

Synthesis and Properties of Dimetallic Complexes Based on a New Oxalamidine-Derived Ligand System with Pendant Pyridine Functionality

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Reaction of sterically hindered bis(imidoyl)chlorides of oxalic acid with picolylamine afforded conformationally locked oxalic acid-derived amidines with pendant pyridine functional-

ities. Based on this new multivalent ligand system, dimetallic complexes were efficiently prepared.

Introduction

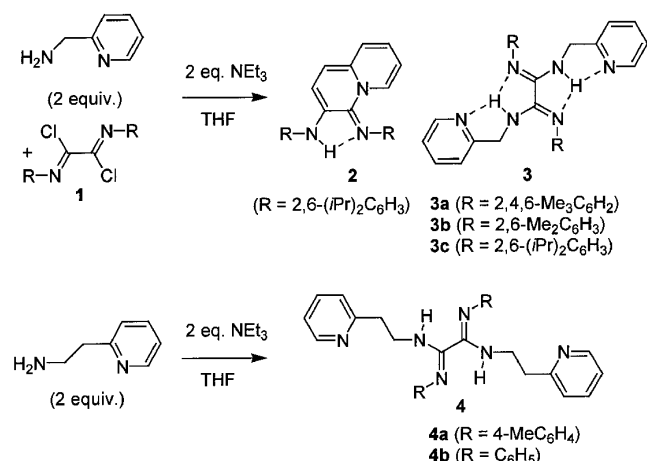
The synthesis of dimetallic complexes, particularly those containing two different transition metals “communicating” with each other, is of considerable current interest for both theoretical and practical reasons.^[1] Important properties have been postulated for these compounds, such as cooperative effects in catalysis, intramolecular electron-transfer reactions, molecular-based ferromagnetic and anti-ferromagnetic interactions and self-organization processes. However, the synthesis of heterodimetallic complexes is associated with severe problems, since two metals exhibiting different demands in terms of their coordination sphere have to be brought close together. Very recently, the preparation of heterodimetallic complexes has been realized using aminopyridines as bridging ligands.^[2] Herein, we report an efficient synthesis of heterodimetallic complexes which relies on the use of a new multivalent ligating system.

The ability of amidinates to act as four-electron-donating, bidentate ligands for main group elements, transition metals, and the lanthanides is well established.^[3] We and others have studied the coordination chemistry of oxalic acid-derived amidines which can act as four-electron-donor ligands (to give five-membered rings) or as bridging ligands.^[4] Very recently, the coordination chemistry of ancillary amidinate ligands with a pendant pyridine functionality has been described by Arnold and co-workers. The metal complexes (Mg, Al, Zr, La) prepared were shown to be monomeric, with the pendant pyridine coordinated intramolecularly.^[5] In most cases, the tridentate ligands coordinated meridionally to the metal centre. This work prompted us to disclose our results related to the coordination chemistry of oxalic acid-derived amidines containing pendant pyridine functionalities. The use of this new ligand

system allowed the efficient synthesis of a variety of heterodimetallic diazadiene complexes.

Results and Discussion

Unfortunately, our initial attempts to prepare the desired ligands **3** by condensation of 2-aminomethylpyridine with the oxalic acid bis(imidoyl)chlorides **1a–c** (R = Tol, Ph, MeOC₆H₄)^[4e] in the presence of triethylamine were unsuccessful, since cyclization products were exclusively obtained.^[4f] The use of oxalic acid bis(imidoyl)esters, prepared by reaction of the corresponding bis(imidoyl)chlorides with ethanol, was equally disappointing and resulted in formation of complex reaction mixtures. Fortunately, the problem could be eventually solved by the use of the sterically hindered bis(imidoyl)chlorides **1d–f** [R = 2,4,6-Me₃C₆H₂, 2,6-Me₂C₆H₃, 2,6-(iPr)₂C₆H₃] which allowed the preparation of the desired oxalamidines **3a–c**, respectively, in good yields (Scheme 1). During the synthesis of **3c**, the cyclization product **2** was obtained as a side-product in 15% yield. The use of sterically undemanding bis(imidoyl)chlorides was possible in the reaction of 2-aminoethylpyridine with



Scheme 1. Preparation of oxalamidines with pendant pyridine functionality

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bis(imidoyl)chlorides to give the amidines **4** (**4a**: R = Tol, **4b**: R = Ph) in good yields.

Amidines represent flexible molecules which usually undergo *E/Z* isomerization by a tautomeric rotation mechanism.^[6a] In the case of oxalamidines, two imino-groups are present and rotation of the central C–C bond can give rise to *s-trans* or *s-cis* conformations.^[6b] Therefore, very complex or coalescent ¹H NMR spectra are normally observed at room temperature due to the highly flexible structure. Interestingly, sharp signals and a low-field NH resonance were observed for compounds **3** which suggested that the latter are conformationally restricted by the presence of intramolecular hydrogen bonds and by the high steric demand of the substituents. Moderately broad signals were observed only for the CH₂ and the NH groups. The location of the NH group was proven by low-temperature ¹H NMR measurements: upon cooling to 0 °C, formation of a doublet is observed for the CH₂ groups due to a ³*J* coupling of the latter with the adjacent NH group.

