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Formation of a Phosphine–phosphinite Ligand in RhCl(PRR′$_2$)[*P*,*P*-R′(R)POCH$_2$P(CH$_2$OH)$_2$] and R′H from *cis*-RhCl(PRR′$_2$)$_2$[P(CH$_2$OH)$_3$] via P–C Bond Cleavage

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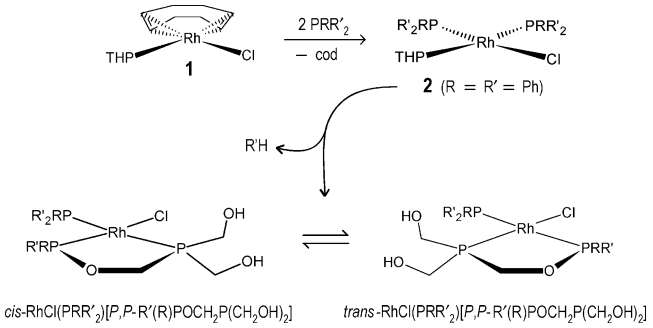
Reaction of RhCl(1,5-cod)(THP), where THP = P(CH$_2$OH)$_3$, with several PRR′$_2$ phosphines (R = or ≠ R′) generates, concomitantly with R′H, the derivatives RhCl(PRR′$_2$)[*P*,*P*-R′(R)POCH$_2$P(CH$_2$OH)$_2$] in two isomeric forms. The hydrogen of the hydrocarbon co-product derives from a THP hydroxyl group which becomes an 'alkoxy' group at the residual PRR′ moiety, this resulting in the *P*,*P*-chelated R′(R)POCH$_2$P(CH$_2$OH)$_2$ ligand. One of the isomers of the PPh$_3$ system, *cis*-RhCl(PPh$_3$)[*P*,*P*-P(Ph)$_2$OCH$_2$P(CH$_2$OH)$_2$], was structurally characterized (cis refers to the disposition of the P atoms with Ph substituents).

Introduction

We have recently reported the syntheses of water-soluble Rh^{I}–THP complexes (THP is tris(hydroxymethyl)phosphine [P(CH$_2$OH)$_3$]),[1] which have potential in the areas of aqueous or aqueous/organic two-phase homogeneous catalysis[2] and in biomedical applications using water-soluble drugs.[3] During a subsequent study of the general reactivity of the complexes with other potential ligands, we have discovered a remarkable reaction of RhCl(cod)(THP) (**1**, cod = 1,5-cyclooctadiene)[1] with PRR′$_2$ tertiary phosphines (R = or ≠ R′). Initially formed rapidly is the *cis*-RhCl(PRR′$_2$)$_2$(THP) species (**2**, detected for the PPh$_3$ and P(*p*-F-C$_6$H$_4$)$_3$ systems), but this slowly converts via a THP-promoted P–C bond cleavage of one of the two PRR′$_2$ ligands to give two isomers of RhCl(PRR′$_2$)[*P*,*P*-R′(R)POCH$_2$P(CH$_2$OH)$_2$] (for example: **3**, R = R′ = Ph; **4**, R = cyclohexyl, R′ = Ph) and the hydrocarbon co-product R′H for which a THP-hydroxy proton provides the hydrogen; the new *P*,*P*-R′(R)POCH$_2$P(CH$_2$OH)$_2$ chelating phosphine–phosphinite ligand contains an 'alkoxy' residue at the residual PRR′ moiety (see Scheme 1). Reaction of **1** with PPh$_3$ provided evidence for intermediate **2** and gave a crystal of **3** that was characterized by X-ray analysis,

Scheme 1. Synthesis of *cis*- and *trans*-RhCl(PRR′$_2$)[*P*,*P*-R′(R)POCH$_2$P(CH$_2$OH)$_2$]



while the corresponding reaction of **1** with PCyPh$_2$ (where Cy = cyclohexyl) to give **4**, in conjunction with the structural data, allowed for analysis of the ^{31}P{^{1}H} NMR data.

