Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alessio, E., Faleschini, P., Sessanta o Santi, A., Mestroni, G. & Calligaris, M. (1993). *Inorg. Chem.* **32**, 5756–5761.
Alessio, E., Sessanta o Santi, A., Faleschini, P., Calligaris, M. & Mestroni, G. (1994). *J. Chem. Soc. Dalton Trans.* In the press.
Calligaris, M., Bresciani-Pahor, N. & Srivastava, R. S. (1993). *Acta Cryst.* C49, 448–451.
Calligaris, M., Faleschini, P. & Alessio, E. (1991). *Acta Cryst.* C47, 747–750.
Davies, J. A. (1981). *Adv. Inorg. Chem. Rev.* **24**, 115–187.
Enraf–Nonius (1988). *CAD-4 Software.* Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Faleschini, P. (1993). PhD thesis, Univ. of Trieste, Italy.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kukushkin, V. Yu., Belsky, V. K., Konovalov, V. E., Aleksandrova, E. A., Pankova, E. Yu. & Moiseev, A. I. (1992). *Phosphorus Sulfur Silicon,* **69**, 103–117.
Lowe, P. A. (1981). *The Chemistry of the Sulphonium Group,* edited by C. J. M. Stirling, pp. 286–288. New York: Wiley.
Yapp, D. T. T., Jaswal, J., Rettig, S. J., James, B. R. & Skov, K. A. (1990). *Inorg. Chim. Acta,* **177**, 199–208.

trans-[Ni(Me₃Ph)(NHPh)(PMe₃)₂], a Monomeric Ni^II–Amide Complex

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Abstract

trans-Phenylamido(2,4,6-trimethylphenyl)bis(trimethylphosphine)nickel(II), [Ni(C₆H₆N)(C₉H₁₁)(C₃H₉P)₂], has been synthesized and its crystal structure determined as part of an ongoing study of the reactivity and stability of late transition metal–amide complexes. The geometry about the amide N atom is planar, with a relatively long interaction with the metal center. The Ni atom exhibits square-planar coordination geometry with the PMe₃ ligands *trans* with respect to each other.

Comment

The chemistry of late transition metal–amide complexes (Groups 8–10) has been studied extensively over the past several years (Bryndza & Tam, 1988; Fryzuk & Montgomery, 1989; Boncella & Villanueva, 1994). In spite of the great interest in these compounds, few have been structurally characterized. The scarcity of these compounds can be attributed to the incompatibility between the electronically saturated metal center and the lone pair of electrons on the amide N atom (Lappert, Power, Sanger & Srivastava, 1980). Knowledge of the structural characteristics is essential for the understanding of the stability and reactivity of these compounds. Determining the geometry about the amide N atom is crucial, since the location of its lone electron pair should lend insight into the reactivity of the metal amide. From a search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983), we have established that there are no examples of primary amides (derived from a primary amine, forming M—NHR) of the Ni triad where the amide proton has been located and refined. Therefore, the exact geometry about the N atom is unknown. Here we report the structure of the title compound, (I).

(I)
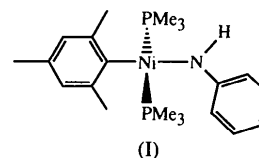
A displacement ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the title molecule with the atom-labelling scheme is given in Fig. 1. The coordination geometry around the Ni atom is square planar with the phosphine ligands *trans* with respect to each other. The Ni atom lies in the coordination plane (the average deviation is 0.01 Å for the plane defined by atoms Ni, P1, N, P2 and C1). The mesityl ring is oriented perpendicular to the coordination plane, forming an angle of 89.7° with it. Since the amide proton was located in the difference Fourier map and refined without constraints at 0.82 (3) Å from N, it was possible to determine the geometry about the N atom unambiguously. This atom lies 0.03 Å from the plane defined by atoms Ni, C7 and H. The planarity around the N atom favors delocalization of its lone pair of electrons.

