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Synthesis and ligand exchange reactions of $P_2Pd(II)$ and $P_2Pt(II)$ salicylaldimates

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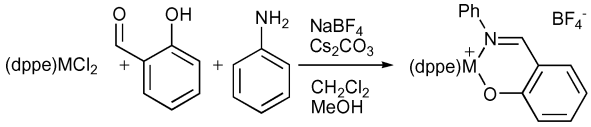
Reaction of (dppe)MCl_2 (dppe = 1,2-bis(diphenylphosphino)ethane) with 2-(*N*-phenyliminomethyl)phenol leads to air-stable (dppe)M(N,O) chelates (M = Pd, **1a**; M = Pt, **1b**). The *N*-4-methylphenyl derivative of **1a** has been characterized by X-ray analysis. The N,O ligands are kinetically labile and exchange occurs in solution in the presence of other salicylaldimines. In the presence of anilines, a metal-mediated imine exchange process occurs. Hammett analysis reveals that the platinum complexes are sensitive to the electronics at N but not at O. Electron donating groups on the N-aryl ring stabilize the metal complex.

Introduction

As part of our continuing interest in developing coordination compounds that provide properties favorable to their molecular imprinting, we recently began investigating a class of previously unreported P_2M(*N*,*O*-salicylaldimine)-cations (M = Pd, Pt). Prior to our work a number of examples of this ligand on Pd/Pt were known, but none had the properties we desired. Some known monomeric complexes for M = Pd and Pt include (but are not limited to): bis(salicylaldimine)M(II);[1] (salen)M(II);[2] (*N*-(2-diphenylphosphinophenyl)salicylaldimate)M(II)(L), (L = Cl, CH_3, CH_3CN);[3] (*N*-(2-hydroxyaryl)salicylaldimate)M(II)-(amine);[4] (salicylaldimate)M(II)(diamine);[5] (salicylaldimate)-Pd(II)(π-allyl);[6] and (salicylaldimate)$Pd(PR_3)(CH_3)$.[7] Additionally, a number of $Ni(Ph)(PPh_3)$(salicylaldimine) complexes have been reported for olefin polymerization catalysis;[8] isoelectronic square planar (salicylaldimate)Rh^I(bis-phosphine) complexes are also known.[9]

Results and discussion

N-Phenylsalicylaldimine chelates of the metal fragment (dppe)M (M = Pt, Pd) were conveniently prepared by stirring (dppe)MCl_2 with salicylaldehyde and aniline in a 1 : 1 mixture of CH_2Cl_2 and MeOH with $NaBF_4$ and Cs_2CO_3 (eqn. (1)).



1a M = Pd 84%
1b M = Pt 82%

(1)

Aqueous workup afforded the yellow crystalline solids **1a** and **1b** in good yields. Both compounds could be stored on the benchtop for months without decomposition.

X-Ray quality crystals of an analog of **1a**, (dppe)Pd(*N*-(4-methylphenyl)salicylaldimate) (**2**), were obtained by vapor diffusion of n-pentane into a saturated CH_2Cl_2 solution. An ORTEP representation is shown in Fig. 1 along with selected bond lengths and angles. The Pd–O bond (2.027(3) Å) is shorter than the Pd–N bond (2.104(4) Å) by 0.077 Å, likely the result of a slightly stronger ionic component to the Pd–O bonding.[10] The Pd–P bonds are nearly equivalent; Pd–P1 is 2.2555(14) Å and Pd–P2 is 2.2558(14) Å. The larger steric demand of the *N*-aryl imine *versus* the phenoxide is apparent from the cisoid angles P–Pd–(N/O); P2–Pd–N is 100.57(12)° while P1–Pd–O is 85.79(11)°. The complex shows almost no deviation from planarity at Pd (Σ bond angles = 359.9°).

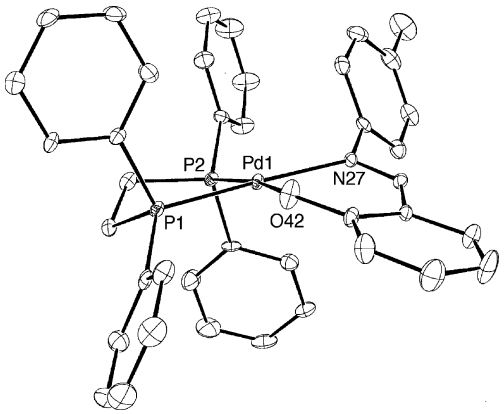
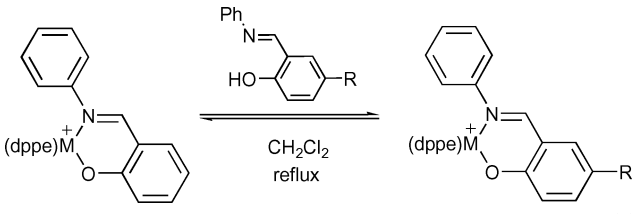


