Supporting Information

Coordinatively Diverse *ortho*-Phosphinoaniline Complexes of Ruthenium and Isolation of a Putative Intermediate in Ketone Transfer Hydrogenation Catalysis

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Table 1. Crystallographic Experimental Details

compound	**2a**	**2b**•C_4H_8O	**2c**	**3b**•$2CH_2Cl_2,H_2O$	**4**	**5**•$0.5CH_2Cl_2$	**6b**	**7**•$0.5C_5H_{12},0.5CH_2Cl_2$
formula	$C_{29}H_{32}Cl_2NPRu$	$C_{33}H_{40}Cl_2NOPRu$	$C_{29}H_{31}ClNPRu$	$C_{32}H_{40}Cl_6NOPRu$	$C_{43}H_{56}Cl_2N_4P_2Ru$	$C_{29.5}H_{35}Cl_3N_4P_2Ru$	$C_{32}H_{34}N_4O_3P_2Ru$	$C_{42}H_{41}ClN_4O_{10}P_2Ru_3$
formula weight	597.50	669.60	561.04	799.39	862.83	714.98	685.64	1162.39
crystal dimens (mm)	0.67 × 0.31 × 0.19	0.51 × 0.22 × 0.08	0.35 × 0.15 × 0.15	0.48 × 0.28 × 0.22	0.32 × 0.28 × 0.14	0.54 × 0.15 × 0.13	0.44 × 0.30 × 0.08	0.38 × 0.16 × 0.12
crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$Pca2_1$ (No. 29)	$Pbca$ (No. 61)	$P2_1$ (No. 4)	$P2_1/n$[a]
a (Å)	7.9672 (4)	15.6106 (13)	8.9830 (4)	10.5904 (7)	36.0666 (14)	16.7298 (14)	11.2706 (12)	17.7363 (5)
b (Å)	18.0587 (9)	11.3767 (9)	15.4775 (6)	14.7948 (9)	10.3284 (4)	16.5689 (14)	12.7184 (14)	12.7680 (3)
c (Å)	18.2121 (9)	18.0365 (15)	18.5190 (8)	22.9421 (14)	22.7085 (9)	22.2494 (19)	11.9508 (13)	21.6124 (6)
α (deg)				96.8793 (9)				
β (deg)	99.7796 (6)	100.2180 (10)	100.5820 (10)	95.4204 (9)			116.9570 (10)	94.7770 (3)
γ (deg)				96.1720 (9)				
V (Å^3)	2582.2 (2)	3152.4 (4)	2530.99 (19)	3527.0 (4)	8459.2 (6)	6167.4 (9)	1526.9 (3)	4877.3 (2)
Z	4	4	4	4	8	8	2	4
ρ_{calcd} (g cm^{-3})	1.537	1.411	1.472	1.505	1.355	1.540	1.491	1.583
μ (mm^{-1})	0.895	0.744	0.806	0.971	0.608	0.899	0.658	1.093
$2\theta_{max}$ (deg)	57.28	55.08	55.08	52.76	54.96	55.06	55.00	54.96
total data collected	23042 (-10 ≤ h ≤ 10, -23 ≤ k ≤ 24, -24 ≤ l ≤ 24)	27171 (-20 ≤ h ≤ 20, -14 ≤ k ≤ 14, -23 ≤ l ≤ 23)	21963 (-11 ≤ h ≤ 11, -20 ≤ k ≤ 19, -24 ≤ l ≤ 24)	28025 (-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28)	71812 (-46 ≤ h ≤ 46, -13 ≤ k ≤ 13, -29 ≤ l ≤ 29)	51801 (-21 ≤ h ≤ 21, -21 ≤ k ≤ 21, -28 ≤ l ≤ 28)	13494 (-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -15 ≤ l ≤ 15)	42128 (-23 ≤ h ≤ 22, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28)
independent reflns (R_{int})	6309 (0.0108)	7228 (0.0416)	5836 (0.0189)	14380 (0.0213)	19378 (0.0401)	7096 (0.0346)	6972 (0.0175)	11166 (0.0214)
obsd reflns [$I \geq 2\sigma(I)$]	6028	5979	5341	12471	17974	6185	6728	9664
restraints/params	0 / 309	0 / 354	0 / 300	6[b] / 771	0 / 939	1[c] / 391	0 / 383	20[d] / 579
Flack abs struct parameter					0.298(12)		–0.005(16)	
goodness-of-fit (all data)[e]	1.045	1.063	1.121	1.070	1.022	1.090	1.097	1.051
R_1 [$I \geq 2\sigma(I)$][f]	0.0198	0.0350	0.0286	0.0332	0.0276	0.0299	0.0239	0.0279
wR_2 [all data][g]	0.0535	0.0897	0.0733	0.0940	0.0647	0.0742	0.0601	0.0860
largest diff peak, hole (e Å^{-3})	0.488, –0.378	0.828, –0.602	0.649, –0.457	2.119, –1.094	0.970, –0.449	0.672, –0.400	0.536, –0.320	1.186 and –0.931 e Å^{-3}

