Carbon-Carbon Bond Formation in the Reaction of Benzoyl Cyanide with Nickel(II) β-Diketonates†

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Nickel β-diketonates react with benzoyl cyanide to give C–C bond formation between the methine and the cyano carbon atoms. The resulting reddish compounds are square-planar iminodiketonato complexes, which are likely catalytic intermediates in the synthesis of β-enaminodiones from β-diketones and PhCOCN. The acetylacetonato derivative [Ni(acac·PhCOCN)$_2$] can be obtained in the solid state in two stable forms; an X-ray single-crystal analysis of form **II** indicates that the unit cell [monoclinic, space group $P2_1/c$, $a = 11.408(5)$ Å, $b = 15.109(4)$ Å, $c = 14.515(5)$ Å, $\beta = 108.93(3)°$] contains two couples of independent, structurally very similar, molecules of the complex. The nickel atom is always centrosymmetrically co-ordinated to the ligand in a N,O bonding configuration, which is preferred to the alternative O,O one.

The metal-promoted addition of β-dicarbonyls to nitriles has recently been shown to represent an important approach for the synthesis of a large variety of β-enaminodiones and of their cyclic derivatives.[1–9] This synthetic procedure is particularly useful not only because of its high chemoselectivity, but also as it does not require the usual basic conditions, in which either the reagents and/or the products may be unstable.[10]

In this context, the role of the metal catalyst has been well established[11] and it implies, in the crucial step, activation *via* co-ordination of the deprotonated β-dicarbonyl and of the nitrile to give the required C–C bond-forming reaction. Despite the large variety of nitriles used in these syntheses, interest in the catalytically relevant iminocarbonylenolate complexes has been mainly limited to cyanogen derivatives.[12–14]

We report here on the isolation and full characterization of the complexes obtained in the reaction of nickel(II) β-diketonates with benzoyl cyanide [equation (1)], which are

$$[\mathrm{Ni}(\beta\text{-dik})_2] + 2\mathrm{PhCOCN} \longrightarrow [\mathrm{Ni}(\beta\text{-dik}\cdot\mathrm{PhCOCN})_2] \quad (1)$$

likely catalytic intermediates in the related synthesis of β-benzoyl-β-enaminodiketones $H_2N(PhCO)C{=}C(COR)$-COR′, hereafter labelled as H-β-dik·PhCOCN, from β-diketones and benzoyl cyanide.[6] Here H-β-dik = acetylacetone (Hacac), benzoylacetone (Hba), or dibenzoylmethane (Hdbm).

Experimental

Infrared and UV/VIS spectra were recorded on Perkin-Elmer 781 and 576 instruments, respectively, mass spectra on a VG Micromass 16F and ^{1}H NMR spectra on a JEOL FX 90Q spectrometer. The TG–DSC data were obtained with Perkin-Elmer TGS-2, DSC-4 equipment. All solvents and reagents were high-purity products used as received. Solvents were from Baker ('Baker Analyzed Reagent'), benzoylacetone and dibenzoylmethane from EGA-Chemie, benzoyl cyanide from Fluka, nickel acetate tetrahydrate from C. Erba, and nickel acetylacetonate from Merck. The complexes [Ni(ba)$_2$] and [Ni(dbm)$_2$][15] and the β-benzoyl-β-enaminodiketones H-β-dik·PhCOCN[6] were prepared by literature procedures.

General Procedures for the Synthesis of [Ni(β-dik·PhCOCN)$_2$] *Complexes*.—The more straightforward procedure (*a*) implies reaction of the required nickel diketonate complex with benzoyl cyanide in 1:2 molar ratio, in dichloroethane. Typically, the complex (4 mmol) was suspended in carefully deoxygenated $C_2H_4Cl_2$ (25 cm^3) and treated with a solution (25 cm^3) of benzoyl cyanide (8 mmol). The suspension was vigorously stirred and kept under argon. The reaction temperatures ranged from room to reflux and times varied from 4 to 70 h. The resulting complex, which slowly precipitated at room temperature, was filtered off (moisture being excluded), washed with $C_2H_4Cl_2$ and dried *in vacuo*.

An alternative procedure (*b*) involves reaction of nickel acetate tetrahydrate with the protonated H-β-dik·PhCOCN ligand in 1:2 molar ratio, in ethanol. Typically the nickel salt (0.5 mmol) and the ligand (1 mmol) were treated with deoxygenated ethanol (50 cm^3). The suspension was stirred at room temperature and the resulting complex started to precipitate after a few minutes. The reaction was complete in about 1 h, after which the solid was filtered off, washed with ethanol and dried *in vacuo*.

