$\omega/2\theta$ scans
Absorption correction:
empirical ψ scan (*SDP/PDP*; Enraf–Nonius, 1985)
$T_{\min} = 0.55$, $T_{\max} = 0.65$
3485 measured reflections
2012 independent reflections

$R_{\text{int}} = 0.012$
$\theta_{\max} = 30°$
$h = -4 \rightarrow 29$
$k = -4 \rightarrow 12$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 240 min
intensity decay: 1.2%

Refinement

Refinement on F
$R = 0.025$
$wR = 0.034$
$S = 1.27$
2012 reflections
70 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} = 0.050$

$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}
Extinction correction:
secondary Zachariasen (1967)
Extinction coefficient:
$4.5(1) \times 10^{-7}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd†	1/2	1/2	0.2300	0.03054 (6)
S1	0.48845 (3)	0.29468 (8)	−0.0090 (1)	0.0311 (2)
S2	0.39918 (4)	0.54239 (9)	0.4142 (1)	0.0339 (2)
O1	0.3828 (1)	0.2498 (2)	0.1585 (2)	0.0360 (7)
C1	0.4204 (1)	0.1972 (3)	0.0315 (3)	0.0283 (7)
C2	0.3258 (1)	0.1655 (3)	0.2226 (4)	0.0387 (9)
C3	0.2731 (2)	0.2818 (4)	0.2498 (5)	0.052 (1)
C4	0.3446 (2)	0.0849 (5)	0.3852 (7)	0.092 (2)

† Site occupancy = 0.50.

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

Cd—S1	2.585 (1)	O1—C1	1.323 (3)
Cd—S2	2.536 (1)	O1—C2	1.479 (3)
S1—C1	1.680 (3)		
S1—Cd—S1^{i}	90.86 (2)	S1^{i}—Cd—S2^{i}	114.60 (2)
S1—Cd—S2	114.60 (2)	S2—Cd—S2^{i}	113.07 (3)
S1—Cd—S2^{i}	110.96 (2)	Cd—S1—C1	108.3 (1)
S1^{i}—Cd—S2	110.96 (2)	Cd—S2—C1^{ii}	101.4 (1)

Symmetry codes: (i) $1 - x, 1 - y, z$; (ii) $x, \frac{1}{2} + y, \frac{1}{2} + z$.

All non-H atoms were located from electron-density maps and were refined anisotropically by full-matrix least squares. H atoms were calculated and were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP for Windows* (Frenz, 1998). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) as implemented in *SDP for Windows*. Program(s) used to refine structure: *SDP for Windows*. Molecular graphics: *Xtal*3.4 (Hall *et al.*, 1995) *ORTEP*. Software used to prepare material for publication: *SDP for Windows*.

DWT acknowledges support from Air Force contract F33615-97-D-5405/TMC97-5405-0006-01. DWT also thanks Dr Doug Dudis for his helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1413). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide.* Version 3.0. Enraf–Nonius, Delft, The Netherlands.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1998). *SDP for Windows.* B. A. Frenz & Associates, College Station, Texas, USA.
Hall, S. R., Flack, H. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *Reference Manual.* Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
Iimura, Y. (1973). *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)*, **67**, 43–46.
Kurtz, S. K. & Dougherty, J. P. (1978). *Systematic Materials Analysis*, edited by J. H. Richardson & R. V. Peterson, pp. 269–342. New York: Academic Press.
Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1999). C**55**, 719–722

[1,3-Bis(pyridine-2-carboxamido)propane]palladium(II) monohydrate and its nickel(II) analogue

MASANA TAMURA,[a] YUJI KAJIKAWA,[a] NAGAO AZUMA,[a] HIROYUKI TANI,[b] KUNIHIKO TAJIMA,[c] KENJI KANAORI,[c] KEISUKE MAKINO[c]† AND TOSHIO TAKAYAMA[d]

[a]*Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790-8577, Japan,* [b]*Advanced Instrumentation Center for Chemical Analysis, Ehime University, Matsuyama 790-8577, Japan,* [c]*Department of Polymer Science & Engineering, Kyoto Institute Technology, Sakyo-ku, Kyoto 606-8585, Japan, and* [d]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221-1293, Japan. E-mail: azuma@dpc.ehime-u.ac.jp*