Experimental Section

General. The RhCl(cod)(THP) complex (**1**) was synthesized by our recently reported method;[1] the phosphines were used as received from Strem Chemicals, and the reactions with the Rh complex were carried out under Ar using standard Schlenk techniques or in a J-Young NMR tube. MeOH was dried over Mg–I$_2$, and distilled under N$_2$. ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{1}H NMR spectra were measured in CD$_3$OD at room temperature (~300 K), unless stated otherwise, on a Bruker AV400 spectrometer. A residual deuterated solvent proton (relative to external SiMe$_4$) and external 85% aq H$_3$PO$_4$ were used as references (d = doublet, m = multiplet; *J* values given in Hz). Elemental analyses were performed on a Carlo Erba 1108

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(1) Lorenzini, F.; Patrick, B. O.; James, B. R. *Dalton Trans.* **2007**, 3224.
(2) Wiebus E.; Cornils, B. In *Catalyst Separation, Recovery and Recycling*; Cole-Hamilton, D., Tooze, R., Eds.; Springer: Dordrecht, 2006; Chapter 5.
(3) (a) Raghuraman, K.; Pillarsetty, N.; Volkert, W. A.; Barnes, C.; Jurisson, S.; Katti, K. V. *J. Am. Chem. Soc.* **2002**, *124*, 7276. (b) Jurisson, S. S.; Ketring, A. R.; Volkert, W. A. *Transition Met. Chem.* **1997**, *22*, 315.

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analyzer. Mass spectrometry was performed on a Bruker Esquire electrospray (ESI) ion-trap spectrometer with samples dissolved in MeOH, with positive-ion polarity scanning from 60 to 1000 *m/z*. GC (HP-17 capillary column, 25 m × 0.25 mm (0.26 μm film), 50 °C for 20 min): t_R = 1.20 min (benzene). GCMS (Agilent Technologies; 6890N Network GC System, 5975B Inert MSD; HP-chiral column, 30 m × 0.25 mm (0.25 μm film), 50 °C for 20 min): t_R 2.25 min, M = 79 (benzene-d_1).

***cis*- and *trans*-RhCl(PPh$_3$)[*P,P*-P(Ph)$_2$OCH$_2$P(CH$_2$OH)$_2$] (3).** Addition of PPh_3 (15 mg, 0.058 mmol) in MeOH or CH_3COCH_3 (0.5 mL) to a yellow MeOH or CH_3COCH_3 solution (0.5 mL) of **1** (10 mg, 0.027 mmol) at room-temperature results in the immediate formation of a brown solution, but over ∼12 h, the solution becomes yellow and, after ∼2 weeks, X-ray quality yellow crystals (13 mg, 70% yield) of the cis isomer were deposited from a methanol solution. The $^{31}P\{^1H\}$ and ^1H NMR spectra of this system were monitored in CD_3OD (see Results and Discussion), while the NMR spectra of the isolated material are given here. A satisfactory elemental analysis for **3** was not obtained even for the crystal (see Results and Discussion). Mass spectrum: 673 (M^+). ^1H NMR: δ 3.41−4.28 (m, 6 H, POCH_2P(CH_2OH)$_2$), 6.95−7.60 (m, 25 H, C$_6H_5$). $^{13}C\{^1H\}$ NMR: δ 54.51−58.92 (m, POCH$_2$P(CH$_2$OH)$_2$), 129.34−137.38 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (see Figure 2 for labeling): δ 29.62 (m, P$_\alpha$Ph$_3$, P$_A$Ph$_3$, *cis*- and *trans*-**3**), 68.70 (ddd, P_B(CH$_2$OH)$_2$ of *trans*-**3**, $J_{PBRh} \cong 130.5$, $J_{PBPA} \cong 32.6$, $J_{PBPC} \cong 321.4$), and 68.98 (ddd, P_β(CH$_2$OH)$_2$ of *cis*-**3**, $J_{P\beta Rh} \cong 130.5$, $J_{P\beta P\alpha} \cong 32.6$, $J_{P\beta P\gamma} \cong 321.4$), 170.47 (ddd, Ph$_2P_C$O of *trans*-**3**, $J_{PCRh} \cong 147.7$, $J_{PCPA} \cong 33.3$, $J_{PCPB} \cong 321.4$), 170.67 (ddd, Ph$_2P_\gamma$O of *cis*-**3**, $J_{P\gamma Rh} \cong 147.7$, $J_{P\gamma P\alpha} \cong 33.3$, $J_{P\gamma P\beta} \cong 321.4$).

