

# Pentachlorophenyl $\beta$ -Carbonylenolate Phosphino Nickel(II) Complexes: Synthesis, Full $^1\text{H}$ , $^{31}\text{P}$ and $^{13}\text{C}$ NMR Characterization and X-ray Structure of Pentachlorophenyl 1-ethoxy-1,3-butanedionate Diphenylmethylphosphino Nickel(II)

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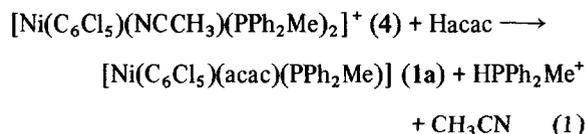
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## Abstract

Reaction of the cationic complex  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{CH}_3\text{CN})\text{L}_2]^+$  ( $\text{L} = \text{PPh}_2\text{Me}$ ) with  $\beta$ -dicarbonyls (diketones and ethyl-2-oxo-butanoate) in the presence of  $\text{NEt}_3$  affords the neutral complexes  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\beta\text{-carbonylenolate})\text{L}]$ . A more convenient synthesis of analogous complexes was found in the reaction of *trans*- $[\text{Ni}(\text{Cl})(\text{C}_6\text{Cl}_5)\text{L}_2]$  ( $\text{L} = \text{PPh}_2\text{Me}_2$ ,  $\text{PMe}_3$ ) and  $[\text{Ti}(\beta\text{-carbonylenolate})]$  derivatives. The isolated complexes have been characterized by  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR and IR spectroscopies. They exhibit a square planar geometry in which the  $\beta$ -carbonylenolate acts as  $O,O'$ -chelating ligand; complexes with unsymmetrically substituted  $\beta$ -ketoenolates give rise in solution to mixtures of geometrical isomers. A single crystal X-ray structure of the ketoester derivative,  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{OEt})(\text{PPh}_2\text{Me})]$ , shows that the isomer bearing the ester carbonyl group *trans* to the phosphine ligand is the only one present in the solid state. The crystal is monoclinic, space group  $P2_1/n$ ,  $Z = 4$  and the cell dimensions are  $a = 13.332(4)$ ,  $b = 23.799(6)$ ,  $c = 8.674(3)$  Å,  $\beta = 97.2(3)^\circ$ .

## Introduction

In the course of our studies on the metal-promoted or -catalysed reactivity of  $\beta$ -dicarbonyls with electrophiles (mainly nitriles) [1] we came across a fairly interesting reaction [2] between a nitrile-containing metal complex and acetylacetonate (Hacac) (eqn. (1)).



The product does not result from the expected [3, 4] addition reaction of Hacac to the electrophilically activated  $\text{C}\equiv\text{N}$  group, but from (i) protonation of  $\text{PPh}_2\text{Me}$  by Hacac, (ii) release of  $\text{HPPh}_2\text{Me}^+$  and acetonitrile from the metal coordination sphere, (iii)  $O,O'$ -coordination of the so generated  $\text{acac}^-$  ligand.

The reaction product, **1a**, is a neutral nickel(II) species in which one  $O,O'$ -bonded-acetylacetonate ligand, one phosphine and one carbanionic ligand are coexisting in the metal coordination sphere. Complexes of this type are relatively rare and they were typically prepared by ligand displacement reactions involving aluminum alkyls or aryls [5] (for Ni) and  $[\text{Ti}(\beta\text{-diketonate})]$  reagents (for Pd) [6].

On the basis of these results we tried to develop a general simpler route to nickel complexes of type  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{R}^1\text{C}(\text{O})\text{CHC}(\text{O})\text{R}^2)\text{PR}_3]$  based on the reaction depicted in eqn. (1). However, the difficulties encountered in obtaining some of the starting cationic complexes as  $\text{BPh}_4^-$  salts in pure crystalline forms, led us to develop an even simpler route based on  $[\text{Ti}(\beta\text{-carbonylenolate})]$  reagents (*i.e.* derivatives of  $\beta$ -ketoesters,  $\beta$ -ketoamides, etc.) and  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{Cl})(\text{PR}_3)_2]$  complexes, which are in fact the precursors of complexes **4**.

Our results show that the  $\text{Ti}^{\text{IV}}$ -based route is not only very effective when applied to nickel(II) complexes but also useful for complex reagents containing phosphines different from  $\text{PPh}_3$  and for diverse  $\beta$ -carbonylenolate ligands. Finally we also report here a single crystal X-ray structure for the complex  $[\text{Ni}(\text{C}_6\text{Cl}_5)(1\text{-ethoxy-1,3-butanedionate})(\text{PPh}_2\text{Me})]$ .

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## Experimental

All manipulations involving air and moisture-sensitive compounds were performed under nitrogen with Schlenk techniques. Solvents were purified by standard methods [7]. Literature methods were used for the preparation of *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)L<sub>2</sub>] (L = PPh<sub>2</sub>Me [8], PPhMe<sub>2</sub>, PMe<sub>3</sub> [9] and PPh<sub>3</sub> [10]). A similar procedure was used for the preparation of the new complex [NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>2</sub>Cy)<sub>2</sub>]. The thallium β-ketoenolates were prepared by reacting equimolar amounts of TIOEt (Aldrich) and the appropriate β-diketone in solution of toluene according to the literature methods [11].

### Instruments

IR and UV–Vis spectra were recorded on Perkin-Elmer 781 and Lambda 5 spectrometers respectively. NMR spectra were recorded on a JEOL FX-90Q spectrometer with the residual solvent peak as an internal reference.

