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Bimetallic nickel complexes supported by 2,5-bis(phosphine)-1,4-hydroquinonate ligands. Structural, electrochemical and theoretical investigations

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ABSTRACT

The coordination chemistries of several 2,5-bis(phosphine)-1,4-hydroquinones, (2,5-bis($PiPr_2$)-3,6-difluoro-1,4-hydroquinone (**1a**), 2,5-bis($PiPr_2$)-1,4-hydroquinone (**1b**), (2,5-bis(PPh_2)-3,6-difluoro-1,4-hydroquinone (**1c**), and 2,5-bis(PPh_2)-1,4-hydroquinone (**1d**)) were investigated. Reactions of these ligands **1a–d** with excess (∼2.5) of bis(cyclopentadienide)nickel, and in case of **1a**, with bis(pentamethylcyclopentadienide)nickel, resulted in the formation of bimetallic nickel complexes **2a–d** and **3a**, where both [P,O] chelating pockets of the ligands were occupied by CpNi or Cp*Ni moieties, respectively. Cyclic voltammetric (CV) scans on complexes **2a–d** contained a common feature of two reversible/quasi-reversible waves and one irreversible redox event. Complex [**2a**][PF_6] was isolated by the oxidation of **2a** with ferrocenium hexafluorophosphate. Spectroscopic, structural, and synthetic studies were carried out in order to elucidate the nature of these redox processes. Our results suggest that the reversible and quasi-reversible redox events are ligand-based processes (hydroquinone/semiquinone/quinone), while the irreversible process was assigned as metal-based. These conclusions were supported by additional experimental data and by theoretical calculations. Investigations of chemical reactivity showed that cyclopentadienide ligands in complexes **2a–d** can be displaced from the metal centers upon reactions with *o*-aminothiophenol. One of these derivatives, **4a**, containing capping [N,S] *o*-aminothiophenolate ligands was isolated and fully characterized. A CV scan of complex **4a** contained one reversible wave and an irreversible wave at higher potentials. The assignment is complicated by the proton transfer processes accompanying the electron transfer events. Complexes **1a**, **2a–c**, [**2a**][PF_6] and **4a** were characterized by single crystal X-ray diffraction experiments.

1. Introduction

The coordination chemistry of redox active ligands has been an active area of research for several decades [1]. Some notable examples include redox-active complexes featuring dimolybdenum units linked by the tetraazatetracene ligand [2], chiral triangular complexes with Rh–Rh bonds [3], and a trinuclear cobalt molecular wire capped by ferrocenylacetylide moieties [4]. It is also known that various hydroquinone derivatives are well suited to serve as redox-active platforms for the buildup of coordination complexes. Both 1,2-hydroquinone and 1,4-hydroquinone display rich

coordination chemistry with various modes of ligation established and well understood [5,6]. Simple *p*-quinone linkages have been used in constructing multimetallic assemblies containing early transition metals [7–12]. Polymetallic networks where the quinoid fragments function both as σ- (through oxygen atoms) and π-ligands (via coordination of a transition metal containing fragment onto the quinone ring) have also been extensively studied [13–16]. More predictable coordination modes and enhanced complex stability can be expected if O groups of the quinoid moieties constitute part of chelation pockets. Various dihydroxybenzoquinones which contain such structural features are well-studied ligands. Coordination polymers supported by such ligands are noted for their higher directionality and for increased stability brought about by the structural rigidity of O,O-chelation pockets [6]. Binucleating

