



## Note

## 4-Hydroxyaryl complexes of group 10 metals



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## ABSTRACT

Attempts have been made to synthesize group 10 metal complexes bearing  $\sigma$ -bonded 4-hydroxyaryl ligands that are potential precursors to metallaquinones. Treatment of 4-bromo-2,6-di-*tert*-butylphenol with  $[\text{Pd}(\text{PPh}_3)_4]$  led to formation of the phosphaquinone  $\text{Ph}_3\text{P} = \text{C}_6\text{H}_3\text{Bu}_2\text{-3,5-O-4}$  (**1**), whereas that with  $[\text{M}(\text{PPh}_3)_4]$  ( $\text{M} = \text{Ni}, \text{Pt}$ ) yielded the biquinone  $[\text{C}_6\text{H}_3\text{Bu}_2\text{-3,5-O-4}]_2$  (**2**). The solid-state structure of **1** features a short  $\text{C}=\text{O}$  double bond and alternate phenyl  $\text{C}-\text{C}$  single and double bonds that are characteristic of quinoidal compounds. Alkylation of  $[\text{NiCl}_2(\text{PPh}_3)_2]$  with  $(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OSiMe}_3\text{-4})\text{MgBr}$  afforded *cis*- $[\text{Ni}(\text{PPh}_3)_2\text{Br}(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OSiMe}_3\text{-4})]$  (**3**) that reacted with  $^t\text{Bu}_4\text{NF}$  to yield  $[\text{Ni}(\text{PPh}_3)(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OH-4})_2(\mu\text{-OH})_2]$  (**4**) containing a  $\sigma$ -bonded 4-hydroxyaryl ligand.

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## 1. Introduction

Quinoidal compounds have attracted considerable attention because of their pivotal roles in biology, and chemistry, and materials science [1]. Although quinone derivatives are well documented, not many heteroatom-substituted quinoidal compounds have been isolated. Examples of isolated quinone compounds bearing  $\text{C} = \text{X}$  ( $\text{X} = \text{B}$  [2],  $\text{P}$  [3],  $\text{Bi}$  [4]) bonds are shown in Scheme 1. Stable metallaquinones (quinone in which one of the oxygen atoms is replaced by a transition metal) remain elusive. By contrast, transition metal complexes with  $\pi$ -bonded quinoidal ligands that have been used as building blocks for polymeric organometallic networks are well known [5].

Heavy element-containing quinoidal compounds are generally synthesized from the hydroxyaryl precursors. For example, reaction of the  $\text{R}(\text{PCl}_2)_2$  ( $\text{R} = 2,4,6\text{-tri-}t\text{-butylphenyl}$ ) with  $\text{Li}(\text{C}_6\text{H}_4\text{Bu}_2\text{-3,5-O-4})$ , followed by dechlorination afforded the phosphaquinone **B** [3], whereas the bismuthaquinone **C** (Scheme 1) was obtained by reaction of  $[(\text{N}^*\text{C}^*\text{N})\text{BiCl}_2]$  ( $\text{N}^*\text{C}^*\text{N} = 2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$ ) with  $\text{Li}(\text{C}_6\text{H}_4\text{Bu}_2\text{-3,5-O-4})$  [4]. Milstein and co-workers reported that deprotonation of a  $\text{Ru}(\text{II})$  complex bearing a hydroxy-PCP pincer ligand yielded a  $\text{Ru}(\text{O})$  quinoid species (**D**) that is readily converted to the zwitterionic form (**E**) by changing the solvent polarity (Scheme 2) [6]. This finding prompted us to synthesize transition metal 4-hydroxyaryl complexes and to explore their deprotonation

reactions.

In an attempt to prepare 4-hydroxyaryl complexes, oxidative addition of  $[\text{M}(\text{PPh}_3)_4]$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ) with substituted 4-bromophenols was studied. In particular, the oxidative addition with 4-bromo-2,6-di-*tert*-butylphenol was explored because all the reported heteroatom-substituted quinoidal compounds **A-C** contain the 2,6-di-*tert*-butylphenoxy moiety. In this work, we found that whereas the reaction of 4-bromo-2,6-di-*tert*-butylphenol with  $[\text{Pd}(\text{PPh}_3)_4]$  gave a phosphaquinone, **1**, presumably via the  $\text{P}-\text{C}$  elimination of a  $\text{Pd}(\text{II})$  4-hydroxyaryl intermediate, those with  $[\text{M}(\text{PPh}_3)_4]$  ( $\text{M} = \text{Ni}, \text{Pt}$ ) afforded a biquinone, **2**. A dinuclear  $\text{Ni}(\text{II})$  hydroxyaryl complex  $[\text{Ni}(\text{PPh}_3)(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OH-4})_2(\mu\text{-OH})_2]$  (**4**) has been synthesized by desilylation of  $[\text{Ni}(\text{PPh}_3)_2\text{Br}(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OSiMe}_3\text{-4})]$  (**3**) and characterized by X-ray crystallography.

