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Syntheses of Transition Metal Complexes of Pentafluorophenylhydrazine

Wolfram Rieber and Wolfgang Beck*

Dedicated to Professor Hanns Peter Boehm on the Occasion of his 90th Birthday

Key Words : Pentafluorophenylhydrazine as Ligand, Transition Metal Chlorides

Abstract. By reaction of pentafluorophenylhydrazine with metal chlorides the complexes $M(NH_2NHC_6F_5)_4Cl_2$ ($M = Co, Ni$), $M(NH_2NHC_6F_5)_2Cl_2$ ($M = Mn, Fe, Pd, Zn, Cd$), $Cu(NH_2NHC_6F_5)Cl$ and $Hg(NH_2NHC_6F_5)_2Cl$ have been obtained. From $Cr(CO)_6$ and pentafluorophenylhydrazine the complex $Cr(CO)_5(NH_2NHC_6F_5)$ was synthesized.

Introduction

Pentafluorophenylhydrazine reacts readily with aldehydes and ketones to give hydrazones and therefore has been applied very often as derivatizing agent for the determination of these carbonyl compounds in air, in water, biological fluids, on surfaces, or cosmetics, using chromatography and mass spectrometry [1, 2]. It has been applied in organic synthesis, e.g. for the synthesis of pyrazoles [1].

To our knowledge, pentafluorophenylhydrazine has been used only in a few cases in coordination and organometallic chemistry:

The ferrocenylhydrazone $(C_5H_5)Fe(C_5H_4CH=NNHC_6F_5)$ was reported [3]. The structures of cobalt(II) complexes of Schiff bases from pentafluorophenylhydrazine and salicyl aldehyde or acetylpyridine have been determined by X-ray diffraction [4]. Reactions of pentafluorohydrazine with (porphyrine)iron and hemoglobin [5] and with $[(C_5H_5)Fe(CO)_2]^-$ [6] have been carried out to give σ -bonded phenyl complexes. $RHgX$ compounds have been prepared by reactions of polyfluoroarylhydrazines $RHNNH_2$ with Hg, HgO or HgX_2 and various oxidizing agents [7]. In a trimeric carbonyl osmium cluster $Os_3(CO)_{10}(NH_2NHC_6F_5)$ the hydrazine group of pentafluorophenylhydrazine was found as bridge between two Os atoms [8].

In the following we present reactions of pentafluorophenylhydrazine with metal halides and with hexacarbonylchromium(0) $[Cr(CO)_6]$. Shortly after the discovery of hydrazine by Curtius in 1894, the latter [9] and others [10] reported several metal halide complexes with hydrazine and phenylhydrazine of type $M(NH_2NHR)_2X_2$ ($R = H$ [9 - 13], Ph [14,15]., e.g. also K. A. Hofmann in Munich [11]. $Mo(CO)_5(NH_2NHPh)$ has been synthesized from the phenyl substituted hydrazine and $[Mo(CO)_5Cl]^-$ [16]. Reviews on the many metal complexes containing monodentate and bridging hydrazine, bidentate and substituted hydrazine ligands [17-19] have been published.

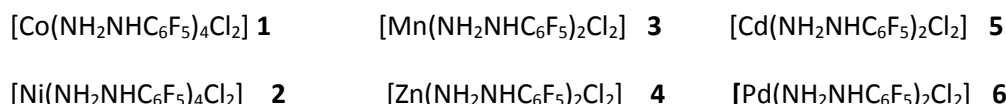
Pentafluorophenylhydrazine is a weaker base than phenylhydrazine ($K_b = 1.4 \cdot 10^{-10}$ compared to $1.6 \cdot 10^{-9}$) [20] and should coordinate through the NH_2 group for steric reasons.

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Results and Discussion

The metal dichlorides MCl_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$), which contain crystal water, and MCl_2 ($\text{M} = \text{Zn}, \text{Cd}$) react with pentafluorophenylhydrazine in ethanol to give the complexes **1-5** in high yields.



