Inorganica Chimica Acta, 130 (1987) 243–250

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

B. LONGATO*, B. CORAIN*, R. ANGELETTI

Centro di Studio Sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., c/o Dipartimento di Chimica Inorganica Metallorganica e Analitica, Via Marzolo 1, 35100 Padua, Italy

and G. VALLE

Centro di Studio Sui Biopolimeri, c/o Dipartimento di Chimica Organica, Via Marzolo 1, 35100 Padua, Italy

(Received September 25, 1986; revised November 25, 1986)

Abstract

Reaction of the cationic complex $[Ni(C_6Cl_5)(CH_3CN)L_2]^+$ ($L = PPh_2Me$) with β-dicarbonyls (diketones and ethyl-2-oxo-butanoate) in the presence of NEt_3 affords the neutral complexes $[Ni(C_6Cl_5)$(β-carbonylenolate)L]. A more convenient synthesis of analogous complexes was found in the reaction of *trans*-$[Ni(Cl)(C_6Cl_5)L_2]$ ($L = PPhMe_2$, PMe_3) and [Tl(β-carbonylenolate)] derivatives. The isolated complexes have been characterized by ^{1}H, ^{31}P and ^{13}C NMR and IR spectroscopies. They exhibit a square planar geometry in which the β-carbonylenolate acts as *O,O'*-chelating ligand; complexes with unsymmetrically substituted β-ketoenolates give rise in solution to mixtures of geometrical isomers. A single crystal X-ray structure of the ketoester derivative, $[Ni(C_6Cl_5)(CH_3C(O)CHC(O)OEt)(PPh_2Me)]$, 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, $\beta = 97.2(3)°$.

Introduction

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

$$[Ni(C_6Cl_5)(NCCH_3)(PPh_2Me)_2]^+ \ (4) + Hacac \longrightarrow [Ni(C_6Cl_5)(acac)(PPh_2Me)] \ (1a) + HPPh_2Me^+ + CH_3CN \qquad (1)$$

The product does not result from the expected [3, 4] addition reaction of Hacac to the electrophilically activated C≡N group, but from (i) protonation of PPh_2Me by Hacac, (ii) release of $HPPh_2Me^+$ and acetonitrile from the metal coordination sphere, (iii) *O,O'*-coordination of the so generated $acac^-$ 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 [Tl(β-diketonate)] reagents (for Pd) [6].

On the basis of these results we tried to develop a general simpler route to nickel complexes of type $[Ni(C_6Cl_5)(R^1C(O)CHC(O)R^2)PR_3]$ based on the reaction depicted in eqn. (1). However, the difficulties encountered in obtaining some of the starting cationic complexes as BPh_4^- salts in pure crystalline forms, led us to develop an even simpler route based on [Tl(β-carbonylenolate)] reagents (*i.e.* derivatives of β-ketoesters, β-ketoamides, etc.) and $[Ni(C_6Cl_5)(Cl)(PR_3)_2]$ complexes, which are in fact the precursors of complexes **4**.

Our results show that the Tl^I-based route is not only very effective when applied to nickel(II) complexes but also useful for complex reagents containing phosphines different from PPh_3 and for diverse β-carbonylenolate ligands. Finally we also report here a single crystal X-ray structure for the complex $[Ni(C_6Cl_5)$(1-ethoxy-1,3-butanedionate)$(PPh_2Me)]$.

---

*Authors to whom correspondence should be addressed.

0020-1693/87/$3.50

Experimental

All manipulations involving air and moisture-sensitive compounds were performed under nitrogen with Schlenk techniques. Solvents were purified by standards methods [7]. Literature methods were used for the preparation of *trans*-[NiCl(C_6Cl_5)L_2] (L = PPh_2Me [8], $PPhMe_2$, PMe_3 [9] and PPh_3 [10]). A similar procedure was used for the preparation of the new complex [NiCl(C_6Cl_5)(PPh_2Cy)$_2$]. The thallium β-ketoenolates were prepared by reacting equimolar amounts of TlOEt (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_6Cl_5)(CH_3CN)(PPh_2Me)$_2$]BF_4

A solution of $AgBF_4$ (390 mg, 2 mmol) in CH_3CN (2 ml) was added to a solution of *trans*-[NiCl(C_6Cl_5)-(PPh_2Me)$_2$] (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 $C_{22}H_{19}Cl_5F_4P_2NiNB$: C, 48.83; H, 3.49; N, 1.67. Found: C, 48.24; H, 3.63; N, 1.58%. ^1H NMR (in $CDCl_3$): 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^{-1}) in nujol: 2290 (ν(CN)).

