New nickel(0) complexes with bulky diphosphine ligands

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Abstract

The synthesis and characterization of new complexes of formula Ni(dp), Ni(dp)C_7H_8 (dp = 1,2-bis-(dicyclohexylphosphino)ethane [dcpe]; 1,3-bis(dicyclohexylphosphino)propane [dcpp]; 1,4-bis(dicyclohexyl-phosphino)butane [dcpb]), $Ni_2(dcpe)_3$, $Ni_2(dcpb)_3$, $Ni(dcpe)_2$ and $Ni(depe)_2$ (depe = 1,2-bis(diethylphosphino)-ethane) are described. The electronic spectra of these complexes are discussed.

Introduction

Diphosphines with general formula $R_2P–(CH_2)_n–PR_2$ allow complexes to be obtained in which, in view of the chelating ability of the ligands, the bond angle P–M–P depends on the dimensions of the heteroatomic ring and therefore on the 'n' value. In complexes of bulky transition metals with $R_2P–(CH_2)_2–PR_2$ (R = alkyl, phenyl) the P–M–P angle value ranges from 75 to 77° (M = Mo, Ta) [1] and from 82 to 85° (M = Os, Ru, Ir, Rh, Pd) [1, 2]; when the transition metal is the smaller nickel atom, the P–M–P angle is larger [3] (from 89 to 92°) as a consequence of the shorter Ni–P bond distances. For complexes with $R_2P–(CH_2)_3–PR_2$, P–M–P angle values of 89,3° (M = Pd; R = Ph) [2] and 103,5° (M = Ni; R = Cy) [4] are reported. To the best of our knowledge no data concerning angle values for complexes with $R_2P–(CH_2)_4–PR_2$ ligands are reported in the literature, although complexes with these ligands are known [5].

We have addressed our attention to complexes of nickel(0) with chelating diphosphines targeted to the purpose of obtaining new carbon dioxide complexes of nickel and of studying the influence of the P–Ni–P bond angle on their stability. We have aimed at the chelating phosphine series $Cy_2P–(CH_2)_n–PCy_2$ (dp) (Cy = cyclo-C_6H_{11}; n = 2, 3 and 4; dp = dcpe, dcpp and dcpb, respectively) since these ligands, owing to their high steric hindrance and basicity, should allow the formation of coordinatively unsaturated complexes suitable for reacting with CO_2 [6]. Indeed, with phosphines

such as dcpe, dcpp and PCy₃, but not with the less bulky ones like $(CH_3)_2P–(CH_2)_2–P(CH_3)_2$ or $P(CH_3)_3$ [7], the arene–nickel(0)complexes with formula (arene)Ni(dp) (dp = dcpe, dcpp; arene-benzene, naphthalene, anthracene) and (naphthalene)Ni(PCy₃)₂ [8] have been obtained.

This paper is concerned with the preparation and some properties of two-coordinated 14-electron nickel(0) complexes of formula Ni(dp) (dp = dcpe, dcpp and dcpb). The preparation of the $Ni_2(dp)_3$ (dp = dcpe and dcpb), $Ni(dcpe)_2$ and $Ni(depe)_2$ complexes is also reported.

The preparation of the complexes was carried out by the same pathway used for the tetracoordinated complexes of cobalt(I) [9a], for some dinitrogen complexes of cobalt(0) and cobalt(-I) [9b], for tri- and tetracoordinated trialkylphosphino–nickel(0) complexes [9c].

Experimental

All the reactions were carried out in anhydrous solvents which were distilled and stored under inert atmosphere.

1,2-Bis(dicyclohexylphosphino)ethane was purchased from Strem and used without further purification; 1,3-bis(dicyclohexylphosphino)propane and 1,4-bis-(dicyclohexylphosphino)butane were prepared by literature procedures [10].

The complexes Ni(dcpe)Cl_2, Ni(dcpp)Cl_2 and Ni(dcpb)Br_2 were prepared as described in ref. 11.

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Samples for decomposition tests or melting point determinations were sealed in capillary tubes under nitrogen.

NMR solvents were dried over activated 5 Å molecular sieves and deoxygenated by repeated freezing–pumping cycles. NMR spectra were recorded on a Varian XL200 spectrometer operating in FT mode. ^{31}P shifts were measured with respect to external 85% H_3PO_4.

IR spectra were recorded with a Perkin-Elmer 883 spectrophotometer.

By treating the solid nickel(0) complexes with sulfuric acid the evolution of H_2 was detected by chromatographic analyses in ratio $H_2/Ni = 1$ for all the compounds.