[a]An alternate setting of $P2_1/c$ (No. 14). [b]Distances involving hydrogens of the solvent water molecules were assigned idealized values during refinement (d(O–H) = 0.85 Å; d(H···H) = 1.39 Å). [c]The Cl–C distances within the solvent CH_2Cl_2 molecule were restrained to be equal (within 0.03 Å) during refinement. [d]Distances within the disordered solvent *n*-pentane and CH_2Cl_2 molecules were subject to the following restraints during refinement: $d(C–C)_{n\text{-pentane}}$ = 1.53(1) Å; $d_{1,3}(C\cdots C)_{n\text{-pentane}}$ = 2.50(1) Å; $d(Cl–C)_{CH_2Cl_2}$ = 1.80(1); $d(Cl\cdots Cl)_{CH_2Cl_2}$ = 2.87(1) Å. [e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ where n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$, and a_0 and a_1 are optimized by the refinement program; for **2a**, a_0 = 0.0289, a_1 = 1.3642; for **2b**, a_0 = 0.0410, a_1 = 2.4231; for **2c**, a_0 = 0.0303, a_1 = 2.3504; for **3b**, a_0 = 0.0443, a_1 = 3.7038; for **4**, a_0 = 0.0326, a_1 = 1.9568; for **5**, a_0 = 0.0350, a_1 = 4.3573; for **6b**, a_0 = 0.0346, a_1 = 0.0654; for **7**, a_0 = 0.0459, a_1 = 5.1261. [f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [g]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Selected Structural Parameters for Monophosphinoaniline Complexes.

	2a	**2b**•C_4H_8O	**2c**	**3b**•$2CH_2Cl_2$,H_2O
Atoms	Distances / Å	Distances / Å	Distances / Å	Distances / Å
Ru–P	2.3633(3)	2.2899(7)	2.2925(6)	2.3059(7), 2.3005(7)[a]
Ru–Cl(1)	2.4258(4)	2.3947(6)	2.4050(6)	2.3944(6), 2.3982(6)
Ru–Cl(2)	2.4035(3)	–	–	–
Cl(1)–H1N	2.43	2.16	–	–
Ru–N	–	2.172(2)	2.0861(19)	2.199(2), 2.209(2)
Atoms	Angles / °	Angles / °	Angles / °	Angles / °
Cl(1)–Ru–P	87.262(12)	85.58(2)	90.48(2)	84.27(2), 83.34(2)
Cl(2)–Ru–P	89.887(12)	–	–	–
Cl(1)–Ru–Cl(2)	86.271(12)	–	–	–
Cl(1)–Ru–N	–	83.32(6)	83.86(6)	83.73(6), 83.56(6)
Cl(2)–Ru–N	–	–	–	–
P–Ru–N	–	80.58(6)	80.41(6)	81.27(6), 81.92(6)

[a] Two crystallographically independent molecules.

