Journal of Organometallic Chemistry 696 (2011) 1787–1791

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and characterisation of complexes of the 2,6-diphenoxyphenyl ligand

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ARTICLE INFO

Article history:
Received 4 June 2010
Received in revised form
1 December 2010
Accepted 20 December 2010

Keywords:
Silane
Stannane
Lithium
Aryl

ABSTRACT

The use of the 2,6-diphenoxyphenyl ligand has facilitated the stabilisation of lithium, silane and stannane complexes. The *ortho*-metallation reaction between 1,3-$(PhO)_2C_6H_4$ and ^nBuLi yields 2,6-$(PhO)_2C_6H_3Li$ (**1**); the crystallographically characterised dimer $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et₂O]₂**) can be obtained by the crystallisation of **1** from diethyl ether. The reaction between **1** and Me_3ECl gives rise to the structurally authenticated complexes 2,6-$(PhO)_2C_6H_3EMe_3$ [E = Si, **2**; E = Sn, **3**].

1. Introduction

The utilisation of ligands featuring intramolecular donors is an area of intense research interest [1]. In particular, aryl ligands featuring alkoxy substituents in the 2 and 6 positions have been used to great effect in the stabilisation of main group and transition metal compounds [2–6]. The rigid structure conferred by these ligands has given rise to unusual planar tetracoordinate carbon atoms in the tetrameric aggregate $[2,6\text{-}(MeO)_2C_6H_3Li]_4$ [2] and T-shaped oxygen coordination within the trimer $[2,6\text{-}(^tBuO)_2C_6H_3Li]_3$ [3]. The use of the lithium complexes of 2,6-dialkyloxyphenyl ligands has been instrumental in opening up new areas of transition metal chemistry, for example with the stabilisation of very short metal-metal bonding interactions in $[2,6\text{-}(MeO)_2C_6H_3M]_2$ (M = V, Cr, Mo) [4]. Moreover, 2,6-dialkyloxyphenyl ligands have been used to stabilise highly reactive main group centres, such as compounds containing Ca–C bonds $[(THF)_2Ca\{\mu\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2\}_3Ca(THF)I]$ [5] and the first germanium radical to exhibit near-planarity at the metal centre, $\bullet Ge[3,5\text{-}^tBu_2\text{-}2,6\text{-}(EtO)_2C_6H]$ [6].

The chemistry of the 2,6-substituted aryls of this type is dominated by these 2,6-dialkoxy species; as part of our ongoing investigations into the use of bulky ligands in the stabilisation of unusual coordination modes [7–9] we are investigating the synthesis of complexes of 2,6-diaryloxy substituted aryl ligands, in order to probe the effect of changing the electronic and steric features of 2,6-substituted aryl ligand systems on their coordination chemistry.

2. Experimental

2.1. General

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or glove box techniques. Hexane, diethyl ether, THF and toluene were pre-dried over Na wire prior to passing through a column of alumina. Benzene-d_6 (Goss) was dried over potassium, while d_8-THF was dried over CaH_2; these NMR solvents were degassed with three freeze–pump–thaw cycles prior to use. $CDCl_3$ was used as received. ^1H, ^{13}C, ^7Li, ^{29}Si and ^{119}Sn NMR spectra for these complexes were collected on a Bruker DPX 400 spectrometer. Chemical shifts are quoted in ppm relative to TMS (^1H, ^{13}C and ^{29}Si), $LiCl/D_2O$ solution (^7Li) or $SnMe_4$ (^{119}Sn). The NMR spectra were assigned according to the ligand numbering scheme (Fig. 1). Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, and by the departmental service at the School of Chemistry, University of Nottingham. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Elemental analyses were performed by Stephen Boyer, London Metropolitan University.

2.2. Syntheses

2.2.1. Synthesis of 2,6-$(PhO)_2C_6H_3Li$ (1) and $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et₂O]₂**)

To a solution of 1,3-$(PhO)_2C_6H_4$ (1.0 g, 3.81 mmol) in hexane (30 cm^3) was added ^nBuLi (1.51 cm^3, 3.81 mmol, 2.5 M in hexanes) and the resulting mixture heated to reflux with stirring for 16 h.

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doi:10.1016/j.jorganchem.2010.12.023

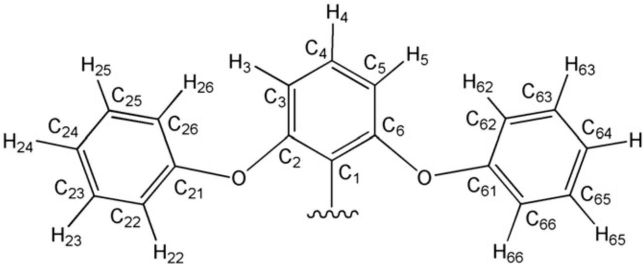

Fig. 1. Numbering scheme for the NMR spectra for the compounds in this investigation.

The reaction mixture was cooled to room temperature and a white precipitate of 2,6-$(PhO)_2C_6H_3Li$ (**1**) was collected by filtration. Yield: 0.78 g; 76%.