[Ni(acac·PhCOCN)$_2$] (*form* **I** *and form* **II**). Procedure (*a*) gave, after 4 h at reflux temperature, an orange-red solid (form **II**), which was recrystallized from $C_2H_4Cl_2$; yield 52%, m.p. (decomp.) *ca.* 300 °C (Found: C, 59.55; H, 4.60; N, 5.20. Calc. for $C_{26}H_{24}N_2NiO_6$: C, 60.15; H, 4.65; N, 5.40%). Procedure (*b*) gave in high yield [> 90%, m.p. (decomp.) *ca.* 290 °C] a product (form **I**) with a very similar elemental analysis (C, 59.30; H, 4.75; N, 5.20%), but slightly different infrared spectrum, mainly in the ν(N–H) region. It can be crystallized from freshly distilled dichloromethane or acetone and in this case the resulting solid

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Fractional coordinates for the two independent molecules of [Ni(acac·PhCOCN)$_2$] (form **II**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	0.000 000	0.500 000	0.500 000	Ni(2)	0.500 000	1.000 000	1.000 000
O(2)	0.220 3(7)	0.190 1(5)	0.628 8(6)	O(4)	0.216 2(8)	0.941 1(6)	0.631 7(6)
O(1)	−0.087 8(6)	0.396 7(4)	0.487 8(6)	N(2)	0.352 8(8)	0.958 8(6)	0.917 4(7)
N(1)	0.148 4(7)	0.444 1(5)	0.551 9(6)	O(5)	0.543 0(7)	1.044 4(5)	0.897 6(5)
O(3)	0.366 8(6)	0.362 1(5)	0.689 1(5)	O(6)	0.175 7(8)	0.833 9(5)	0.786 2(7)
C(1)	−0.049(1)	0.317 1(7)	0.503 5(8)	C(14)	0.310 1(9)	0.956 6(7)	0.824 4(7)
C(2)	−0.156(1)	0.252 1(9)	0.480(1)	C(15)	0.375 6(8)	0.993 3(8)	0.764 1(7)
C(3)	0.076 1(9)	0.292 8(7)	0.542 6(7)	C(16)	0.317(1)	0.979 0(7)	0.659 9(8)
C(4)	0.121(1)	0.202 1(7)	0.564 5(8)	C(17)	0.184(1)	0.913 7(8)	0.782 4(9)
C(5)	0.055(1)	0.123 1(8)	0.507 4(9)	C(18)	0.484(1)	1.038 9(7)	0.805 7(8)
C(6)	0.171 1(9)	0.360 1(7)	0.566 6(7)	C(19)	0.370(1)	1.005(1)	0.580 2(9)
C(7)	0.308(1)	0.337 5(7)	0.607 4(8)	C(20)	0.554(1)	1.095(1)	0.752(1)
C(8)	0.365 8(6)	0.295 5(5)	0.541 4(4)	C(21)	0.087 6(5)	1.064 0(5)	0.761 6(5)
C(9)	0.489 1(6)	0.268 3(5)	0.578 4(4)	C(22)	−0.016 5(5)	1.118 3(5)	0.741 9(5)
C(10)	0.546 8(6)	0.230 5(5)	0.516 6(4)	C(23)	−0.134 1(5)	1.080 7(5)	0.719 8(5)
C(11)	0.481 2(6)	0.220 0(5)	0.417 8(4)	C(24)	−0.147 6(5)	0.988 9(5)	0.717 5(5)
C(12)	0.357 9(6)	0.247 2(5)	0.380 8(4)	C(25)	−0.043 4(5)	0.934 6(5)	0.737 2(5)
C(13)	0.300 2(6)	0.285 0(5)	0.442 6(4)	C(26)	0.074 2(5)	0.972 2(5)	0.759 2(5)

Table 2 Selected bond distances (Å) for the two independent molecules of [Ni(acac·PhCOCN)$_2$] (form **II**)

