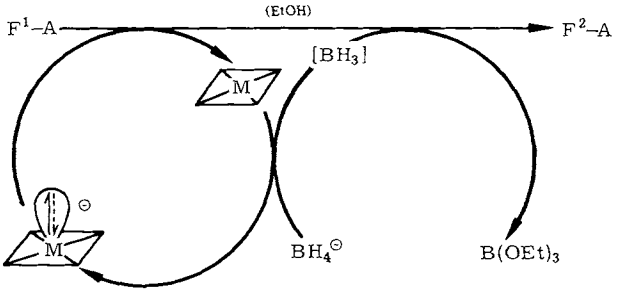
By *Heiner Eckert* and *Yvonne Kiesel*[*]

Transition metal-phthalocyanines (MPc) are extremely stable, both thermally and chemically, and hence some of them find use as fast blue dyes[1]. They can take up electrons reversibly in the d_{z^2} orbital of the central atom M[2]; this predestinates them—in combination with a suitable reducing agent such as $NaBH_4$—as reduction catalysts[3].



MPc

The anions $[MPc]^{\ominus}$ of insoluble metal-phthalocyanines are soluble in polar organic solvents[2]. We recently reported on the use of the cobalt(I)-phthalocyanine anion for the selective reduction of nitro compounds[4] and for the cleavage of β-haloalkyl protecting groups[3]. $NaBH_4$ reductions[5] of nitro-[5a-c], cyano-[5a] and carbamoyl groups[5a], and of activated CC double bonds[5b,d] with addition of transition metal salts[5a,c] or catalyzed by structurally similar, but very expensive vitamin B_{12}[5d] or decomposable "cobaloxime"[5b,d] have also been described. Olefins and nitriles have been reduced with zinc in acidic medium in presence of vitamin B_{12} as catalyst[6].



F^1–A and F^2–A see Table 1; M = VO, Mn, Fe, Co, Pd

The reduction of aliphatic and aromatic nitro- and nitroso-compounds, as well as oximes, Schiff's bases and nitriles with $NaBH_4$ under mild conditions in protic solvents (such as alcohols) at 20–25 °C to the corresponding amines can be homogeneously catalyzed with $[MPc]^{\ominus}$. CC-double bonds are hydrogenated, and halides are reduced to hydrocarbons. Arenes, aromatic halides, carboxylates and carboxamides are not attacked. The simultaneous reduction of several functional groups is also possible. The reaction rates gradually decrease along the series C=C ≈ Hal ≈ NO_2 ≈ NO > C=NOH ≈ C=N–R > CN;

Table 1. $[CoPc]^{\ominus}$-catalyzed reduction of organic compounds with $NaBH_4$ in EtOH at 20 °C. Educt conc. 0.2 M; $NaBH_4$ conc. 1.4 M; CoPc conc. 0.02 M.

Educt F^1–A	t [h]	Product F^2–A	Yield [%]
n-C_3H_7–NO_2	189	*n*-C_3H_7–NH_2	76
p-NO_2–C_6H_4–CH_3	21	*p*-NH_2–C_6H_4–CH_3	88
p-NO_2–C_6H_4–Cl	2–168	*p*-NH_2–C_6H_4–Cl	81–96
p-NO_2–C_6H_4–CH_2–CN	6	*p*-NH_2–C_6H_4–CH_2–CN	85
2,4-$(NO_2)_2C_6H_3$–Cl	214	2,4-$(NH_2)_2C_6H_3$–Cl	79
R–NO_2 [a]	2.5	R–NH_2 [a]	93
p-NO–C_6H_4–Cl	94	*p*-NH_2–C_6H_4–Cl	95
C_6H_5–CH=NOH	47	C_6H_5–CH_2–NH_2	80
C_6H_5–$CH(CH_3)$–CH=NOH	48	C_6H_5–$CH(CH_3)$–CH_2–NH_2	73
c-C_6H_{10}=NOH	48	*c*-C_6H_{11}–NH_2	78
C_6H_5–CH=N–$CH(CH_3)_2$	72	C_6H_5–CH_2–NH–$CH(CH_3)_2$	92
C_6H_5–CN	168	C_6H_5–CH_2–NH_2	53
C_6H_5–CH_2–CN	137	C_6H_5–CH_2–CH_2–NH_2	63
NC–$(CH_2)_4$–CN	188	NH_2–$(CH_2)_6$–NH_2 [b]	27
C_8H_{17}–CH=CH–C_7H_{14}–CO_2Et	40 [c]	$C_{17}H_{35}$–CO_2Et	100
C_6H_5–CH=CH–CO_2Et	0.5	C_6H_5–CH_2–CH_2–CO_2Et	98
$(CH_3)_2C$=CH–CO–NH_2	165	$(CH_3)_2CH$–CH_2–CO–NH_2	80
C_6H_5–CH=CH–CN	1	C_6H_5–CH_2–CH_2–CN	82
n-$C_{12}H_{25}$–Br	21	*n*-$C_{12}H_{26}$	97
2,4-$(CH_3)_2C_6H_3$–CH_2Cl	2	1,2,4-$(CH_3)_3C_6H_3$	63
p-NO_2–C_6H_4–CO–CH_3	48	*p*-NH_2–C_6H_4–CH(OH)–CH_3	79
p-NO_2–C_6H_4–CH_2–CN	156	*p*-NH_2–C_6H_4–CH_2–CH_2–NH_2	77
p-NO_2–C_6H_4–CH=CH–CO_2Et	120	*p*-NH_2–C_6H_4–CH_2–CH_2–CO_2Et	64