(*Received 28 July 1998; accepted 3 December 1998*)

Abstract

The title compounds, [*N*,*N*′-bis(2-pyridylcarbonyl)propane-1,3-diaminato-κ^4N]palladium(II) monohydrate, $[Pd(C_{15}H_{14}N_4O_2)]\cdot H_2O$, and [*N*,*N*′-bis(2-pyridylcarbonyl)propane-1,3-diaminato-κ^4N]nickel(II) monohydrate, $[Ni(C_{15}H_{14}N_4O_2)]\cdot H_2O$, were investigated by means of X-ray diffraction and high-resolution NMR. The Pd^{II} and Ni^{II} ions have regular and distorted square-planar

---

† Current address: Institute of Advanced Energy, Kyoto University, Uji 611-0011, Japan.

© 1999 International Union of Crystallography
Printed in Great Britain - all rights reserved

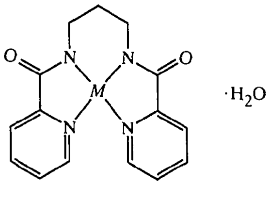
coordination geometries, respectively. Libration of the propanediyl chains in these complexes was observed in both the crystalline and solution states.

Comment

Mono- and binuclear Cu^{II} complexes of 1,3-bis(pyridine-2-carboxamido)propane (H_2ppda) were isolated from aqueous alkaline (Ojima, 1967) and acidic solutions (Kajikawa *et al.*, 1981, 1984; Tsuboyama *et al.*, 1984), respectively. H_2ppda provides [Ni^{II}(ppda)]·H_2O crystals from an alkaline solution and fine powdered crystals from acidic solution which have not yet been characterized. The softer Pd^{II} Lewis acid gives [Pd(ppda)]·H_2O alone both in alkaline and acidic solutions. Crystal structure analyses of these complexes suggest libration of the propanediyl group in their crystalline state.

The crystal structures of palladium(II) complexes of *N*-methyl- and *N*,*N*′-dimethyl-1,2-bis(pyridine-2-carboxamido)ethane, *i.e.* [PdCl(HpedaMe)] and [PdCl$_2$(H_2pedaMe$_2$)], are known (Mulqi *et al.*, 1982). The coordination geometry of these complexes is square planar involving pyridyl (py) N atoms, a deprotonated amide N atom and a chloride ion or ions.

The molecular structure and selected bonding parameters of the present Pd^{II} complex, (I), are shown in Fig. 1 and Table 1, respectively. The coordination geometry is square planar with an N_4 donor set. The average Pd—N(py) distance of 2.067 (3) Å is significantly longer than those in [PdCl$_2$(H_2pedaMe$_2$)] and [PdCl(HpedaMe)] [2.00 (1) and 2.045 (10) Å, respectively], which can be attributed to the *cis* configuration of the pyridyl rings in the [Pd(ppda)] chromophore, in contrast with the *trans* configuration in the latter two complexes. The *cis* configuration causes steric repulsion between the H atoms *ortho* to the respective pyridyl N atoms. The average Pd—N(amide) bond distance of 1.983 (3) Å is the same as that in [PdCl(HpedaMe)], which may be ascribed to the softness of the Pd^{II} Lewis acid and the base-deprotonated amide N atom. Actually, this complex does not protonate even at pH 0.5.