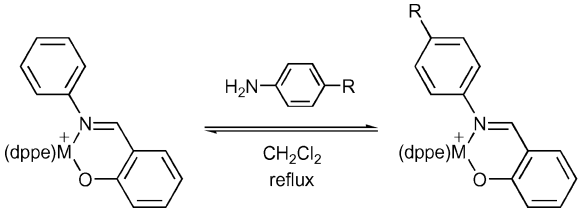
Fig. 1 ORTEP representation of **2**. Hydrogen atoms and counterion omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–O42 = 2.027(3), Pd1–N27 = 2.104(4), Pd1–P1 = 2.2555(14), Pd1–P2 = 2.2558(14); P1–Pd1–P2 = 84.29(5), P1–Pd1–O42 = 85.79(11), P2–Pd1–N27 = 100.57(12), N27–Pd1–O42 = 89.28(16).

While exploring the reactivity of these new complexes, we discovered that two distinct modes of ligand exchange were operative; substitution of the entire salicylaldimine fragment (eqn. (2))



(2)

and substitution of the aniline fragment (eqn. (3)).



(3)

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The former is almost certainly associative in nature[11] and proceeds through a mixed salicylaldimine complex. The latter reactivity can be readily rationalized as a Lewis acid-promoted imine exchange reaction (Fig. 2).[12–16]

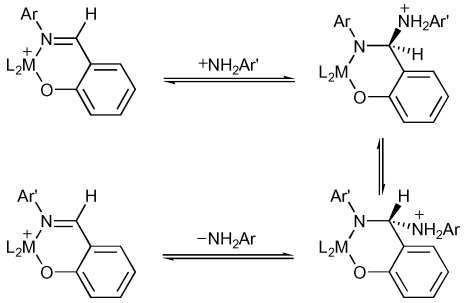


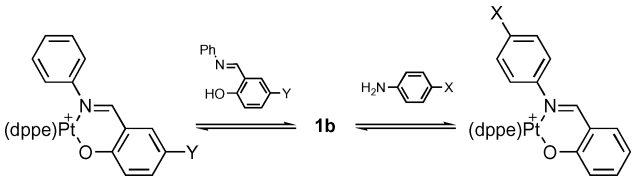
Fig. 2 Possible mechanism for metal-mediated imine exchange.

Complexes **1a** and **1b** undergo both ligand exchange processes in a wide variety of solvents, both protic (MeOH), and aprotic (CH_2Cl_2, PhCl, $MeNO_2$). The palladium complexes reach equilibrium more rapidly than their platinum analogs, however they slowly abstract chloride from chlorinated solvents at elevated temperature to form (dppe)$PdCl_2$. On the other hand, **1b** was stable in refluxing chlorobenzene for several days.

The multiple ligand exchange reactions displayed by these complexes allowed the electronic influence of the salicylaldimine to be easily probed. Complex **1b** was equilibrated with either substituted anilines or salicylaldimines to assess the impact of electron density changes at both the N and O positions (Table 1). Hammett plots[17] using the σ_p substituent parameters[18] indicated a strong correlation between the relative free energy of **1b** and the electronic influence of X on the one hand, and little correlation with the electronic influence of Y on the other (Fig. 3). A large negative slope ($\rho = -3.07$) was observed with X, clearly indicating that the complex is stabilized by increased electron density at N while a relative insensitivity to electronic perturbations was observed at O.

The electronic effect observed at *N* is intuitively reasonable, and presumably reflects bonding between the neutral *N*-ligand and a cationic metal complex that is reliant on the *N*-basicity for stability. More unexpected, however, was the lack of a strong trend in the position *para* to the phenolate oxygen. In the neutral Ni(II) salicylaldimine catalysts mentioned in the introduction, the olefin polymerization activity was moderately sensitive to

Table 1 Salicylaldimine exchange equilibria



Entry[a]	X	Y	K_{eq}[b]	ΔG/kcal mol^{-1}
1	OMe	H	7.20	−1.31
2	Me	H	2.82	−0.685
3	Cl	H	0.188	1.11
4	H	H	1[c]	0
5	H	OMe	0.710	0.226
6	H	Me	1.18	−0.109
7	H	Cl	0.452	0.525

[a] Equimolar amounts of **1b** and the appropriate salicylaldimine or aniline were heated at 60 °C in $MeNO_2$ until equilibrium was reached as judged by ^{31}P NMR. [**1b**] = 0.0250 M. [b] Relative concentrations determined by ^{31}P NMR. Average of three measurements. [c] By definition.

