

NEUTRAL AMINOCARBENE COMPLEXES OF NICKEL FROM THE REACTION OF $[\text{Ni}\{\eta^2\text{-C}(\text{NBu}^t)\text{CH}_2\text{CMe}_3\}$ $(\text{NC}_4\text{H}_2\text{Me}_2)(\text{PMe}_3)]$ WITH DIPROTONIC ACIDS

ERNESTO CARMONA,* PILAR PALMA and MANUEL L. POVEDA

Departamento de Química Inorgánica-Instituto de Ciencia de Materiales,
Universidad de Sevilla-CSIC, Apartado 553, 41071-Sevilla, Spain

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Abstract—The dihaptoiminoacyl complex $[\text{Ni}\{\eta^2\text{-C}(\text{NBu}^t)\text{CH}_2\text{CMe}_3\}(\text{NC}_4\text{H}_2\text{Me}_2)(\text{PMe}_3)]$ (**1**), containing the coordinated 2,5-dimethylpyrrolyl ligand, reacts with CO_2 , in the presence of water, with protolytic cleavage of the Ni—N bond and protonation of the iminoacyl nitrogen atom, to furnish an η^2 -carbonate aminocarbene complex of composition $[\text{Ni}(\eta^2\text{-CO}_3)\{\text{C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{PMe}_3)]$ (**2**). This transformation has been shown to be a general reaction of **1** with diprotonic acids, and compounds related to **2** have been obtained using oxalic, parabanic and salicylic acids. The new compounds have been fully characterized by analytical and spectroscopic methods.

A recent contribution from our laboratory has described the formation of various η^1 -iminoacyl complexes of nickel(II) with the composition $[\text{Ni}\{\eta^1\text{-C}(\text{NBu}^t)\text{R}\}\text{Cl}(\text{PMe}_3)_2]$. Substitution of the chloride ligand by the bulkier 2,5-dimethylpyrrolyl group induces a change in the coordination mode of the iminoacyl ligand and provides the dihapto-iminoacyl compounds $[\text{Ni}\{\eta^2\text{-C}(\text{NBu}^t)\text{R}\}(\text{NC}_4\text{H}_2\text{Me}_2)(\text{PMe}_3)]$.¹ A characteristic feature of the chemistry of the η^1 -iminoacyls is the extreme facility with which the coordinated iminoacyl nitrogen can be protonated, even by water, to form the cationic aminocarbene species,¹ $[\text{Ni}\{\text{C}(\text{NHBu}^t)\text{R}\}\text{Cl}(\text{PMe}_3)_2]^+$.

During studies aimed at the investigation of the chemical properties of the η^2 -iminoacyl complexes containing the 2,5-dimethylpyrrolyl ligand, we have found that these can also be readily protonated and that action of commercial, high purity CO_2 on solutions of a representative member, $[\text{Ni}\{\eta^2\text{-C}(\text{NBu}^t)\text{CH}_2\text{CMe}_3\}(\text{NC}_4\text{H}_2\text{Me}_2)(\text{PMe}_3)]$ (**1**), causes both iminoacyl protonation and Ni—N bond heterolysis, with formation of the neutral aminocarbene $[\text{Ni}(\eta^2\text{-CO}_3)\{\text{C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{PMe}_3)]$ (**2**), which contains a bidentate carbonate ligand. Herein we describe the formation and spectroscopic characterization of **2** and of other

related aminocarbene complexes resulting from the protonation of **1** with various diprotonic acids. Analytical and selected IR and ¹H NMR data for the new compounds are given in the Experimental, selected ¹³C and ³¹P NMR data are collected in Table 1.

RESULTS AND DISCUSSION

Compound **1** is fairly unreactive towards both H_2O and CO_2 as independent reagents. However, upon bubbling CO_2 through a solution of **1** in Et_2O , small amounts of a yellow, finely divided solid, identified as complex **2**, precipitate out of the solution. The addition of one or two drops of water induces further precipitation of this sparingly soluble solid, while if the above transformation is carried out using acetone as the solvent and the reaction mixture is allowed to stand overnight without stirring, complex **2** is obtained in the form of yellow, needle-shaped crystals in good yields. After the reaction is complete, an NMR analysis of the mother liquor reveals the presence of free 2,5-dimethylpyrrole, while IR and NMR studies of the yellow complex **2** show the presence of an aminocarbene and a carbonate ligands (see below). Accordingly, the reaction occurs with both hydrolytic cleavage of the Ni—N bond and protonation of the iminoacyl functionality, presumably by the

* Author to whom correspondence should be addressed.

