metal-organic compounds

Chlorobis(triphenylphosphine)nickel(I)

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Crystals of the title compound, $[NiCl(C_{18}H_{15}P)_2]$, contain one molecule per asymmetric unit with no short intermolecular interactions. This is noteworthy since previous studies have reported that the formally 15-electron species oligomerizes in the solid state. The nickel(I) centre has a distorted trigonal–planar coordination geometry, the origin of which is suggested to be electronic in nature.

Comment

Although little evidence has been presented to confirm the existence of a nickel(II)–boryl compound, nickel(0) (Suginome *et al.*, 1998) and nickel(II) (Gridnev *et al.*, 1993) complexes have been shown to catalyse certain alkyne boration reactions by mechanisms which are proposed to involve such species. As part of our continuing studies into the syntheses of transition metal–boryl complexes, we therefore attempted a direct stoichiometric preparation. The reaction between *B*-chlorocatecholborane and bis(triphenylphosphine)(ethene)nickel(0) failed to afford the desired oxidative–addition product, instead yielding chlorobis(triphenylphosphine)nickel(I), (I), and chlorotris(triphenylphosphine)-nickel(I) as part of a product mixture (Whittell, 2000).
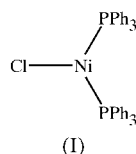
Complexes of nickel(I) are far less numerous than those of either nickel(0) or nickel(II), with most of those isolated as solids containing phosphine or arsine ligands (Sacconi *et al.*, 1987). Of those containing halide ions and monodentate phosphines, only $[NiX(PPh_3)_3]$ (X = Cl, Br) had been characterized by X-ray crystallography prior to this study (Cassidy & Whitmire, 1991; Mealli *et al.*, 1983). These compounds dissociate in benzene solution to afford the title compound (Heimbach, 1964) or its bromide analogue (Porri *et al.*, 1967), respectively, in addition to free triphenylphosphine. While this manuscript was in preparation, a new polymorph of $[NiCl(PPh_3)_3]$ was reported, along with the crystal structure of

a tetrahydrofuran (THF) solvate of (I) (Ellis & Spek, 2000). The latter contains no short intermolecular interactions. Although not characterized crystallographically, other compounds of the formulation $[NiX(PR_3)_2]$ have been studied by different analytical techniques, but these compounds are reported to be either oligomeric (X = Cl, Br; R = Ph; Lappert & Speier, 1974; Cundy & Nöth, 1971) or dimeric with a square-planar configuration [X = Cl, Br; R = cyclohexyl (Cy); Aresta *et al.*, 1975] in the solid state.

Consistent with the findings of Ellis & Spek (2000), complex (I) is monomeric in the crystal, with the nickel(I) coordination geometry being best described as distorted trigonal–planar (Fig. 1). This is particularly noteworthy as the formally 15-electron species might well be expected to oligomerize, as previously suggested (Lappert & Speier, 1974). The Ni—Cl bond length [2.1666 (6) Å; Table 1] is comparable to that observed in $[NiCl(PPh_3)_2]\cdot$THF [2.1481 (6) Å], but significantly shorter than in both polymorphs of $[NiCl(PPh_3)_3]$ [2.2785 (9) and 2.2933 (17) Å; Cassidy & Whitmire, 1991; Ellis & Spek, 2000]. The Ni—P distances [2.2536 (5) and 2.2393 (5) Å] and Cl—Ni—P angles [123.56 (2) and 121.12 (2)°] in (I) differ significantly from one another, and are also different to the corresponding parameters in $[NiCl(PPh_3)_2]\cdot$THF [2.2091 (6) and 2.2012 (6) Å, and 126.98 (2) and 121.33 (2)°, respectively], which also has crystallographically independent triphenylphosphine ligands. This distortion of the trigonal plane is consistent with the chemical inequivalence of the phosphorus nuclei as suggested by electron spin resonance studies on a single crystal of [CuBr-$(PPh_3)_2$] doped with (I) (Nilges *et al.*, 1977). A distorted trigonal–planar geometry is also apparent in [Ni{N(Si-Me_3)_2}(PPh_3)_2] (Bradley *et al.*, 1972), although the Ni—P bond lengths [2.220 (4) and 2.213 (4) Å] are equivalent. These, however, are significantly shorter than those in (I) and longer than those in $[NiCl(PPh_3)_2]\cdot$THF. Nonetheless, common to all
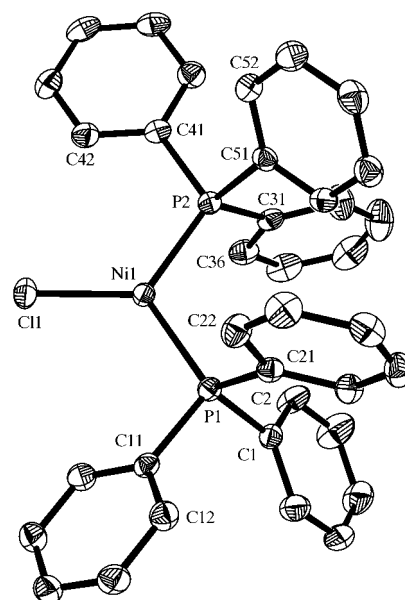

