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Secondary ligand–metal interactions in rhodium(III) and iridium(III) phosphoramidite complexes

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ABSTRACT

The synthesis, characterization, and application in asymmetric catalytic cyclopropanation of Rh(III) and Ir(III) complexes containing (S_a,R_C,R_C)-O,O′-[1,1′-binaphthyl-2,2′-diyl]-N,N′-bis[1-phenyl-ethyl]phosphoramidite (**1**) are reported. The X-ray structures of the half-sandwich complexes [$MCl_2(C_5Me_5)$(**1**,κ*P*)] (M = Rh, **2a**; M = Ir, **2b**) show that the metal–phosphoramidite bond is significantly shorter in the Ir(III) analog. Chloride abstraction from **2a** (with $CF_3SO_3SiMe_3$ or with CF_3SO_3Me) and from **2b** (with $AgSbF_6$) gives the cationic species [$MCl(C_5Me_5)$(1,2-η-**1**,κ*P*)]$^+$ (M = Rh, **3a**; M = Ir, **3b**), which display a secondary interaction between the metal and a dangling phenethyl group ($NCH(CH_3)Ph$) of the phosphoramidite ligand, as indicated by NMR spectroscopic studies. Complexes **3a** and **3b** slowly decompose in solution. In the case of **3b**, the binuclear species [$Ir_2Cl_3(C_5Me_5)_2$]$^+$ is slowly formed, as indicated by an X-ray study. Preliminary catalytic tests showed that **3a** cyclopropanates styrene with moderate yield (35%) and diastereoselectivity (70:30 *trans*:*cis* ratio) and with 32% ee (for the *trans* isomer).

1. Introduction

Secondary metal–ligand interactions (in particular involving a dangling aryl group) have found increasing attention in asymmetric catalysis [1] since the recognition that they play a pivotal role in Pd(II) [2–4], Pd(0) [5], and Pd(I) [6] catalysts for C–C bond formation containing bulky phosphine ligands that feature secondary interactions. Recently, secondary interactions have been recognized also for a class of ligands that has been initially considered as monodentate *par excellence*, that is, phosphoramidites (P*) [7], which have found successful application in asymmetric catalysis [8]. Thus, iridium complexes of methylamino-substituted P* ligands have been shown to undergo C–H activation and give cyclometallated complexes with P,CH_2-bidentate coordination, which efficiently catalyze enantioselective allylic alkylation and amination reactions [9]. Interestingly, phosphoramidites featuring an olefin functionality, which can therefore act as chelating ligands, have been found to be particularly efficient for the latter transformation [10].

A different coordination mode, that is, the η^2-coordination of a dangling aryl substituent at the phosphoramidite nitrogen atom, has been suggested for nickel(0) on the basis of calculations [8b,e] and to explain [1] the enantioselectivity of palladium(II) catalysts [11]. We have reported the first well-characterized example of such an interaction involving the phosphoramidite ligand (S_a,R_C,R_C)-O,O′-[1,1′-binaphthyl-2,2′-diyl]-N,N′-bis[1-phenylethyl]phosphoramidite) (**1**) in the half-sandwich complex [RuCl(η^6-*p*-cymene)(1,2-η-Ph-P*-κ*P*)]PF_6 (**2**), in which one of the phenyl (or naphthyl) substituents at nitrogen of the phosphoramidite (P*) coordinates in an 1,2-η-fashion to ruthenium [12]. Such π-aryl interactions are not restricted to ruthenium(II), though. Phosphoramidite **1** gives analogous η^2-interactions also with d^8 metal ions, such as in [Pd(η^3-allyl)(1,2-η-Ph-**1**-κP]$^+$ and in the rhodium(I) complexes [Rh(diene)(1,2-η-Ph-**1**-κ*P*)]$^+$ (diene = COD or NBD) [13]. Additionally, **1** can act as a 6-electron donor, as in [$RuCl_2$(η^6-Ph-**1**-κ*P*)] [12b], or as a 4-electron donor, as in the rhodium(I) complex [Rh(**1**-κ*P*)(η^6-Ph-**1**-κ*P*)]$^+$ [13]. These versatile coordination modes have been recently suggested as a possible reason for enhanced lifetime of [$RuCl_2$(*p*-cymene)(**1**)] as catalyst (compared to the methyl-substituted ligand) in the formation of β-oxo esters from propargylic alcohols and RCOOH [14].