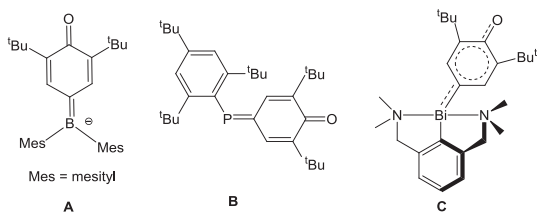
## 2. Experimental section

## 2.1. General considerations

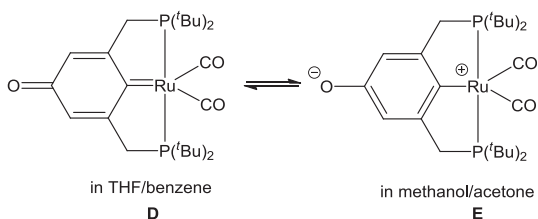
All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were dried, distilled and degassed before use. NMR spectra were recorded on a Bruker AV 400 MHz NMR spectrometer operating at 400, 100 and 162.0 MHz for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ , respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$ ), and  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, United Kingdom. The compounds  $[\text{M}(\text{PPh}_3)_4]$  ( $\text{M} = \text{Ni}$  [7],  $\text{Pd}$  [8],  $\text{Pt}$

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**Scheme 1.** Examples of heteroatom-substituted quinoidal compounds [2–4].



**Scheme 2.** A PCP pincer-based ruthenaquinone [5].

[9] and  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$  [10] were prepared according to literature methods. 2,6-Dimethyl-4-trimethylsilyloxyphenylmagnesium bromide was prepared by treatment of 1-bromo-2,6-dimethyl-4-trimethylsilyloxybenzene, which was obtained from 4-bromo-3,5-dimethylphenol and chlorotrimethylsilane, with Mg in tetrahydrofuran (THF).

## 2.2. Reaction of $[\text{Pd}(\text{PPh}_3)_4]$ with 4-bromo-2,6-di-*tert*-butylphenol

To a suspension of  $[\text{Pd}(\text{PPh}_3)_4]$  (230 mg, 0.2 mmol) in toluene (10 mL) was added 1 equivalent of 4-bromo-2,6-di-*tert*-butylphenol (57 mg, 0.2 mmol). The resulting solution was refluxed for 2 d, and the volatiles were removed in vacuo. The residue was washed with hexanes and then extracted with  $\text{CH}_2\text{Cl}_2$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexanes afforded yellow crystals that were characterized as the phosphoquinone  $\text{Ph}_3\text{P} = \text{C}_6\text{H}_3\text{Bu}_2\text{-3,5-O-4}$  (**1**) by X-ray crystallography. Yield: 50 mg, 54%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.31$  (s, 18H,  $\text{CH}_3$ ), 6.84 (s, 2H, Ph), 7.60–7.72 (m, 15H, Ph) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 28.82$  (s), 34.63 (s), 122.11 (s), 122.99 (s), 140.15 (s), 176.21 (s) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 20.74$  (s) ppm. Anal. Calcd for  $\text{C}_{32}\text{H}_{35}\text{OP}$ : C, 82.37; H, 7.56. Found: C, 81.50; H, 7.24.

## 2.3. Reaction of $[\text{M}(\text{PPh}_3)_4]$ ( $\text{M} = \text{Ni}, \text{Pt}$ ) with 4-bromo-2,6-di-*tert*-butylphenol

A mixture of  $[\text{Ni}(\text{PPh}_3)_4]$  or  $[\text{Pt}(\text{PPh}_3)_4]$  (0.2 mmol) and 4-bromo-2,6-di-*tert*-butylphenol (0.2 mol) in toluene (10 mL) was heated at reflux for 2 d, and the volatiles were removed in vacuo. The residue was washed with hexanes and then extracted with  $\text{CH}_2\text{Cl}_2$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$ /Et<sub>2</sub>O/hexanes afforded yellow crystals that were identified as the biquinone  $[\text{C}_6\text{H}_3\text{Bu}_2\text{-3,5-O-4}]_2$  (**2**) by X-ray crystallography. Yield: 40%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.35$  (s, 36H,  $\text{CH}_3$ ), 7.70 (s, 4H, Ph) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 28.95$  (s), 35.38 (s), 125.38 (s), 135.49 (s), 149.78 (s), 185.92 (s) ppm. Anal. Calcd for  $\text{C}_{28}\text{H}_{40}\text{O}_2$ : C, 82.30; H, 9.87. Found: C, 81.79; H, 10.04.