### Preparation of *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(CH<sub>3</sub>CN)- (PPh<sub>2</sub>Me)<sub>2</sub>]BF<sub>4</sub>

A solution of AgBF<sub>4</sub> (390 mg, 2 mmol) in CH<sub>3</sub>CN (2 ml) was added to a solution of *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>2</sub>Me)<sub>2</sub>] (1.5 g, 2 mmol) in 1,2-dichloroethane (20 ml). The reaction mixture was stirred at room temperature for 30 min and then filtered. Addition of n-hexane to the orange solution afforded an oily precipitate which slowly converted, upon stirring, to a pale yellow powder. This was collected by filtration, washed with hexane and dried under vacuum. Melting point (m.p.) 222–225 °C (dec.). *Anal.* Calc. for C<sub>22</sub>H<sub>19</sub>Cl<sub>5</sub>F<sub>4</sub>P<sub>2</sub>NiNB: C, 48.83; H, 3.49; N, 1.67. Found: C, 48.24; H, 3.63; N, 1.58%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>): 7.38 (complex mult., 10 H), 2.03 (triplet, *J*(PH) 3.7 Hz, 6 H), 1.81 (triplet, *J*(PH) 1.5 Hz, 3 H). IR (cm<sup>-1</sup>) in nujol: 2290 (ν(CN)).

### Preparation of Complexes 1–3

#### Reaction of *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(CH<sub>3</sub>CN)L<sub>2</sub>]BF<sub>4</sub> with β-dicarbonyls

Pentachlorophenyl 2,4-pentanedionate diphenylmethylphosphine nickel(II) (**1a**): a solution of *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(CH<sub>3</sub>CN)(PPh<sub>2</sub>Me)<sub>2</sub>]BF<sub>4</sub> (0.66 g, 0.79 mmol) in DCE (10 ml) containing Hacac (1 ml, 9.7 mmol) and NEt<sub>3</sub> (1 ml, 7.1 mmol) was stirred at room temperature for 2 h. The reaction mixture was evaporated under vacuum and the residuum triturated with EtOH. The yellow–orange precipitate so formed was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/EtOH. Yield of pure product 78%, m.p. 195 °C (dec.). *Anal.* Calc. for C<sub>24</sub>H<sub>20</sub>Cl<sub>5</sub>O<sub>2</sub>PNi: C, 47.46; H, 3.31. Found: C, 47.22; H, 3.39%.

With the same procedure used for the acac<sup>-</sup> derivative, the following complexes were prepared.

Pentachlorophenyl 1-phenyl-1,3-butanedionate diphenylmethylphosphine nickel(II) (**1b**): yellow crystals, yield 64%, m.p. 185 °C (dec.). *Anal.* Calc. for C<sub>29</sub>H<sub>22</sub>Cl<sub>5</sub>O<sub>2</sub>PNi: C, 52.03; H, 3.30. Found: C, 52.35; H, 3.28%.

Pentachlorophenyl 1,1,1-trifluoro-5,5,5-trimethyl-2,4-pentanedionate diphenylmethylphosphine nickel(II) (**1c**): yellow microcrystals, purified from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, yield 58%, m.p. 133 °C. *Anal.* Calc. for C<sub>27</sub>H<sub>22</sub>Cl<sub>5</sub>F<sub>3</sub>O<sub>2</sub>PNi: C, 46.10; H, 3.29. Found: C, 46.04; H, 3.33%.

Pentachlorophenyl 1,1,1,5,5,5-hexamethyl-2,4-pentanedionate diphenylphosphine nickel(II) (**1d**): yellow microcrystals, yield 60%, m.p. 158 °C (dec.). *Anal.* Calc. for C<sub>30</sub>H<sub>32</sub>Cl<sub>5</sub>O<sub>2</sub>PNi: C, 52.10; H, 4.66. Found: C, 51.85; H, 4.67%.

Pentachlorophenyl 1-ethoxy-1,3-butanedionate diphenylmethylphosphine nickel(II) (**1e**): yellow–orange crystals, yield 77%, m.p. 154 °C (dec.). *Anal.* Calc. for C<sub>25</sub>H<sub>22</sub>Cl<sub>5</sub>O<sub>3</sub>PNi: C, 47.10; H, 3.48. Found: C, 47.20; H, 3.47%.

#### Reaction of *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)L<sub>2</sub>] with [thallium (β-carbonylenolate)] complexes

Pentachlorophenyl 2,4-pentanedionate dimethylphenylphosphine nickel(II) (**2a**): a solution of *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>] (1.0 g, 1.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added to a suspension of [Tl(acac)] (0.486 g, 1.6 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred at room temperature for a few minutes and the precipitate of TlCl so formed was filtered. The resulting brown solution was evaporated *in vacuo* and the residuum treated with EtOH to give a yellow precipitate which was purified by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/EtOH. Yield of pure product 73%, m.p. 193 °C (dec.). *Anal.* Calc. for C<sub>19</sub>H<sub>18</sub>Cl<sub>5</sub>O<sub>2</sub>PNi: C, 41.85; H, 3.33. Found: C, 41.76; H, 3.35%.

With the same procedure the following complexes were prepared.

Pentachlorophenyl 1-phenyl-1,3-butanedionate dimethylphenylphosphine nickel(II) (**2b**): yield 60%, m.p. 177 °C. *Anal.* Calc. for C<sub>24</sub>H<sub>20</sub>Cl<sub>5</sub>O<sub>2</sub>PNi: C, 47.46; H, 3.32. Found: C, 47.26; H, 3.47%.

