C17	−0.6538 (3)	0.0617 (2)	−0.3416 (5)	3.6
C18	−0.5941 (3)	0.0844 (2)	−0.2508 (5)	3.6
C19	−0.7577 (3)	−0.0009 (2)	−0.4079 (5)	3.5
C20	−0.8288 (4)	−0.0190 (2)	−0.3758 (6)	5.6
C21	−0.8912 (4)	−0.0378 (3)	−0.4734 (7)	6.5
C22	−0.8819 (4)	−0.0378 (2)	−0.6047 (6)	5.0
C23	−0.8100 (4)	−0.0210 (2)	−0.6356 (6)	5.0
C24	−0.7485 (4)	−0.0024 (2)	−0.5382 (5)	4.6
C25	−0.9455 (4)	−0.0559 (3)	−0.7104 (7)	6.2
C26	−0.9948 (4)	−0.0691 (2)	−0.8038 (7)	6.7
C27	−1.0126 (8)	−0.0910 (6)	−1.088 (1)	19.3
C28	−1.130 (1)	−0.1325 (5)	−0.936 (1)	26.4
C29	−1.1349 (5)	−0.0319 (4)	−0.999 (1)	10.8
C30	−0.3836 (4)	0.0757 (2)	−0.2861 (6)	6.3
C31	−0.2516 (4)	0.1119 (3)	−0.0672 (7)	7.3
C32	−0.3634 (5)	0.1797 (3)	−0.2434 (8)	7.7
C33	−0.3521 (3)	0.1462 (2)	0.2043 (4)	3.0
C34	−0.3124 (3)	0.1872 (2)	0.1808 (5)	3.8
C35	−0.2502 (3)	0.2064 (2)	0.2756 (5)	4.0
C36	−0.2258 (3)	0.1848 (2)	0.3977 (5)	3.4
C37	−0.2635 (3)	0.1431 (2)	0.4203 (5)	4.2
C38	−0.3257 (3)	0.1242 (2)	0.3245 (5)	3.6
C39	−0.1616 (3)	0.2065 (2)	0.5016 (5)	3.8
C40	−0.1465 (4)	0.2536 (2)	0.5018 (6)	5.2
C41	−0.0877 (4)	0.2746 (2)	0.5969 (7)	5.9
C42	−0.0417 (4)	0.2478 (3)	0.6965 (6)	5.4
C43	−0.0568 (4)	0.2015 (3)	0.6976 (7)	7.0
C44	−0.1160 (4)	0.1797 (2)	0.6014 (6)	6.3
C45	0.0206 (4)	0.2701 (2)	0.7952 (6)	5.6
C46	0.0735 (4)	0.2876 (3)	0.8732 (6)	6.3
C47	0.1206 (6)	0.3756 (4)	1.024 (1)	12.4
C48	0.1894 (6)	0.2812 (4)	1.1303 (8)	11.1
C49	0.2447 (6)	0.3223 (4)	0.896 (1)	12.0

Table 6. *Selected geometric parameters* (Å, °) *for* (III)

Co—C1	2.002 (4)	Co—C8	2.052 (6)
Co—C2	1.967 (5)	Co—C9	2.057 (7)
Co—C3	1.990 (5)	C1—C2	1.466 (6)
Co—C4	1.976 (4)	C1—C4	1.468 (7)
Co—C5	2.054 (8)	C2—C3	1.473 (7)
Co—C6	2.065 (6)	C3—C4	1.466 (6)
Co—C7	2.068 (6)		
C2—C1—C4	87.4 (4)	C2—C3—C4	87.2 (4)
C1—C2—C3	92.5 (4)	C1—C4—C3	92.8 (4)

All three structures were solved using the Patterson function with *SHELXS*86 software (Sheldrick, 1985). All the H atoms were calculated. In (II), B_{eq} values for the C atoms in one of the phenyl groups are abnormally large, suggesting rotational disorder. In (III), B_{eq} values for the terminal tri-methylsilyl C atoms (10.8–26.4 Å^2) are abnormally large, again suggesting disorder. Refinements were carried out using *CRYSTAN-GM* software (MAC Science, 1992) on a SUN SPARC2 workstation. Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Ni(Mes)[N(Ph)C(O)N(H)CMe3]-(PMe3)2

