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Synthesis and structural characterization of Groups 10 and 11 mononuclear fluoroaryloxide complexes

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Dedicated to Prof. Malcolm L.H. Green

Abstract

A study of four late-transition metal fluoroaryloxide (OAr^F or OAr') complexes is presented including X-ray crystallography, polynuclear solution NMR spectroscopy, UV–Vis spectroscopy and elemental analyses. The study includes three new compounds: $[(Ph_3P)_2Ni(OAr^F)_2]$ (**1a**), $[(Ph_3P)_2Ni(OAr')_2]$ (**1b**), $[(COD)Pt(OAr^F)_2]$ (**2**) and one compound whose synthesis and elemental analysis were reported previously: $[(Ph_3P)Au(OAr^F)]$ (**3**). These compounds represent the common L_2MX_2 (**1a**, **1b**, **2**) and LMX (**3**) ligand classes in Groups 10 and 11, respectively, but with an uncommon ligand type, the monodentate phenoxide. In the solid state, compounds **1a** and **1b** exhibit square-planar geometry at nickel with *trans* phosphines in each case. In solution, these nickel compounds slowly decompose in CH_2Cl_2. Compound **2** is quite stable in solution at room temperature with the two phenoxide ligands *cis* to one another in the solid state. Compound **3** has a virtually linear geometry at the gold center and is stable in the solid state in the dark but decomposes slowly in solution in the light. Comparison of these four fluoroaryloxide compounds with the protio analogs (or attempts to make such compounds) demonstrate the greater stability to reduction of late-metal aryloxide complexes with highly electron-withdrawing substituents on the phenoxide rings.
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1. Introduction

Phenoxide and aryloxide ligands on transition metal centers are highly important in many disparate areas of science. In biology, metal–phenoxide linkages are formed between a metal (most often a first-row transition metal) and the phenolic side chain of tyrosine. Metal sequestration units often have multiple phenoxide donor atoms for chelation such as transferrin [1] or enterobactin [2]. Metal centers also bind to phenoxide ligands during oxidation of phenols to ke-

tones as in catecholase [3,4] or in aromatic hydroxylation as in tyrosinase [3,4]. Metal phenoxides, metal alkoxides, and mixed-metal combinations of phenoxides and alkoxides are valuable precursors for metal oxide ceramics [5]. Many important chelating ligands in chemistry include phenolate units such as macrocyclic calixarenes [6] and salen systems [7]. Metal-based homogeneous catalysts also make use of phenoxide ligands such as the alkyne metathesis catalysts prepared by the Schrock group [8], hydrogenation systems from the Rothwell group [9], and the zinc [10] and cadmium [11] compounds used in CO_2/epoxide copolymerization developed by the D. Darensbourg group. Late metal aryloxides had been less well studied than

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early transition metal derivatives [12], but more recent work [13], including this paper, addresses the disparity [14].

Phenoxides are anionic oxygen-donor ligands that often bridge metal centers and typically bind hard metal centers in relatively high oxidation states. In transition metal compounds requiring monodentate phenoxides, one method to prevent bridging by the electron-rich oxygen donors, is to furnish the ligand with bulky substituents at the 2- and 6-positions. Our laboratory has demonstrated an alternative approach, namely that the bridging propensity may be reduced by extensive fluorination of the phenyl ring as in OC_6F_5 (OAr^F) or $OC_6H_3(CF_3)_2$ (OAr') [13]. This modification is an electronic approach, instead of a steric one, and thus results in metal centers that may still bind to other ligands for catalysis or more complex structure development. All monodentate phenoxide ligands are simple X-type ligands in the MLXZ classification system [15], but their steric and electronic properties differ significantly. Herein we describe four more compounds with monodentate fluoroaryloxides whose simple OC_6H_5 analogs have not been reported in all cases. These compounds serve to develop further comparisons of OPh and OAr^F as ligands as well as increase the number of known and structurally characterized monodentate $M–OAr^F$ and $M–OAr'$ linkages.