Preparation of Complexes 1–3

Reaction of trans-[Ni(C_6Cl_5)(CH_3CN)L_2]BF_4 with β-dicarbonyls

Pentachlorophenyl 2,4-pentanedionate diphenylmethylphosphine nickel(II) (**1a**): a solution of *trans*-[Ni(C_6Cl_5)(CH_3CN)(PPh_3Me)$_2$]BF_4 (0.66 g, 0.79 mmol) in DCE (10 ml) containing Hacac (1 ml, 9.7 mmol) and NEt_3 (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_2Cl_2/EtOH. Yield of pure product 78%, m.p. 195 °C (dec.). *Anal.* Calc. for $C_{24}H_{20}Cl_5O_2PNi$: C, 47.46; H, 3.31. Found: C, 47.22; H, 3.39%.

With the same procedure used for the acac$^-$ 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 $C_{29}H_{22}Cl_5O_2PNi$: 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_2Cl_2/MeOH, yield 58%, m.p. 133 °C. *Anal* Calc. for $C_{27}H_{22}Cl_5F_3O_2PNi$: 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 $C_{30}H_{32}Cl_5O_2PNi$: 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 $C_{25}H_{22}Cl_5O_3PNi$: C, 47.10; H, 3.48. Found: C, 47.20; H, 3.47%.

Reaction of trans-[NiCl(C_6Cl_5)L_2] with [thallium (β-carbonylenolate)] complexes

Pentachlorophenyl 2,4-pentanedionate dimethylphenylphosphine nickel(II) (**2a**): a solution of *trans*-[NiCl(C_6Cl_5)($PPhMe_2$)$_2$] (1.0 g, 1.6 mmol) in CH_2Cl_2 (20 ml) was added to a suspension of [Tl(acac)] (0.486 g, 1.6 mmol) in 25 ml of CH_2Cl_2. 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_2Cl_2/EtOH. Yield of pure product 73%, m.p. 193 °C (dec.). *Anal.* Calc. for $C_{19}H_{18}Cl_5O_2PNi$: 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 $C_{24}H_{20}Cl_5O_2PNi$: 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 $C_{14}H_{16}Cl_5O_2PNi$: 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_2Cl_2/petroleum ether. Yield of pure product 60%, m.p. 204 °C(dec.). *Anal.* Calc. for $C_{14}H_{17}Cl_5O_2NPNi$:

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 CH_2Cl_2/C_2H_5OH (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 $\theta = 25°$ (scan width = 1.2°, scan speed = $0.02° s^{-1}$). 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 μR 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 introduced 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**

$NiC_{25}H_{22}PCl_5O_3$
Molecular weight = 637.4
λ(Mo Kα) = 0.7107 Å
a = 13.332(4) Å
b = 23.799(6) Å
c = 8.674(3) Å
β = 97.2(3)°
V = 2730.5 Å^3
Space group $P2_1/n$
D_c = 1.433 g cm^{-3}
Z = 4
μ(Mo Kα) = 12 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 ν(CN) band at 2290 cm^{-1} of the coordinated CH_3CN and the concomitant appearance of that due to the free nitrile (2260 cm^{-1}). IR and ^1H 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 CH_3CN takes place, even in the presence of a large excess of β-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 acac$^-$. Thus the IR spectrum of an equimolar solution of $[Ni(C_6Cl_5)(CH_3CN)(PPh_2Me)_2]BF_4$ (5×10^{-2} M)