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Abstract

The title compound, *trans*-(3-*tert*-butyl-1-phenylureido)-(2,4,6-trimethylphenyl)bis(trimethylphosphine)nickel(II), [Ni(C9H11)(C11H15N2O)(C3H9P)2], has been synthesized and its crystal structure determined as part of our continuing investigation into the reactivity and stability of the late-transition-metal amide complexes. The Ni atom has square-planar coordination geometry; two *trans* sites are occupied by PMe3 ligands. The geometry around the amide N atom is planar due to the interaction of its lone pair with the carbonyl π system. A relatively long Ni—N bond, 1.978 (6) Å, is interpreted as arising from a lack of significant π interaction between the amide N atom and the Ni metal centre.

Comment

Recently, the chemistry of late-transition-metal amide complexes (Groups 8–10) has been studied extensively (Bryndza & Tam, 1988; Roundhill, 1992; Boncella & Villanueva, 1994). This interest in transition-metal amide complexes arises from their potential to facilitate C—N bond formation between amine derivatives and unsaturated organic compounds. This chemistry has been slow to develop, mainly because the inability of the electronically saturated metal centre to accommodate π donation from the lone-pair electrons of the amide N atom results in a weak metal–nitrogen bond (Lappert, Power, Sanger & Srivsastrava, 1980). With newer methods for the synthesis of metal amide complexes, the chemistry of these compounds can be explored. We report the structure of the product, (I), of the reaction between a late-transition-metal amide complex and ^{t}BuNCO. The structure reveals that the ^{t}BuNCO has inserted into the N—H bond.

(I)
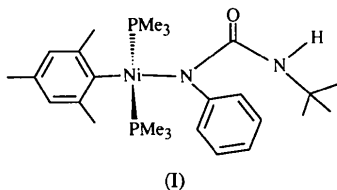
A displacement ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the molecule with the atom-labeling scheme is shown in Fig. 1. The mesityl ring and the amidophenyl ring are oriented perpendicular to the plane of coordination around the Ni atom, thus minimizing steric strain around the Ni atom. The coordination plane forms angles of 93.4 (2) and 90.4 (2)° with the planes of the mesityl and the amidophenyl rings, respectively. The Ni—N1 bond length of 1.978 (6) Å indicates that there is no significant interaction between the lone-pair electrons on N1 and the Ni centre. This bond is considerably longer than the corresponding bond in *trans*-[Ni(Mes)(NHPh)(PMe$_3$)$_2$] [1.932 (3) Å; VanderLende, Boncella & Abboud, 1995] where strong interaction with the N-atom lone pair shortens the Ni—N1 bond. It is, however, comparable with the corresponding bond in *trans*-[Ni(Mes){N(Ph)C(O)CHPh$_2$}(PMe$_3$)$_2$] [1.974 (3) Å; VanderLende, Abboud & Boncella, 1994]. The relatively long N1—C7 and C=O bonds, and short N1—C13 and N2—C13 bonds, suggest electronic interaction between the carbonyl π bond and the N1 and N2 lone pairs. Delocalization of electrons along the four-atom moiety (N1, N2, C13, O1) is further supported by the near planarity of the >N1—C(=O)—N2< fragment (torsion angles vary from −10.7 to 13.5°).
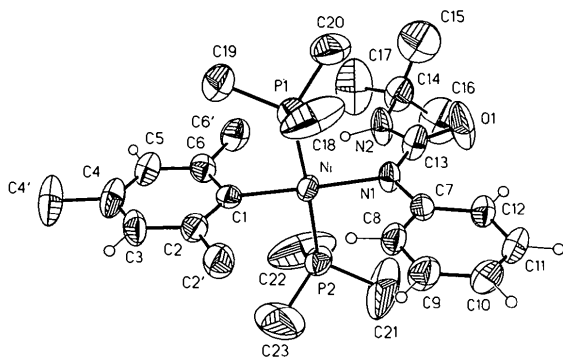

Fig. 1. Molecular structure of (I) with 50% probability ellipsoids and showing the atom-numbering scheme.

Experimental

Using Schlenk techniques, one equivalent of (CH$_3$)$_3$CNCO was added to a solution of [Ni(Mes)(NHPh)(PMe$_3$)$_2$] in benzene. After stirring for 12 h, the solvent was removed under reduced pressure. The solid was dissolved in 20 ml of pentane and concentrated to *ca* 5 ml under reduced pressure. The solution was cooled to 263 K to produce

trans-[Ni(Mes){N(Ph)C(O)N(H)CMe$_3$}(PMe$_3$)$_2$], (I), as bright yellow crystals. Although (I) slowly decomposes in air, crystals were placed in individual thin-walled glass capillary tubes and flame-sealed in the open atmosphere.