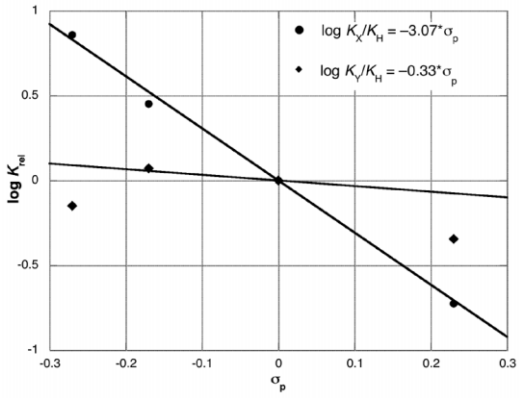


Fig. 3 Hammett plots of K_{rel} *vs.* σ_p. (●) Entries 1–3, Table 1. (◆) Entries 5–7, Table 1. Linear regressions forced through (0,0).

strong electrong withdrawing groups (NO_2), but not to good donors like –OMe.[8b] Computationally, these substituents had only a small effect on the relative energetics of catalyst activation, propagation, and chain transfer.[19] Much more significant were steric effects on the rates of catalysis, which confirmed the experimental observations that catalyst activation, productivity, and especially deactiviation, were sensitive to the size of both halves of the ligand.[20]

In contrast to our late metal case, which has minimal π-donor M–L character, oxophilic early metals have properties that show significantly larger electronic sensitivities to positions *para* to the phenolate oxygen, for example van Koten's NO-chelated V(IV) complexes.[21] This situation can reasonably be ascribed to strengthened π-donor interactions (and hence π-communication) with the electron deficient metals. Similarly, high valent intermediates like those achieved in Jacobsen's Mn(salen)-catalyzed olefin epoxidations are sensitive to electronic perturbations *para* to the salicylaldimine oxygen, which provided a mechanism for tuning of enantioselectivity.[22] Given the magnitude of the effects with strong binding aryloxides and the attenuated affects in the present case, we reason that removing π-donation from the bonding also removes an efficient mechanism for electronic communication.

In summary, we have described the synthesis and structure of a new class of monocationic (dppe)M(II)(salicylaldimate) complexes for M = Pd, Pt. The electronic influence of the (*N*,*O*) ligand was probed through a series of exchange equilibria, and it was found that **1a** is stabilized by electron rich imine donors but it is insensitive to the electronics of phenoxide donors. The relative insensitivity of the oxygen position was rationalized by noting that in contrast to early and/or high valent metal complexes, minimal π-donor interactions are present in square-planar d^8-complexes, and that this appears to attenuate the electronic communication between the ligand and the metal.

Experimental

General

All reagents were used as received without further purification. In all cases, solvents were used without drying or distillation. (dppe)$PtCl_2$, (dppe)$PdCl_2$, and 5-substituted salicylaldimines were prepared from procedures modified from the literature.[23] Compounds **1a** and **1b** were synthesized under dinitrogen and ligand exchange reactions were performed under air. NMR spectra were recorded on a Bruker Avance 400 or 300 MHz spectrometer; chemical shifts are given in ppm and are referenced to residual solvent resonances (^1H, ^{13}C) or an 85% H_3PO_4 external standard (^{31}P). Elemental analysis was performed by Complete Analysis Laboratories, Inc.

Syntheses

(dppe)Pd(2-(*N*-phenyliminomethyl)phenolate)(BF_4) (1a). To a flask containing 20 mg aniline (0.21 mmol) and 26 mg salicylaldehyde (0.21 mmol) in 24 mL 1 : 1 CH_2Cl_2/MeOH was added 123 mg (dppe)$PdCl_2$ (0.214 mmol), 56 mg $NaBF_4$ (0.51 mmol), and 76 mg Cs_2CO_3 (0.233 mmol). The reaction was heated to reflux for four hours, then cooled to ambient temperature and poured into 25 mL water. The biphase was extracted with CH_2Cl_2 (3×) and the combined extracts were washed with water (2×), dried over $MgSO_4$, and evaporated *in vacuo*. The crude yellow solid was recrystallized from CH_2Cl_2/^{t}BuOMe to yield 140 mg (84%) of **1a** containing 0.04 equiv. CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 5H), 7.61 (m, 2H), 7.54 (m, 6H), 7.41 (m, 8H), 7.32 (t, 1H, J = 7.1 Hz), 7.19 (d, 1H J = 8.0 Hz), 6.84 (t, 1H, J = 7.1 Hz), 6.66 (t, 3H, J = 7.6 Hz), 6.55 (m, 3H), 2.71 (m, 2H), 2.52 (m, 2H); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 63.6 (d, $J_{P\text{-}P}$ = 28.2 Hz), 59.6 (d, $J_{P\text{-}P}$ = 28.2 Hz); ^{13}C{^{1}H}{^{31}P} (75 MHz, $CDCl_3$)[24] δ 167.1, 164.4, 153.7, 136.8, 136.0, 133.2, 133.0, 132.7, 132.6, 129.6, 129.5, 128.7, 126.5, 124.9, 122.5, 121.5, 119.1, 33.4, 23.8. Anal. Calcd. for $C_{39}H_{34}BF_4NOP_2Pd$·(0.04 CH_2Cl_2): C, 59.26; H, 4.34; N, 1.77. Found: C, 59.50; H, 4.37; N, 1.76%.

