Journal of Thermal Analysis, Vol. 41 (1994) 161-171

THERMAL $N(CN)_2$-BRIDGING REACTIONS OF DICYANAMIDE COMPLEXES $Ni\{N(CN)_2\}_2L_n$ IN SOLID PHASE*

A:*L* = pyridine and its methyl derivatives

E. Jóna, M. Hvastijová and J. Kohout

Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava
Slovakia

(Received May 17, 1992; in revised form February 20, 1993)

Abstract

The stoichiometry of thermal decomposition reactions was studied for the following compounds: $Ni\{N(CN)_2\}_2py_2$ (I) (py-pyridine), $Ni\{N(CN)_2\}_2(2\text{-}Mepy)_2$ (II), $Ni\{N(CN)_2\}_2(3\text{-}Mepy)_2$ (III) and $Ni\{N(CN)_2\}_2(4\text{-}Mepy)_3$ (IV). In complexes I and II the loss of the volatile heterocyclic ligands occurs in one step while in complexes III and IV in two steps. Magnetic and spectral data indicated pseudooctahedral configuration for all complexes. The course of thermal $N(CN)_2$–bridging reactions of the complexes studied are discussed.

Keywords: complexes, dicyanamide complexes, pyridine, thermal bridging reactions

Introduction

It is known that nickel(II) complexes such as NiX_2L_n release volatile ligands *L* upon heating, as expressed by the equation

$$NiX_2L_n\,(s) \xrightarrow{\Delta T} NiX_2\,(s) + nL\,(g) \qquad (1)$$

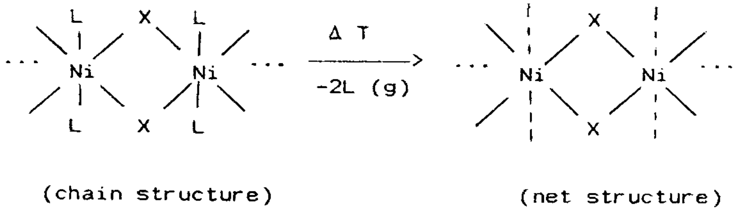
More often, however, it is a multistep process, when the escape of one or more volatile ligands takes place successively. Depending on several factors [1], some of the expected steps are usually not observed.

---

* Part XXV in the series Heterogeneous reactions of solid Ni(II) complexes.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Thermal bridging reactions can be expected when *L* is a volatile ligand (as pyridine or piperidine and its derivatives [2, 3]) and ligand *X* can form a bridge over two or more central atoms, i.e. a heating of the starting complexes will give the intermediates with dimeric [4] or polymeric- (chain or net) structure



We prepared a series of nickel(II) complexes containing pyridine (py) and methylpyridine (2-Mepy, 3-Mepy, 3-Mepy) as a volatile ligand *L* and $N(CN)_2$ as a bridging group *X*, and examined the possibility of these bridge formation reactions.

Experimental

The starting complexes: $Ni\{N(CN)_2\}_2py_2$ (I), $Ni\{N(CN)_2\}_2(2\text{-Mepy})_2$ (II), $Ni\{N(CN)_2\}_2(3\text{-Mepy})_2$ (III) and $Ni\{N(CN)_2\}_2(4\text{-Mepy})_3$ (IV) were prepared according to paper [5]. $Ni\{N(CN)_2\}_2(3\text{-epy})_1$ (V), $Ni\{N(CN)_2\}_2(4\text{-Mepy})_2$ (VI) and $Ni(NCS)_2$ (VII) were prepared by the isothermal decomposition of the starting complexes at about 230°C (complex V), about 80°C (complex VI) and about 300°C (compound VII). The compounds obtained were analysed for nickel, carbon, hydrogen and nitrogen.

The stoichiometry of thermal decomposition was studied using a Derivatograph OD 102. In all thermal decompositions a sample mass of 100 mg was used and the rate of temperature increase was 3 $deg \cdot min^{-1}$. The measurements were carried out in air using open standard crucible. To study the quasi-equilibrium decomposition temperatures (T_D) the Q-derivatograph was used. This experimental technique results in stabilisation of the decomposition temperature, i.e. the experiment proceeds under quasi-isothermal conditions [6]. Using special sample holder types it is possible to keep the pressure of the gaseous products almost constant (conical crucible ≈90 kPa).