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ligands where the quinone oxygens are flanked by other donor atoms, thus, creating chelating [O, E] cavities (E = nitrogen, phosphorus or other donor atom) are somewhat limited in numbers [17–19]. In particular, phosphine-appended *para* hydroquinones have received only limited attention [20–23], and this can be attributed to the incompatibility of the phosphine and quinone functionalities [24]. Bis(phosphine)-*p*-hydroquinonate ligands are less known, and the research here has been mainly limited to complexes of 2,5-bis(diphenyl)phosphosphine-1,4-hydroquinone [25,26]. The coordination chemistry of phosphine-appended *p*-hydroquinones appears to be relatively underdeveloped in contrast to the chemistry developed with tertiary phosphines which are among the most widely utilized class of ligands [27]. Earlier we reported on the syntheses and structural studies of the several 2,5-bis(phosphine)-1,4-hydroquinone and 2,5-bis(phosphoryl)-1,4-hydroquinone derivatives, including preliminary investigations of bimetallic nickel complexes supported by one of these ligands [28]. Herein we describe our continuing investigations showing that 2,5-bis(phosphine)-1,4-hydroquinone ligands (Chart 1, **1a–d**) are excellent platforms to synthesize bimetallic nickel complexes (Chart 1, **2a–d** and **3a**). Complexes **2a–d** were found to display rich redox behavior, which was investigated through electrochemical, structural and spectroscopic studies and by theoretical calculations. Initial investigations of chemical reactivity also revealed that complexes **2a–d** can serve as building blocks for extended linear arrays composed of alternating redox-active units (Chart 1, **4a**).

2. Experimental

2.1. General procedures

All reactions and manipulations were carried out utilizing standard Schlenk techniques involving a double manifold vacuum line and a glovebox both using purified N_2. Diethylether, THF, benzene hexanes and pentane were dried and distilled from Na/benzophenone. Methylene chloride was distilled from CaH_2. Starting materials were purchased from commercial suppliers and were used as received; *o*-aminothiophenol was purified by vacuum distillation. Ligands **1a**, **1c** and **1d** were obtained by following published procedures [25,26].

A Varian INOVA spectrophotometer was used to obtain NMR spectra of ^1H, ^{13}C, ^{31}P, ^{19}F at 400, 100, 161 and 376 MHz, respectively. ^1H & ^{13}C spectra were referenced to tetramethylsilane, ^{31}P spectra was referenced to 85% H_3PO_4 as an external reference, and ^{19}F spectra was referenced to $CFCl_3$ dissolved in benzene-d_6 as an internal reference in a sealed capillary tube. Elemental analysis was carried out at Galbraith Laboratories (PO Box 51610, Knoxville, TN 37950, USA); high resolution mass spectroscopy analyses were performed at Michigan State University Mass Spectrometry Facility (Room 11, Biochemistry Building, East Lansing, MI 48824-1319, USA).

Cyclic voltammetry measurements were carried out in a standard three-electrode cell utilizing a CHI 420 electrochemical analyzer. Glassy carbon, platinum wire, and Ag/Ag+ were used as a working, counter and reference electrode, respectively. A small amount of ferrocene was added to the last scan and used as a reference. All experiments were carried out in 1 mM solutions of analyte with 0.1 M N(^{n}Bu)$_4$PF$_6$ as a supporting electrolyte in CH_2Cl_2. Scan rate for all experiments was 0.05 V/s.

Ultra Violet and Visible spectra (230–1100 nm) were collected using a Perkin Elmer *Lambda 35* spectrometer with a 1 cm path length quartz cuvette.

2.2. Synthesis

2.2.1. 2,5-Bis(diisopropylphosphino)-1,4-hydroquinone (**1b**)

A solution of 1,4-dibromo-2,5-dimethoxybenzene (4.20 g, 14.0 mmol) in diethylether (250 ml), was cooled to 0 °C, and solution of *n*-butyllithium (1.6 M, 17.5 ml, 28 mmol) was added. The reaction mixture was stirred for 15 minutes, and then a solution of chlorodiisopropylphosphine (4.5 ml, 28 mmol) in diethylether (30 ml) was added. The reaction mixture was stirred for 2.5 h, then all volatiles were removed under vacuum yielding an off white solid. The resulting solid was rinsed with cold methanol (40 ml) and then recrystalized from hot methanol (200 ml) yielding crystalline 1,4-bis(diisopropylphosphino)-2,5-dimethoxybenzene (white solid, 2.85 g, after drying under vacuum overnight). Yield: 54.9%. ^1H NMR (CDCl$_3$): δ 6.86 (dd, 2H), 3.75 (s, 6H), 2.18 (m, 4H), 1.08 (dd, 6H), 0.90 (dd, 6H). ^{31}P NMR (CDCl$_3$): δ 4.3 (s). HRMS(ESI+): 371.2274 (MH$^+$); calcd. for $C_{20}H_{37}O_2P_2$: m/z = 371.2269.

