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Tetrakis(trimethylphosphine)nickel(0) *

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Abstract

The title complex, $[Ni(PMe_3)_4]$, has been prepared by metal-vapour synthesis, and characterized by ^1H, ^{13}C, ^{31}P, and ^{61}Ni NMR spectroscopy and ultraviolet photoelectron (PE) spectroscopy. The ^{61}Ni NMR spectrum exhibits a quintet $\{^1J(NiP)$ 285 Hz$\}$, and the t_2 and e ionization energies occur at 5.60 and 6.52 eV, the lowest yet observed for a nickel(0) complex.

The direct synthesis of homoleptic metal phosphine complexes from metal atoms and an excess of phosphine, giving yields of 50% or better based on the metal used, is well established {e.g. $[Mo(PMe_3)_6]$ [1,2] or $[M(dmpe)_3]$ (dmpe = 1,2-bis(dimethylphosphino)ethane; M = Cr, Mo, W, V, Nb, or Ta) [3,4]}. It has been previously reported [4,5] that the nickel(0) complex tetrakis(trimethylphosphine)-nickel(0), $[Ni(PMe_3)_4]$, can also be prepared by metal-vapour synthesis, but no experimental details were given. We report here full details of the synthesis of tetrakis(trimethylphosphine)nickel(0) by the direct reaction of nickel metal and trimethylphosphine, its isolation, and its characterization using ^1H, ^{13}C, ^{31}P, and ^{61}Ni NMR spectroscopy and ultraviolet photoelectron (PE) spectroscopy.

Experimental

All operations, unless otherwise stated, were performed under dry dinitrogen, either using conventional Schlenk techniques or in a Miller–Howe inert atmosphere box ($<$ 5 ppm H_2O, $<$ 1 ppm O_2). Trimethylphosphine was prepared by a modification of Schmidbaur's procedure [6]. Nickel metal (99.9%, ex. Koch-Light) was vacuum melted before use in the co-condensation experiments (in a separate

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operation). Butoxybutane and light petroleum (b.p. 40–60 °C) were distilled from sodium-potassium alloy under dry dinitrogen, and ethanenitrile was distilled from phosphorus(V) oxide under dry dinitrogen; all other solvents used were of spectroscopic grade and were dried on a column of type 4A molecular sieve. The design of the metal-vapour synthesis apparatus has been described elsewhere [7].

All NMR spectra were obtained at room temperature, using C_6D_6 (previously dried over 4A molecular sieve) as solvent, with a Bruker WM-360 spectrometer. All chemical shifts are defined as positive to low field (high frequency) of the reference compound or frequency. Proton and ^{13}C chemical shifts were measured relative to tetramethylsilane, ^{31}P chemical shifts were measured relative to trimethylphosphite and solvent corrected, and ^{61}Ni chemical shifts were measured as discussed. The photoelectron spectra were recorded on a Perkin–Elmer PS16 spectrometer that has been modified to enable He-II spectra to be obtained. The samples were loaded within an argon-filled glove bag. Sufficient vapour pressure to obtain PE spectra was achieved by heating the sample to a lamp temperature of 115 °C and calibration of the spectra was achieved by simultaneous admission of xenon (12.130 eV), and with reference to the helium self-ionization peak (4.991 eV).

Preparation of trimethylphosphine. Butoxybutane (800 cm^3) and magnesium turnings (105 g) were placed in a three-necked flask (3 l) fitted with a stirrer, funnel, water condenser, and dry ice condenser with gas inlet. Iodomethane (560 g) was added gradually over a period of approximately 7 h, during which time it was necessary to cool the flask in a water bath. The mixture was stirred overnight to yield a black, viscous solution containing an excess of magnesium. Triphenylphosphite (310 g) and butoxybutane (ca. 70 cm^3) were then added, over a period of one hour, to the solution (cooled in an ice bath), and this was then allowed to warm up to room temperature overnight to give a viscous grey mixture. The contents of the flask were then heated under reflux (using the −78 °C condenser) for 90 min, and the liquid formed was then removed by distillation, collecting the fraction which boiled below 50 °C. This distillate was then fractionally distilled using a Vigreux column, collecting the fraction boiling in the range 38–40 °C. Finally, the isolated trimethylphosphine (1·25 g) was purified by vacuum distillation immediately prior to use.