The electronic spectra of the solid samples were measured by a Unicam SP 700 photometer. Infrared absorption spectra were recorded with a UR model 20 spectrophotometer. Magnetic moments were measured with a Gouy balance at room temperature.

Results and discussion

Thermal properties of the complexes

The results of thermal analysis are shown in Figs 1–3 and are summarised in Table 1. The TG and DTG curves show that the release of the volatile ligands *L* is a one-step process for complexes I and II, as expressed by the equation

$$\mathrm{Ni\{N(CN)_2\}_2L_2\,(s)} \xrightarrow{\Delta T} \mathrm{Ni\{N(CN)_2\}_2\,(s) + 2L\,(g)} \qquad (3)$$

(L = py (I) and 2-Mepy (II))
while for III and IV it is a two -step process, $\mathrm{Ni\{N(CN)_2\}_2(3\text{-}Mepy)_1}$ (V); $\mathrm{Ni\{N(CN)_2\}_2(4\text{-}Mepy)_2}$ (VI) and $\mathrm{Ni\{N(CN)_2\}_2}$ (VII) being formed as intermediates:

$$\mathrm{Ni\{N(CN)_2\}_2(3\text{-}Mepy)_2\ (III)\ (s)} \xrightarrow{\Delta T} \mathrm{Ni\{N(CN)_2\}_2(3\text{-}Mepy)_1\ (s) + 3\text{–}Mepy(g)} \qquad (4)$$

$$\mathrm{Ni\{N(CN)_2\}_2(3\text{-}Mepy)_1\ (V)\ (s)} \xrightarrow{\Delta T} \mathrm{Ni\{N(CN)_2\}_2\ (VII)\ (s) + 3\text{-}Mepy\ (g)} \qquad (5)$$

$$\mathrm{Ni\{N(CN)_2\}_2(4\text{-}Mepy)_3\ (IV)\ (s)} \xrightarrow{\Delta T} \mathrm{Ni\{N(CN)_2\}_2(4\text{-}Mepy)_2\ (VI)\ (s) + 4\text{-}Mepy\ (g)} \qquad (6)$$

$$\mathrm{Ni\{N(CN)_2\}_2(4\text{-}Mepy)_2\ (VI)(s)} \xrightarrow{\Delta T} \mathrm{Ni\{N(CN)_2\}_2\ (VII)\ (s) + 2(4\text{-}Mepy)\ (g)} \qquad (7)$$

The percent weight loss, as reported in Table 1 shows that there is good agreement between experimental and theoretical values.

The Q-TG curves (Fig. 4), which were traced under quasi-isothermal heating conditions (using conical crucible) provide comprehensive information about the reaction stoichiometry as well as the decomposition temperatures. It is obvious that there are no differences between the stoichiometry of thermal decomposition under quasi-equilibrium (Fig. 4) and non-equilibrium conditions (Figs 1–3), with the exception of $\mathrm{Ni\{N(CN)_2\}_2(3\text{-}Mepy)_2}$ (III). In this

