The First Ru(η^3-PCP) Complexes of the Electron-Rich Pincer Ligand 1,3-Bis((dicyclohexylphosphino)methyl)benzene: Structure and Mechanism in Transfer Hydrogenation Catalysis

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Mild routes to the first Ru(η^3-pincer) derivatives of bis((dicyclohexylphosphino)methyl)-benzene are reported. RuCl(η^3-PCP)(PPh_3) (**3**·PPh_3; PCP = [2,6-(Cy_2PCH_2)$_2C_6H_3$]) is formed quantitatively on reaction of the PC(H)P-arene ligand with $RuCl_2(PPh_3)_3$ at 22 °C in the presence of base. Treatment of **3**·PPh_3 with KHB^sBu_3 under nitrogen atmosphere generates RuH(η^3-PCP)(PPh_3)(N_2), **4**, as a mixture of conformational isomers in which the hydride and N_2 ligands are trans or cis (**4a** or **4b**, respectively). On exposure to H_2, **4a/b** undergo immediate, quantitative exchange of bound N_2 for η^2-H_2, affording the corresponding isomers of RuH(η^3-PCP)(PPh_3)(H_2), **5a/b**. Complex **3**·PPh_3 resists displacement of PPh_3 by H_2 at 22 °C, but on exposure to CO, readily yields RuCl(η^3-PCP)$(CO)_2$, **6**. Transfer hydrogenation of ketones is efficiently catalyzed by **3**·PPh_3 and **4**, in a pathway involving loss of PPh_3 and (for **3**) exchange of chloride for hydride. The duration of pretreatment of **3**·PPh_3 with base (KOH, ^{t}BuOK) in refluxing 2-propanol is critical to activity, and indirect evidence supports formation of a catalytically active dihydride species during this process. X-ray crystal structures are reported for **3**, **4a**, **5a**, and **6**.

Introduction

Organometallic complexes containing monoanionic, terdentate pincer ligands have been intensively studied over the past decade, driven in large part by the potential of such species in catalysis.[1−6] While group 9 and 10 metal complexes with aryl- and alkyl-PCP ligands have received much attention, the PCP pincer chemistry of group 8 metals has focused principally on the important family of arylphosphine derivatives. Such ruthenium pincer complexes exhibit versatile catalytic activity in (e.g.) transfer hydrogenation, Kharasch addition, atom-transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), and oxidative coupling of arenes with alkenes.[1−3,6−9] Electron-rich alkylphosphine derivatives can expand opportunities for modulating activity and selectivity, and for introduction of chirality. Examples of alkylphosphine pincer complexes in group 8 chemistry are confined, however, to *tert*-butyl[10−12] and isopropyl[13] PCP ligands. In view of the profound influence of pincer ligand properties and chelate bite angles on structure and reactivity,[12,14a] and motivated by the remarkably high transfer-hydrogenation activity of the cyclohexylphosphine complex [RuH_3(dcypb)(CO)]$^-$ (dcypb = 1,4-bis-(dicyclohexyl)phosphinobutane),[15] we undertook investigation of the chemistry of the cyclohexyl-PCP pincer systems, group 9 and 10 complexes of which have been studied by the Cross[14] and Park[16] groups. We recently

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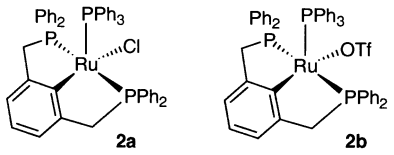
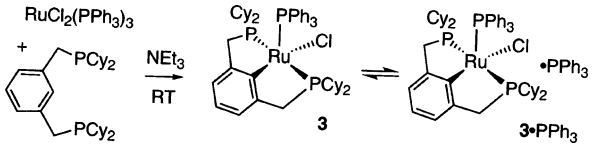
Chart 1



Scheme 1



reported the first ruthenium complex of 1,3-bis(dicyclohexylphosphino)methyl)benzene, 1,3-$(Cy_2PCH_2)_2C_6H_4$, an η^2-PC(H)P-arene complex bearing an alkylidene ligand.[17] Here we describe a mild route to η^3-pincer Ru(II) derivatives containing a chloride or hydride ligand, their reactivity toward small molecules, including N_2, H_2, and CO, and their high activity in transfer hydrogenation of aryl ketones.

Results and Discussion

Convenient access to an η^3-pincer derivative of the bulky ligand 1,3-$(CH_2P^tBu_2)_2C_6H_4$ has been established from $[RuCl_2(COD)]_n$.[10a] RuX[η^3-2,6-$(P^tBu_2CH_2)_2C_6H_3$](CO) (**1a**, X = Cl) was obtained in good yields from these precursors by decarbonylation of isoamyl alcohol in the presence of NEt_3 as base. Attempts to access Ru(η^3-PCP) complexes via the corresponding reaction of 1,3-$(Cy_2PCH_2)_2C_6H_4$ were frustrated by formation of PP-bridged species.[18] We find that $RuCl_2(PPh_3)_3$ functions as a much more tractable precursor to the desired pincer complexes, as earlier found for the synthesis of RuX[η^3-2,6-$(CH_2PPh_2)_2C_6H_3$](PPh_3) (**2a**, X = Cl; Chart 1).[19,20] Thus, we observe quantitative formation of RuCl(η^3-PCP)(PPh_3)·PPh_3 (**3**·PPh_3) on reaction of $RuCl_2(PPh_3)_3$ with the PC(H)P-arene ligand at room temperature in the presence of NEt_3 (Scheme 1; isolated yield ca. 80%). The added base serves to scavenge the HCl liberated. While it has previously been noted that the $RuCl_2(\eta^2$-PC(H)P-arene) intermediate can be sufficiently acidic to be deprotonated by NEt_3,[10,21,22] the driving force for activation of the C−H (arene) bond in the present reaction is sufficient that **3** is observed at 22 °C even in the absence of added base. Direct cyclometalation of electron-donating alkylphosphine pincer ligands typically requires forcing temperatures.[2] Optimum yields of **1a**, for example, require refluxing at 120 °C for 24 h.[10a] Reaction of $RuCl_2(PPh_3)_3$ with 1,3-$(^iPrCH_2)_2C_6H_4$ similarly requires thermolysis at 110 °C in THF using a pressure vessel.[13]

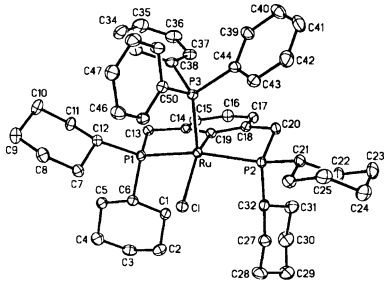


Figure 1. ORTEP diagram of **3**·THF; thermal ellipsoids set at the 30% probability level. Hydrogen atoms and THF solvate are omitted for clarity. Key structural parameters are summarized in Table 2.

