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Diphenylglycoluril as a novel ligand architecture for dirhodium(II) carboxamidates

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Dedicated to Robert J. Angelici.

Abstract

1,6-Bis-(*N*-benzyl)-diphenylglycoluril (1,6-BPGlyc) was used as a ligand in the synthesis of a dinuclear rhodium(II) paddlewheel complex. The ligand exchange reaction from $Rh_2(OAc)_4$ was remarkably selective for the formation of $Rh_2(1,6\text{-BPGlyc})_2(OAc)_2$ with a *cis*-(1,3) ligand arrangement in 46% isolated yield. The bis-substitution pattern and diastereoselective ligand exchange is attributed to the steric bulk of the glycoluril backbone that prevents further ligand substitution. $Rh_2(1,6\text{-BPGlyc})_2(OAc)_2$ catalyzes cyclopropanation reactions *via* decomposition of diazoacetates with reactivities and selectivities that were comparable to those of dirhodium(II) tetrakis-μ-carboxamidates.

Keywords: Dirhodium; Dirhodium carboxamidate; Glycoluril; Cyclopropanation; Catalysis

1. Introduction

Glycoluril derivatives are the subject of numerous studies because of their synthetic accessibility, their curved and rigid structure, and their hydrogen-bond donating/accepting ureidyl functionality. The nature by which these features convey form and function to supramolecular structures continues to receive considerable attention in areas such as crystal engineering [1], self-association, and host/guest chemistry; a number of reviews on these topics are available [2].

Coordination complexes that take advantage of the structural characteristics of glycoluril are less well known. Although glycoluril derivatives are incorporated as elements of phosphine or amine based ligands [3], the coordinating ability of the nascent glycoluril subunit has yet to be explored. This is surprising since glycoluril contains ureidyl functionality that can act as a μ-bridging ligand (μ-NCO) in a metal-coordination complex. We report that one such complex is a dirhodium(II) carboxamidate.

Dirhodium(II) tetrakis-μ-carboxamidates are long known as asymmetric catalysts for carbene transformations [4]. They are constructed with four μ-NCO bridging ligands around a dinuclear rhodium core in a paddlewheel fashion. In complexes prepared for asymmetric catalysis, the two nitrogen atoms and two oxygen atoms are bound to each rhodium in a *cis*-(2,2) orientation. Herein we report the synthesis and structural characterization of a dirhodium(II) bis-μ-carboxamidate (**1**: $Rh_2L_2(OAc)_2$) where the μ-NCO bridging ligand is 1,6-bis-(*N*-benzyl)-diphenylglycoluril (**2**: L = 1,6-BPGlyc). As the general form of glycoluril is similar to the imidazolidinone class of ligands (**3**: HMPPIM = methyl *N*-(3-phenylpropanoyl)-2-oxoimidazolidine-5-carboxylate), the effects of glycoluril ligand structure on the catalysis of diazodecomposition reactions is compared to $Rh_2(OAc)_4$ and $Rh_2(4S\text{-MPPIM})_4$ (Fig. 1).

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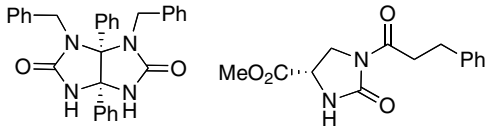

2: 1,6-BPGlyc **3:** HMPPIM

Fig. 1. Comparison of glycoluril and imidizolidinone ligands.

2. Experimental

2.1. General

Tetrakis-μ-acetato-diaquodirhodium(II) and ethyl diazoacetate were obtained commercially. The preparation of 1,6-bis-(*N*-benzyl)-diphenylglycoluril [1c], Rh_2(4*S*-MPPIM)$_4$ [5], and methyl phenyldiazoacetate [6] have been previously described. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ) downfield from Me_4Si (TMS). Gas chromatographic analysis was obtained on a Varian 3900 gas chromatograph equipped with a Varian Factor 4 capillary column (0.25 mm × 30 m). Preparative chromatographic purification was performed using SiliCycle (60 Å, 40–63 mesh) silica gel according to the method of Still [7]. Thin layer chromatography (TLC) was performed on Merck 0.25 mm silica gel 60 F_{254} plates with visualization by fluorescence quenching or chemical stain. UV–Vis spectra were obtained on a Varian Cary 50 spectrophotometer using a xenon flash lamp. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer. Anhydrous CH_2Cl_2 was purified prior to use by nitrogen forced-flow over activated alumina as described by Grubbs [8].