Preparation of tetrakis(trimethylphosphine)nickel(0). In a typical experiment, nickel atoms (3.1 g, 0.05 mol) were evaporated from a premelted ingot (10.7 g) at ca. 1.17 kW (4.5 kV at 260 mA) and co-condensed with trimethylphosphine (30 cm^3) over a period of 2 h. The apparatus was allowed to warm to room temperature under dinitrogen, whence the excess of trimethylphosphine was removed by continuous evacuation. The walls of the reaction vessel were washed with light petroleum (b.p. 40–60 °C; ca. 500 cm^3) and the resultant brown solution was immediately filtered through Celite® to remove the excess of unreacted nickel. The removal of solvent in vacuo, followed by double recrystallization from hot ethanenitrile, yielded tan coloured $[Ni(PMe_3)_4]$ (ca. 10 g, ca. 55%).

Results and discussion

Synthesis

Nickel(0) complexes are known to exist with a wide range of ligands, including those containing Group 15 atoms and alkenes. They have justly received a lot of attention, particularly for their potential catalytic activity and for their ability to undergo oxidative addition reactions with, for example, organic halides [8]. Previously, phosphine complexes of nickel(0) have been prepared by ligand displacement reactions [9], for example by treating bis(cycloocta-1,5-diene)nickel(0) with an excess of a phosphine [10]. The preparation presented here represents a simple, high yield procedure for $[Ni(PMe_3)_4]$.

Nuclear magnetic resonance studies

Each of the nuclei in $[Ni(PMe_3)_4]$ possess an isotope with a nuclear spin, and hence the complex (in C_6D_6 solution) has been examined by ^1H, ^{13}C, ^{31}P, and ^{61}Ni NMR spectroscopy.

Nickel-61 NMR spectroscopy. For highly symmetrical structures (e.g. T_d or D_{4h}), where the quadrupolar effect of the ^{61}Ni nucleus is minimized, ^{61}Ni NMR spectroscopy is capable of providing an effective means of studying diamagnetic nickel(0) complexes. Despite this fact, the range of compounds investigated to date using this technique has been small [11–13]. This is, perhaps, surprising since the natural abundance of the magnetically susceptible nucleus (1.13%; $I = 3/2$) and its relative receptivity ($D_c = 0.24$) [14] make the metal quite amenable to NMR studies using modern instrumentation. However, for less symmetrical systems, it remains to be seen how the lowering of symmetry affects the observed line widths. Drain [15] proposed the use of tetracarbonylnickel(0) as a standard for ^{61}Ni NMR spectroscopy (its T_d configuration gives low quadrupole broadening while, being a liquid, favourable relaxation times can be obtained without recourse to the use of solvents which would otherwise reduce the effective concentration of ^{61}Ni nuclei, 9.2×10^{-2} mol l^{-1}), and subsequent workers [11,12] have adopted this recommendation. The absolute resonance frequency of ^{61}Ni in $[Ni(CO)_4]$ has been previously determined at 8.936050 MHz (relative to the resonance of the protons in