The structure of amidine **3a** was independently confirmed by X-ray crystallography (Figure 1). The amidine moiety is planar and shows an *s-trans*-(*Z/Z*) configuration. The bulky mesityl groups are twisted out-of-plane by 104.9°. It is noteworthy that the oxalamidines **3** represent rare examples of systems containing intramolecular three-centre (“bifurcated”) hydrogen bonds.^[7] Two hydrogen bonds (to the amidine nitrogen N1A and to the pyridine nitrogen N3) are observed for the hydrogen atom located at nitrogen N2 (N1A–H 2.18 Å, N3–H 2.41 Å). Bifurcated hydrogen bonds are of great current interest since they play an important role in DNA conformation^[8] and in protein hydration.^[9] Two types of three-centre interaction can be distinguished, one involving two donors and one acceptor (“HXH”), and the other involving one donor and two acceptors (“XHY”). Very recently, computational studies of a depsipeptide model have shown that addition of a second acceptor (Y) to a hydrogen bond XH has no enthalpic benefit, while addition of a second donor (H) to XH is modestly favourable enthalpically.^[10]

Two conformations are, in principle, possible for oxalamidine ligands coordinated to the metal. The ligand can possess an *s-trans*- or an *s-cis* conformation. We have found that oxalamidinate complexes of molybdenum possess the *s-cis* conformation.^[4c–4d,12] These compounds are thus 1,4-diazadiene complexes.^[11] The reaction of dibenzylidiphenyl-oxalamidine with Mo(CO)₄(nor) resulted in rotation of the central C–C bond and coordination of the aromatic (rather than the aliphatic) imino groups to the metal to give an *s-cis*-configured DAD complex (Scheme 2).^[12] The chemoselectivity can be explained by the fact that protonation of the nitrogen atom would result in interruption of the conjugation of the phenyl and the imino group. Interestingly, formation of the *s-trans*-configured complex **5** was observed in the reaction of ligand **3a** with Mo(CO)₄(nor) (Scheme 2). The structure of complex **5** was determined by spectroscopic means: whereas only two carbonyl absorptions (IR) are observed for Mo(CO)₄(nor), four absorptions are observed for complex **5**. In addition, two sets of signals are

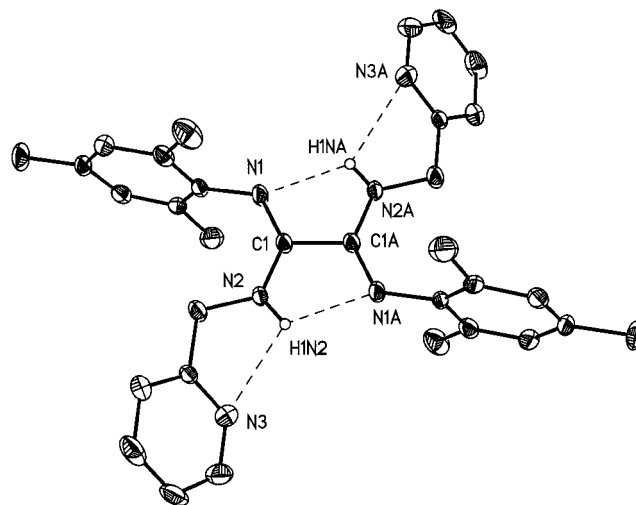
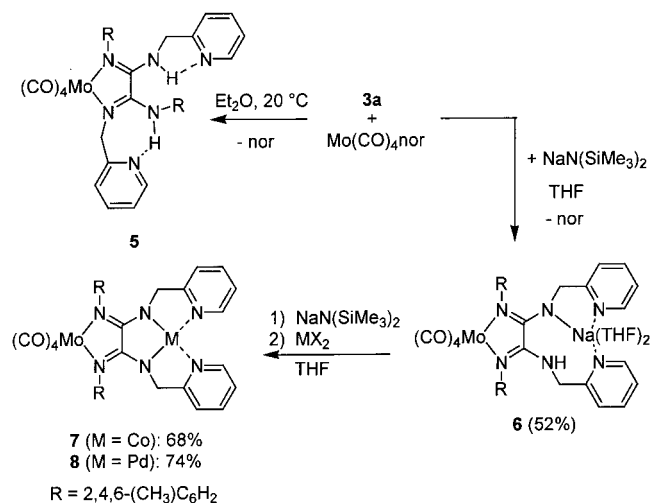


Figure 1. ORTEP plot of **3a** with the atom numbering scheme; the thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths [Å] and angles [°]: N1–C1 1.276(3), N2–C1 1.340(3), C1–C1A 1.526(4); N1–C1–C1A 116.5(2), N2–C1–C1A 113.1(2), C1–N2–C2 128.2(2), N2–C2–C3–N3 40.3, C1–N1–C8–C9 104.9



Scheme 2. Synthesis of hetero-dimetallic complexes **5–8**

observed in the ¹H NMR spectrum. In the ¹³C NMR spectrum of **5**, separate signals are detected for all carbon atoms which could be assigned to the proposed structure. All spectroscopic data indicate that complex **5** adopts an unsymmetrical structure containing an *s-trans*-configured oxalamidine unit rather than a symmetrical structure containing a *cis*-configured oxalamidine unit. The *s-trans* selectivity can be explained by the assumption that the hydrogen bond involving the pyridine nitrogen is more stable than the hydrogen bond located within the oxalamidine substructure. The 2-aminomethylpyridine subunit is planar due to intramolecular hydrogen bonding. Therefore, coordination of two aromatic imino groups to the metal would result in severe steric interactions. Coordination of two aliphatic imino groups to the metal would result in cleavage of two relatively stable pyridine hydrogen bonds. In contrast, formation of complex

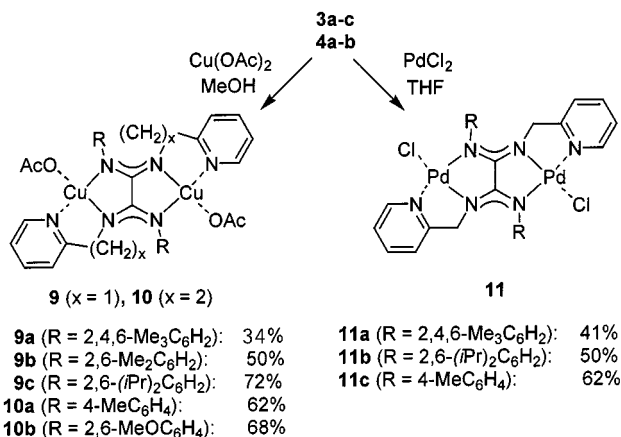
5 involves a prototropic shift, cleavage of a weak hydrogen bond and formation of a strong one.