## 2.4. Synthesis of *cis*- $[\text{Ni}(\text{PPh}_3)_2\text{Br}(\text{C}_6\text{H}_2\text{Me}_2\text{-2,6-O-SiMe}_3\text{-4})]$ (**3**)

To a solution of  $[\text{NiCl}_2(\text{PPh}_3)_2]$  (1 g, 1.60 mmol) in THF (10 mL) was added 1 equivalent of 2,6-dimethyl-4-trimethylsilyloxyphenylmagnesium bromide (3.2 mL of 0.5 M

solution in THF, 1.6 mmol) at 0 °C. The resulting orange mixture was stirred for 15 min at 0 °C and the volatiles were removed in vacuo. Methanol was added and the resulting suspension was cooled to 0 °C. The yellow precipitate was collected by vacuum filtration, washed with two portions of cold methanol (10 mL), and dried under high vacuum. Recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexanes afforded orange crystals which were suitable for X-ray diffraction analysis. Yield: 1.1 g, 80%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.17$  (s, 9H,  $\text{CH}_3$ ), 2.72 (s, 6H,  $\text{CH}_3$ ), 5.93 (s, 2H, Ph), 7.10 (m, 18H, Ph), 7.82 (m, 12H, Ph) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 19.50$  (s) ppm. Anal. Calcd for  $\text{C}_{47}\text{H}_{47}\text{BrNiOP}_2\text{Si}$ : C, 55.88; H, 4.69. Found: C, 55.73; H, 4.73.

## 2.5. Synthesis of $[\text{Ni}(\text{PPh}_3)(\text{C}_6\text{H}_2\text{Me}_2\text{-2,6-OH-4})_2(\mu\text{-OH})_2]$ (**4**)

To a solution of **3** (100 mg, 0.12 mmol) in THF (10 mL) was added 1.5 equivalents of  $^n\text{Bu}_4\text{NF}\cdot\text{H}_2\text{O}$  (0.18 mL of a 1 M solution in THF, 0.18 mmol) at –78 °C. The resulting mixture was then warmed to room temperature and stirred overnight. The volatiles were removed in vacuo. The residue was washed with hexanes and then extracted with MeCN. Recrystallization from MeCN/Et<sub>2</sub>O afforded yellow crystals which were suitable for X-ray diffraction. Yield: 33 mg, 52%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -4.0$  (br, 2H, OH), 2.98 (s, 6H,  $\text{CH}_3$ ), 5.85 (br, 2H, OH), 5.92 (s, 4H, Ph), 7.24–7.37 (m, 30H, Ph) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 21.20$  (s) ppm. Anal. Calcd for  $\text{C}_{52}\text{H}_{50}\text{Ni}_2\text{O}_4\text{P}_2$ : C, 68.01; H, 5.49. Found: C, 68.16; H, 5.28.

## 2.6. X-ray crystallography

Crystal data and experimental details for **1**, **3**, and **4** are summarized in Table 1. Preliminary examinations and intensity data collection were carried out on a Bruker SMART APEX 1000 CCD diffractometer. The collected frames were processed with the software SAINT. The data was corrected for absorption using the program SADABS [11]. Structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [12]. Unless stated otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL97 default parameters. CCDC 1539784, 1540324 and 1540325 contains the supplementary crystallography data for **1**, **3**, and **4**, respectively.

**Table 1**  
Crystallographic data and experimental details for **1**, **3** and **4**.

	1-0.125( $\text{C}_4\text{H}_8\text{O}$ )	3- $\text{CH}_2\text{Cl}_2$	4-2 $\text{CH}_3\text{CN}$
Formula	$\text{C}_{32}\text{H}_{35}\text{OP}$	$\text{C}_{47}\text{H}_{47}\text{BrNiOP}_2\text{Si}$	$\text{C}_{52}\text{H}_{50}\text{Ni}_2\text{O}_4\text{P}_2$
Fw	475.58	941.42	1000.39
<i>a</i> [Å]	10.8259(2)	11.7312(4)	14.01551(11)
<i>b</i> [Å]	18.4075(3)	12.2073(5)	12.82811(10)
<i>c</i> [Å]	14.8443(2)	17.6080(5)	27.58082(19)
$\alpha$ [°]	90	95.260(3)	90
$\beta$ [°]	94.853(2)	93.322(3)	97.8616(7)
$\gamma$ [°]	90	116.250(4)	90
<i>V</i> [Å <sup>3</sup> ]	2947.53(8)	2238.28(14)	4912.22(6)
<i>Z</i>	4	2	4
Cryst system	monoclinic	triclinic	monoclinic
$\rho_{\text{calcd}}$ [ $\text{g}\cdot\text{cm}^{-3}$ ]	1.072	1.397	1.353
Space group	$P2_1/n$	<i>P</i> -1	$P2_1/n$
<i>T</i> [K]	173.15	99.98(6)	100.0(2)
$\mu$ [ $\text{mm}^{-1}$ ]	0.973	3.969	1.947
<i>F</i> (000)	1020	972	2096
No. of reflns	8830	12411	19228
No. of indep reflns	4910	7872	8757
R(int)	0.0626	0.0290	0.0201
$R_1$ , $wR_2$ ( $I > 2\sigma(I)$ )	0.0598, 0.1355	0.0446, 0.1205	0.0268, 0.0657
$R_1$ , $wR_2$ (all data)	0.0971, 0.1560	0.0555, 0.1264	0.0337, 0.06823
GoF	1.002	1.002	1.002

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