Originally, it was the seminal work by Brookhart [15] and Hossain [16] on *cis*-selective cyclopropane formation with cyclopentadienyl complexes of iron(II) that prompted us to prepare half-sandwich complexes based on the [RuCl(arene)(P*)]$^+$ fragment and use them in asymmetric cyclopropanation. Indeed, the latter species cyclopropanate styrene derivatives with high enantioselectivity [12], but with low activity and modest diastereoselectivity. With these preliminary results as a starting point, we have extended our studies to other half-sandwich d^6 complexes. We describe below the synthesis and application in asymmetric

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cyclopropanation of rhodium(III) and iridium(III) pentamethylcyclopentadienyl complexes as further examples of P,C-bidentate coordination of phosphoramidite **1**.

2. Experimental

2.1. General procedures, methods and materials

Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques, or in a glove box under purified nitrogen. (*R*)-(−)-bis(1-phenylethyl)amine hydrochloride was obtained from Aldrich. (*S*)-(−)-1,1′-Bi(2-naphthol), trifluoromethanesulfonic acid trimethylsilyl ester, and PCl_3 were purchased from Fluka. Silver hexafluoroantimonate was purchased from Acros. PCl_3 was distilled immediately before use. NEt_3 was freshly distilled on CaH_2. All other commercially available reagents were used without further purification. Solvents were purified by standard procedures: CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2. $[RhCl_2(C_5Me_5)]_2$ and $[IrCl_2(C_5Me_5)]_2$ were prepared according to literature procedures [17]. Phosphoramidite **1** was prepared by a modification [13] of the one-pot procedure reported by Alexakis [18]. Optical rotations were measured using a Perkin–Elmer 341 polarimeter with a 1 dm cell in $CHCl_3$, unless otherwise stated. The HR MALDI spectra were measured by the MS-service (Laboratorium für Organische Chemie, ETH Zürich) on a IonSpec Ultima HR MALDI-FT-ICR mass spectrometer at 4.7 T using a DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]-malononitrile) matrix. Elemental analyses were carried out by the Laboratory of Microelemental Analysis (Laboratorium für Organische Chemie, ETH Zürich). ^{1}H (700, 500 and 300 MHz), ^{31}P (283, 202 and 121 MHz), ^{13}C (176, 126 and 76 MHz), and ^{19}F (188 MHz) spectra were recorded on Bruker Avance 700, 500, 300, and 200 MHz spectrometers in CD_2Cl_2, unless otherwise stated. Chemical shifts δ are quoted in parts per million (ppm) downfield of tetramethylsilane for ^{1}H and ^{13}C NMR spectra. ^{31}P NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ 0.0). ^{19}F NMR spectra were referenced to external $CFCl_3$. Coupling constants *J* are given in Hz.

2.2. $[RhCl_2(C_5Me_5)]$(**1**, κP)] (**2a**)

