

## Reactivity of Cyanogen towards Compounds Containing Active Hydrogens at Carbon. 6. Addition to $\beta$ -Dicarbonylenolato Complexes of Nickel(II) and Ligand Ability of Bis[1-cyano-2-(1-iminoethyl)butane-1,3-dionate]Nickel(II) towards $\text{PdCl}_2$

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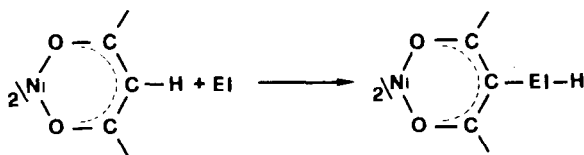
The bis- $[\beta$ -carbonylenolato]nickel(II) complexes  $[\text{Ni}(\text{eaa})_2]$  (eaa = ethylacetoacetato),  $[\text{Ni}(\text{ba})_2]$  (ba = benzoylacetonato),  $[\text{Ni}(\text{dbm})_2]$  (dbm = dibenzoylmethanato),  $[\text{Ni}(\text{dpm})_2]$  (dpm = dipivaloylmethanato) are found to be reactive towards  $\text{C}_2\text{N}_2$  to give selectively square-planar complexes of stoichiometry  $[\text{Ni}(\text{ligand} \cdot \text{C}_2\text{N}_2)_2]$ .

The reaction of  $[\text{Ni}(\text{acac})_2]$  with  $\text{C}_2\text{N}_2$  was reconsidered and the nature of two supposed isomeric products has been thoroughly reinvestigated by a variety of physico-chemical methods, including a combination of thermogravimetry–differential thermal analyses.

The complex  $[\text{Ni}\beta_2]$  ( $\beta$  = 1-cyano-2-(1-iminoethyl)butane-1,3-dionate) reacts quantitatively with  $[\text{PdCl}_2(\text{PhCN})_2]$  to give a coordination polymer of approximate composition  $[(\text{PdCl}_2)(\text{Ni}\beta_2)_{0.25}]$ .

### Introduction

In 1977 Nelson and co-workers described [1] a novel reaction in the chemistry of  $\beta$ -carbonylenolato metal complexes (Scheme 1).



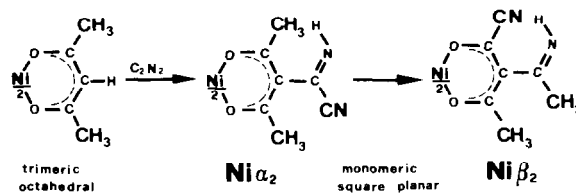
$\text{E1} = \text{R}-\text{N}=\text{C}=\text{O}; \text{CH}_3\text{COO}-\text{C}\equiv\text{C}-\text{COOCH}_3;$   
 $\text{COOC}_2\text{H}_5-\text{N}=\text{N}-\text{COOC}_2\text{H}_5$

† Part of this work was carried out during a visit of B.C. (A. von Humboldt fellow) at the Institute of Inorganic Chemistry, T. U. Munich in 1981, and particular thanks are due to the stimulating interest of Prof. F. Köhler and Dr. F. Kreissl in this work.

In contrast with the typical reaction at the C–H methino group which normally implies substitution of the hydrogen atom by an electrophile, insertion of E1 into the C–H bond took place in this case. The reaction of Scheme 1 leads to metal complexes which maintain the octahedral trimeric configuration of  $[\text{Ni}(\text{acac})_2]$  [2] and no evidence of destabilization of this structure upon insertion of E1 could be observed under any circumstances. This ligand-centered reaction was concomitantly found to be the key-step in the  $[\text{Ni}(\text{acac})_2]$  catalyzed high selective additions of electrophiles to a variety of  $\beta$ -dicarbonyl compounds [1, 3].

We reported in 1979 [4] that cyanogen reacts analogously with  $[\text{Ni}(\text{acac})_2]$  to give insertion of the  $\text{C}_2\text{N}_2$  moiety into the C–H methino bond.

However, in contrast with the findings mentioned above, the octahedral trimeric structure of  $[\text{Ni}(\text{acac})_2]$  was found to be totally de-stabilized in favour of the square planar one (Scheme 2), under many different experimental conditions.



The structure of  $[\text{Ni}\beta_2]$  was established [4] by X-ray single crystal analysis and the structure of  $[\text{Ni}\alpha_2]$  was proposed on the basis of close analogy of the cyanation reaction with those described in Scheme 1.

The X-ray spectra of the powders of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  were found to be quite different from each other, and remarkably the spectrum of  $[\text{Ni}\alpha_2]$  was later found [5] to be very similar to that of a copper complex having a  $[\text{Cu}\beta_2]$  [6] configuration. This casts some doubts on the real nature of  $[\text{Ni}\alpha_2]$  and

prompted us to reinvestigate thoroughly the relationships between  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$ .

We report here on the reaction of  $[\text{Ni}(\beta\text{-carbonyl-enolato})_2]$  complexes with  $\text{C}_2\text{N}_2$  and on further data pertinent to the molecular relationship between  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$ . The ligand ability of  $[\text{Ni}\beta_2]$  towards  $\text{PdCl}_2$  is also described.

## Results and Discussion

### The Relationship between $[\text{Ni}\alpha_2]$ and $[\text{Ni}\beta_2]$

$[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  are both crystalline products which crystallize in form of blood-red arrow tips ( $[\text{Ni}\beta_2]$ ) and of orange-red javelins ( $[\text{Ni}\alpha_2]$ ). Several attempts to obtain single crystals of  $[\text{Ni}\alpha_2]$  suitable for X-ray analysis failed, owing to a tendency to give twinned crystals. This forced us to devise a set of chemical and physico-chemical experiments devoted to ascertain the ligand configuration of  $[\text{Ni}\alpha_2]$ . Some have already been reported [4]; the new and conclusive ones are collected below under separate headings.

### I.R. Spectra

We have carefully checked and confirmed our previously reported data (nujol mull) [4]:

Compound	$\nu_{\text{N-H}}$	$\nu_{\text{C}\equiv\text{N}}$	$\nu_{\text{C}=\text{N}}$
$[\text{Ni}\alpha_2]$	3250(s)	2220(w)	1635(s)
$[\text{Ni}\beta_2]$	3200(s)	2240(vw)	1640(s)

The observed small differences in the wavenumber figures for the significant I.R. bands of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  do not allow discrimination between the hypothesis of isomerism (Scheme 2) and dimorphism (solid state effect). Unfortunately spectra in solution do not help because: a) both species are sparingly soluble in all common solvents except DMSO; b) in DMSO the only existing species is  $[\text{Ni}\beta_2]$  (see below).