Table 1. Selected NMR data for the new complexes

Compound	$^{13}\text{C}\{^1\text{H}\}$								$^{31}\text{P}\{^1\text{H}\}$
	PMe_3	CH_2CMe_3			$\text{Ni}-\text{C}-\text{NHBu}^t$			Others	
		CH_2	C	Me	$\text{C}(\text{Bu}^t)$	$\text{Me}(\text{Bu}^t)$	$\text{Ni}-\text{C}$		
2^a	13.8d (33)	64.0s	35.1s	22.1s	61.6s	31.4s	243.1d (37)	170.2s (CO_3)	-2.2s
3	11.3d (33)	63.1s	35.0s	31.3s	61.0s	30.5s	240.5d (40)	169.2, 169.3 (s, C_2O_4)	4.0s
4	15.7d (33)	67.5s	38.6s	34.9s	65.0s	34.2s	^b	$\text{C}=\text{O}^b$	3.4s
5-6	^c 11.5d (32)	62.9s	34.4s	30.5s	59.9s	29.9s	242.9d (44)	173.5s (COO) ^{e, g}	-4.9s
	^d 11.5d (32)	63.1s	34.1s	30.8s	59.9s	29.9s	242.5d (42)	172.7s (COO) ^f	-3.9s

Coupling constants (Hz) in parentheses. In CD_3OD unless otherwise indicated.

^a In D_2O .

^b Non-observed resonances.

^c Major isomer.

^d Minor isomer.

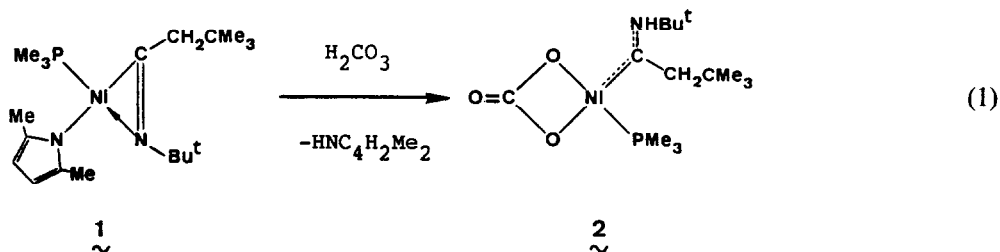
^e $\text{C}-\text{O}-\text{Ni}$: 168.3.

^f $\text{C}-\text{O}-\text{Ni}$: 167.5.

^g Aromatics at 114.0, 115.7, 122.1, 122.8, 122.9, 131.9, 132.6.

action of carbonic acid on complex **1**, as shown in eq. (1):

functionalities,⁴ and appears as a doublet due to its coupling to the ^{31}P nucleus. The value of 37 Hz

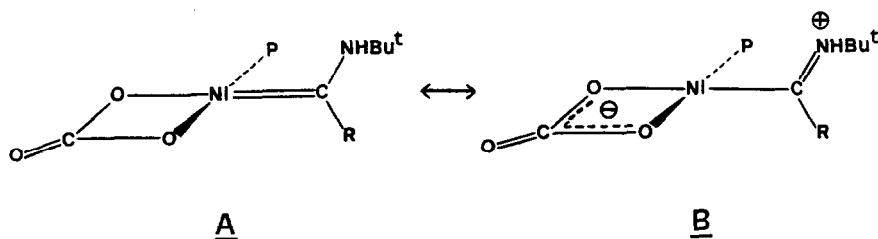


Complex **2** is insoluble in most common organic solvents, but has appreciable solubility in polar solvents such as methanol or water. The presence of a carbonate ligand is indicated by the appearance of a strong IR absorption at *ca* 1580 cm^{-1} , whose frequency suggests bidentate coordination,^{2,3} and by the observation of a ^{13}C resonance at *ca* 170 ppm (^{13}C enriched sample). On the other hand, the aminocarbene ligand gives a characteristic IR absorption at 3200 cm^{-1} due to the $\text{N}-\text{H}$ stretching vibration, but the $\nu(\text{C}-\text{N})$ band cannot be readily discerned since it overlaps with the strong carbonate absorption at 1580 cm^{-1} . Complex **2** crystallizes with one molecule of water of crystallization, and evidence for this and for the existence of a hydrogen-bonded network in the solid-state structure of **2** can be ascertained from IR data.²

The nickel-bound carbon atom of the aminocarbene ligand gives a ^{13}C resonance at 243 ppm, that is, in the range characteristic of aminocarbene