(dppe)Pt(2-(*N*-phenyliminomethyl)phenolate)(BF_4) (1b). To a flask containing 52 mg aniline (0.56 mmol) and 68 mg salicylaldehyde (0.56 mmol) in 50 mL 1 : 1 CH_2Cl_2/MeOH was added 332 mg (dppe)$PtCl_2$ (0.500 mmol), 126 mg $NaBF_4$ (1.15 mmol), and 227 mg Cs_2CO_3 (0.697 mmol). The reaction was heated to reflux for two hours, then cooled to ambient temperature and poured into 50 mL water. The biphase was extracted with CH_2Cl_2 (3×) and the combined extracts were washed with water (2×), dried over $MgSO_4$, and evaporated *in vacuo*. The crude yellow solid was recrystallized from CH_2Cl_2/^{t}BuOMe to yield 361 mg (82%) of **1b** containing 0.03 equiv. CH_2Cl_2. ^{1}H{^{31}P} NMR (400 MHz, $CDCl_3$) δ 8.04 (br s, 1H, $J_{H\text{-}Pt}$ = 460 Hz), 7.86 (d, 4H, J = 7.2 Hz), 7.47 (m, 16H), 7.26 (m, 2H), 6.84 (t, 1H, J = 7.2 Hz), 6.73 (m, 2H), 6.65 (m, 2H), 6.53 (d, 2H, J = 7.6 Hz), 2.54 (m, 2H), 2.32 (m, 2H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 35.9 (d, $J_{P\text{-}P}$ = 11.3 Hz, $J_{Pt\text{-}P}$ = 3314 Hz), 31.9 (d, $J_{P\text{-}P}$ = 11.4 Hz, $^3J_{Pt\text{-}P}$ = 3710 Hz); ^{13}C{^{1}H}{^{31}P} (75 MHz, $CDCl_3$)[24] δ 165.2, 162.4, 153.9, 137.2, 135.5, 133.1, 133.0, 132.5, 129.4, 128.6, 127.1, 126.1, 124.1, 123.0, 121.1, 119.1, 117.6, 34.5, 23.8. Anal. Calcd. for $C_{39}H_{34}BF_4NOP_2Pt$·(0.03 CH_2Cl_2): C, 53.33; H, 3.91; N, 1.59. Found: C, 53.01; H, 3.72; N, 1.55%.

Equilibrium measurements (typical procedure)

A solution of 22.0 mg **1a** (0.0251 mmol) in 1.00 mL of a 0.0250 M stock solution of 4-methylaniline in nitromethane (0.025 mmol) was sealed in a J-Young NMR tube and heated to 60 °C. The reaction was monitored by ^{31}P NMR until no changes were observed in the relative peak areas of the compounds (48–72 hours) at which time three separate ^{31}P spectra were collected.[25] Equilibrium constants were calculated from the average molar ratios of the two $P_2Pt(N,O)$ complexes.

Crystallography

Crystals suitable for X-ray analysis of (dppe)Pd(*N*-(4-methylphenyl)salicyaldimate), prepared analogously to **1b**, were grown at room temperature from a saturated CH_2Cl_2 solution with slow diffusion of pentane. Single crystals were mounted in oil on the end of a fiber. Intensity data were collected on a Siemens SMART diffractometer with CCD detection using Mo-Kα radiation of wavelength 0.710 73 Å (ω scan mode). The structure was solved by direct methods and refined by least squares techniques on F using structure solution programs from the NARCVAX System.[26] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and allowed to ride on the atoms to which they were bonded.

Crystallographic data. Empirical formula = $PdP_2C_{40}H_{36}NOBF_4$; fw (g mol^{-1}) = 801.87; space group = $P2_1/n$; a = 11.8713(10); b = 15.5493(13); c = 20.1471(17) Å; β = 103.517(1)°; V = 3615.9(5) Å^3; Z = 4; T = −100 °C; D_c = 1.473 g cm^{-3}; λ = 0.71073 Å; μ = 0.66 mm^{-1}; R_f = 0.057; R_w = 0.052.

CCDC reference number 269568.

See http://www.rsc.org/suppdata/dt/b5/b501827g/ for crystallographic data in CIF or other electronic format.

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