### NMR Spectra in DMSO

The spectra of both species are identical (Fig. 1) and in agreement with the  $[\text{Ni}\beta_2]$  structure. The resonance at 2.0 ppm is attributed to the  $\text{CH}_3\text{-}\beta$  and that at 4.3 ppm to  $\text{CH}_3\text{-}\alpha$ . The unusual position of the broader peak at 4.3 ppm is attributed to a weak temperature-dependent paramagnetism of these solutions, possibly due to a fast equilibrium between a planar (predominant) and an octahedral configuration. The predominance of the planar configuration is shown by the spectrum in the visible region (band at 550 nm) referring to 0.1 M solutions of  $[\text{Ni}\beta_2]$  in DMSO.

An indirect support of the hypothesis of this equilibrium is given by the effect of the temperature on the  $\Delta\delta$  of the  $\text{CH}_3\text{-}\alpha$  and  $\text{CH}_3\text{-}\beta$  resonances (Fig. 2). It is seen that a temperature increase reduces the magnetic susceptibility of the solution, albeit not

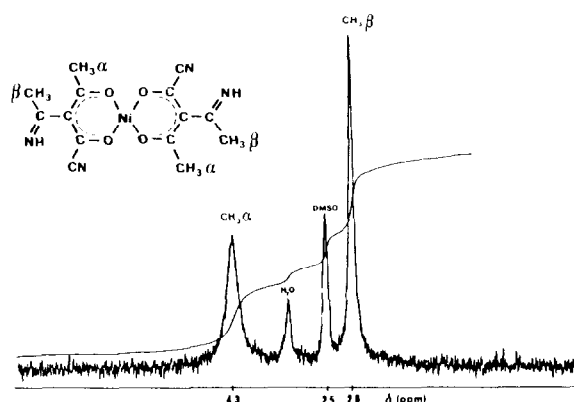


Fig. 1.  $^1\text{H}$  NMR spectrum of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  in DMSO (0.1 M).

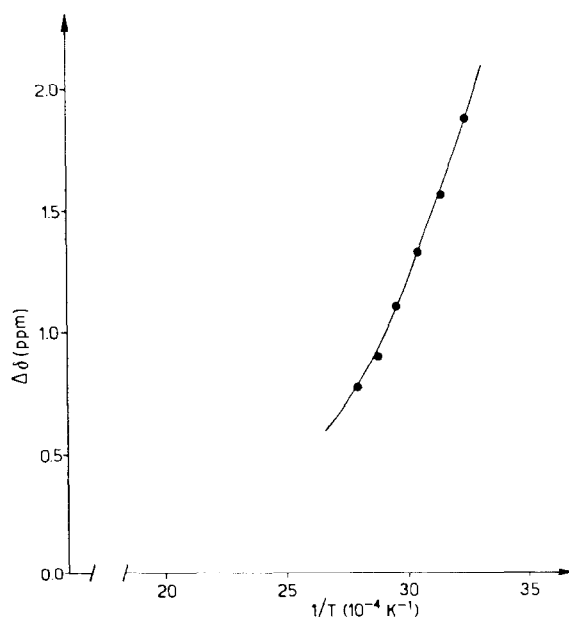


Fig. 2. Plots of  $\Delta\delta$  versus  $T^{-1}$  for  $\text{CH}_3\text{-}\alpha$  and  $\text{CH}_3\text{-}\beta$  resonances referring to  $[\text{Ni}\beta_2]$  in DMSO.

according to the Curie law. The observed behaviour indicates that a paramagnetic centre is contained in solution, whose concentration changes with temperature according to the proposed equilibrium.

### UV-Visible Spectra in $\text{CH}_2\text{Cl}_2$ and in the Solid State

$[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  exhibit well-resolved and identical spectra in solution and very similar ones in nujol mulls. The explored range was 240–800 nm. We did not expect large spectral changes in the electronic spectra of isomers like  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$ , but the perfect identity of the spectra coupled with the NMR data strongly indicate that in  $\text{CH}_2\text{Cl}_2$  the existing species is  $[\text{Ni}\beta_2]$ .

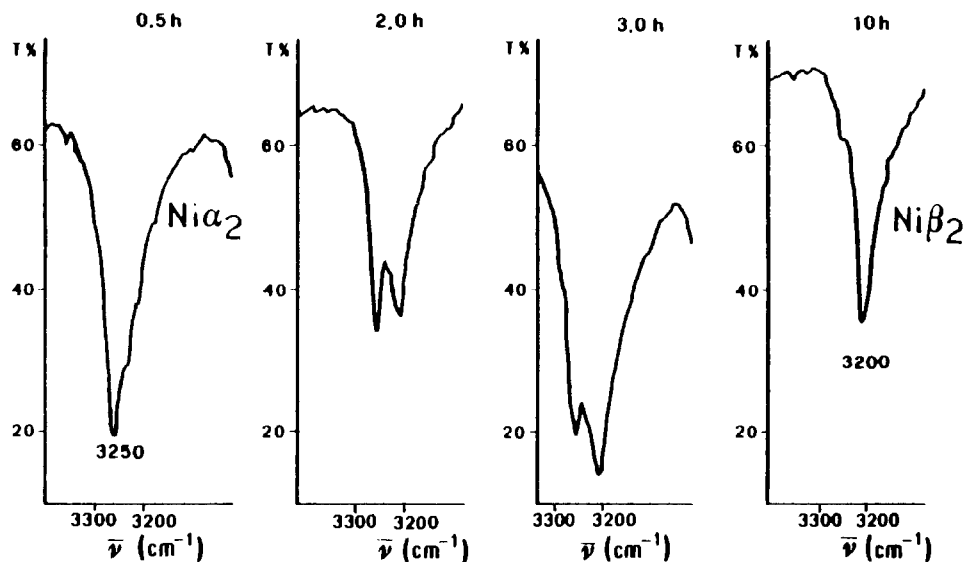


Fig. 3. Infrared spectra ( $\nu_{\text{N-H}}$ ) of the material present in a suspension of  $\text{H}_2\text{O}$ -saturated  $\text{CH}_2\text{Cl}_2$  originally containing  $[\text{Ni}\alpha_2]$ , at various times.