[a] R = 2-acetamino-4-methoxy-5-methoxycarbonylphenyl. [b] Isolated as *N,N'*-dibenzoyl derivative. [c] 3 h at 50 °C.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.

the reaction times are <30 min to 200 h. Hence, reducible groups can be successively reduced selectively under kinetic control, *e.g.* a nitronitrile to an aminonitrile or an α,β-unsaturated to a saturated nitrile (Table 1). The cata-

lysts are used in a concentration of up to 0.001 M; in the reduced soluble form $[MPc]^{\ominus}$ they change color (Table 2), thus allowing the course of the reaction to be monitored. After the reaction (in non-reducing medium), the catalyst MPc is quantitatively recovered; it can be used again for reductions without any further treatment.

Table 2. $[MPc]^{\ominus}$-catalyzed reduction of *p*-chloronitrobenzene with $NaBH_4$ in EtOH at 20–25 °C. Educt conc. 0.2 M; $NaBH_4$ conc. 1.4 M; MPc conc. 0.02 M.

M in MPc	Color of $[MPc]^{\ominus}$ [a]	*t* [h]	Yield of *p*-NH_2—C_6H_4—Cl [%]
$V^{IV}O$	lilac	2	48
$V^{IV}O$		23	91
Mn^{II}	dark green	2	85
Fe^{II}	wine red	3	74
Fe^{II}		96	89
Co^{II}		2	81
Co^{II} [b]	deep yellow-green	71	74
Co^{II} [c]		3	26
Co^{II} [c]		70	76
Pd^{II}	black [d]	2	80
Pd^{II}		120	98
Vitamin B_{12b}	blue green [e]	2	34
Vitamin B_{12b}		20	64

[a] 1–15 min after the combined addition of $NaBH_4$ and MPc in solution. [b] $NaBH_4$ conc. 0.4 M. [c] CoPc conc. 0.002 M. [d] Color of the sparingly soluble crystals. [e] Color of the vitamin B_{12b} solution.

Strong catalyst poisons[7] such as divalent S-compounds (β-naphthalenethiol, 1-octanethiol), or cyanide or iodide ions in tenfold excess (referred to the catalyst; equimolar referred to the educt) do not influence the rate of the reaction, or if so only slightly. This is reflected in the almost identical yields of reduction products in reactions with or without catalyst poison (Table 3). This immunity is understood in the case of $[MPc]^{\ominus}$ catalysts with M = Fe or Co, probably owing to maximal localization of the negative charge in the "central atomic orbitals" of these $[MPc]^{\ominus}$. This finding is consistent with the results of LCAO-MO calculations on the electron-configuration of MPc[2]. The poisoning effects of the metals with d-electrons (*e.g.* Cu^{2+}, Fe^{2+}) are deactivated by their reduction to the metals under the reaction conditions. The M—C bond in alkyl-MPc complexes, which can be formed as intermediates from $[MPc]^{\ominus}$ and alkylating agents, is likewise reductively cleaved by $NaBH_4$. Thus, an organo-MPc, such as 2-hydroxyethyl-Co^{III}Pc, can be used with the same effect as MPc for the catalysis of reduction.

