Synthesis of π-Aryloxide Complexes of Nickel and Palladium

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Summary: *The reaction of the palladium chloroallyl dimer [Pd(μ-Cl)(η³-C₃H₅)]₂,* ***1****, with 2 equiv of the sodium salt of 2,6-di-tert-butyl-4-methylphenol (NaOAr) gives a thermally unstable, aryloxide-bridged binuclear allyl complex, [Pd(μ-OAr)(η³-C₃H₅)]₂. In contrast,* ***2****, the nickel analogue of* ***1****, furnishes an unusual mononuclear allyl derivative,* ***4****, which contains a π,η⁵-aryloxide ligand. Larger amounts of the sodium aryloxide react with* ***1*** *or* ***2****, affording binuclear "ate" complexes containing both σ,μ- and π,η⁵-aryloxide ligands.*

The involvement of late transition metal alkoxides and hydroxides[1] in homogeneous catalysis[2] has triggered intensive research directed toward understanding the factors that control their stability and their reactivity.[3] As a result, a number of alkoxide and aryloxide compounds of group 10 metals are now known.[4] Almost invariably, the ArO functionality is O-bound and acts either as a terminal or as a bridging ligand, π-aryl binding to Ni, Pd, or Pt being very rare.[5] Whereas this may appear surprising in view of the many documented examples of π-aryl coordination in aryloxide compounds of groups 6−9 elements,[6] a similar trend can be encountered for pentadienyl- and π-arene ligands.[7]

Binuclear nickel allyl complexes bridged by aryloxide ligands catalyze the polymerization of dienes to insoluble cross-linked polymers.[4a] Our own interest in polymerization chemistry and the knowledge that the above catalysis relies upon the ability of the dinickel compound to split by cleavage of the bridging structure have led us to attempt the synthesis of analogous binuclear allylnickel and allylpalladium complexes bridged by very bulky aryloxide ligands.

The reaction of the sodium salt of 2,6-di-*tert*-butyl-4-methylphenol with the allyl complexes $[M(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ is complex and gives different products depending upon the metal (M = Ni or Pd), the ratio of the reagents, and the reaction time. For example, treatment of the Pd dimer **1** (Scheme 1) with the sodium aryloxide in a 1:2 molar ratio (THF, 1 h) allows the isolation of yellow crystals of the binuclear allyl **3a**. This compound is thermally unstable and decomposes in solution at room temperature to give free 2,6-di-*tert*-butyl-4-methylphenol and a black deposit of palladium. Nevertheless, full NMR data (^{1}H and ^{13}C) can be acquired.[8] These data are similar to those of closely related Ni complexes

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Scheme 1

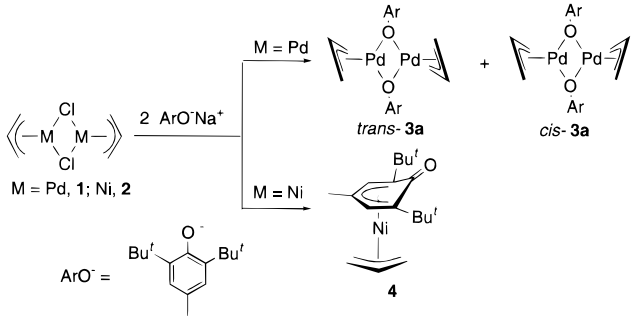
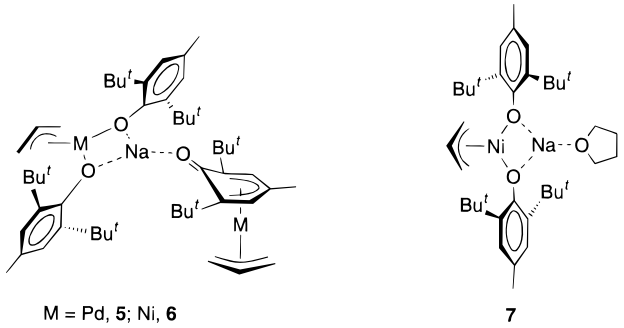


Chart 1



reported previously,[4a] showing that **3a** exists in solution as a 1:1 mixture of *cis* and *trans* isomers. To further confirm this proposal, we have prepared analogous allylpalladium derivatives with bridging 2,6-dialkylphenoxide groups (OC_6H_3-2,6-R_2; R = Me, **3b**; *i*-Pr, **3c**). Both exhibit spectroscopic features comparable to those of **3a** and the same 1:1 *cis*/*trans* isomer ratio in solution (see Supporting Information). Noteworthy, these compounds are more stable than **3a** in solution and do not decompose appreciably at room temperature.