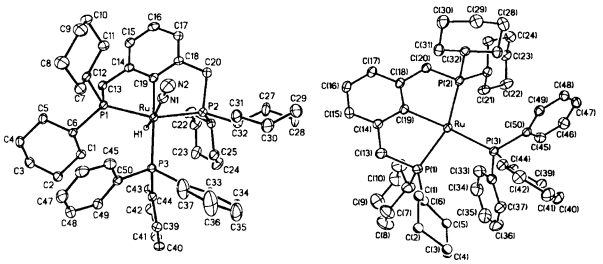


Figure 2. ORTEP diagrams of **4a**·Et_2O (left) and **5a** (right); ellipsoids set at the 30% probability level. Non-hydridic hydrogen atoms and solvent molecule (**4a**) are omitted for clarity. Hydride and dihydrogen ligands are not located for **5a**. Key parameters are given in Table 2. Additional values for **4a** (distances in Å, angles in deg): Ru−N(1), 2.014(4); N(1)−N(2), 1.111(6); H(1)−Ru−N(1), 173(1); Ru−N(1)−N(2), 178.3(4).

Spectroscopic and microanalytical data for **3**·PPh_3 are consistent with a square pyramidal structure, with a basal PCP ligand and a PPh_3 ligand, occupying the apical site. A doublet of virtual triplets is observed for one of the methylene protons in each "elbow" (δ 2.90; $^2J_{HH}$ = 16.7 Hz, $^vJ_{HP}$ = 5.2 Hz) and a broad doublet for the other (δ 2.55; $^2J_{HH}$ = 12.2 Hz). The ^{31}P NMR spectrum (Table 1) consists of an A_2X spin system, indicating trans-disposition of the two equivalent PCy_2 groups, and a singlet for free PPh_3 at −5.46 ppm. While the latter signal does not diminish perceptibly on trituration or reprecipitation, a crystal structure determination reveals the complex devoid of "solvating" PPh_3 (Figure 1).

Hydride derivatives of Ru-pincer complexes are thought to be key intermediates in transfer hydrogenation via **2a**,[2,3] and are also of interest for their potential as precursors to alkylidene derivatives.[17,23] In undertaking transformation of **3**·PPh_3 to the hydride, we chose to use KBH^sBu_3, in preference to more conventional hydride sources, in the hope of circumventing deprotonation of the pincer "arms"[2] or formation of borohydride complexes.[10b] Addition of KHB^sBu_3 to **3**·PPh_3 under nitrogen atmosphere resulted in clean transformation into two new products (ratio 1:1), the ^{31}P NMR signals for which correlate by EXSY-NMR. Two A_2X patterns

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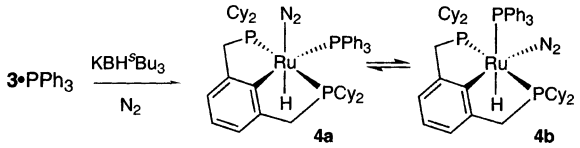
Table 1. Summary of Key NMR Data for Complexes 3−5[a]

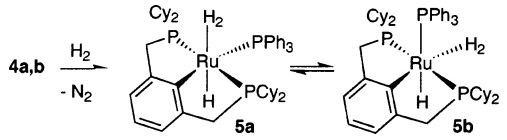
compd	solvent	$\delta_{P(A)}$ PCP	$\delta_{P(B)}$ PPh_3	$^2J_{PP}$	δ_H, Ru*H*	$^2J_{HP}$ cis	$^2J_{HP}$ trans	δ_H, Ru(H_2)
3	C_6D_6	35.7	80.9	32				
	2:1 ^{i}PrOH/C_7D_8	37.0	81.2	31				
4a[b]	C_6D_6	59.6	45.0	17	−12.2 (q)	19.5 (s)		
	2:1 ^{i}PrOH/C_7D_8	60.5	45.6	17				
4b	C_6D_6	54.6	28.8	14	−8.05 (dt)	21.8 (s)	90	
	2:1 ^{i}PrOH/C_7D_8	55.5	29.4	14				
5a	C_6D_6	68.1	56.6	18	−8.70 (q)	18.9 (s)	-	−4.34 (s)
	2:1 ^{i}PrOH/C_7D_8	68.9	57.0 (br s)	16				
5b	C_6D_6	71.1	37.1	14	−10.64 (dt)	21.7 (s)	80	−7.08 (s)
	2:1 ^{i}PrOH/C_7D_8	71.8	37.8 (br s)	15				

[a] 300 MHz (^{1}H); 121 MHz (^{31}P); 295 K, *J* in Hz. All PCP signals doublets; all PPh_3 signals triplets, unless otherwise noted. [b] Spectra at 253 K; unresolved at 295 K.

Scheme 2



Scheme 3



are observed, confirming retention of bound PPh_3: that for **4b** is well resolved at room temperature (295 K), while the doublet for the PCP ligand within **4a** emerges only on cooling to 253 K. These species could not be separated, but were isolated as a mixture in 87% yield. On the basis of X-ray analysis for **4a** (Figure 2), supported by spectroscopic and microanalytical data for the mixture, we identify the products as conformational isomers of RuH(η^3-PCP)(PPh_3)(N_2), **4** (**4a**, hydride trans to N_2; **4b**, hydride cis to N_2; Scheme 2).

