Table 1. *Crystallographic summary for* $NiBr_2(Ph_3AsO)_2$

Data collection[a,b]	
Mode	θ–2θ
Scan rate (° min^{-1})	1·9–6·7
θ range (°)	0—22
Range of *hkl*	$0 \le h \le 19$, $0 \le k \le 11$, $0 \le l \le 18$
Unique reflections	2209
Crystal dimensions approx. (mm)	0·08 × 0·18 × 0·30
Structure refinement[c,d]	
Reflections used [$I > 2\sigma(I)$]	724
Number of variables	126
R, *wR*	0·059, 0·061
S	0·75
Max. shift/e.s.d.	0·1
Max., min. density in difference map (e Å^{-3})	0·55, −0·53

(*a*) Unit-cell parameters by least-squares refinement of the setting angles of 23 reflections with $10 < \theta < 22°$.

(*b*) Enraf–Nonius CAD-4 diffractometer with graphite monochromator was used. Standard reflections showed no significant variation.

(*c*) The intensities were corrected for Lp and for absorption: min. and max. values 0·85–1·02 (Walker & Stuart, 1983).

(*d*) Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0{\cdot}0075|F_o|^2$.

Table 2. *Fractional atomic coordinates and isotropic temperature factors* (Å^2) *(only two* C *atoms for each rigid phenyl ring are given)*

	x	*y*	*z*	B_{iso}
Br(1)	0·4470 (3)	0·6576 (5)	0·4263 (7)	5·8 (2)
Br(2)	0·4620 (3)	1·0272 (5)	0·3441 (7)	5·1 (2)
Ni	0·4762 (3)	0·8070 (6)	0·3285 (7)	3·7 (2)
As(1)	0·6208 (2)	0·7067 (5)	0·2423 (7)	3·7 (2)
As(2)	0·3572 (2)	0·8114 (5)	0·1875 (7)	3·3 (2)
O(1)	0·577 (2)	0·783 (3)	0·310 (2)	5·0 (8)
O(2)	0·430 (2)	0·756 (3)	0·230 (2)	5·7 (9)
C(111)	0·281 (1)	0·840 (3)	0·256 (2)	4 (1)
C(112)	0·221 (1)	0·908 (3)	0·231 (2)	5 (1)
C(121)	0·371 (1)	0·963 (2)	0·133 (2)	2·4 (9)
C(122)	0·365 (1)	1·081 (2)	0·168 (2)	6 (1)
C(131)	0·333 (2)	0·682 (3)	0·115 (2)	5 (1)
C(132)	0·264 (2)	0·665 (3)	0·087 (2)	5 (1)
C(211)	0·583 (1)	0·546 (2)	0·226 (2)	6 (1)
C(212)	0·561 (1)	0·475 (2)	0·289 (2)	7 (1)
C(221)	0·630 (2)	0·803 (3)	0·152 (2)	4 (1)
C(222)	0·692 (2)	0·803 (3)	0·108 (2)	5 (1)
C(231)	0·713 (1)	0·673 (3)	0·277 (2)	4 (1)
C(232)	0·752 (1)	0·565 (3)	0·261 (2)	5 (1)

Table 3. *Selected interatomic distances* (Å) *and angles* (°)

Br(1)—Ni	2·39 (1)	As(1)—C(221)	1·88 (3)
Br(2)—Ni	2·364 (8)	As(1)—C(231)	1·87 (2)
Ni—O(1)	1·94 (3)	As(2)—O(2)	1·66 (3)
Ni—O(2)	2·00 (3)	As(2)—C(111)	1·89 (3)
As(1)—O(1)	1·65 (3)	As(2)—C(121)	1·88 (3)
As(1)—C(211)	1·87 (3)	As(2)—C(131)	1·92 (3)

