

Phenalenyl-based ligand for transition metal chemistry: Application in Henry reaction

ARUP MUKHERJEE^a, TAMAL K SEN^a, SWADHIN K MANDAL^{a,*}, DANIEL KRATZERT^b, DIETMAR STALKE^b, ALEXANDER DÖRING^b and CAROLA SCHULZKE^c

^aDepartment of Chemical Sciences, Indian Institute of Science Education and Research (IISER)-Kolkata, Mohanpur 741252, India

^bGeorg-August-Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany

^cSchool of Chemistry, Trinity College Dublin, Dublin 2, Ireland

e-mail: swadhin.mandal@iiserkol.ac.in

Abstract. We report the synthesis and characterization of the first transition metal complex of a phenalenyl-based ligand. The reaction of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with 9-*N*-methylamino-1-*N'*-methylimino-phenalene (**LH**) in 1:1 stoichiometric ratio results in the formation of a mononuclear copper complex $[\text{LCu}(\text{OAc})]$ (**1**). The molecular structure of **1** was established by X-ray crystallography. The electrochemistry of **1** indicates the formation of an anionic radical by one electron reduction into the non-bonding molecular orbital of the phenalenyl system. The complex **1** efficiently catalyses the C–C bond forming Henry reaction.

Keywords. Cu-complex; phenalenyl; radical; X-ray crystallography; Henry reaction.

1. Introduction

The chemistry of phenalenyl-based ligand systems has not yet been explored except on the development of neutral boron containing free radical conductors.^{1,2} Phenalenyl is well-known odd alternant hydrocarbon with high symmetry (D_{3h}) which has the ability to form three redox species: cation, radical, and anion.³ The formation of this redox triad involves the use of the nonbonding molecular orbital (MO) of the phenalenyl moiety and hence does not affect the stability of the resulting species greatly. The neutral radical state is stabilized by the extended electronic delocalization and this way a number of phenalenyl-based organic conductors (chart 1) have been reported exhibiting the highest room temperature conductivity among any neutral radical solids.^{1,2} Such characteristic features have been widely utilized for exploring new conjugated electronic systems, such as multifunctional electronic and magnetic materials.² The chemistry so far developed in this system is limited to the spiro-conjugated boron system.^{1,2} The chemistry of phenalenyl-based ligand

systems has not yet been explored for designing transition metal catalysts. Herein we report the synthesis and characterization of a copper complex bearing a symmetrical phenalenyl-based N,N-ligand (**LH**). The reaction of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with 9-*N*-methylamino-1-*N'*-methylimino-phenalene (**LH**) in 1:1 stoichiometric ratio results in the formation of a mononuclear copper complex $[\text{LCu}(\text{OAc})]$ (**1**). The molecular structure of **1** was established by X-ray crystallography. The electrochemistry of **1** reveals the presence of a reversible

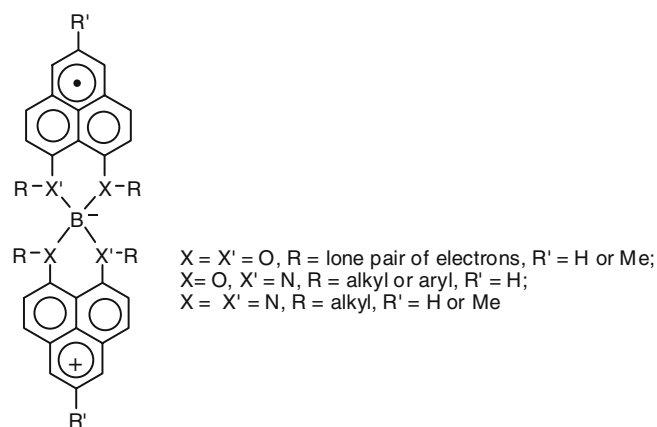


Chart 1. Phenalenyl-based neutral radical conductors.