Table 3. Selected Structural Parameters for Complex **4**.

Atoms	Distances / Å
Ru–Cl(1)	2.3938(6), 2.3928(6)[a]
Ru–P(1)	2.3778(6), 2.3851(7)
Ru–P(2)	2.3313(6), 2.3319(6)
P(1)–C(10)	1.849(2), 1.839(2)
P(2)–C(10)	1.839(2), 1.826(2)
Atoms	Angles / °
Cl(1)–Ru–P(1)	79.60(2), 80.09(2)
Cl(1)–Ru–P(2)	83.60(2), 84.52(2)
P(1)–Ru–P(2)	71.09(2), 71.43(2)
Ru–P(1)–C(10)	91.89(7), 92.03(8)
Ru–P(2)–C(10)	93.67(8), 94.12(8)
P(1)–C(10)–P(2)	95.85(11), 97.43(12)

[a] Two crystallographically independent molecules.

Table 4. Selected Structural Parameters for Complex **5**•$0.5CH_2Cl_2$.

Atoms	Distances / Å	Atoms	Distances / Å
Ru–Cl(1)	2.4793(6)	Ru–P(2)	2.2194(5)
Ru–Cl(2)	2.4903(6)	Ru–N(1)	2.1352(17)
Ru–P(1)	2.2359(9)	Ru–N(3A)	2.168(4)
Atoms	Angles / °	Atoms	Angles / °
Cl(1)–Ru–P(1)	97.215(19)	Cl(2)–Ru–N(3A)	81.72(11)
Cl(2)–Ru–P(2)	103.41(2)	P(1)–Ru–P(2)	72.828(19)
Cl(1)–Ru–N(1)	83.06(5)	Ru–P(1)–C(1)	97.18(6)
Cl(1)–Ru–N(3A)	96.94(11)	Ru–P(2)–C(1)	97.85(6)
Cl(2)–Ru–N(1)	87.08(5)	P(1)–C(1)–P(2)	91.09(9)

Table 5. Selected Structural Parameters for Complex **6b**.

Atoms	Distances / Å
Ru–P(1)	2.3855(6)
Ru–P(2)	2.3878(6)
Ru–C(1)	1.911(2)
Ru–C(2)	1.931(2)
Ru–C(3)	1.905(2)
P(1)–C(10)	1.864(2)
P(2)–C(10)	1.846(2)
Atoms	Angles / °
P(1)–Ru–P(2)	71.41(2)
P(1)–Ru–C(1)	95.99(7)
P(1)–Ru–C(2)	115.59(8)
P(1)–Ru–C(3)	129.55(9)
P(2)–Ru–C(1)	166.34(7)
P(2)–Ru–C(2)	96.74(7)
P(2)–Ru–C(3)	93.43(8)
Ru–P(1)–C(10)	95.44(7)
Ru–P(2)–C(10)	95.83(7)
P(1)–C(10)–P(2)	97.32(10)

Table 6. Selected Structural Parameters for Complex **7**•$0.5C_5H_{12}$,$0.5CH_2Cl_2$.

Atoms	Distances / Å
Ru(1)–Ru(2)	2.8464(3)
Ru(1)–Ru(3)	2.8504(3)
Ru(2)–Ru(3)	2.8567(3)
Ru(1)–P(1)	2.3317(6)
Ru(2)–P(2)	2.3580(6)
Atoms	Angles / °
Ru(1)–Ru(2)–Ru(3)	59.973(7)
Ru(2)–Ru(1)–Ru(3)	60.194(7)
Ru(1)–Ru(3)–Ru(2)	59.833(7)
Ru(1)–Ru(2)–P(2)	94.203(17)
Ru(2)–Ru(1)–P(1)	91.596(7)
P(1)–C(20)–P(2)	118.47(13)