Br(1)—Ni—Br(2)	123·1 (5)	C(211)—As(1)—C(231)	103 (1)
Br(1)—Ni—O(1)	105 (1)	C(221)—As(1)—C(231)	107 (1)
Br(1)—Ni—O(2)	109 (1)	O(2)—As(2)—C(111)	114 (1)
Br(2)—Ni—O(1)	105 (1)	O(2)—As(2)—C(121)	114 (1)
Br(2)—Ni—O(2)	108 (1)	O(2)—As(2)—C(131)	104 (1)
O(1)—Ni—O(2)	104 (1)	C(111)—As(2)—C(121)	107 (1)
O(1)—As(1)—C(211)	111 (1)	C(111)—As(2)—C(131)	110 (1)
O(1)—As(1)—C(221)	112 (1)	C(121)—As(2)—C(131)	108 (1)
O(1)—As(1)—C(231)	109 (1)	Ni—O(1)—As(1)	132 (1)
C(211)—As(1)—C(221)	114 (1)	Ni—O(2)—As(2)	130 (1)

zation were reported. At that time it was not possible to produce single crystals of the blue complex. The present crystals were of poor diffracting quality and did not allow measurements of data with a resolution good enough to perform anisotropic refinements for all the non-H atoms and for accurate calculation of distances and angles. Nevertheless, the main aim of the present study could still be achieved, namely the unambiguous determination of the (somewhat distorted) tetrahedral coordination around the Ni ion.

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Structure of a Bis{[(2,3-η,$\kappa P'$)-1,2-diphospha-2-propene]nickel}

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Abstract. Bis[μ-(3,4-η,κP^5)-5-chloro-2,2,6,6-tetramethyl-3-phenyl-4,5-diphospha-2-silahept-3-ene]bis[carbonylnickel(0)], $C_{30}H_{46}Cl_2Ni_2O_2P_4Si_2$, M_r = 807·0, monoclinic, $P2_1/c$, a = 18·418 (4), b = 10·697 (3), c = 21·080 (7) Å, β = 102·32 (2)°, V = 4057 Å^3, Z = 4, D_x = 1·32 Mg m^{-3}, λ(Mo $K\alpha$) =

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0·71069 Å, $\mu = 1{\cdot}30\ mm^{-1}$, $F(000) = 1680$, $T = 298$ K, $R = 0{\cdot}052$ for 3407 observed reflections. The structure determination revealed an 'anti-parallel' arrangement of two PPCNi(CO) moieties. Thereby, each Ni atom adopts a 16 valence electron configuration being σ coordinated by the phosphino-fragment of one diphosphapropene and η^2 coordinated by the π system (E configuration) of the second phosphino-methylenephosphane. The molecular structure is similar to the structure found for the analogous molecule $[Ph_2P—P{=}C(SiMe_3)_2]_2[Ni(CO)]_2$ [Appel, Casser & Knoch (1985). *J. Organomet. Chem.* **297**, 21–26].