Pentachlorophenyl 2,4-pentanedionate trimethylphosphine nickel(II) (**3a**): yellow–brown crystals, yield 72%, m.p. 196 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>16</sub>Cl<sub>5</sub>O<sub>2</sub>PNi: C, 34.80; H, 3.34. Found: C, 34.54; H, 3.40%.

Pentachlorophenyl 1-methylamino-1,3-butanedionate trimethylphosphine nickel(II) (**3f**): in this case the reaction mixture was stirred at room temperature for 12 h. After filtration of TlCl and evaporation under vacuum of the obtained solution, the residuum was washed with a mixture of petroleum ether 30 ÷ 50 and EtOH (2:1). The solid product so obtained was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether. Yield of pure product 60%, m.p. 204 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>17</sub>Cl<sub>5</sub>O<sub>2</sub>NPNi:

C, 33.75; H, 3.44; N, 2.80. Found: C, 33.54; H, 3.46; N, 2.69%.

### X-ray Structure Analysis and Refinement of 1e

Yellow crystals were obtained upon slow evaporation of a  $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$  (1:1) solution of 1e. Crystal data, obtained from single crystal diffractometry, are listed in Table I. The intensities were collected at *ca.* 20 °C from a prismatic crystal of approximate dimensions 0.25 × 0.25 × 0.25 mm on a Philips PW 1100 four circle diffractometer operating in the  $\theta/2\theta$  scan mode up to  $\theta = 25^\circ$  (scan width =  $1.2^\circ$ , scan speed =  $0.02^\circ \text{ s}^{-1}$ ). 4968 reflections (4641 unique,  $R = 0.05$ ) were measured. The Ni atom was located by a Patterson map; a subsequent Fourier synthesis showed all the non-hydrogen atoms. No absorption correction was applied, being the maximum  $\mu R$  value equal to 0.3. No correction for presence of extinction was made. The refinement was performed by block diagonal least-squares, with anisotropic thermal parameters for all non-hydrogen atoms.  $W$  was taken equal to unity. The H atoms were located from a difference Fourier map and intro-

duced with calculations, but not refined. The final  $R$  value for the 1566 observed reflections with  $I > 3\sigma(I)$  was 0.111. All molecular parameters refer to this refinement degree. The final Fourier difference map showed three significant peaks at *ca.* 0.35 Å around the nickel atom. On accounting for this electron density,  $R$  value dropped to 0.070, thus indicating a considerable degree of lattice disorder. X-ray analysis carried out on two different crystals gave the same results. All the computations were carried out by an IBM 144 computer using SHELX-76 programs and scattering factors therein. For the nickel atom the scattering factors were taken from 'International Tables for X-Ray Crystallography', Vol. IV. Selected molecular parameters and fractional coordinates of 1e are collected in Tables II and III. The molecular arrangement with the atom numbering scheme used in the analysis is presented in Fig. 1.

TABLE I. Crystal Data for 1e

$\text{NiC}_{25}\text{H}_{22}\text{PCl}_5\text{O}_3$
Molecular weight = 637.4
$\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$
$a = 13.332(4) \text{ \AA}$
$b = 23.799(6) \text{ \AA}$
$c = 8.674(3) \text{ \AA}$
$\beta = 97.2(3)^\circ$
$V = 2730.5 \text{ \AA}^3$
Space group $P2_1/n$
$D_c = 1.433 \text{ g cm}^{-3}$
$Z = 4$
$\mu(\text{Mo K}\alpha) = 12 \text{ cm}^{-1}$
Monochromator = graphite

### Results and Discussion

The numbering scheme of the prepared complexes is shown in Scheme 1.

In solution of 1,2-dichloroethane (DCE) at room temperature, reaction 1 occurs in several hours as shown by the disappearance of the  $\nu(\text{CN})$  band at  $2290 \text{ cm}^{-1}$  of the coordinated  $\text{CH}_3\text{CN}$  and the concomitant appearance of that due to the free nitrile ( $2260 \text{ cm}^{-1}$ ). IR and  $^1\text{H}$  NMR spectra of the reaction mixture indicate that compound 1a is the only reaction product, *i.e.* no addition of Hacac to the metal-coordinated  $\text{CH}_3\text{CN}$  takes place, even in the presence of a large excess of  $\beta$ -dicarbonyl. Synthesis of 1a is much faster in the presence of triethylamine as the reasonable consequence of the formation in DCE of appreciable amounts of the nucleophile  $\text{acac}^-$ . Thus the IR spectrum of an equimolar solution of  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{CH}_3\text{CN})(\text{PPh}_2\text{Me})_2]\text{BF}_4$  ( $5 \times 10^{-2} \text{ M}$ )

TABLE II. Selected Bond Distances (Å) and Angles ( $^\circ$ ) for  $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{OEt})\text{PPh}_2\text{Me}]$  (1e) (e.s.d.s in parentheses)

Ni–O(2)	1.845(20)	C(20)–C(21)	1.629(52)
Ni–O(1)	1.838(21)	C(22)–O(3)	1.342(12)
O(1)–C(20)	1.261(44)	C(23)–O(3)	1.461(43)
O(2)–C(22)	1.402(38)	C(23)–C(24)	1.349(69)
C(22)–C(25)	1.430(49)	Ni–P(1)	2.144(8)
C(25)–C(20)	1.325(59)	NiC(1)	1.887(24)
O(2)–Ni–C(1)	93.5(1.0)	O(2)–C(22)–O(3)	117.6(2.8)
C(1)–Ni–P(1)	87.9(0.8)	C(22)–O(3)–C(23)	117.0(2.7)
P(1)–Ni–O(1)	86.1(0.7)	C(18)–P(1)–C(19)	104.1(1.3)
O(2)–Ni–O(1)	92.5(0.9)	C(18)–P(1)–C(12)	102.1(1.2)
Ni–O(2)–C(22)	125.1(1.8)	C(12)–P(1)–C(19)	103.6(1.3)
O(2)–C(22)–C(25)	122.6(2.9)	C(18)–P(1)–Ni	122.0(0.9)
C(25)–C(20)–O(1)	124.1(3.6)	C(19)–P(1)–Ni	107.9(0.9)
Ni–O(1)–C(20)	132.3(2.3)	C(12)–P(1)–Ni	115.2(1.0)