These complexes are formed as nacreous, fine crystalline compounds, which mostly are not soluble in the common organic solvents and are decomposed in water, as shown by the change of colour.

Reduction of Pd(II) to Pd(O) occurs on addition of pentafluorophenylhydrazine to PdCl_2 or $\text{Pd}(\text{NO}_3)_2$ in ethanol. However, complex **6** was available by reaction of $[\text{AsPh}_4]_2[\text{PdCl}_4]$ in aprotic solvents (e.g. dichloromethane).

Long ago, it was already observed, that metal(III) chlorides and hydrazine yield metal(II) complexes [12, 17]. Reduction of Fe(III), Cu(II) and Hg(II) occurs also with pentafluorophenylhydrazine in reactions with FeCl_3 , CuCl_2 and HgCl_2 in ethanol and the complexes **7-9** could be isolated:



Complexes **7** and **8** were also obtained from FeCl_2 and CuCl . No reaction was observed with Hg_2Cl_2 and $\text{NH}_2\text{NHC}_6\text{F}_5$. Hg(II) complexes were reported [11, 21] from HgCl_2 and N_2H_4 .

Analogously to N_2H_4 [17, 22], N_2 and pentafluorophenylaniline are formed by reaction of FeCl_3 with pentafluorophenylhydrazine as reducing agent; $\text{C}_6\text{F}_5\text{NH}_2$ could be identified by boiling point, IR-spectrum and acetyl derivative.

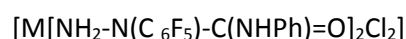
In aqueous solution, CuCl_2 and pentafluorophenylhydrazine afforded a nitrogen free compound under vigorous evolution of gas, which - presumably - is a fluorobenzene derivative [20].

In the IR spectra, besides the N-H absorptions at $3100\text{-}3300\text{ cm}^{-1}$ (νNH) and at $1580\text{-}1610\text{ cm}^{-1}$ (δNH), the $\nu\text{N-N}$ absorption at 950 cm^{-1} is characteristic (see experimental part) and may be indicative for unidentate pentafluorophenylhydrazine as ligand, coordinated through the H_2N group as for phenylhydrazine for which no hydrazine bridged complexes are known, probably for steric reasons [17, 18]. E.g. (For free pentafluorophenylhydrazine $\nu\text{N-N} = 940\text{ cm}^{-1}$).

The palladium(II) complex **6** is monomeric in acetone solution (osmometrically determined), according to a planar tetracoordinated structure. For Zn-complexes with phenylhydrazine ligands a tetrahedral structure was determined [23], which should be present also in **4**, whereas for $[\text{Zn}(\text{N}_2\text{H}_4)_2\text{Cl}_2]$ a polymeric structure with infinite chains $-\text{Zn}-\text{NH}_2-\text{NH}_2-\text{Zn}-$ was found [24].

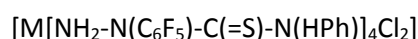
The complexes **1-7** exhibit the same composition as the corresponding phenylhydrazine (NH_2NHPh) metal complexes [14].

The cobalt and nickel complexes **1** and **2** react with phenylisocyanate $\text{PhN}=\text{C}=\text{O}$ and phenylisothiocyanate $\text{PhN}=\text{C}=\text{S}$ to give the complexes **10-13**:



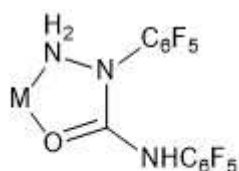
10: M = Co

11: M = Ni



12: M = Co

13: M = Ni



Chelate structure in **10, 11**

For **10** and **11** a six coordinated bischelate structure has to be assumed as in various semicarbazide complexes [25-27], whereas for **12** and **13** a chelate structure is not probable. In good accordance with these proposals the $\text{C}=\text{O}$ absorption of **10** and **11** is shifted from 1698 cm^{-1} of the free semicarbazide to 1640 cm^{-1} in the complexes, whereas no comparable shift is observed for the $\text{C}=\text{S}$ absorption of the thiosemicarbazide compounds **12** and **13** (see e.g. [28]). In the reactions to **10-13** the amino group is protected by the metal atom against attack of an electrophile. By these reactions 1,1-disubstituted hydrazines, which readily can be cleaved from the metal ion by water or weak acids, are available in a directed way.