#### *Thermal Conversion of $[\text{Ni}\alpha_2]$ to $[\text{Ni}\beta_2]$ in $\text{C}_2\text{H}_4\text{Cl}_2$*

We know that  $[\text{Ni}\alpha_2]$  is converted into  $[\text{Ni}\beta_2]$  by refluxing its solutions in reagent grade  $\text{C}_2\text{H}_4\text{Cl}_2$ . We have monitored this process by quenching the 'reacting' solutions of  $[\text{Ni}\alpha_2]$  at different times (see Experimental) and we could verify that the  $[\text{Ni}\alpha_2] \rightarrow [\text{Ni}\beta_2]$  conversion is a real, kinetically-controlled chemical process. In fact, dissolution of  $[\text{Ni}\alpha_2]$  followed by quenching affords mixtures of crystals progressively enriched in  $[\text{Ni}\beta_2]$ .

#### *$\text{H}_2\text{O}$ -Catalyzed Conversion of $[\text{Ni}\alpha_2]$ into $[\text{Ni}\beta_2]$*

Our previous proposal [4] about a possible  $\text{H}_2\text{O}$ -catalyzed pathway for converting  $[\text{Ni}\alpha_2]$  into  $[\text{Ni}\beta_2]$  in chlorinated solvents is now supported by experimental evidence. In fact, while a suspension of  $[\text{Ni}\alpha_2]$  in anhydrous  $\text{CH}_2\text{Cl}_2$  under vigorous stirring is stable for some days at room temperature ( $[\text{Ni}\alpha_2]$  is recovered unaltered), the same experiments carried out in  $\text{H}_2\text{O}$ -saturated solvent leads to rapid transformation of  $[\text{Ni}\alpha_2]$  into  $[\text{Ni}\beta_2]$ , Fig. 3.

This finding is in clear agreement with the view of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  as being isomeric and not dimorphic species.

#### *Attempts to Extract the Ligand upon Protonation*

Various attempts (see Experimental) of obtaining the protonated ligands by reaction of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  with Brönsted acids were unsuccessful.

#### *X-Ray Powder Diffraction Spectrum of $[\text{Ni}\alpha_2]$*

The reflection X-ray powder spectra of  $[\text{Ni}\alpha_2]$  and  $[\text{Cu}\beta_2]$  were recorded by means of an advanced

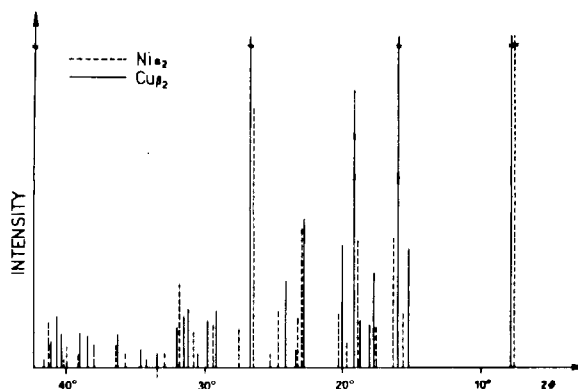


Fig. 4. X-ray powder spectra (reflection) of  $[\text{Cu}\beta_2]$  and  $[\text{Ni}\alpha_2]$ .

apparatus [8] and the results are schematically collected in Fig. 4.

It is seen that the spectra are very similar (as already reported by us on the basis of the data of a flat chamber apparatus [5]) and inspection of the actual diffractograms shows even greater similarities between the two spectra\*. On considering that  $[\text{Cu}\beta_2]$  crystallizes in the triclinic system, the small differences observed can also be expected for isotypic compounds (having slightly different lattice parameters), thus confirming our previous report. In conclusion, while  $[\text{Ni}\beta_2]$  [4] and  $[\text{Cu}\beta_2]$  [6] which have the same molecular structure are not isotypic [5],  $[\text{Ni}\alpha_2]$  and  $[\text{Cu}\beta_2]$  which may not have the same molecular structure, are most likely isotypic.

\*A copy of the diffractograms is available as supplementary material.

### Mass Spectrometry (Electron Impact)

Both species gave almost identical mass spectra, if heated up to 180 °C. The direct analysis of the spectrum prevented the identification of the structure of the 360 mass parent ion (*i.e.* its  $\alpha$  or  $\beta$  structure). For  $[\text{Ni}\alpha_2]$  the 360 peak appears at 180 °C (5% of base peak 84), while for  $[\text{Ni}\beta_2]$  the same peak appears at 50 °C (15% of base peak 84) and at 180 °C it reaches 85% of the base peak 84.

### Thermogravimetry, Differential Thermal Analysis and Differential Scanning Calorimetry

Samples of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  were examined by a combination of thermogravimetric (TG) and differential thermal analysis (DTA) as well as by differential scanning calorimetry (DSC). The thermograms are reported in Fig. 5. It is seen that in the temperature range 170–220 °C a 5–7% loss of weight is observed for both species. The TG patterns however are different in shape and the DTA patterns appear also to be very different. The loss of weight for  $[\text{Ni}\alpha_2]$  is accompanied by two weakly exothermic transitions, while the loss of weight for  $[\text{Ni}\beta_2]$  results to be a single, much more exothermic process. DSC measurements confirm the DTA results and gave for the two decomposition processes 13 Kcal/mol for  $[\text{Ni}\alpha_2]$  (total) and 26 Kcal/mol for  $[\text{Ni}\beta_2]$ .

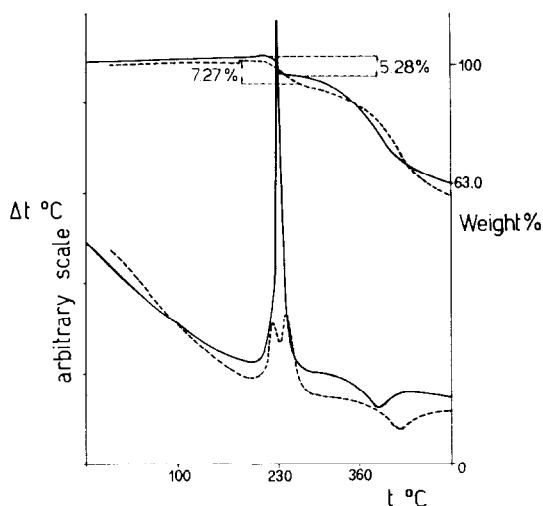


Fig. 5. TG and DTA patterns for  $[\text{Ni}\alpha_2]$  (---) and  $[\text{Ni}\beta_2]$  (—).

