Synthesis and X-ray Structures of New Mononuclear and Dinuclear Diimine Complexes of Late Transition Metals

Timo V. Laine,*[a] Martti Klinga,[a] and Markku Leskelä[a]

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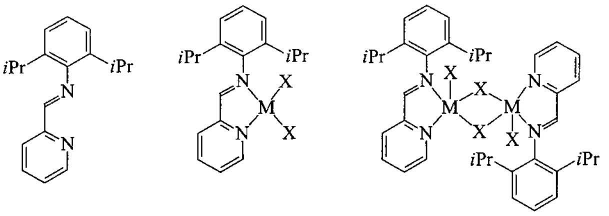
Synthesis of new palladium(II) (**1**), nickel(II) (**2a** and **2b**), and cobalt(II) (**3**) complexes bearing the unsymmetrical, bidentate nitrogen ligand 2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine (**L**) is described. The solid-state structures of **1**, **2a**, and **2b** have been determined by single-crystal X-ray diffraction. The Pd^{II} compound exists in the monomeric form whereas the nickel complexes were observed as centrosymmetric dimers with slightly distorted square-pyramidal coordination sphere around each nickel center.

Introduction

During the past 15 years extensive research effort from academic and industrial laboratories has been devoted to the development of transition-metal-catalyzed polymerization processes.[1] As a result the polyolefin industry has since the early 1990s had the option to transfer from mixture-type systems of the classical Ziegler−Natta technology to more sophisticated single-site catalysts, such as group-4 metallocenes,[2] in which well-defined active centers and catalyst structures enable tailoring of polymer properties by modifying the catalyst precursor itself.[3] Some signs of the next prospective catalyst generation are already emerging:[1] The disclosure by the group of Brookhart in 1995 that they produced high molecular weight polyethylene for the first time with late transition metal complexes[4] has revived the investigation of late transition metal compounds as potential catalyst precursors.[5] Prior reports of the use of group-10 metals exist,[6] but these systems suffer from the highly competitive chain-termination step and produce only short-chain oligomers of up to 40 carbon atoms.[7] Therefore, very little utilization had been found for such systems leaving the nickel-catalyzed oligomerization of ethylene in the Shell Higher Olefin Process (SHOP)[8] as the sole industrial-scale application. This disadvantage was, however, overcome by the use of nickel(II) and palladium(II) complexes bearing sterically demanding 1,4-diazabutadiene ligands,[4] in which bulky aryl groups of the ligand protect the active center by blocking the axial coordination sites thus enhancing chain growth and disfavoring termination processes.[9] Depending on the ligand substitution pattern and process parameters these catalysts can produce a wide variety of products ranging from linear high-density material to highly branched, amorphous polyethylene[4,10] or even short-chain oligomers.[11] Also different types of ethylene copolymers incorporating polar comonomers, such as alkyl acrylates, can be manufactured.[12] Due to the demonstrated versatility and industrial potential[13] a comprehensive patent application covering the syntheses of numerous diazabutadiene-type transition-metal compounds and their use as polymerization catalysts has been filed.[14]

According to recent reports the group of applicable catalyst precursor metals is extending rapidly to cover other, more scarcely utilized transition metals as well. In addition to group-10 metal compounds[4,10,15] some five-coordinate iron(II) and cobalt(II) complexes bearing triimine-type ligands have demonstrated suitability as active ethylene polymerization catalysts after activation with alkylaluminum compounds.[16] Also the first examples of homogeneous chromium(III) catalysts have been published recently.[17] Reported studies, however, have mainly involved symmetrical ligands with two electronically or sterically equivalent imine nitrogen atoms.[5] In this article we present the synthesis and characterization of novel group-9 and -10 metal complexes containing the unsymmetrical, bidentate ligand 2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine (**L**).