Finally, an organometallic complex has been synthesized by photochemical reaction [29] of hexacarbonyl chromium with pentafluorophenylhydrazine and $[\text{Cr}(\text{CO})_5(\text{NH}_2\text{NHC}_6\text{F}_5)]$ (**14**) could be isolated and characterized. The $\nu\text{N}-\text{N}$ absorption at 945 cm^{-1} of **14** is again typical for the unidentate hydrazine ligand. Pentacarbonyl complexes of Cr, Mo and W with N_2H_4 are interesting and valuable starting compounds for the syntheses of Sellmann's diazene (N_2H_2) and dinitrogen complexes [30].

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Experimental Part

The solvents were saturated with nitrogen and distilled. The syntheses were performed under nitrogen atmosphere. Pentafluorophenylhydrazine was purchased from PCR Peninsular Chemresearch Inc., Gainesville, Florida, USA. It can be synthesized by reaction of hydrazine hydrate with hexafluorobenzene [20].

The analyses have been in part performed by Mikroanalytisches Labor Dr. E. Pascher, Bonn, using V_2O_5 as oxidant.

$Co(NH_2NHC_6F_5)_4Cl_2$ (**1**): To a concentrated solution of $CoCl_2 \cdot 6 H_2O$ (0.48 g, 2 mmol) in ethanol a solution of pentafluorophenylhydrazine (1.6 g, 8 mmol) in ethanol was dropped, whereby immediately a rose coloured, acereous precipitate was obtained, which was washed with ethanol and diethylether and dried *in vacuo* for 6 h. IR (nujol): 3330 sh, 3284 s, 3140 sh (νNH), 1590 m (δNH), 1520 vs, 1480 s (C-C), 952 ss ($\nu N-N$) cm^{-1} . $CoC_{24}H_{12}Cl_2F_{20}N_8$ (922.3): Calcd. C 31.20, H 1.30, N 12.15, Cl 7.70, F 41.40, Co 6.40; found C 31.04, H 1.28, N 12.05, Cl 7.89, F 41.60, Co 6.20.

$Ni(NH_2NHC_6F_5)_4Cl_2$ (**2**): By dropping a solution of pentafluorophenylhydrazine (1.6 g, 8 mmol) in ethanol to a solution of $NiCl_2 \cdot 6 H_2O$ (0.48 g, 2 mmol) in ethanol a bright blue, glittering precipitate was obtained, which was washed with ethanol and diethylether and dried *in vacuo* for 6 h. IR (nujol): 3320 sh, 3284 s, 3160 sh (νNH), 1585 m (δNH), 1520 vs, 1478 s (C-C), 948s ($\nu N-N$) cm^{-1} . $NiC_{24}H_{12}Cl_2F_{20}N_8$ (922.0): Calcd. C 31.20, H. 1.30, N 12.15; found C 31.43, H 1.44, N 11.84.

$Mn(NH_2NHC_6F_5)_2Cl_2$ (**3**): To a solution of $MnCl_2 \cdot 4 H_2O$ (0.4g, 2 mmol) in ethanol (10 ml) a solution of pentafluorophenylhydrazine (0.8 g, 4 mmol) in ethanol (5 ml) was added. The gradually formed fine crystalline, flesh-coloured precipitate was filtered off, washed with ethanol and diethylether and dried *in vacuo* for 6 h. IR (nujol): 3312 sh, 3299 s, 3280 vs, 3140 s (νNH), 1608 (δNH), 1536 vs, 1525 vs, 1481 vs (C-C) 947 ($\nu N-N$) cm^{-1} . $MnC_{12}H_6Cl_2F_{10}N_4$ (521.9): Calcd. C 27.60, H 1.16, N 10.72; found C 29.03, H 1.41, N 11.14.- $Mn(NH_2NH)_{2.5}Cl_2$ (621.0): Calcd. C 29.01, H 1.22 N 11.28.