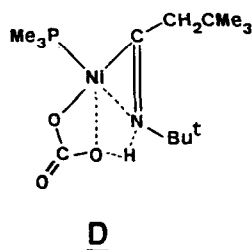
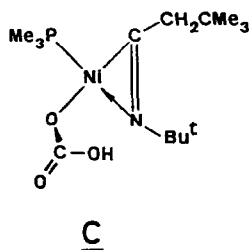
found for the phosphorus-to-carbon coupling constant is indicative of a *cis* distribution of the aminocarbene and phosphine ligands. Interestingly, the methylene protons of the CH_2CMe_3 group appear as an AB quartet in the ^1H NMR spectrum. The inequivalence of these protons indicates that the aminocarbene ligand occupies a rigid position in a plane perpendicular to that containing the nickel centre and the donor atoms of the other ligands, as shown below (A). This, and the low-field chemical shift found for the aminocarbene carbon atom are clearly in accord with an important contribution of the carbene resonance structure A to the ground-state structure of this molecule.

Some brief comments seem appropriate at this point on the formation of the aminocarbene complex **2**. The first step probably involves the protolytic cleavage of the $\text{Ni}-\text{N}$ bond by carbonic acid, with formation of an intermediate bicarbonate complex of possible structure C. This could then be followed by protonation of the iminoacyl nitrogen, in an



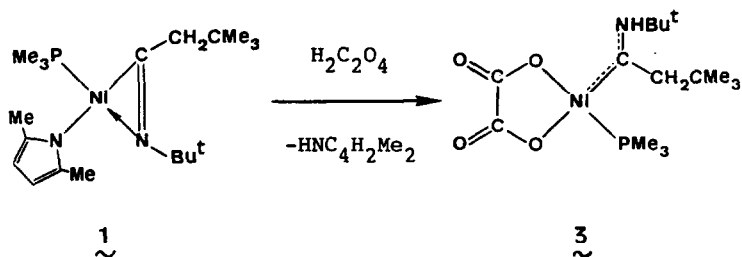
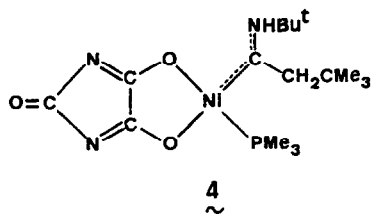
intramolecular, concerted manner, as depicted in D.

below can be proposed on the basis of analytical and spectroscopic data, and also by similarity with



In an attempt to obtain aminocarbene complexes related to **2**, containing the larger, five-membered chelating $\text{O}-\text{C}-\text{C}-\text{O}-\text{Ni}$ ring, the reactions of **1** with oxalic, $\text{H}_2\text{C}_2\text{O}_4$, and parabanic, $\text{H}_2\text{C}_3\text{N}_2\text{O}_3$, acids, have been investigated. Addition of oxalic acid to an acetone solution of **1** yields a yellow, microcrystalline precipitate of complex **3**, with solubility properties very similar to those of **2**. Microanalytical and spectroscopic data are in accord with bidentate oxalate coordination, as shown in eq. (2):

that assigned to the related compounds **2** and **3**. For complex **4**, however, its low solubility has prevented observation of the ^{13}C resonances of the parabanate ligand.



Thus, the IR spectrum of **3** displays several bands in the region $1700\text{--}1600\text{ cm}^{-1}$ which can be assigned to $\nu(\text{C}=\text{O})$ of the bidentate oxalate ligand,^{2,5} while the ^{13}C NMR spectrum of **3** exhibits two nearly coincident ^{13}C signals for the carbon atoms of the oxalate ligand in the proximity of 169 ppm. Other pertinent spectroscopic data for **3** are collected in the Experimental and in Table 1 and will not be discussed any further.

Parabanic acid, $\text{H}_2\text{C}_3\text{N}_2\text{O}_3$, provides an analogous species, **4**, for which the structure shown