Crystal data

[Ni(C$_9$H$_{11}$)(C$_{11}$H$_{15}$N$_2$O)-(C$_3$H$_9$P)$_2$]	Mo *K*α radiation
M_r = 521.28	λ = 0.71073 Å
Monoclinic	Cell parameters from 32
$P2_1/n$	reflections
a = 8.575 (2) Å	θ = 10–11°
b = 20.711 (4) Å	μ = 0.80 mm^{-1}
c = 16.583 (3) Å	T = 293 K
β = 99.91 (2)°	Plate
V = 2901 (1) Å^3	0.46 × 0.34 × 0.17 mm
Z = 4	Yellow
D_x = 1.193 Mg m^{-3}	

Data collection

Siemens *P3m/V* diffractometer	R_{int} = 0.017
ω scans	θ_{max} = 27.5°
Absorption correction:	$h = 0 \rightarrow 10$
analytical	$k = 0 \rightarrow 24$
T_{min} = 0.762, T_{max} = 0.876	$l = -19 \rightarrow 19$
5650 measured reflections	4 standard reflections
5110 independent reflections	monitored every 100
2151 observed reflections	reflections
[$F > 6\sigma(F)$]	intensity decay: 1%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.001
R = 0.0571	$\Delta\rho_{max}$ = 0.82 e Å^{-3}
wR = 0.0627	$\Delta\rho_{min}$ = −0.51 e Å^{-3}
S = 1.70	Extinction correction: none
2151 reflections	Atomic scattering factors
289 parameters	from *International Tables*
H-atom parameters not refined	*for X-ray Crystallography* (1974, Vol. IV)
$w = 1/[\sigma^2(F) + 0.0004F^2]$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
Ni	0.01938 (13)	0.08545 (5)	0.25886 (6)	0.0371 (4)
P1	−0.1409 (3)	0.09515 (12)	0.34935 (13)	0.0479 (9)
P2	0.1880 (3)	0.07969 (14)	0.17252 (14)	0.0545 (10)
O1	−0.3103 (9)	−0.0406 (3)	0.1397 (5)	0.105 (4)
N1	−0.1550 (8)	0.0493 (3)	0.1779 (4)	0.040 (3)
N2	−0.0794 (9)	−0.0520 (3)	0.2261 (4)	0.061 (3)
C1	0.1884 (9)	0.1184 (4)	0.3405 (5)	0.039 (3)
C2	0.2171 (10)	0.1847 (4)	0.3511 (5)	0.046 (3)
C2'	0.1209 (11)	0.2342 (4)	0.2965 (5)	0.064 (4)
C3	0.3324 (10)	0.2063 (5)	0.4173 (5)	0.061 (4)
C4	0.4168 (11)	0.1646 (6)	0.4717 (5)	0.064 (4)
C4'	0.5424 (11)	0.1905 (6)	0.5410 (6)	0.099 (5)
C5	0.3871 (11)	0.0996 (5)	0.4613 (5)	0.057 (4)
C6	0.2767 (10)	0.0766 (5)	0.3971 (5)	0.046 (3)
C6'	0.2448 (10)	0.0047 (4)	0.3926 (5)	0.063 (4)
C7	−0.2433 (9)	0.0912 (4)	0.1203 (4)	0.039 (3)
C8	−0.2209 (11)	0.1572 (4)	0.1301 (5)	0.051 (4)