***cis*- and *trans*-RhCl(PCyPh$_2$)[*P,P*-Ph(Cy)POCH$_2$P(CH$_2$OH)$_2$] (4).** The reaction of **1** with $PCyPh_2$ was carried out under conditions identical to those given above for the PPh_3 system, and the system was again monitored by NMR spectroscopy. Maintaining the 12 h reacted solution at ∼ −18 °C for ∼1 week again deposited yellow crystals (15 mg, 78% yield), but these were too small for successful X-ray analysis. Anal. Calcd for $C_{33}H_{45}ClO_3P_3Rh$: C, 54.97; H, 6.29. Found: C, 54.74; H, 6.59. Mass spectrum: 686 (M^+). ^1H NMR: δ 0.49−1.56 (m, 22 H, C$_6H_{11}$), 3.07−4.18 (m, 6 H, POCH_2P(CH_2OH)$_2$), 6.99−7.67 (m, 15 H, C$_6H_5$). $^{13}C\{^1H\}$ NMR: δ 26.20−36.35 (m, C_6H_{11}), 57.51−60.80 (m, POCH$_2$P(CH$_2$OH)$_2$), 128.44−135.98 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (Figure 2): *cis*-**4**, δ 28.94 (ddd, P_α, $J_{P\alpha Rh}$ = 132.3, $J_{P\alpha P\beta}$ = 292.0, $J_{P\alpha P\gamma}$ = 26.4), 82.25 (ddd, P_β, $J_{P\beta Rh}$ = 139.3, $J_{P\beta P\alpha}$ = 292.0, $J_{P\beta P\gamma}$ = 32.1), 196.02 (P_γ, $J_{P\gamma Rh}$ = 199.2, $J_{P\gamma P\alpha}$ = 26.4, $J_{P\gamma P\beta}$ = 32.1); *trans*-**4**, δ 29.83 (P_A, J_{PARh} = 120.5, J_{PAPB} = 33.7, J_{PAPC} = 352.3), 78.60 (P_B, J_{PBRh} = 180.8, J_{PBPA} = 33.7, J_{PBPC} = 34.6), 184.36 (P_C, J_{PCRh} = 148.0, J_{PCPA} = 352.3, J_{PCPB} = 34.6).

Other Phosphine Systems. The in situ reactions (under conditions identical to those described above) of **1** with PEtPh$_2$, PMePh$_2$, P(*p*-tol)$_3$, P(*p*-F-C$_6$H$_4$)$_3$, and P^{n}Pr$_3$ were monitored by NMR as for the PPh_3 and $PCyPh_2$ systems. No solid complexes were isolated; the δ_H and δ_P shift values and *J* values for all the systems are in Tables S1 and S2, respectively, in the Supporting Information.

X-ray Crystallographic Analysis of *cis*-3. Measurements were made on a Bruker X8 APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); data were collected and integrated using the Bruker SAINT software package[4] and were corrected for absorption effects using the multiscan technique (SADABS),[5] with minimum and maximum transmission coefficients of 0.770 and 0.942, respectively. The data were corrected for Lorentz and polarization effects, and the structures were solved by direct methods.[6] Crystallographic data: $C_{35}H_{41}O_5P_3RhCl$, MW = 772.95, triclinic, $P\bar{1}$ (No. 2), a = 10.472(1) Å, b = 11.607(1) Å, c = 14.588(2) Å, α = 87.553(6)°, β = 78.799(5)°, γ = 83.749(5)°, V = 1728.6(3) Å,[3] T = 173.0(1) K, Z = 2, μ(Mo K$_\alpha$) = 7.51 cm^{-1}, 8381 independent reflections measured, D_{calcd} = 1.485 g cm^{-3}, R1 = 0.051, wR2 = 0.068 (for $I > 2\sigma(I)$), and 424 refined parameters. CCDC No. 651551.

