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RESEARCH ARTICLE



Synthesis, characterization, and crystal structure of novel bulky phenyl-bridged α -diimine binucleating ligands

Ali Mechria 问

Moncef Msaddek

Laboratoire de Chimie Hétérocyclique, Produits naturels et Réactivité: L.C.H.P.N.R, Faculté des sciences de Monastir, Monastir, Tunisia

Correspondence

Ali Mechria, Laboratoire de Chimie Hétérocyclique, Produits naturels et Réactivité : L.C.H.P.N.R, Faculté des sciences de Monastir, Bd de l'environnement, 5000 Monastir, Tunisia. Email: ali.mechria@fsm.rnu.tn

Abstract

A series of sterically and electronically modulated phenyl-bridged α -diimine ligands **L1–L6** of the general formula Ar-N=C(Me)-C(Me)=N-C₆H₄-N=C(Me)-C(Me)=N-Ar have been synthesized (**L1** : Ar = 2,6-iPr₂-C₆H₃; **L2**: Ar = 2,6-Me₂-C₆H₃; **L3**: 4-Me-C₆H₄; **L4**: Ar = 4-Et-C₆H₄; **L5**: Ar = 2,4,6-Cl₃-C₆H₂; **L6**: Ar = 4-Cl-C₆H₄). All of which have been characterized by ¹H NMR, ¹³C NMR, IR, and elemental analysis. In addition, the effect of the electronic modification was studied by UV–Vis spectroscopy, and the structure of a representative ligand was confirmed by single-crystal X-ray diffraction. Moreover, a DFT electronic structure of the same ligand has been determined.

1 | INTRODUCTION

Over the past two decades, a considerable interest was given to alternative ligands to phosphines, for the development of late transition metal catalysts. Examples of this include the important development by Brookhart and co-workers of adiimine ligands for nickel and palladium catalysed olefin polymerization and oligomerization.^[1] Furthermore, interest in these α -diimine systems-based complexes and various derivatives thereof have arose extensively in both academic and industrial research.^[2-9] Recently, a range of sterically encumbered multidentate binucleating nitrogen-ligands, such as organo-bridged iminopyridines, α -diimines, and iminophenolates, were found to be efficient systems achieving active dinickel,^[10-18] dipalladium,^[19] and diiron catalysts^[17,20] for alkene oligomerization/polymerization. The electronic interactions found like some cooperative effects between neighboring active metal centers are the reason of this catalytic performance. The same electronic effects cannot be expected in their mononuclear counterparts.^[21–24] Considering the fact that only limited works on modified α -diimine systems and as a continuation of this type of study that allows us to take advantage of spatial proximities of the binucleating ligands, we have targeted a binucleating version, modulated sterically and electronically, of these intensively studied α -diimine ligands as possible supports for bimetallic complexes. These

bridged ligands by phenyl spacers introducing appended imine functionalities with bulky aryl substituent's on the *N*aryl moiety making them symmetrical. These new phenylbridged α -diimine ligands retains all the essential features of the α -diimine ligands and in addition provides an additional adjacent compartment to accommodate another metal, making them closely the bimetallic mimic of the originally developed and the most studied α -diimine based metal complexes. The present paper provides a full account of our new methodology for the synthesis, isolation, and characterization of a series of novel phenyl-bridged α -diimine ligands.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of new ligands

Novel ligands phenyl-bridged α -diimine L1–L6 have been prepared in a facile and versatile one-pot 2-step manner under mild conditions in two successive condensation reactions. First, the treatment of butane-2,3-dione with one equivalent of aromatic primary amines leads to the corresponding α -iminoketone without isolation of the product. The advancement of the reaction was checked by TLC. When the majority of the reactants are consumed, a half equivalent of para-phenyenediamine was added to the reaction vessel at room temperature with vigorous stirring affording the desired compounds after several hours (Scheme 1):