Molecule A		Molecule B	
Ni(1)–O(1)	1.832(7)	Ni(2)–O(5)	1.836(9)
Ni(1)–N(1)	1.822(8)	Ni(2)–N(2)	1.828(8)
O(1)–C(1)	1.28(1)	O(5)–C(18)	1.29(1)
C(1)–C(2)	1.52(2)	C(18)–C(20)	1.54(2)
C(1)–C(3)	1.40(1)	C(18)–C(15)	1.37(1)
C(3)–C(4)	1.46(2)	C(15)–C(16)	1.46(1)
C(4)–O(2)	1.22(1)	C(16)–O(4)	1.23(1)
C(4)–C(5)	1.51(2)	C(16)–C(19)	1.52(2)
C(3)–C(6)	1.44(1)	C(14)–C(15)	1.43(2)
C(6)–N(1)	1.30(1)	C(14)–N(2)	1.28(1)
C(6)–C(7)	1.52(1)	C(14)–C(17)	1.52(2)
C(7)–O(3)	1.22(1)	C(17)–O(6)	1.21(1)
C(7)–C(8)	1.47(1)	C(17)–C(26)	1.48(1)
Contact distances			
N(1)···O(1)	2.65	N(2)···O(5)	2.62
N(1)···O(1^{I})	2.52	N(2)···O(5^{II})	2.56
N(1)···O(3)	2.91	N(2)···O(6)	2.96

Symmetry relations: I $\bar{x}$, $1 - y$, $1 - z$; II $1 - x$, $2 - y$, $2 - z$.

Table 3 Selected bond angles (°) for the two independent molecules of [Ni(acac·PhCOCN)$_2$] (form **II**)

Molecule A		Molecule B	
O(1)–Ni(1)–N(1)	92.9(4)	O(5)–Ni(2)–N(2)	91.4(4)
Ni(1)–O(1)–C(1)	129.7(8)	Ni(2)–O(5)–C(18)	129.0(7)
Ni(1)–N(1)–C(6)	129.0(8)	Ni(2)–N(2)–C(14)	130.9(8)
O(1)–C(1)–C(2)	111(1)	O(5)–C(18)–C(20)	108(1)
O(1)–C(1)–C(3)	125(1)	O(5)–C(18)–C(15)	125(1)
C(2)–C(1)–C(3)	124(1)	C(20)–C(18)–C(15)	126(1)
C(1)–C(3)–C(4)	125(1)	C(18)–C(15)–C(16)	125.0(9)
C(1)–C(3)–C(6)	120(1)	C(18)–C(15)–C(14)	120.0(9)
C(4)–C(3)–C(6)	115(1)	C(16)–C(15)–C(14)	115.0(9)
C(3)–C(4)–O(2)	119(1)	C(15)–C(16)–O(4)	118(1)
C(3)–C(4)–C(5)	123(1)	C(15)–C(16)–C(19)	126(1)
O(2)–C(4)–C(5)	119(1)	O(4)–C(16)–C(19)	115(1)
C(3)–C(6)–N(1)	124(1)	C(15)–C(14)–N(2)	123(1)
C(3)–C(6)–C(7)	122.1(9)	C(15)–C(14)–C(17)	122.4(9)
N(1)–C(6)–C(7)	114.2(9)	N(2)–C(14)–C(17)	115(1)
C(6)–C(7)–O(3)	119(1)	C(14)–C(17)–O(6)	119(1)
C(6)–C(7)–C(8)	117.7(9)	C(14)–C(17)–C(26)	117(1)
O(3)–C(7)–C(8)	123(1)	O(6)–C(17)–C(26)	123(1)

contains variable amounts of solvent (for example, Found: C, 57.20; H, 4.65; N, 4.90. Calc. for $C_{26}H_{24}N_2NiO_6 \cdot 0.4CH_2Cl_2$: C, 57.35; H, 4.50; N, 5.05%). The complex in form **I** can be transformed into form **II** by refluxing it in dichloroethane for 4 h. This conversion occurs rapidly at room temperature in commercial dichloromethane, containing traces of HCl, and is very slow in acetone.

[Ni(ba·PhCOCN)$_2$]. Procedure (*a*) gave, after 70 h at room temperature, a brown-red solid, which was recrystallized from $C_2H_4Cl_2$; yield 54%, m.p. (decomp.) 246 °C (Found: C, 67.05; H, 4.35; N, 4.35. Calc. for $C_{36}H_{28}N_2NiO_6$: C, 67.20; H, 4.40; N, 4.35%). The same product is obtained with procedure (*b*).

[Ni(dbm·PhCOCN)$_2$]. Procedure (*a*) gave, after 10 h at reflux temperature, a brown-red solid, which was washed with boiling $C_2H_4Cl_2$; yield 49%, m.p. 250 °C (Found: C, 71.00; H, 4.10; N, 3.45. Calc. for $C_{46}H_{32}N_2NiO_6$: C, 72.00; H, 4.20; N, 3.65%). The same product is obtained with procedure (*b*).