TABLE II. Selected Bond Distances (Å) and Angles (°) for $[Ni(C_6Cl_5)(CH_3C(O)CHC(O)OEt)PPh_2Me]$ (**1e**) (e.s.d.s in parentheses) 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	*x/a*	*y/b*	*z/c*
Ni	0.7122(3)	0.9110(1)	0.5224(4)
P1	0.8475(6)	0.8982(3)	0.6800(9)
Cl1	0.8026(7)	0.8384(3)	0.2693(9)
Cl2	0.7996(8)	0.7069(4)	0.2627(12)
Cl3	0.6877(7)	0.6409(3)	0.4959(12)
Cl4	0.5750(8)	0.7056(4)	0.7349(11)
Cl5	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)

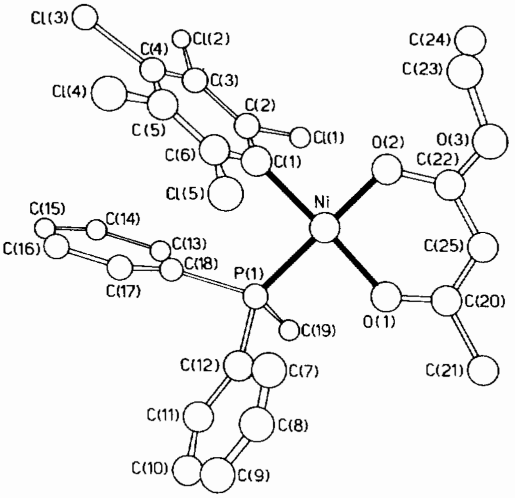
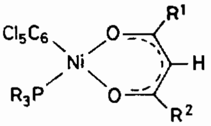


Fig. 1. Molecular structure of pentachlorophenyl 1-ethoxy-1,3-butanedionate diphenylmethylphosphine nickel(II).



	PR3		R1	R2
1	PPh_2Me	a	Me	Me
		b	Me	Ph
		c	CMe_3	CF_3
		d	CMe_3	CMe_3
		e	Me	OEt
2	$PPhMe_2$	a	Me	Me
		b	Me	Ph
3	PMe_3	a	Me	Me
		f	Me	N(H)Me

Scheme 1.

and Hacac in DCE containing an excess of NEt_3 (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 β-dicarbonyls such as the β-diketones (**1a**–**1d**) and β-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 β-carbonylenolate with the neutral complexes *trans*-$[NiCl(C_6Cl_5)(PR_3)_2]$ (L = $PPhMe_2$, PMe_3) in DCE

$$\textit{trans}\text{-}[NiCl(C_6Cl_5)L_2] + [Tl(\beta\text{-carbonylenolate})] \longrightarrow$$
$$[Ni(C_6Cl_5)(\beta\text{-carbonylenolate})L] + L + TlCl \qquad (2)$$

This synthetic route does not require the preparation of the ionic complexes $[Ni(C_6Cl_5)(CH_3CN)L_2]BF_4$, which, in the case of L = $PPhMe_2$ and PMe_3 are uncrystallizable oils, whereas for L = PPh_3 the acetonitrile complex is not accessible owing to the lack of reactivity of *trans*-$[NiCl(C_6Cl_5)(PPh_3)_2]$ with $AgBF_4$ and acetonitrile in 1,2-dichloroethane.

The addition of an equimolar amount of [Tl(β-diketonate)] to a solution of the nickel(II) complexes *trans*-$[NiCl(C_6Cl_5)L_2]$ (L = $PPhMe_2$, PMe_3), leads to immediate precipitation of TlCl. A lower reactivity is displayed by the β-ketoamidate derivative $[Tl(CH_3C(O)CHC(O)NHCH_3)]$ for which reaction (2) requires several hours to go to completion at room temperature. β-Ketoamidate complexes analogous to **3f** could also be obtained quantitatively in solution (NMR control) starting from $[NiCl(C_6Cl_5)(PPh_2Me)_2]$ and $[NiCl(C_6Cl_5)(PPhMe_2)_2]$ by using excess of [Tl(β-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*-$[NiCl(C_6Cl_5)L_2]$ (L =