To support our hypothesis, compound **3a** was deprotonated with $\text{NaN}(\text{SiMe}_3)_2$: reaction of the sodium salt of **3a** with $\text{Mo}(\text{CO})_4(\text{nor})$ gave the *s-cis*-configured heterodimetallic complex **6** (Scheme 2). The structure of complex **6** was independently confirmed by an X-ray structure analysis (Figure 2). The pyridine moieties are located above and below the plane of the chelate system. The mesityl substituents of the ligand are located orthogonal to each other due to steric interactions. The sodium atom is coordinated by two pyridine nitrogens, by an amidinate-derived nitrogen atom and by an oxygen atom of a neighbouring molecule. These atoms define the equatorial square plane of a distorted octahedron. The oxygen atoms of two THF molecules are located at the axial positions. The Mo–C33 bond is shorter than the other Mo–C distances due to the *trans* effect of the nitrogen N1 and the polarizing influence of the sodium ion. The C35–O3 bond is elongated (1.189 Å) and lies in the same range as normal C–O double bonds.^[13]

Deprotonation of the NH group of complex **6** and subsequent reaction with one equivalent of CoBr_2 or PdCl_2 resulted in formation of the heterodimetallic complexes **7** (Mo/Co) and **8** (Mo/Pd). The spectroscopic properties of these products are very similar to those of complex **6**, which suggests that the same type of structure is adopted. For compound **8** only two signals (^1H NMR) are observed for the CH_3 groups and only one signal is observed for the CH_2 groups. The chemical shifts are almost identical to those observed for complex **6**. Due to the anionic character of the ligands, bathochromic shifts (IR) are observed for the equatorial carbonyl ligands of complexes **6**–**8**. Whereas ex-

amples are known where hydrogen bonding influences the selectivity or the rate of organic transformations, such effects are rare in complexation reactions. However, such processes should play an important role in the binding of transition metals to biomolecules.

The synthesis and properties of homodimetallic complexes were next studied. Reaction of $\text{Cu}(\text{OAc})_2$ with the pyridyloxalamidines **3** and **4** resulted in formation of the deeply green to black coloured (Cu/Cu) complexes **9** and **10** (Scheme 3). Reaction of ligands **3** with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ resulted in formation of the orange coloured (Pd/Pd) complexes **11**.



Scheme 3. Synthesis of homo-dimetallic complexes **9**–**11**

The structure of the Cu complex **10a** was independently confirmed by an X-ray structure analysis (Figure 3). Deeply green coloured single crystals of **10a** were obtained from a

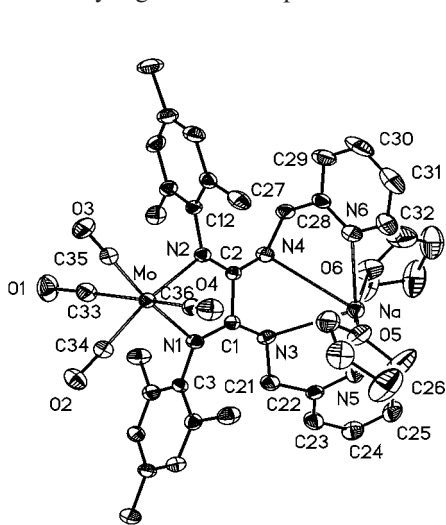


Figure 2. ORTEP plot of **6** with the atom numbering scheme; the thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths [Å] and angles [°]: Mo–N1 2.244(3), Mo–C35 1.916(5), N3–C1 1.310(5), N5–Na 2.426(5), O2–C34 1.172(6), Mo–N2 2.271(3), N1–C1 1.348(5), N3–Na 2.652(4), N6–Na 2.518(4), O3–C35 1.184(5), Mo–C33 2.031(5), N2–C2 1.289(5), N4–C2 1.360(5), O3A–Na 2.378(4), C1–C2 1.524(6), N1–Mo–N2 71.52(12), N1–C1–C2 112.5(3), N4–C2–C1 112.4(4), Mo–N1–C1 119.6(3), N2–C2–C1 117.4(4), C1–N3–Na 112.4(3), N3–Na–N6 109.9(13), Mo–N2–C2 118.3(3), N3–C1–C2 113.4(4), N3–Na–N5 66.94(13)

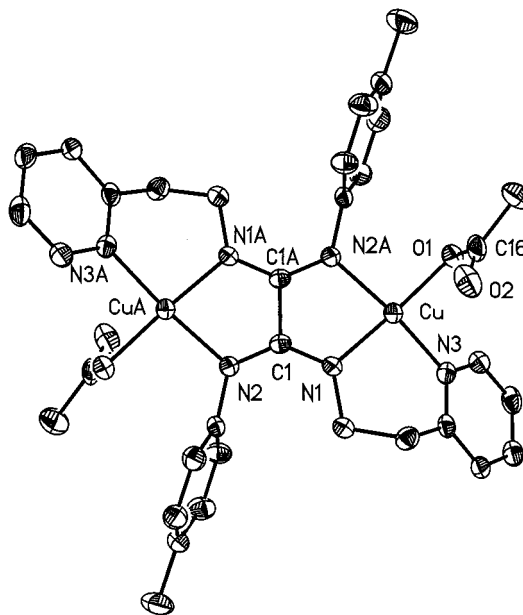


Figure 3. ORTEP plot of **10a** with the atom numbering scheme; the thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths [Å] and angles [°]: N1–C1 1.314(6), Cu–N1 1.940(3), Cu–N3 2.008(3), N2–C1 1.316(4), Cu–N2A 1.973(3), Cu–O1 1.953(3), C1–C1A 1.537(3), N1–C1–C1A 113.4(4), N2A–Cu–O1 94.16(11), C1–N1–Cu 115.6(2), N2–C1–C1A 113.9(4), C1–N2–CuA 114.2(2), N1–Cu–N3 94.22(12), N1–Cu–N2A 82.92(12)