$[RhCl_2(C_5Me_5)]_2$ (0.0494 g, 0.0008 mol) and ligand (S_a,R_C,R_C)-**1** (0.0863 g, 0.0016 mol) were dissolved in $CDCl_3$ (1.2 mL). The solution was stirred for 1 h at room temperature and then stored 3 days for crystallization. The solvent was carefully decanted, the deep-red crystals thus obtained were washed with a small amount of $CDCl_3$ (∼0.4 mL) and dried in air. Complex **2a** cocrystallizes with three $CDCl_3$ molecules (see below). Yield: 0.1023 g, 53%. *Anal.* Calc. for $C_{49}H_{45}D_3NCl_{11}O_2PRh$: C, 48.65; H, 4.25; N, 1.16. Found: C, 48.57; H, 4.22; N, 1.16%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.37 (d, $^4J_{P,H}$ = 4.7, 15H, CpC*H*$_3$), 1.77 (d, $^3J_{H,H}$ = 6.7, 6H, NCHC*H*$_3$) 5.28 (dq, $^3J_{H,H}$ = 6.8, $^3J_{P,H}$ = 15.8, 2H, NC*H*CH$_3$) 6.06 (d, $^3J_{H,H}$ = 8.8, 1H) 6.76–7.46 (m, 17H), 7.81 (d, $^3J_{H,H}$ = 8.2, 1H), 7.85–7.89 (m, 2H), 8.43 (d, $^3J_{H,H}$ = 8.9, 1H, arom). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 9.4 ($^3J_{P,C}$ = 2.0, CpCH$_3$) 22.7 ($^3J_{P,C}$ = 3.4, NCHCH$_3$), 56.2 ($^2J_{P,C}$ = 9.4, NCHCH$_3$), 101.0 ($^1J_{Rh,C}$ = 4.3, $^2J_{P,C}$ = 6.7, Cp), 120.9, 122.6 ($J_{P,C}$ = 2.3), 122.7 ($J_{P,C}$ = 3.2), 124.9 ($J_{P,C}$ = 3.0), 125.2 ($J_{P,C}$ = 3.7), 125.6, 125.8, 126.2, 126.8, 127.4, 127.5, 127.7 ($J_{P,C}$ = 1.2), 128.0, 129.4, 131.2 ($J_{P,C}$ = 0.8), 131.4 ($J_{P,C}$ = 0.9), 132.7 ($J_{P,C}$ = 1.7), 132.8 ($J_{P,C}$ = 2.1), 145.3, 147.6 ($J_{P,C}$ = 5.8), 149.0, 149.2 (arom). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 151.8 (d, $^1J_{Rh,P}$ = 225.1).

2.3. X-ray structure of $[RhCl_2(C_5Me_5)]$(**1**, κP)] (**2a**)

Deep red needles of (S_a,R_C,R_C)-**2a** were obtained by slow evaporation of a $CDCl_3$ solution. Crystal data: $C_{49}H_{48}Cl_{11}NO_2PRh$, monoclinic, $P2_1$, 0.50 × 0.34 × 0.20 mm, a = 11.4151(8), b = 23.2267(17), c = 11.5790(8) Å, V = 2676.3(3) Å^3, Z = 2, F(0 0 0) = 1 224, D_{calc} = 1.497 g cm^{-3}, μ = 0.937 mm^{-1}. Data were collected at 294 K on a Bruker AXS SMART APEX platform in the θ range 1.75–28.28°. The structure was solved with SHELXTL using direct methods. Of the 27 924 measured ($-15 \leqslant h \leqslant 15$, $-30 \leqslant k \leqslant 30$, $-15 \leqslant l \leqslant 15$), 13 159 unique reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement parameters). R_1 = 0.0356 (12 523 data with $F_o > 4\sigma(F_o)$), wR_2 = 0.0937 (all data). Maximum and minimum difference peaks were +0.877 and −0.484 e Å^{-3}. Additionally to **3a**, the asymmetric unit contains three chloroform molecules.

2.4. $[IrCl_2(C_5 Me_5)]$(**1**,κP)] (**2b**)