*2.2.1.1. Data for **1**.* ^{1}H NMR (d_8-THF, 298 K, 400.20 MHz): δ 6.43 (d, 2H, H3 + H5, $J = 7.6$ Hz), 6.74–6.79 (m, 2H, H24 + H64), 6.83 (t, 1H, H4, $J = 7.6$ Hz), 6.86–6.90 (m, 4H, H22 + H26 + H62 + H66), 7.10–7.15 (m, 4H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 100.64 MHz): δ 113.3 (C3 + C5), 117.4 (C24 + C64), 119.7 (C4), 125.6 (C22 + C26 + C62 + C66), 128.9 (C23 + C25 + C63 + C65), 161.8 (C21 + C61), 164.4 (C1), 168.0 (C2 + C6). ^{7}Li NMR (d_8-THF, 298 K, 155.53 MHz): δ −0.79. Elemental analysis: calcd for $C_{18}H_{13}LiO_2$: C 80.56, H 4.89; found C 80.59, H 4.89%. IR (nujol mull) ν/cm^{-1} 1592 md, 1565 md, 1490 st, 1412 st, 1262 w, 1213 st, 1162 st, 1086 md, 1023 md, 994 w, 948 st, 791 md, 761 md, 693 md, 585 w, 491 w.

Recrystallisation of **1** from diethyl ether solution at room temperature yielded $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et$_2$O]$_2$**) as colourless crystals suitable for X-ray diffraction studies. Yield: 0.65 g; 66%.

*2.2.1.2. Data for **[1.Et$_2$O]$_2$**.* ^{1}H NMR (d_8-THF, 298 K, 400.20 MHz): δ 1.17 (t, 12H, OEt$_2$, $J = 7.0$ Hz), 3.43 (q, 8H, OEt$_2$, $J = 7.0$ Hz), 6.47 (d, 4H, H3 + H5, $J = 7.6$ Hz), 6.79–6.83 (m, 4H, H24 + H64), 6.87 (t, 2H, H4, $J = 7.6$ Hz), 6.90–6.94 (m, 8H, H22 + H26 + H62 + H66), 7.14–7.19 (m, 8H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 100.64 MHz): δ 15.4 (OEt$_2$), 66.0 (OEt$_2$), 113.2 (C3 + C5), 117.7 (C24 + C64), 119.6 (C4), 125.4 (C22 + C26 + C62 + C66), 129.1 (C23 + C25 + C63 + C65), 161.8 (C21 + C61), 164.4 (C1), 167.8 (C2 + C6). ^{7}Li NMR (d_8-THF, 298 K, 155.53 MHz): δ 1.04. Elemental analysis: calcd for $C_{44}H_{46}Li_2O_6$: C 77.15, H 6.77; found: C 77.23, H 6.65%. IR (nujol mull) ν/cm^{-1}: 1593 md, 1565 md, 1490 st, 1412 st, 1262 w, 1214 st, 1164 st, 1071 md, 1023 md, 994 w, 947 st, 911 w, 848 w, 815 w, 790 md, 762 md, 693 md, 585 w, 491 w.

2.2.2. Synthesis of 2,6-$(PhO)_2C_6H_3SiMe_3$ (**2**)

To a suspension of **1** (0.21 g, 0.78 mmol) in toluene (20 cm^3) and THF (1 cm^3) was added Me_3SiCl (0.15 cm^3, 1.18 mmol) *via* syringe and the resulting mixture was allowed to react with stirring for 72 h. Volatiles were removed *in vacuo* and the precipitate was extracted with hexane (30 cm^3). Cooling of the saturated hexane solution to −30 °C yielded 2,6-$(PhO)_2C_6H_3SiMe_3$ (**2**) as colourless crystals suitable for X-ray diffraction studies. Yield: 0.19 g, 73%. ^{1}H NMR (CDCl$_3$, 298 K, 400.20 MHz): δ 0.40 (s, 9H, SiMe$_3$), 6.66 (d, 2H, H3 + H5, $J = 8.2$ Hz), 7.05–7.09 (m, 4H, H22 + H26 + H62 + H66), 7.14–7.18 (m, 2H, H24 + H64), 7.26 (t, 1H, H4, $J = 8.0$ Hz), 7.39–7.44 (m, 4H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 298 K, 100.64 MHz): δ 1.2 (SiMe$_3$), 113.5 (C3 + C5), 118.7 (C22 + C26 + C62 + C66), 123.0 (C24 + C64), 129.8 (C23 + C25 + C63 + C65), 131.3 (C4), 157.6 (C21 + C61), 162.9 (C2 + C6), (C1 not observed). $^{29}Si\{^1H\}$ NMR (CDCl$_3$, 298 K, 79.51 MHz): δ −5.27. Elemental analysis: calcd for $C_{21}H_{22}O_2Si$: C 75.41, H 6.63; found: C 75.57, H 6.38%. IR (nujol mull) ν/cm^{-1} 2868 st, 1959 w, 1595 md, 1588 md, 1561 md, 1489 md, 1435 st, 1290 w, 1260 w, 1246 md, 1218 st, 1159 w, 1109 w, 1075 w, 1055 w, 1024 w, 984 w, 889 w, 843 md, 826 w, 753 w, 744 md, 691 md. Mass spec. (EI): *m*/*z* 334 ([M]$^+$, 85%), 319 ([M − Me]$^+$, 100%), 303 ([M − 2Me]$^+$, 15%), 261 ([M − SiMe$_3$]$^+$, 10%), 226 ([M − OPh − Me]$^+$, 15%), 211 ([M − OPh − 2Me]$^+$, 50%). Accurate mass: Calcd for $C_{21}H_{22}O_2Si$: 334.1389, measd 334.1389; Calcd for $C_{20}H_{19}O_2Si$ (*i.e.* M − Me): 319.1145, measd 319.1137.