$PPhMe_2$ and PMe_3) with [Tl(acac)], the complexes containing PPh_3 and PPh_2Cy 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 β-diester, dimethylmalonate. In fact, a solution of equimolar amounts of *trans*-$[Ni(C_6Cl_5)(CH_3CN)(PPh_2Me)_2]BF_4$ and $CH_3OC(O)CH_2C(O)OCH_3$ in the presence of an excess of 1,1,3,3,-tetramethylguanidine showed no reaction after 24 h at room temperature. The Tl^I-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 $\nu(C\overset{\cdots}{-}O)$ and $\nu(C\overset{\cdots}{-}C)$ bands of the metallo-organic rings are generally identifiable in the expected 1500–1650 cm^{-1} 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 $\nu(C\overset{\cdots}{-}O)$ band and that of the CMe_3 radical by CF_3 a significant ipsochromy of the $\nu(C\overset{\cdots}{-}O)$ and $\nu(C\overset{\cdots}{-}C)$ 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-β-diketonate to metal-β-ketoamidate ring.

Finally, as a general comment on the position of the $\nu(C\overset{\cdots}{-}O)$ bands in **1a**, **2a** and **3a** with respect to $[Ni(acac)_2]$, the bathochromic effect (25, 15 and 20 cm^{-1} respectively) caused by the presence of C_6Cl_5 and PR_3 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^{II} square-planar species. Homoleptic nickel(II) planar species bearing two β-carbonylenolate ligands ($\{NiO_4\}$chromophore) display the relevant band in the range 535–560 nm [14, 15] with ε values ranging from 50 to 200 M^{-1} cm^{-1}. Heteroleptic complexes of the type [Ni(β-carbonylenolate)(diphosphine)]$^+$ were found by us [16] to give the same band in the range 425–450 nm with ε varying from 670 to 1740 M^{-1} cm^{-1} ($\{NiO_2P_2\}$ chromophore) and those here described span the range 430–450 nm with ε of 600 to 860 M^{-1} cm^{-1} ($\{NiO_2P_2\}$ chromophore).

^1H, ^{31}P and ^{13}C NMR Spectra

The ^1H NMR spectra (Table V) of the symmetrically substituted β-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_3 ligand which does not exchange in the NMR time scale.

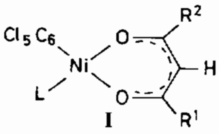
It is interesting to note the change of the differences of the $acac^-$ methyl resonances chemical shifts in the complexes $[Ni(acac)(C_6Cl_5)L]$ as a function of the phosphine ligand. The value of 0.22 ppm found for the PPh_2Me derivative is reduced in fact, to 0.07 ppm when L = $PPhMe_2$ and further reduced to only 0.01 ppm for the PMe_3 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 $[Ni(C_6Cl_5)(PR_3)$(β-carbonylenolate)] Complexes

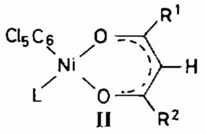
Complex	$\nu(C\overset{\cdots}{-}O)$, $\nu(C\overset{\cdots}{-}C)$ (cm^{-1})	λ_{max} (nm) (ϵ(M^{-1} cm^{-1}))^a
1a	1580(s), 1530(s)	228(46, 500); 447(670)
1b	1560(s), 1520(s)	228(48, 000); 254(40, 550); 290(21, 150)^c 345(8, 250)^c; 440(860)
1c	1610(s), 1590(s)	229(45, 000); 340(4, 000)^c; 447(780)
1d	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^b), 1520(s^b)	228(44, 250); 245(41, 650); 290(19, 490)^c 340(7, 550)^c; 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)^c; 435(600)

^{a}Data were obtained from solutions ranging from 10^{-5} to 10^{-3} M. In this range the spectra obey Lambert–Beer's law. ^{b}Uncertain identification. ^{c}Shoulder.