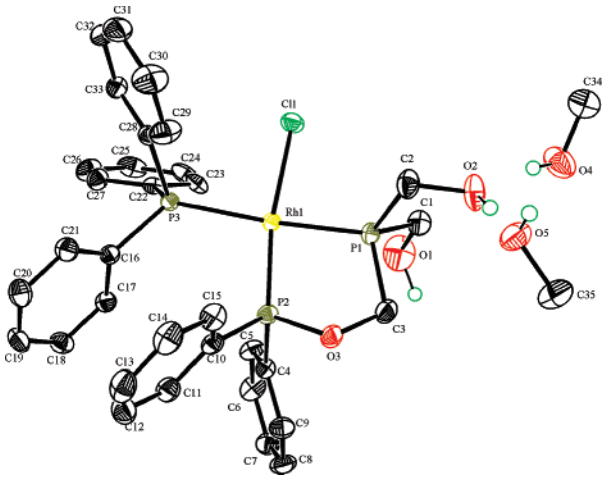

Figure 1. Structure of *cis*-RhCl(PPh$_3$)[*P,P*-P(Ph)$_2$OCH$_2$P(CH$_2$OH)$_2$] (**3**)·2CH$_3$OH, with 50% probability ellipsoids. Selected distances (Å) and angles (deg): Rh(1)−P(1), 2.2174(6); Rh(1)−P(2), 2.1487(6); Rh(1)−P(3), 2.3205(6); Rh(1)−Cl(1), 2.4054(6); P(1)−Rh(1)−P(2), 83.37(2); P(1)−Rh(1)−P(3), 175.04(2); P(1)−Rh(1)-Cl(1), 87.56(2); P(2)−Rh(1)-P(3), 100.62(2); P(2)−Rh(1)-Cl(1), 170.93(2); P(3)−Rh(1)-Cl(1), 88.44(2).

Results and Discussion

The room-temperature reaction of the yellow complex **1** with PPh_3 in MeOH is summarized in Scheme 1. The immediately formed brown solution by $^{31}P\{^1H\}$ and ^1H NMR spectra shows loss of **1** (δ_P 17.7, d, J_{RhP} = 145), essentially complete formation of an intermediate, **2**, free cod, and trace amounts of free PPh_3 (δ_P −4.30, s), free THP (δ_P −25.0, s), and RhCl(cod)(PPh$_3$) (δ_P 31.9, d, J_{RhP} = 150).[7] Species **2** is characterized by three doublets of doublets of doublets for the three inequivalent P atoms: δ 20.07 (P_a(THP), J_{PaRh} = 142.2, J_{PaPb} = 321.4, J_{PaPc} = 38.6),[8] 34.88 (P_bPh$_3$ trans to THP, J_{PbRh} = 130.5, J_{PbPa} = 321.4, J_{PbPc} = 38.6), and 50.89 (P_cPh$_3$ trans to Cl, J_{PcRh} = 192.9, J_{PcPa} = 38.6, J_{PcPb} = 38.6). The $^{31}P\{^1H\}$ spectrum changes over ∼12 h (as the solution becomes yellow) to one unresolved multiplet at δ 29.62, and ddd patterns at δ 68.70 and 68.98 and at δ 170.47 and 170.67, the spectrum being essentially unchanged down to 213 K. After consideration of the corresponding spectrum for the $PCyPh_2$ system (see below), these resonances result from a roughly 1:1 mixture of *cis*- and *trans*-**3**, each isomer having three inequivalent P atoms; some of the *J* values for the δ 29.62 resonance can be retrieved from the other two resonances (see Experimental Section, and Tables S1 and S2).

(4) *SAINT*, Version 7.03A; Bruker AXS Inc.: Madison, WI, 1997−2003.

(5) *SADABS. Bruker Nonius area detector scaling and absorption correction*, V2.10; Bruker AXS Inc.: Madison, WI, 2003.

(6) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(7) Elsevier, C. J.; Kowall, B.; Kragten, H. *Inorg. Chem.* **1995**, *34*, 4836.

(8) Assignment of δ 20.07 to the THP ligand is based on data from ref 1.