TABLE III. Fractional Coordinates for 1e

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.7122(3)	0.9110(1)	0.5224(4)
P1	0.8475(6)	0.8982(3)	0.6800(9)
C11	0.8026(7)	0.8384(3)	0.2693(9)
C12	0.7996(8)	0.7069(4)	0.2627(12)
C13	0.6877(7)	0.6409(3)	0.4959(12)
C14	0.5750(8)	0.7056(4)	0.7349(11)
C15	0.5836(7)	0.8371(4)	0.7469(10)
C1	0.6958(21)	0.8322(10)	0.5156(31)
C2	0.7415(21)	0.8014(12)	0.4047(34)
C3	0.7380(21)	0.7423(13)	0.3931(36)
C4	0.6890(25)	0.7135(11)	0.5004(42)
C5	0.6367(21)	0.7428(12)	0.6079(33)
C6	0.6420(21)	0.8003(12)	0.6130(34)
C7	0.7561(30)	0.9553(14)	0.9031(36)
C8	0.7541(26)	0.9794(13)	1.0529(41)
C9	0.8396(29)	0.9780(12)	1.1633(36)
C10	0.9297(28)	0.9514(13)	1.1267(38)
C11	0.9313(24)	0.9262(11)	0.9775(31)
C12	0.8464(23)	0.9282(11)	0.8700(29)
C13	0.9687(24)	0.8061(13)	0.6312(36)
C14	0.9990(26)	0.7505(16)	0.6560(42)
C15	0.9743(29)	0.7202(14)	0.7793(48)
C16	0.8998(34)	0.7415(15)	0.8722(48)
C17	0.8629(22)	0.7975(12)	0.8435(29)
C18	0.8997(21)	0.8272(9)	0.7260(31)
O1	0.7403(17)	0.9864(9)	0.5429(21)
O2	0.5963(16)	0.9239(8)	0.3871(23)
O3	0.4777(21)	0.9788(11)	0.2306(31)
C19	0.9530(20)	0.9366(11)	0.6009(33)
C20	0.6949(34)	1.0295(17)	0.4848(38)
C21	0.7477(35)	1.0901(12)	0.5290(48)
C22	0.5629(28)	0.9768(14)	0.3307(37)
C23	0.4353(26)	0.9252(15)	0.1717(43)
C24	0.4997(49)	0.9066(20)	0.0439(54)
C25	0.6102(36)	1.0280(14)	0.3872(47)

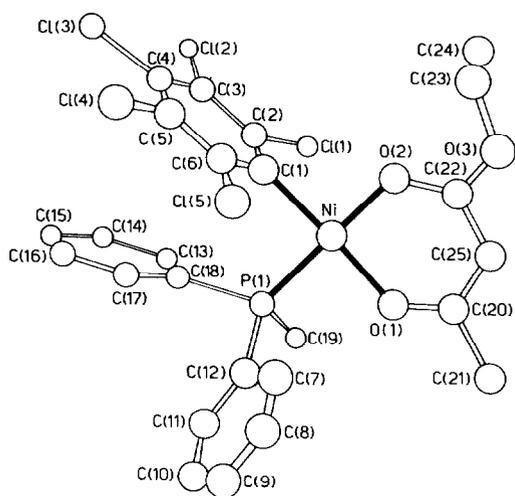
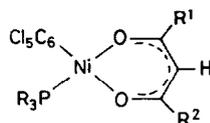


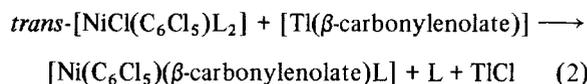
Fig. 1. Molecular structure of pentachlorophenyl 1-ethoxy-1,3-butanedionate diphenylmethylphosphine nickel(II).



	PR <sub>3</sub>		R <sup>1</sup>	R <sup>2</sup>
1	PPh <sub>2</sub> Me	a	Me	Me
		b	Me	Ph
		c	CMe <sub>3</sub>	CF <sub>3</sub>
		d	CMe <sub>3</sub>	CMe <sub>3</sub>
		e	Me	OEt
2	PPhMe <sub>2</sub>	a	Me	Me
		b	Me	Ph
3	PMe <sub>3</sub>	a	Me	Me
		f	Me	N(H)Me

Scheme 1.

and Hacac in DCE containing an excess of NEt<sub>3</sub> (1:10) shows the complete displacement of the nitrile ligand in 2 h at room temperature. We find that under these conditions synthesis of compounds **1** occurs with  $\beta$ -dicarbonyls such as the  $\beta$ -diketones (**1a–1d**) and  $\beta$ -ketoester (**1e**) and the corresponding complexes have been isolated in good yields. Moreover a simpler route leading to the related complexes of type **2** and **3** (Scheme 1) was achieved by reacting the required thallium  $\beta$ -carbonylenolate with the neutral complexes *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PR<sub>3</sub>)<sub>2</sub>] (L = PPhMe<sub>2</sub>, PMe<sub>3</sub>) in DCE



This synthetic route does not require the preparation of the ionic complexes [Ni(C<sub>6</sub>Cl<sub>5</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]BF<sub>4</sub>, which, in the case of L = PPhMe<sub>2</sub> and PMe<sub>3</sub> are uncrystallizable oils, whereas for L = PPh<sub>3</sub> the acetonitrile complex is not accessible owing to the lack of reactivity of *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] with AgBF<sub>4</sub> and acetonitrile in 1,2-dichloroethane.