Table 3. $[MPc]^{\ominus}$-catalyzed reduction of *p*-chloronitrobenzene with $NaBH_4$ in the presence of strong catalyst poisons. For conditions see Table 2; concentration of catalyst poison 0.2 M.

Catalyst poison	M	*t* [h]	Yield [%] of *p*-NH_2—C_6H_4—Cl without catalyst poison	with catalyst poison
β-Naphthalenethiol	Co	2	81	84
n-C_8H_{17}—SH	Co	2	81	72
$CN^{\ominus}$	Co	2	81	58
$CN^{\ominus}$	Co	8	—	83
$CN^{\ominus}$	Fe	3	74	70
$I^{\ominus}$	Co	2	81	77
Cu^{2+}	Co	2	81	93
HO—CH_2—CH_2—Co^{III}Pc		2	81	85
$CN^{\ominus}$	Vitamin B_{12b}	2	34	10

The reduction of a nitro group with $NaBH_4$ can also be catalyzed by the structurally related vitamin B_{12}, but the reaction is slower and susceptible to catalyst poisoning (Tables 2 and 3). Moreover, vitamin B_{12} is not so favorable as the metal-phthalocyanines regarding stability, insolubility in the "non-active state", and price. The easily accessible "cobaloximes"[5b,d] (vitamin B_{12} models) are readily decomposable in the reduced form and tend to undergo side reactions at the ligand[8]. While many metal-macrocycles, *e.g.* the metal-porphyrins[9], can be relatively easily demetalated, the metal in stable MPc is almost irreplaceable even under drastic conditions (e.g. 5 N HCl/reflux; 5 N NaOH/reflux; conc. H_2SO_4)[1a]. The sensitivity of the porphyrins to light, which leads to their photooxidation[9], is not observed in the case of the light-fast dyes MPc. Because of their stability the MPc's are guaranteed a very long life even under "hard" conditions.

The stable MPc's are thus a successful combination of soluble $[MPc]^{\ominus}$ catalysts during the reduction and insoluble MPc-procatalyst under non-reducing conditions.

Procedure

MPc[1] (0.5 g, *ca.* 0.9 mmol) is added under N_2 to a solution of $NaBH_4$ (2.7 g, 70 mmol) in EtOH (50 cm^3). The deep-colored solution (or suspension) is treated with 10 mmol F^1—A (Table 1) and the water-cooled mixture stirred at 20–25 °C under constant pressure (Tables 1 and 2). The ice-cold mixture is then neutralized with 5 N HCl (5–10 min until completion of the initially vigorous evolution of gas; pH 6–7) and the deep-blue precipitate separated by centrifugation (5 min; 3000 rpm) and washed three times with MeOH; the catalyst MPc remains behind. For re-use the catalyst is washed three times with water and dried between 20 and 200 °C. The combined centrifugates are evaporated down and the residue partitioned between water and CH_2Cl_2. In the case of aliphatic amines the residue is partitioned with 1 N NaOH/ether. Volatile amines are isolated from the ether phase as F^2—A · HCl. Concentration and drying of the organic phase affords the products F^2—A. These are purified by filtration of a solution in hexane/ether in the case of neutral substances, and by filtration of their aqueous solutions in hydrochloric acid in the case of amines.

Received: November 26, 1980 [Z 753 IE]
German version: Angew. Chem. *93*, 477 (1981)