These new phenyl-bridged α -diimine ligands L1–L6 were isolated as pale yellow solids sparingly soluble in ethanol and dichloromethane but almost insoluble in all other common solvants. ¹H, ¹³C, NMR, IR spectroscopy and elemental analyses were consistent with the bis-(diimine) ligands formulation. The formation of these bis- α -diimine ligands is easily deduced from the study of their FTIR spectra. In fact, the disappearance of the stong band of the carbonyl at around $1,715 \text{ cm}^{-1}$ and the appearance of a new characteristic intense band at around 1.630 cm^{-1} , which is attributed to the imine function, confirms the creation of ligands L1–L6. The examination of ¹H and ¹³C NMR spectra of ligands L1– L6, in CDCl₃ at room temperature, supports their respective structures and shows similar trends both in the aromatic and aliphatic regions. Furthermore, the number of signals indicates that all ligands are symmetrical. Detailed chemical shift values for all the carbon and protons are given in Section 4. The ¹H NMR spectra of ligands show that the protons of the two methyl groups of the diimine backbone occurs at around δ 2.20 and 2 ppm which is slightly upfield from that of 2,3-butanedione at δ 2.33 ppm.^[25] In the aromatic region, the protons of the phenyl spacer appear as a singlet at around 6.8 ppm. All others signals of the ligands L1-L6 are found in the expected ranges. The ¹³C NMR spectra agreed very well with the proposed structures of the binucleating ligands L1-L6. The disappearance of the carbonyl signals at around 197 ppm and the appearance of two signals around 168 and 167 ppm, attributed to the two azomethine carbons, confirms the identity of these bis- α -diimine ligands. All other signals are in concordance with the structure of the ligands.

Electronic spectra of ligands L1–L6 recorded in dichloromethane over the scan range of 200–800 nm show identical trends. All ligands present in their absorption spectra a strong band at around 240 nm which can be ascribed to $\pi \rightarrow \pi^*$ transition and another weak band at around 360 nm corresponding to $n \rightarrow \pi^*$ transitions^[26,27] (Figure 1): The molecular structure for L1 has been determined by a single crystal X-ray diffraction study at 293 K and is shown in Figure 2. Crystallographic details are provided in Table 1, and relevant geometrical parameters are listed in Tables 2 and 3. Crystals of ligand L1 suitable for structure determination were grown by slow evaporation of ethanolic solution at room temperature. The molecular structure of ligand L1 shows an asymmetric unit formed by a half molecule of Ar- $N=C(Me)-C(Me)=N-C_6H_4-N=C(Me)-C(Me)=N-Ar$ (where $Ar = 2,6-iPr_2-C_6H_3$) while the corresponding molecular structure is generated by symmetry. In the solid state, the molecule exists in the E (anti) configuration at both C=N double bonds, while the conformation of the central C-C bond is s-trans as indicated by the torsion angles N1-C13-C15-N2 and N1-C13–C15–C16 of $170.4(2)^{\circ}$ and $-5.9(4)^{\circ}$, respectively. The N-imine aryl rings lie perpendicular to the diimine backbone plane as indicated by the torsion angles C6-C1-N1-C13 and C13-N1-C1-C2 of 81.9(3) and -104.3(3)° respectively, likely because of steric repulsion between the two bulky diisopropylphenyl groups. Furthermore, the aryl ring spacer is almost perpendicular to the bis(imino) backbone plane as revealed by the dihedral angles C15-N2-C17-C19A and C15-N2-C17-C18 of -74.9(3) and $110.4(3)^{\circ}$. The two imine distances C=N (1.268(2) for N1-C13 and 1.269(3) Å for N2-C15) are identical and agree well with the values for double bond character.^[22-24] The N-Carvl simple bonds (1.429(3) for N1-C1 and 1.424(3) Å for N2–C17) agree with the expected range for this type of bonds.^[28] The C–C bond distances (1.37-1.39 Å) and the C-C-C bond angles (117°-121°) of the phenyl rings are in accordance with the values reported in the literature.^[22-24]