NMR evidence excludes the possibility that the **4a**−**4b** equilibrium involves reversible coordination of N_2, i.e., assignment of **4b** as square pyramidal RuH(η^3-PCP)(PPh_3). The downfield location of the hydride signal (δ_{RuH} −8.05, doublet of triplets; Table 1) indicates that this ligand is not trans to an empty coordination site (for which δ_{RuH} values of −25 to −30 ppm are expected[10b,24]), while its multiplicity confirms that the hydride ligand is trans to one phosphorus ligand and cis to two others. In comparison, the hydride signal for **4a** is poorly resolved at room temperature, appearing as a very broad resonance centered at −12 ppm, barely visible above the baseline. The breadth of the peak suggests increased lability for N_2 trans to hydride. The signal resolves into a quartet on cooling to 253 K: its multiplicity and the magnitude of the coupling constant ($^2J_{PH}$ = 19.5 Hz; Table 1) indicate a cis relationship between the hydride ligand and all three phosphorus nuclei. Both hydride signals display the long T_1(min) relaxation times characteristic of hydride ligands: 359 ms for **4a** (278 K, 500 MHz) and 333 ms for **4b** (282 K, 500 MHz). Observation of only two IR bands for ν(Ru−H) and ν(N≡N) (2114, 2134 cm^{-1}) may indicate the presence of a single isomer in the solid state.

Retention of N_2 within the coordination sphere in **4a** and **4b** contrasts with formation of a coordinatively unsaturated product on reaction of **2a** with sodium hydride under nitrogen atmosphere.[20b] Facile formation of dinitrogen adducts has been reported[10b] in related Ru[η^3-2,6-($P^tBu_2CH_2$)$_2$$C_6H_3$] chemistry, and we earlier noted the potency of N_2 as a stabilizing ligand in Ru-dcypb complexes.[25]

Exchange of bound N_2 for H_2 is facile for **4a/b**, but not for chloride complex **3**. Complex **3** undergoes no spectroscopically observable reaction under 1 atm H_2 after 1 h at RT. After 24 h, a new A_2B system is apparent in the ^{31}P NMR spectrum, but this accounts for only 7% of the total integrated intensity (δ 53.6 (d), 23.2 (t), $^2J_{PP}$ = 16.3 Hz). The multiplicity indicates retention of PPh_3, as well as the pincer ligand, within the coordination sphere, and the structure is tentatively assigned as RuCl(η^3-PCP)(PPh_3)(H_2). Under the same conditions, the N_2 ligand in **4a/b** is displaced within minutes by H_2 (Scheme 3). The reaction yields RuH(η^3-PCP)(PPh_3)(H_2), **5a/b**, again as a mixture of two conformational isomers, with hydride trans (**5a**) or cis (**5b**) to dihydrogen: the cis isomer predominates by a ratio of 3:1. (The high stability of hydride cis to H_2 has been noted[26] and may provide a driving force for exchange in the case of **4**, versus **3**.) Four distinct sets of ^{1}H NMR resonances appear in the hydride region for **5a/b**. Again, the downfield location of the hydride signals (−8.70, −10.64 ppm) argues for a coordinatively saturated structure. Coupling to three cis ^{31}P nuclei splits the hydride signal for **5a** into a quartet, while that for **5b** appears as a doublet of triplets, split by one trans and two cis ^{31}P nuclei. The dihydrogen ligands give rise to two broad singlets, each integrating to twice the intensity of the corresponding hydride. The T_1(min) relaxation time for the dihydrogen ligand in **5b** is longer than that in **5a**, as expected for a dihydrogen ligand perturbed by interaction with a cis-hydride (**5a**, 20 ms; **5b**, 24 ms; both at 265 K, 500 MHz). ^{31}P NMR analysis reveals two A_2X patterns, which do not correlate in EXSY-NMR experiments, indicating that exchange between **5a** and **5b** is slow on the NMR time scale. Indeed, binding of H_2 is sufficiently strong in **5a** that crystals could be grown by evaporation of a benzene

(24) The high trans influence of hydride is manifested in a strong site preference: this ligand normally takes up the apical site in square pyramidal complexes, for which these diagnostic upfield chemical shifts are observed. See, for example: Marchenko, A. V.; Huffman, J. C.; Valerga, P.; Tenorio, M. J.; Puerta, M. C.; Caulton, K. G. *Inorg. Chem.* **2001**, *40*, 6444.

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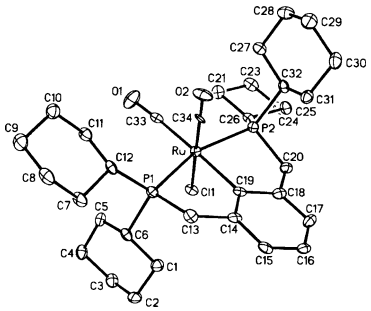
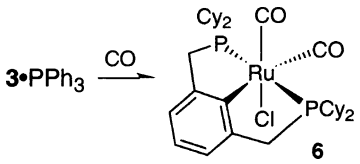


Figure 3. ORTEP diagram for **6**. Selected bond lengths (Å) and angles (deg) (where two values are given, the second is for the mirror image complex); other values shown in Table 2: Ru(1)−C(34), 1.837(11), 1.859(11); Ru(1)−C(33), 1.912(5); Ru(1)−Cl(1), 2.447(4), 2.447(4); C(33)−O(1), 1.167(5); C(34)−O(2), 1.187(11), 1.166(11); C(33)−Ru−C(19), 177.7(2); C(34)−Ru−C(33), 90.4(6), 88.3(6); C(34)−Ru−Cl(1), 178.8(5), 178.6(7); C(34)−Ru−C(19), 91.4(6), 89.9(6); C(19)−Ru−Cl(1), 88.66(16), 89.12(16); 78.88(13).

Scheme 4



solution of **5a/b** in a N_2-filled drybox over a period of 3 days. X-ray analysis revealed the structure shown in Figure 2.

The PPh_3 ligand in **3**·PPh_3, though unperturbed by exposure to H_2, is readily displaced by carbon monoxide (Scheme 4). The deep green color of **3**·PPh_3 dissipates within minutes of exposure to 1 atm CO (RT, benzene), giving a pale yellow solution. Displacement of PPh_3 and formation of six-coordinate RuCl(η^3-PCP)$(CO)_2$ (**6**) are confirmed by spectroscopic, microanalytical, and X-ray data. In situ $^{31}P\{^1H\}$ NMR analysis reveals a singlet for (free) PPh_3 and another singlet, of equal integrated intensity, for the equivalent ^{31}P nuclei of the pincer ligand (δ_P 62.4). The PPh_3 singlet disappears on reprecipitation of the product from CH_2Cl_2/diethyl ether, and **6** is isolated in 88% yield. The presence of two inequivalent carbonyl ligands is indicated by the appearance of two strong ν(CO) bands in the IR spectrum (2018, 1945 cm^{-1}), and two characteristically downfield $^{13}C\{^1H\}$ NMR triplets (199.8 ppm (t, $^2J_{CP}$ = 12 Hz), 198.2 (t, $^2J_{CP}$ = 7 Hz)), the multiplicity of which confirms that only two ^{31}P nuclei remain in the coordination sphere. Both the IR and the ^{13}C NMR data are consistent with cis-disposition of the CO ligands, as also found for RuCl-[η^3-2,6-$(PPh_2CH_2)_2C_6H_3$](CO)$_2$.[20b] X-ray quality crystals were obtained by slow evaporation of a benzene solution; an ORTEP diagram is shown in Figure 3.