L

1: M = Pd, X = Cl

2a: M = Ni, X = Cl
2b: M = Ni, X = Br
3: M = Co, X = Br

Scheme 1

Results and Discussion

Synthetic Aspects

The ligand **L** is prepared by a facile one-step condensation of 2-pyridinecarboxaldehyde and 2,6-bis(1-methylethyl)phenylamine, as shown in Scheme 2, yielding pale yellow, crystalline material after purification and recrystalliza-

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[a] Laboratory of Inorganic Chemistry, Department of Chemistry, P. O. Box 55, FIN-00014 University of Helsinki, Finland
Fax: (internat.) + 358-9/1914-0198
E-mail: timo.laine@helsinki.fi

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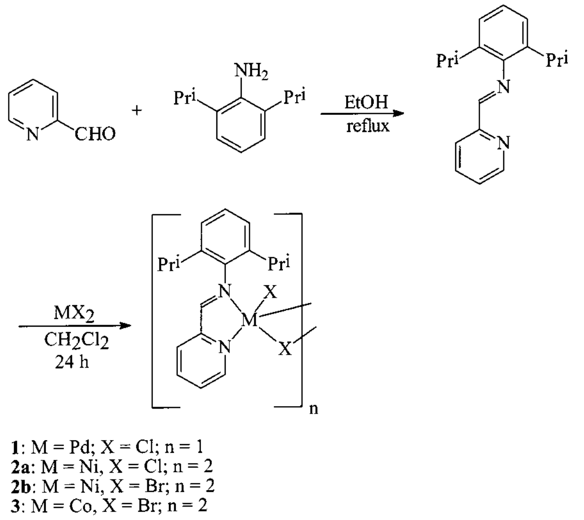
tion from pentane. Due to the limited solubility of anhydrous late transition metal halides in organic solvents only in the case of cobalt the subsequent complex formation step could be performed by a direct reaction of the ligand with the metal halide. Otherwise, solvent-adduct-based precursor compounds were needed (the adduct was 1,2-dimethoxyethane and 1,5-cyclooctadiene for nickel and palladium, respectively). Complexation products were isolated as yellow (**1**), orange (**2a**), orange-red (**2b**), or deep brown (**3**) powders in good yields (70−96%). All compounds gave satisfactory distribution patterns in elemental analysis.



Scheme 2. Synthesis of compounds **1**−**3**

Analysis of the palladium compound **1** by ^{1}H-NMR spectroscopy reveals certain changes in chemical shifts. First of all, the sharp doublet signal from the isopropyl methyl groups of the free ligand at $\delta = 1.17$ has been split into two smaller doublets at $\delta = 1.03$ and $\delta = 1.43$ after complexation. This may be explained by the blocking effect of the chloride ions attached to the palladium center. While in the free ligand the aryl group can rotate unobstructed around the carbon−nitrogen bond, the chloride positioned *cis* to the imine nitrogen atom restricts this movement and subjects the inner methyl groups to some degree of deshielding resulting in the observed separation of peaks. Another distinctive consequence of complex formation is the movement of certain signals in the spectrum. Protons situated in the *ortho* and *para* positions in the aromatic ring systems as well as the proton of the imine carbon atom are especially affected with chemical shifts transferred downfield by 0.30−0.51 ppm. Measurements of the ^{1}H-NMR spectra for the nickel and cobalt complexes (**2a**, **2b**, and **3**) failed apparently as a result from the interfering effect caused by the associated metal center.

Treating the nickel compounds with methylaluminoxane (MAO) provides quite effective catalysts for ethylene polymerization, while the cobalt complex shows nearly negligible activity. In nickel-catalyzed reactions the activities and polymer molecular weights depend on the polymerization temperature: Lowering the temperature to 0 °C leads to an increase in molecular weights by an order of magnitude at the expense of declining catalytic activity.[18] The MAO-activated palladium compound could not be utilized for the polymerization of ethylene but it proved to be highly active with cyclic monomers, such as norbornene.[19] In order to take full advantage of the potential provided by these systems our current work is concentrating on the effects of different ligand substitution patterns on the polymerization behavior of these compounds.

X-ray Crystallography

Crystallization from acetone (for **1**) or a mixture of acetone and pentane (2:1 for **2a**, 1:1 for **2b**) yielded deep orange crystals suitable for structural analysis. The crystal data, together with the data collection and structure refinement parameters are presented in Table 2. Selected bond lengths and angles are given in Table 1. In each compound the solid-state structures are stabilized only by van der Waals forces between the molecules.