Under the same conditions used for the synthesis of **3a**, the nickel chloroallyl derivative **2** generates the thermally stable, red complex **4**, which exhibits NMR and IR spectra notably different from those of **3a**.[9] Only one set of signals can be observed in the ^{1}H NMR spectra of **4** over the temperature range from 193 to 298 K. The resonance attributed to the ring C−H protons experiences a significant upfield shift (δ 6.07, C_6D_6) as compared with the corresponding resonances in both *cis*- and *trans*-**3a**, which appear in the proximity of 7.2 ppm. A similar effect is detected in the $^{13}C\{^1H\}$ NMR spectra of these complexes. In particular, the Me-bound quaternary carbon atom resonates at δ 85.6 (coincident at 115.3 ppm in *cis*- and *trans*-**3a**). These data are in accord with the proposed π-coordination of the ring, which finds additional support in the observation of two strong ν(CO) IR absorptions at 1565 and 1541 cm^{-1} typical of π-coordinated aryloxide ligands.[6] The bonding mode of the ligands in **4** has been confirmed by X-ray structural analysis, but its quality is too poor for publication due to polysynthetic twinning of the crystals.[10]

Reacting the chloroallyl derivatives **1** and **2** with sodium 2,6-di-*tert*-butyl-4-methylphenoxide for longer periods of time (3−4 h) generates low yields (typically 10−15%) of a new type of product of composition [M_2-(η^3-C_3H_5)$_2$(OAr)$_3$Na] (M = Pd, **5**; Ni, **6**)[11,12] (Chart 1). For the Pd compound **5**, somewhat higher yields (ca. 38%) are obtained if a 1:4 ratio of **1** to NaOAr is employed, while a rational synthesis of **6** requires mixing strictly the stoichiometric amounts of the reagents (i.e., 1:3 molar ratio of **2** to the aryloxide). Otherwise (e.g., 1:4 ratio) the new *ate* species **7** (see Chart 1) is formed. This complex is extremely air sensitive and decomposes upon attempted recrystallization, presumably by initial loss of THF. As expected, when equimolecular amounts of **4** and **7** are dissolved in C_6D_6 and mixed together, compound **6** and free THF are cleanly produced.

In agreement with the formulation proposed for **5** and **6**, their NMR spectra display signals for two inequivalent allyl groups and for two kinds of aryloxide entities, the latter in a 2:1 ratio (see Supporting Information for detailed assignments). The observation of two doublets at 7.25 and 7.28 ppm (data for **5**; $^4J_{HH}$ = 2.2 Hz) with relative intensity corresponding to two hydrogen atoms each, suggests O-coordination of the two equivalent ArO groups, whereas a singlet at δ 6.34 (also 2H) may be taken as indicative of π-aryl binding of the third ArO unit. High-field shifts in the $^{13}C\{^1H\}$ resonances of one of the aromatic rings can also be detected, the shifts being more pronounced for the Ni compound **6** than for **5**. For instance, the methyl-bound quaternary aromatic carbon for the unique ArO ring of **5** and **6** resonates at 94.6 and 89.7 ppm, respectively, while the corresponding resonance for the two equivalent M−OAr groups ap-

(8) Selected spectroscopic data for **3a**: ^{1}H NMR (300 MHz, 20 °C, C_6D_6): δ 1.92 (s, 18H, C*Me*$_3$, *cis* isomer), 2.09 (s, 36H, C*Me*$_3$, *trans* isomer), 2.26 (s, 18H, C*Me*$_3$, *cis* isomer), 2.33 (s, 12H, *Me*, *cis*+*trans* isomers), 7.23 (s, 2H, C*H* arom., *cis* isomer), 7.25 (s, 4H, C*H* arom., *trans* isomer), 7.28 (s, 2H, C*H* arom., *cis* isomer). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_6D_6): δ 115.3 (*p*-C_q, *cis* or *trans*), 125.8 (*C*H arom, *cis* isomer), 126.7 (*C*H arom, *trans* isomer), ca. 127.4 (obscured by the solvent signal, *C*H arom., *cis* isomer), 138.7 (*o*-C_q arom., *cis* isomer), 139.4 (*o*-C_q arom., *trans* isomer), 140.2 (*o*-C_q arom., *cis* isomer), 169.5 (C_{ipso} arom., *cis*+*trans*).

(9) Synthesis of **4**. Compound **2** (0.650 g, 2.4 mmol) was dissolved in 40 mL of THF, cooled to −30 °C, and treated with 4.3 mL of a 1.12 M solution of sodium 2,6-di-*tert*-butyl-4-methylphenoxide in THF. The cooling bath was removed and the mixture allowed to stir for 1 h at room temperature. The solvent was evaporated in vacuo, and the residue was extracted with 50 mL of petroleum ether and filtrated. Reducing the volume and cooling the solution to −30 °C, the compound was isolated as red crystals. Yield: 0.74 g, 50%. ^{1}H NMR (300 MHz, 20 °C, C_6D_6): δ 1.43 (s, 3H, C*H*$_3$), 1.51 (s, 18H, C*Me*$_3$), 1.54 (d, 2H, $^3J_{HH}$ = 12 Hz, allyl HC*H* anti), 2.60 (d, 2H, $^3J_{HH}$ = 6.3 Hz, allyl *H*CH syn), 5.14 (m, 1H, allyl C*H*), 6.07 (s, 2H, C*H* arom.). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_6D_6): δ 20.1 (*C*H$_3$), 29.8 (C*Me*$_3$), 35.0 (*C*Me$_3$), 47.6 (allyl *C*H$_2$), 85.6 (C_q−Me), 98.9 (allyl *C*H), 107.7 (C*H* arom.), 123.8 (C_q-Bu^t), 165.7 (*C*=O). IR(Nujol mull): 1565, 1541, st. ν(C=O). MS (EI): *m*/*z* 318 (M^+). Anal. Calcd for $C_{18}H_{28}NiO$: C, 67.75; H, 8.84. Found: C, 67.75; H, 8.56.