2.3 | Density functional theory (DFT) calculations

Geometry optimization reported in this article was done with the Gaussian09^[29] program package supported by



SCHEME 1 Synthetic route for the synthesis of pheny-bridged α -diimine ligands **L1–L6**

GaussView 5.0.8. The DFT^[30,31] calculations has been performed with the popular hybrid-GGA functional B3LYP (Becke, three-parameter combined with Lee–Yang–Parr correlation functional).^[32–35] In this study, we chose the double-zeta Pople-type basis set $6-31++G(d,p)^{[36–38]}$ for all atoms. The initial geometry has been taken from crystal structure. The geometry of L1 in the gas phase has been optimized using tight convergence criteria ignoring symmetry and using S = 0 spin state. Optimized structure obtained from unrestricted B3LYP method was confirmed to

be local minima by performing analytical vibrational frequency analysis at the same level of theory (no imaginary frequency observed). Experimental and theoretical geometric parameters are summarized in Table 2 and 3. It can be seen that the X-ray solid state and the electronic structures are similar. The ligand **L1** adopt an s-trans conformation as shown in Figure 3. Furthermore, the differences between experimental and theoretical bond distances are within the standard uncertainties (0.01 Å). So, the B3LYP functional predicted reasonably accurate geometry.



FIGURE 1 UV-Vis spectra of ligands L1-L6 in dichloromethane



FIGURE 2 ORTEP representation of the molecular structure of ligand L1 with atom labeling scheme and anisotropic displacement ellipsoid depicted at 40% probability. Hydrogen atoms are omitted for clarity

TABLE 1 Crystal data and structure refinement for ligand L1

Chemical formula	C38 H50 N4
Crystal size (mm ³)	$0.09\times0.06\times0.04$
Formula weight	562.82
Crystal system	Monoclinic
Space group	P21/c
a (Å)	12.677(5)
b (Å)	8.791(5)
c (Å)	16.274(5)
β (°)	99.524(5)
$V(\text{\AA}^3)$	1788.6(14)
Ζ	2
<i>T</i> (K)	293(2)
ρ_{calc} (g/cm ³)	1.045
Total reflections	3515
Unique reflections	1292
R(int)	0.0305
$2\theta_{max}$ (°)	53.35
λ (Å)	0.71073
$\mu (mm^{-1})$	0.061
F(000)	612
Goodness-of-fit	1.091
$R_1 \left(I > 2\sigma(I) \right)$	0.0567
wR ₂	0.1024

TABLE 2 Experimental and theoretical bond distances of L1

Bond lengths	Experimental	Theoretical
N1-C1	1.429(3)	1.42
N1-C13	1.268(2)	1.28
N2-C15	1.269(3)	1.28
N2-C17	1.424(3)	1.40
C1–C2	1.400(3)	1.41
C1–C6	1.396(3)	1.41
C13-C14	1.501(3)	1.51
C13-C15	1.500(3)	1.50
C15-C16	1.496(3)	1.51

3 | EXPERIMENTAL

3.1 | General methods and materials

2,6-diisopropylaniline, 2,6-dimethylaniline and 4-ethylani line were distilled under vacuum from potassium hydroxide prior to use. p-Toluidine and p-phenylenediamine were purified by sublimation in vacuo. Butane-2,3-dione, 4-chloroaniline and 2,4,6-trichloroaniline were used as received from Sigma-Aldrich. NMR spectra were recorded