The palladium compound **1** crystallizes in the monomeric form with two chlorine atoms (Cl1 and Cl2) and two nitrogen atoms (N1 and N8) of the bidentate ligand forming the expected square-planar coordination sphere around the palladium center (see Figure 1). The palladium atom is situated exactly in the coordination plane N1−N8−Cl2−Cl1 (0.029 Å above the calculated plane) as the average off-plane deviation is 0.053 Å. The narrow N1−Pd−N8 angle 80.08(11)° resulting from the relatively small bite size of the ligand, however, distorts the square structure in a similar fashion as observed in other pyridylimine[20] or bipyridine[21,22] complexes of palladium, but without any coordination plane distortion out of the ligand plane.[22a] In fact, the significant bond lengths and angles in complex **1** resemble the ones reported for the structure of the C_2-symmetric dichloro(2,2′-bipyridine)palladium(II),[21] which indicates electronic similarity of the two nitrogen coordination sites. The variation between the ligand nitrogen atoms, therefore, originates from the difference in steric environment of the two binding sites: The phenyl ring of the imino side arm adopts a position almost perpendicular to the metal coordination plane with the phenyl−coordination plane angle 86.84(8)° and, thus, shields the metal center from one side.

The nickel complexes **2a** and **2b**, in turn, crystallize as centrosymmetric dimers in which each nickel atom is coordinated to two ligand nitrogen atoms (N1 and N8) as two bridging halogen atoms (Cl1 and Cl1a in **2a**, Br1 and Br1a in **2b**) connect the two metal centers. A terminal halide ion (Cl2 and Br2 in **2a** and **2b**, respectively) completes the square-pyramidal coordination sphere. The intramolecular nickel−nickel distance of the chloro complex **2a** is slightly shorter [3.475(1) Å] than recently reported for other nitrogen-ligand-containing nickel(II) dimers,[23c] which is also reflected in a sharper Ni−Cl−Ni angle. Dimeric structures are commonly known for dichloronickel(II) complexes of this type,[23] while similar bipyridine-based dibromonickel-

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **2a**, and **2b**

1		**2a**		**2b**	
Bond lengths					
Pd−N1	2.028(3)	Ni−N1	2.039(2)	Ni−N1	2.050(9)
Pd−N8	2.022(3)	Ni−N8	2.095(2)	Ni−N8	2.099(9)
Pd−Cl1	2.2809(11)	Ni−Cl1	2.3965(8)	Ni−Br1	2.533(2)
Pd−Cl2	2.2768(10)	Ni−Cl1a$^{\#}$	2.3366(8)	Ni−Br1a*	2.459(2)
C6−C7	1.457(5)	Ni−Cl2	2.2729(9)	Ni−Br2	2.411(2)
C7−N8	1.279(4)	C6−C7	1.463(4)	C6−C7	1.455(16)
N8−C9	1.448(4)	C7−N8	1.278(3)	C7−N8	1.282(14)
		N8−C9	1.440(3)	N8−C9	1.423(14)
Bond angles					
N1−Pd−N8	80.08(11)	N1−Ni−N8	79.37(9)	N1−Ni−N8	79.9(4)
N1−Pd−Cl1	94.33(9)	N1−Ni−Cl1	91.08(6)	N1−Ni−Br1	91.5(2)
N1−Pd−Cl2	174.51(9)	N1−Ni−Cl1a$^{\#}$	161.14(6)	N1−Ni−Br1a*	160.1(3)
N8−Pd−Cl1	172.85(8)	N1−Ni−Cl2	94.00(6)	N1−Ni−Br2	95.0(3)
N8−Pd−Cl2	94.64(8)	N8−Ni−Cl1	148.86(6)	N8−Ni−Br1	153.2(3)
Cl1−Pd−Cl2	91.05(4)	Cl1−Ni−Cl1a$^{\#}$	85.53(3)	Br1−Ni−Br1a*	85.84(7)
		Ni−Cl1−Nia$^{\#}$	94.47(3)	Ni−Br1−Nia*	94.16(7)

Symmetry transformations used to generate equivalent atoms: $^{\#}$ $-x$, $-y$, $-z + 1$; * $-x$, $-y + 2$, $-z + 2$.

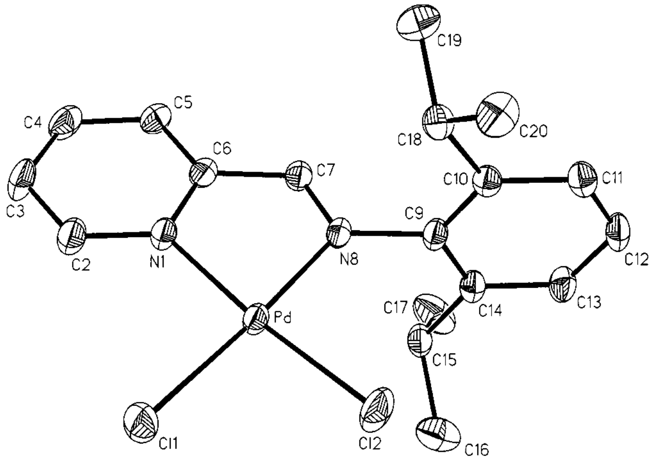


Figure 1. Crystal structure of complex **1** showing the labeling scheme; displacement ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity