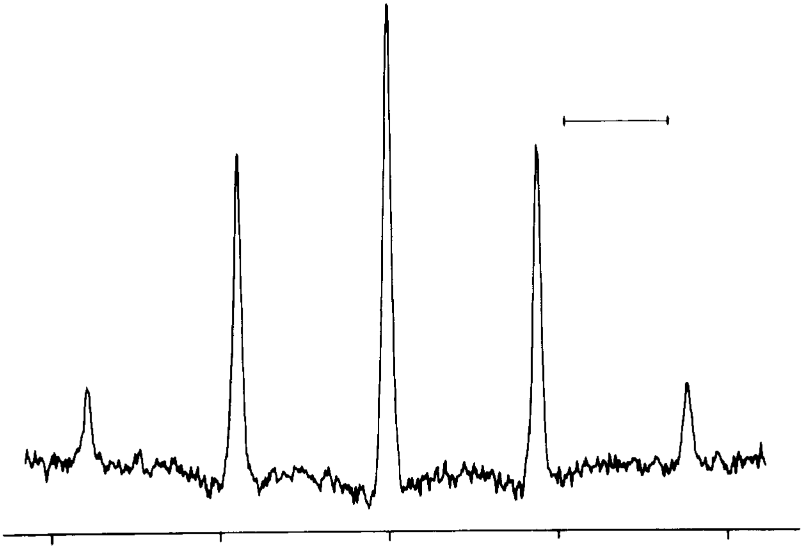

Fig. 1. The ^{61}Ni NMR spectrum of $[Ni(PMe_3)_4]$ in C_6D_6. The bar (|———|) represents 200 Hz.

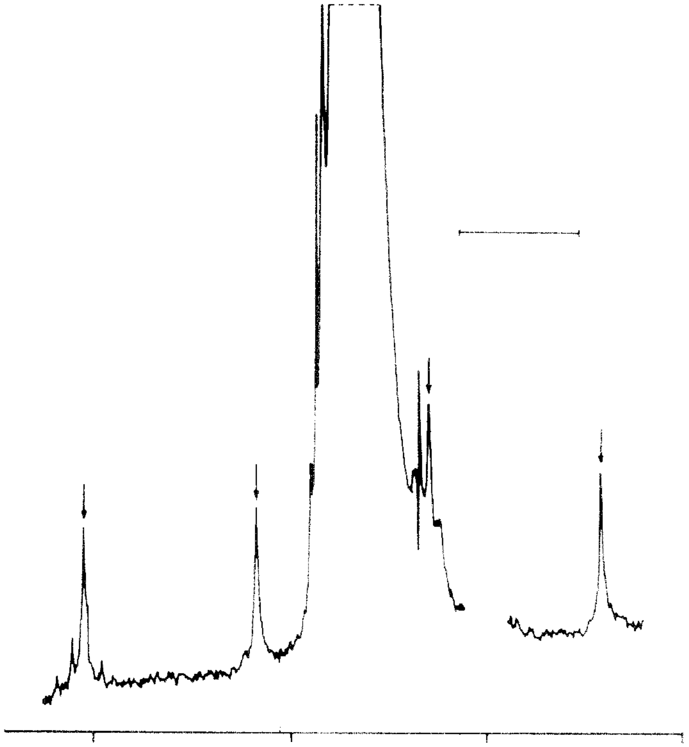

Fig. 2. The $^{31}P\{^{1}H\}$ NMR spectrum of $[Ni(PMe_3)_4]$ in C_6D_6. The arrows (↓) indicate the nickel-61 satellites, and the bar (|———|) represents 200 Hz.

$[Si(CH_3)_4]$ at 100 MHz) [12]. Because of the obvious difficulties in handling such a highly toxic and volatile material, we recommend that all subsequent ^{61}Ni chemical shifts can be referred to this absolute value, thus obviating the need to handle $[Ni(CO)_4]$. This parallels the practice, recommended by Goodfellow (see Appendix (iii) of ref. 16) of referencing ^{195}Pt to an absolute frequency of 21.4 MHz on an instrument for which $[Si(CH_3)_4]$ resonates at exactly 100.00 MHz.

The ^{61}Ni NMR spectrum of $[Ni(PMe_3)_4]$ (see Fig. 1) consists of a quintuplet, $^{1}J(NiP)$ 285 Hz, corresponding to coupling between ^{61}Ni ($I = 3/2$) and ^{31}P ($I = 1/2$), at an absolute frequency of 8.9512529 MHz (relative to the resonance of the protons in $[Si(CH_3)_4]$ at 100.000 MHz), and hence with a chemical shift of + 131.2 ppm. Comparison of this value with those obtained for other nickel(0) complexes [11–13] indicates that it is well within the range that would be expected. The well-defined spectrum indicates that the complex does not undergo dissociation in benzene on the NMR time scale.

