

## Synthesis and Characterisation of Nickel(II) Diphenylalkenylphosphine Complexes

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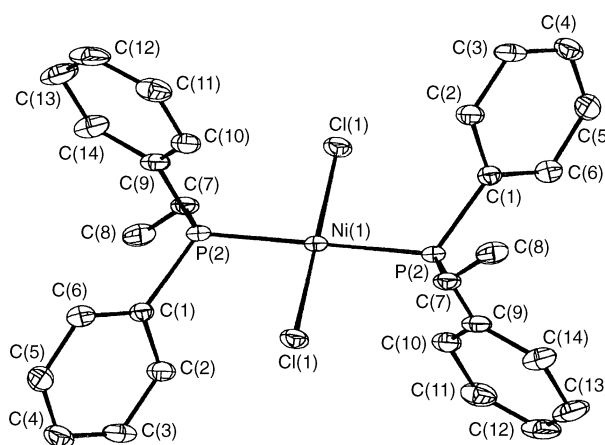
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Nickel(II) phosphine complexes are prepared with a series of diphenylalkenylphosphine ligands and characterised by single crystal X-ray diffraction and spectroscopic techniques.

The investigation of monodentate phosphine coordination by nickel(II) salts reported by Venanzi and co-workers remains a seminal illustration of the various influences which affect transition metal geometric isomerism. Although the coordination of numerous structurally diverse phosphine ligands has been considered since these early studies,<sup>3</sup> a detailed examination of the influence of alkene substituents within the tertiary phosphine ligand has not been undertaken. Thus, the following complexes have been prepared;  $[\text{NiX}_2(\text{PPh}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2)_2]$  ( $\text{X} = \text{Cl}, \text{NCS}$ ,  $n = 0, 1, 3$ ;  $\text{X} = \text{Br}$ ,  $n = 0, 1$ ), along with  $[\text{Ni}(\text{NCS})_2(\text{PPh}_2\text{R})_2]$  ( $\text{R} = \text{Me}, \text{Ph}, \text{CPh}=\text{CH}_2$ ).

$[\text{NiBr}_2(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  **1** and  $[\text{NiBr}_2(\text{PPh}_2\text{CH}_2\text{CH}=\text{CH}_2)_2]$  **2** have been studied in detail by Que and Pignolet and by Venanzi and coworkers, respectively.<sup>5,6</sup> <sup>1</sup>H NMR spectroscopy indicates **1** can exist in both square planar (**1a**) and tetrahedral (**1b**) forms,<sup>5</sup> but we have been able to isolate pure **1b** from polar media, in non-polar solvents mixtures **1a** and **1b** are always isolated. Square planar and tetrahedral **2a** and **2b** could be isolated from ethanol and glacial acetic acid, respectively.<sup>6</sup> The synthesis of these solid state isomers has been repeated; however, UV-VIS studies indicate significant proportions of paramagnetic materials which render the complexes unsuitable for high resolution NMR spectroscopic studies.

All the thiocyanate complexes exist in square planar geometries in both the solid state and in solution. <sup>1</sup>H NMR and IR spectra for the  $[\text{Ni}(\text{NCS})_2(\text{PPh}_2\text{R})]$  complexes [ $\text{R} = \text{CH}=\text{CH}_2$  **3**,  $\text{CH}_2\text{CH}=\text{CH}_2$  **4**,  $(\text{CH}_2)_3\text{CH}=\text{CH}_2$  **5**,  $\text{CPh}=\text{CH}_2$  **6**, Me **7**, Ph **8**] are indicative of non-bonding alkene functions and monodentate isothiocyanate bonding. Differences do exist in <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic shifts of both ligands and complexes as a function of R, Table 2. The former sees a range of shifts for diphenylalkenylphosphines lying between PPh<sub>3</sub> and PPh<sub>2</sub>Me, and moving upfield as a function of increasing chain length. The effect is derived from diamagnetic deshielding by the



**Fig. 2** X-Ray crystal structure of  $[\text{NiCl}_2(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$

alkene which is progressively negated by increasing chain length and its associated alkene free rotation. Upon complexation, all phosphine ligands in **3–8** undergo further deshielding, as a consequence of metal–ligand bonding. However, this effect is smallest in magnitude for the vinyl and  $\alpha$ -styrenyl substituted ligands in **3** and **6**. Although bonding descriptions involving d-orbitals appear unnecessary for coordinated and hypervalent p-block compounds in the light of theoretical calculations,<sup>7</sup> interaction between the alkene  $\pi$ -orbital and the phosphorus centre using s- and p-orbital bonding may be responsible for ameliorating the electron deficiency generated by coordination.