TABLE V. ^{1}H and ^{31}P NMR Data[a] for Complexes [Ni(β-carbonylenolate)(C_6Cl_5)L] (L = PPh_2Me, **1**; $PPhMe_2$, **2**; PMe_3, **3**) in $CDCl_3$ *cis*(R^1, L)



I, *trans*(R^1, L)



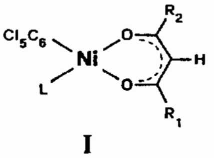
II

Compound	Isomer[f]	β-Carbonylenolate			Phosphine resonances (J(PH) Hz)		^{31}P chemical shifts (δ)
		R^1	CH	R^2	CH_3	C_6H_5	
1a ($R^1 = CH_3$; $R^2 = CH_3$)		1.63	5.40	1.85	1.62 d(10.6)[b]	7.7–7.2 cm	11.24
1b ($R^1 = CH_3$; $R^2 = C_6H_5$)	*cis*	1.79	6.06	c	1.66 d(10.7)	7.9–7.1 cm	11.31
	*trans**	2.01	6.09		1.71 d(10.7)		11.71
1c ($R^1 = C(CH_3)_3$; $R^2 = CF_3$)	*cis*	0.77	6.00	–	1.77 d(10.9)	7.9–7.2 cm	11.98
	*trans**	0.99		–	1.59 d(10.5)		10.97
1d ($R^1 = C(CH_3)_3$; $R^2 = C(CH_3)_3$)		0.76	5.71	0.98	1.72 d(10.5)	7.9–7.2 cm	12.39
1e ($R^1 = CH_3$; $R^2 = OC_2H_5$)	*cis**	1.51	4.81	3.79[d] q, 1.08 t	1.74 d(10.7)	8.0–7.2 cm	11.31
	trans	1.56	4.78	3.23[d] q, 0.83 t	1.66 d(10.2)		10.30
2a ($R^1 = CH_3$; $R^2 = CH_3$)		1.75	5.36	1.82	1.40 d(10.7)	7.8–7.2 cm	−0.53
2b ($R^1 = CH_3$; $R^2 = C_6H_5$)	*cis*	1.90	6.04	c	1.45 d(11.0)	7.8–7.2 cm	−0.43
	*trans**	1.98					0.68
3a ($R^1 = CH_3$; $R^2 = CH_3$)		1.80	5.37	1.81	1.09 d(11.1)		−5.38
3f ($R^1 = CH_3$; $R^2 = NH(CH_3)$)	*cis** or	1.72	4.56	e	1.09 d(11.2)		−5.08
	trans		4.54				−6.63

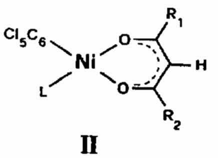
[a] Chemical shifts are in ppm; H_3PO_4 was used as external standard for ^{31}P spectra. [b] d, doublet; t, triplet; q, quartet; cm, complex multiplet. [c] Indiscernible because of overlapping with the phosphine phenyl resonance. [d] $J(CH_2CH_3)$ = 7.5 Hz. [e] NH(CH_3) resonances: δ *ca.* 4.7 (very broad singlet, N*H* CH_3), δ 2.63 (d, J(HH) 5.1 Hz), 2.51 (d, J(HH) 5.1 Hz). [f] Starred is the more abundant isomer.

[Ni(acac)(C_6H_5)PPh_3], which was attributed [17] to the anisotropic shielding of the triphenylphosphine ligand. Thus the higher field resonance was attributed to the acac$^-$ methyl group nearer to the phosphine phenyl substituents, *i.e.* in *cis* position to the PPh_3 ligand. In line with these observation, we find that the 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 PMe_3 derivative the two acac$^-$ methyl groups are virtually isocronous, 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 CH_3 *cis* to the phosphine ligand.

Complexes containing unsymmetrically substituent β-carbonylenolate 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:



I



II

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** (R^2 = 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 $^{31}P\{^1H\}$ 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 R^1, R^2 substituents.