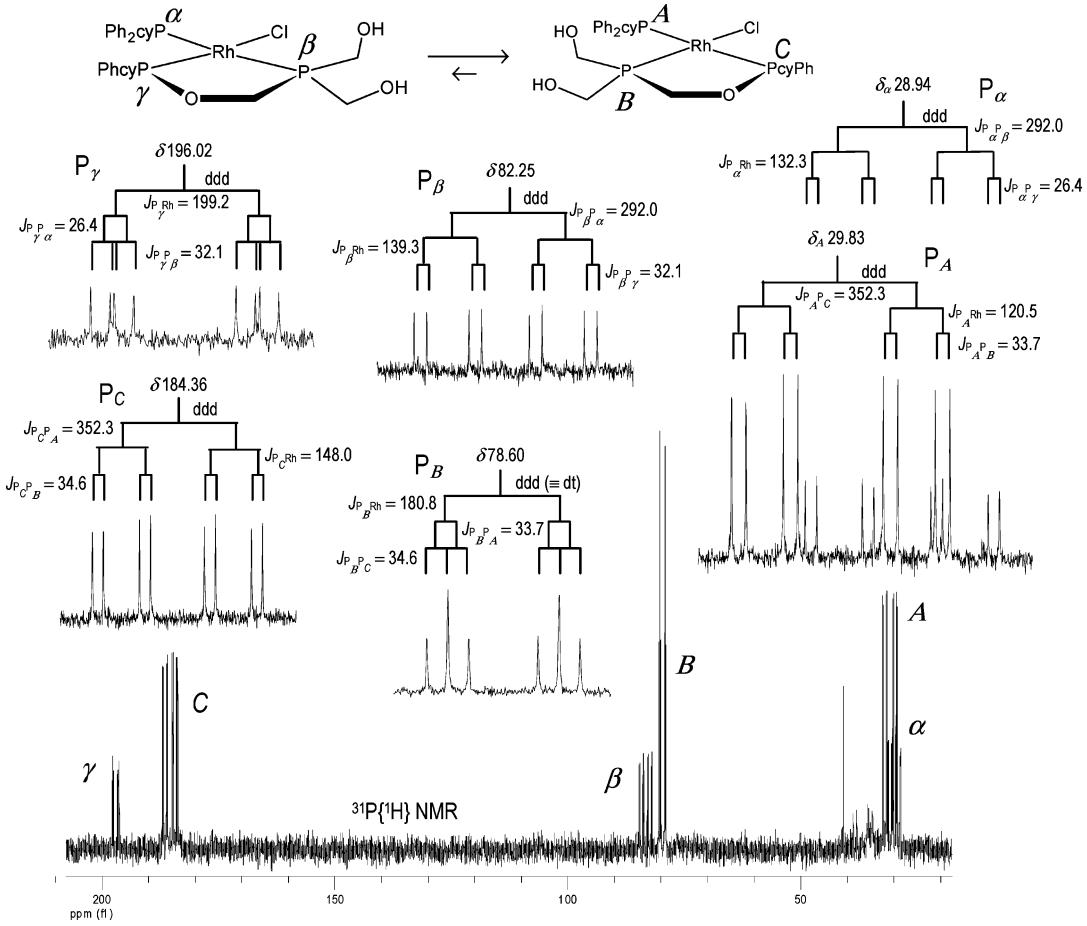

Figure 2. $^{31}P\{^1H\}$ NMR spectrum of *cis*- and *trans*-RhCl(PCyPh$_2$)[*P*,*P*-Ph(Cy)POCH$_2$P(CH$_2$OH)$_2$] (**4**) (cis/trans = 1:4).