The gas analyses (H_2, N_2) were performed with a Carlo Erba chromatograph, model CAT_2 Fractovap (equipped with a column filled with Chromosorb 102) connected to a Varian 4270 integrator using the procedure standardized in our previous report [12] for carbon dioxide analysis.

The analyses of toluene contained in some complexes were carried out by subjecting THF solutions of weighed samples to chromatographic analysis using a Varian 3300 GC, equipped with a SP 2100 Carbowax column in a variable temperature mode.

Electronic spectra were recorded with a Cary 219 Varian spectrophotometer. The UV–Vis spectra of solids were obtained by recording the absorbance of a nujol mull of the sample spread between two quartz discs. We preferred to use this technique as it is simpler and faster than that based on reflectance measurements in MgO, especially when the samples to be analyzed are air sensitive.

1,2-Bis(dicyclohexylphosphino)ethanenickel(0), Ni(dcpe)

A suspension of Ni(dcpe)Cl_2 (1.8 g; 3.26 mmol) and powdered sodium (300 mg; 13 mmol) in toluene (30 ml) was stirred at room temperature under nitrogen until a deep red solution was obtained. After filtration, the toluene was evaporated and the crude was dissolved in 10 ml of n-heptane. By cooling to −30 °C deep red crystals were obtained which were filtered, washed with cold n-heptane and dried *in vacuo*. Yield 1.1 g (70%). m.p. 143–145 °C.

Anal. Calc. for $C_{26}H_{48}NiP_2$: C, 64.88; H, 10.05; Ni, 12.20; P, 12.87. Found: C, 64.61; H, 9.91; Ni, 12.15; P, 12.78%.

δ (^{31}P){H}) in C_7D_8: 43.7 (s) ppm.

When the crystallization is performed with toluene/heptane, the complex contains one mole of toluene per mole of nickel. In a typical reaction the crude obtained from the reduction of 1.4 g of Ni(dcpe)Cl_2 was dissolved in 10 ml of toluene. After filtration, the red solution was concentrated to 2–3 ml. By adding heptane (10 ml) and cooling to −20 °C red crystals

were obtained which were filtered, washed with cold n-heptane and dried *in vacuo*. Yield 217 mg (15%).

Anal. Calc. for $C_{26}H_{48}NiP_2 \cdot C_7H_8$: Ni, 10.24; P, 10.80; C_7H_8, 16.07. Found: Ni, 10.18; P, 10.84; C_7H_8, 16.08%.

1,3-Bis(dicyclohexylphosphino)propanenickel(0), Ni(dcpp)

This complex was obtained in a similar manner starting from Ni(dcpp)Cl_2 and sodium sand (Na/Ni molar ratio = 4). Yield 55%. m.p. 156–158 °C.

Anal. Calc. for $C_{27}H_{50}NiP_2$: C, 65.47; H, 10.17; Ni, 11.85; P, 12.51. Found: C, 64.93; H, 10.80; Ni, 11.82; P, 12.30%.

δ (^{31}P{H}) in C_7D_8: 24.6(s) ppm.

When crystallization was performed in toluene/heptane a complex containing one mole of toluene per mole of nickel was obtained.

Anal. Calc. for $C_{27}H_{50}NiP_2 \cdot C_7H_8$: Ni, 9.99; P, 10.54; C_7H_8, 15.68. Found: Ni, 10.03; P, 10.51; C_7H_8, 15.58%.

1,4-Bis(dicyclohexylphosphino)butanenickel(0), Ni(dcpb)

This complex was obtained in a similar manner starting from Ni(dcpb)Br_2 and sodium sand (Na/Ni molar ratio = 4). Yield 40%. m.p. 215–217 °C.

Anal. Calc. for $C_{28}H_{52}NiP_2$: C, 66.02; H, 10.29; Ni, 11.52; P, 12.16. Found: C, 65.81; H, 9.89; Ni, 11.52; P, 11.95%.

δ (^{31}P{H}) in C_7D_8: 29.5(s) ppm.

When crystallization was performed in toluene/heptane solvent a complex containing one mole of toluene per mole of nickel was obtained.

Anal. Calc. for $C_{28}H_{52}NiP_2 \cdot C_7H_8$: Ni, 9.76; P, 10.30; C_7H_8, 15.31. Found: Ni, 9.68; P, 10.11; C_7H_8, 15.01%.