*For correspondence

one electron reduction process. The complex **1** exhibits high catalytic activity in C–C bond forming Henry reaction.^{4–15}

2. Experimental

2.1 Materials and methods

All manipulations were carried out under dry nitrogen atmosphere using standard Schlenk line technique. Solvents were dried using conventional procedure. 9-*N*-methylamino-1-*N'*-methylimino-phenalene was prepared according to the literature procedure.^{1a} Copper acetate monohydrate was purchased from Merck, India and was used as received. Aldehydes were purchased from Aldrich and were used without further purifications. Triethylamine (Et₃N) was dried over KOH and nitromethane (CH₃NO₂) was dried over CaCl₂. Elemental analyses were performed at the Institut für Anorganische Chemie, Universität Göttingen. The melting point was measured on a Buchi B-545 melting point apparatus. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker 500 MHz spectrometer. Electrochemical measurements were performed with an AUTOLAB PGSTAT12 potentiostat/galvanostat using a platinum disc electrode with a reaction surface of 1 mm² as working electrode. A platinum rod electrode (together with internal referencing versus ferrocene/ferrocenium) was used as reference electrode and a platinum knob electrode as auxiliary electrode. The scan rate of the cyclic voltammetric experiment was 100 mV/s. The sample was dissolved in acetonitrile (0.1 mmol/L) together with the electrolyte tetrabutylammonium hexafluorophosphate (0.1 mol/L). The electrochemical experiments were conducted inside a glovebox under argon atmosphere at 25°C. The crystallographic data for **1** was collected from shock-cooled crystals at 100 K mounted on a glass fibre. The crystals were cooled and protected from air with a low temperature mounting device¹⁶ in inert oil. The data of **1** was collected on a INCOATEC Mo Microsource with Quazar mirror optics equipped with a low temperature device using monochromatic MoK_α radiation (λ = 0.71073 Å). The data was integrated with SAINT,¹⁷ and an empirical absorption correction with SADABS¹⁸ was applied. The structure was solved by direct methods (SHELXS-97)¹⁹ and refined by full-matrix least-squares methods against *F*² (SHELXL-97).¹⁸ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydro-

gen atoms were refined isotropically on calculated positions using a riding model with their *U*_{iso} values constrained to 15 times the *U*_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

2.2 Preparation of complex **1**

9-*N*-methylamino-1-*N'*-methylimino-phenalene (222 mg, 1.0 mmol) and Cu(OAc)₂·H₂O (199 mg, 1.0 mmol) were mixed in dichloromethane (DCM)/ethanol mixture (30 mL, 1:1) and stirred at 25°C overnight. The starting materials slowly dissolved and resulted in a brown-red colour. Finally, the reaction mixture was refluxed for 30 min. It was filtered and kept at 25°C. Red-brown crystals appeared in one day (332 mg, yield 95%). M.pt. 175°C (decomposes to black mass). IR (KBr, 600–4000 cm⁻¹): 3032(w), 2925(w), 2896(w), 2792(w), 2353(w), 1637(s), 1587(s), 1512(w), 1477(w), 1430(w), 1395(m), 1346(w), 1279(s), 1254(w), 1192(m), 1164(s), 1018(m), 927(m), 908(w), 830(s), 812(s), 776(m), 746(w), 720(w), 690(w). Elemental analysis: Anal. Calcd. for CuC₁₇H₁₆N₂O₂: C, 59.47%; H, 4.66%; N, 8.16%; Found: C, 58.44%; H, 4.42%; N, 7.83%.

2.3 General procedure for the catalytic Henry reaction

Complex **1** (0.066 mmol) was dissolved in ethanol (2 mL) and aldehyde (0.66 mmol) was added followed by the addition of nitromethane (3.3 mmol) and triethylamine (0.066 mmol). The mixture was allowed to stir at 25°C for 15 h. The volatiles were removed *in vacuo*, and the residue was purified by flash chromatography to afford the nitroaldol adduct.