To a cold (−80 °C) solution (CH$_2$Cl$_2$, 200 ml) of 1,4-bis(diisopropylphosphino)-2,5-dimethoxybenzene (2.85 g, 7.69 mmol) BBr$_3$ (3.4 ml, 36 mol) was added and the reaction mixture was allowed to warm to room temperature overnight. After that all volatiles were removed under vacuum and then dry methanol (150 ml) was added. This generated a slurry which was then stirred overnight. All volatiles were removed under vacuum, and the remaining solid was re-suspended in dry isopropanol (150 ml), followed by an addition of NEt$_3$ (5.0 ml, 39 mmol) and stirring overnight. The solution was reduced in volume (to ∼40 ml), and degassed H$_2$O (20 ml) was added resulting in precipitation of an off white solid (2.22 g, isolated by filtration). Yield: 84.4%. ^1H NMR (CDCl$_3$): δ 6.83 (dd, 2H), 2.11 (m, 4H), 1.11 (dd, 6H), 0.93 (dd, 6H). ^{31}P NMR (CDCl$_3$): δ −21.7 (s). HRMS(ESI+): 343.1950 (MH$^+$); Calc. for $C_{18}H_{33}O_2P_2$: m/z = 343.1956.

2.2.2. Bis((η^5-cyclopentadienyl)nickel)-μ-(2,5-bis(diisopropylphosphino)-3,6-diflouro-1,4-hydroquinonate), (**2a**)

A solution of **1a** (1.10 g, 2.91 mmol) in THF (150 ml) was slowly added drop wise to a solution of Cp$_2$Ni (1.39 g, 7.37 mmol) which was dissolved in benzene (150 ml). The solution was then heated in a 50 °C oil bath for 39 h. The mixture was then filtered and all volatiles removed under vacuum. Excess Cp$_2$Ni was removed by gently heating the solids under vacuum with a cold finger placed inside the flask. The remaining solid was re-dissolved in THF (20 ml) and pentane (70 ml) added to initiate precipitation. This resulted in 1.36 g of a light brown powder. Yield: 75.4%. ^1H NMR (C$_6$D$_6$): δ 5.08 (s, 10H), 1.87 (m, 4H, $^3J_{HH}$ = 7 Hz, $^2J_{HP}$ = 11 Hz), 1.02 (dd, 12H, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 17 Hz), 0.77 (dd, 12H, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 17 Hz). ^{13}C NMR (C$_6$D$_6$): δ 152.3 (m,C$_{arom}$O), 147.8 (ddt,
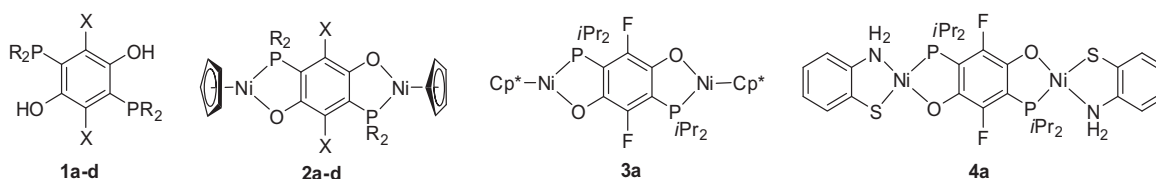
Chart 1. **a** (R = *i*Pr, X = F); **b** (R = *i*Pr, X = H); **c** (R = Ph, X = F); **d** (R = Ph, X = H).