CAS Registry numbers:
n-C_3H_7—NO_2, 108-03-2; *p*-NO_2—C_6H_4—CH_3, 99-99-0; *p*-NO_2—C_6H_4—Cl 100-00-5; *p*-NO_2—C_6H_4—CH_2—CN, 555-21-5; 2,4-$(NO_2)_2C_6H_3$-Cl, 97-00-7; R-NO_2, 4093-41-8; *p*-NO—C_6H_4-Cl, 932-98-9; C_6H_5—CH=NOH, 932-90-1; C_6H_5—$CH(CH_3)$—CH=NOH, 13213-36-0; *c*-C_6H_{10}=NOH, 100-64-1; C_6H_5—CN, 100-47-0; C_6H_5—CH_2—CN, 140-29-4; NC—$(CH_2)_4$—CN, 111-69-3; β-pinene, 127-91-3; C_6H_5—CH=CH—CO_2Et, 103-36-6; $(CH_3)_2C$=CH—CO—NH_2, 4479-75-8; C_6H_5—CH=CH—CN, 4360-47-8; *n*-$C_{12}H_{25}$—Br, 143-15-7; 2,4-$(CH_3)_2C_6H_3$—CH_2Cl, 824-55-5; *p*-NO_2—C_6H_4—CO—CH_3, 100-19-6; *p*-NO_2—C_6H_4—CH=CH—CO_2Et, 953-26-4; $NaBH_4$, 1694-66-2; CoPc, 3317-67-7; VoPc, 13930-88-6; MnPc, 14325-24-7; FePc, 132-16-1; PdPc, 20909-39-1; Vitamin B_{12b}, 13422-52-1; β-naphthalenethiol, 91-60-1; *n*-C_8H_{17}—SH, 111-88-6; CN^-, 57-12-5; I^-, 20461-54-5; Cu^{2+}, 15158-11-9; Ho—CH_2CH_2—Co^{III}Pc, 62450-97-9; *n*-C_3H_7—NH_2, 107-10-8; *p*-NH_2—C_6H_4—CH_3, 106-49-0; *p*-NH_2—C_6H_4—Cl, 106-47-8; *p*-NH_2—C_6H_4—CH_2—CN, 3544-25-0; 2,4-$(NH_2)_2$—C_6H_3—Cl, 5131-60-2; R-NH_2, 77495-40-0; C_6H_5—CH_2—NH_2, 100-46-9; C_6H_5—$CH(CH_2)$—CH_2—NH_2, 582-22-9; *n*-C_6H_5—NH_2, 108-91-8; C_6H_5—CH_2—CH_2—NH_2, 64-04-0; C_6H_5CONH—$(CH_2)_6$—$CNCOC_6H_5$, 5326-21-6; pinane, 473-55-2; C_6H_5—CH_2—CH_2CO_2Et, 2021-28-5; $(CH_3)_2CH$—CH_2—CO—NH_2, 541-46-8; $C_6H_5CH_2$—CH_2—CN, 645-59-0; *n*-$C_{12}H_{26}$, 112-40-3; 1,2,4-$(CH_3)_3C_6H_3$, 95-63-6; *p*-NH_2—C_6H_4—CH(OH)—CH_3, 14572-89-9; *p*-NH_2—C_6H_4—CH_2—CH_2—NH_2, 13472-00-9; *p*-NH_2—C_6H_4—CH_2—CH_2—CO_2Et, 7116-44-1;

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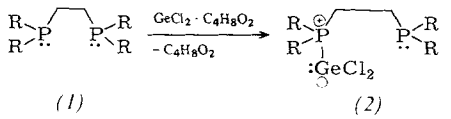
P,P,P',P'-Tetraphenylethylenediphosphanedichlorogermanediyl: A Fluxional Phosphorus Ylide[**]

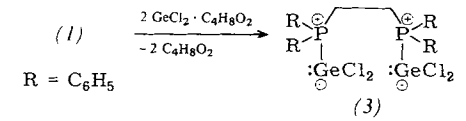
By *Wolf-Walther du Mont, Gero Rudolph,* and *Norbert Bruncks*[*]

The kinetic lability of certain phosphorus ylides, phosphane chalcogenides and halogenophosphonium ions $R_3P{-}X$ ($X = GeCl_2$[1], $SnCl_2$[2], Te[3], Br^+, I^+[3a]) has recently been determined in the presence of non-coordinated R_3P. The transfer of six-electron species of heavy main group elements between phosphanes, which occurs rapidly on the ^1H- and ^{31}P-NMR time scales even at room temperature, can be satisfactorily described as a P^{III}/P^V redox reaction or a "ligand exchange" process at I^+, Te^0, Sn^{II} *etc.* Thus, *Scherer et al.* detected a fluxional redox system *via* transfer of tellurium in a diazadiphosphetidine derivative[3d], in which discrete P^{III}- and P^V-units are present in the crystal[4]. We now report the first fluxional ylide in which the "carbene analogous" dichlorogermanediyl derivative is mobile in solution at $-80\,^\circ C$.