Reactions of Ni(dcpe) with dcpe: synthesis of $Ni_2(dcpe)_3$

To a stirred n-heptane solution (20 ml) containing 250 mg of crude Ni(dcpe), 110 mg of solid dcpe were added. After 30 min the solution turned to violet and a violet solid precipitated which was filtered off, washed with cold heptane and dried *in vacuo*.

Anal. Calc. for $C_{78}H_{144}Ni_2P_6$: Ni, 8.47; P, 13.42. Found: Ni, 8.40; P, 13.24%.

Reactions of Ni(dcpe) with dcpe: synthesis of $Ni(dcpe)_2$

To a stirred toluene solution (10 ml) containing 240 mg of crude Ni(dcpe), 211 mg of solid dcpe were added. After 30 min the solution turned to deep brown and a brown solid precipitated which was filtered off, washed with cold heptane and dried *in vacuo*.

Anal. Calc. for $C_{52}H_{96}NiP_4$: Ni, 6.49; P, 13.71. Found: Ni, 6.44; P, 13.32%.

Bis[1,2-bis(diethylphosphino)ethane]nickel(0), Ni(depe)$_2$

A suspension of Ni(depe)Cl_2 (900 mg; 2.68 mmol) and powdered sodium (290 mg; 12.6 mmol) in toluene (30 ml) was stirred at room temperature under nitrogen.

After 24 h the suspension turned to brown and a light red–violet solution was obtained by filtration, which was concentrated to about 4 ml *in vacuo* and finally treated with absolute alcohol (10 ml). By cooling to −30 °C, ivory needles slowly precipitated, which were filtered at −20 °C, washed with cold ethanol and dried *in vacuo*. The compound becomes irreversibly light violet at room temperature. Decomposes 201–204 °C.

Anal. Calc. for $C_{20}H_{48}NiP_4$: Ni, 12.46; P, 26.29. Found: Ni, 12.40; P, 25.81%.

Results and discussion

The reduction under argon or nitrogen with sodium sand of Ni(II) complexes of formula Ni(dp)X$_2$ (X = Cl, Br; dp = dcpe, dcpp, dcpb) suspended in toluene leads to the formation of red solutions from which, after filtration and evaporation to dryness *in vacuo*, dark red crude products are obtained. The crystallization from n-heptane yields the Ni(dp) complexes. Upon crystallization of the crude products with toluene/n-heptane, the same products containing one mole of toluene per mole of nickel are obtained. Both Ni(dp) and Ni(dp)C$_7$H$_8$ complexes are dark red crystalline solids readily oxidized by air, both in solution and in the solid state. They are soluble in aromatic solvents and in THF; their solubilities in aliphatic hydrocarbons (C$_5$–C$_7$) are fairly high at room temperature, and significantly smaller at low temperatures.

Upon prolonging the reduction time of Ni(dcpe)X$_2$ for some hours, the n-heptane soluble violet complex Ni$_2$(dcpe)$_3$ could be extracted from the crude mixture. This procedure was difficult to standardize, but the same compound could be obtained by reacting dcpe and Ni(dcpe) in a 0.5/1 molar ratio. The complex Ni$_2$(dcpe)$_3$ is an air-sensitive product, soluble in aromatic hydrocarbons.

When the reduction of Ni(dcpe)Cl$_2$ is performed in solvents like THF or n-heptane (which possess a smaller coordinating ability), the light brown compound of formula Ni(dcpe)$_2$ is obtained, from their red–brown (THF) or dark brown (n-heptane) solution, in low yield. This complex can also be prepared by reacting dcpe and Ni(dcpe) in a 1/1 molar ratio (or dcpe with Ni$_2$(dcpe)$_3$ in a 1/1 molar ratio). On the contrary, the reduction of Ni(dcpb)Cl$_2$ in n-heptane (even when stirred for eight days) stops when the violet Ni$_2$(dcpb)$_3$ is produced, probably as the consequence of the larger bulkiness of the dcpb ligand compared with that of the dcpe.

By reducing with sodium in toluene complexes of nickel(II) with less bulky diphosphines like depe and dppe (1,2-bis(diphenylphosphino)ethane) the known Ni(depe)$_2$ [13a] and Ni(dppe)$_2$ [13b] complexes have been obtained.

