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4-Hydroxyaryl complexes of group 10 metals

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ABSTRACT

Attempts have been made to synthesize group 10 metal complexes bearing σ -bonded 4-hydroxyaryl ligands that are potential precursors to metallaquinones. Treatment of 4-bromo-2,6-di-*tert*-butylphenol with [Pd(PPh_3)_4] led to formation of the phosphaquinone Ph_3P = C₆H_3^tBu_2-3,5-O-4 (1), whereas that with [M(PPh_3)_4] (M = Ni, Pt) yielded the biquinone [C₆H_3^tBu_2-3,5-O-4]_2 (2). The solid-state structure of **1** features a short C=O double bond and alternate phenyl C-C single and double bonds that are characteristic of quinoidal compounds. Alkylation of [NiCl_2(PPh_3)_2] with (C₆H_2Me_2-3,5-OSiMe_3-4)](**3**) that reacted with ⁿBu_4NF to yield [Ni(PPh_3)(C₆H_2Me_2-3,5-OH-4)]_2(\mu-OH)_2 (**4**) containing a σ -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 C = X (X = B [2], P [3], 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 π -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 RPCl₂ (R = 2,4,6-tri-*tert*-butylphenyl) with Li(C₆H^t₄Bu₂-3,5-0-4), followed by dechlorination afforded the phosphaquinone **B** [3], whereas the bismuthaquinone **C** (Scheme 1) was obtained by reaction of $[(N^{C}N)BiCl_2]$ (N^CC^N = 2,6-(Me_2NCH_2)_2C_6H_3) with Li(C₆H^t₄Bu₂-3,5-0-4) [4]. Milstein and co-workers reported that deprotonation of a Ru(II) complex bearing a hydroxy-PCP pincer ligand yielded a Ru(0) 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

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In an attempt to prepare 4-hydroxyaryl complexes, oxidative addition of $[M(PPh_3)_4]$ (M = Ni, Pd, Pt) with substituted 4bromophenols 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 $[Pd(PPh_3)_4]$ gave a phosphaquinone, **1**, presumably via the P-C elimination of a Pd(II) 4-hydroxyaryl intermediate, those with $[M(PPh_3)_4]$ (M = Ni, Pt) afforded a biquinone, **2**. A dinuclear Ni(II) hydroxyaryl complex $[Ni(PPh_3)(C_6H_2Me_2-3,5-OH-4]_2(\mu-OH)_2$ (**4**) has been synthesized by desilylation of $[Ni(PPh_3)_2Br(C_6H_2Me_2-3,5-OSiMe_3-4]$ (**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 ¹H, ¹³C and ³¹P, respectively. Chemical shifts (δ , ppm) were reported with reference to SiMe₄ (¹H and ¹³C), and H₃PO₄ (³¹P). 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 [M(PPh₃)₄] (M = Ni [7], Pd [8], Pt



Note



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



Scheme 2. A PCP pincer-based ruthenaquionone [5].

[9]) and [Ni(PPh₃)₂Cl₂] [10] were prepared according to literature methods. 2,6-Dimethyl-4-trimethylsiloxyphenylmagnesium bromide was prepared by treatment of 1-bromo-2,6-dimethyl-4trimethylsiloxybenzene, which was obtained from 4-bromo-3,5dimethylphenol and chorotrimethylsilane, with Mg in tetrahydrofuran (THF).

2.2. Reaction of $[Pd(PPh_3)_4]$ with 4-bromo-2,6-di-tert-butylphenol

To a suspension of $[Pd(PPh_3)_4]$ (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 CH₂Cl₂. Recrystallization from CH₂Cl₂/hexanes afforded yellow crystals that were characterized as the phosphaquinone Ph₃P = C₆H⁴₅Bu₂-3,5-0-4 (1) by X-ray crystallography. Yield: 50 mg, 54%. ¹H NMR (400 MHz, CDCl₃): δ = 1.31 (s, 18H, CH₃), 6.84 (s, 2H, Ph), 7.60–7.72 (m, 15H, Ph) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 28.82 (s), 34.63 (s), 122.11 (s), 122.99 (s), 140.15 (s), 176.21 (s) ppm. ³¹P {¹H} NMR (CDCl₃): δ = 20.74 (s) ppm. Anal. Calcd for C₃₂H₃₅OP: C, 82.37; H, 7.56. Found: C, 81.50; H, 7.24.

