

Synthesis and Structure of Three Unusual Homoleptic Aryloxides of Nickel and Palladium

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Summary: Homoleptic group 10 aryloxides consisting of discrete molecules have been isolated from the reaction of the sodium salts of bulky phenols with $\text{NiBr}_2(\text{dme})$ or $\text{PdCl}_2(\text{MeCN})_2$. The nickel 2,6-diisopropylphenolate is a trimer, displaying σ -coordinated aryloxide ligands, while the Ni and Pd derivatives of 2,6-di-*tert*-butylphenol are monomers that adopt an unprecedented π -allylic, sandwich-like structure.

Alkoxide derivatives of the late transition elements have aroused considerable interest, due to their involvement in several catalytic processes, e.g. C–O bond formation and cleavage, olefin and alkyne alkoxycarbonylation, and olefin polymerization.¹ They also display a high reactivity,² which is sometimes reminiscent of that of the related metal alkyls.³ Despite this interest, late-transition-metal alkoxides have been much less studied. Even though $[\text{M}(\text{OR})_2]_n$ complexes of Mn, Fe, Co, and Zn have been characterized recently,^{4,5} when OR is a bulky alkoxide or aryloxide group, corresponding compounds of G10 elements have been hitherto unreported. Herein we present the synthesis and structural characterization of the first homoleptic aryloxide derivatives of Ni and Pd.

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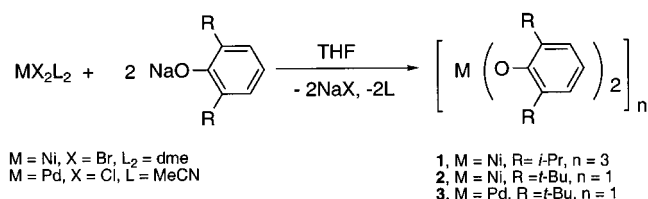
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Scheme 1



The new compounds **1–3**, derived from the bulky 2,6-diisopropylphenolate (O-dipp) and 2,6-di-*tert*-butylphenolate (O-dtbp), have been isolated following the reactions summarized in Scheme 1.

Although our initial attempts to prepare the O-dipp derivatives provided only ill-defined materials, we have subsequently found that a rigorous elimination of the volatiles under vacuum allows the isolation of the extremely air-sensitive nickel compound **1**,⁶ albeit in very low yields (ca. 8%). Notwithstanding its paramagnetism ($\mu_{\text{eff}} = 2.08$ B.M. per Ni atom at 298 K, Evans method⁷), useful ¹H and ¹³C NMR spectra can be recorded, which reveal the unexpected complexity of the molecules of **1**. Except for the linear dependence of the chemical shift with $1/T$, there is no change in the line shape of the NMR resonances in the temperature interval from –80 to +80 °C. This is in accord with the absence of equilibria involving other oligo- or monomeric species and of intramolecular rearrangements. As Figure 1 shows,⁸ the molecules of **1** are trimeric in the solid state and consist of a nearly linear arrangement of the Ni atoms, separated by ca. 2.98 Å and bridged by aryloxide groups.⁹ The coordination geometries of the central and the terminal nickel atoms are remarkably different, the former being in a distorted-square-planar environment while the latter are bonded to one terminal (Ni–O, 1.72 Å) and two bridging (Ni–O, 1.90 Å) aryl-

(6) ¹H NMR (C_6D_6 , 20 °C): δ –117.8 (s, $\nu_{1/2} = 33$ Hz, 2H, *p*-CH, terminal), –24.4 (s, $\nu_{1/2} = 27$ Hz, 4H, CH), –6.0 (s, $\nu_{1/2} = 25$ Hz, 12H, CH(CH₃)₂), –4.8 (s, $\nu_{1/2} = 25$ Hz, 12H, CH(CH₃)₂), 10.7 (br s, $\nu_{1/2} = 46$ Hz, 12H, CH(CH₃)₂), 16.8 (s, $\nu_{1/2} = 25$ Hz, 12H, CH(CH₃)₂), 17.8 (s, $\nu_{1/2} = 25$ Hz, 12H, CH(CH₃)₂), 18.5 (br s, $\nu_{1/2} = 39$ Hz, 12H, CH(CH₃)₂), 38.6 (br s, $\nu_{1/2} = 68$ Hz, 4H, CH), 42.5 (br s, $\nu_{1/2} = 78$ Hz, 4H, CH), 45.8 (s, $\nu_{1/2} = 25$ Hz, 4H, CH), 53.9 (s, $\nu_{1/2} = 23$ Hz, 4H, CH), 54.2 (s, $\nu_{1/2} = 23$ Hz, 4H, CH), 55.8 (br s, $\nu_{1/2} = 87$ Hz, 4H, CH). ¹³C{¹H} NMR (C_6D_6 , 20 °C): δ –319.3, –201.7, –69.4, –61.8, –6.4, 22.7, 34.2, 66.3, 88.0, 99.2, 179.0, 189.7, 195.7, 354.4, 356.2. IR (Nujol mull): 1584, 1556 cm^{-1} $\nu(\text{C}=\text{C})$. μ_{eff} (298 K) = 6.25 B.M. Anal. Calcd for $\text{C}_{72}\text{H}_{102}\text{Ni}_3\text{O}_6$: C, 69.76; H, 8.29. Found: C, 69.74; H, 8.22.