X-Ray Structure Analysis of [Ni(acac·PhCOCN)$_2$] (*form* **II**).—Crystals suitable for the X-ray analysis were obtained by recrystallization of form **I** from acetone. From the solution, kept at room temperature, an orange powder of complex in form **I** was first precipitated and from the resulting suspension heavy red crystals of form **II** slowly separated (*ca.* 60 d), which were isolated by decantation. The X-ray work was carried out on a Philips four-circle diffractometer with monochromatized Mo-Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings ($8 \leqslant 2\theta \leqslant 30°$).

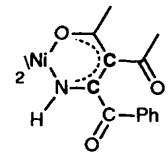
Crystal data $C_{26}H_{24}N_2NiO_6$, $M = 519.2$, $F(000) = 1080$, monoclinic, space group $P2_1/c$, $a = 11.408(5)$, $b = 15.109(4)$, $c = 14.515(5)$, $\beta = 108.93(3)°$, $U = 2366$ Å^3, $D_c = 1.46$ g cm^{-3} for $Z = 4$, μ(Mo-Kα) = 8.2 cm^{-1}, maximum crystal size = 0.5 mm.

Intensities were measured by the θ–2θ scan method with a scan speed of 2° min^{-1} up to $\theta = 25°$ yielding 4162 unique reflections of which 1674 were significantly above background [$I > 3\sigma(I)$]. The data were corrected for Lorentz and polarization factors. The compound is stable under irradiation. The structure was solved by Patterson and Fourier maps alternated with cycles of least-squares refinement of the atomic parameters. The full-matrix refinement proceeded by minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. Convergence was reached at the conventional R factor of 0.066, when the maximum residual of electron density was 0.87 e Å^{-3}. During the refinement the phenyl rings were treated as rigid hexagons (C–C 1.395, C–H 1.08 Å) and a fixed thermal parameter ($U = 0.07$ Å^2) was assigned to the H atoms. Scattering factors for Ni were taken from ref. 16, those for the other atoms being internally supplied by the SHELX program.[17] The scattering factors for Ni were corrected for anomalous dispersion. Final atomic coordinates are reported in Table 1, selected bond lengths and angles in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Nickel β-diketonates react with benzoyl cyanide to give stable red-brown square-planar complexes (Table 4). The X-ray analysis of [Ni(acac·PhCOCN)$_2$] (form **II**; see later for details) indicates a C–C bond formation between the methine and the cyano carbon atoms, as sketched in the structure below.



The reaction formally appears as an insertion of the C≡N into the C–H group and is the result of a multistep process, which, by analogy to other investigated nitriles,[11] should involve end-on co-ordination of the cyano nitrogen to the nickel centre and subsequent C–C bond formation in a metal-promoted electrophile (nitrile)–nucleophile (β-diketonate) interaction.

A number of physicochemical measurements have been undertaken to determine the structures of all [Ni(β-dik·PhCOCN)$_2$] complexes obtained, with particular attention to the two forms in which the acetylacetonato derivative can be isolated.

The UV/VIS spectra in dichloromethane solution are characterized by a series of very intense bands in the range 263–395 nm attributable to the metallo-carbonylenolato ring, and by a broad ligand-field band in the visible region (530–540 nm, ε = 70–200 dm^3 mol^{-1} cm^{-1}) typical of a square-planar geometry. The values obtained are in close agreement, for example, with those observed for [Ni(dpm)$_2$] (Hdpm = dipivaloylmethane; λ = 535 nm, ε = 80 dm^3 mol^{-1} cm^{-1})[18] and for a number of [Ni(β-carbonylenolate·C$_2$N$_2$)$_2$] complexes.[12] Thus, addition of benzoyl cyanide to the metallo-ring causes a collapse of the trimeric octahedral structure of [Ni(acac)$_2$], [Ni(ba)$_2$] and [Ni(dbm)$_2$][15] in favour of a square-planar one. This phenomenon has already been observed in the related reaction with cyanogen and cannot be attributed to a solvent effect, because of the close similarity of the spectra in solution and in Nujol mull. This destabilization of the octahedral structure of [Ni(β-dik)$_2$] complexes can reasonably be related to a change of bonding atoms; it has been reported that substitution of an oxygen by an imino group yields *trans* square-planar complexes.[19–22] It should be also pointed out that the spectra of the two forms of [Ni(acac·PhCOCN)$_2$] are practically identical either in dichloromethane or in acetone, showing only small differences in the relative band intensities in the solid state.