Chloride complexes  $[\text{NiCl}_2(\text{PPh}_2\text{R})_2]$  [ $\text{R} = \text{CH}=\text{CH}_2$  **9**,  $\text{CH}_2\text{CH}=\text{CH}_2$  **10**,  $(\text{CH}_2)_3\text{CH}=\text{CH}_2$  **11**] are isolated as square planar diamagnetic solids. However, whilst <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra are readily obtained for the thiocyanate complexes, the chlorides display complex variable temperature <sup>1</sup>H NMR spectra and poorly resolved or unobservable <sup>31</sup>P{<sup>1</sup>H} NMR spectra. Such properties are commonly associated with the establishment of solution equilibria leading to traces of paramagnetic tetrahedral material. Axial metal–ligand interactions are known in nominally square planar complexes, such as those in  $\text{PdI}_2(\text{PPh}_2\text{Me})_2$ .<sup>11</sup> However, such interactions can be excluded by the X-ray structural characterisation of  $[\text{NiCl}_2(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  **9**. The structure determination demonstrates that **9** exists in the solid state in a conventional square planar geometry with all nickel–vinyl distances exceeding the sum of the relevant covalent radii (Fig. 2). Comparable structurally characterised  $\text{NiCl}_2\text{P}_2$  square planar complexes are relatively few; however nickel-centred bond lengths and angles are similar to those obtained for the square planar clathrate form of  $[\text{NiCl}_2(\text{PPh}_3)_2]$ , Table 3.

**Table 2** <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic data for  $[\text{Ni}(\text{NCS})_2(\text{PPh}_2\text{R})_2]$  complexes **3–8**

Complex	R	Free ligand	$\delta_{\text{P}}$ (CDCl <sub>3</sub> )	
			Complex	Coordination shift (ppm)
<b>3</b>	CH = CH <sub>2</sub>	–10.8	6.2	17.0
<b>4</b>	CH <sub>2</sub> CH = CH <sub>2</sub>	–15.8	8.5	24.3
<b>5</b>	(CH <sub>2</sub> ) <sub>3</sub> CH = CH <sub>2</sub>	–17.8	11.8	29.6
<b>6</b>	CPh = CH <sub>2</sub>	–6.8	12.1	18.9
<b>7</b>	Me	–28.1	4.4	32.5
<b>8</b>	Ph	–5.9	13.3	19.2

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**Table 3** Selected bonds lengths (Å) and angles (°) for **9**

	[NiCl <sub>2</sub> (PPh <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub> ] <b>9</b>	[NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>
Ni-Cl	2.1653(8)	2.155(3)
Ni-P	2.244(2)	2.242(3)
Cl-Ni-P	91.75(5)	93.2(1)

<sup>a</sup>From ref. 12.

*Crystal Data for* [NiCl<sub>2</sub>(PPh<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>] **9**.— C<sub>28</sub>H<sub>26</sub>Cl<sub>2</sub>NiP<sub>2</sub>, *M* = 554.04, monoclinic, space group *P*2<sub>1</sub>/*n*<sub>1</sub>, *a* = 9.8397(13), *b* = 13.4937(5), *c* = 10.537(11) Å, β = 109.141(9)°, *V* = 1321.6(14) Å<sup>3</sup>, *D*<sub>c</sub> = 1.392 g cm<sup>-3</sup>, *T* = 120(2) K, *Z* = 2, μ(Mo-Kα) = 1.072 mmol, unique no. of observed data = 1963 [*I* > 2σ(*I*)], *R*<sub>1</sub> = 0.0422, *wR*<sub>2</sub> = 0.0990. Crystal dimensions 0.20 × 0.15 × 0.15 mm. Intensity data were recorded on a FAST TV area detector. The structure was solved by direct methods and refined by full matrix least squares on *F*<sup>2</sup>, with all non-hydrogen atoms being refined anisotropically.

Techniques used: <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, IR spectroscopy, X-ray diffraction

References: 17

Table 1: Characterisation data for complexes **1–11**Table 4: Bond distances for non-hydrogen atoms in **9**Table 5: Fractional coordinates for the crystallographically characterised **9**Table 6: Thermal parameters for non-hydrogen atoms in the crystallographically characterised **9**Table 7: Bond angles for non-hydrogen atoms in **9**Figure 1: Schematic representation of **9** <sup>1</sup>H NMR spectra at 25 °C and -65 °C in C<sub>7</sub>D<sub>8</sub>

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