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Aliphatic pincer-type POCOP ligands and their complexation behaviour with iridium: Crystal structure of an iridium(III) phosphinite complex

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ABSTRACT

Reaction of 2 equivalents of 1,3-bis-(di-*tert*-butylphosphinito)-2-methyl-propane (**1a**) with $[Ir(COD)Cl]_2$ affords the first aliphatic diphosphinite PCP pincer complex with iridium, $Ir(H)\{(t\text{-}Bu_2POCH_2)_2C(Me)\}Cl$ (**2**). The poor yield of **2** is partly explained by the formation of a di-nuclear byproduct $[IrCl(COD)]_2(\mu_2\text{-}\{(t\text{-}Bu_2POCH_2)_2CH(Me)\})$ (**3**). Reaction of 1,3-bis-(di-*iso*-propylphosphinito)-2-methyl-propane (**1b**) under the same condition does not give any cyclometallation, and reaction with $IrCl_3{\cdot}H_2O$ in DMF leads to complete decomposition of the pincer ligand under the formation of $Ir(H)(i\text{-}Pr_2P(OH))_3(CO)$ (**4**), underpinning the comparatively low thermal stability of aliphatic phosphinite pincer systems.

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1. Introduction

Since the pioneering work of Shaw [1], aliphatic PCP pincer complexes of the late transition metals have drawn limited attention compared to their aromatic counterparts [2]. Nonetheless, more recent work has clearly shown that the hybridisation of the carbon coordinated to the metal highly influences the reactivity of the pincer complex [3–5].

Electronic and steric properties of the pincer complex can be further adjusted by varying the principal structure of the PCP ligand, and the replacement of phosphines for phosphinites acts in both these aspects. These phosphinite ligands (often denoted POCOP ligands) are generally more conveniently prepared than their PCP counterparts and with higher yields. Such POCOP complexes have been reported with aromatic backbones and have found applications in e.g. the palladium catalysed Heck reaction [6] and in iridium catalysed dehydrogenation reactions of ammonia borane [7] along with transfer dehydrogenation of alkanes [8] and primary amines [9].

Examples of POCOP complexes based on aliphatic backbones are less common and mainly involve first row transition metals [10,11]. Previous work in our group has shown that whereas a cyclohexyl based diphosphine $PC_{sp3}P$ ligand readily cyclometallates with palladium, platinum and iridium, the corresponding diphosphinite gives non-cyclometallated mono- or di-nuclear complexes with palladium and platinum [12]; with iridium the phosphinite ligand undergoes dehydrogenation upon coordination to the metal, resulting in a pincer complex with an aromatic backbone [13]. We therefore decided to investigate the cyclometallating properties of aliphatic phosphinite ligands lacking the possibility for aromatisation.

In this paper we report the synthesis of the first aliphatic diphosphinite PCP pincer complex with iridium, $Ir(H)\{(t\text{-}Bu_2POCH_2)_2C(Me)\}Cl$ (**2**). We also report the formation of the dinuclear compound **3**, again showing the decreased propensity for aliphatic phosphinites to cyclometallate. Finally, we report the product of a thermal decomposition of a phosphinite ligand involving cleavage of the C–O bond.

2. Experimental

2.1. General considerations

All compounds were prepared in an inert atmosphere of either nitrogen or argon, in a glove box or using high vacuum techniques. Non-chlorinated solvents were distilled from sodium/benzophenone ketyl and chlorinated solvents were distilled from CaH_2, using high vacuum techniques. Deuterated solvents and commercially available reagents were purchased from Sigma Aldrich and Acros Organics and used as received inside a glove box. Chemical shifts are given in ppm downfield from TMS (^1H- and ^{13}C NMR) using residual solvent peaks or H_3PO_4 (δ 0) as reference. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (m) multiplet, (v) virtual. Elemental analyses were performed by H.

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Table 1
Crystal data for compounds **2**–**4**.

	2	**3**	**4**
Formula	$C_{20}H_{44}ClIrO_2P_2$	$C_{36}H_{68}Cl_2Ir_2O_2P_2$	$C_{19}H_{46}IrO_4P_3$
fw	606.18	1050.21	623.70
Space group	$P2_1/c$	*Pnma*	$P2_1/n$
a (Å)	13.3180(4)	16.229(5)	9.0172(4)
b (Å)	12.3347(3)	13.514(5)	16.7256(7)
c (Å)	17.1377(4)	18.200(5)	17.5259(11)
β (°)	99.099(3)	90.00	90.00
V (Å^3)	2779.85(13)	3992(2)	2643.2(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.539	1.762	1.557
μ (mm^{-1})	5.030	6.905	5.252
θ range (°)	2.39–32.99	2.51–25.02	2.32–33.01
Number of reflections collected	27382	21940	24436
Number of unique reflections	9493	3668	9174
$R(F)$ ($I > 2\sigma(I)$)[a]	0.0274	0.0315	0.0804
$wR_2(F^2)$ (all data)[b]	0.0634	0.0748	0.2416
S[c]	0.979	1.170	1.306
R_{int}	0.0332	0.0421	0.0628

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.
[c] $S = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.

Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. IR spectra were recorded on a Bruker Alpha spectrometer, with diamond ATR–FTIR detection.

2.2. Preparation of 1,3-bis-(di-tert-butylphosphinito)-2-methylpropane (**1a**)

To a solution of 2-methyl-1,3-propanediol (0.50 g, 5.55 mmol) in THF (10 mL) KH (470 mg, 11.2 mmol) was added and the reaction was left to stir at room temperature over night. ClP^tBu_2 (2.01 g, 11.1 mmol) was added and the mixture was stirred for an additional 20 h. The solvent was removed *in vacuo* and replaced with Et_2O. The resulting suspension was filtered through celite and concentrated in vacuo, giving **1a** as an essentially pure colourless oil that was used without further purification (Yield: 1.75 g, 84%). ^{1}H NMR (C_6D_6): δ 3.84–3.79 (m, 2H, OCH_2), 3.72–3.67 (m, 2H, OCH_2), 2.05 (oct, $^3J_{PH}$ = 6.4 Hz, 1H, $CH_3CH(CH_2)_2$), 1.13 (d, $^3J_{PH}$ = 11.2 Hz, 18H, 2 (CH_3)$_3$C), 1.12 (d, $^3J_{PH}$ = 11.1 Hz, 18H, 2 (CH_3)$_3$C), 0.94 (d, $^1J_{HH}$ = 6.9 Hz, 3H, CH_3CH). ^{13}C {^{1}H} NMR (C_6D_6) = δ 75.9 (d, J_{PC} = 20.9 Hz, CH_2O), 38.0 (t, J_{PC} = 7.5 Hz, CH_3CH), 35.4 (d, J_{PC} = 26.2 Hz, (CH_3)$_3$C), 35.2 (d, J_{PC} = 25.7 Hz, (CH_3)$_3$C), 27.7 (d, J_{PC} = 15.5 Hz, (CH_3)$_3$C), 27.6 (d, J_{PC} = 15.5 Hz, (CH_3)$_3$C), 14.6 (s, CH_3CH). ^{31}P {^{1}H} NMR (C_6D_6): δ 161.5 (s).

2.3. Preparation of 1,3-bis-(di-iso-propylphosphinito)-2-methylpropane (**1b**)

A hexane solution of *n*-BuLi (2.5 M, 1.60 mL, 4.00 mmol) was added to an ice-cooled and stirred solution of 2-methyl-1,3-propanediol (0.148 mL, 1.66 mmol) in THF (8 mL). After stirring for 2 h at room temperature, a solution of ClP^iPr_2 (0.557 mL, 3.33 mmol) in THF (1.5 mL) was added at 0 °C and the reaction was left to stir over night. The reaction was concentrated in vacuo, extracted with toluene (15 mL) and filtered through a pad of celite. Removal of solvent gave **1b** as an essentially pure pale yellow oil, that was used without further purification (Yield: 0.490 g, 91%). ^{1}H NMR (C_6D_6): δ 3.79–3.73 (m, 2H, OCH_2), 3.68–3.62 (m, 2H, OCH_2), 2.02 (oct, $^3J_{PH}$ = 6.4 Hz, 1H, $CH_3CH(CH_2)_2$), 1.69–1.59 (m, 4H, $CH(CH_3)_2$), 1.16–1.11 (m, 12H, 2 (CH_3)$_2$CH), 1.05–0.98 (m, 12H, 2 (CH_3)$_2$CH), 0.93 (d, $^1J_{HH}$ = 6.9 Hz, 3H, CH_3CH). ^{13}C {^{1}H} NMR (C_6D_6): δ 74.4 (d, J_{PC} = 19.5 Hz, 2 CH_2O), 37.9 (t, J_{PC} = 7.2 Hz, $CH_3CH(CH_2)_2$), 28.3 (d, J_{PC} = 17.9 Hz, 4 (CH_3)$_2$CH), 18.2 (d, J_{PC} = 5.0 Hz, (CH_3)$_2$CH), 18.0 (d, J_{PC} = 5.1 Hz, (CH_3)$_2$CH), 17.1 (d, J_{PC} = 1.4 Hz, (CH_3)$_2$CH), 17.0 (d, J_{PC} = 1.3 Hz, (CH_3)$_2$CH), 14.1 (s, CH_3CH). ^{31}P {^{1}H} NMR (C_6D_6): δ 152.4 (s).