Phosphorus-31 NMR spectroscopy. There has, as yet, been no report of an observation of $^{31}P/^{61}Ni$ satellites in the ^{31}P spectrum of a nickel(0) complex. The ^{31}P spectrum of $[Ni(PMe_3)_4]$ (Fig. 2) revealed initially a strong singlet at 162.62 ppm. With increased accumulation time, the presence of additional fine structure attributable to ^{61}Ni satellites was observed ($^{1}J(NiP)$ 285 Hz). This is the first time that direct evidence of ^{61}Ni–^{31}P coupling has been observed in this manner.

Proton NMR spectroscopy. The proton spectrum revealed a singlet, corresponding to the methyl protons, at δ 1.167 ppm, compared with 1.23 ppm for the free ligand. As expected, the Ni–P bonding has only a minor effect on the methyl proton signal, a small upfield shift being observed.

Carbon-13 NMR spectroscopy. A single quintuplet was observed at 25.20 ppm $\{J'(\mathrm{CP})$ 8.67 Hz; $^1J(\mathrm{CP}) \simeq 17.34$ Hz [16]$\}$, corresponding to virtual coupling of the methyl carbon atoms to the four equivalent phosphorus atoms. The presence of Ni–P bonding in the complex had a small but noticeable effect on the position of the methyl carbon signal, a downfield shift of 8.1 ppm being measured with respect to the free ligand (δ 17.1 ppm, $^1J(\mathrm{CP})$ 13.5 Hz [17]).

Photoelectron spectroscopic study of [Ni(PMe$_3$)$_4$]

The He-I photoelectron spectrum of [Ni(PMe$_3$)$_4$] is depicted in Fig. 3, and the ionization energies and assignments of the bands in the spectrum are summarized in Table 1. The assignments of the spectra were made on the basis of group theoretical considerations and by analogy with the literature assignments of [Ni(PF$_3$)$_4$] [18–20] and [Ni(CO)$_4$] [21,22]. These last two molecules have received considerable attention from a variety of groups and, although there was initial conflict [18,19] over the precise assignment of the spectrum of [Ni(PF$_3$)$_4$], widely accepted assignments of their photoelectron spectra have now been achieved [20].

The two low ionization energy bands (A and B; see Fig. 3) of all three molecules are very similar in profile, but are markedly different in the ionization energy range

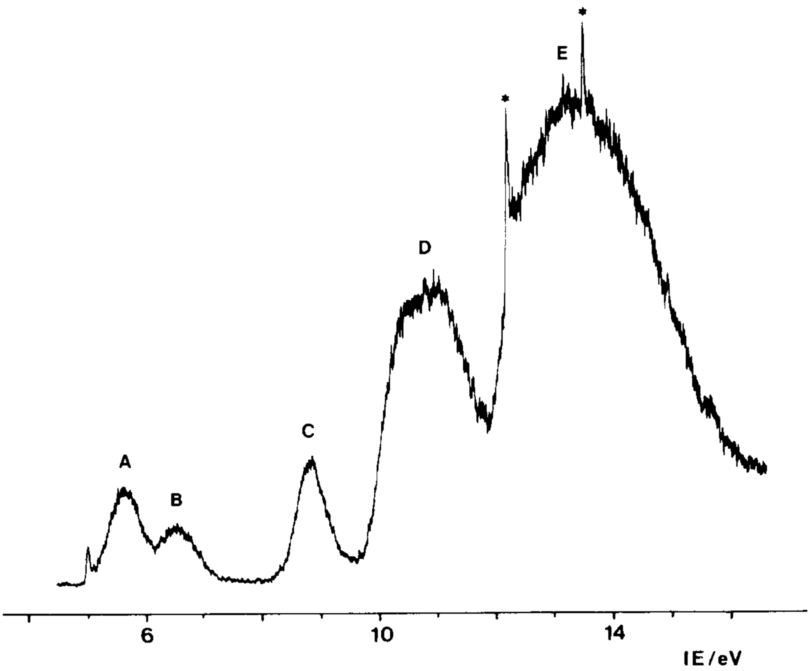

Fig. 3. The He-I PE spectrum of [Ni(PMe$_3$)$_4$]. The peaks marked with an asterisk are due to the xenon calibration gas.