2.3. Reaction of $[M(PPh_3)_4]$ (M = Ni, Pt) with 4-bromo-2,6-di-tert-butylphenol

A mixture of [Ni(PPh₃)₄] or [Pt(PPh₃)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 CH₂Cl₂. Recrystallization from CH₂Cl₂/Et₂O/hexanes afforded yellow crystals that were identified as the biquione [C₆H^t₃Bu₂-3,5-0-4]₂ (**2**) by X-ray crystallography. Yield: 40%. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.35$ (s, 36H, CH₃), 7.70 (s, 4H, Ph) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 28.95$ (s), 35.38 (s), 125.38 (s), 135.49 (s), 149.78 (s), 185.92 (s) ppm. Anal. Calcd for C₂₈H₄₀O₂: C,82.30; H, 9.87. Found: C, 81.79; H, 10.04.

2.4. Synthesis of cis-[Ni(PPh₃)₂Br(C₆H₂Me₂-2,6-OSiMe₃-4)] (**3**)

To a solution of [NiCl₂(PPh₃)₂] (1 g, 1.60 mmol) in THF (10 mL) was added 1 equivalent of 2,6-dimethyl-4-trimethylsiloxyphenylmagnesium 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 CH₂Cl₂/hexanes afforded orange crystals which were suitable for X-ray diffraction analysis. Yield: 1.1 g, 80%. ¹H NMR (400 MHz, C₆D₆): δ = 0.17 (s, 9H, CH₃), 2.72 (s, 6H, CH₃), 5.93 (s, 2H, Ph), 7.10 (m, 18H, Ph), 7.82 (m, 12H, Ph) ppm. ³¹P {¹H} NMR (CDCl₃): δ = 19.50 (s) ppm. Anal. Calcd for C₄₇H₄₇BrNiOP₂Si: C, 55.88; H, 4.69. Found: C, 55.73; H, 4.73.

2.5. Synthesis of $[Ni(PPh_3)(C_6H_2Me_2-2, 6-OH-4)]_2(\mu-OH)_2(4)$

To a solution of **3** (100 mg, 0.12 mmol) in THF (10 mL) was added 1.5 equivalents of ⁿBu₄NF·H₂O (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/Et₂O afforded yellow crystals which were suitable for X-ray diffraction. Yield: 33 mg, 52%. ¹H NMR (400 MHz, CD₃CN): $\delta = -4.0$ (br, 2H, OH), 2.98 (s, 6H, CH₃), 5.85 (br, 2H, OH), 5.92 (s, 4H, Ph), 7.24–7.37 (m, 30H, Ph) ppm. ³¹P {¹H} NMR (CDCl₃): $\delta = 21.20$ (s) ppm. Anal. Calcd for C₅₂H₅₀Ni₂O₄P₂: 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 F² 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.

	$1 \cdot 0.125(C_4H_8O)$	$3 \cdot CH_2Cl_2$	4·2CH ₃ CN
Formula	C ₃₂ H ₃₅ OP	C47H47BrNiOP2Si	C ₅₂ H ₅₀ Ni ₂ O ₄ P ₂
Fw	475.58	941.42	1000.39
a [Å]	10.8259(2)	11.7312(4)	14.01551(11)
b [Å]	18.4075(3)	12.2073(5)	12.82811(10)
c [Å]	14.8443(2)	17.6080(5)	27.58082(19)
α [°]	90	95.260(3)	90
β [°]	94.853(2)	93.322(3)	97.8616(7)
γ [°]	90	116.250(4)	90
V [Å ³]	2947.53(8)	2238.28(14)	4912.22(6)
Ζ	4	2	4
Cryst system	monoclinic	triclinic	monoclinic
$\rho_{calcd} [g \cdot cm^{-1}]$	1.072	1.397	1.353
Space group	P21/n	P-1	P21/n
T [K]	173.15	99.98(6)	100.0(2)
$\mu [{ m mm}^{-1}]$	0.973	3.969	1.947
F(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 , w R_2 ($I > 2\sigma(I)$)	0.0598, 0.1355	0.0446, 0.1205	0.0268, 0.0657
R_1 , w R_2 (all data)	0.0971, 0.1560	0.0555, 0.1264	0.0337, 0.06823
GoF	1.002	1.002	1.002