2.2. Bis-μ-{1,6-(*N*-benzyl)diphenylglycoluril}-bis-μ-acetatodirhodium(II) acetonitrile solvate (*1*)

Tetrakis-μ-acetato-diaquodirhodium(II) (150 mg, 0.31 mmol) and 1,6-bis-(*N*-benzyl)-diphenylglycoluril (1.25 g, 2.50 mmol) were dissolved in a mixture of chlorobenzene/acetonitrile (15 mL, 25:1) [9]. The reaction flask was fitted with a Soxhlet extraction apparatus charged with a thimble containing a mixture of Na_2CO_3/sand (3 g, 2:1) and a condenser. After purging the system with N_2, the reaction mixture was heated to reflux for 48 h. The solvent was removed under reduced pressure to yield a glassy blue solid. The solid was loaded directly onto a preparatory silica gel column and eluted with CH_2Cl_2, then CH_2Cl_2/acetone (99:1), followed by CH_2Cl_2/acetone (98:2). Two sequential recrystallizations from boiling acetonitrile/methanol (15:1) yielded dark red crystals (184 mg, 0.145 mmol, 46% yield). TLC: $R_f = 0.20$ (CH_2Cl_2/MeOH 98:2). ^{1}H NMR: $\delta = 7.33$ (6H, t, $J = 7.6$ Hz), 7.30–7.15 (18H, comp), 7.13 (6H, d, $J = 7.6$ Hz), 7.03 (4H, t, $J = 7.4$ Hz), 6.80–6.70 (6H, comp), 5.46 (2H, s), 4.80 (2H, d, $J = 17.2$ Hz), 3.95–3.90 (4H, comp), 3.84 (2H, d, $J = 16.8$ Hz), 2.09 (6H, s) ppm. ^{13}C NMR: $\delta = 191.5$, 172.3, 161.6, 140.0, 139.4, 137.9, 128.5, 128.3, 128.0, 127.1, 126.9, 126.6, 126.5, 126.2, 126.0, 116.0, 92.3, 86.6, 45.9, 45.1, 23.9 ppm. UV–Vis (CH_3OH) λ_{max} (ε M^{-1} cm^{-1}) nm = 580 (188). IR (neat) 1611 (O–(C=O)–C stretch), 1699 (N–(C=O)–N stretch) cm^{-1}. XRD (CCDC #661587): crystals were grown by slow evaporation from acetonitrile.

2.3. X-ray structure determination of *1*

A purple prism of $Rh_2C_{68}H_{62}N_{10}O_8 \cdot 5CH_3CN$ with approximate dimensions $0.135 \times 0.22 \times 0.435$ mm^3 was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 220(2) K on a three-circle diffractometer system equipped with Bruker Smart1000 CCD area detector. Detection was performed using a graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 50 kV and 30 mA. The

Table 1
Crystal data and structure refinement for $Rh_2C_{68}H_{62}N_{10}O_8 \cdot 5CH_3CN$

Empirical formula	$Rh_2C_{68}H_{62}N_{10}O_8 \cdot 5CH_3CN$
Formula weight (g/mol)	1558.37
Temperature (K)	220(2)
Radiation, l (Å)	Mo Kα, 0.71073
Crystal size (mm)	0.435 × 0.22 × 0.135
Crystal habit	purple prism
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	23.913(2)
b (Å)	15.2843(15)
c (Å)	20.481(2)
α (°)	90
β (°)	93.740(2)
γ (°)	90
Volume (Å^3)	7469.7(13)
Z	4
Density, ρ_{calc} (g/cm^3)	1.386
Absorption coefficient, μ (mm^{-1})	0.508
θ Range (°)	2.40–27.50
Reflections collected	91920
Independent reflections	17118
Observed reflection, $I > 2\sigma(I)$	12875
Maximum and minimum transmission[a]	0.934 and 0.803
Goodness-of-fit on F^2	1.006
Max $\lvert\Delta/\sigma\rvert$	0.001
Final R indices[b]	
R_1, $I > 2\sigma(I)$	0.0498
wR_2, all data	0.1168
R_{int}	0.0418
R_{sig}	0.0313
Minimum, maximum peaks (e/Å^3)	0.952, −1.437

[a] Absorption correction was performed using the semi-empirical from equivalents method (SADABS).

[b] Function minimized was $\sum w(F_o^2 - F_c^2)^2$ where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 \Big/ \sum w(F_o^2)^2\right]^{1/2}$ with a weighting scheme $w = 1 \Big/ \left[\sigma^2(F_o^2) + (0.015P)^2 + 27.8P\right]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$.