Since the geometry about the N atom is planar, the lone pair of electrons from the N atom must be delocalized within the structure. There appears to be an interaction between the lone pair of electrons and the Ni metal center. The Ni—N bond length of 1.932 (3) Å is consistent with the Ni—N bond length of 1.924 (2) Å found in [NiClN(SiMe₂CH₂PPh₂)₂], (II) (Fryzuk, MacNeil, Rettig, Secco & Trotter, 1982). This interaction is not observed in the complexes *trans*-[Ni(Mes){N(Ph)C(O)CHPh₂}(PMe₃)₂], (III) (Van-

derLende, Abboud & Boncella, 1994), and *trans*-[Ni(Mes){N(Ph)C(O)NH'Bu}(PMe_3)_2], (IV) (Penney, VanderLende, Boncella & Abboud, 1995), where the Ni—N bond lengths are 1.974 (3) and 1.978 (6) Å, respectively. This lengthening of the Ni—N bond by at least 0.04 Å is due to the delocalization of the lone pair onto the carbonyl group in compounds (III) and (IV).

Delocalization of the N-atom electron pair onto the phenyl ring is also evidenced. The N—C7 bond length of 1.354 (5) Å is relatively short. In an analogous palladium compound, *trans*-[Pd(Ph)(NHPh)(PMe_3)_2] (Villanueva, Abboud & Boncella, 1994), the N—C_{phenyl} bond length is 1.32 (2) Å. These bonds are much shorter than the N—C_{phenyl} bond lengths in (III) and (IV) of 1.42 and 1.41 Å, respectively, where once again the electrons are delocalized onto the carbonyl group. This is a difference in the N—C_{phenyl} bond length of at least 0.06 Å. A short N—C_{phenyl} bond length is also observed in the Ir^I complex [Ir(CO){NH(p-tolyl)}(PPh_3)_2] [1.385 (5) Å; Rahim, White, Rheingold & Ahmed, 1993].

These data strongly suggest that the lone pair of electrons from the N atom is delocalized over the Ni—N bond as well as onto the phenyl ring.
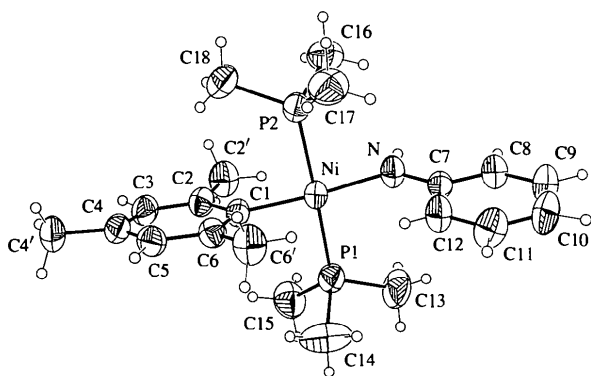

Fig. 1. Molecular structure of (I) showing the atom-numbering scheme and plotted with 50% probability ellipsoids.

Experimental

Using Schlenk techniques, *trans*-[Ni(Mes)Cl(PMe_3)_2] (Mes = 2,4,6-Me_3C_6H_2) (Carmona, Paneque & Poveda, 1989) was allowed to react with one equivalent of KNHPh in Et_2O at 195 K. The reaction was stirred at room temperature for 24 h before the solvent was removed under reduced pressure. The product was extracted with pentane and the volume of the filtrate reduced and cooled to 195 K to afford *trans*-[Ni(Mes)(NHPh)(PMe_3)_2], (I), as an orange crystalline powder. Recrystallization by slowly cooling a pentane solution of (I) to 263 K afforded red crystals after 48 h. The rapid solid-state reactivity of (I) toward H_2O necessitated isolation of the crystals in a dry box. Crystals were placed in individual capillary tubes and flame sealed when removed from the dry box.

Crystal data

$[Ni(C_6H_6N)(C_9H_{11})(C_3H_9P)_2]$
$M_r = 422.15$
Monoclinic
$P2_1/n$
$a = 12.491 (1)$ Å
$b = 12.368 (1)$ Å
$c = 15.655 (1)$ Å
$\beta = 109.72 (1)°$
$V = 2276.7 (3)$ Å³
$Z = 4$
$D_x = 1.232$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10–11°$
$\mu = 1.00$ mm⁻¹
$T = 293$ K
Plate
$0.53 \times 0.38 \times 0.15$ mm
Orange

Data collection

Siemens *P3m/V* diffractom-
eter
ω scans
Absorption correction:
analytical
$T_{min} = 0.685$, $T_{max} = 0.860$
5780 measured reflections
5248 independent reflections
3285 observed reflections
$[F > 6\sigma(F)]$