1:1 solution of MeOH and water. The ligand shows an *s-trans-(E/E)* configuration. The square-planar coordination spheres of the Cu^{II} atoms are distorted. The amidine moiety is planar. In contrast, the tolyl groups are twisted out of plane by ca. 90°. The bond lengths C1–N1 and C1–N2 are almost identical, due to delocalization of the π -electrons (N1–C1–N2). Whereas intense (C=N) absorptions (IR) were observed for the free ligands, no respective absorptions were present for the metal complexes **9–11**, again due to delocalization of the π -electrons. In the electron paramagnetic resonance (EPR) spectrum of complex **10b** a signal was detected at $g = 2.082$. Although the hyperfine structure could not be resolved, the value and the anisotropy of the resonance line were typical for the $g_{\perp}$ signal of Cu^{II}. An antiferromagnetic interaction between the Cu atoms can be anticipated.^[14] Quantitative EPR measurements showed that only ca. 15% of Cu^{II} with $s = 0.5$ was present. The magnetic moment of complex **10b** ($\mu_{\text{eff}} = 1.55$ BM, $T = 296$ K) was lower than the spin-only value of the Cu^{II} ion ($\mu_{\text{eff}} = 1.73$ BM).

In conclusion, we have reported the synthesis of conformationally locked oxalic acid-derived amidines with pendant pyridine functionalities. Based on this multivalent ligand system, new hetero- and homodimetallic complexes were efficiently prepared.

Experimental Section

General: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. Petroleum ether (PE, b.p. 40–70 °C), diethyl ether (E), *tert*-butyl methyl ether (MTBE), toluene and acetone were distilled prior to use. The solvents that were used for the reactions (THF and ether), were distilled from sodium/benzophenone immediately prior to use. The oxalic acid bis(imidoyl)chlorides were prepared according to literature procedures.^[4c] NMR: 200 MHz and 50 MHz (for ¹H and ¹³C, respectively), if not quoted otherwise, on an AC 200 F (Bruker) apparatus. The solvents CDCl₃, CD₂Cl₂ and [D₈]THF were used as received. The multiplicity of the carbon atoms was determined by the DEPT 135 technique and quoted as: CH₃, CH₂, CH and C for primary, secondary, tertiary and quaternary carbon atoms. MS: EI, 70 eV; CI, H₂O: chemical ionization with water. Preparative scale chromatography: J. T. Baker silica gel (60–200 mesh). For the EPR measurements, an ESP 300 E apparatus (Bruker, $\nu = 9.4$ GHz, internal standard: diphenylpicrylhydrazyl). Melting points, uncorrected, were measured using a Büchi apparatus. Elemental analyses: Microanalytical laboratory of the Universities of Hannover and Jena.

General Procedure for the Preparation of Oxalic Acid Amidines (3): A THF solution of **1** (2.0 mmol), 2-picolylamine (0.44 mL) and NEt₃ (0.63 mL, 4.5 mmol) was refluxed for 48 h. After cooling, the precipitated HNEt₃Cl was filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (toluene → toluene/acetone = 1:1).

***N,N'*-Bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)-ethane-1,2-diamine (3a):** Yield: 0.73 g of colourless crystals (72%), m.p. 148–150 °C. – ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 2.10$ (s,

12 H, 2- and 6-CH₃), 2.29 (s, 6 H, 4-CH₃), 4.00 (s, 4 H, CH₂), 6.82 (s, 4 H, CH), 7.02 (br. d, 2 H, Pyr-CH), 7.14 (t, 2 H, Pyr-CH), 7.59 (t, 2 H, Pyr-CH), 8.20 (br. 2 H, NH), 8.48 (d, 2 H, Pyr-CH). – ¹³C NMR (50 MHz, CD₂Cl₂): $\delta = 18.6$ (2,6-CH₃), 20.9 (4-CH₃), 47.6, 121.6, 122.4, 128.3, 128.6, 131.6, 136.7, 144.5, 146.0 (br), 149.5, 158.1. IR (Nujol): $\tilde{\nu} = 3309$ (m, ν_{NH}), 1648 (s, ν_{CN}), 1607 (m), 1592 (m), 1569 (m) cm⁻¹. – MS [CI (H₂O)]: m/z (%) = 505 (100) [$M^+ + 1$], 412 (24), 252 (18) [$M^+ / 2$], 93 (19). – C₃₂H₃₆N₆ (504.7): calcd. C 76.16, H 7.19, N 16.65; found C 76.21, H 7.11, N 16.33.

1,2-Bis(2,6-dimethylphenylimino)-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (3b): Yield: 1.1 g of colourless crystals (58%), m.p. 136–138 °C. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 2.14$ (s, 12 H, CH₃), 4.00 (d, $J = 4.4$ Hz, 4 H, CH₂), 6.87 (t, $J = 6.3$ Hz, 2 H, Pyr-CH), 7.00 (d, $J = 6.7$ Hz, 6 H, Ar), 7.13 (t, $J = 5.0$ Hz, 2 H, Pyr), 7.58 (t, $J = 7.7$ Hz, 2 H, Pyr), 8.19 (br. 2 H, NH), 8.48 (d, $J = 4.8$ Hz, 2 H, Pyr). – ¹³C NMR (50 MHz, CD₂Cl₂): $\delta = 18.6$ (CH₃), 47.5 (CH₂), 121.6, 122.4, 127.6, 128.9, 136.7, 145.6, 147.2, 149.5, 157.9. – IR (Nujol): $\tilde{\nu} = 3301$ (s, ν_{NH}), 1662 (s, ν_{CN}), 1588 (s), 1569 (m), 1492 (s) cm⁻¹. – MS [CI (H₂O)]: m/z (%) = 477 (100) [$M^+ + 1$], 384 (19), 238 (10) [$M^+ / 2$], 147 (4), 126 (7), 110 (5), 93 (12). – C₃₀H₃₂N₆ (476.6): calcd. C 75.60, H 6.77, N 17.63; found C 75.74, H 7.17, N 17.32.