Magnetic susceptibility measurements show that all complexes are weakly paramagnetic; the positive μ values are in contrast with a d^8 square-planar structure, but again consistent with those found in the similar [Ni(β-carbonylenolate·C$_2$N$_2$)$_2$] complexes.[12] As the X-ray structure of [Ni(acac·PhCOCN)$_2$] (form **II**) rules out any tetragonal distortion around the nickel and any long-range octahedral interaction, the source of this low magnetism seems at the moment obscure.

The solid-state infrared spectra of the complexes are characterized by a medium-intensity band in the ν(N–H) region (3301–3275 cm^{-1}), strong ν(C=O) bands between 1676 and 1626 cm^{-1}, and typical absorptions of the metallo-organic and phenyl rings (1598–1557 cm^{-1}).[19,23] The large bond delocalization extending throughout the ring and its substituents makes a detailed attribution of the single bands rather arbitrary. These data, anyway, unambiguously confirm the benzoyl cyanide insertion into the C–H methine bond. Regarding the ligand configuration, the values of ν(N–H), fairly low ($\leqslant$3301 cm^{-1}) for a 'pure' imino stretching,[23] may suggest N,O co-ordination for all complexes, in analogy with the determined structure of [Ni(acac·PhCOCN)$_2$] (form **II**).

The ^{1}H NMR spectra at 90 MHz were recorded only in dimethyl sulfoxide, because of the low solubility of the complexes in other solvents. They all show the typical resonances of the phenyl protons around δ 7.5, which may overlap with the imino signal. The two forms of [Ni(acac·PhCOCN)$_2$] have the same spectrum and exhibit two distinct CH$_3$ resonances at δ 2.25 and 2.42. A variable-temperature study indicates that there is no coalescence of these peaks up to 80 °C; for temperatures above 100 °C the complex partly decomposes. Only one CH$_3$ resonance, as expected, is observed for [Ni(ba·PhCOCN)$_2$] at δ 1.72. The above values for [Ni(acac·PhCOCN)$_2$] are very similar to those found for its ligand H$_2$N(PhCO)C=C(COMe)COMe (δ 2.28 and 2.47),[6] where it can be assumed that one of the two acetyl groups is involved in intramolecular hydrogen bonding with one amino hydrogen. On these bases, the presence of two methyl resonances, at comparable δ values, for [Ni(acac·PhCOCN)$_2$] would suggest that the complex adopts, in dimethyl sulfoxide solution, a configuration in which only one MeCO group is bonded to the nickel centre. No definite conclusion on ligand configuration can be drawn for [Ni(ba·PhCOCN)$_2$] and [Ni(dbm·PhCOCN)$_2$].

The thermal behaviour of the complexes shows interesting features. The complex [Ni(acac·PhCOCN)$_2$] (form **I**) darkens and exhibits a solid aggregation at 245 °C. This phenomenon is exothermic (ΔH = −60 kJ mol^{-1}) and occurs without weight loss. The complex melts with decomposition at *ca.* 290 °C (ΔH = *ca.* 45 kJ mol^{-1}; Δw = −9% in the range 245–320 °C). The complex [Ni(acac·PhCOCN)$_2$] (form **II**) darkens at 250 °C without weight loss in an exothermic process (ΔH = −26 kJ mol^{-1}, ΔT = 230–260 °C), which is followed by decomposition (Δw = −11%, ΔT = 260–330 °C, ΔH = *ca.* 10 kJ mol^{-1}). A much simpler pattern is shown by [Ni(ba·PhCOCN)$_2$] which melts at 246 °C (ΔH = 110 kJ mol^{-1}) and by [Ni(dbm·PhCOCN)$_2$] (m.p. 250 °C, ΔH = 200 kJ mol^{-1}). In both cases extensive decomposition is observed at higher temperatures (Δw = *ca.* −30%, ΔT = 250–300 °C). These results indicate that both forms of [Ni(acac·PhCOCN)$_2$] undergo solid-state rearrangements, which are accompanied by heat evolution, to reach more stable structures.