TABLE 3 Experimental and theoretical bond angles of L1

Bond angles (°)	Experimental	Theoretical
C13-N1-C1	120.6(2)	123.19
C15-N2-C17	121.5(2)	124.13
C6C1N1	118.4(2)	118.65
C2C1N1	119.4(2)	119.91
N1-C13-C15	117.3(2)	116.44
N1-C13-C14	126.2(2)	126.00
C15-C13-C14	116.4(2)	117.54
N2-C15-C16	126.1(2)	126.69
N2-C15-C13	115.7(2)	115.67
C16-C15-C13	118.1(2)	117.63

on a Bruker AMX 300 spectrometer. H and C chemical shifts were given in ppm and referenced to the residual solvent resonance relative to TMS. IR spectra were recorded on a Perkin-Elmer Spectrum two FT-IR instrument with the Universal ATR Sampling Accessory over the range of $4,000-400 \text{ cm}^{-1}$. The electronic spectra were measured on an UviLine 9400, SECOMAM spectrophotometer over the range of 200–800 nm. Melting Points were recorded using a Kofler hot stage apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

3.2 | Synthesis of ligands L1–L6

3.2.1 | General procedure

A 50 mL round bottom flask was charged with methanol (30 mL), primary arylamines (20 mmol), butane-2,3-dione (1.72 g, 20 mmol), and glacial acetic acid (0.4 g, 6.7 mmol). The yellow solution was stirred at room temperature for 24 hours. The progress of the reaction was monitored by TLC by the consumption of reactants. When the reaction was complete, p-phenylenediamine (1.08 g, 10 mmol) was added and the reaction mixture was stirred for 2 days at room temperature. The resulting yellow precipitate was isolated by filtration, washed with methanol (3×10 mL), and dried under vacuum for 12 hours affording the ligands L1–L6 in good to moderate yields. All ligands were obtained as a pale yellow powder.

3.2.2 | Synthesis of ligand L1

L1 was obtained from 2,6-diisopropylaniline (3.56 g, 20 mmol), butane-2,3-dione (1.72 g, 20 mmol), glacial acetic acid (0.4 g, 6.7 mmol), and p-phenylenediamine (1.08 g, 10 mmol). Yield: 3.7 g (67%). Crystals suitable for structure determination were grown by slow evaporation of ethanolic solution at room temperature. m.p. 161°C. IR [ν cm⁻¹]: 1634



FIGURE 3 DFT optimized structure of ligand L1 using the same atom labeling scheme as ORTEP representation. Hydrogen atoms are omitted for clarity

 $(\nu_{C=N})$. Anal. Calc. for $C_{38}H_{50}N_4$ (562.83): C, 81.09; H, 8.95; N, 9.95. Found: C, 80.58; H, 9.12; N, 10.30. ¹H-NMR (300 MHz, CDCl₃): 1.13 (dd, 24H, CH(CH₃)₂); 1.94 (s, 6H, $C10H_3$; 2.18 (s, 6H, C7 H_3); 2.65 (sept, 4H, J = 6.6 Hz, $CH(CH_3)_2$; 6.82 (s, 4H, H_{12}); 7.04 (m, 6H, $H_{3,4,5}$). ¹³C-NMR (75.47 MHz, CDCl₃): 15.22 (C₁₀); 16.17 (C₇); 22.58, 23.12 (CH₃-iPr); 28.40 (CH-iPr); 120.01 (C₁₂); 122.89 (C_{3.5}); 123.55 (C₄); 135.06 (C_{2.6}); 143.15 (C₁₁); 147.08 (C₁); 168.14, 168.30 (C₈, C₉). λ_{max} (nm): 240, 357.

3.2.3 Synthesis of ligand L2

Ligand L2 was obtained from 2,6-dimethylaniline (2.42 g, 20 mmol), butane-2,3-dione (1.72 g, 20 mmol), glacial acetic acid (0.4 g, 6.7 mmol), and p-phenylenediamine (1.08 g, 10 mmol). Yield: 2.67 g (59%). m.p. 158°C. IR [ν cm⁻¹]: 1632 ($\nu_{C=N}$). Anal. Calc. for C₃₀H₃₄N₄ (450.62): C, 79.96; H, 7.61; N, 12.43. Found: C, 80.17; H, 8.09; N, 11.74. ¹H-NMR (300 MHz, CDCl₃): 2.19 (s, 12H, 0,0'-CH₃); 2.25 (s, 6H, C10H₃); 2.39 (s, 6H, C7H₃); 6.87 (s, 4H, H₁₂); 7.06 (m, 6H, H_{3.4.5}). ¹³C-NMR (75.47 MHz, CDCl₃): 15.74 (C₁₀); 17.48 (C₇); 17.67 (0,0'-CH₃); 120.01 (C₁₂); 123.21 (C_{3.5}); 124.63 (C₄), 127.91 (C_{2.6}); 142.00 (C₁₁); 147.08 (C₁); 167.84, 168.10 (C_8, C_9) . λ_{max} (nm): 241, 367.