(10) Compound **4** crystalizes in the monoclinic space group *P*21/*n* with *a* = 6.777(2) Å, *b* = 17.685(4) Å, *c* = 14.319(3) Å, β = 93.531(4)° and D_c = 1.238 g cm^{-3} for *Z* = 2. An ORTEP view of this compound is available in the Supporting Information.

(11) Selected spectroscopic data for compound **5**: ^{1}H NMR (300 MHz, 20 °C, C_6D_6): δ 1.24 (s, 18H, π-bound aryloxide C*Me*$_3$), 1.67 (s, 3H, π-bound aryloxide C*H*$_3$), 1.88, 2.03 (s, 18H each, σ, μ-bound aryloxide C*Me*$_3$), 2.40 (s, 6H, σ, μ-bound aryloxide aryl−C*H*$_3$), 6.34 (s, 2H, π-bound aryloxide C*H*), 7.25, 7.28 (d, 2H each, $^4J_{HH}$ = 2.2 Hz, σ, μ-bound aryloxide C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_6D_6): δ 94.6 (π-bound aryloxide *C*arom−Me), 114.8 (π-bound aryloxide *C*arom−H), 121.9 (σ, μ-bound aryloxide *C*arom−Me), 125.9 and 126.0 (σ, μ-bound aryloxide *C*arom−H), 169.3 and 169.5 (π- or σ,μ-bound aryloxide C_q−O).(12) Selected spectroscopic data for compound **6**: ^{1}H NMR (300 MHz, 20 °C, C_6D_6): δ 1.12 (s, 18H, π-bound aryloxide C*Me*$_3$), 1.24 (s, 3H, π-bound aryloxide C*H*$_3$), 2.00, 2.21 (s, 18H each, σ, μ-bound aryloxide C*Me*$_3$), 2.34 (s, 6H, σ, μ-bound aryloxide aryl−C*H*$_3$), 5.93 (s, 2H, π-bound aryloxide C*H*), 7.19, 7.24 (s, 2H each, σ, μ-bound aryloxide C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_6D_6): δ 89.7 (π-bound aryloxide *C*arom−Me), 107.8 (π-bound aryloxide *C*arom−H), 122.3 (σ, μ-bound aryloxide *C*arom−Me), 125.9 and 126.1 (σ, μ-bound aryloxide *C*arom−H), 162.7 and 168.6 (π- or σ,μ-bound aryloxide C_q−O).

pears at ca. 122 ppm in both complexes. Nearly identical IR absorptions at 1560 and 1520 cm^{-1} can be observed for **5** and **6**, this region being void of bands in the IR spectra of **3** and **7**. Noteworthy, the MS spectra of **5** and **6** show peak clusters with Z/e and isotopic distributions corresponding to the $M(ArO)(C_3H_5)^+$ ions. Growing crystals of **5** or **6** suitable for X-ray studies has, so far, proven elusive. However, analytical and spectroscopic data can be taken in favor of the structure shown in Chart 1, in which the sodium cation is coordinated to the oxygen atom of the ArO groups. The capacity of the ArO oxygen to form hydrogen bonds or to coordinate to Na^+ ions has been observed in other systems.[6a,b,d] A similar structural formulation, in which THF replaces the oxo-cyclohexadienyl moiety, is in agreement with the data obtained for **7**.[13]

In conclusion, our results show that similarly to other middle or late transition metals, Ni and Pd centers can bind to bulky aryloxide groups both in the σ,μ- and π,η^5-fashion. Although the π-coordination mode appears to be less favorable for group 10 metals, it can be preferred when bulky 2,6 substituents are present in the aryloxide ligand. The ability of the latter to undergo coordination changes may be relevant to the mechanism of the *cis-trans* isomerization, as well as to the catalytic polymerization properties of Ni and Pd aryloxide-bridged allyl complexes. Further studies aimed at determining the catalytic activity of compounds **3**−**7** in olefin and diene polymerization or oligomerization are currently in progress.

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for compounds **3**−**7**. ORTEP view of the crystal structure of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Selected spectroscopic data for compound **7**: ^{1}H NMR (300 MHz, 20 °C, C_6D_6): δ 1.11 (m, 4H, CH_2 (THF)), 1.87, 2.09 (s, 18H each, CMe_3), 2.35 (s, 6H, CH_3), 3.05 (m, 4H, CH_2 (THF)), 7.19, 7.23 (d, 2H each, $^4J_{HH}$ = 1.7 Hz, C*H* arom.). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_6D_6): δ 21.2 (*C*H_3), 24.9 (THF), 122.7 (C_q−Me), 125.8, 126.1 (*C*H arom.), 137.6, 139.0 (C_q−Bu^t), 167.9 (C_q−O).