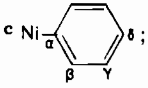
Table VI summarizes the ^{13}C NMR data of the more soluble complexes. Compounds **1a**, **2a** and **3a** exhibit two well separated carbonyl resonances, whose values are insensitive to the nature of the phosphine ligand. In the case of the PPh_2Me derivative the resonance at lower field appears as a doublet due to the coupling with the ^{31}P nucleus and therefore it must be attributed to the carbonyl *trans* to the phosphine ligand. Unlike the carbonyl group, the two acac$^-$ methyl ^{13}C resonances exhibit a slight but

TABLE VI. ^{13}C NMR Data for Complexes [Ni(β-carbonylenolate)(C_6Cl_5)L] (L = PPh_2Me, **1**; $PPhMe_2$, **2**; PMe_3, **3**)[a]

Compound	Isomer[b]	β-carbonylenolate resonances					Phosphine resonances					C_6Cl_5 group[c]		
		R^1CO	CH	R^2CO	R^1	R^2	PCH_3	P–C	*o*-C	*m*-C	*p*-C	C_α	C_β	C_γ
1a		185.1	100.4 ((160))	188.0 (1.4)	26.4 ((127.5))	26.8 (5.1) ((127))	11.6 (30.8) ((132))	131.6 (47)	132.4 (10.3)	127.9 (10.3)	130.2 (2.2)	151.5 (58.3)	137.7 (2.9)	127.4
1b	*cis*	186.9	97.3	180.8	27.2	[e]	11.9 (30.8)	[d]	132.5 (10.2)	127.9 (9.5)	130.3 (2.2)	not detectable		
	trans	189.6 (2.2)	97.3	178.1	27.6 (5.1)		11.7 (30.8)	[d]	132.4 (10.2)	128.1 (9.5)				
1c	*cis*	202.2	91.7	171.7 [34]	41.5; 27.6	118.2 [283]	11.7 (30.0)	130.5 (49.1)	132.2 (10.2)	128.1 (10.3)	130.6 (*ca.* 2)	not detectable		
	trans	203.7	92.0	167.5 [34]	42.0; 27.6 (2.9)			130.7 (48.3)	132.4 (9.5)					
1d		194.9	90.5	197.0 (2.2)	40.3; 28.2	40.8; 28.2 (4.4)	11.7 (30.0)	131.4 (46.9)	132.4 (10.2)	127.8 (9.5)	130.2 (2.9)	not detectable		
2a		185.1	100.5 ((159.7))	188.0	26.6 ((125.3))	26.8 (7.3) ((126.7))	11.7 (30.8) ((131.1))	132.5 (46.2)	130.2 (8.8) ((161))	128.1 (10.1)	129.8 (4)	152.8 (49.1)	137.9 (2.9)	127.4
2b	*cis*	186.8	97.2	180.7	27.4	[e]	12.4 (30.0)	not attributable				not detectable		
	trans	189.5 (1.4)	97.6	178.6	27.5 (5.0)		11.8 (30.0)							
3a		185.2	100.5 ((162))	188.0	26.7 ((126.9))	26.8 (4.9) ((127.9))	12.9 (30.0) ((130))					152.7 (51.3)	137.8 (2.9)	127.5

[a] Measured at 27 °C, in $CDCl_3$ solution. Figures in parentheses, double parentheses and brackets give $J(^{31}P-^{13}C)$, $^1J(^{13}C-^1H)$ and $J(^{19}F-^{13}C)$ in Hz, respectively.

[b] *Cis* and *trans* isomers as in Table V.

[c]  ; the attribution is based on ref. 18 and on the interpretation of the spectrum of the related complex *trans*-[NiCl(C_6Cl_5)(PMe_3)$_2$] (see Text).

[d] Not attributable.

[e] 126.6; 127.1; 127.9.

significant dependence on the phosphine ligand. In agreement with the ^1H NMR data, the methyl group in *cis* position to the 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}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}P nucleus with a $|^4J(^{13}C-^{31}P)| = 5-7$ Hz. The assignment of the ^{13}C resonances in the unsymmetrically substituted β-carbonylenolate ligands is based on the same criteria utilized for the ^1H spectra and the interpretation of the spectral features of the phosphine ligands is based on relevant literature [18].