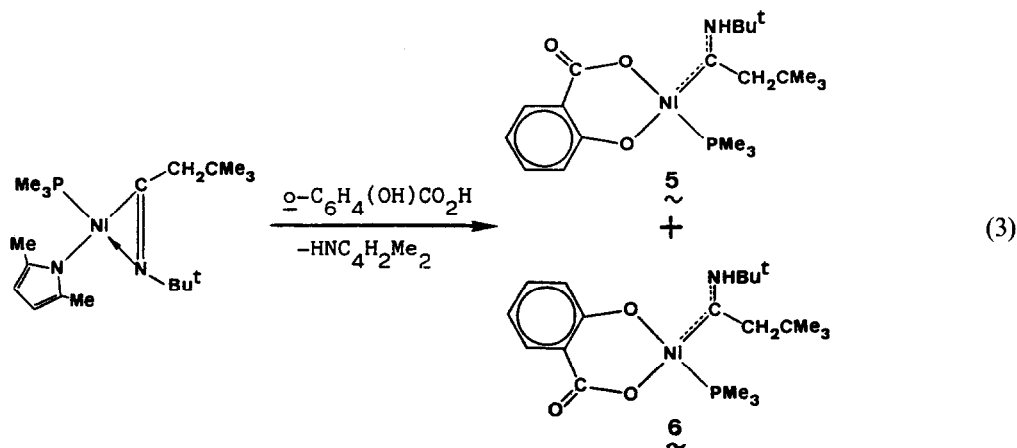
Finally, we have carried out the reaction of **1** with salicylic acid, to obtain a yellow, microcrystalline precipitate, which is shown by NMR to be composed of an isomeric mixture of compounds **5** and **6** [eq. (3)], in an approximate 3:2 ratio. The ^{13}C NMR spectrum of this isomeric mixture displays two doublets at 242.5 and 242.9 ppm ($^2J_{\text{CP}} = 42$ and 44 Hz, respectively) that can be assigned to the nickel-bound aminocarbene carbon in both isomers, as well as two singlets at 173.5 and 172.7 ppm due to the carboxylate carbons. Similarly, the

$^{31}\text{P}\{^1\text{H}\}$ NMR shows two singlets at -4.9 and -3.9 ppm. The above data suggest that the isomerism is due to the geometric distribution of the salicylate group with respect to the other ligands, that is, to its positioning with the carboxylate functionality *trans* either to the phosphine or to the aminocarbene ligand, as indicated in eq. (3).

CMe_3), 1.93, 2.65 (d, dd, $^2J_{\text{HH}} = 12.5$, $^4J_{\text{HP}} = 2.8$ Hz, diastereotopic CH_2 protons).

Preparation of $[\text{Ni}(\eta^2\text{-C}_2\text{O}_4)\{\text{C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{PMe}_3)] \cdot \text{H}_2\text{O}$ (3)

Complex 1 (0.26 g, 0.7 mmol) was dissolved in acetone (40 cm^3) and treated with solid $\text{H}_2\text{C}_2\text{O}_4 \cdot$



EXPERIMENTAL

Microanalyses were by Pascher Microanalytical Laboratory, Remagen (F.R.G.), and the Micro-analytical Service of the University of Seville. The spectroscopic instruments used were Perkin-Elmer models 557 and 684 for IR spectra and Varian XL-200 for ^1H , ^{13}C and ^{31}P NMR spectra. All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. Complex 1 was prepared according to ref. 1 and parabanic acid following a literature method.⁶

Synthesis of $[\text{Ni}(\eta^2\text{-CO}_3)\{\text{C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{PMe}_3)] \cdot \text{H}_2\text{O}$ (2)

A solution of $[\text{Ni}\{\eta^2\text{-C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{NC}_4\text{H}_2\text{Me}_2)(\text{PMe}_3)]$ (1) (0.30 g, 1 mmol) in acetone (100 cm^3) was treated with a few drops of water and then transferred to a Fischer-Porter vessel. The N_2 atmosphere was replaced by CO_2 , the CO_2 pressure increased to 3 atm and the solution was kept undisturbed overnight. The yellow, crystalline precipitate that formed was filtered off, washed with acetone and dried under vacuum. Yield: 90%. IR (Nujol mull): 3200 cm^{-1} (NH), 1580 cm^{-1} (br, CO_3 and $\text{C}=\text{N}$). Found: C, 45.4; H, 8.4; N, 3.7; O, 16.8. Calc. for $\text{C}_{14}\text{H}_{30}\text{NO}_3\text{P}\text{Ni} \cdot \text{H}_2\text{O}$: C, 45.7; H, 8.7; N, 3.8; O, 17.4%. ^1H NMR (D_2O , 200 MHz): δ 1.12 (d, $^2J_{\text{HP}} = 11.4$ Hz, PMe_3), 1.17 (s, CH_2CMe_3), 1.82 (s,