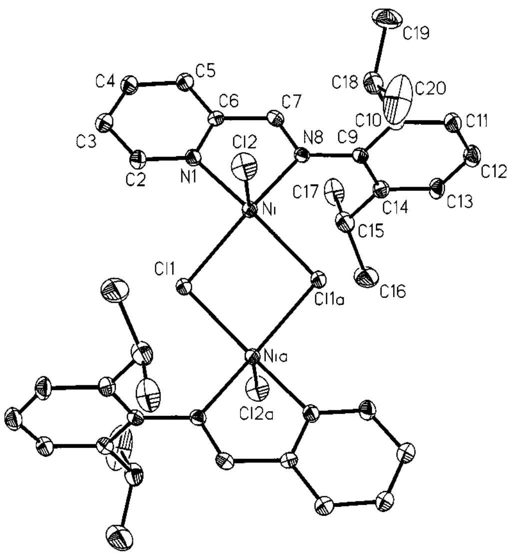


Figure 2. Molecular structure of compound **2a** with the labeling scheme

(II) compounds may exhibit monomeric complexes if additional steric bulk is introduced.[23a]

As with complex **1** also in the case of the nickel analogs the narrow nitrogen−nickel−nitrogen angle [79.37(9)° in **2a** and 79.9(4)° in **2b**] slightly deforms the basal square structure. The effect from dimerization contributes to further structural distortion leading to unequal nickel−nitrogen and nickel−halogen bond lengths: The shorter nickel−halogen bond of the bridge (Ni−Cl1 and Ni−Br1) corresponds to a similarly shorter Ni−N bond (the bond to the imino nitrogen atom N8) situated in the *trans* position. The axial chlorine atom Cl2 or bromine atom Br2, however, has the shortest bond length of all three nickel−halogen bonds.

Another common structural feature between the palladium and nickel complexes is the lack of double-bond delocalization in all three compounds. Relative to other bonds in the imino bridge [values ranging from 1.423(14) to 1.463(4) Å] the C=N double bond (C7−N8) is still the shortest [1.279(4), 1.278(3), and 1.282(14) Å for **1**, **2a**, and **2b**, respectively] even after complexation.

Besides in coordination geometry the nickel compounds differ from their palladium analog in the nature of the coordination plane. In **1** the coordination plane exhibits only slight puckering while more severe puckering was observed in the nickel compounds with average deviations of 0.119 Å for **2a** and 0.071 Å for **2b**, although the calculated value of **2b** is quite close to the average deviation in the palladium complex **1**. Also the palladium atom, as described earlier, is situated in the middle of the coordination plane whereas in the nickel complexes the metal center is elevated from the plane by 0.475(1) and 0.456(4) Å in **2a** and **2b**, respectively.

Analysis of the cobalt coordination sphere in compound **3** revealed a dimeric structure in which one terminal and two bridging bromine atoms as well as two ligand nitrogen

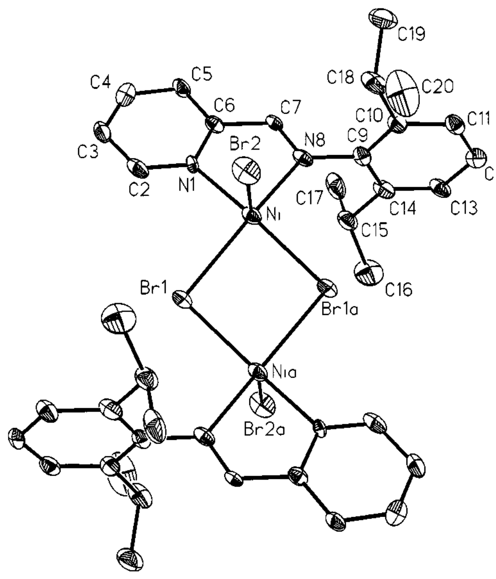


Figure 3. Molecular structure of complex **2b**

atoms create square-based pyramids around each five-coordinate metal center.[24]