(I) M = Pd^{II}
(II) M = Ni^{II}

The [Ni(peda)] chromophore [H_2peda = 1,2-bis(pyridine-2-carboxamido)ethane] assumes a square-planar structure with C_2 symmetry (Stephens & Vagg, 1982*a*). The present [Ni(ppda)]·H_2O crystal is another crystal form of one reported previously (Stephens & Vagg, 1984*b*). Hereafter the former and the present crystals will be referred to as the α and β forms, respectively. There are also two crystal forms reported for [Cu(ppda)(H_2O)]·$2H_2O$, where one modification is obtained by prolonged standing of the aqueous solution after separation of the other modification (Stephens & Vagg, 1982*b*, 1984*a*; Tsuboyama *et al.*, 1984). The β-[Ni(ppda)]·H_2O modification, (II), belongs to space group *P*2/*n* with Z = 2, which imposes a twofold axis through the Ni and C8 atoms (Fig. 1). The coordination geometry is tetrahedrally distorted square planar, which is very similar to that in the α form. The tetrahedral twist, defined by the

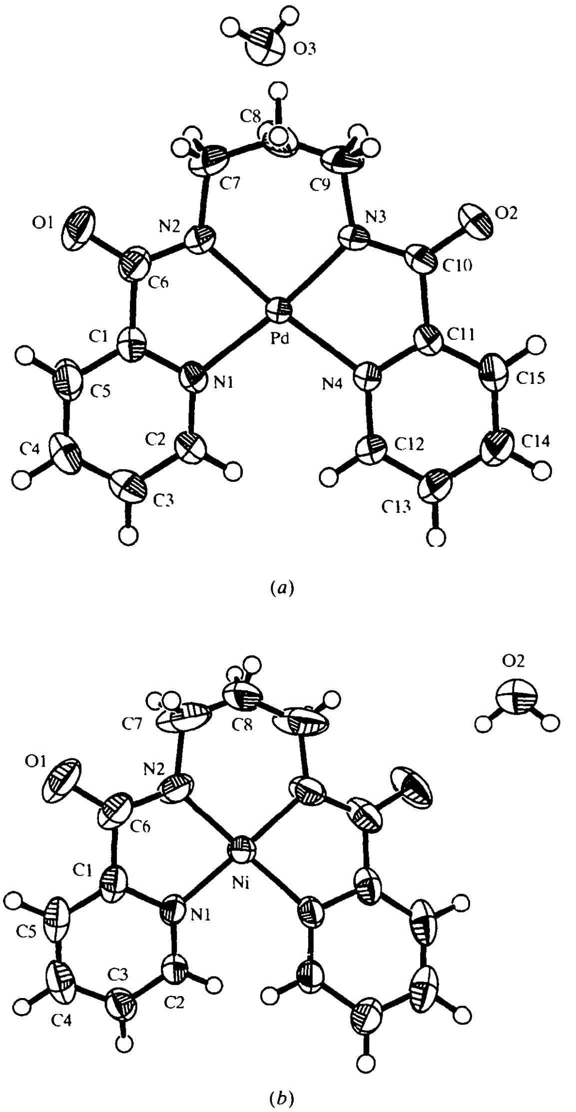


Fig. 1. The molecular structures and atomic numbering systems of (*a*) the [Pd(ppda)] chromophore and (*b*) the β-[Ni(ppda)] chromophore. Displacement ellipsoids are drawn to include 50% probability. H atoms are included with displacement parameters of B = 1.0 Å^2.

dihedral angle between the Ni/N1/N1′ and Ni/N2/N2′ planes is 15.9°, which is identical to that in the α form.

The C8 atom in the [Pd(ppda)] chromophore shows a B_{eq} value (16.8 Å^2) much greater than those of C7 and C9 (5.1 and 6.0 Å^2, respectively). The B_{eq} value of C8 (12.9 Å^2) in β-[Ni(ppda)] is also much greater than those of the other C atoms (3.5–7.8 Å^2), implying flip-flop libration at C8.

High-resolution ^{1}H NMR spectra observed for methanol-d_4 and D_2O solutions of [Pd(ppda)]·H_2O exhibit no spectral change upon addition of DCl or NaOD to the solution. Thus, the coordination of a deprotonated amide N atom to Pd^{II} is more favourable than that of a protonated amide. The spectra observed for H_2ppda in methanol-d_4 at room temperature showed a quintet at 1.92 p.p.m. and a triplet at 3.55 p.p.m. (*versus* TMS) due to α- and β-methylene protons librating rapidly. These signals exhibited high-field shifts to 1.82 and 3.22 p.p.m., respectively, upon coordination to Pd^{II}, which may be attributed to deprotonation at the amide. The chemical shifts due to the aromatic ring protons of H_2ppda were shifted to low-field from 7.5–8.6 to 7.7–8.7 p.p.m.