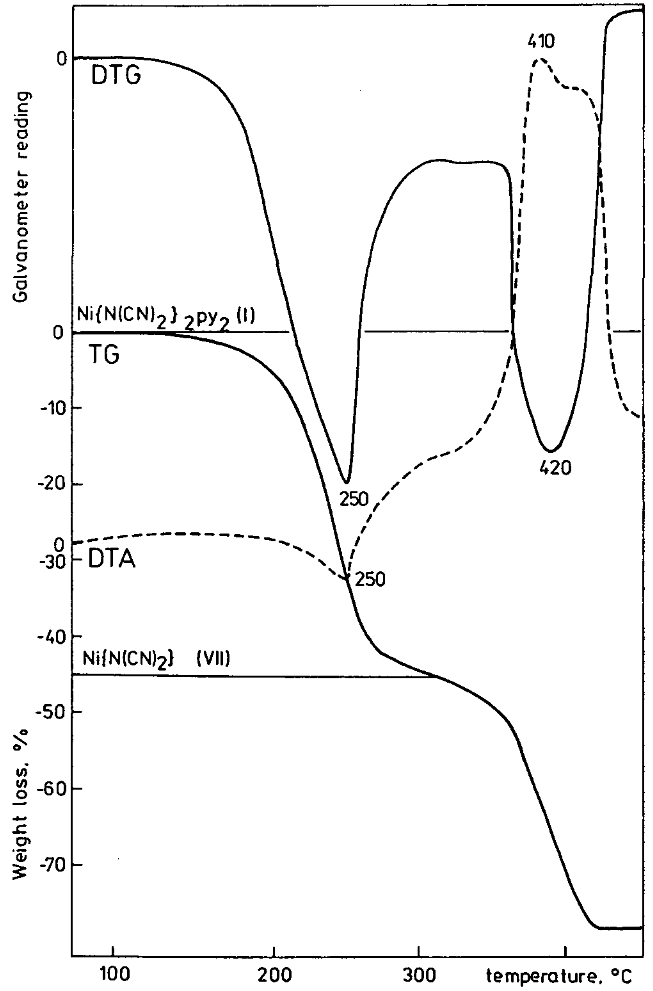


Fig. 1 Thermal curves of complex I

case no stable intermediate $Ni\{N(CN)_2\}_2(3\text{-}Mepy)_1$ is formed and the stoichiometry of thermal decomposition may be described by the equation

$$Ni\{N(CN)_2\}_2(3\text{-}Mepy)_2\ (III) \xrightarrow{Q\text{-}TG} Ni\{N(CN)_2\}_2\ (VII)\ (s) + 2(3\text{-}Mepy)\ (g) \tag{8}$$

The decomposition temperatures derived from the quasi-isothermal measurements can be used to set up a qualitative sequence of the thermodynamic stabilities of the compounds in identical thermal decomposition reactions [7].

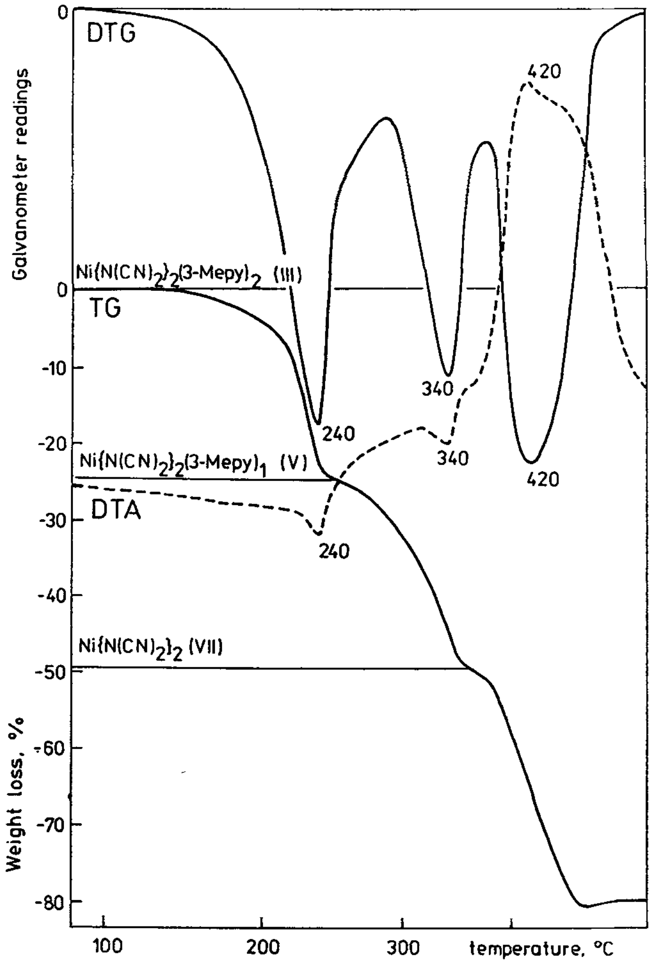


Fig. 2 Thermal curves of complex III

According to the quasi-equilibrium decomposition temperatures (Table 1), the thermodynamic stability of Ni{N(CN)$_2$}$_2$L$_n$ complexes increases in the following sequence:

$$IV < I \approx III < II$$

Magnetic and spectral properties of the complexes

On the basis of the magnetic moments (Table 2), it can be concluded that all the complexes under study are paramagnetic and the values are in the range usually given for octahedral nickel(II) complexes [8].

All the complexes have similar d–d spectra consisting of two spin-allowed bands and a spin-forbidden absorption between them. These spectra are characteristic of octahedral configuration [9]. The spin-allowed bands in the increasing energy order are assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition.