Experimental Section

General: All complex preparations were performed under argon with standard Schlenk techniques. Acetone was dried by storing under argon with $CaSO_4$ granules, other solvents by refluxing with a drying agent (P_2O_5 for dichloromethane and sodium/benzophenone for the non-halogenated solvents) and distillation under argon. Dichloro(1,5-cyclooctadiene)palladium(II)[25] [(COD)-$PdCl_2$] as well as dichloro(1,2-dimethoxyethane)nickel(II) [(DME)$NiCl_2$] and dibromo(1,2-dimethoxyethane)nickel(II) [(DME)$NiBr_2$][26] were prepared according to the literature. Anhydrous $CoBr_2$ (Aldrich, 99%), 2-pyridinecarboxaldehyde (Merck, 98%), and 2,6-bis(1-methylethyl)phenylamine (Aldrich, 90%) were used as received. − ^1H NMR: Varian Gemini 200 spectrometer (200 MHz); $CDCl_3$ or [D_6]acetone as solvent, TMS as internal standard. − EI MS: Finnigen SSQ 7000 spectrometer (70 eV); direct inlet probe. − Elemental analyses were carried out at the University of Ulm, Germany, except for the bromine content determination of complex **3**, which was performed by gravimetric analysis at the University of Helsinki.

2,6-Bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine (L): The ligand was synthesized by modifying the literature procedure[27] reported for the analogous 2,6-dimethyl compound. Ethanol (100 mL), 2,6-bis(1-methylethyl)phenylamine (15.76 g, 80.0 mmol), and 2-pyridinecarboxaldehyde (8.57 g, 80.0 mmol) were combined and refluxed for 20 min. The solvent was removed and the residue was vacuum-distilled followed by chromatography on basic alumina with pentane/ethyl acetate (3:1) as eluent. Recrystallization from pentane yielded pale yellow crystals, 14.36 g (67%). − ^1H NMR ($CDCl_3$): $\delta = 1.17$ (d, 12 H, H_{Me}), 2.97 (m, 2 H, $CHMe_2$), 7.16 (m, 3 H, H_{arom}), 7.42 (m, 1 H, $H_{pyridine,5}$), 7.86 (t, 1 H, $H_{pyridine,4}$), 8.27 (d, 1 H, $H_{pyridine,3}$), 8.31 (s, 1 H, $CH{=}N$), 8.73 (d, 1 H, $H_{pyridine,6}$). − $C_{18}H_{22}N_2$ (266.39): calcd. C 81.16, H 8.32, N 10.52; found C 81.01, H 8.37, N 10.39.

Dichloro[2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)-phenylamine]palladium(II) (1): The ligand **L** (0.76 g, 2.87 mmol) was dissolved in 10 mL of dichloromethane and added to a solution of [(COD)$PdCl_2$] (0.80 g, 2.80 mmol in 40 mL of CH_2Cl_2). Stirring was continued for 24 h at ambient temperature at which time precipitation occurred. The precipitated yellow powder was collected by filtration, washed with diethyl ether (2 × 20 mL) and dried in vacuo; yield 1.07 g (96%). − ^1H NMR ([D_6]acetone): $\delta = 1.03$ (d, 6 H, H_{Me}), 1.43 (d, 6 H, H_{Me}), 3.27 (m, 2 H, $CHMe_2$), 7.12 (m, 3 H, H_{arom}), 7.93 (m, 1 H, $H_{pyridine,5}$), 8.22 (d, 1 H, $H_{pyridine,3}$), 8.36 (t, 1 H, $H_{pyridine,4}$), 8.69 (s, 1 H, $CH{=}N$), 9.18 (d, 1 H, $H_{pyridine,6}$). − $C_{18}H_{22}Cl_2PdN_2$ (443.71): calcd. C 48.73, H 5.00, N 6.31; found C 48.29, H 5.05, N 6.19.

Di-μ-chlorodichlorobis[2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine]dinickel(II) (2a): To a suspension of [(DME)$NiCl_2$] (1.86 g, 8.45 mmol) in 40 mL of dichloromethane was added the yellow ligand solution (2.34 g, 8.77 mmol in 15 mL of CH_2Cl_2). After stirring the brown reaction mixture for 24 h at room temperature, the solvent was evaporated and the resulting solid material was washed with pentane (3 × 20 mL) and dried in vacuo yielding complex **2a** as orange powder, 2.65 g (79%). − $C_{36}H_{44}Cl_4N_4Ni_2$ (791.97): calcd. C 54.60, H 5.60, N 7.07; found C 54.61, H 5.94, N 6.68.