The variable-temperature ^{1}H NMR spectrum of [Pd(ppda)]·H_2O in methanol-d_4 was studied. Two broad lines due to the α- and β-methylene protons were split into two equally intense lines with separations ($\Delta\delta$) of 0.9 and 0.6 p.p.m., respectively, at 198 K. In general, the chemical shift of the axial proton of the cyclohexane ring is about 0.5 p.p.m. up-field compared with that of the equatorial proton (To-ori & Hirota, 1990). The observed splittings can thus be attributed to the chemical shifts of the axial and equatorial protons. Thus, the temperature-dependent libration resulting from concerted rotation about the N—C and C—C bonds is evident in solution.

Experimental

H_2ppda was prepared according to the method of Ojima (1967). [Pd(ppda)]·H_2O was synthesized by mixing a dilute HCl solution of $PdCl_2$ with an equimolar aqueous solution of H_2ppda and allowing the resulting solution to stand at ambient temperature. The isolated product was recrystallized from dimethylformamide as pale-yellow single crystals. Analysis: C 44.3, H 3.86, N 13.84%; calculated for $C_{15}H_{16}N_4O_3Pd$: C 44.3, H 3.97, N 13.77%. A single crystal was sealed in a glass capillary. [Ni(ppda)]·H_2O was prepared by mixing aqueous solutions of $NiCl_2$ and equimolar free base at pH 8–9, adjusted with NaOH solution. The product was recrystallized from alkaline solution (pH 8–9) as red single crystals. High-resolution ^{1}H NMR spectra were recorded on a Jeol JNM-EX400 and Bruker ARX-500 spectrometer.

Compound (I)

Crystal data

[Pd($C_{15}H_{14}N_4O_2$)]·H_2O
M_r = 406.72
Triclinic
$P\bar{1}$
a = 10.762 (2) Å
b = 10.960 (2) Å
c = 7.160 (1) Å
α = 100.76 (1)°
β = 97.53 (1)°
γ = 115.33 (1)°
V = 728.5 (2) Å^3
Z = 2
D_x = 1.854 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 24 reflections
θ = 12.8–13.0°
μ = 1.276 mm^{-1}
T = 298.2 K
Prismatic
0.25 × 0.25 × 0.15 mm
Yellow

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.676, T_{max} = 0.826
3523 measured reflections
3344 independent reflections
2807 reflections with $I > 3\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.5°
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 12$
$l = -9 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: 1.26%

Refinement

Refinement on F
R = 0.032
wR = 0.035
S = 1.570
2807 reflections
217 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.0001
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.0781
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Pd—N1	2.066 (3)	N2—C6	1.322 (5)
Pd—N2	1.983 (3)	N2—C7	1.465 (5)
Pd—N3	1.983 (3)	N3—C9	1.464 (5)
Pd—N4	2.068 (3)	N3—C10	1.322 (5)
N1—Pd—N2	80.1 (1)	N2—Pd—N3	94.6 (1)
N1—Pd—N3	174.6 (1)	N2—Pd—N4	174.4 (1)
N1—Pd—N4	105.4 (1)	N3—Pd—N4	79.9 (1)

Compound (II)

Crystal data

[Ni($C_{15}H_{14}N_4O_2$)]·H_2O
M_r = 359.02
Monoclinic
$P2/n$
a = 7.183 (2) Å
b = 9.307 (3) Å
c = 11.326 (3) Å
β = 105.73 (2)°
V = 728.8 (3) Å^3
Z = 2
D_x = 1.636 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 12.0–12.8°
μ = 1.355 mm^{-1}
T = 298.2 K
Prismatic
0.50 × 0.25 × 0.08 mm
Red

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.723$, $T_{max} = 0.897$
1919 measured reflections
1786 independent reflections
1231 reflections with $I > 3\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: 0.85%