The mass spectra (Table 5) have been recorded with the electron-impact technique, by introducing the complexes directly into the source, at 200 °C, applying an electron potential of 70 eV (*ca.* 1.12 × 10^{-17} J) and an electron intensity of 20 μA. Under these conditions satisfactory spectra are obtained for [Ni(acac·PhCOCN)$_2$] and [Ni(ba·PhCOCN)$_2$], whereas [Ni(dbm·PhCOCN)$_2$] undergoes extensive decomposition, showing mainly low-molecular-weight fragments. Two areas are clearly distinguishable: one at high molecular weight, corresponding to simple fragmentations of the molecular ion, and one at low weights, corresponding to fragmentations of the ligand. Both complexes show the peak corresponding to the molecular ion (*m/z* 518 and 642), albeit with very different intensity, so indicating a greater stability of the acetylacetonato derivative. The more significant fragments still containing the metal indicate easy loss of PhCO, whereas the ligand shows, in particular, the expected methyl, acetyl, benzoyl and benzoyl cyanide fragmentations. Also in this case the two forms of [Ni(acac·PhCOCN)$_2$] exhibit the same behaviour, giving the same spectra, suggesting that one form is easily converted into the other in the electron beam of the spectrometric ion source.

The X-ray powder diffraction pattern of [Ni(acac·PhCOCN)$_2$] is markedly different, both in position and intensity of the peaks, for the two forms. In particular the large differences in the position of the peaks at low angles (< 10°) are clearly indicative of distinct lattice parameters, but cannot, obviously, give information on the molecular structure.

Table 4 Summary of data on [Ni(β-dik·PhCOCN)$_2$] complexes

Complex	Selected IR bands[a] (cm^{-1})			UV/VIS data in CH$_2$Cl$_2$, λ_{max}/nm(log ε)	^{1}H NMR in (CD$_3$)$_2$SO, δ	μ
	ν(N–H)	ν(C=O)	ν(C⋯O), ν(C⋯C), ν(C⋯N)			
[Ni(acac·PhCOCN)$_2$] (form **I**)	3277n	1670s 1633m[b]	1596mw 1557s	260(4.8), 295(4.6), 365(3.5), 530(1.9)	2.25 (s, 3 H, CH$_3$) 2.42 (s, 3 H, CH$_3$) 7.30 (s, *ca.* 1 H, NH) 7.52 (m, 5 H, C$_6$H$_5$)	0.61
[Ni(acac·PhCOCN)$_2$] (form **II**)	3301m	1675s 1665s 1626s	1597mw 1578 (sh) 1564vs	*c*	*c*	0.57
[Ni(ba·PhCOCN)$_2$]	3268m	1676s 1628s	1598m 1565s	264(4.8), 310(4.3), 530(2.2)	1.72 (s, 3 H, CH$_3$) 7.45 (m, 10 H, 2C$_6$H$_5$)	1.23
[Ni(dmb·PhCOCN)$_2$]	3275m	1667s 1637s	1598m 1583m 1558s	272(4.7), 320(4.3), 395(3.6), 540(2.3)	6.80–8.10 (C$_6$H$_5$)	0.56

[a] Nujol mull. [b] Tentative attribution. [c] Solution spectra identical, within experimental errors, with those of form **I**.

Table 5 Electron-impact mass spectra[a] of [Ni(β-dik·PhCOCN)$_2$] complexes[b]

Ionic species	[Ni(acac·PhCOCN)$_2$] (forms **I** and **II**)	[Ni(ba·PhCOCN)$_2$]
[M]$^+$	518(30)	642(0.4)
[M – H$_2$O]$^+$	500(12)	
[M – PhCO]$^+$	413(38)	537(0.5)
[M – (PhCO + H$_2$O)]$^+$	395(13)	
[M + H – L]$^+$	289(20)	
[M + H – (L + H$_2$O)]$^+$	271(25)	
[HL]$^+$	231(54)	293(12)
[HL – CH$_3$]$^+$	216(16)	278(3.6)
[HL – CH$_3$CO]$^+$	188(24)	250(6.0)
[HL – PhCO]$^+$	126(22)	188(13)
[HL – PhCOCN]$^+$		162(10)
[HL – (PhCOCNH + CH$_3$)]$^+$		146(30)
[PhCO]$^+$	105(100)	105(100)
[Ph]$^+$	77(45)	77(78)
[CH$_3$CO]$^+$	43(80)	43(22)

[a] *m/z* (relative intensity). [b] For [Ni(dbm·PhCOCN)$_2$]: *m/z* 504(3.8), [M – 2PhCOCN]$^+$; 224(28), [HL – PhCOCN]$^+$; 223(25), [HL – PhCOCNH]$^+$; 147(16), [HL – (PhCOCN + Ph)]$^+$; 131(23), [PhCOCN]$^+$; 105(100), [PhCO]$^+$; and 77(52), [Ph]$^+$.