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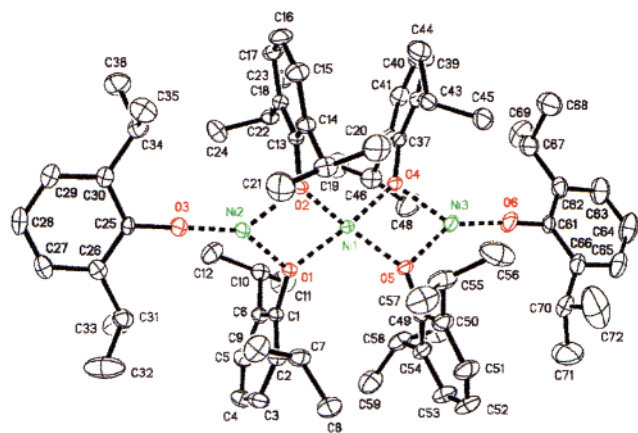
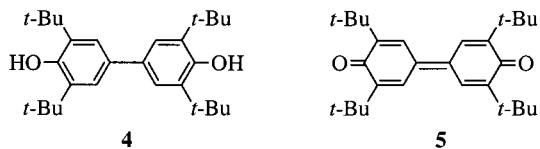


Figure 1. Molecular structure and numbering scheme of **1** (20% probability ellipsoids, hydrogen atoms and C_6H_{14} solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni1–O1 = 1.953(2), Ni1–O2 = 1.927(2), Ni1–O4 = 1.956(2), Ni1–O5 = 1.932(2), Ni2–O1 = 1.901(2), Ni2–O2 = 1.918(2), Ni2–O3 = 1.728(2), Ni3–O4 = 1.905(2), Ni3–O5 = 1.899(2), Ni3–O6 = 1.725(2), Ni1–Ni3 = 2.977(2), Ni1–Ni2 = 2.990(2), O1–C1 = 1.381(3), O2–C13 = 1.381(3), O3–C25 = 1.325(3), O4–C37 = 1.386(3), O5–C49 = 1.382(3), O6–C61 = 1.322(3); O1–Ni1–O2 = 77.3(1), O1–Ni1–O4 = 158.3(1), O1–Ni1–O5 = 107.9(1), O2–Ni1–O4 = 108.7(1), O2–Ni1–O5 = 150.3(1), O4–Ni1–O5 = 77.5(1), O1–Ni2–O2 = 78.8(1), O1–Ni2–O3 = 144.2(1), O2–Ni2–O3 = 136.9(1), O4–Ni3–O5 = 79.6(1), O4–Ni3–O6 = 140.0(1), O5–Ni3–O6 = 140.4(1), Ni2–Ni1–Ni3 = 174.42(2).

oxide ligands in an unusual (for Ni(II)) trigonal-planar coordination.¹⁰ The shorter Ni–O bonds to the terminal O-dipp and the almost linear Ni–O–C bond angles could suggest multiple-bond character. However, the related complexes of Cr, Mn, Fe, and Co exhibit similar structural features,⁴ which are therefore independent of the metal electronic configuration. Hence, according to Power^{4d} it appears reasonable that the above structural properties are a consequence of a predominantly ionic $\text{Ni}^{2+} \cdots (\text{OAr})^-$ bonding interaction. In fact, the Ni $\cdots$ O separations are close to the sum of the effective ionic radii^{4d} of O^{2-} and Ni^{2+} .