The large difference in the TG and DTA patterns exhibited by  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  is in disagreement with the hypothesis of the dimorphism and is in agreement with the proposal that they are isomeric compounds, according to Scheme 1.

Even though the preceding data are either ambiguous or support the hypothesis of the dimorphism, thermal,  $\text{H}_2\text{O}$ -conversion and especially thermogravi-

metric data leave no doubts that  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  are real isomeric compounds. Our data do not prove directly the  $\alpha$  nature of the ligand present in  $[\text{Ni}\alpha_2]$ , but the configuration drawn in Scheme 1 appears extremely likely. NMR and UV-visible data can be interpreted on the basis of an isomerization of  $[\text{Ni}\alpha_2]$  into  $[\text{Ni}\beta_2]$  occurring upon dissolution (apparently relatively fast in the employed conditions), which prevents the direct observation of the moiety  $[\text{Ni}\alpha_2]$  in solution. Finally the substantial identity of EI mass spectra of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  can be explained by the reasonable assumption that one species can be converted into the isomeric one in the electron beam of the spectrometer ion source.

### Synthesis of Complexes $[\text{Ni}(\beta\text{-carbonylenolato}\cdot\text{C}_2\text{N}_2)_2]$

$[\text{Ni}(\beta\text{-carbonylenolato})_2]$  complexes react readily with  $\text{C}_2\text{N}_2$  at ambient conditions in  $\text{C}_2\text{H}_4\text{Cl}_2$  to give compounds of stoichiometry  $[\text{Ni}(\beta\text{-carbonylenolato}\cdot\text{C}_2\text{N}_2)_2]$ , which can be isolated only as single isomers. The general reaction conditions and the essential physico-chemical properties of the obtained complexes are summarized in Table I (see the summary for the adopted symbols). The i.r. data exhibited by the cyanated complexes clearly indicate that they all contain the moiety  $[2/\text{M}\alpha]$  or  $[2/\text{M}\beta]$ , Scheme 2.

The spectral data in the VIS range leave no doubt that all these species are square planar complexes, both in the solid state and in solution. They all display, in fact, a single broad ligand field band around 550 nm with  $\epsilon$ 's ranging from 180 to 200 ( $\text{M}^{-1}\text{cm}^{-1}$ ), in close agreement with the figures observed for the well characterized species  $[\text{Ni}(\text{dpm})_2]$  [2, 9] ( $\lambda = 535$ ;  $\epsilon = 80$ ),  $[\text{Ni}\beta_2]$  [4] ( $\lambda = 555$ ;  $\epsilon = 110$ ) and  $[\text{Ni}(\text{acac})_2]$  in diphenylmethane [2] above 150 °C ( $\lambda \approx 555$ ).

The magnetic moments determined for the various complexes are surprising in that they are definitely greater than zero and the relevant  $\chi_{\text{M}}$ 's are found to be temperature-dependent. The temperature effect was checked for  $[\text{Ni}\alpha_2]$ ,  $[\text{Ni}\beta_2]$  and  $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$  in the range 90–293 K ( $[\text{Ni}\alpha_2]$ ), 90–387 K ( $[\text{Ni}\beta_2]$ ) and 90–298 K ( $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$ ). The persistence of the  $\mu > 0$  down to 90 K strongly suggests that no spin equilibrium phenomenon occurs in the present cases and the solid state structure of  $[\text{Ni}\beta_2]$  rules out any appreciable tetragonal distortion around nickel(II). Only a heavy impurity by a paramagnetic species could justify the observed  $\mu$  values, but careful elemental analysis carried out on all the employed batches rules out this possibility.

For this reason, the source of the lower magnetic moments of  $[\text{Ni}\alpha_2]$ ,  $[\text{Ni}\beta_2]$  and  $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$  remains obscure. E.s.r. measurements carried out on  $[\text{Ni}\beta_2]$  gave no electron spin signal down to 100 K.

The NMR spectra of  $[\text{Ni}\alpha_2]$ ,  $[\text{Ni}\beta_2]$ ,  $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$ , and  $[\text{Ni}(\text{dpm}\cdot\text{C}_2\text{N}_2)_2]$  recorded in DMSO

TABLE I. Summary of the Data Referring to the Complexes  $[\text{Ni}(\beta\text{-carbonylenolato}\cdot\text{C}_2\text{N}_2)_2]$ .

Complex	I.r. data (selected $\text{cm}^{-1}$ ) <sup>a</sup>		UV-vis data <sup>b</sup> in solution, $\lambda_{\text{max}}$ (nm); $\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ ) in parenthesis	UV-vis data, $\lambda_{\text{max}}$ (nm) in solid phase <sup>c</sup>	NMR (DMSO- $d_6$ ) $\delta$ (ppm)	$\mu$ (BM) at 298 K <sup>e</sup>
	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$				
$[\text{Ni}(\text{O}_2)]$	3250(s)	2200(w)	1635(s)	260(18400), 290(26000), 350(3200)	250, 300, 355, 415, 550	0.68
$[\text{Ni}(\beta_2)]$	3200(s)	2240(vw)	1640(s)	420(3300), 555(110)	265, 310, 355, 415, 550	0.50
$[\text{Ni}(\text{eaa}\cdot\text{C}_2\text{N}_2)_2]$	3260(s)	2235(vw)	1715(s)	275(64500), 335(16000), 410(5650), 535(200)	275, 350, 410, 550	1.28
$[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$	3250(s)	2170(vw)	1640(s)	255(54500), 305(27000), 420(5500), 555(200)	260, 335, 575	0.75
$[\text{Ni}(\text{dbm}\cdot\text{C}_2\text{N}_2)_2]$	3290(s)	2230(vw)	1650(s)	260(62000), 315(49500), 360(15000), 435(7500), 550(180)	325, 440, 575	0.00
$[\text{Ni}(\text{dpm}\cdot\text{C}_2\text{N}_2)_2]$	3280(s)	2230(vw)	1675(s)	250(19500), 295(13100), 355(4000), 435(2200), 560(200)	260, 310, 355, 440, 575	f