The addition of an equimolar amount of [Ti( $\beta$ -diketonate)] to a solution of the nickel(II) complexes *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)L<sub>2</sub>] (L = PPhMe<sub>2</sub>, PMe<sub>3</sub>), leads to immediate precipitation of TlCl. A lower reactivity is displayed by the  $\beta$ -ketoamidate derivative [Ti(CH<sub>3</sub>C(O)CHC(O)NHCH<sub>3</sub>)] for which reaction (2) requires several hours to go to completion at room temperature.  $\beta$ -Ketoamidate complexes analogous to **3f** could also be obtained quantitatively in solution (NMR control) starting from [NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PPh<sub>2</sub>Me)<sub>2</sub>] and [NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>] by using excess of [Ti( $\beta$ -ketoamidate)], but the relevant products could not be isolated analytically pure.

In contrast with the fast reaction observed in the case of the complexes *trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)L<sub>2</sub>] (L =

PPhMe<sub>2</sub> and PMe<sub>3</sub>) with [Ti(acac)], the complexes containing PPh<sub>3</sub> and PPh<sub>2</sub>Cy are completely unreactive in DCE, after several hours at room temperature. The lack of reactivity is possibly due to steric effects related to the higher cone angle of these phosphine ligands [12]. In addition, a drastic decrease of reactivity, likely related to electronic effects, is observed in the case of the  $\beta$ -diester, dimethylmalonate. In fact, a solution of equimolar amounts of *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(CH<sub>3</sub>CN)(PPh<sub>2</sub>Me)<sub>2</sub>]BF<sub>4</sub> and CH<sub>3</sub>OC(O)CH<sub>2</sub>C(O)OCH<sub>3</sub> in the presence of an excess of 1,1,3,3-tetramethylguanidine showed no reaction after 24 h at room temperature. The Ti<sup>I</sup>-based route did not appear to be viable with the thallium derivative of dimethylmalonate.

### Optical Spectra

In spite of the presence of phenyl rings, in most of the investigated complexes, the typical  $\nu(\text{C}\cdots\text{O})$  and  $\nu(\text{C}\cdots\text{C})$  bands of the metallo-organic rings are generally identifiable in the expected 1500–1650 cm<sup>-1</sup> range [13], Table IV. They appear as medium to strong, sometime slightly composite, bands, whose positions fit fairly well with the expected [13] effect of the nature of the substituents on the electronics of the ring. Thus Me replacement by Ph causes a bathochromy of the  $\nu(\text{C}\cdots\text{O})$  band and that of the CMe<sub>3</sub> radical by CF<sub>3</sub> a significant ipsochromy of the  $\nu(\text{C}\cdots\text{O})$  and  $\nu(\text{C}\cdots\text{C})$  bands in 1c. The position of the CO band for 1e is also expected as the consequence of the replacement of Me by OEt. The ipsochromy of both bands observed upon replacement of Me by N(H)Me in 3f is also remarkable in that it fits with the known general decrease of covalent character of the M–O bonds observed on going from metal- $\beta$ -diketonate to metal- $\beta$ -ketoamidate ring.

Finally, as a general comment on the position of the  $\nu(\text{C}\cdots\text{O})$  bands in 1a, 2a and 3a with respect to

[Ni(acac)<sub>2</sub>], the bathochromic effect (25, 15 and 20 cm<sup>-1</sup> respectively) caused by the presence of C<sub>6</sub>Cl<sub>5</sub> and PR<sub>3</sub> in the nickel(II) coordination sphere suggests a higher covalent character of the Ni–O bonds in the title complexes.

The electronic spectra of complexes 1, 2 and 3 exhibit the expected ligand field band, which is typical of Ni<sup>II</sup> square-planar species. Homoleptic nickel(II) planar species bearing two  $\beta$ -carbonylenolate ligands ( $\{\text{NiO}_4\}$ chromophore) display the relevant band in the range 535–560 nm [14, 15] with  $\epsilon$  values ranging from 50 to 200 M<sup>-1</sup> cm<sup>-1</sup>. Heteroleptic complexes of the type [Ni( $\beta$ -carbonylenolate)(diphosphine)]<sup>+</sup> were found by us [16] to give the same band in the range 425–450 nm with  $\epsilon$  varying from 670 to 1740 M<sup>-1</sup> cm<sup>-1</sup> ( $\{\text{NiO}_2\text{P}_2\}$  chromophore) and those here described span the range 430–450 nm with  $\epsilon$  of 600 to 860 M<sup>-1</sup> cm<sup>-1</sup> ( $\{\text{NiO}_2\text{P}_2\}$  chromophore).

### <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR Spectra

The <sup>1</sup>H NMR spectra (Table V) of the symmetrically substituted  $\beta$ -carbonylenolate ligands exhibit a single set of resonances consistent with an *O,O'*-chelated configuration. The phosphine methyl protons appear as sharp doublets (*J* = 10–11 Hz) in agreement with the presence of a PR<sub>3</sub> ligand which does not exchange in the NMR time scale.