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Reactions of [M(PPh₃)₄] with 4-bromo-2,6-di-tert-butylphenol

No reaction was found between $[Pd(PPh_3)_4]$ and 4-bromo-2,6di-*tert*-butylphenol in toluene at room temperature. Refluxing $[Pd(PPh_3)_4]$ with 4-bromo-2,6-di-*tert*-butylphenol in toluene for 2 d led to isolation of yellow crystals that were identified as the phosphaquinone Ph₃P = C₆H₃⁴Bu₂-3,5-O-4 (1) (Scheme 3) by X-ray crystallography. The formation of 1 presumably involves the oxidative addition of 4-bromo-2,6-di-*tert*-butylphenol to Pd(0) and subsequent P-C elimination of a Pd(II) hydroxyaryl intermediate. The ¹H NMR spectrum of 1 displayed a sharp singlet at $\delta = 1.31$ ppm due to the *tert*-butyl group; no O-H signal was observed. The ³¹P {¹H} NMR spectrum showed a singlet at $\delta = 20.74$ ppm. The observation of the CO signal at $\delta = 176$ ppm in the ¹³C NMR spectrum together with the IR ν (C-O) band at 1578 cm⁻¹ is indicative of the C=O double bond character in **1**.

The molecular structure of **1** is shown in Fig. 1. Selected bond lengths are listed in Scheme 4. The C-O bond length of 1.273(2) Å is close to those in related quinone compounds, such as $[C_6H_3^tBu_2-3,5-O-4]_2$ [1.228 Å] [13]. The C-C bonds in the 6-member carbocyclic ring displays a long-short-long pattern [1.415(4), 1.374(4), and 1.460(5) Å] that is characteristic of quinoidal compounds. The P-C distance in **1** of 1.755(3) Å is similar to that of the P=C bond in **B** [1.750(2) Å] [3]. Taken together, the structural data in **1** are consistent with the formulation of a phosphaquinone.

Unlike the Pd analogue, the reactions of $[M(PPh_3)_4]$ (M = Ni, Pt) 4-bromo-2,6-di-*tert*-butylphenol in refluxing toluene led to formation of 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (2) (Scheme 3) that was characterized by NMR spectroscopy and elemental analyses. The biquinone 2 was apparently formed by oxidation of the biphenol precursor (3,5-^tBu₂-4-OHC₆H₂)₂ that is derived from metal-mediated homo-coupling of the 3,5-di-*tert*-butyl-4-hydroxyphenyl groups. At this stage, it is not clear why the reactions of 4-bromo-2,6-di-*tert*-butylphenol with the Ni and Pt complexes led to C-C coupling, whereas P-C elimination occurred at the Pd centre.

3.2. Ni(II) hydroxyaryl complex

We next attempted to synthesize hydroxyaryl complexes by transmetallation with Grignard reagents. Treatment of [Ni(PPh₃)₂Cl₂] with the trimethylsilyl-protected Grignard reagent (C₆H₂Me₂-2,6-OSiMe₃-4)MgBr in THF resulted in an immediate color change from maroon to orange. Recrystallization from CH₂Cl₂/



Scheme 3. Reactions of [M(PPh₃)₄] with 4-bromo-2,6-di-*tert*-butylphenol.



Fig. 1. Molecular structure of 1. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.



Scheme 4. Selected bond lengths [Å] in 1.