We think that, on the basis of the literature data mentioned in the introduction, the P–Ni–P bond angle values in Ni complexes with dcpe and dcpp ligands can be expected to be 90 and 103°, respectively. For the complexes containing the dcpb ligand, in the absence of related structural data, we consider that, when *n* passes from 2 to 3, the increase of the P–Ni–P angle (about 13°) is practically equal to the difference between the interior angle of the hexagon (120°) and the pentagon (108°); therefore, we think it is reasonable to increase the angle corresponding to *n* = 3 by a value practically equal to the difference between the interior angles of the heptagon (128.57°) and of the hexagon and to assign to the P–Ni–P angle for *n* = 4 a value of *c*. 111°. This value is supported by observations based on building up Büchi molecular models.

The dp ligand should be electronically similar to two PCy$_3$ molecules and in the Ni(dp) complexes the nickel atom is expected to possess the same very good backbonding ability that it has in the Ni(PCy$_3$)$_2$ fragment [6]. This highly unsaturated complex forms the stable adducts Ni(PCy$_3$)$_2$CO$_2$ [11, 14] and {Ni(PCy$_3$)$_2$}$_2$N$_2$ [6, 9c], upon reaction with carbon dioxide and dinitrogen, respectively.

We find that the Ni(dp) and Ni(dp)$_2$ complexes, but not the Ni(depe)$_2$ one, react with CO$_2$ to give carbon dioxide–nickel(0) complexes, whose stabilities depend upon the P–Ni–P angle bond value [15]. On the contrary they do not react with N$_2$ probably because the P–Ni–P angle cannot widen out [3c, 16] to reach the values that have been calculated (118°) for Ni(PH$_3$)$_2$N$_2$ [17] and found (128°) for the {Ni(PCy$_3$)$_2$}$_2$N$_2$ complex [6].

The ^{31}P NMR spectrum of each Ni(dp) (C$_7$D$_8$ solution, 293 K) shows a single sharp peak which is shifted downfield compared with that of the corresponding free ligand (Table 1). These downfield shifts are possible due to both the coordination and chelation effects in our systems [18]. Unfortunately, to our knowledge, it is not possible to isolate Ni(0) complexes equivalent to the Ni(dp) compounds with the trialkylmonophosphines PMeCy$_2$ and PEtCy$_2$ and therefore it is not possible to estimate separately the effect of coordination and of chelation. The greater shift for Ni(dcpe) is consistent with that reported in the literature for five-membered chelate rings [18].

TABLE 1. ^{31}P data for Ni(dp) complexes (ppm)

	δ complex	δ free ligand	Δ = δ complex − δ free ligand	Chelate ring size
Ni(dcpe)	43.7	−6.6	50.3	5
Ni(dcpp)	24.6	−4.6	29.2	6
Ni(dcpb)	29.5	−4.3	33.8	7

TABLE 2. Absorption maxima (nm) [molar extinction]

Ni(dcpe)·C$_7$H$_8$	nujol		318(max)(s)	374(sh)(m)		492(m-w)	520(sh)
Ni(dcpe)	nujol		310; 316(max)(m)	378(sh)(m)		490(m-w)	520(sh)
Ni(dcpe)	n-heptane	292 [ϵ=2468]				470 [ϵ=1032]	520(sh) [ϵ=903]
Ni(dcpp)	nujol		312(max)(s)	375(sh)	408(sh)(m)	470(sh)(m-w)	500(sh, broad)
Ni(dcpp)	toluene		334	367	408(sh)		516(sh, br)
Ni(dcpb)	nujol		305(max, br)(s)	377(s)		490(sh)(m-w)	
Ni(dcpb)	toluene		330	364(sh)			520(sh)
Ni$_2$(dcpe)$_3$	nujol	280(vs)	300(vs)			484(s)	532(sh)
Ni$_2$(dcpe)$_3$	toluene		300 [ϵ=5049]			470 [ϵ=1078]	528(sh) [ϵ=735]
Ni(dcpe)$_2$	nujol	262(vs) 278(w)	301(s) 326(max)				
Ni(dcpe)$_2$	toluene		314 [ϵ=19238]				
Ni(dcpe)$_2$	n-heptane	262(sh) [ϵ=7744]	316 [ϵ=18362]				
Ni(depe)$_2$	toluene	294 [ϵ=9765]	316(sh) [ϵ=8415]	370(sh) [ϵ=842]			
Ni(depe)$_2$	nujol	271(s) 283(w)	300(sh)				
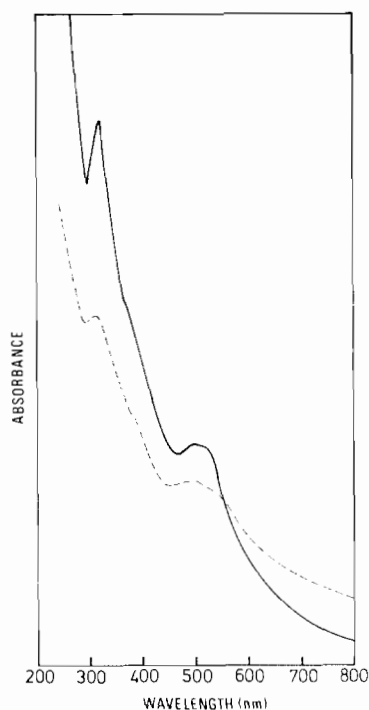
Fig. 1. Electronic absorption spectra (nujol mulls), molar absorbance on arbitrary scale: – – – Ni(dcpe); —— Ni(dcpe)·C$_7$H$_8$.

