$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.779$, $T_{max} = 0.817$
4097 measured reflections
3867 independent reflections

$R_{int} = 0.011$
$\theta_{max} = 24.66°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 0$
$l = -13 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: −0.4%

Refinement

Refinement on F
$R = 0.022$
$wR = 0.031$
$S = 1.16$
3170 reflections
286 parameters
H atoms riding
$w = 4F^2/[\sigma(I)^2 + (PF^2)^2]$, if $F^2 <$ cutoff$[\sigma(I)^2 + (pF^2)^2]$, then the reflection is omitted ($p = 0.04$, cutoff = 3.0)

$(\Delta/\sigma)_{max} = 0.0001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.09$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ni—Cd	3.2274 (5)	Ni—N1	2.039 (2)
Cd—O1	2.260 (1)	Ni—N2	2.021 (2)
Cd—O2	2.263 (2)	O1—C1	1.309 (2)
Cd—O4	2.293 (2)	O2—C17	1.319 (3)
Ni—O1	2.030 (2)	O3—C18	1.246 (3)
Ni—O2	2.012 (1)	O4—C18	1.257 (3)
Ni—O3	2.047 (2)	O5—C20	1.230 (3)
Ni—O5	2.190 (2)		
O1—Cd—O2	73.66 (5)	O5—Ni—N2	88.79 (7)
O1—Cd—O4	84.68 (5)	N1—Ni—N2	97.66 (7)
O2—Cd—O4	86.61 (6)	Cd—O1—Ni	97.44 (5)
O1—Ni—O2	84.26 (6)	Cd—O1—C1	134.0 (1)
O1—Ni—O3	92.88 (7)	Ni—O1—C1	124.1 (1)
O1—Ni—O5	87.98 (7)	Cd—O2—Ni	97.86 (6)
O1—Ni—N1	88.09 (7)	Cd—O2—C17	134.8 (1)
O1—Ni—N2	173.15 (7)	Ni—O2—C17	125.6 (1)
O2—Ni—O3	94.59 (6)	Ni—O3—C18	129.7 (1)
O2—Ni—O5	91.03 (6)	Cd—O4—C18	128.7 (2)
O2—Ni—N1	171.47 (6)	Ni—O5—C20	118.4 (2)
O2—Ni—N2	89.76 (6)	Ni—N1—C7	123.7 (2)
O3—Ni—O5	174.37 (5)	Ni—N1—C8	118.3 (1)
O3—Ni—N1	89.52 (6)	Ni—N2—C10	118.7 (1)
O3—Ni—N2	90.91 (7)	Ni—N2—C11	124.0 (2)
O5—Ni—N1	84.95 (6)		

All non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed geometrically 0.95 Å from their parent C atoms with $U_{iso}(H) = 1.3U_{eq}(C)$. After refining the coordinates of methyl H atoms for a few cycles, a riding model was used for all H atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf-Nonius, 1994). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *MolEN* version of *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1135). Services for accessing these data are described at the back of the journal.

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Bis[*N*-(2,6-diisopropylphenyl)amido][*N*-(2,6-diisopropylphenyl)imido]bis(pyridine-*N*)zirconium

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Abstract

The title compound, $[Zr(C_{12}H_{17}N)(C_{12}H_{18}N)_2(C_5H_5N)_2]$, contains a five-coordinate Zr atom with a distorted square-base pyramidal geometry comprising one *N*-(2,6-diisopropylphenyl)imido, two *N*-(2,6-diisopropylphenyl)amido and two pyridine ligands. There are two independent molecules in the asymmetric unit.

Comment

The chemistry of transition metal imido complexes continues to attract considerable interest (Wigley, 1994). Zirconium terminal imido complexes were first reported in 1988 (Walsh, Hollander & Bergman, 1988) and are still relatively rare species. We have been interested in developing Group 4–imido chemistry (Blake, Mountford, Nikonov & Swallow, 1996, and references therein) and during the course of our studies obtained crystals of the previously described (Arney, Bruck, Huber & Wigley, 1992) zirconium–imido complex $[Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(NH\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2(py)_2]$ (py = pyridine), (I).

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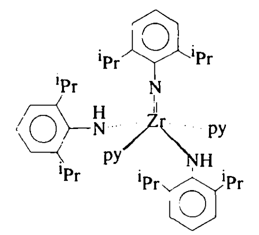

(I)

Crystals of (I) contain two crystallographically independent molecules, the geometric features of which are essentially identical. However, one of the aryl rings in the second molecule (that containing Zr101) exhibits some site disorder. This has been successfully modelled and does not affect the discussion of the general features of the molecular structure of (I).