The key to elucidating the chemistry resulted from slow precipitation (after 2 weeks) of X-ray quality, yellow crystals. The crystallographic analysis revealed that the structure was that of *cis*-**3**, the asymmetric unit containing two CH_3OH solvate molecules (Figure 1); cis refers to the disposition of the P atoms with Ph substituents. The structure revealed that P−C bond cleavage of a P−C_6H_5 moiety had occurred and a −CH_2OH of the THP had been converted to an alkoxy moiety that had replaced the Ph group (Scheme 1); the C_6H_6 co-product was detected quantitatively by GC and, when the reaction was carried out in CD_3OD, which resulted in D/H exchange with the hydroxyl protons of THP, C_6H_5D was detected by GCMS. Thus, the square planar Rh^I complex contains the novel, *P*,*P*-chelating phosphine−phosphinite $Ph_2POCH_2P(CH_2OH)_2$ ligand, with the metal being 0.030(5) Å out of the mean plane. Within the asymmetric unit, there are 12 intermolecular O- -H bonds, which are common within Rh^I−THP complexes.[1] There are three strong H-bonds (O- -H = 1.71−1.73 Å) between the hydroxyl-hydrogen of a P(CH_2OH) and the O atom of CH_3OH, one strong H-bond (O- -H = 1.78 Å) between an O atom of a P(CH_2OH) and the hydroxyl-hydrogen of CH_3OH, and eight weaker H-bonds (O- -H = 2.53−2.62 Å): two between the *m*-H-atom of a Ph and the O atom of P(CH_2OH), two between the *p*-H-atom of a Ph and the O atom of CH_3OH, two between the H atom of a P(CH_2OH)-methylene and the O atom of CH_3-OH, and two between the H atom of the PCH_2OP methylene and the O atom of CH_3OH. The $^{31}P\{^1H\}$ spectrum of a methanol solution of the crystal still revealed a 1:1 mixture of *cis*- and *trans*-**3**, implying rapid equilibrium between the two isomers in solution, and the independence of the isomer ratio with temperature implies a thermoneutral equilibrium, which seems reasonable for the very similar isomeric structures. The $^{31}P\{^1H\}$ and ^1H NMR spectra show that the 1:1 mixture is indefinitely stable in solution under Ar. An unsatisfactory elemental analysis for **3** is thought, based on $^{31}P\{^1H\}$ data, which sometimes showed trace doublet peaks at δ 31.9 (J = 150) and 27.9 (J = 127), to be due to the presence of traces of RhCl(cod)(PPh_3)[7] and *trans*-RhCl(CO)-(PPh_3)$_2$;[9] the carbonyl ligand could arise via decarbonylation of formaldehyde which can be readily formed from transition metal−THP species.[10]

The corresponding reaction of $PCyPh_2$ is qualitatively the same as that with PPh_3, the immediately formed brown solution showing no $^{31}P\{^1H\}$ signal for **1**, some free $PCyPh_2$ (δ −3.03) and a complicated mixture of products showing δ values between 20.23 and 66.67, but we were unable to detect the intermediate *cis*-RhCl($PCyPh_2$)$_2$(THP), analogous to that seen in the PPh_3 system. The $^{31}P\{^1H\}$ NMR spectrum changes over ∼10 h to one showing just two sets of three

(9) O'Connor, J. M.; Ma, J. *Inorg. Chem.* **1993**, *32*, 1866.
(10) (a) Higham, L. J.; Whittlesey, M. K.; Wood, P. T. *J. Chem. Soc. Dalton Trans.* **2004**, 4202. (b) Hoye, P. A. T.; Pringle, P. G.; Smith M. B.; Worboys, K. *J. Chem. Soc. Dalton Trans.* **1993**, 269.

doublets of doublets of doublets due to *cis*- and *trans*-**4** (Scheme 1, Figure 2, and Tables S1 and S2); these species were readily identified because the cis/trans ratio was now 1:4. Benzene was again formed over the 10 h reaction time. The $^{31}P\{^1H\}$ assignments are consistent with literature data: formation of the five-membered ring and the electron-withdrawing effect of the O atom bound to P_γ (in *cis*-**4**) and P_C (in *trans*-**4**) atoms result in the very low-field signals for these P atoms,[11] while the large $^2J_{P\alpha P\beta}$ and $^2J_{PAPC}$ coupling constants define the mutually trans positions of these P atoms, and the $^1J_{RhP}$ values are in the normal range.[12] The ^1H NMR signals in CD_3OD for the inequivalent methylene protons of the reactant THP within *cis*- and *trans*-**4** in CD_3OD appear as a multiplet in the range δ 3.07−4.18 (similar to the corresponding data for the PPh_3 system, Table S1). Some isolated yellow crystals were well characterized as an isomeric mixture by elemental analysis, NMR spectroscopy, and MS data; the $^{31}P\{^1H\}$ NMR spectra of the crystals dissolved in CD_3OD and of the in situ solution reveal (as for the PPh_3 system) that the isomer ratio was unchanged from 298 to 213 K.