<sup>a</sup> Nujol mull. <sup>b</sup> In  $\text{CH}_2\text{Cl}_2$ . Solutions obey Lambert-Beer's law in the range  $10^{-3}$ – $10^{-4}$  M. <sup>c</sup> Nujol mull; transparency spectra. <sup>d</sup> Insolubility prevents reliable spectra from being obtained. <sup>e</sup> Details and data at other temperatures are reported under the relevant headings. <sup>f</sup> Not determined.

gave clear indication on the structure of these species in this solvent. The spectra of  $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$  and of  $[\text{Ni}(\text{dpm}\cdot\text{C}_2\text{N}_2)_2]$  are reported in Fig. 6. The solutions of the first species appear to be weakly paramagnetic (notice the shape of the  $\delta = 5.5$  ppm peak and compare it with the analogous one observed for  $[\text{Ni}\beta_2]$ ), and both the integration ratios and the position of the peaks suggest a  $[\text{Ni}\alpha\beta]$ -like structure for the  $\text{ba}^-$  derivative.

The  $[\text{Ni}\beta]$ -like ring is responsible for the  $\text{CH}_3$  resonance at 2.1 ppm (sharp signal) while the  $[\text{Ni}\alpha]$ -like one gives a broad band centered at 5.5 ppm (a position quite unusual for a  $\text{CH}_3$  proton, but conceivable if the metal center is weakly paramagnetic). Both  $\text{C}_6\text{H}_5$  rings can be reasonably expected to give a cumulative ill-defined signal centered around 7.7 ppm). The source of the weak paramagnetic susceptibility of the solution of  $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$  may be in the occurrence of a fast equilibrium between a predominant square planar species and a minor octahedral one.

The spectrum of  $[\text{Ni}(\text{dpm}\cdot\text{C}_2\text{N}_2)_2]$  clearly refers to a diamagnetic solution, and the  $=\text{N-H}$  resonances can also be detected in this case. This finding deserves some attention, as for other nickel(II) diamagnetic imidate complexes this resonance could not be detected [10] and the position of the resonances of  $=\text{N-H}$  protons does not appear well-documented in the literature. The presence of two well-separated resonances, due to a pair of non equivalent *ter*-butyl groups, can be consistent with either a  $[\text{Ni}\beta_2]$  or a  $[\text{Ni}\alpha_2]$ -like nature of the complex. In this latter case the non-equivalence of the *ter*-butyl protons is the consequence of the steric hindrance of the bulky substituents, which prevents the rotation of the  $-\text{C}(=\text{NH})(\text{CN})$  groups around the  $\text{C}(\text{ring})-\text{C}(=\text{NH})(\text{CN})$  bond.

Apart from the problem of the  $\alpha$  or  $\beta$  nature of the complexes described here, which will be later examined by convenient techniques [11], it is clear that the replacement of a hydrogen atom by  $\text{C}(=\text{NH})(\text{CN})$  or by  $\text{C}(=\text{NH})\text{R}$  groups at the intercarbonyl position causes a collapse of the trimeric octahedral structure [12] of the  $[\text{Ni}(\text{acac})_2]$ ,  $[\text{Ni}(\text{ba})_2]$ ,  $[\text{Ni}(\text{dbm})_2]$  complexes, as well as of whose color and composition are in agreement with an octahedral configuration.

The factors affecting the relative stabilities of the high-spin paramagnetic  $[\text{Ni}(\text{O}-\text{O})_2]_3$  versus the low-spin diamagnetic  $[\text{Ni}(\text{O}-\text{O})_2]$  forms of a variety of  $[\text{Ni}(\beta\text{-diketonato})_2]$  complexes have been thoroughly examined [13]. In the absence of severe steric constraints (absent at the intercarbonyl position) the trend of the increasing basicity towards the proton of the  $\beta$ -diketonato ligands appears to correlate well with the stabilization of the monomeric square-planar structure versus the octahedral one. Thus, increasing basicity towards the proton was proposed to cor-