$Zn(NH_2NHC_6F_5)_2Cl_2$ (**4**): To a solution of $ZnCl_2$ (0.4 g, 2 mmol) in ethanol a solution of pentafluorophenylhydrazine (1.2 g, 4 mmol) in ethanol was added. The gradually formed white bright precipitate was washed with cold ethanol (few ml) and several times with petroleum ether. The compound is moderately soluble in ethanol and diethylether. IR (nujol): 3330 s, 3190m (νNH), 1590 s (δNH), 1526 vs (C-C), 149 s, 950 s ($\nu N-N$) cm^{-1} . $ZnC_{12}H_6Cl_2F_{10}N_4$ (532.5): Calcd. 27.00 H 1.13 N 10.55; found C 26.93, H 1.23, N 10.34.

$Cd(NH_2NHC_6F_5)_2Cl_2$ (**5**): To a solution of $CdCl_2$ (0.36 g, 2 mmol) in ethanol (96 %, 30 ml) a solution of pentafluorophenylhydrazine (0.8 g, 4 mmol) in ethanol (20 ml) was dropped. The white, fine crystalline precipitate was filtered off, washed several times with ethanol and diethylether and dried *in vacuo* for 6 h. IR (nujol): 3280 vs, 3141 s, 3100 sh (νNH), 1610 s (δNH), 1537 vs, 1524 vs, 1481vs (C-C), 948 s ($\nu N-N$) cm^{-1} . $CdC_{12}H_6Cl_2F_{10}N_4$ (579.4): Calcd. C 24.85, H 1.05, N 9.68; found C 24.63, H 1.23, N 9.58.

$Pd(NH_2NHC_6F_5)_2Cl_2$ (**6**): $[AsPh_4]_2[PdCl_4]$ was obtained by adding an aqueous solution of $AsPh_4Cl$ to an aqueous solution of NaCl (in excess) and $Pd(NO_3)_2$ and the formed precipitate was isolated and dried. To a solution of $[AsPh_4]_2[PdCl_4]$ (1 g, 1.8 mmol, from $AsPh_4Cl$, $Pd(NO_3)_2$, and NaCl) in dichloromethane a solution of pentafluorophenylhydrazine (1.1 g, 6 mmol) in dichloromethane was added. From the dark brown solutions after 1 min a gold yellow, nacreous precipitate appeared, which was washed with dichloromethane. The complex is moderately soluble in ethanol and diethylether. IR (nujol):

3280 s, 3218 s 3100sh (ν NH), 1582 s (δ NH), 1523 s, 1517 vs, 1468 s (C-C), 962 s (ν N-N) cm^{-1} . $\text{PdC}_{12}\text{H}_6\text{Cl}_2\text{F}_{10}\text{N}_4$ (573.3): Calcd. C 25.10, H 1.05, N 9.79; found C 25.07, H 1.16 N 9.81, M 540 (osmometrically in acetone).

$\text{Fe}(\text{NH}_2\text{NHC}_6\text{F}_5)_2\text{Cl}_2$ (**7**): Under N_2 atmosphere to a solution of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ (0.4 g, 1.5 mmol) in ethanol a solution of pentafluorophenylhydrazine (1.55 g, 7.8 mmol) in ethanol (20 ml) was added. Under slight evolution of gas a white precipitate appeared, which was filtered off after 1 h, washed with ethanol and diethylether and dried *in vacuo*. The complex turned dark brown on air. From the filtrate by addition of diluted NaOH and extraction with diethylether pentafluoroaniline could be isolated, which was identified by its boiling point 153-155 °C and its acetyl derivative (m.p. 129 °C) [31].

IR (nujol): 3330 vs, 3300 m, 3278 s, 3130 m (ν NH), 1604 m (δ NH), 1535 s, 1520 s, 1481 s (C-C), 943 s (ν N-N) cm^{-1} . $\text{Fe}_{12}\text{H}_6\text{Cl}_2\text{F}_{10}\text{N}_4$ (523.0): Calc. C 27.58 H 1.15, N 10.71, Cl 13.57; found C 28.35, H 1.64, N 10.50, Cl 13.71.