Et₂O/hexanes afforded air-stable orange crystals characterized as *trans*-[Ni(C₆H₂Me₂-2,6-OSiMe₃-4)Br(PPh₃)₂] (**3**) (Scheme 5), the bromide ligand of which apparently came from the Grignard reagent. Attempts to prepare a Ni(II) diaryl complex by alkylation of [Ni(PPh₃)₂Cl₂] with excess (C₆H₂Me₂-2,6-OSiMe₃-4)MgBr failed. The ¹H NMR spectrum of **3** displayed a singlet at δ = 0.17 ppm due to the trimethylsilyl protons. The ³¹P {¹H} NMR spectrum displayed a singlet at δ = 19.50 ppm, consistent with the *trans* arrangement of the two phosphine ligands. Fig. 2 shows the molecular structure of **3**. The geometry around Ni(II) is pseudo square planar with the two PPh₃ ligand trans to each other. The Ni-C distance of 1.907(3) Å is typical for Ni(II) phenyl complexes.

Treatment of **3** with ^{*n*}Bu₄NF·H₂O in THF resulted in formation of a yellow precipitate that was characterized as a dinuclear hydroxobridged Ni(II) 4-hydroxyaryl complex [Ni(PPh₃)(C₆H₂Me₂-2,6-OH-4)]₂(μ -OH)₂ (**4**) (Scheme 5). Thus, the desilylation of **3** also resulted in substitution of the bromide ligand by hydroxide (presumably derived from ^{*n*}Bu₄NF·H₂O) and elimination of the PPh₃ ligand. The structure of **4** that features a Ni₂(OH)₂ core is shown in Fig. 3. The geometry around each Ni is pseudo square planar with the aryl ligand *trans* to the μ -hydroxo group. The Ni-O bond lengths in the



Scheme 5. Synthesis of the Ni(II) 4-hydroxyaryl complex 4. Reagents: (i) $(C_6H_2Me_2-2,6-OSiMe_3-4)MgBr$, THF; (ii) $^nBu_4NF \cdot H_2O$, THF.



Fig. 2. Molecular structure of **3.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å]: Ni(1)-C(1) 1.907(3), Ni(1)-P(1) 2.2255(8), Ni(1)-P(2) 2.2146(9), Ni(1)-Br(1) 2.3645(6).



Fig. 3. Molecular structure of **4.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [deg]: Ni(1)-P(1) 2.1436(4), Ni(1)-O(1) 1.9491(10), Ni(1)-O(2), 1.8979(10), Ni(1)-C(1) 1.9012(15), Ni(2)-P(2) 2.1377(4), Ni(2)-O(1) 1.9164(10), Ni(2)-O(2) 1.9304(10), Ni(2)-C(11) 1.8998(15); Ni(1)-O(1)-Ni(2) 92.91(4), Ni(1)-O(2)-Ni(2) 94.09(5).

 $Ni_2(OH)_2$ core are in the range of 1.8979(10)-1.9304(10) Å and the O-Ni-O angles are 92.91(4) and $94.09(5)^0$. The Ni-C distance in **4** [av. 1.901 Å] is almost the same as that in **3**, whereas the Ni-P distances

[av. 2.1407 Å] are slightly shorter than those in the latter. An attempt has been made to deprotonate **4** with base. Unfortunately, the treatment of **4** in THF with 1 equivalent of Et_4NOH led to immediate formation of a dark insoluble precipitate, indicating that the complex has decomposed.

In summary, we found that reaction of $[Pd(PPh_3)_4]$ with 4bromo-2,6-di-*tert*-butylphenol afforded a phosphaqunione, **A**, presumably via reductive elimination of a Pd(II) 4-hydroxyaryl intermediate, whereas a bi-quinone, **B**, was obtained for the Ni and Pt analogues. A Ni(II) complex bearing a 4-hydroxyaryl ligand, **4**, has been prepared by alkylation of $[NiCl_2(PPh_3)_2]$ with $(C_6H_2Me_2-2,6-OSiMe_3-4)MgBr$, followed by desilylation. The synthesis of 4hydroxyaryl complexes with more substitutionally inert transition metals (e.g. Os) by this method and the study of their deprotonation are underway.

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Supporting information available

Crystallographic data for compounds **1**, **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1539784, 1540324 and 1540325, respectively, in CIF format. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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