$R_{int} = 0.0125$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -20 \rightarrow 19$
4 standard reflections
monitored every 100
reflections
intensity decay: 3%

Refinement

Refinement on F
$R = 0.0445$
$wR = 0.0478$
$S = 1.36$
3285 reflections
258 parameters
$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å⁻³
$\Delta\rho_{min} = -0.30$ e Å⁻³
Atomic scattering factors
from *International Tables*
for X-ray Crystallography
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Ni	0.46691 (4)	0.15944 (3)	0.16912 (3)	0.0384 (2)
P1	0.65065 (8)	0.14007 (8)	0.23537 (7)	0.0511 (4)
P2	0.28275 (8)	0.17495 (8)	0.10725 (6)	0.0495 (4)
N	0.4715 (3)	0.1380 (3)	0.0482 (2)	0.0482 (14)
C1	0.4507 (3)	0.1837 (3)	0.2846 (2)	0.0402 (13)
C2	0.4276 (3)	0.0982 (3)	0.3355 (2)	0.0473 (14)
C2'	0.4185 (4)	−0.0153 (3)	0.2998 (3)	0.064 (2)
C3	0.4055 (3)	0.1182 (4)	0.4154 (3)	0.054 (2)
C4	0.4023 (3)	0.2216 (3)	0.4474 (2)	0.054 (2)
C4'	0.3693 (4)	0.2435 (4)	0.5302 (3)	0.076 (2)
C5	0.4257 (3)	0.3053 (3)	0.3986 (3)	0.053 (2)
C6	0.4493 (3)	0.2886 (3)	0.3186 (2)	0.0443 (13)
C6'	0.4662 (4)	0.3868 (3)	0.2671 (3)	0.063 (2)
C7	0.5083 (3)	0.2050 (3)	−0.0045 (2)	0.0403 (12)
C8	0.5234 (3)	0.1715 (3)	−0.0853 (2)	0.050 (2)
C9	0.5574 (4)	0.2422 (3)	−0.1392 (3)	0.060 (2)
C10	0.5810 (4)	0.3483 (4)	−0.1142 (3)	0.068 (2)
C11	0.5681 (4)	0.3831 (3)	−0.0355 (3)	0.064 (2)
C12	0.5334 (4)	0.3134 (3)	0.0181 (3)	0.056 (2)
C13	0.7286 (3)	0.0901 (5)	0.1651 (3)	0.089 (2)
C14	0.7254 (4)	0.2612 (4)	0.2827 (4)	0.105 (2)
C15	0.6995 (4)	0.0460 (4)	0.3292 (3)	0.075 (2)
C16	0.2183 (3)	0.0664 (4)	0.0283 (3)	0.078 (2)
C17	0.2422 (4)	0.2954 (4)	0.0383 (3)	0.077 (2)
C18	0.1909 (3)	0.1802 (4)	0.1759 (3)	0.078 (2)

Table 2. *Selected geometric parameters* (Å, °)