It is interesting to note the change of the differences of the acac<sup>-</sup> methyl resonances chemical shifts in the complexes [Ni(acac)(C<sub>6</sub>Cl<sub>5</sub>)L] as a function of the phosphine ligand. The value of 0.22 ppm found for the PPh<sub>2</sub>Me derivative is reduced in fact, to 0.07 ppm when L = PPhMe<sub>2</sub> and further reduced to only 0.01 ppm for the PMe<sub>3</sub> complex. Moreover, the resonance at lower field is substantially insensitive to the nature of the phosphine ligand. A larger chemical shift difference between the corresponding resonances was observed in the related complex

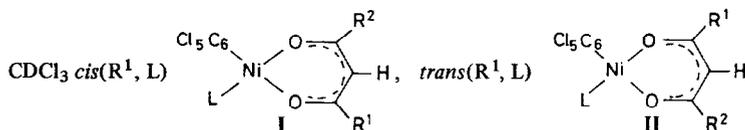
TABLE IV. Spectroscopic Data for [Ni(C<sub>6</sub>Cl<sub>5</sub>)(PR<sub>3</sub>)( $\beta$ -carbonylenolate)] Complexes

Complex	$\nu(\text{C}\cdots\text{O}), \nu(\text{C}\cdots\text{C})$ (cm <sup>-1</sup> )	$\lambda_{\text{max}}$ (nm) ( $\epsilon(\text{M}^{-1} \text{cm}^{-1})$ ) <sup>a</sup>
1a	1580(s), 1530(s)	228(46, 500); 447(670)
1b	1560(s), 1520(s)	228(48, 000); 254(40, 550); 290(21, 150) <sup>c</sup> 345(8, 250) <sup>c</sup> ; 440(860)
1c	1610(s), 1590(s)	229(45, 000); 340(4, 000) <sup>c</sup> ; 447(780)
1d	1550(m), 1530(m)	229(46, 500); 444(650)
1e	1605(s), 1530(s)	231(49, 500); 453(620)
2a	1590(s), 1530(s)	237(41, 700); 442(730)
2b	1560(m <sup>b</sup> ), 1520(s <sup>b</sup> )	228(44, 250); 245(41, 650); 290(19, 490) <sup>c</sup> 340(7, 550) <sup>c</sup> ; 431(920)
3a	1585(s), 1520(s)	229(41, 200); 260(17, 650); 431(600)
3f	1600(s), 1570(s)	229(47, 600); 280(13, 800) <sup>c</sup> ; 435(600)

<sup>a</sup>Data were obtained from solutions ranging from 10<sup>-5</sup> to 10<sup>-3</sup> M. In this range the spectra obey Lambert–Beer's law.

<sup>b</sup>Uncertain identification.

<sup>c</sup>Shoulder.

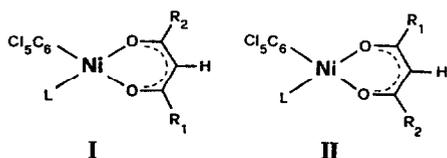
TABLE V.  $^1\text{H}$  and  $^{31}\text{P}$  NMR Data<sup>a</sup> for Complexes  $[\text{Ni}(\beta\text{-carboxylate})(\text{C}_6\text{Cl}_5\text{L})]$  ( $\text{L} = \text{PPh}_2\text{Me}$ , 1;  $\text{PPhMe}_2$ , 2;  $\text{PMe}_3$ , 3) in

Compound	Isomer <sup>f</sup>	$\beta$ -Carboxylate			Phosphine resonances ( $J(\text{PH})$ Hz)		$^{31}\text{P}$ chemical shifts ( $\delta$ )
		$\text{R}^1$	CH	$\text{R}^2$	$\text{CH}_3$	$\text{C}_6\text{H}_5$	
<b>1a</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{CH}_3$ )		1.63	5.40	1.85	1.62 d(10.6) <sup>b</sup>	7.7–7.2 cm	11.24
<b>1b</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{C}_6\text{H}_5$ )	<i>cis</i>	1.79	6.06	c	1.66 d(10.7)	7.9–7.1 cm	11.31
	<i>trans</i> <sup>*</sup>	2.01	6.09		1.71 d(10.7)		11.71
<b>1c</b> ( $\text{R}^1 = \text{C}(\text{CH}_3)_3$ ; $\text{R}^2 = \text{CF}_3$ )	<i>cis</i>	0.77	6.00	–	1.77 d(10.9)	7.9–7.2 cm	11.98
	<i>trans</i> <sup>*</sup>	0.99	6.00	–	1.59 d(10.5)		10.97
<b>1d</b> ( $\text{R}^1 = \text{C}(\text{CH}_3)_3$ ; $\text{R}^2 = \text{C}(\text{CH}_3)_3$ )		0.76	5.71	0.98	1.72 d(10.5)	7.9–7.2 cm	12.39
<b>1e</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{OC}_2\text{H}_5$ )	<i>cis</i> <sup>*</sup>	1.51	4.81	3.79 <sup>d</sup> q, 1.08 t	1.74 d(10.7)	8.0–7.2 cm	11.31
	<i>trans</i>	1.56	4.78	3.23 <sup>d</sup> q, 0.83 t	1.66 d(10.2)		10.30
<b>2a</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{CH}_3$ )		1.75	5.36	1.82	1.40 d(10.7)	7.8–7.2 cm	–0.53
<b>2b</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{C}_6\text{H}_5$ )	<i>cis</i>	1.90	6.04	c	1.45 d(11.0)	7.8–7.2 cm	–0.43
	<i>trans</i> <sup>*</sup>	1.98	6.04				0.68
<b>3a</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{CH}_3$ )		1.80	5.37	1.81	1.09 d(11.1)		–5.38
<b>3f</b> ( $\text{R}^1 = \text{CH}_3$ ; $\text{R}^2 = \text{NH}(\text{CH}_3)$ )	<i>cis</i> <sup>*</sup> or	1.72	4.56	e	1.09 d(11.2)		–5.08
	<i>trans</i>		4.54				–6.63