$2\text{H}_2\text{O}$ (0.088 g, 0.7 mmol). The reaction mixture was stirred at room temperature for 4 h and the resulting yellow precipitate filtered off, washed with acetone and dried under vacuum. Yield: 60%. IR (Nujol mull): 3200 cm^{-1} (NH), $1700\text{--}1600 \text{ cm}^{-1}$ (several bands, C_2O_4 and $\text{C}=\text{N}$). Found: C, 45.9; H, 7.5. Calc. for $\text{C}_{15}\text{H}_{30}\text{NO}_4\text{P}\text{Ni} \cdot \text{H}_2\text{O}$: C, 45.5; H, 8.1%. ^1H NMR (CD_3OD , 200 MHz): δ 1.42 (d, $^2J_{\text{HP}} = 11.6$ Hz, PMe_3), 1.50 (s, CH_2CMe_3), 2.12 (s, CMe_3), 2.35, 2.95 (d, dd, $^2J_{\text{HH}} = 12.3$, $^4J_{\text{HP}} = 3.1$ Hz, diastereotopic CH_2 protons).

Synthesis of $[\text{Ni}(\eta^2\text{-C}_3\text{O}_3\text{N}_2)\{\text{C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{PMe}_3)]$ (4)

A solution of parabanic acid (0.114 g, 1 mmol) in methanol (40 cm^3) was added via canula to a stirred solution of complex 1 (0.38 g, 1 mmol) in acetone (30 cm^3). After stirring overnight, the reaction mixture was taken to dryness and the residue triturated with Et_2O (30 cm^3). The resulting solid was filtered off and dried. Yield: 60%. IR (Nujol mull): 3200 cm^{-1} (NH), 1640 cm^{-1} (br, $\text{C}=\text{O}$ and $\text{C}=\text{N}$). ^1H NMR (CD_3OD , 200 MHz): δ 1.43 (d, $^2J_{\text{HP}} = 11.4$, PMe_3), 1.50 (s, CH_2CMe_3), 2.12 (s, CMe_3), 2.30, 2.94 (d, dd, $^2J_{\text{HH}} = 12.2$, $^4J_{\text{HP}} = 3.2$ Hz, diastereotopic CH_2 protons).

Synthesis of $[\text{Ni}(\eta^2\text{-C}_7\text{H}_4\text{O}_3)\{\text{C}(\text{NHBu}^t)\text{CH}_2\text{CMe}_3\}(\text{PMe}_3)]$ (5) and (6)

Complex 1 (0.18 g, 0.5 mmol) dissolved in acetone

(20 cm³) was reacted with a solution of salicylic acid (0.05 g, 0.5 mmol) in acetone (30 cm³). A yellow solid started precipitating upon mixing of the reactants. The reaction mixture was allowed to stand overnight and the resulting microcrystalline solid filtered off, washed with acetone and dried. Yield: 60%. IR (Nujol mull): 3200 cm⁻¹ (NH), 1600–1540 cm⁻¹ (several bands, C=O and C=C). Found: C, 56.1; H, 7.9; N, 3.2. Calc. for C₂₀H₃₄NO₃PNi: C, 56.4; H, 8.0; N, 3.3%. ¹H NMR (CD₃OD, 200 MHz) major isomer: δ 1.37 (d, ²J_{HP} = 11.1 Hz, PMe₃), 1.55 (s, CH₂CMe₃), 2.18 (s, CMe₃), 2.25, 2.93 (d, dd, ²J_{HH} = 12.1, ⁴J_{HP} = 3.0 Hz, diastereotopic CH₂ protons), 6.4–7.8 (m, aromatics); minor isomer: δ 1.37 (d, ²J_{HP} = 11.1 Hz, PMe₃), 1.56 (s, CH₂CMe₃), 2.17 (s, CMe₃), 2.24, 2.90 (d, dd, ²J_{HH} = 12.1, ⁴J_{HP} = 3.0 Hz, diastereotopic CH₂ protons), 6.4–7.8 (m, aromatics).

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REFERENCES

1. E. Carmona, P. Palma, M. Panque and M. L. Poveda, *Organometallics* 1990, **9**, 583.
2. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn. Wiley Interscience, New York (1986).
3. (a) H. H. Karsh, *Chem. Ber.* 1977, **210**, 2213; (b) D. A. Palmer and R. V. Eldik, *Chem. Rev.* 1983, **83**, 651.
4. B. E. Mann and B. F. Taylor, *¹³C NMR Data for Organometallic Compounds*. Academic Press, London (1981).
5. R. C. Mehrotra and R. Bohra, *Metal Carboxylates*. Academic Press, London (1986).
6. J. I. Murray, *Organic Synthesis*, Vol. IV. Wiley Interscience, New York (1963).