P1—Ni	2.190 (1)	C2'—C2	1.502 (5)
P2—Ni	2.182 (1)	C3—C2	1.390 (6)
N—Ni	1.932 (3)	C4—C3	1.379 (6)
C1—Ni	1.910 (4)	C4'—C4	1.512 (6)
C13—P1	1.807 (5)	C5—C4	1.376 (6)
C14—P1	1.789 (5)	C6—C5	1.394 (6)
C15—P1	1.811 (4)	C6'—C6	1.511 (5)
C16—P2	1.819 (4)	C8—C7	1.404 (5)
C17—P2	1.809 (4)	C12—C7	1.394 (5)
C18—P2	1.819 (5)	C9—C8	1.378 (6)
C7—N	1.354 (5)	C10—C9	1.372 (6)
C2—C1	1.411 (5)	C11—C10	1.366 (7)
C6—C1	1.405 (5)	C12—C11	1.372 (7)
P1—Ni—P2	177.78 (8)	C6—C1—Ni	121.5 (3)
P1—Ni—N	94.36 (10)	C2'—C2—C3	119.2 (4)
P2—Ni—N	87.29 (10)	C2'—C2—C1	119.6 (4)
P2—Ni—C1	88.50 (10)	C3—C2—C1	121.0 (3)
N—Ni—C1	175.72 (13)	C4—C3—C2	122.1 (4)
C1—Ni—P1	89.87 (10)	C4'—C4—C5	120.9 (4)
C13—P1—C14	103.0 (3)	C4'—C4—C3	121.8 (4)
C13—P1—C15	99.8 (2)	C5—C4—C3	117.2 (4)
C13—P1—Ni	116.32 (12)	C6—C5—C4	122.5 (4)
C14—P1—C15	102.5 (2)	C6'—C6—C1	121.2 (3)
C14—P1—Ni	115.0 (2)	C6'—C6—C5	118.1 (3)
C15—P1—Ni	117.8 (2)	C1—C6—C5	120.6 (3)
C16—P2—C17	103.5 (2)	C8—C7—C12	115.2 (4)
C16—P2—C18	101.8 (2)	C8—C7—N	123.0 (3)
C16—P2—Ni	113.29 (15)	C12—C7—N	121.8 (4)
C17—P2—C18	102.6 (2)	C9—C8—C7	121.8 (4)
C17—P2—Ni	112.2 (2)	C10—C9—C8	120.9 (4)
C18—P2—Ni	121.42 (12)	C11—C10—C9	118.6 (5)
C7—N—Ni	129.9 (2)	C12—C11—C10	120.8 (4)
C2—C1—C6	116.5 (3)	C7—C12—C11	122.6 (4)
C2—C1—Ni	121.6 (3)		

The ω scan width was symmetrical over 1.2° about the $K\alpha_{1,2}$ maximum and the background was offset 1.0 and −1.0 in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min^{-1} (depending upon intensity). The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The structure was solved by the heavy-atom method from which the position of the Ni atom was found. The remainder of the non-H atoms were obtained from a difference Fourier map. The amide H and aromatic H atoms were obtained from a subsequent difference Fourier map and refined without constraints; their distances range from 0.86 (4) to 0.99 (4) Å, and their angles between 117 (2) and 121 (2)°, except for atom H10 which makes angles of 114 (2) and 127 (2)°. Their isotropic displacement parameters range from 0.043 (9) to 0.073 (12) Å^2. The methyl H atoms were calculated in idealized positions (0.96 Å) and given fixed displacement parameters.

Programs used: *SHELXTL-Plus* (Sheldrick, 1990) for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics; *SHELX76* (Sheldrick, 1976) for structure refinement (full-matrix least squares); *FUER* (Larson, 1982) for geometric and parameter tables.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Boncella, J. M. & Villanueva, L. A. (1994). *J. Organomet. Chem.* **465**, 297–304.

Bryndza, H. E. & Tam, W. (1988). *Chem. Rev.* **88**, 1163–1188.

Carmona, E., Paneque, M. & Poveda, M. L. (1989). *Polyhedron*, **8**, 285–291.

Fryzuk, M. D., MacNeil, P. A., Rettig, S. J., Secco, A. S. & Trotter, J. (1982). *Organometallics*, **1**, 918–930.

Fryzuk, M. D. & Montgomery, D. C. (1989). *Coord. Chem. Rev.* **95**, 1–40.

Lappert, M. F., Power, P. P., Sanger, A. R. & Srivastava, R. C. (1980). In *Metal and Metalloid Amides*. Chatham: Halsted Press.

Larson, S. B. (1982). *FUER. Program for Generating Positional and Thermal Parameters and Geometrical Quantities*. Univ. of Texas, Austin, TX, USA.

Penney, J. M., VanderLende, D. D., Boncella, J. M. & Abboud, K. A. (1995). *Acta Cryst.* Submitted.

Rahim, M., White, C., Rheingold, A. L. & Ahmed, K. J. (1993). *Organometallics*, **12**, 2401–2403.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

VanderLende, D. D., Abboud, K. A. & Boncella, J. M. (1994). *Inorg. Chem.* In preparation.

Villanueva, L. A., Abboud, K. A. & Boncella, J. M. (1994). *Organometallics*. Submitted.

cis-Dichloro[bis(diphenylphosphino)ethane]palladium(II)

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Abstract

In cis-[PdCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)], the Pd atom is at the centre of an approximately square-planar arrangement of two P and two Cl atoms. The P—Pd—P angle is 88.3 (1)° and the two Pd—P distances are 2.284 (3) and 2.264 (3) Å.