Table 6 Angles (°) between the planes for the two independent molecules of [Ni(acac·PhCOCN)$_2$] (form **II**)

Plane	Atoms	Angle (°)	
I	Ni(1), N(1), O(1)		
II	N(1), O(1), C(1), C(6)	II–I	3.6
III	C(3), C(4), O(2), C(5)	III–I	29.1
IV	C(6), C(7), C(8), O(3)	IV–I	72.0
		IV–II	68.6
V	C(8) to C(13)	V–I	78.6
		V–II	75.3
		V–IV	9.0
VI	Ni(2), N(2), O(5)	VI–I	68.6
VII	N(2), O(5), C(14), C(18)	VII–VI	3.1
VIII	C(15), C(16), O(4), C(19)	VIII–VI	8.8
IX	C(14), C(17), C(26), O(6)	IX–VI	76.8
		IX–VII	79.3
X	C(21) to C(26)	X–VI	79.0
		X–VII	81.7
		X–IX	6.0

X-Ray Structure of [Ni(acac·PhCOCN)$_2$] (*form* **II**).—As the four Ni atoms occupy two different sets of special positions (equipoints 2a and 2b) on inversion centres, the asymmetric unit of the monoclinic cell contains the halves of two independent centrosymmetric molecules of the same compound. In this way corresponding molecular details are determined twice, which allows greater confidence. Moreover, since the two molecules are chemically and structurally almost identical, we will eventually refer to the molecular structure of the compound without always distinguishing between the two independent units present in the crystal, and to the structural details as the averages of the observed values.

As shown in Fig. 1 the nickel atoms are centrosymmetrically co-ordinated to the bidentate ligands in the square-planar geometry. With reference to Fig. 2 the O–Ni–N angle subtended by the ligand has a mean value of 92.1° and the Ni–O and Ni–N distances are very similar, so that no significant distortions from the idealized geometry are present. Identification of the nitrogen atoms (from the chemical point of view there was ambiguity in the relative positions of the atoms co-ordinated) was made on the basis of the associated thermal parameters and confirmed by the circumstance that in both molecules a peak which can be attributed to the hydrogen atom was observed near the nitrogen at the appropriate distance [N–H 0.84–1.01(10) Å]. Mean plane calculations (see Table 6) show that the planes formed by the N, O, and the two adjacent C atoms are slightly inclined (by 3–4°) to the corresponding NiN$_2$O$_2$ co-ordination planes, so that the molecule tends towards the chair conformation. However, the whole molecule, with the exception of the acetyl and of the benzoyl groups, is approximately planar. This fact, along with the observed bond distances, implies that some delocalization of electron density extends, as a mesomeric effect, to the entire six-membered metallocycle. However, a more pronounced double-bond character seems to be attributed to the C–N and C(1)–C(3) [and C(18)–C(15)] bonds. Similar behaviour was found in related complexes of copper(II)[24] and palladium(II),[25] so appearing as a characteristic feature of iminoenolato rings. The external C–O bonds are clearly ketonic, whereas the C–O bond of