2.3a 1-(2-nitrophenyl)-2-nitroethanol: ¹H NMR (500 MHz, CDCl₃, ppm)²⁰: δ 3.33 (br, 1H, OH), 4.55 (dd, 1H, *J* = 9 Hz and 13.8 Hz, CHHNO₂), 4.87 (dd, 1H, *J* = 2.5 Hz and 13.8 Hz, CHHNO₂), 6.05 (d, 1H, *J* = 9 Hz, CHOH), 7.48 (t, 1H, *J* = 7.5 Hz, ArH), 7.68 (t, 1H, *J* = 7.5 Hz, ArH), 7.95 (d, 1H, *J* = 7.8 Hz, ArH), 8.08 (d, 1H, *J* = 7.8 Hz, ArH). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 66.6, 80.0, 125.2, 128.6, 129.6, 134.2, 134.6, 147.0.

2.3b 1-(4-nitrophenyl)-2-nitroethanol: ¹H NMR (500 MHz, CDCl₃, ppm)²⁰: δ 3.3 (br, 1H, OH), 4.61 (m, 2H, CH₂NO₂), 5.6 (m, 1H, CHOH), 7.63 (d, 2H, *J* = 8.6 Hz, ArH), 8.27 (d, 2H, *J* = 8.6 Hz, ArH).

^{13}C (125 MHz, CDCl_3 , ppm): δ 69.9, 80.6, 124.1, 126.9, 145.0, 148.1.

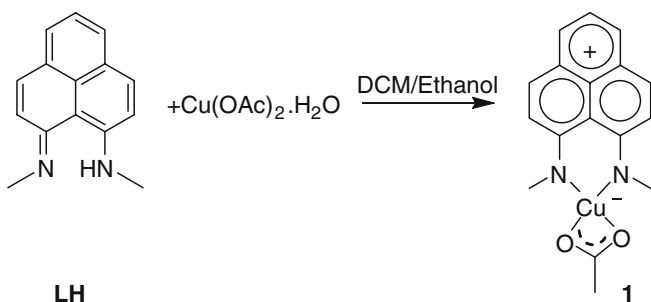
3. Results and discussion

3.1 Synthesis of complex **1**

The title compound was synthesized by the treatment of the ligand 9-*N*-methylamino-1-*N'*-methylimino-phenalene (**LH**) with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in ethanol and dichloromethane mixture (1:1) (scheme 1). The reaction mixture was refluxed for 30 min at the end to ensure complete conversion of the starting materials into the title compound. The compound **1** was characterized by IR spectroscopy, elemental analysis and single crystal X-ray crystallography. The reddish-brown single crystals of **1** were grown from the reaction mixture at 25°C under slow evaporation of the solvents.

3.2 X-ray crystal structures of **1**

The structure of **1** was established by X-ray diffraction study. The molecular structure of **1** is shown in figure 1, and the selected bond lengths and angles are presented in table 1. The X-ray structure reveals a distorted square-planar geometry around the copper (II) centre with two nitrogen atoms of the phenalenyl ligand and two oxygen atoms of the acetate group coordinated to the metal centre. The two Cu–N bond lengths are not equal revealing an inherent asymmetry in the structure. However, the two bond angles N(1)–Cu(1)–O(1) and N(2)–Cu(1)–O(2) are equal (162.7°). The Cu–N bond lengths [Cu(1)–N(2) = 1.907 Å and Cu(1)–N(1) = 1.912 Å] in complex **1** fall in the range reported for other Cu(II) square-planar complexes. For example, the Cu–N bond lengths



Scheme 1. Synthesis of complex **1**.