1,2-Bis(2,6-diisopropylphenylimino)-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (3c): Yield: 0.85 g of colourless crystals (72%), m.p. 144–146 °C. – ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 1.19$, 1.23 (2 × d, $J = 1.9$ Hz, 2 × 12 H, *i*Pr-CH₃), 3.14 (m, 4 H, *i*Pr-CH), 4.11 (s, 4 H, CH₂), 7.01–7.28 (m, 10 H, Ar, Hetar), 7.58 (t, 2 H, $J = 7.7$ Hz, Hetar), 8.21 (br. 2 H, NH), 8.46 (d, $J = 4.8$ Hz, 2 H, Hetar). ¹³C NMR (50 MHz, CD₂Cl₂): $\delta = 22.5$, 22.6 (*i*Pr-CH₃), 29.3 (*i*Pr-C), 47.7, 121.4, 122.4, 122.8, 123.0, 136.8, 138.9, 145.2, 149.6, 157.9. – IR (Nujol): $\tilde{\nu} = 3289$ (s, ν_{NH}), 1658 (s, ν_{CN}), 1592 (s), 1582 (m), 1569 (m) cm⁻¹. – MS [CI (H₂O)]: m/z (%) = 589 (100) [$M^+ + 1$], 294 (8) [$M^+ / 2$]. – C₃₈H₄₈N₆ (588.8): calcd. C 77.51, H 8.22, N 14.27; found C 76.88, H 8.29, N 14.08.

3-(2,6-Diisopropylphenylamino)-4-(diisopropylphenylimino)-4H-pyrido[1,2-*a*]pyrazine (2): During the synthesis of **3c**, **2** was isolated as an orange coloured solid (250 mg, 15%); m.p. 147–148 °C. – ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 1.12$ –1.27 (m, $J = 6.9$ Hz, 12 H, *i*Pr-CH₃), 3.04 (hex, $J = 6.9$ Hz, 4 H, *i*Pr-CH), 6.14 (t, $J = 6.7$ Hz, 1 H, Py), 6.43 (t, $J = 7.6$ Hz, 1 H, Py), 6.92–7.33 (m, 8 H, Ar), 7.42 (s, 1 H, NH), 7.97 (d, $J = 7.7$ Hz, 1 H, Py). – ¹³C NMR (50 MHz, CD₂Cl₂): $\delta = 22.7$, 2.8 (*i*Pr-CH₃), 29.1, 29.5 (*i*Pr-CH), 113.3, 117.4, 120.6, 122.8, 123.1, 123.8, 125.8, 126.1, 127.1, 127.8, 129.8, 134.3, 137.9, 145.1, 146.2, 147.3. – IR (Nujol): $\tilde{\nu} = 3376$ (s, ν_{NH}); 1624 (s, $\nu_{\text{C=N}}$); 1586 (m); 1556 (s) u. 1496 (s) cm⁻¹. – MS [CI (H₂O)]: m/z (%) = 481 (100) [$M^+ + 1$], 437 (8), 293 (10), 187 (7), 146 (6). – C₃₂H₄₀N₄ (480.70): calcd. C 79.96, H 8.39, N 11.66; found C 79.20, H 8.42, N 12.17.

General Procedure for the Preparation of Ligands 4: To a THF solution (100 mL) of 2-(2-aminoethyl)pyridine (20 mmol) and NEt₃ (2.8 mL, 20 mmol) was slowly added a THF solution (50 mL) of **1** (10 mmol) at 0 °C. The mixture was slowly warmed to ambient temperature and was then stirred at 50 °C for 1 h. After cooling, the precipitated HNEt₃Cl was filtered and the solvent of the filtrate was removed in vacuo. The residue was isolated by addition of ether to the crude product and purified by recrystallization from MeOH/H₂O.

***N,N'*-Bis[(2-aminoethyl)-2-pyridyl]-1,2-bis(4-tolylimino)ethane-1,2-diamine (4a):** Yield: 0.51 g of a brown-yellow solid (53%), m.p. 125–126 °C. – ¹H NMR (200 MHz, [D₈]THF): $\delta = 2.22$ (s, 6 H, Tol-CH₃), 2.98 (br, 4 H, CH₂ to Pyr), 3.60 (br, 4 H, CH₂ to NH),

6.43 (br, 4 H, Ar), 6.80 (d, $J = 7.1$ Hz, Pyr, 2 H), 7.12 (m, 6 H, Ar, Pyr), 7.58 (t, $J = 7.2$ Hz, 4 H, Pyr), 8.45 (d, $J = 6.5$ Hz, 2 H, NH). — ^{13}C NMR (50 MHz, $[\text{D}_8]\text{THF}$): $\delta = 20.8$ (CH_3), 37.4 (CH_2 to Pyr), 41.2 (CH_2 to NH), 121.7, 122.6, 123.8, 129.0, 130.9, 136.6, 148.2, 149.8, 151.9, 161.3. — IR (Nujol): $\tilde{\nu} = 3261$ (s, ν_{NH}), 1639 (s, $\nu_{\text{C}=\text{N}}$), 1622 (s), 1605 (s), 1588 (m), 1536 (s), 1507 (s) cm^{-1} . — MS $[\text{EI}]$: m/z (%) = 476 (8) $[\text{M}^+]$, 383 (7), 370 (5), 278 (16) $[\text{M}^+ - 2]$, 145 (6), 134 (9), 118 (12), 106 (100), 94 (17), 91 (13), 78 (14), 65 (5). — $\text{C}_{30}\text{H}_{32}\text{N}_6$ (476.6): calcd. C 75.60, H 6.77, N 17.63; found C 75.63, H 6.77, N 17.63.