Under N_2 atmosphere to a solution of $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ (0.2 g, 1 mmol) in ethanol (5 ml) pentafluorophenylhydrazine (0.4 g, 2 mmol) was added and after 1 min a white precipitate appeared, which showed an IR spectrum, identical with that of the complex from FeCl_3 .

$\text{Cu}(\text{NH}_2\text{NHC}_6\text{F}_5)_2\text{Cl}$ (**8**): Under N_2 atmosphere to a solution of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ (0.4 g, 2.3 mmol) in ethanol (10 ml) a solution of pentafluorophenylhydrazine (1.5 g, 7.5 mmol) in ethanol (20 ml) was added. Immediately – with slight evolution of gas – the white, bright copper(I) complex precipitated, which was washed with ethanol and diethylether. The complex turned brown on air and with NaOH solution red Cu_2O was formed on heating. IR (nujol): 3290 s, 3140 m (ν NH), 1583 (δ NH), 1527 sh, 1518 vs, 1463 m(C-C), 953 s (ν N-N) cm^{-1} . $\text{CuC}_6\text{H}_3\text{ClF}_5\text{N}_2$ (302.1): Calc. 24.20, H 1.01, N 9.45, Cl 11.80; found C 27.02, H 1.33, N 9.50, Cl 12.0.C

Complex **8** was also obtained by addition of a solution of pentafluorophenylhydrazine (0.3 g, 1.5 mmol) in ethanol (4 ml) to a suspension of CuCl (0.1g, 1 mmol) in ethanol (2 ml). The suspension was stirred for 1 d.

$\text{Hg}(\text{NH}_2\text{NHC}_6\text{F}_5)_2\text{Cl}_2$ [**9**]: To HgCl_2 (0.54 g, 2 mmol) in ethanol (14 ml) a solution of pentafluorophenylhydrazine (0.8 g, 4 mmol) in ethanol (10 ml) was added. The formed bright white precipitate was filtered off and washed with diethylether. The complex is moderately soluble in ethanol. IR (nujol): 3242 s, 3124 m, 3092 sh (ν NH), 1604 m (δ NH), 1537 vs. 1524 vs, 1463 s (C-C), 953 s (ν N-N) cm^{-1} . $\text{HgC}_{12}\text{H}_6\text{ClF}_{10}\text{N}_4$ (632.3): Calcd. C 22.80, H 0.86, N 8.86; found c 22.53, H. 1.12, N 9.46.

$\text{Co}[\text{NH}_2\text{-N}(\text{C}_6\text{F}_5)\text{-C}(\text{NHC}_6\text{H}_5)=\text{O})_2\text{Cl}_2$ (**10**): Under N_2 atmosphere to complex **1** (1 g, 1.1 mmol) phenylisocyanate (3 ml) was added. After some min from the dark blue solution a light blue precipitate was formed which - after 2 h - was filtered off and washed several times with petroleum ether and with some ml of diethylether and dried *in vacuo*. The complex is soluble in diethylether, ethanol and acetone. M.P. 130°C. Decomposition with water to give the free semicarbazone and Co (II). IR (nujol): 3290 vs (ν NH), 1640s (CO), 1598 s (δ NH), 1558 s, 1520 vs, 1448 m (C-C), 970 as (ν N-N), 752s, 690 m (CH) cm^{-1} . $\text{CoC}_{26}\text{H}_{16}\text{Cl}_2\text{F}_{10}\text{N}_6\text{O}_2$ (764.3): Calcd. C 40.70, H 2.34, N 10.95; found C 41.44, H 2.58, N 10.42.