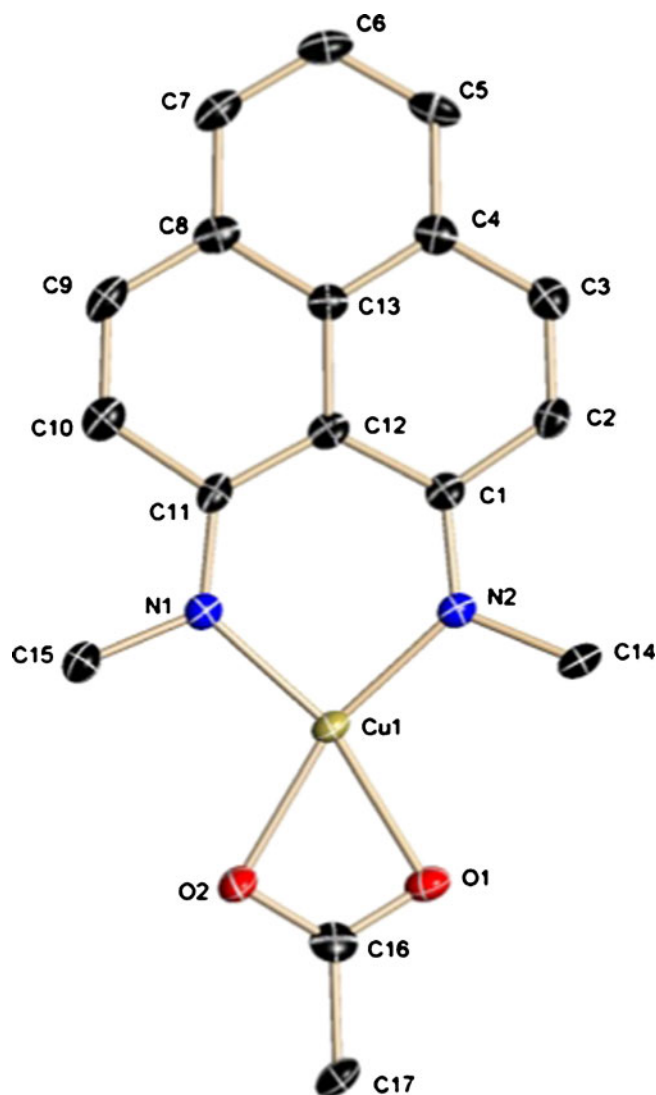


Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn with 50% probability. Hydrogen atoms have been omitted for the sake of clarity.

(~1.92 Å) in propylene-*bis*(biuret)-copper complex, $\text{Na}_2[\text{Cu}(\text{pr}(\text{bi})_2)] \cdot 3\text{Me}_2\text{SO}$ ²¹ and in LCuCl [where $\text{L} = 2,4\text{-bis}(2,6\text{-diisopropylphenylimido})\text{pentane}$]²² are similar to the Cu–N bond length observed in **1**.

The electrochemistry of **1** is presented in figure 2 where it may be seen that complex **1** shows a well-behaved reversible single reduction corresponding to the generation of an anionic radical (scheme 2). Similar reduction process is well-known in related phenalenyl-based spiro-conjugated boron systems.^{1,2} This reduction wave appears at a more negative value (–1.75 V) than the spiro-conjugated boron compounds (~ –1.0 V) bearing the *N,N*-phenalenyl ligands.^{1a} This

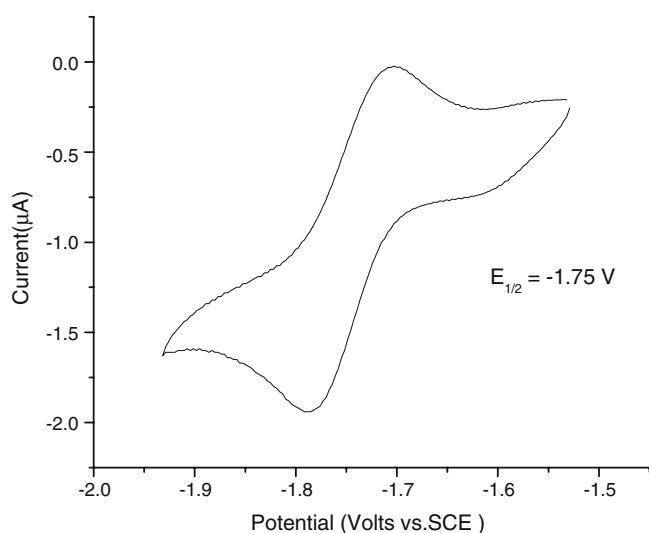
Table 1. Selected bond lengths [\AA] and angles [$^\circ$] for complex **1**.