X-ray Data for 3, 4a, 5a, and 6 (for key, common structural parameters, see Table 2). Square pyramidal **3** is isostructural with **2a**:[20b] consistent with the spectroscopic data, the chloride and η^3-PCP ligands are sited in the basal plane, with PPh_3 occupying the apical site (Figure 1). The single Ru−C bond to the ipso carbon lies in the aromatic plane of the [2,6-$(CH_2PCy_2)_2C_6H_3$] ligand, with a bond length (2.061(4) Å) essentially identical to that in **2a** (2.070(4) Å). Unsurprisingly, some manifestations are seen of the greater steric pressure exerted by the dicyclohexylphosphine moiety versus diphenylphosphine: the P(1)−Ru−P(2) angle is 4° larger in **3** than in **2a** (154.21(4)° versus 150.4(1)°),[20b] and the C(19)−Ru−Cl angle is contracted by ca. 10° (151.42(11)° versus 161.6(1)°).

Table 2. Summary of Key Structural Parameters for Complexes 3−6

	3	4a	5a	6
Ru−C(19)	2.061(4)	2.129(5)	2.133(4)	2.112(4)
Ru−P(1)	2.3247(10)	2.3433(12)	2.3434(11)	2.3649(14)
Ru−P(2)	2.3522(10)	2.3578(12)	2.3148(10)	2.3698(13)
Ru−P(3)	2.1996(10)	2.3655(12)	2.3617(10)	
Ru−X(1) (X = H, Cl)	2.4520(10)	1.60(4)		2.447(4), 2.447(4)
P(1)−Ru−P(2)	154.21(4)	154.95(5)	158.36(4)	160.76(4)
P(1)−Ru−P(3)	95.60(4)	101.15(4)	98.06(4)	
P(1)−Ru−C(19)	82.26(11)	77.61(12)	79.12(11)	78.88(13)
P(2)−Ru−P(3)	102.63(4)	102.30(4)	103.02(4)	
P(2)−Ru−C(19)	80.29(11)	77.68(12)	79.31(11)	81.88(13)
P(3)−Ru−C(19)	88.13(11)	198.96(12)	170.88(10)	

The coordination geometry about Ru in **4a** and **6** is distorted octahedral, as is that deduced for **5a**, for which the crystal quality did not permit location of the hydride and dihydrogen ligands.[27] In all three complexes, the pincer ligand occupies one meridian, and the site trans to the activated ring carbon C(19) is taken up by PPh_3 (**4a**, **5a**) or CO (**6**).[28] The trans influence of the aryl carbon may contribute to the ca. 0.16 Å increase in the Ru−P(3) bond length in **4a** and **5a**, versus **3** (in which the PPh_3 group is trans to the vacant site). Likewise, the slight increase in the Ru−C(19) distance in **4a**, **5a**, and **6**, versus **3**, may reflect the stronger trans influence of phosphine and carbonyl, versus chloride, though a change in metal hybridization associated with the lower coordination number in **3** may also account for these changes. While the P(1)−Ru−P(2) angle of 154.95(5)° in **4a** is very close to that in **3**, the values in **5a** and **6** (158.36(4)°, 160.76(4)°) are significantly less compressed. In the case of **6**, this can be attributed to replacement of the PPh_3 ligand by a sterically undemanding carbonyl group.

The Ru−H distance (1.60(4) Å) in **4a** is comparable, within experimental error, with the value of 1.73(7) Å observed for RuX[η^3-2,6-$(P^tBu_2CH_2)_2C_6H_3$](CO) (**1b**, X = H).[10b] Ru−N (2.014(4) Å) and N−N (1.111(6) Å) distances correlate well with literature values for related complexes (av Ru−N = 2.10 Å; av N−N = 1.13 Å).[10b,29] The C−O bond distance for the nondisordered CO ligand in **6** is within the usual range.[30−33]

Transfer Hydrogenation via PCP Complexes. Ru(II) complexes of both NCN and PCP pincer ligands catalyze the transfer hydrogenation of ketones.[1,3,34]

(27) One cyclohexyl group was also conformationally disordered, with a 50/50 site occupancy distribution.

(28) In complex **6**, the remaining carbonyl and chloride ligands are disordered; the electron density is distributed over C(34), O(2), and Cl(1) and the positions are arbitrarily assigned. The excess of electron density at C(34) results in an unusually small ellipsoid.

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Table 3. Transfer Hydrogenation of Benzophenone[a]

entry	precatalyst	additive[b]	time (h)	conversion (%)
1	**2b**	KOH	108	98
2	**4a/b**		96	88
3	**4a/b**	KOH	24	90
4	**3**·PPh_3	KOH/H_2	24	91
5	**3**·PPh_3	KOH	40	92

[a] Conditions: 20 mmol of Ph_2CO, [Ru] = 0.1 mol %, 20 mL of ^{i}PrOH, reflux (82 °C), N_2 atmosphere, unless otherwise noted. [b] [KOH]/[Ru] = 20.

RuX[η^3-2,6-$(PPh_2CH_2)_2C_6H_3$](PPh_3) (**2b**, X = OTf), with its weakly bound triflate ligand, has demonstrated particularly high activity, as well as versatility toward a range of substrates, including aryl and diaryl ketones targeted as precursors to pharmaceutically desirable benzhydrols.[34] Anionic [RuH(O^iPr)(η^3-PCP)(PPh_3)]$^-$, generated during pretreatment of **2a** or **2b** with KOH in refluxing 2-propanol, was proposed as the resting state in catalysis; a ruthenium hydride species was presumed to be the active catalyst. We find that in the absence of base, "preformed" monohydrides **4a/b** display lower activity for benzophenone reduction than **2b** (Table 3, entries 1, 2). Performance increases dramatically in the presence of KOH (entry 3), consistent with the generally accepted requirement for isopropoxide ion.[34−37] Given this requirement for added base, however, use of the robust chloride complex **3** is preferred over hydride **4**. Activity is significantly higher for reactions carried out under H_2 rather than N_2 (entries 4, 5), suggesting that both H_2- and transfer-hydrogenation pathways are implicated.