2.2.3. Synthesis of 2,6-$(PhO)_2C_6H_3SnMe_3$ (**3**)

To a suspension of **1** (0.20 g, 0.75 mmol) in toluene (20 cm^3) was added a solution of Me_3SnCl (0.15 g, 0.75 mmol) in toluene (10 cm^3) and the resulting mixture was allowed to react with stirring overnight. Volatiles were removed *in vacuo* and the precipitate was extracted with hexane (30 cm^3). Cooling of the saturated hexane solution yielded 2,6-$(PhO)_2C_6H_3SnMe_3$ (**3**) as colourless crystals suitable for X-ray diffraction studies. Yield: 0.14 g, 45%. ^{1}H NMR (C$_6$D$_6$, 298 K, 300.13 MHz): δ 0.52 (s, 9H, SnMe$_3$, $^2J_{117SnH} = 54.9$ Hz, $^2J_{119SnH} = 57.6$ Hz), 6.66 (d, 2H, H3 + H5, $J = 7.8$ Hz), 6.98 (m, 3H, H4 + H24 + H64), 7.06 (m, 4H, H22 + H26 + H62 + H66), 7.17 (m, 4H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 298 K, 100.64 MHz): δ −7.44 (SnMe$_3$, $^1J_{117SnC} = 352.4$ Hz, $^1J_{119SnC} = 369.1$ Hz), 113.3 (C3 + C5), 118.8 (C22 + C26 + C62 + C66), 123.0 (C24 + C64), 129.6 (C23 + C25 + C63 + C65), 131.3 (C4), 158.9 (C21 + C61), 163.5 (C2 + C6), (C1 not observed). $^{119}Sn\{^1H\}$ NMR (C$_6$D$_6$, 298 K, 149.21 MHz): δ −37.9. Elemental analysis: calcd for $C_{21}H_{22}O_2Sn$: C 59.33, H 5.22; found: C 59.25, H 5.26%. IR (nujol mull) ν/cm^{-1} 2869 st, 1957 w, 1739 w br, 1598 w, 1569 md, 1490 md, 1436 st, 1261 md, 1218 st, 1173 w, 1098 w, 1076 w, 1024 md, 976 w, 799 w, 771 w, 750 w, 691 md. Mass spec. (EI): *m*/*z* 411 ([M − Me]$^+$, 100%), 396 ([M − 2Me]$^+$, 10%), 380 ([M − 3Me]$^+$, 20%), 302 ([M − OPh − 2Me]$^+$, 5%), 287 ([M − OPh − 3Me]$^+$, 20%), 261 ([M − SnMe$_3$]$^+$, 20%). Accurate mass: Calcd for $C_{20}H_{19}O_2{}^{112}Sn$, *i.e.* (M − Me): 403.0428, measd 403.0426.

2.3. Crystallography

Crystals of **[1.Et$_2$O]$_2$**, **2** and **3** were mounted on dual-stage glass fibres using YR-1800 perfluoropolyether oil (Lancaster) and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device [10]. Diffraction data were collected on a Bruker SMART APEX diffractometer equipped with a graphite-monochromated Mo-K_α radiation source ($\lambda = 0.71073$ Å). Absorption corrections were applied using a multi-scan method (SADABS) [11]. All non-H atoms were located using direct methods [12] and difference Fourier syntheses. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained in calculated positions and refined with a riding model. For **[1.Et$_2$O]$_2$**, atoms C(19), C(20), C(21) and C(22) of the diethyl ether ligand exhibited disorder over two positions. The disorder was successfully modelled with 22:78 occupancy levels, in conjunction with distance restraints and anisotropic displacement parameter restraints and constraints. Crystal data for **[1.Et$_2$O]$_2$**, **2** and **3** can be found in Table 1.

3. Results and discussion

3.1. Syntheses

The *ortho*-metallation of 1,3-$(PhO)_2C_6H_4$ with ^{n}BuLi proceeds smoothly in hexane under reflux conditions over a period of 16 h to yield 2,6-$(PhO)_2C_6H_3Li$ (**1**) as a colourless powder (Eq. (1)):

$$1,3\text{-}(PhO)_2C_6H_4 + {}^nBuLi \rightarrow 2,6\text{-}(PhO)_2C_6H_3Li + {}^nBuH \qquad (1)$$

Recrystallisation of **1** from Et$_2$O affords $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ **[1.Et$_2$O]$_2$** as colourless crystals suitable for X-ray diffraction studies. Reaction of **1** with one equivalent of Me_3ECl yields