Bond	Distance	Bond	Angles
Cu(1)–N(2)	1.907(6)	N(2)–Cu(1)–N(1)	95.2(3)
Cu(1)–N(1)	1.912(6)	N(2)–Cu(1)–O(2)	162.7(2)
Cu(1)–O(2)	2.051(5)	N(1)–Cu(1)–O(2)	101.1(2)
Cu(1)–O(1)	2.079(5)	N(2)–Cu(1)–O(1)	100.8(2)
N(1)–C(11)	1.31(10)	N(1)–Cu(1)–O(1)	162.7(2)
N(1)–C(15)	1.475(10)	O(2)–Cu(1)–O(1)	63.9(2)
N(2)–C(1)	1.333(10)	C(11)–N(1)–C(15)	119.3(6)
N(2)–C(14)	1.481(10)	C(11)–N(1)–Cu(1)	125.4(5)
O(1)–C(16)	1.271(10)	C(15)–N(1)–Cu(1)	115.1(5)
O(2)–C(16)	1.272(10)	C(1)–N(2)–Cu(1)	127.1(5)
C(1)–C(2)	1.449(11)	C(14)–N(2)–Cu(1)	114.6(5)
C(1)–C(12)	1.461(11)	C(16)–O(1)–Cu(1)	88.1(5)

indicates that the reduction is comparatively more difficult in this system to that of boron-based systems.^{1a} This may be attributed to the lower oxidation state of the copper (+2) in neutral complex **1** as compared to that of cationic spiro-conjugated boron (in +3 oxidation state) compounds.

3.3 Application to Henry reaction

The Henry reaction or the nitroaldol reaction is an important organic transformation leading to the new C–C bonds. It allows access to a range of synthetically

**Figure 2.** Cyclic voltammetry of complex **1** generating an anionic radical by one electron reduction process.

important intermediate such as 1,2-amino alcohol or α -hydroxy carboxylic acids. As a result, there have been considerable efforts towards the development of synthetic methods using Henry reaction.^{4–8} Recent studies have revealed that copper can actively catalyse the Henry reaction.^{9–15}

The new copper complex **1** was tested for its efficiency as catalyst in Henry reaction. The catalytic reaction was carried out at 25°C for 15 h resulting in a moderate yield ($\sim 60\%$) of the corresponding nitroaldol adduct. Addition of Et_3N (10 mol%) greatly enhances the conversion rate ($> 90\%$) of the catalytic reaction (table 2). We carried out the catalytic Henry reaction in a range of solvents such as methanol, ethanol, isopropanol, THF, toluene, dichloromethane, and chloroform to find out the best solvent. Ethanol was found to be the best solvent leading to more than 90% isolated yield (table 3).

After the most productive reaction condition was established, we carried out the Henry reaction on another nitro aldehyde (2-nitro benzaldehyde) using the

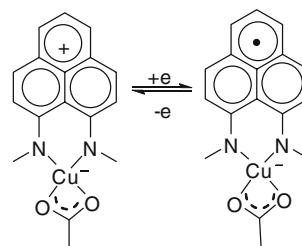
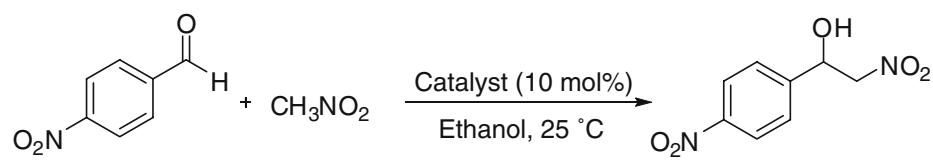
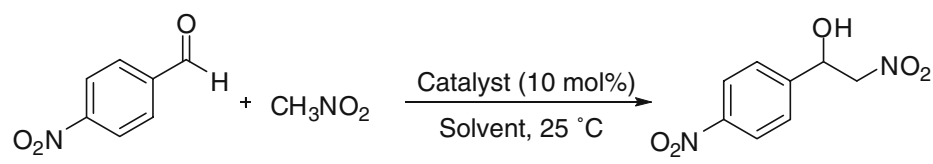
**Scheme 2.** Generation of an anionic radical by one electron reduction of **1**.