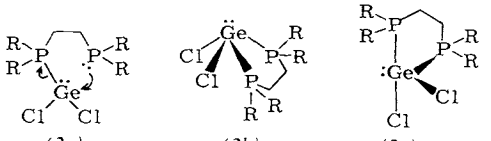
P,P,P',P'-tetraphenylethylenediphosphane *(1)* reacts with the $GeCl_2$-dioxane complex, depending on the stoichiometric ratio, to give the 1:1-complex *(2)* or the 1:2-complex *(3)*. Both dissolve as monomers in benzene and give $^{31}P\{^1H\}$-NMR spectra consisting of *one* signal. While the ^{31}P-singlet for *(3)* occurs at $\delta = -7$ and is consistent



(1) *(2)*



(3)



(2a) *(2b)* *(2c)*

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.

with a diylide structure, the considerable broadening of the ^{31}P-NMR signal of *(2)* at $\delta = -10.2$ presents many structural possibilities. Since only one (sharp) signal appears at $-80\,^\circ C$ in [D_8]toluene, apart from transfer of the ylide functionality between the phosphane groups as in *(2a)*, the chelate complex structures *(2b)* with tetragonal-pyramidal arrangement of ligands at Ge^{II} or the (pseudo)-trigonal bipyramidal arrangement of ligands in *(2c)* might also be present in solution.

In the case of *(2c)*, equilibration of the phosphane functionalities detected in the ^{31}P-NMR spectrum implies that pseudorotation occurs at germanium. A linear Cl—Ge—Cl-arrangement is precluded on the basis of the IR-data. To clarify this problem, an X-ray structure analysis of *(2)* was therefore undertaken[5]. The data, show that the coordination sphere around the germanium in *(2c)* can be described as a distorted trigonal bipyramid, the Ge—P bond lengths are, however, very different ($Ge{-}P_{eq} = 251$ pm, as in $(C_6H_5)_3PGeCl_2$[6], $Ge{-}P_{ax} = 334$ pm, somewhat less than the van der Waals separation). Thus, the equilibration of the phosphorus atoms in solution can be satisfactorily explained by fluxion of the $\overset{\oplus}{P}{-}\overset{\ominus}{Ge}$-ylide *(2a)* as well as by pseudorotation of the chelate complex.

Procedure

(1) (2.15 g, 5.4 mmol) is added to $GeCl_2 \cdot$ dioxane (1.25 g, 5.4 mmol) in 30 cm^3 toluene. The solvent is evaporated off after 1 h, and the already pure *(2)* (2.9 g, 100%) recrystallized from toluene. Decomposition point $\geq 250\,^\circ C$, correct analytical data. IR (CsI/Nujol): $\nu = 270$ s, 305 vw, 335 s cm^{-1} ($PGeCl_2$); ^1H-NMR (C_6D_6): $\delta = 2.3$ (m); ^{31}P-NMR ($C_6D_5CD_3$), 298 K: $\delta = -10.2$ (broad), 193 K: -10.8.

Received: July 4, 1980 [Z 754 IE]
German version: Angew. Chem. *93,* 472 (1981)
CAS Registry numbers:
(1), 1663-45-2; *(2),* 77495-41-1; *(3),* 77495-42-2; $GeCl_2 \cdot C_4H_6O_2$, 28595-67-7

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[(−)-diop]RhCl—Catalyzed Asymmetric Addition of Bromotrichloromethane to Styrene

By *Shinji Murai, Ryoji Sugise,* and *Noboru Sonoda*[*]

Although a number of asymmetric reactions catalyzed by transition metal complexes to form C—H, C—C, C—Si, and C—O bonds with creation of chirality have been reported[1], no reactions of this type which lead to the formation of chiral carbon-halogen bonds have been reported[2] to the best of our knowledge. We describe here the first example of an asymmetric reaction, catalyzed by a chiral transition metal complex, in which the chiral center is formed as a result of carbon-bromine bond formation.

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