***N,N'*-Bis(2-aminoethyl)-2-pyridyl-1,2-bis(4-methoxyphenylimino)ethane-1,2-diamine (4b)**: Yield: 3.9 g of a brown-yellow solid (76%), m.p. 85–87 °C. — ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 2.96$, 3.49 (br, 2×4 H, CH_2), 3.65 (s, 6 H, OCH_3), 3.60, 6.57 ($2 \times$ d, $J = 8.5$ Hz, 2×4 H, Ar), 7.24 (m, 6 H, Pyr), 7.73 (m, 2 H, Pyr), 8.48 (d, $J = 4.5$ Hz, 2 H, NH). — ^{13}C NMR (50 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 36.3$, 40.8 (CH_2), 55.0 (OCH_3), 112.9, 121.3, 122.5, 123.0, 136.3, 143.0, 148.9, 151.2, 154.2, 159.6. — IR (Nujol): $\tilde{\nu} = 3248$ (s, ν_{NH}), 1638 (s), 1618 (s), 1566 (s), 1531 (s), 1504 (s) cm^{-1} . — MS $[\text{CI}(\text{H}_2\text{O})]$: m/z (%) = 509 (100) $[\text{M}^+ + 1]$, 415 (8), 301 (41), 254 (6) $[\text{M}^+ - 2]$, 149 (10), 124 (37), 106 (61), 93 (7). — $\text{C}_{30}\text{H}_{32}\text{N}_6\text{O}_2$ (508.6): calcd. C 70.84, H 6.34, N 16.52; found C 70.49, H 6.58, N 16.07.

Synthesis of Tetracarbonyl[*N,N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine]molybdenum (5): An ether solution of $\text{Mo}(\text{CO})_4(\text{nor})$ (0.30 g, 1.0 mmol) and **3a** (1.0 mmol) was stirred for 24 h. The product was filtered, washed with a small amount of cold ether and dried in vacuo to give 0.39 g of red crystals (55%). ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 2.22$ – 2.38 (m, 18 H, CH_3), 5.00, 5.26 ($2 \times$ s, 2×2 H, CH_2), 6.55–8.86 (m, 12 H, Ar), 10.42 (s, 2 H, NH). — ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 18.8$, 19.3, 21.0 (CH_3), 121.1, 121.6, 121.8, 122.4, 123.1, 123.2, 128.3, 128.8, 128.9, 129.3, 129.5, 130.3, 132.3, 132.8, 132.9, 136.7, 137.1, 138.0, 138.8, 148.9, 149.6, 152.9, 156.1, 160.1, 161.1, 205.4, 206.9, 221.9; IR (Nujol): $\tilde{\nu} = 3400$ (w, ν_{NH}), 2006, 1907, 1893, 1862, 1815, 1803, 1781 (s, $\nu_{\text{C}=\text{O}}$), 1592 (s), 1572 (s), 1561 (s), 1484 (s) cm^{-1} . — $\text{C}_{36}\text{H}_{40}\text{MoN}_6\text{O}_4$ (712.7): calcd. C 60.67, H 5.09, N 11.79; found C 60.11, H 5.03, N 11.72.

Synthesis of Bis(tetrahydrofuran)sodium Tetracarbonyl[*N,N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine]molybdate (6): To a THF solution (25 mL) of **3a** (0.51 g, 1.0 mmol) was slowly added a THF solution of $\text{NaN}(\text{SiMe}_3)_2$ (1 mL, 1 M). After stirring for 30 min the solution was warmed to 20 °C and a THF solution (30 mL) of $\text{Mo}(\text{CO})_4(\text{nor})$ (0.30 g, 1.0 mmol) was added. After stirring for 2 h, the precipitated yellow solid was filtered, washed three times with THF (10 mL) and dried in vacuo to give 0.45 g of yellow crystals (52%). ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 2.00$, 2.13 ($2 \times$ s, 2×9 H, CH_3), 5.32, 4.12 ($2 \times$ s, 2×2 H, CH_2), 6.55–8.27 (m, 12 H, Ar). — IR (Nujol): $\tilde{\nu} = 1991$, 1877, 1863, 1812, 1769, 1754 (s, $\nu_{\text{C}=\text{O}}$), 1593 (m), 1566 (m), 1537 (s) cm^{-1} . — $\text{C}_{44}\text{H}_{51}\text{N}_6\text{MoNaO}_6$ (878.9): calcd. C 60.13, H 5.85, N 9.56; found C 59.59, H 5.65, N 9.26.

Synthesis of Metal Complexes (7a–b): To a THF solution (25 mL) of **6** (0.51 g, 1.0 mmol) was added a THF solution of $\text{NaN}(\text{SiMe}_3)_2$ (2 mL, 1 M). After stirring for 30 min a THF solution (30 mL) of $\text{Mo}(\text{CO})_4(\text{nor})$ (0.30 g, 1.0 mmol) was added. The solution was stirred for 30 min and subsequently a THF solution (25 mL) of $\text{CoBr}_2(\text{THF})_2$ or $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (1 mmol) was added. After stirring for 4 h the solution was filtered (celite) and the filtrate was concentrated in vacuo. An ether layer was added on the top of the THF solution which resulted in precipitation of the product as greenish crystals.