Experimental. The title compound was prepared by the reaction of 1-chloro-1-*tert*-butyl-3-phenyl-3-trimethylsilyl-1,2-diphospha-2-propene (Appel, Kündgen & Knoch, 1985) and $Ni(CO)_4$ in diethyl ether solution at 253 K (Bruder, 1990). The crystals are yellow prisms. A crystal with a size of 0·15 × 0·30 × 0·35 mm was used. X-ray data were measured on a Nicolet *R3m* four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The ω-scan mode was used (scan rate 4·0–29·3° min^{-1}, depending on intensity). The cell constants were determined by least-squares fit of 24 reflections in the range $20 < 2\theta < 25°$. The intensities of 7172 reflections were measured ($2\theta_{max} = 48°$). Three check reflections showed no significant intensity variation (2·0%). The data were averaged to 6367 unique reflections ($R_{int} = 0{\cdot}012$, h −21→20, k 0→12, l 0→24), 3407 of which, with $F > 4\sigma(F)$, were used for all calculations (*SHELXTL*, Sheldrick, 1978; *SHELXTL-Plus*, Sheldrick, 1989). Absorption and extinction corrections were not necessary, but 13 low-angle reflections were ignored during refinement. The structure was solved by direct methods. Full-matrix least-squares refinement on F_o converged to $R = 0{\cdot}052$, $wR = 0{\cdot}046$, and $S = 1{\cdot}22$. All the non-H atoms had anisotropic displacement parameters. All the H atoms were found in a $\Delta\rho$ map, but were refined using a riding model and idealized geometry [U(H) = 1·2 U_{eq}(C)]. A total of 379 parameters were refined, weighting scheme $w^{-1} = \sigma^2(F_o) + 0{\cdot}0003F_o^2$, which led to a featureless analysis of variance of terms of $\sin\theta$ and F_o, a max. value $\Delta/\sigma = 0{\cdot}002$, and max. and min. heights in final $\Delta\rho$ map = 0·38 and −0·36 e $Å^{-3}$, respectively. Atomic scattering factors were those stored in *SHELXTL* and *SHELXTL-Plus* which were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are given in Table 1,* selected bond distances and angles in Table 2. Fig. 1 shows a plot with the atom numbering and Fig. 2 the conformation of the Ni_2P_4 ring.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å² × 10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni(1)	1731 (1)	663 (1)	4446 (1)	48 (1)
C(1')	789 (5)	153 (8)	4236 (4)	77 (4)
O(1')	202 (3)	−166 (7)	4083 (4)	136 (4)
P(1)	2556 (1)	2144 (2)	4809 (1)	51 (1)
P(2)	3202 (1)	2372 (2)	4036 (1)	53 (1)
C(1)	1600 (3)	2529 (6)	4517 (3)	51 (3)
Si(1)	1166 (1)	2903 (2)	5229 (1)	69 (1)
C(1*A*)	139 (4)	2928 (9)	4960 (4)	108 (5)
C(1*B*)	1440 (4)	1696 (8)	5872 (3)	86 (4)
C(1*C*)	1501 (5)	4433 (8)	5602 (4)	116 (5)
C(11)	1272 (4)	3084 (8)	3859 (4)	55 (3)
C(12)	1204 (4)	2401 (9)	3296 (4)	85 (4)
C(13)	905 (6)	2910 (13)	2699 (5)	118 (6)
C(14)	657 (6)	4132 (15)	2639 (6)	126 (7)
C(15)	724 (5)	4812 (10)	3196 (6)	105 (5)
C(16)	1026 (4)	4324 (9)	3809 (4)	79 (4)
Cl(2)	2861 (1)	4066 (2)	3594 (1)	86 (1)
C(20)	4132 (4)	2858 (7)	4526 (4)	61 (3)
C(21)	4635 (4)	3160 (7)	4058 (4)	83 (4)
C(22)	4452 (3)	1718 (7)	4947 (3)	70 (3)
C(23)	4076 (4)	3978 (8)	4967 (4)	92 (4)
Ni(2)	3197 (1)	830 (1)	3358 (1)	54 (1)
C(2')	3124 (5)	1567 (10)	2609 (5)	101 (5)
O(2)	3106 (6)	2103 (8)	2133 (4)	189 (5)
P(3)	3408 (1)	−840 (2)	3997 (1)	48 (1)
P(4)	2382 (1)	−1015 (2)	4398 (1)	46 (1)
C(3)	3217 (4)	−1003 (6)	3137 (3)	52 (3)
Si(3)	4098 (1)	−1360 (3)	2850 (1)	81 (1)
C(3*A*)	3910 (5)	−1114 (12)	1957 (4)	149 (6)
C(3*B*)	4870 (4)	−304 (8)	3248 (4)	85 (4)
C(3*C*)	4430 (5)	−3008 (9)	3049 (5)	155 (7)
C(31)	2517 (5)	−1555 (9)	2728 (3)	61 (3)
C(32)	1910 (5)	−826 (10)	2487 (4)	94 (4)
C(33)	1244 (7)	−1337 (15)	2105 (6)	135 (7)
C(34)	1255 (7)	−2558 (17)	2004 (5)	125 (8)
C(35)	1822 (8)	−3349 (12)	2216 (5)	119 (6)
C(36)	2469 (5)	−2802 (9)	2582 (4)	89 (4)
Cl(4)	1746 (1)	−2435 (2)	3900 (1)	73 (1)
C(40)	2754 (4)	−1829 (7)	5193 (3)	55 (3)
C(41)	3328 (4)	−951 (7)	5606 (3)	72 (3)
C(42)	2101 (4)	−2028 (7)	5525 (3)	72 (3)
C(43)	3117 (4)	−3075 (7)	5091 (3)	72 (4)