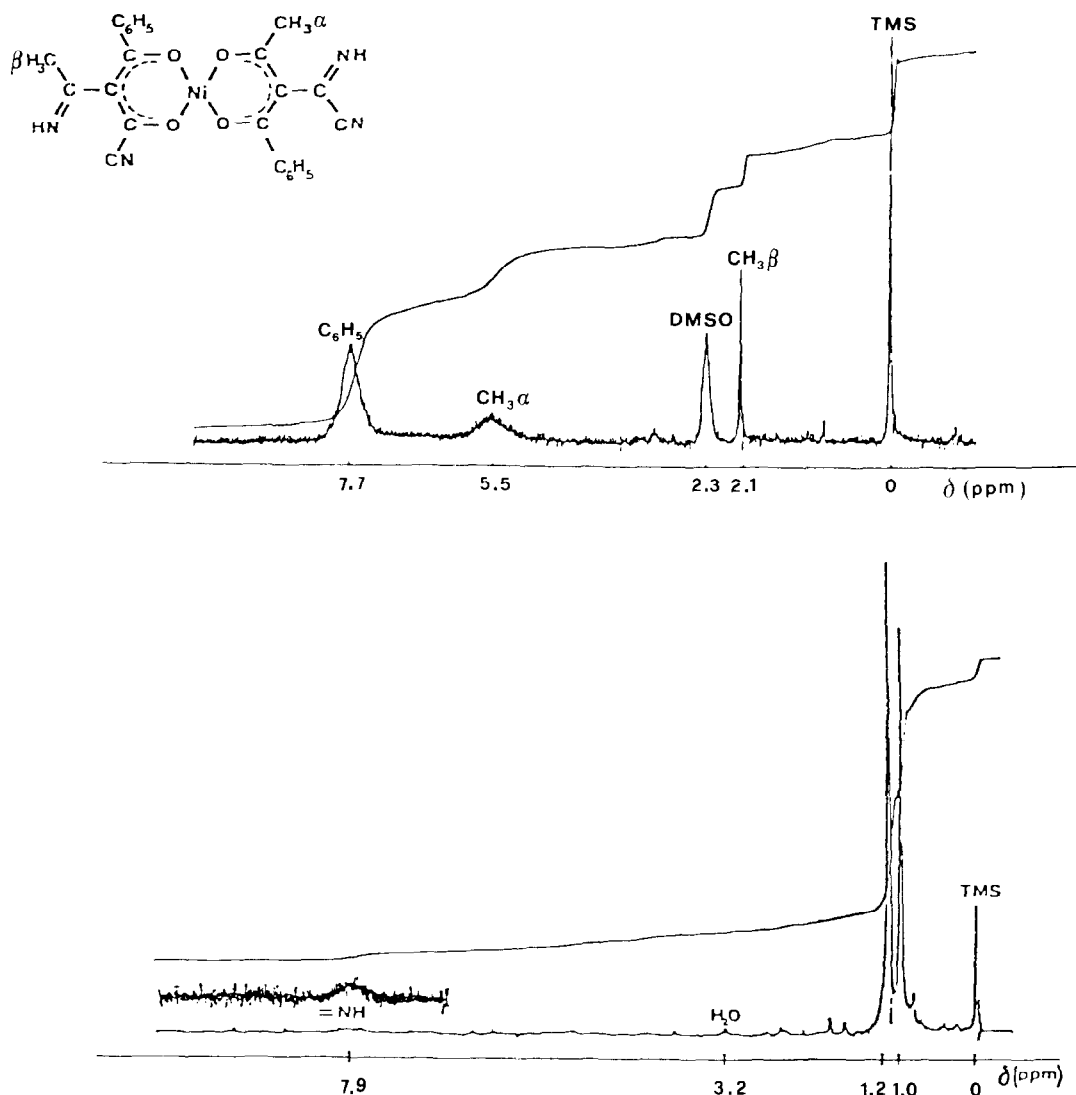


Fig. 6. <sup>1</sup>H NMR spectra of [Ni(ba·C<sub>2</sub>N<sub>2</sub>)<sub>2</sub>] (a) and of [Ni(dpm·C<sub>2</sub>N<sub>2</sub>)<sub>2</sub>] (b) in DMSO-d<sub>6</sub> (internal TMS).

respond to an increase of covalence character in the Ni–ligand bonds leading to preferential formation of [Ni(O–O)<sub>2</sub>] square planar structures.

Inspection of the structures of the [Niα<sub>2</sub>]- and [Niβ<sub>2</sub>]-like complexes leaves little doubt that in both cases inductive and mesomeric effects are expected to stabilize the relevant anions, thus *decreasing* their basicity towards the proton. This apparent contradiction between our results and the line of reasoning recalled above stimulates further investigation on this problem.

#### Ligand Ability of [Niβ<sub>2</sub>]

The metal-coordination ability of imino groups is well established [10, 14] and examples are known of imino groups (connected to metals by a suitable organic skeleton) which display their bonding ability both towards the same metal centre to which the

imino group is indirectly bonded [15] and to an external coordination site [16].

In view of the interest which appears in the literature on the synthesis and coordination properties of coordination compounds [17], we have investigated the ligand ability of [Niβ<sub>2</sub>] towards the acid {PdCl<sub>2</sub>}. Suspensions of [Niβ<sub>2</sub>] were found to react quantitatively with [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] dissolved in CH<sub>2</sub>Cl<sub>2</sub>, containing 0.1 M PhCN, in a molar ratio 1 Pd: 0.25 Ni. The product is a reddish-brown powder, insoluble in the common organic media but soluble in DMSO (up to 0.1 M). A number of chemical and physico-chemical tests in this reaction are summarized under separate items.

#### Titration of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] with [Niβ<sub>2</sub>]

The results are exemplified in Fig. 7 and were checked by four independent tests.

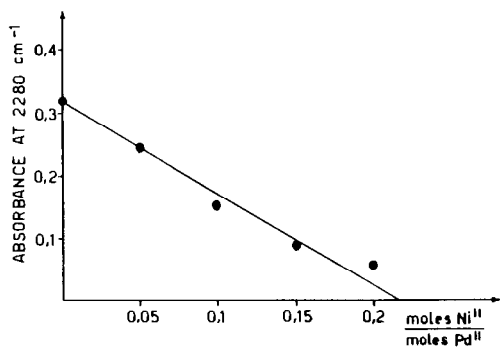


Fig. 7. Typical spectrophotometric titration of  $[\text{PdCl}_2(\text{PhCN})_2]$  by  $[\text{Ni}\beta_2]$  ( $\nu = 2280 \text{ cm}^{-1}$ ).

Addition of solid  $[\text{Ni}\beta_2]$  leads to immediate release of PhCN from  $[\text{PdCl}_2(\text{PhCN})_2]$  and the resulting stoichiometry is 1 Pd: 0.25 Ni (individual values: 0.25; 0.32; 0.22; 0.23). The yield of this reaction evaluated in four independent preparative tests was 84.5, 91.5, 99.5, 84.5 with an average value of 90%. The solubility behaviour of the product, the stoichiometric ratio Pd/Ni and the potential polydentate character of  $[\text{Ni}\beta_2]$  suggest that the product is a three-dimensional coordination polymer containing a  $[\text{PdCl}_2(\text{Ni}\beta_2)_{0.25}]$  repeating unit. VIS, NMR and mass spectra data are in agreement with this suggestion.

#### Infrared Spectrum of the Polymer

The spectrum shows as essential features the bands due to the  $-\text{C}\equiv\text{N}$  ( $2289 \text{ cm}^{-1}$ ),  $\text{C}=\text{N}$  ( $1773 \text{ cm}^{-1}$ ),  $=\text{N}-\text{H}$  ( $3500 \text{ cm}^{-1}$ ),  $\text{Pd}-\text{Cl}$  ( $330 \text{ cm}^{-1}$ ) groups present in the polymer. They indicate that the  $-\text{C}\equiv\text{N}$  moiety of  $[\text{Ni}\beta_2]$  is involved in an 'end on' coordination mode to a metal centre [18], as well as the  $\text{C}=\text{N}$  group [10]. The broad band around  $3500 \text{ cm}^{-1}$  indicates a strong involvement of  $=\text{N}-\text{H}$  groups in hydrogen bonds and the  $\text{Pd}-\text{Cl}$   $330 \text{ cm}^{-1}$  single band is in agreement with the presence of a *trans*- $\text{PdCl}_2$  [19] moiety in the polymer. This set of data shows that the moiety  $[\text{Ni}\beta_2]$  survives in the coordination polymer together with the *trans*- $\{\text{PdCl}_2\}$  one.