3.2.4 Synthesis of ligand L3

Ligand L3 was obtained from 4-methylaniline (2.14 g, 20 mmol), butane-2,3-dione (1.72 g, 20 mmol), glacial acetic acid (0.4 g, 6.7 mmol), and p-phenylenediamine (1.08 g,

10 mmol). Yield: 2.21 g (52%). m.p. 154°C. IR [ν cm⁻¹]: 1632 ($\nu_{C=N}$). Anal. Calc. for C₂₈H₃₀N₄ (422.56): C, 79.59; H, 7.16; N, 13.26. Found: C, 80.23; H, 7.95; N, 12.84. ¹H-NMR (300 MHz, CDCl₃): 2.04 (s, 6H, C10*H*₃); 2.16 (s, 6H, C7*H*₃); 2.24 (s, 6H, p-C H_3); 6.71 (d, 4H, J = 7.2 Hz, $H_{2.6}$); 6.87 (s, 4H, H_{12}); 6.98 (d, 4H, J = 7.5 Hz, $H_{3.5}$). ¹³C-NMR (75.47 MHz, CDCl₃): 13.88 (C₁₀); 15.30 (C₇); 20.86 (p-CH₃); 115.32 (C₁₂); 118.93 (C_{2.6}); 129.52 (C_{3.5}); 133.26 (C₄); 142.87 (C₁₁); 147.08 (C_1) ; 168.01, 168.17 (C_8, C_9) . λ_{max} (nm): 243, 360.

3.2.5 Synthesis of ligand L4

Ligand L4 was obtained from 4-ethylaniline (2.93 g, 20 mmol), butane-2,3-dione (1.72 g, 20 mmol), glacial acetic acid (0.4 g, 6.7 mmol), and p-phenylenediamine (1.08 g, 10 mmol). Yield: 2.21 g (65%). m.p. 156°C. IR [ν cm⁻¹]: 1633 ($\nu_{C=N}$). Anal. Calc. for C₃₀H₃₄N₄ (450.62): C, 79.96; H, 7.61; N, 12.43. Found: C, 80.23; H, 7.35; N, 12.42. ¹H-NMR $(300 \text{ MHz}, \text{CDCl}_3)$: 1.27 (t, 6H, J = 6.9 Hz, CH₃-CH₂); 2.17 (s, 12H, C10 H_3 +C7 H_3); 2.66 (q, 4H, J = 6.9 Hz, CH₃-CH₂); 6.71 (d, 4H, J = 7.2 Hz, $H_{2,6}$); 6.84 (s, 4H, H_{12}); 7.19 (d, 4H, $J = 6.6 \text{ Hz}, H_{3.5}$). ¹³C-NMR (75.47 MHz, CDCl₃): 13.81 (C₁₀); 15.22 (C₇); 15.74 (CH₃-Et); 28.28 (CH₂-Et); 115.27 (C₁₂), 118.91 (C_{2,6}); 128.23 (C_{3,5}); 134.46 (C₄); 144.06 (C₁₁); 147.34 (C₁); 168.23, 168.39 (C₈, C₉). λ_{max} (nm): 244, 357.