The sodium salt of the bulkier phenol 2,6-di-*tert*-butylphenol (NaO-dtbp) reacts with $\text{NiBr}_2(\text{dme})$ or $\text{PdCl}_2(\text{MeCN})_2$ (Scheme 1), giving rise to very air sensitive purple or deep green products, respectively, in low

to moderate yields, whose elemental analysis and mass spectra indicate the composition $\text{M}(\text{O-dtbp})_2$ ($\text{M} = \text{Ni}$ (**2**),¹¹ Pd (**3**)¹²). The synthesis of the Pd derivative **3** is accompanied by the formation of the biphenol **4** and the dibenzoquinone **5**, which were isolated from the reaction



mixture. The presence of **4** and **5** suggests that the oxidation of the phenoxide anion by Pd(II) competes with the formation of **3**, thus lowering the final yield of the latter.¹³ Although the isolated yield of the Ni compound **2** is also low, its synthesis is not accompanied by the formation of **4** or **5**. Instead, and as revealed by the analysis of the mother liquors left after the crystallization of **2**, solvated species of composition $\text{Ni}(\text{O-dtbp})_2\text{L}_2$ ($\text{L}_2 = \text{dme}$ (**6a**), $(\text{THF})_2$ (**6b**))¹¹ are formed, which were isolated by fractional crystallization and characterized by ^1H NMR, IR, and elemental analysis. Compounds **6** may be easily overlooked, due to their high solubility in the crystallization solvent (petroleum ether) and to their paramagnetic character. However, they constitute the main product of the reaction and their presence explains that isolated yields of **2** are as low as 8% if no special caution is taken. In C_6D_6 solution, adducts **6** slowly lose the coordinated solvent, generating **2**. When we take advantage of this observation, the yield of **2** can be improved (up to 30%) by extracting the reaction residue left after evaporation of the THF solvent with toluene, followed by thorough removal of the volatile components of the mixture in vacuo.

Aryloxides **2** and **3** are diamagnetic and soluble in hydrocarbon solvents. Their ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are very simple and show single *tert*-butyl and meta and para aromatic signals, the last two displaying large upfield shifts relative to those of the free HO-dtbp (for instance, the aromatic *p*-H resonates at 3.75 ppm in **2** and 4.74 ppm in **3**). In the IR spectra prominent

(8) Diffraction experiments were performed on a Bruker SMART CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystal data for **1**: triclinic, space group $P\bar{1}$ (No. 2), $a = 14.303(8)$ Å, $b = 16.003(9)$ Å, $c = 19.644(11)$ Å, $\alpha = 86.30(1)^\circ$, $\beta = 71.70(1)^\circ$, $\gamma = 74.89(1)^\circ$, $V = 4121(4)$ Å³, $Z = 2$, $\text{C}_{28}\text{H}_{42}\text{NiO}_2$ (includes two C_6H_{14} solvent molecules that are present in the crystal lattice), $T = 208(2)$ K, data/parameters 14 438/822, $R_1 = 0.064$, $wR_2 = 0.126$ (all data). Crystal data for **2**: orthorhombic, $P2_12_1$ (No. 19), $a = 9.795(5)$ Å, $b = 13.866(7)$ Å, $c = 19.531(11)$ Å, $V = 2653(2)$ Å³, $Z = 4$, $\text{C}_{28}\text{H}_{42}\text{NiO}_2$, $T = 223(2)$ K, data/parameters 3906/196; $R_1 = 0.060$, $wR_2 = 0.097$ (all data). Crystal data for **3**: monoclinic, space group $C2/c$ (No. 15), $a = 20.617(4)$ Å, $b = 7.219(2)$ Å, $c = 18.048(5)$ Å, $\beta = 91.75(1)^\circ$, $V = 2684.9(12)$ Å³, $Z = 4$, $\text{C}_{28}\text{H}_{42}\text{O}_2\text{Pd}$, $T = 213(2)$ K, data/parameters 3813/149, $R_1 = 0.020$, $wR_2 = 0.0482$ (all data).