Fig. 2. Electronic absorption spectrum of a 3.1×10^{-3} M solution of Ni(dcpe) in n-heptane.

The UV–Vis spectra, both in the solid state (nujol mulls) and in solution, of the light brown Ni(dcpe)$_2$ and of the ivory Ni(depe)$_2$ (Table 2) do not show any absorption above 400 nm* and they are consistent with those reported [9c, 19] as characteristic of tetracoordinate Ni(0) complexes. In contrast with complexes of formula NiP$_4$ (P = P{CH$_2$CH$_3$}$_3$, P{CH$_2$CH$_2$CH$_2$CH$_3$}$_3$), which are largely dissociated in solution into tricoor-

dinate NiP$_3$ complexes and free phosphine [6, 9c], Ni(dcpe)$_2$ and Ni(depe)$_2$ are present in solution as tetracoordinated species.

A deep violet compound, obtained by reaction of nickelocene with dcpe, is reported [20] as Ni(dcpe)$_2$ in which one ligating site of the diphosphine ligand should not be coordinated to the metal, so that the nickel should be in fact tricoordinate. This compound is likely to be Ni$_2$(dcpe)$_3$ stemming from the incomplete reaction of the diphosphine with nickelocene.

*Except for a very weak absorption which can be observed at 540 nm ($\epsilon_{apparent}$=16.5) in concentrated n-heptane solution of Ni(depe)$_2$.
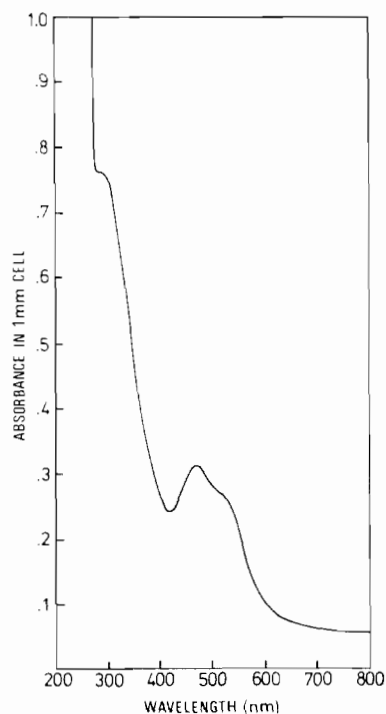
The presence of a strong absorption band at about 500 nm in nujol (Table 2) makes the UV–Vis spectrum of the violet $Ni_2(dcpe)_3$ consistent with those (reflectance) of solid $Ni(PCy_3)_3$ and $\{Ni(PCy_3)_2\}_2N_2$ [9c]. This suggests that, in the complex of formula $Ni_2(dcpe)_3$ in the solid state, the nickel atom is tricoordinated so that one diphosphine molecule has to bridge two adjacent metal atoms.

The UV–Vis spectra of both solid (nujol mulls) Ni(dcpe) and $Ni(dcpe)C_7H_8$ (Fig. 1 and Table 2) are pratically identical and they are just like that of Ni(dcpe) in n-heptane solution (Fig. 2 and Table 2). These observations suggest that the toluene molecule is not really coordinated and that the Ni(dcpe) complex possesses the same coordination number, i.e. geometry, both in solution and in the solid state.

The spectra (solid state and in solution) of this complex are quite similar to those of $Ni(PCy_3)_3$ and $\{Ni(PCy_3)_2\}_2N_2$ in benzene under argon [9c]. This observation confirms our previous proposal [9c] dealing with the solution state of those PCy_3 complexes, i.e. they dissolve to give, under argon, two-coordinated 14-electron Ni^0 species, quite different from the three-coordinated ones present in the solid state.

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