#### Visible Spectrum of the Polymer

The spectrum was recorded in DMSO and is rather featureless (a shoulder at 380 nm and a long tail of a strong UV absorption as far as 520 nm). Remarkably, the ligand field band due to the free  $[\text{Ni}\beta_2]$  moiety at ca. 550 nm cannot be detected at polymer concentrations (calcd. as  $[\text{Pd}_4\text{Cl}_8(\text{Ni}\beta_2)]$ ) at which it can be detected for free  $[\text{Ni}\beta_2]$ . This shows that the chemical environment of Ni(II) in the polymer is strongly altered, in spite of the survival of a  $\beta^-$  ligand environment around the metal.

#### <sup>1</sup>H NMR Spectrum of the Polymer

This was recorded in DMSO. We have seen that free  $[\text{Ni}\beta_2]$  gives two resonances at  $\delta = 2.00$  and  $4.30$  ppm, while the polymer gives two 1:1 resonances at  $\delta = 2.0$  (sharp) and  $7.6$  ppm (very broad). This clearly indicates that the moiety  $[\text{Ni}\beta_2]$  survives in the polymer in DMSO, but the overall environment has been modified with respect to free  $[\text{Ni}\beta_2]$  in the same solvent.

#### Mass Spectrum of the Polymer

This was recorded by heating the sample to  $200^\circ\text{C}$  and  $230^\circ\text{C}$ . In the first case the spectrum does not show any nickel-containing species and a typical pattern attributable to an organic polymer is observed up to mass 2000. At  $230^\circ\text{C}$  the ion peak corresponding to  $[\text{Ni}\beta_2]$ , but not the mass due to  $[\text{PdCl}_2(\text{Ni}\beta_2)_{0.25}]$ , could be detected.

#### Reactivity of the Polymer with $\text{PPh}_3$

The moiety  $\{\text{PdCl}_2\}$  could be quantitatively extracted from the polymer by using a 4:1  $\text{PPh}_3$ : Pd molar ratio in  $\text{CH}_2\text{Cl}_2$  at ambient conditions. The polymer is quantitatively transformed into a mixture of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  and  $[\text{Ni}\beta_2]$  (see Experimental).

## Experimental

### Instruments

Melting points were taken with a Büchi apparatus and are uncorrected. Infrared spectra were determined by a Perkin Elmer model 580 spectrophotometer for  $[\text{Ni}\alpha_2]$ ,  $[\text{Ni}\beta_2]$  and for the polymer, and by a model 257 for the other complexes, and are reported in  $\text{cm}^{-1}$ . Nuclear magnetic resonance (NMR) spectra were measured with a Varian Associates Model 360 A spectrometer using  $\text{Me}_4\text{Si}$  as internal standard ppm. Mass spectra were taken on a VG-ZAB 2F mass spectrometer at an ionization energy of 70 eV. Magnetic measurements were carried out at room temperature on a Gouy apparatus employing a Bruker B-M 6 magnet coupled with a Sartorius electrobalance (Padua) and in Florence (ISSECCE, C.N.R.) by an analogous apparatus equipped for measurements down to 90 K. Electronic spectra were recorded on a Perkin Elmer A 72 spectrophotometer. Thermal analysis (TG and DTA measurements) of  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$  was performed on a DTA-TG 429/3/6 Netzsch instrument.

### Materials

Solvents and reagents were of reagent grade.  $\text{CH}_2\text{Cl}_2$  was purified by treatment with Na/Pb alloy, distillation, treatment with  $\text{P}_2\text{O}_5$  and final distillation. Cyanogen was a Matheson reagent (98.5% purity).  $[\text{Ni}(\text{acac})_2]$  (Schuchardt) was used as received.  $[\text{Ni}(\text{ba})_2]$ ,  $[\text{Ni}(\text{dbm})_2]$  were prepared by literature

procedures [12].  $[\text{Ni}(\text{dpm})_2]$  was prepared from  $[\text{Ni}(\text{dpm})_2\text{H}_2\text{O}]_2$  by sublimation at  $110^\circ\text{C}$  *in vacuo*.  $[\text{Ni}(\text{eaa})_2(\text{H}_2\text{O})_2]$  was prepared by adding to an aqueous solution of  $[\text{Ni}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_4]$  a solution of ethylacetoacetate (dissolved in methanol) and NaOH in ratios 2:1 over nickel, under vigorous stirring. The green precipitate obtained was dried at  $100^\circ\text{C}$  *in vacuo* for one hour and analyzed for C and H.

#### General Procedures for Cyanation Reactions

Conveniently concentrated solutions of  $\text{C}_2\text{N}_2$  were prepared by transferring directly suitable amounts of the gas from the cylinder into the desired volume of solvent. The  $\text{C}_2\text{N}_2$  concentration was determined as previously described [4]. The reaction of  $\text{C}_2\text{N}_2$  with the nickel complexes was carried out typically as follows: *ca.* 1 mmol of complex was dissolved in 10 ml of  $\text{CH}_2\text{Cl}_2$  under stirring (n-hexane for  $[\text{Ni}(\text{dpm})_2]$ ), and the resulting solution was filtered off under moisture exclusion to remove any insoluble impurity. To the nickel(II) solutions so obtained, some 10–20 ml of conveniently concentrated  $\text{C}_2\text{N}_2$  solution was added to reach a  $\text{C}_2\text{N}_2/\text{Ni}$  molar ratio of *ca.* 3. After this operation, the solutions were left to stand and the various products were obtained by spontaneous precipitation and filtered off under moisture exclusion.

Details for the various cases are given below (yields are in parenthesis):

#### $[\text{Ni}\alpha_2]$

Filtration after 24 h gave orange-red crystals (80%). This procedure sometimes gave analytically pure batches, but occasionally and unpredictably, batches containing variable amounts of  $\text{CH}_2\text{Cl}_2$  were also obtained. The presence of trapped solvent was clearly established by mass spectra measurements carried by warming the sample gradually from room temperature to  $250^\circ\text{C}$  and monitoring the  $\text{CH}_2\text{Cl}_2$  mass. All the  $\text{CH}_2\text{Cl}_2$  containing batches gave satisfactory C, H, N, analysis for the composition  $[\text{Ni}(\text{acac}\cdot\text{C}_2\text{N}_2)_2]$ , after allowance for the content of the solvent (quantified by chlorine analysis).