$\text{Ni}[\text{NH}_2\text{-N}(\text{C}_6\text{F}_5)\text{-C}(\text{NHC}_6\text{H}_5)=\text{O})_2$ (**11**): Under N_2 atmosphere to complex **2** (1 g, 1.1 mmol) phenylisocyanate (3 ml) was added. From the dark green solution a light green precipitate was

obtained after some min, which –after 2 h–was filtered off and washed several times with petroleum ether and diethylether and dried *in vacuo*. M. P. 176 °C, The complex is decomposed in water to give the free semicarbazone and Ni(II). IR(nujol): 3265 vs (ν NH), 1640 s (ν CO), 1598 s (δ NH), 1570 s, 1520 ss, 1450 s, 968 s (ν N-N), 750s, 690 s (CH) cm^{-1} : $\text{NiC}_{26}\text{H}_{16}\text{Cl}_2\text{F}_{10}\text{N}_6\text{O}_2$ (764.1): Calcd. C 40.80, H 2.34, N 10.95; found C 39.25, H 2.65, N 9.97.

$\text{Co}[\text{NH}_2\text{-N}(\text{C}_6\text{F}_5)\text{-C}(\text{S})\text{-NHC}_6\text{H}_5]_4\text{Cl}_2$ (**12**): To complex **1** (1 g, 1.1 mmol) phenylthioisocyanate (3 ml) was added and the mixture was stirred for 1 d and its color changed to violet. A light blue precipitate was formed, which was washed several times with petroleum ether and then with some ml of diethylether. The complex is well soluble in ethanol and acetone. IR (nujol): 3340 sh, 3305 sh, 3258 sh, (ν NH), 1595 m (δ NH), 1565 m, 1525 vs, 1455 m (C-C), 1276 (ν CS), 973 s (ν N-N), 735 m, 692 S (CH) cm^{-1} . $\text{CoC}_{52}\text{H}_{32}\text{Cl}_2\text{F}_{20}\text{N}_{12}\text{S}_4$ (1463.0): Calcd. C 42.55, H 2.19, N 11.45; found C 42.58, H 2.27, N 10.87.

$\text{Ni}[\text{NH}_2\text{-N}(\text{C}_6\text{F}_5)\text{-C}(\text{S})\text{-NHC}_6\text{H}_5]_4\text{Cl}_2$ (**13**): The mixture of complex **2** (1 g, 1.1 mmol) and phenylthioisocyanate (3 ml) changed its color to green and after stirring for 1 d a light green precipitate was obtained, which was washed several times with petroleum ether and some ml of diethylether and dried *in vacuo*. The complex is soluble in ethanol and acetone. IR (nujol): 3340 m, 3260 sh, 3150 m (ν NH), 1595 sh (δ NH), 1515 vs, 1448 sh, 1276 m (ν CS), 960 s (N-N), 735 m, 690 s (CH) cm^{-1} . $\text{NiC}_{52}\text{H}_{32}\text{Cl}_2\text{F}_{20}\text{N}_{12}\text{S}_4$ (1462.8): Calcd. C 42.55, H 2.19, n 11.45; found C 43.10, H 1.79, N 11.51.

$\text{Cr}(\text{CO})_5(\text{NH}_2\text{NHC}_6\text{F}_5)$ (**14**): A solution of $\text{Cr}(\text{CO})_6$ (0.22g, 1 mmol) and pentafluorophenylhydrazine (0.4 g, 2 mmol) in THF (20 ml) was irradiated for 100 min with a UV lamp (Quecksilberhochdruckbrenner TQ 81, Fa. Hanau). 4 ml of CO gas were measured and the solution turned its color from yellow to brown. The volume of the solution was reduced to about 7 ml in vacuo and ethanol and water were added to give a dirty-yellow precipitate, which was dissolved in ethanol and then precipitated with water. M.P. 80 °C (dec.). IR (nujol): 3350 m, 3270 sh (ν NH), 2075 s, 1925vs, 1855 s (ν CO), 1605 sh (δ NH), 1505 s, 1495 s, 1460 s (C-C), 945 (ν N-N) cm^{-1} . $\text{CrC}_{11}\text{H}_3\text{F}_5\text{N}_2\text{O}_5$ (390); Calcd. C 33.82, H 0.77, N 7.18,; found C 34.00, H 1.30, N 7.30.

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