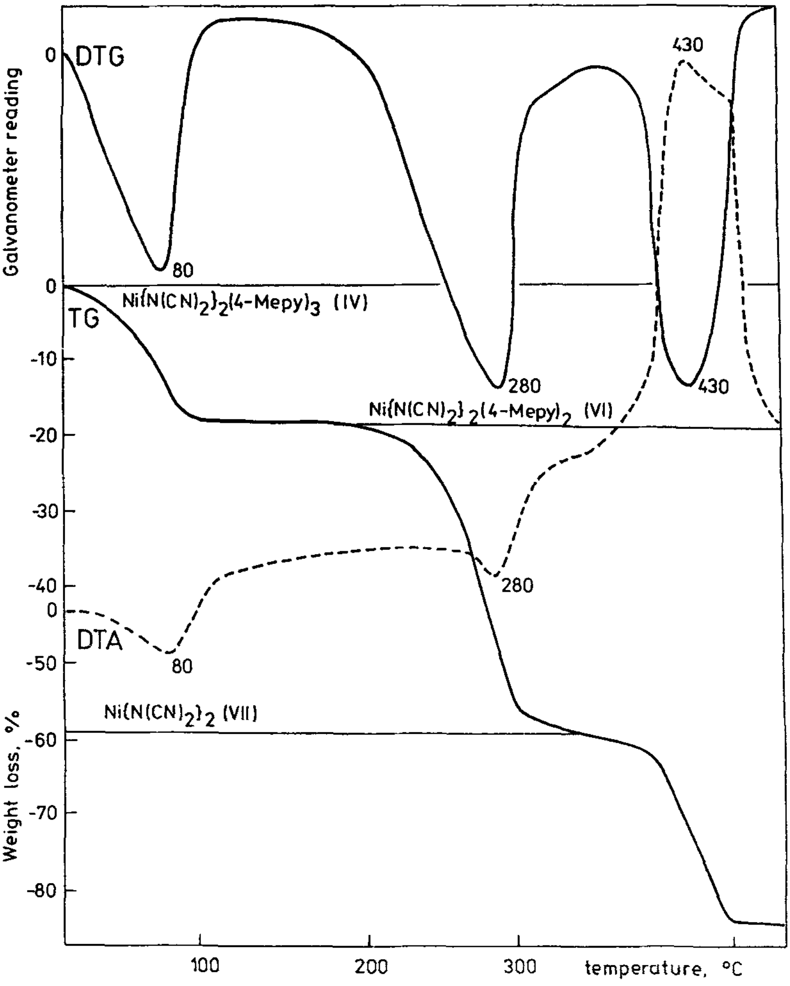


Fig. 3 Thermal curves of complex IV

The highest energy transition $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ is in most cases not observable because of overlapping by other, very intense UV absorptions. The steric effect of 2-Mepy is not connected with the stereochemical change of $Ni\{N(CN)_2\}_2L_2$ complexes (octahedral configuration remains unchanged) but the energy of the

Table 1 Data of the TG, DTG and DTA curves

Complex	T_D / °C	TG / % calcd. / found	DTG / °C	DTA / °C
Ni{N(CN)$_2$}$_2$(py)$_2$ (I)	260	45.3 / 45.0	250	250
Ni{N(CN)$_2$}$_2$(2-Mepy)$_2$ (II)	270	49.4 / 48.0	260	260
Ni{N(CN)$_2$}$_2$(3-Mepy)$_2$ (III)	260	24.7 / 26.5	240	240
		24.7 / 23.5	340	340
Ni{N(CN)$_2$}$_2$(4-Mepy)$_3$ (IV)	105	19.8 / 18.0	80	80
		39.6 / 41.0	280	280