Refinement

Refinement on *F*
$R = 0.043$
$wR = 0.045$
$S = 1.674$
1231 reflections
111 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.0335
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Ni—N1	1.911 (3)	N2—C6	1.326 (5)
Ni—N2	1.862 (3)	N2—C7	1.468 (5)
N1—Ni—N1^{i}	98.7 (2)	N1—Ni—N2^{i}	168.0 (1)
N1—Ni—N2	83.9 (1)	N2—Ni—N2^{i}	96.0 (2)

Symmetry code: (i) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

The positions of the H atoms were idealized (C—H 0.95 Å), assigned isotropic displacement parameters $B(H) = 1.2B_{eq}(C)$, and allowed to ride on their parent C atoms. The water H atoms were refined isotropically.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1076). Services for accessing these data are described at the back of the journal.

References

Kajikawa, Y., Mukai, K., Ishizu, K. & Ojima, H. (1981). *Chem. Lett.* pp. 801–804.
Kajikawa, Y., Sakurai, T., Azuma, N., Kohno, S., Tsuboyama, S., Kobayashi, K., Mukai, K. & Ishizu, K. (1984). *Bull. Chem. Soc. Jpn*, **57**, 1454–1458.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Mulqi, M., Stephens, F. S. & Vagg, R. S. (1982). *Inorg. Chim. Acta*, **62**, 221–229; **63**, 197–207.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ojima, H. (1967). *Nippon Kagaku Zasshi*, **88**, 333–339.
Stephens, F. S. & Vagg, R. S. (1982*a*). *Inorg. Chim. Acta*, **57**, 9–13.
Stephens, F. S. & Vagg, R. S. (1982*b*). *Inorg. Chim. Acta*, **57**, 43–49.
Stephens, F. S. & Vagg, R. S. (1984*a*). *Inorg. Chim. Acta*, **88**, 7–14.
Stephens, F. S. & Vagg, R. S. (1984*b*). *Inorg. Chim. Acta*, **90**, 17–24.
To-ori, M. & Hirota, H. (1990). In *Saishin NMR*. Tokyo: Springer-Verlag. [Translation from Atta-ur-Rahman (1986). *Nuclear Magnetic Resonance*. New York: Springer-Verlag.]
Tsuboyama, S., Sakurai, T., Kobayashi, K., Azuma, N., Kajikawa, Y. & Ishizu, K. (1984). *Acta Cryst.* B**40**, 466–473.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

© 1999 International Union of Crystallography
Printed in Great Britain – all rights reserved

Acta Cryst. (1999). C**55**, 722–724

Dichloro(2,6-diisopropylaniline-*N*)(η^5-pentamethylcyclopentadienyl)rhodium(III)

Soon W. Lee and Jae-Gyung Lee

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746, Korea. E-mail: swlee@chem.skku.ac.kr

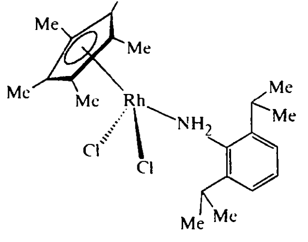
(*Received 29 September 1998; accepted 9 November 1998*)

Abstract

The title compound, $[RhCp^*Cl_2(H_2N\text{–}C_6H_3\text{-}2,6\text{-}{}^iPr_2)]$ (where Cp* is pentamethylcyclopentadienyl) or $[RhCl_2(C_{10}H_{15})(C_{12}H_{19}N)]$, was prepared from the reaction of di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium(III), $[Cp^*RhCl_2]_2$ [White, Yates & Maitlis (1992). *Inorg. Synth.* **29**, 228–234], with 2,6-diisopropylaniline in acetonitrile. This compound has a three-legged piano-stool structure. The ring is almost parallel to the phenyl ring of the 2,6-diisopropylaniline ligand.

Comment

The iridium analogue of the title compound, $[IrCp^*Cl_2(H_2N\text{–}C_6H_3\text{-}2,6\text{-}{}^iPr_2)]$, was prepared by Bergman's group (Glueck *et al.*, 1991). Using the same methodology, we isolated the title compound, (I), which is stable both in the solid state and in solution.



(I)