The reactivity of **1** with $PEtPh_2$, $PMePh_2$, P(*p*-tol)$_3$, P(*p*-F-C_6H_4)$_3$, and P^nPr_3 was qualitatively the same as that described for the PPh_3 and $PCyPh_2$ systems: in situ reactions revealed P−C bond cleavage with formation of *cis*- and *trans*-RhCl(PRR′$_2$)[*P*,*P*-R′(R)POCH$_2$P(CH$_2$OH)$_2$] in a ratio of ∼1, with concomitant generation of the hydrocarbon: benzene for the first two systems and then, respectively, toluene, fluorobenzene, and propane. The $^{31}P\{^1H\}$ and ^1H NMR data for the cis and trans isomer products, using the labeling of Figure 2, are summarized in Tables S1 and S2. Further evidence for an intermediate such as **2** (seen with PPh_3, Scheme 1) was seen only in the P(*p*-F-C_6H_4)$_3$ system, where *cis*-RhCl(P(*p*-F−C_6H_4)$_3$)$_2$(THP) was detected: δ_P 20.00 (ddd, P_a(THP), J_{PaRh} = 130.9, J_{PaPb} = 324.0, J_{PaPc} = 40.7), 33.78 (ddd, P_b(*p*-F−C_6H_4)$_3$ trans to THP, J_{PbRh} = 142.9, J_{PbPa} = 324.0, J_{PbPc} = 38.0), and 49.06 (ddd, P_c(*p*-F−C_6H_4)$_3$ trans to Cl, J_{PcRh} = 192.5, J_{PcPa} = 40.7, J_{PcPb} = 38.0). The aryl-containing phosphine systems took ∼12 h to generate the equilibrium isomer mixture, while the P^nPr_3 system was noticeably slower (>1 day); this is consistent with more general facile, metal-catalyzed cleavage of P−aryl bonds versus P−alkyl bonds, at least as substantiated under homogeneous hydroformylation and hydrogenation conditions, where such cleavage is critical in determining catalytic activity.[13] Of note, reaction of **1** with THP generates RhCl(THP)$_4$ and no P−C bond cleavage is seen.[1]

Reports on cleavage of a P−C bond concurrent with formation of a P−O bond are rare. A close analogue of our system is seen in work from Pringle's group,[10b] which reported P−C bond cleavage at Pt^{II} and Pd^{II} centers during studies on metal complex-catalyzed addition of PH_3 to formaldehyde to give THP: [M{*P*,*P*-(HOCH$_2$)$_2$POCH$_2$P(CH$_2$OH)$_2$}$_2$]Cl$_2$ complexes were isolated as a cis/trans mixture from reaction of *cis*-MCl$_2$(THP)$_2$ (M = Pt, Pd) with excess THP in methanol. Analogous to our Rh systems, a phosphine−phosphinite ligand has been formed, but in contrast to the Rh species, the substituents at each P atom are hydroxymethyl; the Pt and Pd complexes were well characterized but not crystallographically. A complicated multistep mechanism was presented and involved initial formation of a binuclear metal alkoxide derived from deprotonation of a coordinated P(CH$_2$OH)$_3$ and a final ring closure by nucleophilic attack of a coordinated PCH$_2$O$^-$ moiety at a second (mutually cis) coordinated P atom; the proton was incorporated into a phosphonium species, while in our work the proton becomes a component of a hydrocarbon product. A similar proton loss from the THP and ring closure by nucleophilic attack at a *cis*-PRR$_2$′ moiety is likely the essential mechanism in our Rh systems; none of the commonly proposed mechanisms for metal-catalyzed P−C bond cleavage (oxidative insertion of a low-valent metal into the aryl− and alkyl−phosphorus bonds, electrophilic substitution, and *o*-metalation processes)[14,15] seems appropriate for the Rh systems. A related example from Pregosin's group[16] is P−C bond cleavage of a OTf−Ru^{II}−P(OH)Ph$_2$ moiety induced by external MeOH to form a species containing the Ph−Ru^{II}−P(OH)(OMe)Ph moiety with HOTf as co-product; here the MeOH proton removes coordinated triflate which is replaced by a Ph of the phosphine and the methoxide replaces the phosphine phenyl. Less germane examples of P−C bond cleavage within a coordinated PPh_3 with co-formation of a P−O bond include that of an Ir^{III} system, the cleavage being induced by a carbonyl oxygen of a coordinated dibenzoylmethylene moiety,[17] and that of a Pd^{II} system, where an acetate ligand provides the oxygen source.[18] We are unaware of any reports of cleavage of an aryl−phosphine P−C bond induced by a −CH$_2$OH functionality, with co-formation of a hydrocarbon. More common for coordinated THP is loss of formaldehyde with formation