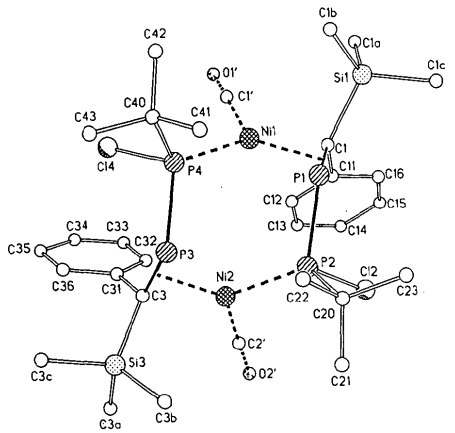

Fig. 1. Plot of the structure with the atom numbering.

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles, non-bonded distances, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53539 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ni(1)—C(1′)	1·783 (8)	Ni(1)—P(1)	2·215 (2)
Ni(1)—C(1)	2·020 (7)	Ni(1)—P(4)	2·172 (2)
C(1′)—O(1′)	1·114 (10)	P(1)—P(2)	2·228 (3)
P(1)—C(1)	1·785 (6)	P(2)—Cl(2)	2·072 (3)
P(2)—C(20)	1·876 (7)	C(1)—Si(1)	1·888 (8)
C(1)—C(11)	1·511 (10)	Ni(2)—C(2′)	1·744 (10)
Ni(2)—P(2)	2·181 (2)	Ni(2)—P(3)	2·220 (2)
Ni(2)—C(3)	2·017 (7)	C(2)—O(2′)	1·151 (13)
P(3)—P(4)	2·238 (3)	P(3)—C(3)	1·778 (6)
P(4)—Cl(4)	2·063 (3)	P(4)—C(40)	1·885 (7)
C(3)—Si(3)	1·887 (8)		

C(1′)—Ni(1)—P(1)	149·8 (3)	C(1′)—Ni(1)—C(1)	101·3 (3)
P(1)—Ni(1)—C(1)	49·6 (2)	C(1′)—Ni(1)—P(4)	104·7 (3)
P(1)—Ni(1)—P(4)	105·2 (1)	C(1)—Ni(1)—P(4)	153·6 (2)
Ni(1)—C(1′)—O(1′)	177·5 (9)	Ni(1)—P(1)—P(2)	105·0 (1)
Ni(1)—P(1)—C(1)	59·5 (2)	P(2)—P(1)—C(1)	111·3 (3)
P(1)—P(2)—Cl(2)	105·4 (1)	P(1)—P(2)—C(20)	101·2 (3)
Cl(2)—P(2)—C(20)	99·1 (3)	P(1)—P(2)—Ni(2)	117·9 (1)
Cl(2)—P(2)—Ni(2)	114·2 (1)	C(20)—P(2)—Ni(2)	116·5 (3)
Ni(1)—C(1)—P(1)	70·9 (2)	Ni(1)—C(1)—Si(1)	110·2 (3)
P(1)—C(1)—Si(1)	109·2 (3)	Ni(1)—C(1)—C(11)	110·5 (5)
P(1)—C(1)—C(11)	125·4 (5)	Si(1)—C(1)—C(11)	119·5 (5)
P(2)—Ni(2)—C(2′)	103·8 (3)	P(2)—Ni(2)—P(3)	103·6 (1)
C(2)—Ni(2)—P(3)	151·9 (4)	P(2)—Ni(2)—C(3)	152·7 (2)
C(2′)—Ni(2)—C(3)	103·5 (4)	P(3)—Ni(2)—C(3)	49·3 (2)
Ni(2)—C(2′)—O(2′)	176·0 (9)	Ni(2)—P(3)—P(4)	104·1 (1)
Ni(2)—P(3)—C(3)	59·4 (2)	P(4)—P(3)—C(3)	112·2 (2)
Ni(1)—P(4)—P(3)	117·9 (1)	Ni(1)—P(4)—Cl(4)	112·0 (1)
P(3)—P(4)—Cl(4)	107·6 (1)	Ni(1)—P(4)—C(40)	116·1 (2)
P(3)—P(4)—C(40)	101·5 (3)	Cl(4)—P(4)—C(40)	99·9 (2)
Ni(2)—C(3)—P(3)	71·3 (2)	Ni(2)—C(3)—Si(3)	109·2 (3)
P(3)—C(3)—Si(3)	110·5 (3)	Ni(2)—C(3)—C(31)	117·1 (5)
P(3)—C(3)—C(31)	125·4 (5)	Si(3)—C(3)—C(31)	115·2 (5)