Cobalt(II) Bis(tetrahydrofuran)[*N,N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine]molybdate (7a): Yield: 0.52 g (68%). — IR (Nujol): $\tilde{\nu} = 1983$, 1929, 1854, 1838, 1805 (s, $\nu_{\text{C}=\text{O}}$), 1610 (s, $\nu_{\text{C}=\text{N}}$), 1579 (s), 1558 (s) cm^{-1} . — $\text{C}_{44}\text{H}_{50}\text{CoMoN}_6\text{O}_6$ (913.78): calcd. C 57.83, H 5.52, N 9.20, Co 6.45; found C 57.19, H 5.93, N 9.42, Co 6.55.

Palladium(II) Bis(tetrahydrofuran)[*N,N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine]molybdate (7b): Yield: 0.71 g (74%). — ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 2.04$, 2.14 ($2 \times$ s, 18 H, CH_3), 4.16 (br, 4 H, CH_2), 6.64, 8.54 (m, 12 H, Ar, Pyr). — IR (Nujol): $\tilde{\nu} = 1995$, 1914, 1883, 1822, 1745 (s, $\nu_{\text{C}=\text{O}}$), 1611 (s, $\nu_{\text{C}=\text{N}}$), 1586 (s), 1562 (s) cm^{-1} . — $\text{C}_{44}\text{H}_{50}\text{MoN}_6\text{O}_6\text{Pd}$ (961.3): calcd. C 54.98, H 5.24, N 8.74; found C 54.43, H 5.13, N 9.00.

Synthesis of the Dimetallic Cu Complexes (9a–c) and (10a–b): A MeOH solution (25 mL) of $\text{Cu}(\text{OAc})_2(\text{H}_2\text{O})$ (0.36 g, 2.0 mmol) and of the ligand **3** or **4** (1 mmol) was stirred for 2 h at 50 °C. The deep green solution was filtered and the solvent of the filtrate was removed in vacuo. To the residue was added ether and the precipitate was filtered and dried in vacuo. The crude product was recrystallized from MeOH or $\text{H}_2\text{O}/\text{MeOH}$ (1:1).

Bis(acetato)[*N,N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine]dicuprate(II) (9a): Yield: 0.25 g of deep green to black crystals (34%). — IR (Nujol): $\tilde{\nu} = 1613$ (s), 1595 (s), 1566 (s) cm^{-1} . — $\text{C}_{36}\text{H}_{40}\text{Cu}_2\text{N}_6\text{O}_4$ (747.8): calcd. C 57.82, H 5.39, N 11.24, Cu 16.99; found C 57.80, H 5.38, N 11.19, Cu 16.41.

Bis(methanol)bis(acetato)[1,2-bis(2,6-dimethylphenylimino)-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine]dicuprate(II) (9b): Yield: 0.40 g of deep green to black crystals (50%). — IR (Nujol): $\tilde{\nu} = 3370$ (br, $\nu_{\text{OH}(\text{MeOH})}$), 1611 (s), 1582 (s), 1567 (s) cm^{-1} . — $\text{C}_{36}\text{H}_{42}\text{Cu}_2\text{N}_6\text{O}_6$ (781.9): calcd. C 55.30, H 5.41, N 10.75, Cu 16.26; found C 55.06, H 5.38, N 10.87, Cu 15.95.

Bis(acetato)[1,2-bis(2,6-diisopropylphenylimino)-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine]dicuprate(II) (9c): Yield: 0.57 g of deep green to black crystals (69%). — IR (Nujol): $\tilde{\nu} = 1625$ (s), 1599 (s), 1582 (s), 1567 (s) cm^{-1} . — $\text{C}_{42}\text{H}_{52}\text{Cu}_2\text{N}_6\text{O}_4$ (832.0): calcd. C 60.63, H 6.30, N 10.10, Cu 15.28; found C 60.71, H 6.42, N 10.11, Cu 14.87.

Bis(methanol)bis(acetato){*N,N'*-bis[(2-aminoethyl)-2-pyridyl]-1,2-bis(4-tolylimino)ethane-1,2-diamine}dicuprate(II) (10a): Yield: 0.49 g of deeply green to black coloured crystals (62%). — IR (Nujol): $\tilde{\nu} = 3265$ (br, $\nu_{\text{OH}(\text{MeOH})}$), 1607 (s), 1571 (s), 1505 (s), 1485 (s) cm^{-1} . — $\text{C}_{36}\text{H}_{42}\text{Cu}_2\text{N}_6\text{O}_6$ (781.9): calcd. C 55.30, H 5.41, N 10.75, Cu 16.26; found C 55.37, H 5.58, N 10.67, Cu 15.74.

Bis(methanol)bis(acetato){*N,N'*-bis[(2-aminoethyl)-2-pyridyl]-1,2-bis(4-methoxyphenylimino)ethane-1,2-diamine}dicuprate(II) (10b): Yield: 0.53 g of deep green to black crystals (68%). — IR (Nujol): $\tilde{\nu} = 3390$ (br, ν_{OH} , MeOH), 1606 (s), 1586 (s), 1502 (s), 1486 (s) cm^{-1} . — $\mu_{\text{eff}} = 1.5$ BM. — EPR (296 K, solid): $g_{\perp} = 2.0036$. — $\text{C}_{35}\text{H}_{40}\text{Cu}_2\text{N}_6\text{O}_7$ (783.8): calcd. C 53.70, H 5.15, N 10.74, Cu 16.09; found C 53.36, H 5.01, N 10.88, Cu 15.87.

Synthesis of the Dimetallic Pd Complexes (11a–c): A THF solution (30 mL) of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.52 g, 2.0 mmol) and of the ligand **3** or **4** (1.0 mmol) was stirred for 24 h at 20 °C. The product, which precipitated as an orange solid, was filtered, washed with THF and dried in vacuo.