C9	−0.3021 (12)	0.2016 (5)	0.0776 (5)	0.063 (4)
C10	−0.4075 (11)	0.1817 (6)	0.0112 (6)	0.068 (4)
C11	−0.4291 (12)	0.1165 (6)	−0.0028 (5)	0.065 (4)
C12	−0.3513 (10)	0.0720 (4)	0.0511 (5)	0.052 (3)
C13	−0.1910 (12)	−0.0150 (5)	0.1767 (5)	0.059 (4)
C14	−0.0874 (15)	−0.1228 (5)	0.2336 (6)	0.067 (5)
C15	−0.234 (2)	−0.1439 (5)	0.2629 (7)	0.117 (7)
C16	−0.083 (2)	−0.1536 (5)	0.1523 (7)	0.122 (7)
C17	0.0537 (15)	−0.1433 (5)	0.2940 (8)	0.141 (7)
C18	−0.2928 (14)	0.1557 (6)	0.3239 (7)	0.126 (7)
C19	−0.0617 (12)	0.1148 (5)	0.4552 (5)	0.088 (5)
C20	−0.2605 (12)	0.0260 (5)	0.3631 (6)	0.093 (6)
C21	0.1101 (13)	0.0643 (9)	0.0694 (6)	0.201 (11)
C22	0.336 (2)	0.0197 (7)	0.1941 (8)	0.177 (10)
C23	0.309 (2)	0.1483 (6)	0.1631 (8)	0.154 (9)

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

P1—Ni	2.212 (3)	C22—P2	1.766 (14)
P2—Ni	2.206 (3)	C23—P2	1.780 (14)
N1—Ni	1.978 (6)	C13—O1	1.220 (12)
C1—Ni	1.930 (7)	C7—N1	1.411 (10)
C18—P1	1.804 (12)	C13—N1	1.366 (12)
C19—P1	1.816 (9)	C13—N2	1.379 (11)
C20—P1	1.798 (11)	C14—N2	1.475 (12)
C21—P2	1.754 (10)		
P1—Ni—P2	176.84 (12)	C20—P1—Ni	116.6 (4)
P1—Ni—N1	90.5 (2)	C21—P2—C22	102.1 (7)
P2—Ni—N1	92.4 (2)	C21—P2—C23	100.9 (7)
P2—Ni—C1	88.7 (3)	C21—P2—Ni	117.4 (4)
N1—Ni—C1	178.0 (3)	C22—P2—C23	99.9 (6)
C1—Ni—P1	88.4 (3)	C22—P2—Ni	115.7 (5)
C18—P1—C19	101.9 (5)	C23—P2—Ni	118.0 (5)
C18—P1—C20	100.3 (5)	C7—N1—C13	119.8 (7)
C18—P1—Ni	114.3 (4)	C7—N1—Ni	118.8 (5)
C19—P1—C20	100.5 (5)	C13—N1—Ni	121.4 (5)
C19—P1—Ni	120.2 (4)	C13—N2—C14	124.3 (8)

The ω-scan width was symmetrically 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). The structure was solved by the heavy-atom method from which the position of the Ni atom was obtained.

SHELXTL-Plus (Sheldrick, 1990) was used for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics. *SHELX*76 (Sheldrick, 1976) was used for structure refinement (full-matrix least-squares).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[bis(triphenylphosphoranylidene)ammonium] Bis[cyanodithiocarbimato-gold(I)], [PPN]₂[Au₂(S₂CNCN)₂]

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Abstract

The title complex, bis[bis(triphenylphosphoranylidene)ammonium] bis[μ-cyanodithiocarbamato(2−)-S:S']-digold(I), [(C₁₈H₁₅P)₂N]₂[Au₂(C₂N₂S₂)₂], displays a short Au···Au contact of 2.813 (1) Å, which is slightly longer than the value of 2.796 (1) Å found in the similar structure of the anionic Au₂(i-mnt)₂²⁻ dimer (i-mnt is 1,1-dicyano-2,2-ethenedithiolate). The complex oxidatively adds halogens to form green Au^II dimers which are unstable at room temperature.

Comment

While gold(I) complexes often display short Au···Au contacts, ranging from 2.7 to 3.3 Å, little is known about the dependence of this interaction on the ligand bound to the Au-atom center. Neutral and anionic bridged dinuclear dithiocarbamate (Heinrich, Wang & Fackler, 1990) and 1,1-dithiolate gold(I) complexes (Khan, Wang & Fackler, 1989) are known to contain some of the shortest Au···Au distances. In addition, both the neutral (Calabro *et al.*, 1981) and the anionic 1,1-dithiolate (Khan, Wang & Fackler, 1989) species are known to add halides oxidatively to form Au^II dimers. As a consequence of better σ donation, the oxidative addition product formed with the dianionic 1,1-dithiolate ligand is more stable than the neutral dithiocarbamate dimer product. Compared with i-mnt (1,1-dicyano-2,2-