Table 2. Standardization of catalytic Henry reaction^a using complex **1** as catalyst.


Entry	Catalyst	Time (h)	Yield (%) ^b
1	Complex 1	22	65
2	Complex 1 + Et ₃ N (10 mol%)	15	92

^aThe reactions were carried out with 0.66 mmol of C₆H₄NO₂CHO and 3.3 mmol of CH₃NO₂ in 2 mL EtOH at 25 °C.

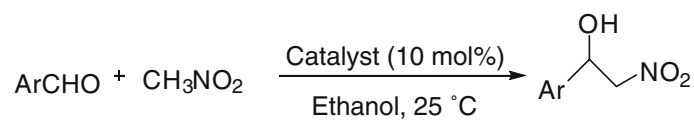
^bIsolated yield after flash chromatographic purification.

Table 3. Effect of solvent on Henry reaction using **1** as catalyst.^a


Entry	Catalyst	Solvent	Time (h)	Yield (%) ^b
1	1 + Et ₃ N	Methanol	15	88
2	1 + Et ₃ N	Ethanol	15	92
3	1 + Et ₃ N	Isopropanol	15	86
4	1 + Et ₃ N	THF	15	75
5	1 + Et ₃ N	Toluene	15	65
6	1 + Et ₃ N	DCM	15	72
7	1 + Et ₃ N	CHCl ₃	15	68

^aThe reactions were carried out with 0.66 mmol of C₆H₄NO₂CHO and 3.3 mmol of CH₃NO₂ in 2 mL solvent for 15 h at 25 °C in the presence of 10 mol% Et₃N.

^bIsolated yield after flash chromatographic purification.

Table 4. Henry reaction using **1** as catalyst on different aldehyde substrates.^a


Entry	Catalyst	Aldehyde	Yield (%) ^b
1	Complex 1	4-NO ₂ C ₆ H ₄ CHO	92
2	Complex 1	2-NO ₂ C ₆ H ₄ CHO	90

^aThe reactions were carried out with 0.66 mmol of C₆H₄NO₂CHO and 3.3 mmol of CH₃NO₂ in 2 mL EtOH for 15 h at 25 °C in the presence of 10 mol% Et₃N.

^bIsolated yield after flash chromatographic purification.

complex **1** as a catalyst. The results of the catalytic reactions are presented in table 4 exhibiting high isolated yield.

4. Conclusion

In summary, we have synthesized and characterized the first transition metal complex of a phenalenyl-based ligand to be utilized as catalyst for carrying out Henry reaction. This result establishes that the phenalenyl-based ligands can be used for the development of transition metal chemistry to design catalyst for homogeneous organic transformation. The complex was synthesized by direct mixing of the reagents in high yield. The electrochemistry of this complex clearly demonstrates that the empty non-bonding orbital of the phenalenyl ligand can accept an electron to generate the anionic radical. This result supports that this system has potential to prepare the mixed organic (free electron in phenalenyl part) inorganic [free electron in copper(II)] hybrid magnetic system. Also it could find application for preparation mixed organic–inorganic tunnel junction by external spin injection. Complex **1** exhibits high catalytic efficiency in the C–C bond forming Henry reactions. This study establishes that the phenalenyl-based ligand system can not only be used as building block for the preparation of molecular conductors but also they can be used as useful ligands for making efficient catalysts. Currently, we have been working on different metals to synthesize active catalysts bearing phenalenyl-based ligands for useful organic catalytic transformations.

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