To gain mechanistic insight into the transfer hydrogenation catalyzed by **3**·PPh_3, we undertook more detailed studies of ligand, base promoter, and reaction conditions. For the sake of both convenience and added insight, we chose to study the more reactive (and enolizable) substrate acetophenone, for which we monitored reactions by gas chromatography. Turnover frequencies (TOF) were evaluated at 20% conversion, to minimize the influence on the rate of decreases in substrate concentration, increases in product concentration, and catalyst decomposition. Results are summarized in Table 4.

At high concentrations, strong bases such as alkali hydroxides can promote hydrogen transfer to ketones,[38−40] a process related to the classical Meerwein−Pondorff−Verlay reduction. While harsh conditions are typical, rates can be significant even at 82 °C. LePage and James, for example, report 60% conversion of acetophenone to 1-phenylethanol within 4 h at 34 mol % NaOH in refluxing 2-propanol.[41] Under our standard conditions (0.02 M KOH, or 2 mol % relative to acetophenone, 82 °C), control experiments in the absence of Ru result in only 2% reduction of acetophenone after 4 h.[42]

Table 4. Transfer Hydrogenation of Acetophenone Using 3·PPh_3 as Precatalyst[a]

entry	pretreatment time[b] (min)	additive	TOF[c] (h^{-1})
6	0	KOH	300
7	10	KOH	450
8	60	KOH	1300
9	60	^{t}BuOK	1200
10	60	KOH + NBu_4Cl[d]	320
11	60	KOH + PPh_3[e]	480
12[f]	60	^{t}BuOK/H_2	2500

[a] Conditions: 2.0 mmol of acetophenone, [Ru] = 0.1 mol %, 2.0 mL of ^{i}PrOH, reflux (82 °C), N_2 atmosphere, unless otherwise noted. [b] Precatalyst heated in the presence of base before addition of substrate. [c] Mol substrate converted per mol Ru per hour at 20% conversion. [d] 2.0 mol % NBu_4Cl. [e] 0.8 mol % PPh_3. [f] Reaction and pretreatment under H_2 (1 atm).

We find that catalyst activity is very sensitive to the duration of pretreatment, during which the precatalyst is heated at reflux in the presence of base (base: Ru = 20:1), prior to addition of substrate. After only 10 min of pretreatment, activity increases by 50% relative to reactions carried out without this initial heating step. Activity increases by 4-fold after 1 h (entries 6−8), declining thereafter. Approximately identical activity was found using KOH or ^{t}BuOK, although the base strength varies by 3 orders of magnitude (pK_a KOH = 16; pK_a ^{t}BuOK = 19; entries 8, 9). This suggests that the base is not involved in the rate-determining step, but rather promotes formation of the catalytically active species, most probably in a rapid preequilibrium involving formation of isopropoxide ion.[36,37]

Addition of the soluble ammonium chloride NBu_4Cl (20 equiv per Ru) reduces the activity to the level of the system without pretreatment (entries 10, 6). Excess chloride is presumed to coordinate to the metal center via exchange with a hydride ligand. Its inhibiting effect is consistent with the earlier report that complex **2b**, containing the weakly coordinating triflate ion, is much more active than its chloride analogue **2a**.[34] Addition of PPh_3 to the system (8 equiv per Ru) also diminishes activity, suggesting that an equilibrium involving loss of PPh_3 precedes the rate-determining step and that excess PPh_3 can compete with the substrate for vacant sites. Both the bound and the solvating PPh_3 present in the precatalyst **3**·PPh_3 will thus diminish the overall activity of the system.

Finally, we note that under hydrogen atmosphere catalyst activity is approximately double that observed under nitrogen atmosphere, presumably due to a H_2-hydrogenation pathway.

NMR Experiments under Catalytically Relevant Conditions. In view of the marked dependence of catalytic activity on pretreatment time, we undertook an in situ $^{31}P\{^1H\}$ NMR study of the precursor **3**·PPh_3 under pretreatment conditions. KO^{t}Bu was employed in preference to KOH in order to ensure solubility of the base without stirring. These experiments are sum-

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(42) While the presence of base can trigger aldol condensation of ketones, only traces of heavier byproducts (<1%) were observed even over the combined time scale of pretreatment and reduction experiments (ca. 3.5 h), reaching 3% after 19 h.

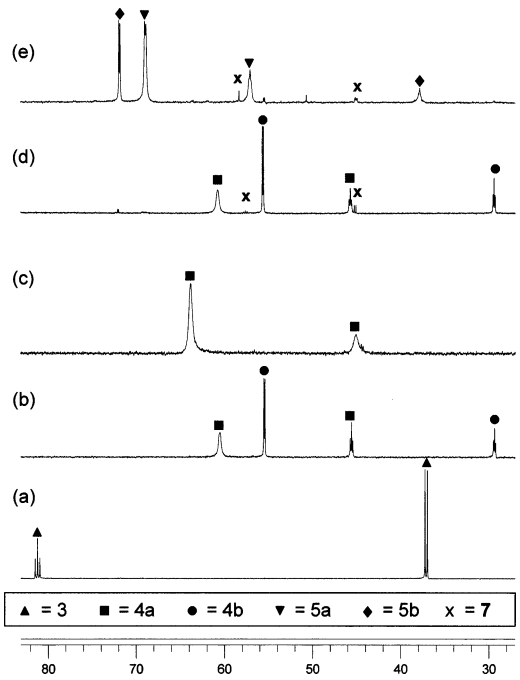

Figure 4. In situ $^{31}P\{^1H\}$ NMR spectra of precursor **3**·PPh_3 under transfer-hydrogenation conditions (2:1 2-propanol/C_7D_8, N_2 atmosphere, 20 equiv KOH): (a) before addition of base, 22 °C; (b) 10 min after adding base, 22 °C; (c) after 10 min at 82 °C (spectrum measured at 82 °C); (d) after 1 h at 82 °C (spectrum measured at 22 °C); (e) after 3 days at 82 °C (spectrum measured at 22 °C).

