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#### Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
 Mean  $\sigma(C-C) = 0.004$  Å  
 Disorder in solvent or counterion  
 $R$  factor = 0.035  
 $wR$  factor = 0.084  
 Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

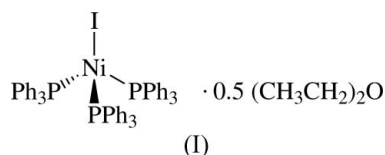
## Iodotris(triphenylphosphine)nickel(I) diethyl ether hemisolvate

A comparison of the title compound,  $[NiI(C_{18}H_{15}P)_3] \cdot 0.5C_4H_{10}O$ , with the previously reported chloro- and bromo-analogues suggests that bond-angle distortion may not always be required for steric relief. The asymmetric unit contains two complex molecules and one disordered diethyl ether molecule.

Received 3 May 2006  
Accepted 30 June 2006

#### Comment

The putative  $Ni^{II}$  species that could be formed by an oxidative addition of the C—I bond in iodomethane to the neutral Ni starting material decomposes readily to yield the title  $Ni^I$  compound, (I). Similar reactivity was observed for tetrakis(trialkylphosphine)nickel(0) with methyl halides (Morvillo & Turco, 1982). This reaction allows for a facile synthesis of the title  $Ni^I$  compound in good yield, allowing a direct structural comparison with the chloro- (Cassidy & Whitmire, 1991; Gernert *et al.*, 2000; Ellis & Spek, 2000) and bromo- (Mealli *et al.*, 1983; Wei *et al.*, 2003) analogues.



The asymmetric unit contains two complex molecules and one disordered diethyl ether molecule. The average Ni—I distance of 2.604 Å in (I) follows the expected Ni—I > Ni—Br > Ni—Cl trend, with previously reported average Ni—halide bond distances of 2.291 Å for Cl and 2.437 Å for Br. This trend is a natural consequence of the increasing atomic radii of the halogen series. Another consequence should be the increasing P—Ni—X angle, given a constant phosphine Tolman cone angle. However, the average angle is less sensitive to halogen substitution: P—Ni—Cl = 106.81, P—Ni—Br = 107.43 and P—Ni—I (this work) = 106.30°. Apparently, moving the halide away from the metal affords enough steric relief so that a distortion in the angles is not required. The deviation of up to 7.5° from the average in the individual symmetry-unique P—Ni—I angles suggests that bond-angle distortion is, in fact, accessible. It might be interesting to see if creating the halide analogue series with a more sterically demanding phosphine or with a smaller metal ion might yield the expected trend.

#### Experimental

The title compound was prepared from 1 equivalent of Ni(cyclooctadiene)<sub>2</sub>, 3.1 equivalents of triphenylphosphine and 1.2 equivalents of methyl iodide in tetrahydrofuran (THF) solvent. After

stirring for 12 h, the mixture was evaporated to dryness and the product extracted with several portions of THF in an inert atmosphere. The combined yield from the THF extractions was 50%. X-ray quality crystals were afforded by slow evaporation of a saturated solution in roughly 50:50 THF–diethyl ether. Sample quality was assessed by polarized microscopy. The selected crystal displayed even and sharp extinction and did not have re-entrant crystal face angles, consistent with untwinned crystals. A single crystal was attached to a fiber loop using Paratone oil for subsequent crystallographic investigation at 120 K.

#### Crystal data

$[\text{NiI}(\text{C}_{18}\text{H}_{15}\text{P})_3] \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$

$M_r = 1009.48$

Triclinic,  $P\bar{1}$

$a = 13.072$  (4) Å

$b = 20.035$  (5) Å

$c = 21.364$  (6) Å

$\alpha = 113.354$  (4)°

$\beta = 105.597$  (4)°

$\gamma = 98.451$  (4)°

$V = 4740$  (2) Å<sup>3</sup>

$Z = 4$

$D_x = 1.415$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\mu = 1.20$  mm<sup>-1</sup>

$T = 120$  (2) K

Block, orange

$0.34 \times 0.28 \times 0.24$  mm

#### Data collection

Bruker APEX diffractometer

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.620$ ,  $T_{\max} = 0.746$

53243 measured reflections

21295 independent reflections

17682 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\text{max}} = 28.3^\circ$

#### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.084$

$S = 1.03$

21295 reflections

1158 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.8632P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 1.50$  e Å<sup>-3</sup>

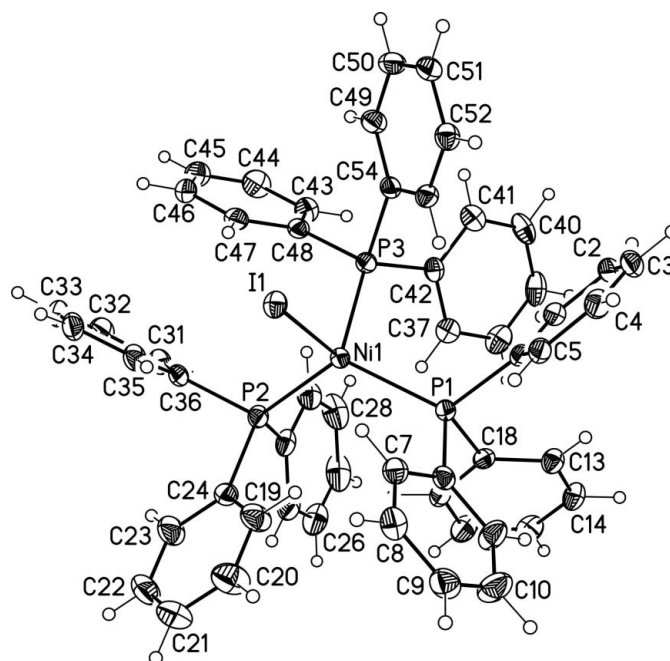
$\Delta\rho_{\text{min}} = -0.52$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

I1–Ni1	2.6028 (7)	Ni1–P2	2.3153 (8)
I2–Ni2	2.6041 (8)	Ni2–P4	2.2800 (9)
Ni1–P3	2.2596 (9)	Ni2–P6	2.2812 (9)
Ni1–P1	2.3054 (9)	Ni2–P5	2.3276 (8)
P3–Ni1–I1	100.38 (2)	P4–Ni2–I2	98.22 (2)
P1–Ni1–I1	113.73 (2)	P6–Ni2–I2	108.67 (2)
P2–Ni1–I1	105.72 (3)	P5–Ni2–I2	111.11 (2)

Two crystallographically distinct molecules of the title compound were located in the asymmetric unit. One molecule of diethyl ether solvent was located in the asymmetric unit, disordered over two positions. In the initial cycles of least-squares refinement, the chemically equivalent atoms in each contributing disordered form were constrained to have equal atomic displacement parameters until the site occupancy converged to 0.86 (1):0.14 (1). The refined site occupancy was then fixed and the displacement parameters allowed to refine. The two contributing disordered positions were restrained



**Figure 1**

The molecular structure of one of the independent molecules of (I), showing the atom-labeling scheme and with 50% probability displacement ellipsoids. The other molecule is very similar.

to have similar interatomic distances. H atoms were assigned calculated positions, with C–H = 0.95–0.99 Å, and treated as riding, with  $U_{\text{iso}}(\text{H}) = 1.0\text{--}1.2U_{\text{eq}}(\text{C})$ . The highest unassigned peak is located 0.877 Å from atom I2.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge support from the National Institutes of Health (GM59191).

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