Related literature. For complexes on 1,2-diphosphapropene see Appel, Casser & Knoch (1985), Casser (1985), and Dunker (1986). For η^2-coordinated phosphoralkene see Cowley, Jones, Stewart & Stuart (1983), and van der Knapp, Jenneskens, Meeuwissen & Bickelhaupt (1983).

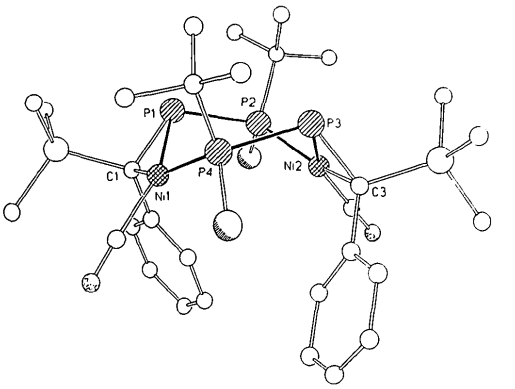

Fig. 2. View on the six-membered NiP ring. The ring adopts a boot conformation (twist conformation of the four P atoms).

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Vaska's Compound* – Dichloromethane Solvate (1/2)

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Abstract. $C_{37}H_{30}ClIrOP_2.2CD_2Cl_2$, $M_r = 954{\cdot}14$, orthorhombic, *Pcab* (alternative *Pbca*, No. 61), $a = 8{\cdot}0054\ (21)$, $b = 20{\cdot}669\ (6)$, $c = 23{\cdot}170\ (5)$ Å, $V = 3834$ Å^3, $Z = 4$, $D_x = 1{\cdot}649$ Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·71073 Å, $\mu = 3{\cdot}94$ mm^{-1}, $F(000) = 1872$, $T = 298$ K, $R = 0{\cdot}0253$ for 1176 unique observed reflections. Despite disordering of the Cl^- and CO ligands, it was possible to resolve the affected atoms and finally to refine without the need for geometric constraints. The solvate molecules associate with the metal complex *via* O···H and Cl···H contacts of 2·415 (25) and 2·672 (16) Å respectively.

Experimental. Crystals were obtained from a CD_2Cl_2 solution of $IrH(CO)(PPh_3)_3$. Yellow columnar crystal, 0·31 × 0·31 × 0·77 mm, Stoe STADI-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values of 46 reflections measured at $\pm\omega$ ($28 < 2\theta < 30°$). For data collection, ω–2θ scans with ω-scan width (1·65

* *trans*-Carbonylchlorobis(triphenylphosphine)iridium.

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