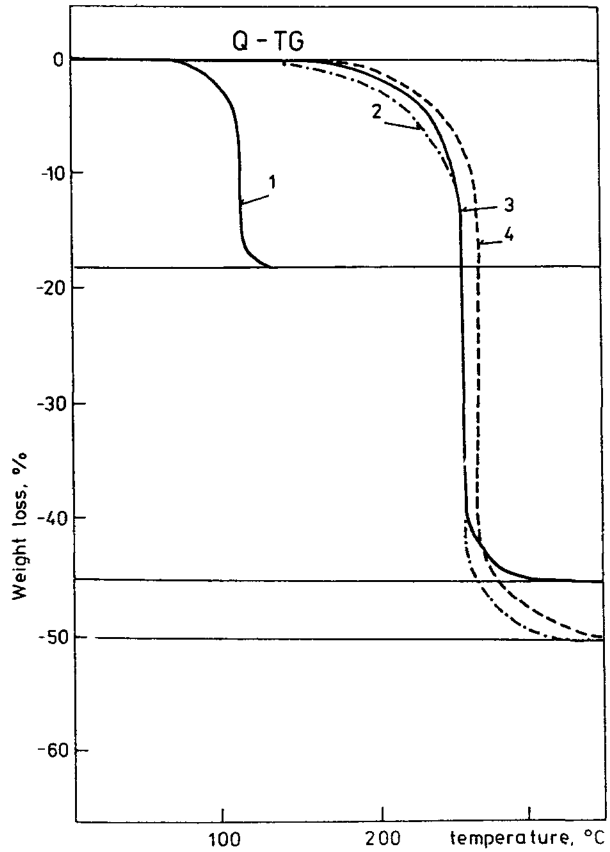


Fig. 4 Q-TG curves of comples I–IV: 1 – complex IV, 2 – complex III, 3 – complex I, 4 – complex II

$^3T_{2g} \leftarrow {}^3A_{2g}$ transition (10 Dg) decreases from about 10 400 cm^{-1} (complex I, III, VI) to 9 400 cm^{-1} (complex II).

The mode of coordination of the $N(CN)_2$ groups in these complexes was investigated by means of infrared absorption spectra. Dicyanamide groups can principally occur as monodentate (bonded through cyanide or amide nitrogen atom), as bidentate (bonded through two cyanide N-atoms or one cyanide and one amide N-atom), tridentate (bonded through two cyanide and one amide N-atom) and tetradentate (one cyanide N-atom is bonded to two central atoms). It follows from literature data summarised in [10] that the main criterion of the mode of coordination are the band positions corresponding to the C–N stretching vibration (usually two or more bands). The regions from 2240 to 2210 cm^{-1} and 2190 to 2160 cm^{-1} are assigned to the monodentate $N(CN)_2$

Table 2 Spectral and magnetic data

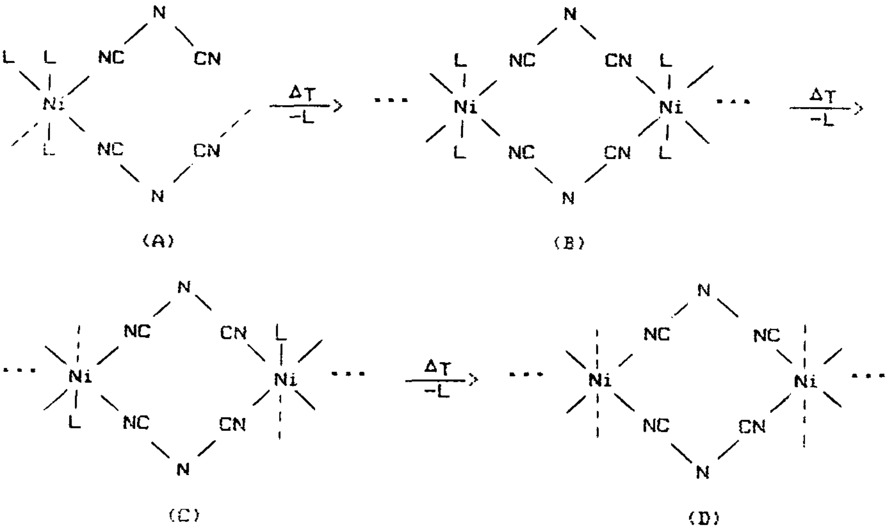
Complex	$\nu(CN)/cm^{-1}$	$\tilde{\nu}_{max}/cm^{-1}$	μ_{ef}, B.M.
I	2255, 2200	10420, ≈13300 (sh) 16900, ≈17170	3.14[a]
II	2254, 2208	9400, ≈13300 27000, ≈27200	2.86[a]
III	2250, 2200	10300. ≈13500 16700, ≈26700	3.15
IV	2252 2240, 2190	10500, ≈13700 16900, ≈27000	3.13
V	2260, 2250 (sh) ~2210	9200, ≈13200 16300, ≈26000	3.07
VI	2253, 2193	10360, ≈13500 16670, ≈26600	3.09[a]
VII	2260, 2210	9700, 16000 ≈26140	3.18[a]