2. Experimental

2.1. General considerations

All studies were carried out at room temperature on a Schlenk line or in a nitrogen- or argon-filled glovebox. For solvents dried in stills, methylene chloride and deuterated methylene chloride were refluxed over CaH_2. THF and hexane were refluxed over potassium and toluene was refluxed over sodium. All solvents were refluxed under nitrogen or argon. Some work was also done with solvents (hexanes, CH_2Cl_2, and toluene) dried in a nitrogen-filled MBraun SPS (solvent purification system) using Al_2O_3. Celite was dried overnight in vacuo while heated to 125 °C with an oil bath. $TlOC_6F_5$ ($TlOAr^F$) and $TlOC_6H_3(CF_3)_2$ ($TlOAr'$) were prepared according to our previously reported procedures [13]. [$(Ph_3P)Au(OPh)$] was prepared from [$(Ph_3P)AuCl$] and KOPh [16]. All other reagents were obtained commercially and were not purified further. NMR spectra were measured on a Varian 300 MHz, Bruker 300 or 400 MHz spectrometer. UV–Vis data were recorded with a Varian Cary 50 spectrometer. [1]H and ^{13}C chemical shifts were referenced to $(CH_3)_4Si$ via the resonance of residual protiosolvent (^{1}H) or the ^{13}C resonance of the solvent. [19]F shifts were referenced to external $CFCl_3$. [31]P shifts were referenced to internal $(MeO)_3PO_4$ or

external 85% H_3PO_4. Microanalyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, BRD.

2.2. Synthesis of [$(Ph_3P)_2Ni(OAr^F)_2$] (1a)

In a 25 ml round bottom flask a portion of $TlOAr^F$ (0.3014 g, 0.7780 mmol) was dissolved in ∼10 ml CH_2Cl_2. $(PPh_3)_2NiCl_2$ (0.2529 g, 0.3866 mmol) was added to the reaction mixture. The reaction mixture turned a dark red-brown color and a white precipitate also evolved. The reaction was left to stir overnight at room temperature, and was filtered through Celite to remove TlCl. The mixture was concentrated in vacuo and recrystallized from CH_2Cl_2 and hexanes (1:1). Dark brown crystals were collected in 56% yield (0.2039 g). ^{1}H NMR, (δ, ppm, CD_2Cl_2) 6.780 (t, 6 H, *para*, $^3J = 7.38$ Hz), 7.347 (t, 12H, *ortho*, $^3J = 7.83$ Hz), 7.696 (t, 12H, *meta*, $^3J = 7.38$ Hz). ^{19}F {^{1}H} NMR, (δ, ppm, CD_2Cl_2) −153.99 (*o*, m), −171.04 (*m*, m), −177.47 (*p*, m). UV–Vis (CH_2Cl_2) [λ_{max}, nm (ε_M, cm^{-1} M^{-1})] 456.0 (3698). *Anal.* Calc. for $C_{48}H_{30}O_2F_{10}P_2Ni$: C, 60.73; H, 3.19. Found: C, 60.68; H, 3.21%.

2.3. Synthesis of [$(PPh_3)_2Ni(OAr')_2$] (1b)

In a 25 ml round bottom flask a portion of $TlOAr'$ (0.3003 g, 0.7744 mmol) was dissolved in ∼10 ml CH_2Cl_2. $(PPh_3)_2NiCl_2$ (0.2535 g, 0.3872 mmol) was added to the reaction mixture. The reaction mixture turned a dark red-brown color and a white precipitate also evolved. The reaction was left to stir overnight at room temperature, and was filtered through Celite to remove TlCl. The mixture was concentrated in vacuo and recrystallized from CH_2Cl_2 and hexanes (1:1). Dark brown crystals (0.3629 g) were collected in 90% yield. ^{1}H NMR, (δ, ppm, CD_2Cl_2) 6.350 (br, 2H, *para*-OAr'), 7.211 (br, 4H, *ortho*-OAr'), 7.260 (t, 12H, *meta*, $^3J = 2.85$ Hz), 7.680 (m, 18H, *ortho* + *para*). ^{19}F {^{1}H} NMR, (δ, ppm, CD_2Cl_2) −63.27 (CF_3, s). UV–Vis (CH_2Cl_2) [λ_{max}, nm (ε_M, cm^{-1} M^{-1})] 446.0 (2905), *Anal.* Calc. for $C_{52}H_{36}O_2F_{12}P_2Ni$: C, 59.97; H, 3.48. Found: C, 59.77; H, 3.41%.

2.4. Synthesis of [$(COD)Pt(OAr^F)_2$] (2)

A portion of [$(COD)_2PtCl_2$] (151.5 mg, 0.4049 mmol) was dissolved in 5 mL of CH_2Cl_2 and 2 equivalents of $KOAr^F$ (179.9 mg, 0.8098 mmol) in 5 mL of THF were added. The solution immediately turned pale yellow and a white precipitate (presumably KCl) was observed. The solution was allowed to stir overnight and then the precipitate was removed via filtration through Celite. The solution was concentrated to dryness in vacuo, and the crude very pale yellow product was recrystallized from CH_2Cl_2 and hexanes. X-ray quality crystals