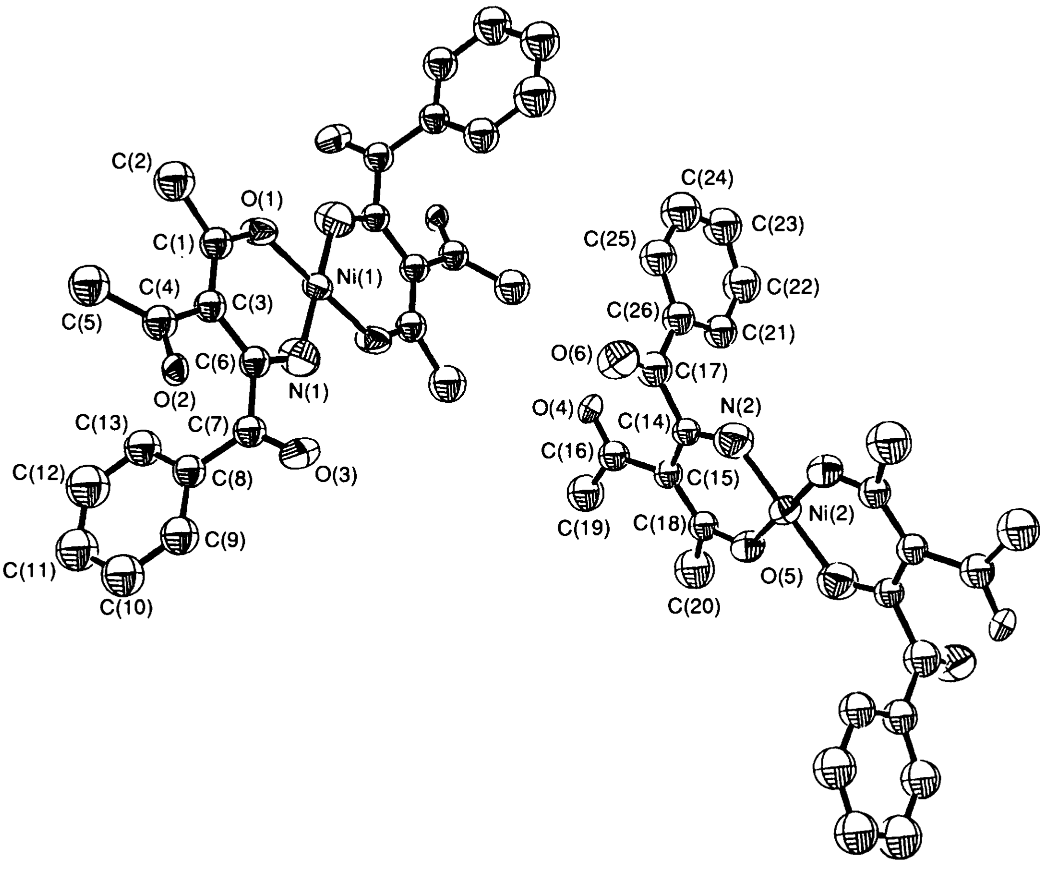


Fig. 1 The crystal structure of the two independent molecules of [Ni(acac•PhCOCN)$_2$] (form **II**). Hydrogen atoms are omitted for clarity

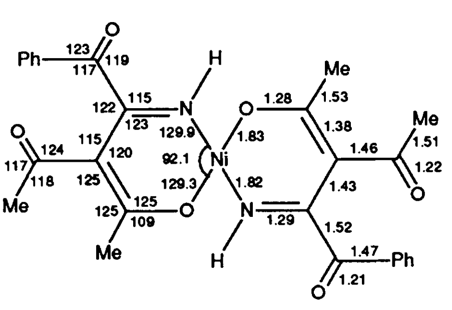


Fig. 2 Schematic drawing of [Ni(acac•PhCOCN)$_2$] (form **II**). Structural parameters (lengths in Å, angles in °) correspond to averages of the values found in the two independent molecules present in the crystal cell

the co-ordinated oxygen atom is significantly longer. The benzoyl group is almost orthogonal to the co-ordination plane (72.0–76.8°), whereas the acetyl group slightly deviates from coplanarity, the deviation being greater for one molecule (29.1 *vs.* 8.8°). Other structural details are normal and need no particular comment.

Conclusion

The results indicate that β-carbonylenolatonickel complexes react with benzoyl cyanide to give insertion at the C–H methine bond of the metallo-organic ring. The reaction rate is lower than with cyanogen and changes with the nature of the co-ordinated ligand (acetylacetone > benzoylacetone > dibenzoylmethane), so following the same reactivity order observed in the catalytic syntheses of the related β-enaminodiones. This strongly suggests that the imino-β-diketonato complexes here described are catalytic intermediates in the organic synthesis and supports our proposal that the rate-determining step in the catalytic cycle is the formation of the C–C bond between the methine and the cyano carbons. The isolated complexes are stable in the solid state and are characterized by a square-planar geometry: the acetylacetonato derivative can be isolated in two forms; form **II** exhibits an iminoenolato configuration characterized by an N,O bonding set, so appearing that the HNC–C(O)Ph is a better co-ordinating group than OC–Me towards the nickel centre. This result is somewhat surprising, as it is generally thought that O,O co-ordination is preferred for moderately hard metal centres like nickel(II),[26] and can perhaps be related to the presence of the benzoyl substitutent at the imino group. The complex [Ni(acac•PhCOCN)$_2$] first precipitates, at room temperature, as form **I**, probably because of its lower solubility, and data do not unambiguously show if it is a polymorphic or an isomeric form of the more stable **II**. Quite remarkably, [Ni(ba•PhCOCN)$_2$] and [Ni(dbm•PhCOCN)$_2$] exhibit only one stable form, independently of temperature and of synthetic procedure. Considering that the benzoyl groups should be poorer ligands than the acetyl group, we may propose for these complexes the same N,O co-ordination demonstrated by X-ray diffraction for the acetylacetonato derivative.

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