A view of one of the molecules of (I) is shown in Fig. 1. Compound (I) is related to the complex $[\mathrm{Zr}(N\text{-}2,6\text{-}\mathrm{C_6H_3}{}^i\mathrm{Pr_2})(\mathrm{NH}\text{-}2,6\text{-}\mathrm{C_6H_3}{}^i\mathrm{Pr_2})_2(L)_2]$ (L = 4-pyrrolidinopyridine) (Profilet, Zambrano, Fanwick, Nash & Rothwell, 1990). It has a distorted square-base pyramidal geometry formed by one apical *N*-(2,6-diisopropylphenyl)imido, two *N*-(2,6-diisopropylphenyl)amido and two pyridine ligands. The two amide and two pyridine ligands adopt mutually *trans* positions. The Zr—N distances for the imide, amide and pyridine ligands are similar to those found in related complexes (Wigley, 1994). In particular, the Zr1—N1 and Zr101—N101 distances, and Zr1—N1—C1 and Zr101—N101—C101 angles are consistent with the imido ligands acting as four-electron donors to the metal centre (Wigley, 1994). In both crystallographically independent molecules of (I), one of the imide–zirconium–amide N angles is substantially larger than the other [compare N1—Zr1—N3 117.0 (2), N101—Zr101—N103 118.0 (2)° and N1—Zr1—N2 101.7 (2), N101—Zr101—N102 100.5 (2)°]. This probably reflects steric crowding at the metal centre, although we cannot rule out an electronic (orbital) origin. In both molecules of (I), it is the amide N atom with its 2,6-diisopropylphenyl substituent oriented towards the arylimido ligand that has the larger angle to the imido N atom.

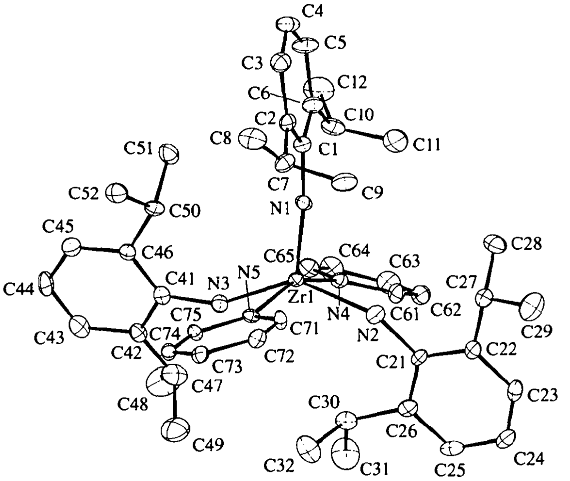

Fig. 1. View of one of the two crystallographically independent molecules of (I) with the atom-numbering scheme. The numbering scheme for the second molecule is the same except that 100 is added to the numerical labels. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity.

Experimental

Bis(tetrahydrofuran)zirconium tetrachloride in tetrahydrofuran was treated sequentially with lithium *N*-(2,6-diisopropylphenyl)amide and pyridine according to previously described procedures (Arney, Bruck, Huber & Wigley, 1992). Crystallization of the crude product from pentane afforded the title compound as yellow sphenoids.

Crystal data

$[\mathrm{Zr(C_{12}H_{17}N)(C_{12}H_{18}N)_2(C_5H_5N)_2}]$
M_r = 777.23
Monoclinic
$P2_1/n$
a = 13.301 (2) Å
b = 32.674 (6) Å
c = 20.381 (5) Å
β = 91.29 (2)°
V = 8855 (3) Å^3
Z = 8
D_x = 1.166 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 52 reflections
θ = 11.1–14.8°
μ = 0.283 mm^{-1}
T = 210.0 (2) K
Sphenoid
0.52 × 0.49 × 0.41 mm
Yellow

Data collection

Stoe Stadi-4 diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω/θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.860, $T_{\max}$ = 0.904
15 850 measured reflections
11 992 independent reflections

8908 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
$\theta_{\max}$ = 25.01°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 37$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 15%

Refinement

Refinement on F^2
$R(F)$ = 0.099
$wR(F^2)$ = 0.098
S = 1.14
8908 reflections
928 parameters
H atoms riding
Chebychev weighting scheme

$(\Delta/\sigma)_{\max}$ = 0.02
$\Delta\rho_{\max}$ = 1.22 e Å^{-3} (near disordered atoms)
$\Delta\rho_{\min}$ = −0.786 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Zr1—N1	1.853 (5)	Zr101—N101	1.850 (4)
Zr1—N2	2.128 (6)	Zr101—N102	2.137 (5)
Zr1—N3	2.134 (5)	Zr101—N103	2.130 (5)