$[IrCl_2(C_5Me_5)]_2$ (0.223 g, 0.0003 mol) and ligand (S_a,R_C,R_C)-**1** (0.302 g, 0.0006 mol) were dissolved in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1 h at room temperature. After evaporating the solvent, the crude product was washed with diethyl ether and pentane. Recrystallization from diethylether gave orange needles, which were washed with diethyl ether and dried in vacuum. The crystals contain one CH_2Cl_2 per complex molecule, as shown by ^{1}H NMR spectroscopy. Yield: 0.3008 g, 57%. $[\alpha]_D^{20} = -17$ (*c* 0.11). *Anal.* Calc. for $C_{47}H_{47}NCl_4IrO_2P$: C, 56.36; H, 4.63; N, 1.36. Found: C, 56.39; H, 4.76; N, 1.37%. HRMS (MALDI): Calcd for $C_{46}H_{44}NO_2PIr$ 866.2733, found 866.2749 [M−H−2Cl]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (d, $^4J_{P,H}$ = 4.5, 15H, CpC*H*$_3$), 1.84 (d, $^3J_{H,H}$ = 6.6, 6H, NCHC*H*$_3$) 5.24 (dq, $^3J_{H,H}$ = 6.9, $^3J_{P,H}$ = 16.2, 2H, NC*H*CH$_3$), 5.91 (d, $^3J_{H,H}$ = 8.7, 1H), 6.74–7.43 (m, 17H), 7.80 (d, $^3J_{H,H}$ = 8.1, 1H), 7.84–7.87 (m, 2H), 8.33 (d, $^3J_{H,H}$ = 9.0, 1H, arom). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 8.9 ($^3J_{P,C}$ = 1.6, CpCH$_3$) 23.3 ($^3J_{P,C}$ = 3.8, NCHCH$_3$), 56.1 ($^2J_{P,C}$ = 8.9, NCHCH$_3$), 95.3 ($^2J_{P,C}$ = 4.1, Cp), 121.0, 122.6 ($J_{P,C}$ = 2.6), 124.6 ($J_{P,C}$ = 3.2), 125.0, 125.1, 125.6, 125.7, 126.1, 126.7, 127.3, 127.4, 127.6, 128.0, 129.2, 131.1 ($J_{P,C}$ = 1.3), 131.4 ($J_{P,C}$ = 1.3), 132.8 ($J_{P,C}$ = 1.8), 145.6, 147.5 ($J_{P,C}$ = 1.5), 148.1, 148.8 (arom). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 114.6.

2.5. X-ray structure of $[IrCl_2(C_5Me_5)]$(**1**, κP)] (**2b**)

Orange needles of (S_a,R_C,R_C)-**3** were grown from diethyl ether. Crystal data: $C_{47}H_{47}Cl_4IrNO_2P$, orthorhombic, $P2_12_12_1$, 0.34 × 0.21 × 0.14 mm, a = 9.4822(6), b = 14.533(1), c = 31.816(2) Å, V = 4384.4(5) Å^3, Z = 4, F(0 0 0) = 2 048, D_{calc} = 1.550 g cm^{-3}, μ = 3.364 mm^{-1}. Data were collected at 200 K on a Bruker AXS SMART APEX platform in the θ range 1.90–28.49°. The structure was solved with SHELXTL using direct methods. Of the 81 792 measured ($-12 \leqslant h \leqslant 12$, $-19 \leqslant k \leqslant 19$, $-42 \leqslant l \leqslant 42$), 11 049 unique reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement parameters). R_1 = 0.0257 (10 718 data with $F_o > 4\sigma(F_o)$), wR_2 = 0.0629 (all data). Maximum and minimum difference peaks were +1.524 and −1.634 e Å^{-3}.

2.6. $[RhCl(C_5Me_5)]$(**1**, κP)]OTf (**3a**)

$[RhCl_2(C_5Me_5)]_2$ (24.7 mg, 0.04 mmol) and ligand (S_a,R_C,R_C)-**1** (43.2 mg, 0.082 mmol) were dissolved in CD_2Cl_2 (1 mL), and the resulting solution was stirred for 30 min at room temperature. Then, $CF_3SO_3SiMe_3$ (15 μL, 17.8 mg, 0.08 mmol) was added. After stirring for 2 h and evaporating the solvent, the crude product was washed with diethyl ether and pentane. The resulting light red powder was dried in vacuum. *Anal.* Calc. for $C_{48}H_{47}NCl_3RhF_3O_5PS$: C, 55.05; H, 4.52; N, 1.33. Found: C, 55.32; H, 4.88; N, 1.24%. HRMS (MALDI): Calc. for $C_{47}H_{45}NO_5PF_3ClSRh$ 962.2586, found 777.2252 [M−OTf−Cl]$^+$. ^{1}H NMR (500.2 MHz, CD_2Cl_2, −90 °C); δ 1.18 (br s, 3H, free NCHC*H*$_3$), 1.21 (d, 15H,