Dichloro[*N,N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine]dipalladate(II) (11a): Yield: 0.36 g of an

orange solid (41%). – IR (Nujol): $\tilde{\nu}$ = 1633 (s), 1610 (m), 1593 (s), 1577 (s), 1568 (s), 1515 cm^{-1} . – $\text{C}_{38}\text{H}_{46}\text{Cl}_2\text{N}_6\text{Pd}_2$ (870.6): calcd. C 52.43, H 5.33, N 9.65, Cl 8.14; found C 51.88, H 5.35, N 10.45, Cl 8.12.

Dichloro[1,2-bis(2,6-diisopropylphenylimino)-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diaminato]dipalladate(II) (11b): Yield: 0.50 g of an orange solid (58%). – IR (Nujol): $\tilde{\nu}$ = 1610 (m), 1593 (s), 1577 (s), 1564 (s) cm^{-1} . – $\text{C}_{38}\text{H}_{46}\text{Cl}_2\text{N}_6\text{Pd}_2$ (870.6): calcd. C 52.43, H 5.33, N 9.65, Cl 8.14; found C 51.88, H 5.35, N 10.04, Cl 8.45.

Dichloro[*N,N'*-bis[(2-aminoethyl)-2-pyridyl]-1,2-bis(4-tolylimino)ethane-1,2-diaminato]dipalladate(II) (11c): Yield: 0.39 g of an orange solid (52%). – ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): δ = 2.18 (s, 6 H, CH_3), 2.97, 3.31 (2 $\times$ br, 2 $\times$ 4 H, CH_2), 6.93 (m, 4 H, Ar), 6.85 (t, J = 7.6 Hz, 1 H, Pyr), 6.93 (d, J = 6.9 Hz, 1 H, Pyr), 7.41 (t, J = 8.4 Hz, 1 H, Pyr), 8.40 (d, J = 5.4 Hz, 1 H, Pyr). – IR (Nujol): $\tilde{\nu}$ = 1673 (s), 1605 (m), 1579 (s), 1504 (m) cm^{-1} . – $\text{C}_{30}\text{H}_{30}\text{N}_6\text{Cl}_2\text{Pd}_2$ (758.4): calcd. C 47.51, H 3.99, N 11.08, Cl 9.35; found C 47.39, H 4.38, N 11.53, Cl 9.51.

Crystal Structure Determinations: The intensity data for the compound were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated $\text{Mo-K}\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.^[15,16]

The structures were solved by direct methods (SHELXS^[17]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97^[18]). The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.^[18] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 3a:^[19] $\text{C}_{32}\text{H}_{36}\text{N}_6$, M_r = 504.67 g mol^{-1} , colourless prism, size $0.40 \times 0.38 \times 0.32 \text{ mm}^3$, monoclinic, space group $P2_1/n$, a = 6.4164(5), b = 21.157(2), c = 10.3108(6) Å, β = 94.085(2)°, V = 1396.2(2) Å³, T = 183 K, Z = 2, $\rho_{\text{calcd.}}$ = 1.200 g cm^{-3} , μ ($\text{Mo-K}\alpha$) = 0.73 cm^{-1} , $F(000)$ = 540, 3067 reflections, Θ_{max} = 26.27°, 2815 independent reflections, 1724 reflections with $F_o > 4\sigma(F_o)$, 208 parameters, R = 0.0568, R_w = 0.1645, largest difference peak and hole: 0.369 e Å⁻³.

Crystal Data for 6:^[19] $\text{C}_{44}\text{H}_{51}\text{MoN}_6\text{NaO}_6$, M_r = 878.84 g mol^{-1} , colourless prism, size $0.30 \times 0.25 \times 0.15 \text{ mm}^3$, monoclinic, space group $P2_1/n$, a = 12.3530(6), b = 20.6111(5), c = 17.2796(8) Å, β = 94.755(1)°, V = 4384.4(3) Å³, T = -90 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.331 g cm^{-3} , μ ($\text{Mo-K}\alpha$) = 3.62 cm^{-1} , $F(000)$ = 1832, 11681 reflections in $h(-13/0)$, $k(-22/21)$, $l(-19/19)$, measured in the range $3.95^\circ \leq \Theta \leq 23.31^\circ$, completeness Θ_{max} = 98.6%, 6126 independent reflections, R_{int} = 0.036, 5706 reflections with $F_o > 4\sigma(F_o)$, 527 parameters, 0 restraints, $R1_{\text{obs}}$ = 0.047, $wR2_{\text{obs}}$ = 0.121, $R1_{\text{all}}$ = 0.066, $wR2_{\text{all}}$ = 1.134, GOOF = 1.084, largest difference peak and hole: 0.485/-0.555 e Å⁻³.

Crystal Data for 10a:^[19] $\text{C}_{36}\text{H}_{44}\text{N}_6\text{O}_6\text{Cu}_2$, M_r = 783.85 g mol^{-1} , brown prism, size $0.40 \times 0.38 \times 0.36 \text{ mm}^3$, orthorhombic, space group $Pbca$, a = 9.173(1), b = 14.853(1), c = 26.275(1) Å, α = β = γ = 90°, V = 3579.9(5) Å³, T = 183 K, Z = 4, $\rho_{\text{calcd.}}$ = 1.454 g cm^{-3} , μ ($\text{Mo-K}\alpha$) = 0.73 cm^{-1} , $F(000)$ = 1632, 3634 reflections, Θ_{max} = 26.31°, 3634 independent reflections, 2228 reflections with $F_o > 4\sigma(F_o)$, 278 parameters, R = 0.0431, R_w = 0.0979, largest difference peak and hole: 0.413 e Å⁻³.

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^[19] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-145494 (**3a**), CCDC-140090 (**6**), and CCDC-145493 (**10a**). Copies of the data can be obtained free

of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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