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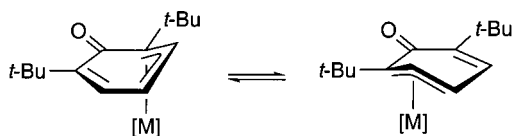
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(11) **2**: ^1H NMR (C_6D_6 , 20 °C) δ 1.39 (s, 36H, CMe_3), 3.75 (t, 2H, $^3J_{\text{HH}} = 3.4$ Hz, *p*-CH arom), 6.52 (d, 4H, $^3J_{\text{HH}} = 6.4$ Hz, *m*-CH arom); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ 29.6 (CMe_3), 35.6 (CMe_3), 61.2 (*p*-CH arom), 117.6 (*m*-CH arom), 128.0 ($\text{C}_q\text{-Bu}^t$), 176.8 (C=O); IR (Nujol mull) 1612, 1582, st. $\nu(\text{C=O})$; MS (EI) m/z 469 (M^+). Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{NiO}_2$: C, 71.66; H, 9.02. Found: C, 71.38; H, 9.00. **6a**: ^1H NMR (C_6D_6 , 20 °C) δ -42.8 (br s, $\nu_{1/2} = 535$ Hz, 2H, *p*-CH arom), 1.0 (s, $\nu_{1/2} = 39$ Hz, 5H, CH_2 (dme)), 8.4 (s, $\nu_{1/2} = 34$ Hz, 6H, CH_3 (dme)), 18.2 (br s, $\nu_{1/2} = 329$ Hz, 36H, CMe_3), 44.3 (s, $\nu_{1/2} = 29$ Hz, 4H, *m*-CH arom); IR (Nujol mull) 1579 st $\nu(\text{C=C})$. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{NiO}_4$: C, 68.70; H, 9.37. Found: C, 68.84; H, 9.14. **6b**: ^1H NMR (C_6D_6 , 20 °C) δ -47.4 (s, $\nu_{1/2} = 24$ Hz, 2H, *p*-CH arom), 1.6 (s, $\nu_{1/2} = 34$ Hz, 8H, CH_2 (THF)), 6.8 (s, $\nu_{1/2} = 31$ Hz, 8H, CH_2 (THF)), 21.5 (br s, $\nu_{1/2} = 49$ Hz, 36H, CMe_3), 44.8 (s, $\nu_{1/2} = 14$ Hz, 4H, *m*-CH arom); IR (Nujol mull) 1579 st $\nu(\text{C=C})$. Anal. Calcd for $\text{C}_{36}\text{H}_{58}\text{NiO}_4$: C, 70.48; H, 9.53. Found: C, 70.22; H, 9.36.

(12) **3**: ^1H NMR (C_6D_6 , 20 °C) δ 1.37 (s, 36H, CMe_3), 4.74 (t, 2H, $^3J_{\text{HH}} = 6.3$ Hz, *p*-CH arom), 6.25 (d, 4H, $^3J_{\text{HH}} = 6.3$ Hz, *m*-CH arom); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C) δ 30.1 (CMe_3), 35.1 (CMe_3), 70.6 (*p*-CH arom), 119.3 (*m*-CH arom), 132.7 ($\text{C}_q\text{-Bu}^t$), 180.7 (C=O); IR (Nujol mull) 1616, 1588, 1571 st $\nu(\text{C=O})$; MS (EI) m/z 516 (M^+). Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{PdO}_2$: C, 65.04; H, 8.19. Found: C, 65.24; H, 8.27.

(13) Compounds **4** and **5** can also be produced by chemical or electrochemical oxidation of HO-dtbp. See: (a) Fujiyama, H.; Kohara, I.; Iwai, K.; Nishiyama, S.; Tsuruya, S.; Masai, M. *J. Mol. Catal.* **1999**, *188*, 417. (b) Torii, S.; Dhimane, A. L.; Araki, Y.; Inokuchi, T. *Tetrahedron Lett.* **1989**, *30*, 2105. (c) Omura, K.; *Tetrahedron Lett.* **2000**, *41*, 685.

Scheme 2



absorptions in the region $1620\text{--}1570\text{ cm}^{-1}$, attributable to the $\nu(\text{C}=\text{O})$ vibration, can be found. Both features resemble closely those recently reported for π -aryloxide complexes of Ni and Pd¹⁴ and suggest that **2** and **3** possess a sandwich-type structure. This conclusion is supported by the X-ray studies summarized in Figure 2.⁸ In the two compounds, which are not isostructural with respect to the crystal lattice, each O-dtbp ligand coordinates to the metal in a η^3 fashion, a rare feature among the π -aryloxo complexes. These compounds constitute unique examples of transition-metal homoleptic π -aryloxides,¹⁵ an observation that appears the more striking when one considers that the iron derivative $[\text{Fe}(\text{O}-2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)_2]_2$ exhibits a σ -aryloxide coordination.^{4c} The bond distances within the rings of the η^3 -coordinated aryloxide ligands suggest that their aromaticity is largely lost. Thus, the C1–O, C1–C2, and C3–C4 bond lengths (mean values 1.238, 1.487, and 1.432 Å, respectively; low-temperature values) are comparable to those of the C=O, C–C, and C=C bonds in organic enones (1.215, 1.44, and 1.36 Å, respectively),¹⁶ while the C4–C5 and C5–C6 distances are close to 1.41 Å, a value characteristic of bis(π -allyl) complexes of Ni and Pd.¹⁷ The loss of aromaticity is also evident in the appreciably puckered rings, where the allylic and enone moieties are contained in planes that form angles of 16.7° in **1** and 18.0° in **2**. Their solution NMR spectra indicate higher molecular symmetry than is found in the solid state. A plausible explanation is fast exchange of the metal center between the two possible η^3 -allylic sites averaging the *t*-Bu and *m*-H resonances (Scheme 2). The symmetrical spectrum is maintained down to -100°C , a noticeable line broadening being observable only at the lowest temperatures studied, indicating a very low energy barrier for the exchange. It is suspected that the same type of process might also be facile in π -quinone complexes of palladium structurally related to **2**,¹⁸ but in contrast some η^3 -hexadienyl palladium systems only undergo this isomerization process above the ambient temperature.¹⁹