Di-μ-bromodibromobis[2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine]dinickel(II) (2b): Analogously to the preparation of **2a**, complex **2b** was prepared from [(DME)$NiBr_2$] (0.40 g, 1.30 mmol) and **L** (0.36 g, 4.89 mmol) in CH_2Cl_2. The orange-red powder was collected by filtration, washed with pentane (3 × 10 mL) and vacuum-dried; yield 0.44 g (70%). − $C_{36}H_{44}Br_4N_4Ni_2$ (969.77): calcd. C 44.59, H 4.57, N 5.78; found C 44.10, H 4.59, N 5.68.

Di-μ-bromodibromobis[2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine]dicobalt(II) (3): Anhydrous $CoBr_2$ (0.55 g, 2.52 mmol) was dissolved in 10 mL of acetone and combined with the ligand solution (0.68 g, 2.55 mmol in 10 mL of acetone). The resulting green-brown solution was stirred for 24 h at room temperature. After solvent evaporation, the residue was washed with hexane (3 × 10 mL) and vacuum-dried. The complex was obtained as brown powder, 1.02 g (83%). − EI MS (70 eV); *m/z*: 483, 485, 487 [1/2 M^+]; 404, 406 [1/2 $M^+ - Br$]; 323 [1/2 $M^+ - 2\ Br$]. − $C_{36}H_{44}Br_4Co_2N_4$ (970.25): calcd. C 44.57, H 4.57, Br 32.94, N 5.77; found C 44.54, H 4.75, Br 32.61, N 5.62.

Crystal-Structure Determinations: The crystals were mounted to a glass fiber with the oil drop method.[28] Crystal data obtained with the $\omega-2\theta$ scan mode were collected on an automated four-circle Rigaku AFC-7S diffractometer using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) at 193 K. Three standard reflections were monitored after every 200 intensity scans. The intensities were corrected for Lorentz and polarization effects. For all compounds ψ-scans were used for absorption correction.[29] Data sets were compressed to reflection files with TEXSAN Single Crystal Structure Analysis Software.[30] The structures were solved with SHELXTL PC 4.1 program package[31] using direct methods while further refinement with full-matrix least squares on F^2 was carried out with SHELXL-93[32] (for **2a**) or SHELXL-97[33] (for **1** and **2b**). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions (riding model) with 1.2 times the displacement factors of the host carbon atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-103369 (for **1**), -103368 (for **2a**), and -103370 (for **2b**). Copies of the data can be obtained on application to CCDC, 12 Union

Table 2. Crystallographic data for complexes **1**, **2a**, and **2b**

	1	**2a**	**2b**
Empirical formula	$C_{18}H_{22}Cl_2N_2Pd$	$C_{36}H_{44}Cl_4N_4Ni_2$	$C_{36}H_{44}Br_4N_4Ni_2$
Formula weight	443.71	791.97	969.77
Crystal color and form	Yellow, prismatic	Orange, prismatic	Orange-brown, prismatic
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no.14)
a [Å]	10.035(2)	9.817(6)	9.885(6)
b [Å]	12.523(3)	14.602(5)	14.515(7)
c [Å]	14.853(3)	13.833(6)	14.127(7)
β [°]	94.70(3)	109.13(4)	106.82(4)
V [Å^3]	1860.3(7)	1873.4(7)	1940.2(18)
Z	4	2	2
$D_{calcd.}$ [Mg/m^3]	1.584	1.404	1.660
Absorption coefficient [mm^{-1}]	1.285	1.321	5.119
F(000)	896	824	968
Crystal size [mm]	0.25 × 0.15 × 0.15	0.25 × 0.25 × 0.25	0.15 × 0.15 × 0.10
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ_{max} [°]	25.00	26.49	25.00
Number of collected reflections	3298	4506	2955
Number of independent reflections	3119	3395	2802
Number of parameters	234	234	212
Goodness-of-fit on F^2	1.066	1.061	1.029
Final R indices [$I > 2\sigma(I)$]	$R = 0.0322$, $wR = 0.0761$	$R = 0.0360$, $wR = 0.0922$	$R = 0.0761$, $wR = 0.1647$
R indices (all data)	$R = 0.0371$, $wR = 0.0779$	$R = 0.0431$, $wR = 0.0955$	$R = 0.1273$, $wR = 0.1848$
Largest differential peak and hole [e/Å^3]	0.539 and −0.981	0.637 and −0.856	0.991 and −0.979

Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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