marized in Figure 4. After 10 min in the presence of base and 2-propanol at ambient temperatures (nitrogen atmosphere), the signals for **3** have nearly disappeared, being replaced by two new A_2B patterns assigned to **4b** and **4a** (ratio 1:1; chemical shifts confirmed with authentic samples). The signals due to **4b** progressively diminish as the NMR probe is warmed: at 82 °C, they are no longer observed. After 1 h at 82 °C, the spectrum is essentially unchanged: resonances for **4a** dominate the spectrum, accompanied by a new A_2B pattern for unknown **7** (<5% integrated intensity) at δ 57.3 and 45.0 ($^2J_{PP}$ = 23 Hz) and emerging signals for **5a/b**. As the probe is cooled back to room temperature, the signals for **4b** reappear, and a 1:1 integration relative to **4a** is reestablished (implying that the equilibrium favors **4a** at elevated temperatures), but the new signals remain. Heating the NMR sample for 3 days at 82 °C resulted in a color change from red to pale yellow: dominating the ^{31}P NMR spectrum are signals assigned to hydride complexes **5b** and **5a** (chemical shifts confirmed by comparison to authentic samples).

The catalytic data indicate that the most active catalytic species is formed by loss of *both choride and triphenylphosphine ligands* from **3** and that maximum activity requires a "pretreatment" period (reaction with base in refluxing 2-propanol) as long as 1 h. The in situ NMR experiments, however, show complete conversion of **3** to monohydrides **4a/b** in <10 min even at room temperature. It may be inferred that the monohydride complexes are not the catalytically most active species, but a resting state which delivers this species, as van Koten has proposed.[34] Furthermore, the emergence of dihydrogen complexes **5a/b** *under nitrogen* strongly suggests the intermediacy of a dihydride species. (The fact that the activity observed for catalysis under H_2 is only double that under N_2, despite a 100-fold increase in concentration of **5a/b**, argues against identification of the dihydrogen complex(es) as the active species.)

Bäckvall recently proposed that a $Ru(H)_2$ complex is formed as the true catalytic species in transfer hydrogenation via related Ru systems,[40] and our observations provide strong circumstantial support for the accessibility of such an entity. The absence of spectroscopic evidence for either a PPh_3-free or a dihydride species points toward operation of a highly active catalyst present in low concentration. Favored candidates include $Ru(H)_2[\eta^2$-PC(H)P](L), formed by elimination of the activated pincer carbon, and anionic $[Ru(H)_2(\eta^3$-PCP)(L)]$^-$ (L = ketone). In favor of the former are its coordinative unsaturation and the enhanced flexibility of such η^2-pincer ligands (both factors that would facilitate substrate entry and hence, catalytic activity). In addition, the ease with which the η^3-PCP structure could be regenerated would give access to a stable resting state, accounting for the thermal stability of the catalyst, as well as the spectroscopic invisibility of the η^2-species.

Conclusions

The foregoing describes facile routes to the first group 8 complexes of a bulky, electron-rich η^3-pincer ligand containing cyclohexylphosphine groups. $RuCl(\eta^3$-PCP)(PPh_3), **3**, prepared via room-temperature reaction of $RuCl_2(PPh_3)_3$ with the PC(H)P ligand, provides a convenient entry point into complexes $RuH(\eta^3$-PCP)(PPh_3)(L) (L = N_2, H_2). The triphenylphosphine ligand is retained within all of these complexes, being displaced only by carbon monoxide or, as judged from the catalytic data, under transfer-hydrogenation conditions. Both chloride and hydride complexes serve as precatalysts for transfer hydrogenation of ketones, with activity comparable to that of the arylphosphine complex **2b**: we speculate that a PPh_3-free dihydride species such as $Ru(H)_2[\eta^2$-PC(H)P](ketone) may be the most active catalyst in each case. While the activity of related species containing the flexible dcypb ligand is higher by several orders of magnitude (TOF 9600 h^{-1} for reduction of benzophenone), the robustness and tunability of the pincer ligand scaffold offer enhanced potential for asymmetric catalysis, and we are currently pursuing development of chiral, PPh_3-free versions of these systems.

Experimental Section

General Procedures. All reactions were carried out at 22 °C under nitrogen atmosphere using standard Schlenk or drybox techniques, unless stated otherwise. Reactions with H_2 were carried out under 1 atm pressure, using Praxair UHP grade H_2, passed through a Deoxo cartridge and Drierite column in series. CO (Praxair) was used as received. Dry, oxygen-free solvents were obtained using an Anhydrous Engineering solvent purification system and stored over Linde 4 Å molecular sieves. $CDCl_3$, C_6D_6, and toluene-d_8 were dried over activated sieves (Linde 4 Å) and degassed by consecutive freeze/pump/thaw cycles. $RuCl_2(PPh_3)_3$[43] and 1,3-$(Cy_2PCH_2)_2C_6H_4$[10] were prepared as previously described.

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Table 5. Details of Crystal Data and Structure Refinement