Figure 1
The molecular structure of the title compound with ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

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three complexes is a contraction of the P—Ni—P angle relative to the ideal value (120°); 114.94 (2), 111.52 (2) and 107.0 (2)° for (I), [NiCl(PPh$_3$)$_2$]·THF and [Ni{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$], respectively. A review article by Eller *et al.* (1977) inferred this to mean, in the case of the Ni^{I}–amide complex, that the amide was of larger steric bulk than the triphenylphosphine ligands, an assertion which is not consistent with the presence of this same structural feature in both (I) and [NiCl(PPh$_3$)$_2$]·THF. Consideration of steric factors alone would predict a P—Ni—P angle for all three complexes greater than 120°, as observed for the P—Cu—P angle [126.0 (1)°] in the copper(I) bromide analogue, [CuBr(PPh$_3$)$_2$] (Davis *et al.*, 1973), the molecular structure of which would be expected to be determined solely by steric effects on account of the d^{10} electron configuration at copper. The angular distortion most probably arises from a first-order Jahn–Teller effect which, for a d^9 metal complex, is expected to destabilize an ML_3 structure from D_{3h} to C_{2v} symmetry (Albright *et al.*, 1985).

Experimental

All manipulations were conducted under an atmosphere of dry dinitrogen or *in vacuo*, using standard glove-box techniques. The solvents were dried over sodium and distilled under dinitrogen immediately prior to use. ClB(cat) (cat is 1,2-O$_2$C$_6$H$_4$) was purchased from commercial sources and used without further purification. [Ni(η-C$_2$H$_4$)(PPh$_3$)$_2$] was prepared in accordance with the literature (Schramm & Ibers, 1980). A solution of ClB(cat) (0.013 g, 0.084 mmol) in toluene (*ca* 1 ml) was prepared in a small sample vial and then transferred to a similar vessel containing [Ni(η-C$_2$H$_4$)(PPh$_3$)$_2$] (0.046 g, 0.076 mmol). After *ca* 5 min at room temperature, a cloudy dark-green solution resulted. Hexane (*ca* 4 ml) was then added to the reaction mixture, resulting in the formation of a dark-green precipitate. This was allowed to settle prior to removal and filtration of the orange mother liquor. The mother liquor was concentrated *in vacuo* to afford an orange oil, which was further diluted with toluene (*ca* 1 ml) and transferred to a small Schlenk tube. A hexane overlayer was added which, upon slow solvent diffusion at 251 K, afforded yellow crystals of (I) and orange crystals of [NiCl(PPh$_3$)$_3$]. The latter were shown by X-ray crystallography to be isomorphous with the polymorph reported by Ellis & Spek (2000).

Crystal data

[NiCl(C$_{18}$H$_{15}$P)$_2$]	$D_x = 1.388$ Mg m^{-3}
$M_r = 618.70$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8192
$a = 11.0778$ (11) Å	reflections
$b = 17.535$ (2) Å	$\theta = 2$–25°
$c = 15.4159$ (18) Å	$\mu = 0.88$ mm^{-1}
$\beta = 98.722$ (8)°	$T = 173$ (2) K
$V = 2960.0$ (6) Å^3	Plate, yellow
$Z = 4$	$0.40 \times 0.25 \times 0.12$ mm

Table 1
Selected geometric parameters (Å, °).

Ni1—Cl1	2.1666 (6)	Ni1—P1	2.2536 (5)
Ni1—P2	2.2393 (5)		
Cl1—Ni1—P1	121.12 (2)	P1—Ni1—P2	114.94 (2)
Cl1—Ni1—P2	123.56 (2)		

Data collection

Bruker SMART CCD area-detector diffractometer	6788 independent reflections
ω scans	4961 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.035$
(*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$
$T_{min} = 0.720$, $T_{max} = 0.924$	$h = -8 \rightarrow 14$
18 753 measured reflections	$k = -22 \rightarrow 22$
	$l = -20 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{max} = 0.001$
6788 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
361 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}

H atoms were constrained to idealized geometries at a distance of 0.95 Å from their parent C atoms and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1484). Services for accessing these data are described at the back of the journal.

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