(11) (a) Hoge, B.; Thösen, C.; Pantenburg, I. *Chem. Eur. J.* **2006**, *12*, 9019. (b) Artyushin, O.; Odinets, I.; Goryunov, E.; Fedyanin, I.; Lyssenko, K.; Mastryukova, T.; Röschenthaler, G.-V.; Kégl, T.; Keglevich, G.; Kollár, L. *J. Organomet. Chem.* **2006**, *691*, 5547. (c) Kim, Y.; Verkade, J. G. *J. Organometal. Chem.* **2003**, *669*, 32. (d) Arena, C. G.; Faraone, F.; Graiff, C.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2002**, 711. (e) Nifantyev, E. E; Koroteev, M. P.; Koroteev, A. M.; Belsky, V. K.; Stash, A. I.; Antipin, M. Y.; Lysenko, K. A.; Cao, L. *J. Organomet. Chem.* **1999**, *587*, 18. (f) Bergamini, P.; Costa, E.; Orpen, A G.; Pringle, P. G.; Smith, M. B. *Organometallics* **1995**, *14*, 3178. (g) Li, Y. W.; Newton, M. G.; King, R. B. *J. Organomet. Chem.* **1995**, *488*, 63. (h) Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095. (i) Allison, D. A.; Clardy, J.; Verkade, J. G. *Inorg. Chem.* **1972**, *11*, 2804.

(12) (a) Cipot, J.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 594. (b) Han, Li-B.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 13698. (c) Marcazzan, P.; Patrick, B. O.; James, B. R. *Organometallics* **2005**, *24*, 1445. (d) Raebiger, J. W.; Dubois, D. L. *Organometallics* **2005**, *24*, 110. (e) Merckle, C.; Blümel, J. *Top. Catal.* **2005**, *34*, 5.

(13) (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. (b) Sakakura, T.; Kobayashi, T.-A.; Hayashi, T.; Kawabata, Y.; Tanaka, M.; Ogata, I. *J. Organomet. Chem.* **1984**, *267*, 171.

(14) Kikukawa, K.; Yamane, T.; Ohbe, Y.; Takagi M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1187.

(15) (a) Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1984**, *3*, 649. (b) Goel, A. B. *Inorg. Chim. Acta* **1984**, *84*, L25. (c) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1310.

(16) Geldbach, T. J.; Drago, D.; Pregosin, P. S. *Chem. Comm.* **2000**, 1629.

(17) Cowie, M.; Gauthier, M. D.; Loeb, S. J.; McKeer, I. R. *Organometallics* **1983**, *2*, 1057.

(18) Kikukawa, K.; Matsuda, T. *J. Organomet. Chem.* **1982**, *235*, 243.

of $PH(CH_2OH)_2$, a reverse step in metal complex-catalyzed synthesis of THP from PH_3 and CH_2O.[10]

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Supporting Information Available: General experimental procedure, ^1H and $^{31}P\{^1H\}$ NMR data (Tables S1, S2), and CIF file for *cis*-**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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