	3·THF	**4a**·Et_2O	**5a**	**6**
formula	$C_{54}H_{74}ClOP_3Ru$	$C_{54}H_{77}N_2OP_3Ru$	$C_{56}H_{74}P_3Ru$	$C_{34}H_{51}ClO_2P_2Ru$
fw	968.56	964.16	941.13	690.21
temperature	203(2) K	293(2) K	203(2) K	203(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, $P2(1)/c$	triclinic, $P\bar{1}$
unit cell dimens	a = 12.9390(8) Å α = 99.9870(10)° b = 14.2861(9) Å β =100.7430(10)° c = 14.9545(9) Å γ = 93.3590(10)°	a = 11.3988(10) Å α = 91.4430(10)° b = 11.4641(10) Å β = 92.0320(10)° c = 19.3073(16) Å γ = 99.1330(10)°	a = 18.886(3) Å α = 90° b = 14.2595(19) Å β = 107.256(2)° c = 19.073(3) Å γ = 90°	a = 11.082(2) Å α = 94.222(2)° b = 11.568(2) Å β = 91.744(2)° c = 14.228(2) Å γ = 115.517(2)°
volume	2662.9(3) Å^3	2488.3(4)Å^3	4905.4(11) Å^3	1637.8(4) Å^3
Z, calcd density	2, 1.208 g/cm^3	2, 1.287 g/cm^3	4, 1.274 g/cm^3	2, 1.400 g/cm^3
absorp coeff	0.469 mm^{-1}	0.451 mm^{-1}	0.453 mm^{-1}	0.687 mm^{-1}
F(000)	1024	1024	1996	724
cryst size, mm	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.10	0.10 × 0.07 × 0.02
θ range for data collection	1.41 to 28.72°	1.06 to 26.37 °	1.13 to 28.71 °	1.44 to 28.74°
limiting indices	$-17 \le h \le 16$, $-19 \le k \le 18$, $0 \le l \le 20$	$-14 \le h \le 14$, $-14 \le k \le 14$, $0 \le l \le 24$	$-25 \le h \le 24$, $0 \le k \le 19$, $0 \le l \le 25$	$-14 \le h \le 14$, $-15 \le k \le 15$, $0 \le l \le 18$
no. of reflns collected/ unique	20833/11993 [R(int) = 0.0299]	22227/10024 [R(int) = 0.0657]	43750/11732 [R(int) = 0.0480]	12803/7413 [R(int) = 0.0616]
completeness to θ	86.8% to θ = 28.72	98.3% to θ = 26.37	92.5% to θ = 28.71	87.3% to θ = 28.74
max. and min. transmn	0.928075 and 0.843640	0.928075 and 0.779621	1.000000 and 0.925298	0.928076 and 0.643412
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/ params	11 993/0/518	10 024/0/553	11 732/36/527	7413/2/388
goodness-of-fit on F^2	1.027	1.024	1.028	1.025
R^a	0.0515	0.0565	0.0580	0.0530
$R_w{}^b$	0.0766	0.0976	0.0976	0.0878
largest diff peak and hole	1.709 and −0.428 e A^{-3}	0.709 and −0.944 e A^3	0.709 and −0.944 e A^3	2.519 and −0.807 e A^{-3}

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w\delta^2/\sum wF_o^2]^{1/2}$.

Potassium tri(*sec*-butyl)borohydride was purchased from Aldrich and used as received. ^{1}H NMR (300 or 500 MHz) spectra were recorded on a Bruker Avance-300 or AMX-500 spectrometer; ^{31}P NMR (121 MHz) and ^{13}C NMR (75 MHz) on the Bruker Avance-300. All 2D experiments were carried out on the Avance-300 instrument. Solid state NMR spectra were recorded on a Bruker ASX-200 MHz spectrometer (81 MHz for ^{31}P). IR spectra were measured on a Bomem MB100 IR spectrometer. Microanalyses were carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

RuCl(η^3-PCP)(PPh_3)·PPh_3 (3·PPh_3). A mixture of $RuCl_2(PPh_3)_3$ (0.505 g, 0.53 mmol), 1,3-$(Cy_2PCH_2)_2C_6H_4$ (0.268 g, 0.54 mmol), and NEt_3 (1 mL, excess) in 5 mL of toluene was stirred under N_2 for 18 h at 22 °C. Quantitative reaction was evident by ^{31}P{^{1}H} NMR. The product was filtered through Celite, stripped to an oil, and treated with cold 2-propanol to precipitate a green solid. The solid was filtered off, washed with 3 × 5 mL each of cold 2-propanol and hexanes, and dried under vacuum. Yield of **3**·PPh_3: 0.478 g (79%; isolated yields are limited by the high solubility of the complex). X-ray quality crystals of **3** deposited on slow evaporation of an ether solution. (A solvating THF molecule is present, owing to earlier attempts to crystallize the sample from THF/hexanes.) ^{1}H NMR ($CDCl_3$): δ 7.0−8.2 (m, Ar, 30H), 6.79 (d, CH_{meta}PCP, $^3J_{HH}$ = 7.1 Hz, 2H), 6.68 (t, CH_{para}PCP, $^3J_{HH}$ = 7.2 Hz, 1H), 2.90 (dvt, ArC*H*HP, $^2J_{HH}$ = 16.7 Hz, $^vJ_{HP}$ = 5.2 Hz, 2H), 2.55 (br d, ArCH*H*P, $^2J_{HH}$ = 12.2 Hz, 2H), 0.7−2.2 (br, Cy, 44H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 80.9 (t, Ru-*P*Ph_3, $^2J_{PP}$ = 32 Hz), 35.7 (d, PCP, $^2J_{PP}$ = 32 Hz), −5.46 (s, PPh_3 solvate). Solid state ^{31}P{^{1}H} CP/MAS NMR (80.9 MHz): 82.7 (br s, Ru-*P*Ph_3), 34.1 (br s, PCP), −6.1 (s, PPh_3 solvate). Anal. Calcd for $C_{68}H_{81}ClP_4Ru$: C, 70.48; H, 7.05. Found: C, 70.37; H, 7.02. All analytical methods, with the exception of X-ray diffraction, consistently reveal the presence of 1 equiv of free PPh_3 even after multiple reprecipitations.

RuH(η^3-PCP)(N_2)(PPh_3) (4). A mixture of **3**·PPh_3 (150 mg, 0.13 mmol) and KHB^sBu_3 (136 μL of a 1.0 M solution in Et_2O) in 4 mL of toluene was stirred for 24 h at RT under N_2, then stripped to a red oil, which crystallized on addition of 2-propanol. Reprecipitation from hexanes/2-propanol afforded 100 mg (87%) of isomers **4a**+**4b**. X-ray quality crystals of **4a** were obtained by slow evaporation of a diethyl ether solution. ^{1}H NMR (C_6D_6): δ 7.96 (t, Ar, J_{HH} = 7.5 Hz, 3H), 7.50 (t, Ar, J_{HH} = 7.0 Hz, 3H), 7.34 (d, CH_{meta}PCP, $^3J_{HH}$ = 6.9 Hz, 2H), 7.24 (t, CH_{para}PCP, $^3J_{HH}$ = 6.9 Hz, 1H), 7.15 (t, Ar, J_{HH} = 7.2 Hz, 3H), 7.04 (m, Ar, 6H), 3.48 (d, ArC*H*HP, $^2J_{HH}$ = 14.9 Hz, 1H), 3.33 (d, ArC*H*HP, $^2J_{HH}$ = 14.9 Hz, 1H), 3.01 (br d, $^2J_{HH}$ = 16 Hz, 1H), 0.9−2.5 (br, Cy, 44H), −8.05 (dt, Ru*H*, **4b**, $^2J_{HP}$ = 21.8 Hz, $^2J_{HP}$ = 90 Hz), −12.2 (br s, Ru*H*, **4a**). The signal at −12.2 ppm resolves into a quartet ($^2J_{HP}$ = 19.5 Hz) in C_7D_8 at 253 K. Hydride T_1(min): 333 ms (**4b**, 282 K, 500 MHz), 359 ms (**4a**, 278 K, 500 MHz). ^{31}P{^{1}H} NMR (C_6D_6): δ 59.6 (br s, 2P; **4a**, PCP), 54.6 (d, 2P, $^2J_{PP}$ = 14 Hz; **4b**, PCP), 45.0 (t, 1P, $^2J_{PP}$ = 17 Hz; **4a**, PPh_3), 28.8 (t, 1P, $^2J_{PP}$ = 14 Hz; **4b**, PPh_3). The signal at 59.6 ppm resolves into a doublet ($^2J_{PP}$ = 17 Hz) in C_7D_8 at 253 K. IR (Nujol): $\nu(N_2)$ 2134 (m), ν(RuH) 2114 (m) cm^{-1}. Anal. Calcd for $C_{50}H_{67}N_2P_3Ru$: C, 67.47; H, 7.59; N, 3.15. Found: C, 67.56; H, 7.77; N, 3.14.