<sup>a</sup>Chemical shifts are in ppm;  $\text{H}_3\text{PO}_4$  was used as external standard for  $^{31}\text{P}$  spectra. <sup>b</sup>d, doublet; t, triplet; q, quartet; cm, complex multiplet. <sup>c</sup>Indiscernible because of overlapping with the phosphine phenyl resonance. <sup>d</sup> $J(\text{CH}_2\text{CH}_3) = 7.5$  Hz. <sup>e</sup> $\text{NH}(\text{CH}_3)$  resonances:  $\delta$  ca. 4.7 (very broad singlet,  $\text{NH CH}_3$ ),  $\delta$  2.63 (d,  $J(\text{HH})$  5.1 Hz), 2.51 (d,  $J(\text{HH})$  5.1 Hz). <sup>f</sup> Starred is the more abundant isomer.

$[\text{Ni}(\text{acac})(\text{C}_6\text{H}_5\text{PPh}_3)]$ , which was attributed [17] to the anisotropic shielding of the triphenylphosphine ligand. Thus the higher field resonance was attributed to the  $\text{acac}^-$  methyl group nearer to the phosphine phenyl substituents, *i.e.* in *cis* position to the  $\text{PPh}_3$  ligand. In line with these observation, we find that the  $\text{acac}^-$  methyl resonance at lower field is substantially insensitive to the nature of the phosphine ligand whereas the upfield shift of the resonance due to the other methyl group increases with the number of phenyl groups in the phosphine ligand. In the case of the  $\text{PMe}_3$  derivative the two  $\text{acac}^-$  methyl groups are virtually isochronous, clearly indicating that the anisotropic shielding of the phosphine phenyl substituents give the major contribution to the shift difference. On the basis of these considerations, we attribute the higher field methyl resonance to the  $\text{CH}_3$  *cis* to the phosphine ligand.

Complexes containing unsymmetrically substituted  $\beta$ -carboxylate ligands show two sets of resonances in ca. 3:2 intensity ratio, for all type of protons, due to the presence of two isomeric species:



On the basis of the reasoning outlined above, it is possible to establish the configuration of the two geometric isomers **I** and **II**. For instance, in the case of the nickel 1-ethoxy-1,3-butanedionate complex **1e**, the isomer **I** ( $\text{R}^2 = \text{OEt}$ ) is the more abundant species in solution (ca. 60%). On the other hand, this configuration is just the one observed in the solid state, as shown by the X-ray molecular structure (Fig. 1). A test for the correctness of the criterion used for the spectroscopic assignment appears to be in the relative (inverted) position of the resonances observed for the O–Et group in the **1e** isomers. The same intensity ratio of the two isomeric species of **1e** is deduced from the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which exhibit two singlets at 11.3 and 10.3. Moreover, it is worth mentioning that the relative abundance of the two isomers **I** and **II** is not very sensitive to the nature of the  $\text{R}^1$ ,  $\text{R}^2$  substituents.

Table VI summarizes the  $^{13}\text{C}$  NMR data of the more soluble complexes. Compounds **1a**, **2a** and **3a** exhibit two well separated carbonyl resonances, whose values are insensitive to the nature of the phosphine ligand. In the case of the  $\text{PPh}_2\text{Me}$  derivative the resonance at lower field appears as a doublet due to the coupling with the  $^{31}\text{P}$  nucleus and therefore it must be attributed to the carbonyl *trans* to the phosphine ligand. Unlike the carbonyl group, the two  $\text{acac}^-$  methyl  $^{13}\text{C}$  resonances exhibit a slight but

TABLE VI.  $^{13}\text{C}$  NMR Data for Complexes  $[\text{Ni}(\beta\text{-carbonylenolate})(\text{C}_6\text{Cl}_5\text{L})]$  (L = PPh<sub>2</sub>Me, 1; PPhMe<sub>2</sub>, 2; PMe<sub>3</sub>, 3)<sup>a</sup>