3.2.6 Synthesis of ligand L5

Ligand L5 was obtained from 2,4,6-trichloroaniline (3.93 g, 20 mmol), butane-2,3-dione (1.72 g, 20 mmol), glacial acetic acid (0.4 g, 6.7 mmol), and p-phenylenediamine (1.08 g, 10 mmol). Yield: 5.17 g (43%). m.p. 156°C. IR [ν cm⁻¹]: 1629 (ν _{C=N}). Anal. Calc. for C₂₆H₂₀Cl₆N₄ (601.17): C, 51.95; H, 3.35; N, 9.32. Found: C, 52.38; H, 4.07; N, 8.96. ¹H-NMR (300 MHz, CDCl₃): 2.04 (s, 6H, CH₃); 2.18 (s, 6H, CH₃); 6.97 (s, 4H, H₁₂); 7.19 (s, 4H, H_{3,5}). ¹³C-NMR (75.47 MHz, CDCl₃): 16.19 (C₁₀); 17.38 (C₇); 121.74 (C₁₂); 127.89 (C_{3,5}); 130.17 (C_{2,6}); 134.78 (C₄); 143.15 (C₁₁); 147.08 (C₁); 167.14, 167.87 (C₈, C₉). λ _{max} (nm): 242, 361.

3.2.7 | Synthesis of ligand L6

Ligand L6 was obtained from 4-chloroaniline (2.55 g, 20 mmol), butane-2,3-dione (1.72 g, 20 mmol), glacial acetic acid (0.4 g, 6.7 mmol), and p-phenylenediamine (1.08 g, 10 mmol). Yield: 4.45 g (48%). m.p. 156°C. IR [ν cm-1]: 1625 ($\nu_{C=N}$). Anal. Calc. for C26H20Cl6N4 (601.17): C, 51.95; H, 3.35; N, 9.32. Found: C, 52.73; H, 4.06; N, 9.16. 1H-NMR (300 MHz, CDCl₃): 1.97 (s, 6H, CH₃); 2.11 (s, 6H, CH₃); 7.03 (d, 4H, J = 7.4 Hz, H_{2.6}); 7.14 (s, 4H, H₁₂); 7.39 (d, 4H, J = 6.8 Hz, H_{3.5}). 13C-NMR (75.47 MHz, CDCl₃): 16.19 (C₁₀); 16.84 (C₇); 121.63 (C₁₂); 123.67 (C_{2.6}); 128.39 (C_{3.5}); 132.35 (C₄); 145.03 (C₁₁); 148.08 (C₁); 168.20, 168.61 (C₈, C₉). λ_{max} (nm): 241, 353.

3.2.8 | Solid state structure determination

X-ray quality crystals of L1 were grown from an ethanolic solution upon standing at ambient temperature. Intensity data were collected at ambient temperature on a Bruker AXS Kappa-CCD Apex II diffractometer equipped with graphite monochromated MoK_{α} radiation.

Reflection data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by direct methods and subsequent difference Fourier techniques (SIR-92)^[39] and refined with SHELXL-2013.^[40] Nonhydrogen atoms were refined with anisotropic thermal parameters. C-bound hydrogen atoms were located as residual electron density peaks and refined isotropically without any restraints or placed in idealized positions on parent atoms in the final refinement. Details of the crystal parameters, data collection, and structure refinement are given in Table 1.

4 | CONCLUSION

A series of novel pheny-bridged α -diimine ligands, namely N, N'-Bis(3-(arylimino)butan-2-ylidene)benzene-1,4diamine **L1–L6**, have been prepared in a facile and versatile one-pot 2-step manner under mild conditions in two successive condensation reactions. The mono-condensation of diacetyl with one equivalent of substituted anilines led to the corresponding iminoketone, which upon condensation with a half equivalent of para-phenyenediamine yielded the bis- α -diimine ligands. These ligands have been characterized by spectroscopic and eventually elemental analysis. The representative ligand **L1** was studied by single crystal X-ray analysis. As continuation for this work, the coordination of these ligands with nickel(II) and palladium(II) metal centers was progressed.

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ORCID

Ali Mechria D http://orcid.org/0000-0003-3203-1357

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