The pentachlorophenyl ^{13}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 $|J(^{13}C-^{31}P)|$, the resonance at lower field is attributed to the carbon bonded to the nickel atom. The resonance at *ca.* 137δ, with a $|J(^{13}C-^{31}P)|$ of *ca.* 3 Hz, is attributed to the *ortho*-carbon atom (C_β). The remaining weak resonance which appears as a singlet at 127δ, should be attributed to the C_γ carbon atom. The related complex *trans*-$[NiCl(C_6Cl_5)(PMe_3)_2]$ exhibits, in fact, a ^{13}C spectrum in which the resonance of C_α, C_β, C_γ and C_δ appear as triplets (poorly resolved in the case of C_δ) with values: C_α, 158.7 ($^2J(^{13}C-^{31}P) = 35.1$ Hz); C_β, 136.0 ($^3J(^{13}C-^{31}P) = 9.7$ Hz); C_γ, 128.2 ($^4J(^{13}C-^{31}P) = 3.9$ Hz); C_δ, 126.5 ($^5J(^{13}C-^{31}P) \simeq 2$ Hz). The peak of C_δ is relatively weak and, therefore, the corresponding resonance for complexes **1**–**3** may be undetectably weak.

It seems worth mentioning that the ^1H and ^{13}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 $\nu(C\overset{\cdots}{-}O)$ 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.

References

1 M. Basato, R. Compostrini, B. Corain, B. Longato, S. Sitran, A. C. Veronese and G. Valle, *J. Chem. Soc., Perkin Trans. II,* 2019 (1985), and refs. therein; (b) B. Corain, B. Longato, M. Basato, R. Angeletti and A. C. Veronese, *Inorg. Chim. Acta, 117,* 39 (1986).
2 B. Corain and B. Longato, *Inorg. Chim. Acta, 83,* L37 (1983).
3 B. N. Starnhoff and H. C. Lewis, *Coord. Chem. Rev., 23,* 1 (1977).
4 T. Uchiyama, K. Takagy, K. Matsumoto, S. Ooi, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn., 54,* 1077 (1981).
5 K. Maruyama, T. Ito and A. Yamamoto, *J. Organomet. Chem., 155,* 359 (1978).
6 K. Yamada, S. Baba, Y. Nakamura, S. Kawaguchi, *Bull. Chem. Soc. Jpn., 56,* 1393 (1983).
7 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', 2nd edn., Pergamon, Oxford, 1980.
8 M. D. Rausch and F. E. Tibbets, *Inorg. Chem., 5,* 512 (1970).
9 M. Wada, K. Sameshima, K. Nishiwaky and Y. Kawasaky, *J. Chem. Soc., Dalton Trans.,* 793 (1982).
10 K. P. Mac Kinnon and B. O. West, *Aust. J. Chem., 21,* 2801 (1968).
11 (a) W. H. Nelson, W. J. Randall and D. F. Martin, *Inorg. Synth., 9,* 52 (1967); C. Z. Moore and W. H. Nelson, *Inorg. Chem., 8,* 143 (1969).
12 C. A. Tolman, *Chem. Rev., 77,* 313 (1977).
13 R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-Diketonates and Allied Derivatives', Academic Press, New York, 1978.
14 F. A. Cotton and J. J. Wise, *Inorg. Chem., 7,* 1200 (1966).
15 B. Corain, M. Basato, C. Ballotta and M. Ahmed, *Inorg. Acta, 122,* 129 (1986).
16 G. Favero, B. Corain, M. Basato and S. Isse, *Inorg. Chim. Acta, 122,* 129 (1986).
17 K. Maruyame, T. Ito and A. Yamamoto, *J. Organomet. Chem., 155,* 359 (1978).
18 P. S. Pregosin and R. W. Kunz, '^{31}P and ^{13}C NMR of Transition Metal Complexes', Springer, Berlin, 1979.