RuH(η^3-PCP)(H_2)(PPh_3) (5). NMR-Scale Experiment. A solution of **4b** and **4a**, generated by treating a C_6D_6 solution (~1 mL) of **3** (25 mg, 0.22 μmol) with KHB^sBu_3 (43.1 μL of a 1.0 M solution in Et_2O), was placed under an atmosphere of H_2. Within minutes, the originally red/brown solution had become yellow in color and no starting material was spectroscopically observable. ^{1}H NMR (C_6D_6): δ −4.34 (br s, Ru(H_2), **5a**), −7.08 (br s, Ru(H_2), **5b**), −8.70 (q, Ru*H*, **5a**, $^2J_{HP,cis}$ = 18.9 Hz), −10.64 (dt, Ru*H*, **5b**, $^2J_{HP,cis}$ = 21.7 Hz, $^2J_{HP,trans}$ = 80.1 Hz.) Dihydrogen T_1(min) values at 500 MHz: **5a**, 20 ms (265 K); **5b**, 24 ms (265 K). ^{31}P{^{1}H} NMR (C_6D_6): δ 71.1 (d, 2P, $^2J_{PP}$ = 15 Hz; **5b**, PCP), 68.1 (d, 2P, $^2J_{PP}$ = 18 Hz; **5a**, PCP), 56.6 (t, 1P, $^2J_{PP}$ = 18 Hz; **5a**, PPh_3), 37.1 (t, 1P, $^2J_{PP}$ = 14 Hz; **5b**, PPh_3). X-ray quality crystals of **5a** were obtained by slow evaporation of a benzene solution.

RuCl((η^3-PCP)(CO)$_2$ (6). A solution of **3** (83 mg, 0.093 mmol) in benzene (5 mL) was placed under an atmosphere of CO, stirred at 294 K for 24 h, and then concentrated to dryness. The yellow residue was redissolved in CH_2Cl_2 (~0.25 mL) and cooled to −35 °C. Addition of cold Et_2O (−35 °C, 1 mL) afforded a pale yellow solid, which was filtered off, washed with cold Et_2O (−35 °C, 3 × 1 mL), and dried under vacuum. Yield: 56 mg (88%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.4 (s). ^1H NMR ($CDCl_3$): δ 7.0 (m, Ar, 2H), 6.85 (m, Ar, 1H), 3.65 (m, C*H*$_2$, 2H), 3.35 (m, C*H*$_2$, 2H), 2.5 (m, aliphatic, 2H), 1.1−2.2 (br, aliphatic, 42H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 199.8 (t, $^2J_{CP}$ = 12 Hz, CO), 198.2 (t, $^2J_{CP}$ = 7 Hz, CO). IR (Nujol, cm^{-1}): ν(CO) 2018 (s), 1945 (s). Anal. Calcd for $C_{56}H_{104}N_2Cl_4P_4Ru_2$: C, 59.04; H, 7.44. Found: C, 59.16; H, 7.45. X-ray quality crystals were obtained by slow evaporation of a benzene solution.

Representative Procedure for Transfer Hydrogenation. A toluene solution of **3**·PPh_3 (0.10 mL, 0.020 M) was mixed with KOH in 2-propanol (0.20 mL, 0.20 M) and heated at 82 °C under N_2. A color change from dark green to red occurred within 5 min. After 1 h at reflux, a solution of acetophenone in 2-propanol (1.7 mL, 1.18 M) was added by syringe. The reaction was monitored for 4 h, sampling every 10 min for the first hour and every 30 min thereafter. Conversions were determined by gas chromatography.

Conditions for in Situ NMR Experiment. A solution of **3**·PPh_3 (6 μmol) in 0.3 mL of C_7D_8 was mixed with a solution of KO^{t}Bu (0.12 mmol) in 0.6 mL of 2-propanol and heated at 82 °C under N_2. The solution was monitored by $^{31}P\{^1H\}$ NMR spectroscopy over 3 days.

Structural Determination for 3·THF, 4a·Et$_2$O, 5a, and 6. Suitable crystals were selected, mounted on thin glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[44] No symmetry higher than triclinic was observed in the diffraction data for **3**·THF, **4a**·Et_2O, or **6**, and solution in the centrosymmetric space group option, $P\bar{1}$ [No. 2], yielded chemically reasonable and computationally stable results of refinement. Systematic absences in the diffraction data and unit-cell parameters for **5a** were uniquely consistent with the reported space group $P2_1/c$ (No. 14). The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2.

For complex **3**, two molecules of THF solvent were found at half-occupancy severely disordered in the asymmetric unit. For **4a**·Et_2O, one molecule of diethyl ether solvent was located in the asymmetric unit. One cyclohexyl group in **5a** and the chloride and carbonyl ligands in **6** were found disordered with a refined site occupancy of 50/50. All non-hydrogen atoms were refined with anisotropic displacement coefficients, except the solvent atoms for **3**·THF and the disordered cyclohexyl carbon atoms for **5a**, which were refined isotropically. All non-hydridic hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.[45] Table 5 compiles the data for the structure determinations.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC publications 183904 (**3**·THF), 232518 (**4a**·Et_2O), 232519 (**5a**), and 232520 (**6**). These data can be obtained free of charge on application to the CCDC at 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information Available: Tables of crystal data collection and refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **3**, **4a**, **5a**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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