#### $[\text{Ni}\beta_2]$

$[\text{Ni}\alpha_2]$  (400 mg) was dissolved in 200 ml of boiling  $\text{C}_2\text{H}_4\text{Cl}_2$  and a dark red solution was obtained. By cooling the solution for 30 min. a reddish-yellow precipitate was obtained and its infrared spectrum showed  $\nu_{\text{N-H}}$  bands at 3250 (predominant) and 3200 (minor). The solid was redissolved in the mother liquor at reflux and cooling for 120 min. gave very dark red crystals (95%) displaying only the 3200 infrared band.  $[\text{Ni}\beta_2]$  always gave satisfactory C, H, N, analysis and showed no tendency to incorporate solvent.

#### $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$

Filtration after 3 h gave red brown microcrystals (70%), which were recrystallized from acetone. *Anal.* Found (calcd. in parenthesis): C = 59.20 (59.40); H = 3.85 (3.70); N = 11.20 (11.50). The crude product was found to contain 0.25 mol of  $\text{CH}_2\text{Cl}_2$  per mol of  $[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$  and calculation of C, H, N percentages with this formula gave quite satisfactory values.

#### $[\text{Ni}(\text{dbm}\cdot\text{C}_2\text{N}_2)_2]$

Filtration after 12 h gave yellow brown crystals (86%). The reactions carried out in  $\text{C}_2\text{H}_4\text{Cl}_2$  gave analytically pure crystals. *Anal.* Found (calcd. in parenthesis): C = 67.43 (67.04); H = 3.75 (3.61); N = 8.95 (9.19).

#### $[\text{Ni}(\text{eaa}\cdot\text{C}_2\text{N}_2)_2]$

The reaction time was limited to 3.5 h and prolonged times led to partial decomposition of the product, which appears as a yellow brown powder (72%). The compound analyzes as  $[\text{Ni}(\text{eaa}\cdot\text{C}_2\text{N}_2)_2]$  containing 0.08 mol of  $\text{CH}_2\text{Cl}_2$ . *Anal.* Found (calcd. in parenthesis): C = 45.42 (45.14); H = 4.47 (4.22); N = 13.22 (13.09).

#### $[\text{Ni}(\text{dpm}\cdot\text{C}_2\text{N}_2)_2]$

The reaction was carried out in n-hexane. After dissolution of  $[\text{Ni}(\text{dpm})_2]$ , filtration and addition of  $\text{C}_2\text{N}_2$  in n-hexane, the solution was left in a refrigerator at *ca.*  $0^\circ\text{C}$ . The brown precipitate was filtered after 12 h. Several attempts carried out under slightly different conditions gave batches exhibiting analyses not in perfect agreement with the desired composition. The best obtained analysis was (calcd. in parenthesis): C = 58.72 (58.80); H = 7.22 (7.16); N = 9.51 (10.55). The poor figure for N analysis prompted us to also characterize the product by mass spectrometry. E. I. mass measurements (ionization chamber *ca.*  $200^\circ\text{C}$ ) gave the expected ion parent peak, albeit very weak. Considerably stronger was the signal 476 due to the  $[\text{Ni}(\text{dpm}_2\cdot\text{C}_2\text{N}_2)]^+$  moiety: m/e (relative intensity) 528 (parent, 0.002), 476 (0.02), 424 (0.26), 419 (0.45), 392 (0.29), 367 (0.50), 127 (1.00), 110 (0.32), 57 (1.00). The probe temperature employed for these measurements was just over  $30^\circ\text{C}$  and the weak intensity of the ion parent peak clearly indicates poor thermal stability of  $[\text{Ni}(\text{dpm}\cdot\text{C}_2\text{N}_2)_2]$ .

#### Reactions of $[\text{Ni}\alpha_2]$ and $[\text{Ni}\beta_2]$ with Acids

Numerous attempts to extract the ligands were carried out by employing  $\text{H}_2\text{S}$  and  $\text{CF}_3\text{COOH}$  in  $\text{CH}_2\text{Cl}_2$  and HCl in  $\text{H}_2\text{O}$ /ether or HCl in  $\text{H}_2\text{O}$  (followed by extraction with ether at room temperature and near  $0^\circ\text{C}$ ). The acids were used either in excess over  $[\text{Ni}\alpha_2]$  and  $[\text{Ni}\beta_2]$ , or in stoichiometric ratios and even in under-stoichiometric conditions (coupled



with careful pH control of the aqueous solution during acid addition to suspensions of  $[\text{Ni}\alpha_2]$ ). All the results were unclear and irreproducible.

#### Reaction of $[\text{PdCl}_2(\text{PhCN})_2]$ with $[\text{Ni}\beta_2]$

This was carried out under various conditions (see *Results*) and the isolated material gave the analysis (calculated values in parenthesis): C = 18.38 (15.70); H = 3.21 (1.32); N = 5.30 (5.68); Ni = 5.50 (5.40). The comparison between the poor values for C and H compared with the acceptable one for Ni suggests that the conventional procedure used for determining C, H and N may be unsuitable in this case. Ni analysis carried out by atomic absorption spectroscopy after mineralization by *aqua regia* did not apparently suffer any limitation.

#### Reaction of the Polymer with $\text{PPh}_3$

50 mg of the polymer were suspended in 5 ml of  $\text{CH}_2\text{Cl}_2$  containing 0.08 M  $\text{PPh}_3$  (2 $\text{PPh}_3$ : 1 Pd), the suspension was left under vigorous stirring for 24 hours. The resulting yellow suspension was filtered off *in vacuo*, giving 99 mg of a product whose IR spectrum is superimposable to that of a mixture of 1  $[\text{PdCl}_2(\text{PPh}_3)_2]/0.25 [\text{Ni}\beta_2]$  down to  $200\text{ cm}^{-1}$  (both compounds are known to be scarcely soluble in  $\text{CH}_2\text{Cl}_2$ ). From the mother liquor evaporated to dryness a further 18 mg of mixture were obtained (after washing with ethyl ether). The total recovery of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  and  $[\text{Ni}\beta_2]$  from the polymer was 117 mg (*ca.* 80% of the theoretical value).

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$[\text{Ni}(\text{ba}\cdot\text{C}_2\text{N}_2)_2]$  at lower temperatures and to Mr. Turiaco (our Institute) for the numerous elemental analyses carried out for this research.

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