2.4. Preparation of Ir(H){(t-Bu$_2$POCH$_2$)$_2$C(Me)}Cl (**2**) and [IrCl(COD)]$_2$(μ_2-{(t-Bu$_2$POCH$_2$)$_2$CH(Me)}) (**3**)

Inside a nitrogen atmosphere glovebox, [Ir(COD)Cl]$_2$ (79 mg, 0.12 mmol) was added to a solution of **1a** (90 mg, 0.24 mmol) in CH_2Cl_2 (1 mL) in a J. Young NMR tube. The tube was evacuated under high vacuum and H_2 was added at −196 °C. The reaction mixture was heated to 80 °C over night and after standing at RT for 24 h, orange–red crystals of **3** could be collected. (Yield: 0.011 g, 8.7%). ^{1}H NMR (C_6D_6): δ 5.35–5.27 (m, 4H C*H*=C*H*), 3.87–3.82 (m, 2H, OCH_2), 3.70–3.66 (m, 2H, OCH_2), 3.62–3.57 (m, 4H C*H*=C*H*), 2.21–2.12 (m, 4H, 2 CH=CH–CH_2), 2.04–1.98 (m, 4H, 2 CH=CH–CH_2), 1.94–1.90 (m, 1H, $CH_3CH(CH_2)_2$), 1.57–1.48 (m, 8H, 4 CH=CH–CH_2), 1.50 (s, 18 H, 2 (CH_3)$_3$C), 1.47 (s, 18 H, 2 (CH_3)$_3$C), 0.74 (d, $^1J_{HH}$ = 6.9 Hz, 3H, CH_3CH). ^{31}P {^{1}H} NMR (C_6D_6): δ 142.7 (s). *Anal.* Calcd. for $C_{36}H_{68}Cl_2Ir_2O_2P_2$: C, 41.17; H, 6.53. Found: C, 40.77; H, 6.80%.

The remaining reaction mixture was filtered through celite, concentrated in vacuo and re-dissolved in hexane, before a second filtration through celite. Reduction of solvent and cooling to −28 °C gave an orange precipitate of **2** (Yield: 35 mg, 24%). ^{1}H NMR (C_6D_6): δ 3.28–3.19 (m, 2H, OCH_2), 3.04–3.00 (m, 2H, OCH_2), 1.50 (vt, J_{HP} = 14.0 Hz, 18 H, 2 (CH_3)$_3$C), 1.29 (vt, J_{HP} = 13.5 Hz, 18 H, 2 (CH_3)$_3$C), 1.13 (s, 3H, $CH_3C(CH_2)_2$), −37.4 (t, J_{PH} = 13.4 Hz, 1H, Ir-*H*). ^{13}C {^{1}H} NMR (toluene-d8): δ 90.0 (vt, J_{PC} = 6.7 Hz, OCH_2), 46.6 (vt, J_{PC} = 24.1 Hz, $C(CH_3)_3$), 45.8 (vt, J_{PC} = 26.7 Hz, $C(CH_3)_3$), 39.0 (d, $^2J_{CH}$ = 5.5 Hz, Ir-*C*), 33.8 (vt, J_{PC} = 5.7 Hz, (CH_3)$_3$C), 33.4 (vt, J_{PC} = 6.2 Hz, (CH_3)$_3$C), 32.7 (s, CH_3C). ^{31}P {^{1}H} NMR (C_6D_6): δ 180.0 (d, J_{PH} = 13.4).

2.5. Preparation of Ir(H)(i-Pr$_2$P(OH))$_3$(CO) (**4**)

$IrCl_3 \cdot H_2O$ (0.01 g, 0.03 mmol) and **1b** (0.02 g, 0.062 mmol) was mixed in *N,N*-dimethylformamide (DMF, 0.6 mL) in a J. Young NMR-tube. The reaction was heated to 160 °C for 48 h, and upon cooling to RT **4** was obtained as an off-white, sparingly soluble material that was partly redissolved in methanol. Crystals for X-ray analysis was obtained upon standing over night. IR: υ_{CO} = 1722 cm^{-1}.

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