Zr1—N4	2.423 (5)	Zr101—N104	2.387 (5)
Zr1—N5	2.390 (5)	Zr101—N105	2.409 (5)
N1—Zr1—N2	101.7 (2)	N101—Zr101—N102	100.5 (2)
N1—Zr1—N3	117.0 (2)	N101—Zr101—N103	118.0 (2)
N2—Zr1—N3	141.2 (2)	N102—Zr101—N103	141.4 (2)
N1—Zr1—N4	100.6 (2)	N101—Zr101—N104	101.7 (2)
N2—Zr1—N4	87.7 (2)	N102—Zr101—N104	87.9 (2)
N3—Zr1—N4	83.5 (2)	N103—Zr101—N104	82.3 (2)
N1—Zr1—N5	100.7 (2)	N101—Zr101—N105	104.9 (2)
N2—Zr1—N5	87.2 (2)	N102—Zr101—N105	86.2 (2)
N3—Zr1—N5	87.7 (2)	N103—Zr101—N105	86.3 (2)
N4—Zr1—N5	158.7 (2)	N104—Zr101—N105	153.4 (2)

The *ortho*-, *meta*- and *para*-C atoms of one of the 2,6-diisopropylamide ligands of Zr101 were found to be disordered over two sites as indicated by examination of their anisotropic displacement parameters in the final stages of structure refinement; half-occupancy isotropic atoms were refined. Suitable restraints were applied to the displacement parameters and to the C—C distances both between the two ring fragments and within the two rings. No attempt was made to model two sites for the two *ortho*-isopropyl group substituents or the *ipso*-C atom.

Data collection: *STADI*4 (Stoe & Cie, 1995*a*). Cell refinement: *STADI*4. Data reduction: *XRED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1159). Services for accessing these data are described at the back of the journal.

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μ-Bromo-μ-cyclohexylphosphido-bis(tetracarbonylmanganese) and μ-Bromo-μ-(pentacarbonylmanganese)phosphido-bis(tetracarbonylmanganese)†

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Abstract

The central molecular fragment of the first title complex, $[Mn_2Br(C_6H_{12}P)(CO)_8]$, is a four-membered non-planar Mn_2BrP ring with a cyclohexyl ring and a H atom attached to the bridging P atom. In the related second title complex, $[Mn_3Br(PH)(CO)_{13}]$, the cyclohexyl ligand is substituted by an $Mn(CO)_5$ group which displays an unusual ecliptic arrangement with the axial carbonyl ligands of the ring Mn atoms.

Comment

There exist few structural characterizations of dinuclear metal carbonyl complexes with one phosphido and one halogeno bridging group as the central molecular fragment $MM'(\mu\text{-}X)(\mu\text{-P})$ (X = halogen). Most of the complexes comprise a direct metal–metal bond and show butterfly-like structures (*e.g.* Taylor, Mott & Carty, 1980; Fischer & Vahrenkamp, 1981; Geoffroy, Rosenberg, Herlinger & Rheingold, 1986; Jungbluth, Stöckli-Evans & Süss-Fink, 1989). A nearly planar arrangement of the $MM'(\mu\text{-}X)(\mu\text{-P})$ core as well as a non-bonding metal–metal separation are found in the complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-I})(\mu\text{-PPh}_2)Mn(CO)_4]$ (Horton, Mays, Adatia, Henrick & McPartlin, 1988) and $[Ph_3P(CO)_3Re(\mu\text{-I})(\mu\text{-PPh}_2)Re(CO)_4]$ (Flörke & Haupt, 1991). The recent work (Flörke, 1996) on $[(CO)_4Mn(\mu\text{-Br})(\mu\text{-PH}_2)Mn(CO)_4]$, hereafter referred to as (III), was the first X-ray structure determination of a corresponding dimanganese complex with the bridging ligand X = Br.

We present here the two related title structures, $[(CO)_4Mn(\mu\text{-Br})\{\mu\text{-PH}(C_6H_{11})\}Mn(CO)_4]$, (I), and $[(CO)_4Mn(\mu\text{-Br})\{\mu\text{-PH}[Mn(CO)_5]\}Mn(CO)_4]$, (II), which may be derived formally from (III) by substitution of one H atom attached to the μ-P atom by a cyclohexyl ligand or an $Mn(CO)_5$ group, respectively. In both complexes, each Mn atom is approximately octahedrally

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† Alternative names: μ-bromo-octacarbonyl-$1\kappa^4C,2\kappa^4C$-μ-cyclohexylphosphanido-$1{:}2\kappa^2P$-dimanganese and μ-bromo-$1{:}2\kappa^2Br$-tridecacarbonyl-$1\kappa^4C,2\kappa^4C,3\kappa^5C$-$\mu_3$-phosphanido-$1{:}2{:}3\kappa^3P$-trimanganese.

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