Table 1

Vertical ionization energies and assignments of the photoelectron spectra of $[\mathrm{Ni(PMe_3)_4}]$

Band	Ionization energy (eV)	Assignment
A	5.60	t_2 (metal-based)
B	6.52	e (metal-based)
C	8.76	t_2
D	10.80	
E	13.13	

they encompass. In each case these bands are attributed to ionization from the t_2 (A) and e (B) nickel-based $3d$ orbitals, which are fully occupied in the neutral molecule (the local symmetry at the metal centre is assumed to be T_d). The ionization energies of bands A and B in $[\mathrm{Ni(PMe_3)_4}]$ are compared with the values for the respective bands in the carbonyl and trifluorophosphine analogues in Table 2. The weighted mean [23] of the first two ionization energies of $[\mathrm{Ni(PMe_3)_4}]$ is 3.28 eV below that of $[\mathrm{Ni(CO)_4}]$, 4.14 eV below that of $[\mathrm{Ni(PF_3)_4}]$, and 1.67 eV below that of free nickel atoms. These observations demonstrate that $[\mathrm{Ni(PMe_3)_4}]$ is extremely electron-rich, and rationalize its high reactivity (it is spontaneously inflammable in air). The excess of electron density at the metal cannot be reduced to any significant extent by π back-bonding, in line with the empirical order for this effect: $\mathrm{PF_3} > \mathrm{CO} \gg \mathrm{PMe_3}$. However, the energy differences, $E_B - E_A$, show very little change (see Table 2), and decrease in the order $\mathrm{PF_3} > \mathrm{PMe_3} > \mathrm{CO}$, indicating (as first emphasized by Hamnett and coworkers [24]) that this energy difference cannot be equated with the spectroscopically determined ligand field parameter, Δ, although such comparisons have been made elsewhere [25].

Under T_d symmetry, the HOMOs of four trimethylphosphine molecules combine to give orbitals of t_2 and a_1 symmetry, which become Ni–P σ-bonding in the complex. By analogy with the assignment for the PE spectrum of $[\mathrm{Ni(PF_3)_4}]$ [20], band C (8.76 eV) in the spectrum of $[\mathrm{Ni(PMe_3)_4}]$ is attributed to ionization from the t_2 orbitals: ionization from the a_1 orbital is believed to contribute towards band D. The difference in first ionization energy of free trimethylphosphine (8.62 eV) [26] and band C of $[\mathrm{Ni(PMe_3)_4}]$ is only 0.14 eV, much smaller than the corresponding energy difference (0.89 eV) for trifluorophosphine [27] and $[\mathrm{Ni(PF_3)_4}]$ [20], indicating that the metal–ligand σ interaction in $[\mathrm{Ni(PMe_3)_4}]$ is also weak. Assuming the validity of Koopmans' theorem, the interaction diagram reported [20] for $[\mathrm{Ni(PF_3)_4}]$ is also valid for $[\mathrm{Ni(PMe_3)_4}]$.

Table 2

Comparison of the vertical ionization energies, weighted means and energy differences of the two lowest energy bands in the photoelectron spectra of $[\mathrm{NiL_4}]$ (L = $\mathrm{PMe_3}$, CO or $\mathrm{PF_3}$)

L	E_A (eV)	E_B (eV)	$\bar{E}$ (eV) [a]	$(E_B - E_A)$ (eV)	Ref.
$\mathrm{PMe_3}$	5.60	6.52	5.97	0.92	This work
CO	8.90	9.77	9.25	0.87	19
$\mathrm{PF_3}$	9.69	10.74	10.11	1.05	20

[a] Weighted mean of the A and B ionization energies, $(3E_A + 2E_B)/5$.

The remaining bands (D and E) in the PE spectrum of [Ni$(PMe_3)_4$] are similar in profile and ionization energy to the high energy bands in the PE spectrum of PMe_3 [26], suggesting that the lower lying orbitals of the ligands are relatively little affected by the proximity of the nickel atom.

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