In summary, we have shown that group 10 homoleptic aryloxides that consist of discrete molecules can be prepared by simple ligand exchange reactions, provided that the aryloxide group contains bulky substituents. While the nickel derivative of O-dipp is a trimer displaying a structure related to that of other 3d transition-metal homoleptic alkoxides and aryloxides,

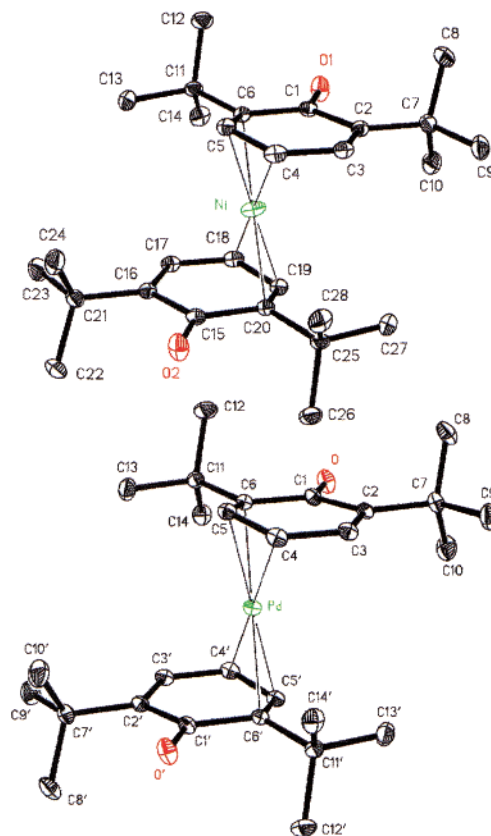


Figure 2. Molecular structures and numbering schemes of **2** and **3** (20% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å): **2**, Ni–C4 = 2.052(2), Ni–C5 = 2.003(2), Ni–C6 = 2.139(2), Ni–C18 = 2.052(2), Ni–C19 = 2.004(2), Ni–C20 = 2.140(2), O1–C1 = 1.242(3), C1–C2 = 1.485(3), C2–C3 = 1.372(3), C3–C4 = 1.424(3), C4–C5 = 1.399(3), C5–C6 = 1.422(3), C6–C1 = 1.481(3), O2–C15 = 1.242(3), C15–C16 = 1.485(3), C16–C17 = 1.372(3), C17–C18 = 1.423(3), C18–C19 = 1.399(3), C19–C20 = 1.421(3), C20–C15 = 1.480(3); **3**, Pd–C5 = 2.163(1), Pd–C4 = 2.224(1), Pd–C6 = 2.276(1), O–C1 = 1.234(1), C1–C2 = 1.489(1), C2–C3 = 1.361(2), C3–C4 = 1.441(2), C4–C5 = 1.405(2), C5–C6 = 1.414(2), C6–C1 = 1.499(1).

the Ni and Pd derivatives of the more hindered O-dtbp ligand adopt an unprecedented π -allylic structure. The high stability of Ni and Pd π -allyl complexes undoubtedly favors the latter configuration, but it remains an open question whether stable σ -aryloxides of the heavier group 10 elements can be obtained. Although we have been hitherto unable to isolate and characterize a well-defined $[\text{Pd}(\text{O-dipp})_2]_n$ compound, the synthesis of new homoleptic alkoxides and aryloxides of Ni, Pd, and Pt is being actively pursued in our laboratory.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles for **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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