[a] from paper [5]

groups. For bidentate groups (very likely bonded through cyanide N-atoms) are characteristic frequencies between 2260–2240 cm^{-1} and 2210–2180 cm^{-1} while for tridentate $N(CN)_2$ groups there are significant frequencies betwen 2280–2260 and 2220–2210 cm^{-1}. In complexes I, II, III and VI, two bands around 2250 cm^{-1} and 2200 cm^{-1} were found for the C–N stretches which obviously indicate the bidentate bridging nitrogen function of the $N(CN)_2$ ligands. In the case of complex IV, the bands about 2252, 2240 and 2190 cm^{-1} can be assigned predominantly to the bidentate and monodentate coordination, while in complex V the bands about 2260, 2250 (sh) and ≈2180 cm^{-1} very probably correspond to the tridentate and bidentate $N(CN)_2$ groups. These facts are in agreement with the pseudooctahedral configuration of these complexes. For $Ni\{N(CN)_2\}_2$ (VII) in contrast to the above mentioned complexes, the pseudooctahedral coordination sphere with bridging but tridentate $N(CN)_2$ groups is predicted [11].

Thermal bridging reactions

The results obtained indicate that all the complexes studied are pseudooctahedral. The hexacoordination can be achieved through the bonding of $N(CN)_2$ as bidentate ligand (complexes I, II, III and VI), monodentate and bidentate ligands (complex IV), bidentate and tridentate ligands (complex V) and tridentate ligand only (compound VII). On the basis of these data the following thermal $N(CN)_2$ bridging reactions are suggested:



(the hexacoordination in cases (A), (C) and (D) is completed by the adjacent structural units)

Based on our experimental results we consider the most probable course of thermal bridging reactions to be by steps B → D (complexes I, II), B → C → D (complex III) and A → B → D (complex IV).

References

1 E. Jóna, T. Sramko and J. Gazo, J. Thermal Anal., 16 (1979) 213.
2 E. Jóna, M. Jamnicky and I. Kostelny, J. Thermal Anal., 32 (1987) 513.
3 E. Jóna and M. Koman, J. Thermal Anal., 34 (1988) 657.
4 R. Tsuchiya, S. Nakagawa, A. Nehara and E. Kynno, Bullet. Chem. Soc. Jap., 46 (1973) 169.
5 H. Köhler, H. Hartung, B. Siefert, Z. Anorg. Allg. Chem., 347 (1966) 30.
6 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.
7 V. A. Logvinenko, Thermal Analysis of Coordination Compounds and Clathrates (in Russian). Izd. Nauka, Novosibirsk 1982.
8 D. Nickols, Comprehensive Inorganic Chemistry (I. C. Bailar, Jr. Ed.), Vol. 42. Pergamon Press, Oxford 1973, p.1152.

9 A. B. P. Lever, Inorganic Electronic Spectroscopy, p.507. Elsevier, Amsterdam 1984.
10 J. Kohout, DCs. Thesis, Bratislava 1989.
11 H. Köhler, A. Kolbe and G. Lux, Z. Anorg. Allg. Chem., 428 (1977) 103.

Zusammenfassung — Für folgende Verbindungen wurde die Stöchiometrie der thermischen Zersetzungsreaktionen untersucht: $Ni[N(CN)_2]_2py_2$ (I) (Py-Pyridin), $Ni[N(CN)_2]_2(2\text{-}Mepy)_2$ (II), $Ni[N(CN)_2]_2(3\text{-}Mepy)_2$ (III) und $Ni[N(CN)_2]_2(4\text{-}Mepy)_3$ (IV). In den Komplexen I und II werden die flüchtigen heterocyclischen Liganden in einem Schritt abgegeben, bei den Komplexen III und IV in zwei Schritten. Magnetische und spektroskopische Angaben zeigen eine pseudooktaedrische Konfiguration für alle Komplexe. Der Verlauf der thermischen $N(CN)_2$-Brückenbildungsreaktion der untersuchten Komplexe wird diskutiert.