Compound	Isomer <sup>b</sup>	$\beta$ -carbonylenolate resonances				Phosphine resonances				$\text{C}_6\text{Cl}_5$ group <sup>c</sup>				
		R <sup>1</sup> CO	CH	R <sup>2</sup> CO	R <sup>1</sup>	R <sup>2</sup>	PCH <sub>3</sub>	P-C	o-C	m-C	p-C	C <sub><math>\alpha</math></sub>	C <sub><math>\beta</math></sub>	C <sub><math>\gamma</math></sub>
1a	<i>cis</i>	185.1	100.4	188.0	26.4	26.8	11.6	131.6	132.4	127.9	130.2	151.5	137.7	127.4
			((160))	(1.4)	((127.5))	(5.1)	(30.8)	(47)	(10.3)	(10.3)	(2.2)	(58.3)	(2.9)	
1b	<i>trans</i>	186.9	97.3	180.8	27.2		11.9	d	132.5	127.9				
							(30.8)		(10.2)	(9.5)	130.3			not detectable
1c	<i>cis</i>	189.6	97.3	178.1	27.6	118.2	11.7	d	132.4	128.1	130.6			
		(2.2)			(5.1)	[283]	(30.8)		(10.2)	(9.5)	( <i>ca.</i> 2)			
1d	<i>trans</i>	202.2	91.7	171.7	41.5; 27.6		11.7	130.5	132.2	128.1	130.2			
		[34]					(30.0)	(49.1)	(10.2)	(10.3)	(2.9)			
2a	<i>cis</i>	194.9	90.5	197.0	40.3; 28.2	40.8; 28.2	11.7	131.4	132.4	127.8	130.2			
		(2.2)			(2.9)	(4.4)	(30.0)	(46.9)	(10.2)	(9.5)	(2.9)			
2b	<i>trans</i>	185.1	100.5	188.0	26.6	26.8	11.7	132.5	130.2	128.1	129.8	152.8	137.9	127.4
			((159.7))		((125.3))	(7.3)	(30.8)	(46.2)	(8.8)	(10.1)	(4)	(49.1)	(2.9)	
3a	<i>cis</i>	186.8	97.2	180.7	27.4		12.4	not attributable						
							(30.0)							
3b	<i>trans</i>	189.5	97.6	178.6	27.5		11.8							
		(1.4)			(5.0)		(30.0)							
3c	<i>cis</i>	185.2	100.5	188.0	26.7	26.8	12.9					152.7	137.8	127.5
			((162))		((126.9))	(4.9)	(30.0)				(4)	(51.3)	(2.9)	

<sup>a</sup>Measured at 27 °C, in CDCl<sub>3</sub> solution. Figures in parentheses, double parentheses and brackets give  $J(^3\text{P}-^{13}\text{C})$ ,  $^1J(^{13}\text{C}-\text{H})$  and  $J(^{19}\text{F}-^{13}\text{C})$  in Hz, respectively. <sup>b</sup>*Cis* and *trans*

isomers as in Table V. <sup>c</sup>Ni <sub>$\alpha$</sub> ; the attribution is based on ref. 18 and on the interpretation of the spectrum of the related complex *trans-trans*-[NiCl(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>] (see Text).



<sup>d</sup>Not attributable. <sup>e</sup>126.6; 127.1; 127.9.

significant dependence on the phosphine ligand. In agreement with the  $^1\text{H}$  NMR data, the methyl group in *cis* position to the  $\text{PR}_3$  ligand is shifted to higher fields with the increase of the number of the phenyl substituents at the phosphorous atom. The other  $^{13}\text{C}$  methyl resonance is insensitive to the nature of the phosphine and, in accordance with its *trans* position with respect to the phosphine ligand, it is coupled to the  $^{31}\text{P}$  nucleus with a  $|^4J(^{13}\text{C}-^{31}\text{P})| = 5-7$  Hz. The assignment of the  $^{13}\text{C}$  resonances in the unsymmetrically substituted  $\beta$ -carbonylenolate ligands is based on the same criteria utilized for the  $^1\text{H}$  spectra and the interpretation of the spectral features of the phosphine ligands is based on relevant literature [18].

The pentachlorophenyl  $^{13}\text{C}$  resonances are characterized by a very weak intensity compared with those of the phosphine phenyl carbon atoms. This has to be the consequence of the quadrupolar effect due to the directly bonded or adjacent chlorine atom(s). On the basis of the larger coupling constant  $|J(^{13}\text{C}-^{31}\text{P})|$ , the resonance at lower field is attributed to the carbon bonded to the nickel atom. The resonance at *ca.* 137 $\delta$ , with a  $|J(^{13}\text{C}-^{31}\text{P})|$  of *ca.* 3 Hz, is attributed to the *ortho*-carbon atom ( $\text{C}_\beta$ ). The remaining weak resonance which appears as a singlet at 127 $\delta$ , should be attributed to the  $\text{C}_\gamma$  carbon atom. The related complex *trans*- $[\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{PMe}_3)_2]$  exhibits, in fact, a  $^{13}\text{C}$  spectrum in which the resonance of  $\text{C}_\alpha$ ,  $\text{C}_\beta$ ,  $\text{C}_\gamma$  and  $\text{C}_\delta$  appear as triplets (poorly resolved in the case of  $\text{C}_\delta$ ) with values:  $\text{C}_\alpha$ , 158.7 ( $^2J(^{13}\text{C}-^{31}\text{P}) = 35.1$  Hz);  $\text{C}_\beta$ , 136.0 ( $^3J(^{13}\text{C}-^{31}\text{P}) = 9.7$  Hz);  $\text{C}_\gamma$ , 128.2 ( $^4J(^{13}\text{C}-^{31}\text{P}) = 3.9$  Hz);  $\text{C}_\delta$ , 126.5 ( $^5J(^{13}\text{C}-^{31}\text{P}) \approx 2$  Hz). The peak of  $\text{C}_\delta$  is relatively weak and, therefore, the corresponding resonance for complexes 1-3 may be undetectably weak.

It seems worth mentioning that the  $^1\text{H}$  and  $^{13}\text{C}$  resonances of the methino group in the complexes 1 appear to be sensitive to the nature of the substituents at the metallo-organic rings. However, no correlation of the methino resonances with the wavenumbers of the relevant  $\nu(\text{C}=\text{O})$  bands and, therefore with the degree of the covalent character of the Ni-O bonds (see the discussion of the IR data) can be established. Unfortunately, the poorer quality of the X-ray structure data obtained for 1e (as the consequence of molecular disorder) makes impossible any reliable speculation on the Ni-O distances.

## Supplementary Material

For 1e: fractional coordinates, thermal parameters, *F* lists and selected least-squares planes with their dihedral angles and deviations of the atoms to the respective planes. Available from the authors on request.

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